Supplementary Methods

***N*-glycan preparation.** Gastropod hemolymph 20 µl was mixed with 30 µl of 330 mM ammonium bicarbonate and 60 µl of 0.02 % (w/v) PHM-LIPOSORB (Merck) in 0.5 mM ammonium bicarbonate, and incubated at 37 °C for 10 min. As an internal standard, 2 µl of 0.5 mM maltohexaose was added. Then the samples were reduced by 10 µl of 120 mM dithiothreitol (DTT) at 60 °C for 30 min and alkylated with 20 µl of iodoacetamide (IAA) by incubation in the dark at room temperature for 1 h (Kita *et al.,* 2007). Trypsin (Sigma-Aldrich) 400 units was added and incubated at 37 °C over night, followed by inactivation at 90 °C for 10 min. After cooling to room temperature, *N*-glycans were released with 2 units of PNGase F (Roche) at 37 °C over night. Glycoblotting by means of BlotGlyco beads (Sumitomo Bakelite) was performed according to the procedure described previously (Amano *et al.,* 2010, Furukawa *et al.,* 2008, Hirose *et al.,* 2011, Nagahori *et al.,* 2013, Nishimura *et al.,* 2004). BlotGlyco beads (10 mg/ml suspension; Sumitomo Bakelite Co., Ltd.) were aliquoted onto one well of a MultiScreen Solvinert filter plate (Millipore, Billerica, MA). To capture total glycans in sample mixtures specifically onto beads via stable hydrazone bonds, 20 µl of PNGase F-digested samples and 180 µl of 2 % acetic acid in acetonitrile were added and incubated at 85 °C for 45 min. The beads were washed with 200 µl of 2 M guanidine HCl in ammonium bicarbonate followed by washing with the same volume of water and 1 % triethylamine in methanol (MeOH). Each washing step was performed in triplicate, respectively. Unreacted hydrazide functional groups on beads were capped by incubation with 10 % acetic anhydride in MeOH for 30 min at room temperature. The solution was removed by vacuum, and then the beads were serially washed by MeOH, 10 mM HCl, water, and dimethyl sulfoxide (DMSO), respectively. On-beads methyl esterification of carboxyl groups in sialic acids was carried out by incubation with 100 µl of 500 mM 3-methyl-1-*ρ*-tolytriazene in a 1:1 mixture of acetonitrile and DMSO at 60 °C for 1 h (Miura *et al.,* 2007). Then the beads were serially washed by 200 µl of MeOH and water. The glycans blotted on beads were subjected to the *trans*-iminization reaction with aoWR (N^{α}-((aminooxy)acetyl)tryptophanylarginine methyl ester) (Shimaoka *et al.,* 2007, Shinohara *et al.,* 2004, Uematsu *et al.,* 2005). 2µl of 20 mM aoWR and 18 µl of 2 % acetic acid in acetonitrile were added and incubated at 85 °C for 45 min. WR-tagged glycans were eluted by adding 50 µl of water and then purified using HILIC spin columns. The purified samples were immediately subjected to

MALDI-TOF MS analysis or dried and stored at -30 °C until use.

Supplementary References

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