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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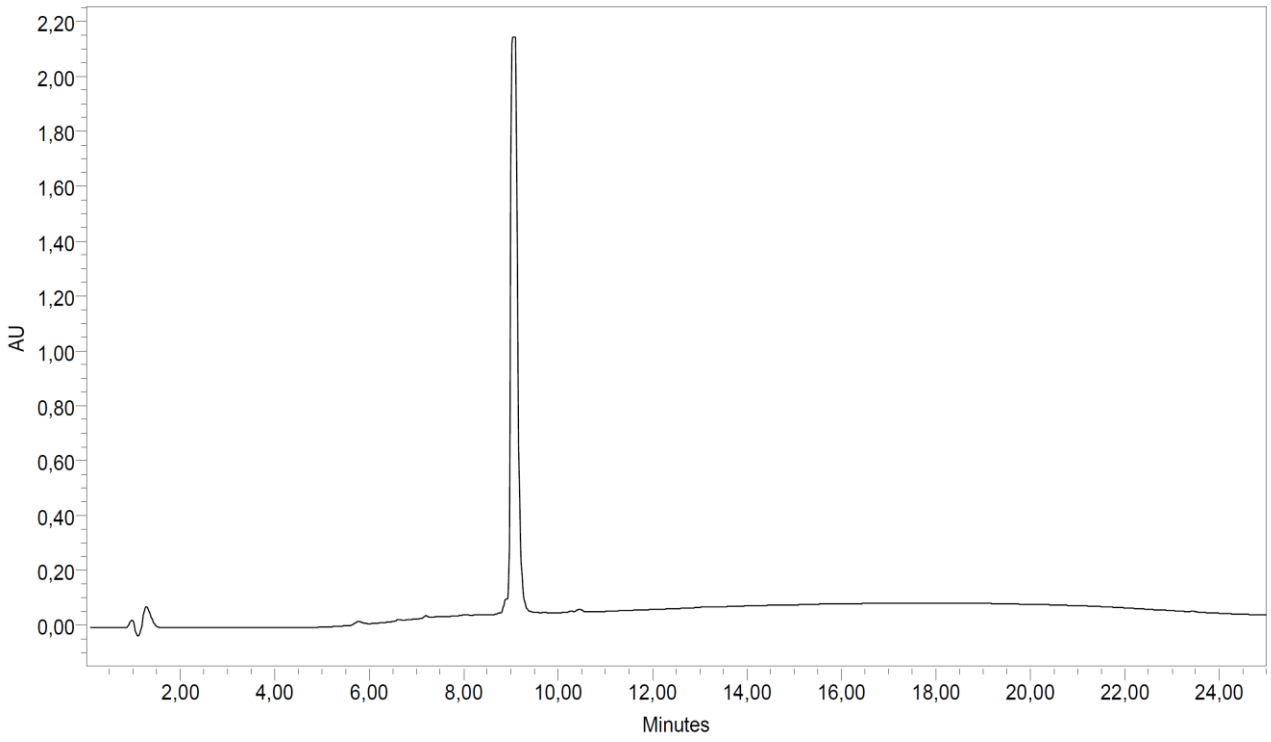
General details

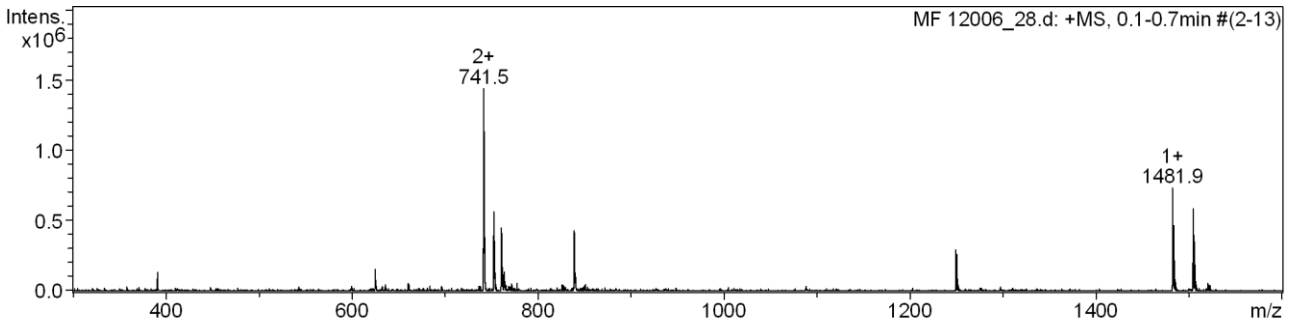
All chemical reagents were purchased from Aldrich (Saint Quentin Fallavier, France) or Acros (Noisy-Le-Grand, France) and were used without further purification. Protected amino acids and Fmoc-Gly-Sasrin resin were obtained from Advanced ChemTech Europe (Brussels, Belgium), Bachem Biochimie SARL (Voisins-Les-Bretonneux, 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 C_{18} columns. Analytical and preparative separation was carried out at 1.0 mL/min (EC 125/3 nucleosil 300-5 C_{18}) and at 22 mL/min (VP 250/21 nucleosil 300-7 C_{18}) with UV monitoring at 214 nm and 250 nm by using a linear A–B gradient (buffer A: 0.09% CF_3CO_2H in water; buffer B: 0.09% CF_3CO_2H 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 D_2O 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, λ = 250 nm)

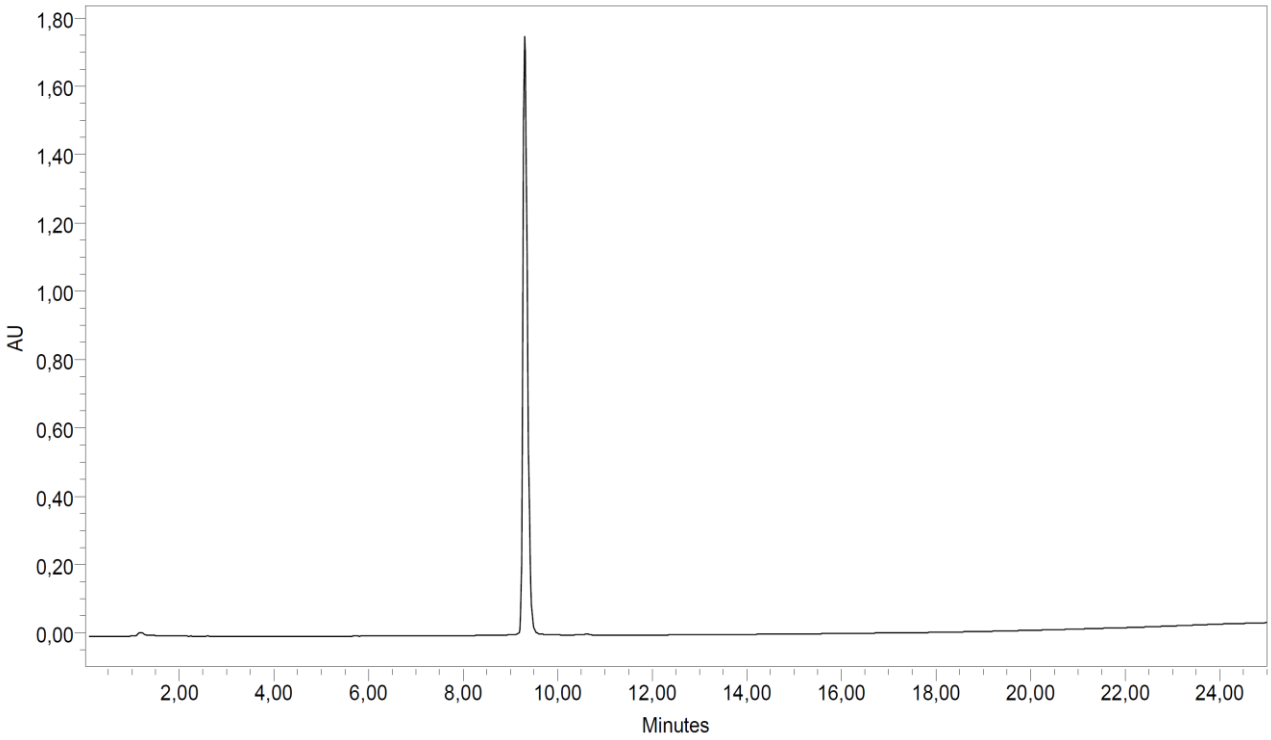


ESI-MS (positive mode): calcd for $C_{60}H_{97}N_{20}O_{24}$ 1481.7, found: *m*/*z* 1481.9 $[M + H]^+$

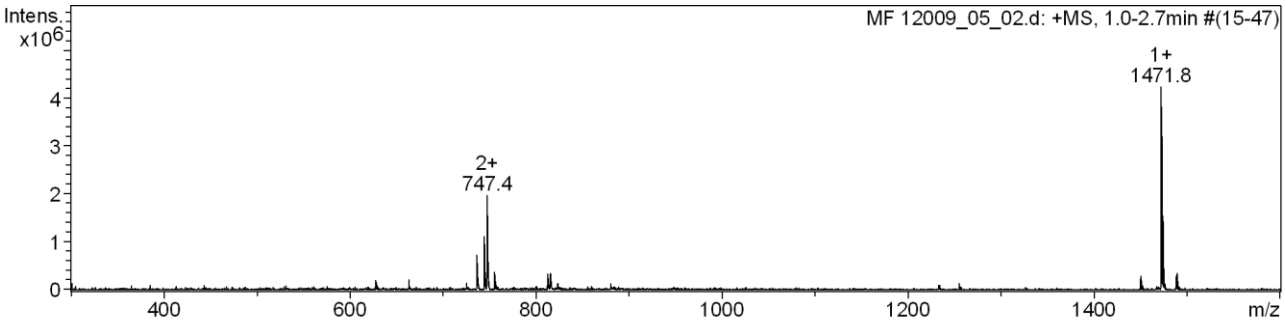


2. Analytical data for compound **5-Fuc**

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

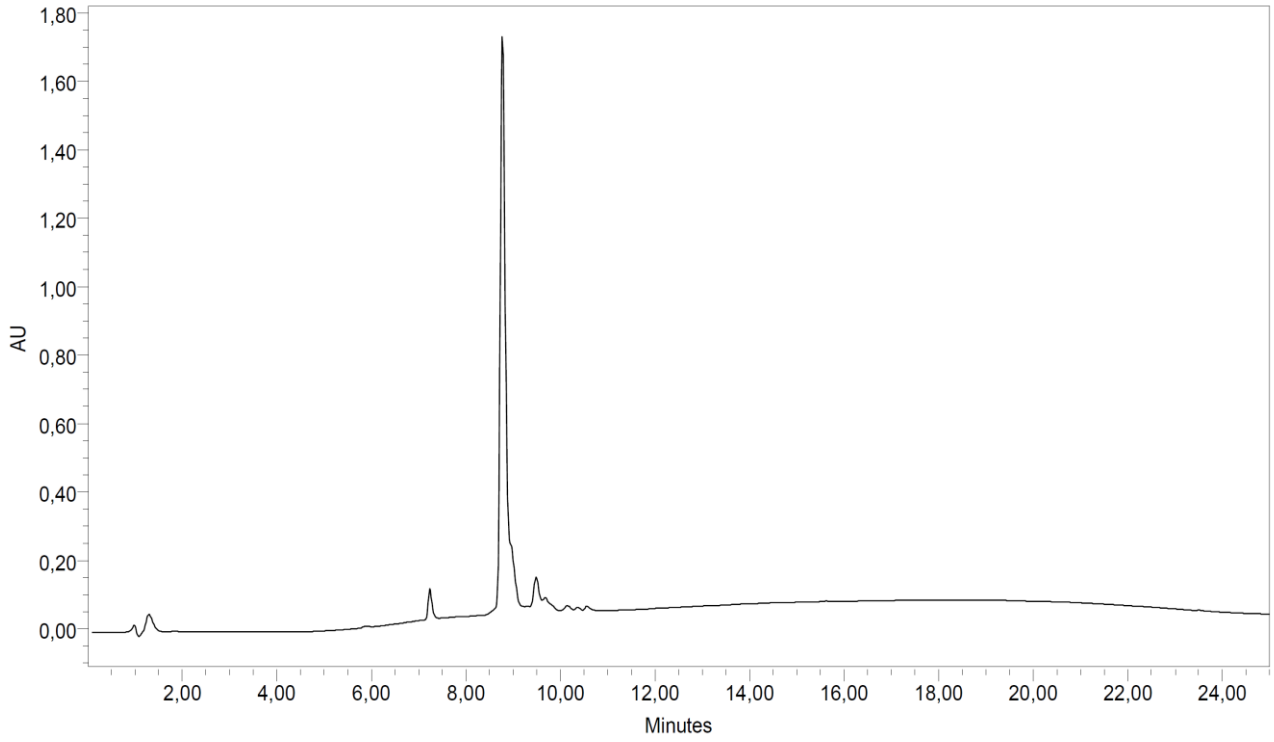


ESI-MS (positive mode): calcd for $C_{60}H_{96}N_{20}O_{22}Na$ 1471.7, found: *m/z* 1471.8 $[M + Na]^+$

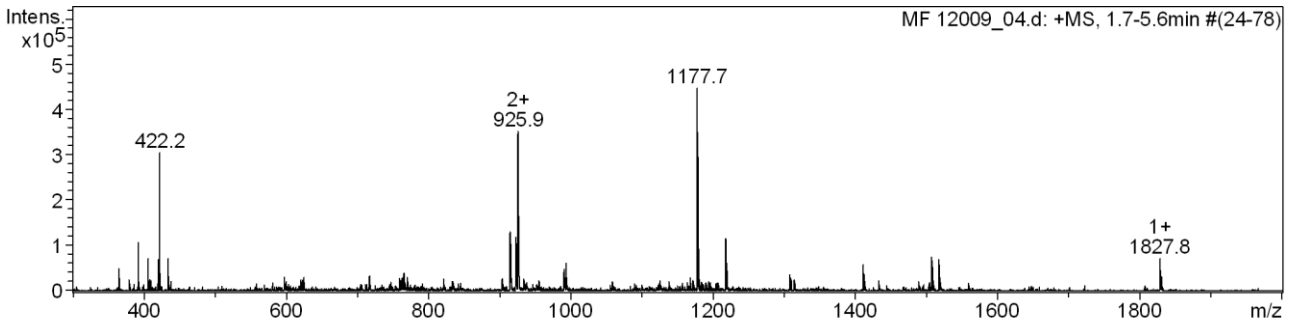


3. Analytical data for compound **5-Lac**

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

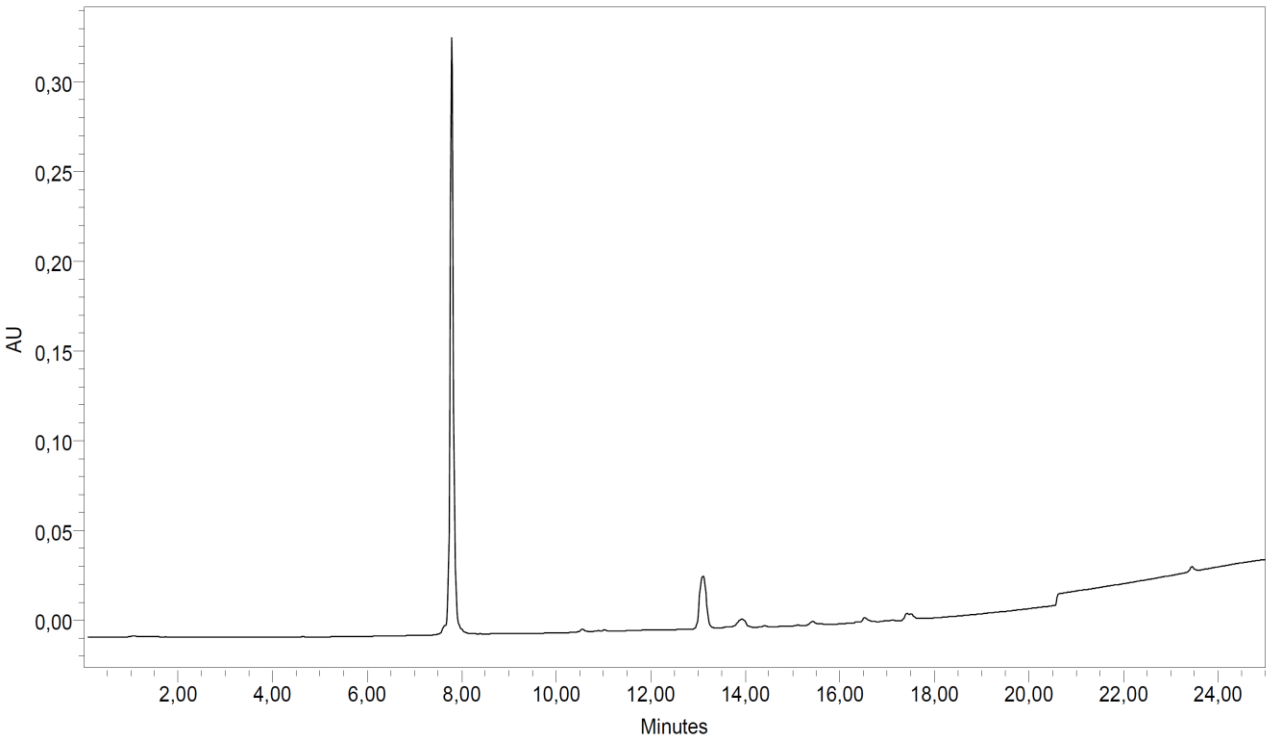


ESI-MS (positive mode): calcd for $C_{72}H_{117}N_{20}O_{34}$ 1805.8, found: *m*/*z* 1806.0 $[M + H]^+$

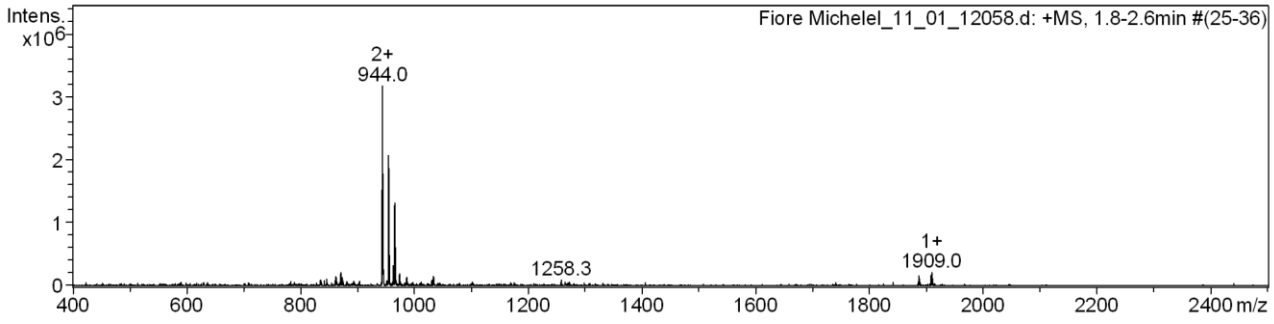


4. Analytical data for compound **6-Man/Fuc**

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

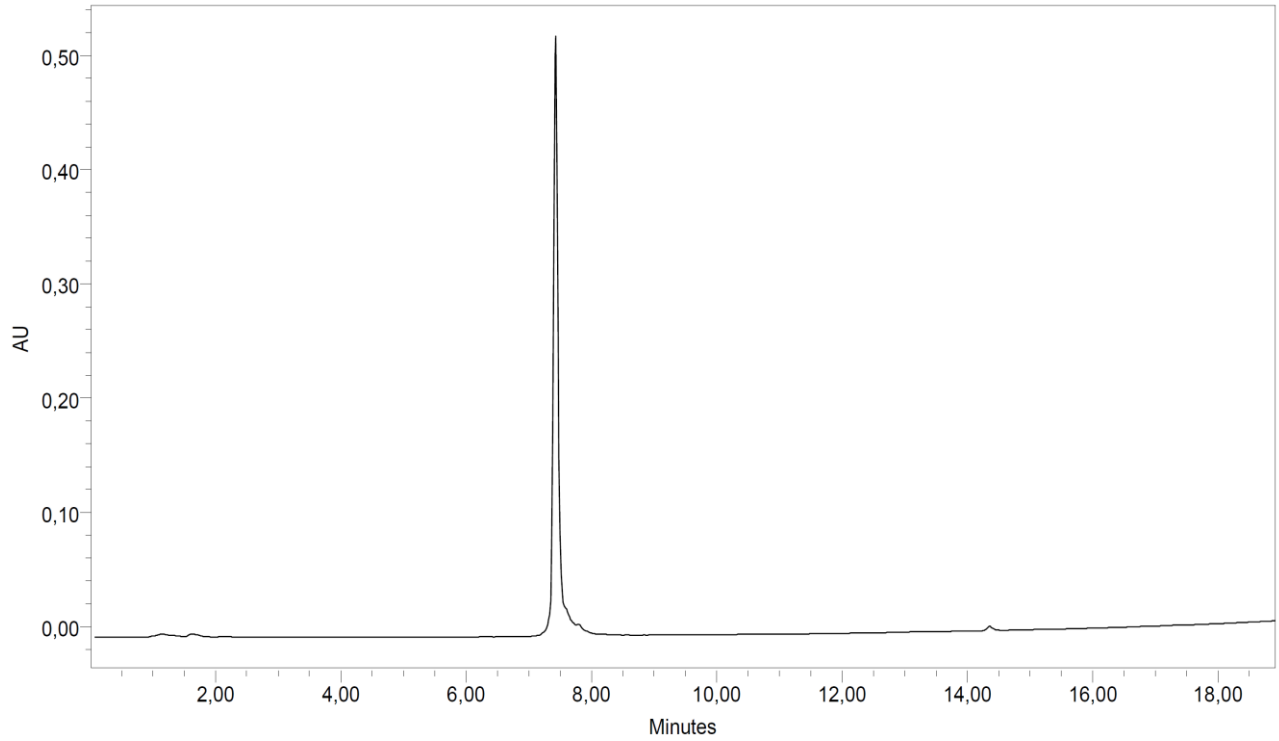


ESI-MS (positive mode): calcd for $C_{78}H_{124}N_{20}O_{34}$ 1885.9, found: *m/z* 1886.0$[M + H]^+$

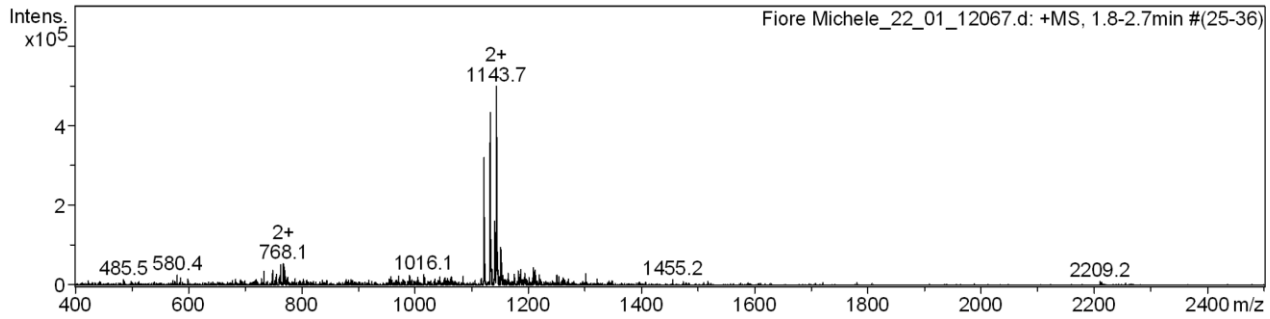


5. Analytical data for compound **6-Man/Lac**

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

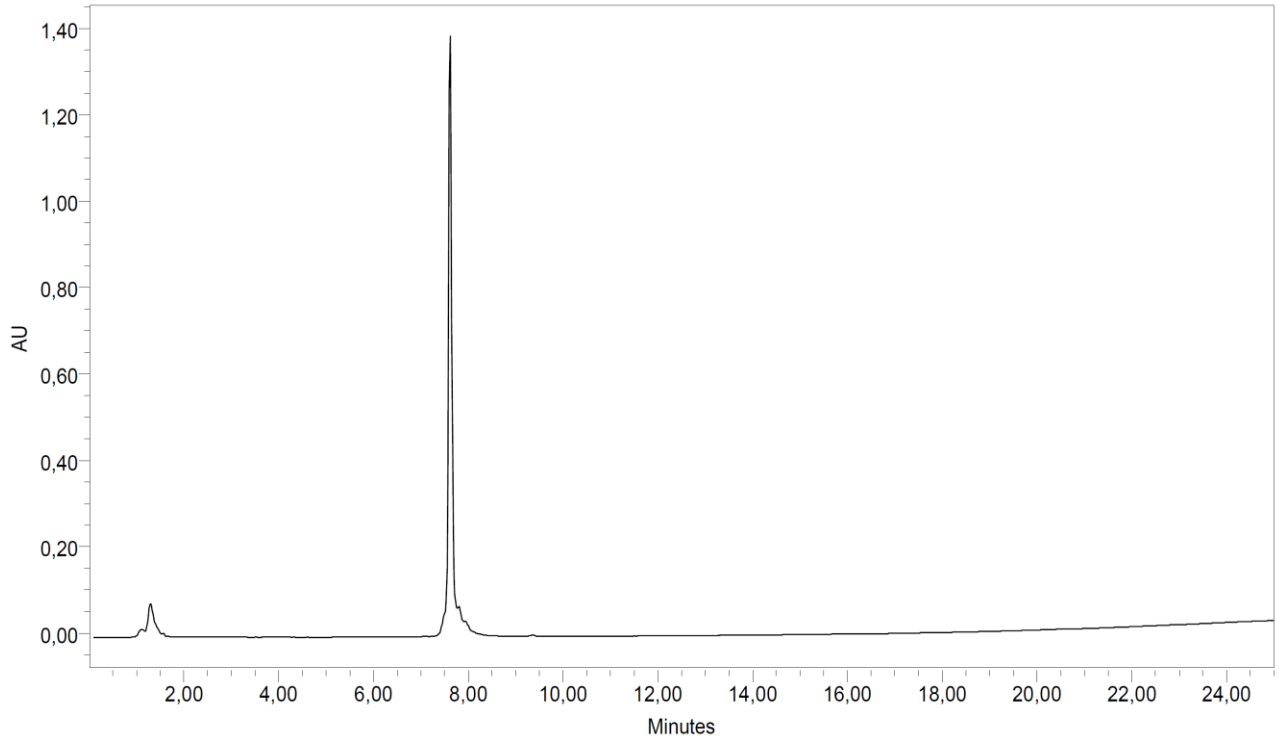


ESI-MS (positive mode): calcd for $C_{90}H_{144}N_{20}O_{46}$ 2242.9, found: *m/z* 2242.3 $[M + H]^+$

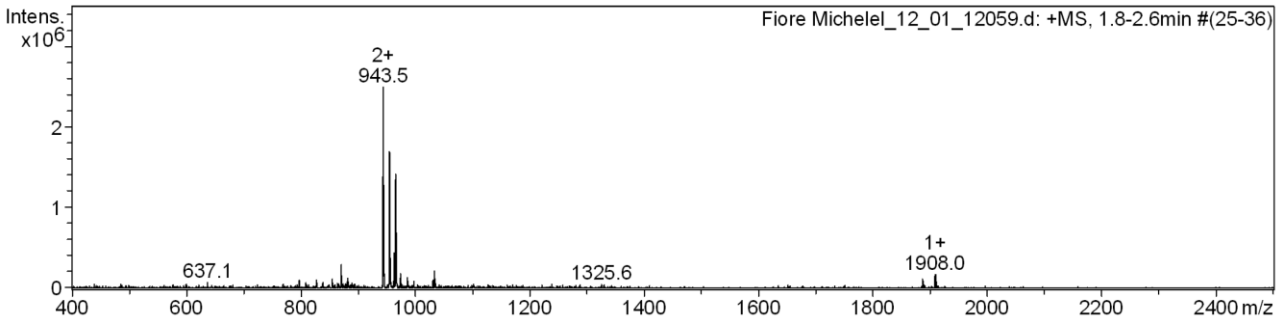


6. Analytical data for compound **6-Fuc/Man**

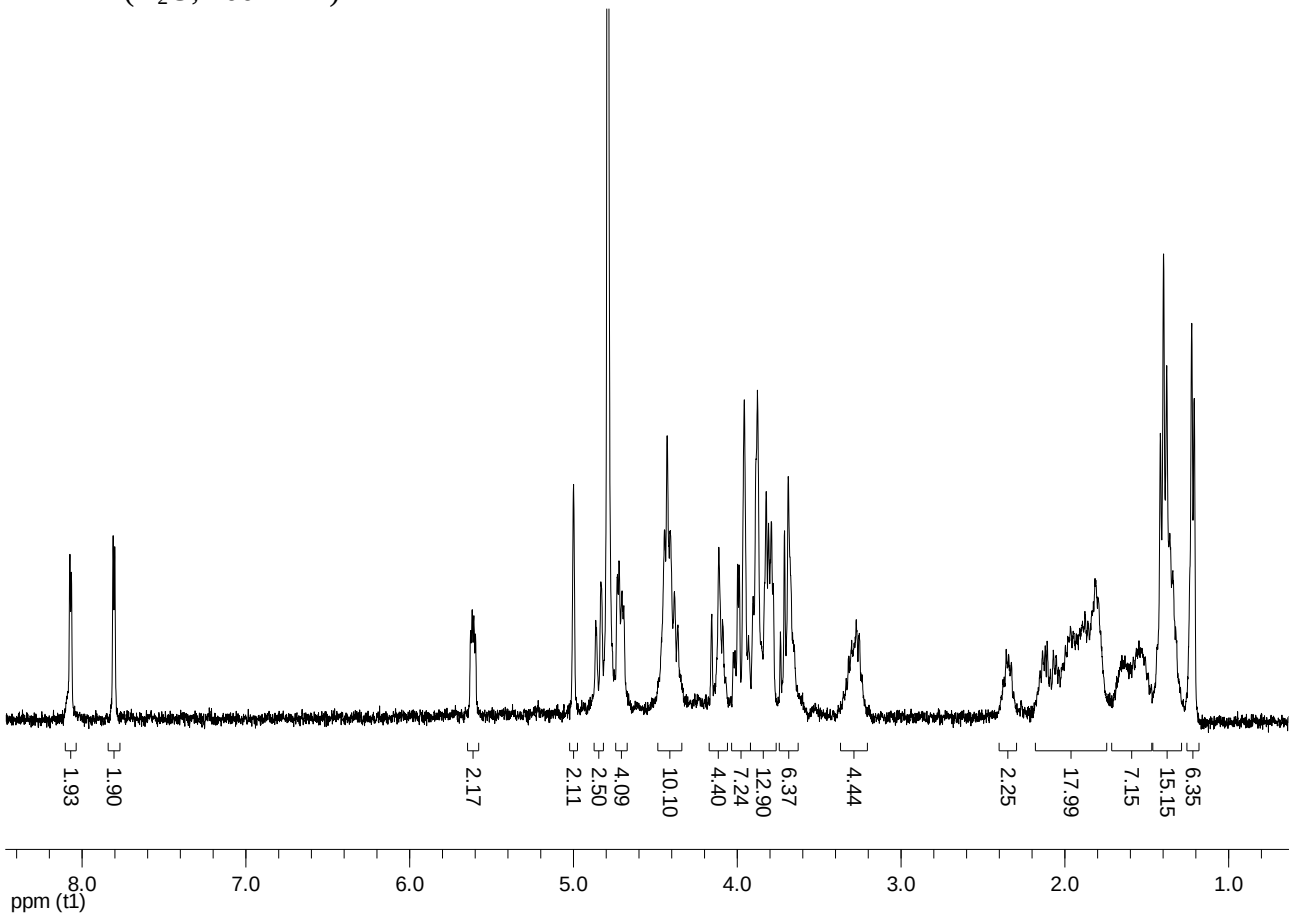
Crude RP-HPLC profile (5 to 100% B in 20 min, λ = 250 nm)



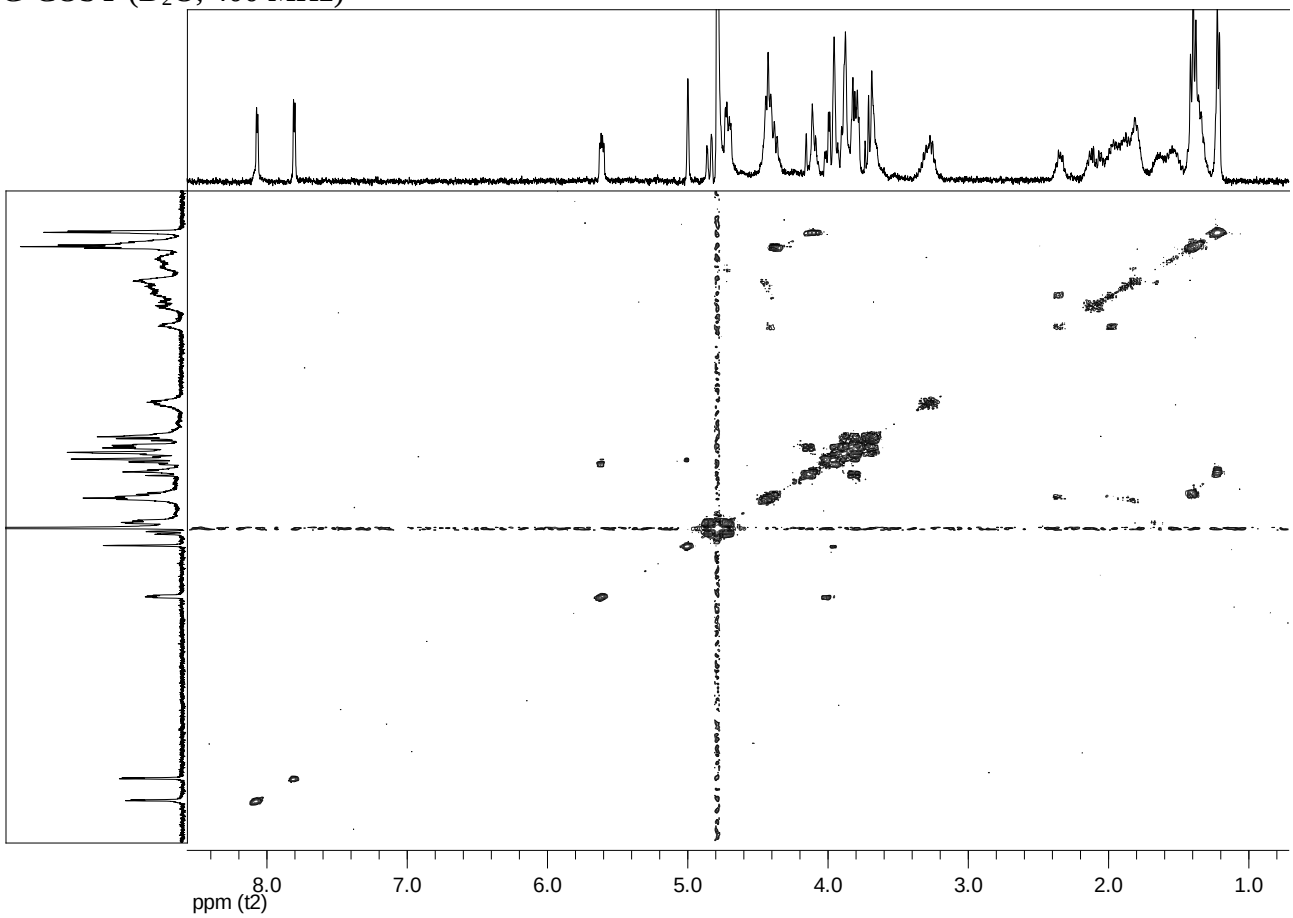
ESI-MS (positive mode): calcd for $C_{78}H_{124}N_{20}O_{34}$ 1885.9, found: *m*/*z* 1886.0 $[M + H]^+$



^{1}H NMR (D_2O, 400 MHz)

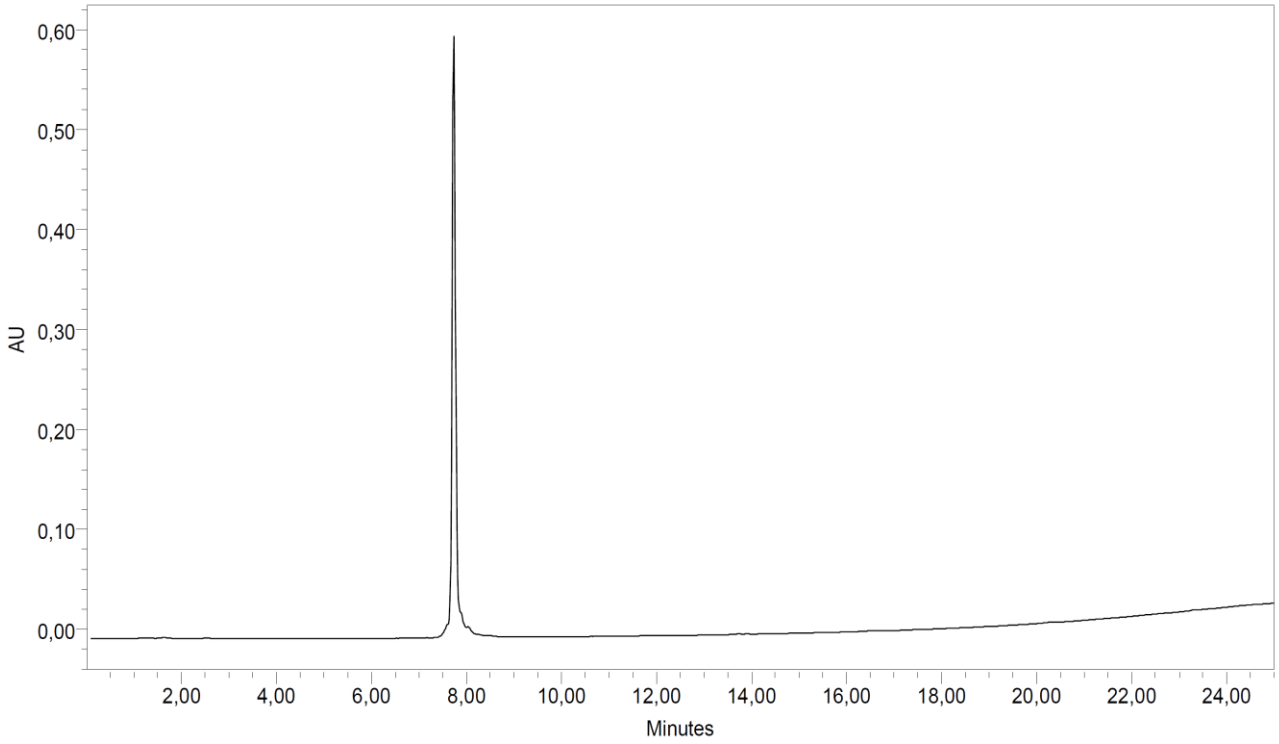


G-COSY (D_2O, 400 MHz)

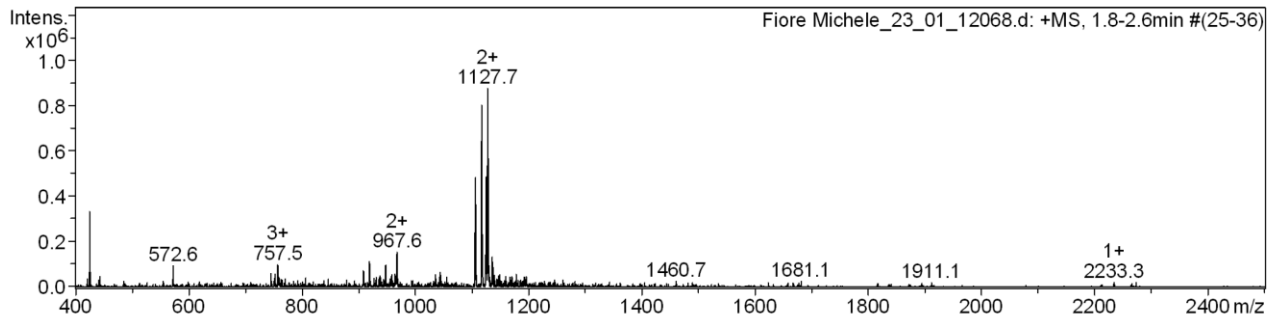


7. Analytical data for compound **6-Fuc/Lac**

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

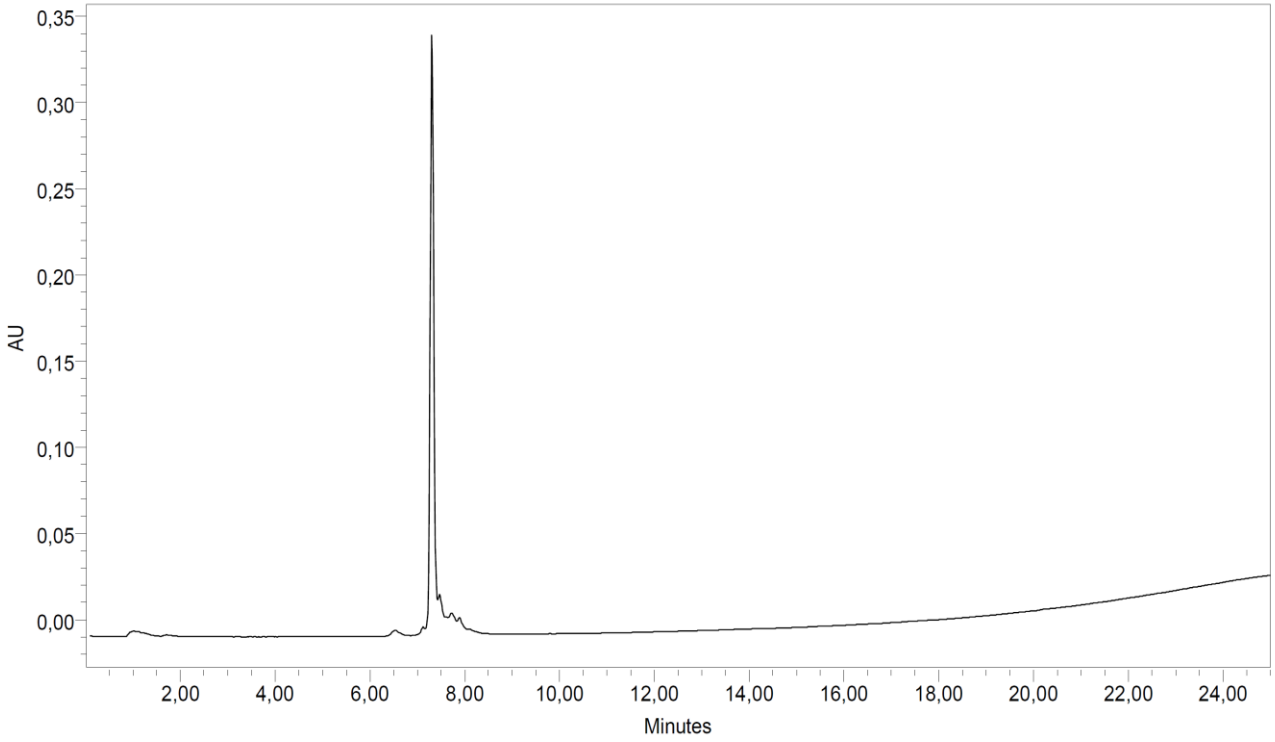


ESI-MS (positive mode): calcd for $C_{90}H_{144}N_{20}O_{44}$ 2210.0, found: *m*/*z* 2210.3 $[M + H]^+$

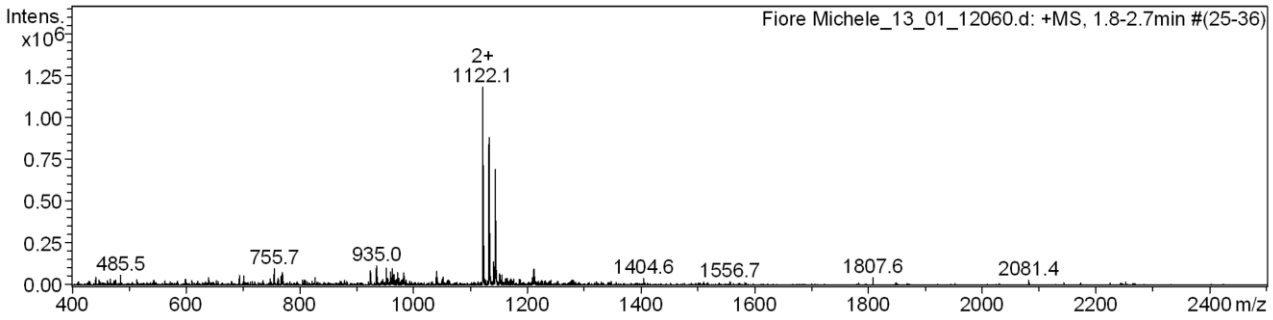


8. Analytical data for compound **6-Lac/Man**

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

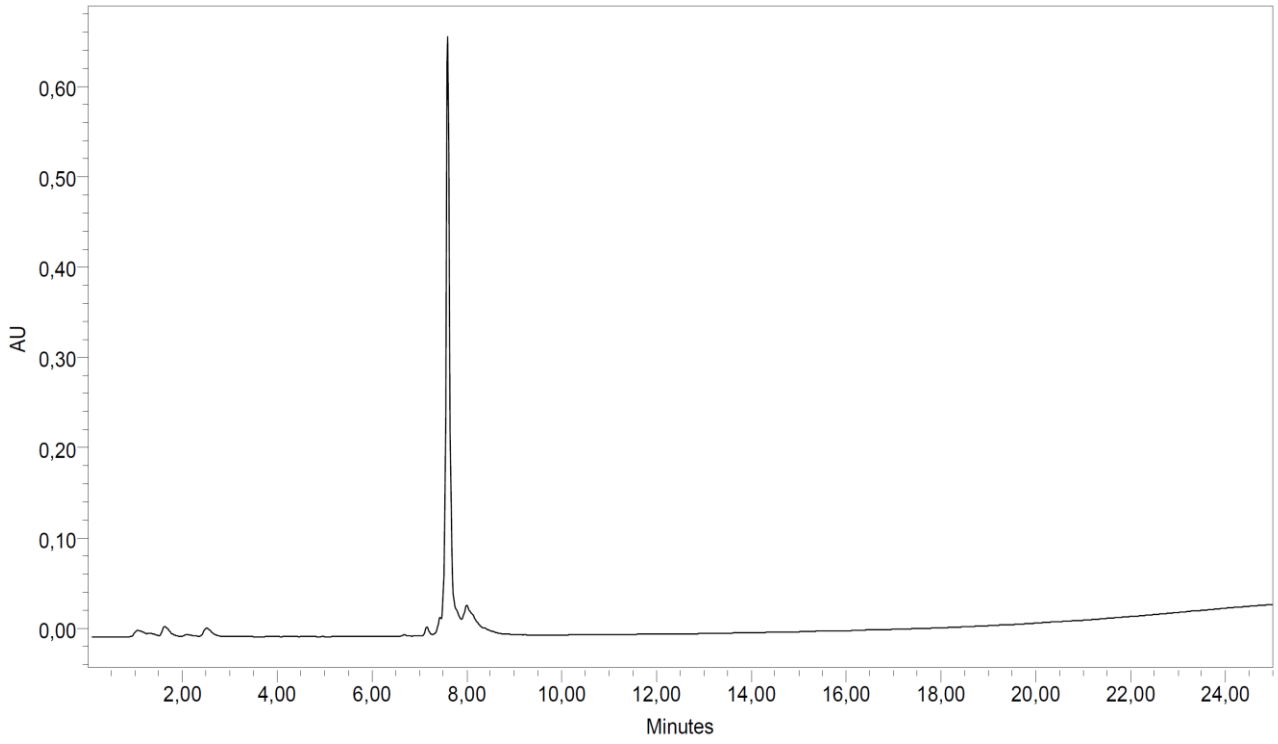


ESI-MS (positive mode): calcd for $C_{90}H_{145}N_{20}O_{46}$ 2242.9, found: *m*/*z* 2242.2 $[M + H]^+$

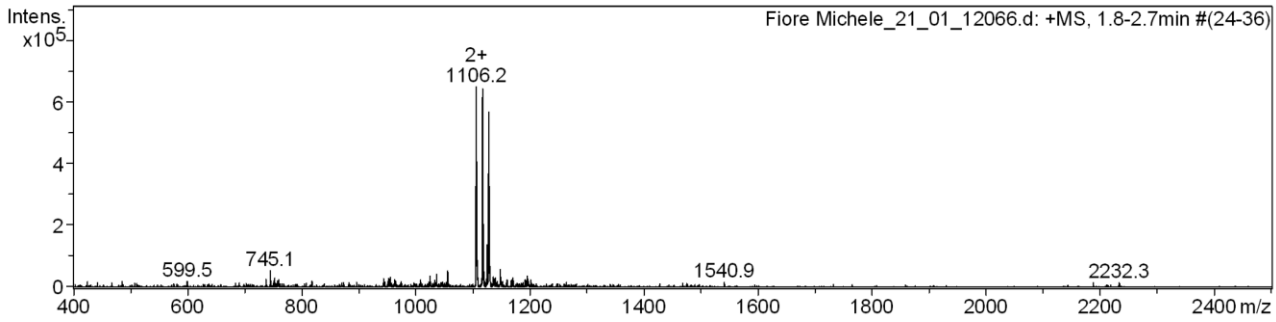


9. Analytical data for compound **6-Lac/Fuc**

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

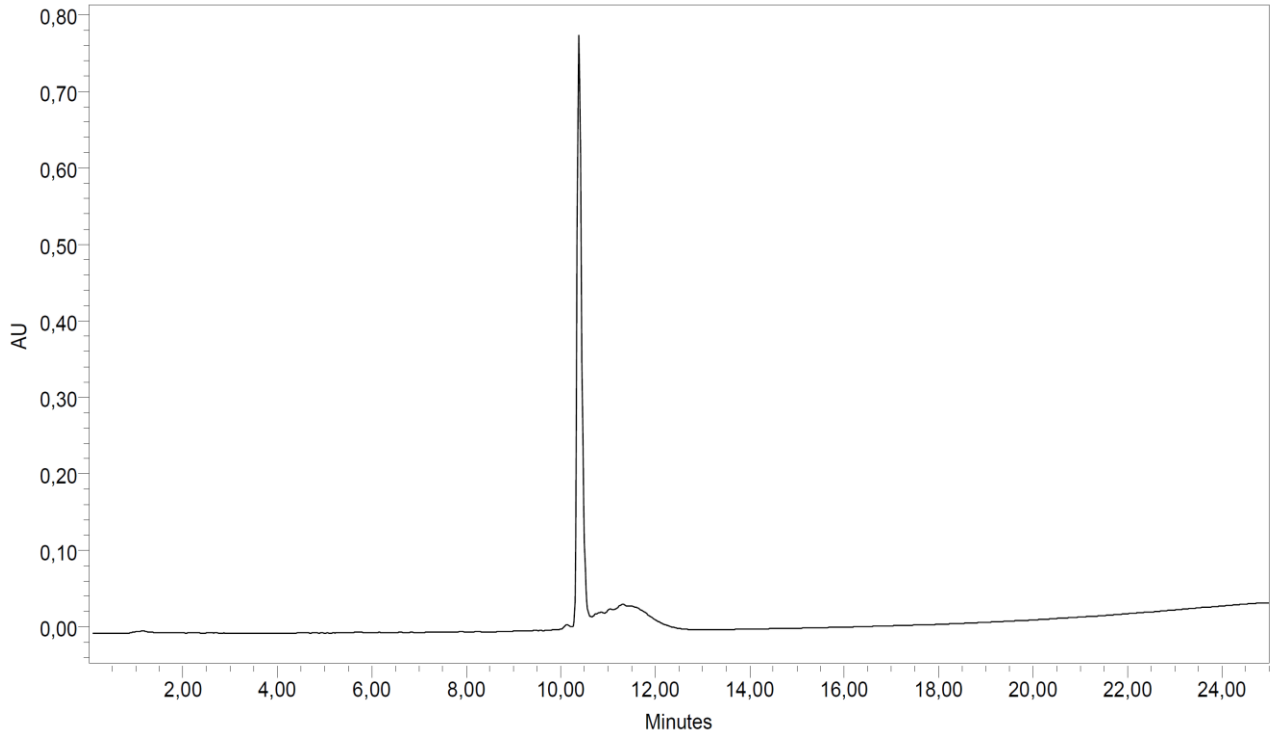


ESI-MS (positive mode): calcd for $C_{90}H_{145}N_{20}O_{44}$ 2210.0, found: *m*/*z* 2210.3 $[M + H]^+$

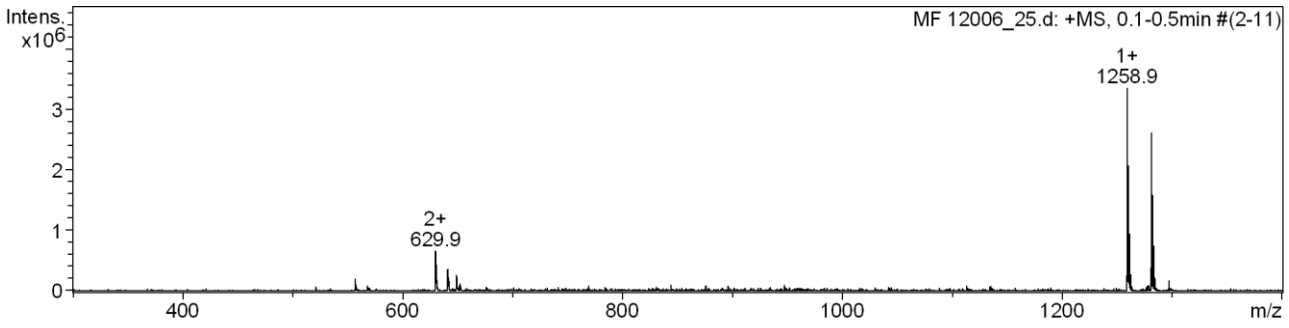


10. Analytical data for compound **7-Man**

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

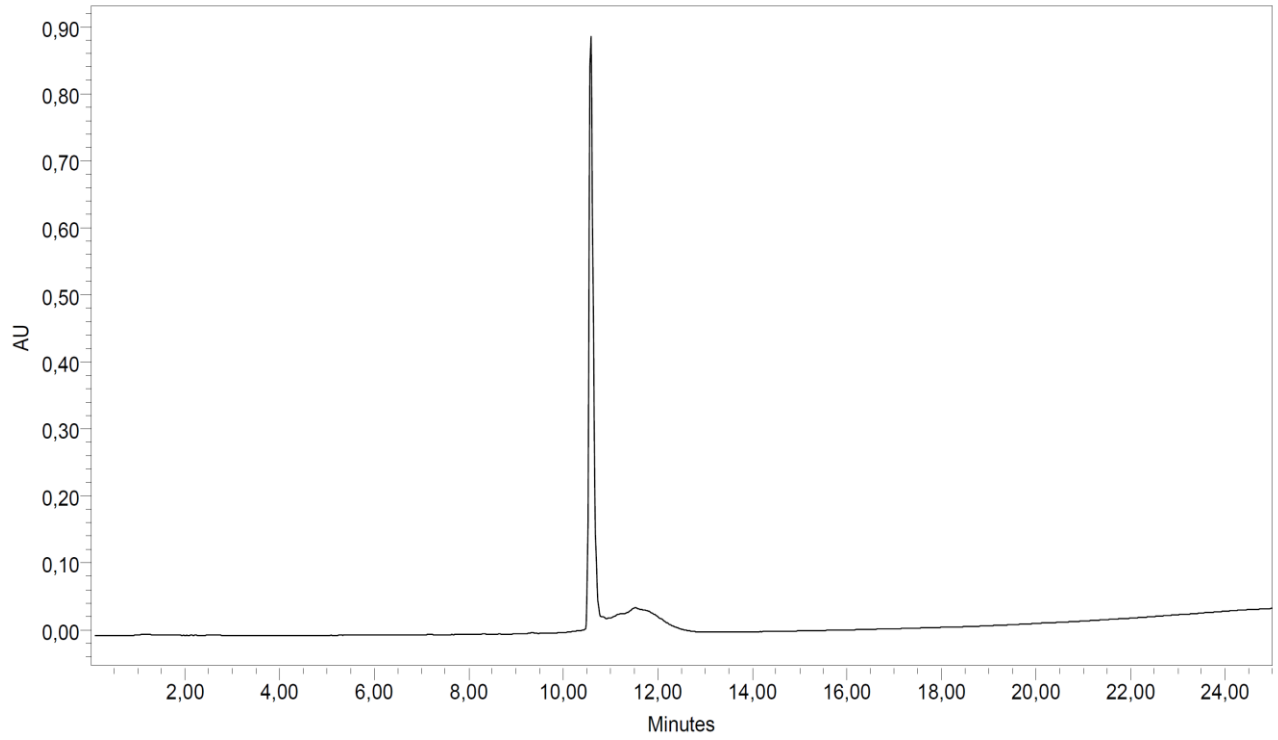


ESI-MS (positive mode): calcd for $C_{52}H_{84}N_{21}O_{16}$ 1258.6, found: *m*/*z* 1258.8 $[M + H]^+$

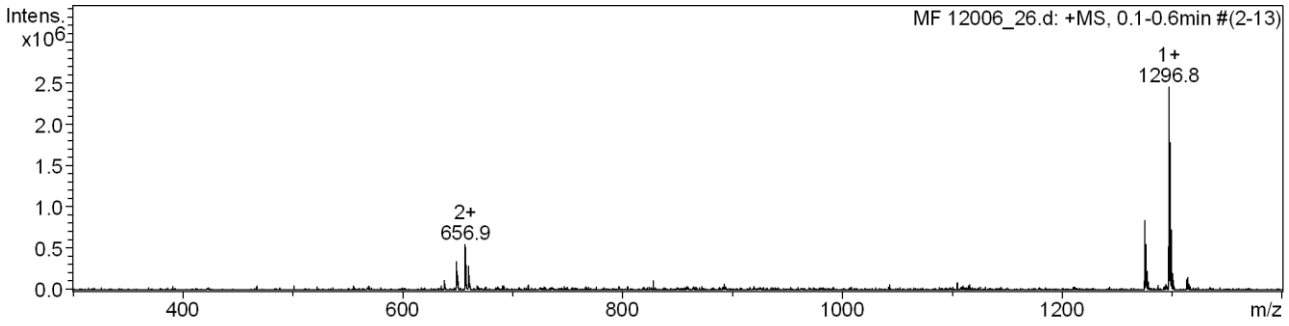


11. Analytical data for compound **7-Fuc**

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

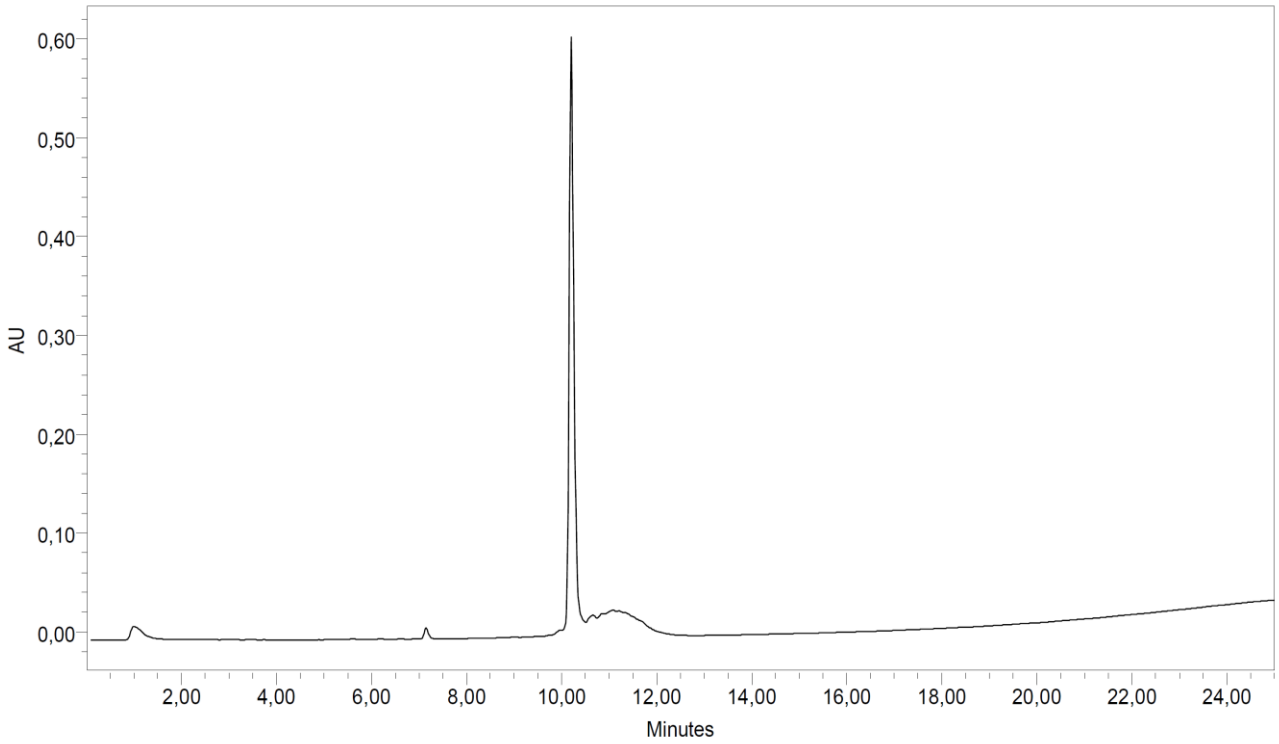


ESI-MS (positive mode): calcd for $C_{52}H_{84}N_{21}O_{17}$ 1274.6, found: *m/z* 1274.8 $[M + H]^+$

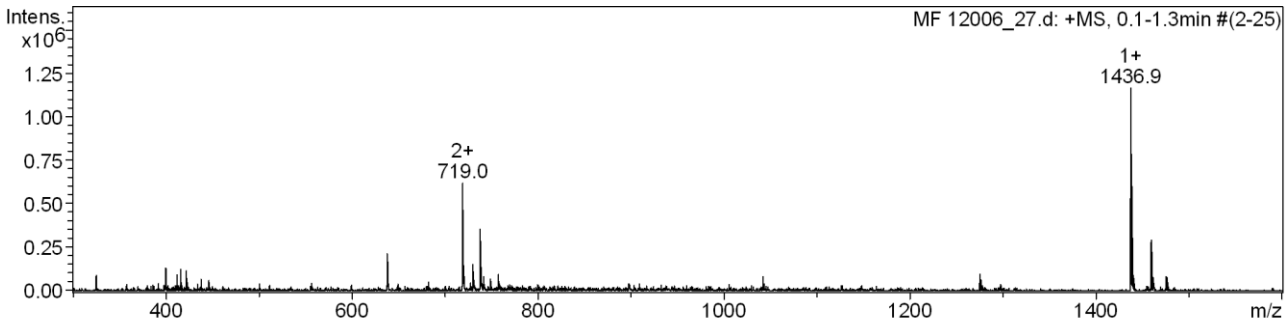


12. Analytical data for compound **7-Lac**

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

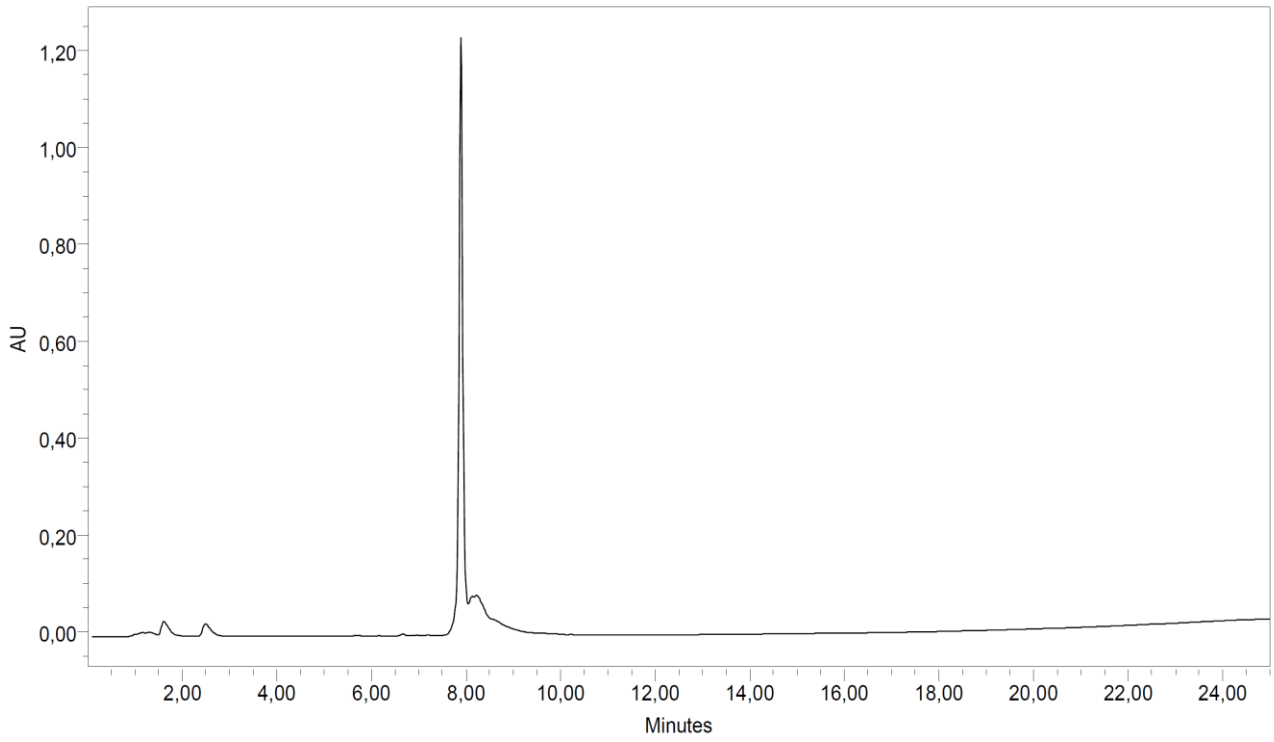


ESI-MS (positive mode): calcd for $C_{58}H_{94}N_{21}O_{22}$ 1436.7, found: *m*/*z* 1436.9 $[M + H]^+$

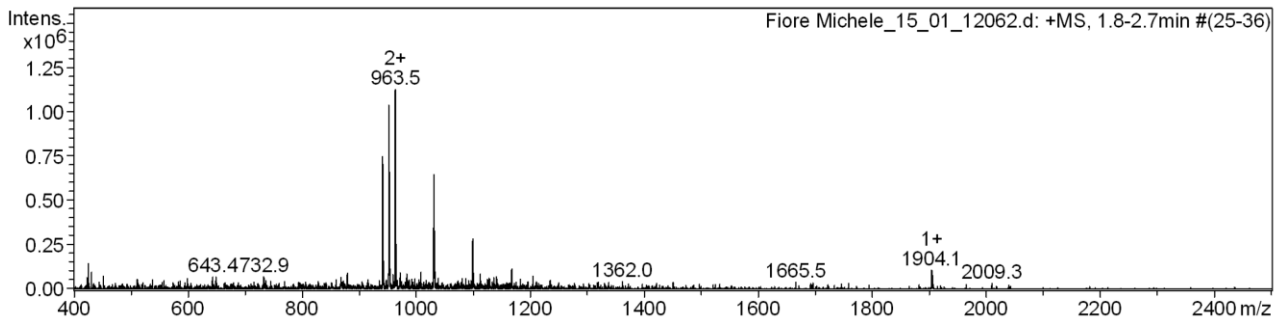


13. Analytical data for compound **8-Man/Fuc**

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

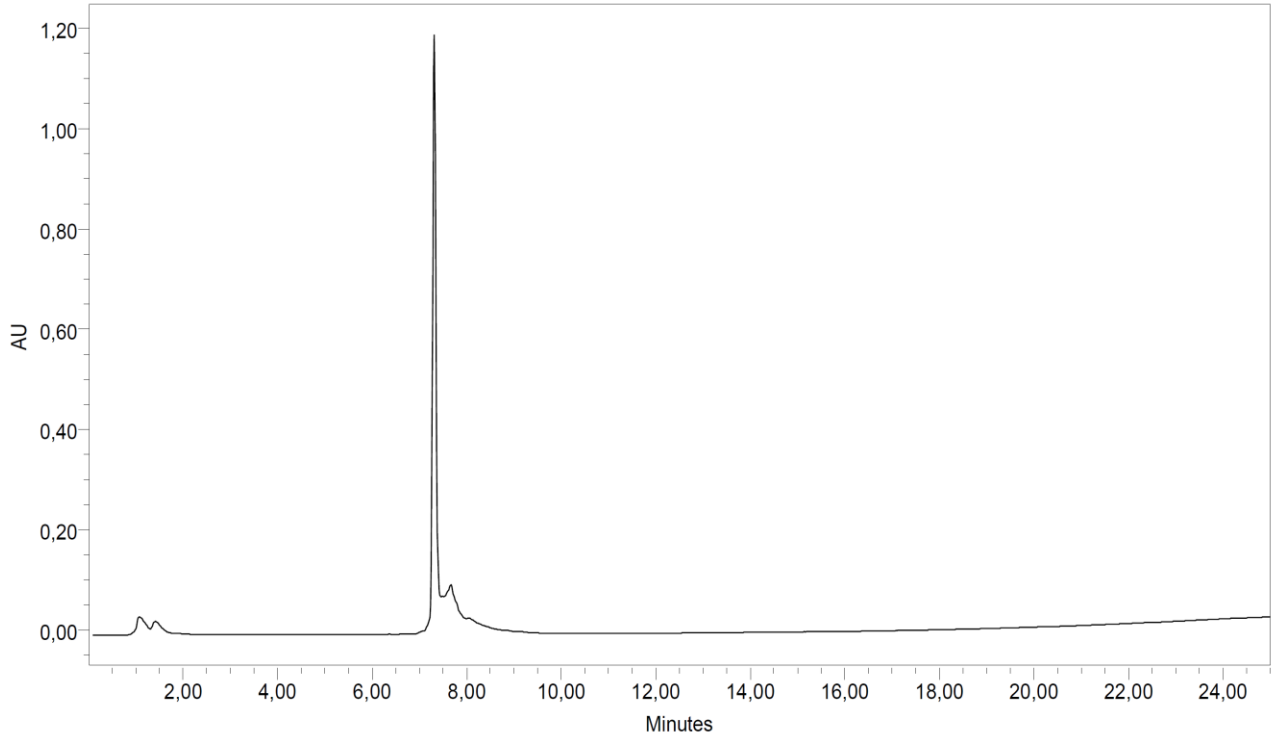


ESI-MS (positive mode): calcd for $C_{79}H_{126}N_{21}O_{32}$ 1880.9, found: *m*/*z* 1881.1 $[M + H]^+$

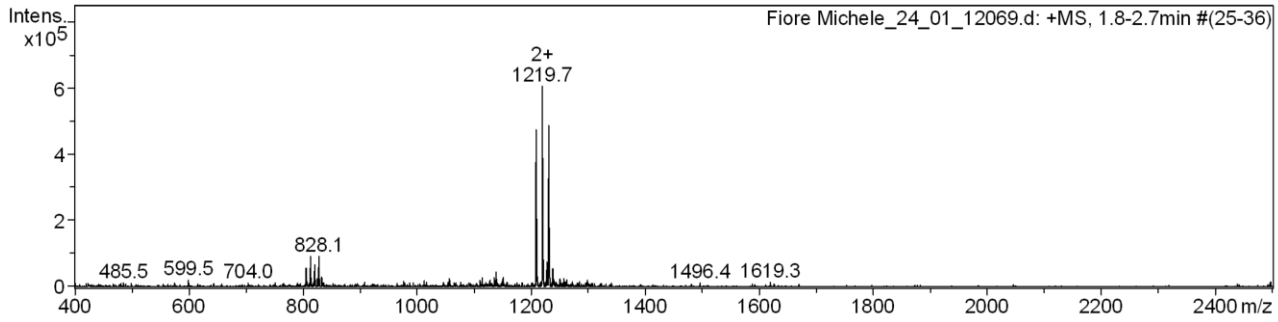


14. Analytical data for compound **8-Man/Lac**

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

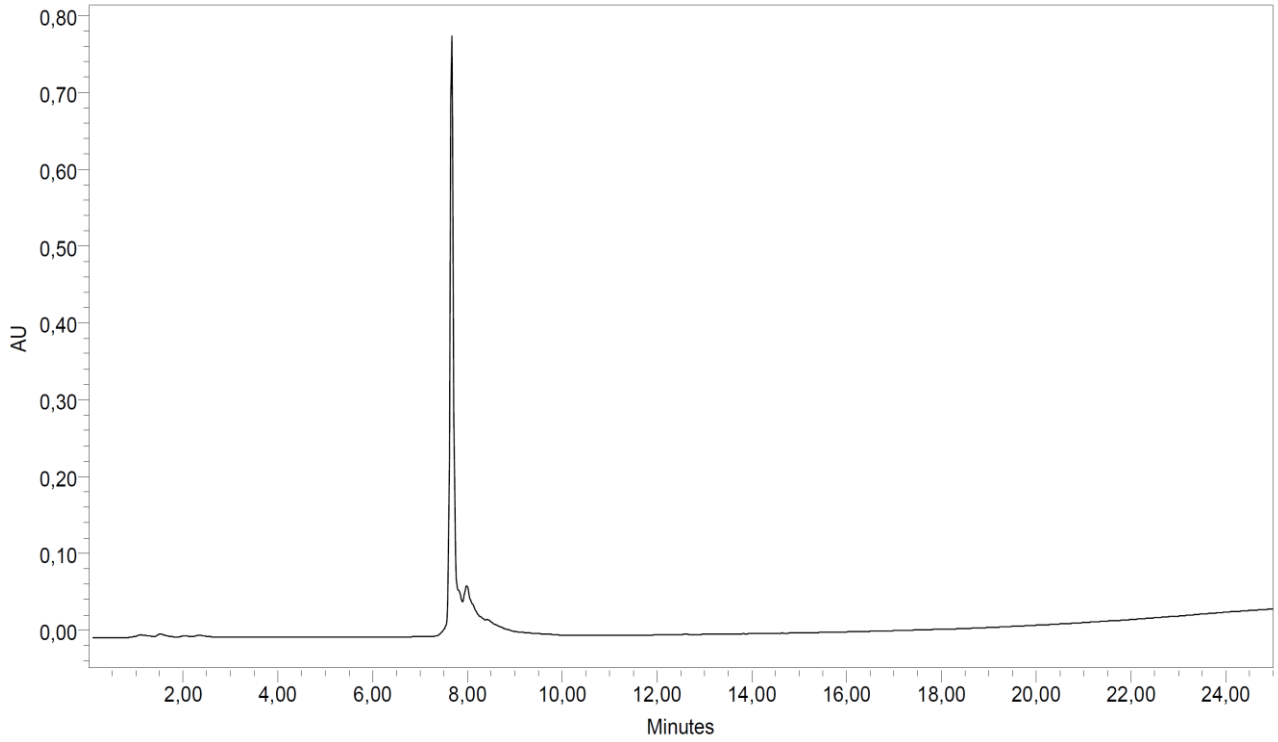


ESI-MS (positive mode): calcd for $C_{97}H_{156}N_{21}O_{50}$ 2415.0, found: *m/z* 2415.4 $[M + H]^+$

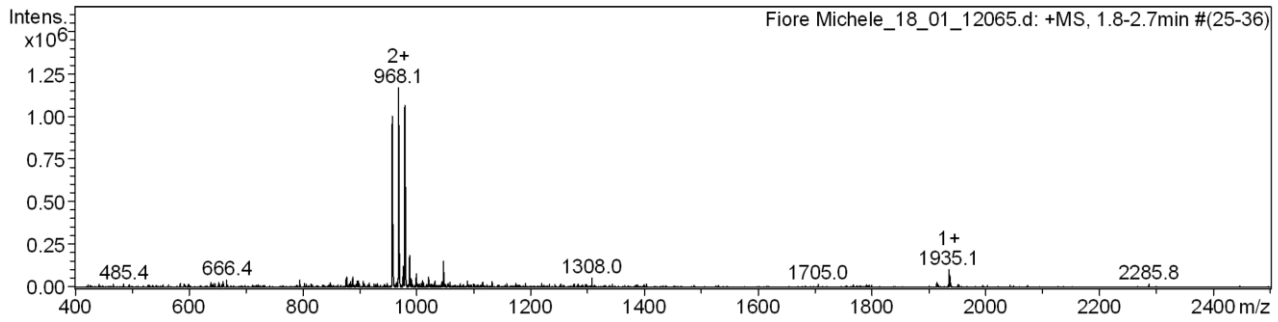


15. Analytical data for compound **8-Fuc/Man**

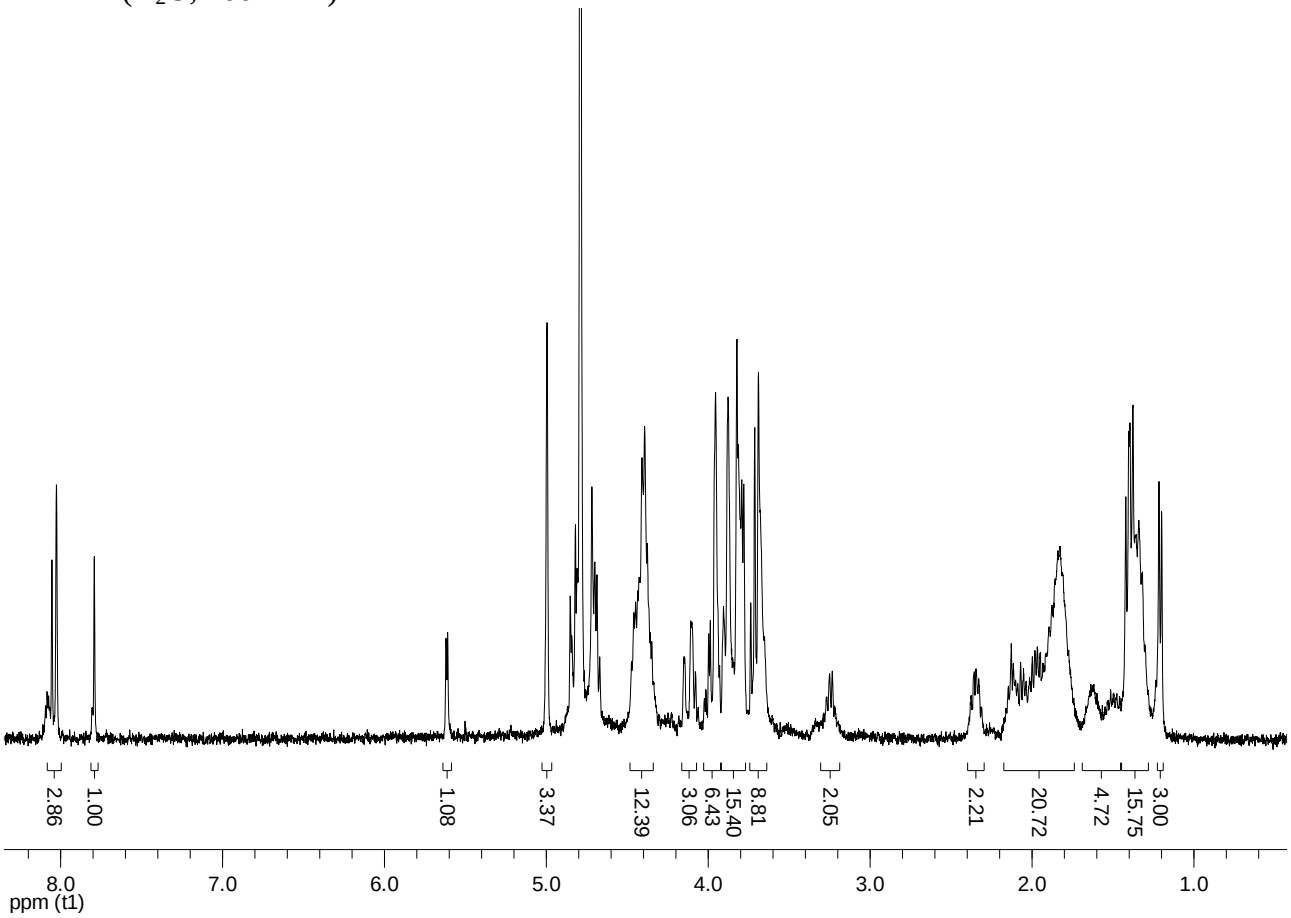
Crude RP-HPLC profile (5 to 100% B in 20 min, λ = 250 nm)



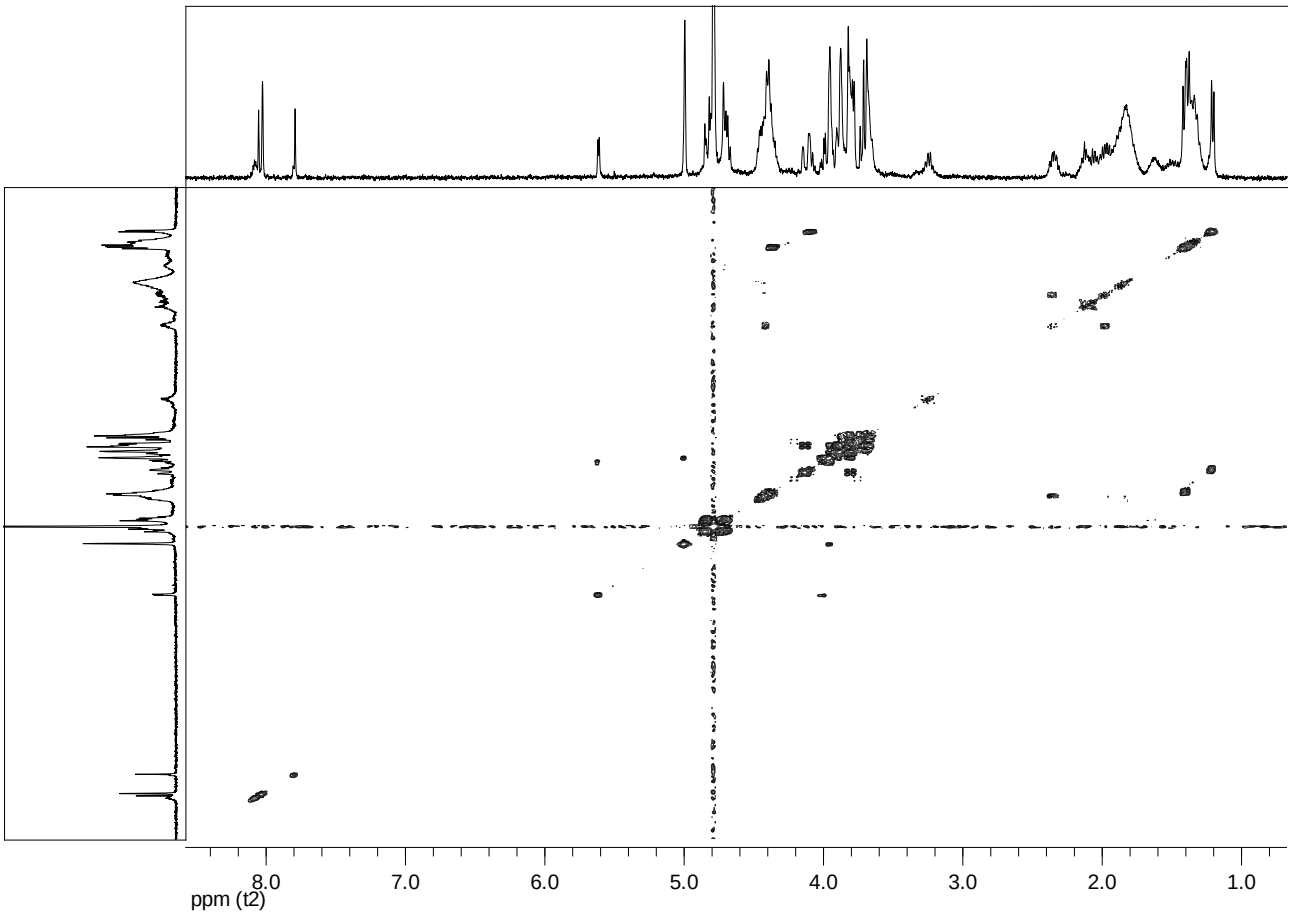
ESI-MS (positive mode): calcd for $C_{79}H_{126}N_{21}O_{34}$ 1912.9, found: *m/z* 1913.2 $[M + H]^+$



^{1}H NMR (D_2O, 400 MHz)

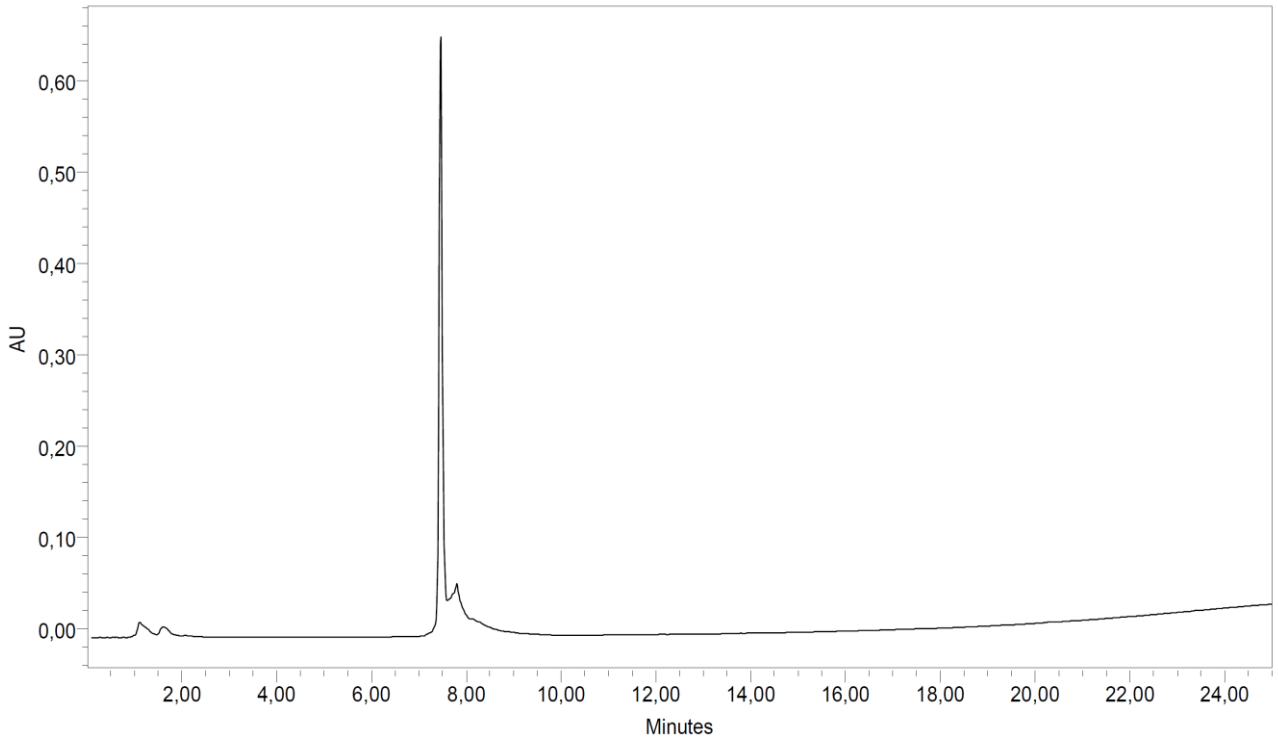


G-COSY (D_2O, 400 MHz)

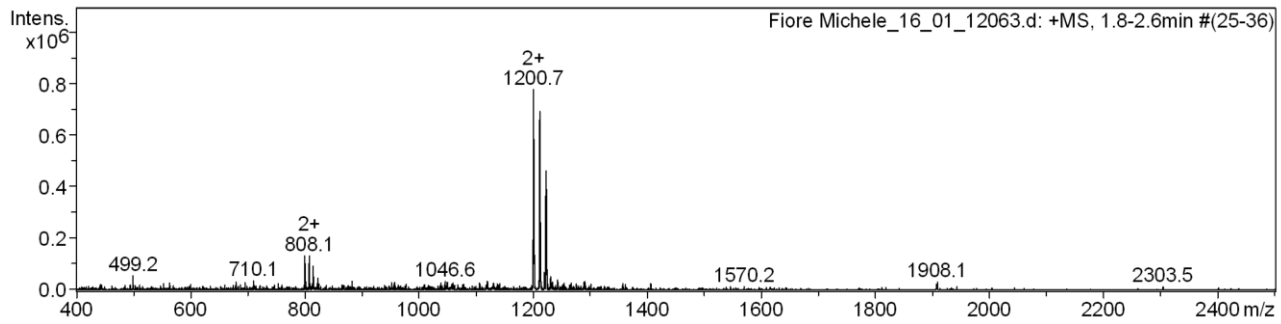


16. Analytical data for compound **8-Fuc/Lac**

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

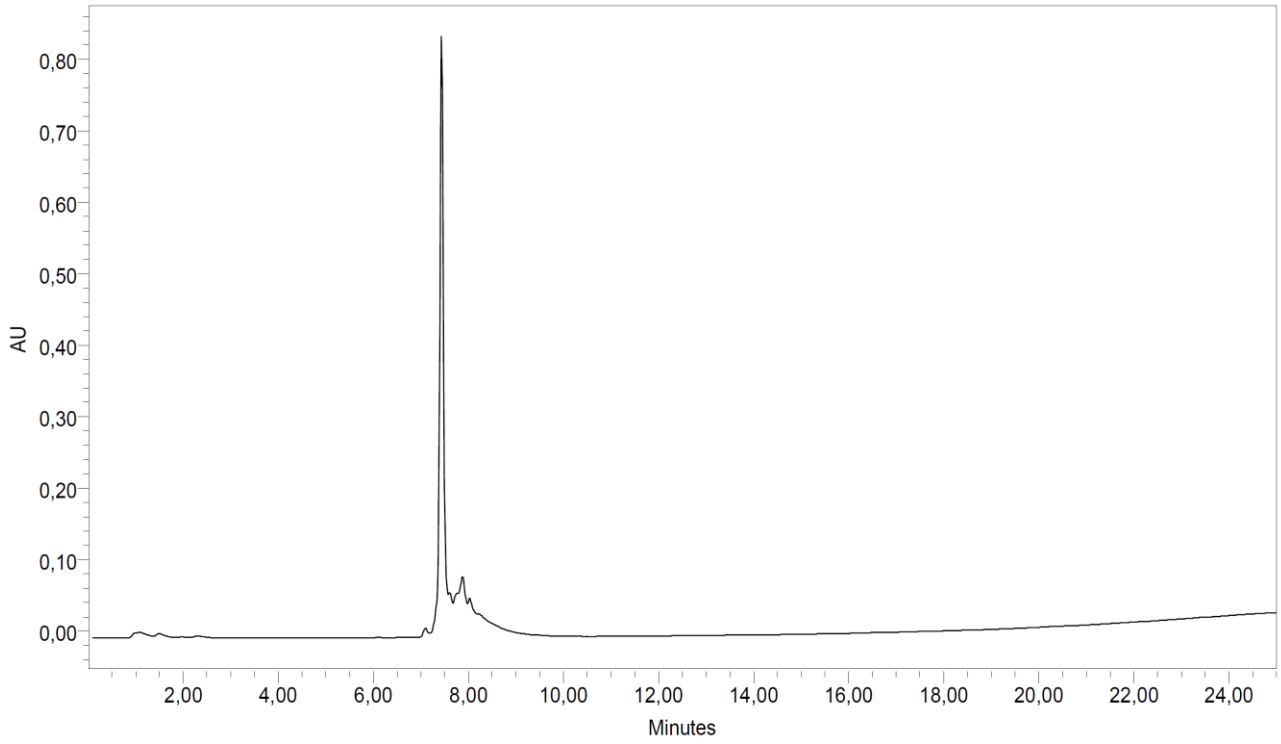


ESI-MS (positive mode): calcd for $C_{97}H_{156}N_{21}O_{49}$ 2400.0, found: *m/z* 2399.0 $[M + H]^+$

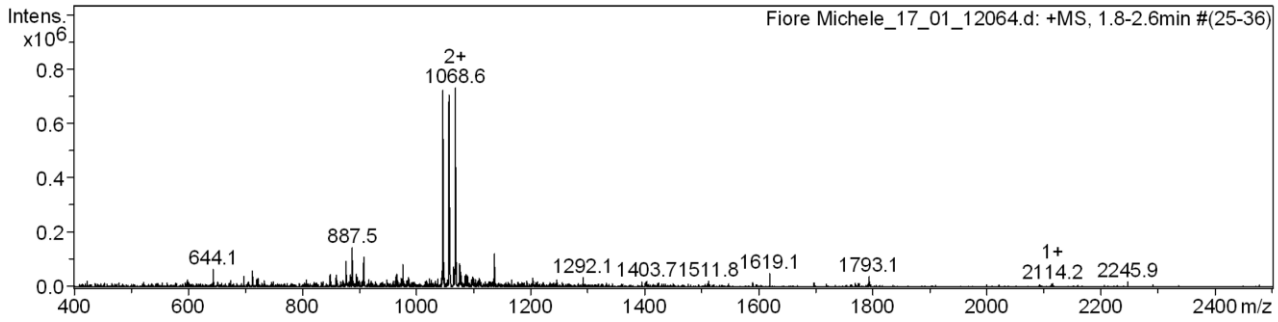


17. Analytical data for compound **8-Lac/Man**

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

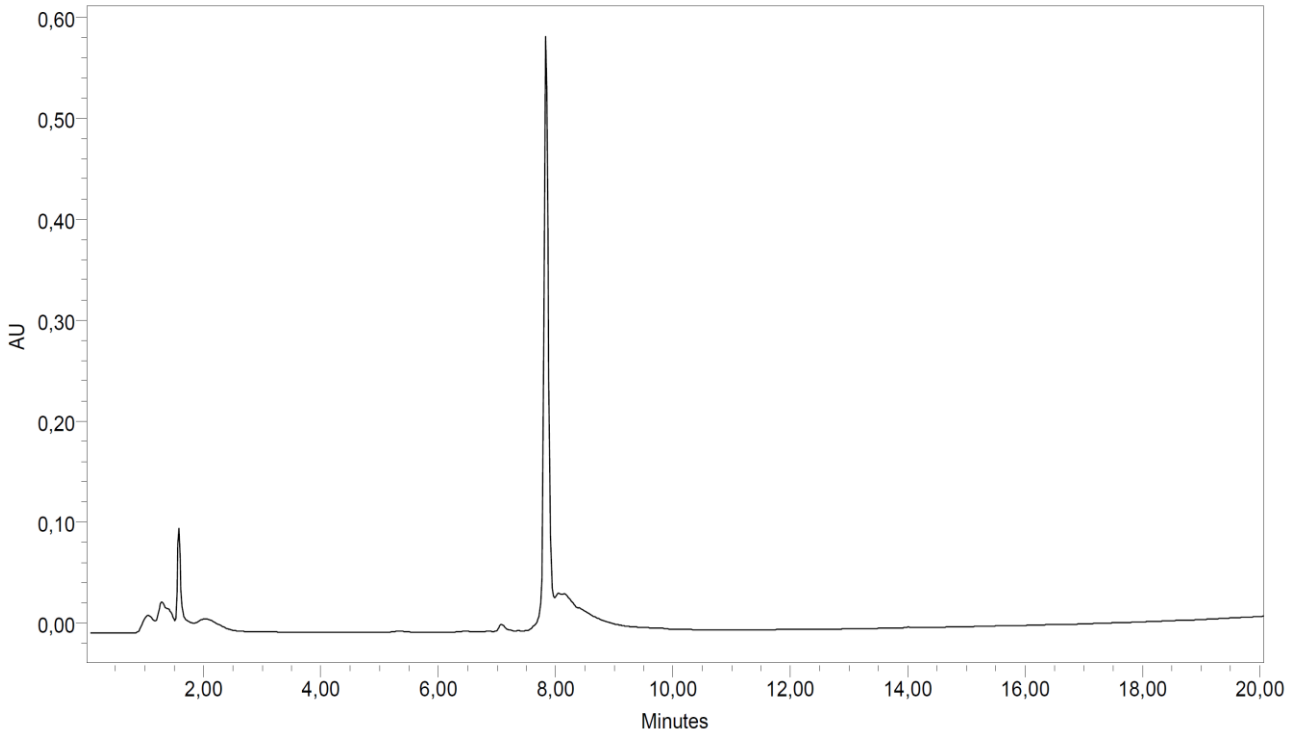


ESI-MS (positive mode): calcd for $C_{85}H_{136}N_{21}O_{40}$ 2092.0, found: *m/z* 2091.2 $[M + H]^+$



18. Analytical data for compound **8-Lac/Fuc**

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



ESI-MS (positive mode): calcd for $C_{85}H_{136}N_{21}O_{37}$ 2043.1, found: *m/z* 2043.9 $[M + H]^+$