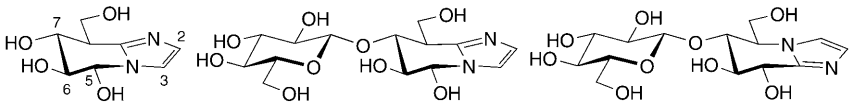
Synthesis of a Fusion-Isomeric Cellobionoimidazole and Its Evaluation against the *syn*-Protonating Glycosidase Cel7A

by **Narinder Mohal**, **Bruno Bernet**, and **Andrea Vasella***

Laboratorium für Organische Chemie, ETH-Hönggerberg, HCI, CH-8093 Zürich

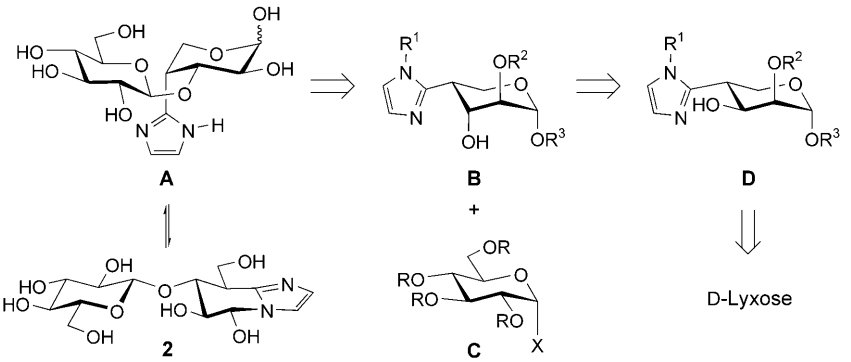
The fusion-isomeric cellobinoimidazole **2**, a potential inhibitor of the *syn*-protonating β-glycosidase Cel7A, was synthesised by *Koenigs–Knorr* glycosylation of the α-D-arabinopyranoside **32**, followed by selective hydrolysis. Glycosylation of **32** with acetobromoglucose **6** proceeded with poor diastereoselectivity, giving the desired 1,3-linked β-D-disaccharide **35** as minor product, besides the major 1,3-linked α-D-disaccharide **36**. Hg^{2+}-Promoted glycosylation of **32** led predominantly to the 1,2-ortho ester **33**. Sequential removal of the silyl, acetyl, and allyl groups of **35** led to a 45:55 equilibrium mixture **2** and the *manno*-configured isomer **39**. Similarly, deprotection of **36** gave a mixture of the maltonoimidazole **42** and the *manno*-configured isomer **43**. According to a known protocol, the glycosyl acceptor **32** was synthesised in eleven steps and an overall yield of 8–13% from D-lyxose. The silylated arabinopyranosyl moiety of the α-D-glucosides **13**–**19**, **33**, **34**, and **36** adopts a $^4C_1$ conformation, while the arabinopyranosyl moiety of the β-D-glucosides **17** and **35** exists as a 1:3 mixture of $^4C_1$ and $^1C_4$ conformers, as a result of the combined preferred axial orientation of bulky vicinal substituents and the anomeric effect. MM3* Modelling evidences a preferred $^4C_1$ conformation of **35** and **36**, and stronger steric interactions between the pyranosyl moieties of **35**. The equilibrium mixture **2**/**39** proved a poor inhibitor of Cel7A with an IC_{50} value of *ca.* 4 mM.

Introduction. – We have recently disclosed the synthesis of fusion-isomeric *gluco*-configured imidazoles of type **1** [1]. As predicted, they do not inhibit *anti*-protonating β-glycosidases from family 1 [2] being devoid of a 'glycosidic heteroatom' that could interact with the catalytic acid of an *anti*-protonating β-glycosidase [3–15]. The imidazole **1** does not inhibit Cel7A (formerly named CBH I), a *syn*-protonating β-glycosidase from family 7 [16] and one of the industrially most important cellulase components of *Trichoderma reesei* [17]. The inhibitory inactivity may be due to the requirement of Cel7A for di- or oligosaccharide substrates, and/or to an unsuitable position of the glycosidic heteroatom. An appreciation of these factors requires the synthesis of at least a disaccharide analogue **2** of **1** [18]. As the isomeric cellobionoimidazole **3** [19] is a potent inhibitor of the *anti*-protonating β-glycosidase Cel5A of family 5, a comparison of the inhibitory activity of **2** and **3** promised to be meaningful. We decided to synthesise this fusion-isomeric cellobionoimidazole **2**.



We considered that **2** – a tautomer of the corresponding hemiacetal **A** – should be accessible by regioselective hydrolysis, or acetolysis and deacetylation, of a suitably masked β-linked disaccharide which, in turn, should be available by standard glucosylation of the acceptor **B** with a glucosyl donor **C** (*Scheme 1*). The α-D-arabinopyranoside **B** is accessible by oxidoreduction of the α-D-lyxopyranoside **D**; a representative of **B** (**4** in *Scheme 2*) has already been prepared from D-lyxose in eleven steps and in *ca.* 9–12% overall yield [1].

Scheme 1

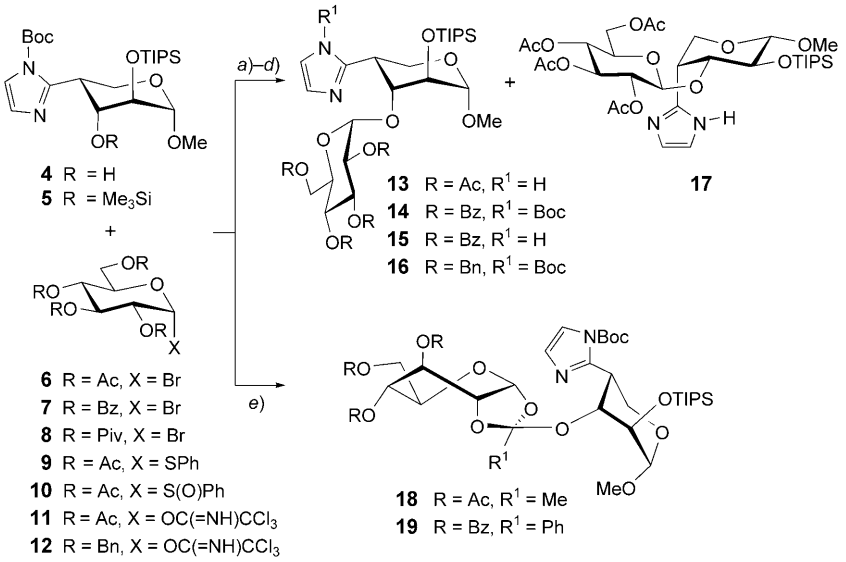


Results and Discussion. – We first attempted to glucosidate the branched-chain α-D-arabinopyranoside **4** [1] with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**6**) [20] under *Koenigs–Knorr* conditions [21] but met with considerable difficulties[1]) (*Scheme 2*). AgOTf-Promoted glucosidation of **4** with **6** in CH_2Cl_2 resulted in an inseparable 2:1 mixture of disaccharides, which were de-bocylated and then separated by chromatography into **13** (26%) and **17** (19%). The unexpected preferential formation of the undesired α-D-glucopyranoside **13** was rationalised by postulating an *in situ* anomerisation of the initially formed β-D-glucopyranoside **17** (*cf.* [22][23]). However, glucosidation in the presence of an acid scavenger such as *N*,*N*,*N*′,*N*′-tetramethyl urea (TMU) [24][25] led exclusively to the 1,2-ortho ester **18** that was isolated in *ca.* 90% yield. Similarly, glucosidation of **4** with **6** in the presence of $Hg(CN)_2/HgBr_2$ in CH_2Cl_2 under *Helferich* conditions [26] gave exclusively **18** by preferred *exo*-attack on the intermediate 1,3-dioxolenium cation [27–30].

We investigated several glucosyl donors to improve the stereoselectivity of the glucosidation of **4** in favour of the desired β-D-anomer (*Scheme 2*). *Koenigs–Knorr*-type glucosidation by the more reactive perbenzoylated bromide **7** [31] provided a mixture of **14** (30%) and *N*-debocylated **15** (29%) that was transformed into **14** by treatment with Boc_2O and DMAP in MeCN. There was no evidence of the desired β-linked anomer. Glucosidation of **4** by **7** in the presence of TMU led exclusively to the 1,2-ortho ester **19** (86%). It was stable to chromatography and stored for months without

[1]) A range of solvents and promoters were tested without success in search of a diastereoselective glycosidation. Glycosidation at temperatures between −20 and 10° led to mixtures, with the 1,2-ortho ester **18** as main product.

Scheme 2



a) i. **6**, AgOTf (Tf = CF_3SO_2), 4-Å mol. sieves, CH_2Cl_2. ii. CF_3COOH/CH_2Cl_2 1:9; 26% of **13**, 19% of **17**, and 18% of **4**. *b*) **7**, AgOTf, 4-Å mol. sieves, CH_2Cl_2; 30% of **14**, 29% of **15**. *c*) **11**, TMSOTf (TMS = Me_3Si), CH_2Cl_2; 99% of **5**. *d*) **12**, $Zn(OTf)_2$, 4-Å mol. sieves, CH_2Cl_2; 30% of **16** and 27% of **4**. *e*) AgOTf, *N,N,N′N′*-tetramethylurea (TMU), 4-Å mol. sieves, CH_2Cl_2; 96% of crude **18** (*ca.* 90% pure); 86% of **19**.

noticeable decomposition. Attempts to rearrange the ortho esters **18** and **19** under well-precedented conditions ($BF_3 \cdot Et_2O$ in CH_2Cl_2, TMSOTf in THF, or $HgBr_2$ in CH_2Cl_2 [32][33]) led either to hydrolysis to the corresponding glucopyranoses or to recovery of starting material. In an exploratory experiment, **4** was glucosidated with the pivaloylated bromide **8** [34] under *Koenigs–Knorr* conditions. The 1,2-ortho ester was the only isolable product, besides the glycosyl acceptor **4**. Yields were rather poor due to the limited stability of the ortho ester to chromatography. Almost no reaction occurred under *Helferich* conditions, and only traces of the pivaloylated ortho ester were observed.

Treatment of **4** with the thioglucoside **9** [35], benzenesulfinyl piperidine (BSP), and Tf_2O [36] led to a *ca.* 3:2 mixture of *N*-Boc-disaccharides that were transformed to **13** and **17** (*Scheme 2*). Similarly, glucosidation of **4** with the phenyl sulfoxide **10** [37] in the presence of Tf_2O and 2,6-di(*tert*-butyl)-4-methylpyridine (DTBMP) [38] provided only the ortho ester **18** in poor yield; in the absence of DTBMP, a complex mixture of Boc-disaccharides was isolated as major product. Treatment with CF_3COOH (TFA) transformed these disaccharides to **13** and **17**. *Schmidt* glycosidation [39] of **4** with the trichloroacetimidate **11** [40][41] and TMSOTf as promoter led only to silylation of **4** to **5** (99%). No disaccharide was formed. A similar glycosidation in the presence of $BF_3 \cdot OEt_3$ induced extensive decomposition of the glycosyl acceptor **4**. Treatment of **4** with the benzylated trichloroacetimidate **12** [42] in CH_2Cl_2, Et_2O, MeCN, or toluene led only to intractable mixtures, presumably due to decomposition of **4**. The $Zn(OTf)_2$-

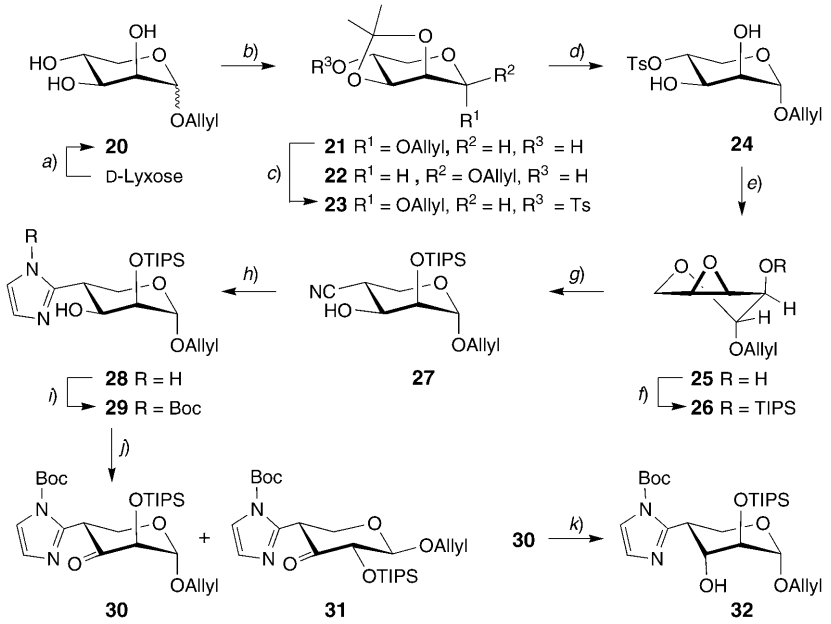
promoted glucosidation of **4** with **12** in CH_2Cl_2 gave the α-D-glucopyranoside **16** in 30% yield without any indication of the β-D-anomer.

Unfortunately, all experiments directed at a regioselective hydrolysis [43] of the C(1)–OMe bond of **17** failed. No reaction was observed when **17** was treated at low temperature with BCl_3 in CH_2Cl_2, Me_3SiI in MeCN, or Me_3SiCl and NaI in MeCN, while higher temperatures and prolonged treatment led to intractable mixtures without any indication of the desired product. There is precedent for regioselective acetolysis [44–50], but acetolysis of **17** (cat. H_2SO_4 in Ac_2O or $FeCl_3$ in Ac_2O) gave a complex mixture of monomers.

In view of these results, we decided to replace the MeO group of **4** by an allyloxy group. We preferred preparing the corresponding allyl glycoside **32** from D-lyxose to hydrolysing **4** and glycosidation of the resulting hemiacetal with allyl alcohol (*Scheme 3*). Accordingly, *Fischer* glycosidation of D-lyxose with 1% of H_2SO_4 in allyl alcohol gave crude **20** in high yields. Isopropylidenation of crude **20** with *Amberlyst-15* in acetone followed by chromatography provided the α- and β-D-lyxopyranosides **21** and **22** in 59 and 6% yield, respectively, from D-lyxose. Tosylation of **21** to **23** (89%) followed by deisopropylidenation in 80% aqueous AcOH at 110° gave the diol **24**. Treatment of **24** with *t*-BuOK gave the 3,4-anhydro-β-L-ribopyranoside **25** (71% from **23**) which was silylated with triisopropyl trifluoromethanesulfonate (TIPSOTf) to **26** (83%). With Et_2AlCN [51][52], the oxirane ring of **26** underwent ring opening with complete control of regioselectivity to provide the 4-cyano-α-D-lyxopyranoside **27** in 78% yield. As described for the analogous methyl lyxoside [1], **27** was treated with a 1:1 mixture of $NH_2CH_2CH(OMe)_2$ and Me_3Al in toluene at 80° to yield 67% of the imidazole **28** that was *N*-bocylated to **29**. *Dess–Martin* periodinane [53] oxidised **29** to the desired α-D-*threo*-pentopyranosid-3-ulose **30** (68% from **28**) and its doubly-epimerised β-D-*erythro*-pentopyranosid-3-ulose **31** (10% from **28**; *cf.* [1]) that is presumably formed by elimination followed by addition of allyl alcohol during purification. *Luche* reduction of **30** with $NaBH_4$ and $CeCl_3 \cdot 7\ H_2O$ [54] proceeded highly stereoselectively to yield the α-D-arabinopyranoside **32** (80%). The stereoselectivity is presumably the result of a complexation of Ce^{III} with O=C(3) and the axial allyloxy group of **30**.

The flattened $^4C_1$ conformation of **21**–**23** is consistent with $J(1,2) = 1.5–3.3$, $J(2,3) = 6.0–6.3$, $J(3,4) = 5.4–6.6$, $J(4,5_{ax}) = 6.6–9.9$, and $J(4,5_{eq}) = 4.5–4.8$ Hz (*Table 3* in the *Exper. Part*). The $[\alpha]_D^{25}$ values (**21**: +62.6, **22**: −86.5) are in accordance with *Hudson*'s rule. The β-L-riboside **25** adopts predominantly the ^1H_o conformation, as evidenced by $J(1,2) = 2.4$, $J(2,3) = 4.5$, $J(3,4) = 4.5$, $J(4,5_{ax}) \approx 1$, and $J(4,5_{eq}) = 1.5$ Hz, whereas the silylated β-L-riboside **26** exists as *ca.* 1:1 mixture of ^1H_o and $^oH_1$ conformers, as indicated by $J(1,2) = 2.4$, $J(2,3) = 3.0$, $J(3,4) = 3.9$, $J(4,5_{ax}) = 1.5$, and $J(4,5_{eq}) = 1.5$ Hz. The carbonitrile **27** shows the C≡N *s* at 118.34 ppm, and a characteristic *td* for H–C(4) at 3.01 ppm with $J(3,4) = J(4,5_{ax}) = 10.8$ and $J(4,5_{eq}) = 5.1$ Hz. Together with $J(1,2) = 2.4$ and $J(2,3) = 3.0$ Hz, these values evidence the predominant $^4C_1$ conformation of **27**. The imidazolyl moiety of **28** gives rise to a br. *s* at 6.99 for H–C(4′) and H–C(5′), a br. *d* at 121.2 ppm for C(4′) and C(5′), and a *s* at 146.4 for C(2′), whereas the imidazolyl moiety of **29**–**32** shows two *d*s ($J = 1.5–2.1$ Hz) for H–C(4′) at 6.86–6.90 and H–C(5′) at 7.31–7.34, two *d*s for C(4′) at 127.2–128.9 and C(5′) at 118.6–119.0, and a *s* for C(2′) at 143.7–148.3 ppm. These values evidence a tautomeric equilibrium of the *N*-unprotected imidazole **28** (*cf.* [1][55][56]). The α-D-*lyxo*-configuration and the $^4C_1$ conformation of **28** and **29** agree well with $J(1,2) = 1.5–1.8$, $J(2,3) = 2.4–3.0$, $J(3,4) = 10.8$, and $J(4,5_{ax}) = 11.4$, $J(4, 5_{eq}) = 3.6–4.8$ Hz. The C=O group of **30** and **31** resonates at 201.0–201.3 ppm. Characteristic shifts are observed for C(1) of the α-D-configured **30** (102.5 ppm) and **32** (99.2 ppm) and the β-D-configured **31** (105.4 ppm; *Table 4* in the *Exper. Part*). The α-D-*threo*-configuration of **30**, the α-D-*arabino*-configuration of **32**, and their $^4C_1$ conformation is evidenced by $J(1,2) \leq 1.8$, $J(4,5_{ax}) = 11.4$, $J(4,5_{eq}) = 4.2–6.6$ Hz, and corroborated for **32** by $J(2,3) = 3.0$, $J(3,4) = 2.1$, and $J(3,5_{eq}) = 1.2$ Hz.

Scheme 3



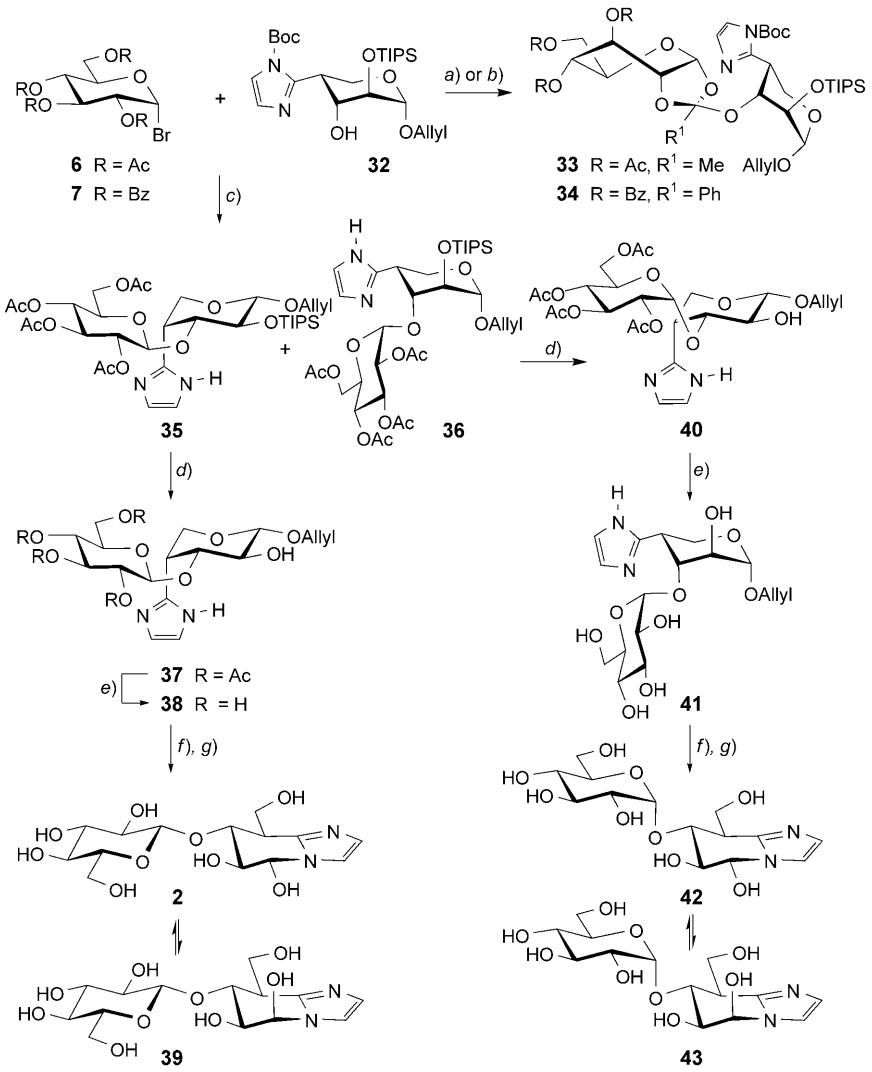
a) Allyl alcohol/conc. H_2SO_4 99:1; 95°. *b*) *Amberlyst-15*, 4-Å mol. sieves, acetone; 59% of **21**, 6% of **22**, and 13% of **21**/**22**. *c*) TsCl, pyridine; 89%. *d*) AcOH/H_2O 4:1, 110°. *e*) *t*-BuOK, THF; 71% from **23**. *f*) TIPSOTf (TIPS = (i-Pr)$_3$Si), 2,6-lutidine, DMF; 83%. *g*) Et_2AlCN, Et_2O, toluene; 78%. *h*) Me_3Al, NH_2-$CH_2CH(OMe)_2$, toluene; 67%. *i*) Boc_2O, 4-(dimethylamino)pyridine (DMAP), MeCN. *j*) *Dess–Martin* periodinane, CH_2Cl_2; 68% of **30** and 10% of **31** from **28**. *k*) $NaBH_4$, $CeCl_3 \cdot 7\ H_2O$, MeOH; 80%.

The downfield shift of the br. *d* ($J = 6.0$ Hz) for HO–C(3) of **32** at 4.73 ppm hints to an intramolecular H-bond to N(3′) of the imidazoyl moiety. $J(1,2) = 7.5$, $J(4,5_{ax}) = 11.7$, and $J(4,5_{eq}) = 6.3$ Hz of **31** are consistent with the β-D-*erythro*-configuration and a flattened $^4C_1$ conformation.

Glucosidation of **32** with **6** in the presence of $Hg(CN)_2$ and $HgBr_2$ led to the 1,2-ortho ester **33** (39%; *Scheme 4*). Similarly, the AgOTf-promoted glucosidation of **32** with the benzoylated bromide **7** gave 70% of the 1,2-ortho ester **34**. AgOTf-Promoted glucosidation of **32** with **6** in CH_2Cl_2 gave 27% of recovered **32** and a *ca.* 7:3 mixture of anomeric *N*-Boc-disaccharides, which could only be separated after their conversion to the desired β-D-glucopyranoside **35** (13%) and the α-D-anomer **36** (31%). We were not successful in improving the α/β ratio in favour of the β-D-anomer **35**, and thus proceeded to deprotect **35** and **36**. Desilylation of **35** to **37** and deacetylation gave the deprotected allyl glycoside **38** (78% overall yield) that was heated in the presence of Pd on charcoal for 24 h. Isomerisation of **38** to the (*E*)/(*Z*)-propenyl glycosides[2]) was evident from the disappearance of the ^{1}H-NMR signals of the allyl group and the appearance of Me *doublets* ($J = 6.9$ Hz) at 1.8 and 1.6 ppm in a *ca.* 4:1 ratio. This mixture was hydrolysed in acidic MeOH to yield 45% of a 45:55 equilibrium mixture of the

[2]) In several experiments, it was necessary to replace the catalyst to drive the isomerisation to completion; we assume that the catalyst was deactivated by the imidazole moiety.

Scheme 4



a) **6**, $Hg(CN)_2$, $HgBr_2$, 4-Å mol. sieves, CH_2Cl_2; 39% of **33** and 21% of **32**. *b*) **7**, AgOTf, TMU, 4-Å mol. sieves, CH_2Cl_2; 70% of **34**. *c*) i. AgOTf, 3-Å mol. sieves, CH_2Cl_2. ii. CF_3COOH/CH_2Cl_2 1:20; 13% of **35**, 31% of **36**, and 27% of **32**. *d*) $Bu_4NF \cdot 3\ H_2O$, THF; 92% of **37**; 92% of **40**. *e*) NH_3, MeOH; 85% of **38**; 82% of **41**. *f*) 10% Pd/C, MeOH, reflux. *g*) 10% aq. HCl, MeOH; 45% of **2**/**39** 45:55; 64% of **42**/**43** *ca*. 1:1.

cellobionoimidazole **2** and its *manno*-analogue **39**. In an analogous sequence, the α-D-glucopyranoside **36** was transformed *via* **40** and **41** to a *ca*. 1:1 mixture of the maltonoimidazole **42** and its *manno*-analogue **43** (48% overall yield).

A $^3S_5$ conformation of the α-D-glucopyranosyl ring of the 1,2-ortho esters **18**, **19**, **33**, and **34** is evidenced by the vicinal coupling constants $J(1^{II},2^{II}) = 5.1-5.4$, $J(2^{II},3^{II}) = 2.7-3.0$, $J(3^{II},4^{II}) = 1.6-2.1$, and $J(4^{II},5^{II}) = 8.5-9.6$

Hz, and by a long-range *w*-coupling of $\leq$1.2 Hz between H–C(2^{II}) and H–C(4^{II}) (see *Table 1* in the *Exper. Part*). H–C(1^{II}) and H–C(2^{II}) of the phenyl ortho esters **19** and **34** resonate 0.40–0.57 ppm downfield to H–C(1^{II}) and H–C(2^{II}) of the methyl ortho esters **18** and **33** (5.52/5.55 and 4.04/4.25 ppm, resp.) whereas C(1^{II}) of these four ortho esters resonates in the narrow range of 96.8–97.5 ppm (see *Table 2* in the *Exper. Part*). The β-D-configuration of **17**, **35**, **37**–**39**, and **2**, and the α-D-configuration of **13**–**16**, **36**, and **41**–**43** are evidenced by $J(1^{II},2^{II})$ of 7.5–7.8 and 3.2–3.9 Hz, respectively, and by the upfield shift of H–C(1^{II}) of the β-D-anomers ($\Delta\delta$ = 0.54–0.67 ppm). The large $J(2,3)=J(3,4)=J(4,5)$ = 9.0–10.5 Hz reveal the $^4C_1$ conformation of the glucopyranosyl moiety of these disaccharides.

Sterically demanding 1,2-disilyl ethers and related vicinal sterically demanding substituents prefer a diaxial orientation (see [57–59] and refs. cit. therein). This preference and the anomeric effect should force the α-D-arabinopyranosyl ring of the TIPS-protected disaccharides to prefer a $^4C_1$ conformation. This is indeed found for the silylated arabinopyranosyl moiety of the α-D-glucosides **13**–**19**, **33**, **34**, and **36** that adopt exclusively the $^4C_1$ conformation, as evidenced by $J(1^I,2^I)<1$, $J(2^I,3^I)=J(3^I,4^I)$ = 2.1–3.0, $J(4^I,5_{ax}{}^I)$ = 10.5–12.0, and $J(4^I,5_{eq}{}^I)$ = 3.0–4.3 Hz (see *Table 1* in the *Exper. Part*). In contradistinction, the silylated arabinopyranosyl moiety of the β-D-glucosides **17** and **35** exists as a *ca.* 1:3 mixture of $^4C_1$ and $^1C_4$ conformers, as shown by $J(1^I,2^I)$ = 4.4–5.1, $J(2^I,3^I)$ = 6.8–6.9, $J(3^I,4^I)$ = 3.0–3.8, $J(4^I,5_{ax}{}^I)$ = 5.1–6.3, and $J(4^I,5_{eq}{}^I)$ = 3.0–3.8 Hz. This observation suggests destabilising steric interactions between the glycosyl units of the β-D-glucosides. Indeed, MM3* modelling (programme Macromodel V. 6.0 [60]) of **35** and **36** confirmed this hypothesis. Minimisation of the $^4C_1$ conformers of **35** and **36** led to a single favoured conformer, with the one of **36** by 1.2 kcal/mol more stable than the one of **35** (*Fig.*). The $^1C_4$ conformer of **36** (ΔE = 5.1 kcal/mol) is more destabilised than the one of **35** (ΔE = 2.3 kcal/mol). The higher stability of the $^4C_1$ conformer of **36** may contribute to the preferred formation of this unwanted anomer in the glucosidation. Replacing the TIPS group of **32** by the sterically less demanding Bn group may lead to ring inversion to the $^1C_4$ conformer; conceivably it would preferentially lead to the desired β-D-glucopyranoside.

The desilylated β-D-glucopyranoside **37** and the α-D-glucopyranoside **40** adopt exclusively the $^1C_4$ conformation ($J(1^I,2^I)$ = 6.6–7.2, $J(2^I,3^I)$ = 9.0, $J(3^I,4^I)$ = 5.6–5.7, $J(4^I,5_{ax}{}^I)=J(4^I,5_{eq}{}^I)$ = 1.8–2.7 Hz; see *Table 1* in the *Exper. Part*). The deacetylated β-D-glucoside **38** in CD_3OD ($J(1^I,2^I)$ = 6.0, $J(2^I,3^I)$ = 8.7, $J(3^I,4^I)$ = 5.4, $J(4^I,5_{ax}{}^I)$ = 3.6 Hz) also prefers the $^1C_4$ conformation to about 85% and the α-D-glucopyranoside **41** ($J(1^I,2^I)$ = 1.8, $J(2^I,3^I)$ = 4.8, $J(3^I,4^I)$ = 3.9, $J(4^I,5_{ax}{}^I)$ = 10.8, $J(4^I,5_{eq}{}^I)$ = 3.9 Hz) flips to about 80% back into the $^4C_1$ conformation. These conformational changes are also reflected by the chemical shift of C(1^I) (**13**–**18**, **33**–**36**, and **41**: 98.3–101.6 ppm; **37**, **38**, and **40**: 102.3–103.6 ppm) and C(3^I) (**13**–**18**, **33**–**36**, and **41**: 70.2–77.4 ppm; **37**, **38**, and **40**: 80.1–82.5 ppm; *Table 2* in the *Exper. Part*).

Remarkably, the *dt*s of H–C(5^{II}) of **13**, **14**, **36** (each resonating at 2.73 ppm), **15** (3.20 ppm), and **41** (2.40 ppm) are strongly shifted to higher fields (compare their chemical shift with 3.70–4.10 ppm for the other disaccharides; *Table 1* in the *Exper. Part*). A weaker upfield shift ($\leq$0.2 ppm) is observed for the signals of both H–C(6^{II}). These H-atoms are located in the π-plane of the imidazolyl moiety, with H–C(5^{II}) nearly in the centre of the ring (see modelled $^4C_1$ conformer of **36** in the *Fig.*), and the upfield shifts reflect its anisotropy. The strong shift difference for H–C(5^{II}) of the benzoates **14** and **15** (0.47 ppm) suggests a different orientation of the imidazolyl ring; an elec-

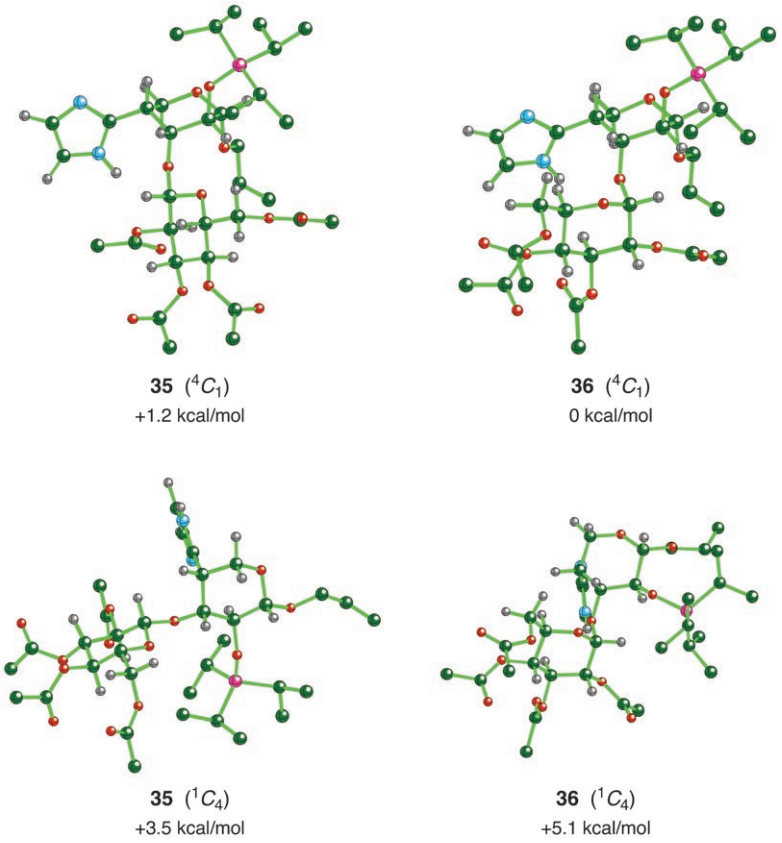


Figure. *Relative stability of the MM3*-calculated* $^4C_1$ *and* $^1C_4$ *conformers of the TIPS protected disaccharides* **35** *and* **36** (for enhanced clarity, the H-atoms of the allyl, TIPS, and Ac groups are omitted).

tronic influence of the Boc group can be excluded since H–C(5^{II}) of the bocylated **14** and the unbocylated **13** resonate at 2.73 ppm. The strongest upfield shift for H–C(5^{II}) of **41** (2.40 ppm) is due to the deacetylation and the change of the solvent to CD_3OD. There is precedent for such upfield shifts of H–C(5) and H–C(6) of an α-linked disaccharide, as reported by our group [61]. Also shielded is C(1^{II}) of the *N*-unprotected *α*-D-glucosides **13**, **15**, and **16** (92.0–92.7 ppm), and the *β*-D-glucosides **17** and **35** (97.3–97.9 ppm; compare with 94.8–96.2 and 103.6–105.1 ppm of 3-*O*-glucosylated *α*-D-altropyranosides [62]). The MeO signal of the benzoylated *α*-D-glucopyranosides **14** and **15** is shifted upfield to 2.95 and 2.70 ppm, respectively, due to an anisotropy effect of BzO–C(2^{II}). The more flexible BnO–C(2^{II}) group of the parent benzyl ether **16** can avoid such a close contact; hence, MeO of **16** resonates at 3.30 ppm.

The D-*gluco*-configuration and the $^7H_6$ conformation of the imidazopyridine moiety of **2** and **42** agree with $J(5,6) = 6.6$ Hz. The D-*manno*-epimers **39** and **43** also prefer the $^7H_6$ conformation and show a smaller $J(5,6)$ value of 3.6 Hz.

Inhibition Studies. The cellobionoimidazole **2** and its *manno*-configured epimer **39** are very weak inhibitors of the *syn*-protonating Cel7A from *T. reesi* (family 7;

IC_{50} = 4 mM at 50°). This weak inhibition strongly suggests that N(1) cannot interact with the flexible catalytic acid. Not surprisingly, the maltonoimidazole **42** and its *manno*-analogue **43** are also weak inhibitors of Cel7A.

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Experimental Part

General (including inhibition experiments). See [1].

Glycosylation of **4** *with* **6**. *a*) A suspension of **4** [1] (200 mg, 0.425 mmol), AgOTf (200 mg, 0.78 mmol) and 4-Å mol. sieves (400 mg) in CH_2Cl_2 (10 ml) was cooled to −10°, treated slowly with a suspension of **6** [20] (200 mg, 0.486 mmol) and 4-Å mol. sieves (200 mg) in CH_2Cl_2 (2 ml) over 30 min, stirred for 16 h at 0 → 16°, treated with sat. aq. $NaHCO_3$ soln. (10 ml), and extracted with AcOEt (3×35 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (10 ml) and dried (Na_2SO_4). Evaporation and FC (25 g of silica gel; hexane/AcOEt 3:2) gave an inseparable mixture of Boc-disaccharides (120 mg, *ca.* 90% pure, traces of impurity derived from **6**) and **4** (36 mg, 18%). The soln. of these Boc-disaccharides (120 mg) in CH_2Cl_2 (10 ml) was cooled to 0°, treated with CF_3COOH (0.1 ml), stirred for 4 h, neutralised with sat. aq. $NaHCO_3$ soln. (5 ml), and extracted with AcOEt (30 ml). The org. layer was washed with H_2O and brine, dried (Na_2SO_4), and evaporated. FC (4 g of silica gel, AcOEt/hexane 1:1 → AcOEt → AcOEt/MeOH 49:1) gave **13** (90 mg, 26%) and **17** (66 mg, 19%).

b) A suspension of **4** (22.5 mg, 0.048 mmol) and **6** (22 mg, 0.053 mmol) in CH_2Cl_2 (2 ml) was treated with 4-Å molecular sieves (141 mg), stirred for 1 h, cooled to 2°, treated with AgOTf (27 mg, 0.105 mmol) and *N*,*N*,*N*′,*N*′-tetramethylurea (TMU, 20 µl, 0.16 mmol), stirred for 2 h at 2 → 23° (complete consumption of **4**), and treated with sat. aq. $NaHCO_3$ soln. (2 ml). After extraction with dil. AcOEt (20 ml), the org. layer was washed with H_2O (5 ml) and brine (5 ml), dried (Na_2SO_4), and evaporated. FC (2 g of silica gel; AcOEt/hexane 2:3) gave crude **18** (37 mg, 96%; *ca.* 90% pure).

Methyl 2,3,4,6-Tetra-O-*acetyl*-α-D-*glucopyranosyl-(1 → 3)-4-deoxy-4-(1*H-*imidazol-2-yl)-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**13**). Colourless solid. R_f (AcOEt) 0.48. M.p. 174.2–174.5°. $[\alpha]_D^{25}$ = +155.4 (c = 0.35, $CHCl_3$). IR ($CHCl_3$): 3457*w*, 3233*w*, 3028*w*, 2947*m*, 2868*w*, 1750*s*, 1549*w*, 1464*w*, 1367*m*, 1236*s*, 1123*m*, 1075*m*, 1039*s*, 988w, 883*m*, 845*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 9.44 (br. *s*, exchanged with D_2O, NH); 7.06 (br. *s*, H−C(4′), H−C(5′)); 3.37 (*s*, MeO); 2.09, 2.06, 2.04, 1.98 (4*s*, 4 AcO); 1.23–1.00 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignment based on a HSQC spectrum): see *Table 2*; additionally, 170.46, 170.31, 169.75, 169.35 (4*s*, 4 C=O); 145.35 (*s*, C(2′)); 128.0 (br. *d*, C(4′)); 116.5 (br. *d*, C(5′)); 55.70 (*q*, MeO); 20.90 (*q*, 2 Me); 20.82, 20.73 (2*q*, 2 Me); 18.18 (*q*, $(Me_2CH)_3Si$); 12.39 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 723.3119 ($[M+Na]^+$, $C_{32}H_{52}N_2NaO_{13}Si^+$; calc. 723.3131). Anal. calc. for $C_{32}H_{52}N_2O_{13}Si \cdot 0.5\ H_2O$ (709.854): C 54.14, H 7.53, N 3.92; found: C 54.26, H 7.42, N 3.95.

Methyl 2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl-(1 → 3)-4-deoxy-4-(1*H-*imidazol-2-yl)-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**17**). Colourless syrup. R_f (AcOEt) 0.22. $[\alpha]_D^{25}$ = −25.4 (c = 0.5, $CHCl_3$). IR ($CHCl_3$): 3428*w*, 3027*w*, 2945*m*, 2867*w*, 1755*s*, 1602*w*, 1545*w*, 1463*m*, 1368*s*, 1256*m*, 1140*m*, 1066*s*, 1041*s*, 968*w*, 864*m*, 845*m*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 9.50 (br. *s*, exchanged with D_2O, NH); 6.97 (br. *s*, H−C(4′), H−C(5′)); 3.46 (*s*, MeO); 2.07, 2.02, 1.98, 1.84 (4*s*, 4 AcO); 1.23–1.00 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 2*; additionally, 170.54, 170.07, 169.35, 169.13 (4*s*, 4 C=O); 145.34 (*s*, C(2′)); 130–120 (br. hump; C(4′), C(5′)); 56.64 (*q*, MeO); 20.87, 20.82, 20.80, 20.71 (4*q*, 4 Me); 18.26, 18.23 (2*q*, $(Me_2CH)_3Si$); 12.57 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 723.3139 ($[M+Na]^+$, $C_{32}H_{52}N_2NaO_{13}Si^+$; calc. 723.3131). Anal. calc. for $C_{32}H_{52}N_2O_{13}Si$ (700.854): C 54.84, H 7.48, N 4.00; found: C 54.58, H 7.40, N 4.04.

Crude Methyl (S)-*3,4,6-Tri*-O-*acetyl-1,2*-O-*(methylmethanediyl)*-α-D-*glucopyranose-(1² → 3)-(4-[1-[(*tert-*butoxy)carbonyl]-1*H-*imidazol-2-yl]-4-deoxy-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**18**; *ca.* 90% pure). Colourless oil. R_f (AcOEt/hexane 4:1) 0.31. $[\alpha]_D^{25}$ = +102.1 (c = 0.9, $CHCl_3$). IR ($CHCl_3$): 2960*m*, 2947*m*, 2868*m*, 1755*m*, 1463*w*, 1371*s*, 1335*w*, 1306*s*, 1260*s*, 1140*s*, 1094*s*, 1042*s*, 986*m*, 926*w*, 883*w*, 844*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; impurity was not assigned): see *Table 1*; additionally, 7.24 (*d*, J = 1.8, H−C(5′)); 6.83 (*d*, J = 1.8, H−C(4′)); 3.30 (*s*, MeO); 2.08, 2.06, 2.04 (3*s*, 3 AcO); 1.58 (*s*, *t*-Bu); 1.22 (*s*, Me); 1.14–1.08 (*m*,

$(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 170.47, 169.36, 169.62 (3*s*, 3 OC=O); 148.64 (*s*, NC=O); 147.27 (*s*, C(2′)); 127.47 (*d*, C(4′)); 120.86 (*s*, *C*(OR)$_3$); 117.96 (*d*, C(5′)); 85.01 (*s*, Me_3C); 55.15 (*q*, MeO); 27.77 (*q*, *Me*$_3$C); 20.78 (*q*, 3 *Me*C=O); 19.72 (*q*, Me); 18.03 (*q*, (*Me*$_2$CH)$_3$Si); 12.33 (*d*, (Me$_2$*C*H)$_3$Si). HR-MALDI-MS: 723.3121 ([*M* – Boc + Na]$^+$, $C_{32}H_{52}N_2NaO_{13}Si^+$; calc. 723.3131).

Glycosidation of **4** *with* **7**. *a*) A suspension of **4** (112 mg, 0.24 mmol), **7** [31] (182 mg, 0.445 mmol), and 4-Å mol. sieves (520 mg) in CH_2Cl_2 (2 ml) was stirred for 45 min at 24°, cooled to 2°, treated with AgOTf (126 mg, 0.49 mmol), warmed to 24°, stirred further for 24 h, treated with sat. aq. $NaHCO_3$ soln. (1 ml), and extracted with AcOEt (3 × 15 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (10 ml) and dried (Na_2SO_4). Evaporation and FC (8 g of silica gel; hexane/AcOEt 7:3 → 11:9) gave **14** (76 mg, 30%) and **15** (65 mg, 29%).

b) A suspension of **4** (120 mg, 0.255 mmol) and **7** (274 mg, 0.42 mmol) in CH_2Cl_2 (6 ml) was treated with 4-Å mol. sieves, stirred at 27° for 1 h, cooled to 2°, treated with AgOTf (192 mg, 0.75 mmol) and TMU (100 µl, 0.835 mmol), stirred for 14 h at 2 → 23° (disappearance of **4**), diluted with AcOEt (50 ml), washed with H_2O (5 ml) and brine (5 ml), dried (Na_2SO_4), and evaporated. FC (5 g of silica gel; CH_2Cl_2/hexane 1:19) gave **19** (229 mg, 86%).

Methyl 2,3,4,6-Tetra-O-*benzoyl*-α-D-*glucopyranosyl-(1 → 3)-4-{1-[(*tert-*butoxy)carbonyl]imidazol-2-yl}-4-deoxy-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**14**). Colourless oil. R_f (hexane/AcOEt 4:1) 0.21, R_f (hexane/AcOEt 7:3) 0.32. $[\alpha]_D^{25} = +168.8$ ($c = 1.05$ $CHCl_3$). IR ($CHCl_3$): 2946*m*, 2868*w*, 1762*m*, 1728*s*, 1602*w*, 1585*w*, 1494*w*, 1452*m*, 1373*m*, 1334*m*, 1304*s*, 1271*s*, 1141*s*, 1104*s*, 1070*m*, 1039*s*, 1028*s*, 991*m*, 882*w*, 843*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 8.04–8.01 (*m*, 4 arom. H); 7.92–7.86 (*m*, 4 arom. H); 7.56–7.24 (*m*, (12 arom. H); 7.33 (*d*, *J* = 2.1, H–C(5′)); 6.97 (*d*, *J* = 1.5, H–C(4′)); 2.95 (*s*, MeO); 1.58 (*s*, *t*-Bu); 1.10–1.00 (*m*, (Me$_2$-CH)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 166.05, 166.03, 165.03, 164.88 (4*s*, 4 OC=O); 149.06 (*s*, NC=O); 147.06 (*s*, C(2′)); 133.18, 133.03, 132.87, 132.81 (4*s*); 130.08–128.61 (several *d*); 127.71 (*d*, C(4′)); 118.53 (*d*, C(5′)); 85.77 (*s*, Me_3C); 54.55 (*q*, MeO); 27.86 (*q*, *Me*$_3$C); 18.09, 18.02 (2*q*, (*Me*$_2$CH)$_3$Si); 12.24 (*d*, (Me$_2$*C*H)$_3$Si). HR-MALDI-MS: 1071.4290 ([*M* + Na]$^+$, $C_{57}H_{68}N_2NaO_{15}Si^+$; calc. 1071.4281).

Methyl 2,3,4,6-Tetra-O-*acetyl*-β-D-*glucopyranosyl-(1 → 3)-4-(1*H-*imidazol-2-yl)-4-deoxy-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**15**). Colourless oil. R_f (hexane/AcOEt 3:2) 0.20. $[\alpha]_D^{25} = +160.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3457*w*, 3226*w*, 2947*m*, 2868*w*, 1728*s*, 1602*w*, 1585*w*, 1548*w*, 1452*m*, 1370*m*, 1334*m*, 1316*m*, 1271*s*, 1111*s*, 1104*s*, 1070*m*, 1038*s*, 1028*s*, 882*w*, 846*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; *ca.* 90% pure): 9.98 (br. *s*, exchanged with D_2O, NH); see *Table 1*; additionally, 8.07–7.99 (*m*, 4 arom. H); 7.92–7.85 (*m*, 4 arom. H); 7.55–7.28 (*m*, 12 arom. H); 7.22 (br. *s*, H–C(5′)); 6.97 (br. *s*, H–C(4′)); 2.70 (*s*, MeO); 1.05–1.00 (*m*, (Me$_2$-CH)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 166.30 165.99, 165.46, 164.79 (4*s*, 4 C=O); 145.70 (*s*, C(2′)); 133.40 (*s*, 2 C); 133.37, 133.01 (2*s*); 129.77–128.37 (several *d*); 128.09 (*d*, C(4′)); 116.35 (*d*, C(5′)); 55.10 (*q*, MeO); 18.15 (*q*, (*Me*$_2$CH)$_3$Si); 12.35 (*d*, (Me$_2$*C*H)$_3$Si). HR-MALDI-MS: 971.3745 ([*M* + Na]$^+$, $C_{52}H_{60}N_2NaO_{13}Si^+$; calc. 971.3757).

Methyl (S)-*3,4,6-Tri*-O-*benzoyl-1,2*-O-*(phenylmethanediyl)*-α-D-*glucopyranose-(1² → 3)-(4-{1-[(*tert-*butoxy)carbonyl]-1*H-*imidazol-2-yl}-4-deoxy-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**19**). Colourless oil solidifying upon storage. R_f (CH_2Cl_2/MeOH 4:1) 0.31. M.p.: 143.3–144.1°. $[\alpha]_D^{25} = +63.9$ ($c = 0.38$, MeOH). IR ($CHCl_3$): 3017*s*, 2976*m*, 2945*m*, 2895*m*, 2868*m*, 1762*m*, 1725*s*, 1602*w*, 1584*w*, 1522*w*, 1476*m*, 1451*w*, 1421*w*, 1372*w*, 1337*w*, 1307*s*, 1228*s*, 1142*s*, 1096*s*, 1043*s*, 970*w*, 880*m*, 848*m*. ^{1}H-NMR (500 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 8.07 (br. *dq*, *J* = 8.2, 1.2, 2 arom. H); 7.96 (br. *dq*, *J* = 8.3, 1.2, 2 arom. H); 7.72 (br. *dq*, *J* = 8.3, 1.2, 2 arom. H); 7.55–7.44 (*m*, 4 arom. H); 7.50 (*tt*, *J* = 7.5, 1.3, 1 arom. H); 7.32–7.26 (*m*, 7 arom H); 7.20–7.18 (*m*, 2 arom H); 7.17 (*d*, *J* = 1.7, H–C(5′)); 6.89 (*d*, *J* = 1.7, H–C(4′)); 3.31 (*s*, MeO); 1.38 (*s*, *t*-Bu); 1.05–1.00 (*m*, (Me$_2$CH)$_3$Si). ^{13}C-NMR (75 MHz, $CDCl_3$; assignments based on a HSQC spectrum): see *Table 2*; additionally, 166.08, 165.13, 164.44 (3*s*, 3 OC=O); 148.91 (*s*, NC=O); 146.74 (*s*, C(2′)); 135.19, 133.62, 133.33, 133.06 (4*s*); 129.94–127.80 (several *d*); 127.56 (*d*, C(4′)); 126.41 (*d*); 121.12 (*s*, (Ph*C*O$_3$); 118.22 (*d*, C(5′)); 84.35 (*s*, Me$_3$*C*); 55.14 (*q*, MeO); 27.68 (*q*, *Me*$_3$C); 18.09, 18.06 (2*q*, (*Me*$_2$CH)$_3$Si); 12.19 (*d*, (Me$_2$*C*H)$_3$Si). HR-MALDI-MS: 1071.4279 ([*M* + Na]$^+$, $C_{57}H_{68}N_2NaO_{15}Si^+$; calc. 1071.4281). Anal. calc. for $C_{57}H_{68}N_2O_{15}Si$ (1048.44): C 65.25, H 6.53, N 2.67; found: C 65.33, H 6.40, N 2.64.

Attempted Glycosidation of **4** *with* **11**. A mixture of **4** (40 mg, 0.085 mmol), **11** [40][41] (43.7 mg, 0.088 mmol), and 4-Å molecular sieves (92 mg) in dry CH_2Cl_2 (3 ml) was cooled to −78°, treated with trimethylsilyl triflate (TMSOTf; twice 3 µl, 0.033 mmol), stirred for 2 h at −30°, treated with sat. aq. $NaHCO_3$ soln. (3 ml), and diluted with AcOEt (20 ml). The org. layer was separated, washed with H_2O (25 ml), dried (Na_2SO_4), and evaporated. FC (4 g of silica gel; hexane/AcOEt 4:1) provided **5** (18 mg, 99%) and a mixture of **4** and **11** (42 mg).

Table 1. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Ortho Esters* **18**, **19**, **33**, *and* **34**, *the* α-D-*Glucopyranosides* **13**–**16**, **36**, **40**, *and* **41**, *and* β-D-*Glucopyranosides* **17**, **35**, **37**, *and* **38** *in* $CDCl_3$[a])

	18[b])	**33**	**19**[c])	**34**[b])	**13**[c])	**14**[b])	**15**	**16**
H–C(1^I)	4.55	4.71	4.56	4.71	4.57	4.46	4.44	4.64
H–C(2^I)	3.91	3.96	4.16	4.25	3.92	3.71	3.71	4.07
H–C(3^I)	4.33	4.35	4.10	4.10–4.04	4.00	4.47	4.15	4.395
H–C(4^I)	4.17	4.22	4.08	4.10–4.04	3.87	4.24	3.94	4.27
H_a–C(5^I)	4.48	4.54	4.62	4.67	4.25	4.76	4.30	4.755
H_b–C(5^I)	3.71	3.71	3.71	3.72	3.67	3.67	3.67	3.79
H–C(1^{II})	5.52	5.55	5.92	5.98	5.44	5.49	5.72	5.11
H–C(2^{II})	4.04	4.25	4.61	4.74	4.77	5.03	5.15	3.48
H–C(3^{II})	5.06	5.10	5.55	5.58	5.29	6.08	5.99	3.75
H–C(4^{II})	4.84	4.86	5.37	5.36	4.96	5.67	5.68	3.59
H–C(5^{II})	3.80	3.80	4.04	4.10	2.73	2.73	3.20	2.54
H_a–C(6^{II})	4.16	4.18	4.49	4.53	4.01	4.16	4.35	3.47
H_b–C(6^{II})	4.09	4.09	4.32	4.34	3.82	4.00	4.23	3.23
$J(1^I,2^I)$	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.9	<1.0
$J(2^I,3^I)$	2.7	3.0	3.0	[d])	3.0	2.1	3.0	2.4
$J(3^I,4^I)$	2.7	3.0	[d])	[d])	3.3	3.0	2.7	3.0
$J(4^I,5a^I)$	11.1	11.4	11.2	10.5	12.0	11.1	10.8	11.7
$J(4^I,5b^I)$	3.6	3.6	3.7	3.0	4.2	4.3	4.2	3.9
$J(5a^I,5b^I)$	10.8	10.8	11.2	10.5	10.8	10.8	10.8	11.4
$J(1^{II},2^{II})$	5.1	5.4	5.2	5.1	3.8	3.8	3.6	3.2
$J(2^{II},3^{II})$	2.7	3.0	3.0	3.0	10.5	10.1	10.1	9.3
$J(3^{II},4^{II})$	2.1	1.9	1.5	1.6	9.6	9.9	9.9	9.3
$J(4^{II},5^{II})$	9.6	9.6	8.7	8.5	9.6	9.9	9.7	9.6
$J(5^{II},6a^{II})$	4.8	4.7	2.7	2.7	3.3	3.3	3.0	1.8
$J(5^{II},6b^{II})$	3.0	2.7	5.6	5.6	2.1	2.1	3.0	1.8
$J(6a^{II},6b^{II})$	12.1	12.0	12.1	12.0	12.3	12.3	12.3	10.8
$^4J(2^{II},4^{II})$	<0.5	1.2	0.8	1.2	–	–	–	–

	36[b])	**40**[c])	**41**[a])	**17**[c])	**35**[b])	**37**[b])	**38**[a])
H–C(1^I)	4.74	4.39	4.68	4.32	4.51	4.35	4.41
H–C(2^I)	3.89	3.63	3.75	3.79	3.645	3.54	3.67–3.57
H–C(3^I)	4.02	3.88	4.05	4.12	3.89	3.94	4.05
H–C(4^I)	3.88	3.58	3.60	3.72	3.72	3.45	3.42–3.23
H_a–C(5^I)	4.32	4.37	4.39	4.20	4.17	4.44	4.36
H_b–C(5^I)	3.67	3.72	3.74	3.66	3.64	3.64	3.67–3.57
H–C(1^{II})	5.40	5.45	4.94	4.90	4.85	4.78	4.55
H–C(2^{II})	4.76	4.89	3.23	4.96	4.97	5.02	3.42–3.23
H–C(3^{II})	5.28	5.33	3.39	5.17	5.18	5.30	3.67–3.57
H–C(4^{II})	4.96	5.07	3.21	5.11	5.11	5.06	3.42–3.23
H–C(5^{II})	2.73	4.19	2.40	3.71	3.71	3.78	3.42–3.23
H_a–C(6^{II})	3.99	4.28	3.45	4.21	4.23	4.20	3.86
H_b–C(6^{II})	3.82	4.16	3.32	4.16	4.14	4.14	3.73
$J(1^I,2^I)$	<1.0	6.6	1.8	5.1	4.4	7.2	6.0
$J(2^I,3^I)$	3.0	9.0	4.8	6.9	6.8	9.0	8.7
$J(3^I,4^I)$	4.8	5.6	3.9	4.5	4.5	5.7	5.4
$J(4^I,5a^I)$	12.0	2.7	10.8	5.1	6.3	1.8	3.6
$J(4^I,5b^I)$	3.8	2.7	3.9	3.0	3.8	2.1	[d])
$J(5a^I,5b^I)$	10.8	12.0	10.8	11.1	11.4	12.0	12.6
$J(1^{II},2^{II})$	3.6	3.6	3.6	7.8	7.8	7.5	7.5
$J(2^{II},3^{II})$	10.4	10.2	9.6	9.0	9.0	9.3	[d])

Table 1 (cont.)

	36[b])	**40**[c])	**41**[a])	**17**[c])	**35**[b])	**37**[b])	**38**[a])
$J(3^{II},4^{II})$	9.6	9.9	9.6	9.3	9.3	9.3	[d])
$J(4^{II},5^{II})$	9.9	9.9	9.6	9.9	9.3	9.6	[d])
$J(5^{II},6a^{II})$	3.3	3.0	3.6	3.9	3.6	4.2	2.1
$J(5^{II},6b^{II})$	2.1	2.1	2.4	2.6	2.6	2.4	2.6
$J(6a^{II},6b^{II})$	12.4	12.0	12.0	12.0	12.3	13.2	12.0

[a]) **38** and **41** in CD_3OD. [b]) Assignments based on selective homodecoupling experiments. [c]) Assignments based on a DQFCOSY and a HSQC spectrum. [d]) Not assigned.

Table 2. *Selected* ^{13}*C-NMR Chemical-Shift Values* [ppm] *of the Ortho Esters* **18**, **19**, **33**, *and* **34**, *the* α-D-*Glucopyranosides* **13**–**16**, **36**, **40**, *and* **41**, *and* β-D-*Glucopyranosides* **17**, **35**, **37**, *and* **38** *in* $CDCl_3$[a])

	18	**33**	**19**[b])	**34**	**13**[b])	**14**	**15**	**16**
$C(1^I)$	101.39	99.55	101.65	101.21	101.32	101.46	101.01	101.45
$C(2^I)$	66.69	66.67	67.41	67.51	64.48	66.98[c])	64.39	65.25
$C(3^I)$	70.25	70.42	70.18	70.19	72.78	76.04	72.91	71.85
$C(4^I)$	35.47	35.48	35.27	35.29	36.86	36.02	35.90	35.67
$C(5^I)$	56.82	57.09	57.01	57.17	56.66	56.42	56.47	56.78
$C(1^{II})$	96.80	96.98	97.37	97.45	92.03	95.79	92.36	94.15
$C(2^{II})$	72.81	73.03	72.50	72.37	71.06	72.63	72.25	79.44
$C(3^{II})$	69.95	69.88	69.40	68.83	69.71	70.31	71.20	81.39
$C(4^{II})$	68.29	68.35	68.47	68.33	67.52	67.18[c])	68.13	76.66
$C(5^{II})$	68.29	68.47	67.73	67.75	67.74	68.99[c])	68.42	70.39
$C(6^{II})$	62.90	63.02	61.14	64.26	61.21	62.62	62.33	67.84

	36	**40**[b])	**41**[a])	**17**[b])	**35**	**37**	**38**[a])
$C(1^I)$	98.32	102.26	101.34	104.32	101.59	102.52	103.60
$C(2^I)$	65.05	71.04	73.99	70.65	70.30	70.50	71.48
$C(3^I)$	73.38	80.79	77.48	77.01	77.35	82.50	80.10
$C(4^I)$	36.86	40.51	37.27	36.82	36.65	39.11	38.95
$C(5^I)$	56.62	64.36	58.86	61.74	61.16	61.69	62.75
$C(1^{II})$	92.65	97.88	99.67	97.37	97.88	100.04	103.06
$C(2^{II})$	70.94	71.39	75.61	71.64	71.72	71.01	75.05
$C(3^{II})$	69.76	70.05	73.50	73.21	73.22	72.34	78.34
$C(4^{II})$	67.48	68.04	70.33	68.33	69.44	68.27	71.08
$C(5^{II})$	67.69	68.12	70.64	71.84	71.87	72.07	78.13
$C(6^{II})$	61.14	61.88	61.90	61.87	61.79	63.92	62.96

[a]) **38** and **41** in CD_3OD. [b]) Assignments based on a HSQC spectrum. [c]) Assignments may be interchanged.

*Methyl 4-[1-[(*tert-*Butoxy)carbonyl)]-1*H-*imidazol-2-yl]-4-deoxy-2*-O-*(triisopropylsilyl)-3*-O-*(trimethylsilyl)*α-D-*arabinopyranoside* (**5**). Colourless oil. R_f (hexane/AcOEt 7:3) 0.10. $[\alpha]_D^{25} = +154.3$ ($c = 0.5$, $CHCl_3$). IR ($CHCl_3$): 2947*m*, 2867*m*, 1762*m*, 1500*w*, 1463*w*, 1372*w*, 1333*w*, 1306*s*, 1262*m*, 1141*s*, 1100*m*, 1119*m*, 1055*m*, 1036*m*, 991*w*, 898*m*, 843*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.27 (*d*, $J = 1.5$, H–C(5′)); 6.87 (*d*, $J = 1.5$ H–C(4′)); 4.59 (*t*, $J = 11.4$, H_{ax}–C(5)); 4.58 (br. *s*, H–C(1)); 4.39 (br. *t*, $J \approx 3.6$, H–C(3)); 4.15 (*dt*, $J \approx 11.1$, 3.6, H–C(4)); 3.74 (br. *d*, $J = 3.6$, H–C(2)); 3.70 (br. *dd*, $J \approx 10.8$, 3.6, H_{eq}–C(5)); 3.36 (*s*, MeO); 1.59 (*s*, *t*-Bu); 1.13 (br. *s*, $(Me_2CH)_3Si$); 0.18 (*s*, Me_3Si). ^{13}C-NMR (75 MHz, $CDCl_3$): 149.50 (*s*, C=O); 147.36 (*s*, C(2′)); 127.62 (*d*, C(4′)); 117.91 (*d*, C(5′)); 102.02 (*d*, C(1)); 84.78 (*s*, Me_3C); 70.63, 69.73 (2*d*, C(2), C(3)); 56.58 (*t*, C(5)); 55.20 (*q*, MeO); 37.01 (*d*, C(4)); 27.95 (*q*, Me_3C); 18.25, 18.19 (*q*, $(Me_2CH)_3Si$); 12.49 (*d*, $Me_2CH)_3Si$); −0.29 (*q*, Me_3Si).

Glycosidation of **4** *with* **12**. A suspension of **4** (15 mg, 0.031 mmol), **12** [42] (41 mg, 0.67 mmol), and 4-Å mol. sieves (198 mg) in CH_2Cl_2 (2 ml) was stirred for 45 min at 23°, cooled to −20°, treated with $Zn(OTf)_2$ (15 mg, 0.041 mmol), stirred for 2 h, warmed to 23°, stirred for another 2 h, treated with sat. aq. $NaHCO_3$ soln. (2 ml), and extracted with AcOEt (3×5 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (2 ml) and dried (Na_2SO_4). Evaporation and FC (2 g of silica gel, hexane/AcOEt 9:1 → 17:3) gave **16** (12 mg, 30%) and **4** (4 mg, 27%).

Methyl 2,3,4,6-Tetra-O-*benzyl*-α-D-*glucopyranosyl-(1 → 3)-4-[1-[(*tert-*butoxy)carbonyl]-2*H-*imidazol-2-yl]-4-deoxy-2*-O-*(triisopropylsilyl)*-α-D-*arabinopyranoside* (**16**). Colourless oil. R_f (hexane/AcOEt 4:1) 0.60. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.44–7.39 (*m*, 2 arom. H); 7.35–7.22 (*m*, 16 arom. H); 7.20–7.15 (*m*, 2 arom. H); 7.17 (*d*, *J* = 1.8, H–C(5′)); 6.84 (*d*, *J* = 1.8, H–C(4′)); 4.91, 4.64 (2*d*, *J* = 10.8, PhCH_2); 4.82, 4.42 (2*d*, *J* = 11.8, PhCH_2); 4.81, 4.65 (2*d*, *J* = 12.0, PhCH_2); 4.52, 4.44 (2*d*, *J* = 12.3, PhCH_2); 3.30 (*s*, MeO); 1.51 (*s*, *t*-Bu); 1.14–1.10 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 148.98 (*s*, NC=O); 147.38 (*s*, C(2′)); 139.41, 138.96, 138.86, 137.94 (4*s*); 128.40–126.86 (several *d* including *d* of C(4′)); 118.14 (*d*, C(5′)); 85.02 (*s*, Me_3C); 75.70, 73.97, 73.64, 71.68 (4*t*, 4 PhCH_2); 55.06 (*q*, MeO); 27.81 (*q*, Me_3C); 18.13, 18.10 (2*q*, $(Me_2CH)_3Si$); 12.30 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS (complete debocylation during the measurement): 915.4584 (94, $[M+Na]^+$, $C_{52}H_{68}N_2NaO_9Si^+$; calc. 915.4586), 893.4697 (93, $[M+H]^+$, $C_{52}H_{69}N_2O_9Si^+$; calc. 893.4767), 861.4439 (100, $[M-MeO]^+$, $C_{51}H_{65}N_2O_9Si^+$; calc. 861.4505).

*Allyl α/β-*D-*Lyxopyranoside* (**20**). An ice cold soln. of D-lyxose (41.63 g, 277 mmol) in anh. AllOH (180 ml) was treated dropwise with conc. H_2SO_4 (1.8 ml, 14.08 mmol), warmed to 23°, heated to 95° for 3 h (disappearance of D-lyxose), cooled, neutralised with Ag_2CO_3 (*ca.* 4.8 g, pH *ca.* 7), filtered, and evaporated. Filtration through a short plug of silica gel (25 g; MeOH/CH_2Cl_2 1:4) and evaporation gave crude **20** (60 g), which was used for the next step without further purification. A pure sample of α-D-**20** was obtained by FC (silica gel; MeOH/CH_2Cl_2 1:4). Thick oil solidifying upon storage. R_f (CH_2Cl_2/MeOH 4:1) 0.55. M.p.: 76–79°. $[\alpha]_D^{25} = +60.7$ (*c* = 1.3, MeOH). IR (ATR): 3301*m*, 2989*w*, 2943*w*, 2892*w*, 2864*w*, 1646*w*, 1466*w*, 1409*w*, 1375*w*, 1300*m*, 1149*w*, 1129*m*, 1103*m*, 1084*m*, 1070*s*, 1008*s*, 921*m*, 883*m*, 856*w*. ^{1}H-NMR (300 MHz, D_2O): 5.85 (*dddd*, *J* = 16.8, 10.5, 6.3, 5.7, $CH_2=CH$); 5.26 (*dq*, *J* = 17.1, 1.5), 5.12 (*dq*, *J* = 10.2, 1.2) (CH_2=CH); 4.72 (*d*, *J* = 3.0, H–C(1)); 4.13 (*ddt*, *J* = 12.9, 5.6, 1.5), 3.96 (*ddt*, *J* = 12.9, 6.3, 1.5) (CH_2=CHCH_2); 3.80–3.66 (*m*, H–C(2), H–C(3), H–C(4), H_{eq}–C(5)); 3.43 (*dd*, *J* = 10.6, 8.4, H_{ax}–C(5)). ^{13}C-NMR (75 MHz, D_2O): 133.05 (*d*, CH_2=CH); 118.36 (*t*, CH_2=CH); 99.16 (*d*, C(1)); 70.50, 69.47 (2*d*, C(2), C(3)); 68.64 (*t*, CH_2=CHCH_2); 66.74 (*d*, C(4)); 62.50 (*t*, C(5)). Anal. calc. for $C_8H_{14}O_5 \cdot 0.1\ H_2O$ (191.99): C 50.09, H 7.49; found: C 49.64, H 6.95.

Isopropylidenation of Crude **20**. A soln. of crude **20** (60 g, 54.7 mmol) in anh. acetone (400 ml) was treated with powdered 4-Å mol. sieves (73 g) and *Amberlyst-15* (H^+ form, 13.2 g). The resulting suspension was stirred at 23° for 20 h (disappearance of **20**) and filtered through a short plug of *Celite* (4×4 cm; washing with additional 100 ml of acetone). Evaporation and FC (156 g of silica gel; hexane/AcOEt 4:1 → 2:1 → 1:1) gave **21** (37.5 g, 59% from D-lyxose), **21**/**22** (8.3 g, 13%), and **22** (4.2 g, 6%).

Allyl 2,3-O-*Isopropylidene*-α-D-*lyxopyranoside* (**21**). Viscous oil solidifying to a colourless solid upon storage. R_f (hexane/AcOEt 1:1) 0.62. M.p. 43.1–44.4°. $[\alpha]_D^{25} = +62.6$ (*c* = 0.81, $CHCl_3$). IR ($CHCl_3$): 3591*w* (sh), 3454*w*, 3017*s*, 2991*w*, 2939*w*, 1457*w*, 1384*m*, 1375*m*, 1234*m*, 1164*m*, 1141*m*, 1075*s*, 1005*m*, 936*m*, 908*w*, 873*w*, 856*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.90 (*dddd*, *J* = 17.4, 10.5, 6.3, 5.7, $CH_2=CH$); 5.32 (*dq*, *J* = 17.1, 1.5), 5.23 (*dq*, *J* = 10.5, 1.5) (CH_2=CH); 4.28 (*ddt*, *J* = 12.9, 5.1, 1.5), 4.07 (*ddt*, *J* = 12.9, 6.3, 1.5) (CH_2=CHCH_2); 3.08 (*d*, *J* = 7.8, exchanged with D_2O, HO–C(4)); 1.50, 1.36 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 133.40 (*d*, CH_2=CH); 118.20 (*t*, CH_2=CH); 109.57 (*s*, Me_2C); 68.86 (*t*, CH_2=CHCH_2); 27.54, 25.62 (2*q*, Me_2C). Anal. calc. for $C_{11}H_{18}O_5$ (230.26): C 57.38, H 7.88; found: C 57.50, H 8.04.

Allyl 2,3-O-*Isopropylidene*-β-D-*lyxopyranoside* (**22**). Colourless oil. R_f (hexane/AcOEt 1:1) 0.43. $[\alpha]_D^{25} = -86.5$ (*c* = 4.5, $CHCl_3$). IR ($CHCl_3$): 3458*w*, 2991*w*, 2939*w*, 1457*w*, 1384*w*, 1375*w*, 1263*m*, 1163*m*, 1140*m*, 1073*s*, 1009*s*, 937*m*, 856*w*, 823*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.89 (*dddd*, *J* = 17.1, 10.2, 6.6, 5.1, $CH_2=CH$); 5.29 (*dq*, *J* = 17.1, 1.5), 5.16 (*dq*, *J* = 10.5, 1.5) (CH_2=CH); 4.30 (*ddt*, *J* = 12.6, 4.8, 1.5), 4.08 (*ddt*, *J* = 12.6, 6.6, 1.5) (CH_2=CHCH_2); 3.08 (*d*, *J* = 4.5, exchanged with D_2O, HO–C(4)); 1.50, 1.39 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 133.92 (*d*, CH_2=CH); 117.97 (*t*, CH_2=CH); 110.50 (*s*, Me_2C); 68.86 (*t*, CH_2=CHCH_2); 27.04, 25.96 (2*q*, Me_2C). Anal. calc. for $C_{11}H_{18}O_5$ (230.26): C 57.38, H 7.88; found: C 57.50, H 8.04.

Allyl 2,3-O-*Isopropylidene-4*-O-*[4-methylphenylsulfonyl]*-α-D-*lyxopyranoside* (**23**). A soln. of **21** (8.5 g, 36.9 mmol) in dry pyridine (20 ml, 245 mmol) was treated with TsCl (9.65 g, 50.79 mmol; → thick slurry), stirred at 23° for 20 h, diluted with Et_2O (500 ml), washed with 10% aq. HCl (2×50 ml), H_2O (2×50 ml), and brine (25 ml), dried (Na_2SO_4), and evaporated. FC (*ca.* 120 g of silica gel; 600 ml of hexane/AcOEt 9:1 and 300 ml of hex-

Table 3. *Selected ^{1}H-NMR Chemical-Shift Values* [ppm] *and Coupling Constants* [Hz] *of the Monosaccharides* **21**–**32** *in $CDCl_3$*

	21	**22**[a])	**23**	**24**	**25**[a])	**26**
H–C(1)	4.81	4.74	4.88	4.77	4.53	4.44
H–C(2)	4.17	4.20	4.08	4.01–3.92	3.75	3.97
H–C(3)	4.26	4.07	4.17	4.01–3.92	3.49[b])	3.36[c])
H–C(4)	3.80–3.78	3.87	4.40	4.62	3.34	3.41
H_a–C(5)	3.80–3.78	3.96	3.77	3.67–3.58	3.98[b])	4.04
H_b–C(5)	3.70	3.25	3.66	3.67–3.58	3.90	3.92[c])
J(1,2)	2.7	3.3	1.5	2.7	2.4	4.4
J(2,3)	6.3	6.0	6.3	[d])	4.5	2.9
J(3,4)	5.4	5.4	6.6	8.1	4.5	3.9
J(4,5a)	[d])	4.5	5.0	6.3	1.5	2.4
J(4,5b)	6.9	6.6	9.8	8.1	0.9	1.0
J(5a,5b)	12.9	10.8	11.4	[d])	13.4	13.4
	27	**28**	**29**	**30**	**31**[a])	**32**
H–C(1)	4.61	4.87	4.86	5.02	4.48	4.79
H–C(2)	3.98	4.02	4.09	4.12	4.44	3.97
H–C(3)	4.03	4.08	4.26–4.23	–	–	4.27[e])
H–C(4)	3.01	3.32	4.26–4.23	5.28	4.63	4.19
H_a–C(5)	3.87	4.28	4.02	4.56	4.51	4.35
H_b–C(5)	3.79	3.90	3.82	4.28	4.13	3.70[e])
J(1,2)	2.4	2.0	1.8	2.0	7.5	1.2
J(2,3)	3.0	3.3	2.5	–	–	3.0
J(3,4)	9.6	10.8	[d])	–	–	2.1
J(4,5a)	5.1	4.8	10.8	11.1	6.3	11.4
J(4,5b)	9.6	10.8	3.6	6.6	11.7	4.1
J(5a,5b)	11.3	11.4	10.8	11.1	11.4	11.4

[a]) Assignments based on selective homodecoupling experiments. [b]) $^4J(3,5a) = 0.5$ Hz. [c]) $^4J(3,5b) = 1.0$ Hz. [d]) Not assigned. [e]) $^4J(3,5b) = 1.2$ Hz.

Table 4. *Selected ^{13}C-NMR Chemical Shift Values* [ppm] *of the Monosaccharides* **21**–**32** *in $CDCl_3$*

	21	**22**	**23**	**24**	**25**	**26**
C(1)	97.63	96.14	96.53	98.35	97.70	99.73
C(2)	74.44	72.93	74.60	69.05	64.84	69.51
C(3)	77.26	77.97	75.68	70.45	51.92[a])	54.18[a])
C(4)	67.17	67.91	77.00	77.28	51.37[a])	53.07[a])
C(5)	63.12	62.91	58.61	59.83	57.98	60.66
	27	**28**	**29**	**30**	**31**	**32**
C(1)	98.93	99.17	99.83	102.47	105.43	99.16
C(2)	69.94[a])	70.73[a])	71.30[a])	76.53	79.81	69.92[a])
C(3)	67.62[a])	69.37[a])	70.99[a])	201.28	201.01	69.10[a])
C(4)	32.53	38.43	38.62	47.84	51.21	36.15
C(5)	59.06	61.12	61.92	62.82	63.65	57.02

[a]) Assignments may be interchanged.

ane/AcOEt 3:1) gave **23** (12.6 g, 89%). Colourless oil. R_f (hexane/AcOEt 4:1) 0.38. $[\alpha]_D^{25} = -0.7$ ($c = 0.92$, $CHCl_3$). IR ($CHCl_3$): 2992*w*, 2937*w*, 1599*w*, 1495*w*, 1451*w*, 1375*m*, 1308*w*, 1190*m*, 1141*m*, 1081*m*, 1015*m*, 994*m*, 964*w*, 927*m*, 829*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.83 (*d*, $J = 8.4$, 2 arom. H); 7.34 (*d*, $J = 9.3$, 2 arom. H); 5.87 (*dddd*, $J = 17.1$, 10.5, 6.0, 5.1, CH_2=C*H*); 5.29 (*dq*, $J = 17.1$, 1.5), 5.21 (*dq*, $J = 10.5$, 1.2) (C*H*$_2$=CH); 4.25 (*ddt*, $J = 12.9$, 4.8, 1.5), 3.98 (*ddt*, $J = 12.6$, 6.3, 1.5) (CH_2=CHC*H*$_2$); 2.44 (*s*, Me); 1.25, 1.17 (2*s*, Me_2C). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 145.06 (*s*); 133.33 (*d*, CH_2=*C*H); 133.14 (*s*); 129.82 (*d*, 2 C); 128.37 (*d*, 2 C); 118.20 (*t*, *C*H$_2$=CH); 109.76 (*s*, Me_2*C*); 68.48 (*t*, CH_2=CH*C*H$_2$); 27.45, 26.21 (2*q*, *Me*$_2$C); 21.72 (*q*, Me). Anal. calc. for $C_{18}H_{24}O_7S$ (384.45): C 56.24, H 6.29; found: C 56.11, H 6.19.

*Allyl 4-*O*-(4-methylphenylsulfonyl)-α-*D*-lyxopyranoside* (**24**). A soln. of **23** (56 g, 145.8 mmol) in glacial AcOH (240 ml) was heated to 110°, stirred for 5 min, treated with H_2O (60 ml), stirred for 40 min at 110° (disappearance of **23**), and evaporated without any further heating. The resulting thick oil was dissolved in Et_2O (600 ml), washed with H_2O (50 ml), sat. aq. $NaHCO_3$ soln. (2 × 50 ml), and dried (Na_2SO_4). Evaporation gave crude **24** (51 g, 89%), which was used for next step without further purification. A pure sample of **24** was obtained by FC (silica gel; hexane/AcOEt 3:2). Colourless oil. R_f (hexane/AcOEt 1:1) 0.34. $[\alpha]_D^{25} = -106.0$ ($c = 0.38$, EtOH). IR ($CHCl_3$): 3574*w*, 3382*w* (sh), 3019*w*, 2925*w*, 1598*m*, 1495*w*, 1405*w*, 1365*m*, 1292*w*, 1190*m*, 1176*s*, 1132*m*, 1099*m*, 1065*m*, 1016*s*, 988*m*, 956*m*, 880*m*, 824*m*, 814*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.82 (*d*, $J = 8.4$, 2 arom. H); 7.35 (*d*, $J = 8.4$, 2 arom. H); 5.86 (*dddd*, $J = 17.1$, 10.5, 6.3, 5.1, CH_2=C*H*); 5.29 (*dq*, $J = 17.1$, 1.5), 5.19 (*dq*, $J = 10.2$, 1.5) (C*H*$_2$=CH); 4.17 (*ddt*, $J = 12.9$, 5.1 1.5), 3.96 (*ddt*, $J = 13.2$, 6.9, 1.5) (CH_2=CHC*H*$_2$); 2.99 (*d*, $J = 3.9$, exchanged with D_2O), 2.68 (*d*, $J = 3.3$, exchanged with D_2O) (HO–C(2), HO–C(3)); 2.46 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 145.54 (*s*); 133.40 (*d*, CH_2=*C*H); 133.40 (*s*); 130.12 (*d*, 2 C); 128.11 (*d*, 2 C); 117.93 (*t*, *C*H$_2$=CH); 68.57 (*t*, CH_2=CH*C*H$_2$); 21.78 (*q*, Me). HR-MALDI-MS: 367.0823 ([*M* + Na]$^+$, $C_{15}H_{22}NaO_7S^+$; calc. 367.0822). Anal. calc. for $C_{15}H_{20}O_7S$ (344.38): C 52.31, H 5.85; found: C 52.13, H 5.85.

*Allyl 3,4-Anhydro-β-*L*-ribopyranoside* (**25**). A suspension of *t*-BuOK (2.77 g, 24.7 mmol) in anh. THF (50 ml) was cooled to 3°, treated dropwise with a soln. of **24** (6.45 g, 20.6 mmol) in anh. THF (200 ml) over a period of 35 min, stirred for 45 min (during this time the stirring became sluggish), and poured into sat. aq. NH_4Cl soln. (60 ml). After stirring for 30 min, the liquor was decanted and filtered through a short pad of *Celite* (2×2 cm). The residue in the flask was treated with AcOEt (150 ml) and filtered. Evaporation of the combined filtrates and FC (*ca.* 240 g of silica gel; hexane/AcOEt 2:3) gave **25** (18.2 g, 71% from **23**). Low-melting colourless solid. R_f (hexane/AcOEt 1:1) 0.40. M.p. <25°. $[\alpha]_D^{25} = +189.9$ ($c = 0.64$, $CHCl_3$). IR ($CHCl_3$): 3553*w*, 3085*w*, 2959*m*, 2920*m*, 2870*w*, 1448*w*, 1406*w*, 1342*m*, 1322*w*, 1246*m*, 1148*s*, 1097*s*, 1045*s*, 1069*s*, 1023*m*, 996*s*, 936*m*, 866*m*, 802*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.99 (*dddd*, $J = 17.1$, 10.5, 6.3, 5.1, CH_2=C*H*); 5.30 (*dq*, $J = 17.1$, 1.5), 5.21 (*dq*, $J = 10.5$, 1.5) (C*H*$_2$=CH); 4.19 (*ddt*, $J = 12.6$, 5.1, 1.5), 4.00 (*ddt*, $J = 12.9$, 6.6, 1.5) (CH_2=CHC*H*$_2$); 2.51 (*d*, $J = 9.9$, exchanged with D_2O, HO–C(2)). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 133.46 (*d*, CH_2=*C*H); 117.95 (*t*, *C*H$_2$=CH); 68.74 (*t*, CH_2=CH*C*H$_2$). Anal. calc. for $C_8H_{12}O_4$ (172.18): C 55.81, H 7.02; found: C 55.56, H 7.00.

*Allyl 3,4-Anhydro-2-*O*-(triisopropylsilyl)-β-*L*-ribopyranoside* (**26**). A soln. of **25** (18.0 g, *ca.* 104 mmol) in anh. DMF (30 ml) was treated with 2,6-lutidine (26 ml, 238 mmol), cooled to 0°, treated dropwise with TIPS-OTf (28 ml, 103 mmol) over a period of 5 min, and stirred at 0° until disappearance of **25** (*ca.* 4 h). The mixture was diluted with Et_2O (500 ml) and washed with 10% aq. HCl (2×30 ml), H_2O (50 ml), and brine (25 ml), dried (Na_2SO_4), and evaporated. FC (*ca.* 180 g of silica gel; hexane/AcOEt 19:1 → 9:1) gave **26** (28.3 g, 83%). Colourless oil. R_f (hexane/AcOEt 1:1) 0.80. $[\alpha]_D^{25} = +99.9$ ($c = 0.7$, $CHCl_3$). IR ($CHCl_3$): 2946*s*, 2894*m*, 2868*s*, 1464*m*, 1384*w*, 1318*w*, 1129*s*, 1092*m*, 1046*m*, 996*s*, 956*w*, 882*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.89 (*dddd*, $J = 17.4$, 10.2, 6.3, 5.1, CH_2=C*H*); 5.29 (*dq*, $J = 17.1$, 1.5), 5.19 (*dq*, $J = 10.5$, 1.5) (C*H*$_2$=CH); 4.21 (*ddt*, $J = 12.9$, 5.1, 1.5), 3.96 (*ddt*, $J = 12.9$, 6.6, 1.5) (CH_2=CHC*H*$_2$); 1.08–1.03 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 133.98 (*d*, CH_2=*C*H); 117.60 (*t*, *C*H$_2$=CH); 68.84 (*t*, CH_2=CH*C*H$_2$); 18.04 (*q*, $(Me_2CH)_3Si$); 12.39 (*d*, $(Me_2CH)_3Si$). Anal. calc. for $C_{17}H_{32}O_4Si$ (328.51): C 62.15, H, 9.82; found: C 62.09, H, 9.92.

*Allyl 4-Cyano-4-deoxy-2-*O*-(triisopropylsilyl)-α-*D*-lyxopyranoside* (**27**). A soln. of **26** (13.8 g, 42.07 mmol) in anh. Et_2O (250 ml) was cooled to 0°, treated portionwise with *ca.* 1M Et_2AlCN in toluene (46.5 ml, 46.5 mmol), allowed to warm up, and refluxed for *ca.* 4 h until complete disappearance of **26**. The mixture was cooled to −40° and treated dropwise with sat. aq. NH_4Cl soln. (*ca.* 50 ml; *caution*: exothermic reaction!). After stirring for 2 h, the liquor was decanted, and the solid was thoroughly washed with AcOEt (2×25 ml). After evaporation of the combined filtrate and washings, FC (220 g of silica gel; hexane/AcOEt 21:4 → 17:3) gave **27** (9.6 g, 78%). Colourless solid. R_f (hexane/AcOEt 9:1) 0.33. M.p. 43.3–44.2° (hexane). $[\alpha]_D^{25} = 0.7$ ($c = 0.86$, $CHCl_3$). IR ($CHCl_3$):

3562*w*, 3024*w*, 2946*s*, 2869*s*, 2247*w*, 1464*m*, 1389*w*, 1264*w*, 1126*s*, 1089*s*, 1024*s*, 997*w*, 883*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 5.84 (*dddd*, *J* = 16.8, 10.8, 6.6, 5.4, CH_2=C*H*); 5.29 (*dq*, *J* = 16.8, 1.5), 5.19 (*dq*, *J* = 10.5, 1.5) (CH_2=CH); 4.16 (*ddt*, *J* = 12.9, 5.1, 1.5), 3.95 (*ddt*, *J* = 12.9, 6.3, 1.5, CH_2=CHCH_2); 2.44 (*d*, *J* = 9.3, exchanged with D_2O, HO–C(3)); 1.07–1.02 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 133.29 (*d*, CH_2=*C*H); 118.34 (*s*, CN); 117.98 (*t*, *C*H_2=CH); 68.30 (*t*, CH_2=CH*C*H_2); 18.18, 18.10 (2*q*, $(Me_2CH)_3Si$); 12.65 (*d*, $(Me_2CH)_3Si$). Anal. calc. for $C_{18}H_{33}NO_4Si$ (355.55): C 60.81, H 9.35, N 3.94; found: C 60.96, H 9.26, N 3.94.

*Allyl 4-Deoxy-4-(1*H*-imidazol-2-yl)-2-*O*-(triisopropylsilyl)-α-*D*-lyxopyranoside* (**28**). A soln. of **27** (7.3 g, 20.56 mmol) in anh. toluene (85 ml) was treated with $NH_2CH_2CH(OMe)_2$ (4 ml, 37.1 mmol), cooled to −18°, treated portionwise with 2M Me_3Al in toluene (19 ml, 38 mmol), warmed slowly to 23°, and heated to 80° for 26 h. The mixture was allowed to cool and treated carefully with sat. aq. NH_4Cl soln. (6 ml) to allow precipitation of the aluminium salts. After filtration and washing with AcOEt (400 ml), the combined org. layers were washed with H_2O (2×40 ml) and brine, dried (Na_2SO_4), and evaporated. FC (*ca.* 150 g of silica gel; hexane/AcOEt 85:17 → 2:3) gave **28** (5.5 g, 67%). Yellow syrup. R_f (AcOEt) 0.34. $[\alpha]_D^{25} = +7.5$ (*c* = 0.56, $CHCl_3$). IR ($CHCl_3$): 3551*w*, 3423*m*, 2946*s*, 2869*s*, 1541*m*, 1464*m*, 1436*w*, 1372*w*, 1218*m*, 1127*s*, 1111*s*, 1085*m*, 1016*s*, 997*m*, 967*m*, 910*m*, 884*m*, 838*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 6.98 (br. *s*, H–C(4′), H–C(5′)); 5.87 (*dddd*, *J* = 16.8, 10.8, 6.6, 5.1, CH_2=C*H*); 5.22 (*dq*, *J* = 16.8, 1.5), 5.19 (*dq*, *J* = 10.2, 1.5) (CH_2=CH); 4.18 (*ddt*, *J* = 12.9, 5.1, 1.5), 3.97 (*ddt*, *J* = 12.6, 6.3, 1.5) (CH_2=CHCH_2); 1.09–1.05 (*m*, $(Me_2CH)_3Si$); signals of NH and OH not observed. ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 146.40 (*s*, C(2′)); 133.58 (*d*, CH_2=CH); 121.22 (br. *d*, C(3′), C(4′)); 117.41 (*t*, *C*H_2=CH); 67.72 (*t*, CH_2=CH*C*H_2); 18.06, 18.00 (2*q*, $(Me_2CH)_3Si$); 12.57 (*d*, $(Me_2CH)_3Si$). Anal. calc. for $C_{20}H_{36}N_2O_4Si$ (396.60): C 60.57, H 9.15, N 7.06; found: C 60.50, H 9.06, N 7.08.

*Allyl 4-[1-[(*tert*-Butoxy)carbonyl]-1*H*-imidazol-2-yl]-4-deoxy-2-*O*-(triisopropylsilyl)-α-*D*-lyxopyranoside* (**29**). A soln. of **28** (1.45 g, 3.65 mmol) in anh. MeCN (7 ml) was treated with Boc_2O (876 mg, 4.02 mmol) and DMAP (47 mg, 0.385 mmol), stirred at 23° for 2 h (complete disappearance of **28**), treated with sat. aq. NH_4Cl soln. (20 ml), and extracted with AcOEt (100 ml). The org. layer was washed with H_2O (5 ml) and brine (5 ml), dried (Na_2SO_4), and evaporated affording crude **29** (1.726 g of a thick oil), which was used for the next step without further purification. An pure sample of **29** was obtained by FC (silica gel; hexane/AcOEt 4:1). Colourless oil. R_f (hexane/AcOEt 4:1) 0.23. $[\alpha]_D^{25} = +26.6$ (*c* = 0.52, $CHCl_3$). IR ($CHCl_3$): 3555*w*, 2945*m*, 2868*m*, 1749*s*, 1464*w*, 1414*w*, 1372*m*, 1307*s*, 1263*w*, 1142*s*, 1124*s*, 1065*m*, 1017*s*, 934*w*, 883*w*, 854*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.33 (*d*, *J* = 2.1, H–C(5′)); 6.90 (*d*, *J* = 1.8, H–C(4′)); 5.90 (*dddd*, *J* = 17.1, 10.5, 6.3, 5.1, CH_2=C*H*); 5.30 (*dq*, *J* = 16.8, 1.5), 5.19 (*dq*, *J* = 10.2, 1.5) (CH_2=CH); 4.22 (*ddt*, *J* = 12.9, 5.4, 1.5), 3.97 (*ddt*, *J* = 12.9, 6.3, 1.5) (CH_2=CHCH_2); 2.84 (br. *d*, *J* = 9.0, exchanged with D_2O, HO–C(3)); 1.60 (*s*, *t*-Bu); 1.14–1.08 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 149.04 (*s*, C=O); 148.27 (*s*, C(2′)); 133.92 (*d*, CH_2=*C*H); 127.64 (*d*, C(4′)); 118.73 (*d*, C(5′)); 117.49 (*t*, *C*H_2=CH); 85.70 (*s*, Me_3C); 67.90 (*t*, CH_2=CH*C*H_2); 28.01 (*q*, *Me*$_3$C); 18.24, 18.21 (2*q*, $(Me_2CH)_3Si$); 12.76 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 519.2855 ($[M+Na]^+$, $C_{25}H_{44}N_2NaO_6Si^+$; calc. 519.2861). Anal. calc. for $C_{25}H_{44}N_2O_6Si$ (496.71): C 60.45, H, 8.93, N 5.64; found: C 60.57, H, 8.93, N 5.64.

Oxidation of **29** *with Periodinane.* A soln. of crude **29** (1.722 g, *ca.* 3.54 mmol) in anh. CH_2Cl_2 (20 ml) was cooled to 0°, treated with a 15% soln. of *Dess–Martin* periodinane in CH_2Cl_2 (11.2 ml, 3.92 mmol), stirred for 4 h (complete disappearance of **29**), diluted with Et_2O (200 ml), washed with sat. aq. $NaHCO_3$ soln. (2×25 ml), dried (Na_2SO_4), and evaporated. FC (50 g of silica gel, hexane/AcOEt 85:15) gave **30** (1.225 g, 68% from **28**) and **31** (70 mg, 10% from **28**).

*Allyl 4-[1-[(*tert*-Butoxy)carbonyl]-1*H*-imidazol-2-yl]-4-deoxy-2-*O*-(triisopropylsilyl)-α-*D*-*threo*-pentopyranosid-3-ulose* (**30**). Colourless oil. R_f (hexane/AcOEt 4:1) 0.21. $[\alpha]_D^{25} = +69.6$ (*c* = 0.67 $CHCl_3$). IR ($CHCl_3$): 3035*w*, 2945*m*, 2868*m*, 1762*s*, 1740*m*, 1499*w*, 1464*m*, 1412*m*, 1372*m*, 1338*w*, 1309*s*, 1264*m*, 1141*s*, 1116*m*, 1077*m*, 1036*m*, 1013*m*, 941*w*, 882*m*, 869*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.31 (*d*, *J* = 1.8, H–C(5′)); 6.89 (*d*, *J* = 1.8, H–C(4′)); 5.86 (*dddd*, *J* = 17.1, 10.2, 6.3, 4.8, CH_2=C*H*); 5.27 (*dq*, *J* = 17.1, 1.5), 5.19 (*dq*, *J* = 10.5, 1.5) (CH_2=CH); 4.22 (*ddt*, *J* = 12.9, 4.8, 1.5), 4.02 (*ddt*, *J* = 12.9, 6.3, 1.5) (CH_2=CHCH_2); 1.54 (*s*, *t*-Bu); 1.18–1.09 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 147.33 (*s*, NC=O); 144.77 (*s*, C(2′)); 133.38 (*d*, *C*H=CH_2); 128.87 (*d*, C(4′)); 118.78 (*d*, C(5′)); 118.11 (*t*, *C*H_2=CH); 85.09 (*s*, Me_3C); 67.88 (*t*, CH_2=CH*C*H_2); 27.82 (*q*, *Me*$_3$C); 17.9 (br. *q*, $(Me_2CH)_3Si$); 12.13 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 517.2711 ($[M+Na]^+$, $C_{25}H_{42}N_2NaO_6Si^+$; calc. 517.2704). Anal. calc. for $C_{25}H_{42}N_2O_6Si$ (494.69): C 60.70, H 8.56, N 5.66; found: C 60.54, H 8.42, N 5.76.

*Allyl 4-[1-[(*tert*-Butoxy)carbonyl]-1*H*-imidazol-2-yl]-4-deoxy-2-*O*-(triisopropylsilyl)-β-*D*-erythro-pentopyranosid-3-ulose* (**31**). Colourless oil. R_f (hexane/AcOEt 4:1) 0.12. $[\alpha]_D^{25} = -22.1$ (*c* = 0.65, $CHCl_3$). IR

(ATR): 2942*w*, 2866*m*, 1753*s*, 1745*s* (sh), 1502*w*, 1463*m*, 1410*m*, 1370*m*, 1338*m*, 1306*s*, 1258*m*, 1136*s*, 1114*s*, 1101*s*, 1068*s*, 1017*m*, 995*w*, 917*w*, 882*m*, 845*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.34 (*d*, *J* = 1.5, H–C(5′)); 6.88 (*d*, *J* = 1.5, H–C(4′)); 5.96 (*dddd*, *J* = 16.8, 10.5, 6.0, 5.1, CH_2=C*H*); 5.34 (*dq*, *J* = 17.1, 1.5), 5.20 (*dq*, *J* = 10.2, 1.5) (C*H*$_2$=CH); 4.42 (*ddt*, *J* = 12.6, 5.1, 1.5), 4.20 (*ddt*, *J* = 12.6, 6.3, 1.5) (CH_2=CHC*H*$_2$); 1.55 (*s*, *t*-Bu); 1.12–1.05 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 147.60 (*s*, NC=O); 143.69 (*s*, C(2′)); 133.77 (*d*, CH_2=*C*H); 127.85 (*d*, C(4′)); 119.03 (*d*, C(5′)); 117.95 (*t*, *C*H$_2$=CH); 85.43 (*s*, Me_3C); 70.89 (*t*, CH_2=CH*C*H$_2$); 27.83 (*q*, *Me*$_3$C); 17.96, 17.93 (2*q*, (*Me*$_2$CH)$_3$Si); 12.48 (*d*, (Me$_2$*C*H)$_3$Si). HR-MALDI-MS: 417.2865 ($[M - Boc + Na]^+$, $C_{25}H_{42}N_2NaO_6Si^+$; calc. 517.2861).

*Allyl 4-{1-[(*tert*-Butoxy)carbonyl)]-1*H*-imidazol-2-yl}-4-deoxy-2-*O*-(triisopropylsilyl)-α-*D*-arabinopyranoside* (**32**). A soln. of **30** (1.18 mg, 2.38 mmol) in dry MeOH (6 ml) was cooled to 0°, treated with $CeCl_3 \cdot 7\,H_2O$ (896 mg, 2.40 mmol) and $NaBH_4$ (79 mg, 2.14 mmol), stirred for 15 min (disappearance of **30**), treated with sat. aq. NH_4Cl soln. (25 ml), and diluted with AcOEt (150 ml). The org. layer was separated, washed with H_2O (25 ml), dried (Na_2SO_4), and evaporated. FC (45 g of silica gel; hexane/AcOEt 4:1) provided **32** (954 mg, 80%). Colourless oil. R_f (hexane/AcOEt 4:1) 0.10. $[\alpha]_D^{25} = +78.8$ (*c* = 0.83, $CHCl_3$). IR ($CHCl_3$): 3507*w*, 3342*w*, 3014*w*, 2945*m*, 2868*m*, 1762*m*, 1462*w*, 1372*w*, 1353*w*, 1305*s*, 1264*m*, 1141*s*, 1100*m*, 1025*m*, 932*w*, 882*w*, 817*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 3*; additionally, 7.33 (*d*, *J* = 2.1, H–C(5′)); 6.86 (*d*, *J* = 2.1 H–C(4′)); 5.91 (*dddd*, *J* = 17.1, 10.8, 6.9, 5.1, CH_2=C*H*); 5.30 (*dq*, *J* = 17.1, 1.5), 5.20 (*dq*, *J* = 10.8, 1.5) (C*H*$_2$=CH); 4.73 (br. *d*, *J* = 6.0, exchanged with D_2O, HO–C(3)); 4.25 (*ddt*, *J* = 12.9, 5.1, 1.5), 4.05 (*ddt*, *J* = 12.9, 6.3, 1.5) (CH_2=CHC*H*$_2$); 1.60 (*s*, *t*-Bu); 1.14–1.04 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 4*; additionally, 149.14 (*s*, C=O); 147.26 (*s*, C(2′)); 133.78 (*d*, CH_2=*C*H); 127.16 (*d*, C(4′)); 118.60 (*d*, C(5′)); 117.96 (*t*, *C*H$_2$=CH); 85.62 (*s*, Me_3C); 68.36 (*t*, CH_2=CHCH$_2$); 27.97 (*q*, *Me*$_3$C); 18.19 (*q*, (Me$_2$*C*H)$_3$Si); 12.38 (*d*, *Me*$_2$CH)$_3$Si). HR-MALDI-MS: 519.2865 ($[M + Na]^+$, $C_{25}H_{44}N_2NaO_6Si^+$; calc. 519.2861). Anal. calc. for $C_{25}H_{44}N_2O_6Si$ (496.71): C 60.45, H 8.93, N 5.64; found: C 60.54, H 8.42, N 5.73.

Glycosidation of **32** *with* **6**. *a*) A suspension of **32** (64 mg, 0.13 mmol), **6** (68 mg, 0.164 mmol), and 4-Å mol. sieves (260 mg) in CH_2Cl_2 (10 ml) was stirred for 1 h at 23°, treated with $Hg(CN)_2$ (35 mg, 0.14 mmol) and $HgBr_2$ (17 mg, 0.047 mmol), heated to reflux for 8 h, cooled to r.t., diluted with AcOEt (40 ml), washed with sat. aq. $NaHCO_3$ soln. (5 ml) and brine (5 ml), and dried (Na_2SO_4). Evaporation and FC (6 g of silica gel; CH_2Cl_2/hexane 1:19) gave **32** (14 mg, 21%) and **33** (42 mg, 39%).

b) At 24°, a suspension of **32** (1.975 g, 3.98 mmol), **6** (2.1 g, 5.1 mmol) and 3-Å mol. sieves 3 (5.2 g) in CH_2Cl_2 (60 ml) was stirred for 30 min, cooled to 0°, treated with AgOTf (1.7 g, 6.6 mmol), allowed to warm to 23°, stirred for 17 h, treated with sat. aq. $NaHCO_3$ soln. (10 ml), and extracted with AcOEt (300 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (30 ml) and dried (Na_2SO_4). Evaporation and FC (60 g of silica gel; hexane/AcOEt 3:2) gave **32** (552 mg, 27%) and an inseparable mixture of crude Boc-disaccharides (1.641 g; *ca.* 90% pure, contaminated with impurities derived from **6**). A soln. of this mixture in CH_2Cl_2 (20 ml) was cooled to 0°, treated with CF_3COOH (1 ml), stirred for 4 h (disappearance of the Boc-disaccharides), neutralised with sat. aq. $NaHCO_3$ soln. (10 ml), extracted with AcOEt (60 ml). The org. layer was washed with H_2O (10 ml) and brine (10 ml), dried (Na_2SO_4) and evaporated. FC (40 g of silica gel; AcOEt/hexane 7:3 → 9:1) gave **36** (892 mg, 31%) and **35** (360 mg, 13%).

*Allyl (*S*)-3,4,6-Tri-*O*-acetyl-1,2-*O*-(methylmethanediyl)-α-*D*-glucopyranose-(1*^{2}*→3)-4-{1-[(*tert*-butoxy)carbonyl]-1*H*-imidazol-2-yl}-4-deoxy-2-*O*-(triisopropylsilyl)-α-*D*-arabinopyranoside* (**33**). Colourless oil. R_f (hexane/AcOEt 2:3) 0.46. $[\alpha]_D^{25} = +88.9$ (*c* = 0.7, $CHCl_3$). IR ($CHCl_3$): 3014*w*, 2946*m*, 2868*m*, 1756*s*, 1462*w*, 1391*w*, 1372*m*, 1335*w*, 1306*s*, 1242*s*, 1140*s*, 1094*s*, 1059*s*, 1041*s*, 980*m*, 927*w*, 882*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 7.26 (*d*, *J* = 1.8, H–C(5′)); 6.85 (*d*, *J* = 1.7, H–C(4′)); 5.86 (*dddd*, *J* = 17.1, 10.5, 6.3, 5.1, CH_2=C*H*); 5.24 (*dq*, *J* = 17.1, 1.8), 5.12 (*dq*, *J* = 10.2, 1.2) (C*H*$_2$=CH); 4.22 (*ddt*, *J* = 12.3, 5.1, 1.5), 3.93 (*ddt*, *J* = 12.3, 6.3, 1.2) (CH_2=CHC*H*$_2$); 2.08, 2.07, 2.04 (3*s*, 3 AcO); 1.59 (*s*, *t*-Bu); 1.21 (*s*, Me); 1.15–1.09 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 170.79, 169.69, 168.82 (3*s*, 3 OC=O); 148.94 (*s*, NC=O); 147.56 (*s*, C(2′)); 134.50 (*d*, CH_2=*C*H); 127.90 (*d*, C(4′)); 121.06 (*s*, Me*C*O$_3$); 118.15 (*d*, C(5′)); 117.26 (*t*, *C*H$_2$=CH); 85.18 (*s*, Me_2C); 68.25 (*t*, CH_2=CH*C*H$_2$); 27.83 (*q*, *Me*$_3$C); 20.98, 20.94, 20.92 (3*q*, 3 *Me*C=O); 19.30 (*q*, Me); 18.20, 18.17 (2*q*, (*Me*$_2$CH)$_3$Si); 12.31 (*d*, (Me$_2$*C*H)$_3$Si). HR-MALDI-MS: 849.3812 ($[M + Na]^+$, $C_{39}H_{62}N_2NaO_{15}Si^+$; calc. 849.3812).

*Allyl 2,3,4,6-Tetra-*O*-acetyl-β-*D*-glucopyranosyl-(1→3)-4-deoxy-4-(1*H*-imidazol-2-yl)-2-*O*-(triisopropylsilyl)-α-*D*-arabinopyranoside* (**35**). Colourless oil. R_f (CH_2Cl_2/AcOEt 1:4) 0.32. $[\alpha]_D^{25} = -12.2$ (*c* = 1.35, $CHCl_3$). IR ($CHCl_3$): 3430*w*, 3029*w*, 2946*m*, 2867*m*, 1754*s*, 1545*w*, 1462*w*, 1367*w*, 1237*s*, 1139*m*, 1067*s*, 1040*s*, 909*w*, 883*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 9.50 (br. *s*, exchanged with D_2O, NH); 6.99 (br. *s*, H–C(4′), H–C(5′)); 5.93 (*dddd*, *J* = 17.1, 10.5, 6.0, 5.1, CH_2=C*H*); 5.32 (*dq*, *J* = 17.1, 1.5), 5.17 (*dq*, *J* = 10.5, 1.5) (C*H*$_2$=CH); 4.31 (*ddt*, *J* = 12.6, 4.8, 1.5), 4.03 (*ddt*, *J* = 12.6, 6.0, 1.5) (CH_2=CHC*H*$_2$); 2.06, 2.02,

1.98, 1.86 (4*s*, 4 AcO); 1.08–1.01 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 170.53, 170.09, 169.32, 169.03 (4*s*, 4 C=O); 145.39 (*s*, C(2′)); 134.01 (*d*, CH_2=*C*H); 130–120 (2 br. *d*, C(4′), C(5′)); 117.13 (*t*, *C*H_2=CH); 68.22 (*t*, CH_2=CH*C*H_2); 20.86, 20.15 (2*q*, 2 Me); 20.80 (*q*, 2 Me); 18.27, 18.24 (2*q*, $(Me_2CH)_3Si$); 12.58 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 749.3277 ($[M+Na]^+$, $C_{34}H_{54}N_2NaO_{13}Si^+$; calc. 749.3287). Anal. calc. for $C_{34}H_{54}N_2O_{13}Si$ (726.89): C 56.18, H 7.49, N 3.85; found: C 56.06, H 7.31, N 3.93.

Allyl 2,3,4,6-Tetra-O*-acetyl-α*-D*-glucopyranosyl-(1 → 3)-4-deoxy-4-(1*H*-imidazol-2-yl)-2*-O*-(triisopropylsilyl)-α*-D*-arabinopyranoside* (**36**). Colourless solid. R_f (CH_2Cl_2/AcOEt 1:4) 0.59. M.p. 116–118°. $[\alpha]_D^{25} = +135.8$ ($c = 2.25$, $CHCl_3$). IR (2.2%, $CHCl_3$): 3456*w*, 3233*w*, 2946*m*, 2868*m*, 1750*s*, 1548*w*, 1463*m*, 1368*m*, 1254*s*, 1120*m*, 1102*s*, 1071*m*, 1036*s*, 932*w*, 883*m*, 845*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 9.73 (br. *s*, exchanged with D_2O, NH); 7.05, 7.01 (2 br. *s*, H–C(4′), H–C(5′)); 5.86 (*dddd*, *J* = 17.1, 10.5, 6.3, 4.8, CH_2=C*H*); 5.30 (*dq*, *J* = 17.1, 1.5), 5.20 (*dq*, *J* = 10.2, 1.5) (CH_2=CH); 4.16 (*ddt*, *J* = 13.5, 4.5, 1.5), 4.06 (*ddt*, *J* = 13.5, 6.6, 1.5) (CH_2=CHCH_2); 2.06, 2.04, 2.02, 1.97 (4*s*, 4 AcO); 1.10–1.05 (*m*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 170.63, 170.40, 169.99, 169.40 (4*s*, 4 C=O); 145.46 (*s*, C(2′)); 134.01 (*d*, CH_2=*C*H); 130–120 (br. *d*, C(4′), C(5′)); 117.96 (*t*, *C*H_2=CH); 68.10 (*t*, CH_2=CH*C*H_2); 20.90 (*q*, 3 Me); 20.60 (*q*, Me); 18.02 (*q*, (*Me*$_2$CH)$_3$Si); 12.22 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 749.3276 ($[M+Na]^+$, $C_{34}H_{54}N_2NaO_{13}Si^+$; calc. 749.3287). Anal. calc. for $C_{34}H_{54}N_2O_{13}Si$ (726.89): C 56.18, H 7.49, N 3.85; found: C 56.31, H 7.47, N 3.97.

Glycosidation of **32** *with* **7**. A suspension of **32** (30 mg, 0.06 mmol), **7** (71 mg, 0.42 mmol), and 4-Å mol. sieves (71 mg) in CH_2Cl_2 (4 ml) was stirred for 1 h at 23°, cooled to 2°, treated with AgOTf (43 mg, 0.17 mmol) and TMU (40 µl, 0.334 mmol), stirred for 4 h (disappearance of **32**), diluted with AcOEt (50 ml), washed with H_2O (5 ml) and brine (5 ml), and dried (Na_2SO_4). Evaporation and FC (6 g of silica gel; CH_2Cl_2/hexane 1:19) gave **34** (42 mg, 70%).

Allyl (S)*-3,4,6-Tri*-O*-benzoyl-1,2*-O*-(phenylmethanediyl)-α*-D*-glucopyranose-(1² → 3)-4-[1-[(*tert*-butoxy)-carbonyl]-1*H*-imidazol-2-yl]-4-deoxy-2*-O*-(triisopropylsilyl)-α*-D*-arabinopyranoside* (**34**). Colourless oil. R_f (hexane/AcOEt 4:1) 0.16. $[\alpha]_D^{25} = +70.1$ ($c = 1.55$, $CHCl_3$). IR ($CHCl_3$): 2945*m*, 2867*m*, 1761*m*, 1724*s*, 1602*w*, 1493*w*, 1452*m*, 1410*w*, 1372*m*, 1338*w*, 1307*s*, 1267*s*, 1142*s*, 1097*s*, 1071*s*, 1028*s*, 993*m*, 961*m*, 883*w*, 845*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 8.08 (br. *dq*, *J* = 8.4, 1.2, 2 arom. H); 7.96 (br. *dq*, *J* = 8.4, 1.2, 2 arom. H); 7.63 (br. *dq*, *J* = 8.4, 1.2, 2 arom. H); 7.59 (*tt*, *J* = 6.0, 1.3, 1 arom. H); 7.51–7.42 (*m*, 5 arom. H); 7.30–7.10 (*m*, 8 arom. H); 7.18 (*d*, *J* = 1.7, H–C(5′)); 6.93 (*d*, *J* = 1.7, H–C(4′)); 5.78 (*ddt*, *J* = 17.1, 10.5, 6.0, CH_2=C*H*); 5.06 (*dq*, *J* = 17.1, 1.5), 4.73–4.67 (*m*) (CH_2=CH); 4.19 (*ddt*, *J* = 12.0, 6.0, 1.2), 3.84 (*ddt*, *J* = 12.0, 6.0, 1.2) (CH_2=CHCH_2); 1.38 (*s*, *t*-Bu); 1.05 (br. *s*, $(Me_2CH)_3Si$). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 166.09, 165.08, 164.26 (3*s*, 3 OC=O); 148.91 (*s*, NC=O); 144.67 (*s*, C(2′)); 135.12 (*s*); 134.11 (*d*, CH_2=*C*H); 133.61, 133.24, 133.06 (3*d*); 130.06–128.18 (several *d*); 129.73, 129.18, 129.13 (3*s*); 127.68 (*d*, C(4′)); 126.41 (2*d*); 123.32 (*s*, Ph*C*O$_3$); 118.20 (*d*, C(5′)); 117.93 (*t*, *C*H_2=CH); 84.40 (*s*, Me_3C); 68.83 (*t* CH_2=CH*C*H_2); 27.70 (*q*, *Me*$_3$C); 18.10, 18.06 (2*q*, $(Me_2CH)_3Si$); 12.21 (*d*, $(Me_2CH)_3Si$). HR-MALDI-MS: 1097.4430 ($[M+Na]^+$, $C_{59}H_{70}N_2NaO_{15}Si^+$; calc. 1097.4438).

Allyl 2,3,4,6-Tetra-O*-acetyl-β*-D*-glucopyranosyl-(1→3)-4-deoxy-4-(1*H*-imidazol-2-yl)-α*-D*-arabinopyranoside* (**37**). A soln. of **35** (142 mg, 0.195 mmol) in THF (2 ml) was cooled to 0°, treated with a soln. of TBAF·3 H_2O (72 mg, 0.23 mmol) in THF (3 ml), stirred for 3 h (disappearance of **35**), and evaporated to dryness. FC (4.8 g of silica gel; AcOEt → AcOEt/MeOH 24:1) gave **37** (106 mg, 92%). Colourless solid. R_f (CH_2Cl_2/MeOH 9:1) 0.42. $[\alpha]_D^{25} = -55.5$ ($c = 2.5$, $CHCl_3$). IR ($CHCl_3$): 3516*w*, 3434*w*, 3029*w*, 3015*w*, 2957*m*, 2867*m*, 1756*s*, 1544*w*, 1437*w*, 1368*m*, 1258*s*, 1069*s*, 1040*s*, 998*w*, 960*w*, 909*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): see *Table 1*; additionally, 6.94 (br. *s*, H–C(4′), H–C(5′)); 5.92 (*dddd*, *J* = 16.8, 10.8, 6.0, 5.1, CH_2=C*H*); 5.30 (*dq*, *J* = 17.1, 1.5), 5.17 (*dq*, *J* = 10.2, 1.5) (CH_2=CH); 4.34 (*ddt*, *J* = 13.5, 5.1, 1.5), 4.12 (*ddt*, *J* = 13.5, 6.0, 1.5) (CH_2=CHCH_2); 2.06, 2.0, 1.97, 1.94 (4*s*, 4 AcO). ^{13}C-NMR (75 MHz, $CDCl_3$): see *Table 2*; additionally, 170.62, 170.06, 170.04, 169.41 (4*s*, 4 C=O); 144.51 (*s*, C(2′)); 133.84 (*d*, CH_2=*C*H); 121.57 (br. hump, C(4′), C(5′)); 117.88 (*t*, *C*H_2=CH); 69.96 (*t*, CH_2=CH*C*H_2); 21.67, 20.58 (2*q*, 4 Me); NH and OH hidden by coalescence. HR-MALDI-MS: 571.2127 ($[M+H]^+$, $C_{25}H_{35}N_2O_{13}^+$; calc. 571.2134). Anal. calc. for $C_{25}H_{34}N_2O_{13}\cdot 0.5\ H_2O$ (579.55): C 51.81, H 6.09, N 4.83; found: C 51.93, H 6.04, N 4.85.

Allyl β-D*-Glucopyranosyl-(1 → 3)-4-deoxy-4-(1*H*-imidazol-2-yl)-α*-D*-arabinopyranoside* (**38**). A soln. of **37** (50 mg, 0.088 mmol) in MeOH (3 ml) was treated with *ca.* 7M NH_3 in MeOH (400 µl), stirred for 23 h at 24°, and evaporated to dryness. FC (3 g of silica gel, $CHCl_3$/MeOH/NH_4OH 15:4:1) gave **38** (30 mg, 85%). Colourless hygroscopic solid. R_f ($CHCl_3$/MeOH/NH_4OH 15:4:1) 0.24. M.p. 211–215° (dec.). $[\alpha]_D^{25} = -25.3$ ($c = 1.49$, MeOH). IR (ATR): 3227*m*, 3092*w*, 2881*m*, 1662*w*, 1548*w*, 1444*w*, 1373*w*, 1247*m*, 1067*s*, 1039*s*, 996*s*, 963*m*, 922*m*, 894*w*. ^{1}H-NMR (300 MHz, CD_3OD): see *Table 1*; additionally, 7.04 (br. *s*, H–C(4′), H–C(5′)); 5.92 (*dddd*, *J* = 17.1, 10.8, 6.0, 5.4, CH_2=C*H*); 5.34 (*dq*, *J* = 17.1, 1.8), 5.16 (*dq*, *J* = 10.5, 1.8) (CH_2=CH); 4.32 (*ddt*,

J = 12.6, 5.4, 1.5), 4.14 (*ddt*, J = 12.6, 6.0, 1.5) (CH_2=CHCH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 2*; additionally, 146.31 (*s*, C(2′)); 135.38 (*d*, CH_2=*C*H); 121.90 (*d*, C(4′), C(5′)); 117.47 (*t*, *C*H_2=CH); 70.68 (*t*, CH_2=CH*C*H_2). HR-MALDI-MS: 425.1535 ($[M+Na]^+$, $C_{17}H_{26}N_2NaO_9^+$; calc. 425.1531). Anal. calc. for $C_{17}H_{26}N_2O_9$·0.5 H_2O (411.40): C 49.63, H 6.62, N 6.81; found: C 49.63, H 6.62, N 6.63.

*(5*R/S*,6*R*,7*S*,8*S*)-7-(β-*D*-Glucopyranosyloxy)-5,6,7,8-tetrahydro-8-(hydroxymethyl)imidazo[1,2-*a*]pyridine-5,6-diol* (**2**/**39**). A soln. of **38** (29 mg, 0.072 mmol) in MeOH (5 ml) was treated with 10% Pd/C (24 mg), heated to reflux at 80° for 24 h, cooled to 24°, and filtered over *Celite*. After evaporation of the filtrate, a soln. of the residue (28 mg, 4:1 mixture of propenyl acetals) in MeOH (5 ml) was cooled to 0°, treated with 10% aq. HCl soln. (100 µl), and stirred for 21 h at r.t. Evaporation and FC (5 g of silica gel; 100 ml of CH_3Cl/MeOH/NH_4OH 7:2:1) gave **2**/**39** 45:55 (16 mg, 45%). Off-white solid. R_f (AcOEt/MeOH/NH_4OH 7:2:1) 0.20. M.p. 184–194° (dec.). $[\alpha]_D^{25}$ = −34.9 (c = 0.6, MeOH). IR (ATR): 3286*m*, 2884*w*, 1638*w*, 1528*w*, 1447*w*, 1367*m*, 1256*m*, 1098*s*, 1065*s*, 1019*s*, 909*w*. ^{1}H-NMR (300 MHz, CD_3OD; **2**/**39** 45:55): 7.15 (*d*, J = 1.8, 0.45 H), 7.11 (*d*, J = 1.5, 0.55 H), 6.99 (*d*, J = 1.5, 0.45 H), 6.96 (*d*, J = 1.5, 0.55 H) (H−C(2), H−C(3)); 5.93 (*d*, J = 3.0, 0.55 H), 5.26 (*d*, J = 6.6, 0.45 H) (H−C(5)); 4.54 (*d*, J = 7.8, H−C(1′)); 4.46 (*d*, J = 3.0), 4.23 (*dd*, J = 8.1, 5.7), 4.16 (*t*, $J \approx$ 9.0), 4.15 (*d*, J = 4.2), 4.08 (*dd*, J = 8.1, 3.0), 3.90 (*dd*, J = 12.0, 2.1), 3.86 (*dd*, J = 12.0, 1.8), 3.82 (*dd*, J = 9.0, 6.9), 3.68 (*dd*, J = 12.0, 5.7), 3.45–3.20 (*m*) (H−C(6), H−C(7), CH_2–C(8), H−C(2′), H−C(3′), H−C(4′), H−C(5′), 2 H_2−C(6′)); 3.14–3.04 (*m*, H−C(8)). ^{13}C-NMR (75 MHz, CD_3OD; **2**/**39** *ca.* 1:1): 145.02/144.38 (2*s*, C(8a)); 129.22/128.88 (2*d*, C(2)); 118.78/117.75 (2*d*, C(3)); 104.85/104.82 (2*d*, C(1′)); 82.36/79.36 (2*d*, C(5)); 78.45, 78.30 (2 C), 77.99, 77.90, 77.83, 75.28, 75.03 (2 C), 71.28, 71.43, 71.35 (10*d*, C(6), C(7), C(2′), C(3′), C(4′), C(5′)); 62.65/61.96, 62.49/60.32 (4*t*, C(6), CH_2–C(8)); 45.20/44.64 (2*d*, C(8)). HR-ESI-MS: 363.1397 ($[M+H]^+$, $C_{14}H_{23}N_2O_9^+$; calc. 363.1398).

*Allyl 2,3,4,6-Tetra-*O*-acetyl-α-*D*-glucopyranosyl-(1 → 3)-4-deoxy-4-(1*H*-imidazol-2-yl)-α-*D*-arabinopyranoside* (**40**). A soln. of **36** (174 mg, 0.24 mmol) in THF (2 ml) was cooled to 0°, treated with $Bu_4NF \cdot 3\ H_2O$ (138 mg, 0.44 mmol) stirred for 3 h (complete disappearance of **36**), and evaporated to dryness. FC (4.8 g of silica gel; AcOEt → AcOEt/MeOH 24:1) gave **40** (125 mg, 92%). Colourless syrup solidifying to an off-white powder upon storage. R_f (AcOEt/MeOH 24:1) 0.16. M.p. 106–108° (at 97–98° becoming transparent). $[\alpha]_D^{25}$ = +76.7 (c = 1.8, $CHCl_3$). IR ($CHCl_3$): 3431*w*, 3027*w*, 3016*w*, 1751*s*, 1602*w*, 1542*w*, 1433*w*, 1367*m*, 1250*s*, 1139*m*, 1074*s*, 1067*s*, 1038*s*, 959*w*, 939*w*, 909*w*. ^{1}H-NMR (300 MHz, $CDCl_3$; assignments based on a DQFCOSY and a HSQC spectrum): see *Table 1*; additionally, 7.02 (br. *s*, H−C(4′), H−C(5′)); 5.92 (*dddd*, J = 17.1, 11.4, 6.6, 5.1, CH_2=C*H*); 5.34 (*dq*, J = 17.1, 1.5), 5.26 (*dq*, J = 11.4, 1.5) (CH_2=CH); 4.35 (*ddt*, J = 12.3, 5.1, 1.5), 4.14 (*ddt*, J = 12.3, 6.6, 1.5) (CH_2=CHCH_2); 2.08, 2.03, 2.02, 2.00 (4*s*, 4 AcO); NH and OH hidden by coalescence. ^{13}C-NMR (75 MHz; $CDCl_3$, assignments based on a HSQC spectrum): see *Table 2*; additionally, 170.68, 170.08, 169.82, 169.54 (4*s*, 4 C=O); 145.09 (*s*, C(2′)); 134.42 (*d*, CH_2=*C*H); 123.0 (br. hump, C(4′), C(5′)); 118.42 (*t*, *C*H_2=CH); 70.24 (*t*, CH_2=CH*C*H_2); 20.92, 20.86 (2*q*, 2 Me); 20.84 (*q*, 2 Me). HR-MALDI-MS: 571.2135 ($[M+H]^+$, $C_{25}H_{35}N_2NaO_{13}^+$; calc. 571.2134).

*Allyl α-*D*-Glucopyranosyl-(1 → 3)-4-deoxy-4-(1*H*-imidazol-2-yl)-α-*D*-arabinopyranoside* (**41**). A soln. of **40** (87 mg, 0.15 mmol) in MeOH (5 ml) was treated with *ca.* 7M NH_3 in MeOH (650 µl), stirred for 17 h at 24° (complete disappearance of **40**), and evaporated to dryness. FC (*ca.* 2 g of silica gel; AcOEt/MeOH 24:1 → 4:1) gave **41** (52 mg, 82%). Colourless solid. R_f (AcOEt/MeOH/NH_4OH 7:2.5:0.5) 0.15. M.p. 184–194° (dec.). $[\alpha]_D^{25}$ = +69.6 (c = 0.67, $CHCl_3$). IR (ATR): 3381*m*, 2921*w*, 1162*w*, 1558*w*, 1452*w*, 1409*w*, 1250*w*, 1132*m*, 1067*s*, 1020*s*, 1000*s*, 943*m*, 880*w*. ^{1}H-NMR (300 MHz, CD_3OD, >90% pure): see *Table 1*; additionally, 6.99 (br. *s*, H−C(4′), H−C(5′)); 5.93 (*dddd*, J = 16.8, 10.5, 6.6, 5.4, CH_2=C*H*); 5.28 (*dq*, J = 16.8, 1.5), 5.18 (*dq*, J = 10.5, 1.5) (CH_2=CH); 4.24 (*ddt*, J = 12.3, 5.7, 1.5), 4.08–4.02 (*m*) (CH_2=CHCH_2). ^{13}C-NMR (75 MHz, CD_3OD): see *Table 2*; additionally, 147.17 (*s*, C(2′)); 135.18 (*d*, CH_2=*C*H); 122.5 (br. hump, C(4′), C(5′)); 118.98 (*t*, *C*H_2=CH); 67.36 (*t*, CH_2=CH*C*H_2). HR-MALDI-MS: 425.1535 ($[M+H]^+$, $C_{17}H_{26}N_2NaO_{13}^+$; calc. 425.1531). Anal. calc. for $C_{17}H_{26}N_2O_9 \cdot 0.25\ H_2O$ (411.40): C 50.18, H 6.56, N 6.90; found: C 50.11, H 6.44, N 6.90.

*(5*R/S*,6*R*,7*S*,8*S*)-7-(α-*D*-Glucopyranosyloxy)-5,6,7,8-tetrahydro-8-(hydroxymethyl)imidazo[1,2-*a*]pyridine-5,6-diol* (**42**/**43**). A soln. of **41** (38 mg, 0.094 mmol) in MeOH (5 ml) was treated with 10% Pd/C (35 mg), heated to reflux at 80° for 48 h, cooled to 24°, filtered over *Celite*, and evaporated. A cold soln. of the residue (33 mg, mixture of propenyl acetals) in MeOH (5 ml) was treated with 10% aq. HCl soln. (100 µl), slowly warmed to 27°, and stirred for 21 h. Evaporation and FC (5 g of silica gel, 100 ml of CH_3Cl/MeOH/NH_4OH 60:32:8) gave **42**/**43** *ca.* 1:1 (22 mg, 64%). Off-white solid. R_f (CH_3Cl/MeOH/NH_4OH 60:32:8) 0.17. M.p. 180–195° (dec. → brown residue). $[\alpha]_D^{25}$ = +47.9 (c = 0.45, MeOH). IR (ATR): 3258*m*, 2987*w*, 1653*w*, 1567*w*, 1449*m*, 1410*m*, 1343*m*, 1252*m*, 1139*m*, 1068*s*, 1018*s*, 910*m*, 823*m*. ^{1}H-NMR (300 MHz, CD_3OD; **42**/**43** *ca.* 1:1, >90% pure): 7.30, 7.28 (2*d*, J = 1.8, H−C(2)); 7.20, 7.16 (2*d*, J = 1.8, H−C(3)); 5.74 (*d*, J = 3.3), 5.34 (*d*, J = 6.0) (H−C(5)); 5.19 (*d*, J = 3.6), 5.16 (*d*, J = 3.9) (H−C(1′)); 4.39 (*dd*, J = 7.8, 5.7, 0.5 H), 4.24–4.14 (*m*, 1.5 H), 4.08–3.98 (*m*, 1 H),

3.88–3.82 (*m*, 1 H), 3.75–3.45 (*m*, 6 H) (H–C(6), H–C(7), CH_2–C(8), H–C(2′), H–C(3′), H–C(4′), H–C(5′), 2 H–C(6′)); 3.24–3.14 (*m*, H–C(8)). ^{1}H-NMR (300 MHz, D_2O; **42**/**43** *ca.* 1:1, >90% pure): 7.09, 7.05 (2 br. *s*, H–C(2)); 6.96, 6.94 (2 br. *s*, H–C(3)); 5.65 (*d*, *J* = 3.6), 5.31 (*d*, *J* = 6.3) (H–C(5)); 5.26 (*d*, *J* = 3.9), 5.22 (*d*, *J* = 3.6) (H–C(1′)); 4.20 (*t*, *J* = 8.1, 0.5 H), 4.18–4.03 (*m*, 2 H), 3.98–3.91 (*m*, 1.5 H), 3.78–3.49 (*m*, 5 H), 3.30 (*t*, *J* = 9.0, 1 H) (H–C(6), H–C(7), CH_2–C(8), H–C(2′), H–C(3′), H–C(4′), H–C(5′), 2 H–C(6′)); 3.08–3.02 (*m*, H–C(8)). ^{1}H-NMR (300 MHz, CD_3OD; **42**/**43**·HCl 7:3, *ca.* 90% pure): 7.62 (*d*, *J* = 1.8), 7.66 (*d*, *J* = 2.1) (H–C(2)); 7.55 (*d*, *J* = 1.8), 7.51 (*d*, *J* = 2.1) (H–C(3)); 5.91 (*d*, *J* = 3.0), 5.55 (*d*, *J* = 6.0) (H–C(5)); 5.24, 5.18 (2*d*, *J* = 3.9) (H–C(1′)); 4.44–4.34 (*m*, 1 H), 4.26–3.96 (*m*, 3 H), 3.85 (br. *t*, *J* = 8.1, 1 H), 3.76–3.46 (*m*, 5 H) (H–C(6), H–C(7), CH_2–C(8), H–C(2′), H–C(3′), H–C(4′), H–C(5′), 2 H–C(6′)); 3.37–3.24 (*m*, H–C(8)). ^{13}C-NMR (75 MHz, CD_3 OD; **42**/**43**·HCl (7:3), *ca.* 90% pure): 144.74/144.24 (2*s*, C(8a)); 121.29, 120.84, 120.56, 120.35 (4*d*, C(2), C(3)); 102.21/101.31 (2*d*, C(1′)); 83.74/80.30 (2*d*, C(5)); 77.19, 75.19, 74.87 (2 C), 74.75, 74.65, 73.53, 73.26, 71.55, 71.34, 69.22 (11*d*, C(6), C(7), C(2′), C(3′), C(4′), C(5′)); 62.57 (*t*, C(6′)); 61.80, 60.59 (2*t*, CH_2–C(8)); 44.37 (*d*, C(8)). HR-ESI-MS: 363.1394 ($[M+H]^+$, $C_{14}H_{23}N_2O_9^+$; calc. 363.1398).

REFERENCES

[1] N. Mohal, A. Vasella, *Helv. Chim. Acta* **2005**, *88*, 100.
[2] M. Kurogochi, S. I. Nishimura, Y. C. Lee, *J. Biol. Chem.* **2004**, *279*, 44704.
[3] T. D. Heightman, A. T. Vasella, *Angew. Chem., Int. Ed.* **1999**, *38*, 750.
[4] N. Panday, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 1205.
[5] N. Panday, A. Vasella, *Synthesis* **1999**, 1459.
[6] N. Panday, M. Meyyappan, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 513.
[7] N. Panday, T. Granier, A. Vasella, *Helv. Chim. Acta* **1998**, *81*, 475.
[8] N. Panday, Y. Canac, A. Vasella, *Helv. Chim. Acta* **2000**, *83*, 58.
[9] T. Granier, A. Vasella, *Helv. Chim. Acta* **1998**, *81*, 865.
[10] T. Granier, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 1738.
[11] T. Granier, N. Panday, A. Vasella, *Helv. Chim. Acta* **1997**, *80*, 979.
[12] M. Terinek, A. Vasella, *Helv. Chim. Acta* **2004**, *87*, 719.
[13] M. Terinek, A. Vasella, *Helv. Chim. Acta* **2003**, *86*, 3482.
[14] T. D. Heightman, M. Locatelli, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 2190.
[15] T. D. Heightman, P. Ermert, D. Klein, A. Vasella, *Helv. Chim. Acta* **1995**, *78*, 514.
[16] C. Divne, J. Ståhlberg, T. T. Teeri, T. A. Jones, *J. Mol. Biol.* **1998**, *275*, 309; C. Divne, J. Ståhlberg, T. Reinikainen, L. Ruohonen, G. Pettersson, J. K. C. Knowles, T. T. Teeri, T. A. Jones, *Science* **1994**, *265*, 524.
[17] T. T. Teeri, *Trends Biotechnol.* **1997**, *15*, 160.
[18] A. Varrot, C. A. Tarling, J. M. Macdonald, R. V. Stick, D. L. Zechel, S. G. Withers, G. J. Davies, *J. Am. Chem. Soc.* **2003**, *125*, 7496; W. M. Best, J. M. Macdonald, B. W. Skelton, R. V. Stick, D. Matthew, G. Tilbrook, A. H. White, *Can. J. Chem.* **2002**, *80*, 857.
[19] A. Varrot, M. Schülein, M. Pipelier, A. Vasella, G. J. Davies, *J. Am. Chem. Soc.* **1999**, *121*, 2621.
[20] R. U. Lemieux, *Methods Carbohydr. Chem*. **1963**, *2*, 221.
[21] W. Koenigs, E. Knorr, *Chem. Ber.* **1901**, *34*, 957.
[22] S. K. Chatterjee, P. Nuhn, *Chem. Commun.* **1998**, 1729.
[23] N. Ikemoto, O. K. Kim, L. C. Lo, V. Satyanarayana, M. Chang, K. Nakanishi, *Tetrahedron Lett.* **1992**, *33*, 4295.
[24] E. M. Arnett, *Prog. Phys. Org. Chem.* **1963**, *1*, 223.
[25] J. Bogusiak, W. Szeja, *Synlett* **1997**, 661.
[26] B. Helferich, K. F. Wedemeyer, *Angew. Chem.* **1949**, *61*, 34; B. Helferich, K. F. Wedemeyer, *Liebigs Ann. Chem.* **1949**, *563*, 139; B. Helferich, K. F. Wedemeyer, *Chem. Ber.* **1950**, *83*, 538.
[27] J. Xu, A. Vasella, *Helv. Chim. Acta* **1999**, *82*, 1728.
[28] C. Foces-Foces, A. Alemany, M. Bernabe, M. Martín-Lomas, *J. Org. Chem.* **1980**, *45*, 3502.
[29] S. Sato, S. Nunomura, T. Nakano, Y. Ito, T. Ogawa, *Tetrahedron Lett.* **1988**, *29*, 4097.
[30] W. E. Dick, D. Weisleder, J. E. Hodge, *Carbohydr. Res.* **1975**, *42*, 65.
[31] R. K. Ness, H. G. Fletcher Jr., C. S. Hudson, *J. Am. Chem. Soc.* **1950**, *72*, 2200; H. G. Fletcher Jr., *Methods Carbohydr. Chem.* **1963**, *2*, 226.
[32] N. K. Kochetkov, A. J. Khorlin, A. F. Bochkov, *Tetrahedron* **1967**, *23*, 693.
[33] T. Ogawa, K. Beppu, S. Nakabayashi, *Carbohydr. Res.* **1981**, *93*, C6.
[34] H. Kunz, A. Harreus, *Liebigs Ann. Chem.* **1982**, 41.

[35] K. C. Nicolaou, R. E. Dolle, D. P. Papahatjis, J. L. Randall, *J. Am. Chem. Soc.* **1984**, *106*, 4189; K. C. Nicolaou, A. Chucholowski, R. E. Dolle, J. L. Randall, *J. Chem. Soc., Chem. Commun.* **1984**, 1155.
[36] D. Crich, M. Smith, *J. Am. Chem. Soc.* **2001**, *123*, 9015; D. Crich, M. Smith, Q. J. Yao, J. Picione, *Synthesis* **2001**, 323; D. Crich, S. X. Sun, *J. Org. Chem.* **1996**, *61*, 4506.
[37] D. Ramkumar, S. Sankararaman, *Synthesis* **1993**, 1057.
[38] D. Kahne, S. Walker, Y. Cheng, D. Vanengen, *J. Am. Chem. Soc.* **1989**, *111*, 6881.
[39] R. R. Schmidt, J. Michel, *Angew. Chem., Int. Ed.* **1980**, *19*, 731.
[40] F. A. W. Koeman, J. P. Kamerling, J. F. G. Vliegenthart, *Tetrahedron* **1993**, *49*, 5291.
[41] C.-W. T. Chang, Y. Hui, B. Elchert, J. Wang, J. Li, R. Rai, *Org. Lett.* **2002**, *4*, 4603.
[42] R. R. Schmidt, M. Stumpp, *Liebigs Ann. Chem.* **1983**, 1249; R. R. Schmidt, J. Michel, M. Roos, *Liebigs Ann. Chem.* **1984**, 1343.
[43] Z. Pakulski, A. Zamojski, O. Holst, U. Zähringer, *Carbohydr. Res.* **1991**, *215*, 337.
[44] Z. Szurmai, J. Kerekgyarto, J. Harangi, A. Liptak, *Carbohydr. Res.* **1987**, *164*, 313.
[45] N. K. Kochetkov, N. E. Nifant'ev, L. V. Backinowsky, *Tetrahedron* **1987**, *43*, 3109.
[46] A. Lubineau, K. Basset-Carpentier, C. Augé, *Carbohydr. Res.* **1997**, *300*, 161.
[47] J. E. M. Basten, C. M. Dreef-Tromp, B. de Wijs, C. A. A. van Boeckel, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1201; M. Petitou, P. Duchaussoy, A. Bernat, P. Hoffmann, J. M. Herbert, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2067.
[48] J. Xia, T. Srikrishnan, J. L. Alderfer, R. K. Jain, C. F. Piskorz, K. L. Matta, *Carbohydr. Res.* **2000**, *329*, 561.
[49] D. V. Yashunsky, Y. E. Tsvetkov, M. A. J. Ferguson, A. V. Nikolaev, *J. Chem. Soc., Perkin Trans. 1* **2002**, 242.
[50] J. K. Fairweather, M. Hrmova, S. J. Rutten, G. B. Fincher, H. Driguez, *Chem.–Eur. J.* **2003**, *9*, 2603.
[51] W. Nagata, M. Yoshioka, T. Okumura, *J. Chem. Soc. C* **1970**, 2365.
[52] A. Knierzinger, A. Vasella, *J. Chem. Soc., Chem. Commun.* **1984**, 9.
[53] D. B. Dess, J. C. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 7277.
[54] J. L. Luche, *J. Am. Chem. Soc.* **1978**, *100*, 2226.
[55] P. Magdolen, A. Vasella, *Helv. Chim. Acta* **2005**, *88*, 2454.
[56] I. I. Padilla-Martínez, A. Ariza-Castolo, R. Contreras, *Magn. Reson. Chem.* **1993**, *31*, 189.
[57] M. A. Tius, J. Busch-Petersen, *Tetrahedron Lett.* **1994**, *35*, 5181.
[58] J. Xu, A. Egger, B. Bernet, A. Vasella, *Helv. Chim. Acta* **1996**, *79*, 2004.
[59] K. Okajima, T. Mukae, H. Imagawa, Y. Kawamura, M. Nishizawa, H. Yamada, *Tetrahedron* **2005**, *61*, 3497; H. Yamada, K. Tanigakiuchi, K. Nagao, K. Okajima, T. Mukae, *Tetrahedron Lett.* **2004**, *45*, 9207; H. Yamada, K. Tanigakiuchi, K. Nagao, K. Okajima, T. Mukae, *Tetrahedron Lett.* **2004**, *45*, 5615; H. Yamada, K. Okajima, H. Imagawa, T. Mukae, Y. Kawamura, M. Nishizawa, *Tetrahedron Lett.* **2004**, *45*, 3157.
[60] F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, C. Caufield, M. Lipton, G. Chang, T. Hendrickson, W. C. Still, *J. Comput. Chem.* **1990**, *11*, 440.
[61] K. Briner, B. Bernet, J.-L. Maloisel, A. Vasella, *Helv. Chim. Acta* **1994**, *77*, 1969.
[62] E. Bózo, A. Vasella, *Helv. Chim. Acta* **1992**, *75*, 2613.

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