The Pent-4-enoyl Group: A Novel Amine-Protecting Group That Is Readily Cleaved under Mild Conditions[1]

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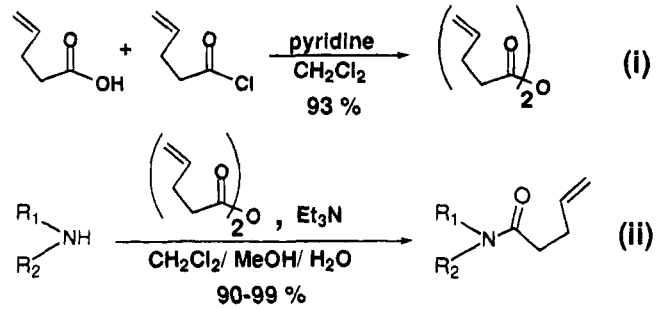
Primary and secondary amines are readily protected as *N*-pent-4-enoyl derivatives, the resulting *N*-pent-4-enamides being usually highly crystalline. Deprotection is rapidly and efficiently effected under mild conditions by treatment with 3 equiv of iodine in aqueous THF solution. Although an oxidizing medium, these deprotection conditions do not affect oxidizable functionalities including *p*-methoxybenzyl ethers and alkyl sulfides.

Introduction

The importance of protecting groups for synthetic manipulations in organic chemistry is ably catalogued in several compendia dedicated to the topic.[3] Deprotection is arguably even more important because synthetic projects have been known to founder in the face of an intransigent protecting group. Amine functions occur in most families of natural products, and thus appropriate protecting strategies geared toward their use have traditionally attracted much attention. Indeed a recent compendium devotes nearly 25% of its pages to amine protection.[3b] Nevertheless currently available choices are compromised for a variety of reasons including high expense, difficulty with installation (imides), lack of stability to acids and/or bases (imines, some carbamates), and difficulty toward removal (amides, alkylamines). Such deficiencies are particularly problematic for aminated carbohydrates which are widespread among the growing number of complex biologically important oligosaccharides. In such structures, protection/deprotection experiments must not only be mild but also preferably chemoselective so as to allow for differentiation between several aminated sites.[4]

Indeed it was our synthetic work with glycoproteins[5] and GPI anchors[6] that sparked our interest in this area of chemistry. Our success in developing hydroxyl-protecting groups that could be installed and/or removed under neutral conditions[7,8] provided a logical launching point. The latter in turn grew out of *n*-pentenyl glycoside (NPG) chemistry which has been explored in our group over the last 7 years.[9] Thus we have shown that NPGs, e.g., **1**, and glycosyl *n*-pentenoates,[10] e.g., **3**, can be hydrolyzed by reaction with an electrophile in the presence of water (Scheme 1a,b). We reasoned that an *n*-pentenamide, e.g., **4**, would react with an electrophile and water through a similar cascade of ionic intermediates (Scheme 1c) to give the oxoiminium ion **5** and thence the free amine **6**. In this manuscript we provide details[11] of our work on the fulfillment of this idea.

N-Pent-4-enoylation. Installation of the pent-4-enoyl group was readily carried out under standard conditions using n-pent-4-enoic anhydride, this being prepared from pent-4-enoyl chloride and pent-4-enoic acid, eq i. The reagent was used in slight excess to acylate the amines dissolved in methylene chloride/methanol/water solvent mixture with triethylamine as base, eq ii. Yields were



consistently in the 90–99% range. After normal workup, isolation of the amides was achieved by direct crystallization, flash chromatography, or, in some cases, passage through mixed-bed ion exchange resin to remove salts and amines. It was encouraging to find that many of the pent-4-enamides that we have so far prepared are readily crystallized, a fact that encourages their use as synthetic intermediates.

Deprotection. *N*-Pent-4-enoylproline benzyl ester (**7**) was chosen as a test substrate for investigating condi-

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(2) (a) R.M. thanks the Danish Technical Research Council for a P.D. fellowship. (b) C.R. is the recipient of a NIH award for underrepresented minorities.
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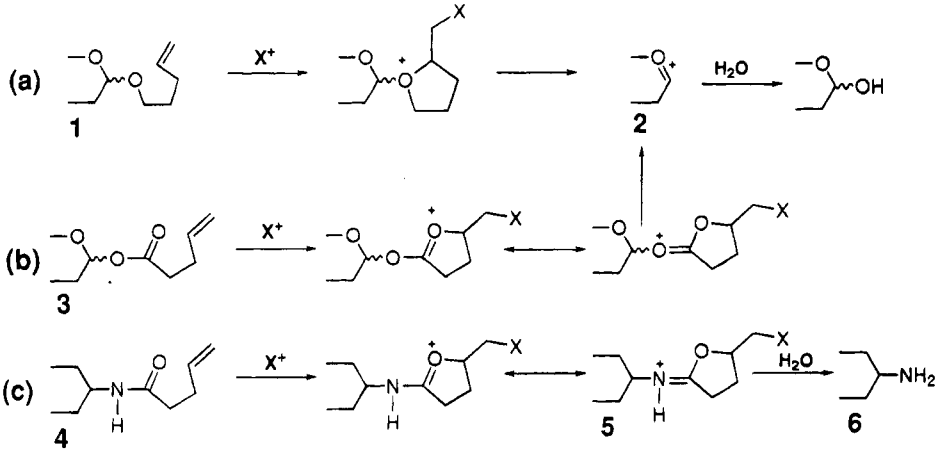
Scheme 1

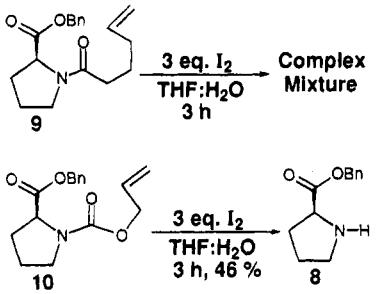


tions for electrophile-induced deprotection. In our work on NPGs, **1**, we have found that *N*-iodosuccinimide/triethylsilyl triflate is an exceedingly potent source of iodonium ion, which causes "instantaneous" cleavage to the oxocarbenium ion **2**.[12] However when this reagent mixture was applied to the test substrate **7**, there were multiple products, Table 1, entry i. *N*-Iodosuccinimide/acetic acid, and even *N*-iodosuccinimide by itself, also gave complex mixtures.

With iodine, the outcome proved to be strongly concentration dependent. Thus with 1 or 2 equiv (Table 1, entries iv and v), there was absolutely no reaction as judged by TLC. However with 3 equiv, cleavage was rapid and efficient as reported in entry vi. This observation is in accordance with the conditions established for iodolactonization.[13]

The solvent used in the above experiments was 1:1 THF/H_2O, but in view of the high crystallinity of these pent-4-enamides, it was deemed appropriate to experiment with other solvent mixtures. The question of solubility aside, the results reported in Table 1 indicate that the choice of solvent can have a profound effect on the cleavage experiment. Thus although yields remained high with aqueous acetonitrile, the process was much slower (entries vii versus vi). By contrast with NPGs, we have found aqueous acetonitrile to be one of the best solvent systems.[9] In the heterogeneous mixture of methylene chloride and water, entry x, deprotection was found to be extremely slow—but reasonably effective. The conditions in Table 1, entry vi, were adopted for general use. Notably the benzylic group of **7** was unaffected under these conditions, and there was absolutely no evidence of epimerization.

We decided to examine the analogues **9** and **10** bearing hex-5-enoyl and (allyloxy)carbonyl groups, respectively. The latter is a popular protecting group for amines, deprotection being normally effected by use of Pd^0 catalysis.[14] Under our standard deprotecting conditions (Table 1, entry vi), **9** gave a complex mixture while **10** gave only a moderate yield of **8**. In both cases there was evidence for addition across the double bond leading to iodohydrin formation. The observation with **9** accords well with our recent finding that the *n*-hexenyloxy group does not cyclize in the presence of electrophiles but instead experiences addition across the double bond.[15]



With these pilot experiments now complete, we examined a wide assortment of substrates as reported in Table 2. The prolinol derivative **11a** was deprotected in good yield under the standard conditions. However the reaction was slower than observed with the ester counterpart **7** (Table 1, entry vi). Deprotection of the emetine alkaloid **12a** was even slower, but the yield of product **12b** was excellent. In this connection, we have found that substrates with a basic nitrogen tend to react more slowly.

The primary amides **13a**, **14a**, and **15a** were cleaved faster, and the yields of the corresponding amines **13b**, **14b**, and **15b**, respectively, were entirely satisfactory. The absence of oxidative attack upon the indole ring of **13a** or the sulfide of **14a** deserves to be noted.

For purposes of solubility, deprotection of the iminoaldonamide **16a** was carried out in aqueous ethanol. Although the yield in the deprotection step was good, it is seen from Table 2 that the reaction was exceedingly slow. The reason for this result is unclear, but it can hardly be attributed to a solvent effect, if one bears in mind that in entry viii of Table 1 deprotection was rapid.

Owing to the importance of D-glucosamine in glyco science, special attention was devoted to some reactions of this substrate. Acylation with pent-4-enoic anhydride, carried out using the well-known procedure for N-acetylation of D-glucosamine hydrochloride, **17a**,[16] gave the crystalline pentenamide **17b** in almost quantitative yield (Scheme 2). Subsequent treatment with acetyl

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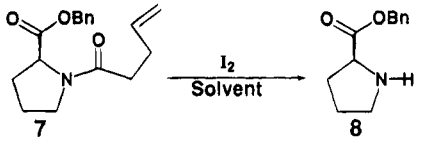
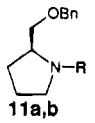
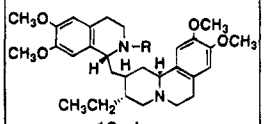
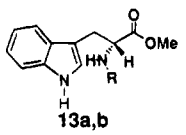
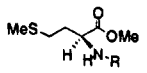
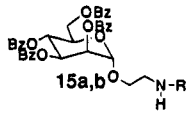
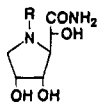
Table 1. Exploratory Conditions for Deprotecting Pent-4-enamides



7 8

entry	electrophile	conditions	reaction time	yield (%)
i	NIS/Et3SiOTf	1:1 THF:H2O	slow reaction, complex mixture	
ii	NIS/HOAc	1:1 THF:H_2O	slow reaction, complex mixture	
iii	NIS	1:1 THF:H_2O	slow reaction, complex mixture	
iv	I_2 (1 equiv)	1:1 THF:H_2O	no reaction	
v	I_2 (2 equiv)	1:1 THF:H_2O	no reaction	
vi	I_2 (3 equiv)	1:1 THF:H_2O	5–10 min	93
vii	I_2 (3 equiv)	1:1 MeCN:H_2O	45 min	92
viii	I_2 (3 equiv)	5:1 EtOH:H_2O	5–10 min	84
ix	I_2 (3 equiv)	1:1 DMF:H_2O	5–10 min	70
x	I_2 (3 equiv)	1:1 CH_2Cl_2:H_2O	3 h	78

Table 2. Deprotection of n-Pent-4-enamides with Iodine (3 equiv)

Substrate (a) R =  Product (b) R = H	Solvent	Reaction Time (Yield)
 11a,b	THF:H_2O	30 min (85 %)
 12a,b	THF:H_2O	6 h (92 %)
 13a,b	THF:H_2O	5-10 min (94 %)
 14a,b	THF:H_2O	5-10 min (89 %)
 15a,b	THF:H_2O	5-10 min (85 %)
 16a,b	EtOH:H_2O	2 h (83 %)

chloride[17] gave the glucosyl chloride **20** ready for Koenigs–Knorr coupling. Silver triflate proved to be an efficient promoter for coupling with alcohols, affording the glucosyl, allyl, *n*-pentenyl, and *p*-methoxybenzyl β-D-glucosaminides **18a**, **19a**, **21a**, and **23**, respectively, all being isolated by direct crystallization. The *p*-methoxybenzyl glycoside **23** was then benzylidenated to give **24a** as a high-melting material (mp 222–224 °C).

In all cases removal of the *N*-pentenoyl group was accomplished in 5–10 min using the standard conditions of 3 equiv of iodine in aqueous THF solution (Scheme 2). The chemoselectivity of the deprotection is clearly evident by the survival of the anomeric allyl and *n*-pentenyl groups in **19b** and **21b**, respectively. Both benzylic centers in **24a** were also unaffected during the oxidative cleavage leading to **24b**.

Attempts to couple the chloride **20** and the hindered alcohol **25** failed, giving instead complete recovery of the latter along with the oxazoline **22** in 73% yield. It may therefore be concluded that, in accordance with a precedent for the corresponding *N*-acetyl analogue,[18] chloride **20** couples very well to primary alcohols but not to hindered secondary alcohols.

In conclusion, the pent-4-enoyl group has been shown to be a facile protecting group for amines. It is easily installed in high yield using pent-4-enoic anhydride. The *N*-pent-4-enamides so obtained are usually highly crystalline, and being amides they should be stable to a wide variety of reaction conditions. However, deprotection is readily effected under mild conditions by treatment with 3 equiv of iodine in aqueous THF solution. In addition the glucosaminyl chloride **20** has been prepared and coupled with primary alcohols to give β-glucosaminides as the only products, these being useful for further synthetic transformations.

Experimental Section

Please see refs 6b,c and 7 for General Procedures.

General Deprotection Procedure for Pent-4-enamides. The pentenoyl amide (0.30 mmol) was dissolved in organic solvent (1 mL), and an equal volume of H_2O (1 mL) was added subsequently, resulting in a cloudy suspension. Additional organic solvent was then added slowly until the turbid solution became clear. The reaction mixture was treated with I_2 (3 equiv) and allowed to stir until completion. The reaction was quenched with solid $NH_4S_2O_3$ (note disappearance of brown color) and the mixture concentrated.

Workup A: The crude material was concentrated *in vacuo* and then flash chromatographed directly to produce the desired amine.

Workup B: The crude material was dissolved in $CHCl_3$ and washed with brine. The organic phase was dried (Na_2SO_4), filtered, concentrated, and chromatographed to afford the desired amine.

Workup C: The crude material was dissolved in MeOH and poured on a column of Amberlite IRA 400 (OH^-) ion exchange resin (50 mL). The column was eluted with MeOH, and the eluate was concentrated to afford the desired amine.

The hydrohalide salts were prepared by concentrating the amines in $CHCl_3$ solutions of the corresponding hydrogen halide.

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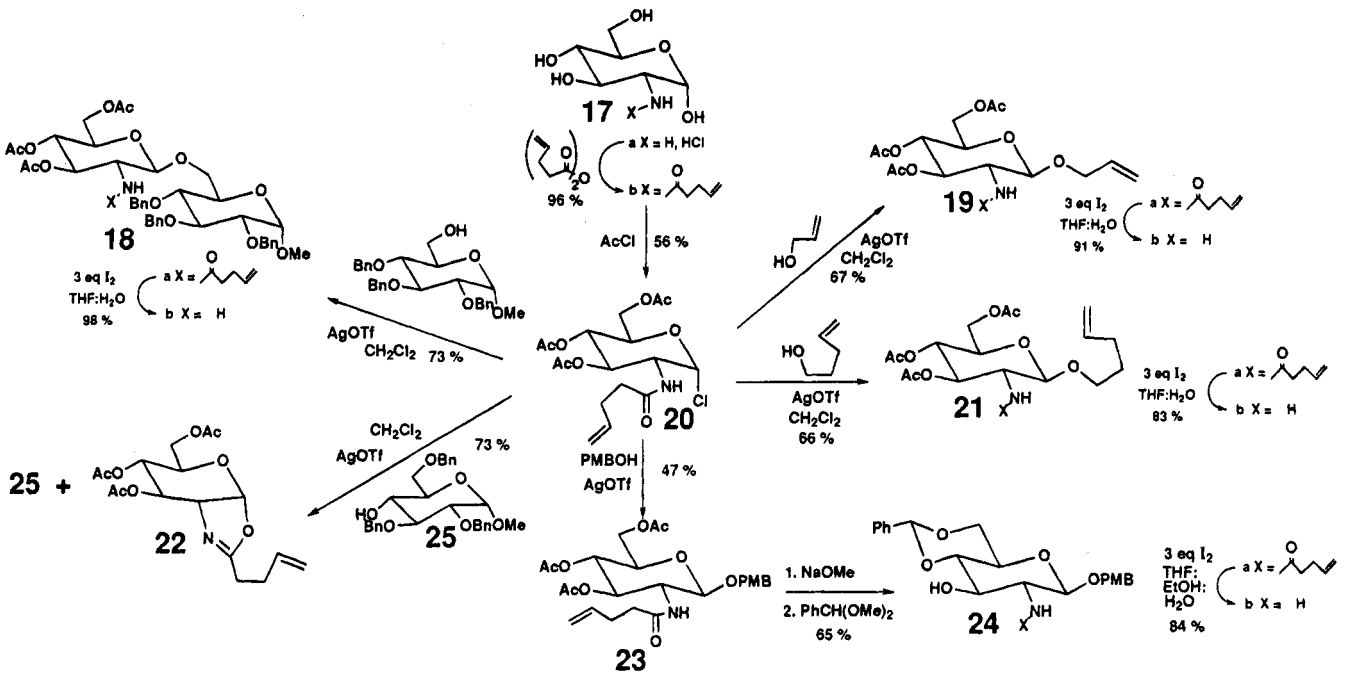
Scheme 2



Pent-4-enoic Anhydride. To an ice-cooled solution of pent-4-enoic acid (33 mL, 32 mmol) and pyridine (33 mL, 41 mmol) in CH_2Cl_2 (400 mL) was added pent-4-enoyl chloride[20] (42 mL, 37 mmol) during 5 min. The reaction mixture was stirred at rt for 30 min and then washed successively with ice-cooled 2% aqueous H_2SO_4 (400 mL) and ice-cooled 5% aqueous $NaHCO_3$ (300 mL). The organic solution was dried and concentrated and the residue distilled to give the title compound (58.6 g, 93%): bp 78–81 °C/0.4 mmHg (lit.[21] bp 105 °C/18 mmHg); δ 0.973; ^1H and ^{13}C NMR in accordance with literature values.[21] Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.94; H, 7.80.

Hex-5-enoic Anhydride.[22] Hex-5-enoic acid[23] (2.9 mL, 24.0 mmol) and pyridine (2.7 mL, 33 mmol) in CH_2Cl_2 (30 mL) were treated with hex-5-enoyl chloride[24] (4.18 g, 32 mmol) as described above. Workup and distillation gave 5.4 g (93%): bp 108–111 °C/0.6 mmHg; δ 0.945; ^1H NMR δ 5.76 (m, 2 -CH=), 5.09–4.98 (m, 2 $=CH_2$), 2.46 (t, J = 7.3 Hz, 2 CH_2), 2.13 (bq, J = 7.1 Hz, 2 -CH_2), 1.77 (p, J = 7.3 Hz, 2 CH_2); ^{13}C NMR 169.4, 137.2, 115.9, 34.4, 32.7, 23.3. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.34; H, 8.50.

***N*-Pent-4-enoyl-L-proline Benzyl Ester (7).** To an ice-cooled solution of L-proline benzyl ester hydrochloride (2.0 g, 8.3 mmol) and Et_3N (2.3 mL, 17 mmol) in CH_2Cl_2 (10 mL) and MeOH (4 mL) was added pent-4-enoic anhydride (2.2 mL, 11.7 mmol). The reaction mixture was stirred at 0 °C for 20 min and then diluted with $CHCl_3$ (20 mL). The solution was washed with saturated aqueous $NaHCO_3$ (20 mL), dried, and concentrated. The residue was purified by flash chromatography (35:65 petroleum ether/EtOAc) to afford 2.23 g (94%) of **7**: R_f = 0.53; $[\alpha]^{20}_D$ −82.9° (*c* 1, $CHCl_3$); ^1H NMR (main rotamer) δ 7.38–7.32 (m, 5H, Ph), 5.87 (m, -CH=), 5.20 (d, J = 12.3 Hz, 1H), 5.13 (d, J = 12.3 Hz, 1H), 5.08–4.96 (m, $=CH_2$), 4.56 (dd, J = 3.6, 8.5 Hz, 1H), 3.64 (m, 1H), 3.51 (dt, J = 6.9, 6.9, 9.4 Hz, 1H), 2.46–2.35 (m, 4H), 2.25–1.87 (m, 4H); ^{13}C NMR 172.2, 171.2, 137.5, 115.1, 66.7, 58.7, 47.0, 33.7, 29.2, 28.7, 24.8. Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.66; H, 7.37; N, 4.79.

L-Proline Benzyl Ester (8). Deprotection was carried out under standard conditions (5 min) in 93% yield using THF as the organic solvent and workup procedure A. Hydrochloride salt: $[\alpha]^{20}_D$ −39.6° (*c* 1, MeOH); mp 141–143 °C (lit.[25] $[\alpha]^{25}_D$ −43.3° (*c* 1, MeOH); mp 148–149 °C); ^1H NMR δ 7.38–7.27 (m, 5H), 5.29–5.14 (m, 2H), 4.48 (m, 1H), 3.54–3.46 (m, 2H), 2.50–2.31 (m, 2H), 2.20–1.91 (m, 2H); ^{13}C NMR 169.9, 134.6, 68.1, 60.6, 46.2, 45.2, 29.1, 23.9.

***N*-Hex-5-enoyl-L-proline benzyl ester (9).** L-Proline benzyl ester hydrochloride (600 mg, 2.48 mmol) was treated with hex-5-enoic anhydride as described above for **7** to give 716 mg (96%) of **9**: R_f = 0.58 (2:3 petroleum ether/EtOAc); $[\alpha]^{20}_D$ −73.9° (*c* 1, $CHCl_3$); ^1H NMR (main rotamer) δ 7.39–7.30 (m, 5H, Ph), 5.79 (m, -CH=), 5.19 (d, J = 12.4 Hz, 1H), 5.12 (d, J = 12.4 Hz, 1H), 5.06–4.95 (m, $=CH_2$), 4.55 (dd, J = 3.6, 8.5 Hz, 1H), 3.64 (m, 1H), 3.50 (dt, J = 6.9, 6.9, 9.6 Hz, 1H), 2.33 (m, 2H), 2.22–1.90 (m, 6H), 1.76 (m, 2H), ^{13}C NMR 172.2, 171.9, 138.2, 115.2, 66.8, 58.8, 47.0, 33.6, 33.2, 29.3, 24.8, 23.8. Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.54; H, 7.75; N, 4.50.

***N*-[(Allyloxy)carbonyl]-L-proline Benzyl Ester (10).** L-Proline benzyl ester hydrochloride (1.86 g, 7.69 mmol) was treated with allyl chloroformate as described above for **7** to give 2.00 g (90%) of **10**: R_f = 0.58 (3:1 petroleum ether/EtOAc); $[\alpha]^{20}_D$ −60.0° (*c* 1, $CHCl_3$); ^1H NMR (1:1 mixture of two rotamers) δ 7.40–7.30 (m, 5H, Ph), 5.94, 5.78 (2 m, -CH=), 5.34–5.10 (m, 4H), 4.61, 4.50 (2 d, J = 5.3, 4.9 Hz, OCH_2), 4.44, 4.38 (2 dd, J = 3.1, 8.7, 3.6, 8.5 Hz, 1H), 3.66–3.55 (m, 1H), 3.55–3.44 (m, 1H), 2.32–2.14 (m, 1H), 2.07–1.84 (m, 3H); ^{13}C NMR 172.7, 172.5 154.8, 154.2, 133.0, 132.8, 117.4, 117.2, 66.8, 66.7, 66.0, 65.9, 59.3, 59.0, 46.9, 46.4, 31.0, 29.9, 24.4, 23.6. Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.30; H, 6.63; N, 4.82.

***N*-Pent-4-enoyl-(*S*)-2-[(benzyloxy)methyl]pyrrolidine (11a).** (*S*)-2-Pyrrolidinemethanol (2.2 mL, 22.1 mmol) was treated with pent-4-enoic anhydride as described above for **7**. The reaction mixture was poured onto a column of Amberlite MB-3 (270 mL, H^+ and OH^-) ion exchange resin which was eluted with MeOH. The eluate was concentrated to yield 4.20 g of a syrup. To an ice-cooled solution of this material in THF (35 mL) were added NaH (1.6 g of 60% oil dispersion, 40 mmol) and Bu_4NI (700 mg). The mixture was stirred for 5 min followed by addition of BnBr (4.5 mL, 38 mmol) and then at rt for 1 h before the reaction was quenched with AcOH. The mixture was filtered through Celite and the filtrate concen-

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trated to remove THF. The residue was dissolved in CH_2Cl_2 (80 mL) and washed with water (80 mL). The organic solution was dried, concentrated, and flash chromatographed (2:3 petroleum ether/EtOAc) to give 6.0 g (99%) of **11a**: $R_f = 0.58$; bp 176–180 °C/0.1 mmHg; $[\alpha]^{20}_D$ −83.1° (*c* 1, $CHCl_3$); ^{1}H NMR (main rotamer) δ 7.38–7.25 (m, 5H, Ph), 5.85 (m, -CH=), 5.08–4.96 (m, =CH_2), 4.54 (d, *J* = 12 Hz, 1H), 4.48 (d, *J* = 12 Hz, 1H), 4.32 (m, 1H), 3.66 (dd, *J* = 3.3, 9.3 Hz, 1H), 3.52 (dd, *J* = 6.8, 9.3 Hz, 1H), 3.55–3.34 (m, 2H), 2.45–2.31 (m, 4H), 2.10–1.84 (m, 4H); ^{13}C NMR 170.9, 137.5, 114.9, 73.0, 70.0, 56.3, 47.1, 34.0, 28.7, 27.4, 24.0. Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.55; H, 8.44; N, 5.09.

(*S*)-2-[(Benzyloxy)methyl]pyrrolidine (11b). Deprotection of **11a** was carried out under standard conditions (30 min) in 85% yield using THF as the organic solvent and workup procedure C: $[\alpha]^{20}_D$ −19° (*c* 1, H_2O); ^{1}H NMR δ 7.37–7.16 (m, 5H), 4.56 (s, 2H), 3.96 (m, 1H), 3.79–3.68 (m, 2H), 3.41–3.23 (m, 2H), 2.11–1.89 (m, 3H), 1.75 (m, 1H); ^{13}C NMR 137.3, 73.2, 68.0, 46.6, 45.8, 26.9, 23.9. Characterization data were consistent with literature precedent.[26]

***N*-Pent-4-enoylemetine (12a).** (+)-Emetine dihydrochloride hydrate (500 mg, 0.903 mmol) was treated with pent-4-enoic anhydride as described above for **7** to give 457 mg (90%) of **12a**: $R_f = 0.53$ (98:2 EtOAc/Et_3N); $[\alpha]^{20}_D$ −48.9° (*c* 1, $CHCl_3$); ^{1}H NMR δ 6.99 (s, 1H), 6.56 (s, 1H), 6.55 (s, 1H), 6.54 (s, 1H), 5.95–5.82 (m, 2H), 5.09-4.96 (m, 2H), 3.96 (s, OMe), 3.85 (s, OMe), 3.83 (s, OMe), 3.82 (s, OMe), 3.47 (dt, *J* = 4.2, 12 Hz, 1H), 3.15–2.85 (m, 6H), 2.76 −2.37 (m, 8H), 2.23 (t, *J* = 12 Hz, 1H), 2.03 (m, 1H), 1.59 (m, 1H), 1.46–1.32 (m, 2H), 1.24–1.04 (m, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR 171.1, 137.6, 115.4, 56.2, 56.1, 55.9, 55.9, 11.1. Anal. Calcd for $C_{34}H_{46}N_2O_5$: C, 72.57; H, 8.24; N, 4.98. Found: C, 72.31; H, 8.25; N, 4.99.

(+)-Emetine (12b). Deprotection of **12a** was carried out under standard conditions (6 h) in 92% yield using THF as the organic solvent and workup procedure A. Dihydrochloride hydrate: $[\alpha]^{20}_D$ +6.3° (*c* 1, H_2O); mp 227 °C dec (lit.[27] $[\alpha]^{25}_D$ +9.0° (*c* 1, H_2O); mp 235 °C dec; ^{13}C NMR 137.3, 73.2, 68.0, 46.6, 45.8, 26.9, 23.9. Characterization data were consistent with the starting material for **12a** and literature precedent.[27]

***N*-Pent-4-enoyl-D-tryptophan Methyl Ester (13a).** D-Tryptophan methyl ester hydrochloride (1.25 g, 4.91 mmol) was treated with pent-4-enoic anhydride as described above for **7** to give 1.4 g (95%) of **13a**: $R_f = 0.51$ (2:3 petroleum ether/EtOAc); $[\alpha]^{20}_D$ −63.3° (*c* 1, $CHCl_3$); ^{1}H NMR δ 8.31 (bs, NH), 7.53 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 6.2, 7.8 Hz, 1H), 7.12 (dd, *J* = 6.2, 8.0 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.04 (bd, *J* = 7.6 Hz, 1H), 5.76 (m, -CH=), 5.04–4.93 (m, 3H), 3.70 (s, OMe), 3.33 (d, *J* = 5.2 Hz, 2H), 2.38–2.22 (m, 4H); ^{13}C NMR 172.5, 172.0, 136.9, 136.2, 127.8, 122.8, 122.3, 119.7, 118.6, 115.7, 111.4, 110.1, 53.0, 52.4, 35.7, 29.3, 27.7. Anal. Calcd for $C_{17}H_{20}N_2O_3$: C, 67.98; H, 6.71; N, 9.33. Found: C, 67.84; H, 6.67; N, 9.33.

D-Tryptophan Methyl Ester (13b). Deprotection of **13a** was carried out under standard conditions (6 h) in 92% yield using THF as the organic solvent and workup procedure A. Hydrochloride of **13b**: $[\alpha]_D$ −12.1° (*c* 1, MeOH); mp 210 °C dec (lit.[28] $[\alpha]^2_D$ −17.5° (*c* 1, MeOH); mp 212 °C dec; ^{1}H NMR δ 8.23 (bs, NH), 7.60–7.05 (m, 5H), 3.84 (m, 1H), 3.71 (s, OMe), 3.29 (m, 1H), 3.05 (m, 1H), 1.73 (bs, NH_2). Characterization data were consistent with the starting material for **13a** and literature precedent.[28]

***N*-Pent-4-enoyl-L-methionine Methyl Ester (14a).** To an ice-cooled solution of L-methionine methyl ester hydrochloride (1.0 g, 5.01 mmol) and Et_3N (1.39 mL, 10 mmol) in CH_2Cl_2 (6 mL) and MeOH (2.4 mL) was added pent-4-enoic anhydride (1.33 mL, 7.05 mmol). The reaction mixture was stirred at 0 °C for 20 min and then diluted with $CHCl_3$ (12 mL). The solution was washed with saturated aqueous $NaHCO_3$ (12 mL), dried, and concentrated. The residue was purified by flash chromatography (2:3 petroleum ether/EtOAc) to afford **14a**: 1.12 g (91%); $R_f = 0.55$; $[\alpha]^{20}_D$ +52.2° (*c* 1, $CHCl_3$); ^{1}H NMR δ 6.22 (bd, *J* = 7.3 Hz, NH), 5.82 (m, -CH=), 5.11–4.98 (m, =CH_2), 4.73 (dt, *J* = 5.2, 7.3 Hz, 1H), 3.75 (s, OMe), 2.53–2.30 (m, 6H), 2.15 (m, 1H), 2.08 (s, SMe), 1.97 (m, 1H); ^{13}C NMR 172.6, 172.1, 136.9, 115.8, 52.6, 51.5, 35.7, 31.8, 30.0, 29.5, 15.5. Anal. Calcd for $C_{11}H_{19}NO_3S$: C, 53.85; H, 7.81; N, 5.71; S, 13.07. Found: C, 53.95; H, 7.87; N, 5.73; S, 13.03.

L-Methionine Methyl Ester (14b). Deprotection of **14a** was carried out under standard conditions (10 min) in 89% yield using THF as the organic solvent and workup procedure A. Hydrochloride salt: $[\alpha]^{20}_D$ +22.1° (*c* 1, H_2O); mp 144–149 °C (lit.[25] values on hydrochloride salt of **14b** $[\alpha]^{19.5}_D$ +25.2° (*c* 5.1, H_2O); mp 147–150 °C); ^{1}H NMR δ 3.69 (s, OMe), 3.58 (dd, *J* = 5.1, 7.2 Hz, 1H), 2.58 (m, 2H), 2.08 (s, SMe), 2.00 (m, 1H), 1.77 (m, 1H); ^{13}C NMR δ 176.2, 53.2, 52.1, 33.8, 30.4, 15.4. Characterization data were consistent with the starting material for **14a** and literature precedent.[25]

2-(Pent-4-enoylamino)ethyl 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranoside (15a). To a solution of ethanolamine (0.5 mL, 8.28 mmol) and Et_3N (1.2 mL, 8.61 mmol) in MeOH (15 mL) was added pent-4-enoic anhydride (2.1 mL, 11.2 mmol). After being stirred for 15 min, the mixture was poured onto a column of Amberlite MB-3 (150 mL, H^+ and OH^-) ion exchange resin which was eluted with MeOH. The eluate was concentrated to give 1.18 g of a hygroscopic, crystalline residue. To a sample of this material (470 mg, 3.28 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide[29] (1.7 g, 2.58 mmol) in CH_2Cl_2 (20 mL) containing powdered, activated 4 Å molecular sieves (0.4 g) was added at −10 °C AgOTf (880 mg, 3.42 mmol). The reaction mixture was stirred vigorously in the dark at −10 °C for 2 h before the reaction was quenched with saturated aqueous $NaHCO_3$ and brine. The mixture was filtered through Celite and the filter cake washed with CH_2Cl_2 (10 mL). The filtrate was washed with saturated aqueous $NaHCO_3$ (25 mL), dried, and concentrated to a syrupy residue which was crystallized from Et_2O to afford 1.43 g (77%) of **15a**: mp 148–149 °C; $[\alpha]^{20}_D$ −61.3° (*c* 1, $CHCl_3$); ^{1}H NMR δ 8.06 (d, *J* = 8 Hz, 2H), 8.04 (d, *J* = 8 Hz, 2H), 7.95 (d, *J* = 8 Hz, 2H), 7.85 (d, *J* = 9 Hz, 2H), 7.65–7.25 (m, 12H, Ph), 6.10 (t, *J* = 10.0 Hz, 1H), 6.07 (m, NH), 5.90 (dd, *J* = 3.0, 10.0 Hz, 1H), 5.86 (m, -CH=), 5.72 (dd, *J* = 2.8, 3.0 Hz, 1H), 5.10 (d, *J* = 2.8 Hz, 1H), 5.15–5.03 (m, =CH_2), 4.69 (dd, *J* = 2.3, 12.1 Hz, 1H), 4.50 (dd, *J* = 4.4, 12.1 Hz, 1H), 4.44 (m, 1H), 3.93 (m, 1H), 3.75–3.63 (m, 2H), 3.50 (m, 1H), 2.49–2.35 (m, 4H); ^{13}C NMR 172.6, 137.1, 115.7, 97.9, 70.3, 70.0, 69.0, 67.8, 66.9, 62.9, 39.1, 35.8, 29.6. Anal. Calcd for $C_{41}H_{39}NO_{11}$: C, 68.23; H, 5.45; N, 1.94. Found: C, 68.09; H, 5.50; N, 1.91.

2-Aminoethyl 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranoside (15b). Deprotection of **15a** was carried out under standard conditions (10 min) to give **15b** in 85% yield using THF as the organic solvent and workup procedure B: $R_f = 0.37$ (18:1 CH_2Cl_2/MeOH); $[\alpha]^{20}_D$ −46.4° (*c* 1, $CHCl_3$); ^{1}H NMR δ 8.11–7.20 (m, 20H), 6.15 (t, *J* = 10.0 Hz, 1H), 5.91 (dd, *J* = 3.1, 10.1, 1H), 5.80 (bs, 1H), 5.21 (bs, 1H), 4.73 (m, 1H), 4.49 (m, 2H), 4.00 (m, 1H), 3.73 (m, 1H), 3.19 (m, 2H); ^{13}C NMR 166.2, 166.1, 165.5, 165.4, 97.9, 70.7, 69.9, 69.2, 51.1, 66.3, 62.7, 40.6. Anal. Calcd for $C_{36}H_{33}NO_{10}$: C, 67.60; H, 5.20; N, 2.19. Found C, 67.34; H, 5.32; N, 2.09.

***N*-Pent-4-enoyl-3,6-dideoxy-3,6-imino-D-allonamide (16a).** To a solution of 3,6-dideoxy-3,6-imino-D-allonamide hydrobromide[30] (1.81 g, 7.04 mmol) and Et_3N (2 mL 14.3 mmol) in MeOH (15 mL) and water (5 mL) was added pent-4-enoic anhydride (2 mL, 10.7 mmol). The reaction mixture was stirred for 15 min and then poured on a column of Amberlite MB-3 (200 mL, H^+ and OH^-) ion exchange resin. The column was eluted with MeOH, and the eluate was concentrated to afford 1.69 g (93%) of crystalline **16a**: mp 160–161 °C; $[\alpha]^{20}_D$ +32.9° (*c* 1, H_2O); ^{1}H NMR (D_2O) δ 5.90 (m, -CH=), 5.13–5.02 (m, =CH_2), 4.71 (d, *J* = 2.8 Hz, 1H), 4.40 (ddd, *J* = 4.3, 4.4, 5.4 Hz, 1H), 4.30 (dd, *J* = 3.9, 4.4 Hz, 1H), 4.15 (dd, *J* = 2.8, 3.9 Hz, 1H), 3.75 (dd, *J* = 5.4, 11.5 Hz, 1H), 3.60 (dd, *J* =

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4.3, 11.5 Hz, 1H), 2.56–2.48 (m, 2H), 2.40–2.30 (m, 2H); ^{13}C NMR (D_2O) 179.3, 178.0, 139.0, 118.1, 73.7, 72.5, 71.4, 67.9, 54.9, 35.8, 30.9. Anal. Calcd for $C_{11}H_{18}N_2O_5$: C, 51.16; H, 7.02; N, 10.85. Found: C, 51.18; H, 6.99; N, 10.86.

3,6-Dideoxy-3,6-imino-D-allonamide (16b). Deprotection of **16a** was carried out under standard conditions (2 h) to give **16b** in 83% yield using EtOH as the organic solvent and workup procedure A. Hydrobromide: $[\alpha]^{20}_D$ −0.81° (*c* 5.0, H_2O); mp 222–227 °C (lit.[30] $[\alpha]^{20}_D$ −1.63° (*c* 5.0, H_2O); mp 231–233 °C). Characterization data were consistent with the starting material for **16a** and literature precedent.[30]

2-Deoxy-2-(pent-4-enoylamino)-α-D-glucopyranose (19b). To a vigorously stirred solution of NaOMe in MeOH (2.2 g, 95.7 mmol of sodium in 100 mL of MeOH) was added D-glucosamine hydrochloride (**17a**) (20 g, 92.7 mmol). The mixture was stirred for 5 min. The precipitated NaCl was removed by filtration through Celite and the filter cake was rinsed with MeOH (10 mL). The filtrate was placed in an ice bath, and pent-4-enoic anhydride (22 mL, 117 mmol) was added immediately. Crystallization began almost instantaneously. The mixture was stirred for 10 min and then kept at −20 °C overnight. Filtration gave the title compound **17b** (23.2 g, 96%): mp 214–215 °C dec.; $[\alpha]^{20}_D$ + 38.8° (*c* 1, H_2O); ^{1}H NMR (α-anomer) δ 5.85 (m, -CH=), 5.15 (d, *J* = 3.0, Hz, 1H), 5.14–5.00 (m, =CH_2), 3.85–3.40 (m, 6H), 2.41–2.30 (m, 4H); ^{13}C NMR 179.3, 139.6, 118.3, 93.6, 74.2, 73.2, 72.8, 63.2, 56.7, 37.6, 32.1. Anal. Calcd for $C_{11}H_{19}NO_6$: C, 50.57; H, 7.33; N, 5.36. Found: C, 50.61; H, 7.41; N, 5.28.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-α-D-glucopyranosyl Chloride (20). A mixture of **17b** (1.6 g, 6.12 mmol) in acetyl chloride (4 mL) was stirred in a sealed flask for 8 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and poured into a beaker containing ice (15 g) and water (5 mL). The phases were separated, and the organic phase was washed successively with ice-cooled water (15 mL) and ice-cooled saturated aqueous $NaHCO_3$ (15 mL). The organic solution was dried and concentrated and the residue flash chromatographed (3:1 CH_2Cl_2/EtOAc) to give 1.38 g (56%) of **20**: R_f = 0.60; $[\alpha]^{20}_D$ +127° (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 6.18 (d, *J* = 3.7 Hz, 1H), 5.85 (d, *J* = 8.8 Hz, NH), 5.78 (m, -CH=), 5.32 (t, *J* = 9.8 Hz, 1H), 5.21 (t, *J* = 9.8 Hz, 1H), 5.10–5.00 (m, =CH_2), 4.54 (m, 1H), 4.32–4.24 (m, 2H), 4.13 (bd, *J* = 10.6 Hz, 1H), 2.38–2.25 (m, 4H), 2.10 (s, Ac), 2.05 (s, Ac), 2.04 (s, Ac); ^{13}C NMR 172.4, 171.5, 170.6, 169.2, 136.4, 116.0, 93.7, 70.9, 70.1, 66.9, 61.2, 53.4, 35.5, 29.2, 20.7, 20.7, 20.6. Anal. Calcd for $C_{17}H_{24}ClNO_8$: C, 50.31; H, 5.96; Cl, 8.74; N, 3.45. Found: C, 50.05; H, 6.00; Cl, 8.59; N, 3.36.

Allyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-β-D-glucopyranoside (19a). To a mixture of **20** (1.2 g, 2.96 mmol), allyl alcohol (0.4 mL, 5.88 mmol), and powdered, activated 4 Å molecular sieves (0.9 g) in CH_2Cl_2 (9 mL) at −20 °C was added AgOTf (960 mg, 3.74 mmol). The reaction mixture was stirred with protection from light for 1 h and allowed to warm to rt. The reaction was quenched with saturated aqueous $NaHCO_3$ and brine and the mixture filtered through Celite. The filter cake was washed with CH_2Cl_2 (15 mL), and the combined filtrate was washed with saturated aqueous $NaHCO_3$ (20 mL). The solution was dried and concentrated and the residue crystallized from Et_2O to afford 843 mg (67%) of **19a**: mp 119–120 °C; $[\alpha]^{20}_D$ −8.32° (*c* 2, $CHCl_3$); ^{1}H NMR δ 5.90–5.73 (m, 2 -CH=), 5.56 (d, *J* = 8.6 Hz, NH), 5.32 (t, *J* = 9.4 Hz, 1H), 5.28–5.18 (m, =CH_2), 5.07 (t, *J* = 9.4 Hz, 1H), 5.07–4.97 (m, =CH_2), 4.73 (d, *J* = 8.3 Hz, 1H), 4.33 (dd, *J* = 5.0, 12.9 Hz, 1H), 4.26 (dd, *J* = 4.8, 12.2 Hz, 1H), 4.13 (dd, *J* = 2.2, 12.2 Hz, 1H), 4.07 (dd, *J* = 6.3, 12.9 Hz, 1H), 3.87 (ddd, *J* = 8.3, 8.6, 9.4 Hz, 1H), 3.70 (m, 1H), 2.38–2.30 (m, 2H), 2.26–2.18 (m, 2H), 2.08 (s, Ac), 2.02 (s, 2Ac); ^{13}C NMR 172.4, 170.9, 170.9, 169.5, 136.9, 133.5, 117.9, 115.7, 99.7, 72.3, 71.8, 70.1, 68.7, 62.2, 54.8, 35.9, 29.4, 20.8, 20.8, 20.7. Anal. Calcd for $C_{20}H_{29}NO_9$: C, 56.20; H, 6.84; N, 3.28. Found: C, 56.00; H, 6.91; N, 3.22.

Allyl 3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (19b). Deprotection of **19a** was carried out under standard conditions (10 min) to give **19b** in 91% yield using THF as the organic solvent and workup procedure B: R_f = 0.5 (3:1 CH_2Cl_2/EtOAc); $[\alpha]^{20}_D$ +5.00° (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 5.93 (m, -CH=), 5.35–5.22 (m, =CH_2), 5.06–4.96 (m, 2H), 4.47–4.26 (m, 3H), 4.15–4.09 (m, 2H), 3.69 (m, 1H), 2.97 (dd, *J* = 8.03, 10.1, 1H), 2.19 (s, Ac), 2.08 (s, Ac), 2.02 (s, Ac); ^{13}C NMR 172.3, 170.9, 170.8, 133.5, 118.3, 102.8, 75.3, 71.8, 70.6, 68.8, 62.2, 55.8, 20.9, 20.8, 20.7. Anal. Calcd for $C_{15}H_{23}NO_8$: C, 52.17; H, 6.71; N, 4.06. Found: C, 52.16; H, 6.59; N, 4.02.

Pent-4-enyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-β-D-glucopyranoside (21a). A mixture of 3,4,6-tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-α-D-glucopyranosyl chloride (**20**) (6.1 g, 15.0 mmol), pent-4-enyl alcohol (3.0 mL, 29.0 mmol), and 4 Å molecular sieves (4 g) in CH_2Cl_2 (40 mL) was treated with AgOTf (4.9 g, 19.1 mmol) as described above. Workup and crystallization from Et_2O gave 4.51 g (66%) of **21a**: mp 112–113 °C; $[\alpha]^{20}_D$ −6.75° (*c* 1, $CHCl_3$); ^{1}H NMR δ 5.84–5.71 (m, 2 -CH=), 5.65 (d, *J* = 8.5 Hz, NH), 5.31 (t, *J* = 9.5 Hz, 1H), 5.07–4.93 (m, 5H), 4.68 (d, *J* = 8.3 Hz, 1H), 4.25 (dd, *J* = 4.7, 12.3 Hz, 1H), 4.12 (dd, *J* = 2.2, 12.3 Hz, 1H), 3.88–3.78 (m, 2H), 3.69 (m, 1H), 3.47 (ddd, *J* = 8.3, 8.5, 9.5 Hz, 1H), 2.38–2.30 (m, 2H), 2.25–2.17 (m, 2H), 2.10–2.00 (m, 2H), 2.06 (s, Ac), 2.02 (s, 2 Ac), 1.70–1.60 (m, 2H); ^{13}C NMR 172.4, 170.8, 170.8, 169.5, 137.9, 136.8, 115.6, 115.0, 100.7, 72.3, 71.8, 69.2, 68.8, 62.2, 54.8, 35.8, 30.0, 29.3, 28.7, 20.8, 20.8, 20.7. Anal. Calcd for $C_{22}H_{33}NO_9$: C, 58.01; H, 7.30; N, 3.07. Found: C, 58.20; H, 7.35; N, 3.10.

Pent-4-enyl 2,3,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (21b). Deprotection of **21a** was carried out under standard conditions (10 min) to give **21b** in 83% yield using THF as the organic solvent and workup procedure B: $[\alpha]^{20}_D$ +5.41° (*c* 1.1, $CHCl_3$); R_f = 0.35 (9:1 CH_2Cl_2/MeOH); ^{1}H NMR δ 5.81 (m, -CH=), 5.06–4.94 (m, 4H), 4.31–4.25 (m, 2H), 4.10 (m, 1H), 3.93 (m, 1H), 3.68 (m, 1H), 3.52 (m, 1H), 2.93 (m, 1H), 2.14 (m, 1H), 2.11 (s, 2 Ac), 2.04 (s, Ac), 1.72 (m, 2H); ^{13}C NMR 172.3, 170.9, 170.8, 137.9, 115.1, 103.9, 75.3, 71.8, 69.7, 68.9, 62.3, 55.9, 30.1, 28.7, 20.9, 20.8, 20.7. Anal. Calcd for $C_{15}H_{23}NO_8$: C, 54.68; H, 7.29; N, 3.75. Found: C, 54.28; H, 7.51; N, 3.99.

***p*-Methoxybenzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-β-D-glucopyranoside (23).** To a mixture of **20** (4.0 g, 9.86 mmol), *p*-methoxybenzyl alcohol (2.2 g, 15.9 mmol) and 4 Å molecular sieves (2.5 g) in CH_2Cl_2 (25 mL) at −30 °C was added AgOTf (3.2 g, 12.5 mmol). The reaction mixture was stirred for 15 min before the reaction was quenched with saturated aqueous $NaHCO_3$ and brine. Workup as described above and crystallization from Et_2O gave 2.36 g (47%) of the title compound **23**: mp 138–140 °C, $[\alpha]^{20}_D$ −36.7° (*c* 1, $CHCl_3$); ^{1}H NMR δ 7.25–7.20 (m, 2H, Ph), 6.90–6.85 (m, 2H, Ph), 5.78 (m, -CH=), 5.31 (d, *J* = 8.4 Hz, NH), 5.22 (dd, *J* = 9.4, 10.5 Hz, 1H), 5.08 (t, *J* = 9.4 Hz, 1H), 5.07–4.96 (m, =CH_2), 4.82 (d, *J* = 11.7 Hz, 1H), 4.63 (d, *J* = 8.4 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.28 (dd, *J* = 4.8, 12.2 Hz, 1H), 4.17 (dd, *J* = 2.5, 12.2 Hz, 1H), 3.94 (dt, *J* = 8.4, 10.5 Hz, 1H), 3.81 (s, OMe), 3.66 (m, 1H), 2.36–2.28 (m, 2H), 2.21–2.15 (m, 2H), 2.11 (s, Ac), 2.01 (s, Ac), 2.00 (s, Ac); ^{13}C NMR 172.3, 170.6, 170.6, 169.2, 159.3, 136.7, 129.7, 128.7, 115.4, 113.7, 99.1, 72.2, 71.7, 70.2, 68.6, 62.2, 55.2, 54.3, 35.8, 29.7, 20.8, 20.7, 20.7. Anal. Calcd for $C_{25}H_{33}NO_{10}$: C, 59.16; H, 6.55; N, 2.76. Found: C, 59.13; H, 6.58; N, 2.78.

Methyl 6-*O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (18a). A mixture of **20** (1.5 g, 3.70 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[31] (1.3 g, 2.80 mmol), and 4 Å molecular sieves (1.2 g) in CH_2Cl_2 (12 mL) was treated with AgOTf (1.2 g, 4.67 mmol) as described above. Workup and crystallization from Et_2O gave 1.70 g (73%) of **18a**: mp 191–192 °C; $[\alpha]^{20}_D$ +9.14° (*c* 1, $CHCl_3$); ^{1}H NMR δ 7.38–7.25 (m, 15H, Ph), 5.70 (m, -CH=), 5.33 (d, *J* = 8.9 Hz, NH), 5.27 (t, *J* = 10.1 Hz, 1H), 5.06–4.92 (m, 4H), 4.85–4.76 (m, 3H), 4.70–4.55 (m, 4H), 4.21 (dd, *J* = 4.6, 12.3 Hz, 1H), 4.09 (dd, *J* = 1.9, 12.3 Hz, 1H), 4.05–3.94 (m, 2H), 3.86 (ddd, *J* = 8.7, 8.9, 10.1 Hz, 1H), 3.78 (m, 3H), 3.51 (dd, *J* = 3.4, 9.5 Hz, 1H), 3.46 (t, *J* = 8.8 Hz, 1H), 3.35 (s, Me), 2.28–2.20 (m, 2H), 2.13–2.05 (m, 2H), 2.01 (s, 3Ac); ^{13}C NMR 172.1, 170.8, 170.7, 169.4, 136.7, 115.6, 100.5, 98.0, 55.2, 54.4, 35.7, 29.2,

(31) Liptak, A.; Jodal, I.; Nanasi, P. *Carbohydr. Res.* **1975**, *44*, 1. Eby, R.; Schuerch, C. *Carbohydr. Res.* **1974**, *34*, 79.

20.7, 20.7, 20.7. Anal. Calcd for $C_{45}H_{55}NO_{14}$: C, 64.81; H, 6.65; N, 1.68. Found: C, 64.84; H, 6.64; N, 1.54.

Methyl 6-*O*-(2,3,6-Tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl] 2,3,4-tri-*O*-benzyl-α-glucopyranoside (18b). Deprotection of **18a** was carried out under standard conditions (10 min) to give **18b** in 98% yield using THF as the organic solvent and workup procedure B: $[\alpha]_D^{20}$ +19.2° (*c* 3.63, $CHCl_3$); R_f = 0.36 (9:1 CH_2Cl_2/MeOH); ^{1}H NMR δ 7.35–7.26 (m, 15H), 5.01–4.89 (m, 3H), 4.82–4.75 (m, 2H), 4.70–4.52 (m, 3H), 4.2 (m, 1H), 4.15–3.94 (m, 3H), 3.82 (m, 1H), 3.71–3.60 (m, 2H), 3.57–3.27 (m, 6H), 2.97 (m, 1H), 2.07 (s, Ac), 2.04 (s, Ac), 2.01 (s, Ac); ^{13}C NMR 170.8, 170.7, 169.8, 104.5, 98.1, 20.9, 20.8, 20.7. Anal. Calcd for $C_{40}H_{49}NO_{13}\cdot H_2CO_3\cdot H_2O$: C, 59.20; H, 6.42; N, 1.68. Found: C, 59.46; H, 6.20; N, 1.70.

***p*-Methoxybenzyl 4,6-*O*-Benzylidene-2-deoxy-2-(pent-4-enoylamino)-β-D-glucopyranoside (24a).** To a solution of *p*-methoxybenzyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(pent-4-enoylamino)-β-D-glucopyranoside (**23**) (1.33 g, 2.62 mmol) in CH_2Cl_2 (1 mL) was added 0.03 M methanolic NaOMe (15 mL), and the reaction mixture was stirred for 1 h. Precipitated triol was filtered off. The filtrate was diluted with MeOH (10 mL) and the reaction quenched with Amberlite IR-120 (H^+) ion exchange resin. The mixture was filtered and the filtrate concentrated to a crystalline residue which was combined with the crystals above. This material was taken up in DMF (10 mL), and benzaldehyde dimethyl acetal (0.55 mL, 3.66 mmol) and pyridinium *p*-toluenesulfonate (100 mg) were added. The mixture was heated at 40 °C under vacuum (~50 mmHg) for 2 h before the reaction was quenched with Et_3N. The solution was concentrated to a crystalline residue which was recrystallized from MeOH to give 800 mg (65%) of **24a**: mp 222–224 °C; $[\alpha]^{20}_D$ −62.3° (*c* 0.5, MeOH); ^{1}H NMR (DMSO-d_6) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.50–7.35 (m, 5H, Ph), 7.24–7.18 (m, 2H, Ph), 6.92–6.85 (m, 2H, Ph), 5.82 (m, -CH=), 5.62 (s, PhCH), 5.28 (d, *J* = 4.9 Hz, 1H), 5.06–4.91 (m, =CH_2), 4.68 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.25 (dd, *J* = 4.8, 10.1 Hz, 1H), 3.75 (s, OMe), 3.75–3.42 (m, 5H), 2.28–2.12 (m, 4H); ^{13}C NMR (DMSO-d_6) 171.4, 158.8, 137.9, 137.8, 129.7, 129.1, 128.9, 128.0, 126.4, 114.9, 113.5, 101.1, 100.7, 81.3, 70.3, 69.8, 67.9, 66.1, 56.1, 55.1, 35.0, 29.3. Anal. Calcd for $C_{26}H_{31}NO_7$: C, 66.51; H, 6.65; N, 2.98. Found: C, 66.36; H, 6.58; N, 2.96.

***p*-Methoxybenzyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (24b).** Deprotection of **24a** was carried out under standard conditions (10 min) to give **24b** in 84% yield using THF as the organic solvent and workup procedure B: $[\alpha]^{20}_D$ +18.4° (*c* 2.13, $CHCl_3$); R_f = 0.4 (9:1 EtOAc/petroleum ether); ^{1}H NMR δ 7.50–7.23 (m, 7H, Ph), 6.91–6.85 (m, 2H, Ph), 5.51 (s, PhCH), 4.79 (d, *J* = 11.4 Hz, 1H), 4.49 (m, 1H), 4.32 (m, 2H), 3.79 (s, OMe), 3.77 (m, 2H), 3.52 (m, 2H), 2.81 (m, 1H); ^{13}C NMR 159.5, 113.9, 103.1, 101.9, 81.4, 72.8, 71.2, 68.8, 66.5, 57.8, 55.3; MS (CI) *m*/*e* 388 $(M + H)^+$.

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