Supplementary Information

Modifying the phenyl group of PUGNAc: Reactivity tuning to deliver selective inhibitors for N-acetyl-D-glucosaminidases

Mitchell Hattie, a Nevena Cekic, b Aleksandra W. Debowski, a,c David J. Vocadlo, b,d and Keith A. Stubbs a*

a School of Chemistry and Biochemistry, The University of Western Australia, Crawley, WA, 6009, Australia.
E-mail: keith.stubbs@uwa.edu.au

b Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada

c School of Pathology and Laboratory Medicine, The University of Western Australia, Crawley, WA 6009, Australia

d Department of Molecular Biology and Biochemistry, Simon Fraser University, Burnaby, British Columbia, V5A 1S6, Canada
Experimental

General

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained on Bruker ARX500 (500 MHz for $^1$H and 126 MHz for $^{13}$C) or Bruker AV600 or AV600III HD (600 MHz for $^1$H and 151 MHz for $^{13}$C) spectrometers. Solvents used for NMR were: deuteriochloroform (CDCl$_3$) with CHCl$_3$ ($^1$H, $\delta$, 7.26 CDCl$_3$ ($^{13}$C, $\delta$ 77.16) used as an internal standard, tetradeuteriomethanol (CD$_3$OD) with CD$_2$HOD ($^1$H, $\delta$ 3.31) or CD$_3$OD ($^{13}$C, $\delta$ 49.00) used as an internal standard, hexadeuteriodimethyl sulfoxide (d$_6$-DMSO) with CD$_2$S(O)CD$_2$H ($^1$H, $\delta$ 2.50) or (CD$_3$)$_2$SO ($^{13}$C, $\delta$ 39.52) used as an internal standard, deuterium oxide (D$_2$O) with DHO ($^1$H, $\delta$ 4.79) or CH$_3$OH ($^{13}$C, $\delta$ 49.50) used as an internal standard.$^1$ All compounds were dried under vacuum to constant weight before analysis. High resolution mass spectra (HR-MS) were recorded with a Waters LCT Premier XE spectrometer, run in W-mode, using ESI or APCI ionisation methods as indicated, with MeCN:water (9:1) as a matrix. Flash chromatography was performed on BDH silica gel with the specified solvents. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 aluminium-backed plates that were stained by heating (>200 °C) with 5% solution of sulfuric acid in EtOH.

$O$-(2-Acetamido-3,4,6-tri-$O$-acetyl-2-deoxy-D-glucopyranosylidene)amino $O'$-(4-nitrophenyl)carbonate 1

$N,N$-Diisopropylethylamine (37 µL, 0.21 mmol) and 4-nitrophenylchloroformate (0.21 mmol) were added to a stirred solution of hydroximolactone 2$^2$ (70 mg, 0.19 mmol) in THF (3.5 mL) at 0°C. After 1.5 h., the reaction mixture was concentrated. Flash chromatography (EtOAc:hexane 7:3) of the residue afforded the carbonate 1 as a colourless oil (43 mg, 36%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.27 (AA‘BB’, 2H), 7.41 (AA‘BB’, 2H), 7.07 (d, $J = 8.0$ Hz, 1H), 5.43 (dd, $J = 9.2$, 9.2 Hz, 1H), 5.32 (dd, $J = 8.8$, 8.8 Hz, 1H), 4.80 (dd, $J = 8.2$, 9.2 Hz, 1H), 4.59 (ddd, $J = 2.5$, 3.5, 8.6 Hz, 1H), 4.46 (dd, $J = 3.5$, 13.0 Hz, 1H), 4.31 (dd, $J = 2.5$, 13.0 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 171.1, 170.3, 170.0, 169.2, 158.8, 155.0, 151.1, 145.6, 125.4, 121.6, 77.6, 71.3, 67.0, 61.2, 49.8, 22.6, 20.6, 20.44, 20.4. HR-MS (APCI) $m/z$ 548.1138; [M+Na]$^+$ requires 548.1129.
**O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-phenyl carbamate 3**

**Method 1:** Aniline (21 µL, 0.23 mmol) was added to a stirred solution of DIPEA (13 µL, 0.080 mmol) and the 4-nitrophenylcarbonate 1 (40 mg, 0.076 mmol) in THF (2.0 mL) at 0°C. After 24 h., the reaction mixture was concentrated and the residue dissolved in CH₂Cl₂, washed with water (15 mL), brine (15 mL), dried (MgSO₄), filtered and concentrated. Flash chromatography (EtOAc:hexane 7:3) of the residue yielded the triacetate 3 as a colourless oil (30 mg, 50%). The ¹H and ¹³C NMR spectra was consistent with that found in the literature.²

**Method 2:** N,N-Diisopropylethylamine (37 µL, 0.21 mmol) and 4-nitrophenylchloroformate (43 mg, 0.21 mmol) were added to a stirred solution of hydroximolactone 2² (70 mg, 0.19 mmol) in THF (3.5 mL) at 0°C. After 1.5 h., aniline (0.21 mmol) and DIPEA (37 µL, 0.21 mmol) were added at 0°C and the reaction mixture was concentrated once all the *in situ* carbonate 1 was consumed, as judged by TLC. Flash chromatography of the resultant residue (EtOAc:hexane 7:3) yielded the triacetate 3 as a colourless oil (56 mg, 69%).

**General preparation of 3,4,6-tri-O-acetyl carbamates 4-33, using the in situ method.**

**Procedure 1**

N,N-Diisopropylethylamine (1.1 equiv) and 4-nitrophenylchloroformate (1.1 equiv) were added to a stirred solution of 2² (1.0 equiv) in THF (20 mL/mmol) at 0°C. After 1.5 h., the appropriate amine (1.1 equiv) and DIPEA (1.5 equiv) were added at 0°C and the reaction mixture was concentrated once all the *in situ* carbonate 1 was consumed, as judged by TLC.

**Procedure 2**

N,N-Diisopropylethylamine (1.1 equiv) and 4-nitrophenylchloroformate (1.1 equiv) were added to a stirred solution of 2² (1.0 equiv) in THF (20 mL/mmol) at 0°C. After 1.5 h., the appropriate amine hydrochloride (1.1 equiv) and DIPEA (2.5 equiv) were added at 0°C and the reaction mixture was concentrated once all the *in situ* carbonate 1 was consumed, as judged by TLC.
O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino \( N - (4\text{-methylphenyl}) \) carbamate 4

Using 2 and 4-methylaniline according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate 4 as a colourless oil (60 mg, 64%). \( R_f \) 0.32 (EtOAc:hexane 7:3). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.51 (br s, 1H), 7.29 (AA'BB', 2H), 7.13 (AA'BB', 2H), 6.41 (d, \( J = 8.0 \) Hz, 1H), 5.36-5.32 (m, 2H), 4.96 (dd, \( J = 8.5, 9.0 \) Hz, 1H), 4.47-4.41 (m, 2H), 4.33 (dd, \( J = 2.0, 12.5 \) Hz, 1H), 2.31 (s, 3H), 2.14 (s, 3H), 2.08 (s, 6H), 2.04 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 170.5, 170.4, 170.3, 169.1, 154.8, 151.7, 134.2, 134.0, 129.9, 119.4, 77.4, 71.3, 67.2, 61.3, 49.5, 23.0, 20.8, 20.7, 20.6, 20.5. HR-MS (APCI) \( m/z \) 494.1775; [M+H]\(^+\) requires 494.1775.

O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino \( N - (4\text{-methoxyphenyl}) \) carbamate 5

Using 2 and 4-anisidine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate 5 as a colourless oil (60 mg, 95%). \( R_f \) 0.30 (EtOAc:hexane, 4:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.47 (br s, 1H), 7.32 (AA'BB', 2H), 6.87 (AA'BB', 2H), 6.44 (d, \( J = 8.5 \) Hz, 1H), 5.37-5.31 (m, 2H), 4.97 (dd, \( J = 8.5, 8.5 \) Hz, 1H), 4.46-4.32 (m, 3H), 3.79 (s, 3H), 2.14 (s, 3H), 2.08 (s, 6H), 2.03 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 170.5, 170.4, 170.3, 169.1, 154.8, 141.7, 134.0, 129.9, 119.4, 77.4, 71.3, 67.2, 61.3, 55.5, 49.5, 23.0, 20.7, 20.6, 20.5. HR-MS (APCI) \( m/z \) 532.1525; [M+Na]\(^+\) requires 532.1543.

O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino \( N - (4\text{-bromophenyl}) \) carbamate 6

Using 2 and 4-bromoaniline according to Procedure 1 and flash chromatography (EtOAc:hexane 7:3) yielded the triacetate 6 as a colourless oil (20 mg, 23%). \( R_f \) 0.27 (EtOAc:hexane 7:3). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.76 (br s, 1H), 7.42 (AA'BB', 2H), 7.33 (AA'BB', 2H), 6.87 (d, \( J = 7.5 \) Hz, 1H), 5.39 (dd, \( J = 8.5, 8.5 \) Hz, 1H), 5.33 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 4.84 (d, \( J = 8.5, 8.5 \) Hz, 1H), 4.51 (dd, \( J = 2.5, 3.0, 8.5 \) Hz, 1H), 4.41 (dd, \( J = 3.5, 13.0 \) Hz, 1H), 4.31 (dd, \( J = 2.5, 13.0 \) Hz, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04, (s, 3H), 2.02 (s, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 170.6, 170.4, 170.2, 169.1, 155.6, 154.7, 151.2, 136.1, 132.1, 120.1, 116.8, 77.2, 71.3, 67.1, 61.2,
49.7, 22.9, 20.62, 20.6, 20.5. HR-MS (APCI) m/z 558.0717; [M+H]^+ requires 558.0723.

*O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-benzyl carbamate 7*

Using **2** and BnNH₂ according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate 7 as a colourless oil (54 mg, 55%). *Rf* 0.35 (EtOAc:hexane 9:1).¹H NMR (500 MHz, CDCl₃): δ 7.36-7.27 (m, 5H), 6.14 (d, *J* = 9.0 Hz, 1H), 5.97 (t, *J* = 5.0 Hz, 1H), 5.34 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.26 (dd, *J* = 10.0, 10.0 Hz, 1H), 4.97 (dd, *J* = 8.5, 10.0 Hz, 1H), 4.49-4.37 (m, 3H), 4.29 (dd, *J* = 1.5, 12.5 Hz, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.95 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 170.5, 170.4, 170.1, 128.8, 127.6, 77.5, 71.4, 67.3, 61.4, 49.4, 45.3, 22.9, 20.64, 20.6, 20.5. HR-MS (APCI) m/z 516.1590; [M+Na]^+ requires 516.1594.

*O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-cyclopropylcarbamate 8*

Using **2** and cyclopropylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate 8 as a colourless oil (68 mg, 89%). *Rf* 0.28 (EtOAc:hexane 3:1).¹H NMR (500 MHz, CDCl₃): δ 6.52 (d, *J* = 6.0 Hz, 1H), 5.49 (s, 1H), 5.34-5.27 (m, 2H), 5.28 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.94 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.45-4.39 (m, 2H), 4.29 (dd, *J* = 3.0, 13.0 Hz, 1H), 2.67-2.61 (m, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 0.79-0.73 (m, 2H), 0.58-0.54 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 170.4, 170.3, 169.1, 155.4, 154.3, 71.5, 67.3, 61.4, 49.3, 22.9, 22.6, 20.63, 20.6, 20.5, 6.8. HR-MS (APCI) m/z 444.1603; [M+H]^+ requires 444.1618.

*O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-cyclobutylcarbamate 9*

Using **2** and cyclobutylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate 9 as a colourless oil (72 mg, 53%). *Rf* 0.29 (EtOAc:hexane 9:1).¹H NMR (500 MHz, CDCl₃): δ 6.40 (d, *J* = 8.5 Hz, 1H), 5.78 (d, *J* = 7.5 Hz, 1H), 5.33 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.28 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.96
Using 2 and cyclohexylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate 11 as a colourless oil (67 mg, 76%). Rf 0.25 (EtOAc:hexane 7:3). 1H NMR (500 MHz, CDCl₃): δ 6.18 (d, J = 8.5 Hz, 1H), 5.54 (d, J = 8.0 Hz, 1H), 5.35 (dd, J = 8.5, 8.5 Hz, 1H), 5.25 (dd, J = 10.0, 10.0 Hz, 1H), 5.00 (dd, J = 9.0, 9.0 Hz, 1H), 4.41 (dd, J = 3.5, 12.5 Hz, 1H), 4.35 (ddd, J = 2.5, 3.5, 12.5 Hz, 1H), 4.30 (dd, J = 2.5, 12.5 Hz, 1H), 3.58-3.56 (m, 1H), 2.14 (s, 3H), 2.08 (br s, 2H), 2.07 (s, 3H), 2.03, (s, 3H), 1.97-1.94 (m, 2H), 1.72-1.68 (m, 2H), 1.41-1.31 (m, 3H), 1.22-1.15 (m, 3H). 13C NMR (126 MHz, CDCl₃): δ 170.44, 170.4, 170.1, 169.1, 153.6, 153.4, 71.4, 67.3, 61.4, 50.1, 49.5, 33.0, 25.4, 24.6, 23.0, 20.7, 20.6, 20.5. HR-MS (APCI) m/z 486.2081; [M+H]^+ requires 486.2088.
Using 2 and adamant-1-ylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate 12 as a colourless oil (99 mg, 86%). $R_f$ 0.29 (EtOAc:hexane 3:1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.22 (d, $J$ = 7.0 Hz, 1H), 5.44 (br s, 1H), 5.36 (dd, $J$ = 9.0, 10.0 Hz, 1H), 5.00 (dd, $J$ = 9.0, 10.0 Hz, 1H), 4.40 (dd, $J$ = 3.0, 12.0 Hz, 1H), 4.35-4.29 (m, 2H), 2.14 (s, 3H), 2.09 (br s, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.96 (br s, 6H), 1.68 (br s, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 170.43, 170.4, 170.3, 153.2, 152.0, 77.4, 71.5, 67.3, 61.4, 51.4, 49.4, 41.5, 36.2, 29.4, 23.0, 20.7, 20.6, 20.5. HR-MS (APCI) $m/z$ 538.2423; [M+H]$^+$ requires 538.2401.

Using 2 and glycinamide 3 according to Procedure 1 and flash chromatography (MeOH:EtOAc 1:9) yielded the triacetate 13 as a colourless oil (43 mg, 61%). $R_f$ 0.15 (EtOAc:hexane:MeOH 75:23:2). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.17 (d, $J$ = 8.4 Hz, 1H), 7.15 (dd, $J$ = 5.4, 6.0 Hz, 1H), 6.62 (br s, 1H), 6.17 (br s, 1H), 5.38 (dd, $J$ = 9.0, 9.0 Hz, 1H), 5.34 (dd, $J$ = 9.0, 9.0 Hz, 1H), 4.98 (dd, $J$ = 9.0, 9.0 Hz, 1H), 4.58-4.55 (m, 1H), 4.41 (dd, $J$ = 2.4, 12.6 Hz, 1H), 4.31 (dd, $J$ = 1.8, 12.6 Hz, 1H), 3.96 (dd, $J$ = 6.0, 16.2 Hz, 1H), 3.82 (dd, $J$ = 5.4, 16.2 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02, (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 171.9, 171.1, 170.6, 170.4, 169.2, 155.8, 154.8, 71.4, 67.2, 61.2, 49.2, 43.9, 22.8, 20.6, 20.5. HR-MS (APCI) $m/z$ 461.1514; [M+H]$^+$ requires 461.1520.

Using 2 and (S)-alaninamide 4 according to Procedure 1 and flash chromatography (MeOH:EtOAc 3:97) yielded the triacetate 14 as a colourless oil (90 mg, 89%). $R_f$ 0.40 (MeOH:EtOAc 1:19). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.00-6.98 (m, 2H), 6.12 (br s, 1H), 5.71 (br s, 1H), 5.39 (dd, $J$ = 9.0, 9.0 Hz, 1H), 5.33 (dd, $J$ = 10.0, 10.0 Hz, 1H), 5.01 (dd, $J$ = 9.5, 9.5 Hz, 1H), 4.67-4.64 (m, 1H), 4.40 (dd, $J$ = 2.5, 13.0 Hz, 1H), 4.30 (dd, $J$ = 1.5, 13.0 Hz, 1H), 4.22 (quintet, $J$ = 6.5 Hz, 1H), 2.12 (s, 3H), 2.07
Using 2 and (S)-2-amino-3-hydroxypropanamide\(^5\) according to Procedure 1 and flash chromatography (MeOH/EtOAc 3:47) gave the triacetate 15 as a colourless oil (70 mg, 64%). \(R_f\) 0.15 (MeOH/EtOAc 3:47). \(^1\)H NMR (500 MHz, CD\(_3\)OD) \(\delta\) 5.44 (dd, \(J = 8.9, 8.9\) Hz, 1H), 5.34 (dd, \(J = 8.9, 8.9\) Hz, 1H), 4.87 (dd, \(J = 9.1, 9.1\) Hz, 1H), 4.60-4.56 (m, 3H), 4.45 (dd, \(J = 4.0, 12.9\) Hz, 1H), 4.41-4.28 (m, 2H), 4.25 (dd, \(J = 4.6, 4.6\) Hz, 1H), 3.85 (dd, \(J = 4.7, 11.2\) Hz, 1H), 3.80 (dd, \(J = 4.7, 11.2\) Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). \(^{13}\)C NMR (126 MHz, CD\(_3\)OD) \(\delta\) 174.6, 173.7, 172.1, 171.4, 171.0, 156.9, 156.4, 78.4, 72.5, 62.7, 57.8, 50.6, 22.6, 20.6, 20.5, 20.5. HR-MS (APCI) \(m/z\) 491.1619; [M+H]\(^+\) requires 491.1625.

Using 2 and (S)-phenylalaninamide\(^6\) according to Procedure 1 and flash chromatography (MeOH:EtOAc 1:39) yielded the triacetate 16 as a colourless oil (83 mg, 78%). \(R_f\) 0.17 (EtOAc:hexane:MeOH 75:23:2). \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.31-7.24 (m, 6H), 7.02 (d, \(J = 8.4\) Hz, 1H), 5.95 (br s, 1H), 5.72 (br s, 1H), 5.38 (dd, \(J = 9.0, 9.0\) Hz, 1H), 5.28 (dd, \(J = 9.6, 9.6\) Hz, 1H), 5.01 (dd, \(J = 9.0, 9.0\) Hz, 1H), 4.68-4.66 (m, 1H), 4.39-4.34 (m, 2H), 4.29 (dd, \(J = 2.4, 12.0\) Hz, 1H), 4.20 (dd, \(J = 7.2, 14.8\) Hz, 1H), 3.10 (dd, \(J = 7.8, 13.8\) Hz, 1H), 2.11 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 174.2, 170.7, 170.6, 170.4, 169.1, 155.4, 154.3, 72.0, 66.7, 60.8, 57.1, 49.2, 38.0, 22.8, 20.7, 20.6, 20.5. HR-MS (APCI) \(m/z\) 551.1979; [M+H]\(^+\) requires 551.1989.

Using 2 and the hydrochloride\(^7\) according to Procedure 2 and flash chromatography
(MeOH/EtOAc 1:19) gave the triacetate 17 as a white solid (85 mg, 70%). $R_t$ 0.35 (EtOAc). $^1$H NMR (600 MHz, CDCl$_3$) δ 7.10 (t, $J$ = 5.7 Hz, 1H), 6.91 (d, $J$ = 8.5 Hz, 1H), 6.21 (t, $J$ = 5.6 Hz, 1H), 5.38 (dd, $J$ = 9.0, 9.0 Hz, 1H), 5.33 (dd, $J$ = 8.6, 8.6 Hz, 1H), 4.98 (dd, $J$ = 8.9, 8.9 Hz, 1H), 4.58 (ddd, $J$ = 2.9, 2.9, 8.7 Hz, 1H), 4.42 (dd, $J$ = 3.3, 12.9 Hz, 1H), 4.28 (dd, $J$ = 2.5, 12.9 Hz, 1H), 3.94 (dd, $J$ = 5.9, 16.4 Hz, 1H), 3.77 (dd, $J$ = 5.2, 16.3 Hz, 1H), 3.36-3.12 (m, 2H), 2.12 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.52-1.47 (m, 2H), 1.38-1.18 (m, 6H), 0.88 (app t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 170.9, 170.6, 170.3, 169.3, 169.01, 155.8, 154.7, 77.4, 71.6, 67.4, 61.3, 49.4, 44.6, 40.0, 31.6, 29.5, 26.7, 23.0, 22.7, 20.8, 20.7, 14.1. HR-MS (APCI) $m/z$ 545.2458; [M+H]$^+$ requires 545.2459.

$O$-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino $N$-methyl carbamate 18

Using 2 and methylamine hydrochloride according to Procedure 2 and flash chromatography (MeOH/EtOAc 3:97) gave the triacetate 18 as a white solid (40 mg, 57%). The $^1$H NMR spectrum was consistent with that found in the literature.8

$O$-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino $N$-ethyl carbamate 19

Using 2 and ethylamine hydrochloride according to Procedure 2 and flash chromatography (EtOAc) gave the triacetate 19 as a colourless oil (59 mg, 83%). $R_t$ 0.32 (EtOAc). $^1$H NMR (500 MHz, CDCl$_3$) δ 6.54 (d, $J$ = 8.5 Hz, 1H), 5.69 (br s, 1H), 5.46-5.22 (m, 2H), 4.97 (dd, $J$ = 8.9, 8.9 Hz, 1H), 4.45-4.26 (m, 3H), 3.36 – 3.25 (m, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.18 (app t, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 170.5, 170.5, 169.3, 154.8, 154.2, 71.7, 67.5, 61.5, 49.4, 36.3, 23.1, 20.8, 20.8, 20.7, 15.1. HR-MS (APCI) $m/z$ 432.1621; [M+H]$^+$ requires 432.1618.

$O$-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino $N$-(prop-1-yl)carbamate 20

Using 2 and 1-propylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 17:3) yielded the triacetate 20 as a colourless oil (64 mg, 71%). $R_t$ 0.26 (EtOAc:hexane 4:1). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.01 (d, $J$ = 8.5 Hz, 1H),
5.93 (t, \(J = 5.5\) Hz, 1H), 5.32 (dd, \(J = 8.0, 8.0\) Hz, 1H), 5.28 (dd, \(J = 8.5, 8.5\) Hz, 1H), 4.88 (dd, \(J = 8.5, 8.5\) Hz, 1H), 4.50 (ddd, \(J = 2.5, 3.5, 8.0\) Hz, 1H), 4.40 (dd, \(J = 3.5, 12.5\) Hz, 1H), 4.27 (dd, \(J = 2.5, 13.0\) Hz, 1H), 3.19-3.15 (m, 2H), 2.09 (s, 3H), 2.04 (s, 6H), 1.99 (s, 3H), 1.54 (heptet, \(J = 7.5\) Hz, 2H) 0.91 (t, \(J = 7.5\) Hz, 3H). 13C NMR (126 MHz, CDCl3): \(\delta\) 170.4, 170.4, 170.0, 169.1, 155.1, 154.1, 76.7, 71.4, 67.3, 61.2, 49.3, 42.8, 22.8, 22.76, 20.5, 20.55, 20.5, 11.1. HR-MS (APCI) \(m/z\) 446.1781; [M+H]+ requires 446.1775.

**O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino \(N\)-(but-1-yl)carbamate 21**

Using 2 and 1-butylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate 21 as a colourless oil (67 mg, 71%). \(R_f\) 0.28 (EtOAc:hexane 4:1). 1H NMR (500 MHz, CDCl3): \(\delta\) 6.96 (d, \(J = 8.0\) Hz, 1H), 5.87 (t, \(J = 5.5\) Hz, 1H), 5.32 (dd, \(J = 8.5, 8.5\) Hz, 1H), 5.29 (dd, \(J = 8.0, 8.0\) Hz, 1H), 4.89 (dd, \(J = 8.5, 8.5\) Hz, 1H), 4.90 (ddd, \(J = 2.5, 3.5, 8.0\) Hz, 1H), 4.40 (dd, \(J = 3.5, 12.5\) Hz, 1H), 4.28 (dd, \(J = 2.5, 12.5\) Hz, 1H), 3.23-3.18 (m, 2H), 2.10 (s, 3H), 2.04 (s, 6H), 2.00 (s, 3H), 1.52-1.47 (m, 2H), 1.37-1.31 (m, 2H), 0.91 (t, \(J = 7.5\) Hz, 3H). 13C NMR (126 MHz, CDCl3): \(\delta\) 170.41, 170.4, 170.0, 169.1, 155.0, 154.1, 71.4, 67.3, 61.2, 49.3, 40.9, 31.6, 22.8, 20.6, 20.5, 19.8, 13.6. HR-MS (APCI) \(m/z\) 460.1938; [M+H]+ requires 460.1931.

**O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino \(N\)-(hex-1-yl)carbamate 22**

Using 2 and 1-hexylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate 22 as a colourless oil (69 mg, 69%). \(R_f\) 0.33 (EtOAc:hexane 4:1). 1H NMR (600 MHz, CDCl3): \(\delta\) 6.99 (d, \(J = 8.4\) Hz, 1H), 5.88 (t, \(J = 5.4\) Hz, 1H), 5.32 (dd, \(J = 8.4, 8.4\) Hz, 1H), 5.28 (dd, \(J = 7.8, 7.8\) Hz, 1H), 4.87 (dd, \(J = 7.8, 7.8\) Hz, 1H), 4.99 (ddd, \(J = 2.4, 3.0, 8.4\) Hz, 1H), 4.40 (dd, \(J = 3.0, 12.6\) Hz, 1H), 4.28 (dd, \(J = 2.4, 12.6\) Hz, 1H), 3.24-3.17 (m, 2H), 2.09 (s, 3H), 2.04 (s, 6H), 1.99 (s, 3H), 1.51-1.49 (m, 2H), 1.33-1.23 (m, 6H), 0.86 (t, \(J = 6.6\) Hz, 3H). 13C NMR (151 MHz, CDCl3): \(\delta\) 170.4, 170.0, 169.1, 155.0, 154.1, 76.7, 71.4, 67.3, 61.2, 49.3, 41.2, 31.3, 29.5, 26.3, 22.8, 22.5, 20.6, 20.54, 20.5, 13.9. HR-MS (APCI) \(m/z\) 488.2259; [M+H]+ requires 488.2244.
Using 2 and 2-propylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate 23 as a colourless oil (48 mg, 67%). *R*$_f$ 0.34 (EtOAc:hexane 4:1). ¹H NMR (500 MHz, CDCl$_3$): δ 6.23 (d, *J* = 8.0 Hz, 1H), 5.47 (d, *J* = 7.0 Hz, 1H), 5.34 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.27 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.97 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.43-4.37 (m, 2H), 4.30 (dd, *J* = 2.5, 12.5 Hz, 1H), 3.92-3.84 (m, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.20 (t, *J* = 6.5 Hz, 6H). ¹³C NMR (126 MHz, CDCl$_3$): δ 170.4, 170.2, 169.1, 153.7, 153.7, 71.5, 67.3, 61.4, 49.4, 43.5, 23.0, 22.8, 22.7, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 446.1776; [M+H]$^+$ requires 446.1775.

Using 2 and 2-methylpropylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate 24 as a colourless oil (73 mg, 74%). *R*$_f$ 0.23 (EtOAc:hexane 4:1). ¹H NMR (500 MHz, CDCl$_3$): δ 6.22 (d, *J* = 8.5 Hz, 1H), 5.78 (t, *J* = 5.5 Hz, 1H), 5.35 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.27 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.98 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.44-4.38 (m, 2H), 4.30 (dd, *J* = 2.0, 12.5 Hz, 1H), 3.13-3.04 (m, 2H), 2.13 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.81 (septet, *J* = 7.5 Hz, 1H) 0.93 (d, *J* = 6.5 Hz, 6H). ¹³C NMR (126 MHz, CDCl$_3$): δ 170.4, 170.4, 170.2, 169.1, 154.8, 153.7, 77.3, 71.4, 67.3, 61.4, 49.4, 48.5, 28.5, 23.0, 20.6, 20.6, 20.5, 19.9. HR-MS (APCI) *m/z* 460.1943; [M+H]$^+$ requires 460.1931.

Using 2 and 2-methylprop-2-ylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 7:3) yielded the triacetate 25 as a colourless oil (62 mg, 62%). *R*$_f$ 0.45 (EtOAc:hexane 7:3). ¹H NMR (500 MHz, CDCl$_3$): δ 6.84 (d, *J* = 6.5 Hz, 1H), 5.61 (br s, 1H), 5.32-5.30 (m, 2H), 4.93 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.43-4.38 (m, 2H), 4.28 (dd, *J* = 2.0, 12.5 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.40 (s, 9H). ¹³C NMR (126 MHz, CDCl$_3$): δ 170.7, 170.4, 170.2, 169.1, 153.7, 153.1, 77.1, 71.5, 67.3, 61.3, 51.1, 49.4, 28.6, 22.8, 20.6, 20.5, 20.5. HR-MS
O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-(prop-2-en-1-yl)carbamate 26

Using 2 and allylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate 26 as a colourless oil (66 mg, 63%). R\textsubscript{f} 0.32 (EtOAc:hexane 4:1). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \textsuperscript{\delta} 6.94 (d, \textit{J} = 8.4 Hz, 1H), 6.00 (t, \textit{J} = 5.4 Hz, 1H), 5.83 (ddt, \textit{J} = 5.2, 10.2, 16.8 Hz, 1H), 5.33 (dd, \textit{J} = 8.4, 8.4 Hz, 1H), 5.29 (dd, \textit{J} = 8.4, 8.4 Hz, 1H), 5.19 (dd, \textit{J} = 1.2, 16.8 Hz, 1H), 5.14 (dd, \textit{J} = 1.2, 10.2 Hz, 1H), 4.88 (dd, \textit{J} = 8.4, 8.4 Hz, 1H), 4.51 (ddd, \textit{J} = 1.2, 3.6, 16.8 Hz, 1H), 4.41 (dd, \textit{J} = 3.6, 13.2 Hz, 1H), 4.28 (dd, \textit{J} = 2.4, 13.2 Hz, 1H), 3.84 (dd, \textit{J} = 2.5, 5.4 Hz, 2H) 2.10 (s, 3H), 2.04 (s, 6H), 1.99 (s, 3H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \textsuperscript{\delta} 170.4, 170.4, 170.0, 169.1, 154.9, 154.4, 133.6, 116.5, 71.4, 67.2, 61.2, 49.3, 43.4, 22.9, 20.6, 20.6, 20.5. HR-MS (APCI) \textit{m/z} 444.1619; [M+H]\textsuperscript{+} requires 444.1618.

O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-(prop-2-yn-1-yl)carbamate 27

Using 2 and propargylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 17:3) yielded the triacetate 27 as a colourless oil (65 mg, 79%). R\textsubscript{f} 0.39 (EtOAc:hexane 9:1 ). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \textsuperscript{\delta} 7.11 (d, \textit{J} = 8.1 Hz, 1H), 6.32 (t, \textit{J} = 5.4 Hz, 1H), 5.34 (dd, \textit{J} = 8.6, 8.6 Hz, 1H), 5.28 (dd, \textit{J} = 8.6, 8.6 Hz, 1H), 4.89 (dd, \textit{J} = 8.5, 8.5 Hz, 1H), 4.51 (ddd, \textit{J} = 2.5, 3.4, 8.8 Hz, 1H), 4.40 (dd, \textit{J} = 3.4, 12.8 Hz, 1H), 4.27 (dd, \textit{J} = 2.5, 12.8 Hz, 1H), 4.08-3.91 (m, 2H), 2.28 (t, \textit{J} = 2.5 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \textsuperscript{\delta} 170.6, 170.4, 169.9, 169.1, 154.9, 154.4, 79.2, 76.9, 72.0, 71.3, 67.2, 61.2, 49.1, 30.8, 22.8, 20.5, 20.5, 20.4. HR-MS (APCI) \textit{m/z} 442.1447; [M+H]\textsuperscript{+} requires 442.1462.

O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N-(2-chloroethyl) carbamate 28

Using 2 and 2-chloroethanolamine hydrochloride according to Procedure 2 and flash chromatography (EtOAc:hexane 9:1) gave the triacetate 28 as a colourless oil (65 mg, 64%). R\textsubscript{f} 0.35 (EtOAc:hexane 9:1). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 6.26 (s, 1H), 6.14 (d, \textit{J} = 8.6 Hz, 1H), 5.35 (dd, \textit{J} = 8.3, 8.3 Hz, 1H), 5.28 (dd, \textit{J} = 9.3, 9.3 Hz, 1H), 4.99
Using 2 and dimethylamine hydrochloride according to Procedure 2 and flash chromatography (EtOAc) gave the triacetate 29 as a colourless oil (77 mg, 88%). $R_f$ 0.34 (EtOAc). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J = 8.2$ Hz, 1H), 5.38 (dd, $J = 9.4$, 9.4 Hz, 1H), 5.31 (dd, $J = 9.1$, 9.1 Hz, 1H), 4.88 (dd, $J = 8.2$, 9.6 Hz, 1H), 4.41 (ddd, $J = 2.4$, 4.0, 9.0 Hz, 1H), 4.37 (dd, $J = 4.0$, 12.6 Hz, 1H), 4.29 (dd, $J = 2.4$, 12.6 Hz, 1H), 2.96 (s, 6H), 2.11 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 171.0, 170.5, 170.3, 169.4, 156.4, 154.8, 77.4, 72.2, 67.6, 61.7, 49.8, 37.0, 36.1, 23.0, 20.8, 20.7, 20.7. HR-MS (APCI) m/z 432.1638; [M+H]$^+$ requires 432.1618.

$O$-(2-Acetamido-3,4,6-tri-$O$-acetyl-2-deoxy-$D$-glucopyranosylidene)amino $N,N$-(diethyl) carbamate 30

Using 2 and diethylamine according to Procedure 2 and flash chromatography (EtOAc) gave the triacetate 30 as a colourless oil (64 mg, 63%). $R_f$ 0.37 (EtOAc). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.03 (s, 1H), 5.46-5.26 (m, 2H), 4.99 – 4.85 (m, 1H), 4.39 (ddd, $J = 2.4$, 3.9, 8.6 Hz, 1H), 4.34 (dd, $J = 4.1$, 12.5 Hz, 1H), 4.28 (dd, $J = 2.4$, 12.7 Hz, 1H), 3.31 (br s, 4H), 2.11 (s, 3H), 2.05 (s, 6H), 1.99 (s, 3H), 1.16 (app t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 170.8, 170.5, 170.3, 169.3, 156.3, 154.2, 77.4, 72.3, 67.5, 61.8, 49.8, 42.7, 41.9, 23.1, 20.8, 20.8, 20.7, 14.1, 13.5. HR-MS (APCI) m/z 460.1922; [M+H]$^+$ requires 460.1931.

$O$-(2-Acetamido-3,4,6-tri-$O$-acetyl-2-deoxy-$D$-glucopyranosylidene)amino $N,N$-(dibutyl) carbamate 31

Using 2 and dibutylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 17:3) gave the triacetate 31 as a white solid (69 mg, 60%). $R_f$ 0.59 (EtOAc). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.0$ Hz, 1H), 5.44 (dd, $J = 9.3$, 14.4 Hz, 2H), 4.98 (dd, $J = 8.0$, 14.4 Hz, 2H), 4.35 (dd, $J = 8.0$, 12.4 Hz, 2H), 4.25 (dd, $J = 8.0$, 12.4 Hz, 2H), 2.18 (br s, 6H), 1.34 (app t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 171.0, 170.5, 170.3, 169.3, 156.3, 154.2, 77.4, 72.3, 67.5, 61.8, 49.8, 42.7, 41.9, 23.1, 20.8, 20.8, 20.7, 14.1, 13.5. HR-MS (APCI) m/z 504.2245; [M+H]$^+$ requires 504.2234.
9.3 Hz, 1H), 5.29 (dd, J = 9.4, 9.4 Hz, 1H), 4.79 (dd, J = 8.6, 8.6 Hz, 1H), 4.44 (ddd, J = 3.0, 3.0, 9.4 Hz, 1H), 4.35 (dd, J = 3.6, 12.7 Hz, 1H), 4.23 (dd, J = 2.4, 12.7 Hz, 1H), 3.33-3.11 (m, 4H), 2.08 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.93 (s, 3H), 1.51 (br s, 4H), 1.29 (br s, 4H), 0.90 (app t, J = 7.3 Hz, 6H). 13C NMR (151 MHz, CDCl 3) δ 171.0, 170.4, 170.1, 169.3, 156.5, 154.5, 76.4, 72.4, 67.3, 61.4, 49.9, 47.9, 47.1, 30.8, 30.2, 22.8, 20.7, 20.7, 20.6, 20.1, 13.9, 13.9. HR-MS (APCI) m/z 516.2574; [M+H]+ requires 516.2557.

**O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N,N-(pentylene) carbamate 32**

Using 2 and piperidine according to Procedure 1 and flash chromatography (EtOAc) gave the triacetate 32 as a colourless oil (90 mg, 86%). Rf 0.35 (EtOAc). 1H NMR (500 MHz, CDCl 3) δ 7.44 (d, J = 8.3 Hz, 1H), 5.39 (dd, J = 9.4, 9.4 Hz, 1H), 5.30 (dd, J = 9.1, 9.1 Hz, 1H), 4.83 (dd, J = 8.2, 9.5 Hz, 1H), 4.42 (dd, J = 2.4, 4.1, 9.0 Hz, 1H), 4.37 (dd, J = 4.1, 12.6 Hz, 1H), 4.28 (dd, J = 2.4, 12.7 Hz, 1H), 3.44 (br s, 4H), 2.11 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.69-1.46 (m, 6H). 13C NMR (126 MHz, CDCl 3) δ 171.0, 170.5, 170.3, 169.4, 156.3, 153.7, 77.4, 72.2, 67.5, 61.7, 49.8, 45.3, 25.7, 24.3, 22.9, 20.8, 20.8, 20.7. HR-MS (APCI) m/z 472.1984; [M+H]+ requires 472.1931.

**O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranosylidene)amino N,N-(ethyleneoxyethylene) carbamate 33**

Using 2 and morpholine according to Procedure 1 and flash chromatography (MeOH/EtOAc 1:24) gave the triacetate 33 as a colourless oil (71 mg, 68%). Rf 0.41 (MeOH/EtOAc 1:19). 1H NMR (600 MHz, CDCl 3) δ 7.09 (d, J = 8.1 Hz, 1H), 5.40 (dd, J = 9.4, 9.4 Hz, 1H), 5.30 (dd, J = 9.1, 9.1 Hz, 1H), 4.82 (dd, J = 8.1, 9.5 Hz, 1H), 4.44 (dd, J = 2.4, 3.8, 8.9 Hz, 1H), 4.37 (dd, J = 3.9, 12.7 Hz, 1H), 4.31 (dd, J = 2.5, 12.7 Hz, 1H), 3.69 (s, 4H), 3.51 (s, 4H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H). 13C NMR (151 MHz, CDCl 3) δ 170.9, 170.4, 170.2, 169.4, 156.7, 153.5, 72.0, 67.5, 66.6, 61.6, 49.9, 44.4, 44.2, 23.0, 20.8, 20.8, 20.7. HR-MS (APCI) m/z 474.1725; [M+H]+ requires 474.1724.
General preparation of carbamates 34-63

A saturated solution of NH₃ in MeOH (10 mL) prepared at 0°C was added to a solution of the appropriate 3,4,6-tri-O-acetyl carbamate (1.0 equiv) in MeOH (25 mL/mmol) at 0°C. After 2 h. at 0°C, the reaction mixture was concentrated.

**O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-(4-methylphenyl) carbamate 34**

Using 4 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 34 as a white solid (15 mg, 26%). m.p. 182-184°C (dec.). Rₖ 0.21 (MeOH:EtOAc 3:17). ¹H NMR (500 MHz, CD₃OD): δ 7.31 (AA'BB', 2H), 7.10 (AA'BB', 2H), 4.57 (d, J = 9.0 Hz, 1H), 3.97-3.94 (m, 2H), 3.85 (dd, J = 4.5, 13.0 Hz, 1H), 3.75 (dd, J = 8.5, 8.5 Hz, 1H), 3.73 (dd, J = 8.5, 8.5 Hz, 1H), 2.28 (s, 3H), 2.07 (s, 3H). ¹³C NMR (126 MHz, CD₃OD): δ 173.8, 159.3, 154.8, 136.7, 134.4, 130.4, 120.4, 84.1, 74.5, 69.8, 61.7, 52.9, 22.8, 20.8. HR-MS (APCI) m/z 368.1462; [M+H]+ requires 368.1458.

**O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-(4-methoxyphenyl) carbamate 35**

Using 5 and flash chromatography (MeOH:EtOAc 9:91) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 5 as a white solid (20 mg, 28%). m.p. 136-140°C (dec.). Rₖ 0.15 (MeOH:EtOAc 3:17). ¹H NMR (600 MHz, CD₃OD): δ 7.34 (AA'BB', 2H), 6.88 (AA'BB', 2H), 4.59 (d, J = 9.6 Hz, 1H), 4.57 (s, 1H), 3.98-3.95 (m, 2H), 3.86 (dd, J = 4.8, 13.2 Hz, 1H), 3.80-3.72 (m, 5H), 2.06 (s, 3H). ¹³C NMR (126 MHz, CD₃OD): δ 173.8, 159.2, 157.7, 155.1, 132.1, 122.2, 115.1, 84.1, 74.5, 69.8, 61.7, 55.9, 52.9, 22.8. HR-MS (APCI) m/z 384.1418; [M+H]+ requires 384.1407.

**O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-(4-bromophenyl) carbamate 36**

Using 6 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 36 as a white solid (30 mg, 43%). m.p. 176-180°C (dec.). Rₖ 0.30 (MeOH:EtOAc 3:17). ¹H NMR (600 MHz, (CD₃)₂SO): δ 9.81 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.53-7.39 (m,
6H), 5.50 (t, J = 5.1 Hz 1H), 4.52 (dd, J = 6.5, 14.2 Hz, 1H), 4.37 (t, J = 8.2 Hz, 1H), 3.97-3.91 (m, 1H), 3.79-3.74 (m, 1H), 3.70-3.61 (m, 2H), 3.58 (t, J = 7.3 Hz, 1H), 1.88 (s, 3H). 13C NMR (151 MHz, (CD3)2SO): δ 169.2, 158.4, 151.7, 138.1, 131.6, 120.5, 114.4, 82.4, 72.2, 68.6, 60.0, 51.1, 22.7. HR-MS (APCI) m/z 432.0414; [M+H]+ requires 432.0406.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-benzylcarbamate 37

Using 7 and flash chromatography (MeOH:EtOAc 1:9) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 37 as a white solid (15 mg, 40%). m.p. 150-156°C (dec.). Rf 0.23 (MeOH:EtOAc 3:17). 1H NMR (600 MHz, CD3OD): δ 7.33-7.25 (m, 5H), 4.57 (s, 1H), 4.54 (d, J = 9.3 Hz, 1H), 4.39-4.34 (m, 2H), 3.95-3.91 (m, 2H) 3.84 (dd, J = 4.4, 12.9 Hz, 1H), 3.75 (dd, J = 9.0, 9.0 Hz, 1H), 3.71 (dd, J = 8.4, 8.4 Hz, 1H), 1.99 (s, 3H). 13C NMR (126 MHz, CD3OD): δ 173.8, 158.6, 158.1, 140.0, 129.6, 128.4, 84.1, 74.4, 69.7, 61.6, 52.8, 45.6, 22.7. HR-MS (APCI) m/z 368.1460; [M+H]+ requires 368.1458.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-cyclopropylcarbamate 38

Using 8 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 38 as a white solid (21 mg, 46%). m.p. 148-152°C (dec.). Rf 0.15 (MeOH:EtOAc 3:17). 1H NMR (600 MHz, CD3OD): δ 4.57 (s, 1H), 4.53 (d, J = 9.0 Hz, 1H), 3.93-3.91 (m, 2H), 3.84 (dd, J = 4.2, 12.6 Hz, 1H), 3.74 (dd, J = 8.4, 8.4 Hz, 1H), 3.70 (dd, J = 9.0, 9.0 Hz, 1H), 2.59 (tt, J = 3.8, 7.2 Hz, 1H), 2.04 (s, 3H), 0.73-0.71 (m, 2H), 0.53-0.51 (m, 2H). 13C NMR (126 MHz, CD3OD): δ 173.8, 158.7, 158.6, 84.0, 74.5, 69.7, 61.6, 52.8, 24.0, 22.8, 6.8. HR-MS (APCI) m/z 318.1297; [M+H]+ requires 318.1301.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-cyclobutylcarbamate 39

Using 9 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 39 as a white solid (38 mg, 77%). m.p. 130-134°C (dec.). Rf 0.17 (MeOH:EtOAc 3:17). 1H NMR (600 MHz, CD3OD): δ 4.57 (s, 1H), 4.54 (d, J = 9.6 Hz, 1H), 4.12 (q, J = 8.3 Hz, 1H), 3.94-3.92 (m, 2H), 3.84 (dd, J = 3.6, 12.6 Hz, 1H), 3.75 (dd, J = 9.0, 9.0 Hz, 1H), 3.71 (dd, J = 9.0, 9.0 Hz, 1H), 2.31-2.25 (m, 2H), 2.05 (s, 3H), 2.01-1.96 (m,
2H), 1.75-1.67 (m, 2H). $^{13}$C NMR (151 MHz, CD$_3$OD): $\delta$ 173.8, 158.5, 156.7, 84.0, 74.2, 69.8, 61.7, 52.9, 47.5, 31.5, 22.8, 15.6. HR-MS (APCI) $m/z$ 332.1473; [M+H]$^+$ requires 332.1458.

$O$-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino $N$-cyclopentylcarbamate 40
Using 10 and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 40 as a white solid (24 mg, 50%). m.p. 140-144°C (dec.). $R_f$ 0.17 (MeOH:EtOAc 3:17). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 4.56 (s, 1H), 4.52 (d, $J = 9.6$ Hz, 1H), 3.97-3.90 (m, 3H), 3.84 (dd, $J = 4.2$, 12.6 Hz, 1H), 3.75 (dd, $J = 8.4$, 8.4 Hz, 1H), 3.71 (dd, $J = 9.0$, 9.0 Hz, 1H), 2.04 (s, 3H), 1.96-1.91 (m, 2H), 1.75-1.68 (m, 2H), 1.65-1.58 (m, 2H), 1.53-1.47 (m, 2H). $^{13}$C NMR (151 MHz, CD$_3$OD): $\delta$ 173.7, 158.2, 157.3, 84.0, 74.3, 69.8, 61.6, 54.1, 52.9, 33.7, 24.5, 22.8. HR-MS (APCI) $m/z$ 346.1611; [M+H]$^+$ requires 346.1614.

$O$-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino $N$-cyclohexylcarbamate 41
Using 11 and flash chromatography (MeOH:EtOAc 1:9) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 41 as a white solid (32 mg, 66%). m.p. 158-162°C (dec.). $R_f$ 0.24 (MeOH:EtOAc 3:17). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 4.57 (s, 1H), 4.53 (d, $J = 8.0$ Hz, 1H), 3.94-3.90 (m, 3H), 3.84 (dd, $J = 4.2$, 12.6 Hz, 1H), 3.75 (dd, $J = 9.0$, 9.0 Hz, 1H), 3.70 (dd, $J = 9.0$, 9.0 Hz, 1H), 3.49-3.42 (m, 1H), 2.04 (s, 3H), 1.92-1.86 (m, 2H), 1.76-1.71 (m, 2H), 1.64-1.60 (m, 1H), 1.41-1.34 (m, 2H), 1.31-1.22 (m, 3H). $^{13}$C NMR (126 MHz, CD$_3$OD): $\delta$ 173.7, 158.2, 157.0, 84.0, 74.3, 69.8, 61.6, 52.9, 51.4, 33.8, 26.6, 25.9, 22.8. HR-MS (APCI) $m/z$ 360.1765; [M+H]$^+$ requires 360.1771.

$O$-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino $N$-(adamant-1-yl)carbamate 42
Using 12 and flash chromatography (MeOH:EtOAc 1:9) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 42 as a white solid (46 mg, 63%). m.p. 154-160°C (dec.). $R_f$ 0.19 (MeOH:EtOAc 3:17). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 4.57 (s, 1H), 4.51 (d, $J = 10.2$ Hz, 1H), 3.93 (dd, $J = 2.4$, 12.6 Hz, 1H), 3.89 (ddd, $J = 2.4$, 3.6, 9.0 Hz, 1H), 3.84 (dd, $J = 3.6$, 12.6 Hz, 1H),
3.74 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.70 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 2.08 (br s, 3H), 2.04 (s, 3H), 2.00-1.97 (m, 6H), 1.75-1.70 (m, 6H). \(^{13}\)C NMR (126 MHz, CD\(_3\)OD): \( \delta \) 174.0, 157.6, 155.4, 84.0, 74.2, 69.8, 61.7, 52.9, 52.0, 42.5, 37.4, 30.9, 22.8. HR-MS (APCI) \( m/z \) 412.2077; [M+H]\(^+\) requires 412.2084.

\( \text{O-}(2\text{-Acetamido-2-deoxy-D-glucopyranosylidene})\text{amino N-}(2\text{-amino-2-oxoeth-1-yl})\text{carbamate 43} \)

Using 13 and flash chromatography (MeOH:EtOAc 3:7) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 43 as a white solid (16 mg, 55%). m.p. 136-140°C (dec.). \( R_f \) 0.17 (MeOH:EtOAc 3:7). \(^1\)H NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.55 (d, \( J = 9.0 \) Hz, 1H), 3.96-3.93 (m, 2H), 3.89-3.83 (m, 3H), 3.76 (dd, \( J = 8.4, 8.4 \) Hz, 1H), 3.72 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 2.06 (s, 3H). \(^{13}\)C NMR (126 MHz, CD\(_3\)OD): \( \delta \) 173.91, 173.86, 158.7, 158.0, 84.2, 74.3, 69.7, 61.6, 52.8, 44.4, 22.8. HR-MS (APCI) \( m/z \) 335.1200; [M+H]\(^+\) requires 335.1203.

\( \text{O-}(2\text{-Acetamido-2-deoxy-D-glucopyranosylidene})\text{amino (S)-N-}(1\text{-amino-1-oxoprop-2-yl})\text{carbamate 44} \)

Using 14 and flash chromatography (MeOH:EtOAc 1:4) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 44 as a white solid (35 mg, 56%). m.p. 108-112°C (dec.). \( R_f \) 0.24 (MeOH:EtOAc 3:7). \(^1\)H NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.57 (s, 1H), 4.53 (d, \( J = 9.0 \) Hz, 1H), 4.22 (q, \( J = 7.2 \) Hz, 1H), 3.97-3.92 (m, 2H), 3.85 (dd, \( J = 3.6, 12.4 \) Hz, 1H), 3.75 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.72 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 2.07 (s, 3H), 1.39 (d, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (126 MHz, CD\(_3\)OD): \( \delta \) 177.1, 173.9, 158.4, 157.0, 84.2, 74.1, 69.7, 61.6, 52.9, 51.4, 22.8, 19.2. HR-MS (APCI) \( m/z \) 349.1352; [M+H]\(^+\) requires 349.1359.

\( \text{O-}(2\text{-Acetamido-2-deoxy-D-glucopyranosylidene})\text{amino (S)-1-amino-3-hydroxy-1-oxo-prop-2-yl) carbamate 45} \)

Using 15 and flash chromatography (MeOH/EtOAc 3:7) of the resultant residue gave a colourless oil which was treated with EtOAc to give 45 as a white solid (16 mg, 31%). \( R_f \) 0.26 (MeOH/EtOAc 7:13). \(^1\)H NMR (600 MHz, D\(_2\)O) \( \delta \) 4.62 (d, \( J = 9.9 \) Hz, 1H), 4.30 (dd, \( J = 4.6, 4.6 \) Hz, 1H), 4.13-4.07 (m, 1H), 4.01 (dd, \( J = 2.2, 12.9 \) Hz, 1H), 3.94-3.77 (m, 5H), 2.09 (s, 3H). \(^{13}\)C NMR (151 MHz, D\(_2\)O) \( \delta \) 175.5, 175.3,
O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino \((S)-N\)-(1-amino-1-oxo-3-phenylprop-2-yl)carbamate 46

Using 16 and flash chromatography (MeOH:EtOAc 3:7) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 46 as a white solid (28 mg, 46%). m.p. 118-122°C (dec.). Rf 0.32 (MeOH:EtOAc 3:7). \(^1\)H NMR (600 MHz, CD\(_3\)OD): \(\delta\) 7.29-7.18 (m, 5H), 4.57 (s, 1H), 4.53 (d, \(J = 9.6\) Hz, 1H), 4.46 (dd, \(J = 5.4, 7.8\) Hz, 1H), 3.93-3.89 (m, 2H), 3.83 (dd, \(J = 4.2, 12.6\) Hz, 1H), 3.75 (dd, \(J = 8.4, 8.4\) Hz, 1H), 3.69 (dd, \(J = 9.6, 9.6\) Hz, 1H), 3.14 (dd, \(J = 5.4, 13.8\) Hz, 1H), 2.94 (dd, \(J = 8.4, 13.8\) Hz, 1H), 2.01 (s, 3H). \(^{13}\)C NMR (151 MHz, CD\(_3\)OD): \(\delta\) 175.7, 173.8, 158.4, 157.0, 137.9, 130.4, 129.5, 127.9, 84.2, 74.2, 69.7, 61.6, 57.1, 52.8, 39.6, 22.8. HR-MS (APCI) \(m/z\) 425.1679; [M+H]\(^+\) requires 425.1672.

O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino \(N\)-(2-hexylamino-2-oxoeth-1-yl) carbamate 47

Using 17 and flash chromatography (MeOH:EtOAc 1:3) of the resultant residue gave a colourless oil which was treated with EtOAc to give 47 as a white solid (21 mg, 34%). Rf 0.33 (MeOH:EtOAc 1:3). \(^1\)H NMR (600 MHz, CD\(_3\)OD) \(\delta\) 4.56 (d, \(J = 9.3\) Hz, 1H), 3.99-3.91 (m, 2H), 3.88-3.68 (m, 5H), 3.20 (app t, \(J = 7.2\) Hz, 2H), 2.06 (s, 3H), 1.55-1.45 (m, 2H), 1.39-1.23 (m, 6H), 0.91 (app t, \(J = 6.7\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CD\(_3\)OD) \(\delta\) 173.8, 171.1, 158.7, 158.0, 84.1, 74.3, 69.7, 61.6, 52.8, 44.7, 40.5, 32.7, 30.4, 27.6, 23.6, 22.8, 14.4. HR-MS (APCI) \(m/z\) 419.2124; [M+H]\(^+\) requires 419.2142.

O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino \(N\)-methyl carbamate 48

Using 18 and flash chromatography (MeOH:EtOAc 1:3) of the resultant residue gave a colourless oil which was treated with EtOAc to give 48 as a white solid (18 mg, 65%). The \(^1\)H NMR spectrum was consistent with that found in the literature.\(^8\)

O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino \(N\)-ethyl carbamate 49

Using 19 and flash chromatography (MeOH:EtOAc 1:4) of the resultant residue gave
a colourless oil which was treated with EtOAc to give 49 as a white solid (9 mg, 22%). \( R_f \) 0.26 (MeOH/EtOAc 1:4). \(^1\text{H}\) NMR (600 MHz, CD\(_3\)OD) \( \delta \) 4.61-4.48 (m, 2H), 3.99-3.89 (m, 2H), 3.84 (dd, \( J = 4.5, 13.0 \) Hz, 1H), 3.75 (dd, \( J = 8.7, 8.7 \) Hz, 1H), 3.71 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.21 (q, \( J = 7.2 \) Hz, 2H), 2.04 (s, 3H), 1.14 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\text{C}\) NMR (151 MHz, CD\(_3\)OD) \( \delta \) 173.8, 158.4, 157.8, 84.0, 74.4, 69.7, 61.6, 52.8, 36.8, 22.8, 15.2. HR-MS (APCI) \( m/z \) 306.1311; \([\text{M+H}]^+\) requires 306.1301.

\textit{O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-(prop-1-yl)carbamate} 50

Using 20 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 50 as a white solid (31 mg, 72%). m.p. 130-136°C (dec.). \( R_f \) 0.11 (MeOH:EtOAc 3:17). \(^1\text{H}\) NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.54 (d, \( J = 9.6 \) Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, \( J = 4.2, 13.2 \) Hz, 1H), 3.75 (dd, \( J = 8.4, 8.4 \) Hz, 1H), 3.71 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.14 (t, \( J = 7.2 \) Hz, 2H), 2.04 (s, 3H), 1.54 (tq, \( J = 7.2, 7.2 \) Hz, 2H), 0.93 (t, \( J = 7.2 \), Hz, 3H). \(^{13}\text{C}\) NMR (151 MHz, CD\(_3\)OD): \( \delta \) 173.7, 158.3, 158.0, 84.0, 74.4, 69.7, 61.6, 52.8, 43.7, 23.9, 22.8, 11.5. HR-MS (APCI) \( m/z \) 320.1453; \([\text{M+H}]^+\) requires 320.1458.

\textit{O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-(but-1-yl)carbamate} 51

Using 21 and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 51 as a white solid (32 mg, 68%). m.p. 84-88°C. \( R_f \) 0.24 (MeOH:EtOAc 3:17). \(^1\text{H}\) NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.54 (d, \( J = 9.3 \) Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, \( J = 3.6, 12.0 \) Hz, 1H), 3.75 (dd, \( J = 8.6, 8.6 \) Hz, 1H), 3.71 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.18 (t, \( J = 7.0 \) Hz, 2H), 2.04 (s, 3H), 1.51 (tt, \( J = 7.0, 7.0 \) Hz, 2H), 1.36 (tq, \( J = 7.0, 7.4 \) Hz, 2H), 0.94 (t, \( J = 7.4 \) Hz, 3H). \(^{13}\text{C}\) NMR (151 MHz, CD\(_3\)OD): \( \delta \) 173.7, 158.3, 158.0, 84.0, 74.4, 69.7, 61.6, 52.8, 41.6, 32.8, 22.8, 20.9, 14.0. HR-MS (APCI) \( m/z \) 334.1611; \([\text{M+H}]^+\) requires 334.1614.

\textit{O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino N-(hex-1-yl)carbamate} 52

Using 22 and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 52 as a
white solid (30 mg, 62%). m.p. 134-138°C (dec.). \( R_f \) 0.14 (MeOH:EtOAc 3:22). \(^1\)H NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.54 (d, \( J = 9.0 \) Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, \( J = 4.2, 13.2 \) Hz, 1H), 3.75 (dd, \( J = 8.4, 8.4 \) Hz, 1H), 3.71 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.18 (t, \( J = 6.6 \) Hz, 2H), 2.04 (s, 3H), 1.54-1.49 (m, 2H), 1.38-1.29 (m, 6H), 0.91 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (151 MHz, CD\(_3\)OD): \( \delta \) 173.7, 158.3, 158.0, 84.0, 74.4, 69.7, 61.6, 52.8, 42.0, 32.7, 30.7, 27.5, 23.6, 22.8, 14.4. HR-MS (APCI) \( m/z \) 362.1915; [M+H]\(^+\) requires 362.1927.

\( O-(2\text{-Acetamido}-2\text{-deoxy-}\text{D-glucopyranosylidene})\text{amino} \) \( N-(\text{prop-2-yl})\text{carbamate} \) 53

Using 23 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 53 as a white solid (23 mg, 71%). m.p. 132-136°C (dec.). \( R_f \) 0.14 (MeOH:EtOAc 3:17). \(^1\)H NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.56 (s, 1H), 4.53 (d, \( J = 8.4 \) Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, \( J = 3.6, 12.6 \) Hz, 1H), 3.80-3.69 (m, 3H), 2.04 (s, 3H), 1.17 (d, \( J = 6.6 \) Hz, 6H). \(^{13}\)C NMR (151 MHz, CD\(_3\)OD): \( \delta \) 173.7, 158.3, 157.0, 84.0, 74.4, 69.8, 61.7, 52.9, 44.5, 22.8. HR-MS (APCI) \( m/z \) 320.1464; [M+H]\(^+\) requires 320.1458.

\( O-(2\text{-Acetamido}-2\text{-deoxy-}\text{D-glucopyranosylidene})\text{amino} \) \( N-(2\text{-methylprop-1-yl})\text{carbamate} \) 54

Using 24 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 54 as a white solid (32 mg, 63%). m.p. 120-124°C (dec.). \( R_f \) 0.18 (MeOH:EtOAc 3:17). \(^1\)H NMR (600 MHz, CD\(_3\)OD): \( \delta \) 4.54 (d, \( J = 9.6 \) Hz, 1H), 3.97-3.93 (m, 2H), 3.84 (dd, \( J = 3.0, 12.0 \) Hz, 1H), 3.75 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.71 (dd, \( J = 8.4, 8.4 \) Hz, 1H), 3.01 (d, \( J = 6.0 \) Hz, 2H), 2.04 (s, 3H), 1.81-1.76 (m, 1H), 0.91 (d, \( J = 6.6 \) Hz, 6H). \(^{13}\)C NMR (151 MHz, CD\(_3\)OD): \( \delta \) 173.7, 158.3, 158.1, 84.0, 74.3, 69.7, 61.6, 52.9, 49.4, 29.9, 22.8, 20.2. HR-MS (APCI) \( m/z \) 334.1605; [M+H]\(^+\) requires 334.1614.

\( O-(2\text{-Acetamido}-2\text{-deoxy-}\text{D-glucopyranosylidene})\text{amino} \) \( N-(2\text{-methylprop-2-yl})\text{carbamate} \) 55

Using 25 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 55 as a white solid (23 mg, 51%). m.p. 112-116°C (dec.). \( R_f \) 0.15 (MeOH:EtOAc 4:21). \(^1\)H
NMR (600 MHz, CD$_3$OD): $\delta$ 4.52 (d, $J = 9.6$ Hz, 1H), 3.93 (dd, $J = 2.4$, 12.6 Hz, 1H), 3.90 (ddd, $J = 2.4$, 3.6, 9.0 Hz, 1H), 3.84 (dd, $J = 3.6$, 12.6 Hz, 1H), 3.74 (dd, $J = 9.0$, 9.0 Hz, 1H), 3.70 (dd, $J = 9.6$, 9.6 Hz, 1H), 2.04 (s, 3H), 1.33 (s, 9H). 13C NMR (151 MHz, CD$_3$OD): $\delta$ 173.7, 157.7, 155.9, 84.0, 74.3, 69.8, 61.7, 52.9, 51.6, 28.9, 22.7. HR-MS (APCI) m/z 334.1627; [M+H]$^+$ requires 334.1614.

$O$-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino $N$-(prop-2-en-1-yl)carbamate 56

Using 26 and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 56 as a white solid (28 mg, 58%). m.p. 80-84°C. $R_f$ 0.14 (MeOH:EtOAc 9:4). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 5.87 (ddt, $J = 4.8$, 10.8, 17.4 Hz, 1H), 5.20 (dd, $J = 1.2$, 17.4 Hz, 1H), 5.11 (dd, $J = 1.2$, 10.8 Hz, 1H), 4.54 (d, $J = 9.6$ Hz, 1H), 3.94-3.92 (m, 2H), 3.85 (dd, $J = 4.2$, 13.2 Hz, 1H), 3.80 (d, $J = 4.8$ Hz, 2H), 3.76 (dd, $J = 9.0$, 9.0 Hz, 1H), 3.71 (dd, $J = 9.0$, 9.0 Hz, 1H), 2.03 (s, 3H). 13C NMR (151 MHz, CD$_3$OD): $\delta$ 173.7, 158.5, 157.8, 135.6, 116.1, 84.1, 74.4, 69.7, 61.6, 52.8, 44.2, 22.8. HR-MS (APCI) m/z 318.1297; [M+H]$^+$ requires 318.1301.

$O$-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino $N$-(prop-2-yn-1-yl)carbamate 57

Using 27 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound 57 as a white solid (26 mg, 56%). m.p. 104-110°C (dec.). $R_f$ 0.19 (MeOH:EtOAc 4:1). $^1$H NMR (600 MHz, CD$_3$OD): $\delta$ 4.56 (d, $J = 9.0$ Hz, 1H), 3.96 (d, $J = 3.0$ Hz, 2H), 3.95-3.92 (m, 2H), 3.85 (dd, $J = 4.8$, 13.2 Hz, 1H), 3.76 (dd, $J = 9.0$, 9.0 Hz, 1H), 3.72 (dd, $J = 9.0$, 9.0 Hz, 1H), 2.61 (t, $J = 2.5$ Hz, 1H), 2.05 (s, 3H). 13C NMR (151 MHz, CD$_3$OD): $\delta$ 173.8, 158.9, 157.5, 84.1, 80.6, 74.4, 72.4, 69.7, 61.6, 52.8, 31.2, 22.8. HR-MS (APCI) m/z 316.1137; [M+H]$^+$ requires 316.1145.

$O$-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino $N$-(2-chloroethyl) carbamate 58

Using 28 and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a colourless oil which was treated with EtOAc to give 58 as a white solid (27 mg,
O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino N,N-(dimethyl) carbamate 59
Using 29 and flash chromatography (MeOH/EtOAc 1:3) of the resultant residue gave a colourless oil which was treated with EtOAc to give 59 as a white solid (37 mg, 74%). \( R_f \) 0.16 (MeOH/EtOAc 4:21). \(^1\)H NMR (600 MHz, CD\(_2\)OD) \( \delta \) 4.58 (d, \( J = 9.8 \) Hz, 1H), 3.93 (dd, \( J = 2.2, 12.3 \) Hz, 1H), 3.90 (dddd, \( J = 2.2, 3.9, 9.2 \) Hz, 1H), 3.85 (dd, \( J = 4.0, 12.3 \) Hz, 1H), 3.76 (dd, \( J = 9.0, 9.0 \) Hz, 1H), 3.69 (dd, \( J = 9.6, 9.6 \) Hz, 1H), 2.96 (m, 6H), 2.04 (s, 3H). \(^{13}\)C NMR (151 MHz, CD\(_2\)OD) \( \delta \) 173.8, 160.1, 156.5, 83.9, 74.8, 69.8, 61.7, 52.8, 36.9, 36.1, 22.8. HR-MS (APCI) \( m/z \) 306.1301; [M+H]\(^+ \) requires 306.1301.

O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino N,N-(diethyl) carbamate 60
Using 30 and flash chromatography (MeOH/EtOAc 4:21) of the resultant residue gave a colourless oil which was treated with EtOAc to give 60 as a white solid (37 mg, 85%). \( R_f \) 0.23 (MeOH/EtOAc 4:21). \(^1\)H NMR (600 MHz, CD\(_2\)OD) \( \delta \) 4.59 (d, \( J = 9.9 \) Hz, 1H), 3.93-3.83 (m, 3H), 3.77 (dd, \( J = 8.9, 8.9 \) Hz, 1H), 3.69 (dd, \( J = 9.6, 9.6 \) Hz, 1H), 3.41-3.32 (m, 4H), 2.04 (s, 3H), 1.17 (br s, 6H). \(^{13}\)C NMR (151 MHz, CD\(_2\)OD) \( \delta \) 173.8, 160.2, 156.5, 84.0, 74.8, 69.8, 61.7, 52.8, 43.5, 42.9, 22.8, 14.3, 13.7. HR-MS (APCI) \( m/z \) 334.1619; [M+H]\(^+ \) requires 334.1614.

O-(2-Acetamido-2-deoxy-d-glucopyranosylidene)amino N,N-(dibutyl) carbamate 61
Using 31 and flash chromatography (MeOH/EtOAc 3:17) of the resultant residue gave a colourless oil which was treated with EtOAc to give 61 as a white solid (38 mg, 79%). \( R_f \) 0.22 (MeOH/EtOAc 7:43). \(^1\)H NMR (600 MHz, CD\(_2\)OD) \( \delta \) 4.59 (d, \( J = 10.0 \) Hz, 1H), 4.02-3.84 (m, 3H), 3.80 (dd, \( J = 8.8, 8.8 \) Hz, 1H), 3.69 (dd, \( J = 9.4, 9.4 \) Hz, 1H), 3.29-3.13 (m, 2H), 2.04 (s, 3H), 1.62-1.49 (m, 4H), 1.41-1.23 (m, 4H), 0.95 (ap t, \( J = 7.3 \) Hz, 6H). \(^{13}\)C NMR (151 MHz, CD\(_2\)OD) \( \delta \) 173.8, 160.1, 156.9, 83.9, 74.8, 69.7, 61.6, 52.8, 48.1, 31.8, 31.2, 22.8, 21.0, 14.2. HR-MS (APCI) \( m/z \) 390.2236; [M+H]\(^+ \) requires 390.2240.
Using 32 and flash chromatography (MeOH/EtOAc 1:4) of the resultant residue gave a colourless oil which was treated with EtOAc to give 62 as a white solid (45 mg, 72%). $R_f$ 0.21 (MeOH/EtOAc 1:4). $^1$H NMR (600 MHz, D$_2$O) $\delta$ 4.68 (d, $J$ = 8.8 Hz, 1H), 4.10-4.07 (m, 1H), 4.05-3.98 (m, 1H), 3.95-3.84 (m, 3H), 3.57-3.42 (m, 4H), 2.12 (s, 3H), 1.70-1.44 (m, 6H). $^{13}$C NMR (151 MHz, D$_2$O) $\delta$ 175.1, 159.9, 155.8, 82.5, 72.8, 68.4, 60.5, 51.8, 46.0, 25.8, 24.1, 22.7. HR-MS (APCI) m/z 346.1625; [M+H]$^+$ requires 346.1614.

Using 33 and flash chromatography (MeOH/EtOAc 3:17) of the resultant residue gave a colourless oil which was treated with EtOAc to give 63 as a white solid (20 mg, 42%). $R_f$ 0.25 (MeOH/EtOAc 1:4). $^1$H NMR (600 MHz, D$_2$O) $\delta$ 4.68 (d, $J$ = 9.6 Hz, 1H), 4.10 (ddd, $J$ = 2.2, 4.3, 9.4 Hz, 1H), 4.02 (dd, $J$ = 2.3, 13.0 Hz, 1H), 3.95-3.84 (m, 3H), 3.77 (br s, 4H), 3.57 (br s, 4H), 2.12 (s, 3H). $^{13}$C NMR (151 MHz, D$_2$O) $\delta$ 175.2, 160.2, 155.6, 82.6, 72.7, 68.3, 66.7, 60.5, 51.8, 44.6, 22.7. HR-MS (APCI) m/z 348.1396; [M+H]$^+$ requires 348.1407.

**Kinetic Analysis of Inhibitors**

Assays against β-hexosaminidase B and NAGLU were carried out in triplicate at 37 ºC for 30 minutes using a stopped assay procedure in which the enzymatic reactions were quenched by the addition of a 4-fold excess of quenching buffer (200 mM glycine, pH 10.75). Assays against OGA were carried out in triplicate at 37°C for 20 minutes using a continuous assay procedure where reactions were initiated by the addition of substrate. Assays against β-hexosaminidase B were conducted in buffer (50 mM citrate, 100 mM NaCl, pH 4.25) and OGA (PBS, pH 7.4 buffer, 0.03% BSA) using 4-methylumbelliferyl N-acetyl-β-D-glucosaminide as substrate. For NAGLU, assays were performed in acetate buffer (100 mM, pH 4.3), containing bovine serum albumin (0.5 mg ml$^{-1}$) using 4-methylumbelliferyl N-acetyl-α-D-glucosaminide as substrate. For β-hexosaminidase B and NAGLU assays, release of 4-methylumbelliferone was monitored using a Varian CARY Eclipse Fluorescence Spectrophotometer 96-well plate system with readings taken at excitation and
emission wavelengths of 368 nm and 450 nm respectively, with 5 mm slit openings. For OGA the extent of 4-methylumbelliferone release was determined using a BioTek Synergy Plate Reader at excitation and emission wavelengths of 350 and 445 nm respectively. Assays contained substrate at the previously determined $K_m$ value of the substrate for the enzyme, and the enzyme was at a concentration of 0.5-10 nM for $\beta$-hexosaminidase B, 10-100 nM for NAGLU and 10 nM for OGA. For $K_I$ analysis, inhibitors were tested at a range of concentrations that encompassed their $K_I$ values. The rates at each inhibitor concentration were plotted and a best fit line through the points was ascertained. The $-1/K_I$ was taken as the point where the line of best fit intersected with $1/V_{max}$.

References
$^{1}H$ NMR spectrum of 1

$^{13}C$ NMR spectrum of 1
\textbf{1H NMR spectrum of 4}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{1H_NMR_spectrum.png}
\end{figure}

\textbf{13C NMR spectrum of 4}

\begin{figure}[h]
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$^1$H NMR spectrum of 5

$^{13}$C NMR spectrum of 5
$^1$H NMR spectrum of 6

$^{13}$C NMR spectrum of 6
$^1$H NMR spectrum of 7

$^{13}$C NMR spectrum of 7
$^1$H NMR spectrum of 8

$^{13}$C NMR spectrum of 8
$^1$H NMR spectrum of 9

$^{13}$C NMR spectrum of 9
$^1$H NMR spectrum of 10

$^{13}$C NMR spectrum of 10
$^1$H NMR spectrum of 11

$^{13}$C NMR spectrum of 11
$^1$H NMR spectrum of 12

$^{13}$C NMR spectrum of 12
$^{1}H$ NMR spectrum of 13

$^{13}C$ NMR spectrum of 13
$^1$H NMR spectrum of 14

$^{13}$C NMR spectrum of 14
$^{1}$H NMR spectrum of 15

$^{13}$C NMR spectrum of 15
$^1$H NMR spectrum of 16

$^{13}$C NMR spectrum of 16
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$^{13}$C NMR spectrum of 24
$^1$H NMR spectrum of 25

$^{13}$C NMR spectrum of 25
$^{1}H$ NMR spectrum of 26

$^{13}C$ NMR spectrum of 26
\(^1\)H NMR spectrum of 27

\(^{13}\)C NMR spectrum of 27
$^{1}$H NMR spectrum of 28

$^{13}$C NMR spectrum of 28
$^{1} \text{H NMR spectrum of 29}$

$^{13} \text{C NMR spectrum of 29}$
$^{1}$H NMR spectrum of 30

$^{13}$C NMR spectrum of 30
$^1$H NMR spectrum of 31

$^{13}$C NMR spectrum of 31
$^1$H NMR spectrum of 32

$^{13}$C NMR spectrum of 32
$$^1$$H NMR spectrum of 33

$$^{13}$$C NMR spectrum of 33
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$^1$H NMR spectrum of 39

$^{13}$C NMR spectrum of 39
$^1$H NMR spectrum of 40

$^{13}$C NMR spectrum of 40
$^1$H NMR spectrum of **41**

$^{13}$C NMR spectrum of **41**
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$^{13}$C NMR spectrum of 63