

$$\begin{array}{c} Ac \ (-80\%) & 1-Fucp \\ al \\ \frac{1}{2} \\ \end{array} \\ S \ \textbf{O45} \\ \rightarrow 4)\text{-D-GlcpA-}(\beta l \rightarrow 4)\text{-L-Fucp-}(\alpha l \rightarrow 3)\text{-D-Riby-}(\beta l \rightarrow 4)\text{-D-Galp-}(\beta l \rightarrow 3)\text{-D-GlcpNAc-}(\beta l \rightarrow 4) \\ S \ \textbf{O47} \\ \rightarrow 2)\text{-D-Ribitol-S-P-}((O\rightarrow 6)\text{-D-Galp-}(\alpha l \rightarrow 3)\text{-L-FucpNAm-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 4) \\ S \ \textbf{O48} \\ \rightarrow 4)\text{-NeupSAc-}(\alpha 2 \rightarrow 3)\text{-L-FucpNAm-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-Galp-}(\alpha 2 \rightarrow 3)\text{-L-FucpNAm-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-GlcpNAc-}(\alpha 2 \rightarrow 3)\text{-L-FucpNAm-}(\alpha l \rightarrow 3)\text{-D-GlalpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-GlcpNAc-}(\beta l \rightarrow 3)\text{-D-GalpNAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-GlcpNAc-}(\alpha l \rightarrow 4)\text{-D-Galp-}(\beta l \rightarrow 3)\text{-D-GlalpNAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-Glcp-NAc-}(\alpha l \rightarrow 4)\text{-D-GalpNAc-}(\alpha l \rightarrow 4)\text{-L-Rhap-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-Glcp-NAc-}(\beta l \rightarrow 4)\text{-D-ManpNAc-}(\beta l \rightarrow 4)\text{-D-GalpNAc-}(\beta l \rightarrow 4)\text{-D-GalpNAc-}(\beta l \rightarrow 4) \\ -2 \text{-D-Glcp-NAc-}(\beta l \rightarrow 2)\text{-D-Fucp3NAc-}(\beta l \rightarrow 6)\text{-D-Glcp-}(\alpha l \rightarrow 4)\text{-D-GalpNAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 4) \\ -2 \text{-D-Glcp-NAc-}(\beta l \rightarrow 2)\text{-D-Fucp3NAc-}(\beta l \rightarrow 6)\text{-D-Glcp-}(\alpha l \rightarrow 4)\text{-D-GalpNAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 4) \\ -2 \text{-D-Glcp-NAc-}(\beta l \rightarrow 3)\text{-D-Fucp3NAc-}(\beta l \rightarrow 6)\text{-D-Glcp-NAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3) \\ -2 \text{-D-Glcp-NAc-}(\beta l \rightarrow 3)\text{-D-Fucp3NAc-}(\beta l \rightarrow 6)\text{-D-Glcp-NAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3) \\ -2 \text{-D-Glcp-NAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3) \\ -2 \text{-D-Glcp-NAc-}(\alpha l \rightarrow 3)\text{-D-Fucp3NAc-}(\beta l \rightarrow 6)\text{-D-Glcp-NAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3) \\ -2 \text{-D-Glcp-NAc-}(\alpha l \rightarrow 3)\text{-D-GlcpNAc-}(\alpha l \rightarrow 3)\text{-D-Glcp$$

supplementary Fig.1

WbwH \rightarrow 3)-D-Quip4N(D-Ala-S3Hb)-(β 1 \rightarrow 6)-D-GlcpNAc-(α 1 \rightarrow 3)-L-QuipNAc-(α 1 \rightarrow 3)-D-GlcpNAc-(α 1 \rightarrow S O58 \rightarrow 2)-D-Galp-(β 1 \rightarrow 3)-D-GlcpNAc-(α 1 \rightarrow 4)-L-Rhap-(α 1 \rightarrow 3)-D-GlcpNAc-(β 1 \rightarrow S O59 D-Fuc p3NFo $\alpha 1$ \rightarrow 2)-D-Manp-(β 1 \rightarrow 3)-D-Glcp-(β 1 \rightarrow 3)-D-GlcpNAc-(β 1 \rightarrow S 060 \rightarrow 8)-8eLegp5R3Hb7Ac-(α 2 \rightarrow 3)-L-FucpNAmp-(α 1 \rightarrow 3)-D-GlcpNAc-(α 1 \rightarrow S 061 α-D-GalpNAcA6NH₂ \rightarrow 3)-L-Rhap-(α 1 \rightarrow 2)-L-Rhap-(α 1 \rightarrow 3)-L-Rhap-(α 1 \rightarrow 3)-D-GlcpNAc-(β 1 \rightarrow S 062 D-Fuc*p*3NAc $\alpha 1$ \rightarrow 3)-D-Galp-(β 1 \rightarrow 4)-D-Glcp-(α 1 \rightarrow 4)-D-GalpNAc-(α 1 \rightarrow 3)-D-GalpNAc-(β 1 \rightarrow S 063 D-Glcp Ac (~90%) S 066 \rightarrow 2)-D-Galp-(α 1 \rightarrow 6)-D-Galp-(α 1 \rightarrow 4)-D-GalpNAc-(α 1 \rightarrow 3)-D-GalpNAc-(β 1 \rightarrow