Supplementary Material (ESI) for New Journal of Chemistry

Supporting information for:

Bis spin labelled cyclodextrins

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General details.

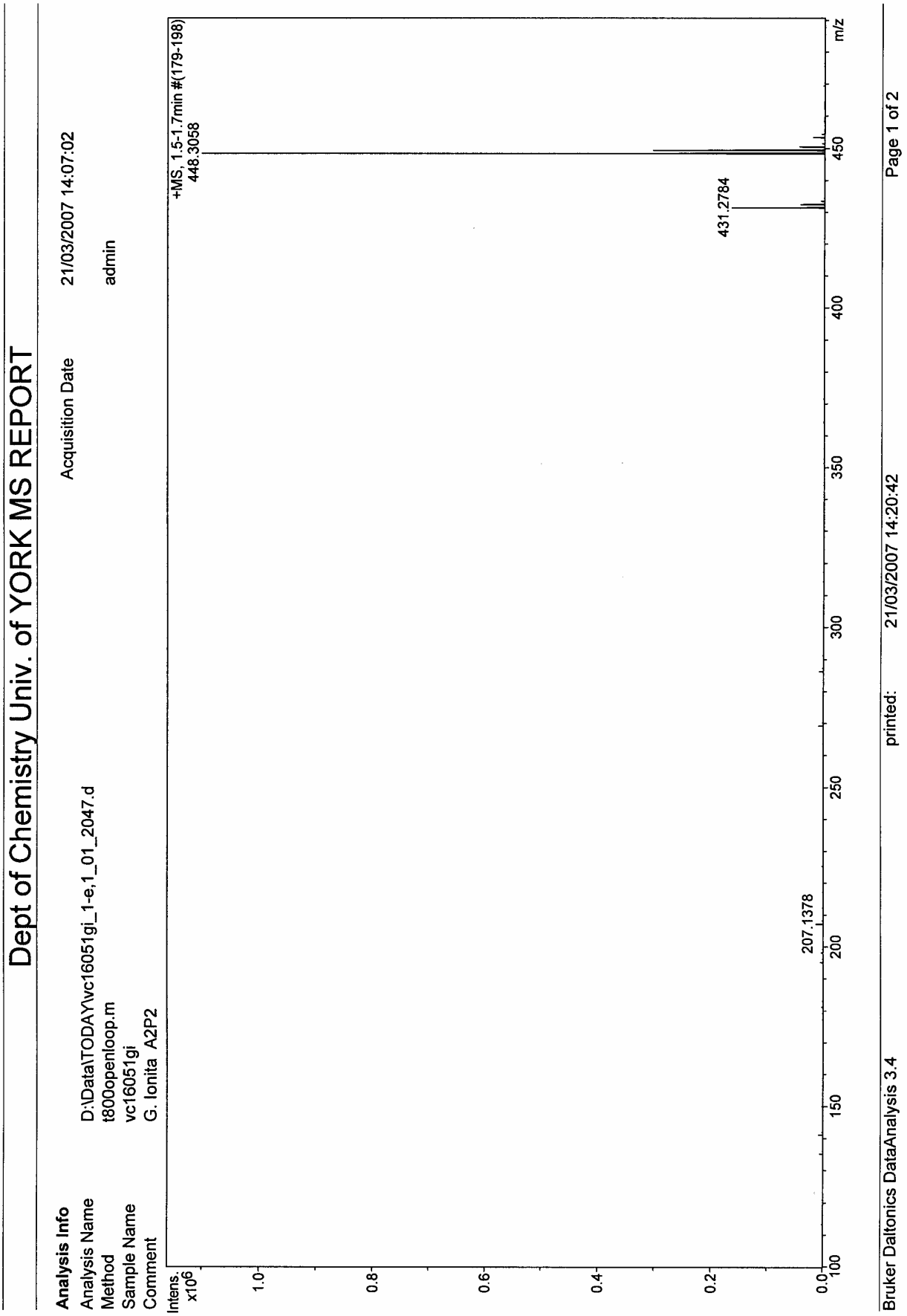
EPR spectra were recorded on Bruker ESP-300E spectrometer at microwave frequency 9.49 GHz with a 100 kHz modulation frequency, a microwave power 1 mW, modulation amplitude 0.1 mT, scan time 335 s, scan width 100 G for spectra at room temperature and 200 G for spectra at 120 K.

Synthesis of **A2P2**: Adamantane-1-carbonyl chloride (322 mg, 2.4 mmol) was added to a solution of diethylene glycol (106 mg, 1 mmol) in dichloromethane (20 ml) in the presence of triethylamine (one drop). After stirring for one day at room temperature, the reaction mixture was washed successively with 0.1 M HCl and saturated $NaHCO_3$ aqueous solutions. The organic layer was dried (Na_2SO_4). The solution was concentrated and purified by column chromatography using 10% ethyl acetate/dichloromethane as an eluent. R_f 0.43. Yield 60 %. ESI-HR-MS data for **A2P2**: calc. for $[C_{26}H_{38}O_5 + H]^+$ 431.2797, found for $[M+H]^+$ 431.2784. $[C_{26}H_{38}O_5 + NH_4]^+$ 448.3063, found for $[M+H]^+$ 448.3058.

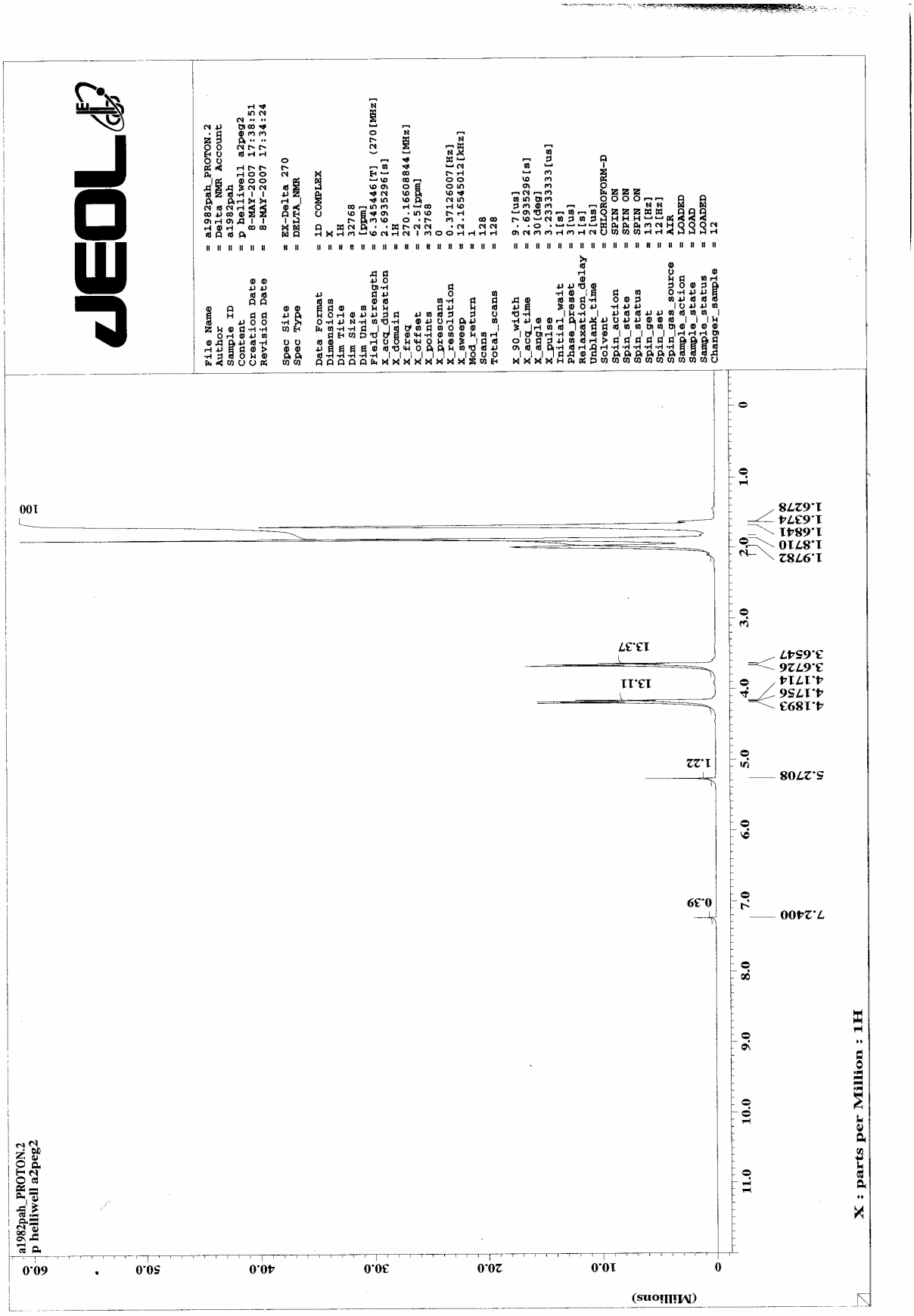
Synthesis of dihydroxy permethylated-β-cyclodextrin isomers. The procedure reported by Z. Chen et al, *J. Org. Chem.* **1997,** *62,* 8529, was followed in order to obtain 6^A, 6^D- and 6^A, 6^B-dihydroxy permethylated β-cyclodextrin. β-CD (2.27 g, 2 mmol) and imidazole (0.47, 14 mmol) were mixed in dry DMF (100 ml) under stirring. Then tert-butyldimethylsilyl chloride (1.08 g, 14 mmol) was added in one portion. This mixture was stirred for 1.5 h at rt and then cooled to 0 °C and NaH (3.2 g, 260 mmol) was added. The mixture was stirred at 0 °C for 30 min and then at rt for 1 h. The mixture was again cooled to 0 °C and CH_3I (17 ml, 253 mmol) was added drop-wise. The mixture was kept at 0 °C for 1 h and then overnight at rt. The reaction was quenched by careful addition of ice-water mixture (10 ml) with stirring and extracted with $CHCl_3$ (100 mL × 3). The combined organic layers were washed successively with 6% aqueous solution of $Na_2S_2O_3$ (50 mL) and water (50 mL × 2) and then dried ($MgSO_4$). After concentration, the

obtained solid residue was refluxed with ammonium fluoride in 200 mL of CH_3OH overnight. The mixture was evaporated and the residue dissolved in $CHCl_3$ (100 mL) and then filtered and concentrated. The diols were separated twice by column chromatography on silica gel (200-400 mesh) using $CHCl_3$/MeOH (50:1) mixture as an eluent. First separation gave a mixture of AB, AC and AD isomers, which were separated on a second column Yield: 6.6 % (AD), 8 % (AB). R_f: 0.40 (AD, $CHCl_3$/MeOH 10/1); 0.30 (AB, $CHCl_3$/MeOH 10/1). ESI-MS data for AB/AC/AD mixture: calc. for $[C_{61}H_{108}O_{35} + Na]^+$ 1423.6568, found for $[M + H]^+$ 1423.7.

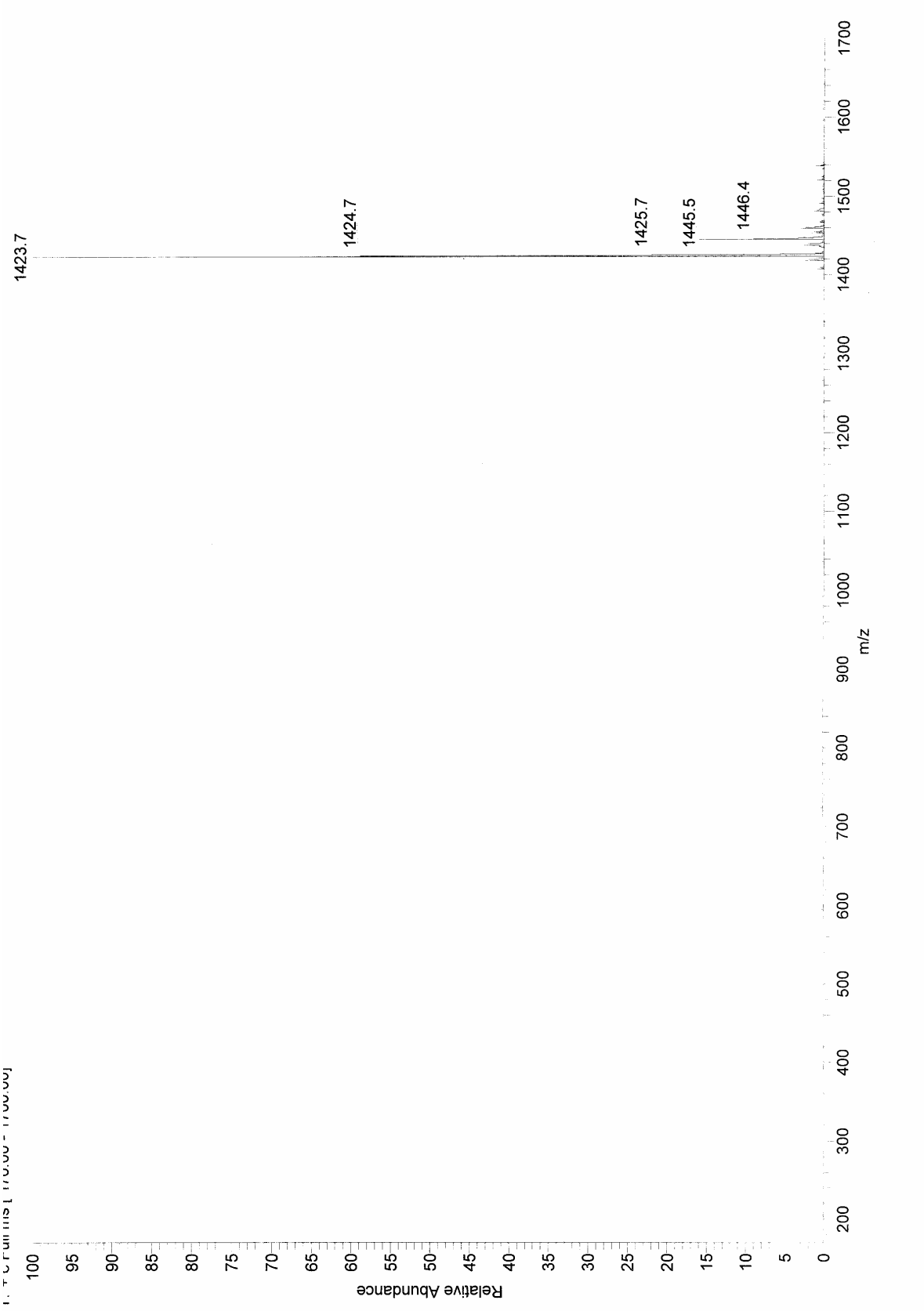
ESI-MS spectrum for **A2P2**



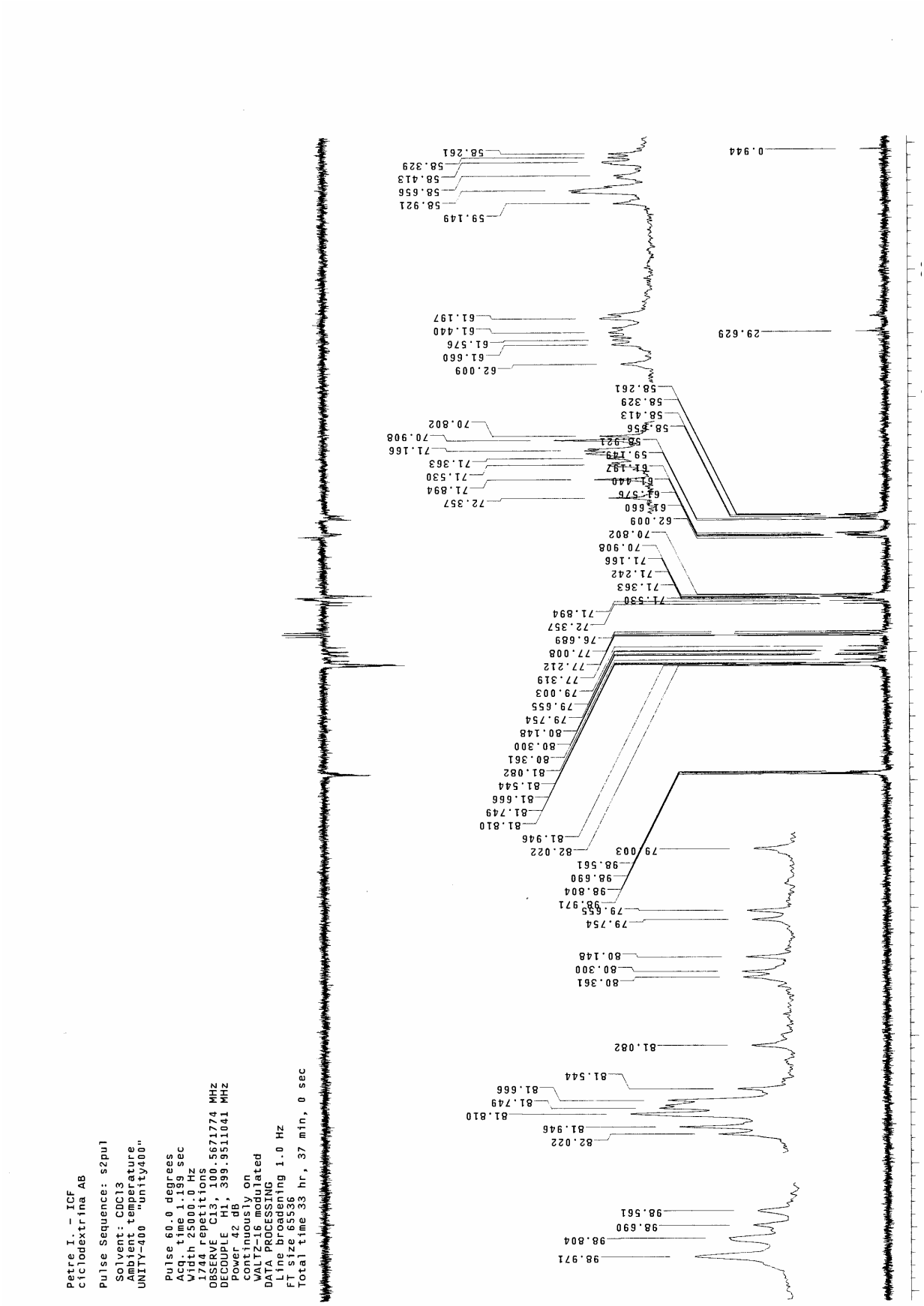
^{1}H NMR spectrum of **A2P2**



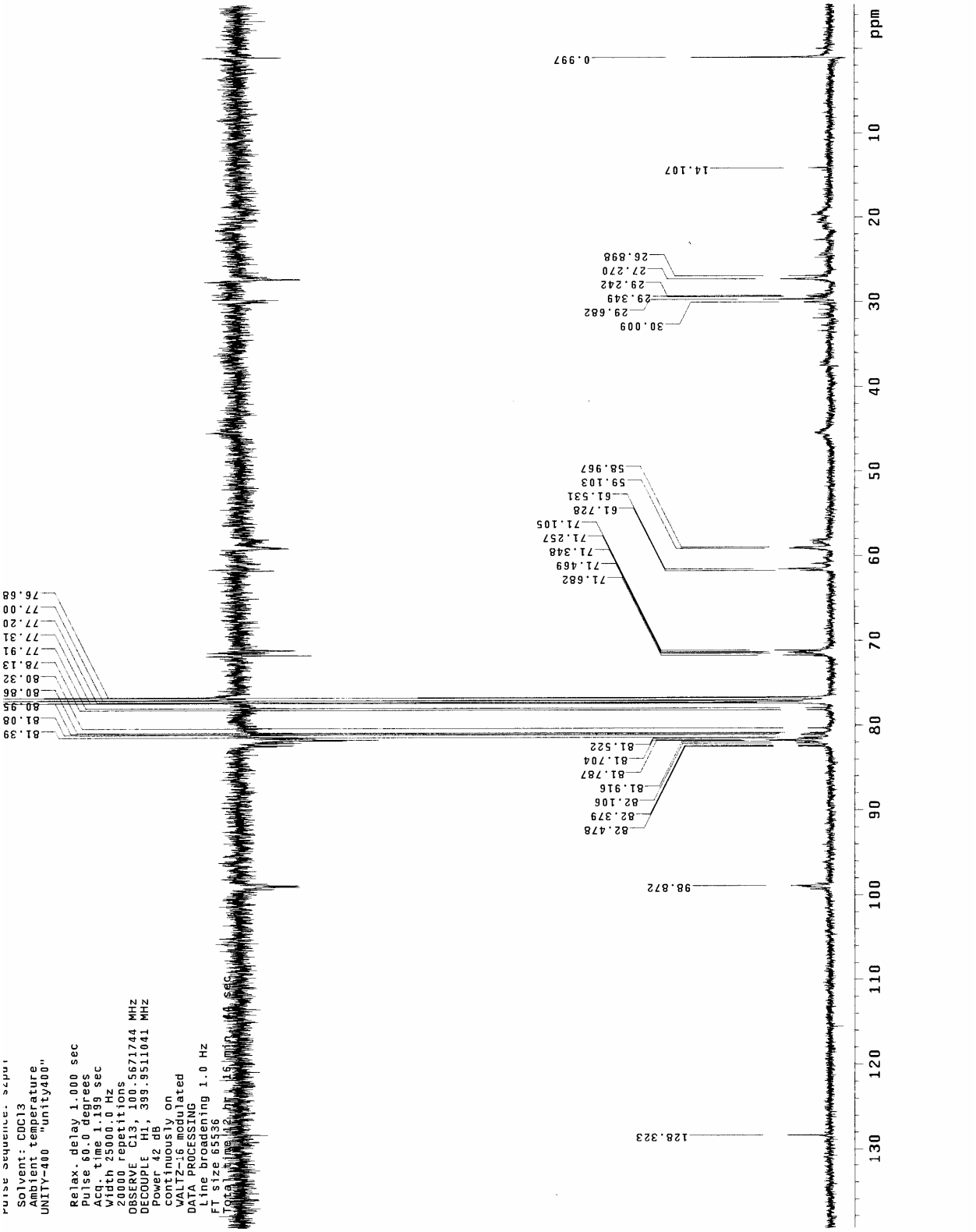
ESI-MS spectrum for dihydroxy permethylated β-cyclodextrin (mixture of AB, AC and AD isomers).



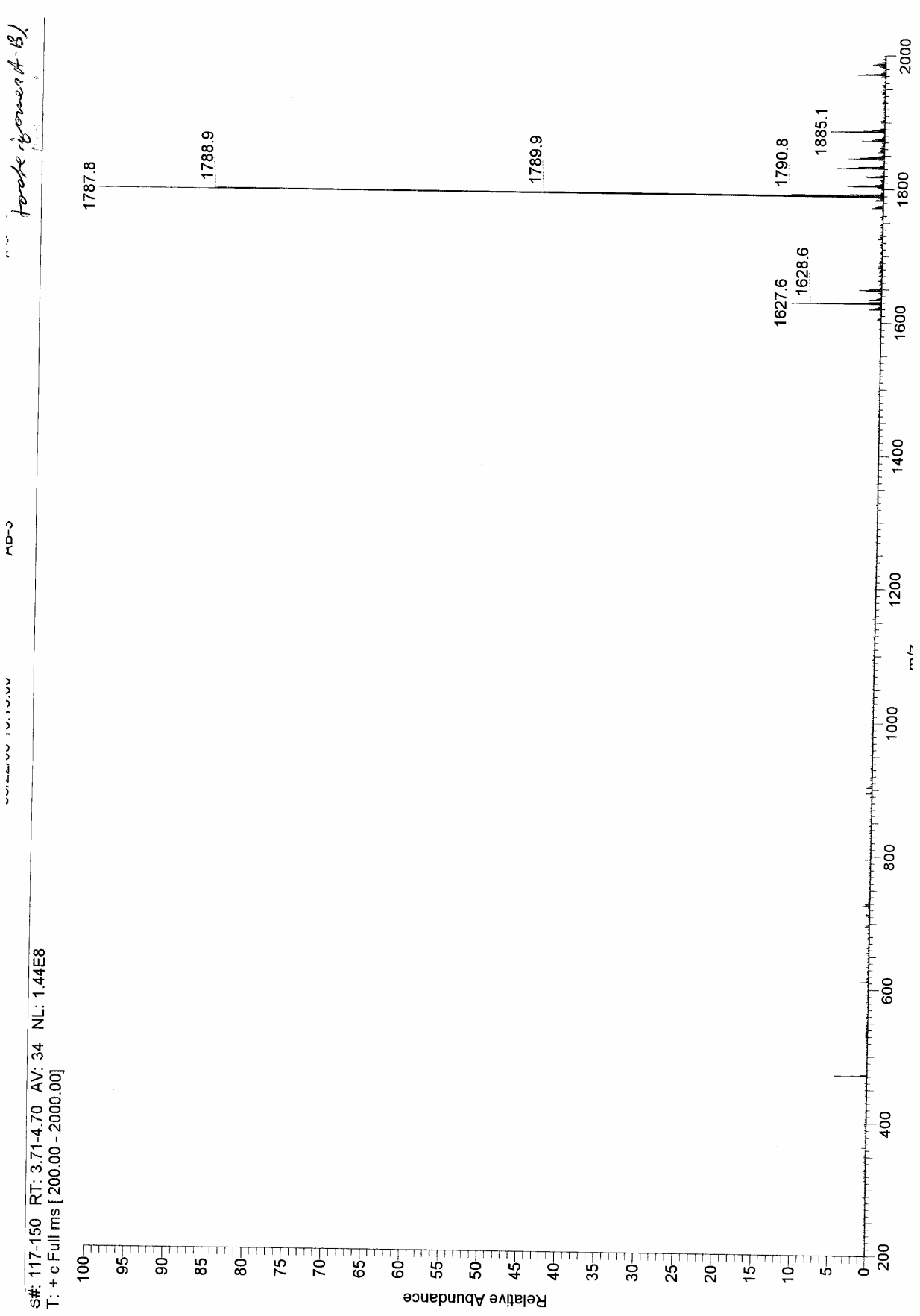
^{13}C NMR for dihydroxy permethylated β-cyclodextrin (AB isomer)



^{13}C NMR for dihydroxy permethylated β-cyclodextrin (AD isomer)



ESI-MS for the **AB** diradical.



ESI-MS for **AD** diradical.