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Note

$FeCl_3$-catalyzed α-glycosidation of glycosamine pentaacetates

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ABSTRACT

An efficient method for the large-scale preparation of α-*N*-acetylglycosaminides, such as fluorogenic T_N-antigen probes and an α-GalNAc-Ser derivative, has been achieved using $FeCl_3$-catalyzed one-step condensation between commercially available D-glycosamine pentaacetates and fluorogenic acceptors (or serine acceptor) in refluxing 1,2-dichloroethane. Experimental simplicity, high α-stereoselectivity, low cost, satisfactory yield, and the environmentally benign nature are major advantages of our approach.

1,2-*cis*-2-Amino-2-deoxy glycosides are essential residues incorporated in a variety of oligosaccharides and glycoconjugates with biologically important roles.[1] However, stereoselective preparation of 1,2-*cis* glycosidic bond for 2-amino-2-deoxy sugar remains a major challenge in complex oligosaccharide synthesis.[2] Much work has been done on this α-glycosidation in order to improve the yield, stereoselectivity, and operational simplicity. Among them, the corresponding 2-azido,[3] 2,3-*trans*-oxazolidinone,[4] 4,6-*O*-benzylidenyl,[5] and 4,6-*O*-di-*tert*-butylsilylene[6] glycosamine derivatives are frequently used as key building blocks. Although great advances have been achieved applying these modified donors, the synthetic efficacy is always hampered because of laborious protecting group manipulations when converting the intermediates to the desired α-*N*-acetylglycosaminides. In a collaborative project, we were required to provide hundred-gram scale products of fluorogenic T_N-antigen probes. Many published α-glycosidation strategies were thus tried, but no encouraging results were obtained that were cost-effective. We would like to disclose here a practical method, which encompasses the condensation of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucopyranose (or galactopyranose) and an aglycon acceptor in refluxing 1,2-dichloroethane in the presence of anhyd ferric chloride.

Ferric chloride has been applied in O-isopropylidenation, acetylation, anomerization, detritylation, debenzylation, deprotection of acetals, and anomeric deacylation.[7] In particular, Kiso and coworkers[8] applied anhyd ferric chloride and 2-acylamino-1-*O*-acetyl-2-deoxy-β-D-glucopyranoses to make β-glycosides in CH_2Cl_2 at room temperature, while Nuhn[9] reported an α-glycosidation by reaction of peracetylated sugar moieties with several acceptors in the presence of $FeCl_3$ in CH_2Cl_2 at 5 °C. Our model study started from the reaction of cheap 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose and *n*-nonyl alcohol in CH_2Cl_2. We first applied Nuhn's method to our substrates, and obtained only the corresponding bicyclic oxazoline derivative. When the reaction was carried out in refluxing dichloromethane, a mixture of *N*-acetylglucosaminides (α:β = 1:1) was observed. Changing the solvent to 1,2-dichloroethane (DCE), and repeating the reaction under reflux conditions gave plausible α product **1a** with a 72% isolated yield (Table 1, entry 1). Further investigation suggested that the reaction was equally effective for either α-, β-, or α,β-mixture of *N*-acetyl-D-glucosamine 1-acetate. On searching in the literature it was found that ferric chloride might cause alkyl β-D-glycopyranoside anomerization, forming the corresponding α-isomer.[10] However, the same report has also clearly revealed that this anomerization is not suitable for the *N*-acetyl-D-glucosamine substrate. Interestingly, when we treated pure nonyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose, prepared according to Kiso's procedure,[8] with anhyd $FeCl_3$ in refluxing DCE, a mixture in favor of α product (α:β = 5:1) was observed. Careful monitoring of the process of our model reaction on TLC indicated a concomitance of oxazoline intermediate, β isomer, and α isomer in the early

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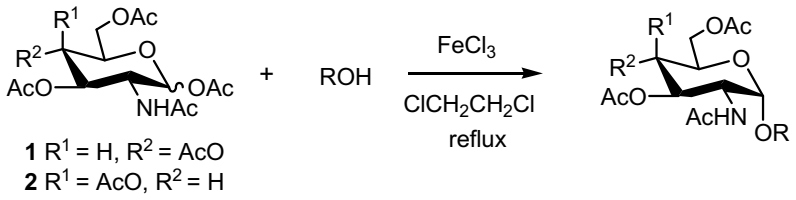
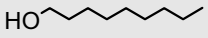
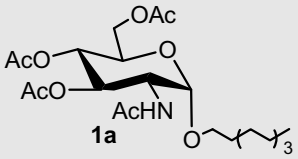
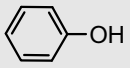
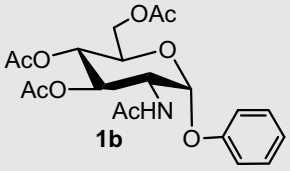
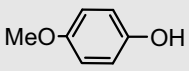
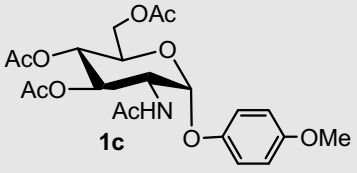
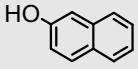
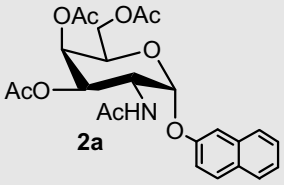
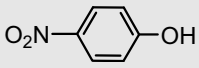
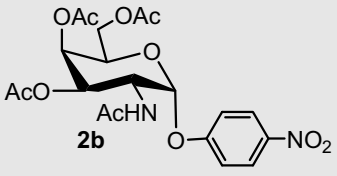
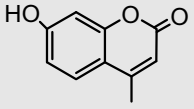
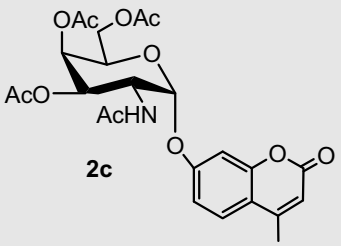
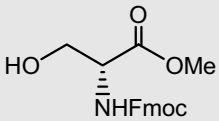
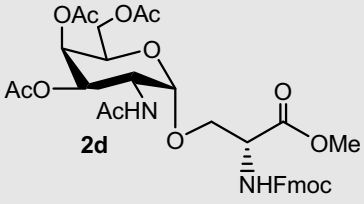
Table 1
Ferric chloride-catalyzed formation of α-*N*-acetylglycosaminides



1 R^1 = H, R^2 = AcO
2 R^1 = AcO, R^2 = H

Entry	Donor	Acceptor	Product	Isolated yield (%)	Stereoselectivity[b]
1	**1**		 **1a**	72	α
2	**1**		 **1b**	75	α
3	**1**		 **1c**	82	α
4	**2**		 **2a**	70	α
5	**2**		 **2b**	54	α
6	**2**		 **2c**	75	α
7	**2**		 **2d**	71[a]	α/β = 4:1

[a] Overall yield.
[b] Pure β isomers were not obtained, except for **2d**.

stage of the reaction. The desired α anomer increased, and was the major product after 16 h in refluxing DCE. This phenomenon suggested that the acid-catalyzed anomerization might have been occurred in situ.[11] To verify the reliability of this reaction, phenol and 4-methoxyphenol (Table 1, entries 2–3) were also subjected to the same reaction conditions. As we expected, α products **1b** and **1c** were obtained in a yield of 75% and 82%, respectively.

Encouraged by this finding, we next turned our attention to the $FeCl_3$-catalyzed condensation between 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-galactopyranose and fluorogenic acceptors (2-naphthol, 4-nitrophenol, and 4-methylumbelliferone) in refluxing DCE. The reactions proceeded smoothly under the above reaction conditions, and the products **2a**, **2b**, and **2c** were obtained in moderate to good yields (Table 1, entries 4–6), respectively. We have successfully prepared compounds **2a** (70% isolated yield) and **2c** (75% isolated yield) at 100-g scale with reproducible yields. The efficient large-scale synthesis of these substrates would facilitate the substrate specificity testing of α-*N*-acetylgalactosaminedase, or new species screening from other living organisms. More impressively, the α-O-linked T_N-serine (Table 1, entry 7), which accumulates on the surface of tumor cells due to incomplete glycan formation in malignant cells,[12] could also be prepared in 71% yield under the above reaction conditions as a separable α,β-mixture (4:1) in favor of α isomer. This fast and efficient synthesis may provide an easily adaptable way toward commercial production of mucin type glycopeptides that are currently under investigation as vaccines against cancers.[13]

In summary, we have developed an efficient method for the large-scale preparation of α-*N*-acetylglycosaminides, such as fluorogenic T_N-antigen probes and an α-GalNAc–Ser derivative. Anhydrous $FeCl_3$ was successfully applied to one-step condensation of commercially available D-galactosamine pentaacetates and fluorogenic acceptors (or serine acceptor), generating expected α products in moderate to good yields in refluxing 1,2-dichloroethane. Experimental simplicity, high α-stereoselectivity, low cost, acceptable yield, and its environmentally benign nature are major advantages of our approach.

1. Experimental

1.1. General methods

The reactions were carried out in dry solvents under an N_2 atmosphere. Optical rotations were determined at 25 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^1H and ^{13}C NMR spectra were recorded with ARX 400 spectrometers for solutions in $CDCl_3$. Chemical shifts are given in ppm downfield from internal Me_4Si. Mass spectra were measured using MALDI-TOFMS with dihydroxybenzoic acid (DHB) as the matrix. Thin layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV lamp.

1.2. Typical procedure for $FeCl_3$-promoted α-O-glycosidation

For a small-scale reaction: To a solution of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucopyranose (1.2 g, 3.1 mmol) in dry 1,2-dichloroethane (30 mL) were added anhyd $CaSO_4$ (1.0 g), anhyd $FeCl_3$ (750 mg), and the acceptor (2 equiv). The suspension was stirred vigorously under reflux for 16 h, at the end of which time TLC indicated that the reaction was complete. Filtration, concentration of the filtrate, and purification of the residue on a silica gel column, using 1:1 or 2:3 EtOAc–petroleum ether as eluent, gave the desired α product. The yield is shown in Table 1.

For a large-scale preparation, compound **2a** is taken as an example: To a pre-heated (40 °C) 1,2-dichloroethane (500 mL) in three-necked flask, equipped with mechanical stirrer, were successively added anhyd $CaSO_4$ (50 g), anhyd $FeCl_3$ (100 g), 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-galactopyranose (150 g, 0.385 mol), and 2-naphanol (84 g, 0.58 mol) under an N_2 atmosphere. The mixture was vigorously stirred under reflux for 16 h. When the reaction was completed (monitored by TLC), 1,2-dichloroethane and satd aq $NaHCO_3$ were added with stirring until the reaction mixture became slightly basic. Centrifuging the reaction mixture and concentrating the supernatant under diminished pressure furnished a residue, which was then subjected to silica gel column chromatography, to obtain **2a** (128 g, 70%) as a yellowish syrup.

1.2.1. Nonyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (1a)

$[\alpha]_D$ +35 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.82 (t, 3H, *J* 6.8 Hz, CH_2CH_3), 1.17–1.24 (m, 12H), 1.53–1.55 (m, 2H), 1.88, 1.95, 1.98, 2.03 (4s, 12H, Ac), 3.56–3.38 (m, 1H, OCH_aH_b), 3.60–3.63 (m, 1H, OCH_aH_b), 3.86–3.90 (m, 1H, H-5), 4.03 (dd, 1H, *J* 2.2, 12.3 Hz, H-6b), 4.18 (dd, 1H, *J* 4.6, 12.3 Hz, H-6a), 4.25–4.30 (m, 1H, H-2), 4.77 (d, 1H, *J* 3.6 Hz, H-1), 5.06 (t, 1H, *J* 9.6 Hz, H-4), 5.16 (t, 1H, *J* 9.6 Hz, H-3), 5.69 (d, 1H, *J* 9.6 Hz, N*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 20.4, 20.5, 20.6, 22.5, 23.0, 26.0, 29.0, 29.1, 29.2, 29.4, 31.7, 51.7, 61.9, 67.5, 68.1, 68.3, 71.2, 97.0 (C-1), 169.1, 169.7, 170.4, 171.1; MALDI-TOFMS: calcd for $C_{23}H_{39}NO_9$: 473.26; found: 496.17 $(M+Na)^+$.

1.2.2. Phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (1b)

Mp 118–120 °C; $[\alpha]_D$ +139 (*c* 1.8, $CHCl_3$), [lit.[14] mp 119–120 °C; $[\alpha]_D^{23}$ +150 (*c* 0.7, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$): δ 1.97, 2.02, 2.04, 2.06 (4s, 12H, Ac), 4.03–4.12 (m, 2H, H-5, H-6b), 4.23 (dd, 1H, *J* 4.6, 12.3 Hz, H-6a), 4.52-4.58 (m, 1H, H-2), 5.22 (t, 1H, *J* 9.8 Hz, H-4), 5.48 (t, 1H, *J* 9.8 Hz, H-3), 5.58 (d, 1H, *J* 3.6 Hz, H-1), 6.40 (d, 1H, *J* 9.3 Hz, N*H*), 7.05-7.10 (m, 3H, Ph), 7.30–7.33 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 20.5, 20.6, 22.9, 51.7, 61.6, 68.0, 68.3, 70.9, 95.7 (C-1), 116.4, 123.0, 129.6, 155.8, 169.2, 170.2, 170.4, 171.2; MALDI-TOFMS: calcd for $C_{20}H_{25}NO_9$: 423.15; found: 446.13 $(M+Na)^+$.

1.2.3. *p*-Methoxyphenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (1c)

Mp 108–110 °C; $[\alpha]_D$ +139 (*c* 1.6, $CHCl_3$), [lit.[15] mp 111 °C; $[\alpha]_D^{20}$ +144 (*c* 1.5, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$): δ 1.97, 2.05, 2.07, 2.09 (4s, 12H, Ac), 3.78 (s, 3H, OCH_3), 4.04–4.10 (m, 2H, H-5, H-6b), 4.23 (dd, 1H, *J* 4.8, 12.3 Hz, H-6a), 4.50–4.51 (m, 1H, H-2), 5.22 (t, 1H, *J* 10.5 Hz, H-4), 5.44 (t, 1H, *J* 10.5 Hz, H-3), 5.46 (d, 1H, *J* 3.5 Hz, H-1), 5.86 (d, 1H, *J* 9.6 Hz, N*H*), 6.84–7.02 (2d, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 20.6, 20.7, 23.1, 51.9, 55.6, 61.7, 67.9, 68.3, 71.0, 96.4 (C-1), 114.7, 117.6, 149.7, 155.4, 169.3, 170.0, 170.5, 171.4; MALDI-TOFMS: calcd for $C_{21}H_{27}NO_{10}$: 453.16; found: 476.13 $(M+Na)^+$.

1.2.4. 2-Naphthnyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranoside (2a)

$[\alpha]_D$ +33 (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.80, 1.96, 2.06, 2.20 (4s, 12H, Ac), 4.06 (dd, 1H, *J* 7.3, 11.3 Hz, H-6b), 4.12 (dd, 1H, *J* 6.6, 11.3 Hz, H-6a), 4.31–4.35 (m, 1H, H-5), 4.79–4.85 (m, 1H, H-2), 5.44–5.46 (m, 2H, $J_{1,2}$ 2.8, $J_{3,4}$ 3.5 Hz, H-1, H-3), 5.76 (d, 1H, *J* 3.6 Hz, H-4), 5.85 (d, 1H, *J* 9.3 Hz, N*H*), 7.21–7.24 (m, 1H, Ph), 7.40–7.47 (m, 3H, Ph), 7.74–7.81 (m, 3H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 20.6, 20.7, 23.3, 47.9, 61.7, 67.2, 67.6, 68.2, 96.4 (C-1), 118.2, 124.7, 126.7, 127.1, 127.6, 129.7, 129.9,

134.1, 153.5, 170.1, 170.2, 170.3, 171.0; MALDI-TOFMS: calcd for $C_{24}H_{27}NO_9$: 473.17; found: 496.13 $(M+Na)^+$; Anal. Calcd for $C_{24}H_{27}NO_9$: C, 60.88; H, 5.75; N, 2.96. Found: C, 60.54; H, 5.64; N, 3.12.

1.2.5. *p*-Nitrophenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranoside (2b)

$[\alpha]_D$ +81 (*c* 1.4, $CHCl_3$), [lit.[16] $[\alpha]_D$ +80 (*c* 0.4, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$): δ 1.83, 1.97, 2.09, 2.20 (4s, 12H, Ac), 4.08 (dd, 1H, *J* 7.3, 11.3 Hz, H-6b), 4.15 (dd, 1 H, *J* 6.6, 11.3 Hz, H-6a), 4.33–4.36 (m, 1H, H-5), 4.83–4.86 (m, 1H, H-2), 5.54–5.56 (m, 2H, $J_{1,2}$ 2.8, $J_{3,4}$ 3.5 Hz, H-1, H-3), 5.84 (d, 1H, *J* 3.6 Hz, H-4), 5.92 (d, 1H, *J* 9.3 Hz, N*H*), 7.17, 8.20 (2d, 4H, *J* 9.0 Hz, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 20.7, 20.72, 23.2, 48.0, 61.7, 67.3, 67.8, 68.4, 96.6 (C-1), 117.7, 125.4, 145.7, 162.4, 169.7, 170.1, 170.2, 171.1; MALDI-TOFMS: calcd for $C_{20}H_{24}N_2O_{11}$: 468.14; found: 491.11 $(M + Na)^+$; Anal. Calcd for $C_{20}H_{24}N_2O_{11}$: C, 51.28; H, 5.16; N, 5.98. Found: C, 51.49; H, 5.02; N, 6.10.

1.2.6. 4-Methylumbelliferyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranoside (2c)

$[\alpha]_D$ +179 (*c* 1, $CHCl_3$), [lit.[16] $[\alpha]_D$ +180 (*c* 1.5, $CHCl_3$)]; ^1H NMR (400 MHz, $CDCl_3$): δ 1.93, 1.98, 2.06, 2.19 (4s, 12H, Ac), 2.41 (d, 3H, *J* 1.1 Hz), 4.02–4.13 (m, 2H, H-6b, H-6a), 4.21–4.25 (m, 1H, H-5), 4.75–4.81 (m, 1H, H-2), 5.40 (dd, 1H, *J* 3.5, 11.5 Hz, H-3), 5.45 (d, 1 H, *J* 3.2 Hz, H-1), 5.68 (d, 1H, *J* 3.5 Hz, H-4), 5.85 (d, 1H, *J* 9.5 Hz, N*H*), 6.20 (d, 1H, *J* 1.0 Hz), 6.95 (dd, 1H, Ph), 7.07 (d, 1H, Ph), 7.69–7.72 (m, 1H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6, 20.5, 20.7, 20.8, 23.2, 47.8, 61.4, 66.9, 67.8, 67.9, 96.5 (C-1), 104.7, 113.0, 113.2, 115.5, 125.8, 152.0, 154.8, 158.6, 160.7, 167.7, 170.1, 170.2, 170.2; MALDI-TOFMS: calcd for $C_{24}H_{27}NO_{11}$: 505.16; found: 528.13 $(M+Na)^+$. Anal. Calcd for $C_{24}H_{27}NO_{11}$: C, 57.03; H, 5.38; N, 2.77. Found: C, 56.84; H, 5.25; N, 2.89.

1.2.7. *N*-(Fluoren-9-yl-methoxycarbonyl)-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-L-serine methyl ester (2d)

$[\alpha]_D$ +58 (*c* 1.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.94, 1.99, 2.05, 2.17 (4s, 12H, Ac), 3.80 (s, 3H, OCH_3), 3.94–3.97 (m, 2H), 4.04–4.13 (m, 3H, H-5, H-6b, H-6a), 4.25 (t, 1H, *J* 6.8 Hz), 4.46–4.60 (m, 3H), 4.52–4.60 (m, 1H, H-2), 4.84 (d, 1H, *J* 3.4 Hz, H-1), 5.10 (dd, 1H, *J* 3.5, 11.5 Hz, H-3), 5.38 (d, 1H, *J* 3.5 Hz, H-4), 5.65 (d, 1H, *J* 9.5 Hz, N*H* of serine), 5.79 (d, 1H, *J* 9.5 Hz, N*H*), 7.31–7.36 (t, 2H, Ph), 7.40–7.44 (t, 2H, Ph), 7.60–7.63 (m, 2H, Ph), 7.75–7.80 (d, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 20.8, 20.9, 23.3, 47.2, 51.1, 52.8, 54.2, 61.4, 66.6, 66.8, 69.0, 69.9, 70.9, 96.5 (C-1), 120.0, 120.1, 125.1, 125.2, 127.1, 127.2, 127.8, 128.8, 141.3, 141.4, 143.7, 143.8, 156.1, 170.2, 170.3, 170.4, 170.6, 170.8; MALDI-TOFMS: calcd for $C_{33}H_{38}N_2O_{13}$: 670.24; found: 693.27 $(M+Na)^+$. Anal. Calcd for $C_{33}H_{38}N_2O_{13}$: C, 59.10; H, 5.71; N, 4.18. Found: C, 59.36; H, 5.62; N, 4.25.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.09.003.

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