

Electronic Supporting Information **Part 2**

*meso*-Tetra(pentafluorophenyl)porphyrin as an Efficient  
Platform for Combinatorial Synthesis and the Selection  
of New Photodynamic Therapeutics using a Cancer Cell

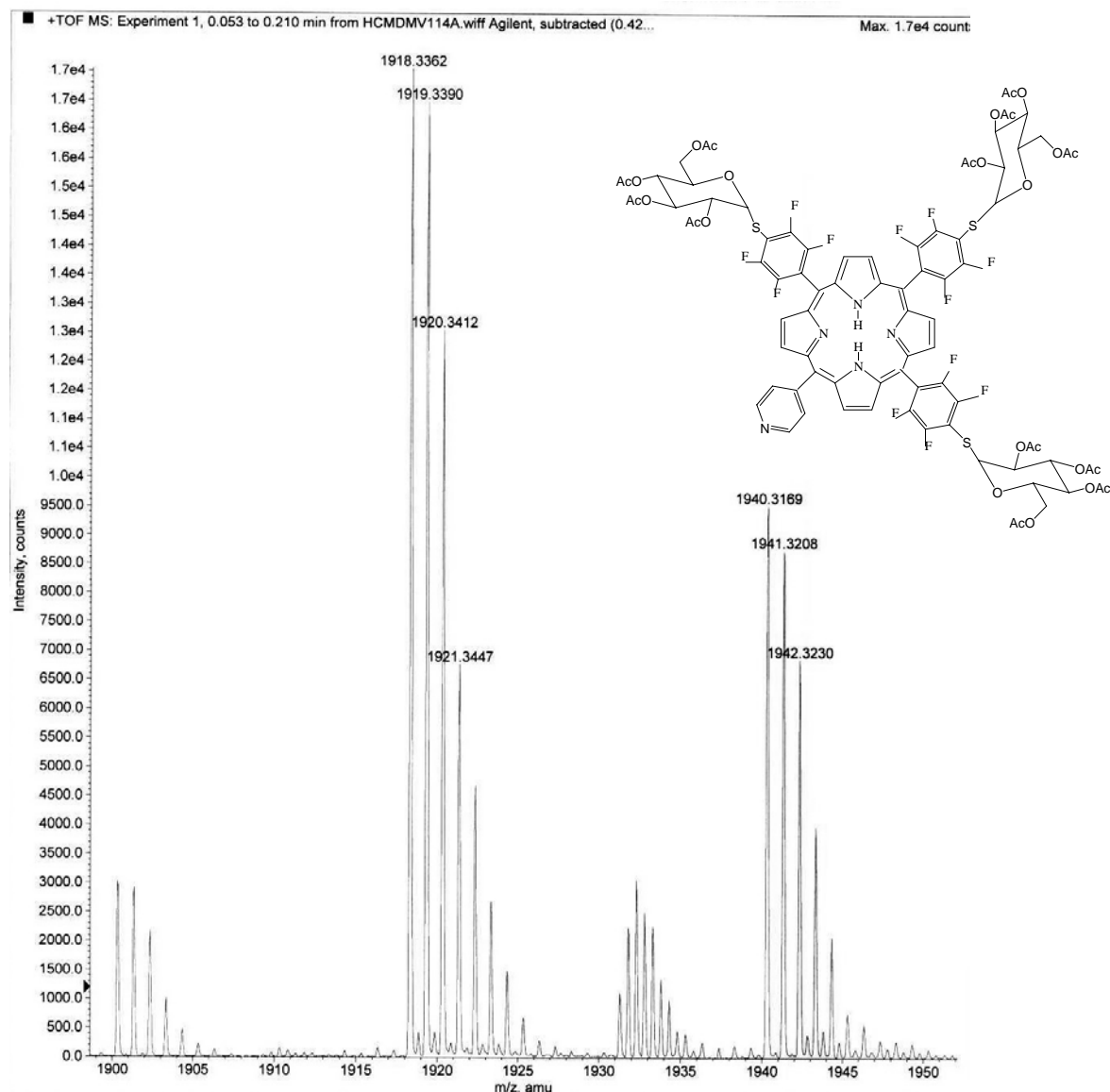
Line<sup>†</sup>

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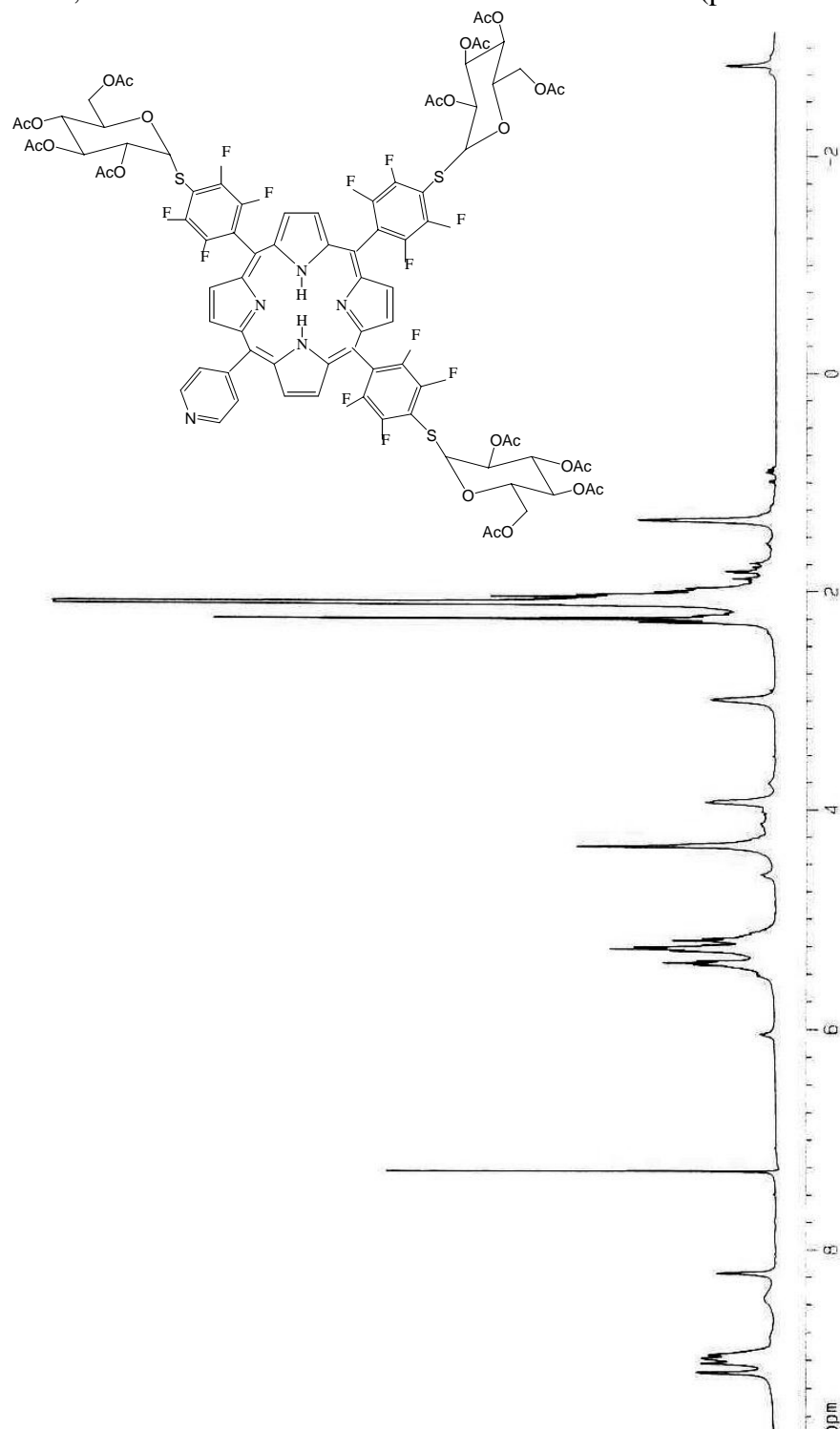
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University of New York, 695 Park Avenue, New York, NY 10021, <sup>b</sup>The Rockefeller University, 1230  
York Avenue, New York, NY 10021

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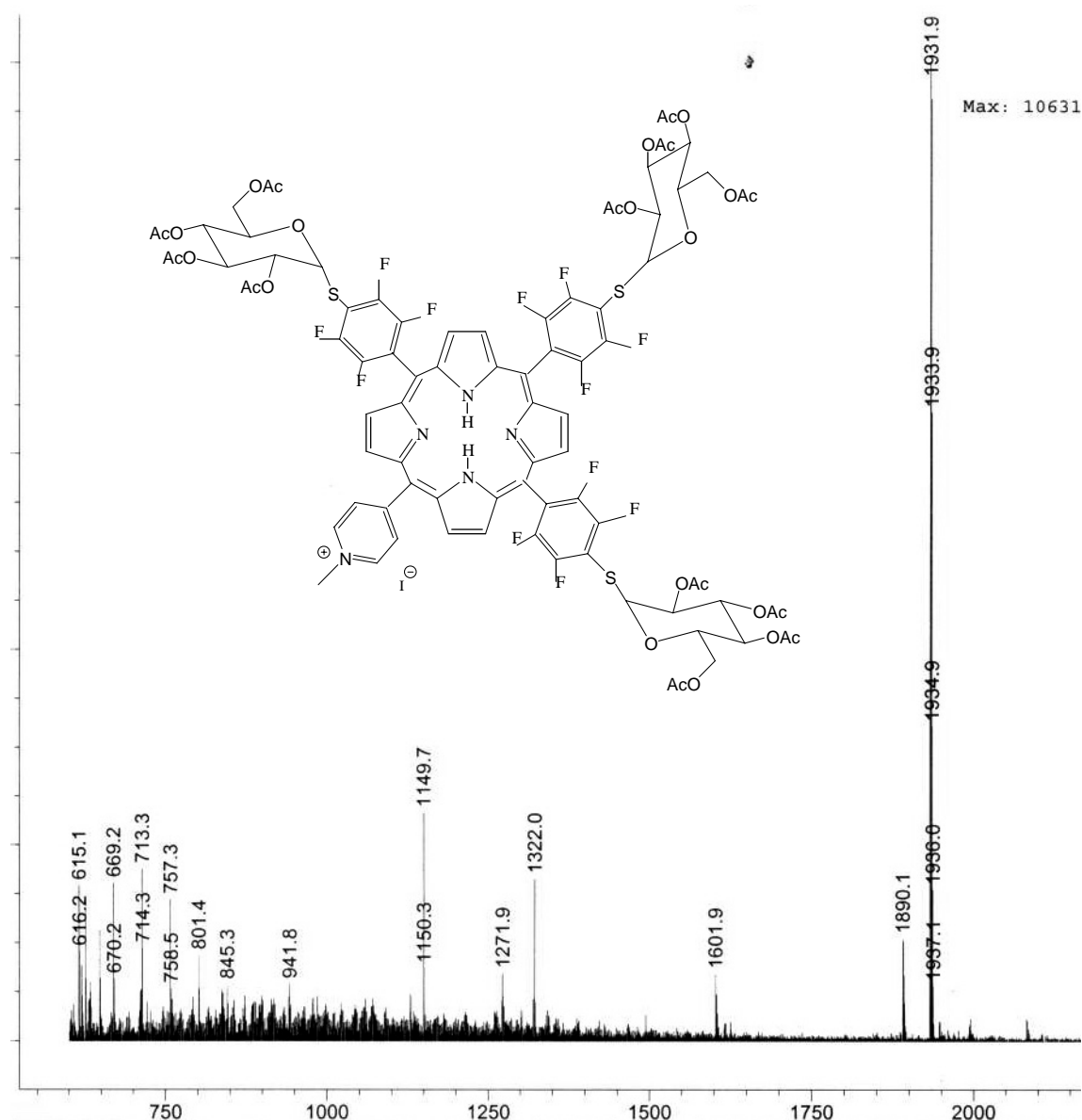
†Dedicated to the memory of R. Bruce Merrifield, friend and colleague.

**Spectral characterization of the newly synthesized mixed aryl porphyrin systems: meso pyridyl and tetrafluorophenyl glycosyl porphyrins.**

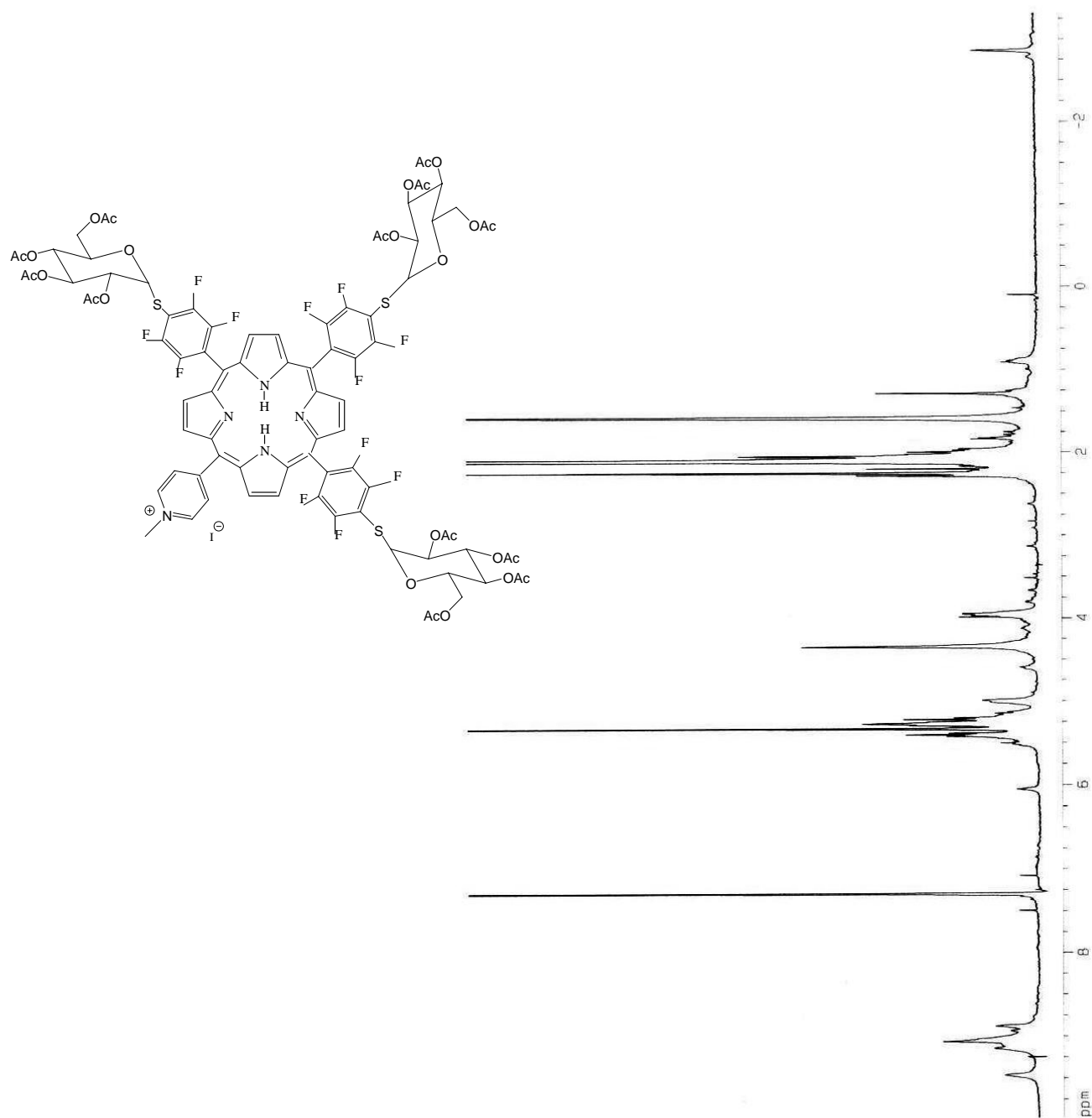
**Figure ESI-22:** ESI-TOF-MS of **GluAc/GluAc/GluAc/Py**: Peak at m/z 1918 is for  $M+H^+$ , 1940 is  $M+Na^+$



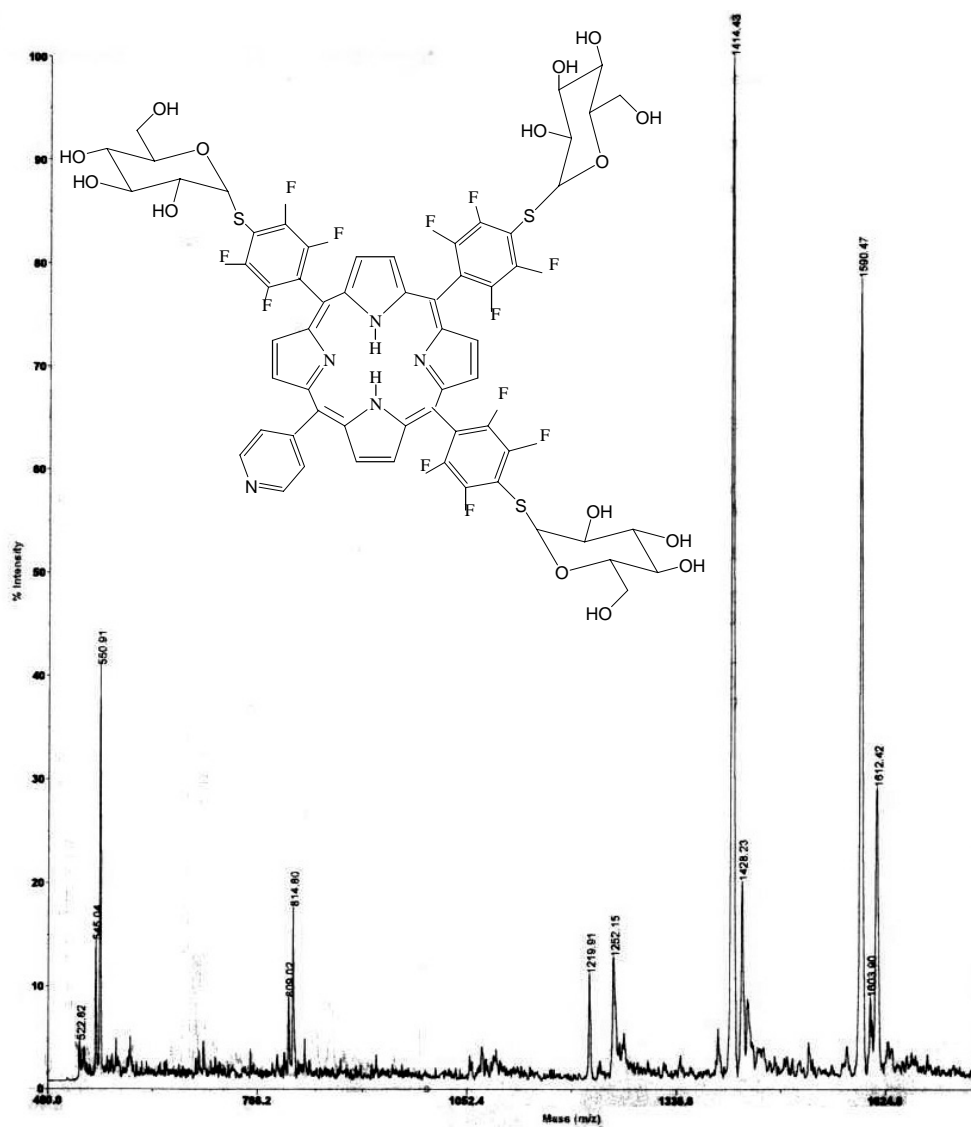
**Figure ESI-23: GluAc/GluAc/GluAc/Py:** NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  = 9.12 (d,  $J$  = 2.5Hz, 2H), 8.99 (m, 8H), 8.22 (d,  $J$  = 4.7 Hz, 2H), 5.41 (t, 3H), 5.24 (m, 9H), 4.34 (s, 6H), 3.92 (m, 3H), 2.25 (m, 9H), 2.10 (m, 27H) and -2.82 (s, 2H). (Solvent peaks are at 7.28, 2.99 and 1.34)



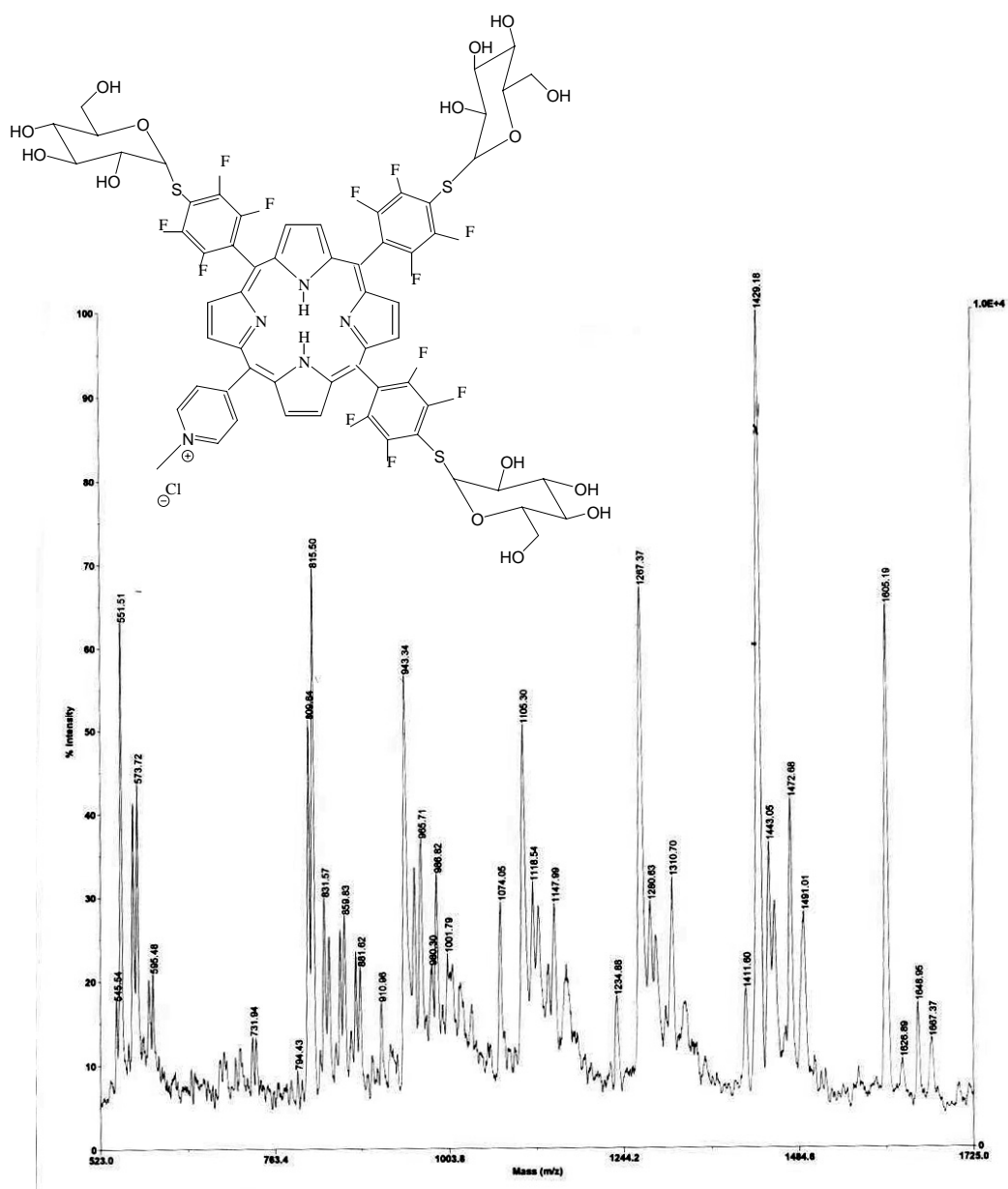
**Figure ESI-24:** ESI-MS (API) of  $\text{GluAc/GluAc/GluAc/Py}^+$ : Peak at 1931 is for  $\text{M} - \text{I}$ .



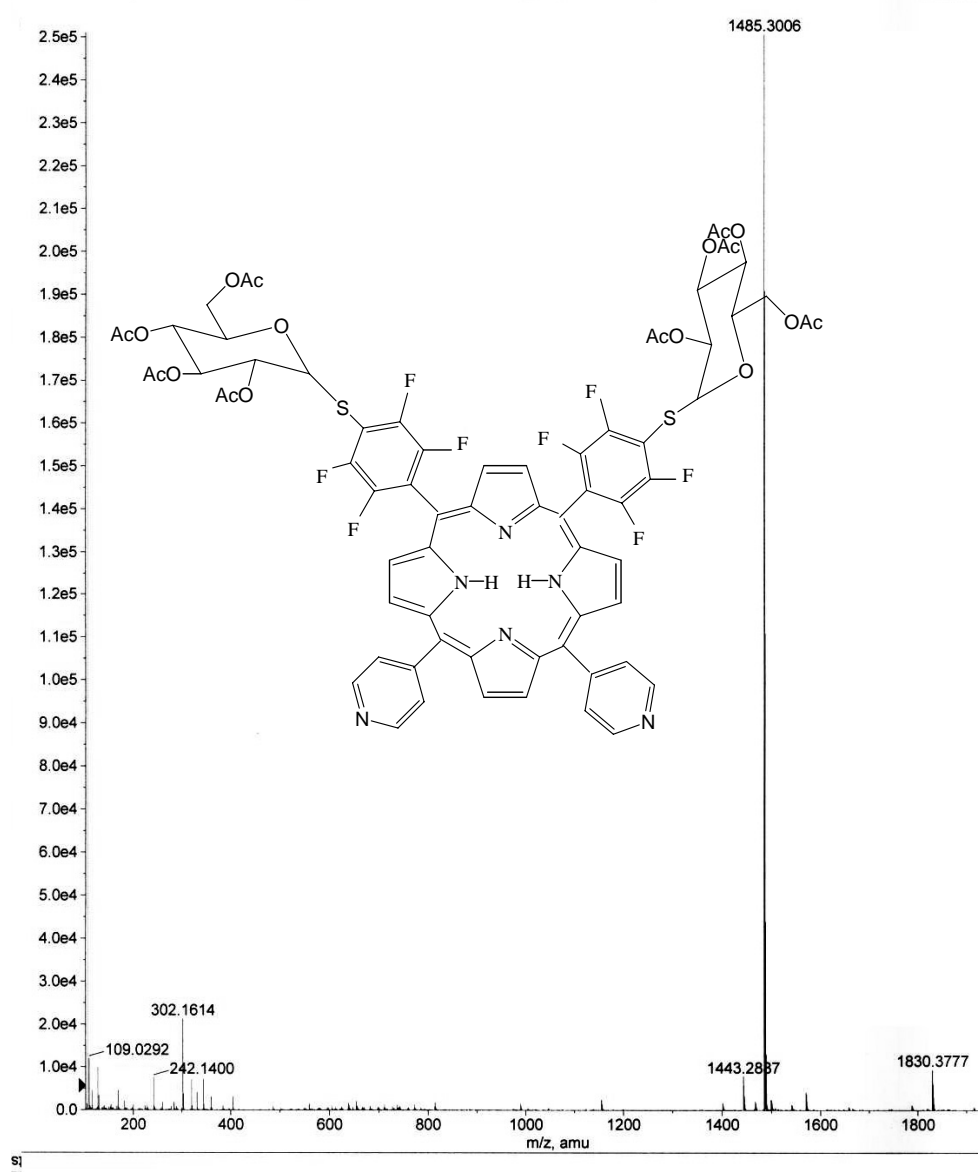
**Figure ESI-25: GluAc/GluAc/GluAc/Py<sup>+</sup>:** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  = 9.46 (S (br), 2H), 9.10 (m, 8H), 8.87 (s (br) 2H), 5.41 - 5.19 (m, 12H), 4.99 (s, 3H), 4.34 (s, 6H), 3.96 (m, 3H), 2.25 (m, 9H), 2.10 (m, 27H) and -2.86 (s, 2H). (Solvent peaks at 7.28, 5.32, 1.58 and 1.29)



**Figure ESI-26:** MALDI-MS of **Glu/Glu/Glu/Py**: Peak at 1414 is for  $M+H^+$ , 1590 is  $M + Na^+ + 2,5$ -dihydroxybenzoic acid (matrix).

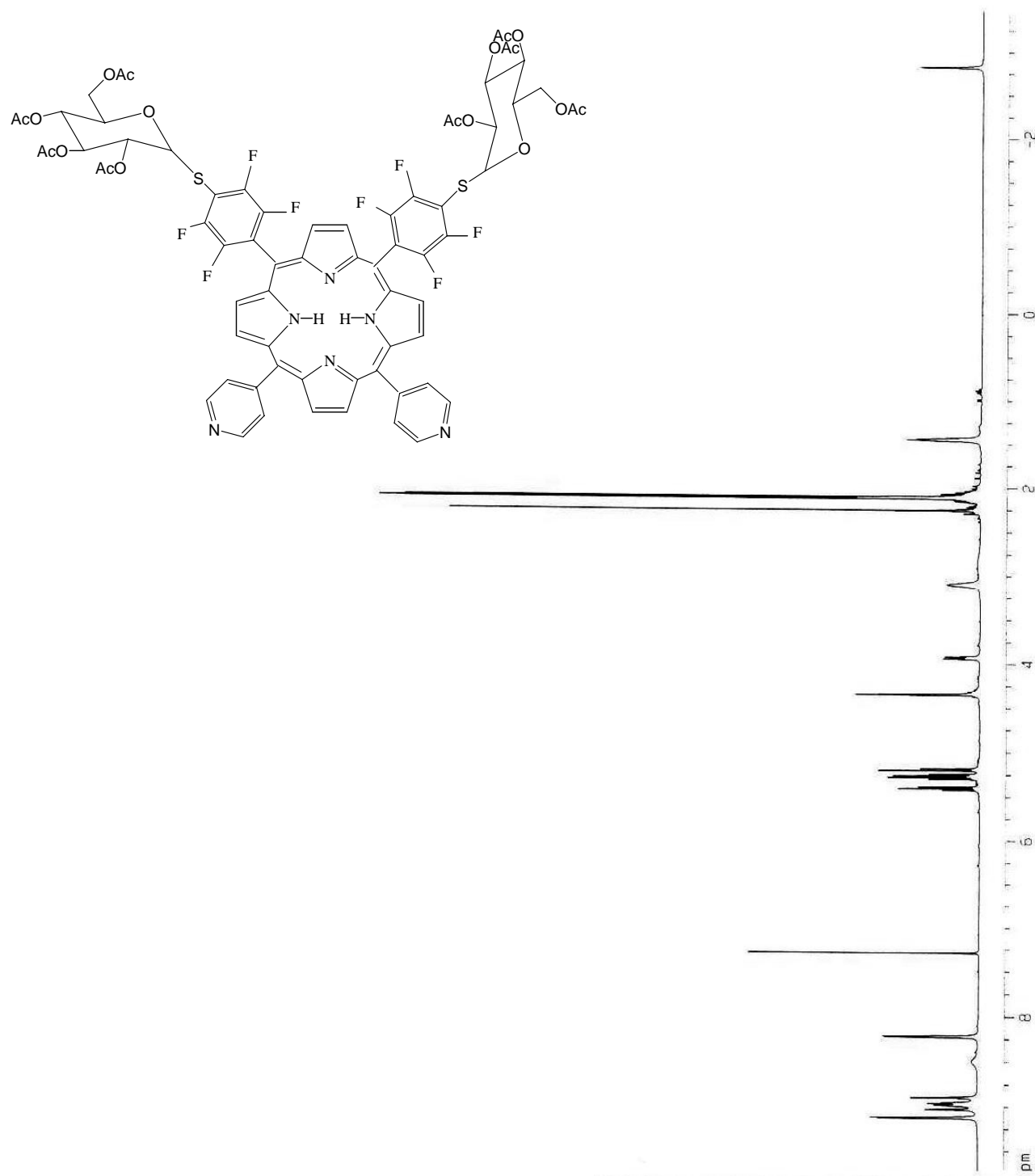


**Figure ESI-27:** MALDI-MS of  $\text{Glu/Glu/Glu/Py}^+$ : Peak at  $m/z$  1429 is for  $\text{M-Cl}^-$ , 1605 is  $\text{M-Cl}^- + \text{Na} + 2,5\text{-dihydroxybenzoic acid}$  (calibration matrix), other major peaks are -162 mass units indicating some S<sub>Glu</sub> fractions were lost during MALDI measurements.

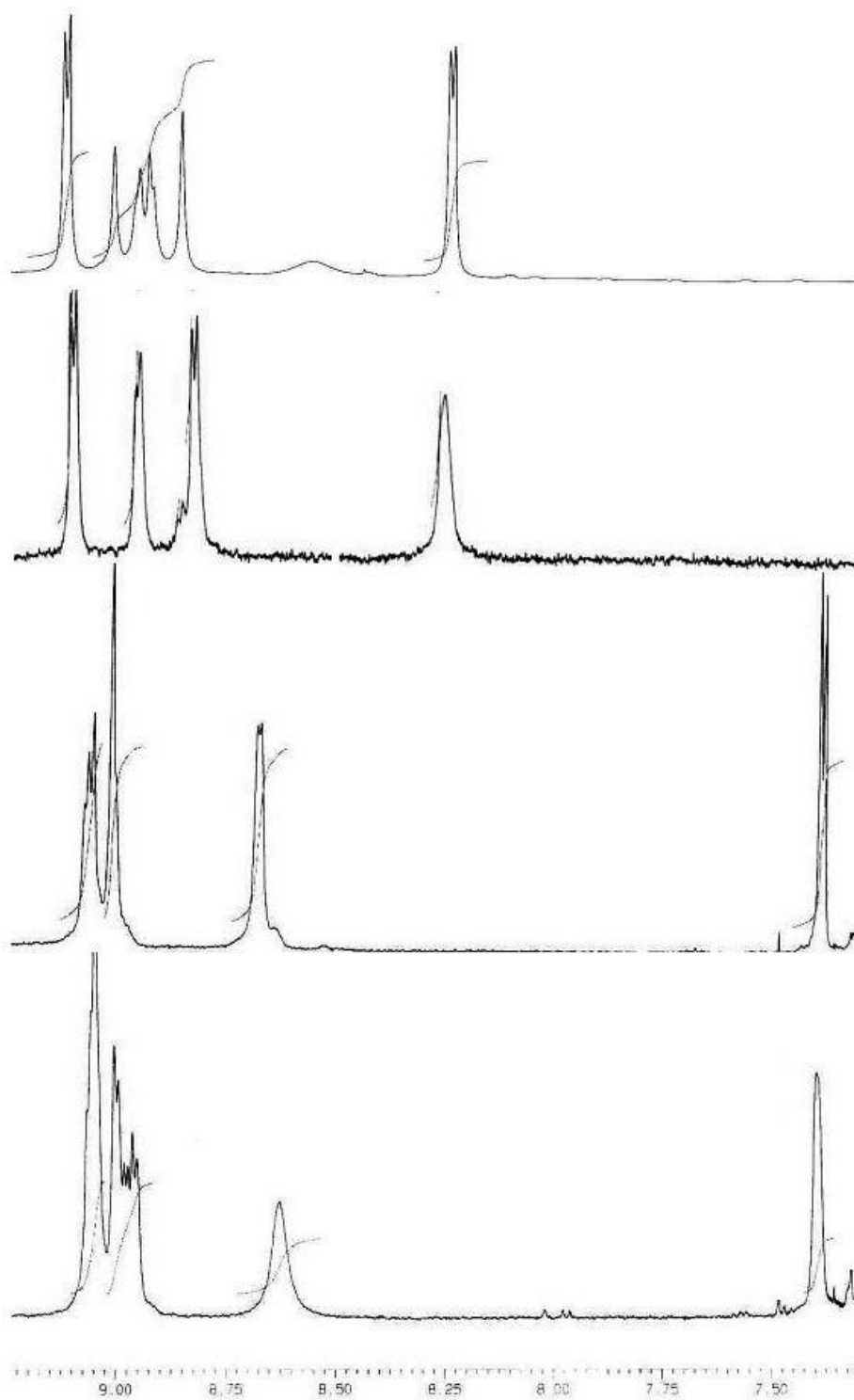


**Figure ESI-28:** ESI-TOF-MS of GluAc/GluAc/Py/Py: Peak at  $m/z$  1485 is for  $M+H^+$ .



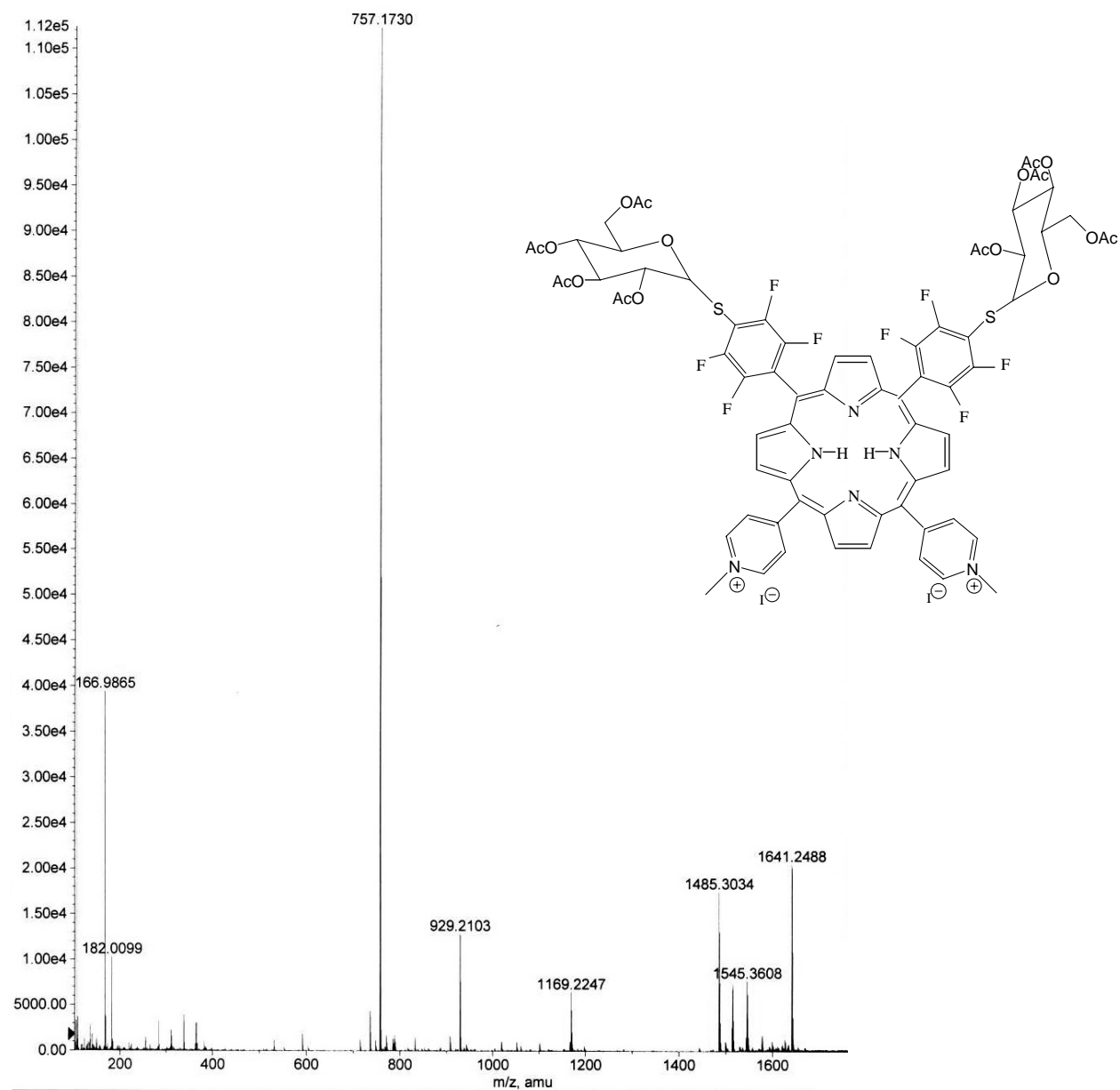


**Figure ESI-29: GluAc/GluAc/Py/Py:** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  = 9.12 (d, J = 5.1 Hz, 4H), 8.96 (m, 8H), 8.22 (d, J = 5.1 Hz, 4H), 5.40 (t, 2H), 5.23 (m, 6H), 4.33 (s, 4H), 3.92 (m, 2H), 2.25 (m, 6H), 2.10 (m, 18H) and -2.81 (s, 2H). (Solvent peaks at 7.28, 3.00 and 1.44)

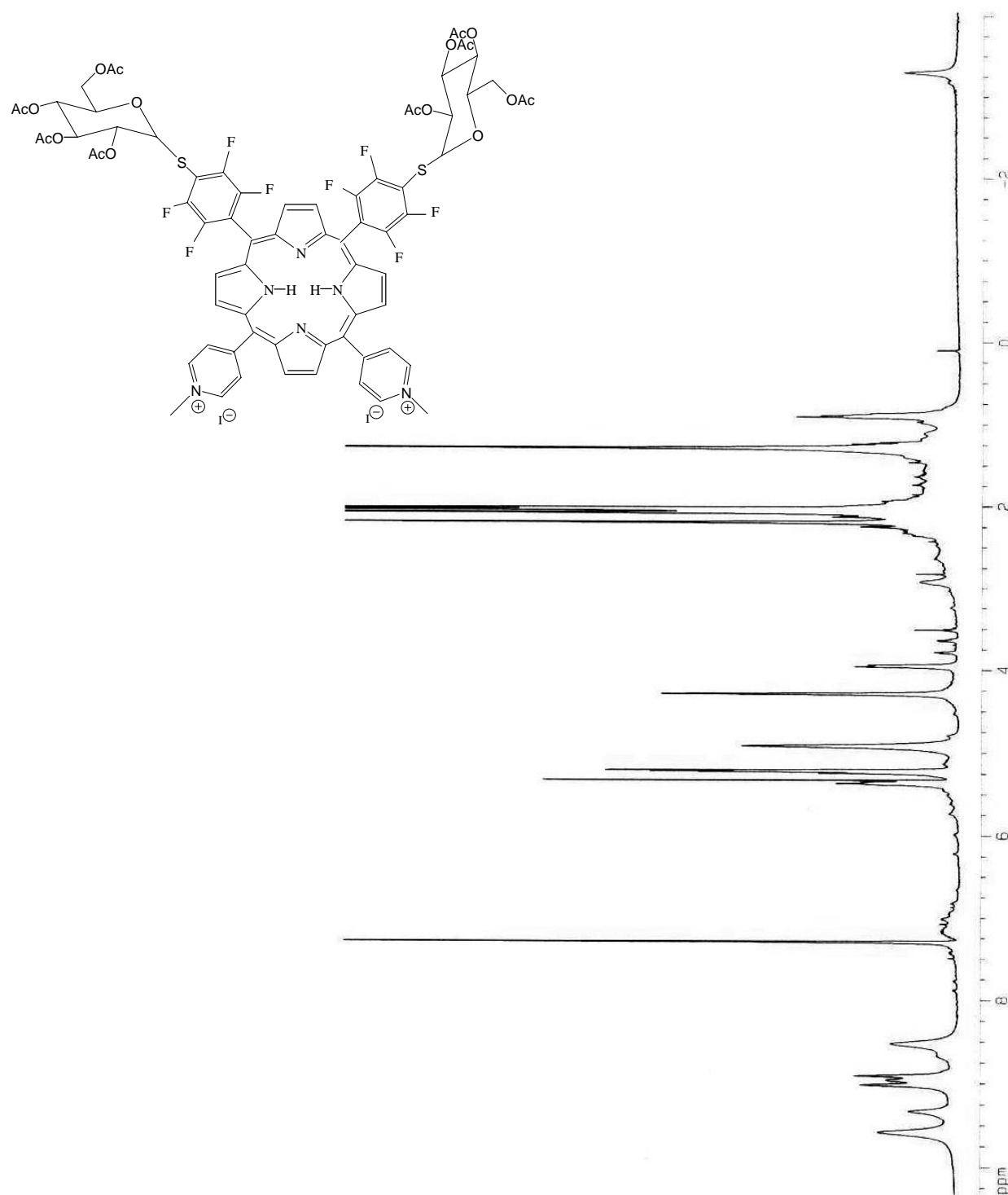


**Figure ESI-30:** Comparison of the aromatic regions in the  $^1\text{H}$  NMR of 5,10 and 5,15 pyridyl porphyrins, from the top: 1. **GluAc/GluAc/Py/Py**, 2. **GluAc/Py/GluAc/Py**, 3. **GluAc/GluAc/SPy/SPy** and 4. **GluAc/GluAc/SPy/SPy**.

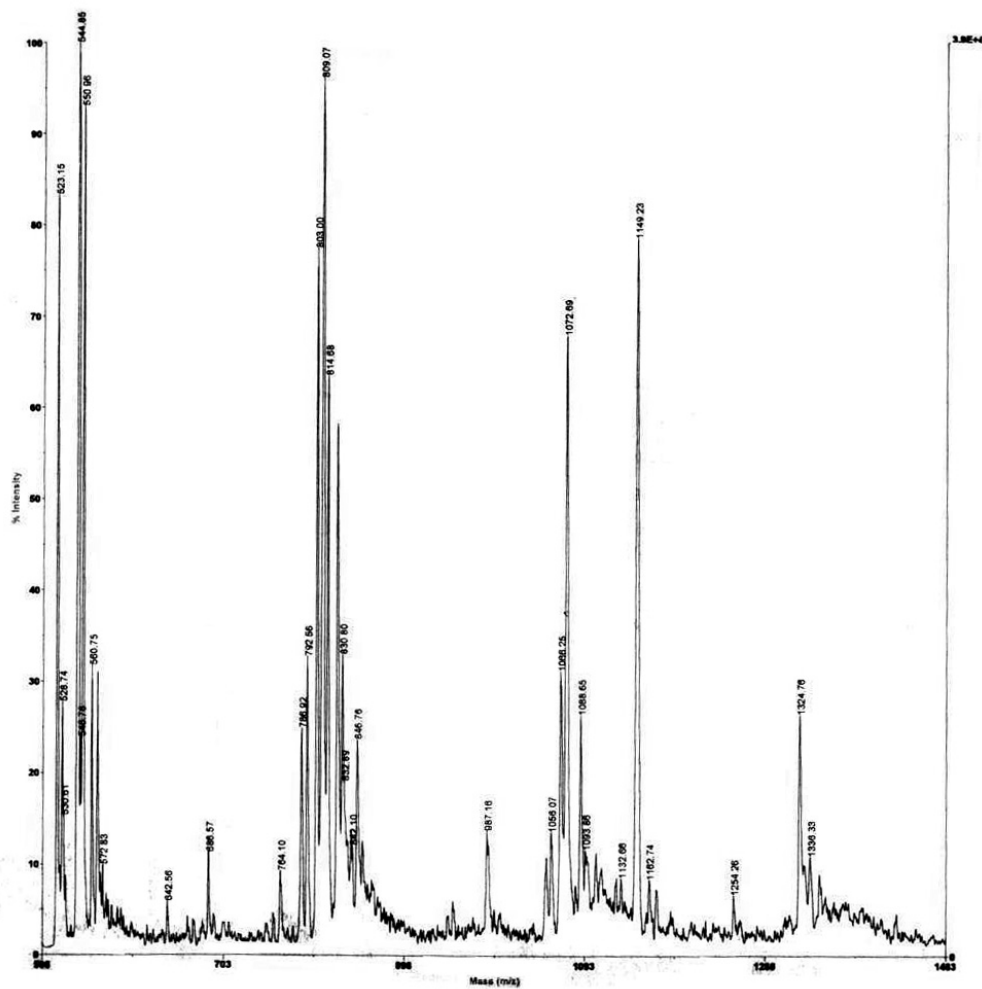
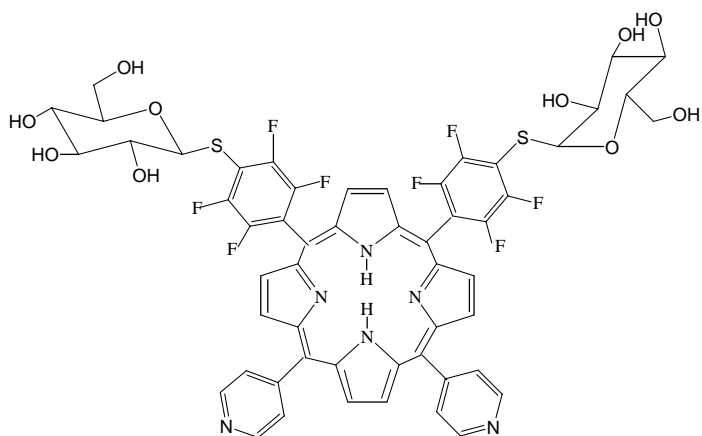
+TOF MS: Experiment 1, 0.068 to 0.225 min from HCMDMV113A.wiff Agilent, subtracted (0.50...



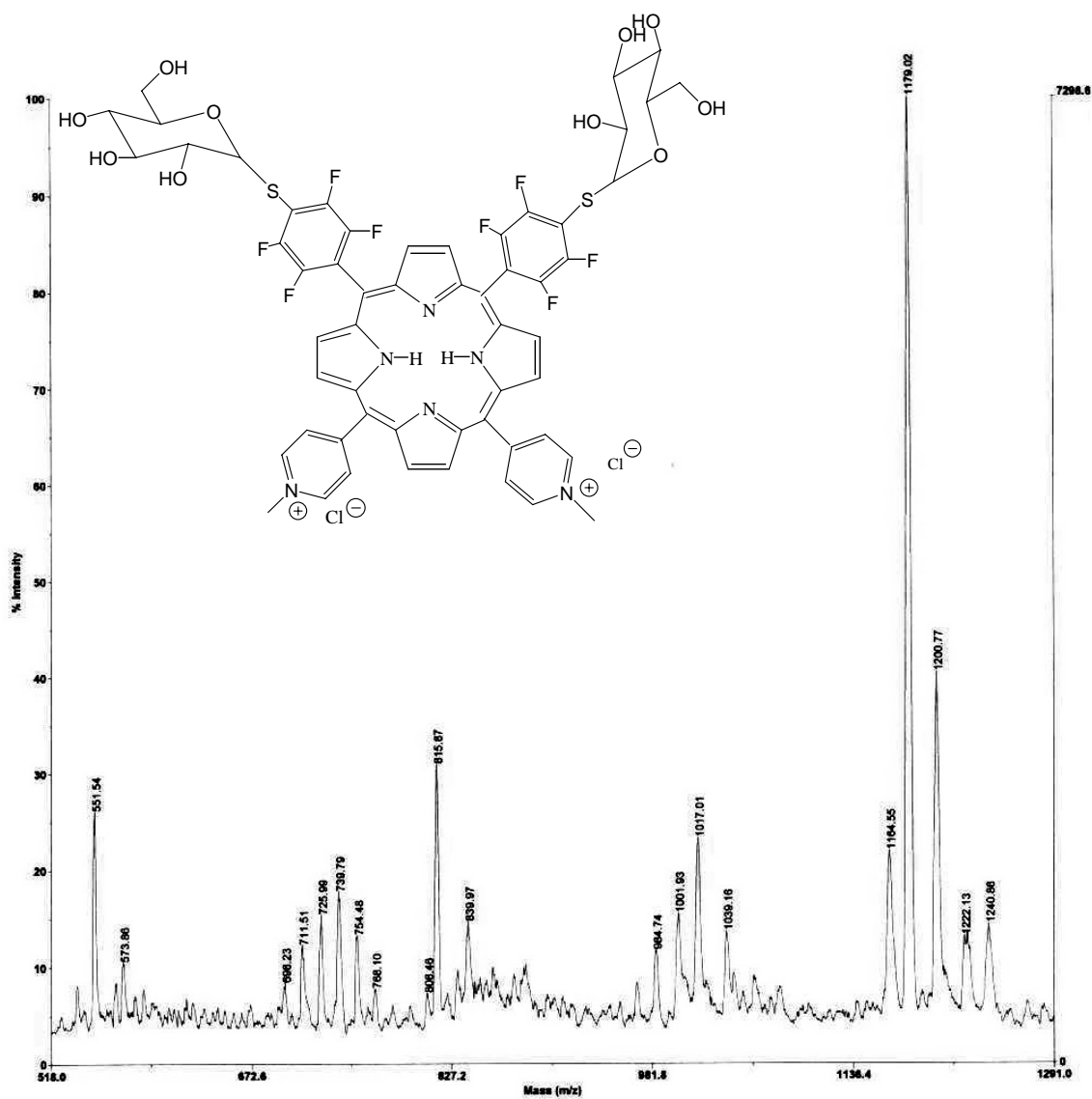
**Figure ESI-31:** ESI-TOF-MS of **GluAc/GluAc/Py<sup>+</sup>/Py<sup>+</sup>**: m/z peak at 1641 is for M - I, and at 757 is for (M - 2I)/2.



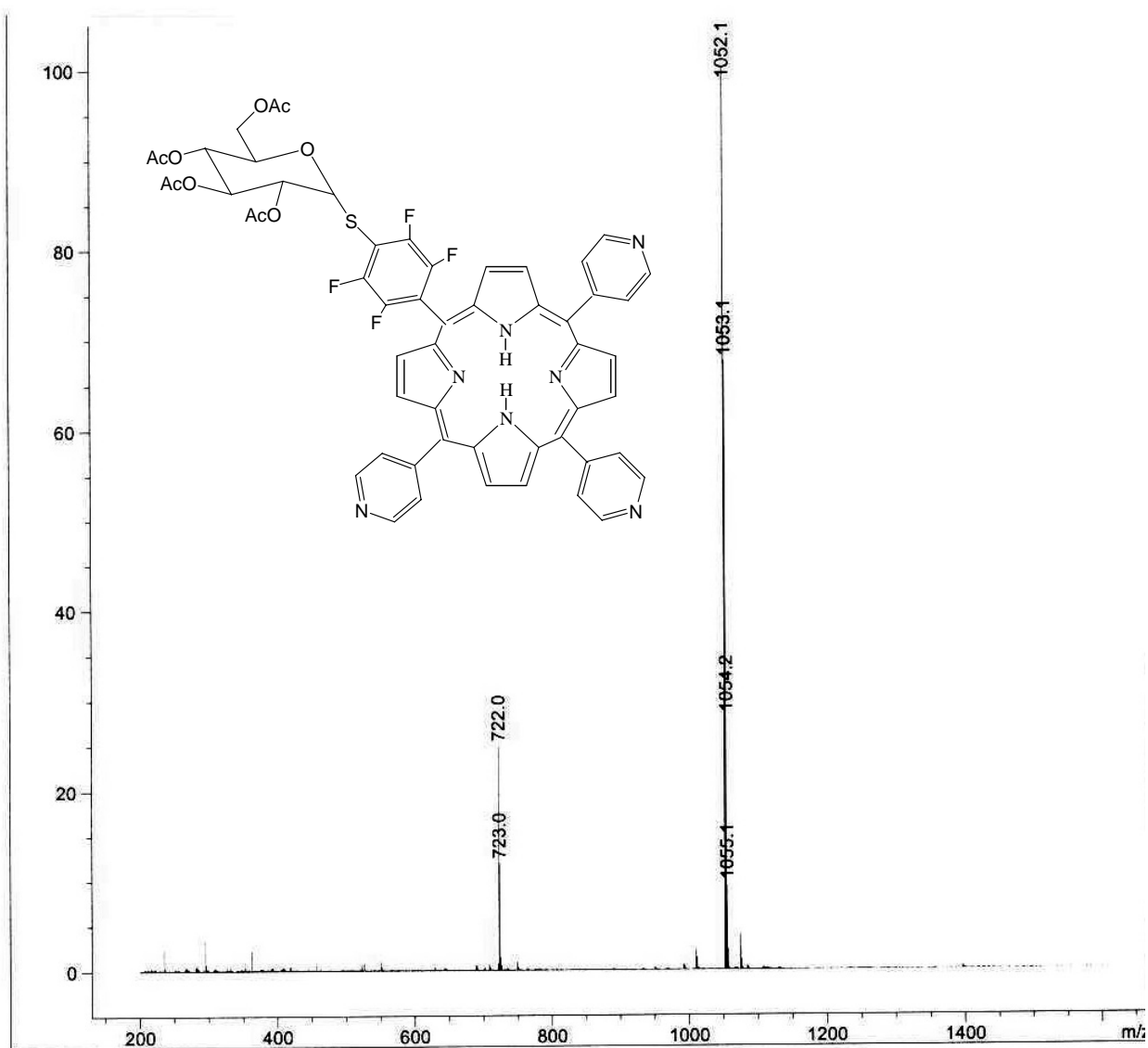
**Figure ESI-32: GluAc/GluAc/Py<sup>+</sup>/Py<sup>+</sup>:** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  = 9.58 (S, 4H), 9.33-8.90 (m, 8H), 8.52 (s, 4H), 5.38 - 5.20 (m, 8H), 4.91 (s, 6H), 4.28 (s, 4H), 3.94 (m, 2H), 2.19 (m, 6H), 2.03 (m, 18H) and -3.30 (s, 2H). (Solvent peaks at 7.28, 5.32, 1.28 and 0.88)



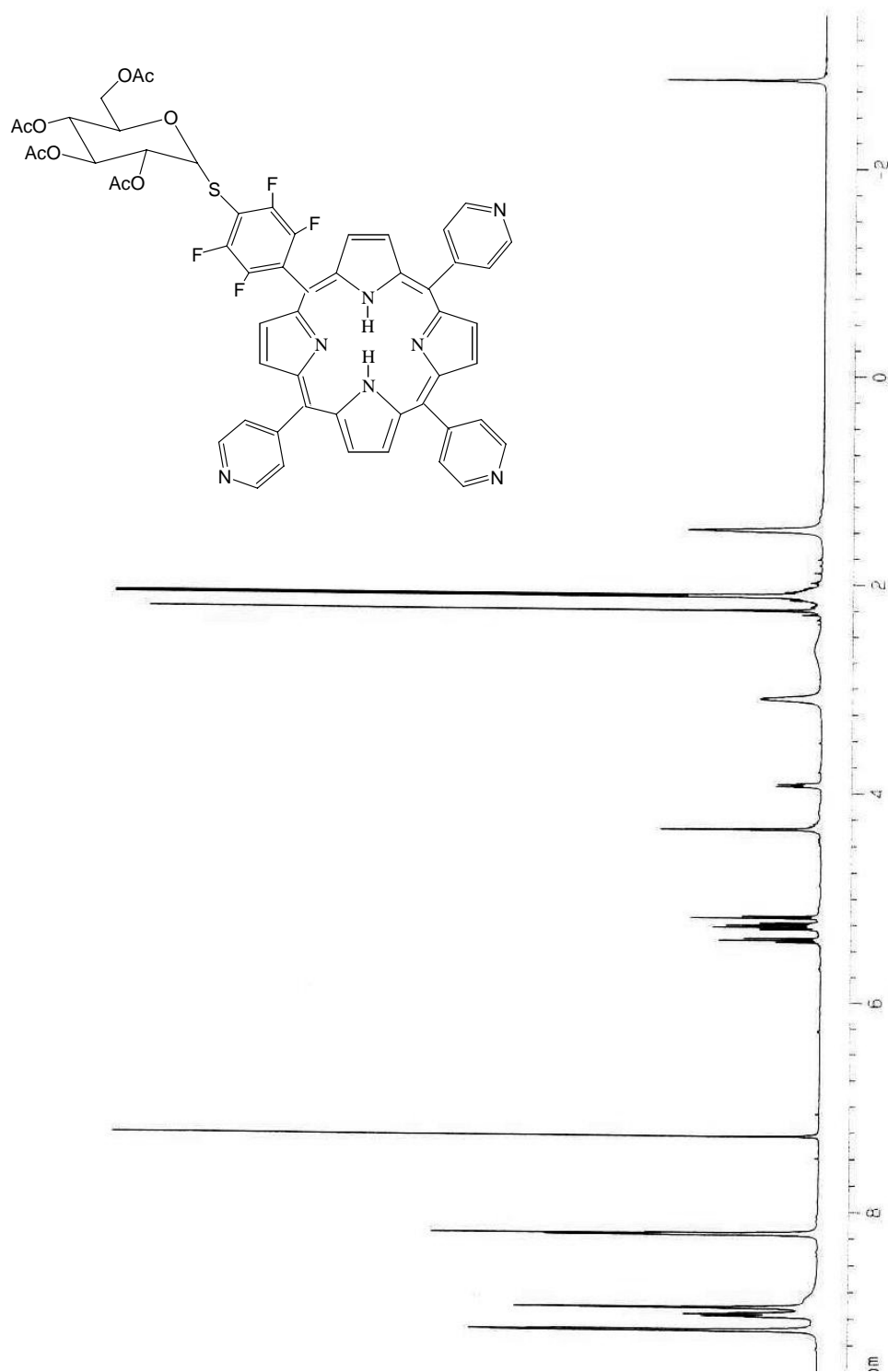
**Figure ESI-33:** MALDI-MS of **Glu/Glu/Py/Py**: the peak at  $m/z$  1149 is for  $M+H^+$ , 1324 is for  $M + Na^+ + 2,5$ -dihydroxybenzoic acid (matrix), and 1073 is for  $M$ -pyridine



**Figure ESI-34:** MALDI-MS of **Glu/Glu/Py<sup>+</sup>/Py<sup>+</sup>**: Peak at m/z 1179 is for M-2Cl<sup>-</sup>, and at 1201 is for M - 2Cl<sup>-</sup> + Na<sup>+</sup>)

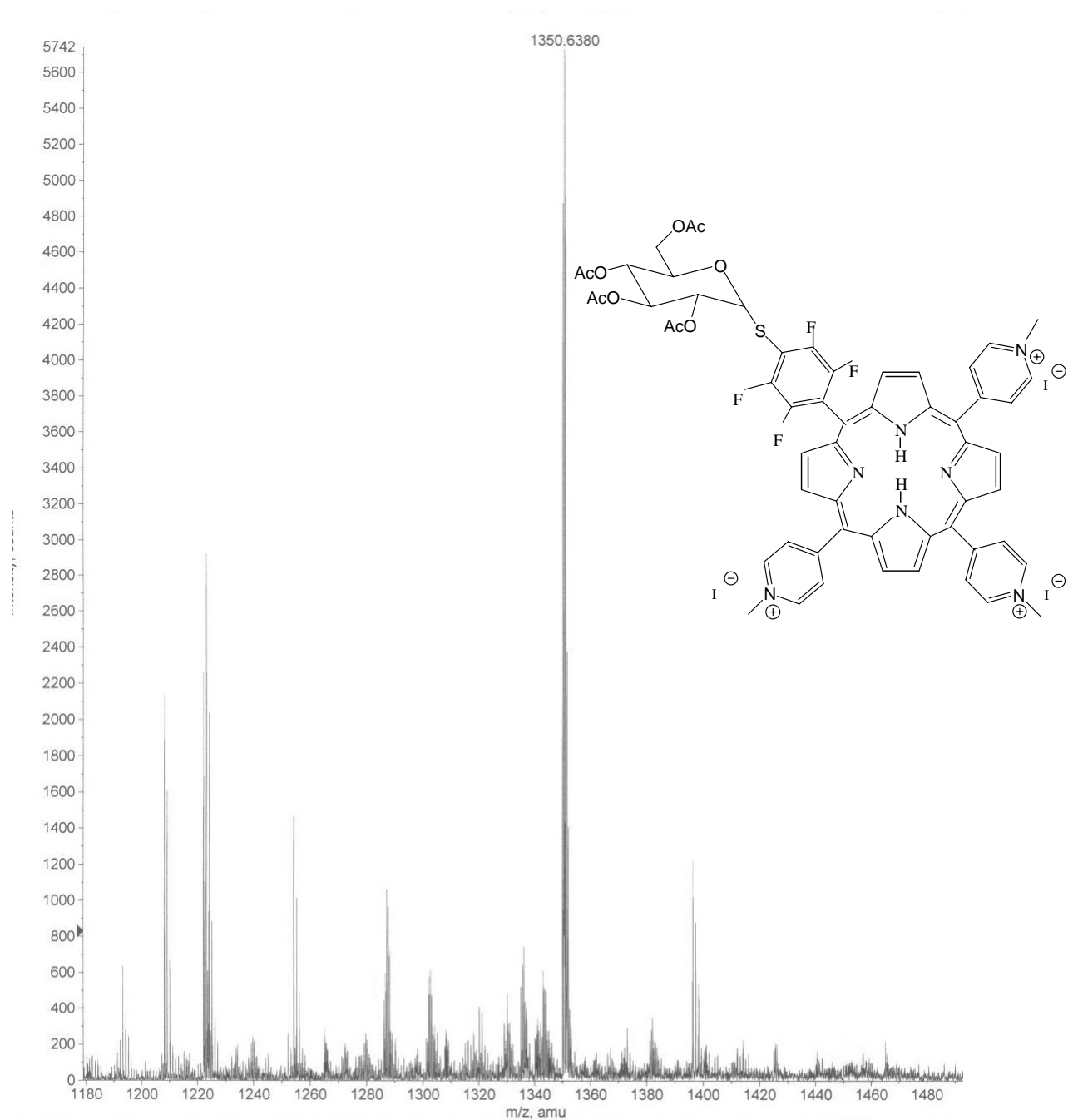


**Figure ESI-35:** ESI-MS (API) of **GluAc/Py/Py/Py**: Peak at m/z 1052 is for  $M+H^+$ .

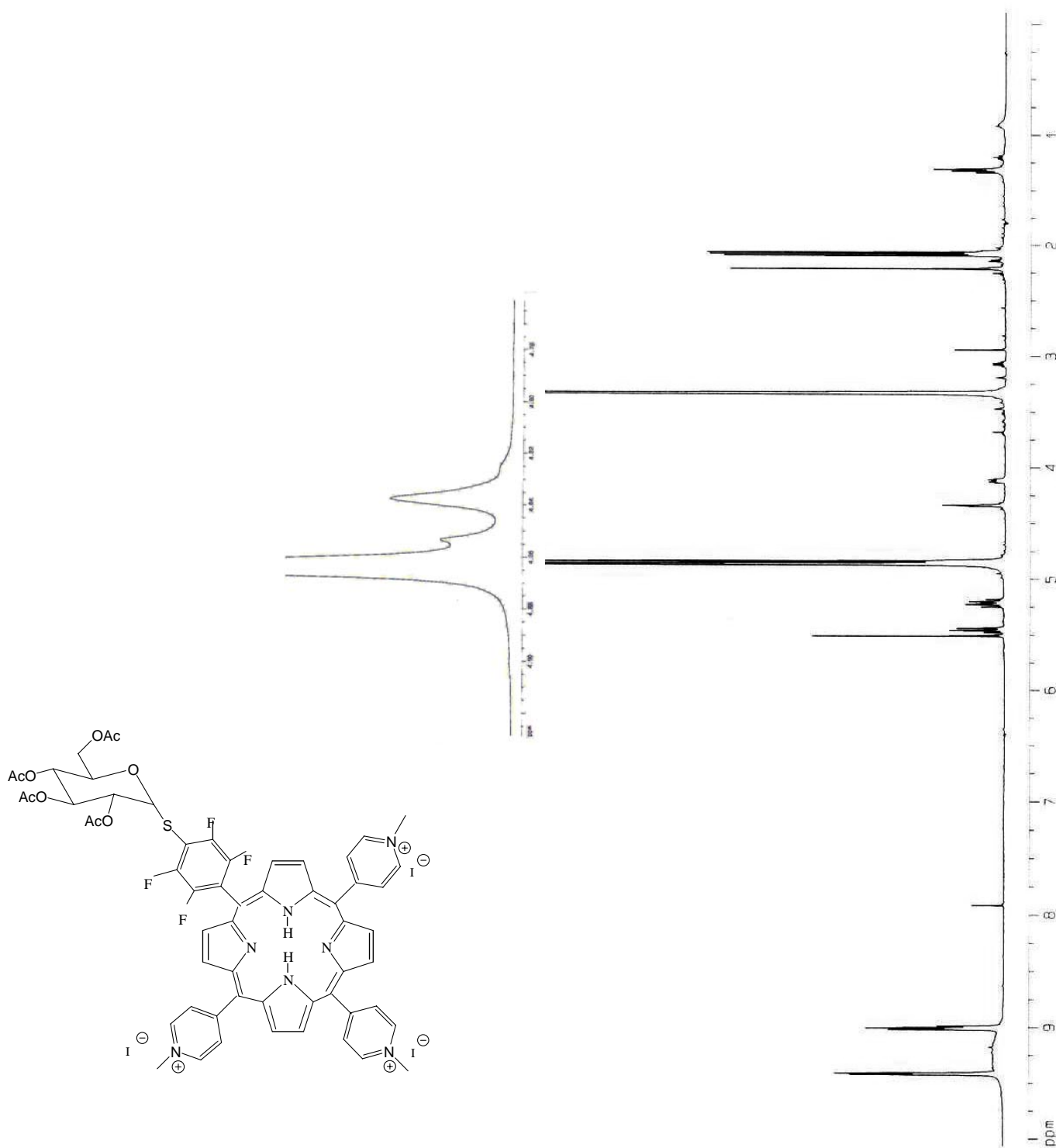


**Figure ESI-36: GluAc/Py/Py/Py** <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  = 9.11 (d, J 4.8 Hz, 6H), 8.94 (m, 8H), 8.21 (d, J = 5.3 Hz, 6H), 5.39 (t, 1H), 5.23 (m, 3H), 4.33 (s, 2H), 3.90 (m, 1H), 2.25 (m, 3H), 2.11 (m, 9H) and -2.85 (s, 2H). (Solvent peaks at 7.28, 3.10 and 1.48)





**Figure ESI-37:** ESI-TOF-MS of **GluAc/Py<sup>+</sup>/Py<sup>+</sup>/Py<sup>+</sup>**: peak at m/z 1350 is for M – I)



**Figure ESI-38: GluAc/Py<sup>+</sup>/Py<sup>+</sup>/Py<sup>+</sup>: <sup>1</sup>H NMR (500MHz, CD<sub>3</sub>OD):  $\delta$  = 9.42- 8.98 (m (20H), 5.50 - 5.19 (m, 4H), 4.83 (s, 9H), 4.33 (s, 2H), 4.10 (m, 1H), 2.21 (s, 3H), 2.07 (m, 9H). (Solvent peaks are at 5.50, 4.85, 3.33 and 1.31). Enlarged spectra between 4.92 and 4.76 are also shown to distinguish methanol peak and N<sup>+</sup>-CH<sub>3</sub> peaks**

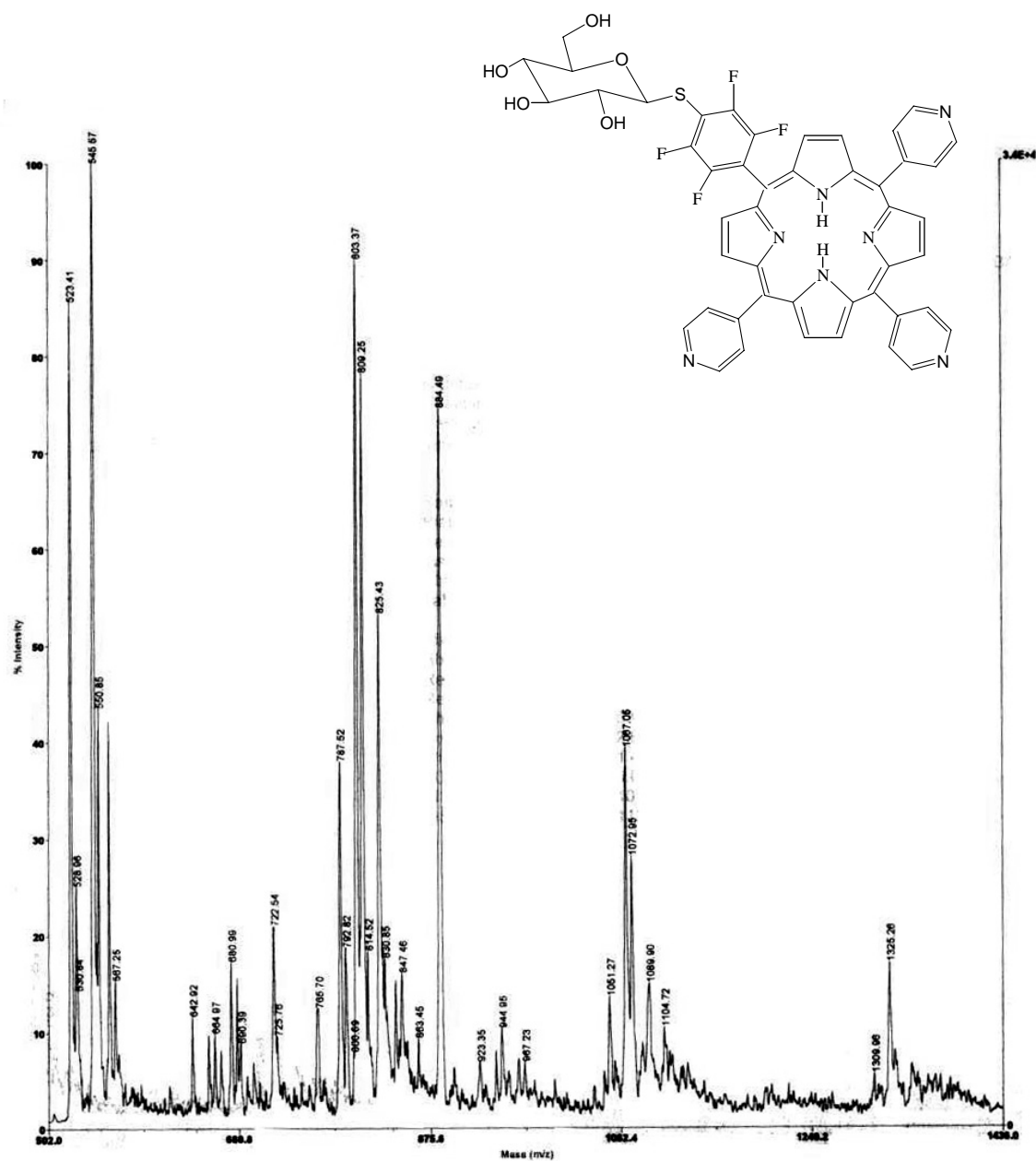
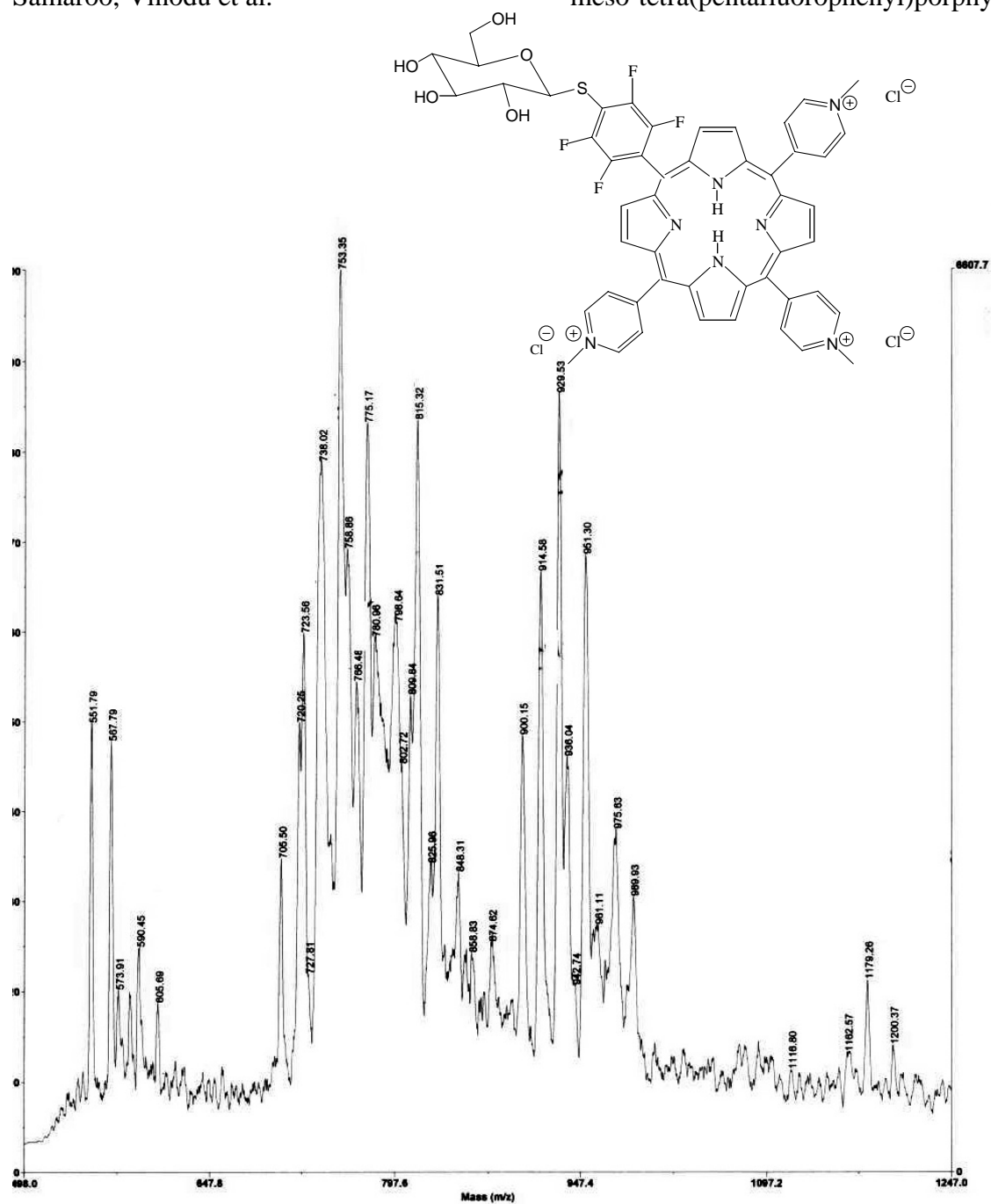
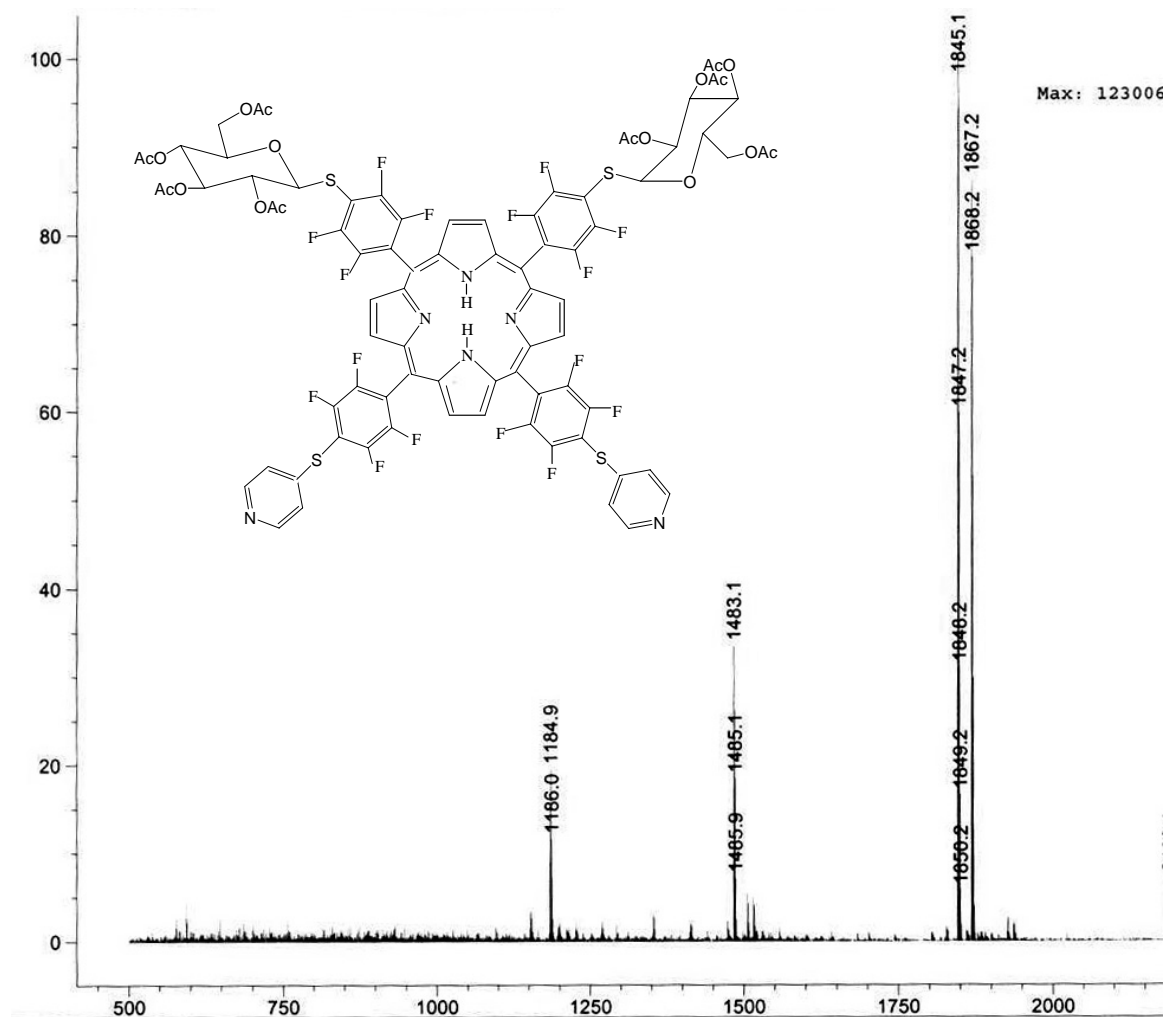


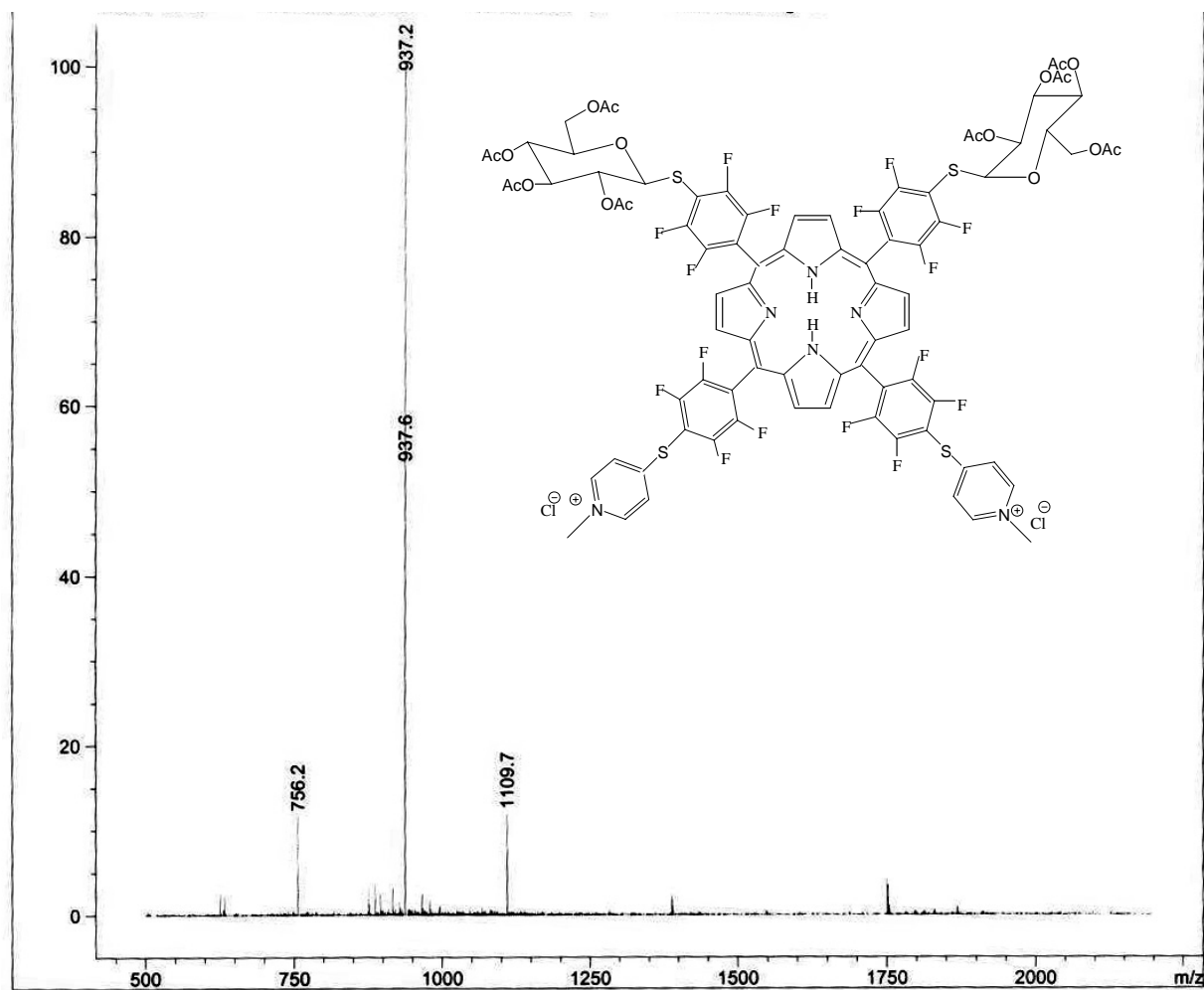
Figure ESI-39: MALDI-MS of Glu/Py/Py/Py: Peak at  $m/z$  884 is for  $M+H^+$ .



**Figure ESI-40:** MALDI-MS of  $\text{Glu/Py}^+/\text{Py}^+$ : Peak at  $m/z$  929 is for  $M - 3\text{Cl}^-$ , 952 is  $M - 3\text{Cl}^- + \text{Na}^+$ , The other major peaks corresponds to the loss of Glu or  $\text{CH}_3$  groups.



**Figure ESI-41:** ESI-MS (API) of **GluAc/GluAc/SPy/SPy**: peak at  $m/z$  1845 is for  $M+H^+$ , 1867 is for  $M+Na^+$ , 1483 is for  $M - \text{Glu}$ , and 1184 is  $M - 2\text{Glu}$ .



**Figure ESI-42:** ESI-MS (API) of **GluAc/GluAc/SPy<sup>+</sup>/SPy<sup>+</sup>**: peak at m/z 937 is for (M- 2Cl<sup>-</sup>)/2.

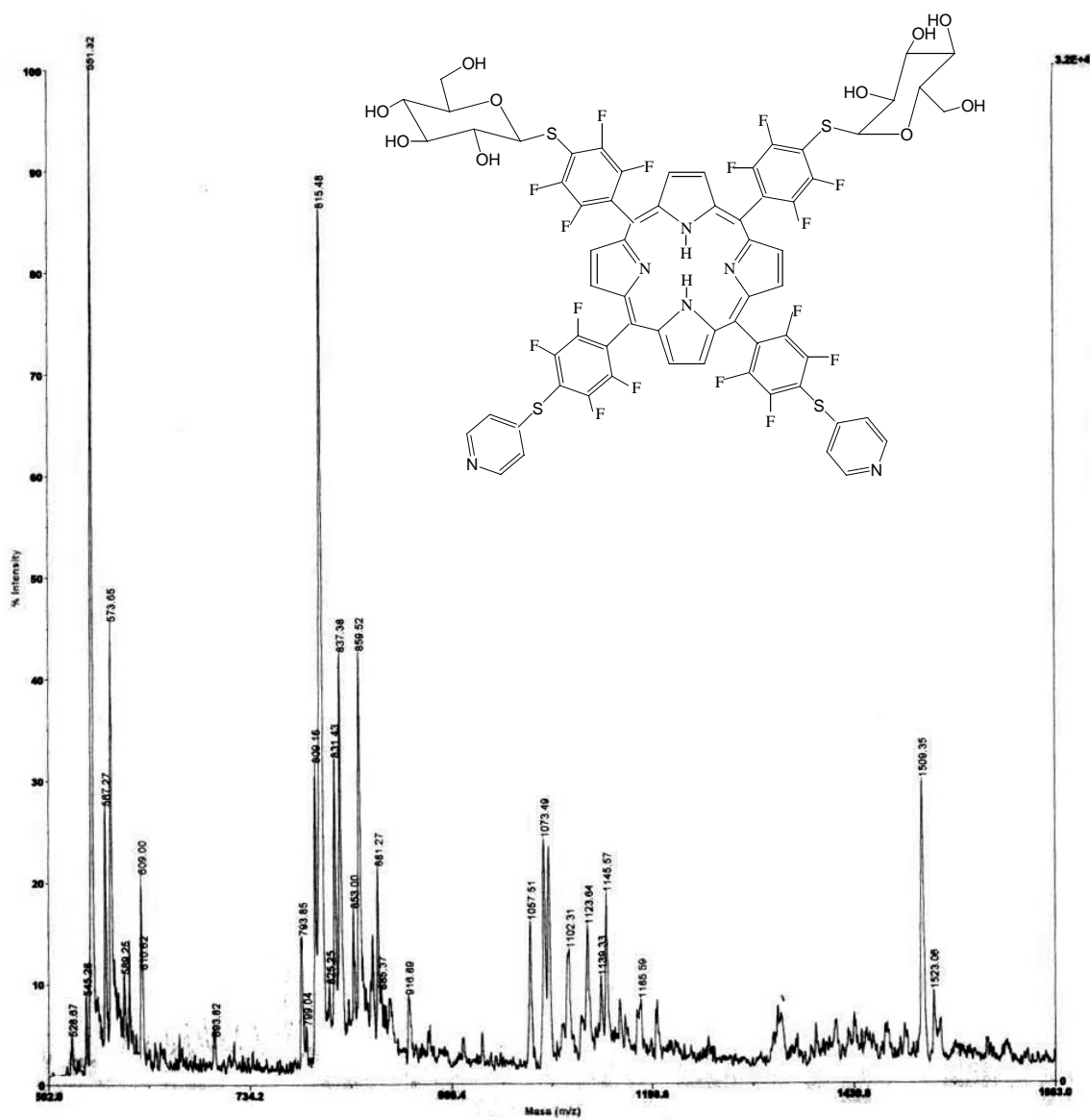


Figure ESI-43: MALDI-MS of Glu/Glu/SPy/SPy: Peak at m/z 1509 is for  $M+H^+$ .

MALDI-MS were obtained as a service from the University of Illinois mass spectrometry facility. ESI-MS were taken at the CUNY mass spectrometry facility at Hunter College.