Supporting Information

General Methods for Chemical Synthesis.

PhoSL[1] and protected-PhoSL bound to resin **S1** (Figure S1) was purchased from SCRUM. Inc., Japan. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was conducted using a Bruker Ultraflex mass spectrometer with detection in the reflector mode. 2,5-Dihydroxy benzoic acid (DHB) was used as the matrix, with positive ionization mode. Preparative reverse-phase high performance liquid chromatography (RP-HPLC) was performed on a JASCO apparatus HPLC analytical Develosil (20×250 mm, Nomura Chemical Co., Ltd) with flow rate of 5 mL/min. Analytical RP-HPLC was performed on a JASCO apparatus HPLC analytical Wakosil-II (4.6 × 250 mm, Wako Pure Chemical Industries, Ltd.) with flow rate of 1 mL/min. Detection of products was made by UV detector (JASCO, UV-2075 Plus). All RP-HPLC procedure was carried out with a liner gradient using H_2O and MeCN with 0.1 wt% TFA.

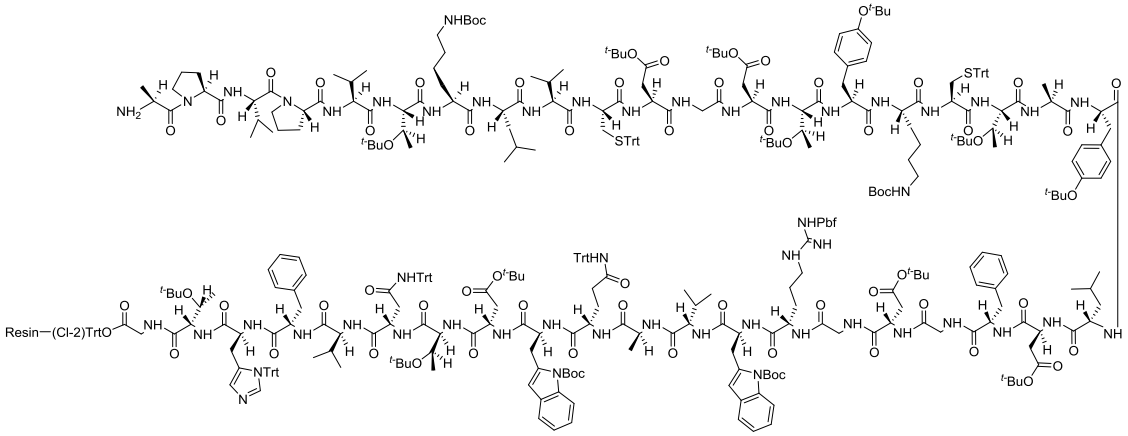

Figure S1. The chemical structure of protected-PhoSL bound to resin **S1**.

Synthesis of Compounds 2 and 3.

To the resin **S1** (100 mg, 100 μmol/g) was added a premixed solution of TBTU (64.2 mg, 200 μmol, 200 mM), NEM (23.0 mg, 200 μmol, 200 mM), and anthraquinone-2-carboxylic acid (**1**) (50.4 mg, 200 μmol, 200 mM) in DMF (1.00 mL), and the resulting mixture was gently shaken at room temperature for 14 h. After filtration, the resin was washed three times with CH_2Cl_2 (1.00 mL) and three times with DMF (1.00 mL) to give anthraquinone bound to resin **S2**. Completion of the coupling reaction was monitored by the Kaiser test. To the resin **S2** was added a premixed solution of TFA (0.820 mL, 107 mmol), 1,2-ethandithiol (12.5 μL, 149 μmol),

thioanisole (25.0 µL, 213 µmol), PhOH (75.0 mg, 797 µmol), and H_2O (25.0 µL), and the resulting mixture was shaken at room temperature for 4 h. After filtration, the resin was washed one time with a solution of the reaction solution. The combined filtrates were added to cooled Et_2O (15.0 mL) to precipitate the product. The resulting precipitate was purified by reversed-phase HPLC (Develosil, 20×250 mm, Nomura Chemical Co., Ltd, 40 ºC, detection by UV (220 nm), 90:10 to 35:65 H_2O/MeCN with 0.1 wt% TFA 60 min, flow rate 5 mL/min) to obtain the hybrid **3** (0.77 mg, 160 nmol, 1.6%). Data for **3**: HPLC (Wakosil-II C18 3.0 µm, 4.6 × 250 mm; 40 ºC; detection by UV (220 nm); 90:10 to 35:65 H_2O/MeCN with 0.1 wt% TFA 40 min; flow rate 1 mL/min); Rt 23.6 min; LRMS (MALDI-TOF-MS) *m*/*z* 4681.2 (4682.1). The compound **2** was obtained from **1** and protected-PhoSL+ lysine bound to resin **S3** in a similar solid synthesis manner in Toray Research Center, Inc., Japan. Data for **2**: HPLC (Wakosil-II C18 3.0 µm, 4.6 × 250 mm; 40 ºC; detection by UV (220 nm); 90:10 to 35:65 H_2O/MeCN with 0.1 wt% TFA 40 min; flow rate 1 mL/min); Rt 20.3 min; LRMS (MALDI-TOF-MS) *m*/*z* 4810.2 (4810.3).

Fluorescent Labeling of Oligosaccharides with 8-Aminopyrene-1,3,6-trisulfonate (APTS).[2]

Sample of glycoprotein (1 mg/mL) 1.9 µL was added to water 100 µL and freeze-dried in a freeze dryer after being frozen at -80 ºC for 15 min. The residue was added to 0.2 M APTS aqueous solution/1.2 M citric acid 2 µL and 1.0 M $NaBH_3CN$ in tetrahydrofuran 2 µL. The mixture was kept at 55 ºC for 2 h. After water 46 µL was added to the mixture, the mixture was shaded by aluminum foil and stored at -20 ºC.

Capillary Affinity Electrophoresis (CAE).[2]

CAE was performed on a Beckman Coulter P/ACE MDQ Glycoprotein System with a helium-cadmium laser induced fluorescence detection system (Ex: 488 nm, Em: 520 nm). The compounds were separated using an eCAP N-CHO capillary (Beckman Coulter; 20 cm effective length, 30 cm total length, 50 µm inner diameter). The inner surface is chemically modified with polyvinyl alcohol and is ideal for affinity electrophoresis using lectins due to negligible levels of lectin-capillary surface interaction. 0.1 M Tris-acetate buffer (pH 7.0) and MeCN were used as the electrolyte. The electrolyte was run by 10 kV for 15 min. The data were collected and analyzed with standard 32 Karat software (Beckman Coulter). Before CAE analysis, a mixture of APTS-labeled oligosaccharides (Manα1-3Man **4**, Fucα1-6GlcNAc **5**, GN5 **6**, NGA2 **7**, and NGA2F **8** (0.083 pmol/mL)) was analyzed in the absence of a lectin. Sample

solutions were infected using a pressure method (0.5 p.s.i., 5s). Their migration times are expressed as glucose units (GU). GU values were determined with an APTS-labeled glucose oligomer mixture prepared from a partial hydrolysate of dextran as an external standard. For CAE analysis, the capillary was filled with the same electrolyte containing a solution of **2** (0, 0.05, 0.1, 0.15, or 0.2 mg/mL) in 0.1 M Tis-acetate buffer (pH 7.0)/MeCN = 7/3, **3** (0 or 0.5 mg/mL) in 0.1 M Tris-acetate buffer (pH 7.0)/MeCN = 1/1, **PhoSL** (0, 0.1, 0.2, 0.4, 0.6, or 0.8 mg/mL) in 0.1 M Tris-acetate buffer (pH 7.0), or **3** (0, 0.1, 0.2, 0.3, 0.4, 0.6, and 0.7 mg/mL) in 0.1 M Tris-acetate buffer (pH 7.0)/MeCN = 7/3 (20 p.s.i., 1.5 min), and the same mixture of the oligosaccharides was analyzed. Changes in the migration of each oligosaccharide were detected.

Analysis of Interaction Between 3 and APTS-labeled Oligosaccharides by CAE.

Capillary electrophoresis of the fluorescently (APTS) labeled oligosaccharides was performed in the presence of PhoSL and the hybrid **3** at the concentrations indicated. Capillary electrophoresis profile using the hybrid **3** was shown in Figure S2.

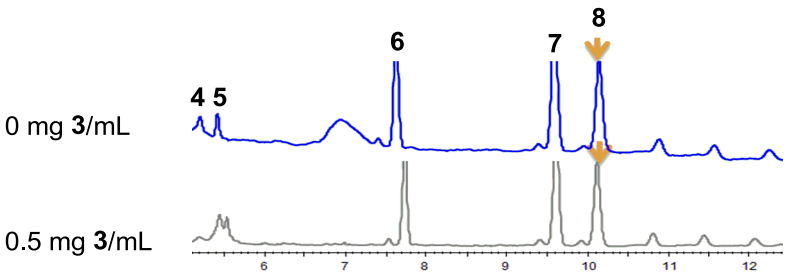

Figure S2. The interaction analysis o the hybrid **3** with the fluorescence (8-aminopyrene-1,3,6-trisulfonic acid, APTS)-labeled oligosaccharides **4-8** by capillary affinity electrophoresis. Capillary electrophoresis of the fluorescently (APTS) labeled oligosaccharides was performed in the presence of the hybrid **3** at the concentrations indicated.

Photo-degradation of Target Oligosaccharide.

PA-labeled[3] oligosaccharide **9** (500 nM) was incubated with **2** in Tris-acetate buffer (100 mM, pH7.0):MeCN = 7:3 at 25 ºC for 2 h under irradiation with a UV lamp (365 nm, 100 W) placed 10 cm from the vessel and the mixture was concentrated. The residue in H_2O:MeCN = 7:3 was analyzed by HPLC methods (Amide-80, 4.6 ×250 mm, TOSOH Co.; 40 ºC; detection by FP (Ex: 310 nm, Em: 380 nm); 10 wt% acetic acid-trimethylamine (pH 7.3, 500 mM) MeCN:10 wt% acetic acid-trimethylamine (pH

7.3, 500 mM) H_2O = 80:20 to 50:50; flow rate 1 mL/min).

EPR Spectrometry.

EPR spectrum was recorded using a Bruker BioSpin EMX EPR operating at 9.5 GHz with 100 kHz modulation. **2** (21 μM) and DMPO (500 mM) were incubated in 2%DMSO/PBS (pH 7.4, 137 mM NaCl, 2.7 mM KCl, 6.5 mM Na_2HPO_4, 1.5 mM KH_2PO_4) containing 1 mM DETAPAC under irradiation with a UV lamp (365 nm, 100 W) placed 40 cm from a flat cell.

Photo-degradation of Glycoproteins.

A solution of glycoprotein (3 μM/lane) and compound (7, 3, 1, 0.3 equivalent to glycoproteins) in 2% DMSO/PBS (pH 7.4, 137 mM NaCl, 2.7 mM KCl, 6.5 mM Na_2HPO_4, 1.5 mM KH_2PO_4) was incubated with or without photo-irradiation using a UV lamp (365 nm, 100 W) placed at 10 cm from the vessel at 25 ºC for 2 h. 4.80 μL of electrophoresis buffer consisted of SDS (5%, wt/vol), glycerol (27%, vol/vol), and bromophenol blue (0.007%, wt/vol) was added to the photo-irradiated samples, and the proteins were separated by SDS-PAGE in 12% polyacrylamidegels. The gels were run by applying 30 mA for 90 min, stained with SYPRO Ruby Protein Gel Stain (Bio-Rad Lab. Inc.) for 14 h, destained in acetic acid (7%, vol/vol) and methanol (10%, vol/vol) for 0.5 h, and washed with deionized water. The gels were scanned with a Molecular Image FX (Bio-Rad Lab. Inc.). Molecular weight markers were used in each gel for calibration purpose.

MALDI TOF MS analysis.

3.00 μL of sample was mixed with a matrix solution (3.00 μL) of 3,5-dimethoxy 4-hydroxycinnamic acid (in 50:50 MeCN/H_2O containing 0.1% TFA). Analyses by MALDI TOF MS were performed in the positive ion mode on an Autoflex III (Bruker).

Cell Culture.

<HuH-7>: The HuH-7 cell line was routinely grown in RPMI supplemented with 5% (v/v) fetal bovine serum, 10% (v/v) horse serum, 0.5% (v/v) penicillin and streptomycin. The cells were maintained at 37 ºC in a humidified atmosphere containing 5% CO_2 plus air.

<A549>: The A549 cell line was routinely grown in Dulbecco's modified Eagle's medium (DMEM) supplemented with 5% (v/v) fetal bovine serum, 10% (v/v) horse serum, 0.5% (v/v) penicillin and kanamycin. The cells were maintained at 37 ºC in a

humidified atmosphere containing 5% CO_2 plus air.

<HeLa>: The HeLa cell line was routinely grown in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% (v/v) fetal bovine serum, 0.5% (v/v) penicillin and kanamycin. The cells were maintained at 37 ºC in a humidified atmosphere containing 5% CO_2 plus air.

<HLE>: The HLE cell line was routinely grown in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% (v/v) fetal bovine serum, 0.5% (v/v) penicillin and kanamycin. The cells were maintained at 37 ºC in a humidified atmosphere containing 5% CO_2 plus air.

MTT Assay.[4]

The cells were seeded into 96-well microplates at 2.00×10^4 cells/mL in 100 μL of complete medium per well and incubation for 24 h at 37 ºC under 5% CO_2 plus air. The cells were treated with a solution of compounds (0, 0.1, 0.3, 1.0 μM) in DMSO (final concentration, 1%) for 24 h at 37 ºC under 5% CO_2 plus air. The cells was preincubated under irradiation UV lamp (368 nm, 30 W) placed at 20 cm form the vessel at 25 ºC for 30 min, and then incubated for 72 h at 37 ºC under 5% CO_2 plus air. And then 10 μL of 5 mg/mL MTT dissolved in PBS was added to each well. After incubation for 3 h at 37 ºC under 5% CO_2 plus air, 100 μL of DMSO was added to each well. The absorbance of the mixture was measured at 540 nm.

References.

1 Y. Kobayashi, H. Tateno, H. Dohra, K. Moriwaki, E. Miyoshi, J. Hirabayashi, H. Kawagishi, *J. Biol. Chem.* 2012, **287**, 33973.

2 K. Nakajima, M. Kinoshita, Y. Oda, T. Masuko, H. Kaku, N. Shibuya, K. Kakehi, *Glycobiology* 2004, **14**, 793.

3 H. Hase, T. Ikenaka, Y. Matsushima, *Biochem. Biophys. Res. Commun.* 1978, **85**, 257.

4 T. Mosmann, *J. Immunol. Methods* 1983, **65**, 55.