Supporting Information

for

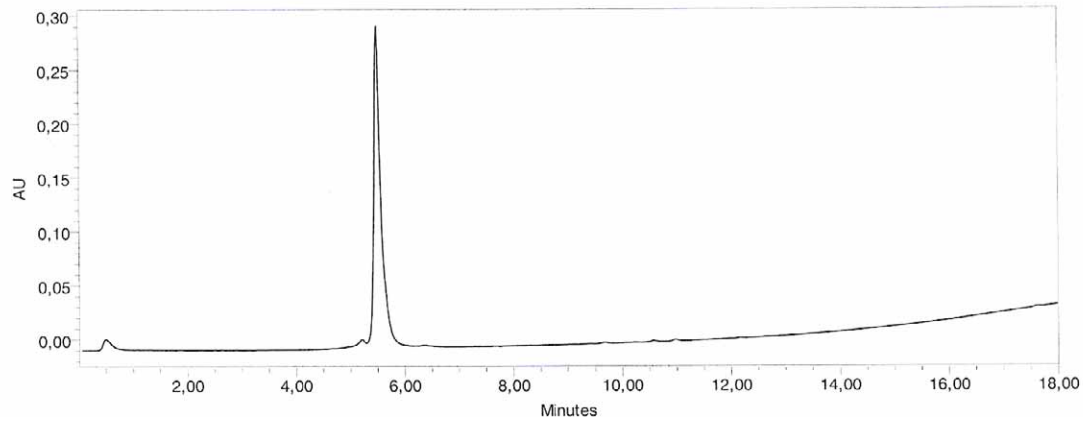
Dendri-RAFTs: A Second Generation of Cyclopeptide-Based Glycoclusters

1. Sample preparation for MALDI-TOF-MS

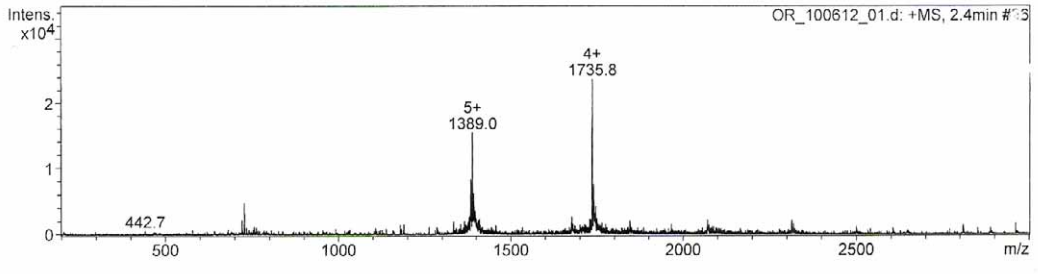
Mass spectra were acquired for all RAFT conjugates on a MALDI-TOF/TOF UltraFlex III mass spectrometer equipped with a nitrogen laser (Bruker-Daltonics, Bremen, Germany) using an external calibration of Protein Mixture 2 standard (Bruker-Daltonics, Germany). A 50 mg/ml solution of 2,5-dihydrobenzoic acid (DHB) in 50% CH_3CN/0.1% CF_3COOH was used as a MALDI matrix and a 1.0 µl of pre-treated sample dissolved in water was after becoming dry over-laid with a 0.5 µl of the matrix solution on the target. The MALDI-TOF positive spectra were collected in linear mode. Every sample before mass spectrometric analysis was diluted in 20 µL 0.1% CF_3COOH and pre-treated on OligoR3 (Applied Biosystems, CA, USA) reverse phase microcolumn. Prepared OligoR3 microcolumn (in Eppendorf gel-loader tips) was regenerated with 100 µL 80% CH_3CN, 0.1% CF_3COOH, washed with 100 µL 0.1% CF_3COOH, and after loading of 20 µL of sample again washed with 50 µL 0.1% CF_3COOH, 100 µL 100 mM CH_3COONH_4 (pH 8.1), and 50 µL 0.1% CF_3COOH. To elute sample a 40 µL of 80% CH_3CN, 0.1% CF_3COOH was used, dried on Speed-Vac, dissolved in 7 µL of deionized water and loaded on MALDI target.

2. *Analytical data for RR-Ser$_{16}$ 7*

RP-HPLC (5 to 100% B in 15 min, λ = 214 and 250 nm)

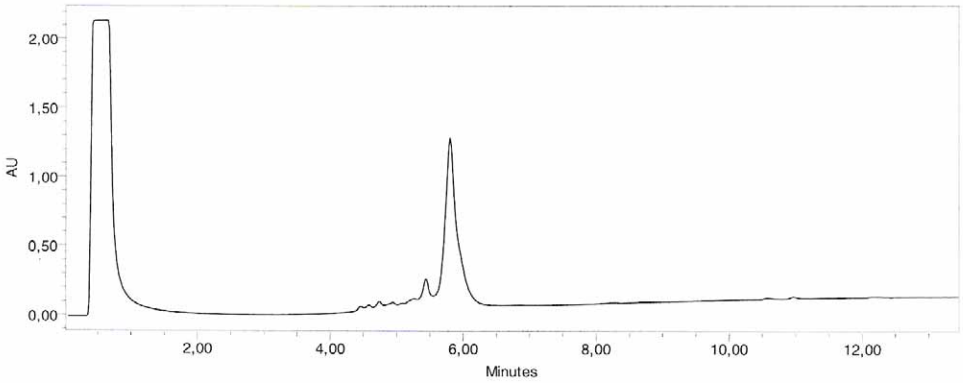


- ESI-MS (positive mode): calcd for $C_{299}H_{509}N_{95}O_{94}$ 6939.0, found: m/z 6940.5 $[M+H]^+$

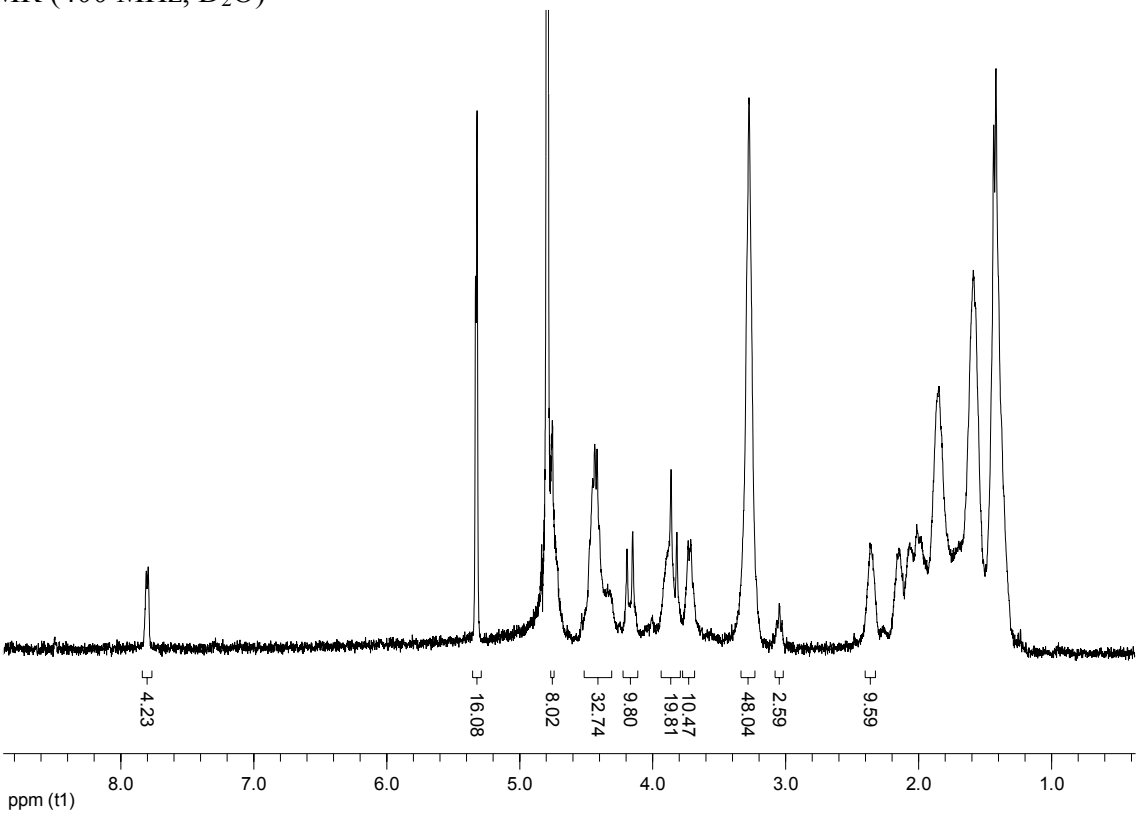


3. Analytical data for RR-CHO$_{16}$ ***8***

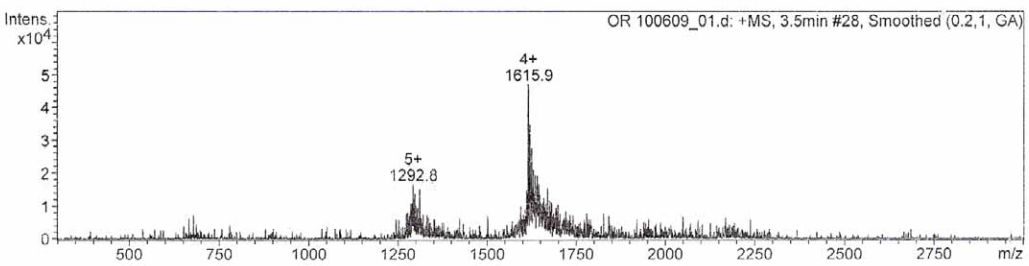
RP-HPLC (5 to 100% B in 15 min, λ = 214 and 250 nm)



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

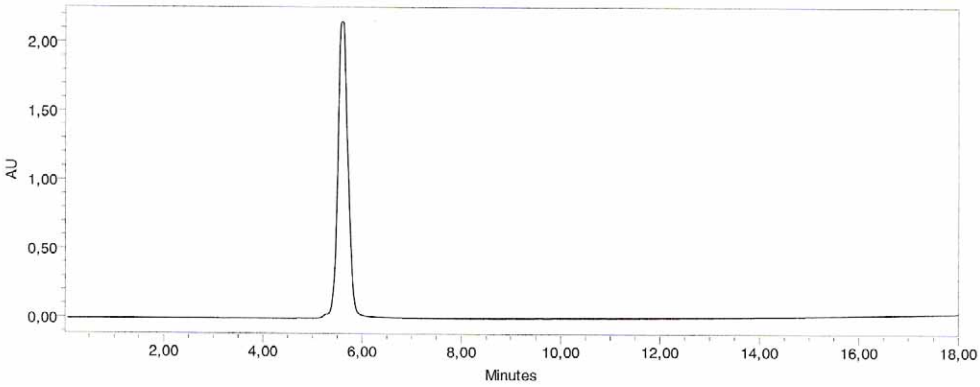


- ESI-MS (positive mode): calcd for $C_{283}H_{429}N_{79}O_{94}$ 6442.0, found: m/z 6460.3 $[M+H_2O]^+$

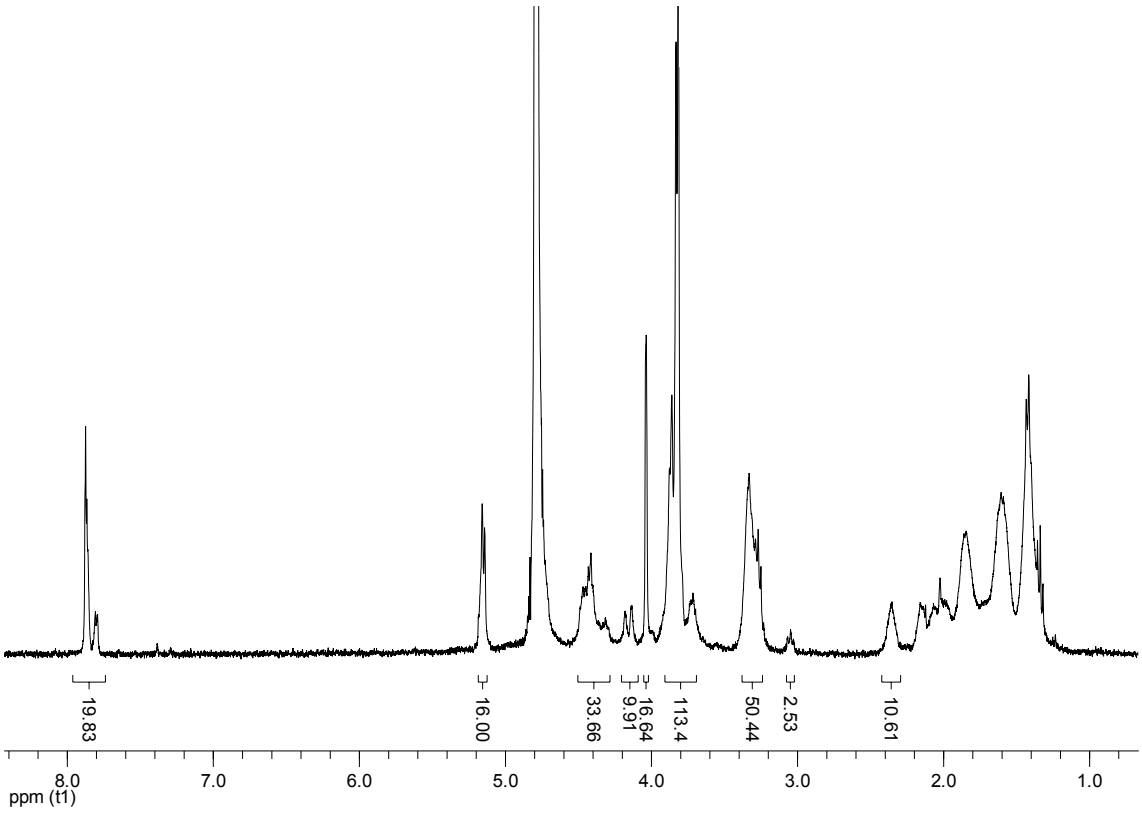


4. Analytical data for RR-βGal$_{16}$ ***9***

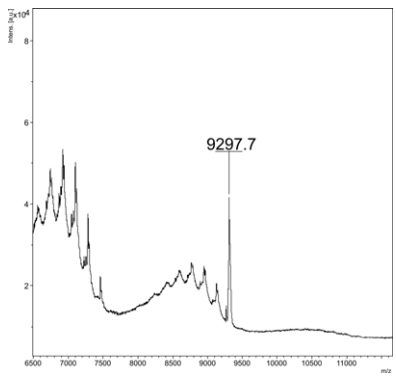
- RP-HPLC (5 to 100% B in 15 min, λ = 214 and 250 nm)



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

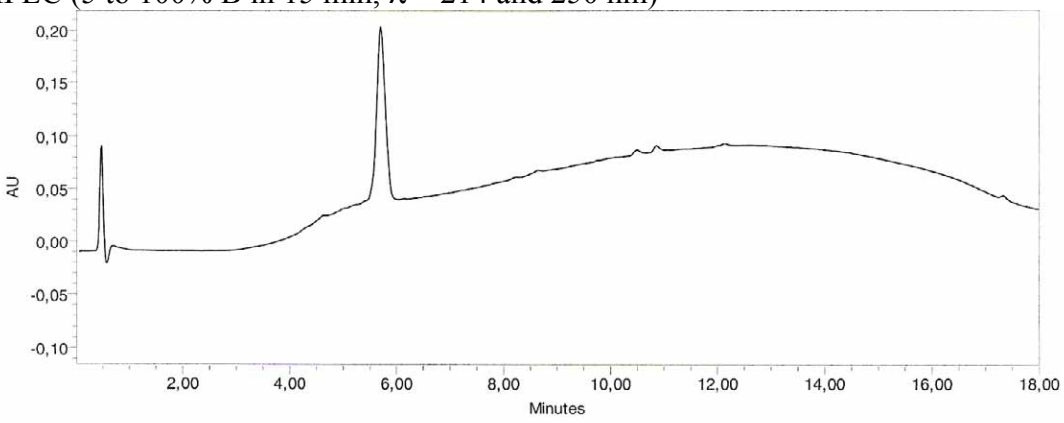


- MALDI-TOF-MS: calcd for $[C_{379}H_{605}N_{95}O_{174}Na]^+$ 9299.4983; found: *m/z* 9297.7 $[M+Na]^+$.

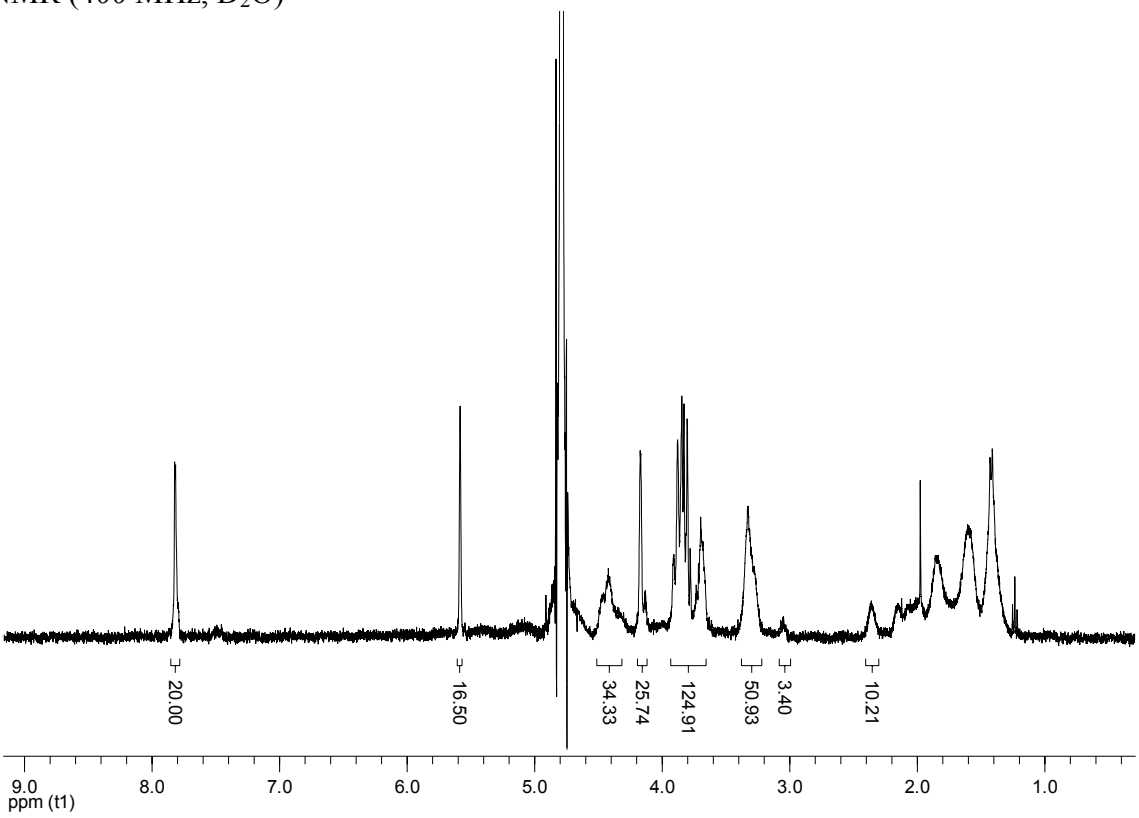


5. Analytical data for RR-αMan$_{16}$ ***10***

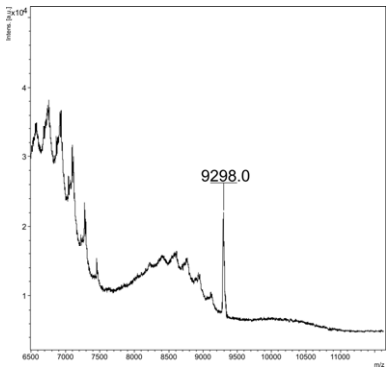
- RP-HPLC (5 to 100% B in 15 min, λ = 214 and 250 nm)



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

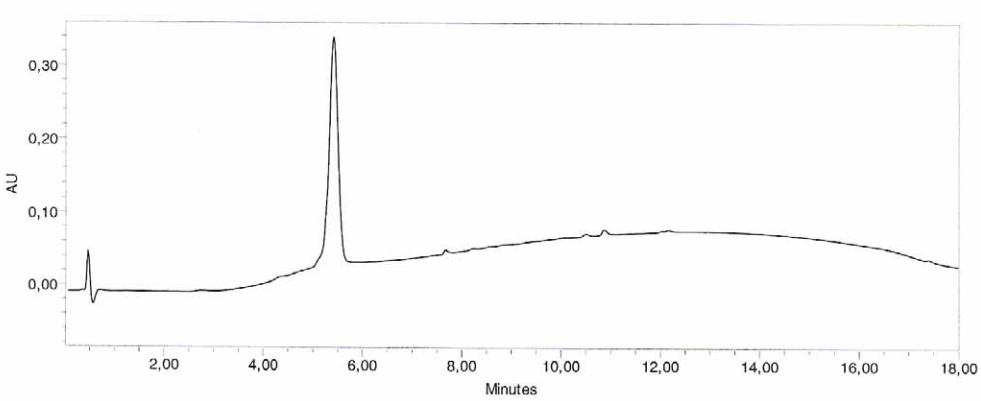


- MALDI-TOF-MS: calcd for $[C_{379}H_{605}N_{95}O_{174}Na]^+$ 9299.4983; found: *m/z* 9298.0 $[M+Na]^+$.

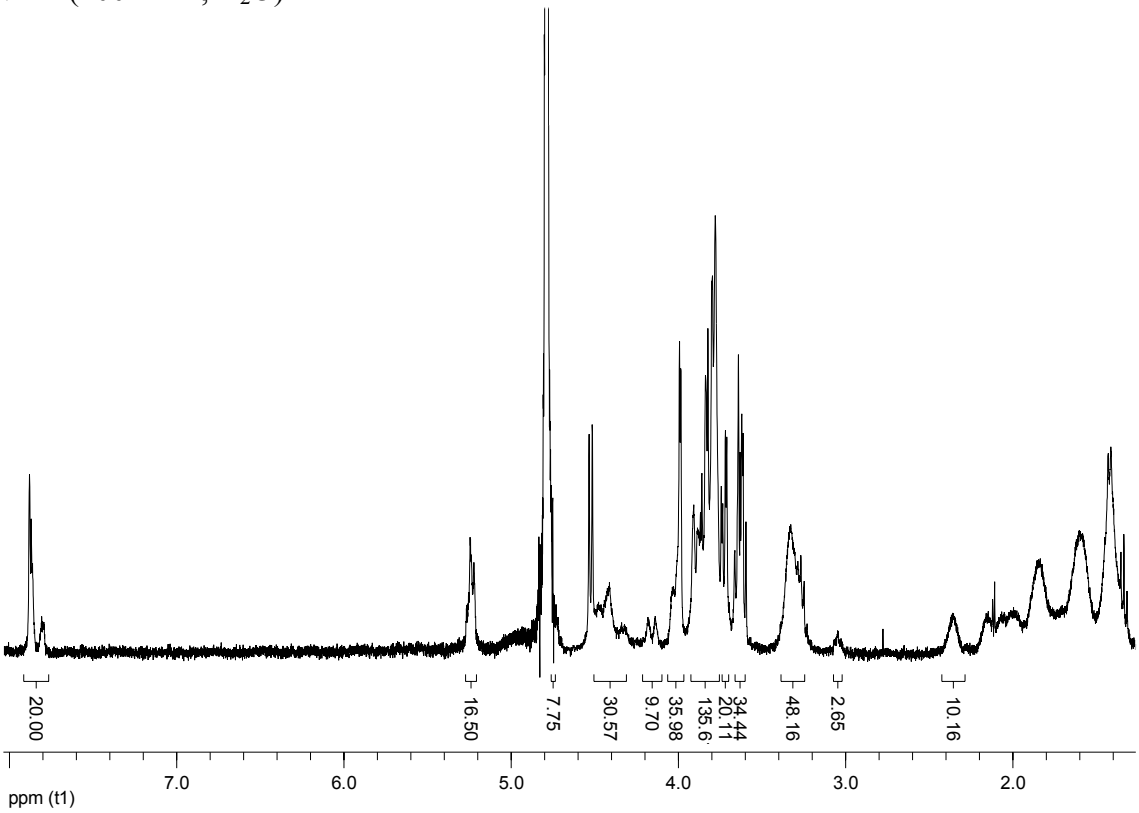


6. Analytical data for RR-βLac$_{16}$ ***11***

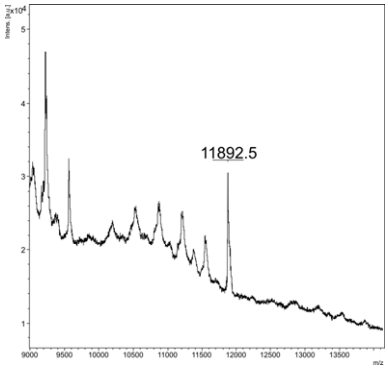
- RP-HPLC (5 to 100% B in 15 min, λ = 214 and 250 nm)



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

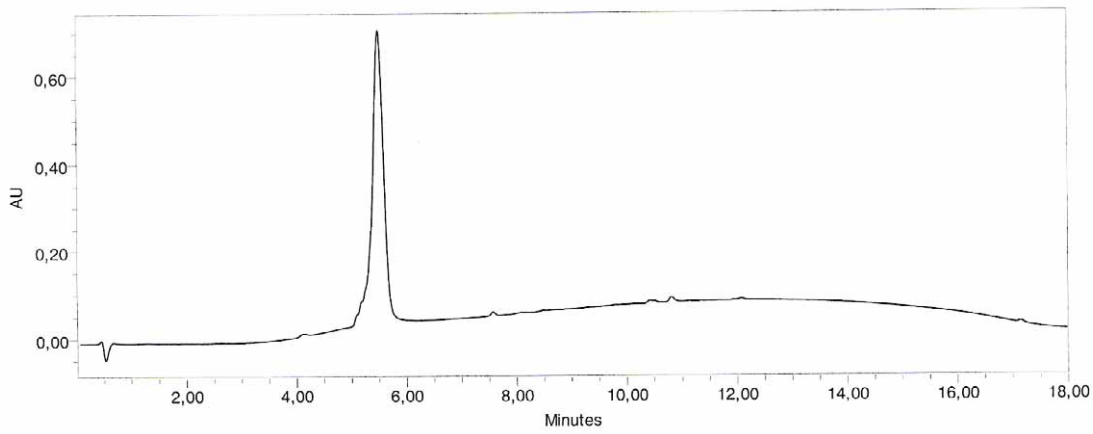


- MALDI-TOF-MS: calcd for $[C_{475}H_{765}N_{95}O_{254}Na]^+$ 11893.7767; found: *m/z* 11892.5 $[M+Na]^+$.

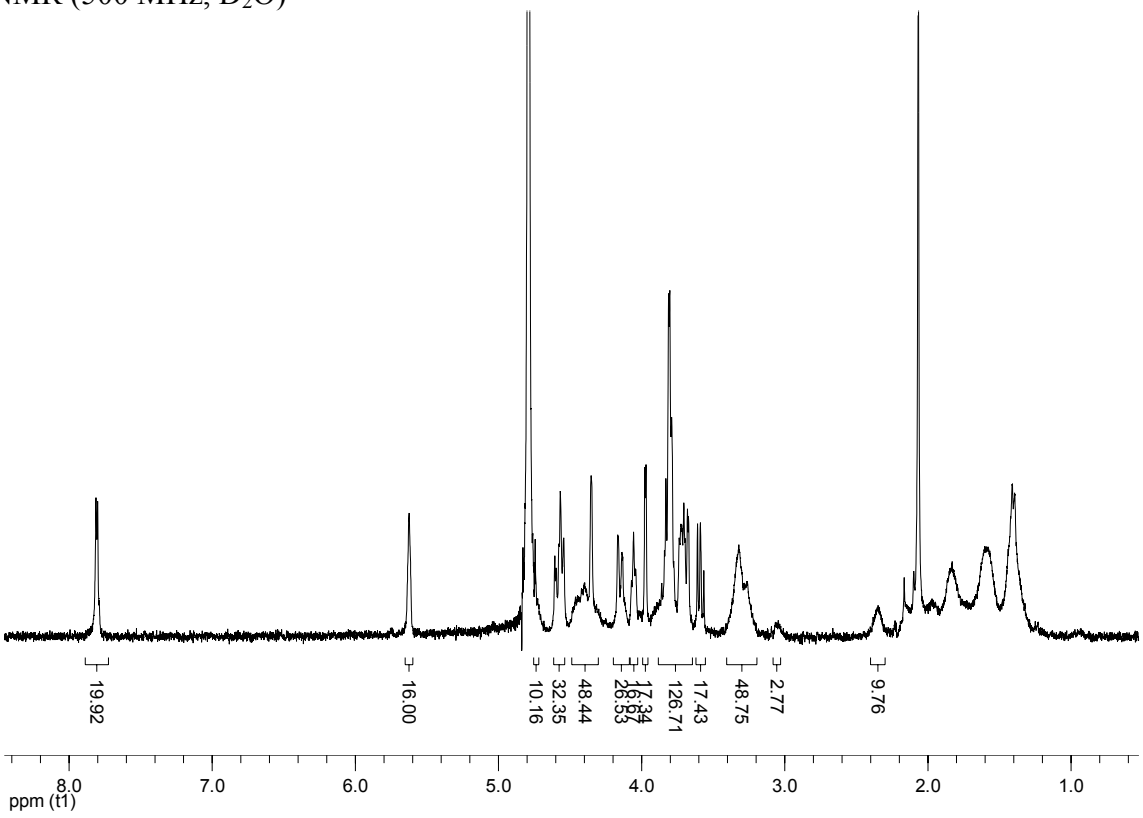


7. Analytical data for RR-αTF$_{16}$ ***12***

- RP-HPLC (5 to 100% B in 15 min, λ = 214 and 250 nm)

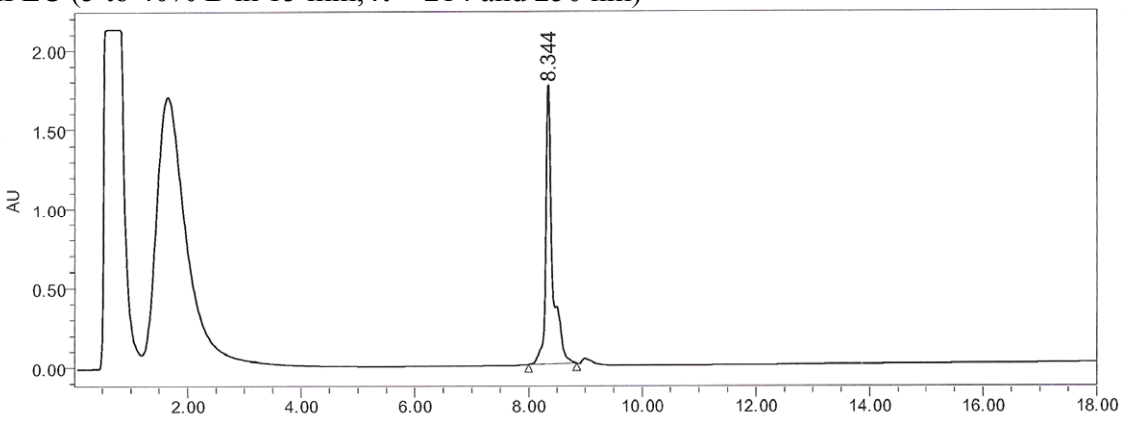


- ^{1}H NMR (500 MHz, D_2O)

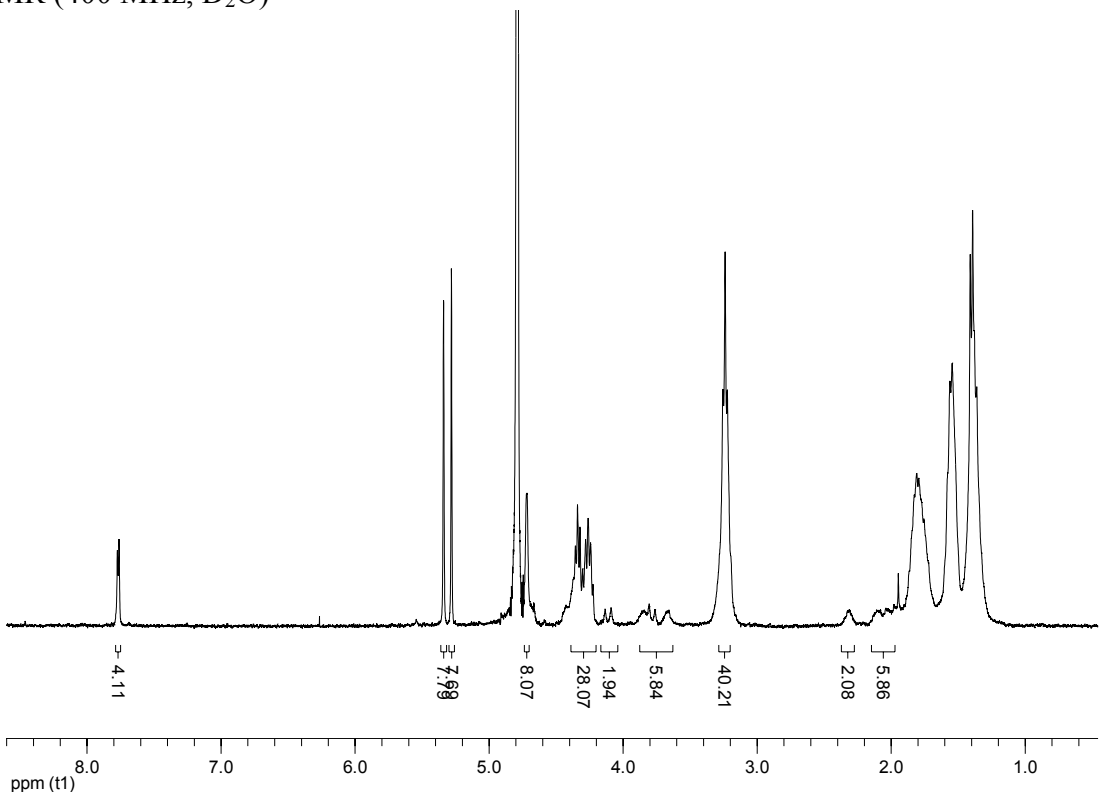


8. Analytical data for RK-CHO$_{16}$

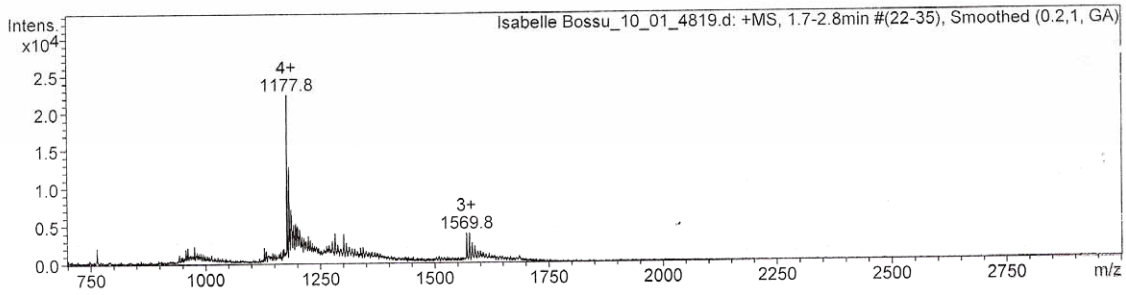
- RP-HPLC (5 to 40% B in 15 min, λ = 214 and 250 nm)



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

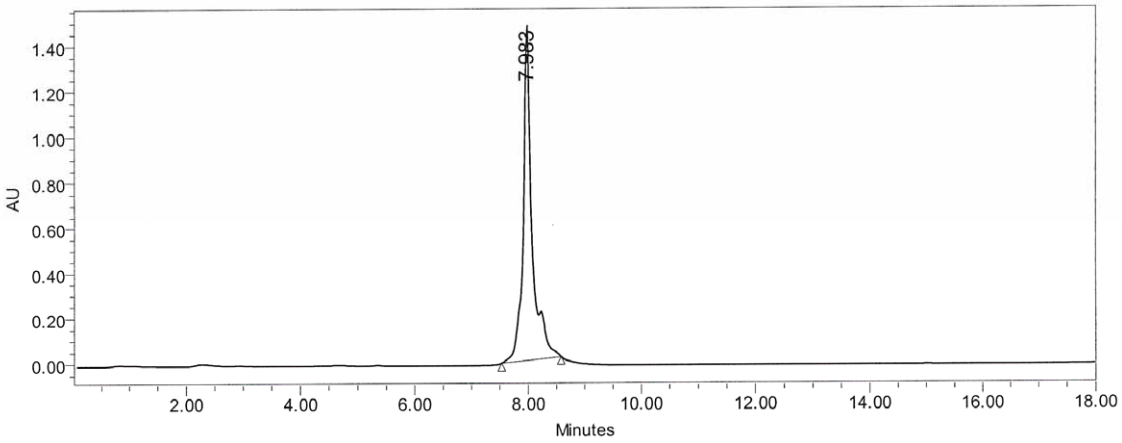


- ESI-MS: calcd for $C_{200}H_{306}N_{58}O_{74}$ 4707.0; found: *m/z* 4707.8 $[M+H]^+$.

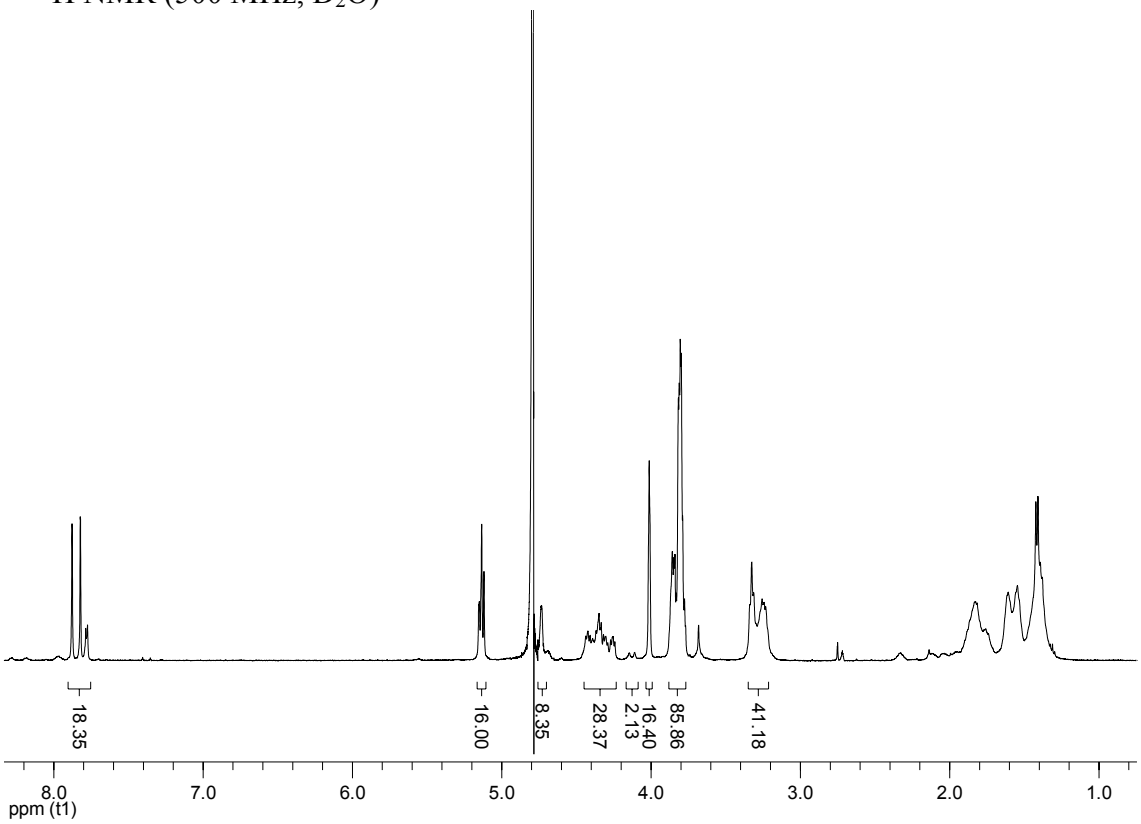


9. Analytical data for RK-βGal$_{16}$ ***18***

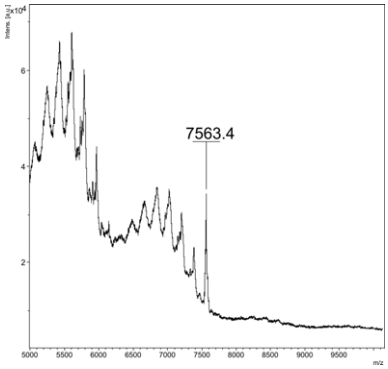
- RP-HPLC (5 to 40% B in 15 min, λ = 214 and 250 nm)



- ^{1}H NMR (500 MHz, D_2O)

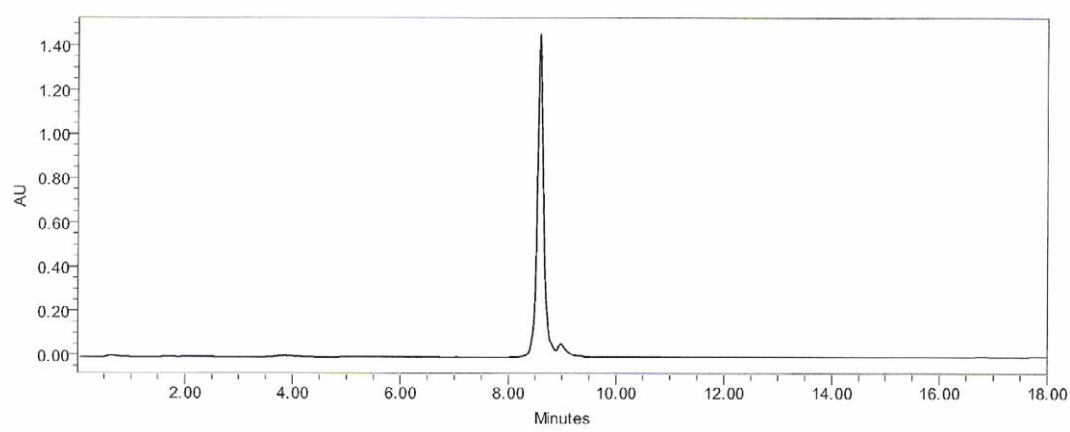


- MALDI-TOF-MS: calcd for $[C_{296}H_{482}N_{74}O_{154}Na]^+$ 7564.4792; found: *m/z* 7563.4 $[M+Na]^+$.

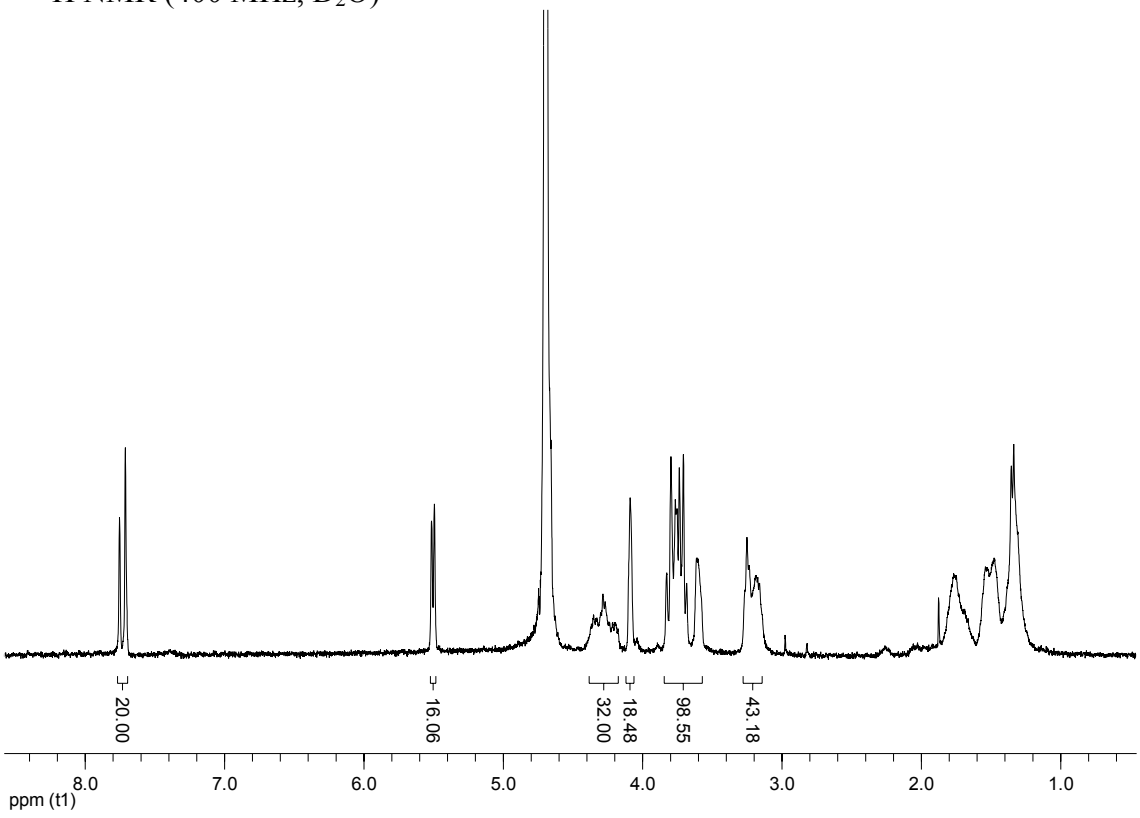


10. Analytical data for RK-αMan$_{16}$ ***19***

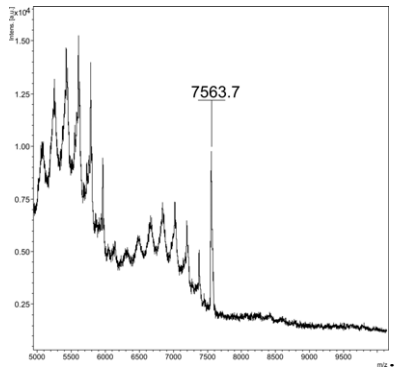
- RP-HPLC (5 to 40% B in 15 min, λ = 214 and 250 nm)



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



- MALDI-TOF-MS: calcd for $[C_{296}H_{482}N_{74}O_{154}Na]^+$ 7564.4792; found: *m/z* 7563.7 $[M+Na]^+$.



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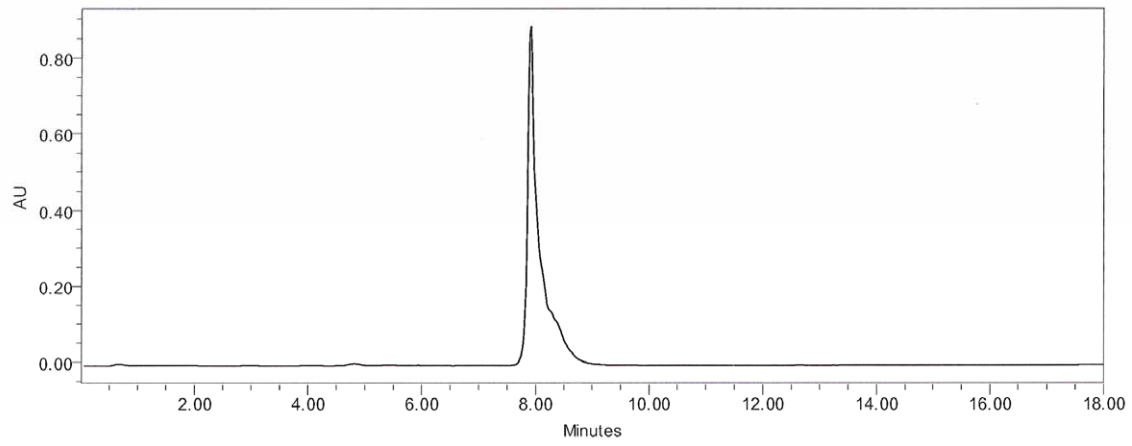
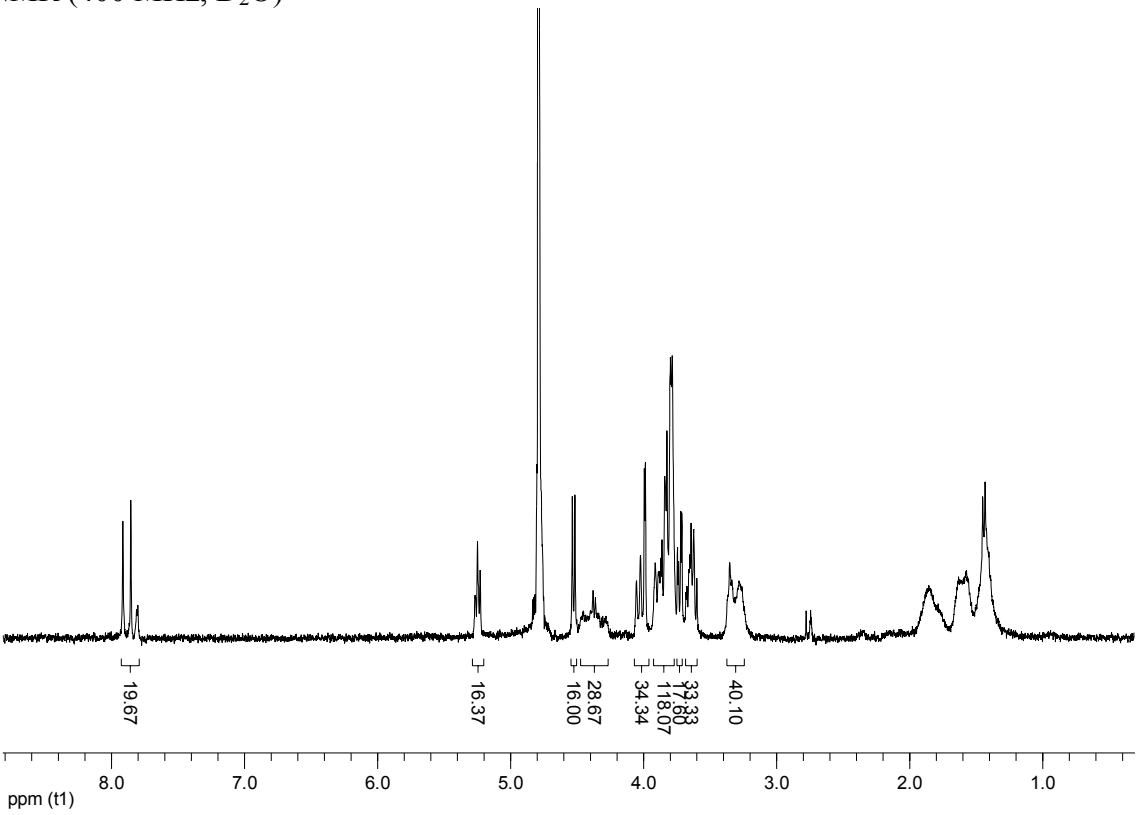
11. Analytical data for RK-βLac$_{16}$ ***20***

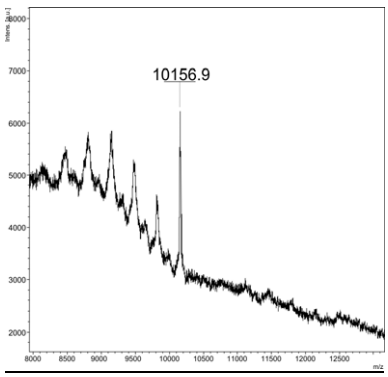
- RP-HPLC (5 to 40% B in 15 min, λ = 214 and 250 nm)



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

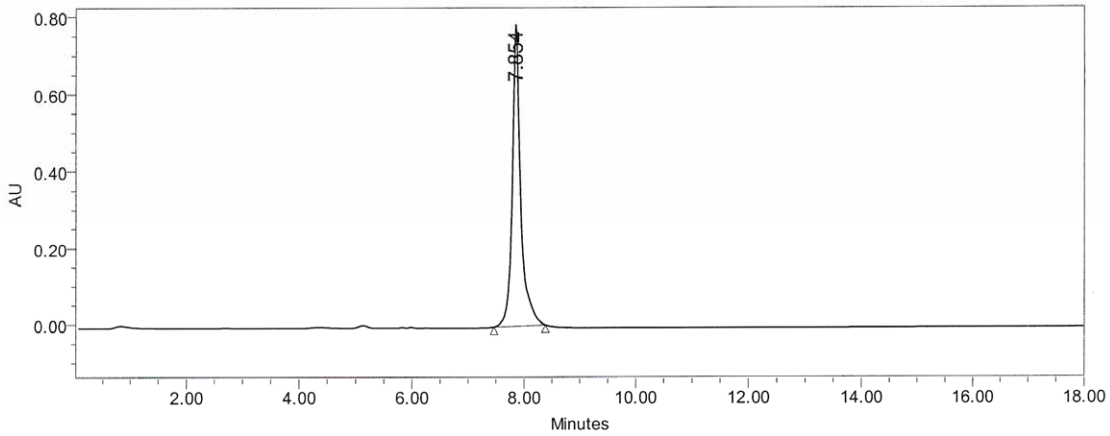


- MALDI-TOF-MS: calcd for $[C_{392}H_{642}N_{74}O_{234}Na]^+$ 10158.7576; found: *m/z* 10156.9 $[M+Na]^+$.

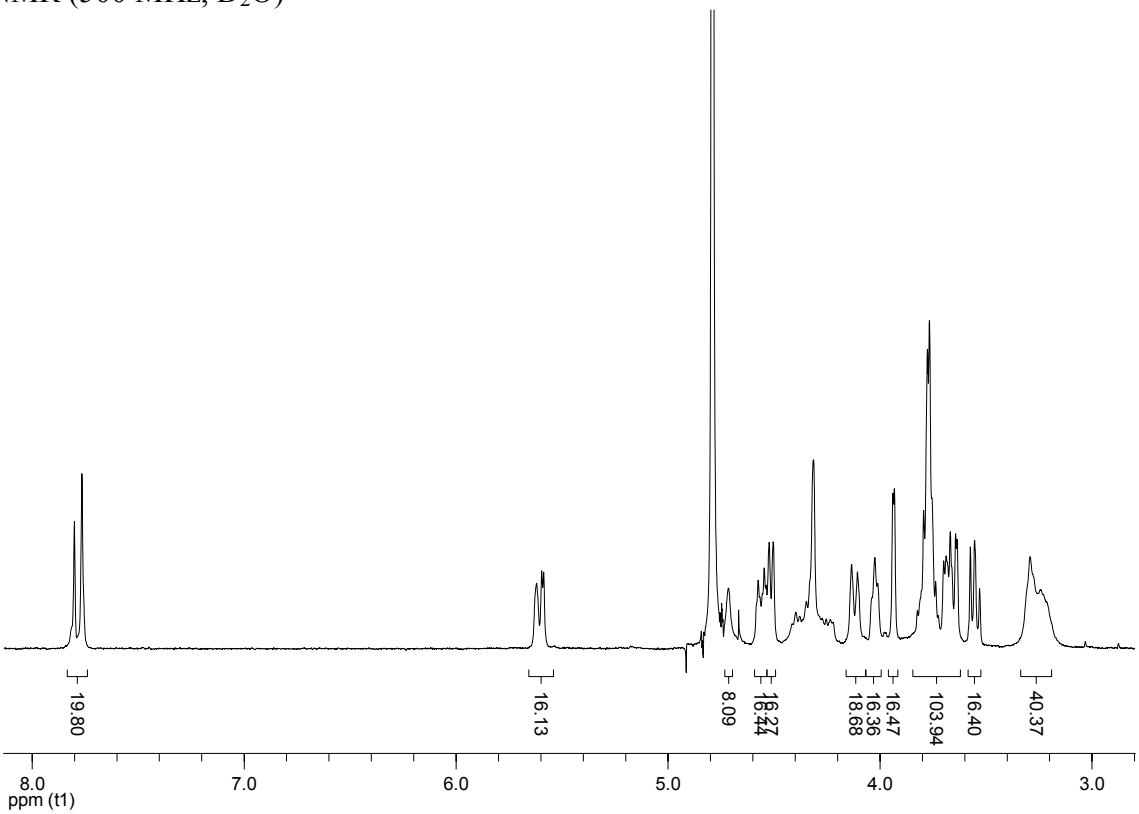


12. Analytical data for RK-αTF_{16} ***21***

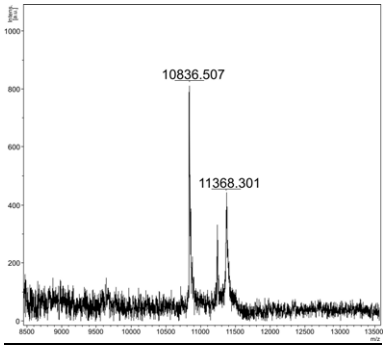
- RP-HPLC (5 to 40% B in 15 min, λ = 214 and 250 nm)



- ^{1}H NMR (500 MHz, D_2O)

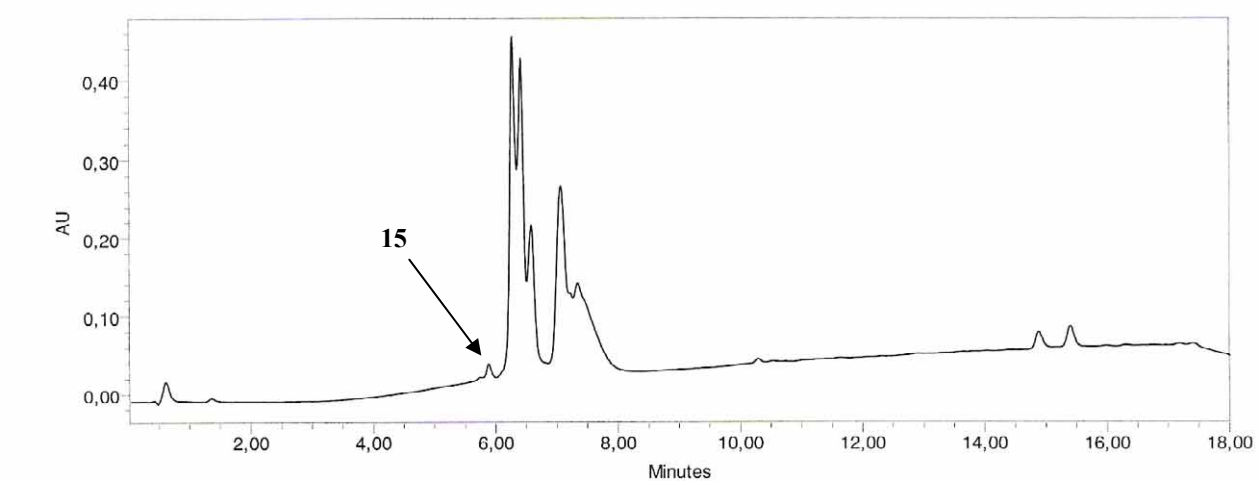


- MALDI-TOF-MS: calcd for $C_{424}H_{690}N_{90}O_{234}Na_2$ 10838.6; found: *m/z* 10836.5 $[M+2Na]^+$.

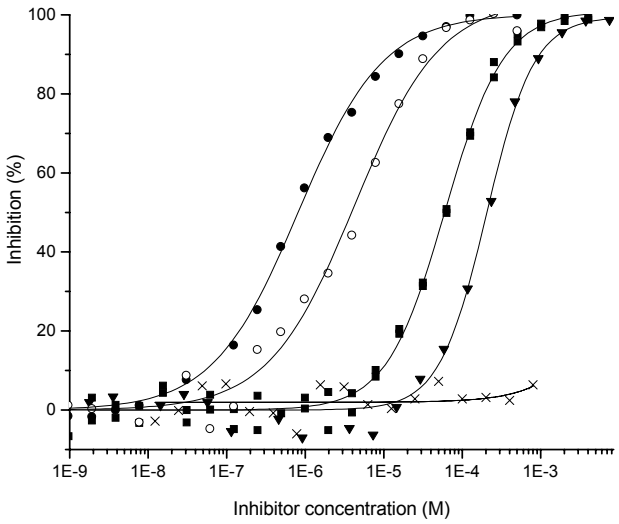


13. Stability of R-αMan$_4$ONH$_2$ ***15***: analytical RP-HPLC after 12 h at 37°C in solution in 0.1% TFA in H_2O

- RP-HPLC (5 to 60% B in 15 min, λ = 214 and 250 nm)



14. Inhibition curves of ELLA test with ConA



Inhibition of binding of Con A to PAA-α-D-Man by Man-α-D-OCH$_3$ (▼), R-αMan$_4$ **13** (■), dendri-RAFTs RR-αMan$_{16}$ **10** (○) and RR-αMan$_{16}$ **19** (●). RR-βGal$_{16}$ **9** (×) was used as negative control.