SUPPLEMENTARY MATERIALS

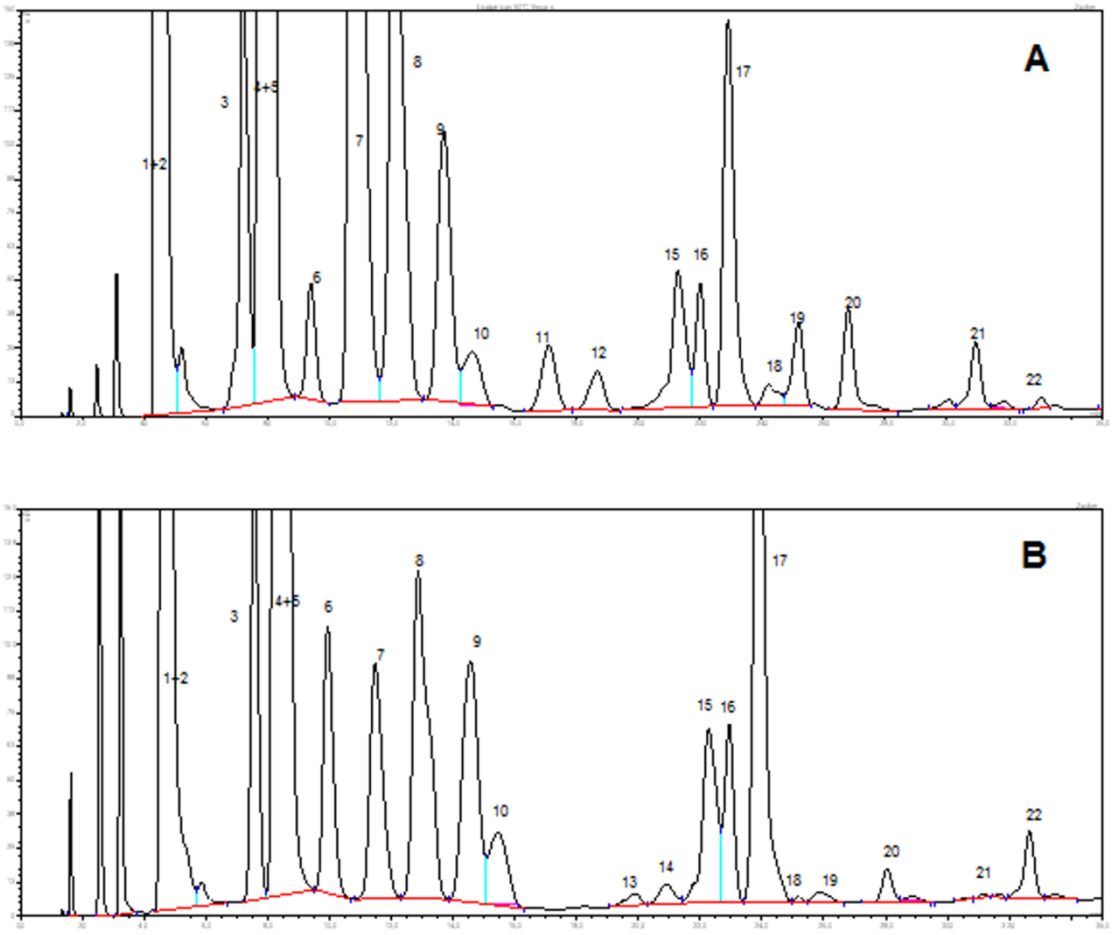

Figure S1. Separation and quantification by HPAEC-PAD of individual GOS produced during lactose conversion catalyzed by (**A**) *L. bulgaricus* β-gal and (B) *B. breve* β-gal I. The identified compounds are (1) D-Gal, (2) D-Glc, (3) β-D-Gal*p*-(1→6)-D-Gal, (4) β-D-Gal*p*-(1→6)-D-Glc (allolactose), (5) β-D-Gal*p*-(1→4)-D-Glc (lactose), (6) β-D-Gal*p*-(1→3)-D-Gal, (7) β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→4)-D-Glc, (9) β-D-Gal*p*-(1→3)-D-Glc, (15) β-D-Gal*p*-(1→3)-β-D-Gal*p*-(1→4)-D-Glc, (17) β-D-Gal*p*-(1→4)-β-D-Gal*p*-(1→4)-D-Glc. Peaks 8, 10-14, 16, 18-22 were not identified.

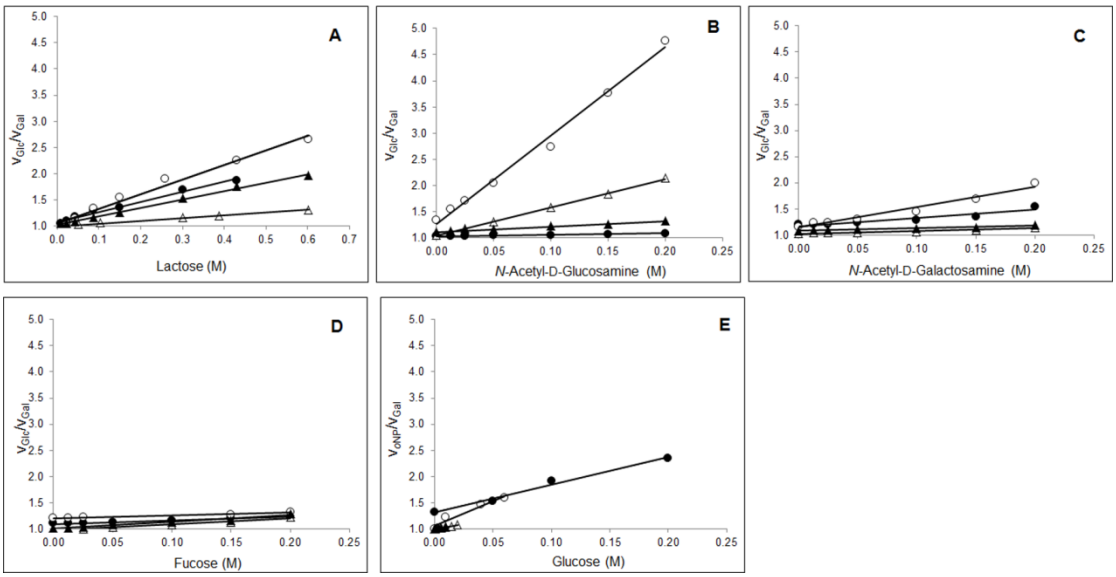

Figure S2. Ratio of initial velocities v_{Glu}/v_{Gal} in the presence of different exogenous nucleophiles, which are lactose (A), *N*-acetyl-D-glucosamine (B), *N*-acetyl-D-galactosamine (C), L- fucose (D); and v_{oNP}/v_{Gal} in the presence of D-Glucose (E). The enzymes are β-galactosidases from *L. reuteri* (●), *L. bulgaricus* (○), *B. breve* β-gal I (▲), and *B. breve* β-gal II (Δ).

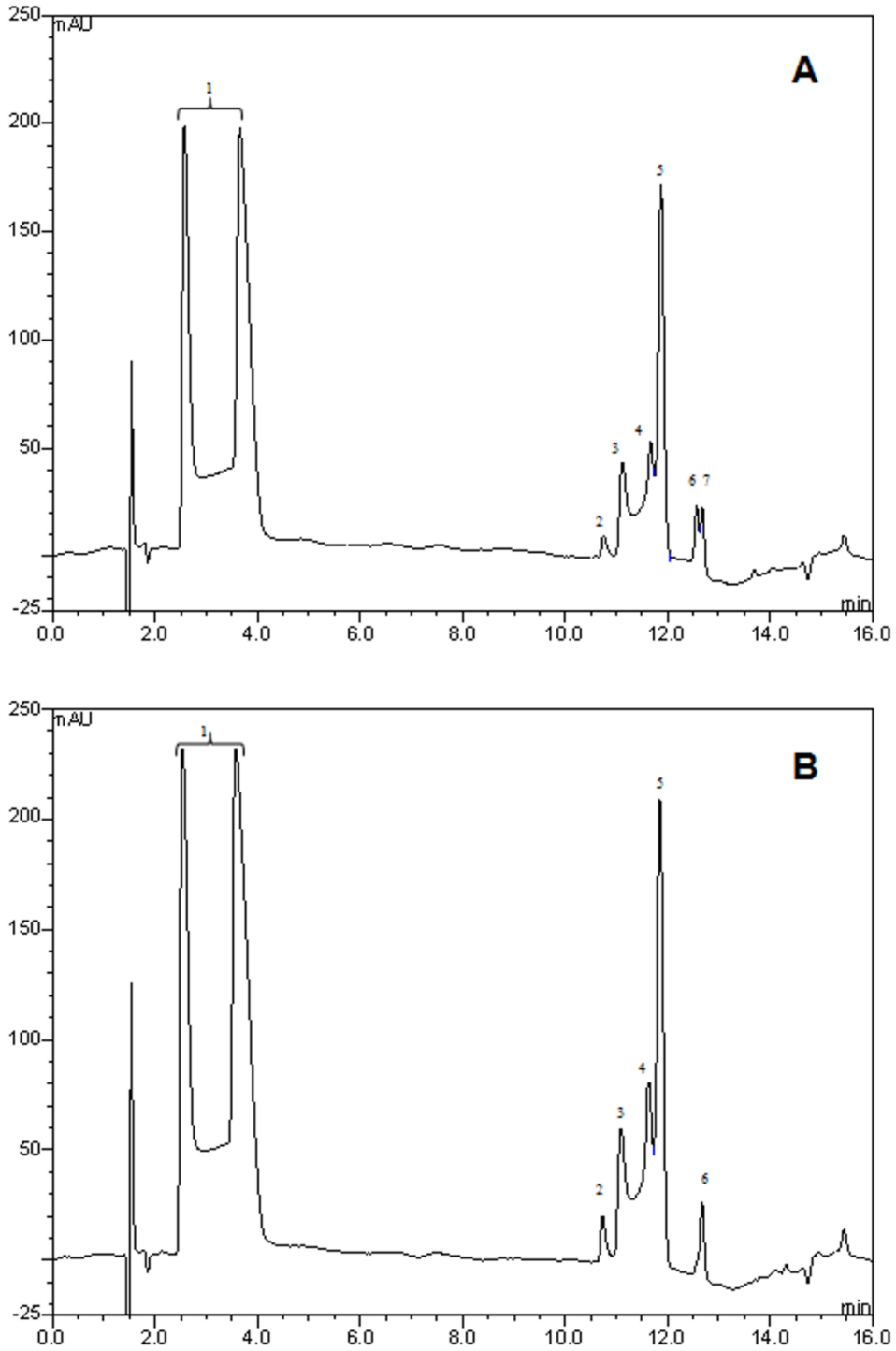

Figure S3. HPLC-UV chromatogram of *N*-acetyl oligosaccharides produced by β-galactosidases from (A) *L. bulgaricus* and (B) *B. breve* βgal-II using equimolar concentration of lactose and GlcNAc dissolved in 50 mM sodium phosphate buffer (pH 6.5) containing 1 mM $MgCl_2$. Peak Identification: (1) the anomeric isomers of GlcNAc, (3) and (5) the anomeric isomers of Gal*p*-(1→6)-D-GlcNAc. Peaks 2, 4, 6 and 7 were not identified.

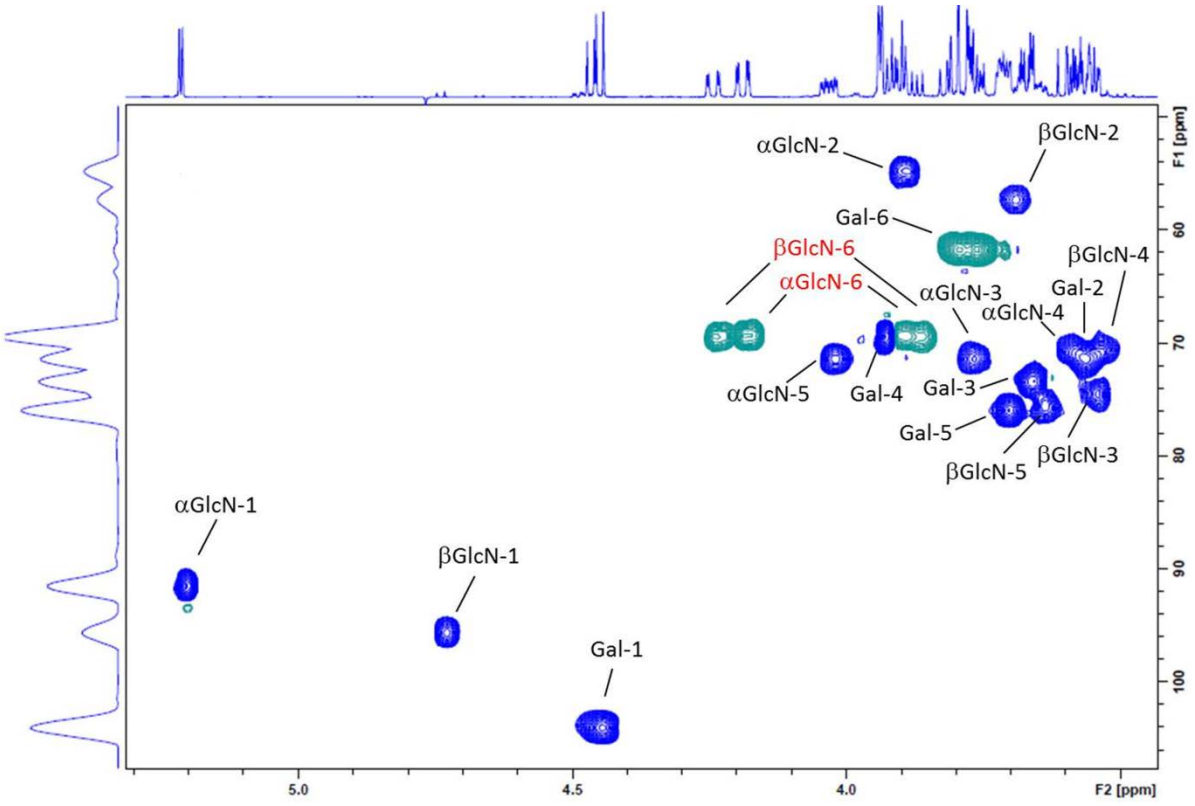

Figure S4. Multiplicity edited HSQC spectrum of β-D-Gal*p*-(1→6)-D-GlcNAc.

Table S1. NMR assignments[a] for *N*-acetyl-allolactosamine

Residue	Position	^{1}H δ (ppm)	*J* (Hz)	^{13}C δ (ppm)
β-Gal*p*-(1→6)	1	4.47 (β)	7.9	104.1
	1	4.45 (α)	7.9	104.1
	2	3.57	10.0	71.3
	3	3.67	3.4	73.4
	4	3.94	<1.0	69.5
	5	3.71	n.d.[b]	75.9
	6a	3.81	7.9, 11.8	61.7
	6b	3.76	2.3	
α-Glc*p*NAc	1	5.21	3.6	91.6
	2	3.90	10.7	54.7
	3	3.78	9.4	71.4
	4	3.60	10.0	70.7
	5	4.03	2.1	71.4
	6a	4.19	11.4	69.4
	6b	3.91	5.5	
β-Glc*p*NAc	1	4.74	8.3	95.6
	2	3.71	n.d.	57.3
	3	3.55	n.d.	74.5
	4	3.54	n.d.	70.7
	5	3.65	9.6	75.5
	6a	4.24	2.0, 11.5	69.4
	6b	3.88	5.9	
NHAc	CH_3	2.06		22.7

[a] Spectra were recorded at 300 K. ^{13}C shifts were referenced to 1,4-dioxane (δ 67.40) and derived from HSQC spectra.
[b] n.d. Not determined.