Supporting information

N-Hexyl-4-aminobutyl Glycosides in Investigating Structures and Biological Functions of Carbohydrates

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Energy-resolved mass spectrometry (ERMS) for compounds 1(α,β) and 8(α,β). In ERMS, the end-cap rf amplitude was raised in 0.02-V increments until the precursor ion could no longer be detected (plateau at less than 0.9% of the total ion current). The averages of $n - 4$ spectra were used in CID experiments (n = 9–15, where n is the number of spectra obtained during the experiments); the first and last two datasets, which correspond to a transient period in an rf amplitude step before it reaches the steady state, were not used in order to avoid inaccuracies.

Isotopic peaks with $[I^i + 1]$ and $[I^i + 2]$, where I^n represents a fragment ion, were included in the calculations (see also "Data handling"). For the isolation of a product ion, $m/z \pm 2$ (range of isotopes, $w = 2$) were isolated and subjected to the CID experiments to include isotopes. In such a case, we set $w = 2$, thus $m/z \pm 0.8$ were isolated to exclude unintended isotopes. Standard MS/MS spectra are the parts of these ERMS spectra corresponding to a designated amplitude.

Data Handlings. The following equations were used to obtain graphs for ERMS data. When an ion "I^P" produces a series of product ions I^1, I^2, I^3, … I^i, the relative ion currents for individual ions are defined by the following equation:

$$^{rel}C = \frac{C^{I^i}}{C^{I^P} + \sum_{i=1}^{n} C^{I^i}} \times 100 \quad (1)$$

where ^{rel}C is the ion current of a given observed ion and is expressed as a percentage of the total ion current, C^{I^i} is the ion current of the observed ion of interest, and C^{I^P} is the ion current of a precursor ion. The calculations were performed using a program developed by us using Excel 2000 (Microsoft

Co.); the program utilized the DSUM function and was written to take a range of isotopes (w) into consideration (w = 0.8 or 2 in the experiments).

Sigmoidal Curve-Fitting. A set of MS^n data obtained at various rf end-cap amplitudes on a mass spectrometer was analyzed using Excel. In the analysis, sets of peaks having certain m/z values were treated as a series of data. The relative intensities were obtained in terms of the total ion current for individual signals at each amplitude (Eq. 1). The data were analyzed using Prism 4 software (GraphPad Software, Inc.). Individual data points were fitted by nonlinear regression analysis using the Boltzmann sigmoidal function (Eq. 2: growth; Eq. 3: decay).

$$y = \frac{a}{1 + e^{[(b-x)/c]}} \quad (2)$$

$$y = \frac{a}{1 + e^{[-(b-x)/c]}} \quad (3)$$

Here, the parameters "a," "b," and "c," which indicate the maximum response, half the maximum response, and a slope factor, respectively, were obtained for each curve.

For each series of data used in this study, the sigmoidal curves and the parameters were obtained by plotting the regression curves using all the data obtained from the abovementioned Excel program.

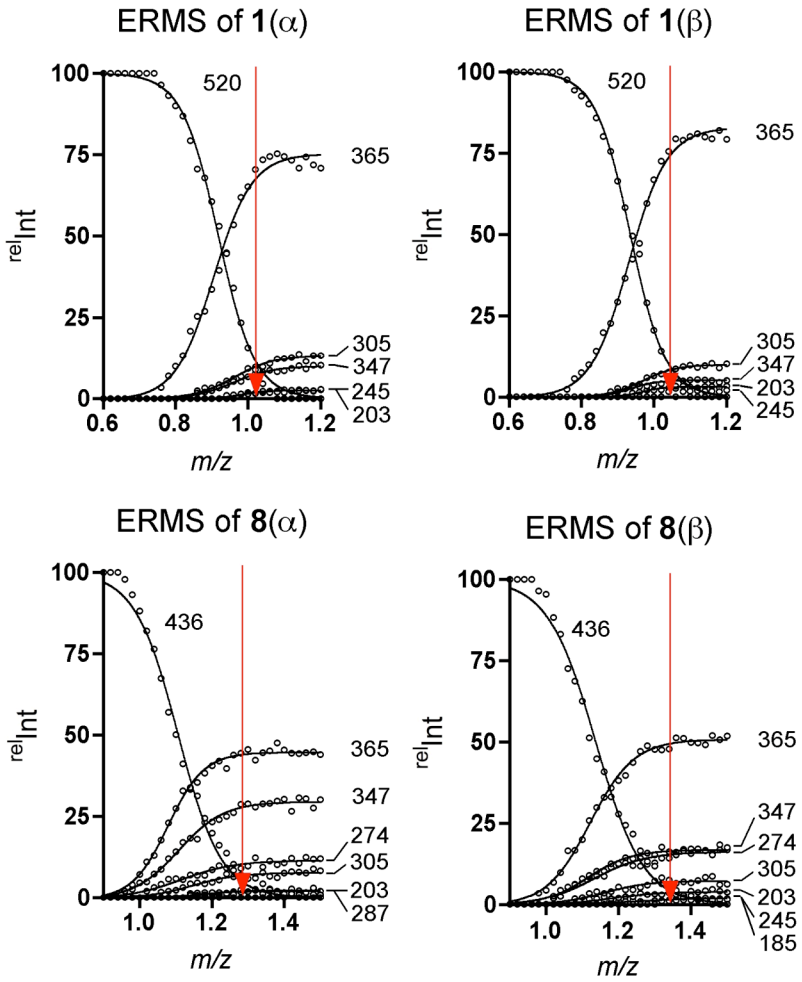
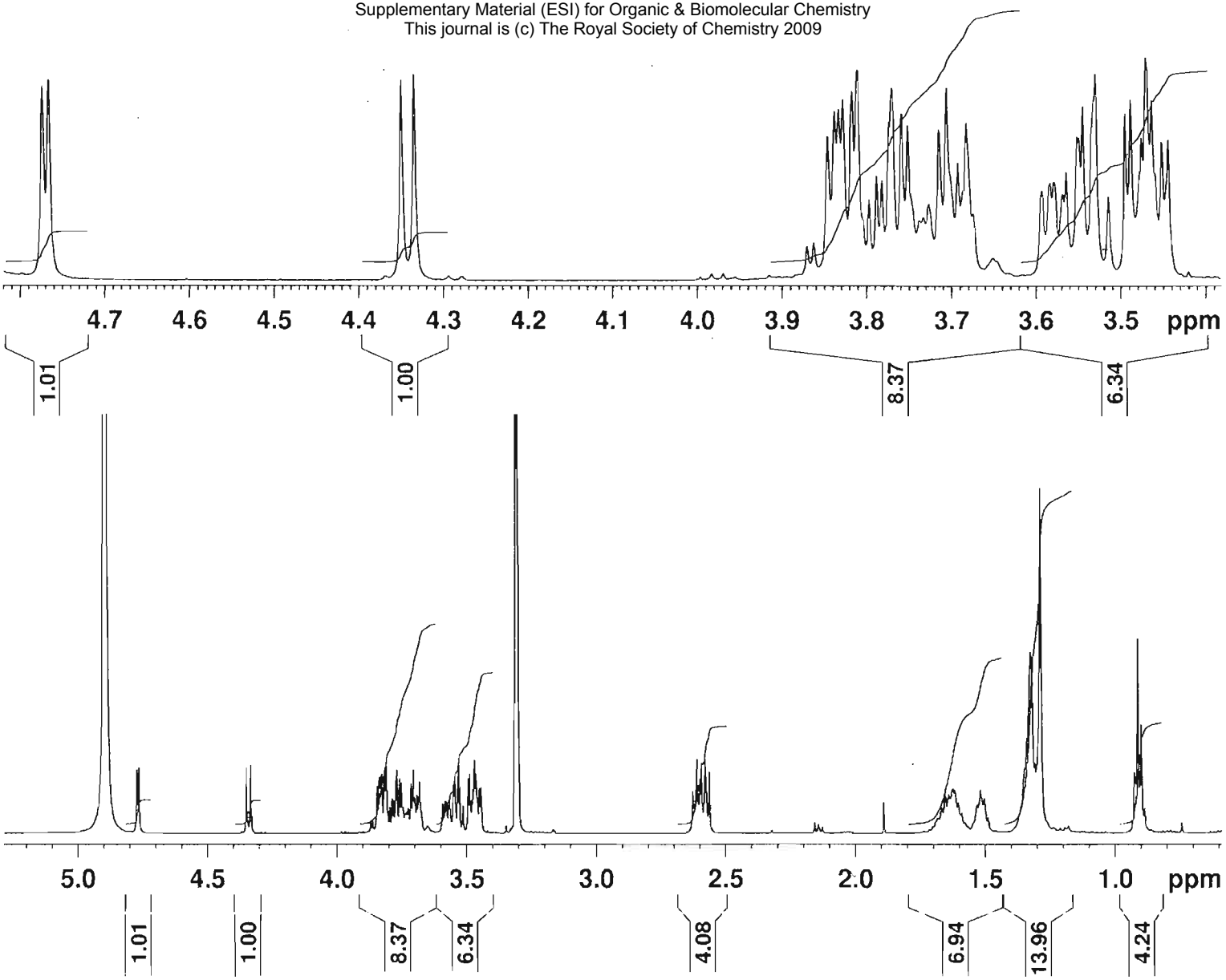
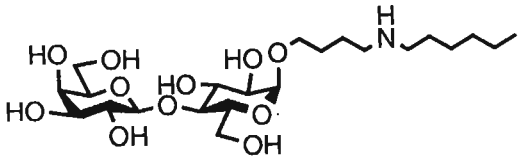
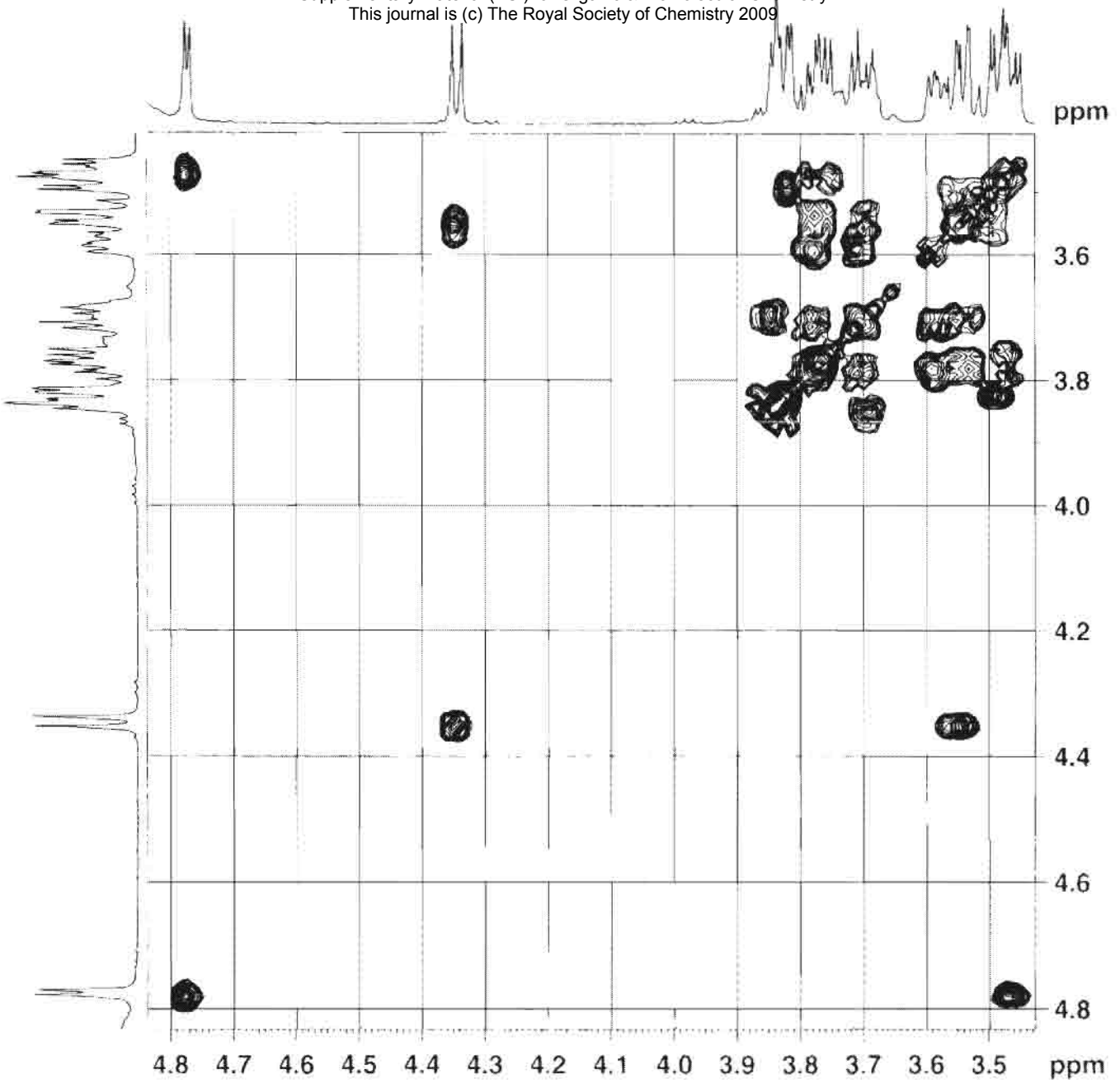


Figure S1. ERMS spectra of compounds **1**(α,β) and **8**(α,β). Red arrows indicate the rf amplitudes corresponding to the data sets that were extracted and used to obtain the MS/MS spectra presented in the manuscript.

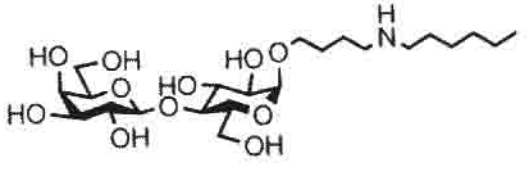


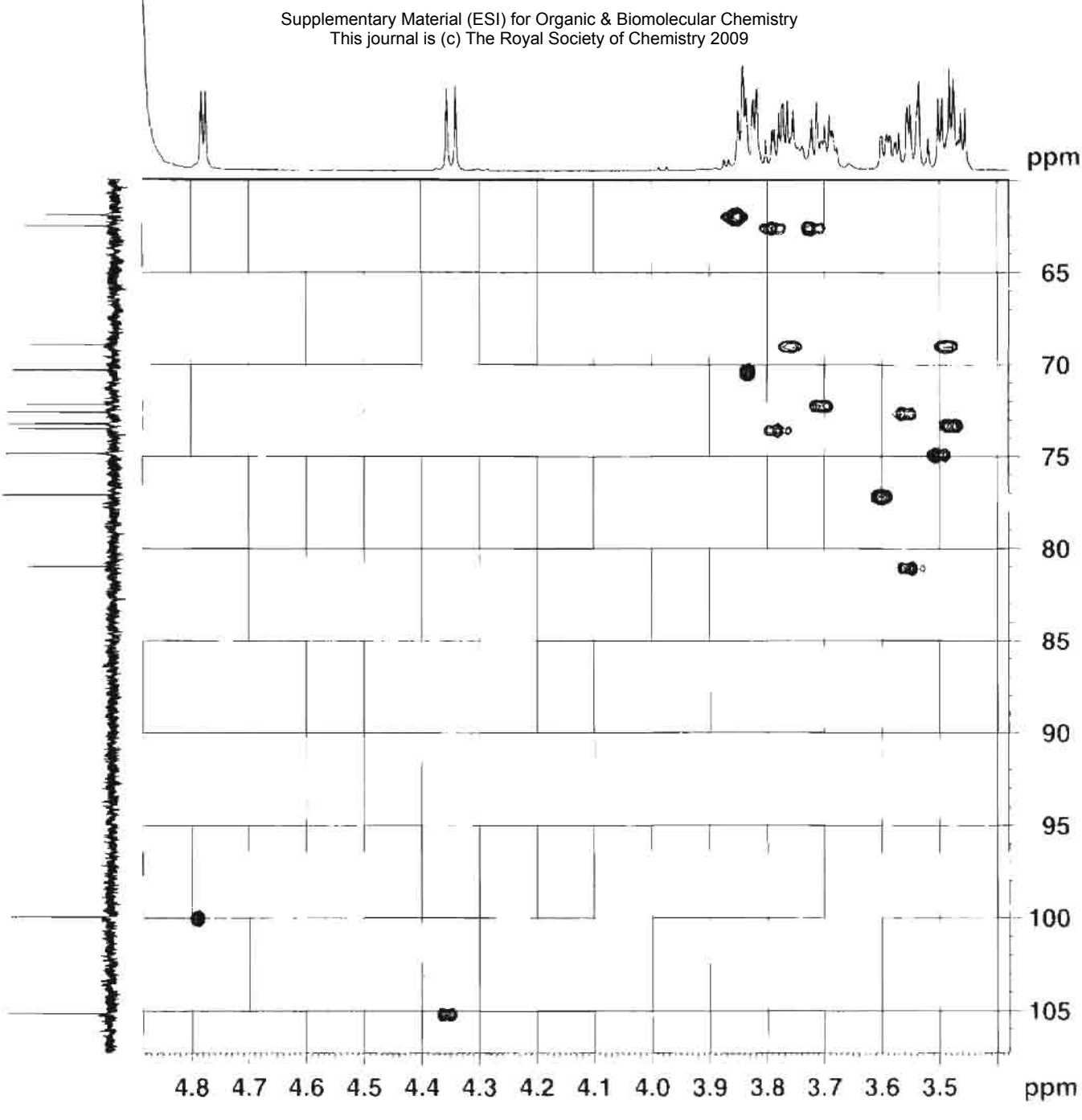
1H NMR of compound 1 alpha



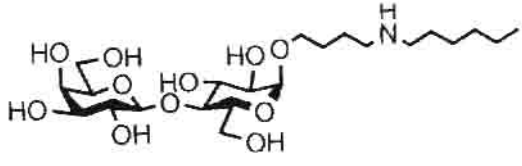


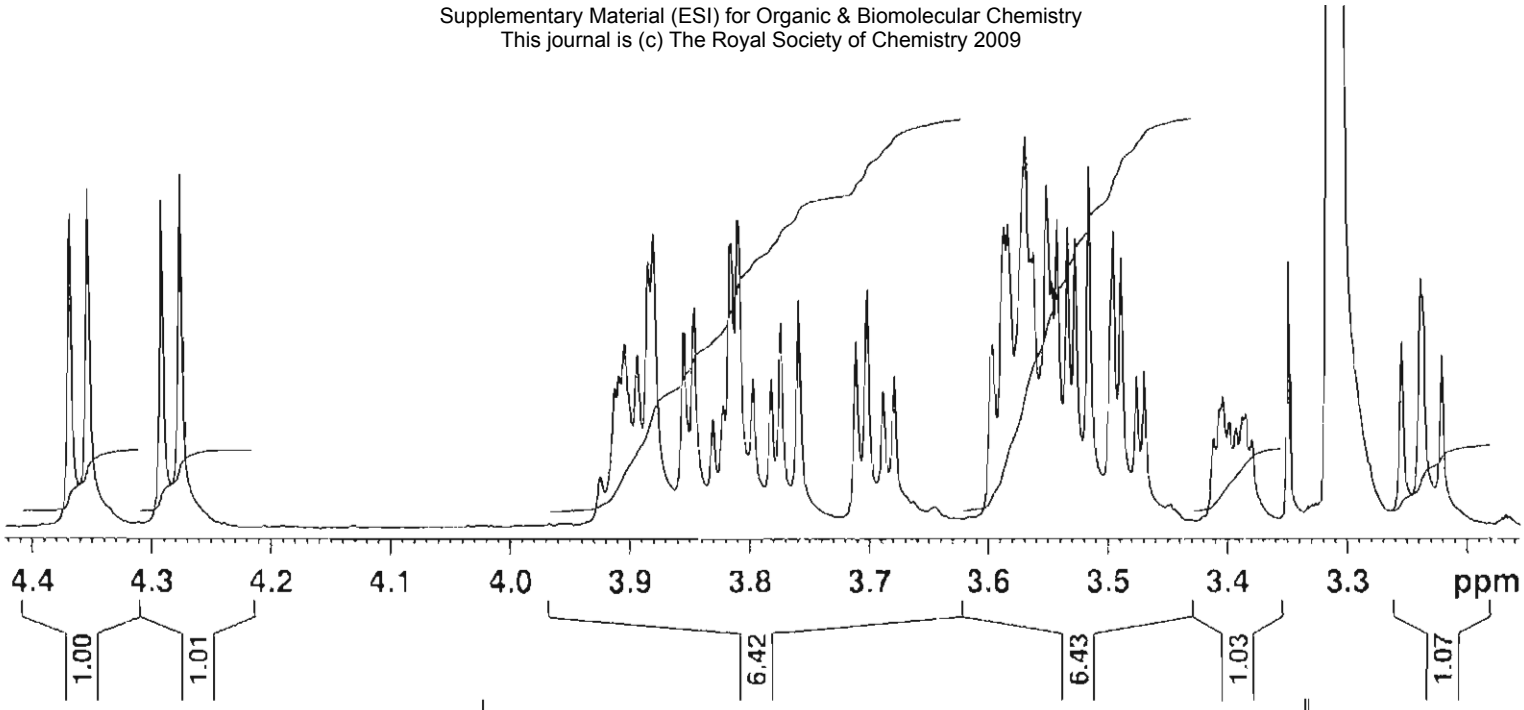
COSY of compound 1 alpha

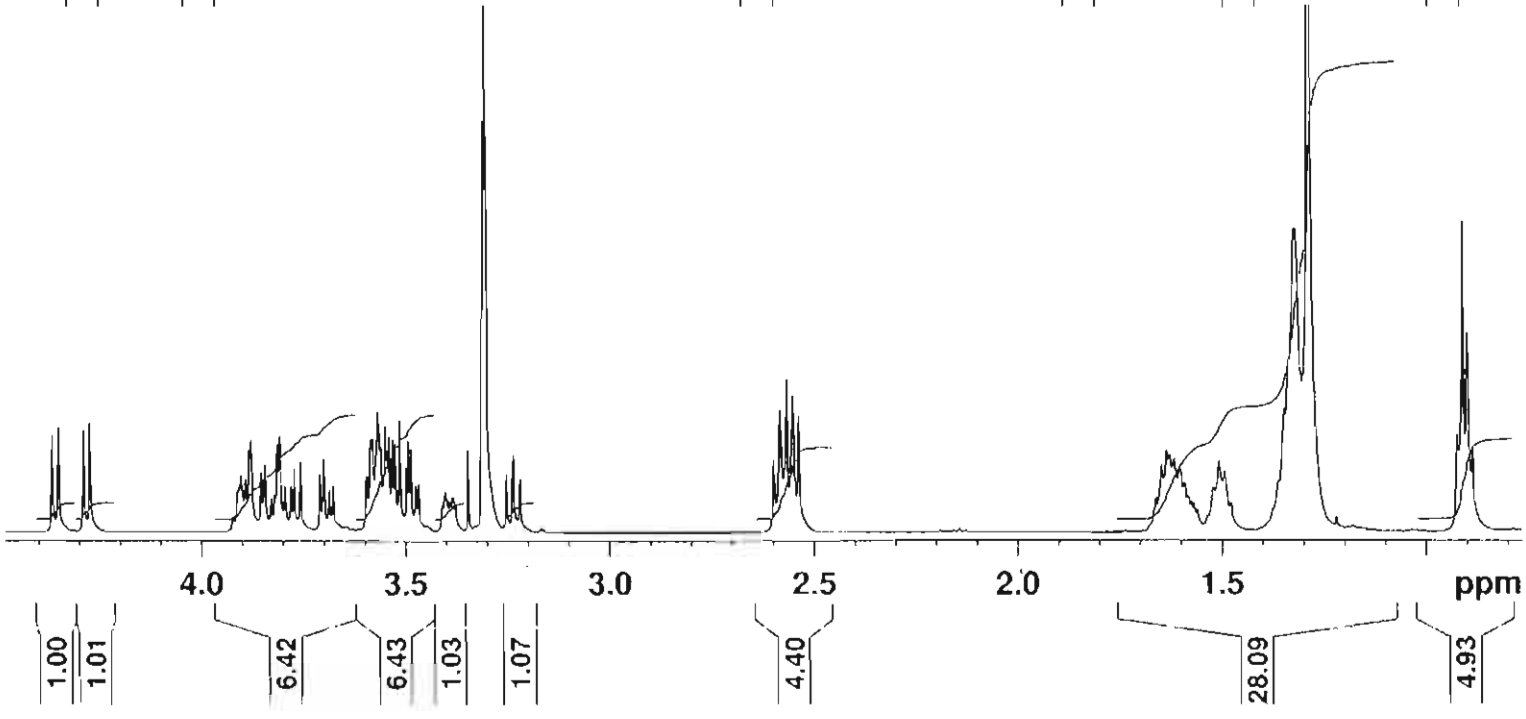




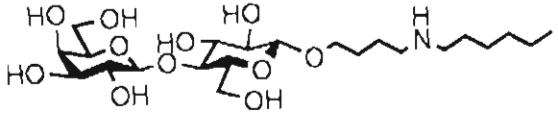
HSQC of compound 1 alpha

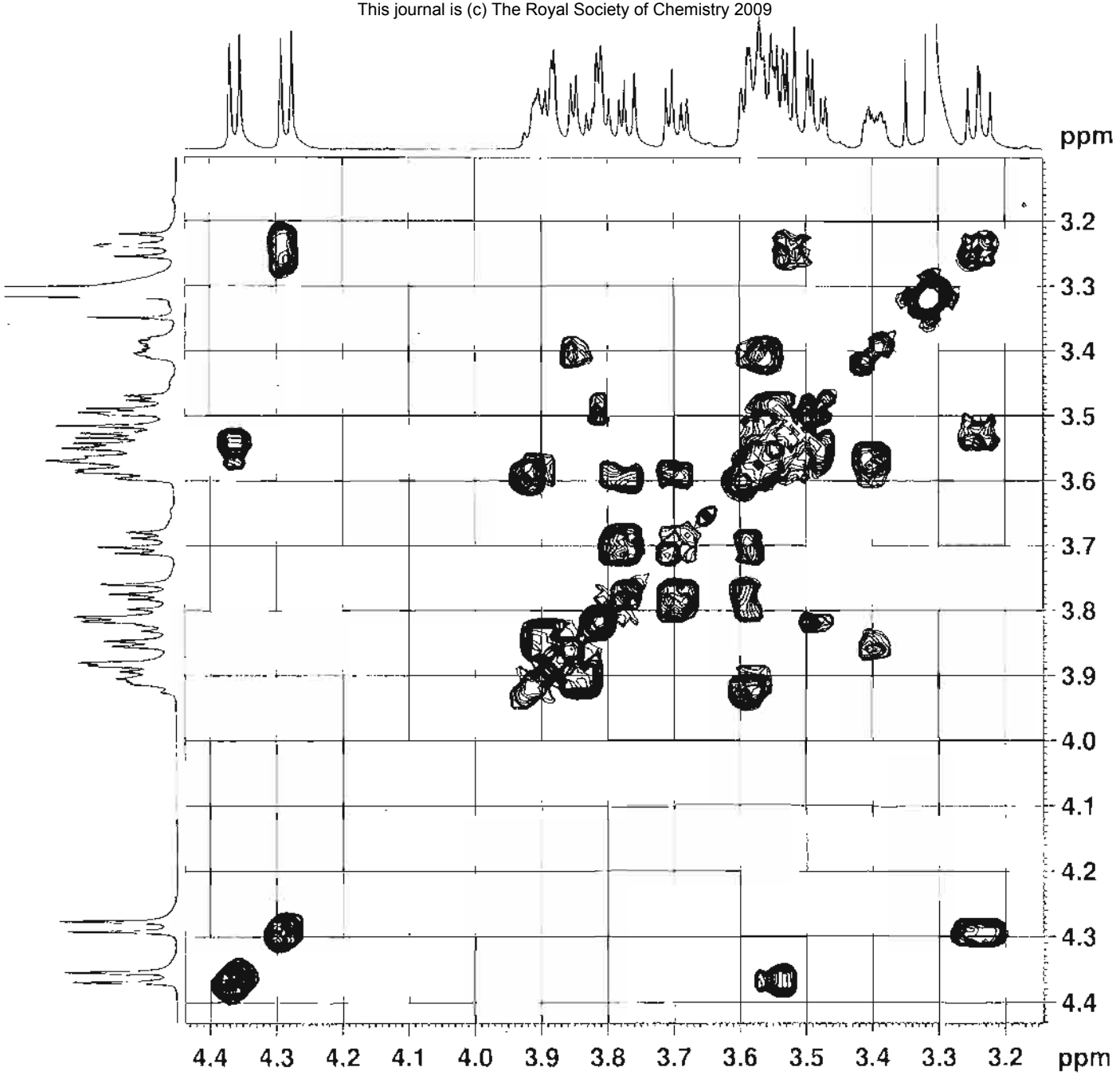




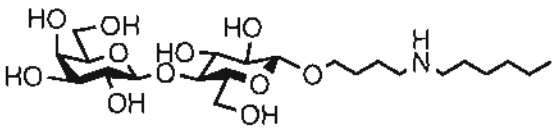


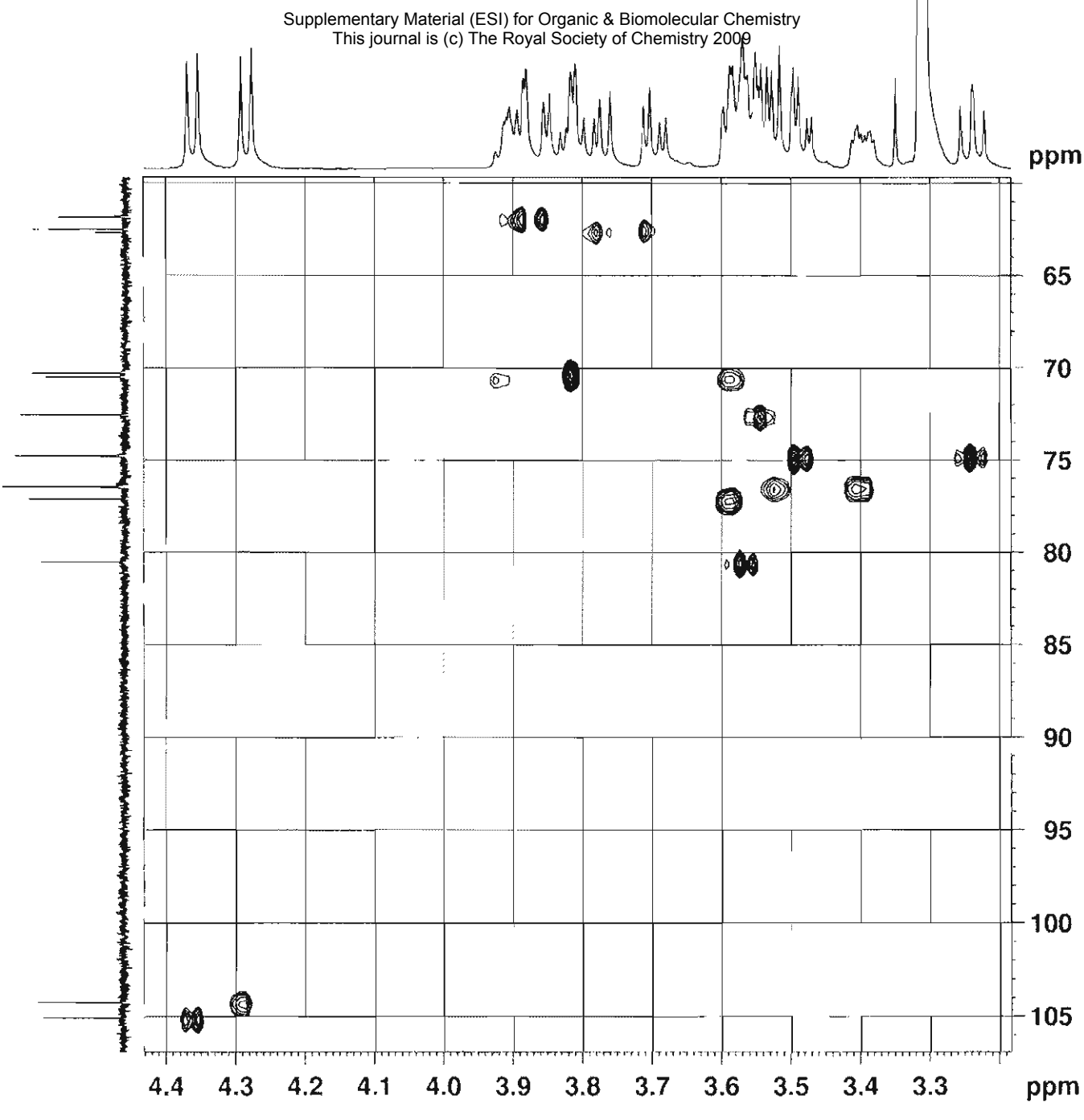
1H-NMR of compound 1 beta



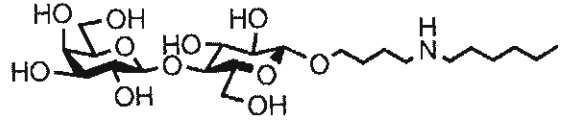


COSY of compound 1 beta



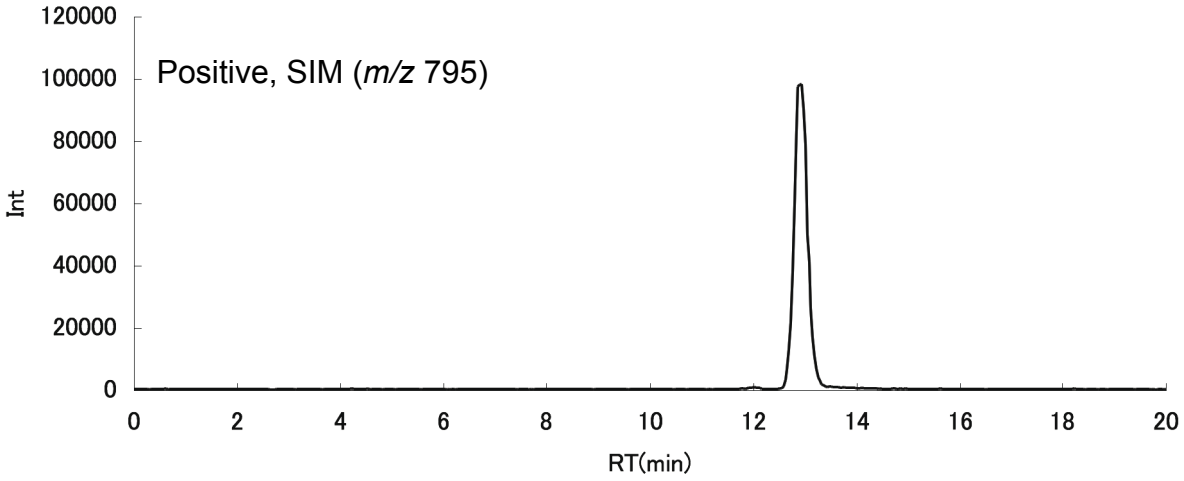


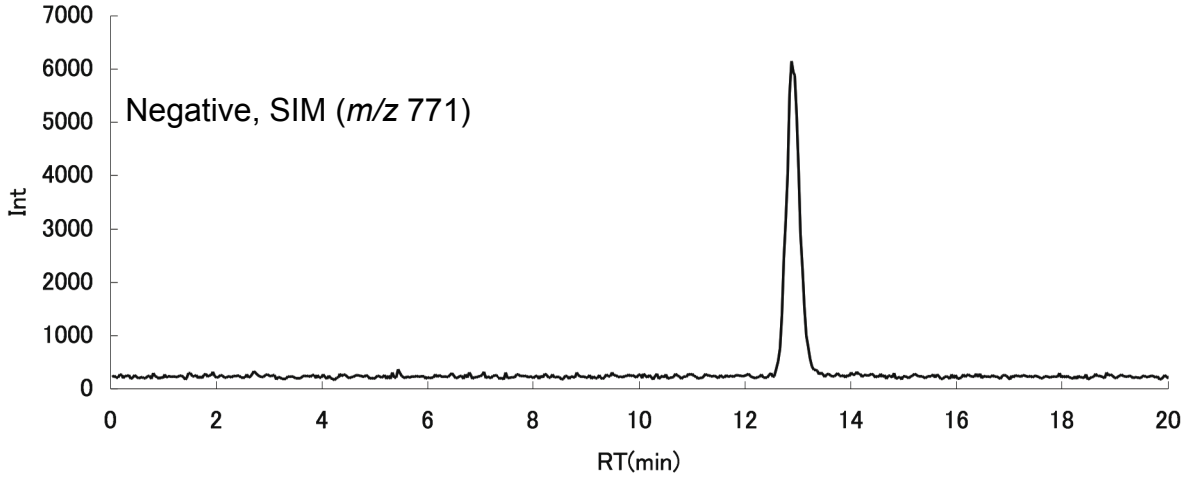
HSQC of compound 1 beta



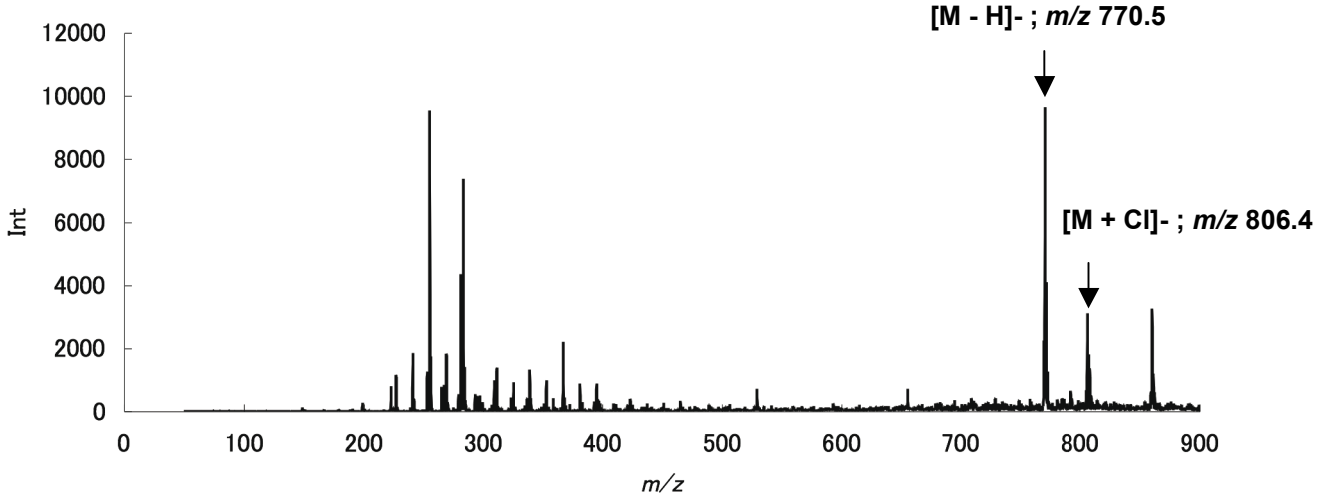
LC-MS chromatogram of compound **9**

Analysis condition
Column ; Cadenza UK-C18 250mmL×4.6mmI.D. (3μm)
Mobile phase ; Isocratic MeCN 40%, H_2O 60%
Flow rate ; 1mL/min
Column Temp. ; 40˚C
Polarity ; Positive & Negative

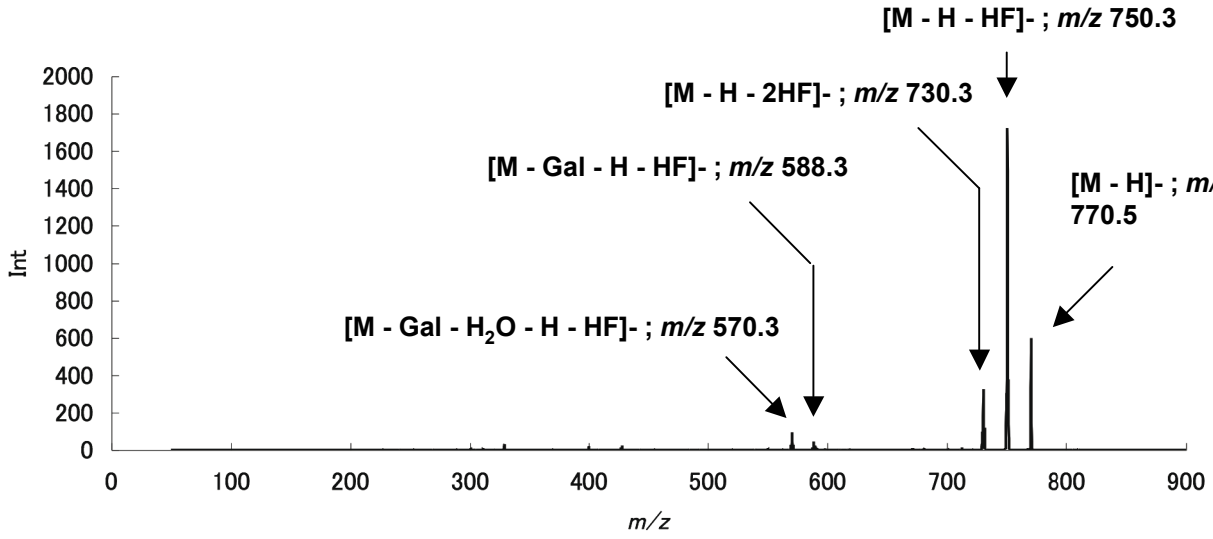


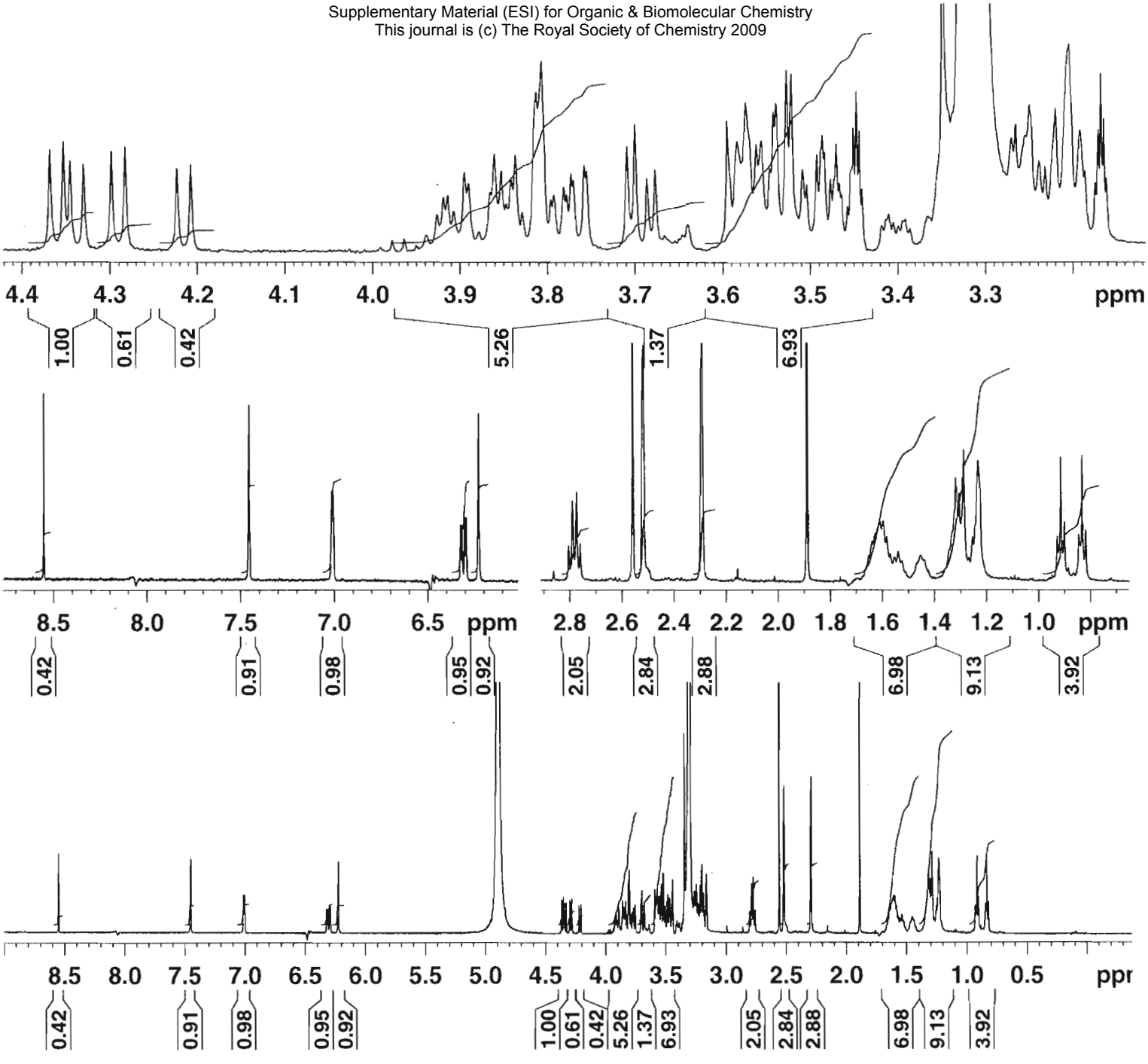


Negative MS spectrum of compound **9**

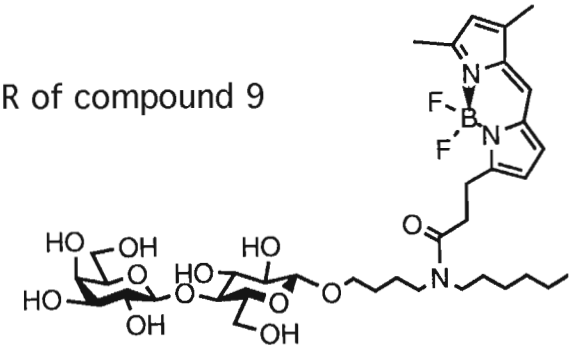


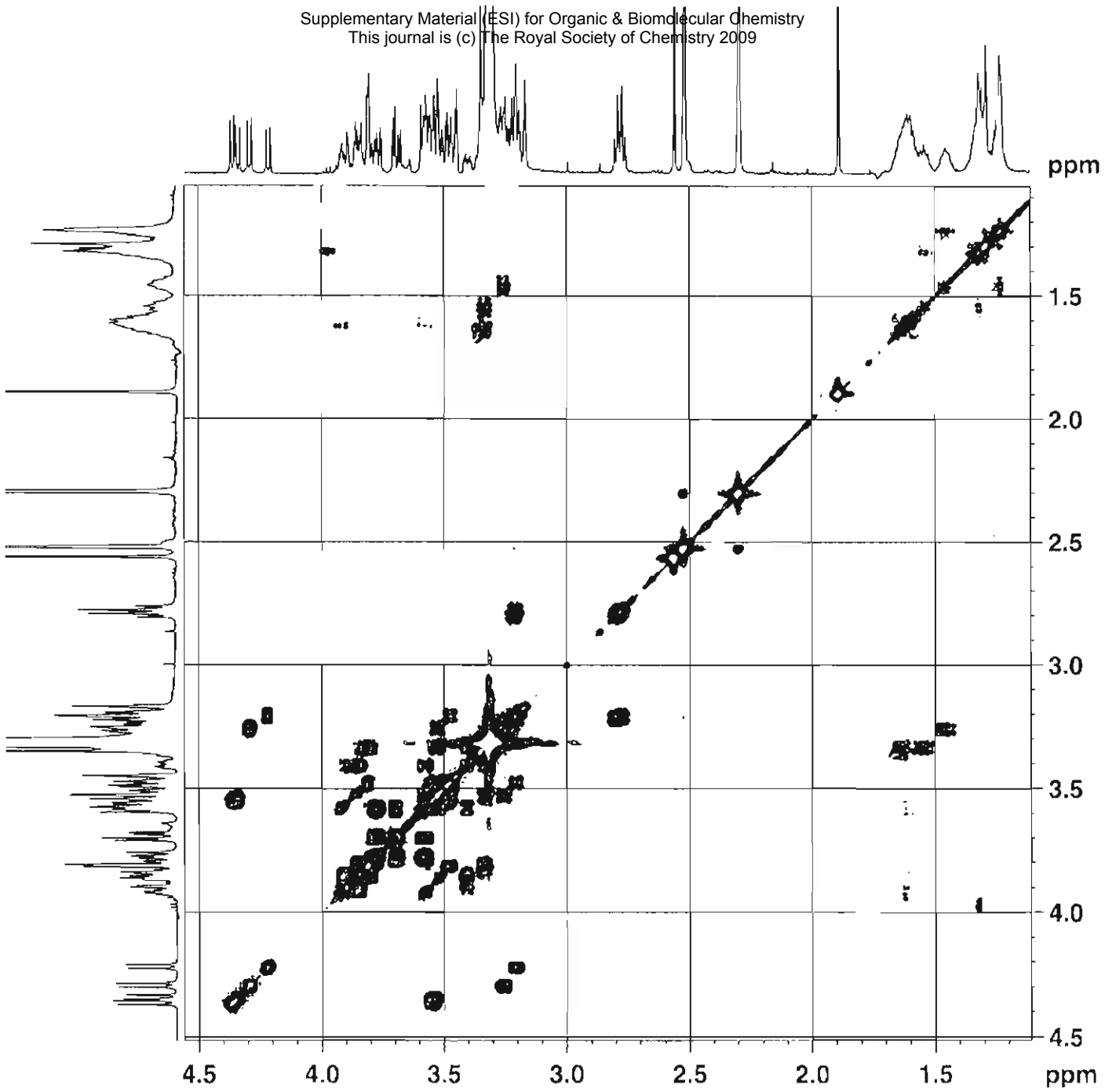
Negative MS/MS spectrum of compound **9**



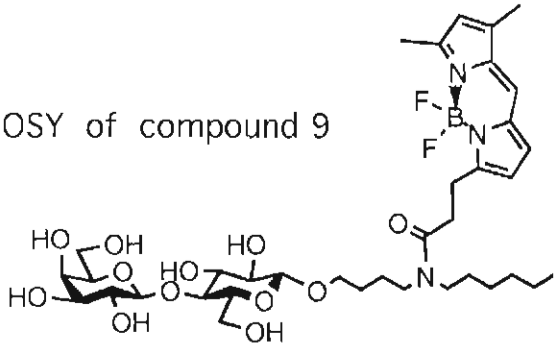


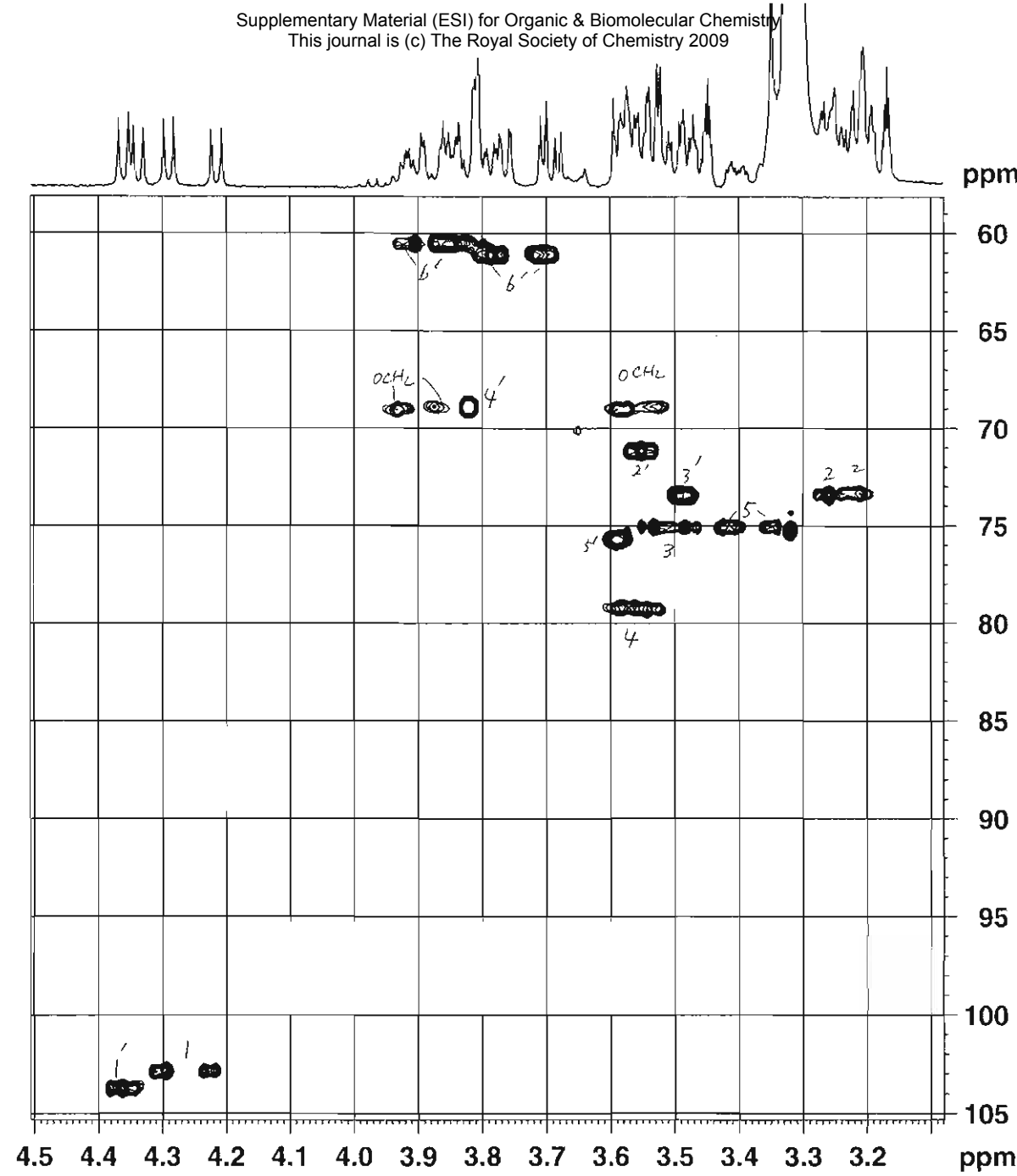
1H-NMR of compound 9



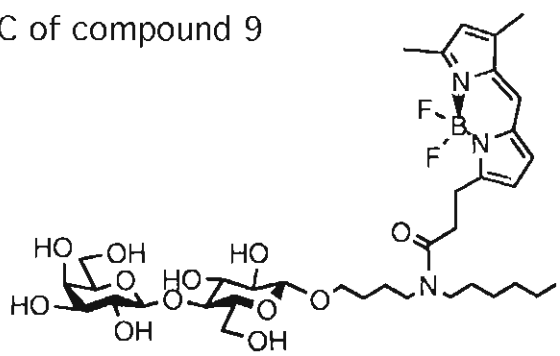


COSY of compound 9



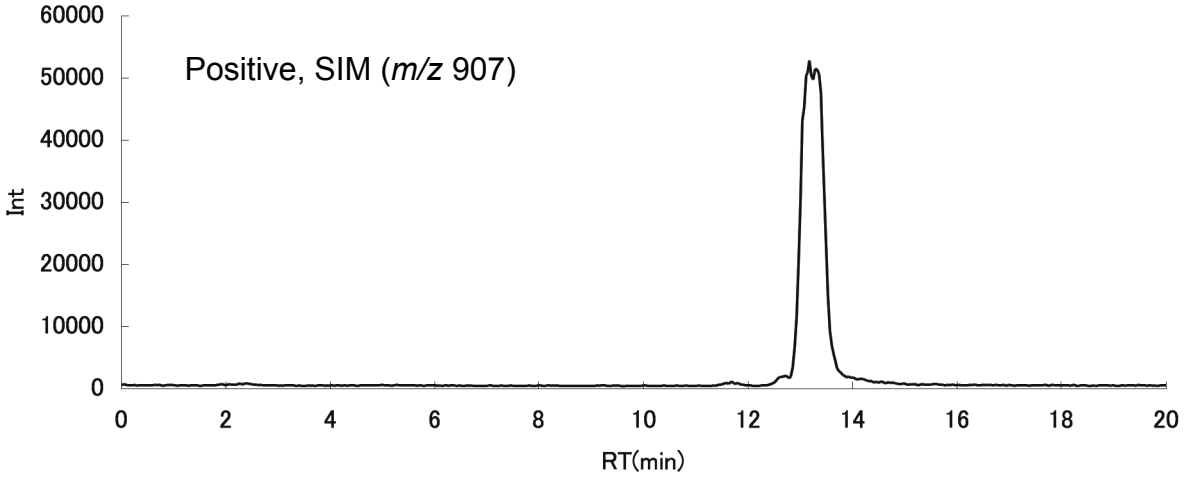


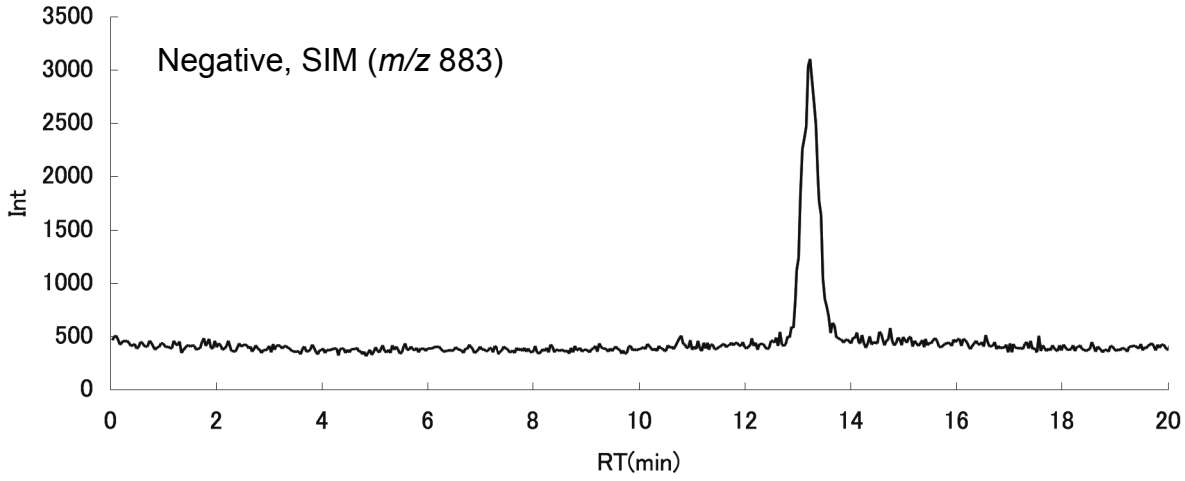
HSQC of compound 9



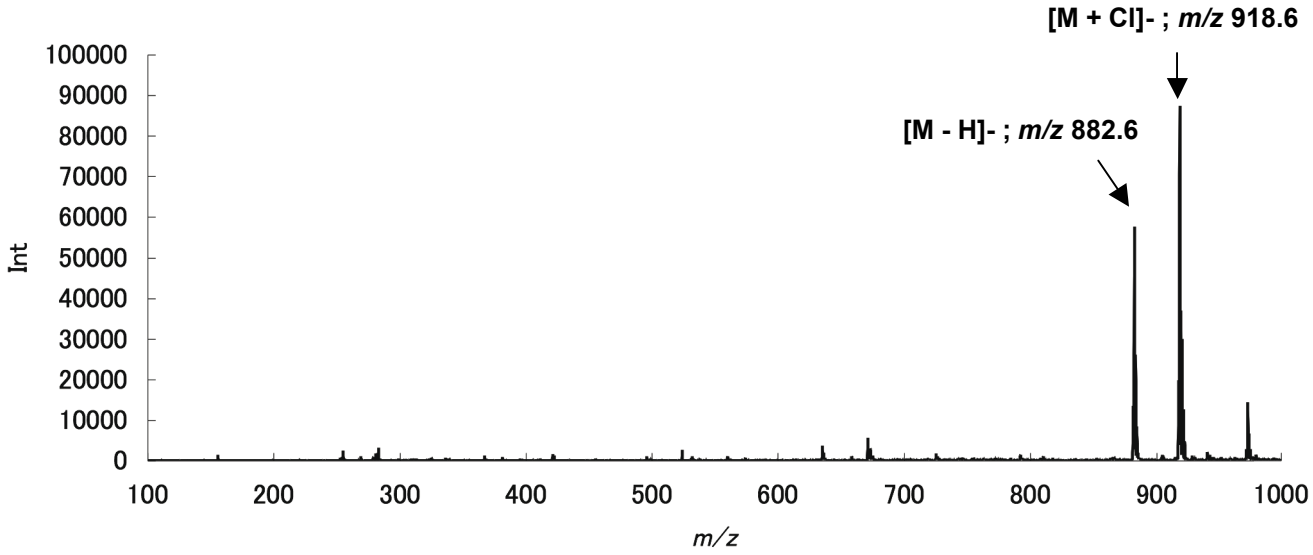
LC-MS chromatogram of compound **10**

Analysis condition
Column ; Cadenza UK-C18 250mmL×4.6mmI.D. (3μm)
Mobile phase ; Isocratic MeCN 30%, H_2O 70%
Flow rate ; 1mL/min
Column Temp. ; 30˚C
Polarity ; Positive & Negative

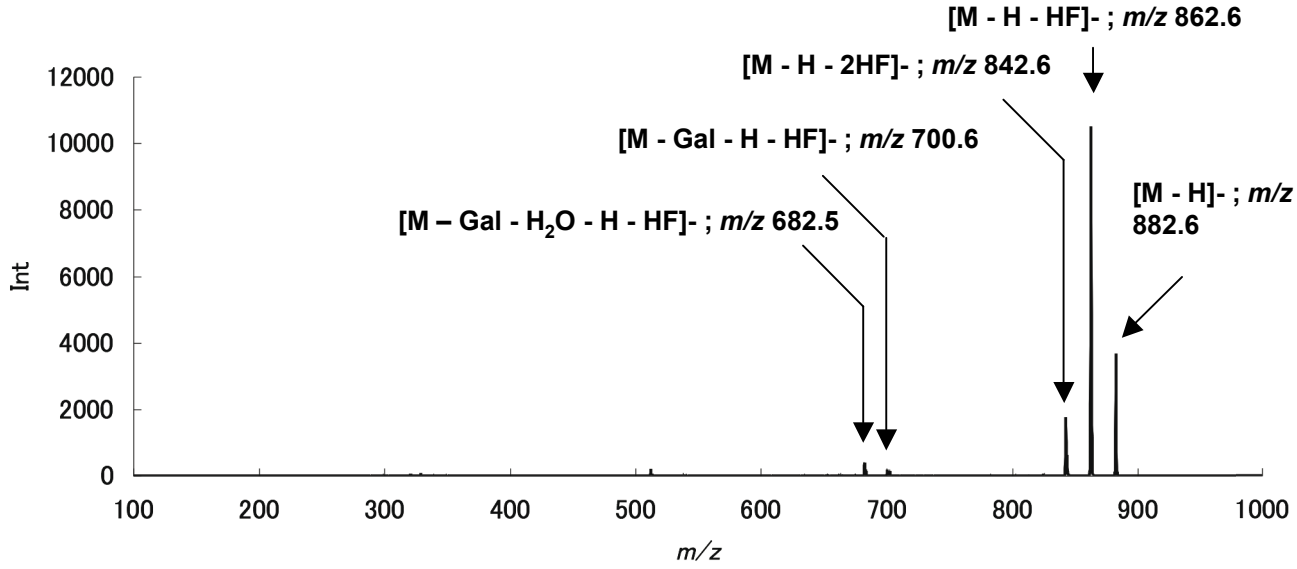


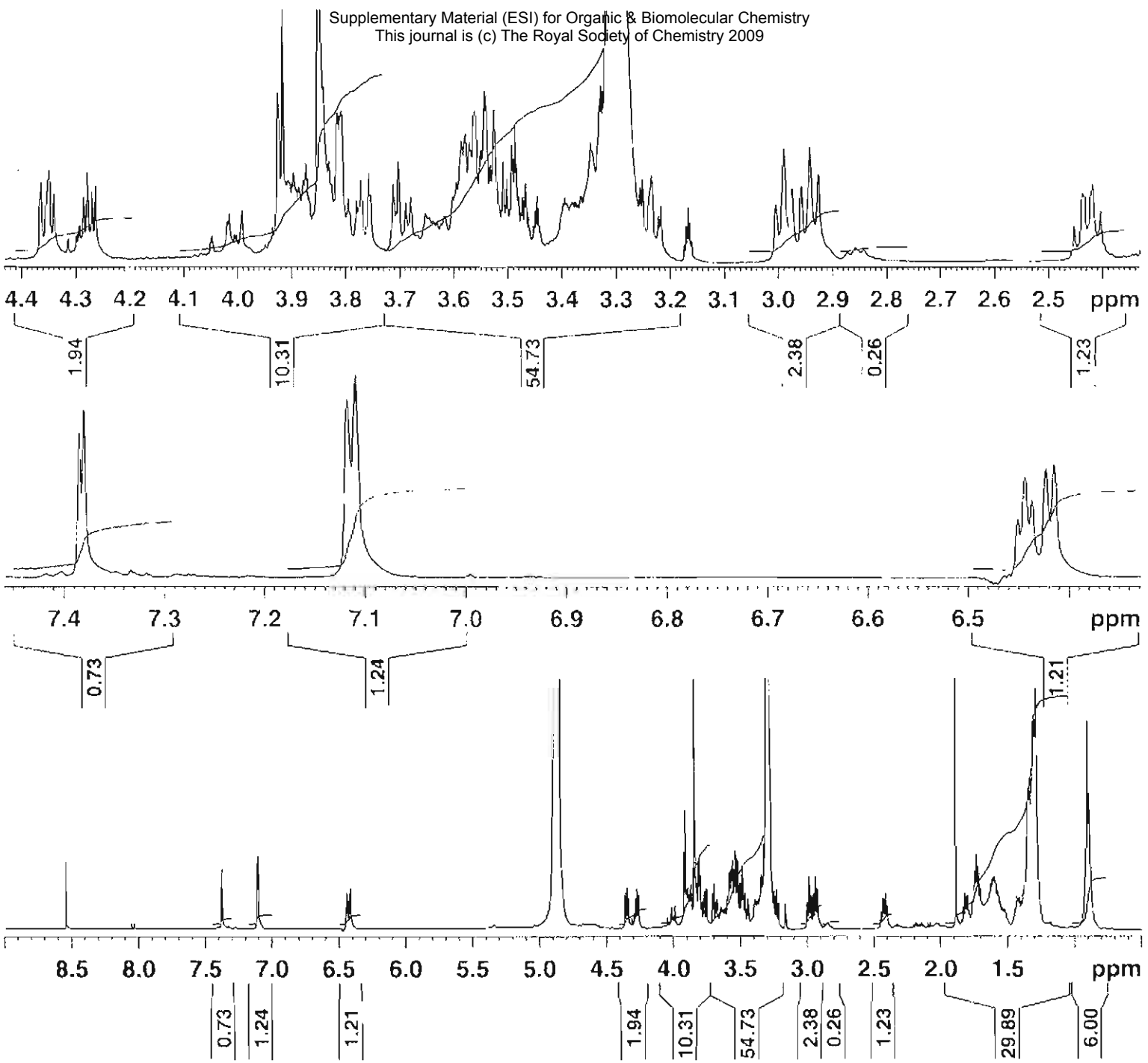


Negative MS spectrum of compound **10**

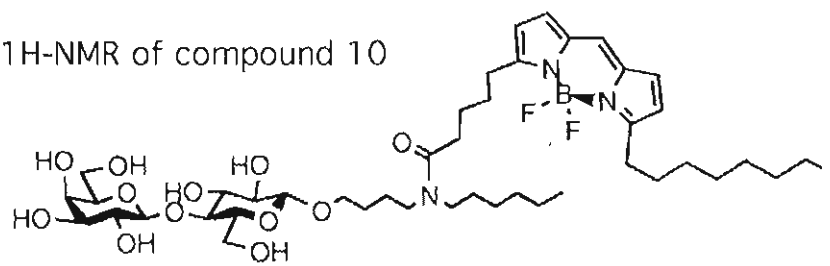


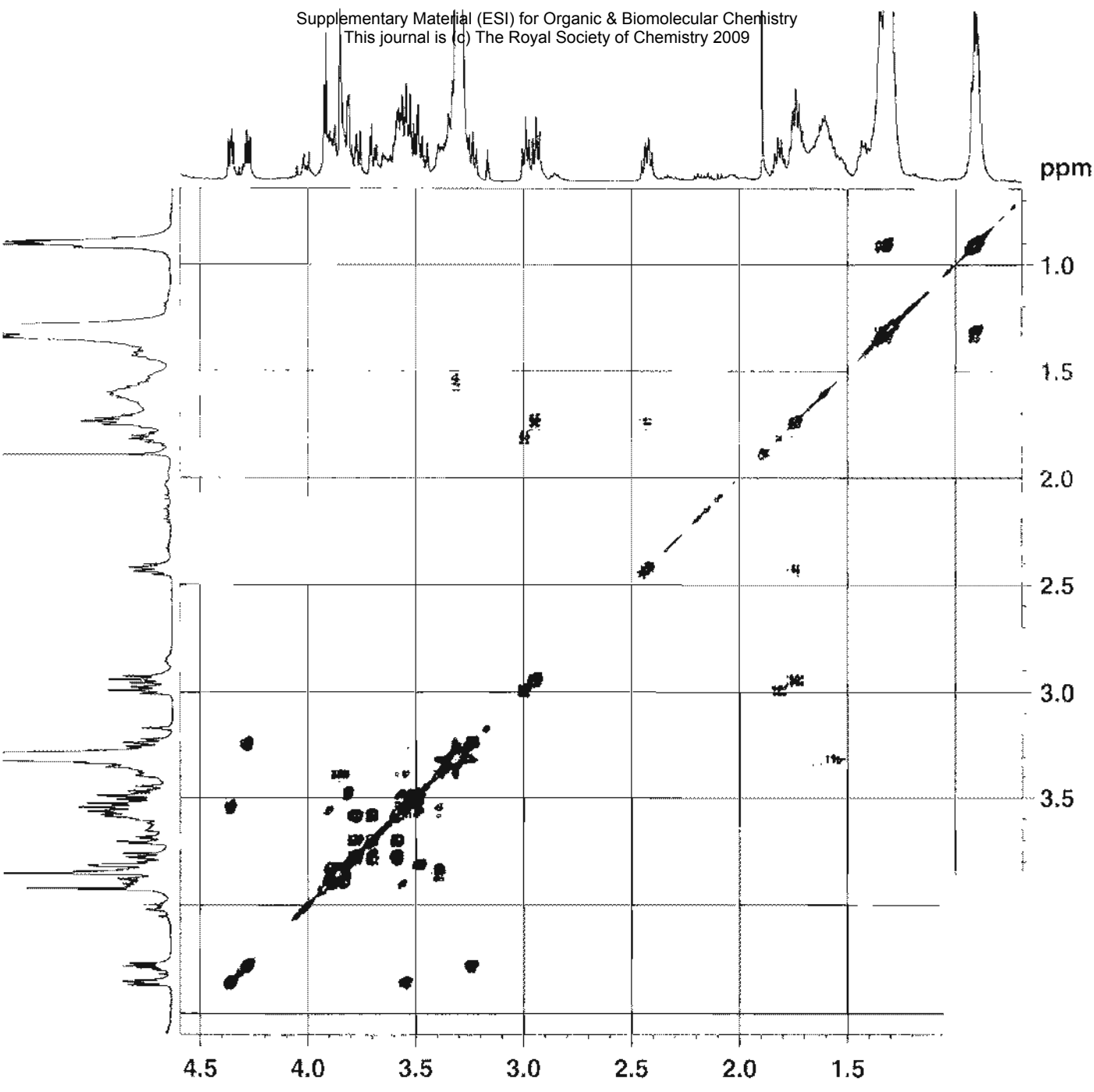
Negative MS/MS spectrum of compound **10**



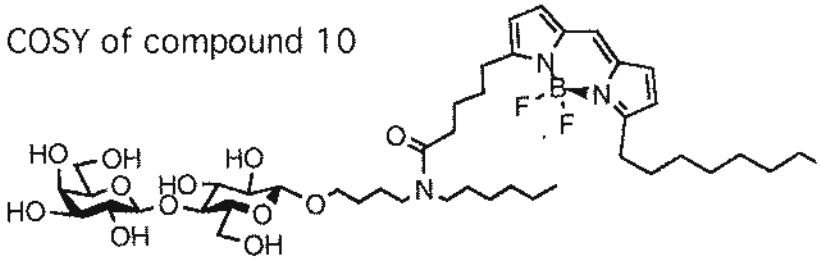


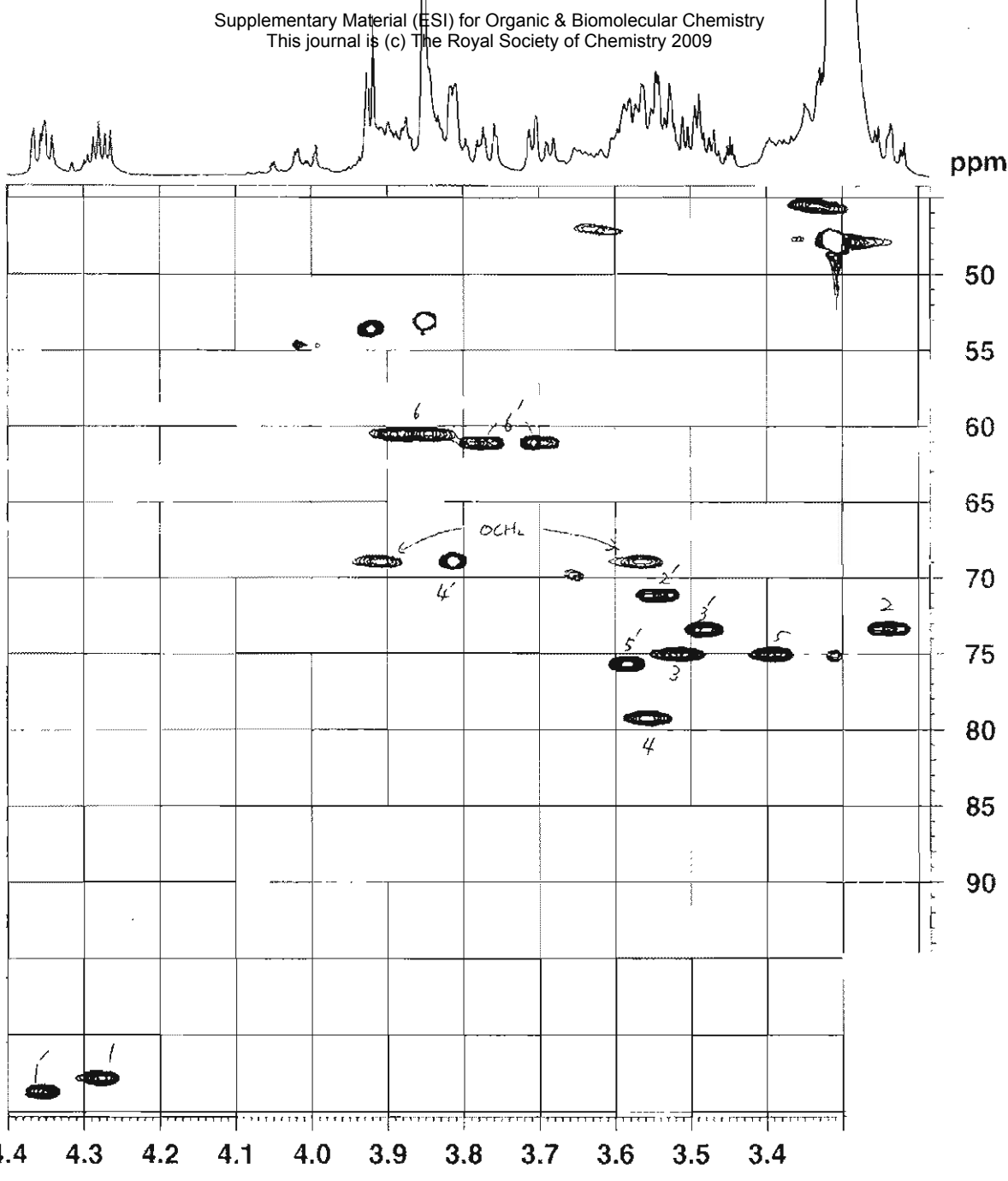
1H-NMR of compound 10





COSY of compound 10





HSQC of compoun 10