Supporting Information
for

Synthesis of heteroglycoclusters by using orthogonal chemoselective ligations

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Crude RP-HPLC profiles and ESI-MS spectra for the heteroglycoclusters

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General details

All chemical reagents were purchased from Aldrich (Saint Quentin Fallavier, France) or Acros (Noisy-Le-Grand, France) and were used without further purification. Protected amino acids and Fmoc-Gly-Sasrin resin were obtained from Advanced ChemTech Europe (Brussels, Belgium), Bachem Biochimie SARL (Voisins-Les-Bretonneux, France) and France Biochem S.A. (Meudon, France). PyBOP was purchased from France Biochem. Reaction progress was monitored by reverse-phase HPLC on Waters equipment by using C18 columns. Analytical and preparative separation was carried out at 1.0 mL/min (EC 125/3 nucleosil 300-5 C18) and at 22 mL/min (VP 250/21 nucleosil 300-7 C18) with UV monitoring at 214 nm and 250 nm by using a linear A–B gradient (buffer A: 0.09% CF3CO2H in water; buffer B: 0.09% CF3CO2H in 90% acetonitrile). Each glycopeptide was analyzed by mass spectrometry by using electrospray ionization on an Esquire 3000+ Bruker Daltonics in positive mode. 1H NMR and G-COSY were recorded in D2O at 400 MHz with a Bruker Avance 400 spectrometer.
1. **Analytical data for compound 5-Man**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $\text{C}_{60}\text{H}_{97}\text{N}_{20}\text{O}_{24}$ 1481.7, found: $m/z$ 1481.9 [M + H]$^+$
2. **Analytical data for compound 5-Fuc**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $C_{60}H_{96}N_{20}O_{22}Na$ 1471.7, found: $m/z$ 1471.8 [M + Na]$^+$
3. **Analytical data for compound 5-Lac**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $\text{C}_{72}\text{H}_{117}\text{N}_{20}\text{O}_{34}$ 1805.8, found: $m/z$ 1806.0 [M + H]$^+$
4. Analytical data for compound 6-Man/Fuc

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

![HPLC profile graph]

ESI-MS (positive mode): calcd for C$_{78}$H$_{124}$N$_{20}$O$_{34}$ 1885.9, found: $m/z$ 1886.0[M + H]$^+$
5. **Analytical data for compound 6-Man/Lac**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

![HPLC profile](image)

ESI-MS (positive mode): calcd for C$_{90}$H$_{144}$N$_{20}$O$_{46}$ 2242.9, found: $m/z$ 2242.3 [M + H]$^+$

![ESI-MS spectrum](image)
6. Analytical data for compound 6-Fuc/Man

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $C_{78}H_{124}N_{20}O_{34}$ 1885.9, found: $m/z$ 1886.0 [M + H]$^+$
$^1$H NMR (D$_2$O, 400 MHz)

G-COSY (D$_2$O, 400 MHz)
7. **Analytical data for compound 6-Fuc/Lac**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $\text{C}_{90}\text{H}_{144}\text{N}_{20}\text{O}_{44}$ 2210.0, found: $m/z$ 2210.3 [M + H]$^+$
8. **Analytical data for compound 6-Lac/Man**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

![Crude RP-HPLC profile](image)

ESI-MS (positive mode): calcd for $\text{C}_{90}\text{H}_{145}\text{N}_{20}\text{O}_{46}$ 2242.9, found: $m/z$ 2242.2 [M + H]$^+$

![ESI-MS](image)
9. **Analytical data for compound 6-Lac/Fuc**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for C$_{90}$H$_{145}$N$_{20}$O$_{44}$ 2210.0, found: $m/z$ 2210.3 [M + H]$^+$
10. **Analytical data for compound 7-Man**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $\text{C}_{52}\text{H}_{84}\text{N}_{21}\text{O}_{16}$ 1258.6, found: $m/z$ 1258.8 [M + H]$^+$
11. Analytical data for compound 7-Fuc

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $\text{C}_{52}\text{H}_{84}\text{N}_{21}\text{O}_{17}$ 1274.6, found: $m/z$ 1274.8 $[\text{M} + \text{H}]^+$
12. Analytical data for compound 7-Lac

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for C$_{58}$H$_{94}$N$_{21}$O$_{22}$ 1436.7, found: $m/z$ 1436.9 [M + H]$^+$
13. **Analytical data for compound 8-Man/Fuc**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

![HPLC profile graph]

ESI-MS (positive mode): calcd for $C_{79}H_{126}N_{21}O_{32}$ 1880.9, found: $m/z$ 1881.1 [M + H]$^+$

![MS spectrum graph]
14. Analytical data for compound 8-Man/Lac

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for C$_9$H$_{156}$N$_{21}$O$_{50}$ 2415.0, found: $m/z$ 2415.4 [M + H]$^+$
15. Analytical data for compound 8-Fuc/Man

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for C$_{79}$H$_{126}$N$_{21}$O$_{34}$ 1912.9, found: $m/z$ 1913.2 [M + H]$^+$
$^1$H NMR (D$_2$O, 400 MHz)

G-COSY (D$_2$O, 400 MHz)
16. **Analytical data for compound 8-Fuc/Lac**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for $C_{97}H_{156}N_{21}O_{49}$ 2400.0, found: $m/z$ 2399.0 [M + H]$^+$
17. **Analytical data for compound 8-Lac/Man**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

![Crude RP-HPLC profile graph](image)

ESI-MS (positive mode): calcd for C$_{85}$H$_{136}$N$_{21}$O$_{40}$ 2092.0, found: $m/z$ 2091.2 [M + H]$^+$

![ESI-MS spectrum](image)
18. Analytical data for compound **8-Lac/Fuc**

Crude RP-HPLC profile (5 to 100% B in 20 min, $\lambda = 250$ nm)

ESI-MS (positive mode): calcd for C$_{85}$H$_{136}$N$_{21}$O$_{37}$ 2043.1, found: $m/z$ 2043.9 [M + H]$^+$