Supplementary Information

Synthesis and Properties of Weakly Coupled Dendrimeric Multiporphyrin Light-Harvesting Arrays and Hole-Storage Reservoirs

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I. Multiphoton effects

When the larger multiporphyrin arrays were examined with high light intensities, the amplitudes of the spectral features associated with Zn* immediately after excitation were much larger than expected for the production of one Zn* per array based on the relative absorbances (extinction coefficients) in the static ground-state optical spectra (as well as transient studies on the isolated chromophores and dyads). The most likely process that will occur if more than one Zn-porphyrin is excited in a given array is singlet-singlet annihilation. In this process, if two adjacent Zn-porphyrins are excited (either directly or as a consequence of energy migration) then the result of the Zn*Zn* → Zn*Zn annihilation process is that one excited state is returned to the ground state and one is left in the excited S_1 state (via an intermediate in which the S_2 state is formed followed by rapid $S_2 \rightarrow S_1$ nonradiative internal conversion).[64] Subsequently, the energy from the remaining Zn* excited state will be transferred (perhaps via several steps depending on its location in the array) to the central Fb-porphyrin to produce Fb*. However, the total number of Fb* states ultimately produced relative to the number of Zn* states initially prepared by photon absorption will be smaller than if only one Zn* had been formed in each array. Thus, a fraction of the transient absorption features (including ground-state bleachings) associated with Zn* at early times will decay to the ground state during the time of the annihilation process, and the absorbance changes at longer times associated with Fb* will be less than expected if no multiphoton effects had taken place.

Although multiphoton-induced annihilation events may occur in a fraction of either the Zn_8Fb or $Zn_{20}Fb$ arrays, these events will not significantly impact the measured time constants for the average overall energy-transfer process from the Zn-porphyrin pool to the Fb-porphyrin core. This is true because there will be a distribution of Zn* excitation sites produced if only one photon is absorbed per array, and a distribution of sites will also exist in the fraction of the arrays in which two photons were originally absorbed after energy migration and the annihilation event that also leaves behind one Zn*. Furthermore, the direct consequences of returning a Zn* to the ground state via annihilation will not affect the time constant for growth of Fb* via energy transfer from the Zn-porphyrin pool, as assayed by the development of bleaching in the ground-state absorption bands of the Fb-porphyrin. Indeed, we have found that the average time constant for arrival of energy at the core is the same within experimental error at high and low excitation intensities.

The finding of a fast time constant (~10 ps or less depending on the array) due to excited-state annihilation may be one indicator that energy transfer between the Zn-porphyrins in a given array may occur roughly on this time scale. The time constant for Zn*Zn* $\rightarrow$ Zn*Zn annihilation will not strictly reflect the inverse rate constant for Zn*Zn $\rightarrow$ ZnZn* energy transfer. Nonetheless, given the dominant through-bond nature of energy transfer between diarylethyne-linked porphyrins,[19,20,53] the annihilation rate constant should be similar to that for energy transfer from Zn* to an adjacent ground-state Zn-porphyrin. Further studies on the arrays described here as well as other arrays containing multiple Zn-porphyrins joined by diarylethyne linkers are underway to elucidate the rate constant for energy transfer between adjacent Zn-porphyrins in these systems.

II. Experimental

General

^{1}H NMR spectra (300 MHz) were collected in $CDCl_3$ unless noted otherwise. Mass spectra of porphyrins were obtained via laser desorption mass spectrometry in the absence of an added matrix (LD-MS)[55] or in the presence of an added matrix (MALDI-MS) such as 4-hydroxy-α-cyanocinnamic acid or ferulic acid,[56] and/or by high resolution fast atom bombardment mass spectrometry (FAB-MS). Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), triphenylarsine ($AsPh_3$), tetrabutylammonium fluoride (TBAF) on silica gel (1.0-1.5 mmol F^-/g resin), mesitaldehyde, $Zn(OAc)_2{\cdot}2H_2O$ and trimethylsilylacetylene were used as received from Aldrich. 4-Iodobenzaldehyde was obtained from Karl Industries, Inc.

Solvents

All solvents used in reactions were dried by standard methods. Toluene and triethylamine were distilled from CaH_2. $CHCl_3$ (Fisher, certified ACS grade, stabilized with 0.8% ethanol) was distilled from K_2CO_3. CH_2Cl_2 and CS_2 (Fisher, certified ACS grade) were used as received.

Chromatography

Analytical scale SEC was used routinely to follow the progress of the reactions, to determine the composition of fractions from chromatography and to assess the purity of the arrays. Unless otherwise specified, analytical SEC was performed on an HPLC using three PLgel columns (Polymer Laboratories, 5 μm, 7.5 x 300 mm) of pore sizes 10^3, 500 and 100 Å connected in series. A Styragel HR 4 column (Waters, 10 μm, 7.8 x 300 mm, ~10^4 Å pore size; we designate this column as 10^4 Å for simplicity) was also used in the SEC column survey. Conditions: mobile phase = THF (Fisher, HPLC grade), flow rate = 0.8 mL/min, injection volume = 20 μL. Sample detection was achieved by absorption spectroscopy using a diode array detector at 420 nm (±10 nm band width).[2,22,47]

Adsorption column chromatography was performed using flash silica (Baker, 40 μm) or alumina (Fisher A540, 80-200 mesh). Preparative-scale SEC was performed either on the benchtop using glass columns (gravity flow) packed with Bio-Beads SX-1 (BioRad) in toluene or THF, or on a Hewlett-Packard 1090 HPLC using a 10^3 Å column (Polymer Laboratories, 10 μm, 300 x 25 mm) in series with a PLgel guard column (10 μm, 25 x 25 mm). Conditions for semi-preparative HPLC: mobile phase = THF, flow rate = 3 mL/min, injection volume = 100-250 μL, detection: UV/Vis, $\lambda = 550 \pm 10$ nm. Porphyrin samples were filtered through glass fiber filters (Fisherbrand 6G) before injection.

Static absorption and emission

Absorption spectra and fluorescence spectra (including quantum yields) were collected in toluene at room temperature as described previously unless noted otherwise.[16,19,20]

Time-resolved absorption

Transient absorption spectra and kinetic date were acquired as described previously using 130-fs 2-10 μJ excitation flashes at 550 nm and weak white-light probe pulses of comparable duration

(10 Hz).[65] Non-degassed samples (25-50 μM) in toluene were contained in 2 mm pathlength cuvettes.

Electrochemistry

The electrochemical studies were performed in benzonitrile (Aldrich) using previously described instrumentation.[3] The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich; recrystallized three times from methanol and dried at 110 °C in vacuo). The electrochemical cell was housed in a Vacuum Atmospheres glovebox (Model HE-93) equipped with a Dri-Train (Model 493). The optical spectra of the oxidized arrays were obtained with a PC card CCD spectrometer (Ocean Optics, Dunedin, Fl, PC2000 with an LS-1 tungsten-halogen light source). The sample compartment of the spectrometer was housed in the glovebox and linked to an external light source and detector (which reside on a PC board mounted in a computer) via a fiber-optic cable.

5,10,15-Tris(4-iodophenyl)-20-{2,6-dimethyl-4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (I_3-Fb-TMS)

Pyrrole (1.11 mL, 16.0 mmol), 4-iodobenzaldehyde (2.76 g, 12.0 mmol), and 2,6-dimethyl-4-[2-(trimethylsilyl)ethynyl]benzaldehyde[23] (0.92 g, 4.0 mmol) were dissolved in $CHCl_3$ (1.6 L). Then $BF_3{\cdot}OEt_2$ (0.59 mL, 4.8 mmol) in $CHCl_3$ (2 mL) was added dropwise over 10 min to the solution with stirring under Ar. The reaction was allowed to proceed for 1.5 h at room temperature. A sample of DDQ (2.72 g, 12.0 mmol) was added in portions over 10 min. After stirring for 30 min, the solvent was removed. The residue was suspended in CH_2Cl_2 (100 mL) and filtered through Celite. The filtrate was set aside and the solids collected in the filtration were suspended in CS_2 (100 mL). The suspension was stirred for 30 min and filtered. This process was repeated for the collected solids of this latter filtration. The filtrates collected from the three filtration steps were combined and concentrated to dryness. The residue was taken up in CS_2 (10 mL, with sonication) and loaded onto a silica column (5 x 40 cm, $CHCl_3$). The mixture of porphyrins eluted as the first band. All fractions that contained porphyrins (with the exception of several late fractions containing *meso*-tetrakis(4-iodophenyl)porphyrin, which was poorly soluble in CS_2) were combined and the solvent was evaporated. The residue was dissolved in CS_2 and chromatographed in two equal portions [alumina (3 x 40 cm), hexanes/CH_2Cl_2 (2.5:1)]. The desired product eluted as the fifth major band. Some leading fractions containing a mixture of the desired porphyrin, the preceding porphyrin, and some tailing fractions containing the desired porphyrin and *meso*-tetrakis(4-iodophenyl)porphyrin were separately resubmitted to chromatographic purification under the same conditions to obtain additional amounts of desired porphyrin. Finally, the combined portions of the desired porphyrin were dissolved in CS_2 (10 mL) in a beaker and CH_2Cl_2 (50 mL) and hexanes (50 mL) were added. The mixture was placed in a fume hood so that a good air flow was pulled over the beaker. This facilitated evaporation of the CS_2 and CH_2Cl_2 within 3 h and resulted in the precipitation of the desired product as a purple powder (785 mg, 18%). ^{1}H NMR and LD-MS data agree with that previously reported.[23]

Zn$_3$Fb-TMS

Following a procedure for Pd-mediated coupling,[47] Zn-H[47] (250 mg, 0.301 mmol) and I$_3$-Fb-TMS (93.5 mg, 83.7 µmol) were reacted in the presence of $AsPh_3$ (31 mg, 0.10 µmol) and $Pd_2(dba)_3$ (12 mg, 13 µmol) in toluene/triethylamine (75 mL, 4:1) at 35 °C under Ar for 6 h. Then additional amounts of $AsPh_3$ (31 mg, 100 µmol) and $Pd_2(dba)_3$ (12 mg, 13 µmol) were added. The reaction was monitored by analytical SEC [retention time (min)/compound]: 22.5 and 23.6/HMWM, 23.8/Zn$_3$Fb-TMS, 24.6/trimers, 26.1/dimers, 28.4/monomers. After 20 h, the reaction was deemed complete. The solvents were evaporated and the residue was chromatographed twice [silica (3 x 10 cm), hexanes/CH_2Cl_2 (2:1→1:1)] to remove traces of low molecular weight material. The fractions containing the desired tetramer were concentrated to dryness and chromatographed [preparative SEC (5 x 60 cm), THF]. The composition of each fraction was determined by using analytical SEC. Following a broad leading band of HMWM, the desired tetramer eluted as the second band (dark red fractions) followed by a third band consisting of trimeric and dimeric products. A second preparative SEC was performed on the leading and trailing fractions of the second band under the same conditions. The combined tetramer-containing fractions from both columns were concentrated. The residue was dissolved in CS_2 (1 mL) and then CH_2Cl_2 (1 mL) and hexanes (1 mL) were added. This solution was chromatographed [silica (3 x 15 cm), hexanes/CH_2Cl_2 (1:1)]. The solvent was removed and the residue was suspended in pentane (20 mL) and sonicated for 1 min. Filtration afforded a reddish-pink powder (165 mg, 61%): ^{1}H NMR δ –2.60 (s, 2H), 0.40 (s, 9H), 1.88 (s, 54H), 1.93 (s, 6H), 2.64 and 2.65 (two s, 27H), 7.29 (s, 6H), 7.31 (s, 12H), 7.70 (s, 2H), 8.08-8.15 (m, 12H), 8.32-8.35 (m, 12H), 8.73 (s, 12H), 8.78 (d, *J* = 5.0 Hz, 2H), 8.82 (d, *J* = 5.1 Hz, 6H), 8.95-8.99

(m, 8H), 9.03 (s, 4H); LD-MS obsd 3215.4, calcd 3218.1 ($C_{216}H_{174}N_{16}SiZn_3$). HRMS was carried out on Zn_3Fb-TMS at greater than unit resolution. Signal-to-noise levels were not sufficient to allow measurement of the nominal exact mass ion (3211.18 amu), but the base peak in the isotope cluster was observed at *m/z* 3217.25. This reaction was performed three times on similar scale and the product was obtained in an average 58% yield. This compound was synthesized earlier in a similar manner.[1]

Zn_4-TMS

Following a standard procedure,[47] a solution of Zn_3Fb-TMS (0.665 g, 0.207 mmol) in CH_2Cl_2 (180 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (68 mg, 0.31 mmol) in methanol (20 mL) for 4.5 h at room temperature under Ar. The reaction mixture was concentrated and the residue was chromatographed [silica, CH_2Cl_2/hexanes (1.2:1)]. The reddish-pink solid obtained was suspended in pentane, sonicated and filtered to afford a reddish-pink powder (625 mg, 92%): ^{1}H NMR δ 0.40 (s, 9H), 1.89 (s, 54H), 1.92 (s, 6H), 2.64 and 2.65 (two s, 27H), 7.29 (s, 6H), 7.30 (s, 12H), 7.69 (s, 2H), 8.08-8.14 (m, 12H), 8.32-8.37 (m, 12H), 8.73 (s, 12H), 8.82-8.86 (m, 8H), 8.96 (d, *J* = 5.1 Hz, 6H), 9.06 (d, *J* = 4.7 Hz, 2H), 9.12 (s, 4H); LD-MS obsd 3283.2, calcd 3281.4 ($C_{216}H_{172}N_{16}SiZn_4$). HRMS was carried out on Zn_4-TMS at greater than unit resolution. Signal-to-noise levels were not sufficient to allow measurement of the nominal exact mass ion (3273.09 amu), but the base peak in the isotope cluster was observed at *m/z* 3281.09. This compound was synthesized earlier in a similar manner.[1]

Zn_4-H

A mixture of Zn_4-TMS (50 mg, 15 μmol) and Bu_4NF/SiO_2[47] (1.0-1.5 mmol F^-/g resin, 31 mg) in THF (5.0 mL) was stirred under Ar at room temperature. After 1 h, ^{1}H NMR analysis of the reaction mixture showed complete desilylation of the starting material. The reaction mixture was then diluted with ethyl acetate (30-40 mL), washed (5% aq $NaHCO_3$, water and brine), dried (Na_2SO_4), filtered and concentrated to dryness. The crude product was dissolved in a minimum amount of toluene and chromatographed (silica, CH_2Cl_2/hexanes 3:1) to afford a reddish-pink solid (46 mg, 94%). Solubility: very soluble in toluene or THF; slightly soluble in CH_2Cl_2. ^{1}H NMR δ 1.87 (s, 54H), 1.93 (s, 6H), 2.64 and 2.65 (two s, 27H), 3.29 (s, 1H), 7.28 (s, 6H), 7.30 (s, 12H), 7.70 (s, 2H), 8.09-8.15 (m, 12H), 8.32-8.37 (m, 12H), 8.73 (s, 12H), 8.82 (d, *J* = 5.1 Hz, 6H), 8.86 (d, *J* = 4.4 Hz, 2H), 8.96 (d, *J* = 5.1 Hz, 6H), 9.06 (d, *J* = 4.4 Hz, 2H), 9.12 (s, 4H);

LD-MS obsd 3207.6, calcd 3209.3 ($C_{213}H_{164}N_{16}Zn_4$). HRMS was carried out on Zn_4-H at greater than unit resolution. Signal-to-noise levels were not sufficient to allow measurement of the nominal exact mass ion (3201.05 amu), but the base peak in the isotope cluster was observed at *m/z* 3209.04. This compound was synthesized earlier in a similar manner.[1]

Asymmetric pentamer Zn_4Fb

Tetramer Zn_4-H (32 mg, 9.97 mmol) was added to a solution of I-Fb[23] (10.4 mg, 12.0 mmol) and $AsPh_3$ (1.2 mg, 3.9 μmol) in 4.4 mL of toluene/triethylamine (5:1). The solution was deaerated with argon for 30 min. A sample of $Pd_2(dba)_3$ (2.0 mg, 1.8 μmol) was added and deaeration was continued for 15 min. The flask was immersed in an oil bath at 40 °C. After 24 h, column chromatography (Bio-Beads SX-1, 5 cm dia x 100 cm, toluene) yielded the following components (in order of elution): HMWM, octamer Zn_8, title pentamer, and unreacted tetramer Zn_4-H and mono-iodo porphyrin. The pentamer was rechromatographed a second time under identical conditions, affording a purple solid (32 mg, 81%): LD-MS obsd 3947.9, calcd avg mass 3948.2 ($C_{266}H_{210}N_{20}Zn_4$); λ_{abs} 423, 429, 515, 550, 590, 647 nm. The ^{1}H NMR spectrum showed signs of aggregation. Treatment of an analytical sample of Zn_4Fb with $Zn(OAc)_2{\cdot}2H_2O$ yielded the all-zinc asymmetric pentamer Zn_5: LD-MS obsd 4012.1, calcd avg mass 4011.6 ($C_{266}H_{208}N_{20}Zn_5$); λ_{abs} 424, 432, 512, 550, 590 nm. This compound was synthesized earlier in a similar manner.[1]

Zn_8Fb

Following a procedure for Pd-mediated coupling,[47] Zn_4-H (20 mg, 6.2 μmol) and I-Fb-I[54] (2.5 mg, 2.6 μmol) were reacted in the presence of $Pd_2(dba)_3$ (0.7 mg, 0.8 μmol) and $AsPh_3$ (1.9 mg, 6.2 μmol) in toluene/triethylamine (5:1, 2.5 mL) at 35 °C under Ar. The reaction was monitored by analytical SEC [retention time (min)/compound]: 20-21/HMWM, 21.7/Zn_8Fb, 23.5/Zn_4Fb-I, Zn_4Fb-Ph, 29.3/monomers. After 2.5 h, a mixture of $Pd_2(dba)_3$ (0.70 mg, 0.80 μmol) and $AsPh_3$ (1.9 mg, 6.2 μmol) was added and the reaction was allowed to proceed overnight (total reaction time = 19 h). The final reaction mixture was concentrated to dryness and the residue dissolved in the minimum amount of toluene. A preliminary purification by column chromatography (silica, CH_2Cl_2/hexanes 3:1) afforded a major red band, which was collected in two fractions. Analytical SEC showed both fractions contained HMWM, the desired nonamer Zn_8Fb, and presumed pentameric and tetrameric species, with the first fraction presenting a higher percentage of Zn_8Fb (10-20%) than the second fraction. A deep red residue remained on top of the silica column. The first and second fractions collected from the silica column were further purified (separately) by preparative SEC (65 x 4.5 cm, toluene). A yellowish leading band containing HMWM was immediately followed by a red band; the latter consisted of the desired Zn_8Fb (collected in 10-13 fractions). The second and third band (red) corresponding to the reaction side-products eluted later. The composition of the Zn_8Fb-containing fractions, determined by analytical SEC, showed a higher percentage of HMWM in the early fractions, while the latter ones contained pure Zn_8Fb. The impure fractions were then divided in three groups (B, C and D) based on the percentage of HMWM present, with D showing the highest percentage of HMWM. These fractions were rechromatographed separately by SEC, and the Zn_8Fb band was collected as described above. A total of nine SEC columns were carried out, although 80-90% of the product was obtained after five columns. The combined pure Zn_8Fb-containing fractions yielded 3.6 mg (20%) of product. Three side-products were isolated and examined by LD-MS: Zn_4Fb-I + Zn_4Fb-Ph (0.9 mg; co-elute on SEC) and Zn_4-Ph (0.4 mg, 2%). Zn_8Fb: ^1H NMR δ –2.53 (s, 2H), 1.88 (s, 108H), 1.92 (m, 12H), 2.04 (s, 12H), 2.64, 2.65 and 2.68 (three s, 60H), 7.29 (s, 12H), 7.31 (s, 24H), 7.35 (s, 4H), 7.91 (s, 4H), 8.09-8.17 (m, 28H), 8.32-8.41 (m, 28H), 8.73 (s, 24H), 8.80 (d, *J* = 5.1 Hz, 4H), 8.83 (d, *J* = 4.4 Hz, 12H), 8.94 (d, *J* = 5.1 Hz, 4H), 8.96-8.99 (m, 16H), 9.12 (d, *J* = 5.1 Hz, 4H), 9.15 (s, 8H); LD-MS obsd 7118.2, calcd 7113.4 ($C_{476}H_{366}N_{36}Zn_8$); λ_{abs} 424, 433, 513, 551, 592, 657 nm; λ_{em} (λ_{ex} = 550 nm) 599, 653, 721 nm.

Zn_4Fb-I: LD-MS obsd 4030.3, calcd 4032.03 ($C_{263}H_{203}IN_{20}Zn_4$). Zn_4Fb-Ph: LD-MS obsd 3983.1, calcd 3982.22 ($C_{269}H_{208}N_{20}Zn_4$). Zn_4-Ph: ^1H NMR data agree with that reported below (see procedure for the synthesis of Zn_5-TMS); LD-MS obsd 3281.2, calcd 3285.35 ($C_{219}H_{168}N_{16}Zn_4$).

Zn_9

Following a standard procedure,[47] treatment of Zn_8Fb with $Zn(OAc)_2{\cdot}2H_2O$ in CH_2Cl_2/methanol (9:1) followed by standard work-up afforded Zn_9: ^1H NMR δ 1.88, 1.91 (two s, 120H), 2.04 (s, 12H), 2.64, 2.65 and 2.68 (three s, 60H), 7.29 (s, 12H), 7.31 (s, 24H), 7.35 (s, 4H), 7.91 (s, 4H), 8.09-8.17 (m, 28H), 8.32-8.41 (m, 28H), 8.73 (s, 24H), 8.83 (d, *J* = 5.1 Hz, 12H), 8.89 (d, *J* = 4.4 Hz, 4H), 8.96-8.99 (m, 16H), 9.03 (d, *J* = 5.1 Hz, 4H), 9.12 (d, *J* = 4.4 Hz, 4H), 9.15 (s, 8H);

LD-MS obsd 7168.9 (neat form), 7171.5 (ferulic acid matrix); calcd 7176.8 ($C_{476}H_{364}N_{36}Zn_9$); λ_{abs} 424, 434, 551, 592 nm; λ_{em} (λ_{ex} = 550 nm) 600, 648 nm.

Zn_5-TMS

Following a procedure for Pd-mediated coupling,[47] Zn_4-H (25 mg, 7.8 μmol) and I-Zn-TMS[2] (8.7 mg, 8.6 μmol) were reacted in the presence of $Pd_2(dba)_3$ (1.1 mg, 1.2 μmol) and $AsPh_3$ (2.9 mg, 9.4 μmol) in toluene/triethylamine (3.3 mL, 5:1) for 4 h at 35 °C under Ar. The reaction was monitored by analytical SEC [retention time (min)/compound]: 22-23/HMWM, 24.1/Zn_5-TMS, 24.8/Zn_4-H, Zn_4-Ph, 28.9/monomers. The final reaction solution was concentrated to dryness. A preliminary purification by column chromatography [silica, CH_2Cl_2/hexanes (2:1)] of the crude material afforded a major red band, which was collected in two fractions. Analytical SEC showed both fractions contained HMWM, the desired pentamer, and presumed unreacted materials. Both fractions were further purified by preparative SEC (toluene). The pentameric product eluted as the second band following a yellowish leading band of HMWM. Leading and tailing fractions containing HMWM, pentamer and tetrameric side-product were concentrated and resubmitted to preparative SEC. The combined pure pentamer-containing fractions afforded a reddish-pink solid (21 mg, 66%). Zn_4-Ph (2.5 mg, 10%) was isolated as a side-product. Zn_5-TMS: ^{1}H NMR δ 0.37 (s, 9H), 1.88 (s, 72H), 2.03 (s, 6H), 2.64 (s, 12H), 2.65 (s, 21H), 7.29 (s, 6H), 7.30 (s, 16H), 7.63 (s, 2H), 7.90 (s, 2H), 8.08-8.16 (m, 14H), 8.31-8.41 (m, 14H), 8.66 (d, *J* = 4.4 Hz, 2H), 8.73-8.74 (m, 16H), 8.82-8.85 (m, 8H), 8.95-8.98 (m, 8H), 9.11 (d, *J* = 5.1, 2H), 9.14 (s, 4H); LD-MS obsd 4093.2, calcd 4093.8 ($C_{270}H_{214}N_{20}SiZn_5$). Zn_4-Ph: ^{1}H NMR δ 1.87 (s, 54H), 1.96 (s, 6H), 2.63 (s, 9H), 2.65 (s, 18H), 7.28 (s, 6H), 7.30 (s, 12H), 7.43-7.46 (m, 3H), 7.69-7.72 (m, 2H), 7.75 (s, 2H), 8.09 (dd, *J* = 8.1, 2.2 Hz, 6H), 8.12-8.15 (m, 6H), 8.30-8.37 (m, 12H), 8.73 (s, 12H), 8.82 (d, *J* = 4.4 Hz, 6H), 8.90 (d, *J* = 4.4 Hz, 2H), 8.95 (d, *J* = 4.4 Hz, 6H), 9.07 (d, *J* = 4.4 Hz, 2H), 9.12 (s, 4H); LD-MS obsd 3285.7, calcd 3285.4 ($C_{219}H_{168}N_{16}Zn_4$). HRMS of Zn_4-Ph was carried out at greater than unit resolution. Signal-to-noise levels were not sufficient to allow measurement of the nominal exact mass ion (3277.08 amu), but the base peak in the isotope cluster was observed at the expected *m/z* = 3285.1.

Zn_5-H

Following the procedure described for the desilylation of Zn_4-TMS, a mixture of Zn_5-TMS (15 mg, 3.7 μmol) and Bu_4NF/SiO_2 (1.0-1.5 mmol F^-/g resin, 15 mg) in THF (1.9 mL) was stirred at room temperature under Ar. After 1 h, ^{1}H NMR analysis of the reaction mixture showed complete desilylation of the starting material. The final reaction mixture was diluted with toluene (20 mL), washed (5% aq $NaHCO_3$, water then brine), dried (Na_2SO_4), filtered and concentrated to dryness. Purification by column chromatography [silica, toluene/hexanes (10:1)] afforded a red solid (14 mg, 95%). Solubility: very soluble in toluene; slightly soluble in ethyl acetate, CH_2Cl_2, or THF. LD-MS obsd 4024.6, calcd 4021.6 ($C_{267}H_{206}N_{20}Zn_5$). The ^{1}H NMR spectrum showed signs of aggregation.

Zn_{20}Fb

Following a procedure for Pd-mediated coupling,[47] Zn_5-H (14 mg, 3.5 μmol) and I_4-Fb[23] (0.7 mg, 0.6 μmol) were reacted in the presence of $Pd_2(dba)_3$ (0.4 mg, 0.4 μmol) and $AsPh_3$ (1.0 mg, 3.4 μmol) in toluene/triethylamine (5:1, 1.0 mL) at 35 °C under Ar. The reaction was monitored by analytical SEC using a guard and 1000 Å columns in series [retention time (min)/compound]: 7-8/HMWM, 8.2/Zn_{20}Fb, 8.4 and 8.8/side products, 9.7/Zn_5-H, 12.0/monomers. (Note that in some of the chromatograms included herein, the use of a guard column resulted in slightly different retention times.) After 3.5 h, a mixture of $Pd_2(dba)_3$ (0.4 mg, 0.4 μmol) and $AsPh_3$ (1.0 mg, 3.4 μmol) was added, and the reaction was allowed to proceed overnight (total reaction time = 22 h). Then the reaction mixture was concentrated to dryness, dissolved in the minimum amount of toluene, and chromatographed [silica, CH_2Cl_2/hexanes (3:1)]. A broad red band containing all porphyrin products was collected and concentrated. Preparative SEC of this porphyrin mixture was carried out on a gravity flow column (48 x 2 cm) using toluene as eluant. The first band (containing the desired Zn_{20}Fb) was collected in several fractions. Analytical SEC showed that each fraction contained a mixture of HMWM, Zn_{20}Fb, and three lower molecular weight species, presumably reaction side-products arising from incomplete coupling. The collected fractions were then divided into three groups (B, C and D) based on the percentage of Zn_{20}Fb present, with B showing the highest percentage of Zn_{20}Fb. These fractions were rechromatographed separately by preparative SEC-HPLC. The band containing the 21-mer (retention time = 22.1 min) was collected again in several fractions, which were examined by analytical SEC (guard and 10^3 Å columns in series) and the impure fractions were divided and combined as described above. After two SEC-HPLC columns, fraction B afforded pure Zn_{20}Fb, while C and D required 2-4 re-injections. The combined pure Zn_{20}Fb fractions yielded 1.9 mg (19%) of product. MALDI-MS (ferulic acid) obsd 16635.5, calcd 16693.0 ($C_{1112}H_{846}N_{84}Zn_{20}$);

λ_{abs} 424, 434, 513, 551, 592, 657 nm; λ_{em} (λ_{ex} = 550 nm) 596, 655, 721 nm. The ^{1}H NMR spectrum showed signs of aggregation.

Zn_{21}

Following a standard procedure,[47] treatment of an analytical sample of $Zn_{20}Fb$ with $Zn(OAc)_2{\cdot}2H_2O$ in CH_2Cl_2/methanol (9:1) followed by standard work-up afforded Zn_{21}: MALDI-MS (ferulic acid) obsd 16704.3, calcd 16756.4 ($C_{1112}H_{844}N_{84}Zn_{21}$); λ_{abs} 424, 434, 512, 551, 592 nm; λ_{em} (λ_{ex} = 550 nm) 600, 647 nm.

Synthesis of a diphenylbutadiyne-linked octamer Zn_8.[1]

A rapid synthesis of the Zn_8 octamer was accomplished via Glaser oxidative homocoupling of Zn_4-H under Eglinton conditions.[66] The Zn_8 octamer contains a diphenylbutadiyne linker joining the two tetrameric halves and lacks a Fb-porphyrin (Scheme S1). The synthesis was performed as follows: Tetramer Zn_4-H (10 mg, 3.1 μmol) was added to a mixture of copper acetate (6.0 mg, 3.2 μmol) in pyridine (1 mL). After 19 h, the product distribution consisted of octamer Zn_8 and a small amount of unreacted Zn_4-H. Purification by two identical chromatographic procedures (SEC, 5 x 100 cm, toluene) afforded 7.2 mg (72%): ^{1}H NMR (CD_2Cl_2) δ 1.89 (s, 108H), 2.06 (s, 12H), 2.67 (s, 36H), 2.69 (s, 18H), 7.26 (s, 12H), 7.27 (s, 24H), 7.82 (s, 4H), 8.06-8.14 (m, 24H), 8.29-8.38 (m, 24H), 8.66-8.67 (m, 24H), 8.74 (d, *J* = 4.6 Hz, 12H), 8.89 (d, *J* = 4.5 Hz, 4H), 8.92 (d, *J* = 4.6 Hz, 12H), 9.08 (d, *J* = 4.5 Hz, 4H), 9.11 (s, 8H); LD-MS obsd 6416.8, calcd 6416.5 ($C_{426}H_{326}N_{32}Zn_8$) λ_{abs} 424, 432, 512, 550, 590 nm. Analytical data are included in Section VII.

III. Exploratory studies on the purification of $Zn_{20}Fb$ (2 pages of data).

Attempted preliminary purification of the 21-mer $Zn_{20}Fb$ on silica as well as alumina using a variety of solvent systems ($CHCl_3$, CH_2Cl_2, toluene, THF, ethyl acetate with hexanes) did not provide desired results; instead, in all cases the porphyrin mixture eluted as one band. Attempts to achieve separation on silica (Alltech, 5 μm, 250 x 4.6 mm) or cyano-propyl (Alltech, 5 μm, 250 x 4.6 mm) HPLC columns using different solvent systems (CH_2Cl_2/hexanes, toluene, toluene/hexanes, toluene/hexanes/isopropanol) resulted in broad unresolved peaks. Treatment of the porphyrin mixture under heterogeneous magnesium insertion conditions with MgI_2,[67] in order to impart higher polarity to the molecule by inserting magnesium into the core Fb-porphyrin moiety of the 21-mer array, did not facilitate separation from the porphyrin mixture. The use of graphite (activated C/Celite (1:1)) as stationary phase[68] on a gravity-flow column with toluene or benzene as eluants, resulted in almost complete elimination of the HMWM from the mixture, but a substantial amount (30-40%) of the 21-mer remained strongly adsorbed to the graphite.

The use of polystyrene gel columns (SEC-HPLC) for the separation of fullerenes[69] and *meso*,*meso*-linked porphyrin arrays[9d] has been recently reported. We investigated three analytical SEC columns with pore sizes of 500 Å (MW range = 500-20,000 Da), 10^3 Å (MW range = 1,000-40,000 Da) and 10^4 Å (MW range = 5,000-600,000 Da). The results are shown below (two pages of data). The best peak resolution was obtained with the 10^3 Å column, whose HPLC trace clearly showed the presence of four species in the mixture: HMWM, 21-mer, and two lower molecular weight by-products. The use of two 10^3 Å columns in series increased the separation of the peaks, while addition of a third column (10^3 Å) did not improve the separation but contributed to band spreading. A change in the flow rate (from 0.4-1.4 mL/min) had no effect on the peak resolution. Despite the high solubility of all arrays in both toluene and THF, toluene could not be used as the mobile phase in SEC-HPLC because it exerts a strong interaction of the porphyrin arrays (from tetramer to 21-mer) with the aromatic gel matrix,[70] resulting in the elution of very broad, unresolved bands at retention times 5-10 min higher than those observed when THF is employed as the eluant. In summary, the optimum set of conditions for analysis of these large arrays on analytical SEC-HPLC was determined to be a 10^3 Å column or two 10^3 Å columns in series, a flow rate of 0.8 mL/min, and THF as the mobile phase.

IV. SEC elution times for diverse arrays (7 pages of data).

We examined the elution time of diverse arrays (ZnTPP, Zn_2, Zn_3, Zn_4-TMS, Zn_5-TMS, Zn_9, and Zn_{21}) with various columns individually. Data are shown for the entire chromatogram and in expanded mode focusing on the region showing the elution peaks. A subset of these data is shown in the main text (Figure 3).

V. LD-MS analysis of the larger arrays (3 pages of data).

We show representative mass spectral data obtained with or without a matrix. These spectra include the following:

(1) The crude reaction mixture and purified sample of Zn_8Fb recorded without a matrix (i.e., LD-MS).

(2) A pure sample of Zn_9 examined under different mass spectral conditions: (a) neat sample (i.e., LD-MS); (b) MALDI-MS using α-cyano-4-hydroxycinnamic acid; (c) ferulic acid.

(3) MALDI-MS spectra using ferulic acid of samples related to the 21-mer arrays: (a) crude reaction mixture of $Zn_{20}Fb$; (b) purified $Zn_{20}Fb$; (c) purified sample of Zn_{21}.

VI. Selected absorption and fluorescence data (4 pages of data).

We show representative fluorescence data obtained in toluene at room temperature for Zn_8Fb, $Zn_{20}Fb$, Zn_9, and Zn_{21}. These spectra include both fluorescence emission spectra and fluorescence excitation spectra. The absorption spectrum of $Zn_{20}Fb$ in toluene at room temperature is also included. Note that the $Q_X(0,0)$ band of the Fb-porphyrin is barely visible at ~650 nm in the presence of the large absorption due to the twenty Zn-porphyrins.

VII. Analytical data of new compounds (28 pages of data).

References.

1-63 See main text.

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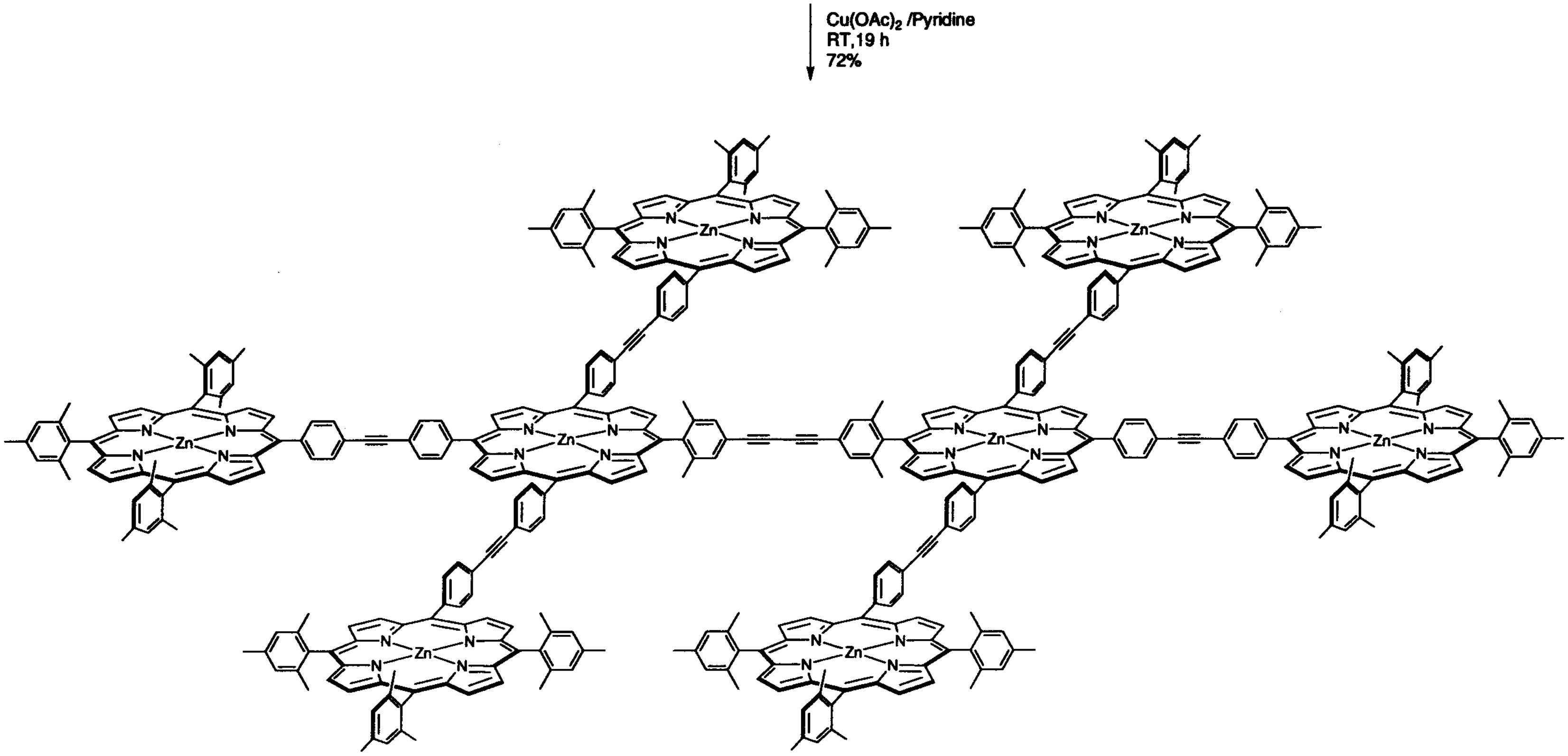
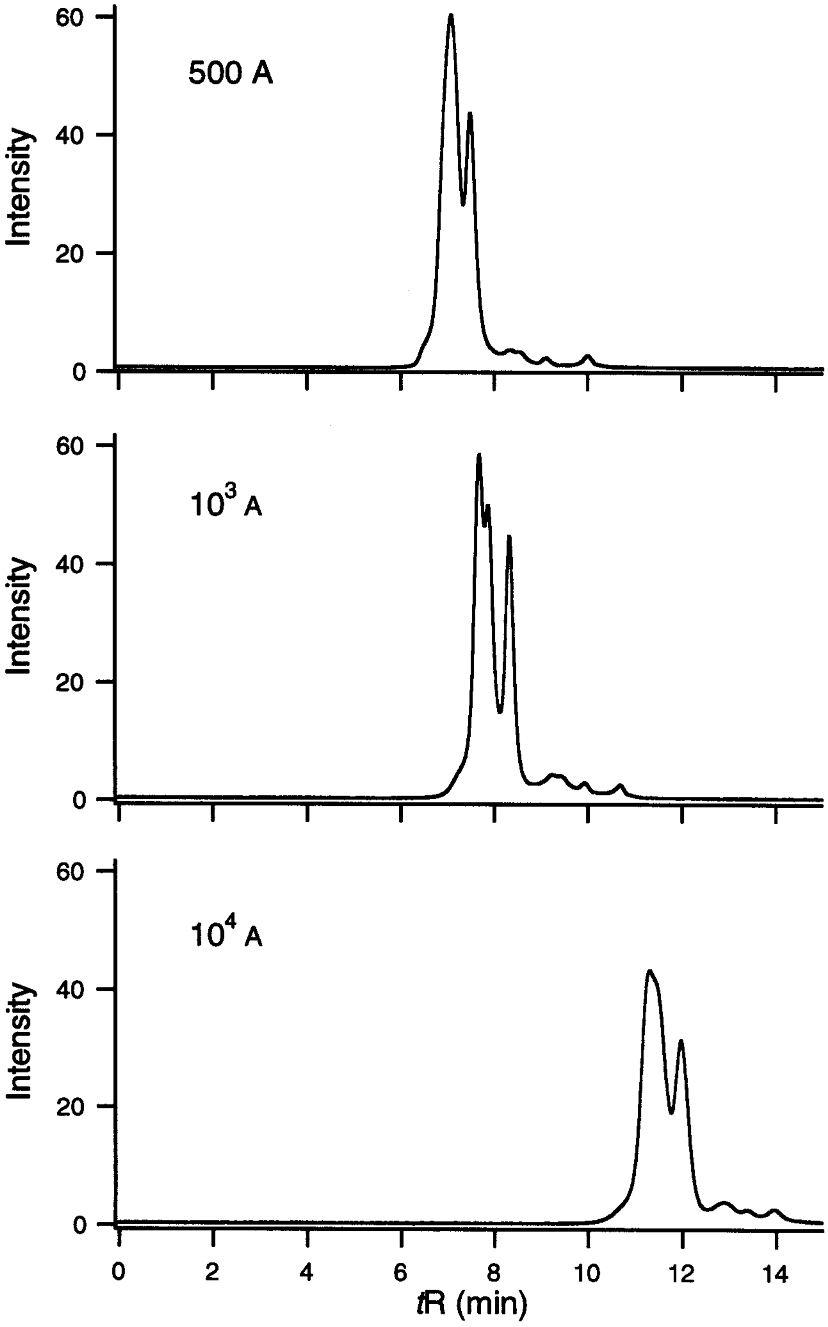
Scheme S1. Synthesis of Octamer

Zn_4-H

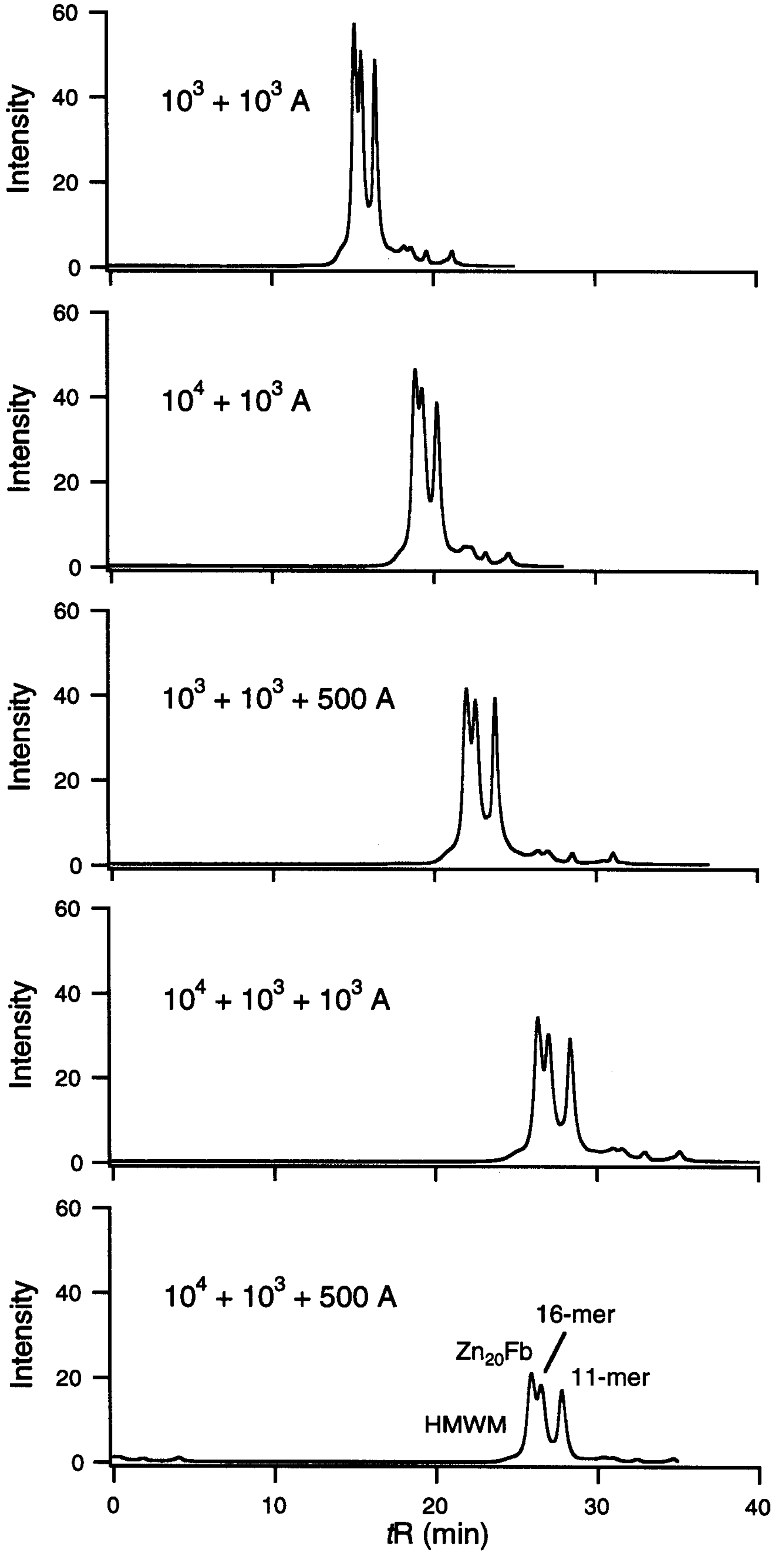


Cu(OAc)$_2$ /Pyridine
RT,19 h
72%

Zn_8

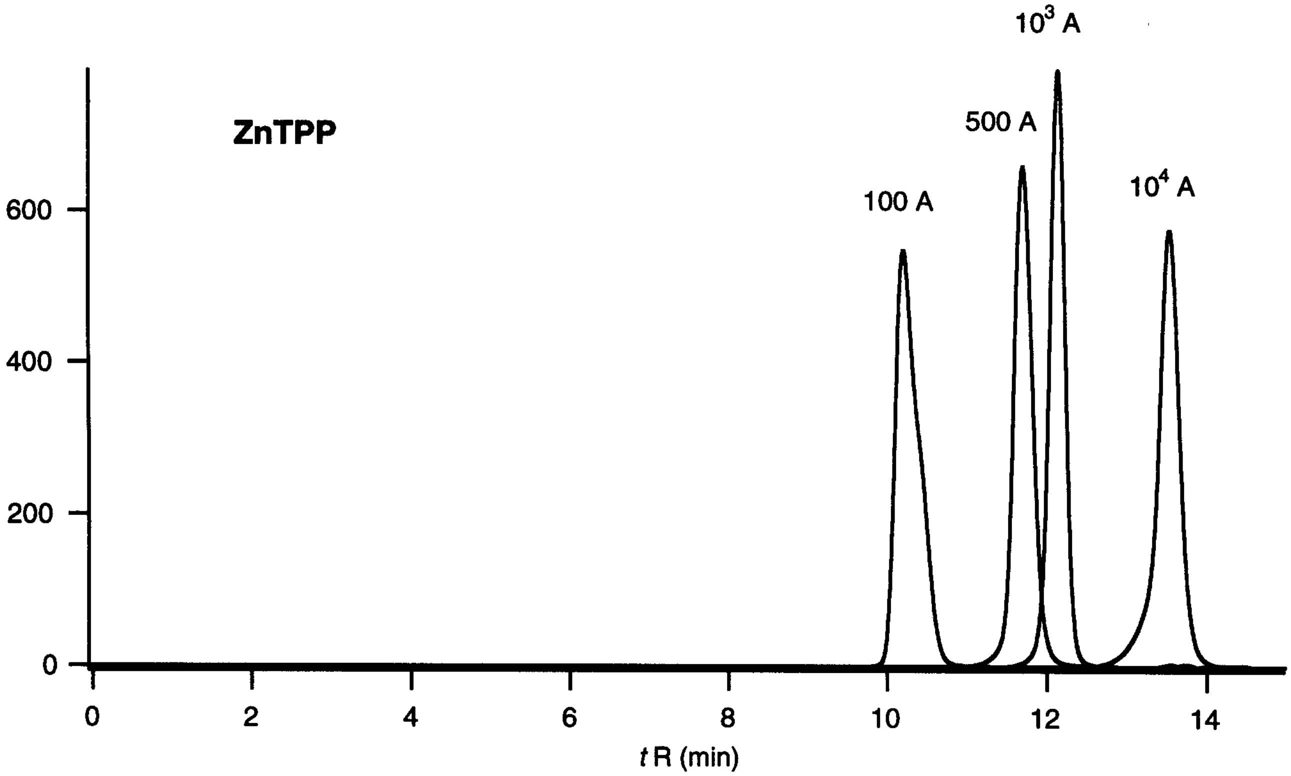


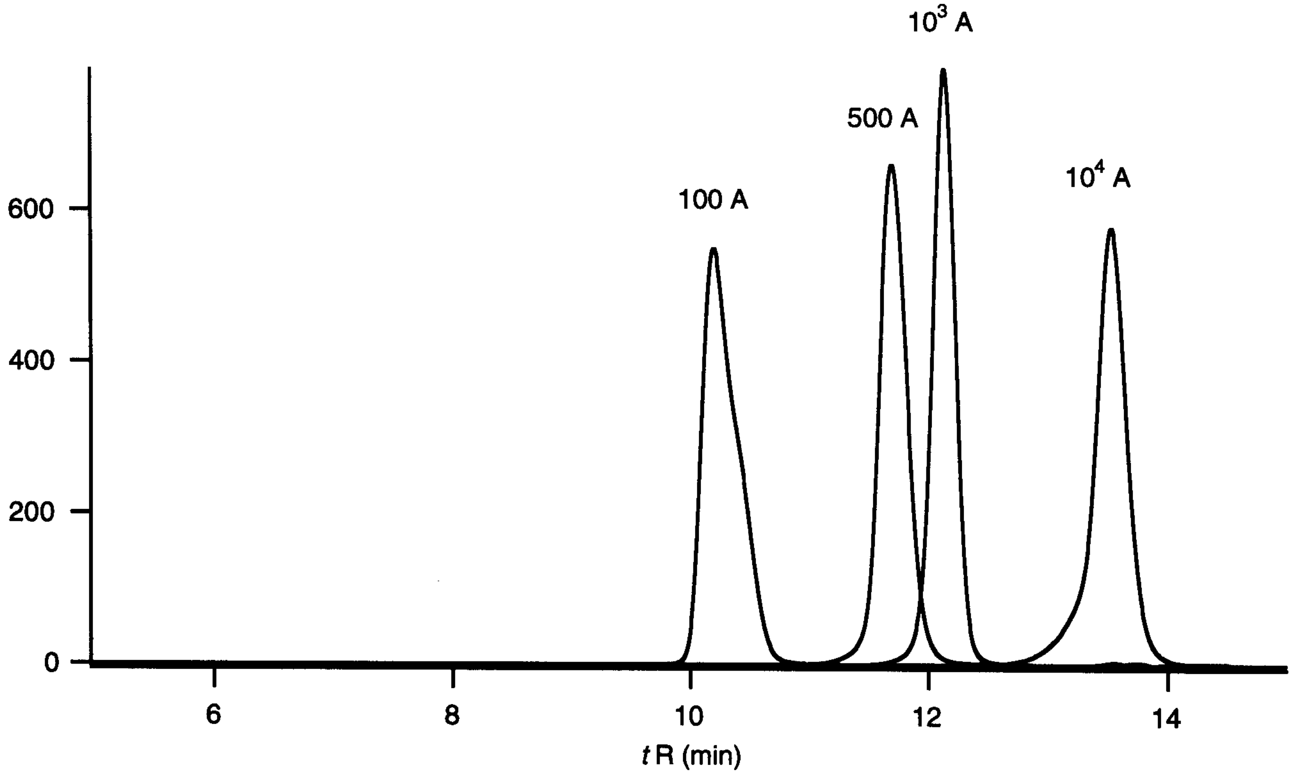
SEC-HPLC Separation of 21-mer array based on column pore size



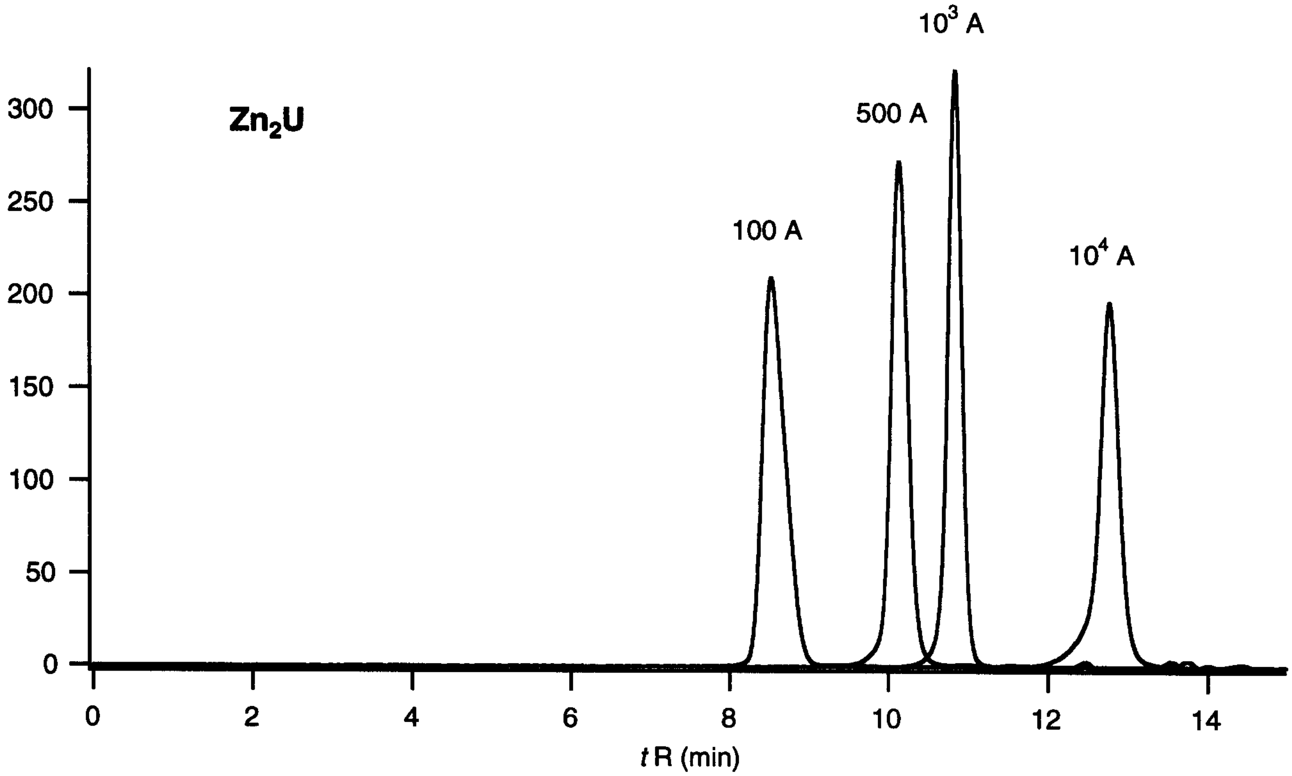
SEC-HPLC Separation of 21-mer array using 2 and 3 columns in series

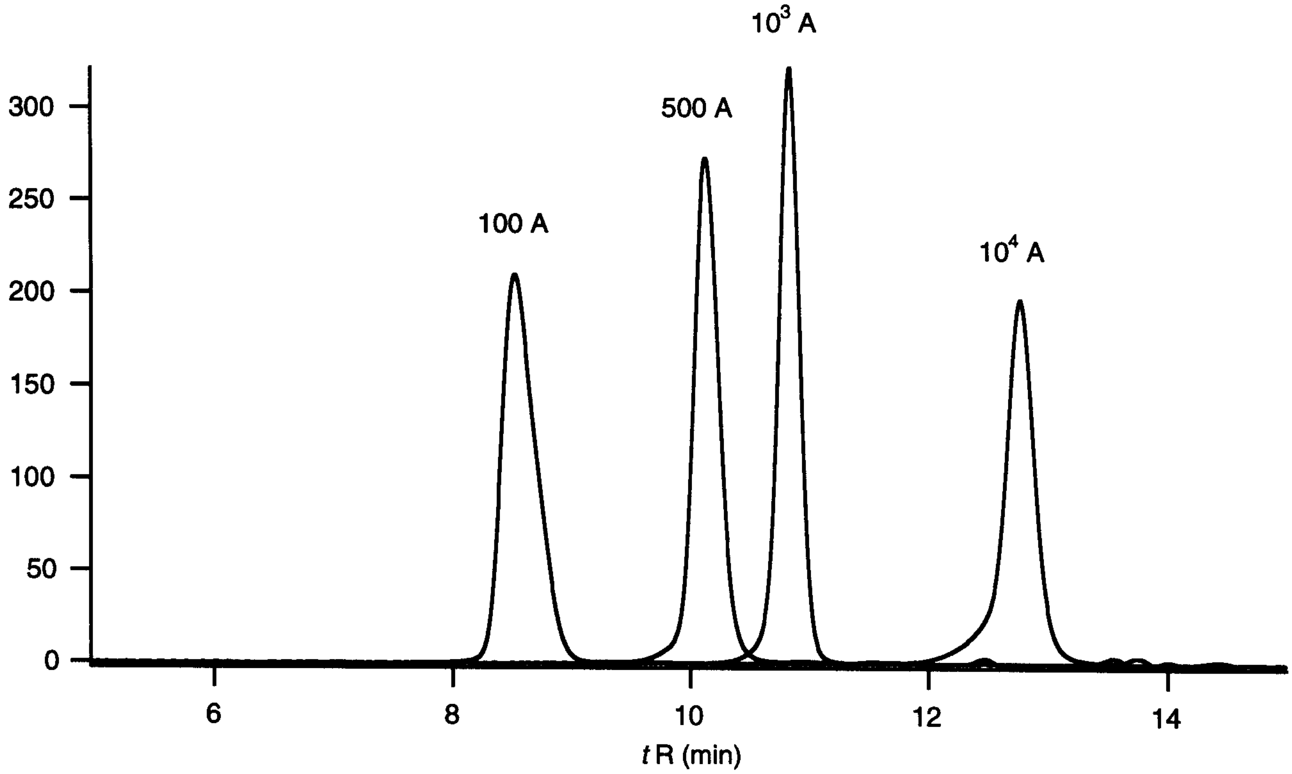
Elution Pattern of ZnTPP on SEC-HPLC Columns



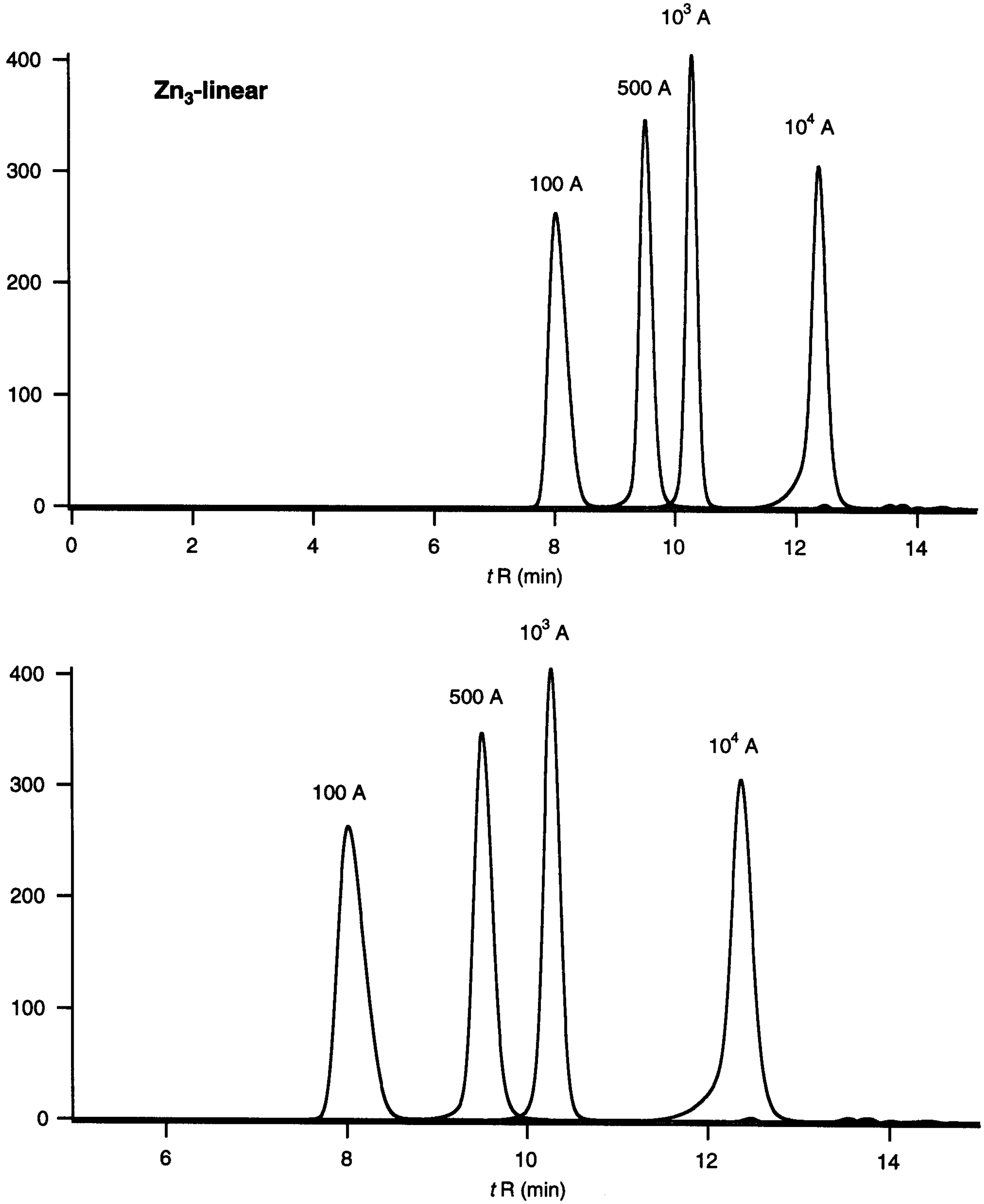


Elution Pattern of Zn_2U on SEC-HPLC columns

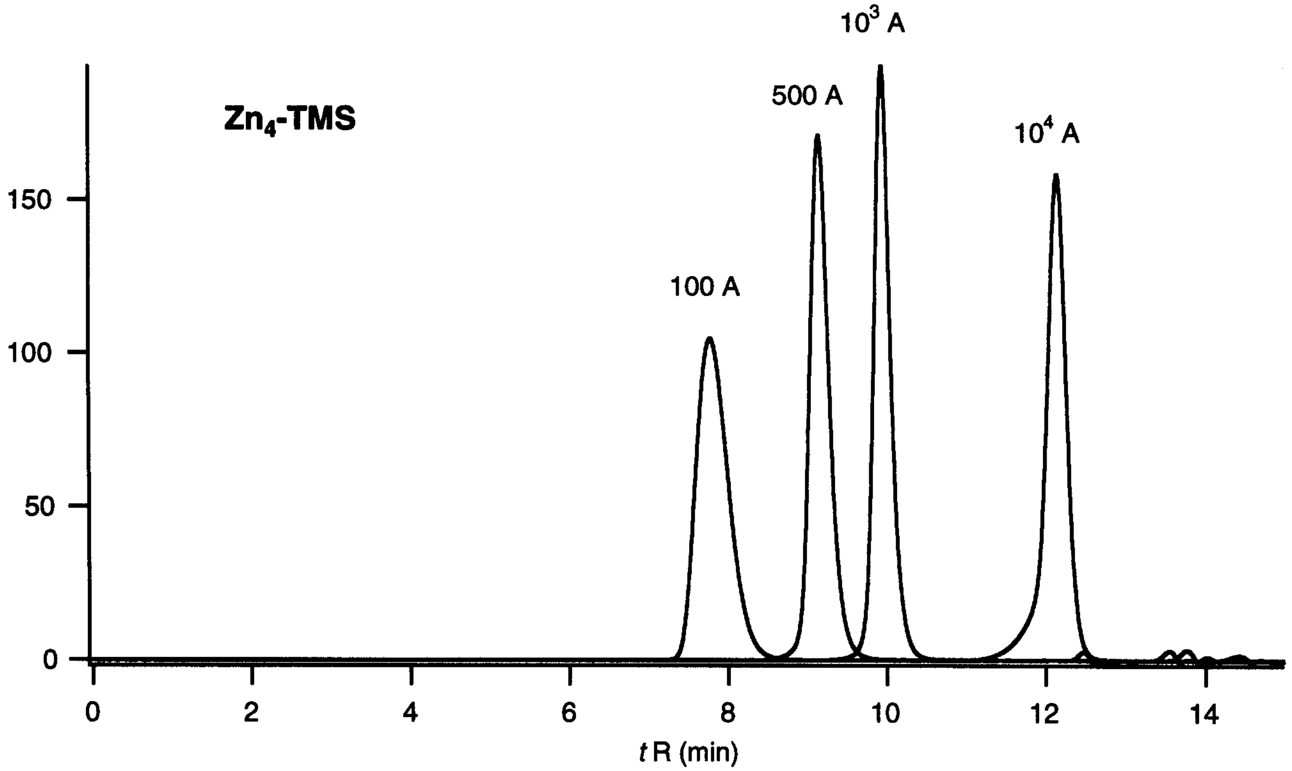


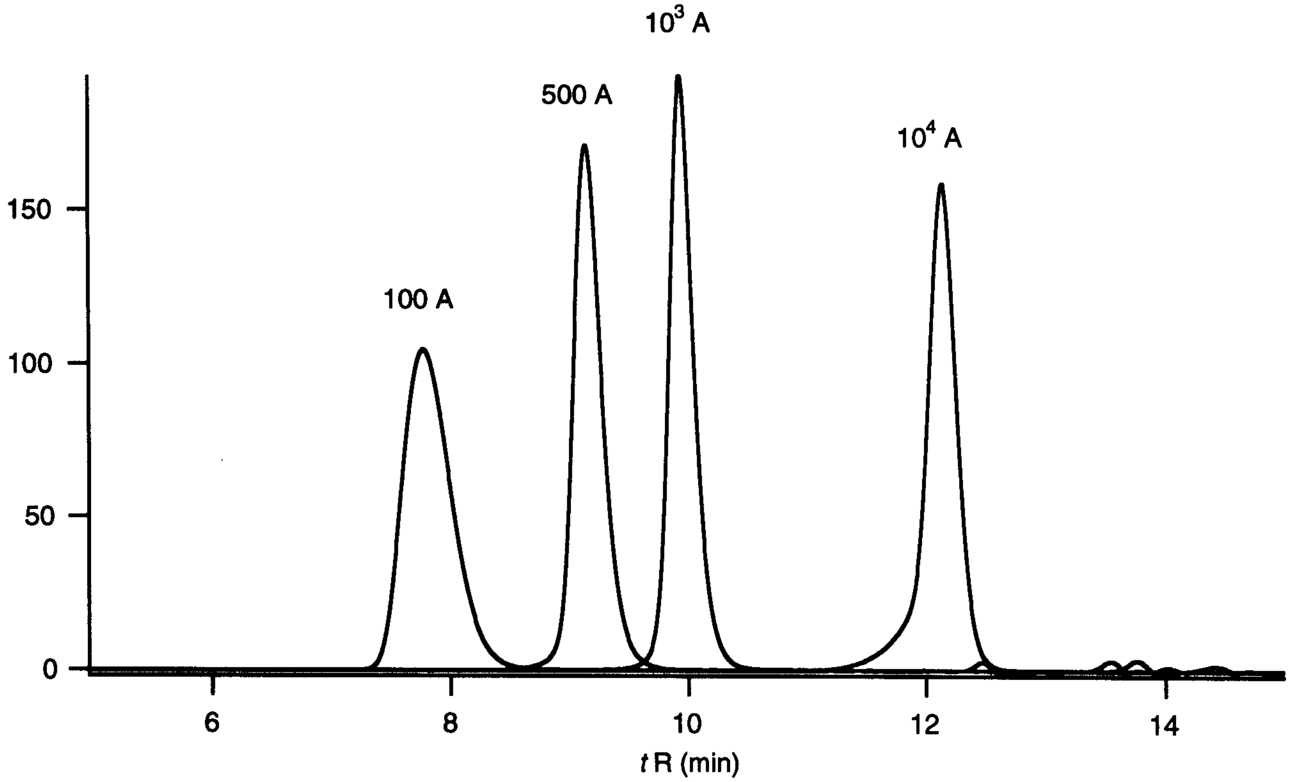


Elution Pattern of Zn_3-linear on SEC-HPLC columns

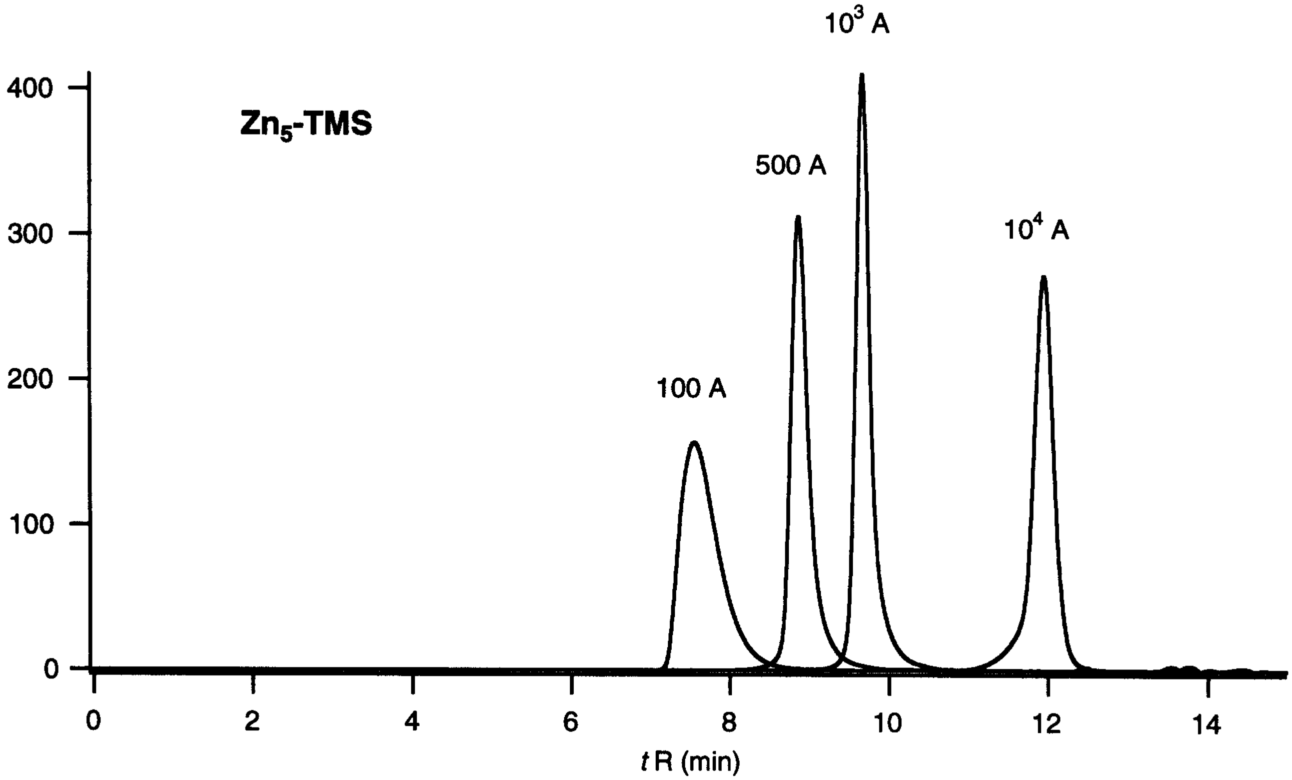


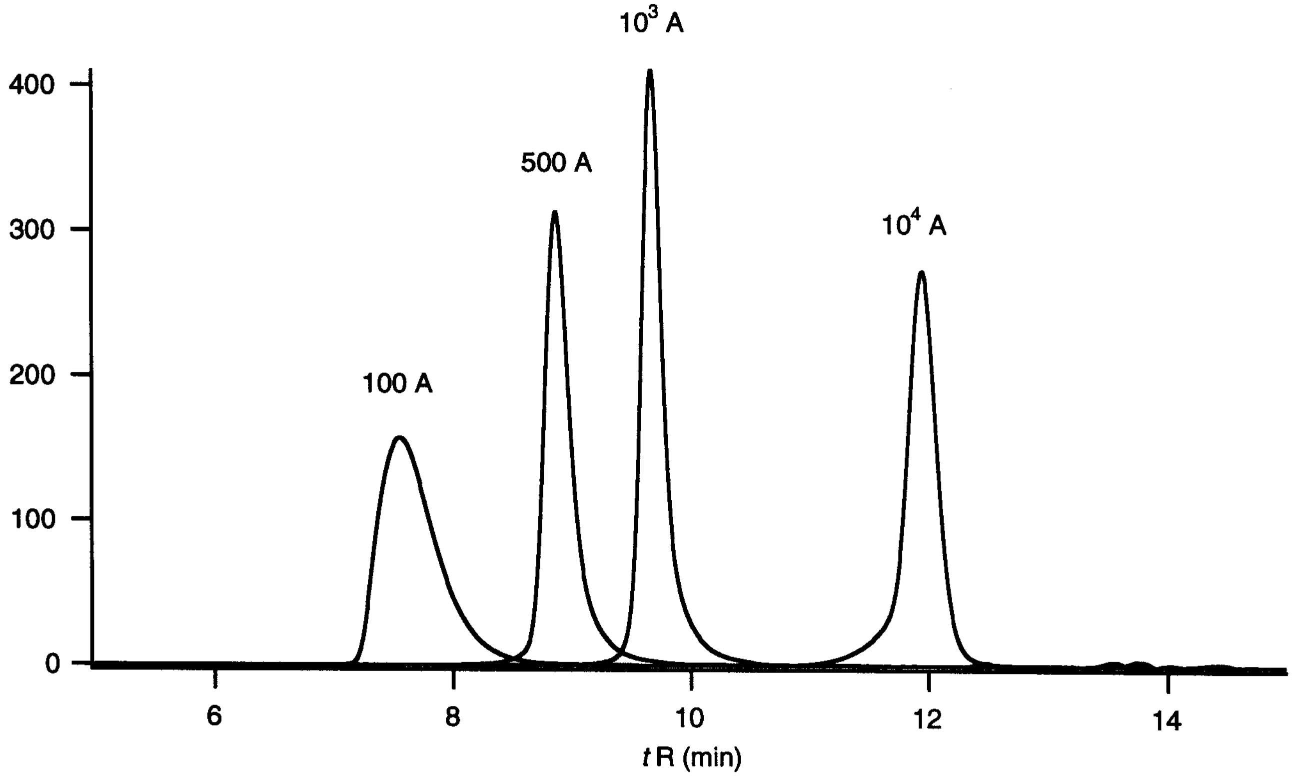
Elution Pattern of Zn$_4$-TMS on SEC-HPLC columns



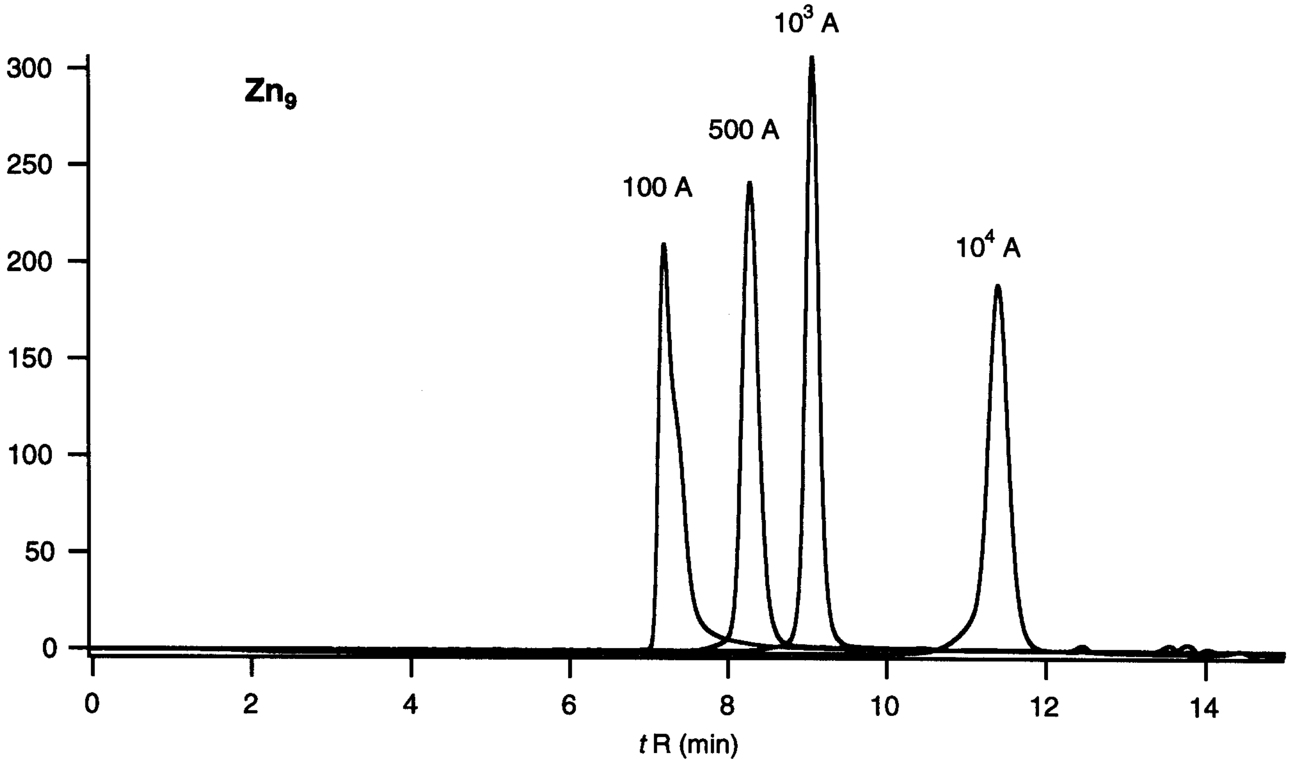


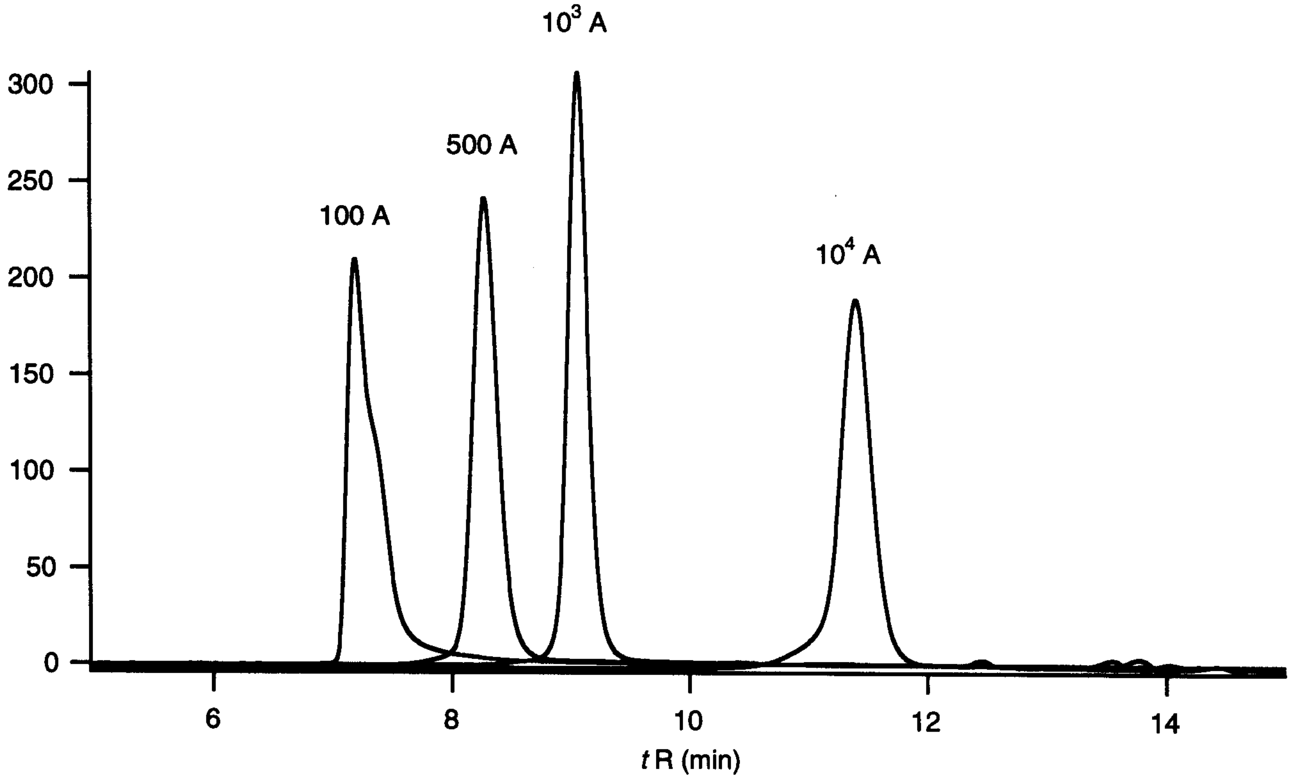
Elution Pattern of Zn_5-TMS on SEC-HPLC columns



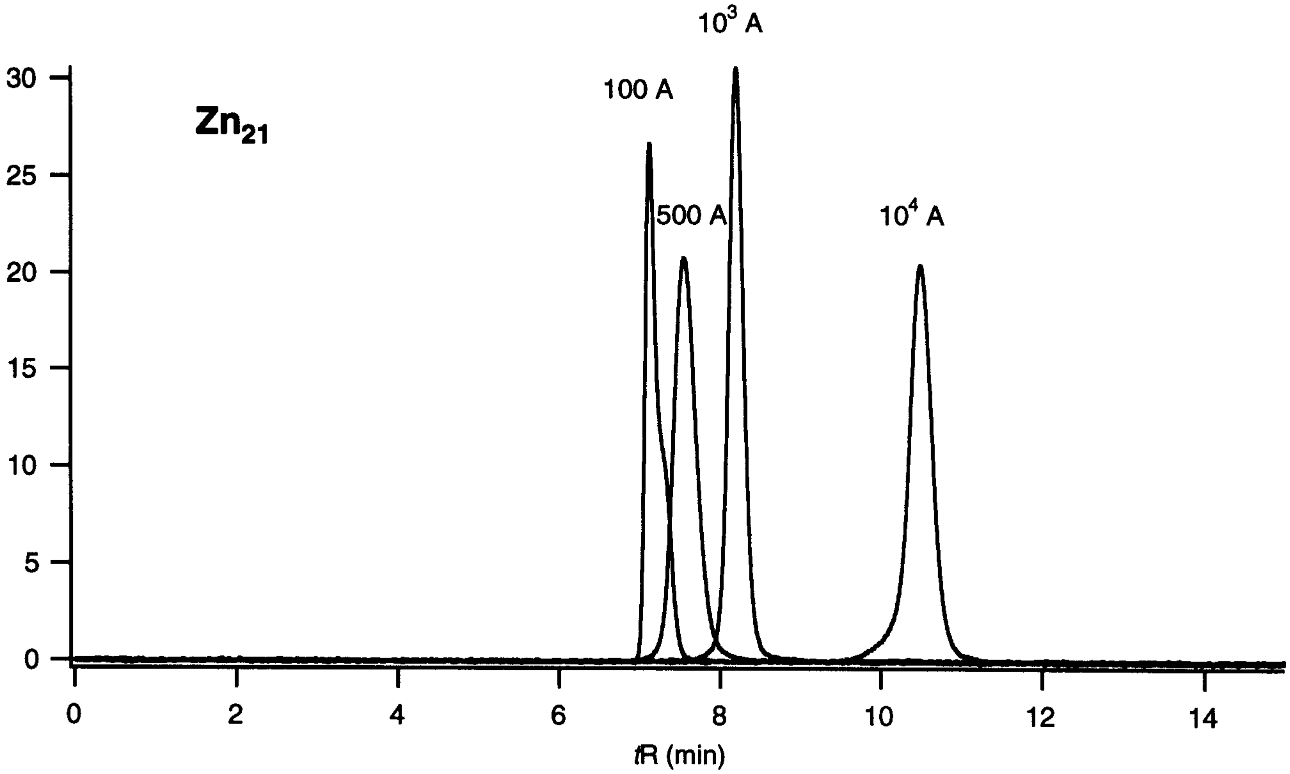


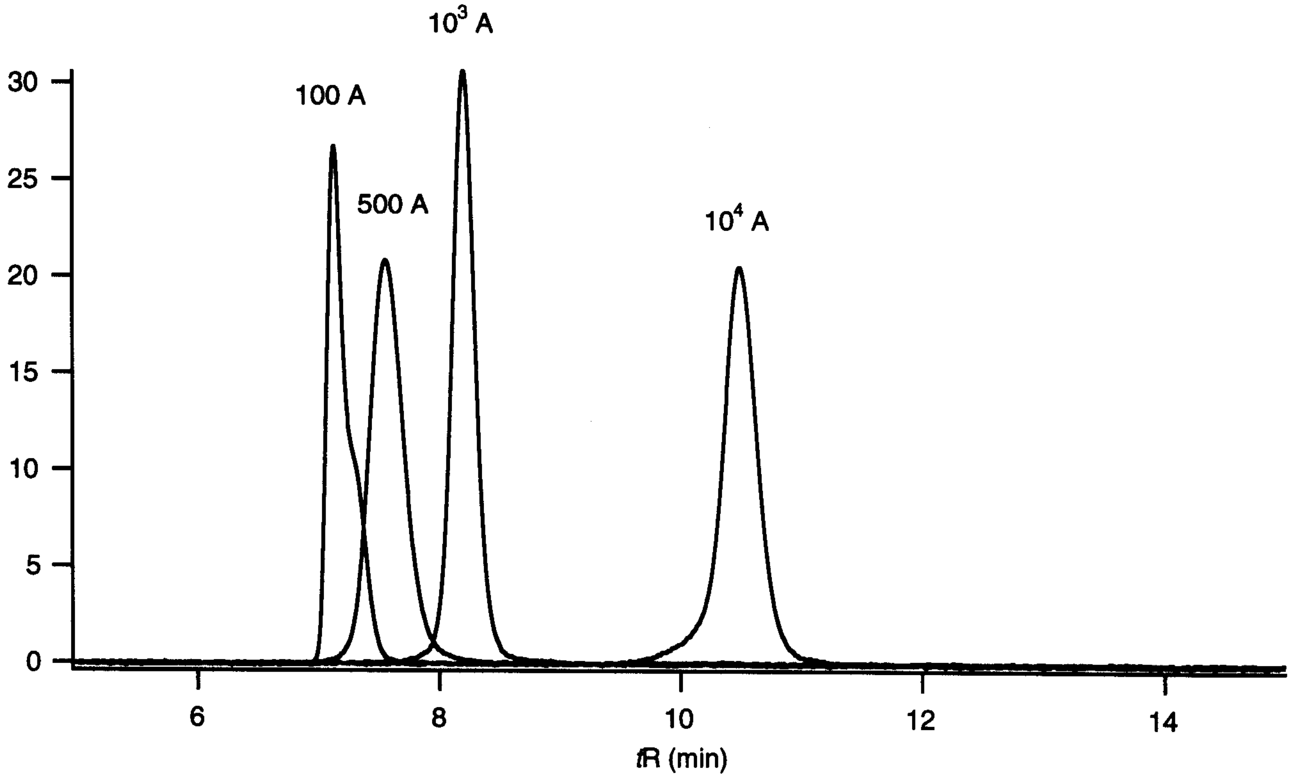
Elution Pattern of Zn_9 on SEC-HPLC columns



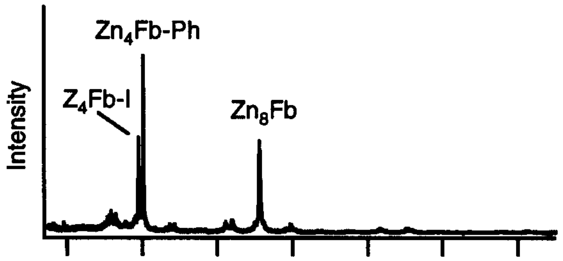


Elution Pattern of Zn_{21} on SEC-HPLC columns

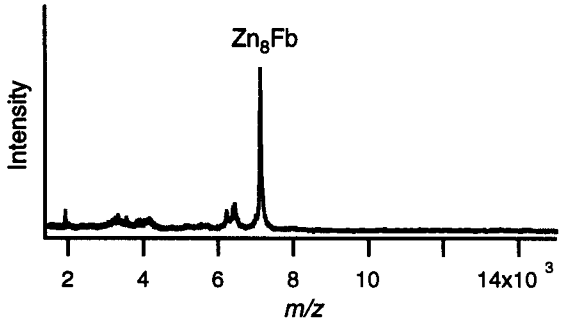


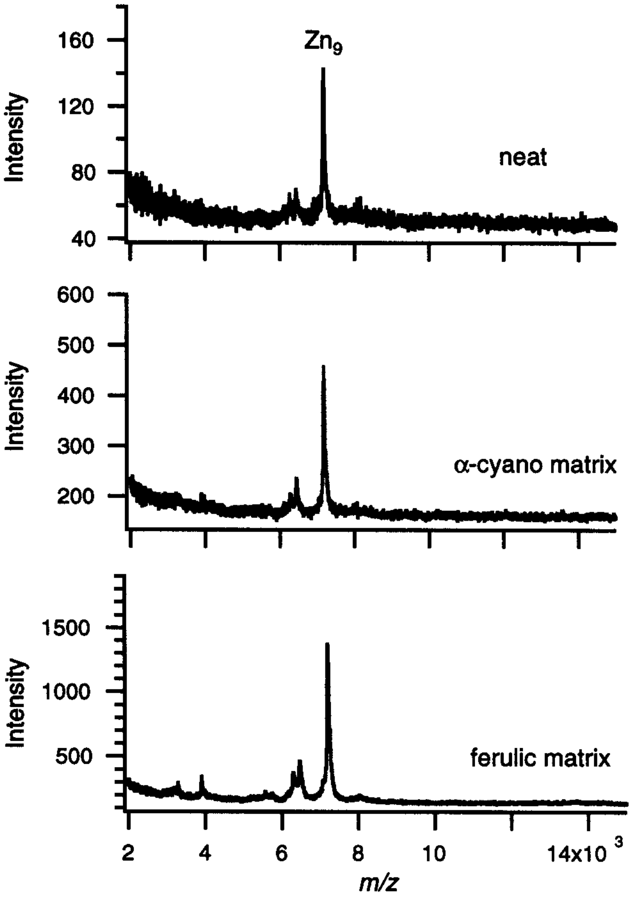


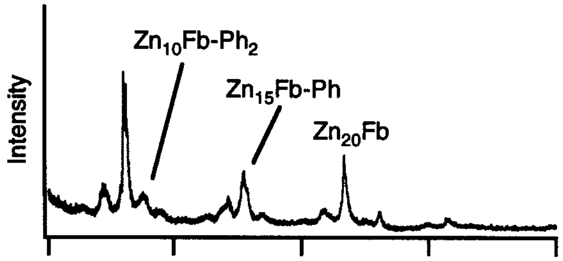
a) Zn_8Fb-reaction mixture



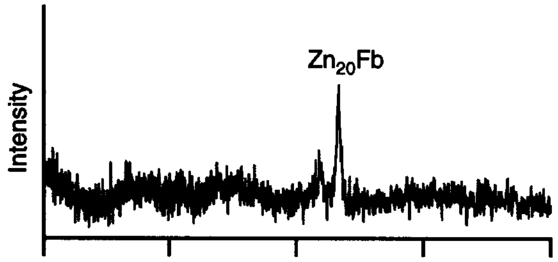
b) purified Zn_8Fb



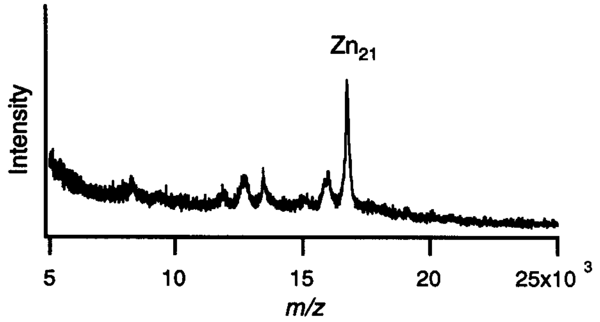

Zn$_9$
Intensity
160
120
80
40
neat
Intensity
600
500
400
300
200
α-cyano matrix
Intensity
1500
1000
500
ferulic matrix
2
4
6
8
10
14x10^3
m/z



a) $Zn_{20}Fb$-reaction mixture



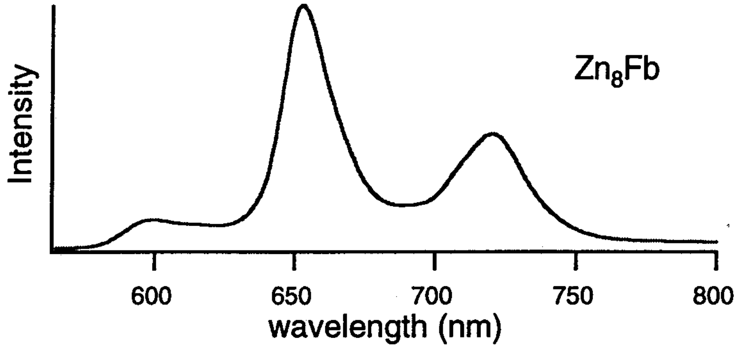
b) purified $Zn_{20}Fb$

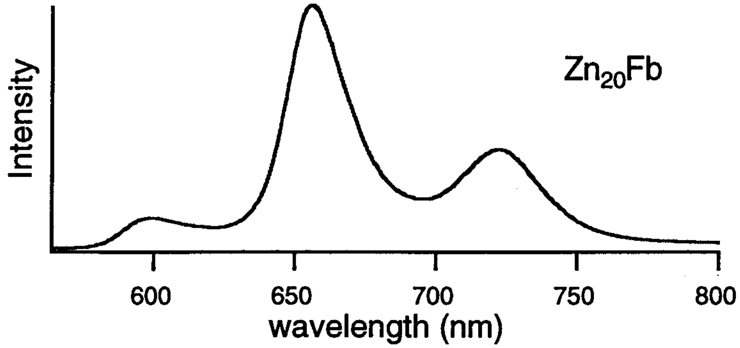


c) Zn_{21}

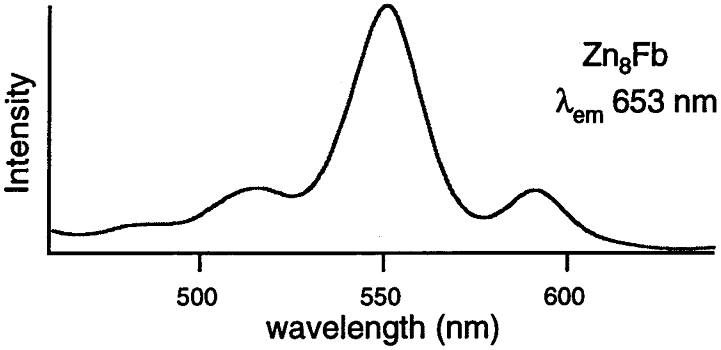
Fluorescence Emission

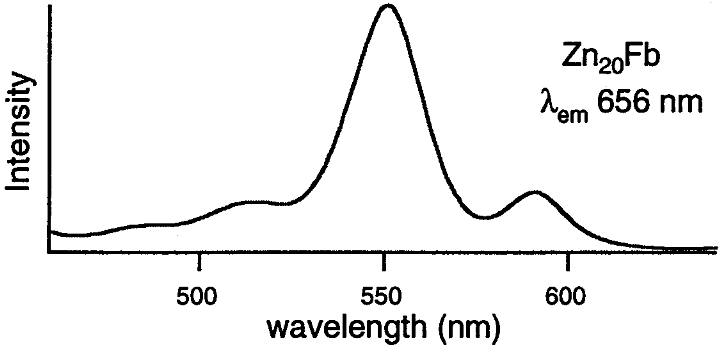
λ_{ex} 550 nm

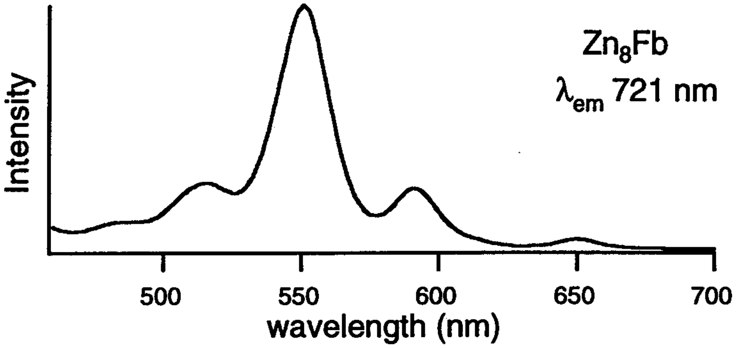


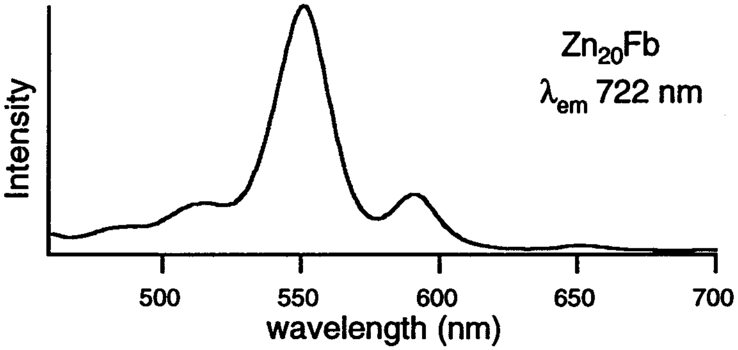


Fluorescence Excitation



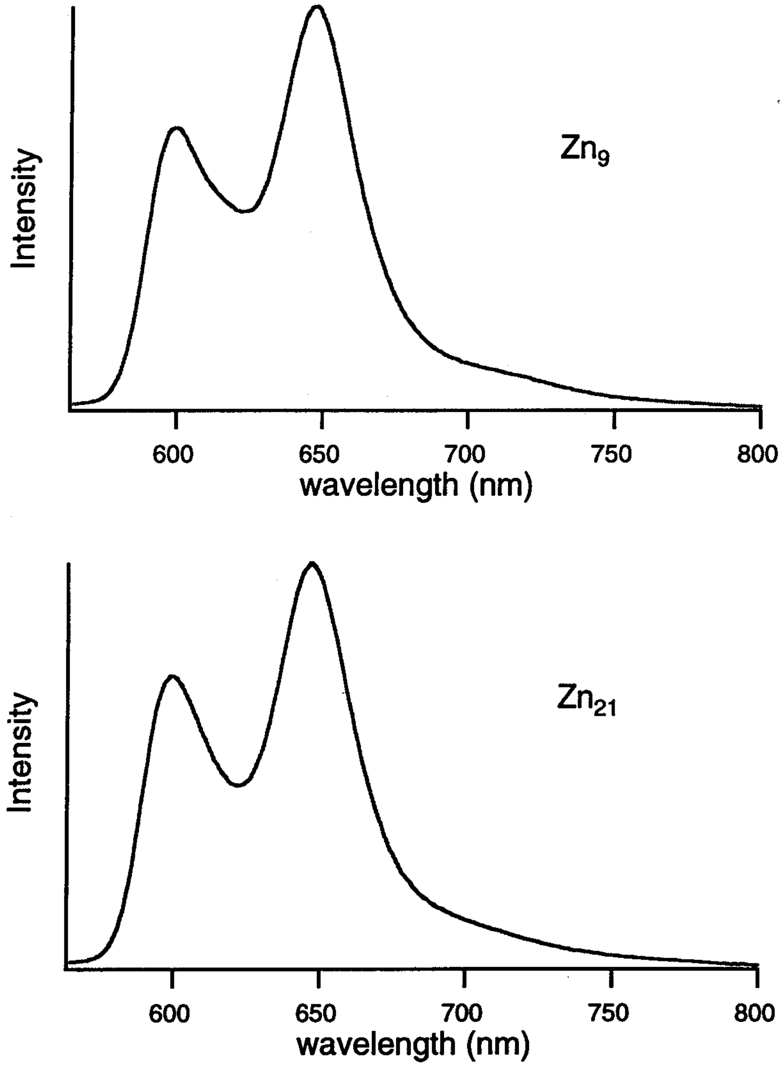






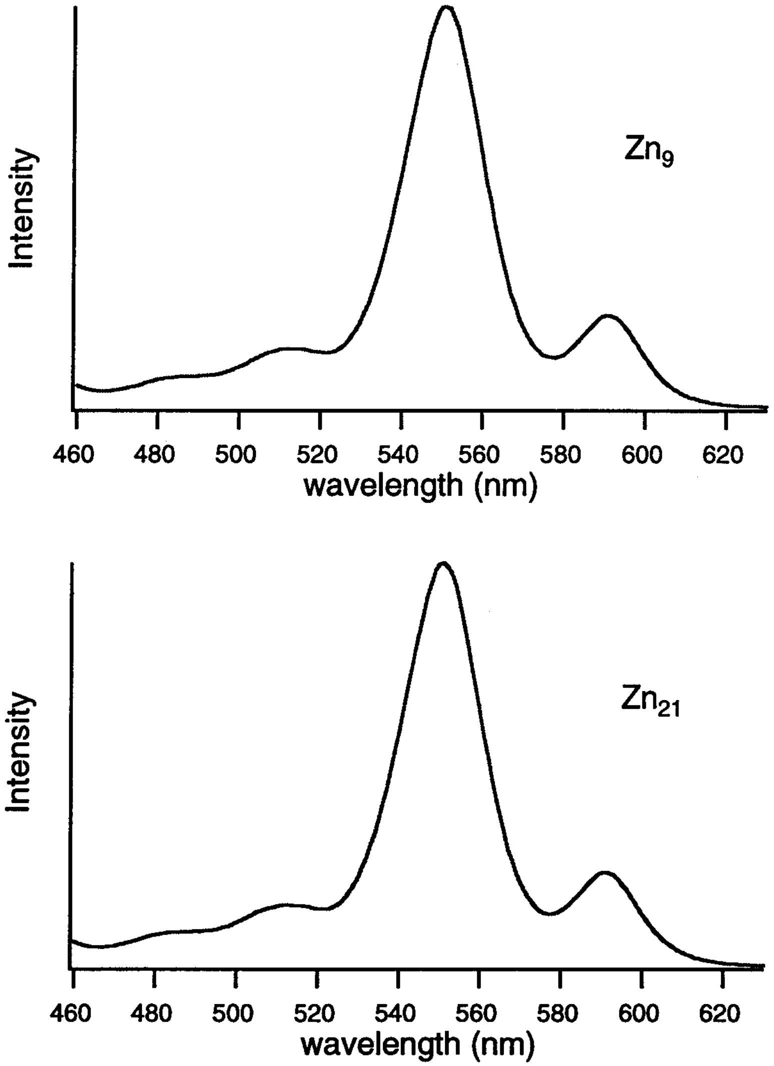
Fluorescence Emission

λ_{em} 550 nm



Fluorescence Emission

λ_{ex} 648 nm



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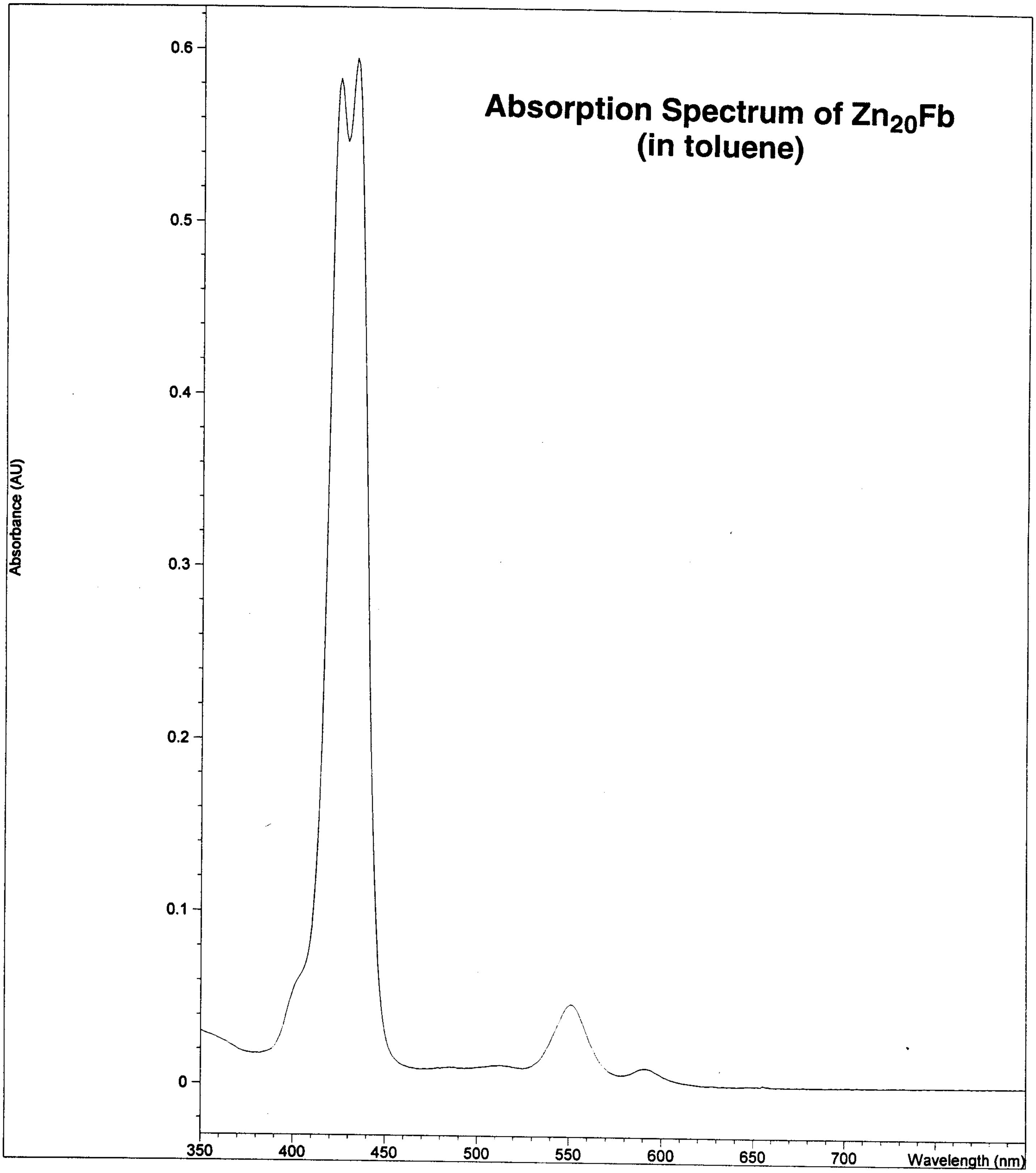

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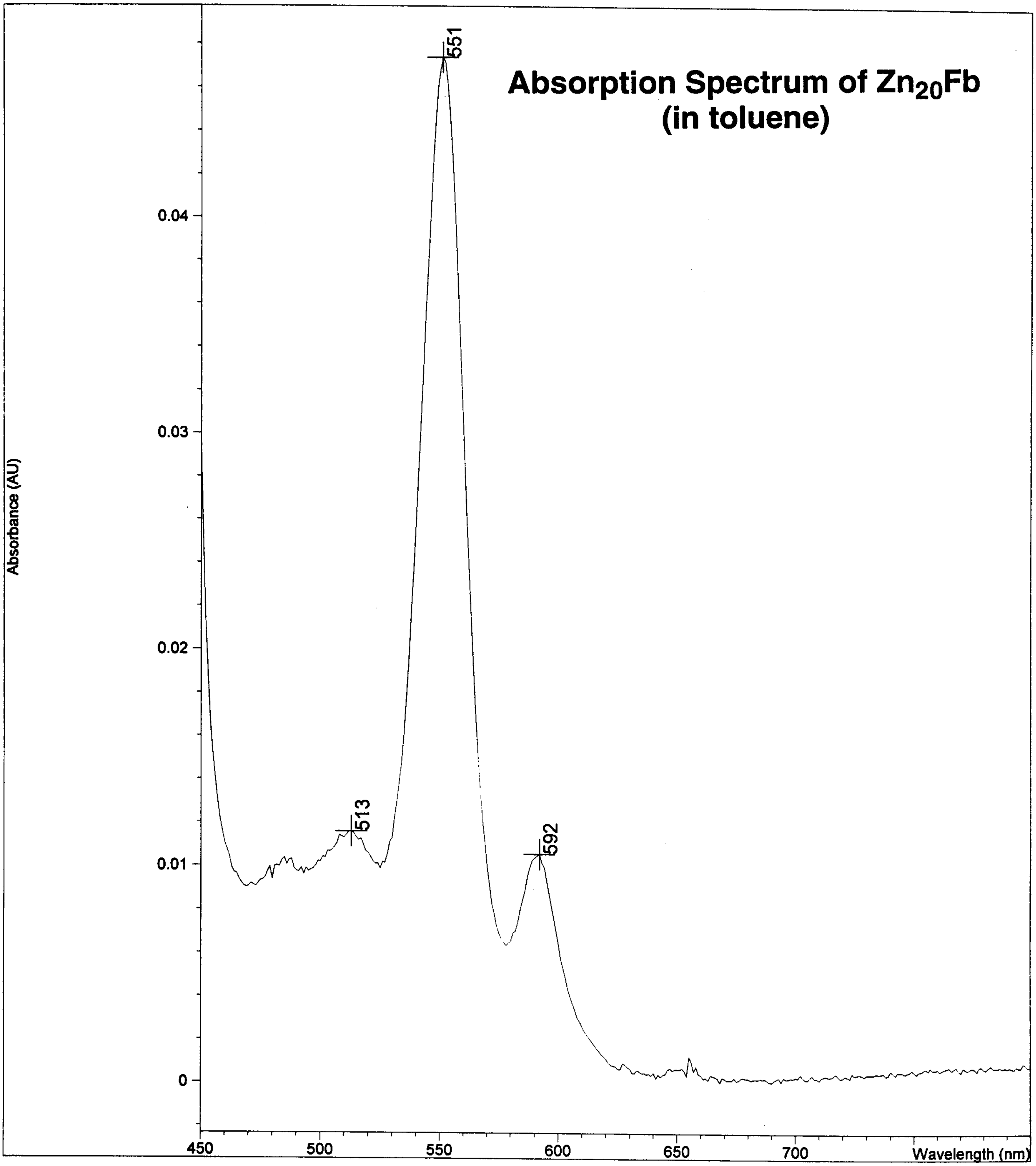

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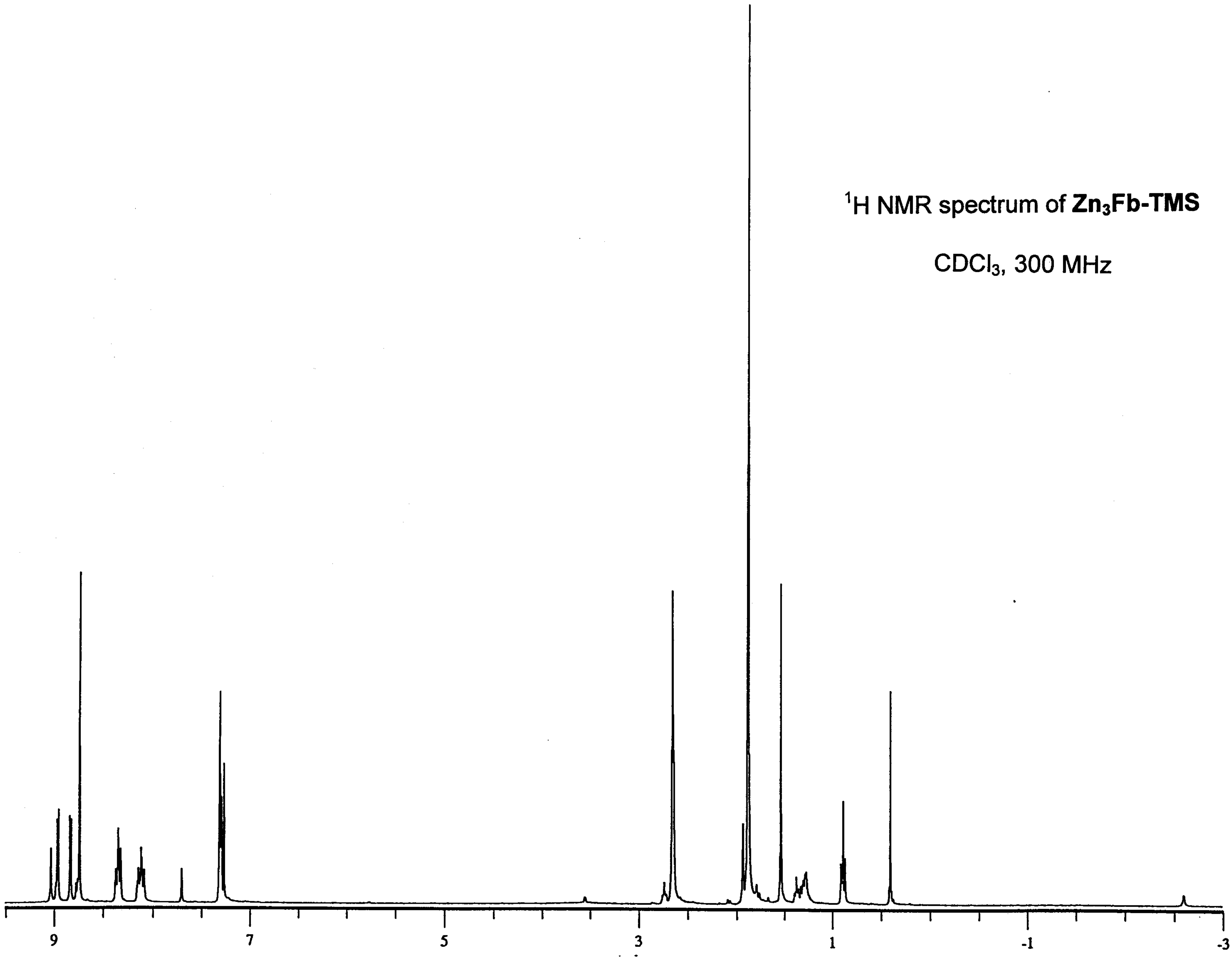
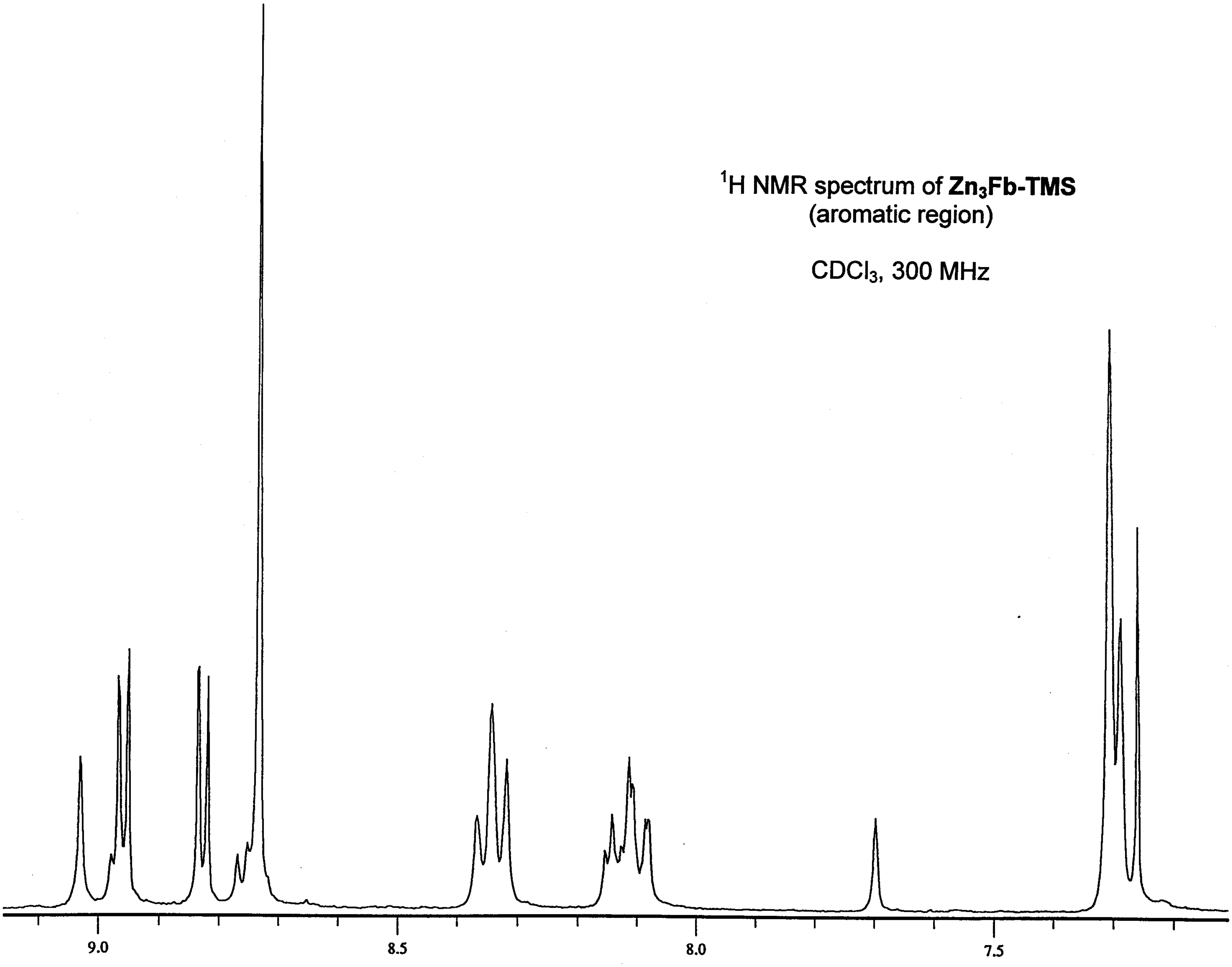


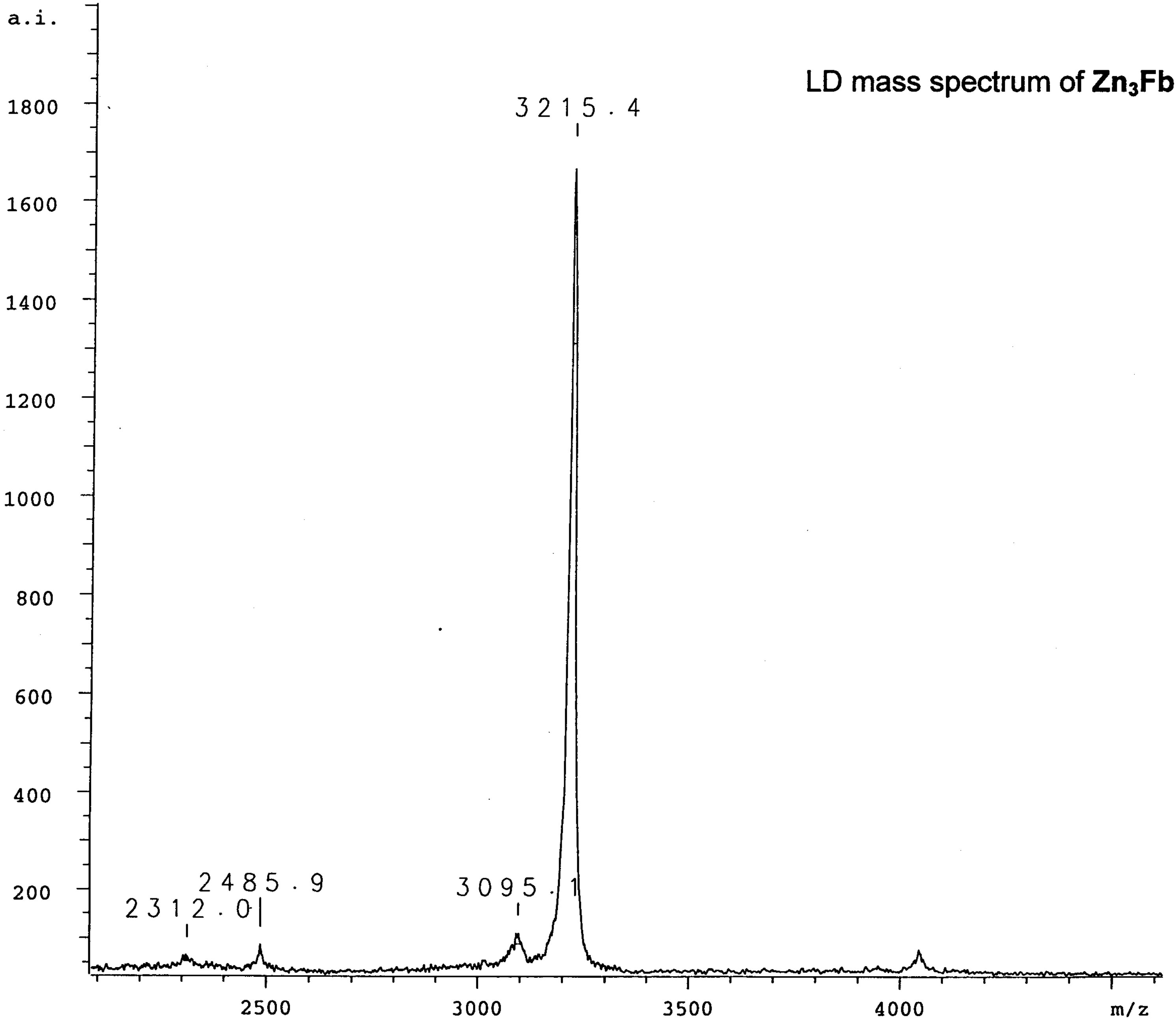
^{1}H NMR spectrum of **Zn_3Fb-TMS**

$CDCl_3$, 300 MHz

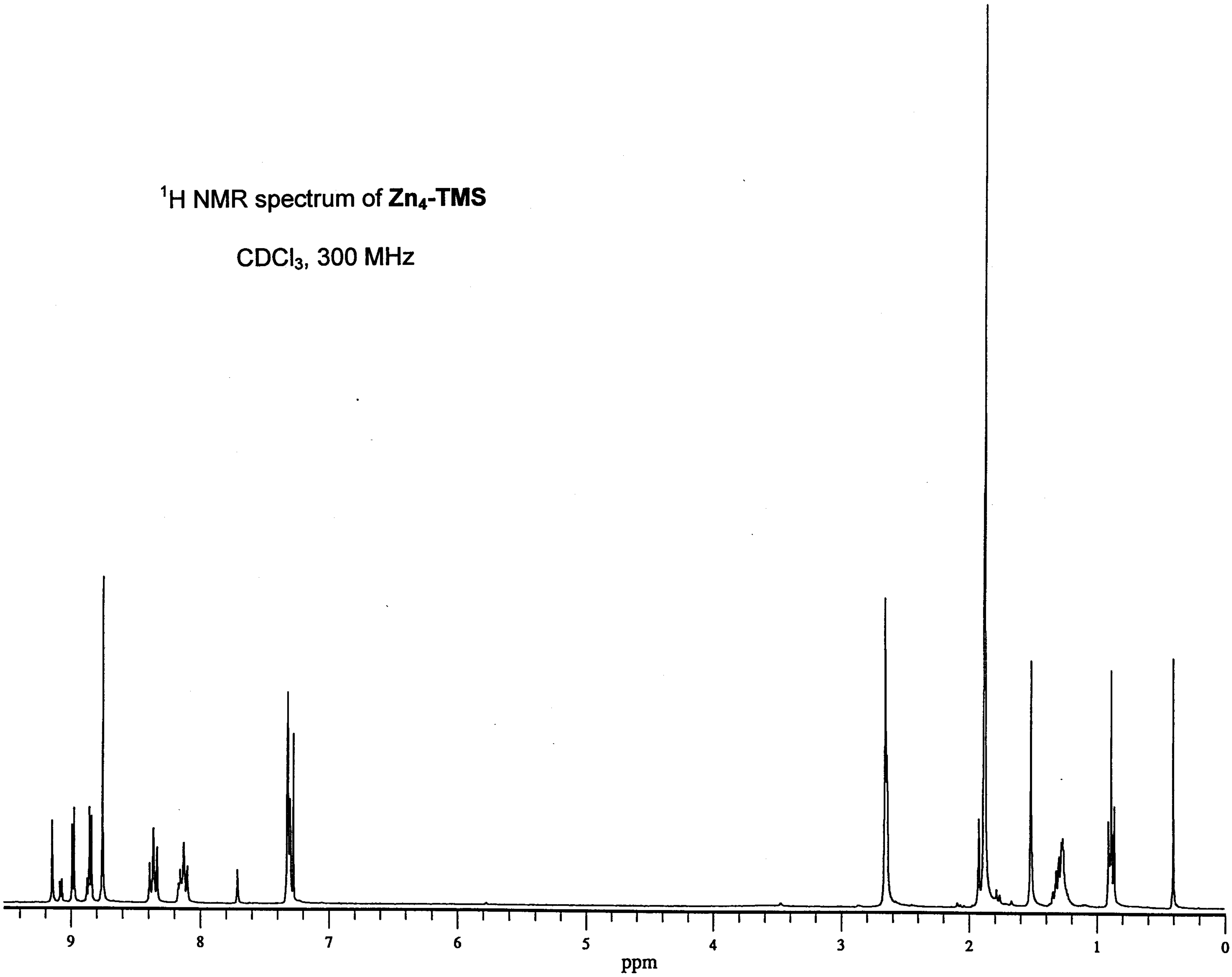


^{1}H NMR spectrum of **Zn_3Fb-TMS** (aromatic region)

$CDCl_3$, 300 MHz



LD mass spectrum of **Zn_3Fb-TMS**



^{1}H NMR spectrum of **Zn$_4$-TMS**

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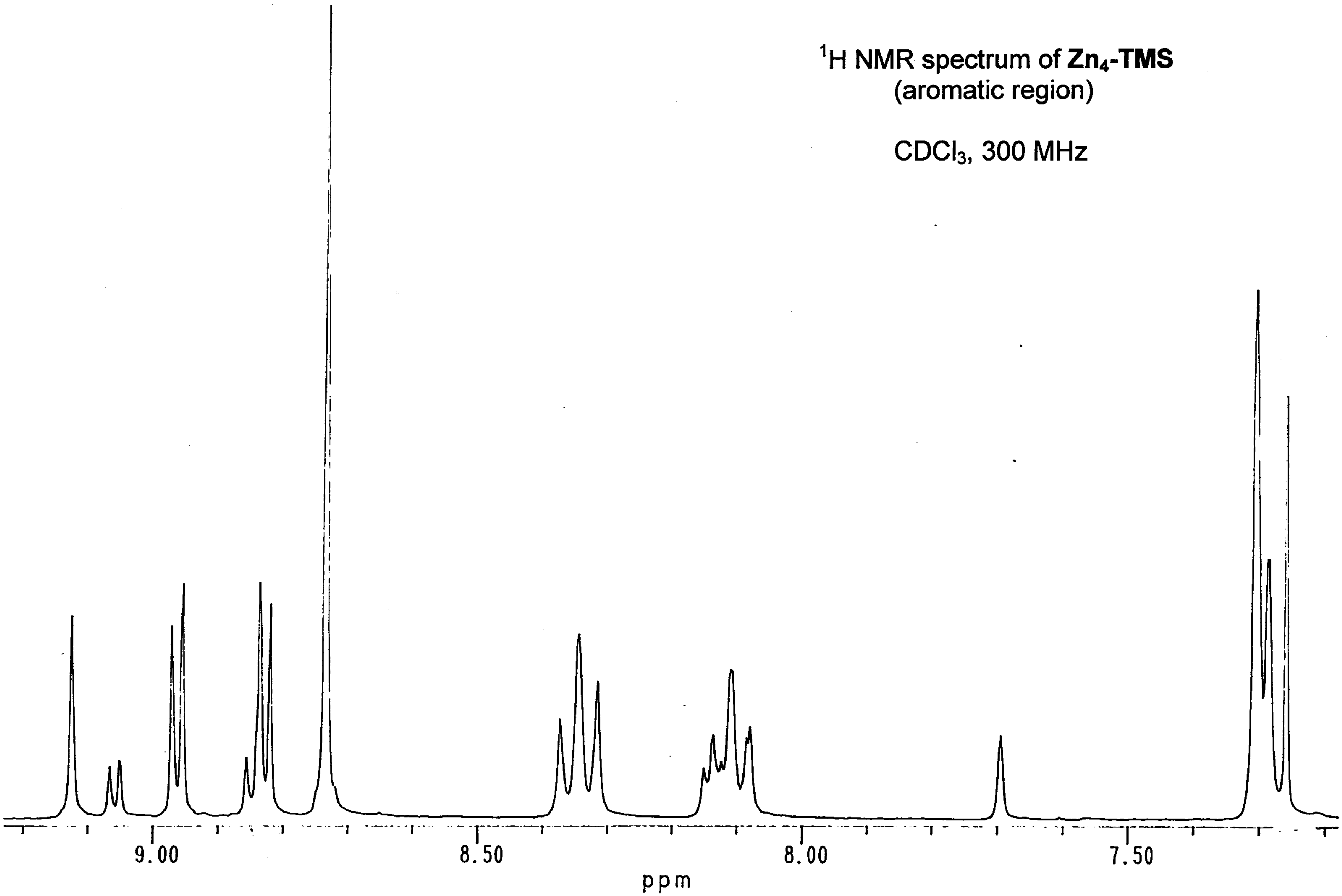
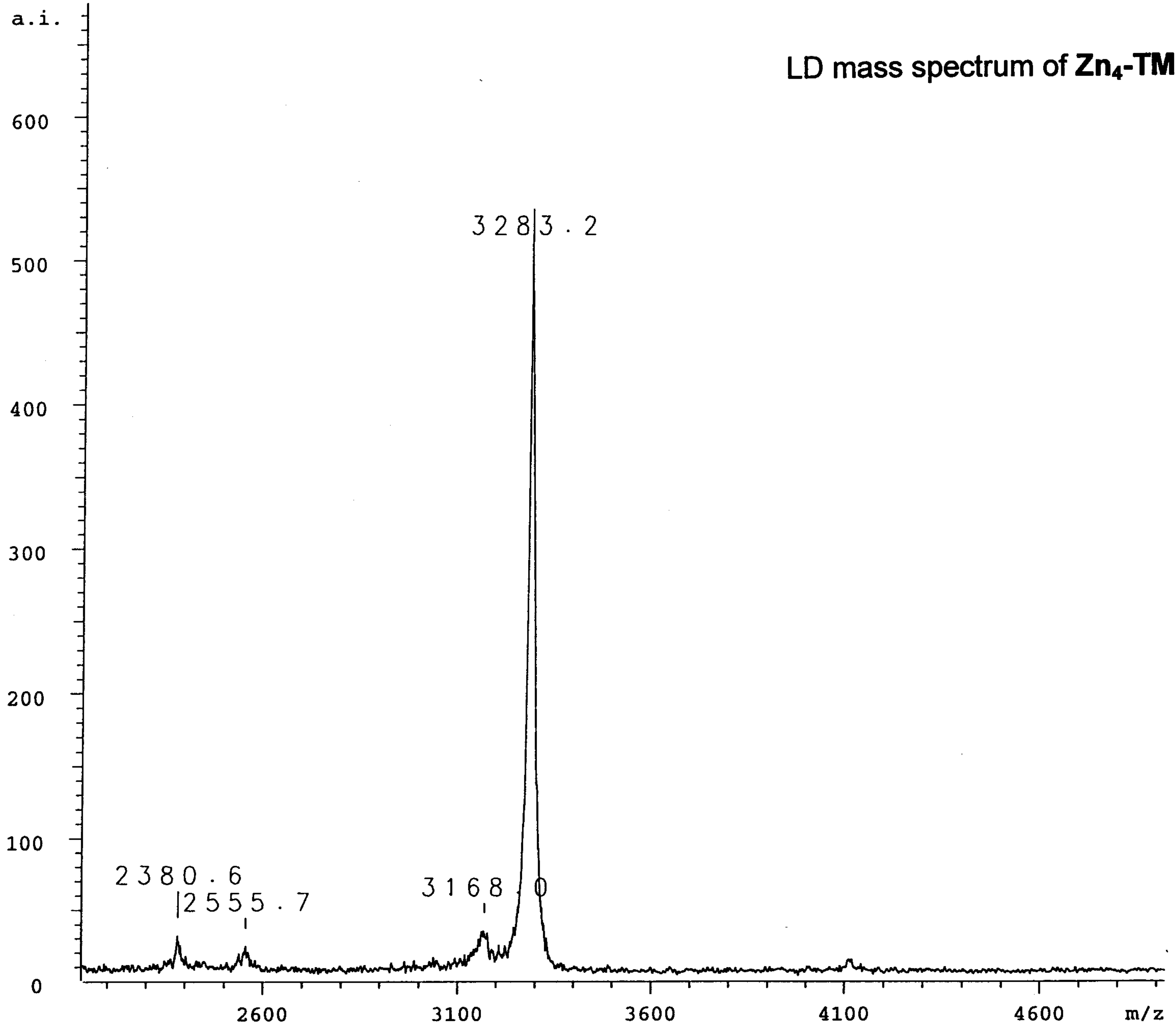


^{1}H NMR spectrum of **Zn_4-TMS**
(aromatic region)

$CDCl_3$, 300 MHz

LD mass spectrum of **Zn_4-TMS**



^{1}H NMR spectrum of **Zn_4-H**

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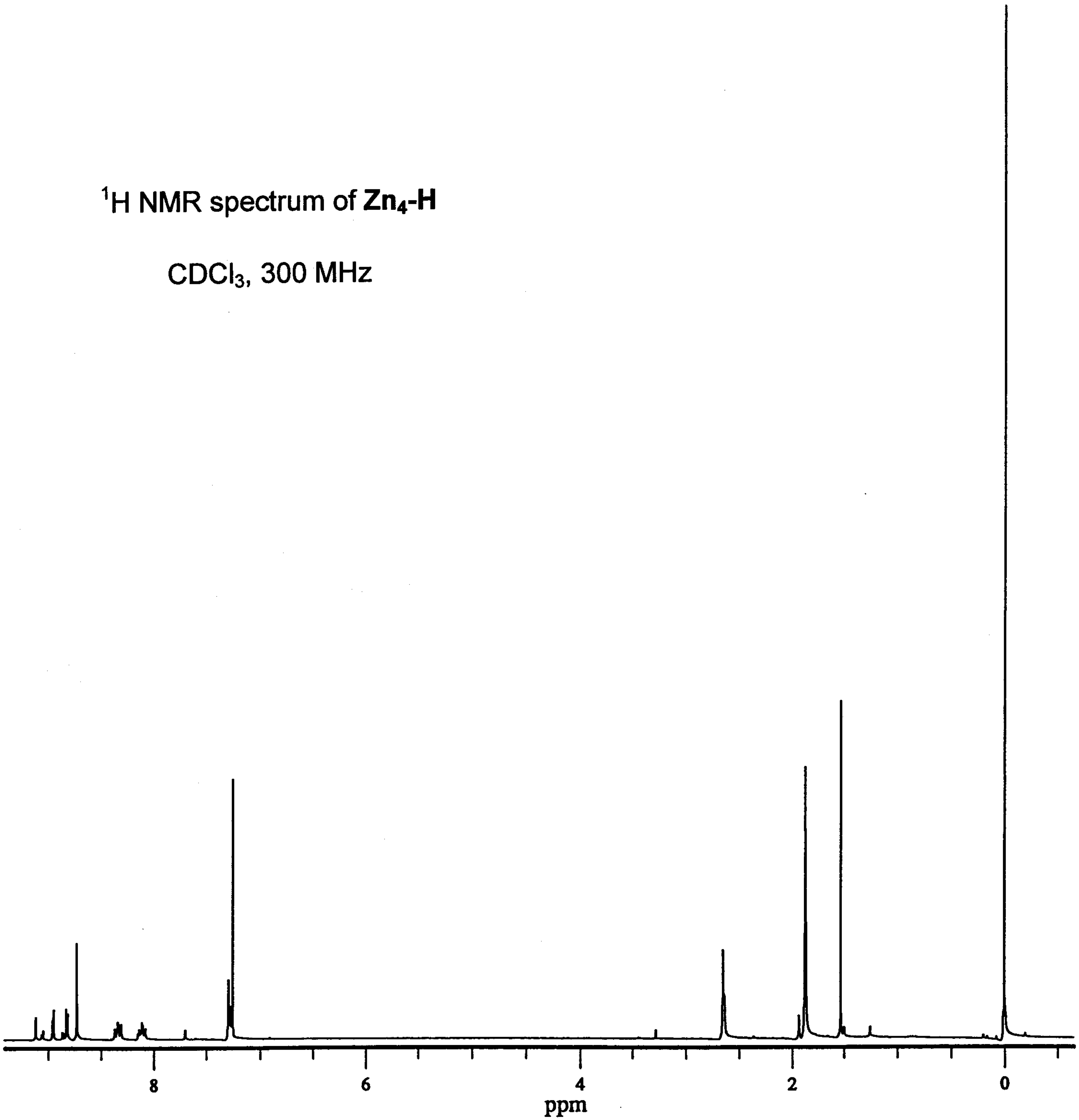

GE NMR OMEGA

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  X  From  9.42   TO  -0.66  ppm
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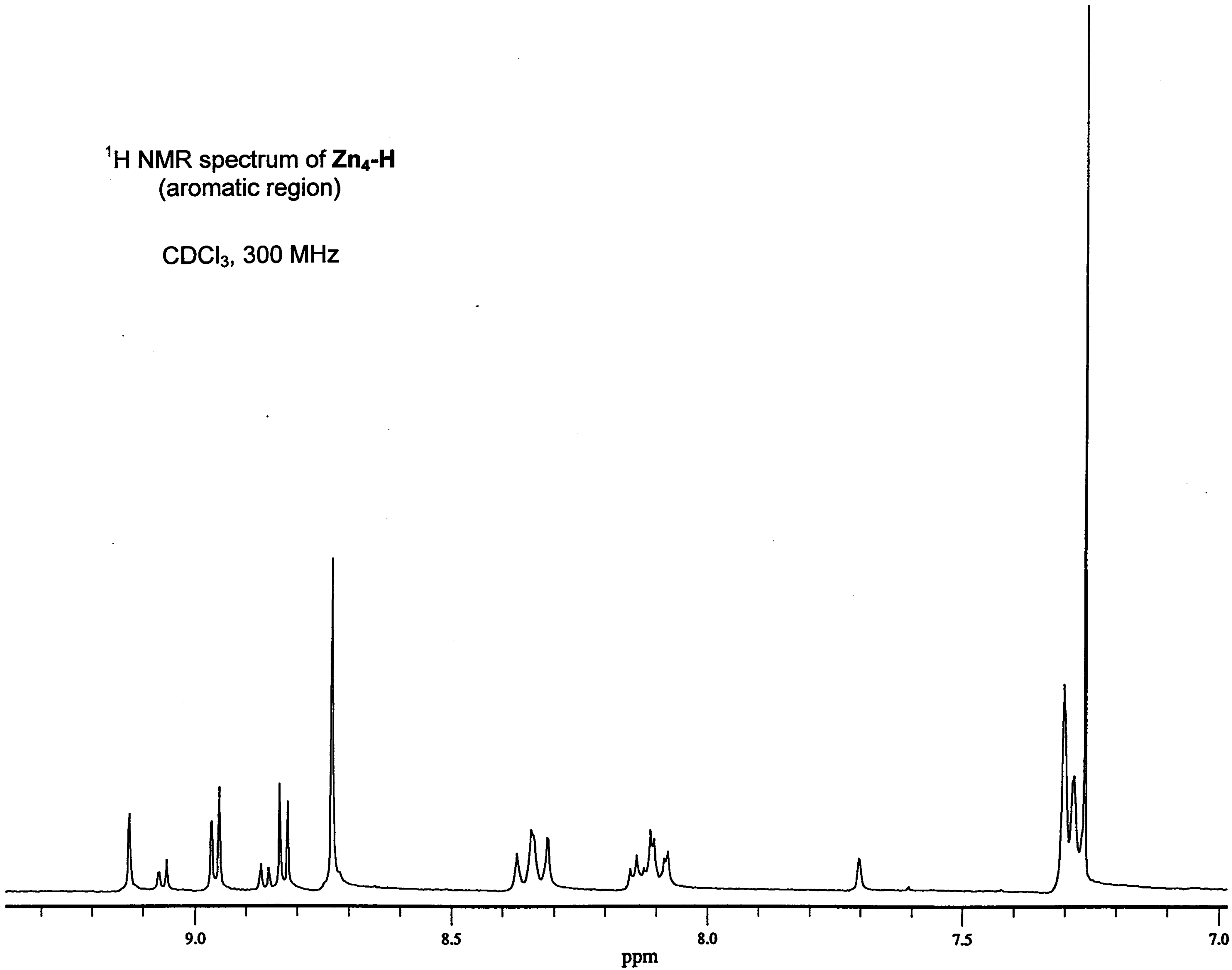
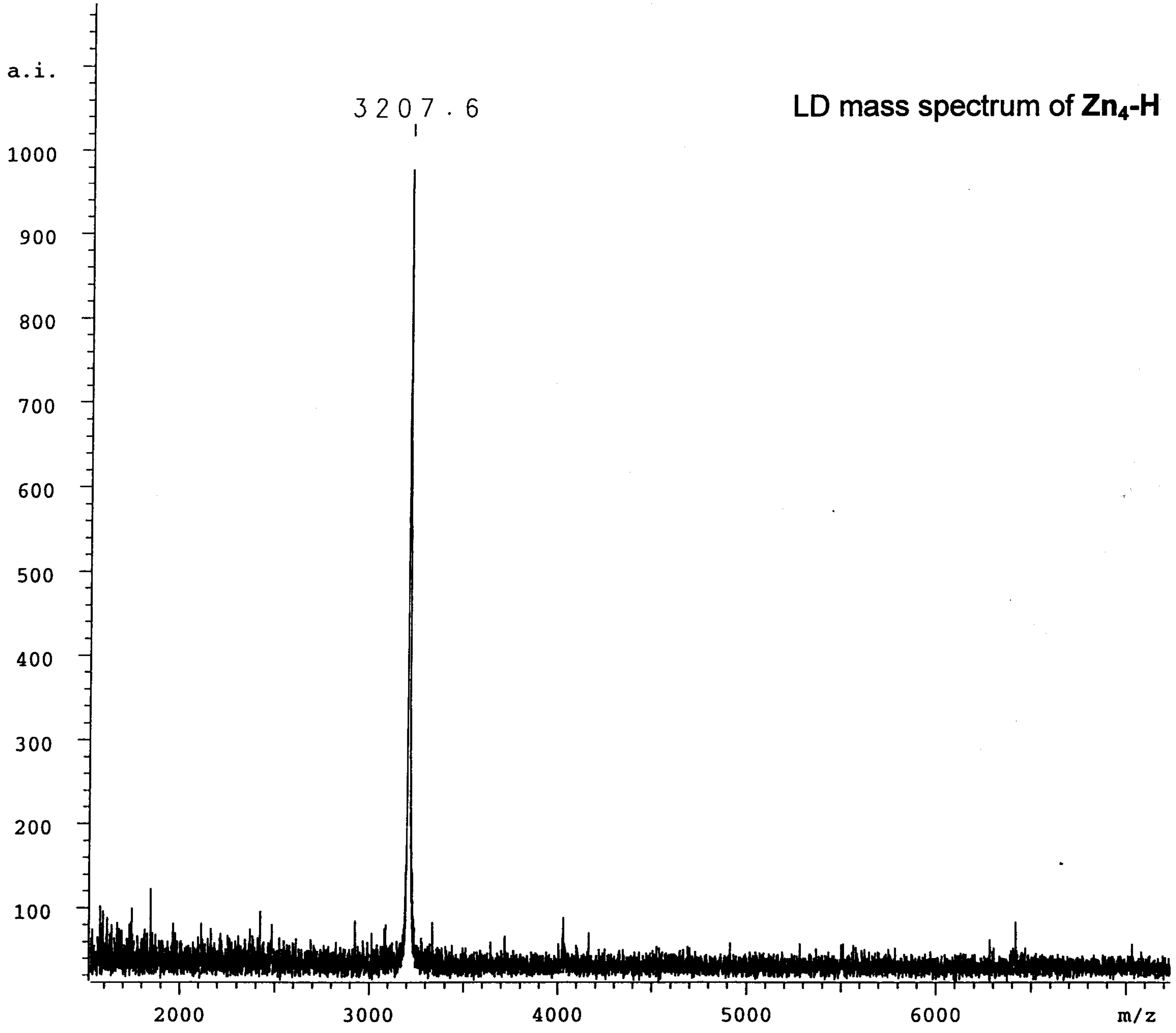


^{1}H NMR spectrum of **Zn$_4$-H**
(aromatic region)

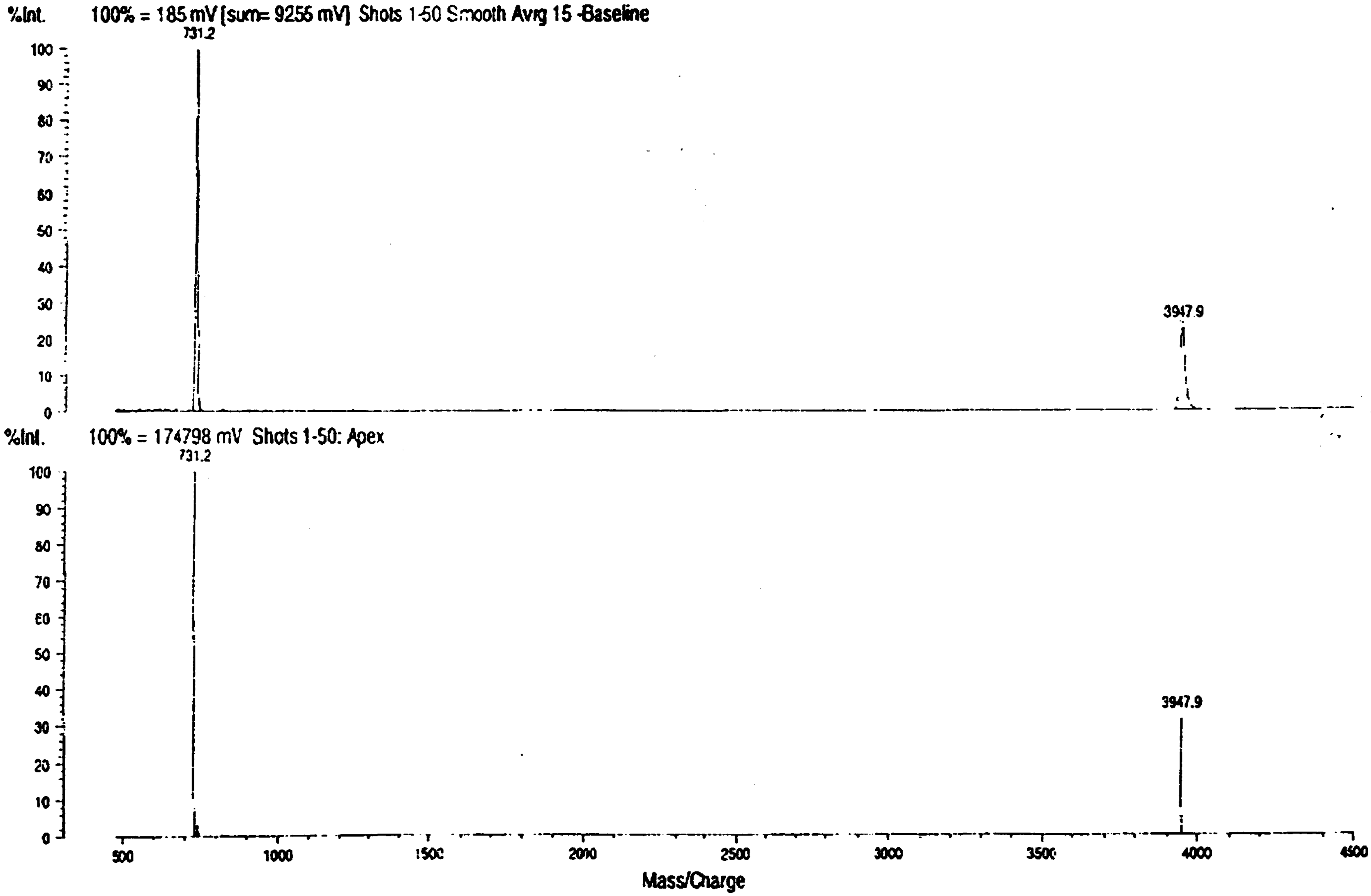
CDCl$_3$, 300 MHz



LD mass spectrum of Zn_4-H

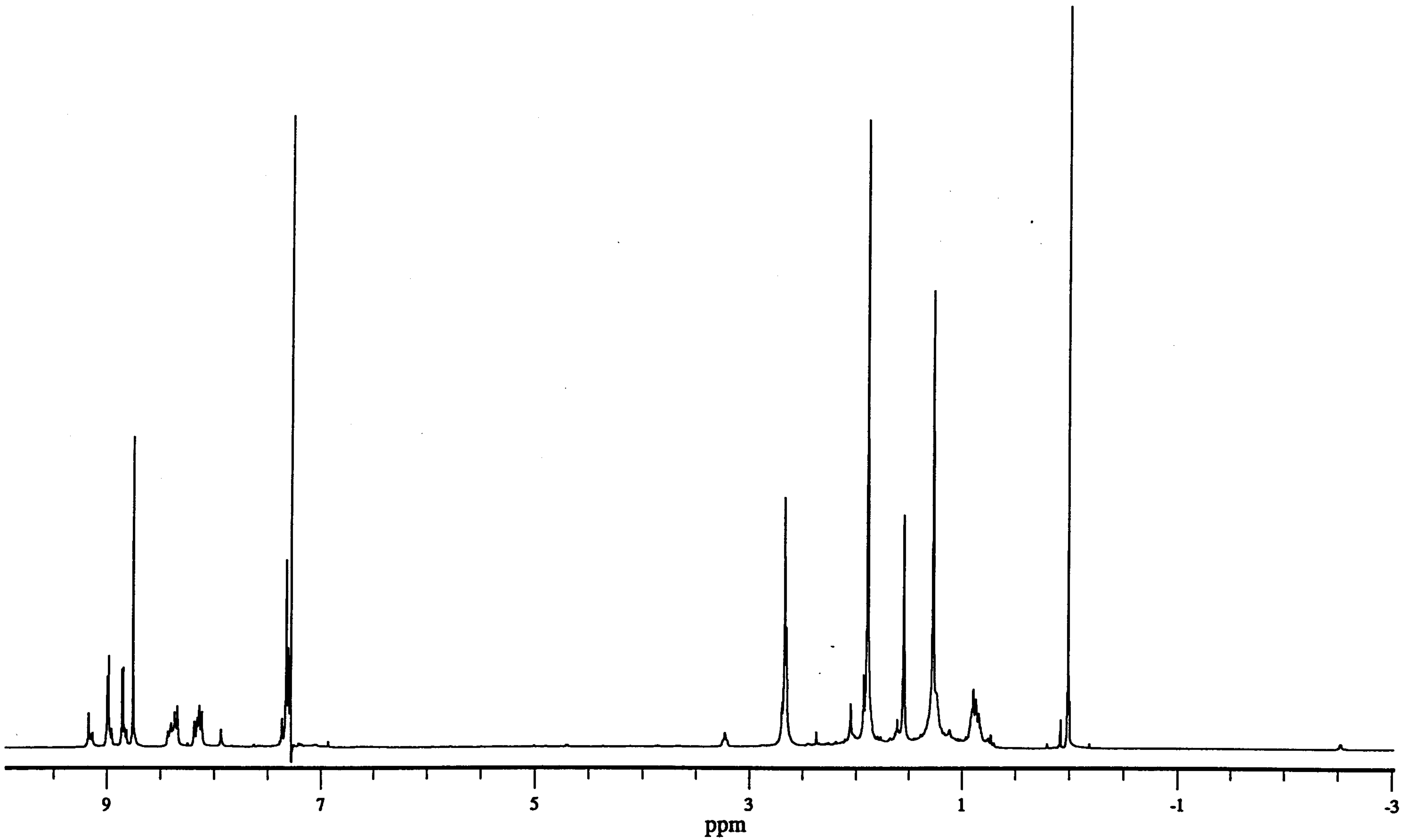
LD-MS Spectrum of Asymmetric Zn_4Fb

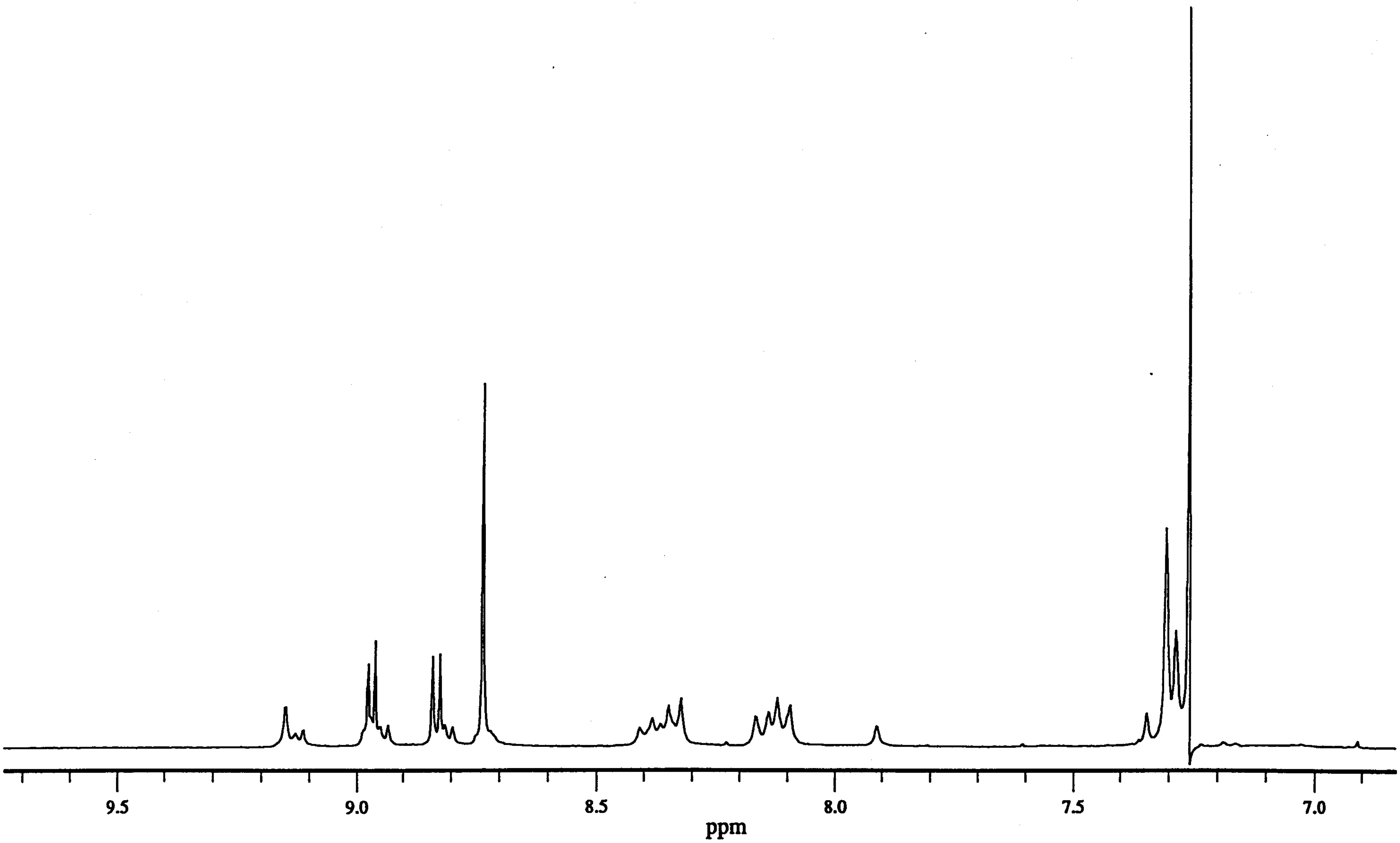
B WANG 10-13-94
Kratos Kompact MALDI 3 V3.0: Run <none> 13 Oct 94 11:29 +Lin Lo Pwr 15
Sample 13: TEJ72



^{1}H NMR spectrum of **Zn$_8$Fb**

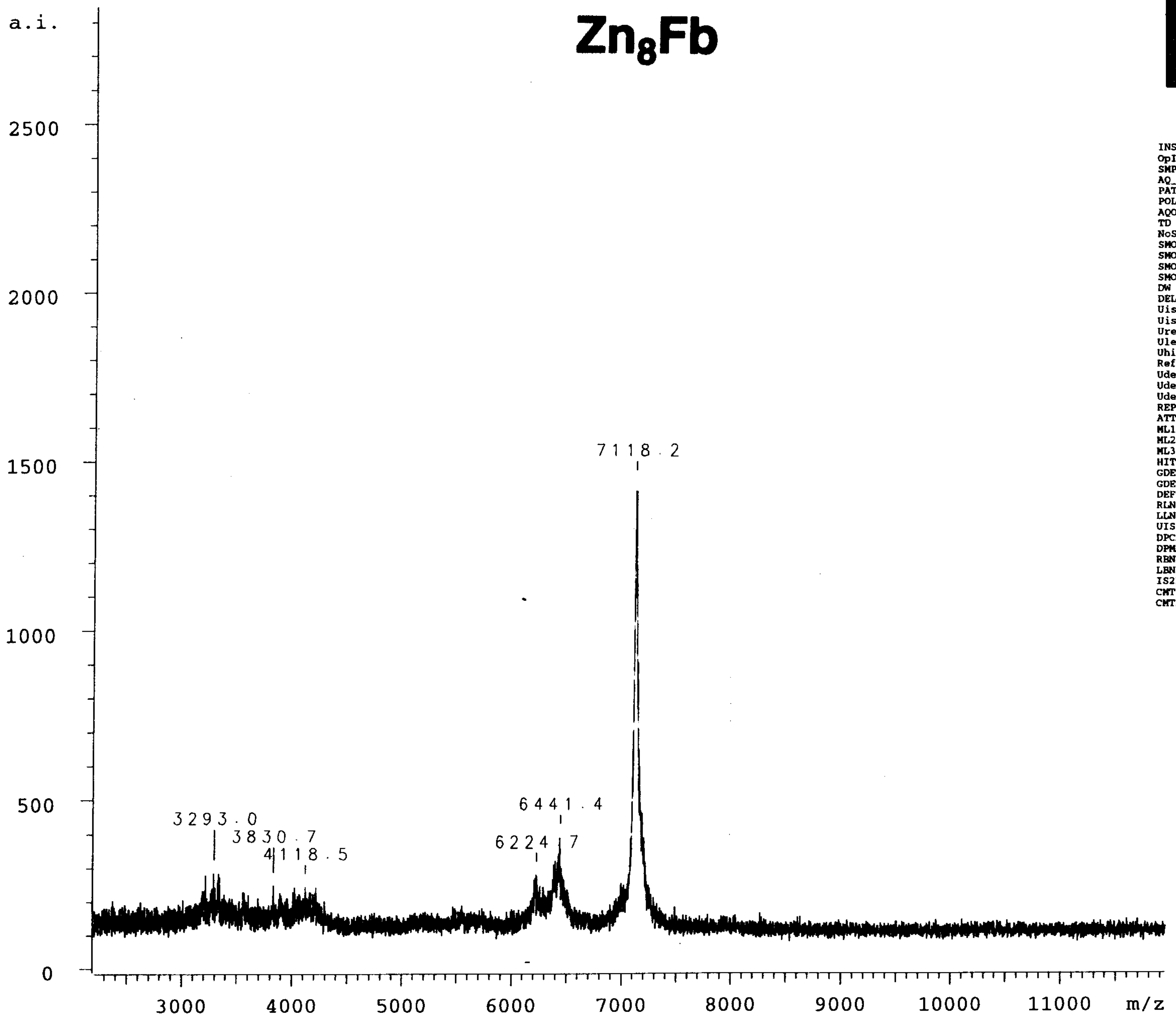
CDCl$_3$, 300 MHz





^{1}H NMR spectrum of **Zn$_8$Fb**
(aromatic region)

CDCl$_3$, 300 MHz



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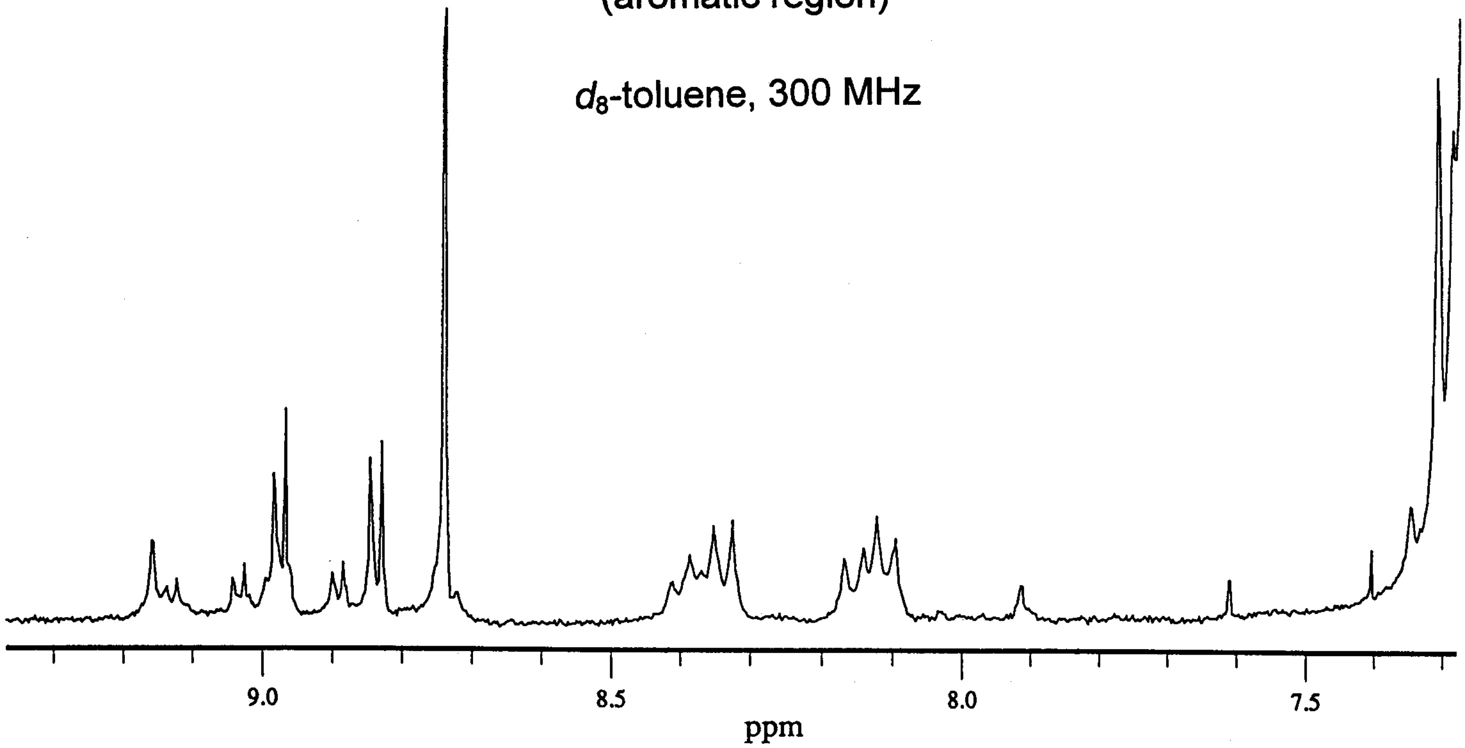
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  981004
AQ_DATE Fri May  1 11:11:49 1998
PATH    /export/home/data/chemistry/LINDSEY/CHARO
POLARI  POS
AQOP_m  Reflector
TD           40000
NoSHOTS        300
SMONUM           0
SMOPTS1          0
SMOPTS2          0
SMOPTS3          0
DW              4.00  [ns]
DELAY          0 [ns]
Uis1           20.00  [kV]
Uis2           18.20  [kV]
Urefl           0.00  [kV]
Ulens           7.50  [kV]
Uhimass         0.00  [kV]
RefFull         0.00  [kV]
UdetL           1.50  [kV]
UdetR           0.00  [kV]
Udefl           2.00  [kV]
REPHZ           1.00  [Hz]
ATTEN          35.0
ML1       2082168.558
ML2           443.732
ML3             0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1        510.84
DPMASS        700.00  [Da]
RBNDVAL         0.33
LBNDVAL         0.28
IS2BNDV         0.91
CMT1    NONAMER, IN CHCL3
CMT2    Shots 300, atten=35
```

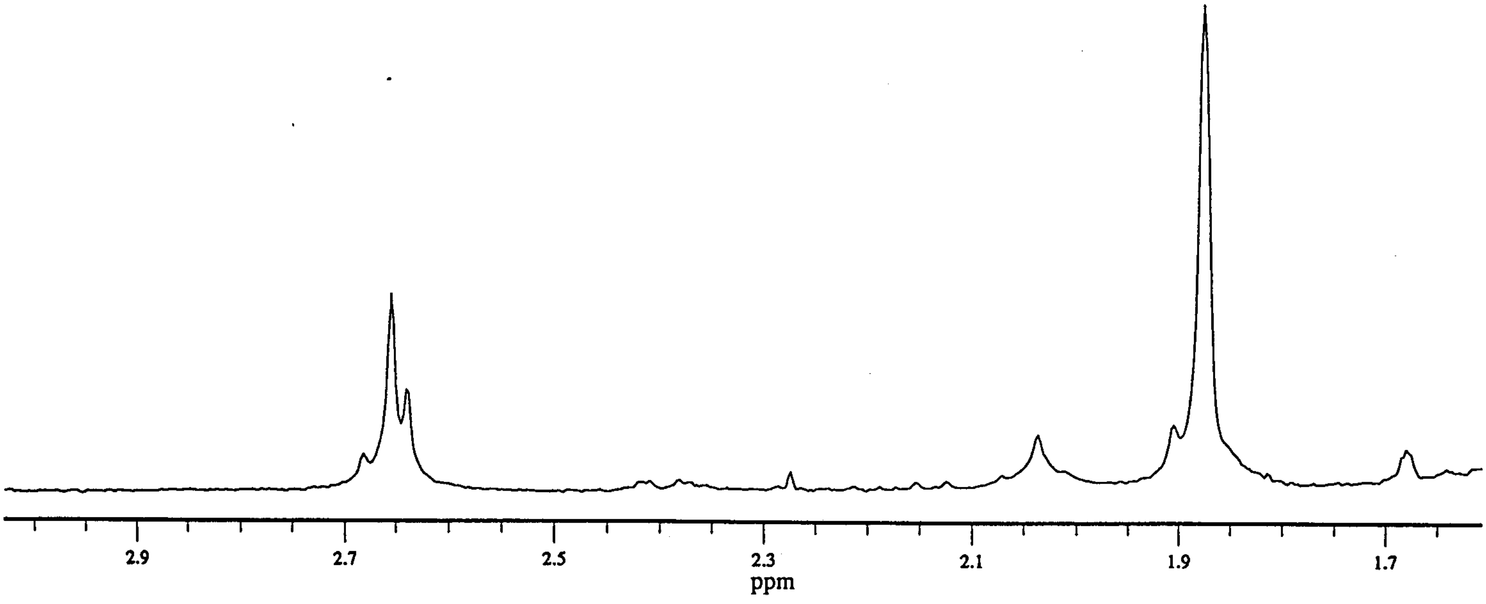
```
/export/home/data/chemistry/LINDSEY/CHARO/981004/1SRef/pdata/1   tof   Fri May  1 11:33:10 1998
```

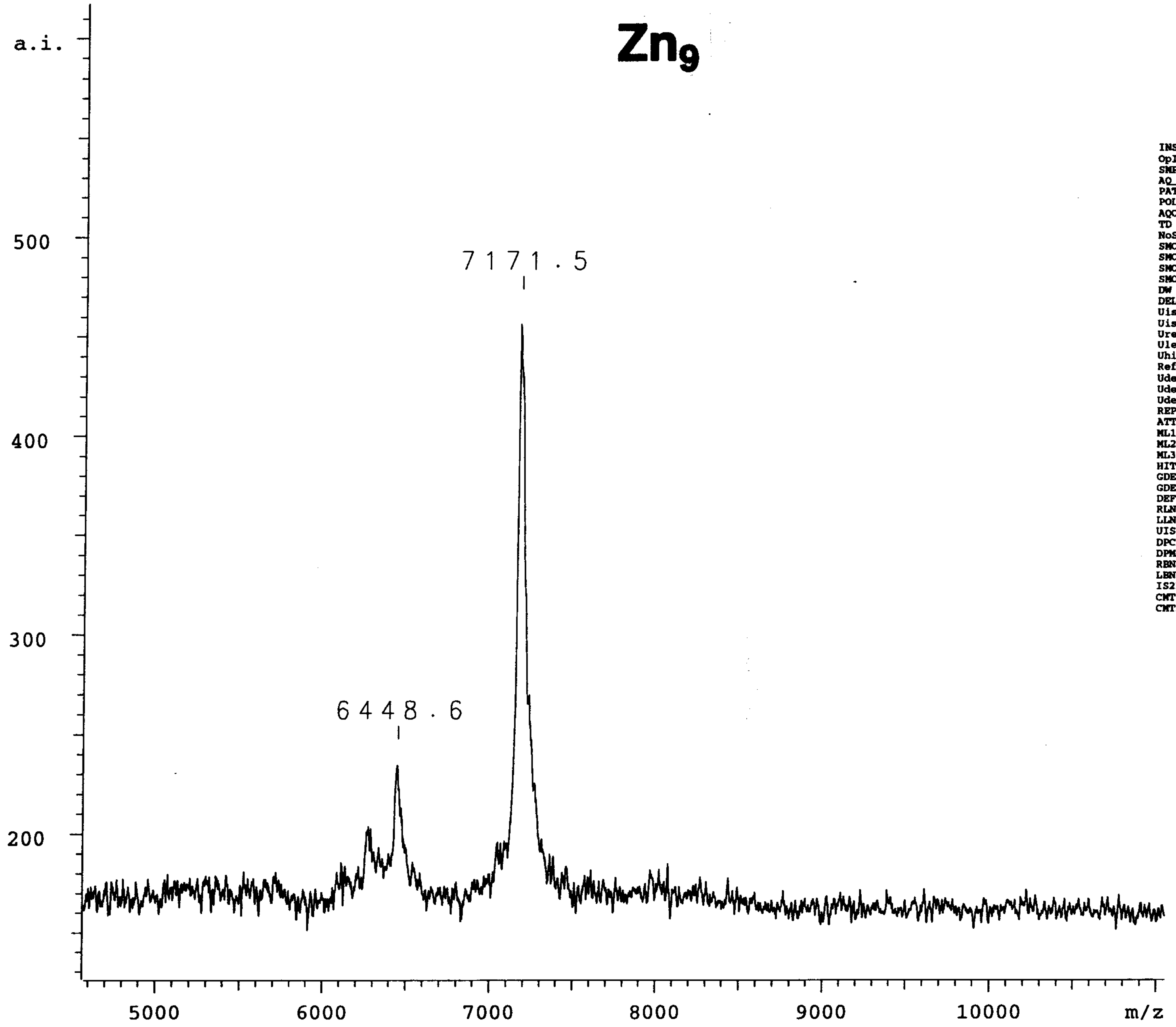
^{1}H NMR spectrum of **Zn$_9$**
(aromatic region)

d_8-toluene, 300 MHz



^{1}H NMR spectrum of **Zn$_9$**
(aliphatic region)





Zn$_9$

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INSTRUM TOF
OpId     N. Srinivasan
SMPNAM   982478
AQ_DATE Mon Aug 17 18:56:24 1998
PATH     /export/home/data/chemistry/LINDSEY/CHARO
POLARI   POS
AQOP_m   Reflector
TD            40000
NoSHOTS         372
SMONUM            1
SMOPTS1          10
SMOPTS2           0
SMOPTS3           0
DW             4.00  [ns]
DELAY         0 [ns]
Uis1          20.00  [kV]
Uis2          18.50  [kV]
Urefl          0.00  [kV]
Ulens          7.50  [kV]
Uhimass        0.00  [kV]
RefPull        0.00  [kV]
UdetL          1.50  [kV]
UdetR          0.00  [kV]
Udefl          2.00  [kV]
REPHZ          1.00  [Hz]
ATTEN         40.0
ML1        2079437.913
ML2          420.660
ML3            0.000
HITURBO no
GDEON    yes
GDEDLY   short
DEFLON   no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1        510.84
DPMASS        700.00  [Da]
RBNDVAL         0.33
LBNDVAL         0.28
IS2BNDV         0.91
CMT1     znp + ferulic acid/toluene
CMT2     att=40
```

```
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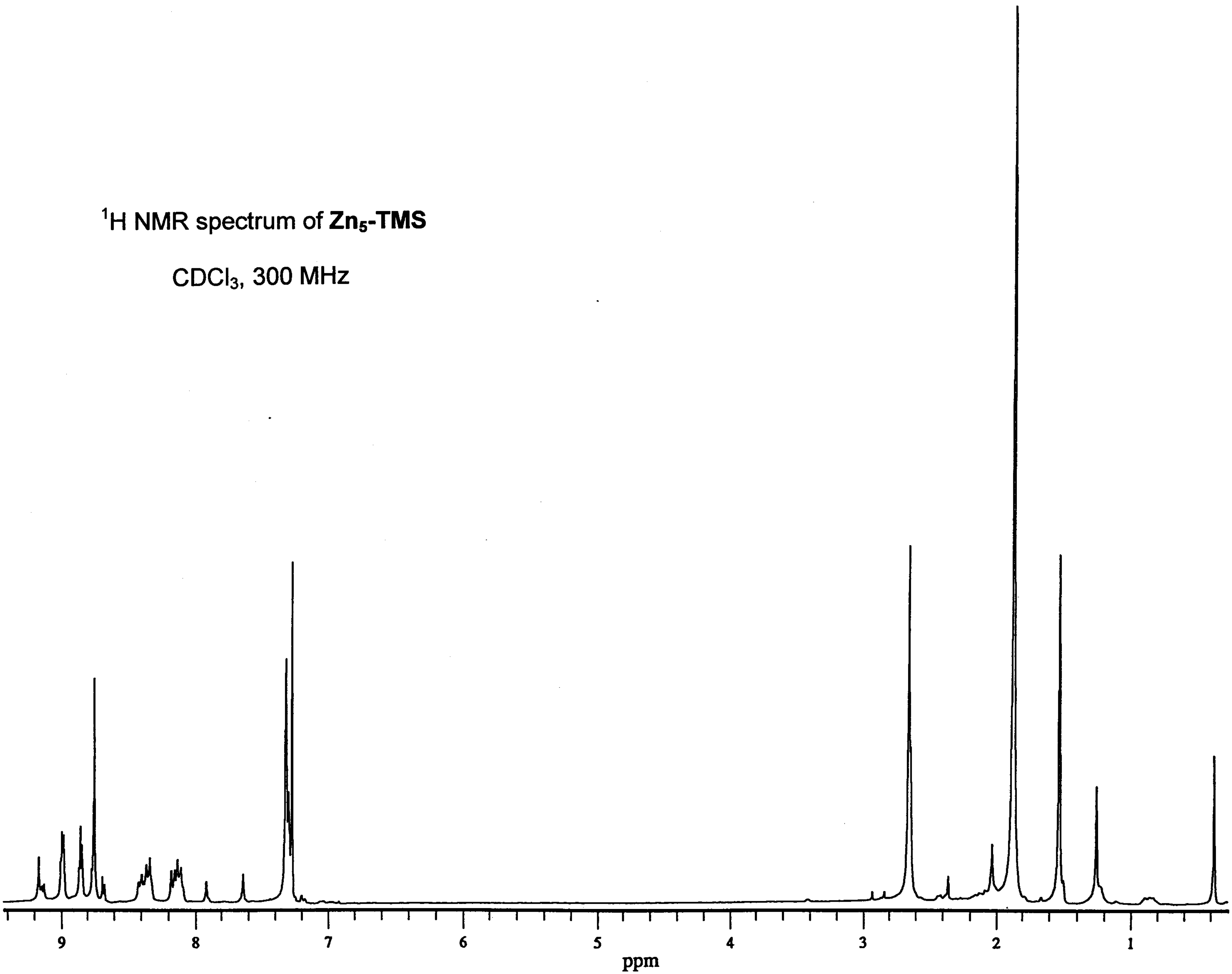
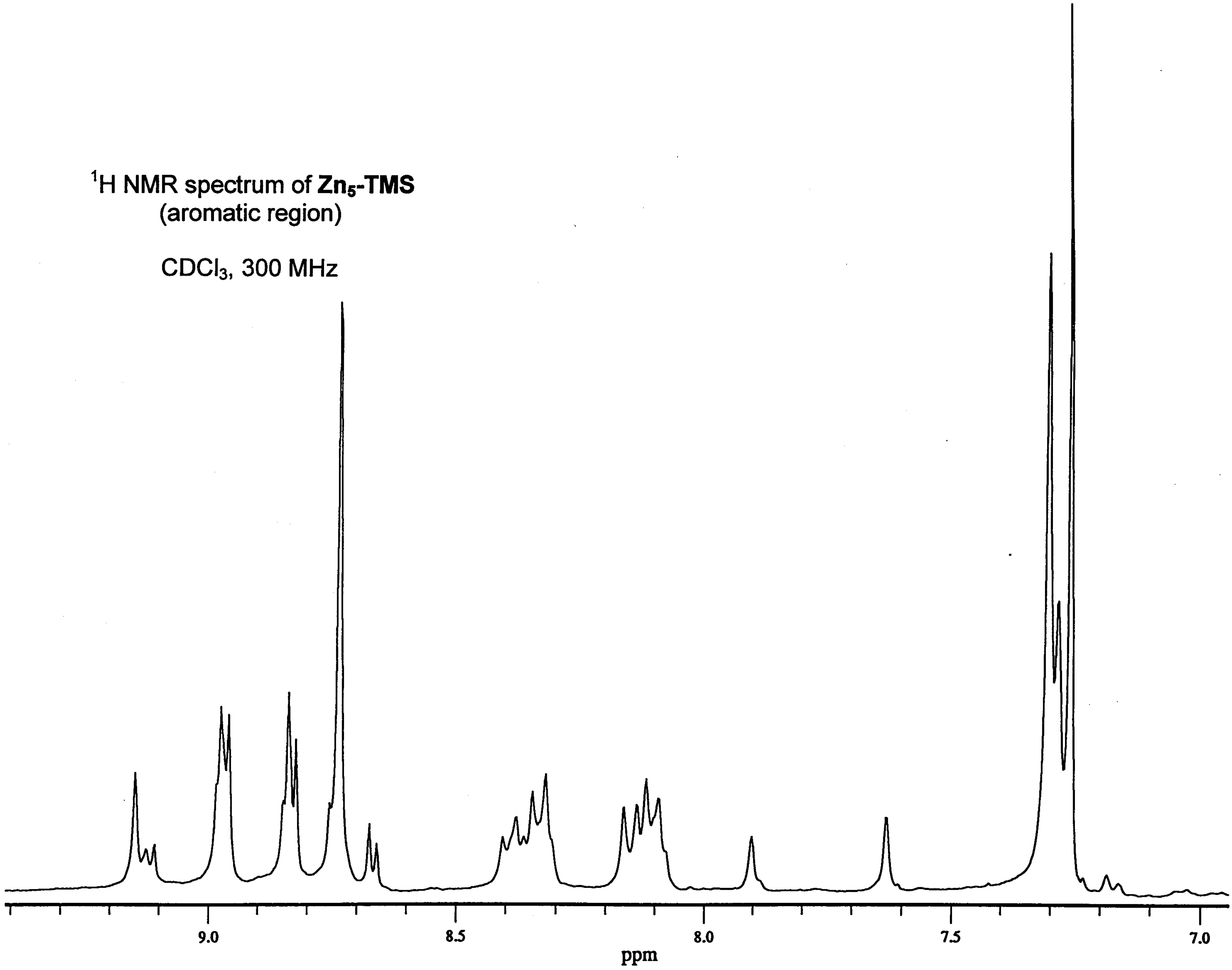


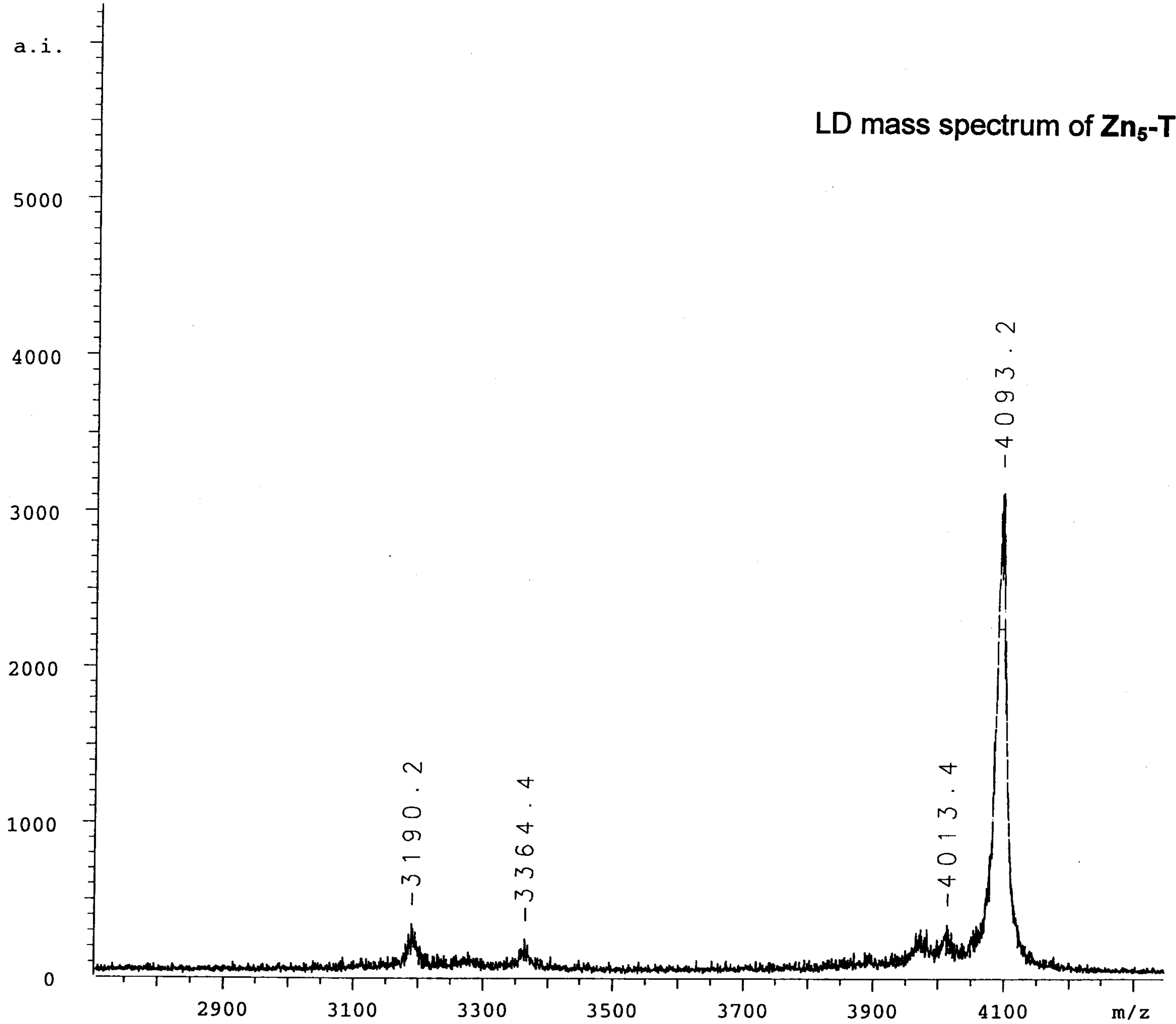
^{1}H NMR spectrum of **Zn$_5$-TMS**

CDCl$_3$, 300 MHz



^{1}H NMR spectrum of **Zn_5-TMS**
(aromatic region)

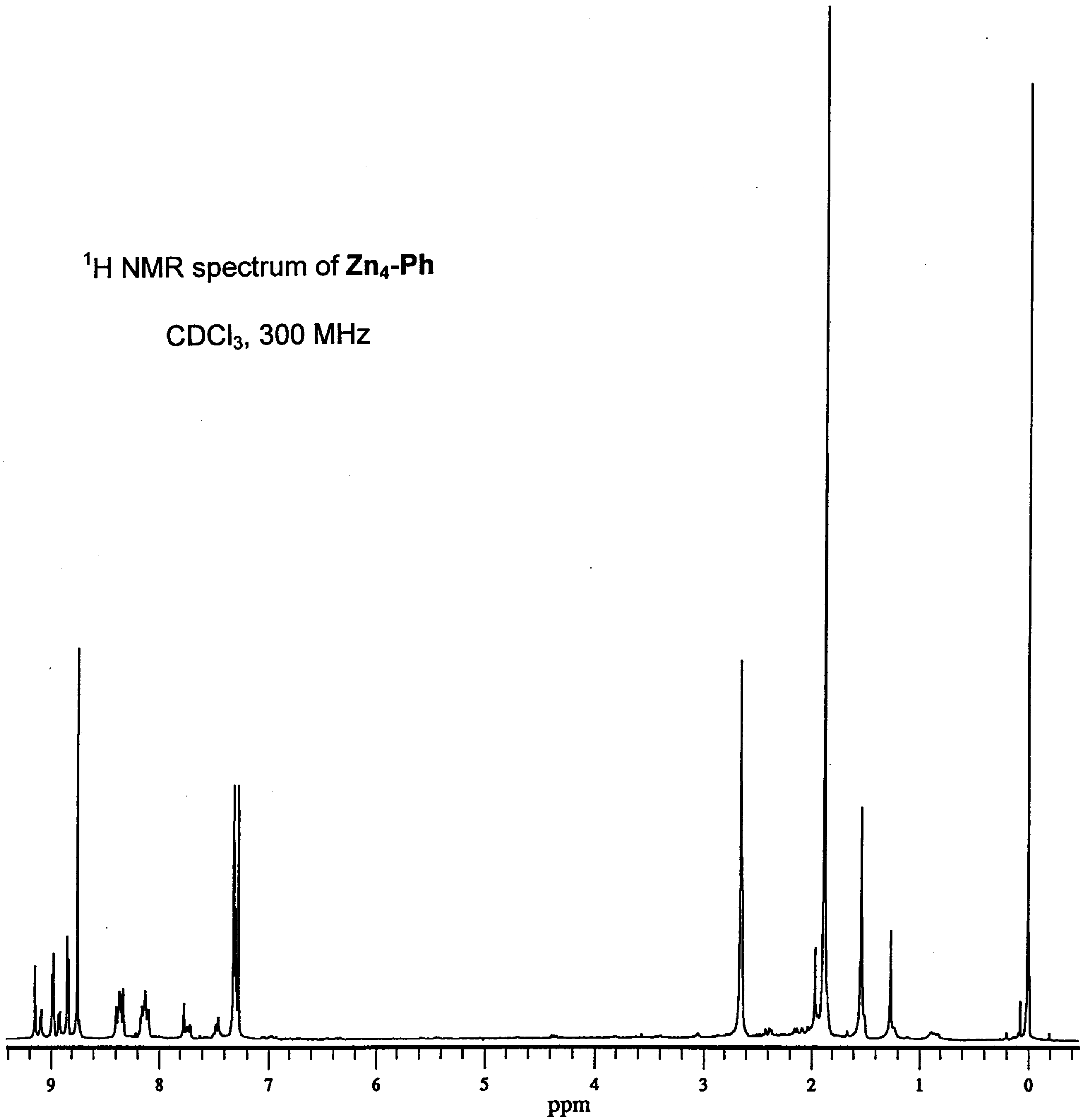
$CDCl_3$, 300 MHz



LD mass spectrum of **Zn_5-TMS**

^{1}H NMR spectrum of **Zn$_4$-Ph**

CDCl$_3$, 300 MHz



GE NMR OMEGA

```
/home/general/acq.data

Date:  Wed Jul 29 14:29:22 1998
OPERATOR: ********

ACQ TIME          = 1.36 sec
DATA SIZE         = 8192
NUM OF BLKS       = 1
NUM OF SCANS      = 120

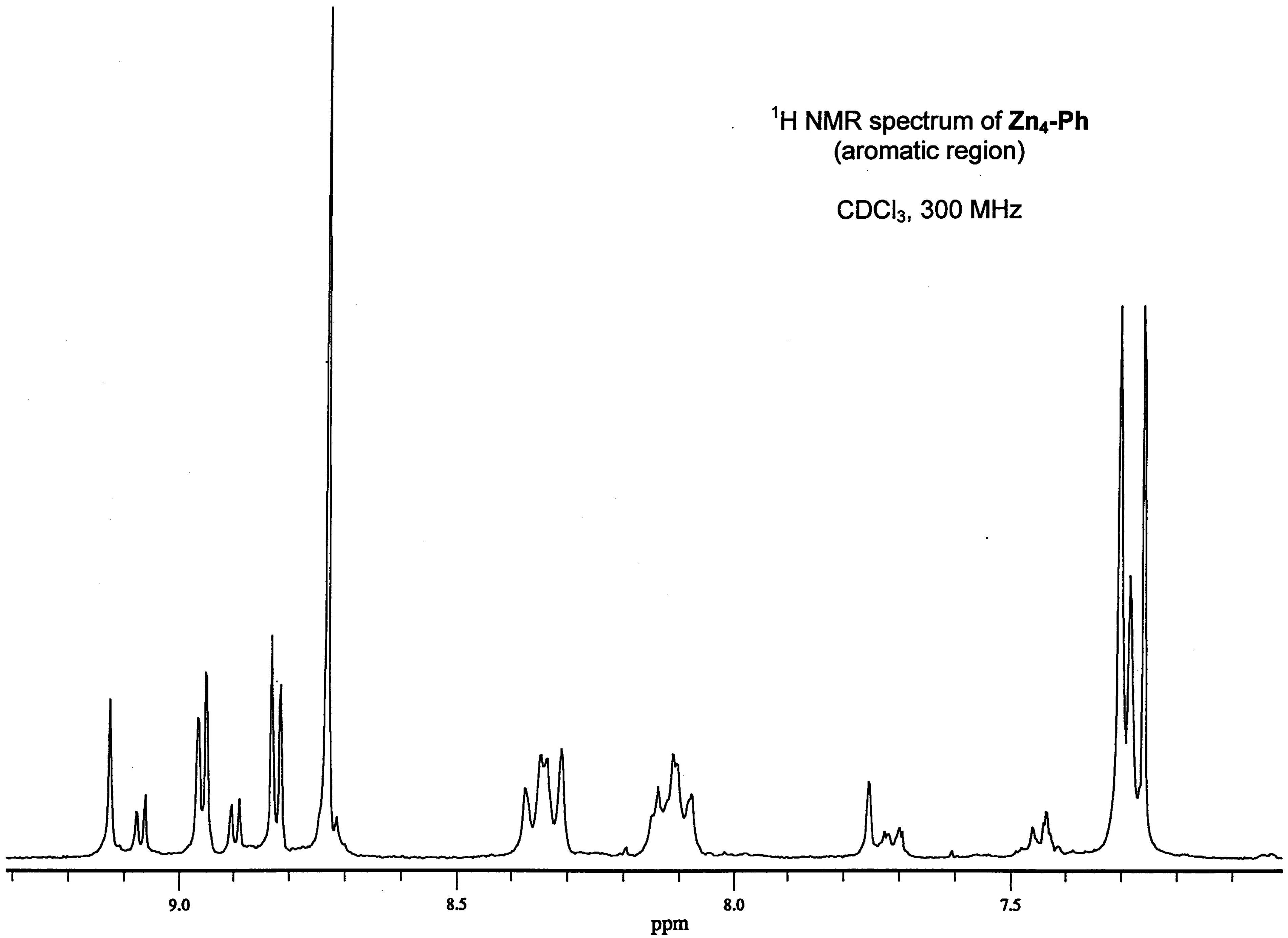
PULSE SEQUENCE:
  SEQUENCE NAME   = 1puls.s

OBSERVE:
  f1 FREQ         = 300.5215058 MHz
  SPEC WIDTH      = 6006.01 Hz
  SPEC OFFSET     = 1502.42 Hz
  GAIN            = 1006.1
  POWER LEVEL     = 63
  HIGH POWER      = ON

DECOUPLER:
  f2 FREQUENCY    = 300.5215058 MHz
  f2 POWER        = 0 db
  f2 MODULATION   = CW

PROCESSING:
  PHASE A         = 95.51
  PHASE B         = -6.62

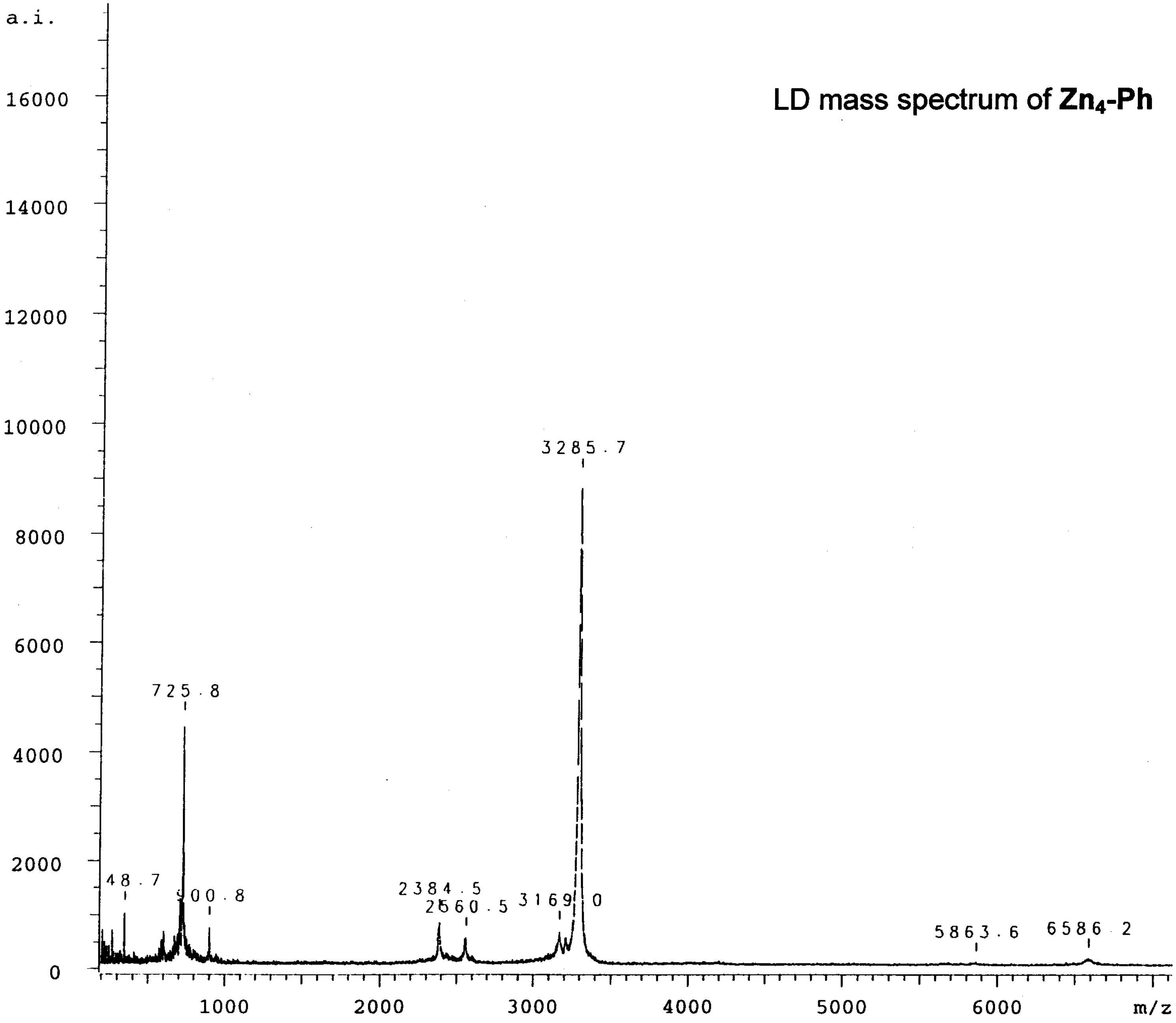
PLOT RANGE:
  X From 9.39  TO  -0.47 ppm
```

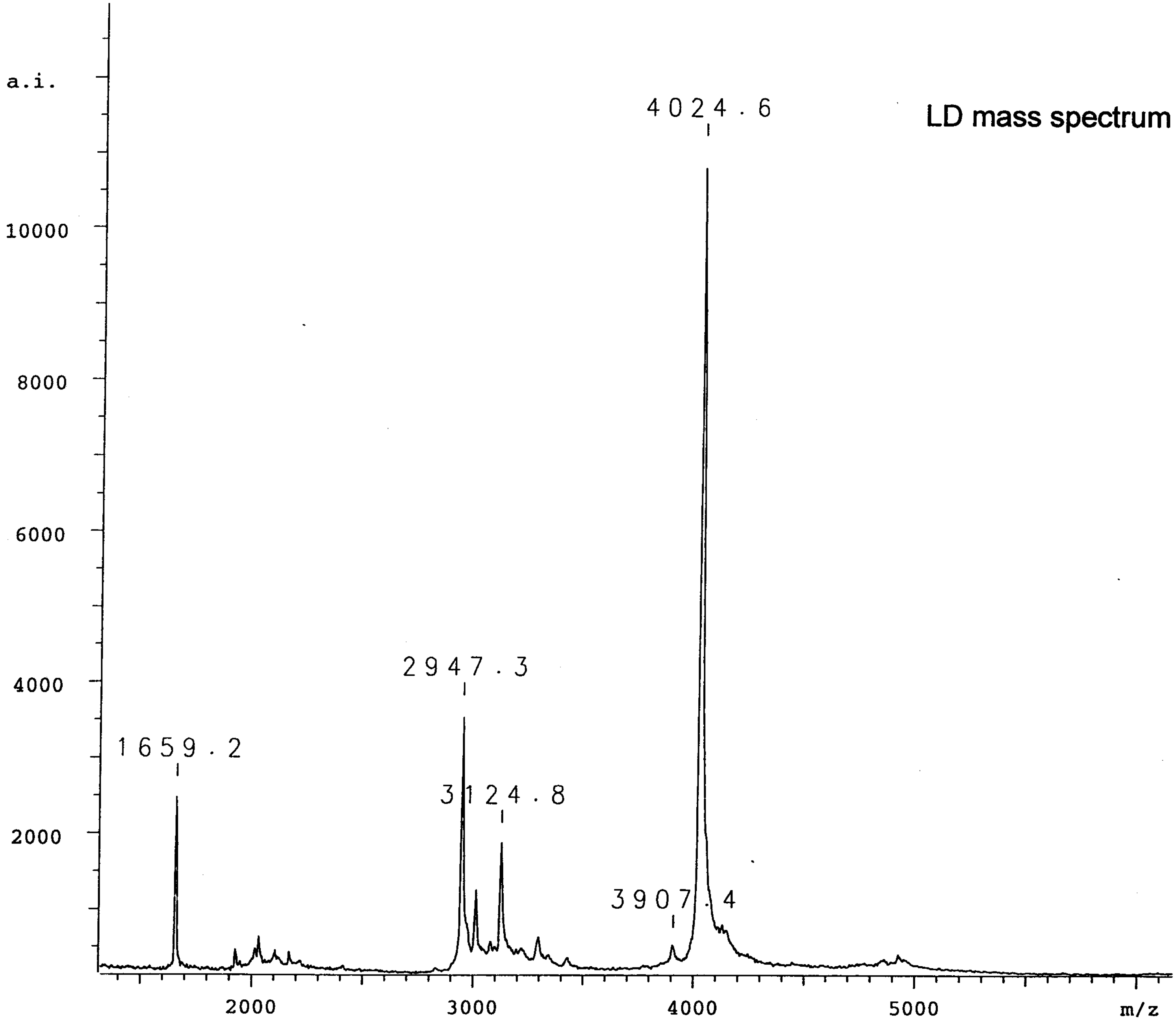


^{1}H NMR spectrum of **Zn_4-Ph**
(aromatic region)

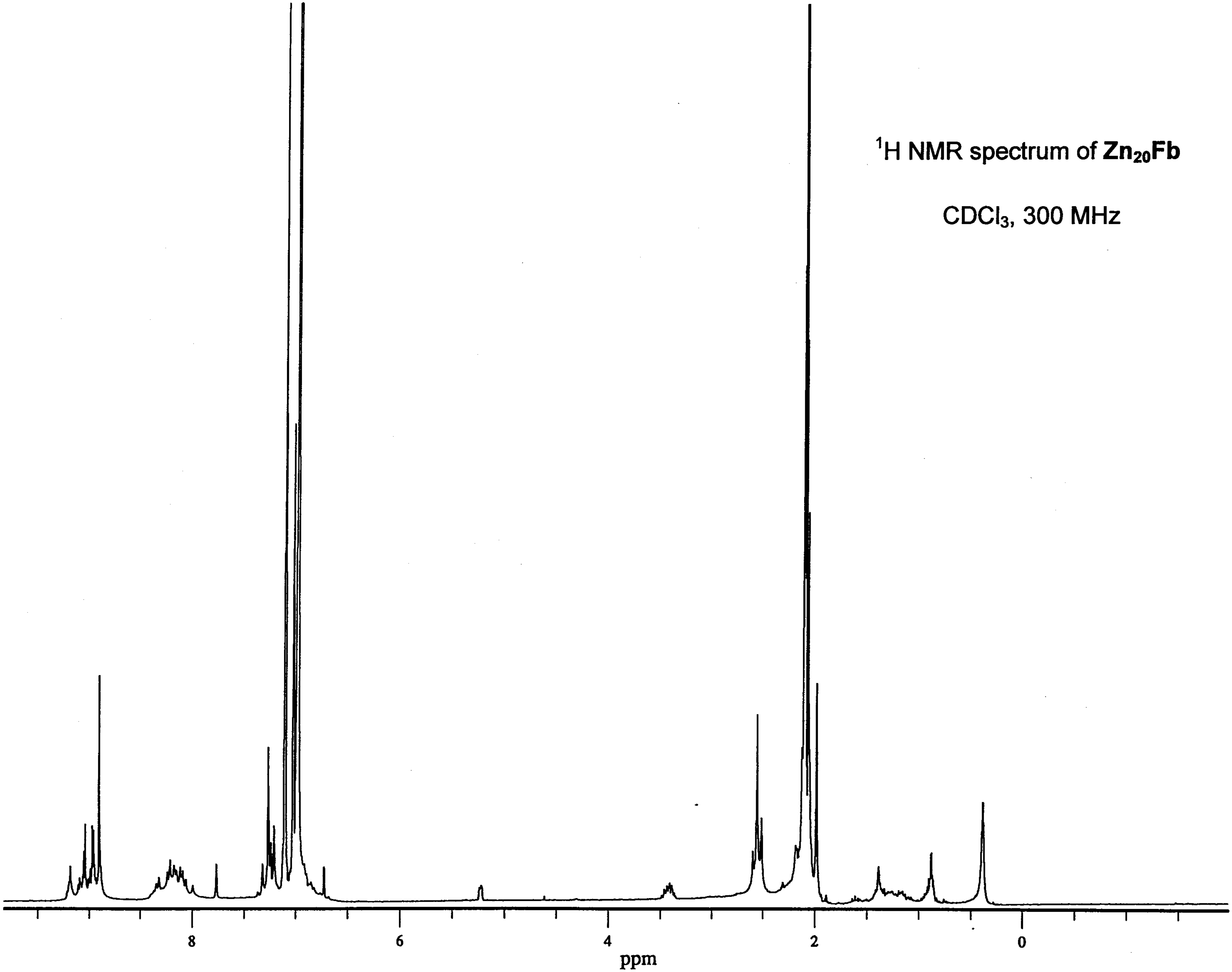
$CDCl_3$, 300 MHz

LD mass spectrum of **Zn_4-Ph**



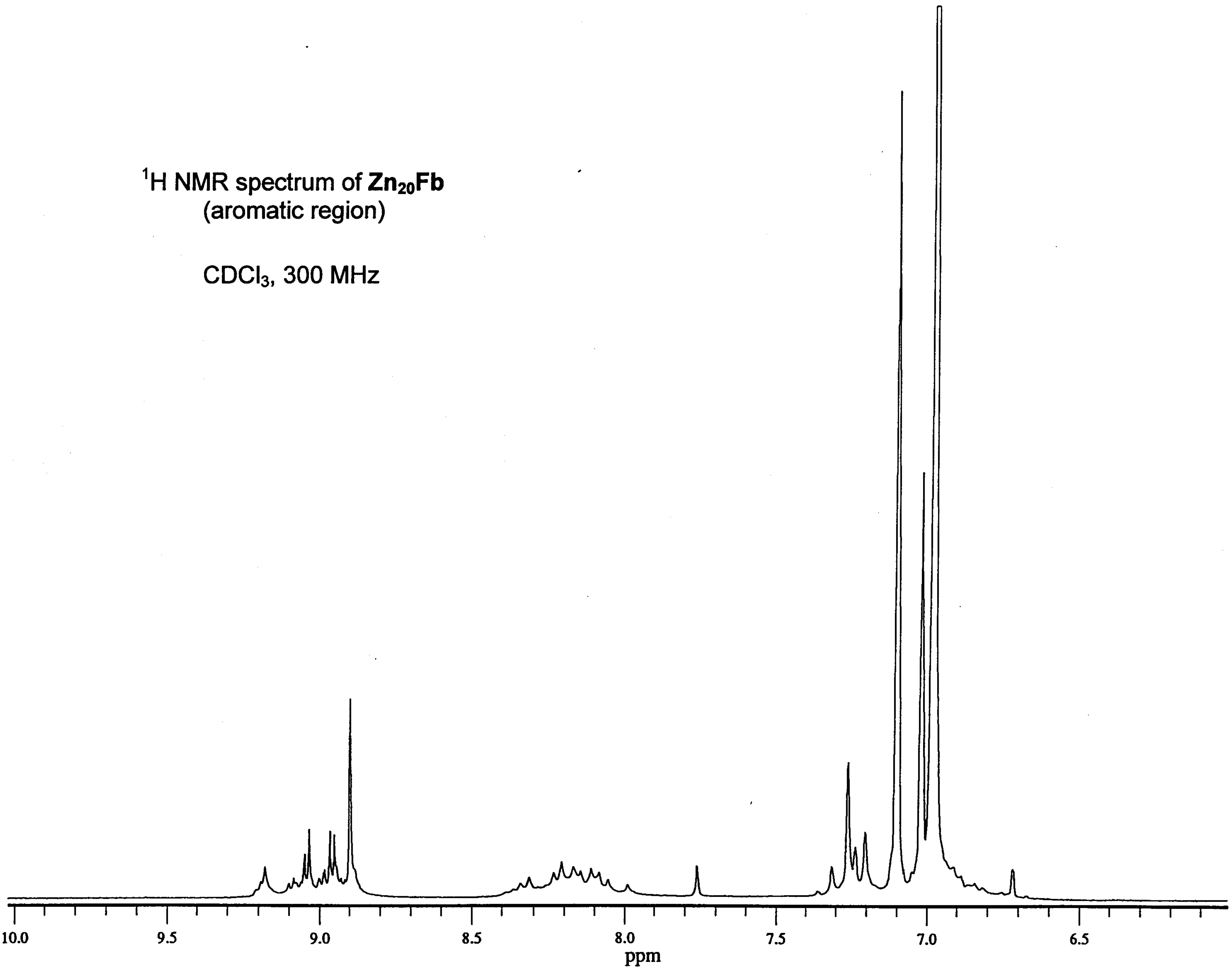


LD mass spectrum of **Zn_5-H**



^{1}H NMR spectrum of **Zn$_{20}$Fb**

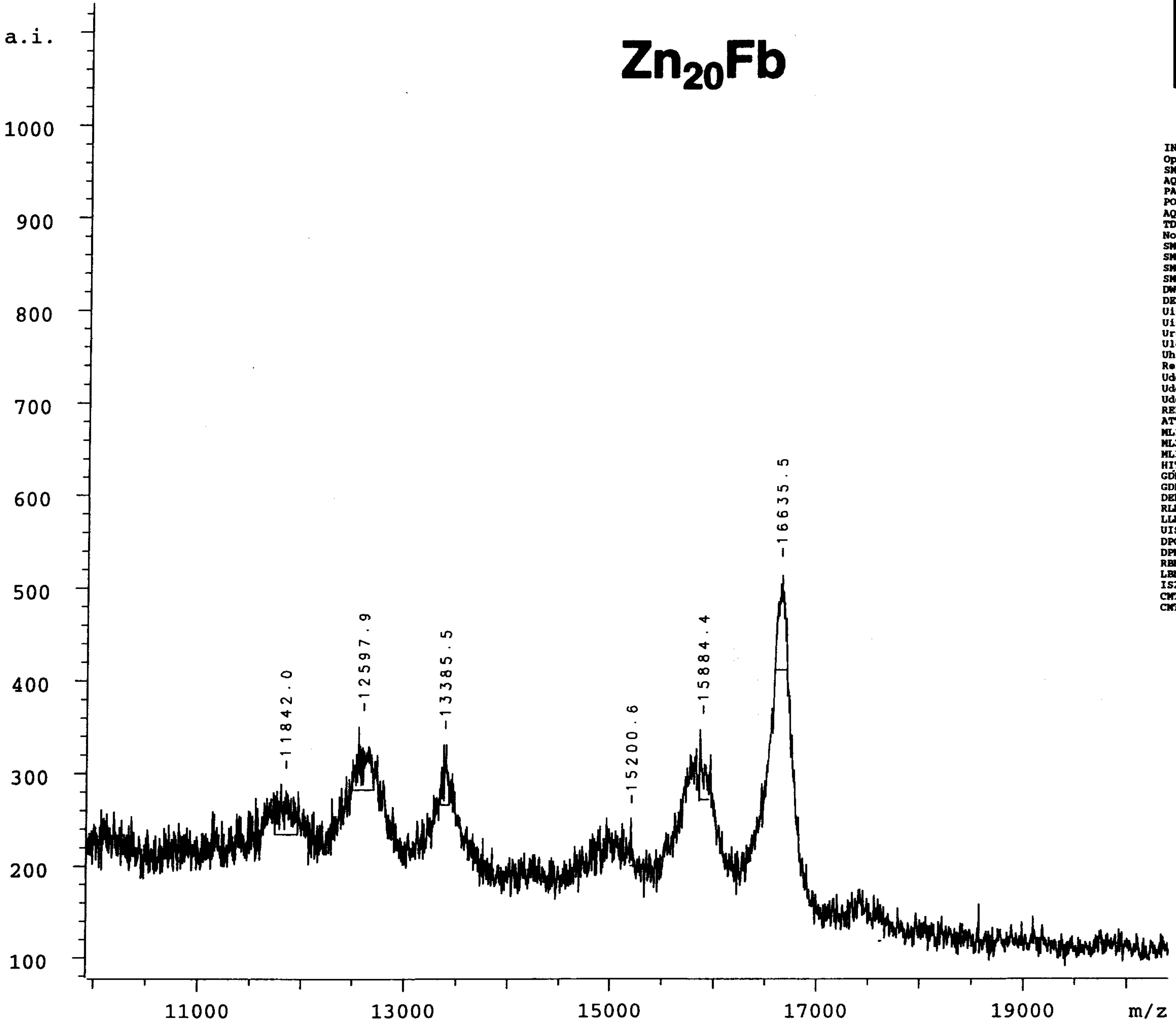
CDCl$_3$, 300 MHz



^{1}H NMR spectrum of **Zn$_{20}$Fb**
(aromatic region)

CDCl$_3$, 300 MHz

Zn$_{20}$Fb



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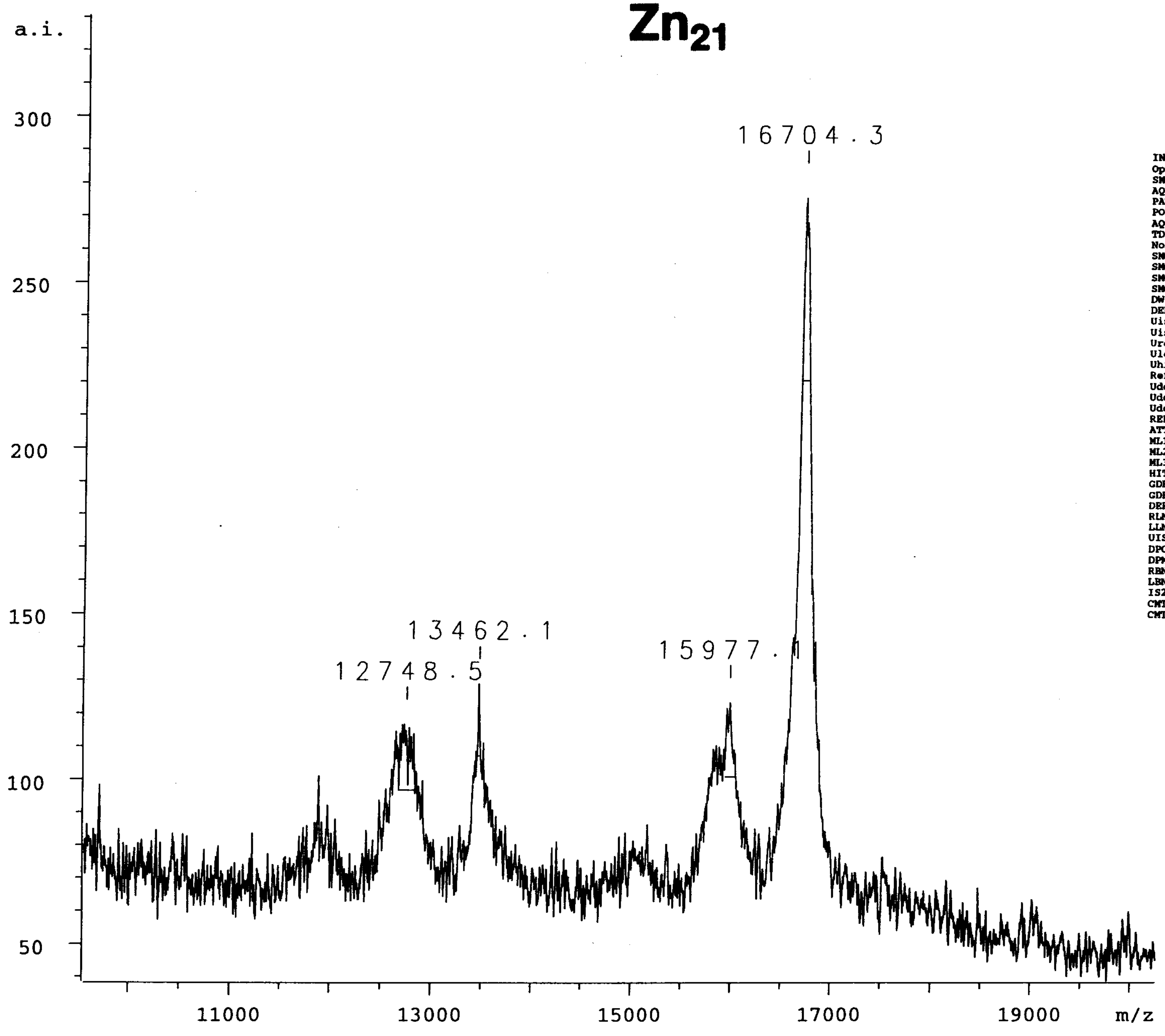
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  983024
AQ_DATE Thu Oct 29 14:27:04 1998
PATH    /export/home/data/chemistry/LINDSEY/CHARO
POLARI  POS
AQOP_m  Reflector
TD            50000
NoSHOTS         300
SMONUM            1
SMOPTS1          10
SMOPTS2           0
SMOPTS3           0
DW             2.00  [ns]
DELAY         0 [ns]
Uis1          20.00  [kV]
Uis2          16.90  [kV]
Urefl          0.00  [kV]
Ulens          7.40  [kV]
Uhimass        0.00  [kV]
RefFull        0.00  [kV]
UdetL          1.50  [kV]
UdetR          0.00  [kV]
Udefl          2.00  [kV]
REPHZ          1.00  [Hz]
ATTEN         30.0
ML1      2074274.974
ML2          392.563
ML3            0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  yes
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1       510.84
DPMASS       700.00  [Da]
RBNDVAL        0.33
LBNDVAL        0.28
IS2BNDV        0.91
CMT1    zn20fb/ferulic acid
CMT2    attn=30; is/2=16.9; lens=7.4
```

/export/home/data/chemistry/LINDSEY/CHARO/983024/1SRef/pdata/1   tof   Thu Oct 29 14:46:27 1998

Zn$_{21}$



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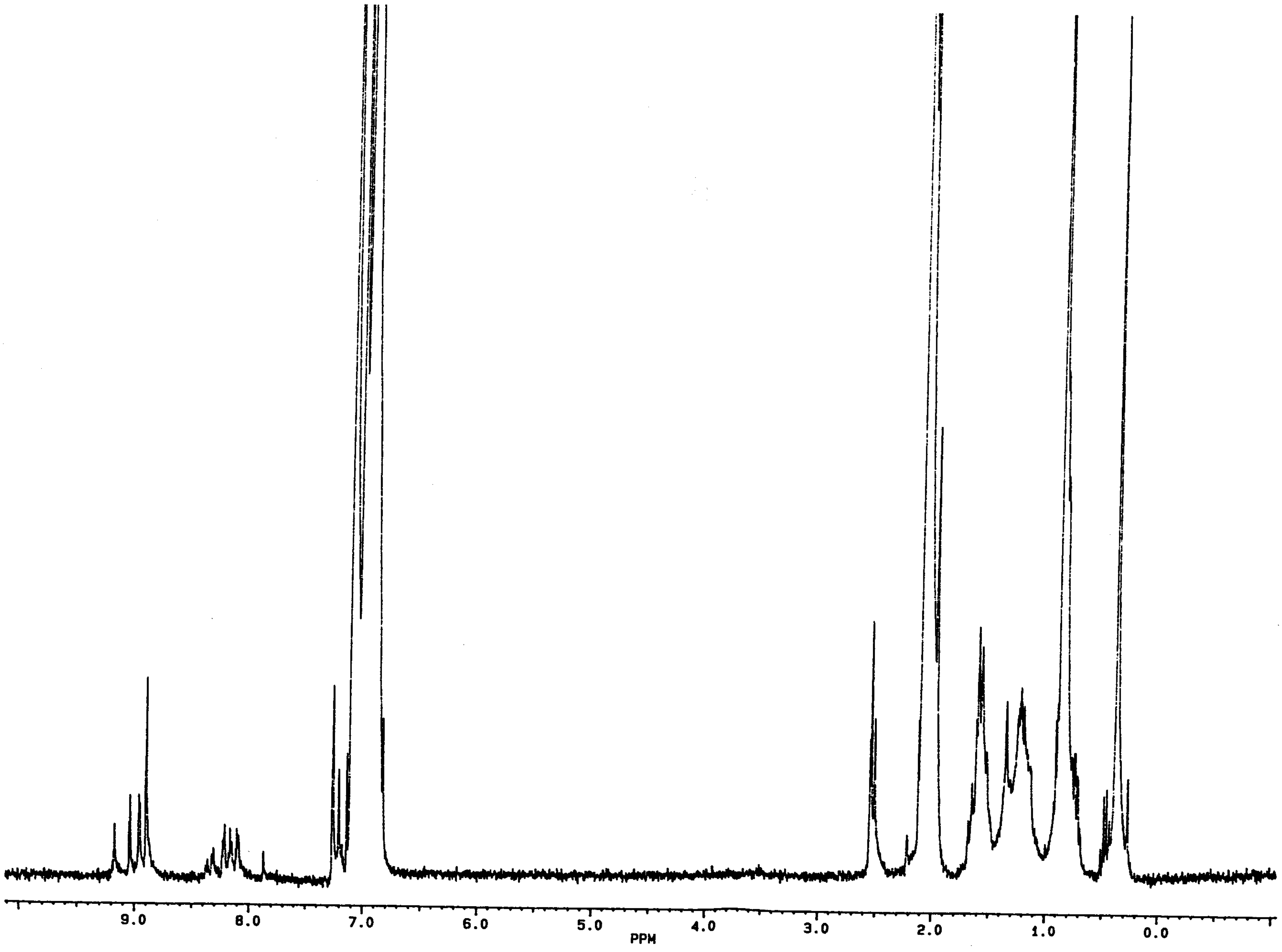
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  982906
AQ_DATE Thu Oct 22 11:05:11 1998
PATH    /export/home/data/chemistry/LINDSEY/CHARO
POLARI  POS
AQOP_m  Reflector
TD           40000
NoSHOTS        300
SNONUM           1
SMOPTS1         10
SMOPTS2          0
SMOPTS3          0
DW               4.00  [ns]
DELAY          0 [ns]
Uis1            20.00  [kV]
Uis2            17.50  [kV]
Urefl            0.00  [kV]
Ulens            7.50  [kV]
Uhimass          0.00  [kV]
RefFull          0.00  [kV]
UdetL            1.50  [kV]
UdetR            0.00  [kV]
Udefl            2.00  [kV]
REPHZ            1.00  [Hz]
ATTEN           30.0
ML1        2075235.788
ML2            300.964
ML3              0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1         510.84
DPMASS         700.00  [Da]
RBNDVAL          0.33
LBNDVAL          0.28
IS2BNDV          0.91
CMT1    Zn21/ferulic acid-toluene; atten=30
CMT2
```

```
/export/home/data/chemistry/LINDSEY/CHARO/982906/1SRef/pdata/1   tof   Fri Oct 23 18:40:39 1998
```

^{1}H NMR Spectrum of Octamer



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DATE 23-9-93

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O1      9034.690
SI    16384
TD    16384
SW    10000.000
HZ/PT     1.221

PW         12.0
RD         2.000
AQ          .819
RG      1024
NS        16
TE       298

FW    12500
O2      9034.690
DP    35L PO

LB          0.0
GB          .200
CX        35.00
CY          0.0
F1        10.113P
F2        -1.054P
HZ/CM   159.563
PPM/CM     .319
SR      5534.57
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LD-MS Spectrum of Octamer