Supplementary Information

Non Catalytic Synthesis of Chromogen I and III from *N*-acetyl-$_D$-glucosamine in High-temperature Water

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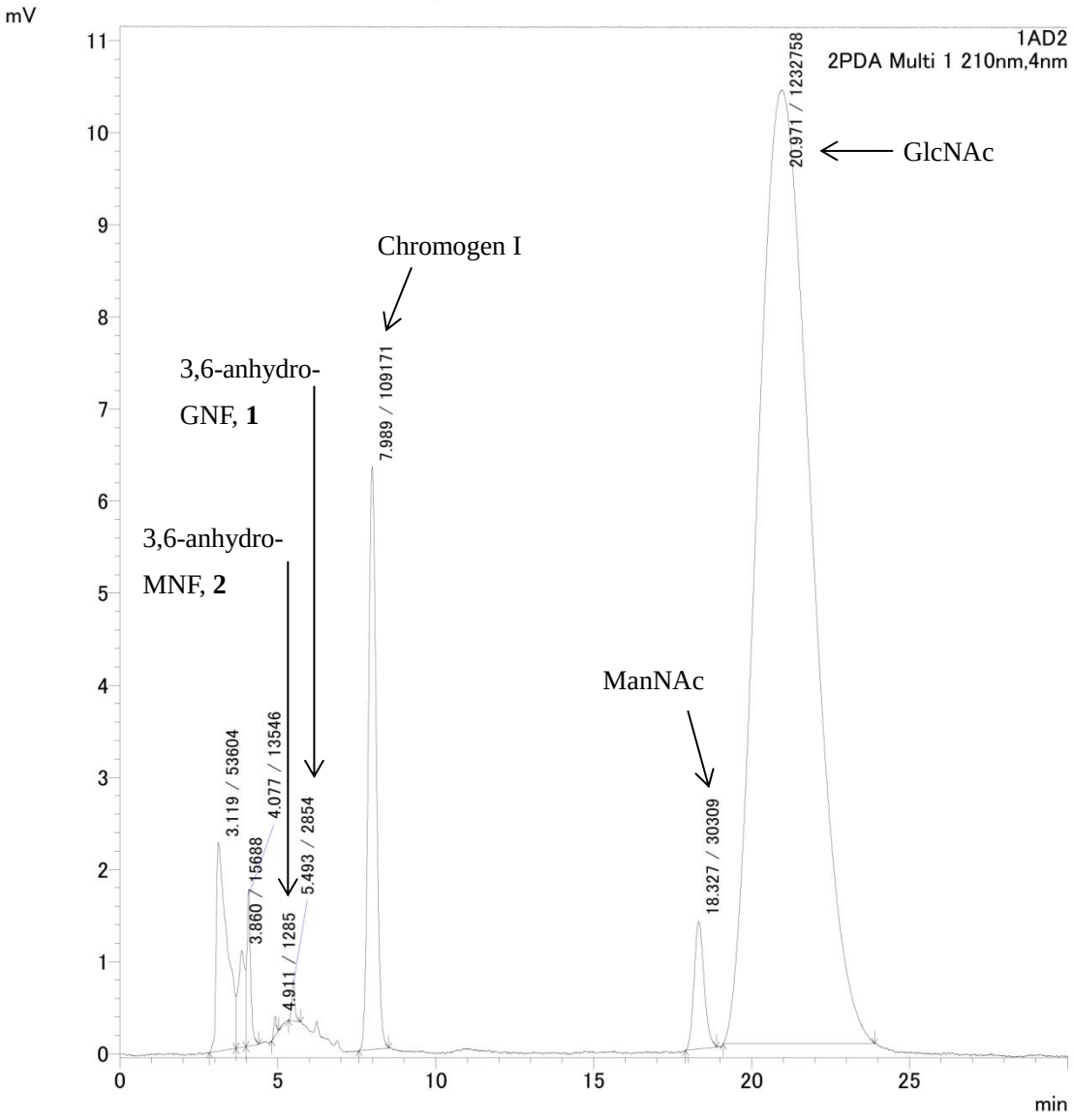
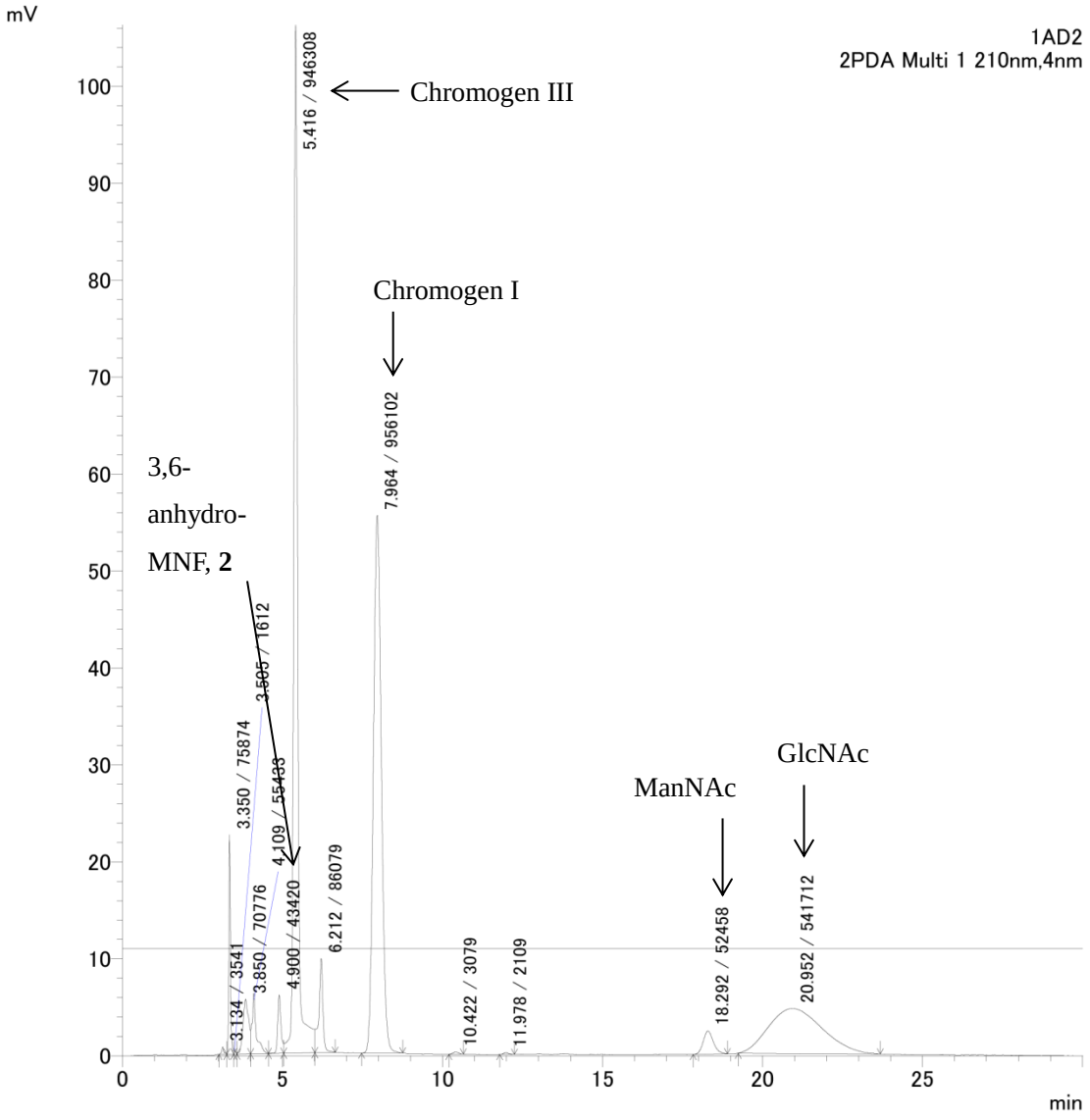
S1. HPLC chromatograph examples

(a) 180ºC, 25 MPa, reaction time 17 sec



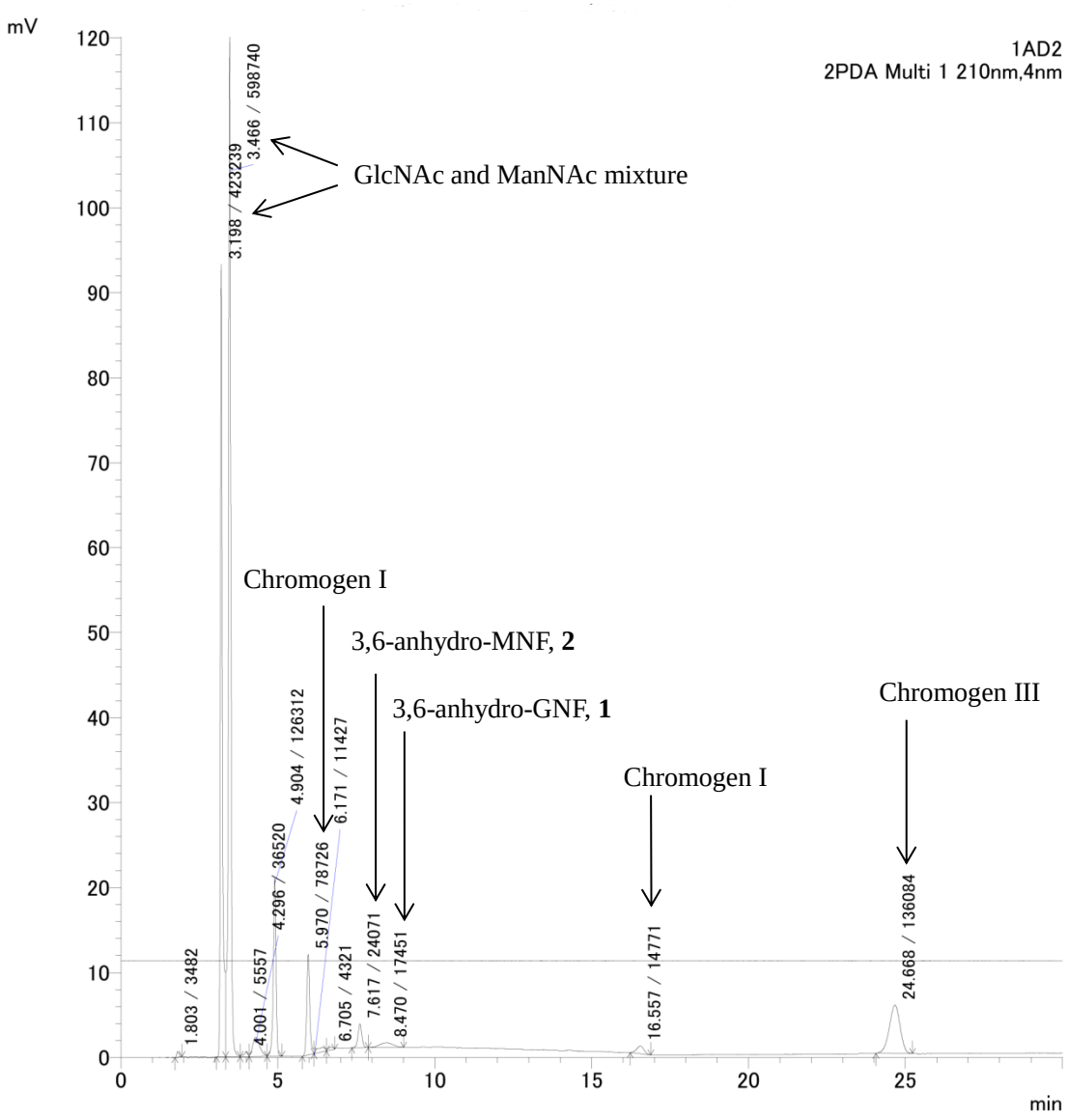
(b) 180ºC, 25 MPa, reaction time 33 sec



When Chromogen III was high concentration as the product, the peaks of Chromogen III and 3,6-anhydro-GMF, **1** overlapped. To analyze these compounds separately, we conducted the following HPLC method too. However, GlcNAc and ManNAc were not separated and Chromogen I showed two peaks in this method

Column: Unison US-C18 (4.6 × 250mm, Imtakt)
Mobile phase: water
Flow rate: 1.0 mL min^{-1}
Column oven temperature: 40ºC

(c) 180ºC, 25 MPa, reaction time 19 sec



S2. Characterization of Chromogen I, 3,6-anhydro-GNF, **1**, 3,6-anhydro-MNF, **2**, and Chromogen III

Chromogen I ; HRESIMS: *m/z* 226.06893 $[M+Na]^+$ (calcd for $C_8H_{13}N_1Na_1O_5$, 226.06914). ^{1}H NMR (D_2O, 500 MHz) α-anomer: δ 6.16 (1H, H-3), 6.04 (1H, H-1), 5.06 (1H, H-4), 3.83–3.57 (3H, H-5, H-6b, H-6a), 2.13 (s, 3H, C*H*$_3$CONH–); β-anomer: δ 6.21 (1H, H-3), 5.99 (1H, H-1), 4.83 (1H, H-4), 3.83–3.57 (3H, H-5, H-6b, H-6a), 2.13 (s, 3H, C*H*$_3$CONH–); ^{13}C NMR (D_2O, 125 MHz) α-anomer: δ 176.1 (CH_3CONH–), 137.0 (C-2), 112.0 (C-3), 102.2 (C-1), 87.5 (C-4), 76.2 (C-5), 65.2 (C-6), 25.4 (CH_3CONH–); β-anomer: δ 176.1 (CH_3CONH–), 136.5 (C-2), 112.7 (C-3), 102.0 (C-1), 87.2 (C-4), 76.5 (C-5), 65.1 (C-6), 25.4 (CH_3CONH–).

3,6-anhydro-GNF, **1** ; HRESIMS: *m/z* 226.07013 $[M+Na]^+$ (calcd for $C_8H_{13}N_1Na_1O_5$, 226.06914). ^{1}H NMR (D_2O, 500 MHz) α-anomer: δ 5.62 (d, 1H, J1,2 = 5.0 Hz, H-1), 4.76 (t, 1H, $J_{3,4}$ = 5.0, $J_{4,5}$ = 5.0 Hz, H-4), 4.66 (t, 1H, $J_{2,3}$ = 5.0, $J_{3,4}$ = 5.0 Hz, H-3), 4.33–4.29 (1H, H-5), 4.27 (t, 1H, $J_{1,2}$ = 5.0, $J_{2,3}$ = 5.0 Hz, H-2), 4.00 (dd, 1H, $J_{5,6b}$ = 6.5, $J_{6a,6b}$ = 8.5 Hz, H-6b), 3.66 (t, 1H, $J_{5,6a}$ = 8.5, $J_{6a,6b}$ = 8.5 Hz, H-6a), 2.06 (s, 3H, C*H*$_3$CONH–); β-anomer: δ 5.44 (1H, H-1), 4.79 (t, 1H, J3,4 = 5.0, J4,5 = 5.0 Hz, H-4), 4.52 (d, 1H, $J_{3,4}$ = 5.0 Hz, H-3), 4.33–4.29 (1H, H-5), 4.18 (1H, H-2), 3.96 (t, 1H, $J_{5,6b}$ = 8.0, $J_{6a,6b}$ = 8.0 Hz, H-6b), 3.88 (t, 1H, $J_{5,6a}$ = 8.0, $J_{6a,6b}$ = 8.0 Hz, H-6a), 2.02 (s, 3H, C*H*$_3$CONH–); ^{13}C NMR (D_2O, 125 MHz) α-anomer: δ 177.1 (CH_3CONH–), 100.4 (C-1), 88.5 (C-3), 81.7 (C-4), 73.0 (C-5, C-6), 61.5

(C-2), 24.56 (CH_3CONH–); β-anomer: δ 176.8 (CH_3CONH–), 105.2 (C-1), 88.6 (C-3), 85.6 (C-4), 73.8 (C-6), 73.5 (C-5), 64.7 (C-2), 24.60 (CH_3CONH–).

3,6-anhydro-MNF, **2** ; HRESIMS: *m/z* 226.06938 $[M+Na]^+$ (calcd for $C_8H_{13}N_1Na_1O_5$, 226.06914). ^{1}H NMR (D_2O, 500 MHz) α-anomer: δ 5.53 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 4.70 (t, 1H, $J_{3,4}$ = 5.5, $J_{4,5}$ = 5.5 Hz, H-4), 4.65–4.62 (1H, H-3), 4.42–4.38 (1H, H-5), 4.35 (t, 1H, $J_{1,2}$ = 5.5, $J_{2,3}$ = 5.5 Hz, H-2), 3.96–3.89 (2H, H-6b, H-6a), 2.07 (s, 3H, C*H*$_3$CONH–); β-anomer: d 5.31 (d, 1H, $J_{1,2}$ = 6.0 Hz, H-1), 4.81 (t, 1H, $J_{3,4}$ = 4.6, $J_{4,5}$ = 4.6 Hz, H-4), 4.65–4.62 (1H, H-3), 4.42–4.38 (1H, H-5), 4.25 (t, 1H, $J_{1,2}$ = 6.0, $J_{2,3}$ = 6.0 Hz, H-2), 4.02 (dd, 1H, $J_{5,6b}$ = 6.7, $J_{6a,6b}$ = 8.4 Hz, H-6b), 3.55 (t, 1H, $J_{5,6a}$ = 8.4, $J_{6a,6b}$ = 8.4 Hz, H-6a), 2.05 (s, 3H, C*H*$_3$CONH–); ^{13}C NMR (D_2O, 125 MHz) α-anomer: δ 177.0 (CH_3CONH–), 98.3 (C-1), 84.7 (C-4), 83.0 (C-3), 73.95 (C-5), 73.5 (C-6), 57.5 (C-2), 24.4 (CH_3CONH–); β-anomer: δ 177.2 (CH_3CONH–), 103.7 (C-1), 83.5 (C-4), 82.7 (C-3), 74.3 (C-5), 73.90 (C-6), 61.8 (C-2), 24.5 (CH_3CONH–).

Chromogen III ; HRESIMS: *m/z* 393.12810 $[2M+Na]^+$ (calcd for $C_{16}H_{22}N_2Na_1O_8$, 393.12739). ^{1}H NMR (D_2O, 270 MHz) δ 7.68 (1H, H-1), 6.25 (1H, H-3), 4.59 (1H, H-5), 3.69–3.67 (2H, H-6b, H-6a), 2.00 (s, 3H, C*H*$_3$CONH–).