Practical Stereo- and Regioselective, Copper(I)-Promoted *Strecker* Synthesis of Sugar-Modified α,β-Unsaturated Imines

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The regio- and stereoselective, *Lewis* acid catalyzed *Strecker* reaction between Me_3SiCN and different aldimines incorporating a 2,3,4,6-tetrakis-*O*-pivaloyl-D-glucopyranosyl (Piv_4Glc) chiral auxiliary has been worked out. Depending on the conditions used, high yields (up to 95%) and good diastereoselectivities (de >86%) were achieved under mild conditions (*Table 1*), especially with $CuBr \cdot Me_2S$ as catalyst. Our protocol allows the ready preparation of asymmetric β,γ-unsaturated α-amino acids such as (*R*)-2-amino-4-phenylbut-3-enoic acid (**13**; *Scheme 2*) and congeners thereof.

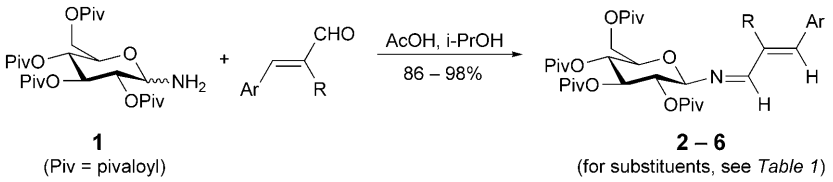
1. Introduction. – Carbohydrates have emerged as versatile auxiliaries and reagents in regio- and stereoselective biological and chemical reactions over the last two decades [1]. Among all the carbohydrates, D-glucose (Glc) has attracted much synthetic attention because of its great contribution to regio- and stereoselective bond construction [2]. It is relatively stable, inexpensive, nontoxic, and readily available owing to its wide occurrence in Nature.

α,β-Unsaturated imine derivatives are useful intermediates in organic synthesis, which can be accessed by simple condensation of parent ketones or aldehydes with amines [3]. Thanks to their *two* electrophilic centers, asymmetric nucleophilic addition reactions often proceed both regio- (1,2- or 1,4-addition) and stereoselectively [4]. The 1,4-addition of silyl ketene acetals to α,β-unsaturated imines, catalyzed by Fe^{III}-exchanged montmorillonites, generally proceeds in fair yield, but, unfortunately, with poor diastereoselectivity [4a]. *Shimizu et al.* [5] have developed a procedure for the addition reaction of two nucleophiles to α,β-unsaturated aldimines promoted by titanium tetrahalides or $AlCl_3$ in a single step, involving both 1,2- and 1,4-addition as the major protocol [5]. Although *Strecker* reactions of α,β-unsaturated imines have been elaborated for the synthesis of β,γ-unsaturated α-amino acids, *Greenlee*'s protocol [4c] suffers from low yields of the arylaldimine, racemic amino acids, and reversion of configuration at the C=C bond. *Snapper* and co-workers [4d] reported Ti-catalyzed asymmetric cyanide 1,2-addition to α,β-unsaturated imines, using *Schiff* base tripeptides as chiral ligands [4d].

In this work, we report on the reactivity and stereo control of metal-promoted *Strecker* reactions between imines containing Glc derivatives as chiral auxiliaries and trimethylsilyl cyanide (Me_3SiCN).

2. Results and Discussion. – We began to examine the addition of cyanides to α,β-unsaturated imines incorporating a 2,3,4,6-tetrakis-*O*-pivaloyl-D-glucopyranosyl (Piv_4-Glc) moiety as the chiral auxiliary at the N-atom. Starting from the glucosamine **1** and a series of substituted cinnamaldehydes, the chiral imines **2**–**6** were prepared under acidic conditions (*Scheme 1*).

Scheme 1

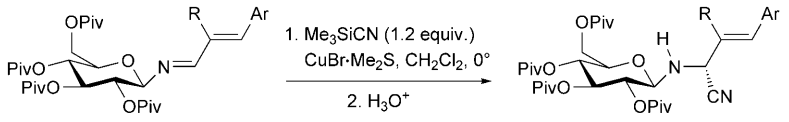


1
(Piv = pivaloyl)

2 – 6
(for substituents, see *Table 1*)

Next, the nucleophilic addition of Me_3SiCN to the aldimines **2**–**6** in CH_2Cl_2 was examined, which afforded the products **7**–**11**. We found that the reaction required 1 equiv. of $CuBr \cdot Me_2S$ to go to completion. As can be seen from *Table 1*, high yields and diastereoselectivities were observed under the given conditions.

Table 1. *Copper(I)-Induced Regio- and Diastereoselective 1,2-Additons of Trimethylsilyl Cyanide to Sugar-Functionalized α,β-Unsaturated Imines*



2 – 6 **7 – 11**

Entry	Substrate	Ar	R	Product	Yield [%][a])	de [%][b])	$[\alpha]_D^{20}$[c])	δ(C) [ppm][d])
1	**2**	C_6H_5	H	**7**	92	86	+5.4	48.32
2	**3**	4-NO_2–C_6H_4	H	**8**	95	88	+5.3	48.87
3	**4**	4-Me_2N–C_6H_4	H	**9**	83	87	+14.8	48.75
4	**5**	4-MeO–C_6H_4	H	**10**	90	88	−2.0	48.42
5	**6**	C_6H_5	Me	**11**	95	89	+11.0	54.34

[a]) Yield of isolated material. [b]) Diastereoisomeric excess; determined by HPLC. [c]) $c = 0.7$, $CHCl_3$. [d]) For *C*H(CN).

We also investigated *Lewis* acids other than Cu, using the reaction of **2** with Me_3SiCN to afford **7** as a model (*Table 2*). With $SnCl_4$, $TiCl_4$, $AlCl_3$, and $ZnCl_2$ as catalysts, (*Entries 2–5* in *Table 2*), the reactions were messy due to the formation of unknown products. *Onaka*'s results of exclusive 1,4-addition [4a] were rationalized by the plausible transition state **12a** (*Figure*) in which the electron density at the γ-C-atom in the α,β-unsaturated imine is decreased. We carried out the corresponding reaction catalyzed by Fe^{III}/montmorillonite (*Entry 6*), which, however, resulted in a poor yield of the 1,2-addition product **7**.

Table 2. *Influence of Different* Lewis *Acids and Conditions on the* Strecker *Reaction*

Entry	Lewis acid	Equiv. of **2**	Time [h]	Yield of **7** [%]
1	$SnCl_4$	1.0	6	71
2	$TiCl_4$	1.0	6	60
3	$AlCl_3$	1.0	6	58
4	$ZnCl_2$	1.0	6	42
5	ZnI_2	1.0	6	45
6	$FeCl_3$/montmorillonite	1.0	6	10
7	$CuBr \cdot Me_2S$	1.0	6	90
8	$CuBr \cdot Me_2S$	0.1	24	50
9	$CuBr \cdot Me_2S$	0.25	12	60
10	$CuBr \cdot Me_2S$	0.5	12	72
11	$CuBr \cdot Me_2S$	1.25	6	90
12	$CuBr \cdot Me_2S$	2.5	6	89
13	$CuBr \cdot Me_2S$	5.0	6	90

In summary, only 1,2- rather than 1,4-addition products were observed in all reactions (*Table 2*). This indicates that the Piv_4Glc group plays a significant role in controlling the regio- and diastereoselective 1,2-addition of cyanide to α,β-unsaturated aldimines. For this reaction, we propose the key transition state **12b** (*Figure*), in which Cu^I is coordinated to both the N-atom of the imine and one of the O-atoms of the 2′-*O*-pivaloyl group. This would decrease the electron density at the C-atom of the C=N moiety and direct the attack of CN^-.

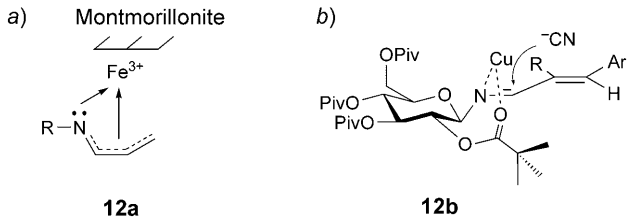
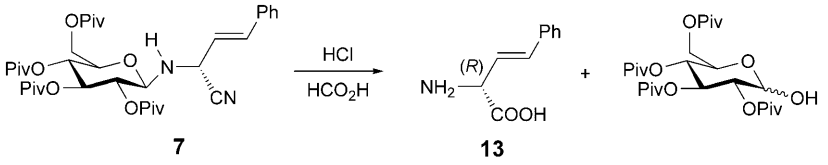


Figure. *Proposed transition-state structures of complexes of regular and sugar-modified imines with* a) *Fe^{III}/montmorillonite and* b) *Cu^I, respectively, in* Strecker *reactions*

β,γ-Unsaturated α-amino acids are of great interest due to their interesting biological properties as antibiotics and enzyme inhibitors [6]. They are also potential building blocks for new, α-branched α-amino acids or synthetic intermediates [7]. Thus, synthetic methods targeting β,γ-unsaturated α-amino acids have attracted much attention [8].

Notably, the chiral amino nitriles **7**–**11**, prepared by stereoselective *Strecker* reaction, are precursors of chiral β,γ-unsaturated α-amino acids. In a first attempt, we, thus, hydrolyzed compound **7** in acidic medium (*Scheme 2*), which, indeed, afforded (*R*)-2-amino-4-phenylbut-3-enoic acid (**13**) [3a][8d]. Further work is currently going on to extend our synthetic protocol.

Scheme 2



7 **13**

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Experimental Part

General. All chemicals are commercially available, and were purchased in *reagent-grade* quality; CH_2Cl_2 was distilled from CaH_2 prior to use. TLC: precoated silica gel *60* F_{254} plates (*Merck*). M.p.: *X4-Data* microscopic melting-point apparatus; uncorrected. IR Spectra: *Nicolet NEXUS-470 FT-IR* spectrometer, with KBr pellets; in cm^{-1}. NMR Spectra: *Bruker Avance DRX-500* spectrometer; δ in ppm rel. to Me_4Si, *J* in Hz. ESI-MS: *Bruker Esquire 3000 plus* spectrometer; in *m*/*z*.

General Procedure (*GP 1*) *for the Preparation of the Imines* **2**–**6**. To a soln. of 2,3,4,6-tetrakis-*O*-pivaloyl-D-glucopyranosylamine (**1**; 0.515 g, 1 mmol) and the appropriate aldehyde (1.3 mmol) in i-PrOH (2.5 ml), two drops of AcOH were added, and the mixture was stirred at r.t. for 20–180 min. The appearance of a precipitate indicated the formation of the imine, which was filtered off, washed rapidly with cold i-PrOH, and dried *in vacuo*.

2,3,4,6-Tetrakis-O-*(2,2-dimethylpropanoyl)*-N-*[(2*E*)-3-phenylprop-2-en-1-ylidene]*-D-*glucopyranosylamine* (**2**). Prepared according to *GP 1*. Yield: 89%. Colorless solid. M.p. 182.2–183.3°. $[\alpha]_D^{20} = -42.5$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2972, 1743, 1638, 1480, 1397, 1281, 1140, 753. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.12 (*d*, *J* = 8.7, 1 H); 7.47 (br., 2 H); 7.36 (br., 2 H); 7.27 (*s*, 2 H); 7.02 (*d*, *J* = 15.9, 1 H); 6.87 (*q*, *J* = 3.9, 1 H); 5.43 (*t*, *J* = 9.5, 1 H); 5.25 (*t*, *J* = 9.6, 1 H); 5.06 (*t*, *J* = 9.2, 1 H); 4.71 (*d*, *J* = 8.6, 1 H); 4.24 (*d*, *J* = 12.3, 1 H); 4.17 (*q*, *J* = 4.8, 1 H); 3.86 (*t*, *J* = 2.6, 1 H); 1.13–1.23 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.4; 177.5; 176.6; 176.4; 163.9; 144.6; 135.5; 129.9; 129.1; 127.8; 111.4; 94.6; 74.4; 73.2; 72.1; 68.1; 62.1; 39.1; 39.0; 27.4; 27.3; 27.3. HR-MS: 630.3625 ($[M+H]^+$, $C_{35}H_{52}NO_9^+$; calc. 630.3642).

2,3,4,6-Tetrakis-O-*(2,2-dimethylpropanoyl)*-N-*[(2*E*)-3-(4-nitrophenyl)prop-2-en-1-ylidene]*-D-*glucopyranosylamine* (**3**). Prepared according to *GP 1*. Yield: 98%. Colorless solid. M.p. 163.5–165.3°. $[\alpha]_D^{20} = -38.5$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2973, 1743, 1640, 1517, 1480, 1345, 1281, 1140, 765. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.24 (*t*, *J* = 8.8, 2 H); 7.66 (*d*, *J* = 8.3, 1 H); 7.62 (*t*, *J* = 8.4, 2 H); 7.06 (*d*, *J* = 15.8, 1 H); 6.96 (*t*, *J* = 8.6, 1 H); 5.45 (*t*, *J* = 9.5, 1 H); 5.22 (*t*, *J* = 9.7, 1 H); 4.99 (*t*, *J* = 9.2, 1 H); 4.83 (*d*, *J* = 8.6, 1 H); 4.27 (*d*, *J* = 12.2, 1 H); 4.17 (*q*, *J* = 4.8, 1 H); 3.88 (*t*, *J* = 5.9, 1 H); 1.09–1.23 (*m*, 36 H). ^{13}C-NMR (125 MHz; $CDCl_3$): 178.4; 177.5; 176.6; 176.3; 164.2; 161.8; 148.2; 141.2; 131.9; 128.3; 124.5; 113.4; 93.0; 74.4; 73.1; 72.2; 70.4; 68.1; 62.0; 39.1; 39.0; 27.3. HR-MS: 697.3291 ($[M+Na]^+$, $C_{35}H_{50}N_2NaO_{11}^+$; calc. 697.3312).

N-*{(2*E*)-3-[4-(Dimethylamino)phenyl]prop-2-en-1-ylidene}-2,3,4,6-tetrakis*-O-*(2,2-dimethylpropanoyl)*-D-*glucopyranosylamine* (**4**). Prepared according to *GP 1*. Yield: 93%. Colorless solid. M.p. 201.2–203.9°. $[\alpha]_D^{20} = -65.65$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2971, 1740, 1642, 1601, 1526, 1480, 1367, 1280, 1128, 1077, 809. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.01 (*s*, *J* = 8.5, 1 H); 7.45 (*d*, *J* = 8.4, 2 H); 7.20 (*d*, *J* = 15.2, 1 H); 6.90 (*t*, *J* = 5.0, 1 H); 6.67 (*t*, *J* = 8.8, 2 H); 5.43 (*t*, *J* = 9.4, 1 H); 5.25 (*t*, *J* = 9.7, 1 H); 5.20 (*t*, *J* = 9.0, 1 H); 4.71 (*d*, *J* = 7.0, 1 H); 4.24 (*d*, *J* = 12.0, 1 H); 4.11 (*q*, *J* = 4.8, 1 H); 3.90 (*t*, *J* = 5.9, 1 H); 3.0 (*s*, 6 H); 0.92–1.27 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.4; 177.6; 176.5; 176.3; 165.4; 151.6; 141.2; 129.3; 123.4; 122.9; 112.1; 111.9; 95.9; 74.3; 73.2; 72.1; 68.2; 64.5; 62.2; 40.4; 39.1; 39.0; 38.9; 27.4; 27.3. HR-MS: 695.3776 ($[M+Na]^+$, $C_{37}H_{56}N_2NaO_9^+$; calc. 695.3884).

2,3,4,6-Tetrakis-O-*(2,2-dimethylpropanoyl)*-N-*[(2*E*)-3-(4-methoxyphenyl)prop-2-en-1-ylidene]*-D-*glucopyranosylamine* (**5**). Prepared according to *GP 1*. Yield: 94%. Colorless solid. $[\alpha]_D^{20} = -3.7$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2972, 1741, 1637, 1602, 1512, 1480, 1398, 1282, 1182, 1142, 1033, 821. ^{1}H-NMR

(500 MHz, $CDCl_3$): 8.08 (*d*, *J* = 8.8, 1 H); 7.43 (*d*, *J* = 8.5, 2 H); 6.94 (*t*, *J* = 2.7, 1 H); 6.92 (*t*, *J* = 4.7, 2H); 6.76 (*q*, *J* = 8.9, 2 H); 5.42 (*t*, *J* = 9.5, 1 H); 5.25 (*t*, *J* = 9.6, 1 H); 5.06 (*t*, *J* = 9.1, 1 H); 4.66 (*d*, *J* = 8.7, 1 H); 4.23 (*d*, *J* = 12.1, 1 H); 4.16 (*q*, *J* = 4.6, 1 H); 3.87 (*t*, *J* = 3.3, 1 H); 3.83 (*s*, 3 H); 1.09–1.22 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.4; 177.6; 176.5; 176.4; 164.4; 161.1; 135.0; 129.4; 128.3; 125.6; 114.1; 95.1; 74.3; 73.2; 72.1; 69.3; 68.1; 62.1; 55.6; 39.1; 39.0; 38.9; 27.4. HR-MS: 682.3553 ($[M+Na]^+$, $C_{36}H_{53}NNaO_{10}^+$; calc. 682.3567).

2,3,4,6-Tetrakis-O-*(2,2-dimethylpropanoyl)*-N-*[(2*E*)-2-methyl-3-phenylprop-2-en-1-ylidene]*-D-*glucopyranosylamine* (**6**). Prepared according to *GP 1*. Yield: 86%. Colorless solid. M.p. 101.7–104.3°. $[\alpha]_D^{20} = -28.4$ (*c* = 1.0, $CHCl_3$). IR (KBr): 2973, 2873, 1743, 1629, 1480, 1398, 1336, 1282, 1142, 760, 696. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.11 (*s*, 1 H); 7.39 (br., 5 H); 7.24–7.29 (*m*, 1 H); 6.87 (*s*, 1 H); 5.4 (*t*, *J* = 9.5, 1 H); 5.23 (*t*, *J* = 9.7, 1 H); 5.01 (*t*, *J* = 9.1, 1 H); 4.82 (*d*, *J* = 8.8, 1 H); 4.27 (*d*, *J* = 12.3, 1 H); 4.17 (*q*, *J* = 4.3, 1 H), 3.88 (*q*, *J* = 4.1, 1 H); 2.07 (*d*, *J* = 5.8, 1 H); 1.04–1.23 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.4; 177.5; 176.7; 176.6; 166.1; 141.8; 136.9; 136.5; 129.7; 128.6; 128.3; 94.6; 74.4; 73.1; 72.4; 72.5; 68.3; 62.2; 39.1; 39.0; 38.9; 27.4; 13.1. HR-MS: 644.3795 ($[M+H]^+$, $C_{36}H_{54}NO_9^+$; calc. 644.3799).

General Procedure (*GP 2*) *for the Preparation of the Amino Nitriles* **7**–**11**. To a soln. of Me_3SiCN (0.14 g, 1.2 mmol) and $CuBr \cdot Me_2S$ (0.31 g, 1 mmol) in CH_2Cl_2 (10 ml) at −30°, a soln. of the appropriate imine (1 mmol) in CH_2Cl_2 (3 ml) was added dropwise. Then, the temp. was raised to 0°, and the mixture was stirred for 3 h (TLC control). When the reaction was finished, 2M aq. HCl (10 ml) was added, and the mixture was washed with sat. aq. $NaHCO_3$ soln. (3 × 10 ml) and H_2O (10 ml). The org. layer was dried ($MgSO_4$) and concentrated *in vacuo*, and the crude product was recrystallized from heptane.

N-*[(2*E*)-1-Cyano-3-phenylprop-2-en-1-yl]-2,3,4,6-tetrakis*-O-*(2,2-dimethylpropanoyl)*-D-*glucopyranosylamine* (**7**). Prepared according to *GP 2*. Yield: 92%. Colorless crystals. M.p. 198.3–200.5°. $[\alpha]_D^{20} = +5.4$ (*c* = 0.7, $CHCl_3$). IR (KBr): 3447, 2973, 2245, 1743, 1480, 1398, 1368, 1146, 761. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.32–7.40 (*m*, 5 H); 6.85 (*d*, *J* = 15.9, 1 H); 6.08 (*dt*, *J* = 15.8, 6.0, 1 H); 5.34–5.42 (*m*, 1 H); 5.11 (*t*, *J* = 9.7, 1 H); 4.88–4.94 (*m*, 1 H); 4.68 (*d*, *J* = 5.6, 1 H); 4.26 (br., 1 H); 4.23–4.25 (*m*, 1 H); 4.10 (*dd*, *J* = 12.6, 5.5, 1 H); 3.75–3.78 (*m*, 1 H); 2.05 (br., 1 H); 1.12–1.43 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.3; 178.0; 177.3; 176.7; 135.4; 129.1; 129.1; 127.1; 117.9; 87.0; 73.9; 72.4; 70.7; 68.2; 62.1; 48.3; 39.1; 39.0; 38.9; 27.4; 27.3; 27.1. HR-MS: 679.3580 ($[M+Na]^+$, $C_{36}H_{52}N_2NaO_9^+$; calc. 679.3571).

N-*[(2*E*)-1-Cyano-3-(4-nitrophenyl)prop-2-en-1-yl]-2,3,4,6-tetrakis*-O-*(2,2-dimethylpropanoyl)*-D-*glucopyranosylamine* (**8**). Prepared according to *GP 2*. Yield: 95%. Colorless crystals. M.p. 176.2–178.1°. $[\alpha]_D^{20} = +5.3$ (*c* = 1.0, $CHCl_3$). IR (KBr): 3333, 2974, 2240, 1732, 1599, 1522, 1481, 1398, 1346, 1282, 1134, 1034, 859, 762. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.17 (*d*, *J* = 8.3, 2 H); 7.50 (*d*, *J* = 8.3, 2 H); 6.86 (*d*, *J* = 15.9, 1 H); 6.27 (*q*, *J* = 5.3, 1 H); 5.35 (*t*, *J* = 10.7, 1 H); 5.09 (*t*, *J* = 9.6, 1 H); 4.90 (*t*, *J* = 9.2, 1 H); 4.55 (*s*, 1 H); 4.25 (*d*, *J* = 4.2, 1 H); 4.03 (*q*, *J* = 4.5, 1 H); 3.71 (*t*, *J* = 5.5, 1 H); 2.49 (*s*, 1 H); 1.07–1.19 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.2; 177.8; 177.2; 176.6; 147.1; 141.5; 131.9; 129.6; 127.7; 124.4; 124.3; 117.7; 87.7; 73.8; 72.3; 70.7; 70.6; 67.9; 48.8; 39.1; 39.0; 38.9; 27.4; 27.3; 27.2. HR-MS: 724.3400 ($[M+Na]^+$, $C_{36}H_{51}N_3NaO_{11}^+$, calc. 724.3421).

N-*{(2*E*)-1-Cyano-3-[4-(dimethylamino)phenyl]prop-2-en-1-yl}-2,3,4,6-tetrakis*-O-*(2,2-dimethylpropanoyl)*-D-*glucopyranosylamine* (**9**). Prepared according to *GP 2*. Yield: 83%. Colorless solid. M.p. 198.4–200.6°. $[\alpha]_D^{20} = +14.8$ (*c* = 1.0, $CHCl_3$). IR (KBr): 3427, 2974, 1742, 1526, 1481, 1398, 1283, 1147, 1034, 893, 562. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.01 (*s*, 1 H); 7.45 (*d*, *J* = 8.5, 2 H); 7.20 (*d*, *J* = 15.2, 1 H); 6.90 (*t*, *J* = 5.0, 1 H); 6.67 (*t*, *J* = 8.8, 2 H); 5.43 (*t*, *J* = 9.4, 1 H); 5.25 (*t*, *J* = 9.7, 1 H); 5.20 (*t*, *J* = 9.0, 1 H); 4.71 (*d*, *J* = 7.0, 1 H); 4.24 (*d*, *J* = 12.0, 1 H); 4.11 (*q*, *J* = 4.8, 1 H); 3.90 (*t*, *J* = 5.9, 1 H); 3.0 (*s*, 6 H); 0.92–1.27 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.4; 177.4; 176.4; 176.3; 170.3; 154.3; 131.4; 130.7; 121.7; 118.7; 112.7; 111.9; 87.5; 74.7; 72.5; 72.4; 67.6; 64.6; 61.7; 49.2; 40.3; 39.1; 39.0; 38.9; 27.4; 27.3; 27.1. HR-MS: 722.4153 ($[M+Na]^+$, $C_{38}H_{57}N_3NaO_9^+$; calc. 722.3993).

N-*[(2*E*)-1-Cyano-3-(4-methoxyphenyl)prop-2-en-1-yl]-2,3,4,6-tetrakis*-O-*(2,2-dimethylpropanoyl)*-D-*glucopyranosylamine* (**10**). Prepared according to *GP 2*. Yield: 90%. Colorless crystals. M.p. 155.6–157.8°. $[\alpha]_D^{20} = -2.0$ (*c* = 1.0, $CHCl_3$). IR (KBr): 3342, 2973, 1739, 1514, 1481, 1397, 1162, 1033, 815. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.33 (*d*, *J* = 8.4, 2 H); 6.87 (*d*, *J* = 8.4, 2 H); 6.76 (*d*, *J* = 15.8, 1 H); 5.92 (*q*, *J* = 6.2, 1 H); 5.39 (*t*, *J* = 9.5, 2 H); 5.10 (*t*, *J* = 9.6, 1 H); 4.88 (*t*, *J* = 9.3, 1 H); 4.64 (*d*, *J* = 5.8, 1

H); 4.23 (*d*, *J* = 12.0, 1 H); 4.08 (*q*, *J* = 5.4, 1 H); 3.82 (*s*, 3 H); 3.73–3.75 (*m*, 1 H); 2.25 (br., 1 H); 1.09–1.22 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.2; 178.0; 177.2; 176.7; 160.3; 152.9; 135.0; 130.6; 128.4; 119.2; 114.7; 114.3; 86.7; 73.8; 72.4; 70.6; 68.1; 62.1; 55.6; 48.4; 39.1; 39.0; 38.9; 27.4; 27.3. HR-MS: 709.3711 ($[M+Na]^+$, $C_{37}H_{54}N_2NaO_{10}^+$; calc. 709.3676).

N-*[(2*E*)-1-Cyano-2-methyl-3-phenylprop-2-en-1-yl]-2,3,4,6-tetrakis*-O-*(2,2-dimethylpropanoyl)*-D-*glucopyranosylamine* (**11**). Prepared according to *GP 2*. Yield: 95%. Colorless crystals. M.p. 123.4–125.6. $[\alpha]^{20}_D = +11.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3321, 2974, 2249, 1744, 1480, 1398, 1367, 1282, 1145, 1034, 761, 701. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.37 (*t*, *J* = 6.5, 2 H); 7.25–7.29 (*m*, 3 H); 6.68 (*s*, 1 H); 5.42 (*t*, *J* = 9.4, 1 H); 5.10 (*t*, *J* = 9.6, 1 H); 4.90 (*t*, *J* = 9.3, 1 H); 4.59 (*s*, 1 H); 4.38 (*d*, *J* = 8.4, 1 H); 4.21 (*d*, *J* = 12.3, 1 H); 4.10 (*q*, *J* = 4.3, 1 H); 3.77–3.79 (*m*, 1 H); 2.07 (*s*, 1 H); 1.97 (*s*, 3 H); 1.01–1.24 (*m*, 36 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 178.2; 178.0; 177.1; 176.8; 136.0; 131.6; 130.8; 129.1; 128.6; 128.5; 127.8; 86.5; 73.8; 72.4; 70.8; 68.3; 54.3; 48.7; 39.1; 39.0; 38.9; 27.4; 27.3; 15.0. HR-MS: 671.3881 ($[M+H]^+$, $C_{37}H_{55}N_2O_9^+$; calc. 671.3908).

Hydrolysis of Compound **7**. Anh. HCl gas was bubbled through a soln. of **7** (0.66 g, 1 mmol) in HCOOH (20 ml) for 24 h at r.t. The soln. was concentrated *in vacuo*, and filtered over silica gel (20 g), eluting with light petroleum ether/AcOEt 1:1. The silica gel (containing the product) was dried, and repeatedly extracted with 2N aq. HCl (400 ml). The combined acidic soln. was concentrated to a volume of *ca*. 10 ml, diluted with conc. HCl (10 ml), and heated to 80° for 48 h. After concentration to dryness, the hydrochloride of **13** was obtained, which was converted to **13** by ion-exchange chromatography.

*Data of (*R*)-2-Amino-4-phenylbut-3-enoic Acid* (**13**). Yield: 95%. Colorless crystals. M.p. 197.3–198.6°. (lit. m.p. 198–200° [4c]). $[\alpha]^{20}_D = +12.0$ ($c = 0.70$, 0.1M aq. HCl) (lit. $[\alpha]^{20}_D = -20$, $c = 1.0$, 0.1M aq. HCl [8h]). IR (KBr): 3453–2500 (br.), 1696, 1625 1474, 1403, 1152, 969, 749. ^{1}H-NMR (500 MHz, D_2O): 7.48–7.50 (*m*, 2 H); 7.35–7.40 (*m*, 3 H); 6.97 (*d*, *J* = 15.8, 1 H); 6.26 (*dd*, *J* = 15.7, 9.0, 1 H); 4.74 (*d*, *J* = 9.1, 1 H). ^{13}C-NMR (125 MHz, D_2O): 171.1; 139.6; 135.4; 129.9; 129.5; 127.59; 119.5; 70.1. ESI-MS: 178 ($[M+H]^+$).

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