Supplementary Material

Flow Chemistry System for Carbohydrate Analysis by Rapid Labeling of Saccharides after Glycan Hydrolysis

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**Figure S1.** Vapourtec easy-MedChem, E-Series flow chemistry system set in the Genomics Research Center of Academia Sinica for sugar tagging and glycan hydrolysis.
Figure S2. The hydrolysis efficiency of maltose (1.0 mg/mL) on treatment with 4 M HCl for 10 min at different temperatures (80, 120 and 150 °C) in a flow chemistry system. The reaction was monitored by MALDI-TOF-MS measurement. Reaction volume: 2.0 mL. Collect volume: 5.0 mL. The hydrolysis of maltose was estimated to be 60% at 80 °C, 99% at 120 °C, and substantial decomposition at 150 °C. Glucose and maltose appeared as the sodiated ions at m/z 202 and 365, respectively.
Figure S3. The hydrolysis efficiency of maltotriose (1.0 mg/mL) on treatment with 4 M HCl for 10 min at different temperatures (25–120 °C) in a flow chemistry system. The reaction was monitored by MALDI-TOF-MS measurement.
Figure S4. Comparison of the hydrolysis efficiency of maltotriose (1.0 mg/mL) on treatment with 4 M or 2 M HCl at 120 °C for 10 min in a flow chemistry system. The reaction was monitored by MALDI-TOF-MS measurement.
Figure S5. Hydrolysis of lactose (1.0 mg/mL) with 4 M HCl at 120 °C for 10 min in a flow chemistry system. The reaction was monitored by LC-MS analysis: LC diagram (A) and LTQ-FTMS spectra (B).
Figure S6. $^1$H-NMR spectrum of Lac-NAIM (600 MHz) in D$_2$O solution (1.0 mL) containing 0.1% (CH$_3$)$_2$SO as internal standard. The aromatic protons of NAIM derivatives in the range of δ 7.2–8.2 ppm are not shown for clarity. The signal of HDO was set at δ 4.80 ppm, and the signal of (CH$_3$)$_2$SO occurred at δ 2.73 ppm.
Digestion of maltohexose (α1,4-linkage) by amylase

Digestion of laminarihexose (β1,3-linkage) by endo-β-1,3-glucanase
Figure S7. CE analysis of enzymatic digestion of oligosaccharides. (A) Electropherograms of maltohexaose-NAIM derivative (trace a) and after digestion by α-amylase (trace b). Peaks 1–6 indicate the NAIM derivatives of saccharides containing 1–6 glucose units. (B) Electropherograms of laminarirexaose-NAIM derivative (trace c, containing minor components of pentamer and heptamer) and after digestion by endo-β-1,3-glucanase (trace d). Peaks 2–7 indicate the NAIM derivatives of saccharides containing 2–7 glucose units. (C) Electropherograms of cellohexaose-NAIM derivative (trace e) and after cellulase digestion (trace f). Peaks 1–6 indicate the NAIM derivatives of saccharides containing 1–6 glucose units. CE conditions: uncoated fused-silica capillary of 30 cm (effective length) × 50 μm id; phosphate buffer (300 mM, pH 3.0); applied voltage of 15 kV (detector at cathode side); sample loaded by pressure for 5s; detection wavelength at 254 nm.