

Electronic Supplementary Information

Divergent and convergent synthesis of GalNAc-conjugated dendrimers using dual orthogonal ligations

Baptiste Thomas, Gour Chand Daskhan, Carlo Pifferi, Michele Fiore and Olivier Renaudet*

Table of Contents

• ¹ H NMR, ¹³ C NMR and HRMS spectra of compound 1a	S 2
• ¹ H NMR, ¹³ C NMR and HRMS spectra of compound 1b	S 3
• ¹ H NMR, ¹³ C NMR and HRMS spectra of compound 4a	S 4
• ¹ H NMR, ¹³ C NMR and HRMS spectra of compound 4b	S 5
• Analytical RP-HPLC and HRMS spectra of compound 5	S 6
• Analytical RP-HPLC and HRMS spectra of compound 8	S 7
• Analytical RP-HPLC and HRMS spectra of compound 9	S 8
• Analytical RP-HPLC and HRMS spectra of compound 10	S 9
• Analytical RP-HPLC and HRMS spectra of compound 11	S 10
• Analytical RP-HPLC and MALDI-TOF spectra of compound 12	S 11
• Analytical RP-HPLC and MALDI-TOF spectra of compound 13	S 12
• ¹ H NMR and ESI-MS spectra of compound 13	S 13
• Analytical RP-HPLC and MALDI-TOF spectra of compound 14	S 14
• ¹ H NMR and ESI-MS spectra of compound 14	S 15
• Analytical RP-HPLC and HRMS spectra of compound 15	S 16

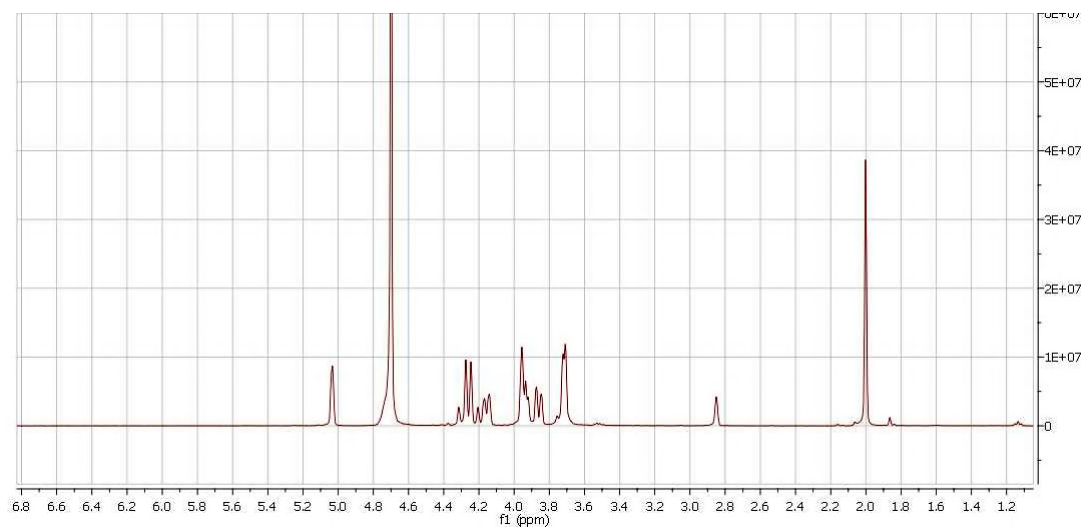


Figure 1. ^1H NMR (D_2O , 400 MHz) of compound **1a**

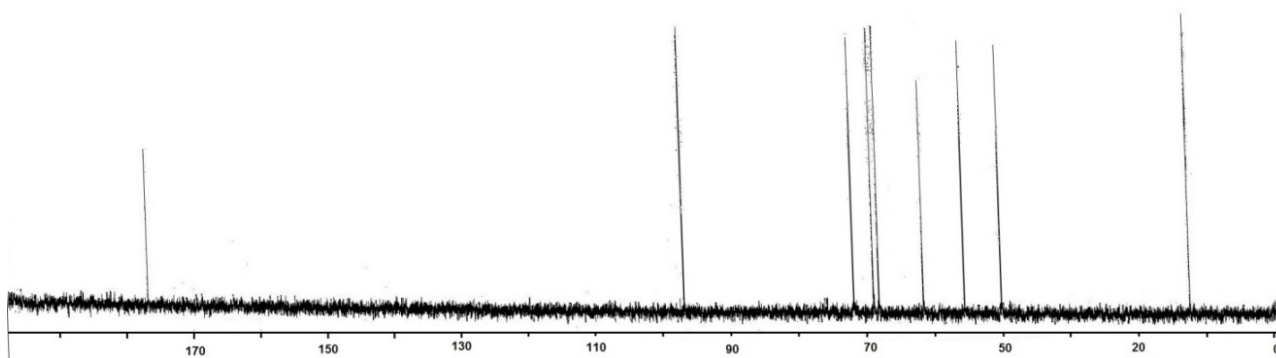


Figure 2. ^{13}C NMR (D_2O , 100 MHz) of compound **1a**

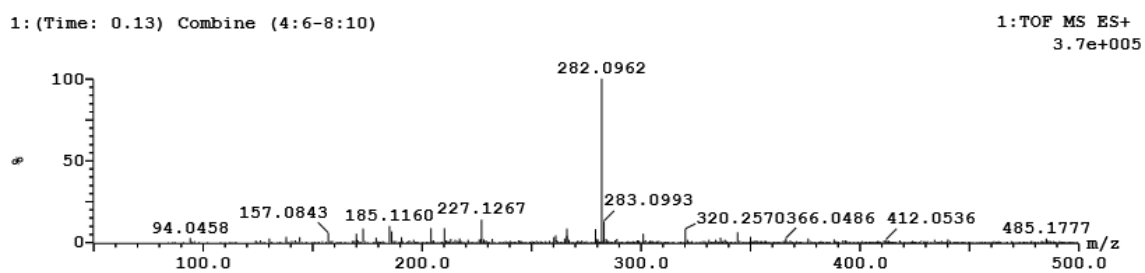


Figure 3. HRMS (ESI^+ -TOF) of compound **1a**

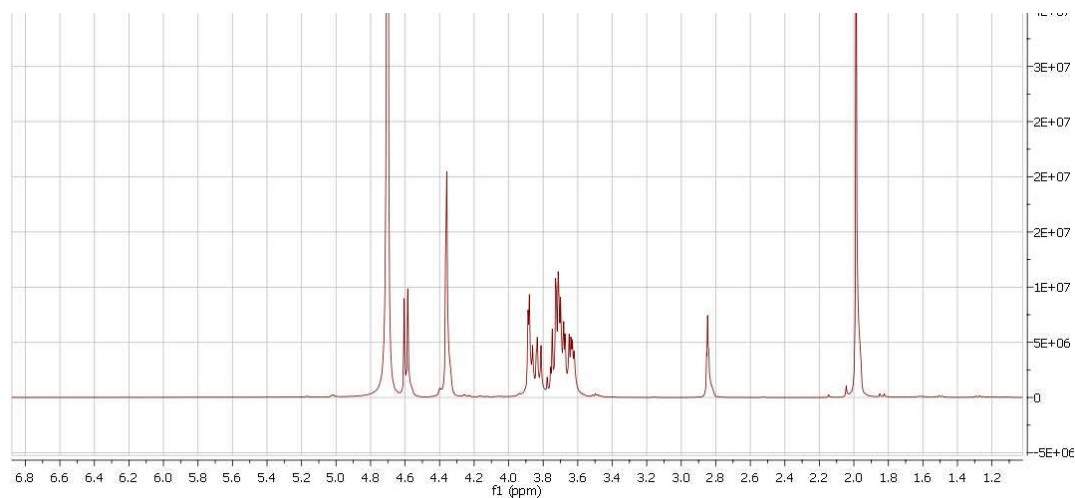


Figure 4. ^1H NMR (D_2O , 400 MHz) of compound **1b**

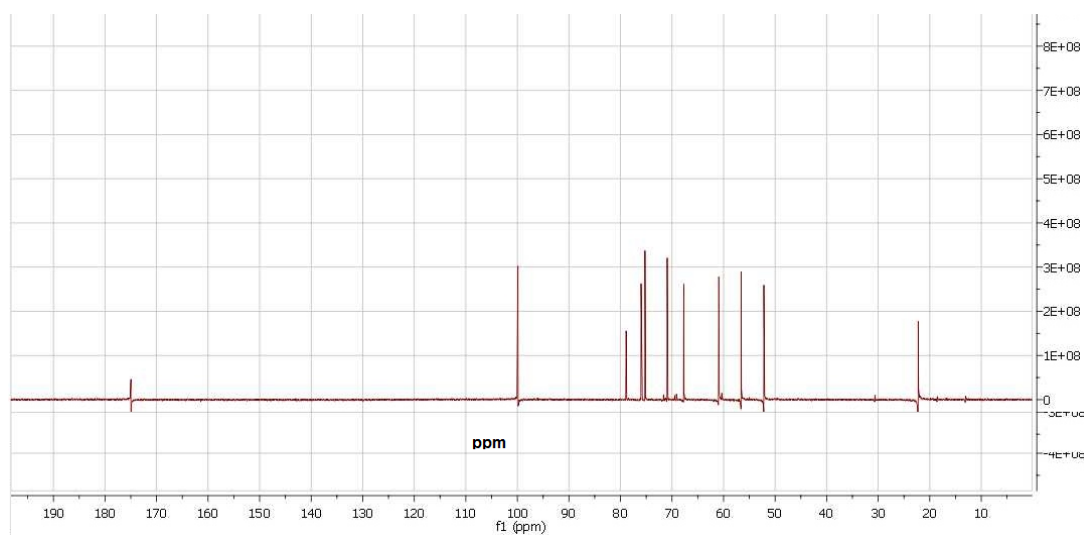


Figure 5. ^{13}C NMR (D_2O , 100 MHz,) of compound **1b**

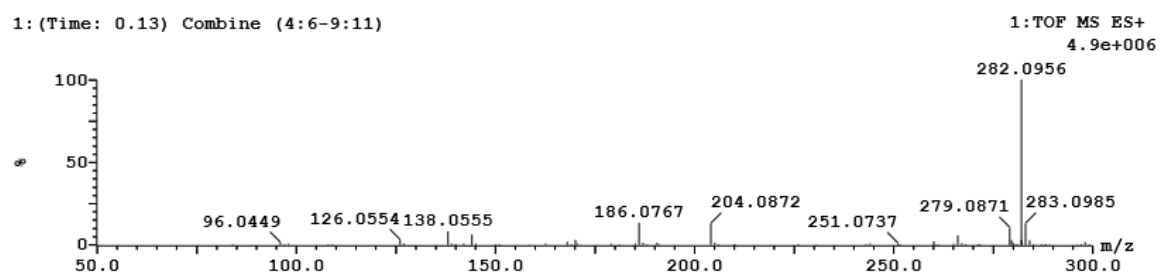


Figure 6. HRMS (ESI^+ -TOF) of compound **1b**

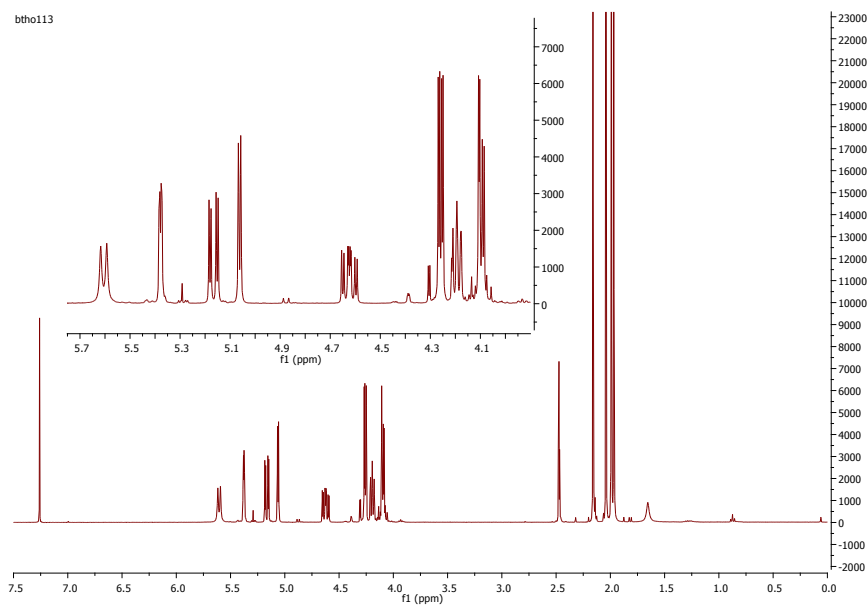


Figure 7. ^1H NMR (CDCl_3 , 400 MHz) of compound **4a**

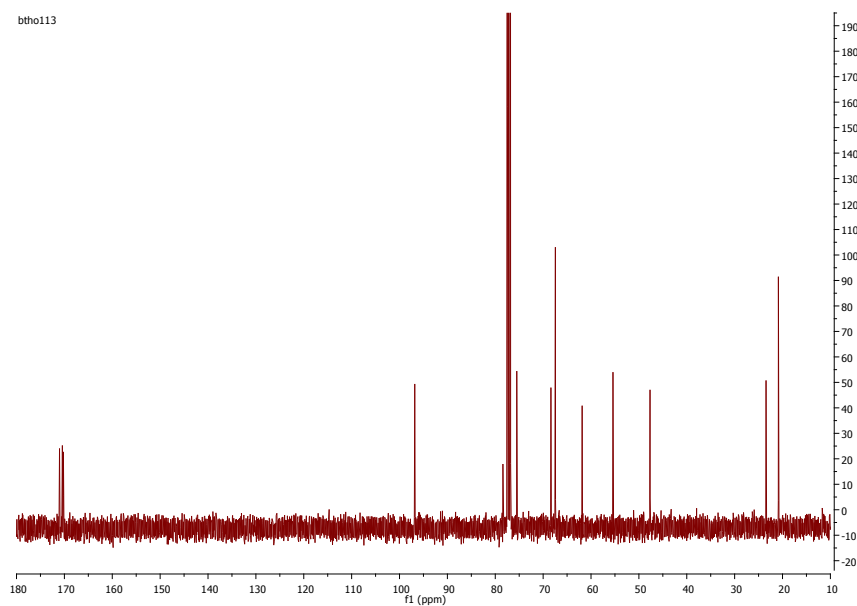


Figure 8. ^{13}C NMR (CDCl_3 , 100 MHz,) of compound **4a**

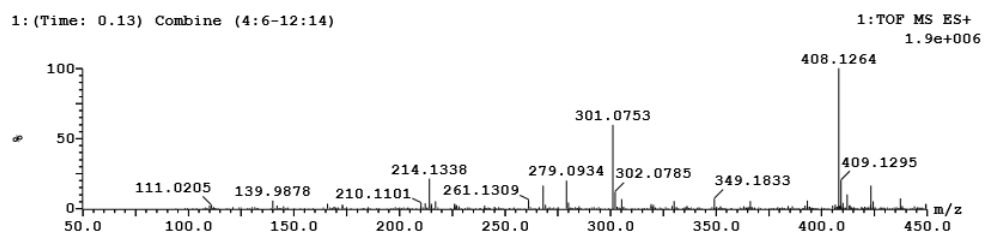


Figure 9. HRMS ($\text{ESI}^+\text{-TOF}$) of compound **4a**

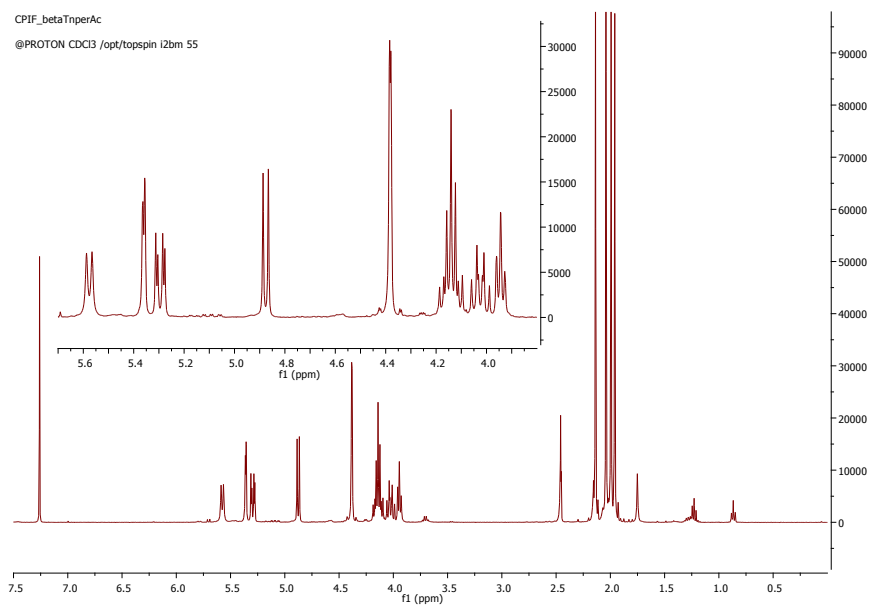


Figure 10. ^1H NMR (CDCl_3 , 400 MHz) of compound **4b**

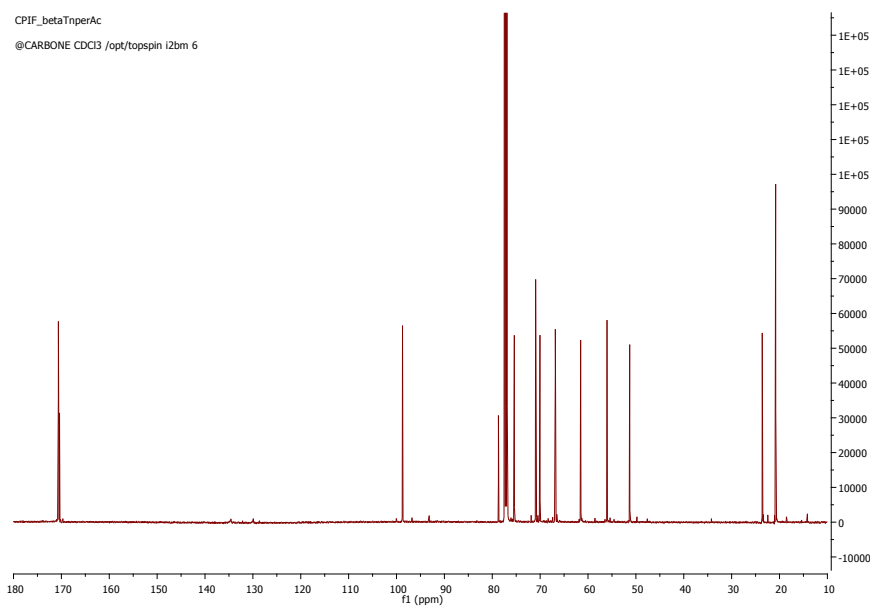


Figure 11. ^{13}C NMR (CDCl_3 , 100 MHz,) of compound **4b**

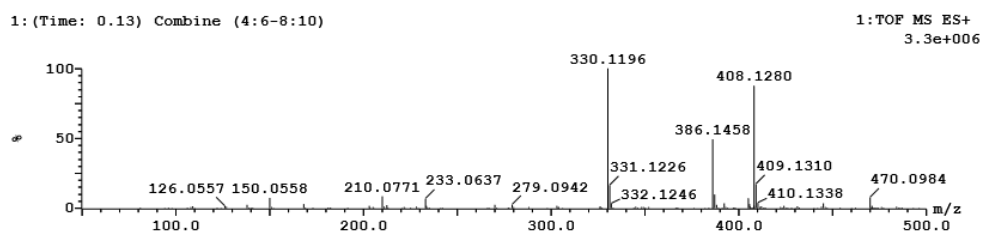


Figure 12. HRMS (ESI^+ -TOF) of compound **4b**

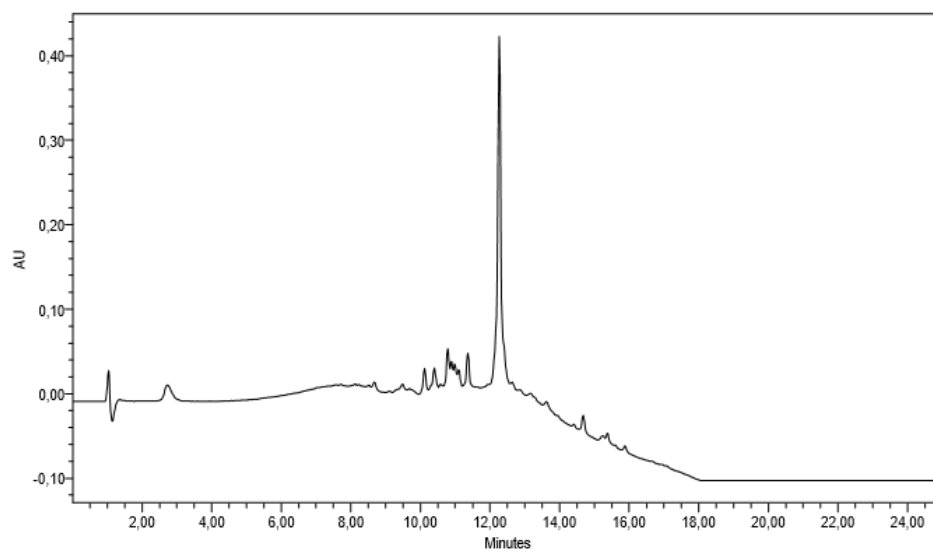


Figure 13. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **5**

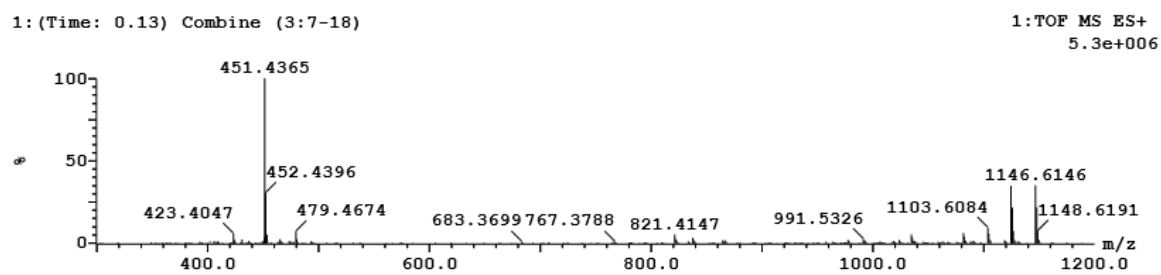


Figure 14. HRMS (ESI^+ -TOF) of compound **5**

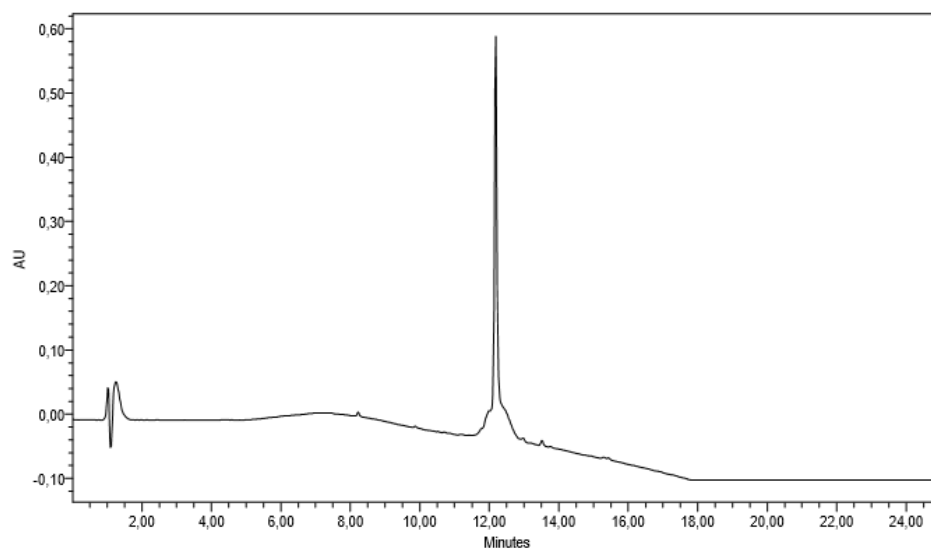


Figure 15. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **8**

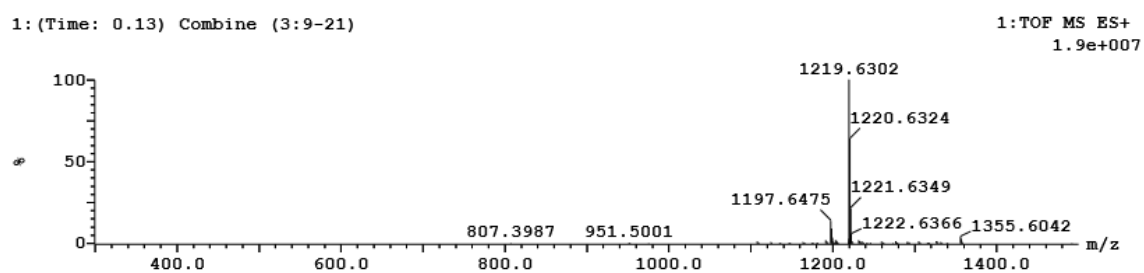


Figure 16. HRMS (ESI^+ -TOF) of compound **8**

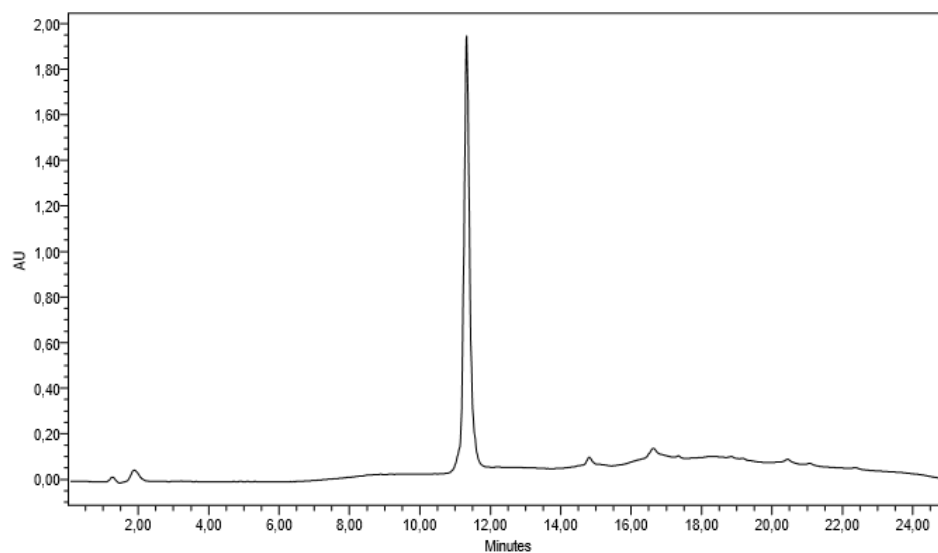


Figure 17. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **9**

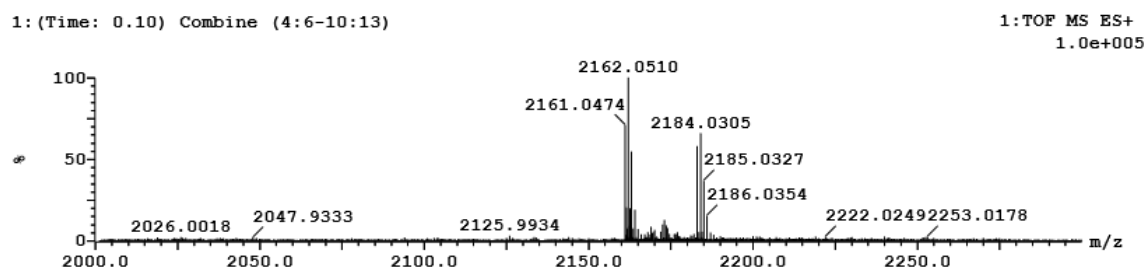


Figure 18. HRMS (ESI^+ -TOF) of compound **9**

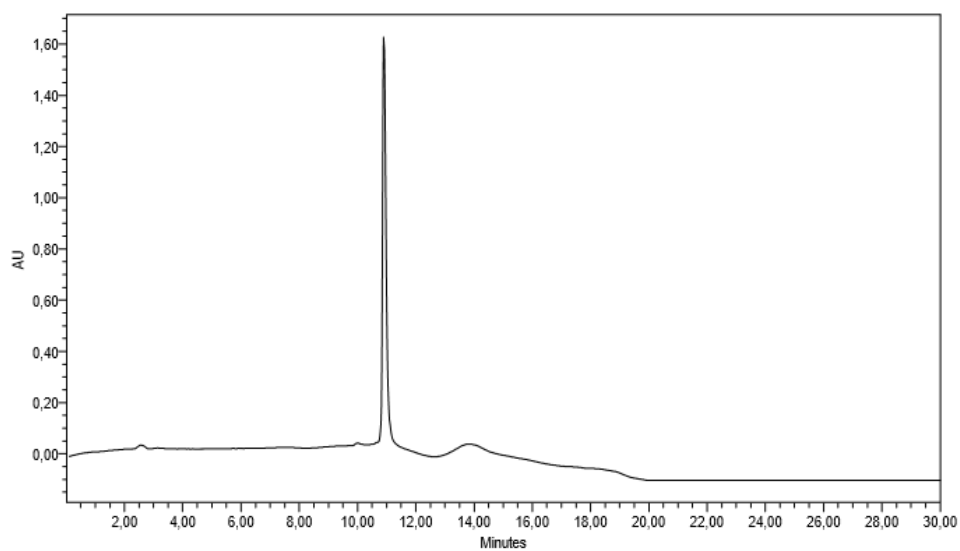


Figure 19. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **10**

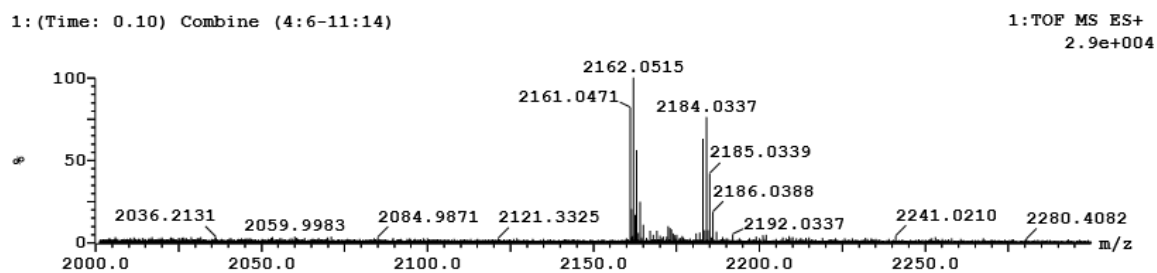


Figure 20. HRMS (ESI^+ -TOF) of compound **10**

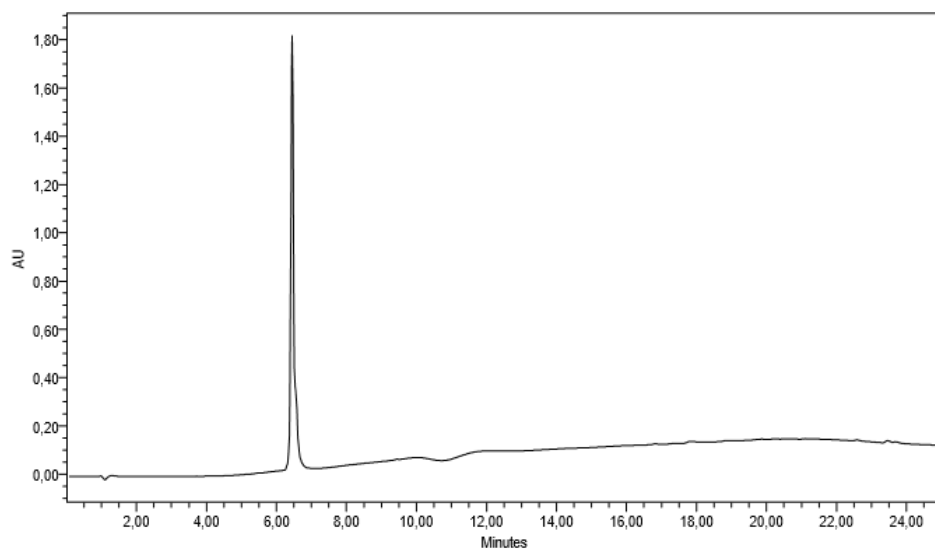


Figure 21. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **11**

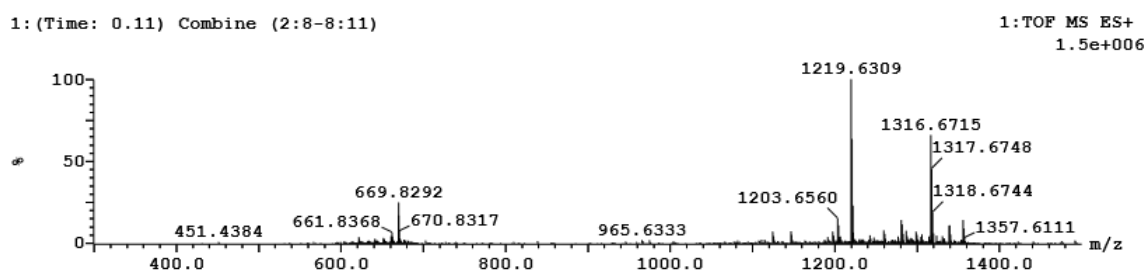


Figure 22. HRMS (ESI^+ -TOF) of compound **11**

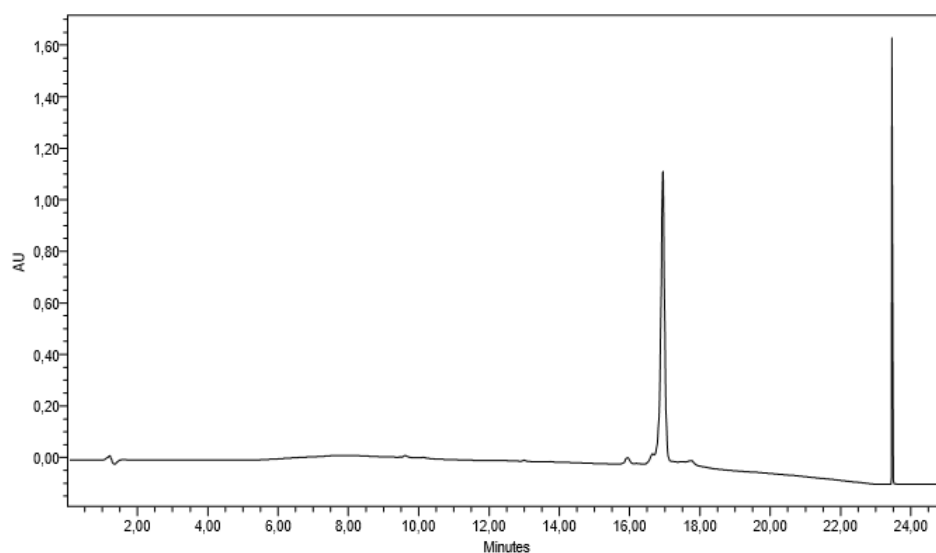


Figure 23. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **12**

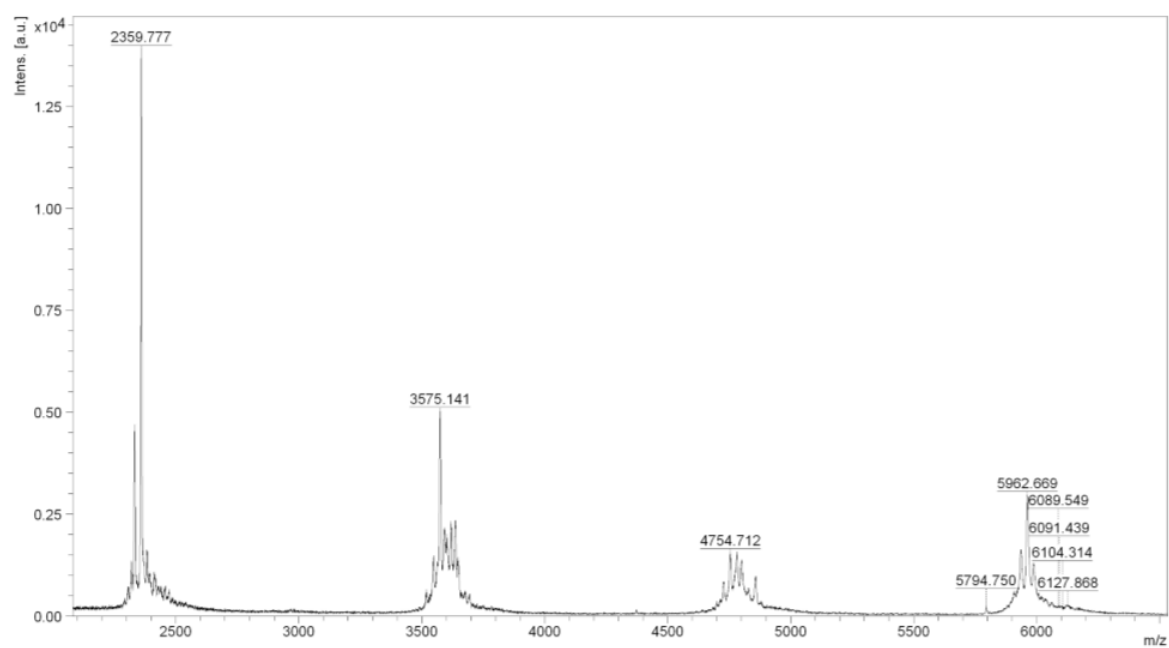


Figure 24. MALDI-TOF of compound **12**

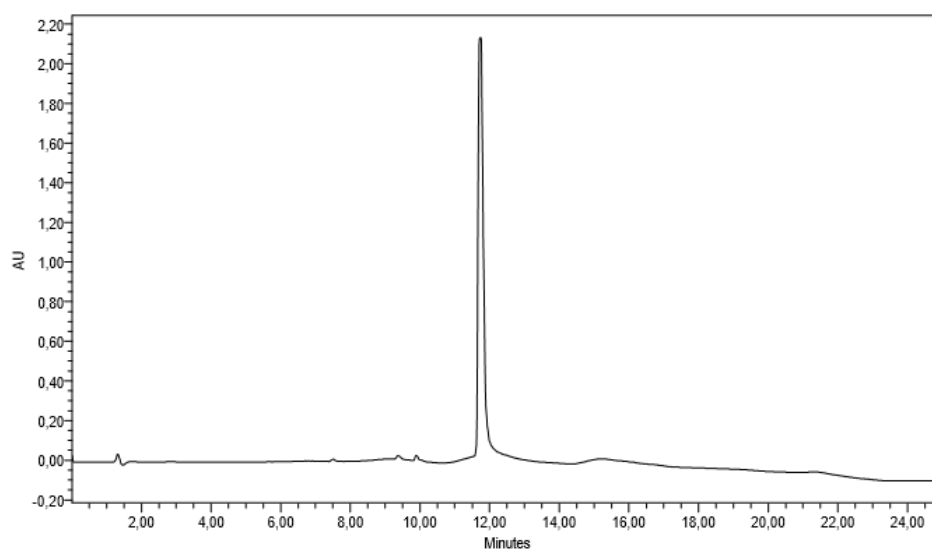


Figure 25. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **13**

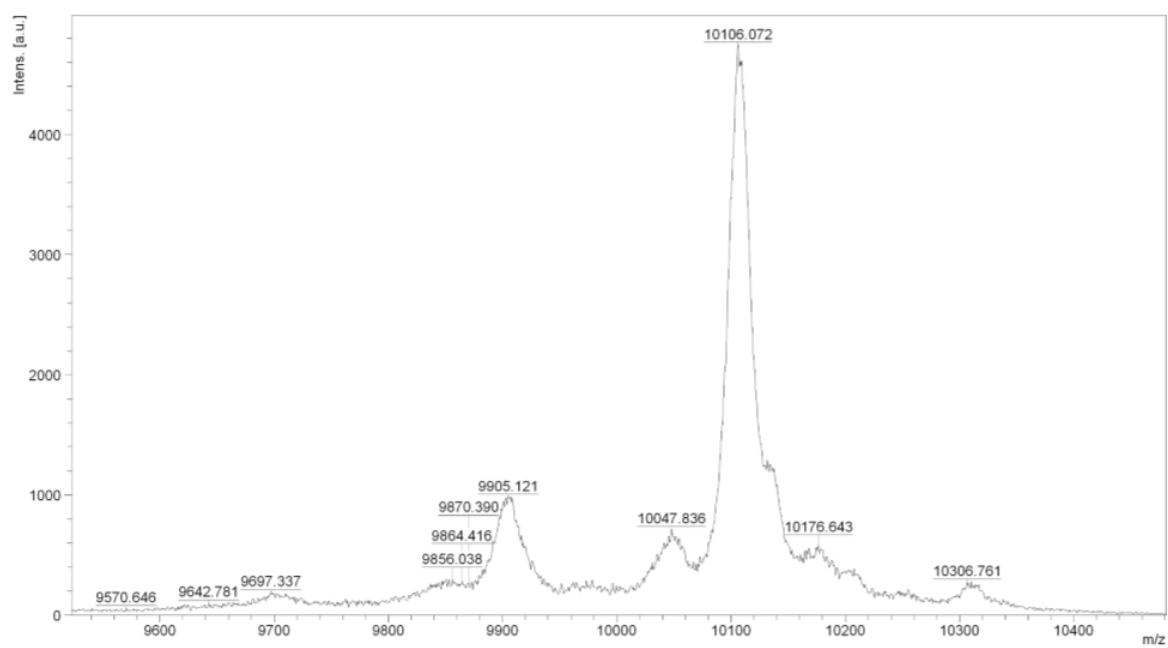
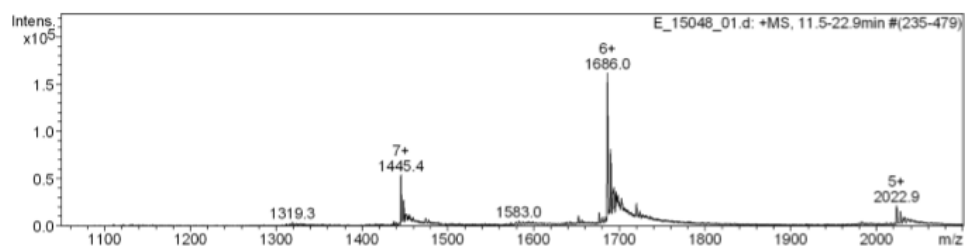


Figure 26. MALDI-TOF of compound **13**

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	1050 m/z	Scan End	2100 m/z
Capillary Exit	181.0 Volt	Skim 1	40.0 Volt	Trap Drive	148.5
Accumulation Time	409 μ s	Averages	20 Spectra	Auto MS/MS	off



Component	Molecular Mass	Molecule	Absolute Abundance	Relative Abundance
A	10111.2	10111.2 [M + H] ⁺	238874	100.00

Component A Detail

Actual Peak	Charge	Isotopic Mass ([M + H] ⁺)	Predicted Peak
1264.9	8+	10112.0	1264.9
1445.4	7+	10111.6	1445.3
1686.0	6+	10111.1	1686.0
2022.9	5+	10110.7	2023.0

Molecular Mass ([M + H]⁺): 10111.2 Std. Deviation: 0.340912

Average Mass ([M + H]⁺): 10111.2

Figure 27. ESI⁺-MS of compound 13

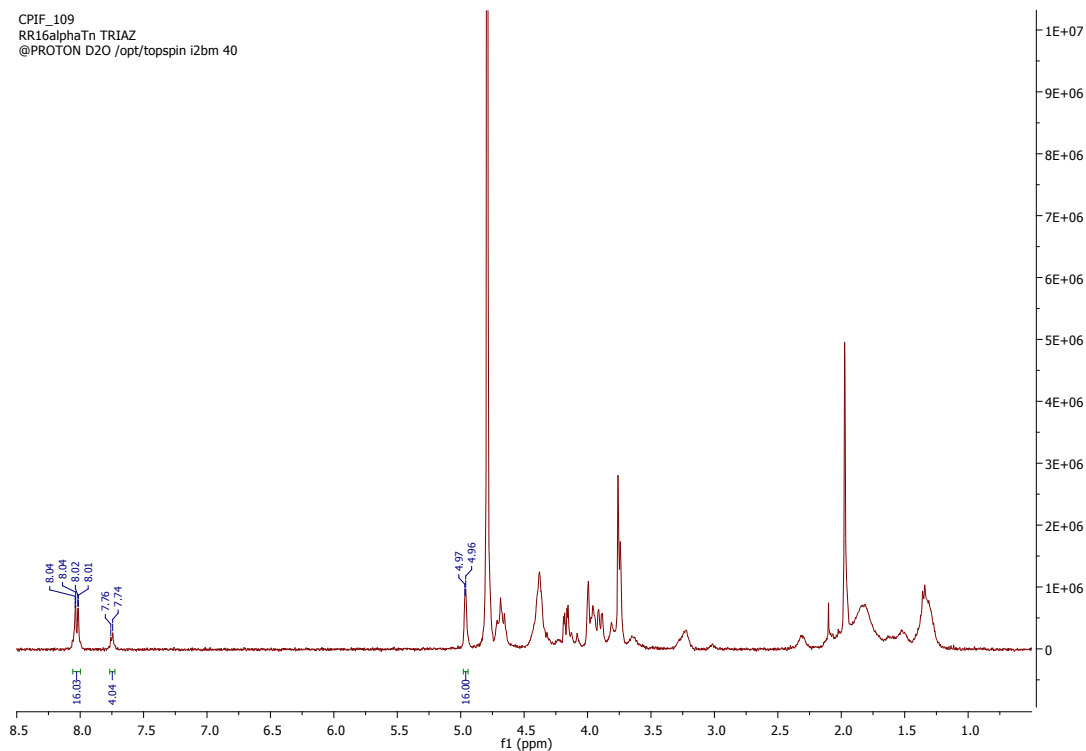


Figure 28. ¹H NMR (D₂O, 400 MHz) of compound 13

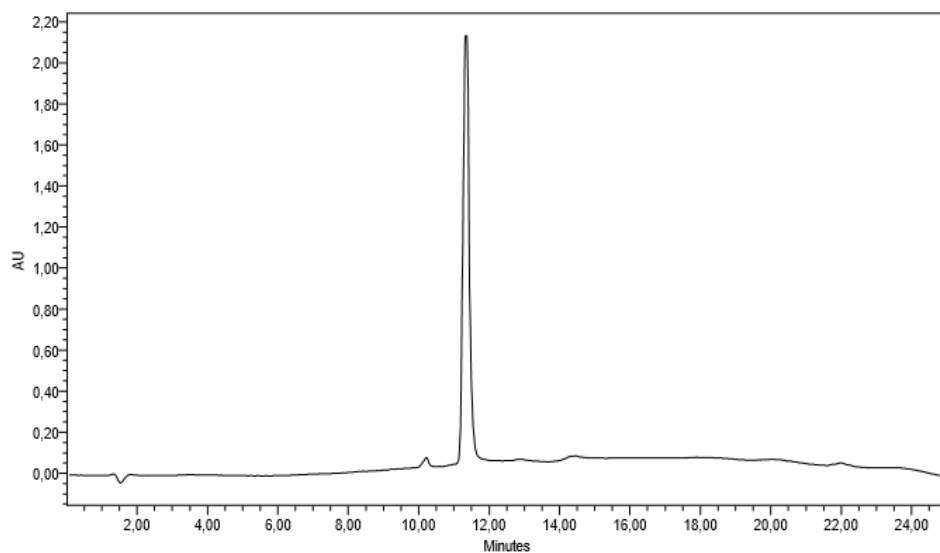


Figure 29. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **14**

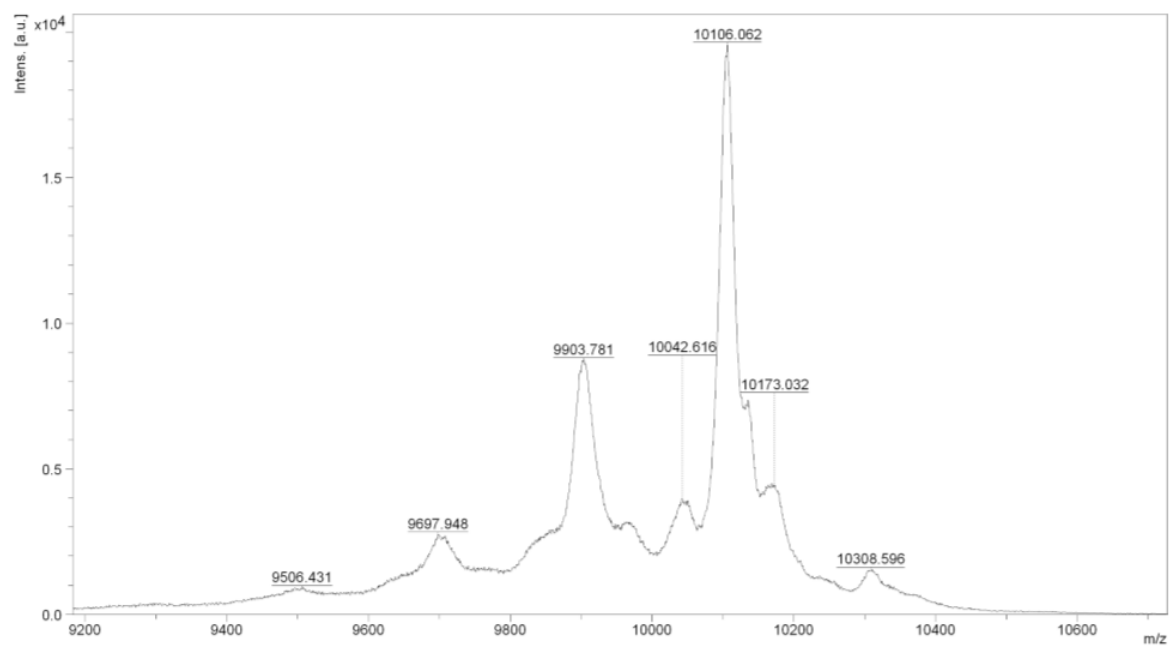


Figure 30. MALDI-TOF of compound **14**

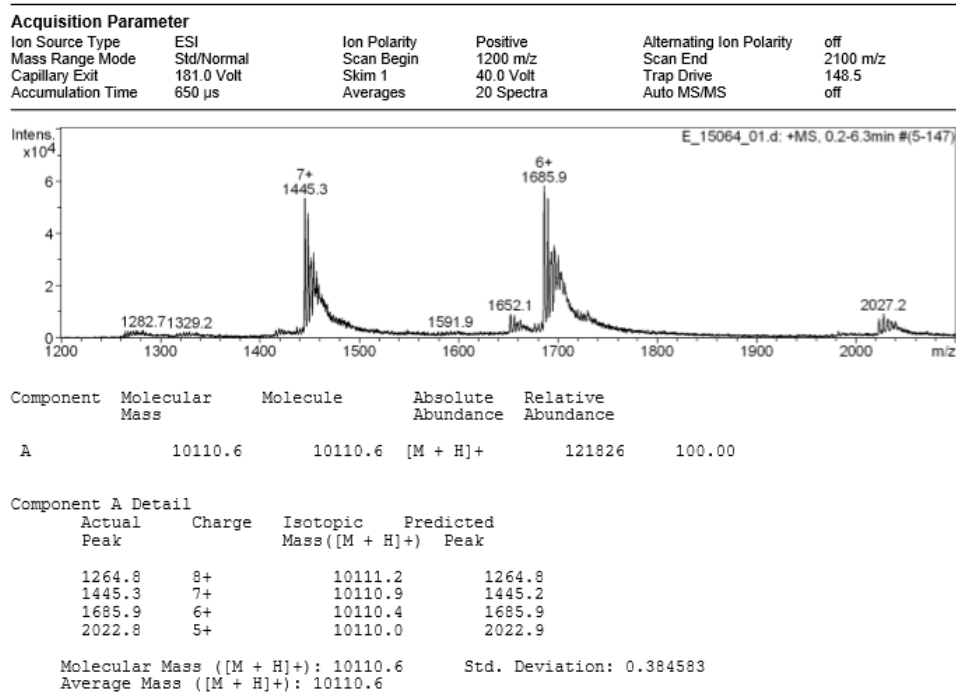


Figure 31. ESI⁺-MS of compound **14**

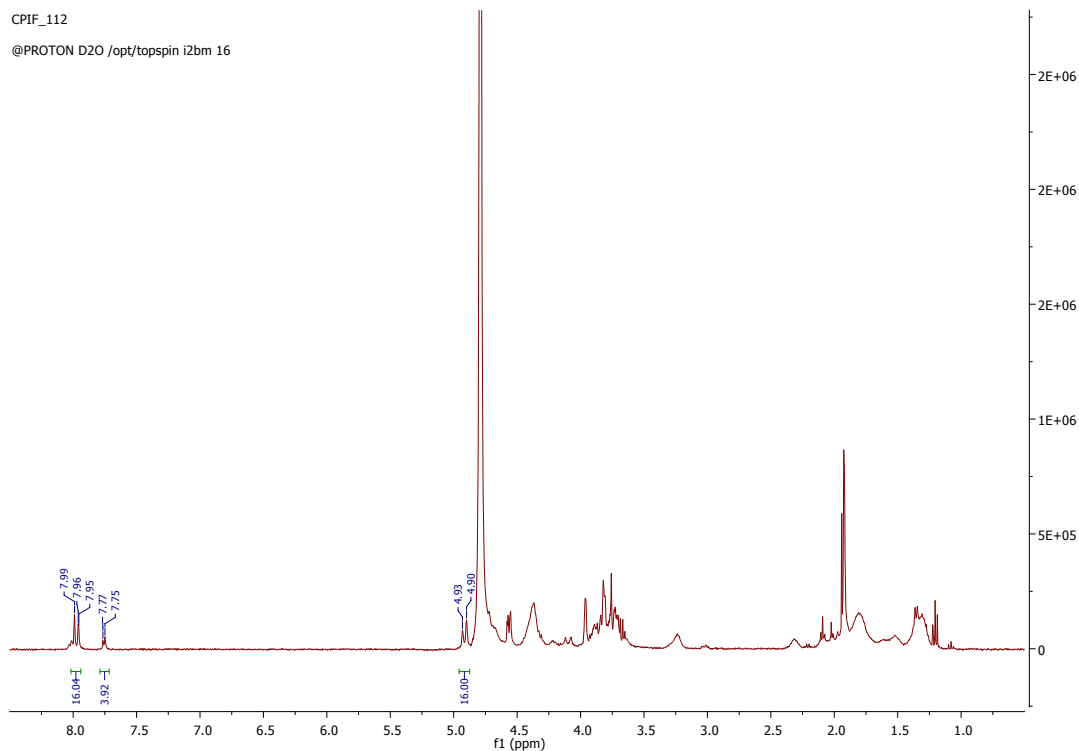


Figure 32. ¹H NMR (D₂O, 400 MHz) of compound **14**

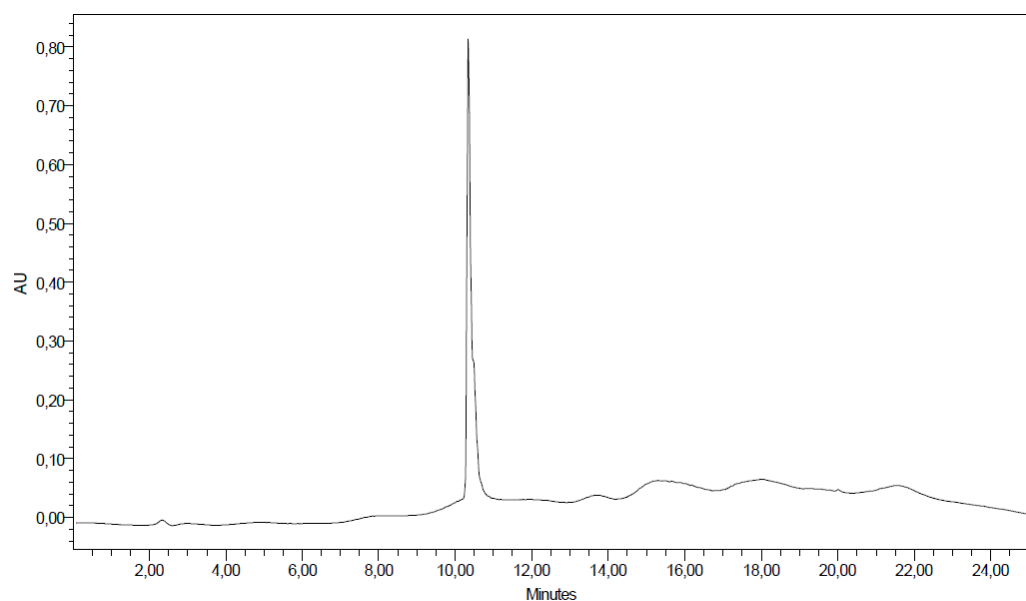


Figure 33. RP-HPLC (C_{18} , $\lambda = 214$ nm 5-100% B in 20 min) of compound **15**

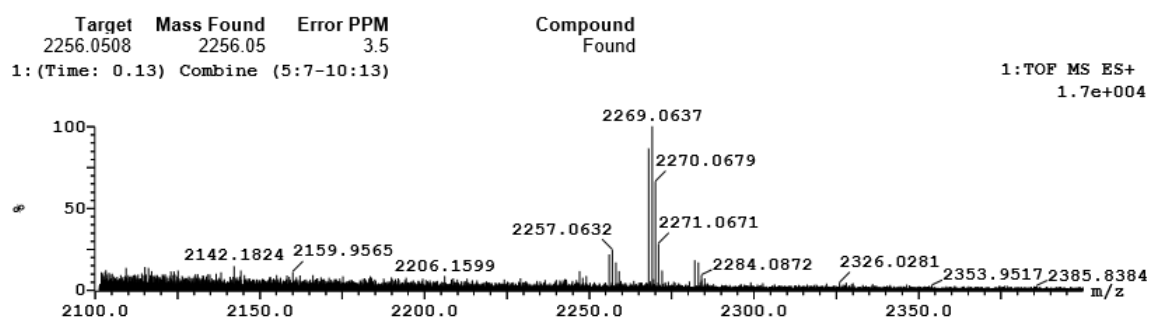


Figure 34. HRMS (ESI⁺-TOF) of compound **15**