Supporting Information

Excited-State Energy-Transfer Dynamics in Self-Assembled Triads Composed of Two Porphyrins and an Intervening Bis(dipyrrinato)metal Complex

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I. Results

1. Attempts to prepare bis(dipyrrinato)metal complexes with $CaCl_2$, $MgBr_2{\cdot}OEt_2$, MgI_2, or $Cd(OAc)_2{\cdot}2H_2O$. We explored the preparation of the dipyrrin metal complexes with $CaCl_2$, $MgBr_2{\cdot}OEt_2$, (DIEA-MgI_2) or $Cd(OAc)_2{\cdot}2H_2O$ (Scheme SI-1). The results were as follows: (1) A solution of **2a** in $CHCl_3$ was treated overnight with TEA (5 equiv) and $CaCl_2$ (5 equiv) in methanol at room temperature. TLC and UV-Vis analysis indicated no **Ca-2a** was formed. (2) A solution of **2a** in $CHCl_3$ was treated overnight with TEA (20 equiv) and $Cd(OAc)_2{\cdot}2H_2O$ (200 equiv) in methanol. TLC and UV-Vis analysis showed no **Cd-2a** was formed. (3) A solution of **2a** in CH_2Cl_2 was treated with TEA (40 equiv) and $MgBr_2{\cdot}OEt_2$ (20 equiv) at room temperature. TLC and UV-Vis analysis showed no reaction even after overnight. (4) Further experiments to prepare **Mg-2j** also failed. In this case, two methods were examined to attempt to prepare **Mg-2j**. We have developed methods for the preparation of Mg-porphyrins at room temperature employing heterogeneous or homogeneous procedures.[1] The same procedures were also employed for preparing **Mg-2j**: (a) Heterogeneous procedure: A solution of **2j** in CH_2Cl_2 was treated with DIEA (20 equiv) and MgI_2 (10 equiv) at room temperature. UV-Vis analysis showed no reaction even after 24 h. (b) Homogeneous procedure: A solution of **2j** in CH_2Cl_2 was treated with a freshly prepared "DIEA-MgI_2" reagent at room temperature. UV-Vis analysis of the crude reaction mixture indicated no reaction occurred even after overnight.

2. Control experiments (Suzuki coupling).

Suzuki coupling reactions were performed in the presence of a dipyrrin, a dipyrrin-zinc(II) complex, a dipyrrin-copper(II) complex or a dipyrrin-palladium(II) complex. We performed a Suzuki cross-coupling reaction (Scheme SI-2) of an iodo-porphyrin (**13**)[2] and a boronate-porphyrin (**14**)[2] in the presence of an equimolar amount of free base dipyrrin **2a** under conditions similar to those used previously:[2] $Pd(PPh_3)_4$ (15 mol%) as catalyst; K_2CO_3 (8 eq) as base; DMF/toluene (1:2, 20 mM) as solvent and at temperature of 90-95 °C under argon. The analytical SEC trace of the reaction mixture (after 22 h at 90-95 °C) indicated no formation of dimer (**15**).

The same Suzuki coupling reaction was carried out as shown in Scheme SI-2, but in the presence of an equimolar amount of bis(dipyrrinato)copper(II) complex **Cu-2b** instead of free base dipyrrin **2a**. Analytical SEC indicated only a 5.3% yield of the dimer was formed after 17 h at 90-95 °C. However, LD-MS analysis of this reaction mixture did not show the presence of the desired dimer peak. We next examined the same Suzuki coupling in the presence of an equimolar amount of the bis(dipyrrinato)zinc(II) complex **Zn-2a**. TLC and analytical SEC analysis showed no reaction occurred after overnight. However, when the same Suzuki coupling

reaction was carried out in the presence of an equimolar amount of bis(dipyrrinato)palladium(II) **Pd-2b** instead of 5-phenyldipyrrin (**2b**), analytical SEC indicated that the dimer was formed in 64% yield (t_R = 10.79 min) after 15 h at 90-95 °C. In summary, Suzuki coupling can be performed in the presence of a bis(dipyrrinato)palladium(II) complex.

(ZnP-dp)$_2$ triad. We first attempted to synthesize the (ZnP-dp)$_2$ triad **12** by direct coupling of the boronate-substituted porphyrin **Zn-5** and bis(dipyrrinato)zinc(II) complex **Zn-2c** via the Suzuki reaction (Scheme SI-3). However, no triad was formed under the conditions we employed in the construction of phenylene-linked porphyrin arrays, i.e., $Pd(PPh_3)_4$ (30 mol%) as catalyst, K_2CO_3 (16 eq relative to boronate porphyrin) as base, toluene/DMF (2:1) as solvent at 90 °C for 15-24 h.[2] Reaction of the bromo-substituted porphyrin **Zn-4** and boronate-substituted bis(dipyrrinato)zinc(II) complex **Zn-2d** under the above mentioned conditions also failed to give the desired (ZnP-dp)$_2$ triad. This is consistent with the results from control experiments.

3. Dipyrromethane-dicarbinol + dipyrrin under Yb(OTf)$_3$/CH$_2$Cl$_2$ conditions.

To examine the reactivity of a dipyrrin towards the new acid-catalyzed condensation conditions (porphyrin formation via dipyrromethane-dicarbinol + dipyrromethane route), three control experiments were performed as follows:

(i) Dipyrromethane-dicarbinol + dipyrrin (in the absence of dipyrromethane). A direct examination of the reactivity of a dipyrrin towards a dipyrromethane-dicarbinol was carried out as follows: A solution containing equimolar amounts of 5-phenyldipyrrin (**2a**) and the dipyrromethane-dicarbinol **11a-diol** derived from 1,9-bis(*p*-toluoyl)-5-phenyldipyrromethane (2.5 mM each in CH_2Cl_2) was treated with Yb(OTf)$_3$ (3.2 mM) (Scheme SI-4). LD-MS analysis of the oxidized reaction mixture after 40 min indicated a weak peak at *m/z* = 641.6, corresponding to the trans-substituted porphyrin. UV-Vis analysis of the crude reaction mixture indicated ~2.5% yield of porphyrin product.

(ii) Dipyrromethane-dicarbinol + dipyrrin (in the absence of dipyrromethane) + AcOH (100 molar equivalents): Deactivation of the dipyrrin. UV-Vis spectroscopic analysis of a 2.5 mM solution of 5-phenyldipyrrin (**2a**) in CH_2Cl_2 showed that at least 100 molar equivalents of AcOH was required to completely protonate the free base dipyrrin. Accordingly, 100 molar equivalents of AcOH was added to a solution of 5-phenyldipyrrin (**2a**) and the condensation with a dipyrromethane-dicarbinol (**11a-diol**) was carried out under the same conditions as in (i). LD-MS and UV-Vis analysis of the oxidized reaction mixture at 40 min showed no detectable peaks corresponding to a porphyrin. An equimolar amount of 5-phenyldipyrromethane (**1a**) was added to the reaction mixture followed by stirring for 40 min; removal of a sample and oxidation with DDQ followed by spectroscopic analysis indicated porphyrin formation in 13% yield (based on ε_{Soret} = 500,000 $M^{-1}cm^{-1}$). However, LD-MS analysis also showed scrambled products (total of four porphyrin peaks were observed: *m/z* = 613.2, *meso*-tetraphenylporphyrin; 627.1, 5-(4-methylphenyl)-10,15,20-triphenylporphyrin; 641.2, the desired product 5,15-bis(4-methylphenyl)-10,20-diphenylporphyrin; 655.2, 5,10,15-tris(4-methylphenyl)-20-phenylporphyrin (Scheme SI-5). While titration of the dipyrrin with acid suppressed reaction of the dipyrrin, this approach also caused acidolytic scrambling, leading to the formation of undesired porphyrin products. We next performed a competitive reaction between a dipyrromethane and a dipyrrin towards a dipyrromethane-dicarbinol.

(iii) Dipyrromethane-dicarbinol + dipyrrin + dipyrromethane: Competitive reaction between dipyrromethane and dipyrrin towards dipyrromethane-dicarbinol. A competitive reaction between a dipyrromethane and a free base dipyrrin towards a dipyrromethane-dicarbinol under the new acid-catalyzed porphyrin-forming conditions (3.2 mM of Yb(OTf)$_3$ in CH_2Cl_2) was examined as follows. A solution containing an equimolar amount of 5-

phenyldipyrromethane (**1a**), 5-(4-*tert*-butylphenyl)dipyrrin (**2b**) and dipyrromethane-dicarbinol **11a-diol** (2.5 mM each) was treated with $Yb(OTf)_3$ (3.2 mM) in CH_2Cl_2 (Scheme SI-6). LD-MS analysis showed only those porphyrin species derived from reaction of 5-phenyldipyrromethane (**1a**) and the dipyrromethane-dicarbinol **11a-diol** at *m/z* = 641.9. No porphyrin peak derived from 5-(4-*tert*-butylphenyl)dipyrrin (**2b**) and the dipyrromethane-dicarbinol **11a-diol** was observed. The usual work up and column chromatographic purification afforded the desired porphyrin **16** in 18% yield. LD-MS and ^{1}H NMR spectroscopic analysis showed the expected porphyrin free of any scrambled product.

Conclusion: The dipyrrin reacts with the dipyrromethane-dicarbinol affording the porphyrin in ~2.5% yield. However, a dipyrromethane reacts with a dipyrromethane-dicarbinol in the presence of an equimolar amount of dipyrrin affording the desired porphyrin without formation of scrambled products. In other words, no competing reaction between the dipyrrin and the dipyrromethane-dicarbinol was detected in the presence of the dipyrromethane.

4. Notes on chromatography.

The purification of all free base dipyrrins (**2**) and the metal complexes **Zn-2**, **Cu-2** and **Pd-2** was accomplished by chromatography on silica gel. The following observations are noteworthy: (1) The free base dipyrrins and their Zn and Pd complexes (with no porphyrins attached) showed streaking on silica chromatography, preventing any discrete bands to be observed. During metalation, any remaining free base dipyrrin was easily removed by washing with methanol since the zinc complexes prepared herein have poor solubility in methanol. On the other hand, the Cu complex did not streak and the starting dipyrrin was readily removed by chromatography. (2) The zinc complexes demetalate on alumina column and the free base dipyrrin binds very tightly to alumina. (3) Porphyrin–dipyrrin **7** was chromatographed on silica and give a tight band similar to those of porphyrins lacking a dipyrrin unit. (4) The all-zinc triad **12** could not be chromatographed on silica owing to the complete demetalation of the zinc-dipyrrin complex, affording the porphyrin-substituted free base dipyrrin **7**. However, the $(ZnP\text{-}dp)_2Pd$ triad **6** was successfully chromatographed on a silica column without any demetalation of the bis(dipyrrinato)Pd complex.

5. Static and Time-Resolved Optical Spectroscopy.

(i) Static Absorption Spectroscopy. The absorption spectra of triad **12a** and **12b** and their reference compounds in toluene or benzonitrile are shown in Figures SI-1 to SI-7 (solid spectra). The absorption spectrum of $(ZnP\text{-}dp)_2Zn$ triad **12b** is essentially the sum of the spectra of reference zinc porphyrin **Zn-8b** and bis(dipyrrinato)zinc complex **Zn-2b** in toluene (Figure SI-1), as is the case for triad **12a** and its reference compounds **Zn-8a** and **Zn-2a**. For each triad, the ultimate porphyrin absorption characteristics in the triad derive mainly from the addition of the aryl ring at the linker site to the starting porphyrin (e.g., **Zn-3**) to give **Zn-8a** or **8b**, with little change upon attachment of the dipyrrin to give porphyrin–dipyrrin **Zn-7a** or **Zn-8b**, or upon self-assembly to produce $(ZnP\text{-}dp)_2Zn$ triad **12a** or **12b** (Figure SI-2 and SI-3). Similar findings were obtained for the compounds in benzonitrile, except that metal coordination red shifts the zinc porphyrin absorption bands by 5-10 nm and alters the Q-band ratios; in contrast, the $(dp)_2Zn$ features are unperturbed (Figures SI-4 to SI-7).

(ii) Static Fluorescence Spectra. The spectral differences of **12a** or **12b** (and their component parts) in toluene or benzonitrile are shown in Figures SI-1 to SI-7 (dashed or dotted spectra) and further described as follows. (1) The emission from the triads **12a** and **12b** in both solvents occurs primarily from the porphyrin(s), showing the same features present for reference

compounds **Zn-8a** or **Zn-7a** and **Zn-8b** or **Zn-7b** (using direct excitation of either the porphyrin or the $(dp)_2Zn$ complex). (2) Due to solvent ligation, the porphyrin emission bands are red shifted and the intensity-ratios altered in parallel with the absorption spectra. (2) The fluorescence from bis(dipyrrinato)zinc reference complex **Zn-2a** has rough mirror symmetry to the absorption in both toluene and benzonitrile. (3) The absorption-emission (Stokes) shift for complex **Zn-2a** decreases to ~460 cm^{-1} from ~660 cm^{-1}; this change is due solely to a blue shift of the emission in benzonitrile, namely to an excited-state effect.

(ii) Time-resolved Absorption Spectra and Kinetics. Transient absorption spectra and kinetics traces obtained for triad **12b** in toluene (Figure SI-8) are similar to those for the triad **12a** in toluene as described in the paper. These findings include the same $[(dp)_2Zn]^*$ lifetime of 1.4 ps, which is the average value from several probe wavelengths. Using standard methods,[3] energy transfer from $[(dp)_2Zn]^*$ to a zinc porphyrin subunit has rate constant $k_{EnT} = (2\bullet 1.4\ ps)^{-1} - (93\ ps)^{-1} = (2.8\ ps)^{-1}$ and yield $\Phi_{EnT} = [1 - 2\bullet(1.4\ ps)/(93\ ps)] = 0.97$. The factors of 2 derive from the presence of two zinc porphyrin energy acceptors per central $(dp)_2Zn$ complex in each $(ZnP\text{-}dp)_2Zn$ triad. The overall yield of energy transfer from $[(dp)_2Zn]^*$ to the porphyrin units in each triad is $\Phi_{EnT}^{total} = [1 - (1.4\ ps)/(93\ ps)] = 0.985$. Furthermore, for each dyad in toluene, once ZnP* is formed from $[(dp)_2Zn]^*$, the ZnP* decay profile obtained the transient absorption data is in qualitative agreement with the fluorescence lifetime within experimental error, indicating little change from the reference porphyrins. Thus, ZnP* for the triads in toluene is not quenched appreciable (<10%) by deleterious processes such as charge transfer.

The excited-state dynamics are somewhat more complex for triads **12a** or **12b** in benzonitrile, is also the case for reference $(dp)_2Zn$ complex **Zn-2a** (the latter to be described in detail elsewhere). Figure SI-9a shows representative transient absorption difference spectra for **12a** in benzonitrile using primary excitation of the central $(dp)_2Zn$ moiety with a 484-nm 130-fs flash. Similar data are obtained for triad **12b** in benzonitrile. The spectrum at 0.5 ps spectrum has common characteristics to those found for each triad in toluene (Figure 4 of the paper and Figure SI-8), and can be assigned mainly to $[(dp)_2Zn]^*$ based on the sharp trough in the 500-525 nm region. This feature primarily reflects excited-state stimulated (by the white-light probe pulse) emission that coincides with the red side of the spontaneous emission from reference complex **Zn-2a** (Figure SI-4, dashed). State ZnP* also contributes to the 0.5 ps spectrum based on partial bleaching of the porphyrin Q(1,0) ground-state band at ~555 nm, Q(0,0) bleaching plus stimulated emission at ~600 nm, and Q(0,1) stimulated emission at ~660 nm. A contribution of the excited zinc porphyrin at early times likely derives from direct porphyrin excitation in a fraction of the arrays (in which $(dp)_2Zn$ is not excited) and the early stage of energy transfer.

By 2.7 ps for **12a** and 2.5 ps for **12b** (Figures SI-9a and SI-10a, dashed lines), the $[(dp)_2Zn]^*$ stimulated emission has decayed and is replaced by ZnP* excited-state absorption along with further development of the ZnP* features noted above.[4] Additional measurements using excitation at 500 nm that allow probing of the $(dp)_2Zn$ ground-state absorption to shorter wavelengths do not rule out the possibility that some associated bleaching remains after $[(dp)_2Zn]^*$ decay. Such a bleaching would indicate that the ~2.5 ps spectrum for each dyad contains a contribution from a charge-separated state such as $[(dp)_2Zn]^-$ ZnP^+ formed by hole/electron transfer from $[(dp)_2Zn]^*$ in parallel with energy transfer to produce ZnP*. In other words, the spectrum at 2.7 ps may contain some charge-separated state in addition to ZnP*. The kinetic traces and fits in Figure SI-9b and Figure SI-10b show that decay of $[(dp)_2Zn]^*$ stimulated emission and growth of ZnP* (and perhaps some $[(dp)_2Zn]^-$ ZnP^+) absorption; this time profile combined with those at other probe wavelengths gives a $[(dp)_2Zn]^*$ lifetime of 0.8 ps for triads **12a** and **12b** in benzonitrile. These findings will be analyzed below along with other

results to estimate the relative yields of the $[(dp)_2Zn]^*$ energy- versus charge-transfer processes in the triads.

As time evolves past ~2.5 ps, the spectrum for each dyad shows relatively small readjustments (increased transient absorption to the red of the porphyrin Q(1,0) absorption bleaching at 555 nm and some reduction of transient absorption to the blue) to give the spectrum shown at 83 ps for **12a** and 200 ps for **12b** (Figures SI-9a and SI-10A, dashed-dotted lines). These changes clearly involve the porphyrin part of the triad, and could reflect electronic or conformational or ligation readjustment of ZnP*, or recombination within any charge-separated state such as $[(dp)_2Zn]^- ZnP^+$ formed from $[(dp)_2Zn]^*$. The kinetic traces shown in Figure SI-9b and SI-10b (insets) combined with results at other probe wavelengths indicate that the time constant of this process is ~85 ps for **12a** and ~105 ps for **12b**.

The last kinetic stage seen for **12a** or **12b** in benzonitrile involves the decay of the ZnP*. For the triad in toluene this decay occurs mainly by intersystem crossing to form the triplet excited state ZnP^T (as occurs in reference zinc porphyrins); this process is indicated by the porphyrin bleachings remaining at about the same amplitude during ZnP* decay, along with disappearance of stimulated emission (Figure 4 of paper). On the other hand, the spectra at 3.4-3.7 ns for **12a** or **12b** in benzonitrile (Figures SI-9a and SI-10a, dotted lines) shows that the decay of stimulated emission (e.g. the dip at ~650 nm at earlier times) is accompanied by significant decay of the porphyrin ground-state bleachings and the overall transient absorption, indicating that significant ground-state recovery has occurred. The simplest interpretation of these observations is that a significant fraction of the ZnP* decay for each triad in benzonitrile occurs by a process such as charge transfer, with the charge-separated product then decaying by charge recombination to the ground state with a time constant < 1 ns. Thus, the spectrum at 3.4-3.7 ns for each triad can be assigned largely to ZnP^T, which appears to form from ZnP* with a yield of ~30% based on the magnitude of the long-time porphyrin bleaching compared to the amplitude at 83-200 ps (when referenced to the transient absorption; Figures SI-9a and SI-10a). The kinetic traces shown in Figures SI-9b and SI-10b (insets) combined with measurements at other probe wavelengths gives an average time constant of 0.7 ns for the third kinetic component for each triad. This value likely largely reflects the ZnP* lifetime but may contain a contribution from the decay of the charge-separated state formed from ZnP*.

These transient absorption data along with the fluorescence data described in the paper are analyzed to estimate the yields of the competing energy- and charge-transfer decay processes for both $[(dp)_2Zn]^*$ and ZnP* in triads **12a** and **12b**. First, consider the decay of the $[(dp)_2Zn]^*$ excited state, which is a lifetime of 0.8 ps that is shorter than the value of 1.4 ps in toluene. If energy transfer is not particularly dependent on solvent (as we have found for through-bond mediated porphyrin–porphyrin transfer), then this shortening would be entirely due to a quenching process such as charge transfer not operable to an appreciable degree in toluene. In this case, the yield of this process would be ≤40% in benzonitrile, giving a ≥60% yield of energy transfer to the porphyrin to produce ZnP*. In a separate analysis, the 0.8 ps lifetime of $[(dp)_2Zn]^*$ in each triad when compared to the shorter decay component of ~6.5 ps in $(dp)_2Zn$ reference complex **Zn-2a** gives a combined energy- and charge-transfer yield to each of the two porphyrins in each triad of $[1- 2\bullet(0.8/6.5)]\bullet100 \sim 75\%$. This is the upper limit to the yield of energy transfer to each porphyrin assuming no competing charge transfer. However, the yield would approach 100% depending on the extent to which the 1000 ps kinetic component observed for reference $(dp)_2Zn$ complex **Zn-2a** contributes along with the 6.5 ps component to the $[(dp)_2Zn]^*$ reference lifetime. The porphyrin fluorescence yields obtained using excitation of one component of the triad versus the other described in the paper (Table 3) give an energy-transfer yield of ~100% for **12a** and ~70% for **12b**. Collectively these data indicate a yield of 80

± 20% for energy transfer from $[(dp)_2Zn]^*$ to each zinc porphyrin in each triad, with part of the remainder deriving from a competing quenching process such as charge transfer.

Turn now to the ZnP* decay pathways triads **12a** and **12b** in benzonitrile. The 0.7 ns kinetic component that can be associated in part if not large measure to the ZnP* decay (and perhaps in part to decay of a charge-separated state) is comparable to the faster (0.9 ns) of the two lifetime components observed for **12a** and **12b** by fluorescence decay (the other being ~2.2 ns, each with ~50% amplitude). Given these data and the associated possibility that more than one electronic/conformational/ligated form may contribute to the photophysics for each triad in benzonitrile, the effective ZnP* lifetime is ~ 1 ns. The ZnP* lifetime for the reference porphyrins in benzonitrile is ~2.6 ns (Table 3 of the paper). These effective lifetime data indicate that the quenching processes operable for the triads in benzonitrile have a yield of [1–(1/2.6)]•100 ~ 60%. A yield of 70% is estimated from the relative amplitudes of porphyrin bleaching for states ZnP* and ZnP^T in the transient absorption data for the triads described above. Given the complexities associated with the data and analysis, an average yield of 60 ± 20% for quenching of ZnP* in triads **12a** and **12b** in benzonitrile is reported in Table 3 of the paper.

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II. Characterization Data

Figure Captions.

Figure SI-1. Electronic absorption spectra (solid) and fluorescence spectra (dashed and dotted) for the triad **12b** (A) and reference porphyrin **Zn-8b** (B) and bis(dipyrrinato)zinc complex **Zn-2a** (C) in toluene at room temperature. The absorption spectra in the 450–650 nm region in A and B have been multiplied by the factors shown. The triad emission in A and B was obtained using predominant zinc porphyrin excitation (dashed spectrum) at 400 nm or bis(dipyrrinato)zinc excitation (dotted spectrum) at 487 nm. Spectra in the respective regions have been normalized to the same peak intensity, and the maxima (± 1 nm) indicated.

Figure SI-2. Electronic absorption spectra (solid) and fluorescence spectra (dashed) for the triad **12a** (A), porphyrin–dipyrrin **Zn-7a** (B), reference porphyrin **Zn-8a** (C) porphyrin **Zn-3** (D) and bis(dipyrrinato)zinc complex **Zn-2a** (E) in toluene at room temperature. Other details are the same as those for Figure SI-1.

Figure SI-3. Electronic absorption spectra (solid) and fluorescence spectra (dashed) for the triad **12b** (A), porphyrin–dipyrrin **Zn-7b** (B), reference porphyrin **Zn-8b** (C) porphyrin **Zn-3** (D) and bis(dipyrrinato)zinc complex **Zn-2a** (E) in toluene at room temperature. Other details are the same as those for Figure SI-1.

Figure SI-4. Electronic absorption spectra (solid) and fluorescence spectra (dashed and dotted) for the triad **12a** (A), reference porphyrin **Zn-8a** (B) and bis(dipyrrinato)zinc complex **Zn-2a** (C) in benzonitrile at room temperature. The triad emission in A

and B was obtained using predominant zinc porphyrin excitation (dashed spectrum) at 400 nm or bis(dipyrrinato)zinc excitation (dotted spectrum) at 453 nm. Other details are the same as those for Figure SI-1.

Figure SI-5. Electronic absorption spectra (solid) and fluorescence spectra (dashed and dotted) for the triad **12b** (A) and reference porphyrin **Zn-8b** (B) and bis(dipyrrinato)zinc complex **Zn-2a** (C) in benzonitrile at room temperature. The triad emission in A and B was obtained using predominant zinc porphyrin excitation (dashed spectrum) at 400 nm or bis(dipyrrinato)zinc excitation (dotted spectrum) at 487 nm. Other details are the same as those for Figure SI-1.

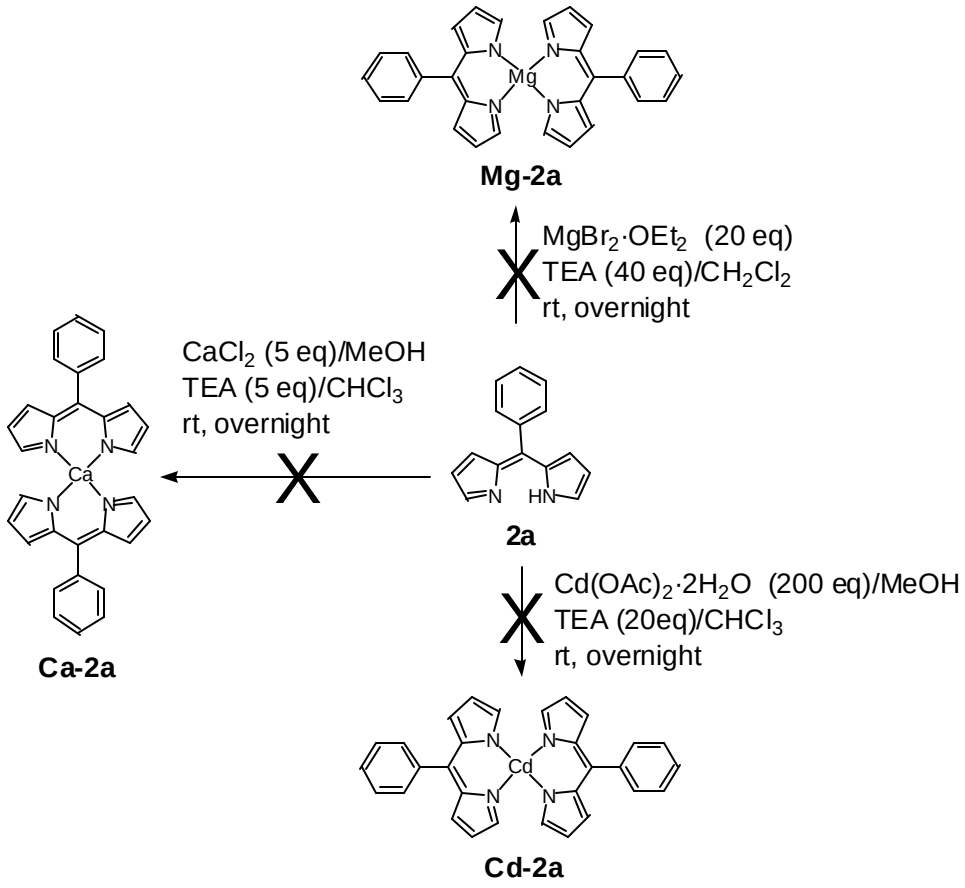
Figure SI-6. Electronic absorption spectra (solid) and fluorescence spectra (dashed) for the triad **12a** (A), porphyrin–dipyrrin **Zn-7a** (B), reference porphyrin **Zn-8a** (C) porphyrin **Zn-3** (D) and bis(dipyrrinato)zinc complex **Zn-2a** (E) in benzonitrile at room temperature. Other details are the same as those for Figure SI-1.

Figure SI-7. Electronic absorption spectra (solid) and fluorescence spectra (dashed) for the triad **12b** (A), porphyrin–dipyrrin **Zn-7b** (B), reference porphyrin **Zn-8b** (C) porphyrin **Zn-3** (D) and bis(dipyrrinato)zinc complex **Zn-2a** (E) in benzonitrile at room temperature. Other details are the same as those for Figure SI-1.

Figure SI-8. Representative time-resolved absorption spectra (A) and a kinetic profile at 538 nm (B) for the triad **12b** in toluene at room temperature using predominant excitation of the bis(dipyrrinato)zinc subunit with a 490-nm 130-fs flash. The 0.5 ps spectrum (solid line) was constructed from spectra at closely spaced time intervals in order to account for the time-dispersion of wavelengths in the white-light probe pulse. The fit to the data in (B) is the convolution of the instrument response with a dual exponential plus a constant, giving time constants of 1.3 ps and ~1.2 ns (inset). The average $(dp)_2Zn^*$ and ZnP* lifetimes, respectively, deduced from measurements at a number of probe wavelengths (and fluorescence decays for ZnP*) are given in Table 3 of the paper.

Figure SI-9. Representative time-resolved absorption spectra (A) and a kinetic profile at 503 nm (B) for the triad **12a** in benzonitrile at room temperature using predominant excitation of the bis(dipyrrinato)zinc subunit with a 484-nm 130-fs flash. The three-exponential fit gives the time constants shown, with average values from a number of probe wavelengths of 0.8 ps, 85 ps, and 0.7 ns. The fast component reflects $[(dp)_2Zn]^*$ decay and the assignment of the other two components are described in the Supporting Information text. Other details are the same as those for Figure SI-8.

Figure SI-10. Representative time-resolved absorption spectra (A) and a kinetic profile at 508 nm (B) for the triad **12b** in benzonitrile at room temperature using predominant excitation of the bis(dipyrrinato)zinc subunit with a 490-nm 130-fs flash. The three-exponential fit gives the time constants shown, with average values from a number of probe wavelengths of 0.8 ps, 105 ps, and 0.7 ns. Other details are the same as those for Figure SI-9.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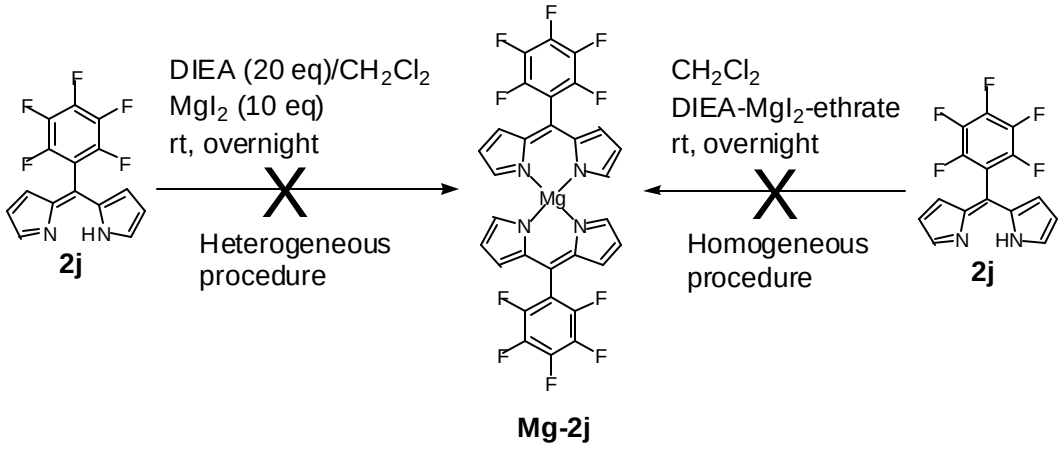
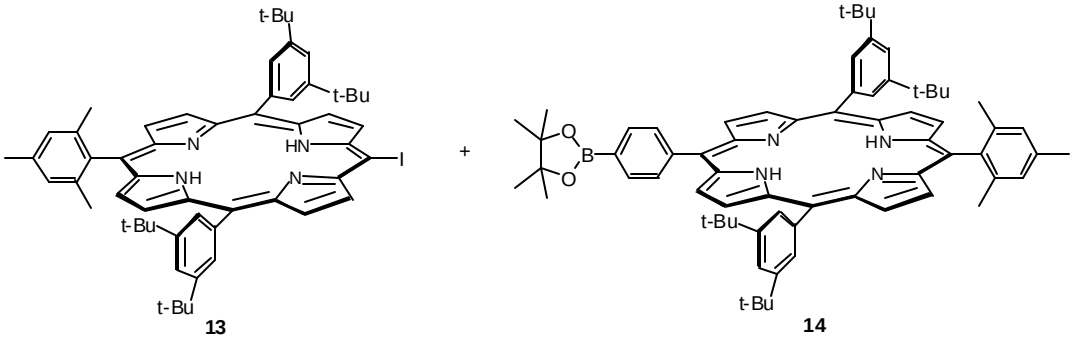
CaCl2 (5 eq)/MeOH
TEA (5 eq)/CHCl3
rt, overnight
2a
Ca-2a
Cd(OAc)2·2H2O (200 eq)/MeOH
TEA (20eq)/CHCl3
rt, overnight
Cd-2a

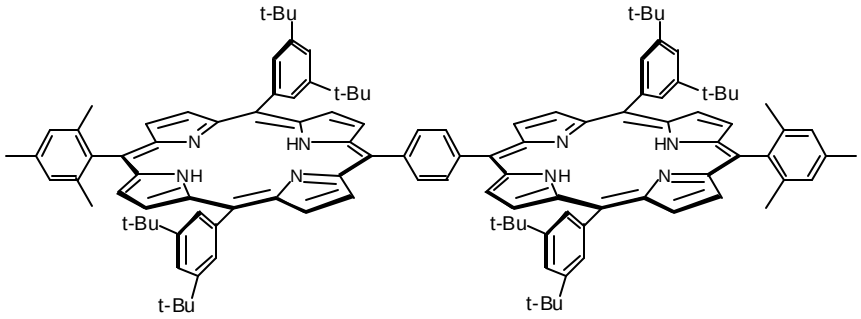

DIEA (20 eq)/CH2Cl2
MgI2 (10 eq)
rt, overnight
Heterogeneous procedure
CH2Cl2
DIEA-MgI2-ethrate
rt, overnight
Homogeneous procedure
2j
2j
Mg-2j

Scheme SI-2



+ equimolar **2a**, **Zn-2a**, **Cu-2b** or **Pd-2b**

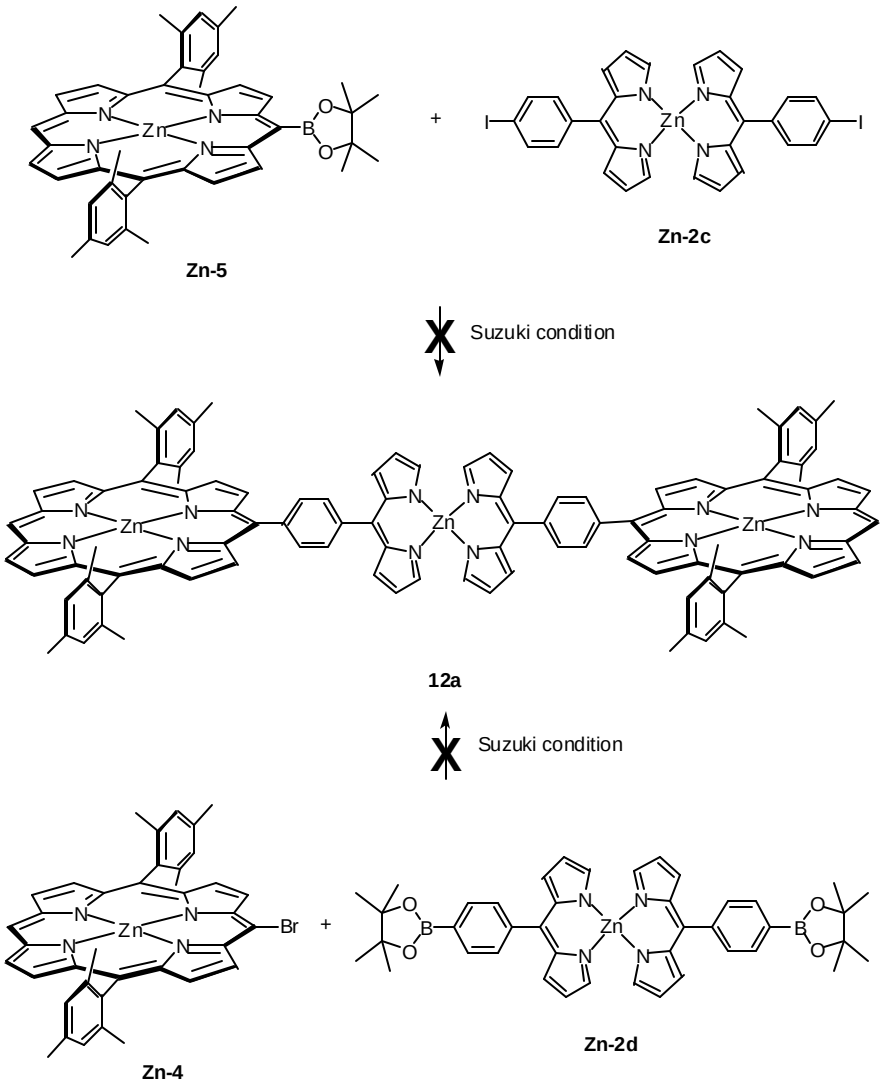
? $Pd(PPh_3)_4/K_2CO_3$, Toluene/DMF (2:1), 90-95 °C, overnight



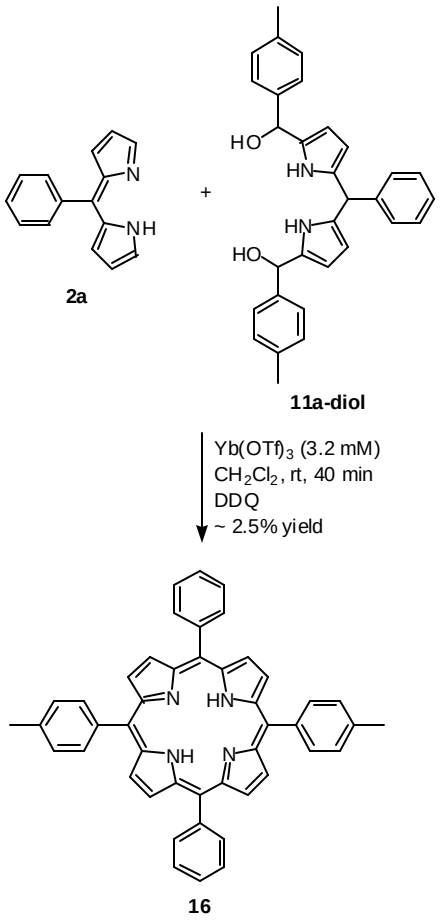
15

(1) In the presence of **2a**: no Suzuki coupling
(2) In the presence of **Zn-2a**: no Suzuki coupling
(3) In the presence of **Cu-2b**: no Suzuki coupling
(4) In the presence of **Pd-2b**: the yield of dimer was 64% (based on SEC)

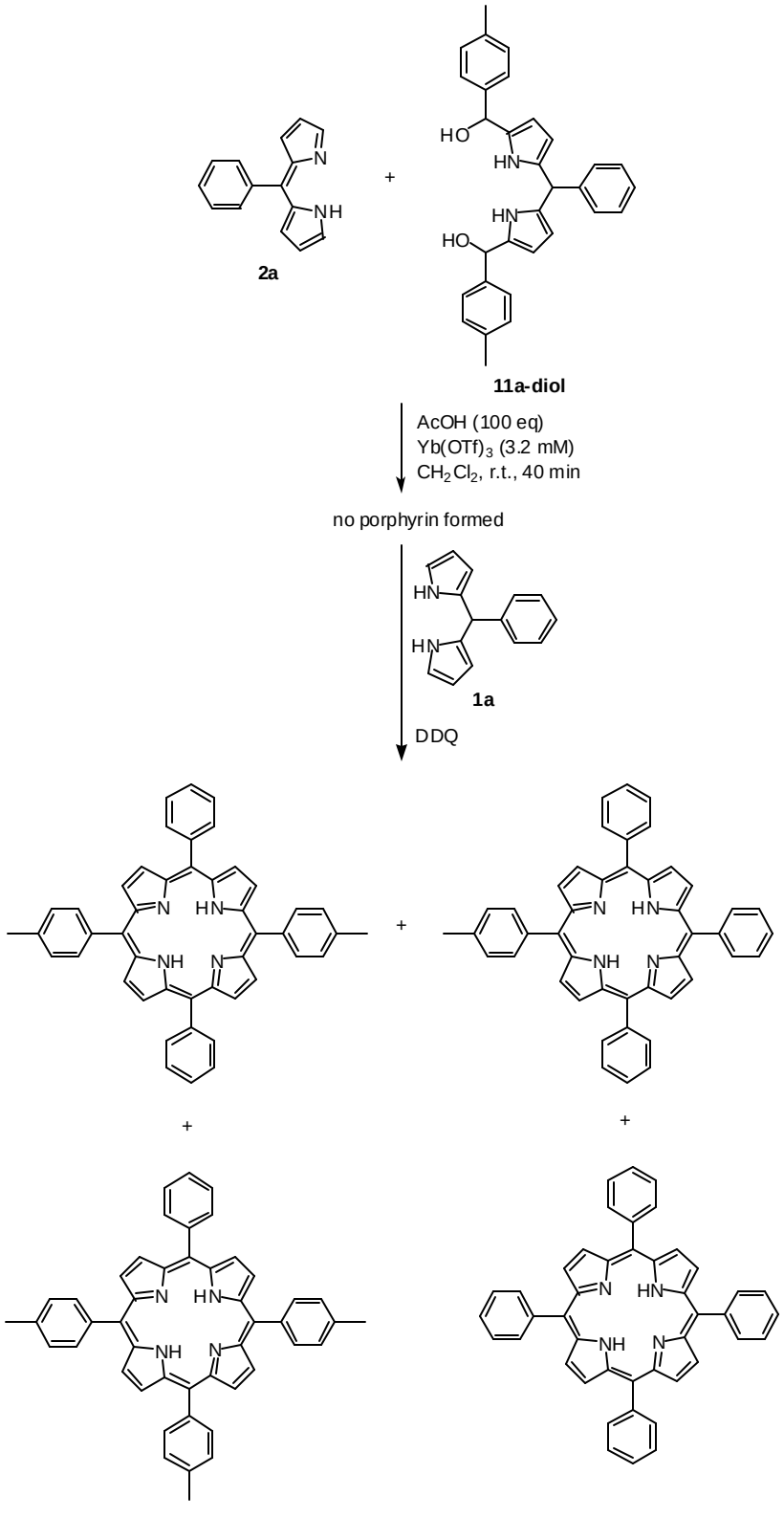
Scheme SI-3



Scheme SI-4

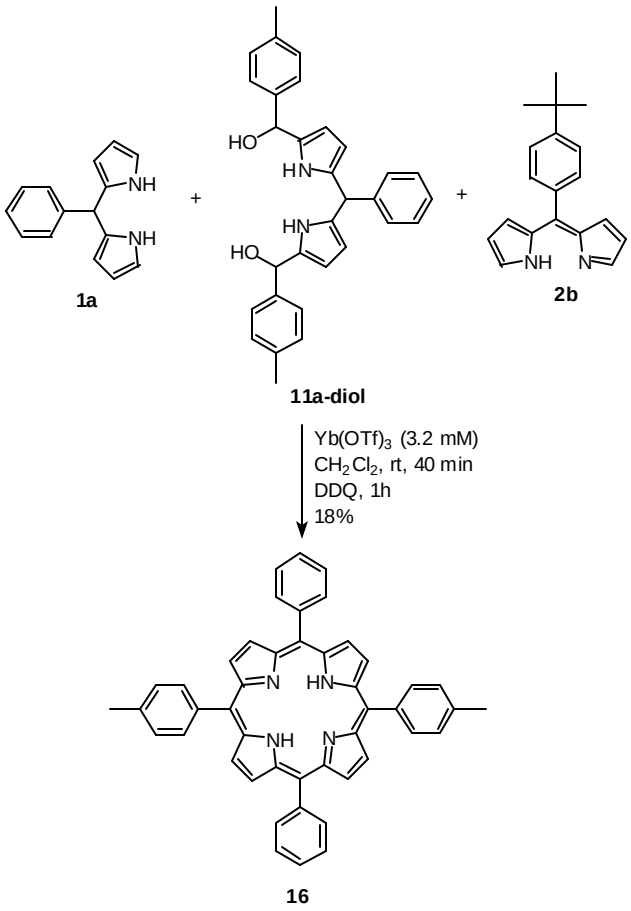

N
NH
2a
+
HO
HN
HN
HO
11a-diol
Yb(OTf)3 (3.2 mM)
CH2Cl2, rt, 40 min
DDQ
~ 2.5% yield
N
HN
NH
N
16

Scheme SI-5



13% total yield

Scheme SI-6


NH
NH
1a
+
HO
HN
HN
HO
11a-diol
+
NH
N
2b
Yb(OTf)3 (3.2 mM)
CH2Cl2, rt, 40 min
DDQ, 1h
18%
N
HN
NH
N
16

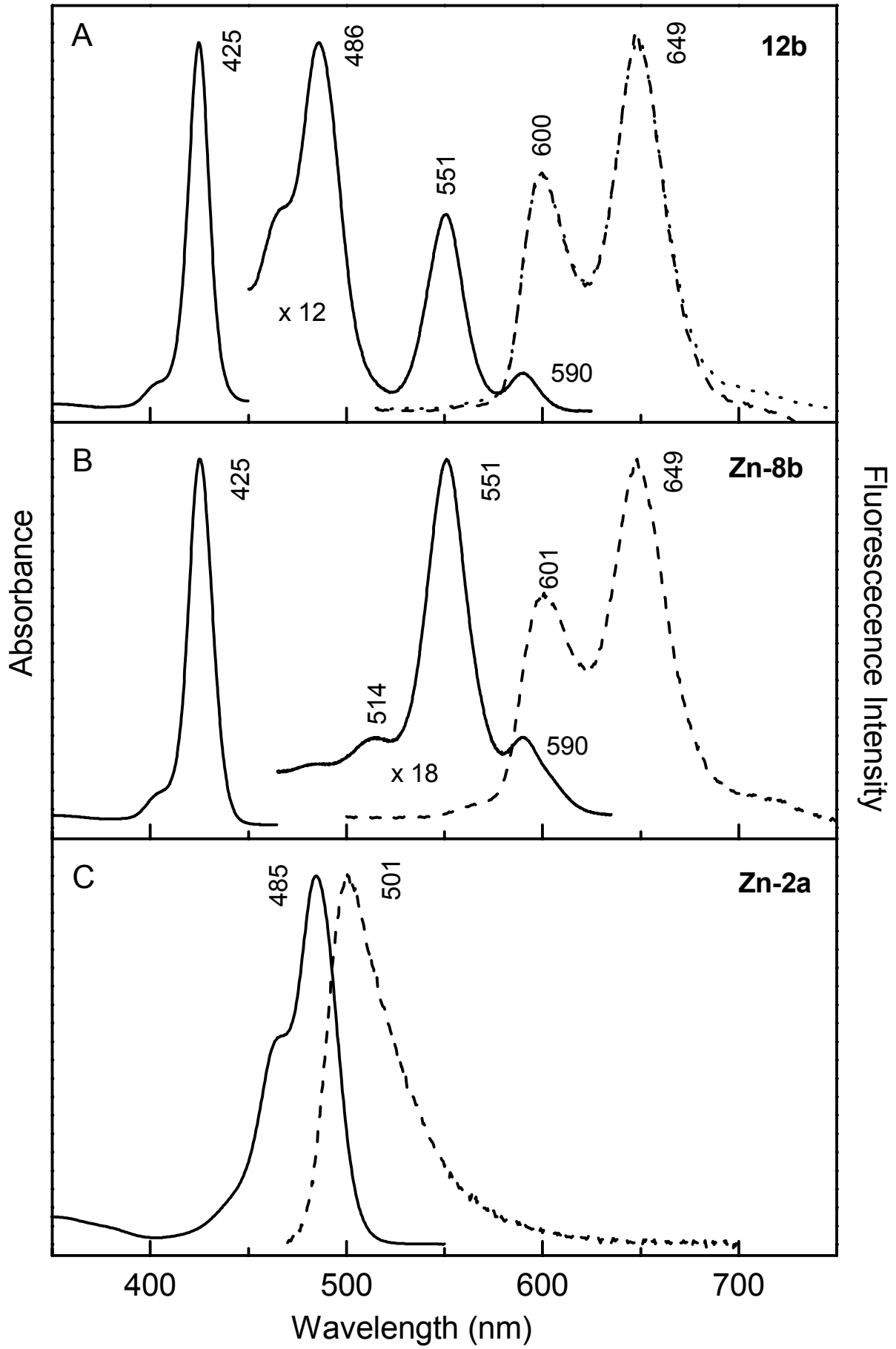

A
425
486
551
600
649
12b
x 12
590
B
425
551
649
Zn-8b
601
514
590
x 18
C
485
501
Zn-2a
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-1

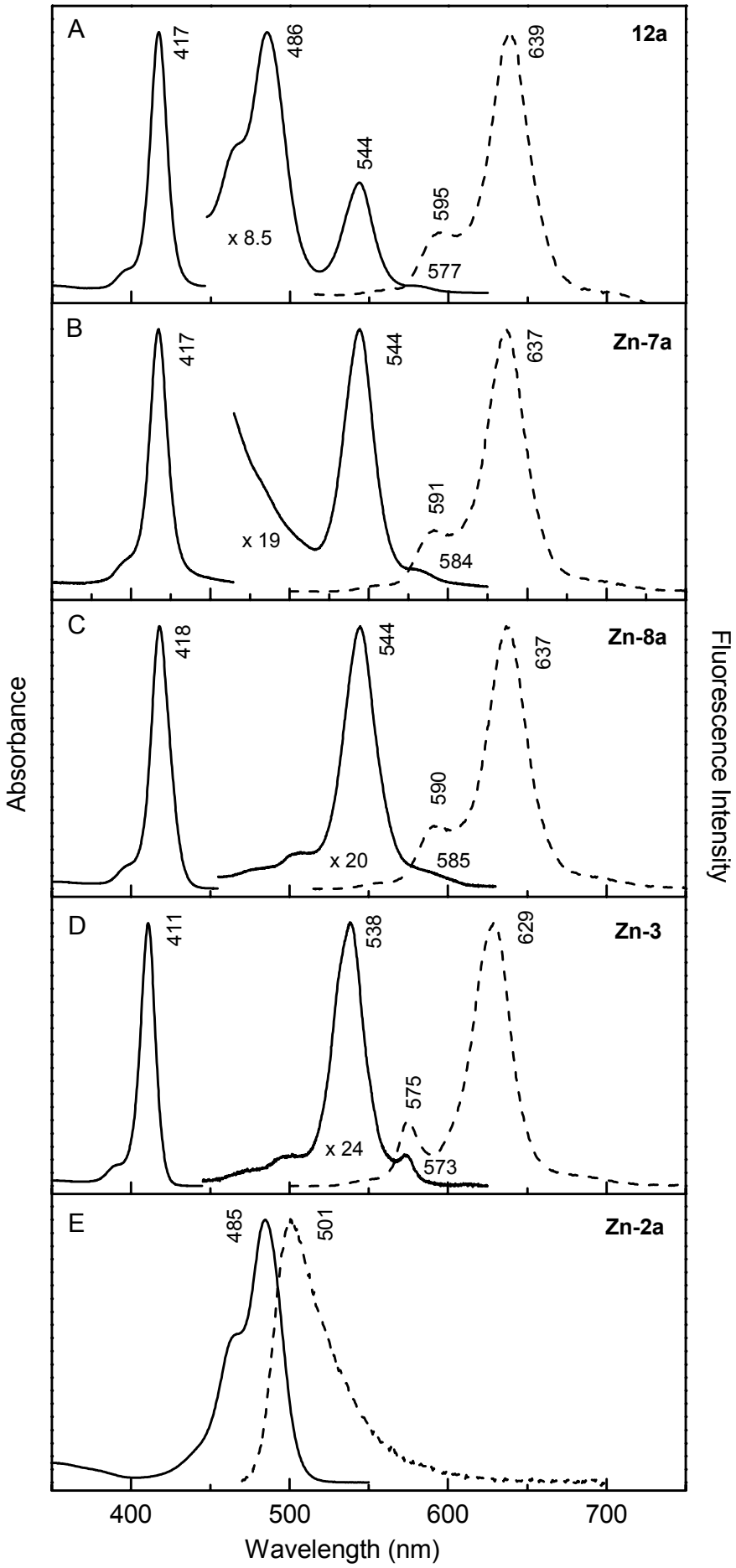

A
12a
417
486
544
595
639
x 8.5
577
B
Zn-7a
417
544
637
591
x 19
584
C
Zn-8a
418
544
637
590
x 20
585
D
Zn-3
411
538
629
575
x 24
573
E
Zn-2a
485
501
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-2

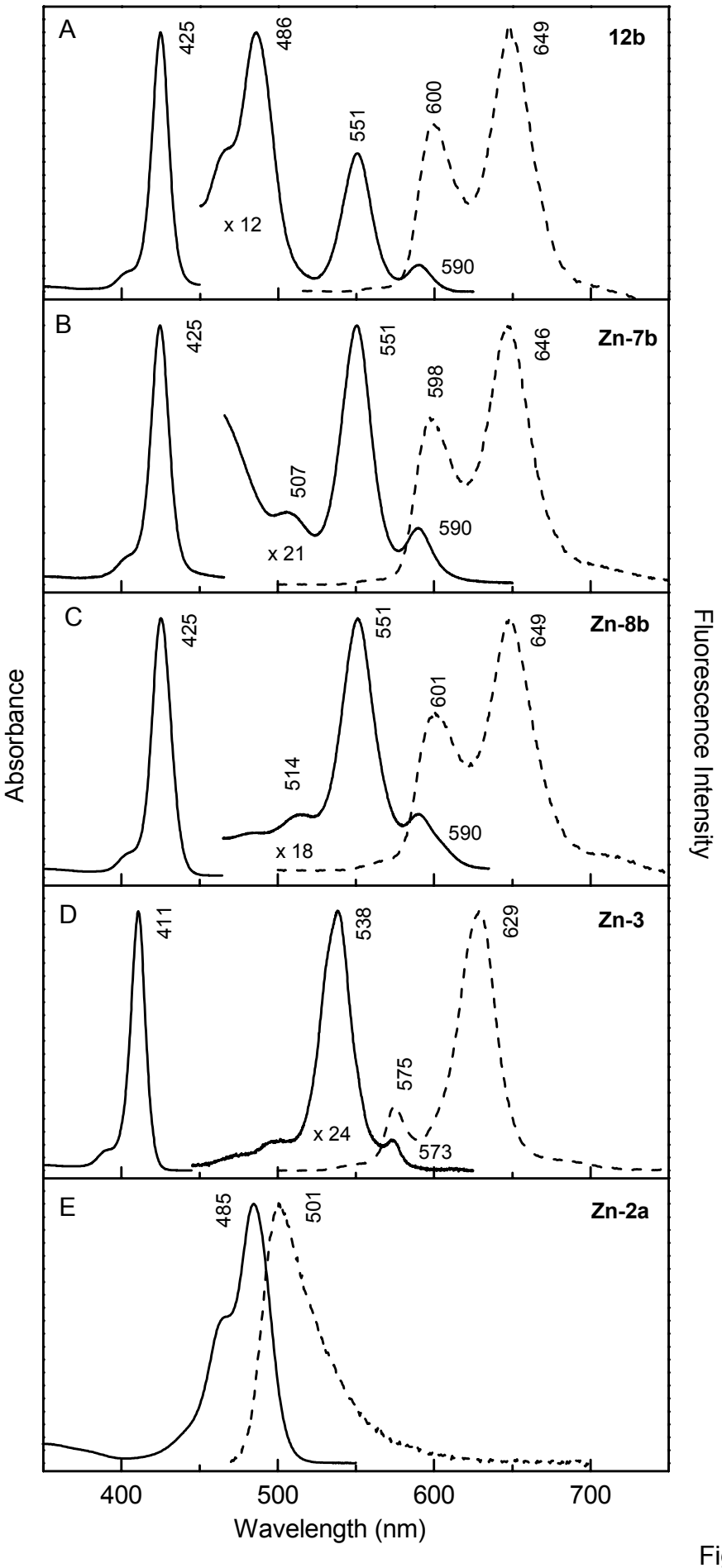

A
425
486
551
600
649
12b
x 12
590
B
425
551
598
646
Zn-7b
507
590
x 21
C
425
551
649
Zn-8b
601
514
590
x 18
D
411
538
629
Zn-3
575
x 24
573
E
485
501
Zn-2a
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-3

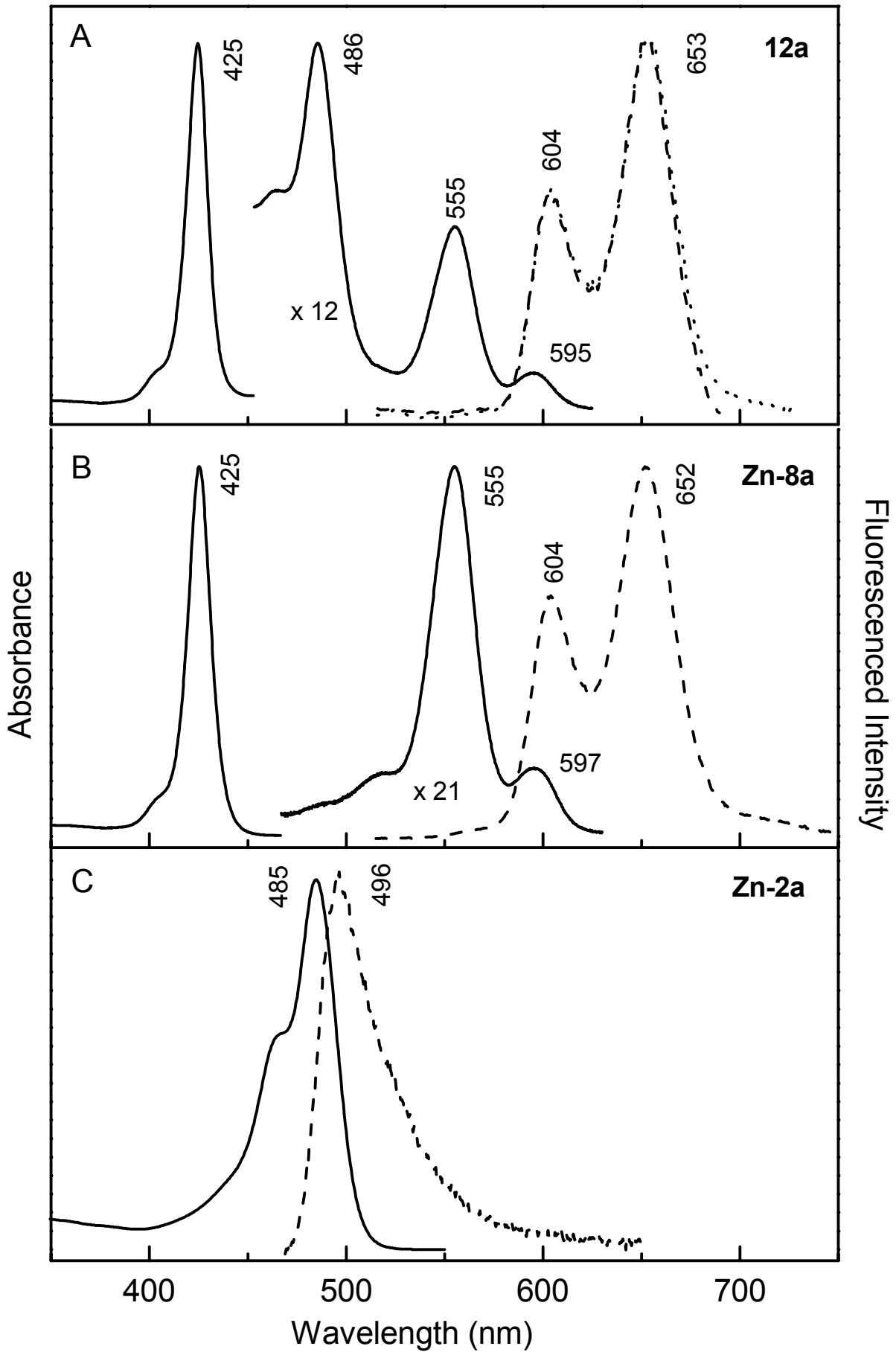

A
425
486
555
604
653
12a
x 12
595
B
425
555
604
652
Zn-8a
x 21
597
C
485
496
Zn-2a
Absorbance
Fluorescenced Intensity
400
500
600
700
Wavelength (nm)

Figure SI-4

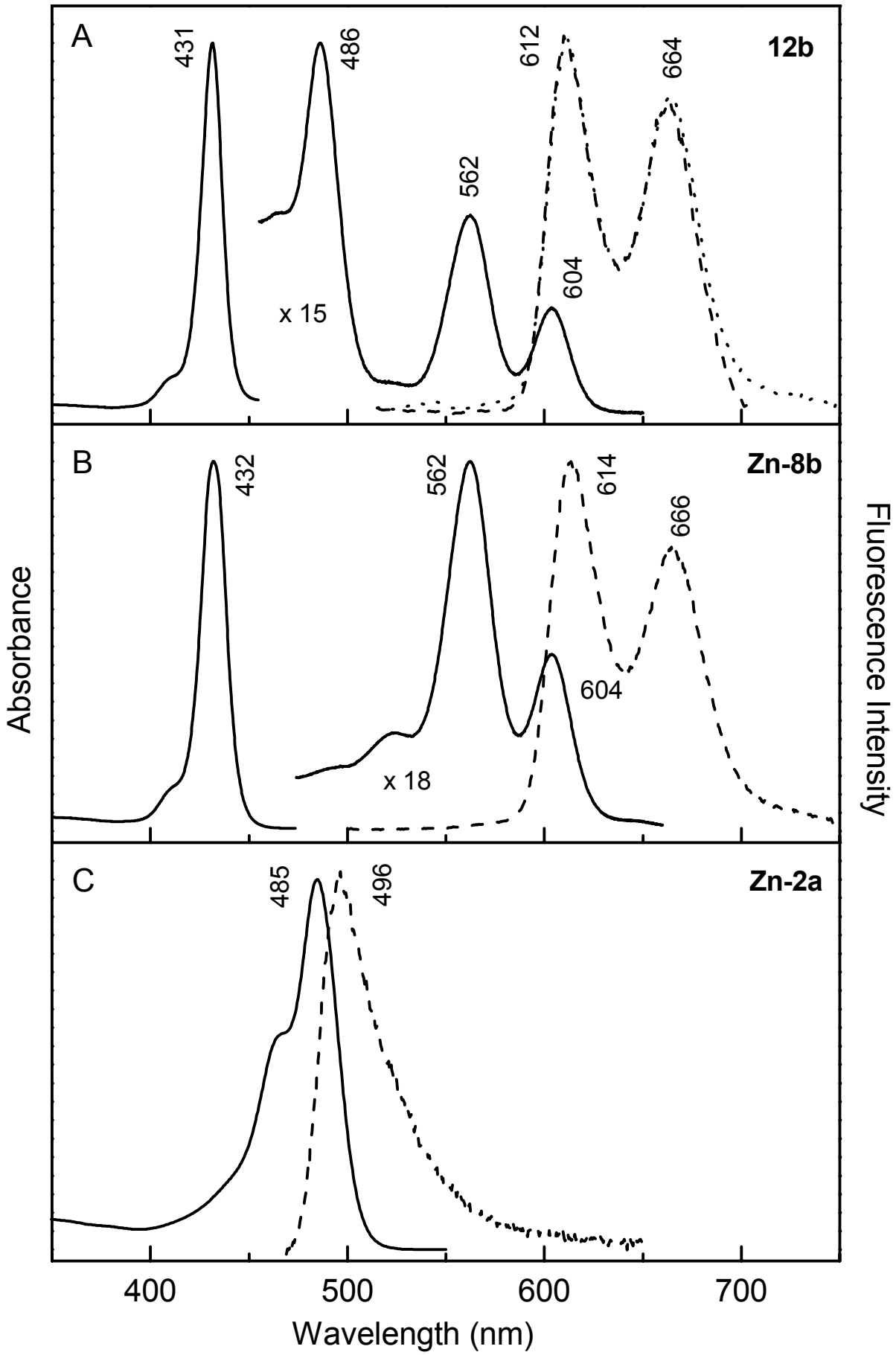

A
12b
431
486
562
612
604
664
x 15
B
Zn-8b
432
562
614
604
666
x 18
C
Zn-2a
485
496
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-5

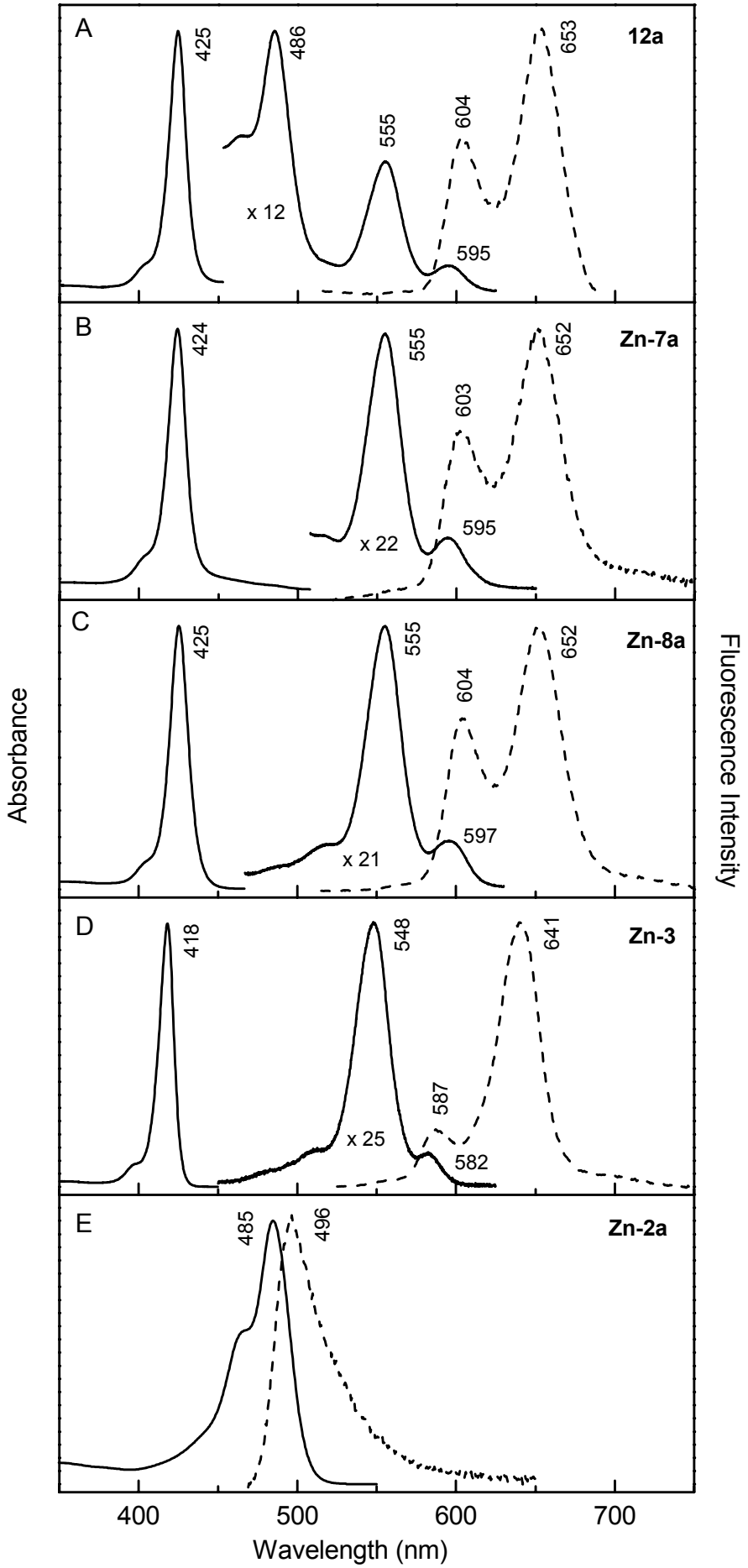

A
425
486
555
604
653
12a
x 12
595
B
424
555
652
Zn-7a
603
595
x 22
C
425
555
652
Zn-8a
604
597
x 21
D
418
548
641
Zn-3
587
582
x 25
E
485
496
Zn-2a
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-6

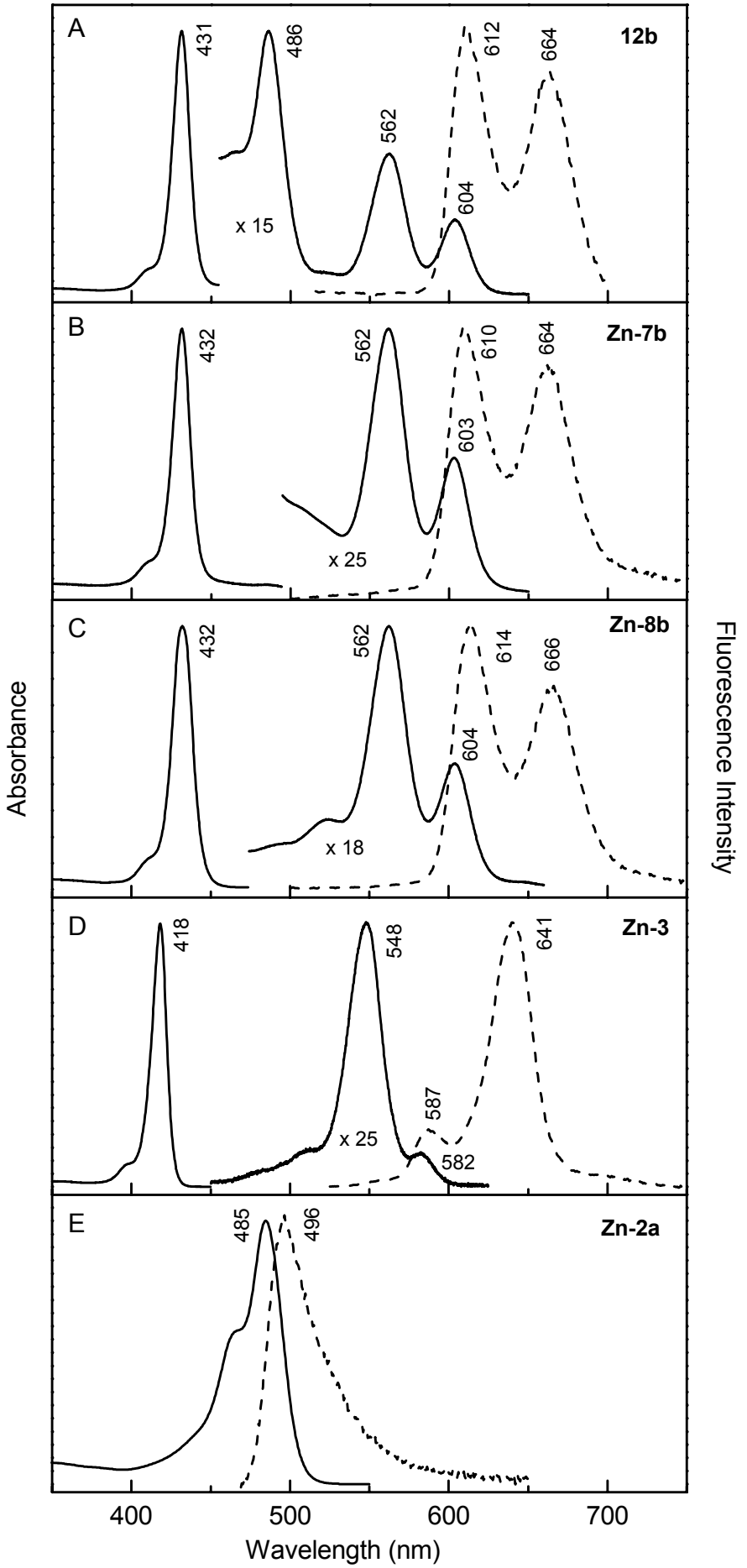
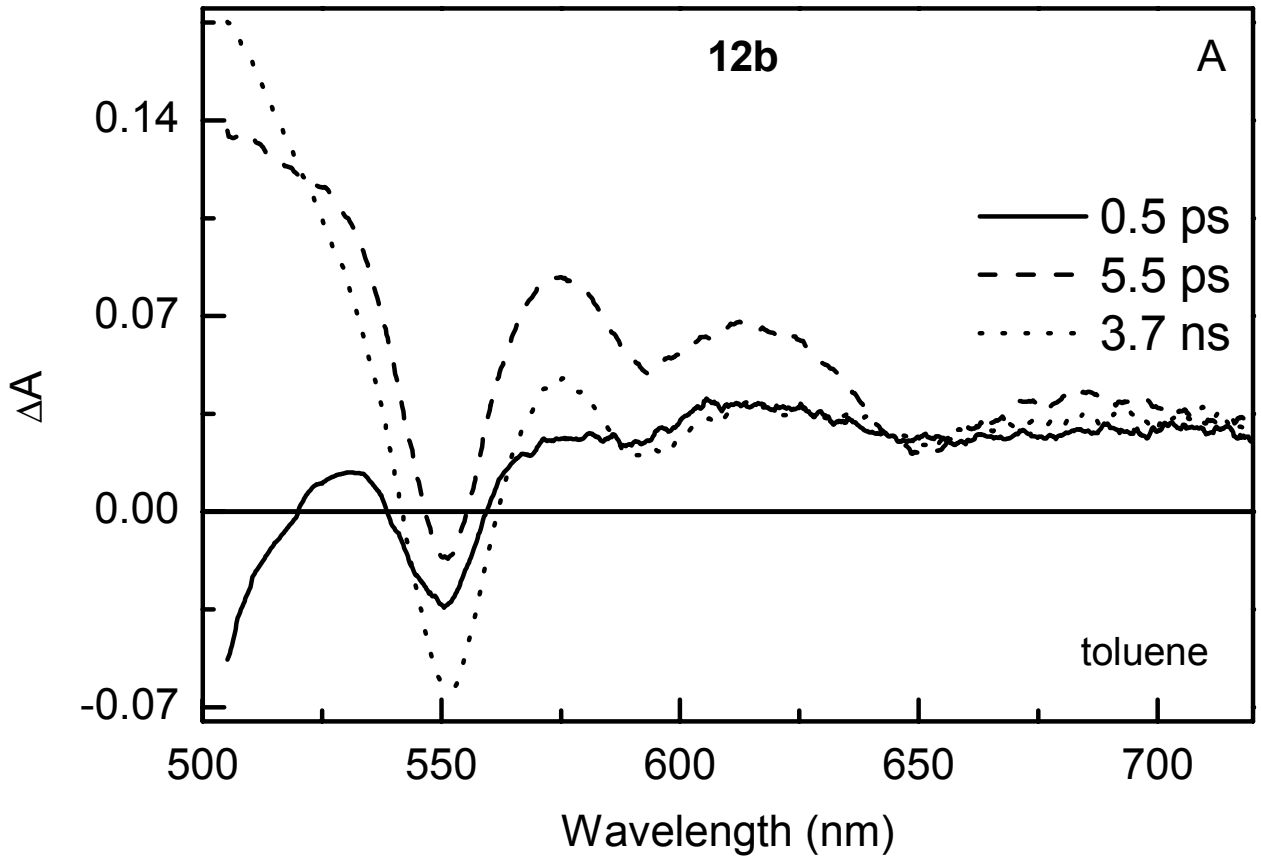

A
12b
431
486
562
604
612
664
x 15
B
Zn-7b
432
562
603
610
664
x 25
C
Zn-8b
432
562
604
614
666
x 18
D
Zn-3
418
548
587
582
641
x 25
E
Zn-2a
485
496
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-7


12b
A
0.14
0.07
0.00
-0.07
ΔA
0.5 ps
5.5 ps
3.7 ns
toluene
500
550
600
650
700
Wavelength (nm)

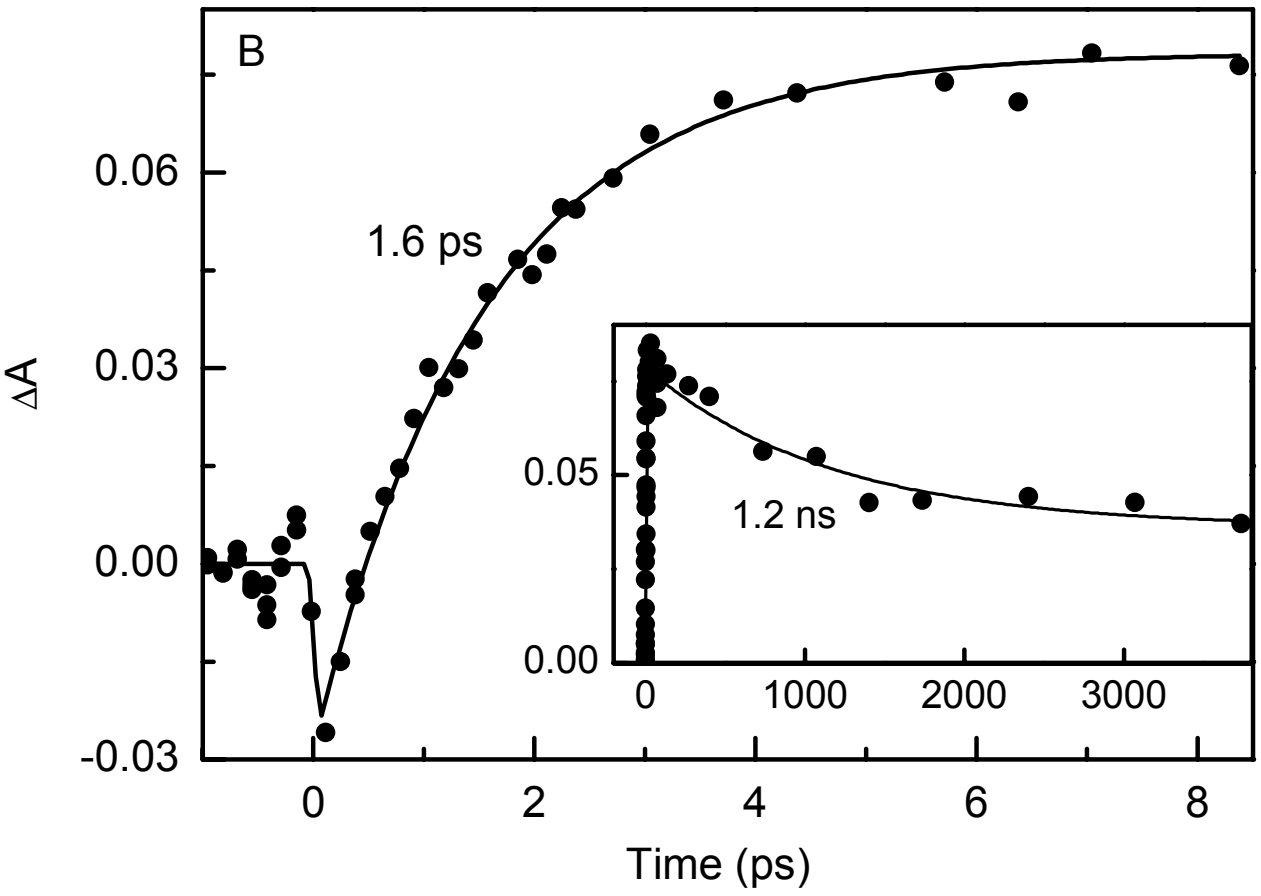

B
0.06
0.03
0.00
-0.03
ΔA
1.6 ps
0.05
0.00
1.2 ns
0
1000
2000
3000
0
2
4
6
8
Time (ps)

Figure SI-8

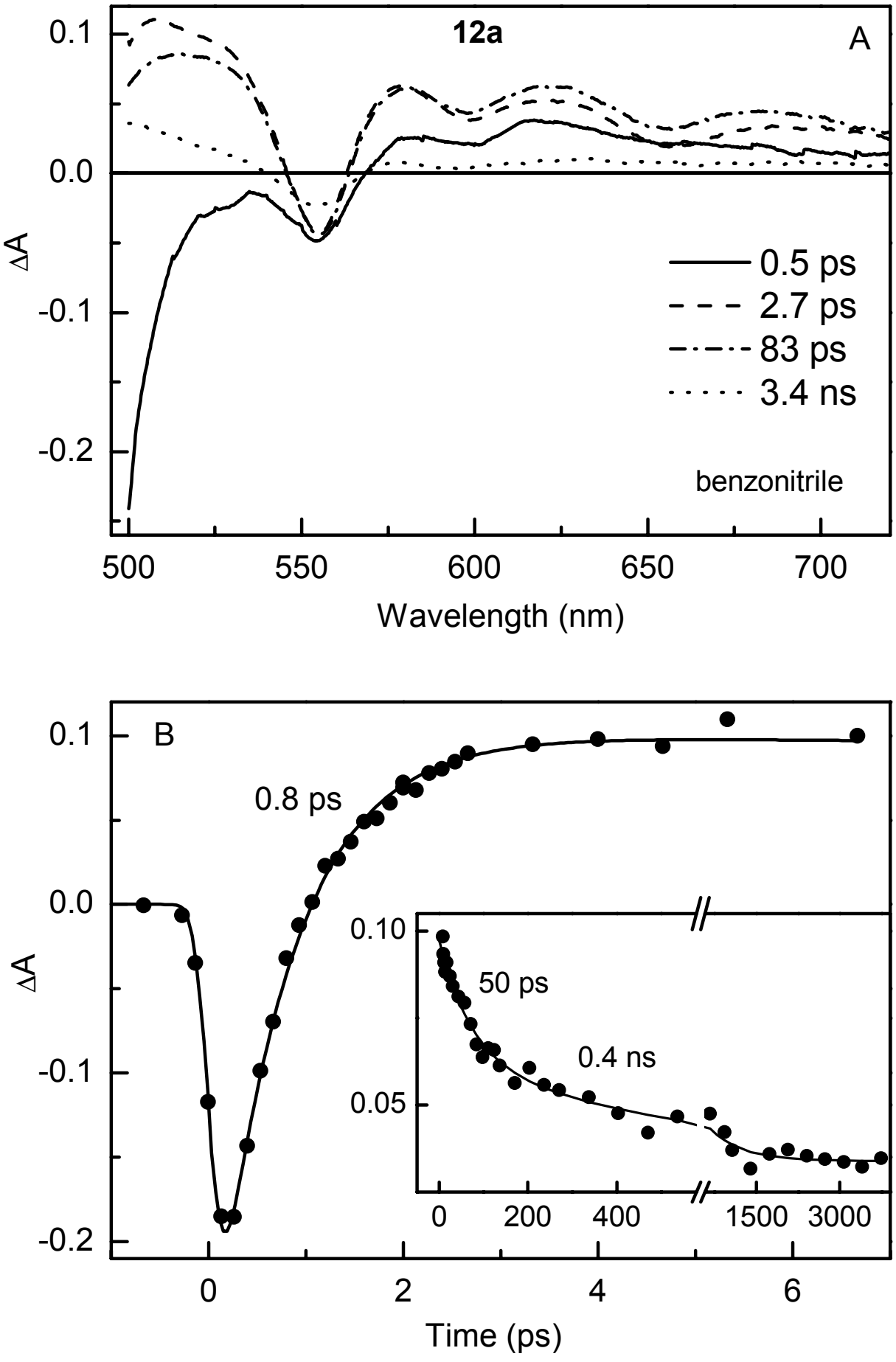

12a
A
0.1
0.0
-0.1
-0.2
ΔA
0.5 ps
2.7 ps
83 ps
3.4 ns
benzonitrile
500
550
600
650
700
Wavelength (nm)
B
0.8 ps
0.10
0.05
50 ps
0.4 ns
0
200
400
1500
3000
0
2
4
6
Time (ps)

Figure SI-9

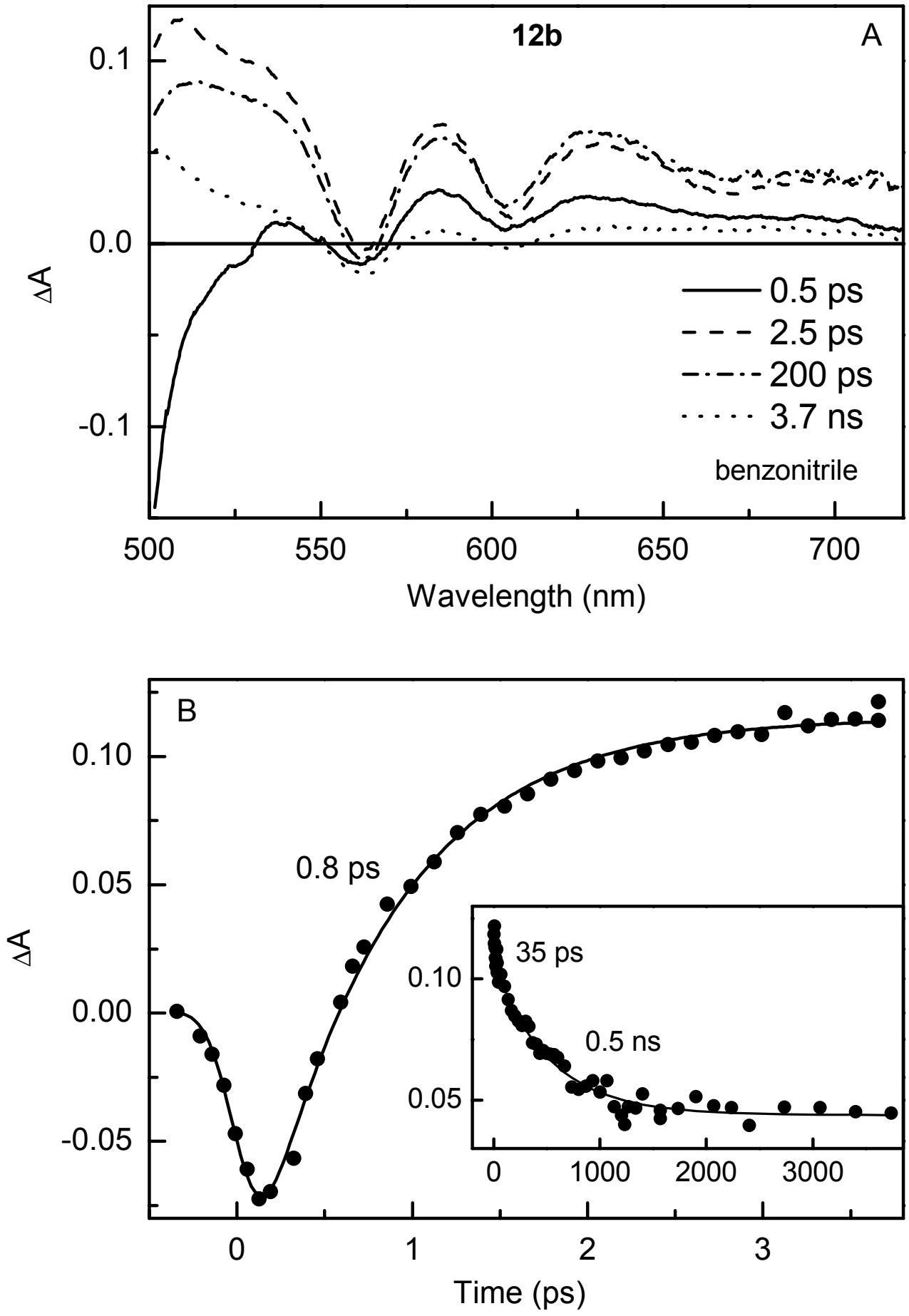
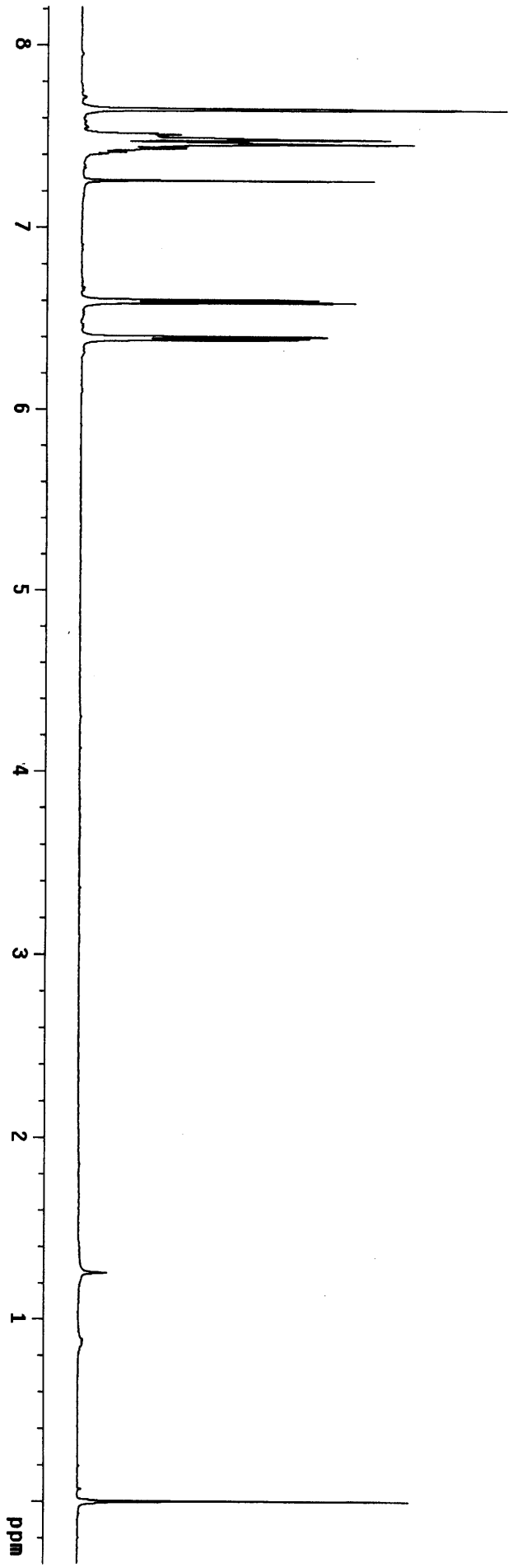
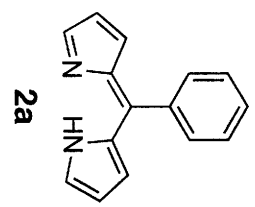
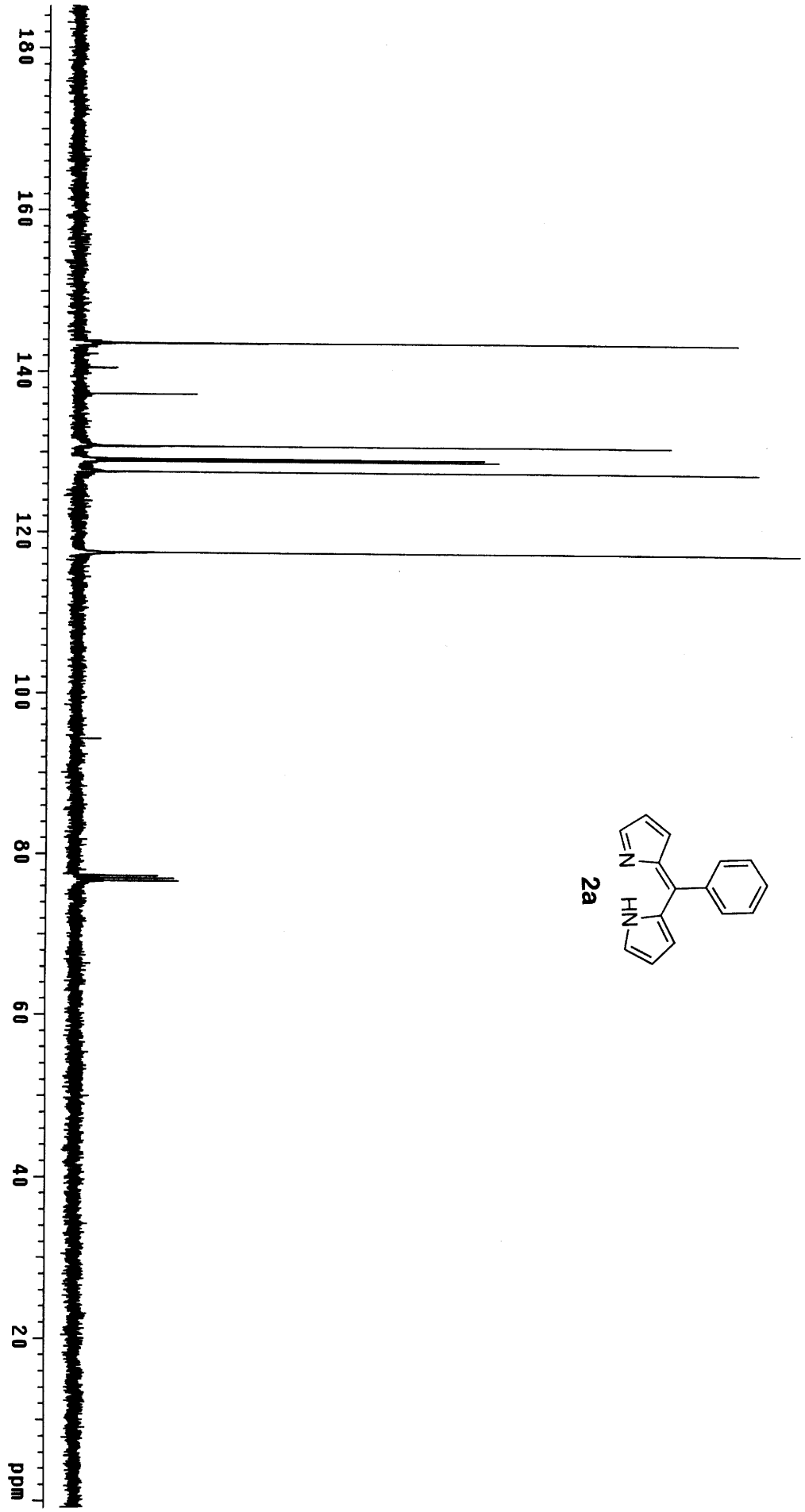

12b
A
0.1
0.0
-0.1
ΔA
0.5 ps
2.5 ps
200 ps
3.7 ns
benzonitrile
500
550
600
650
700
Wavelength (nm)
B
0.10
0.05
0.00
-0.05
ΔA
0.8 ps
35 ps
0.5 ns
0.10
0.05
0
1000
2000
3000
0
1
2
3
Time (ps)

Figure SI-10

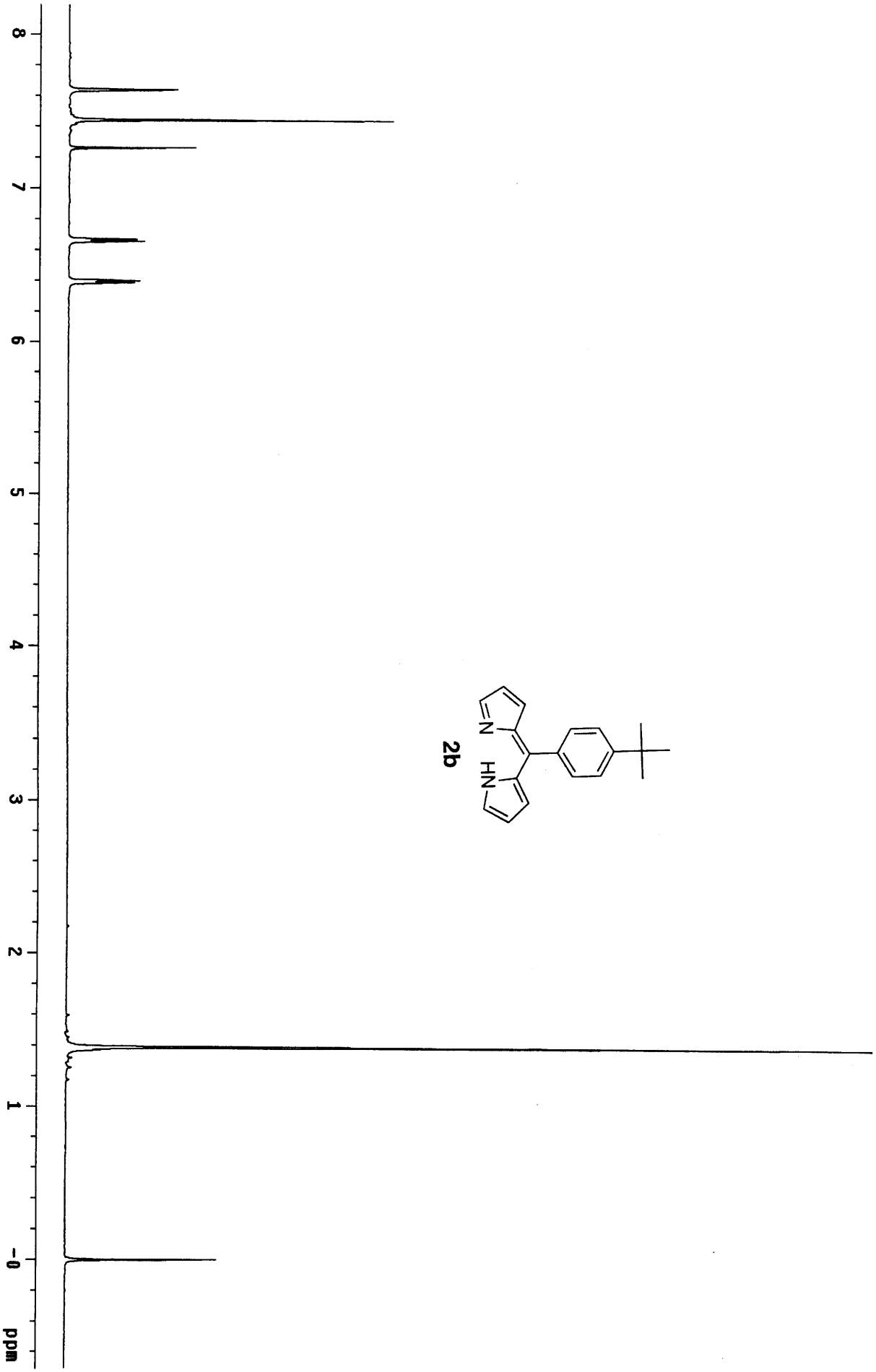




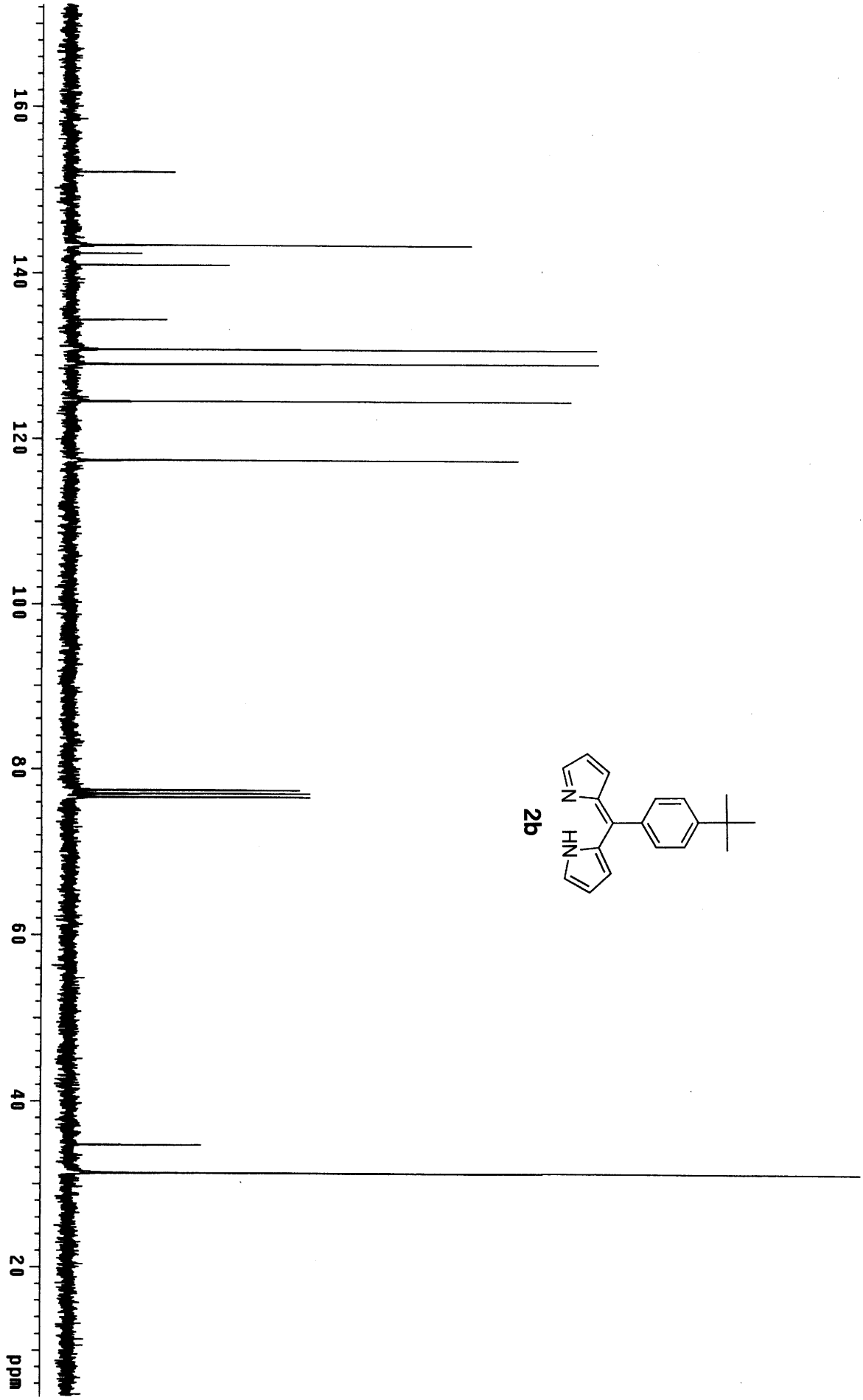
2a



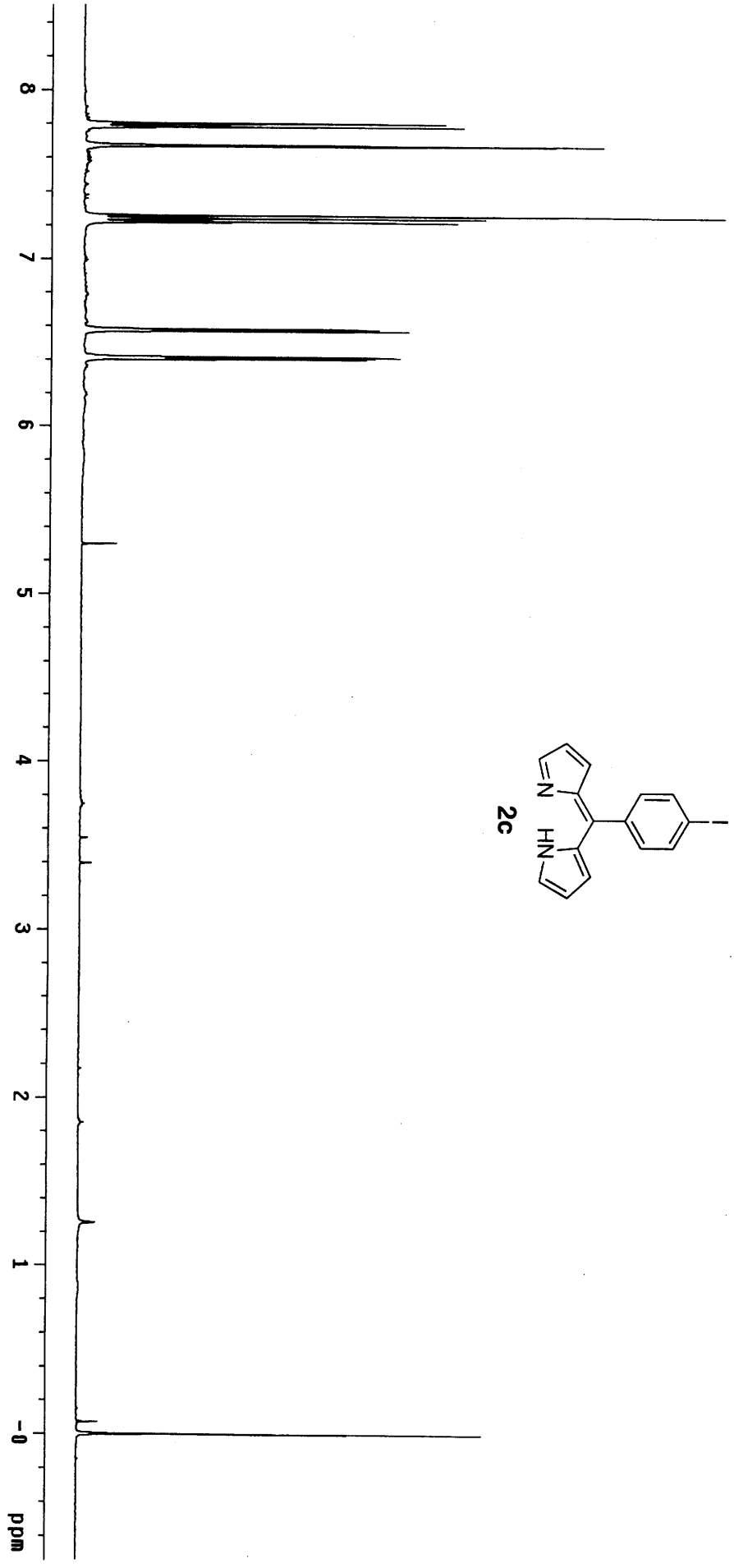
2a



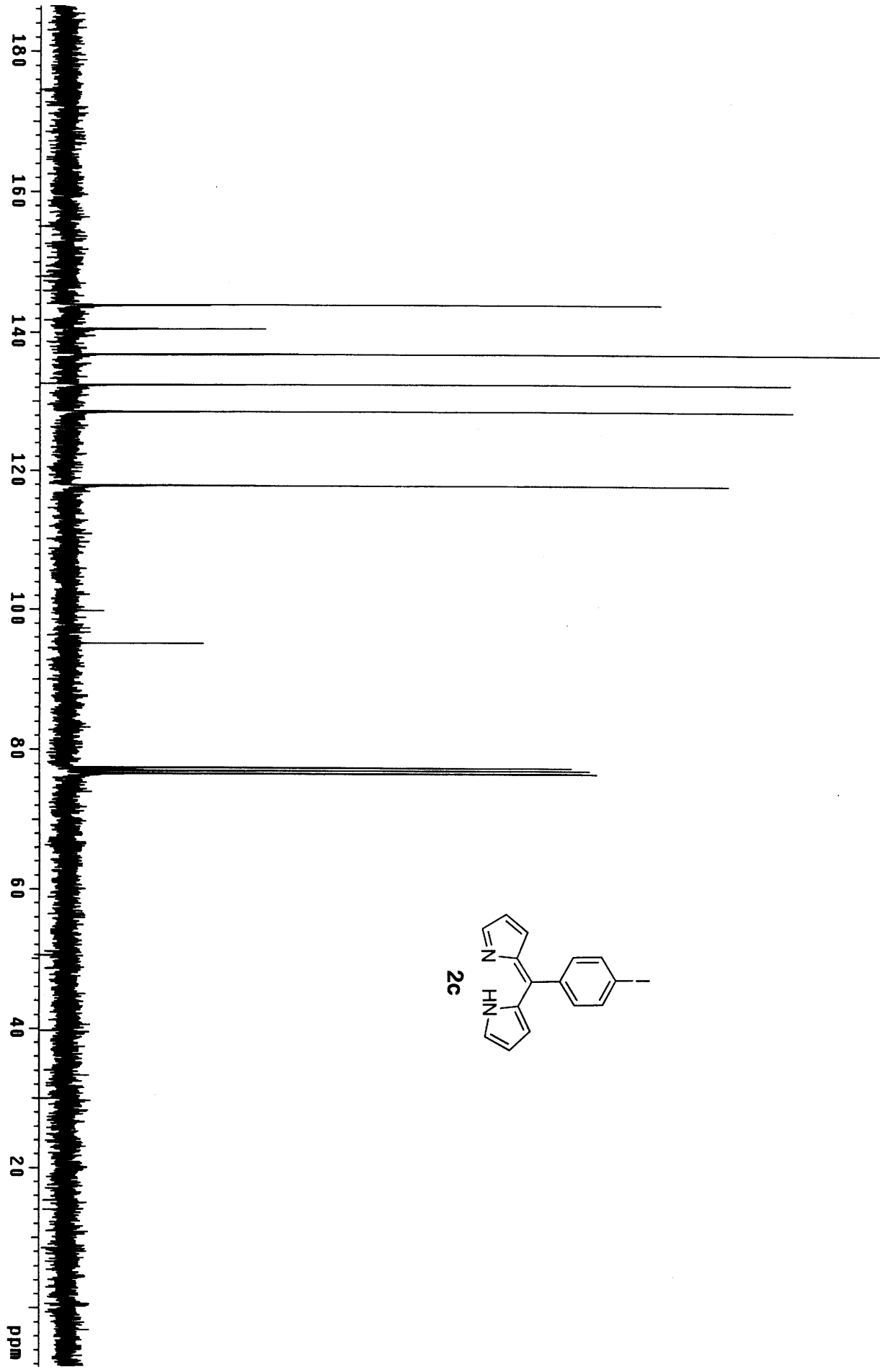
2b



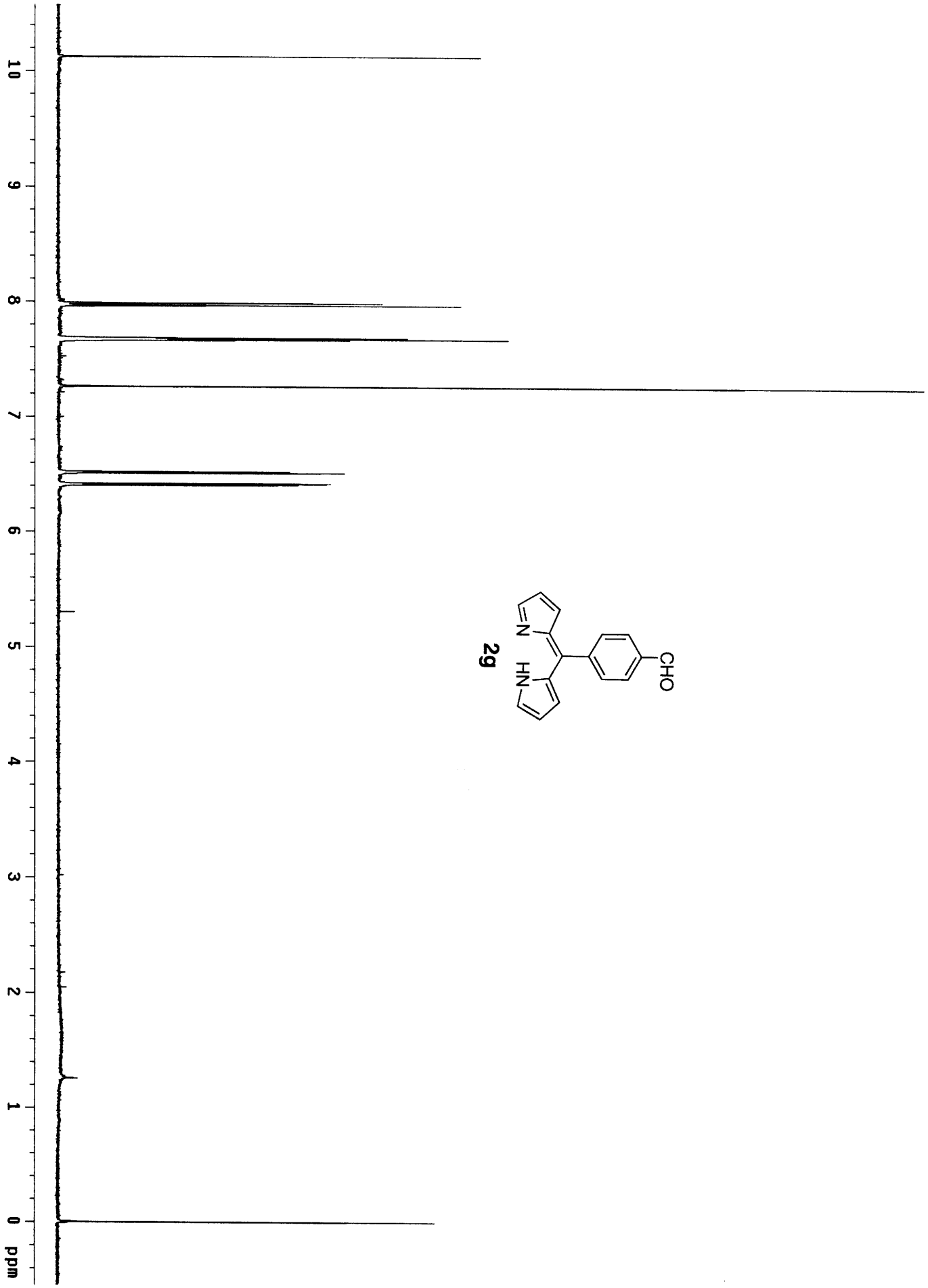
2b



2c

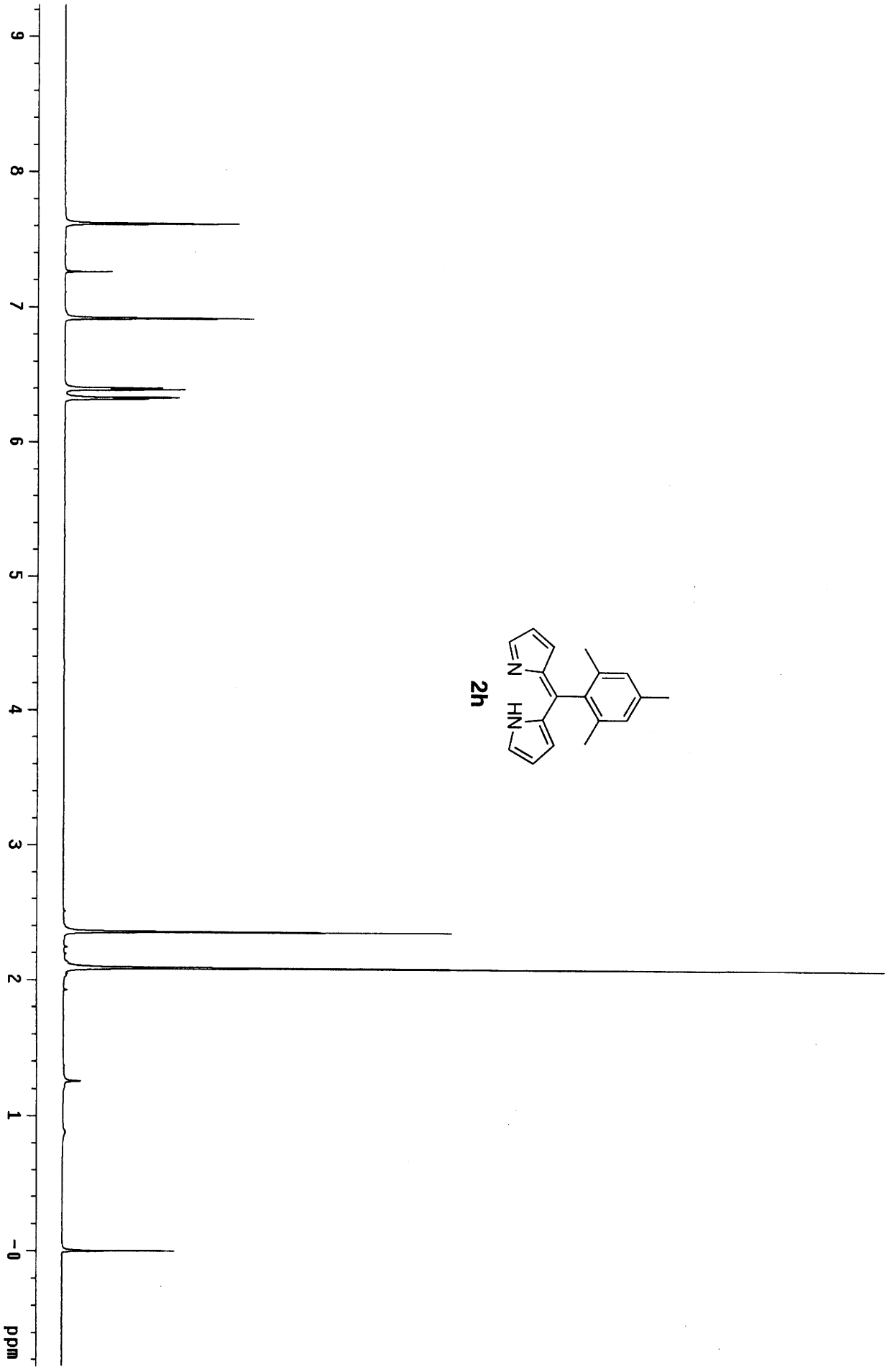


2c

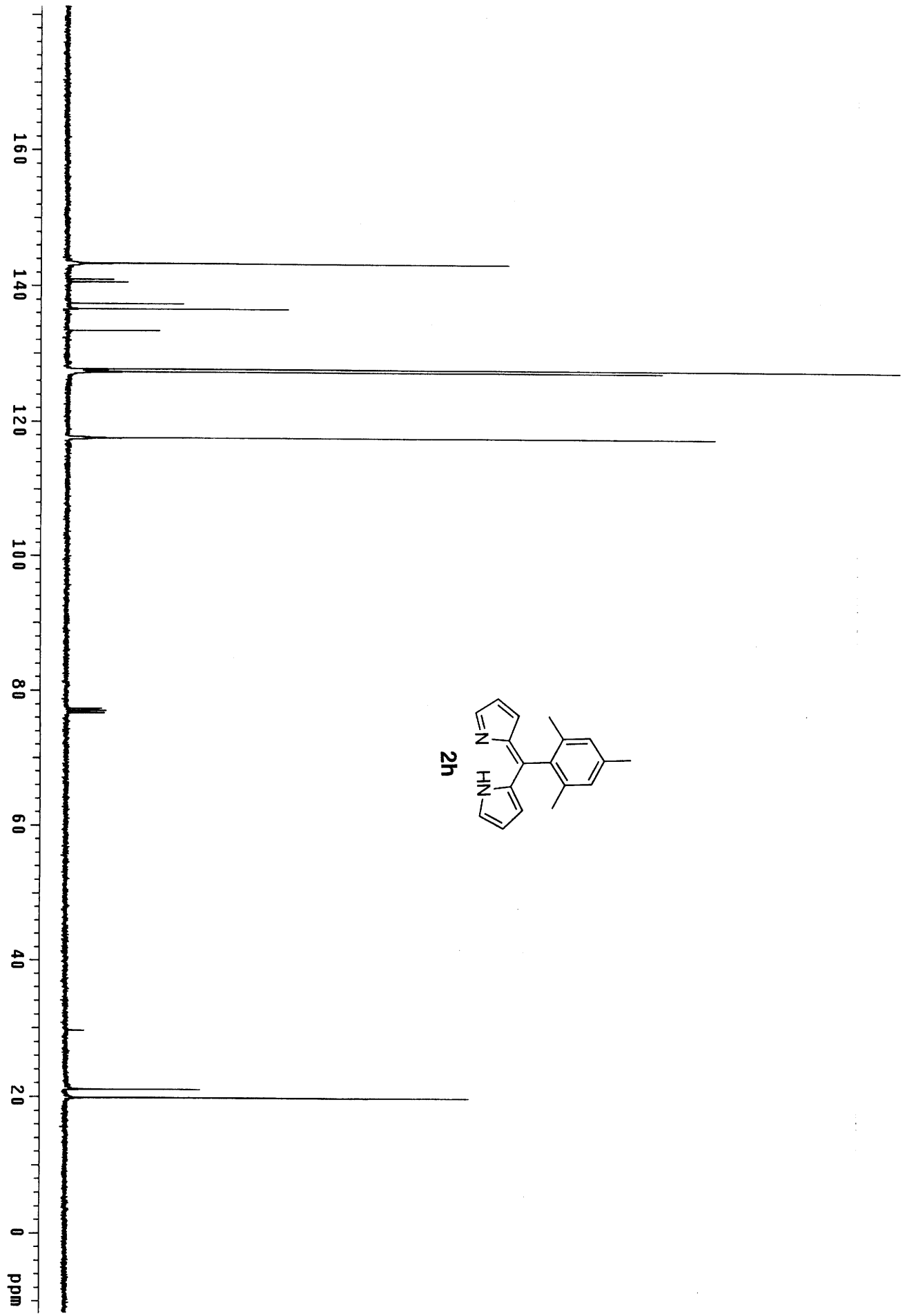


2g

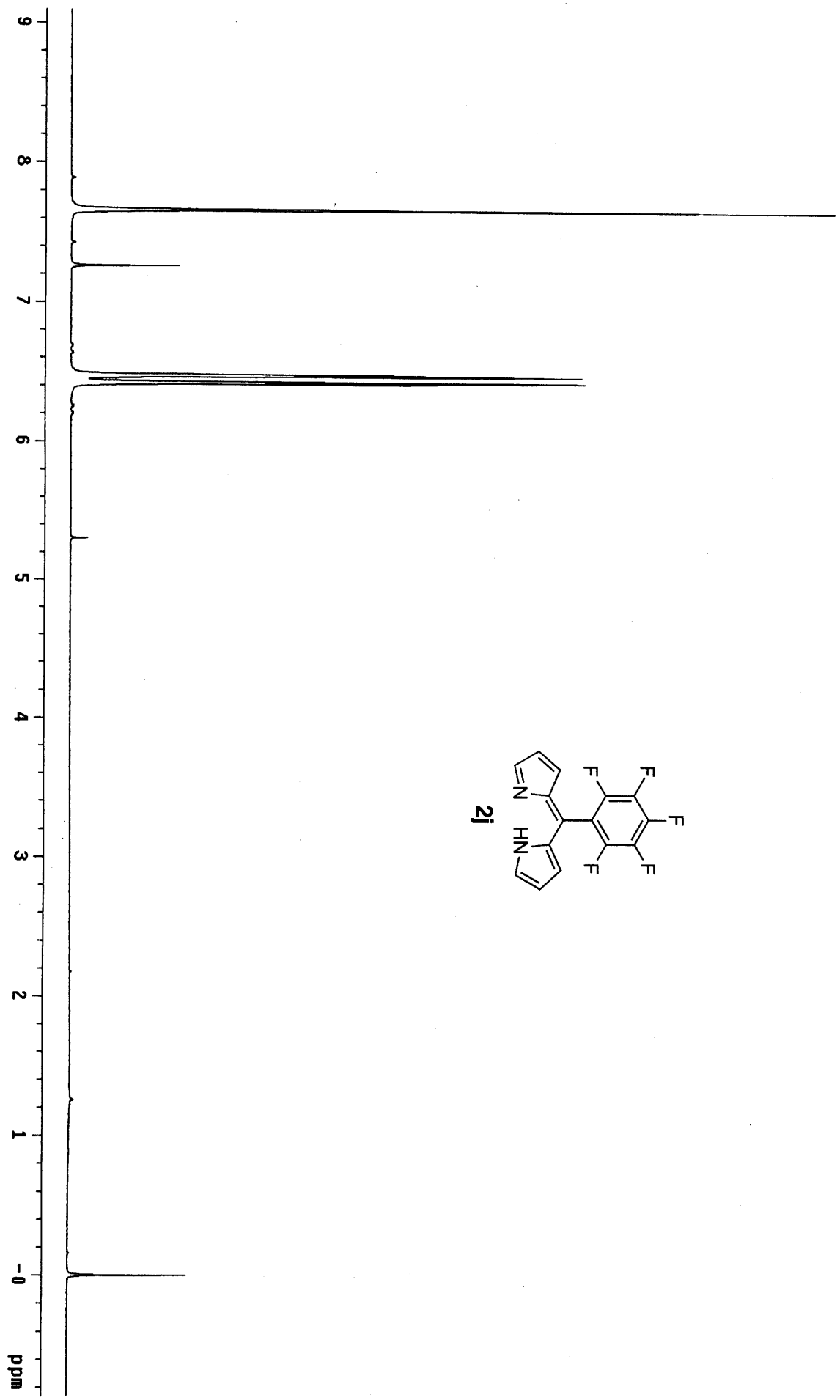
2g



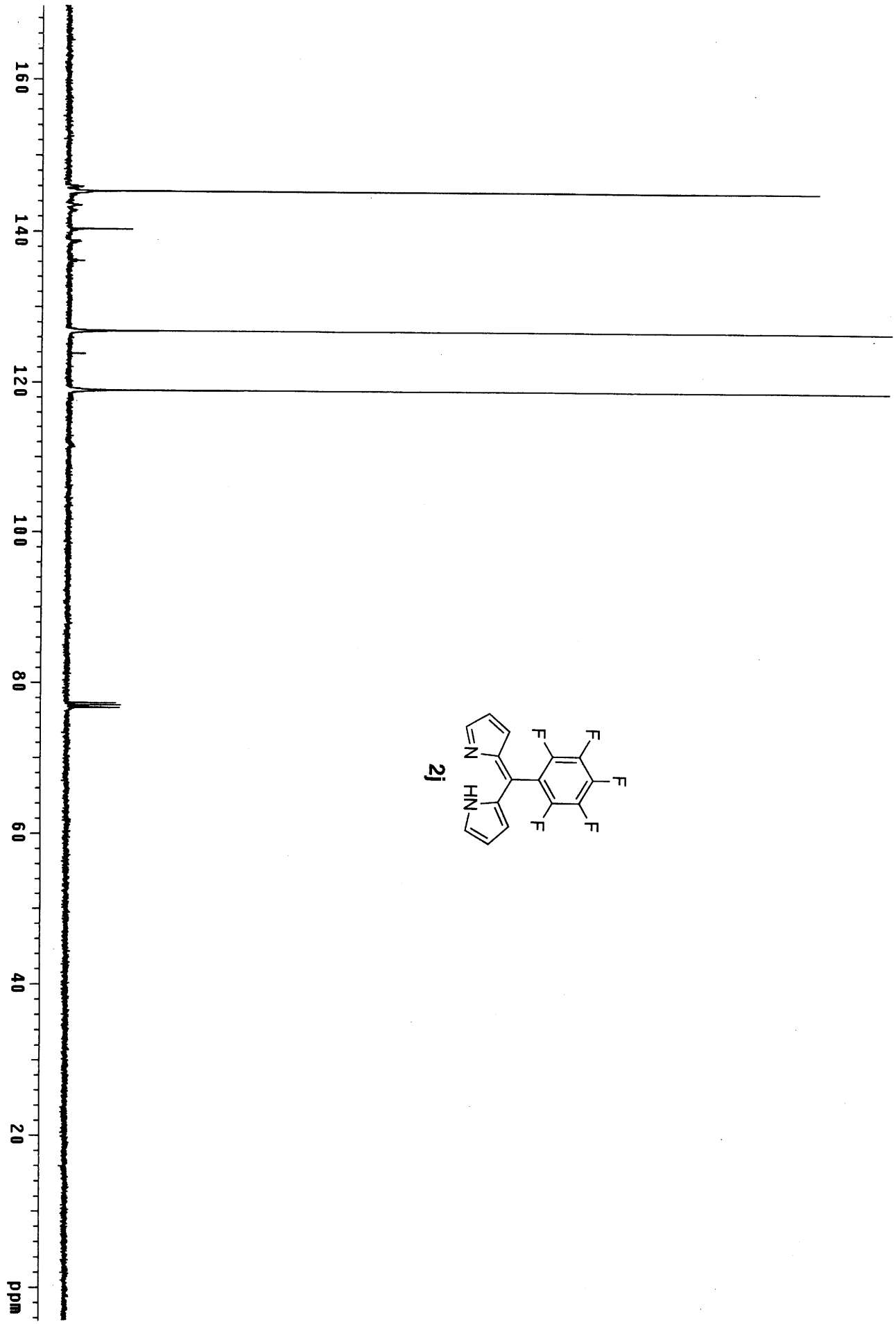
2h



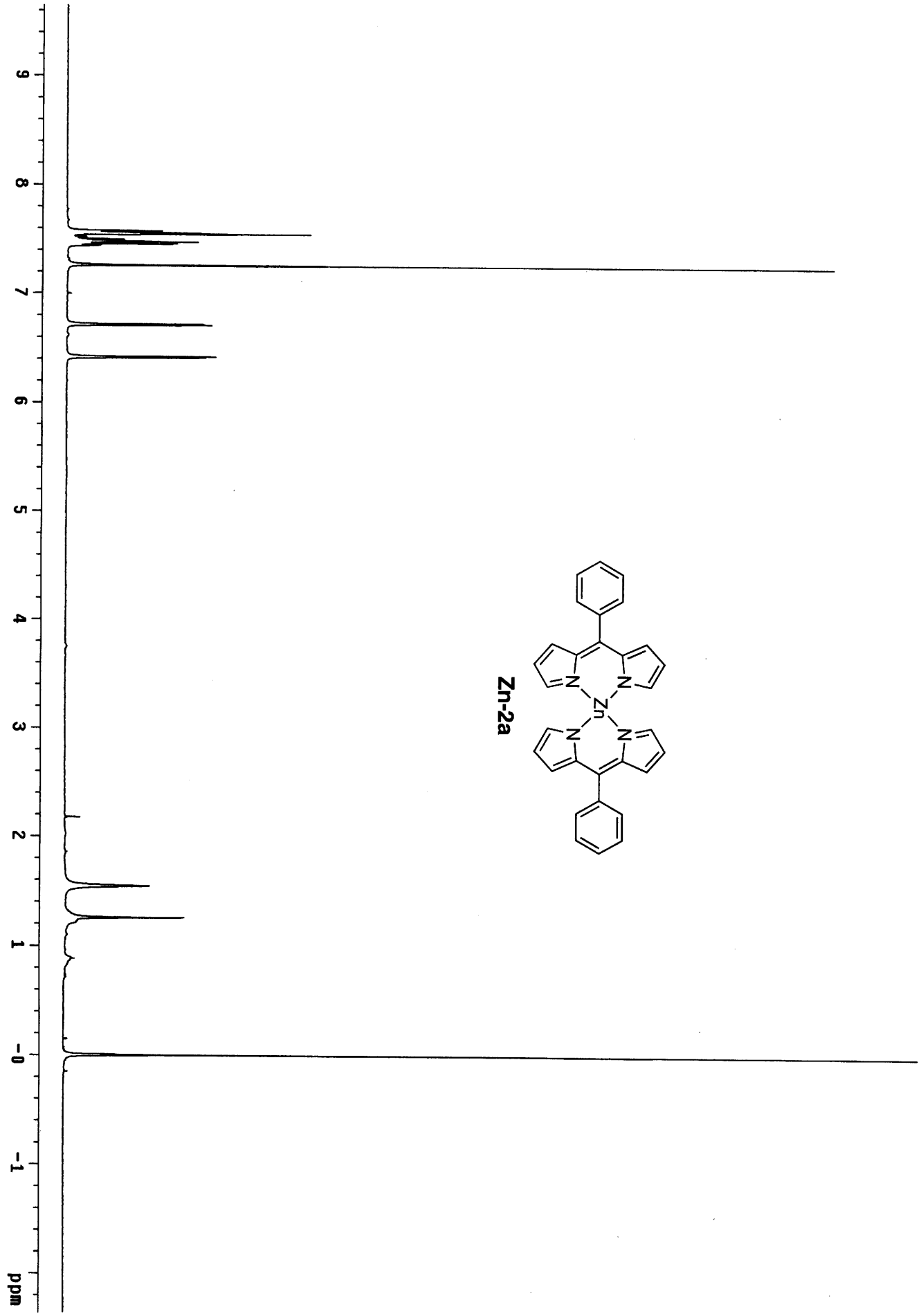
2h



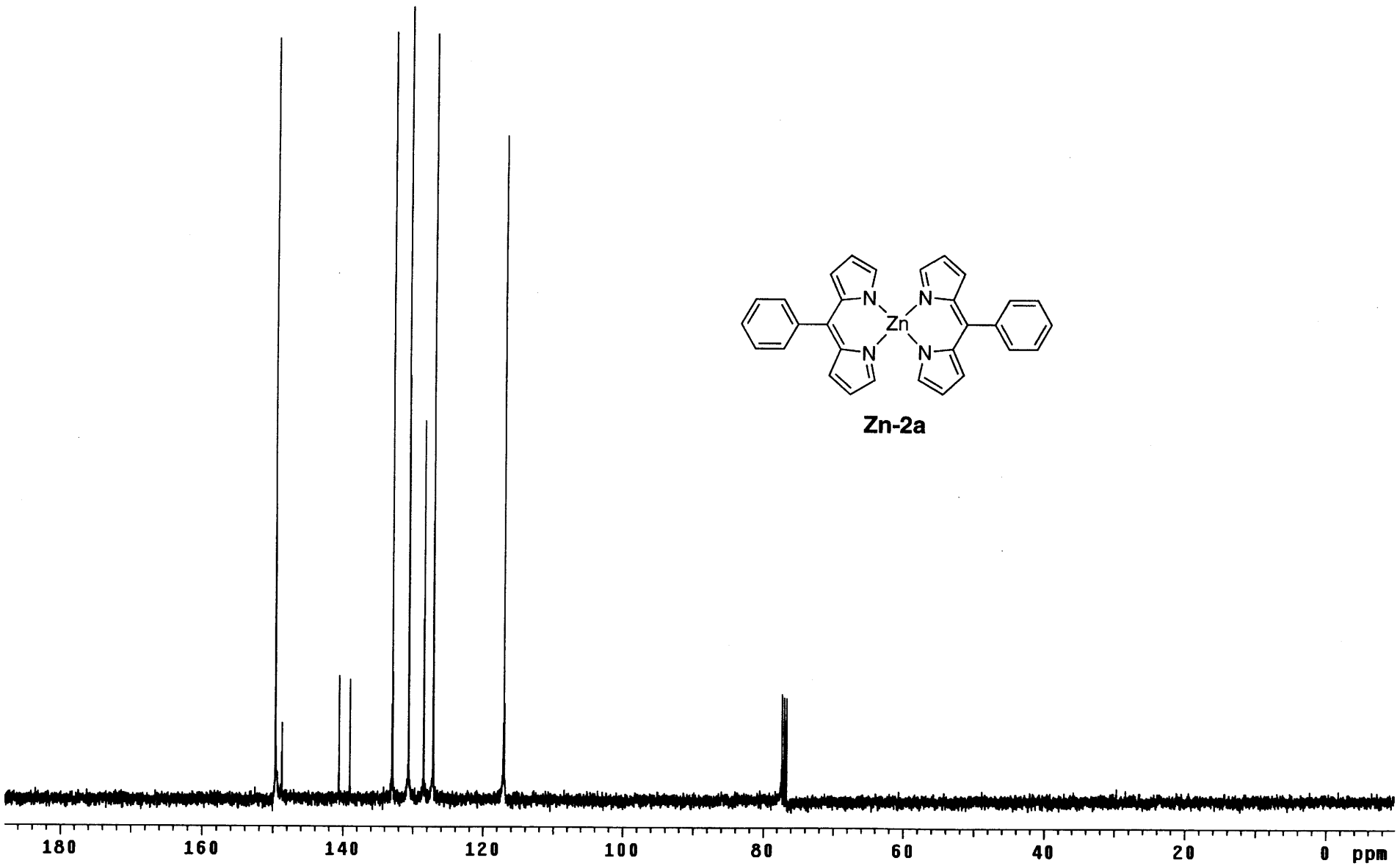
2j



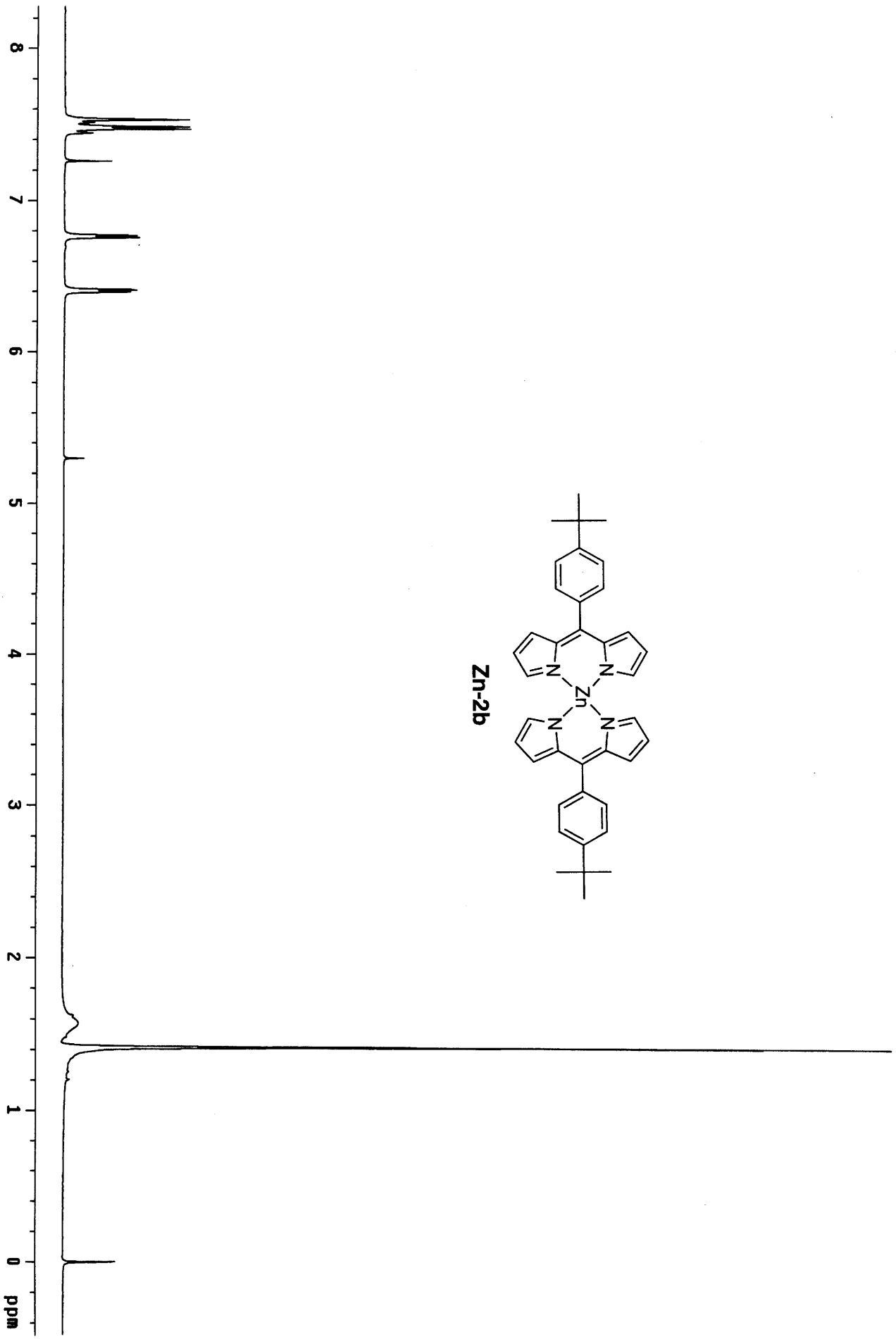
2j



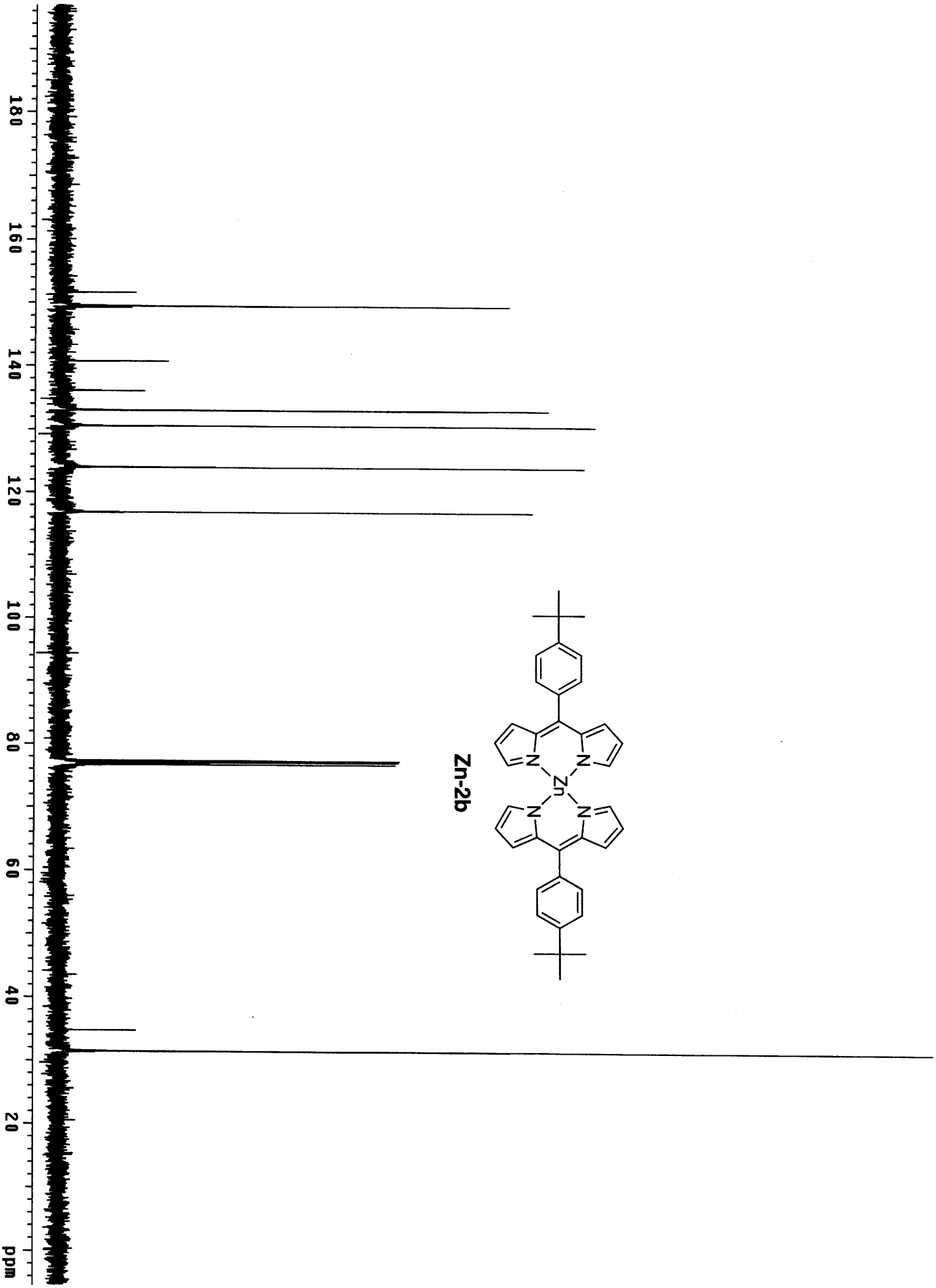
Zn-2a



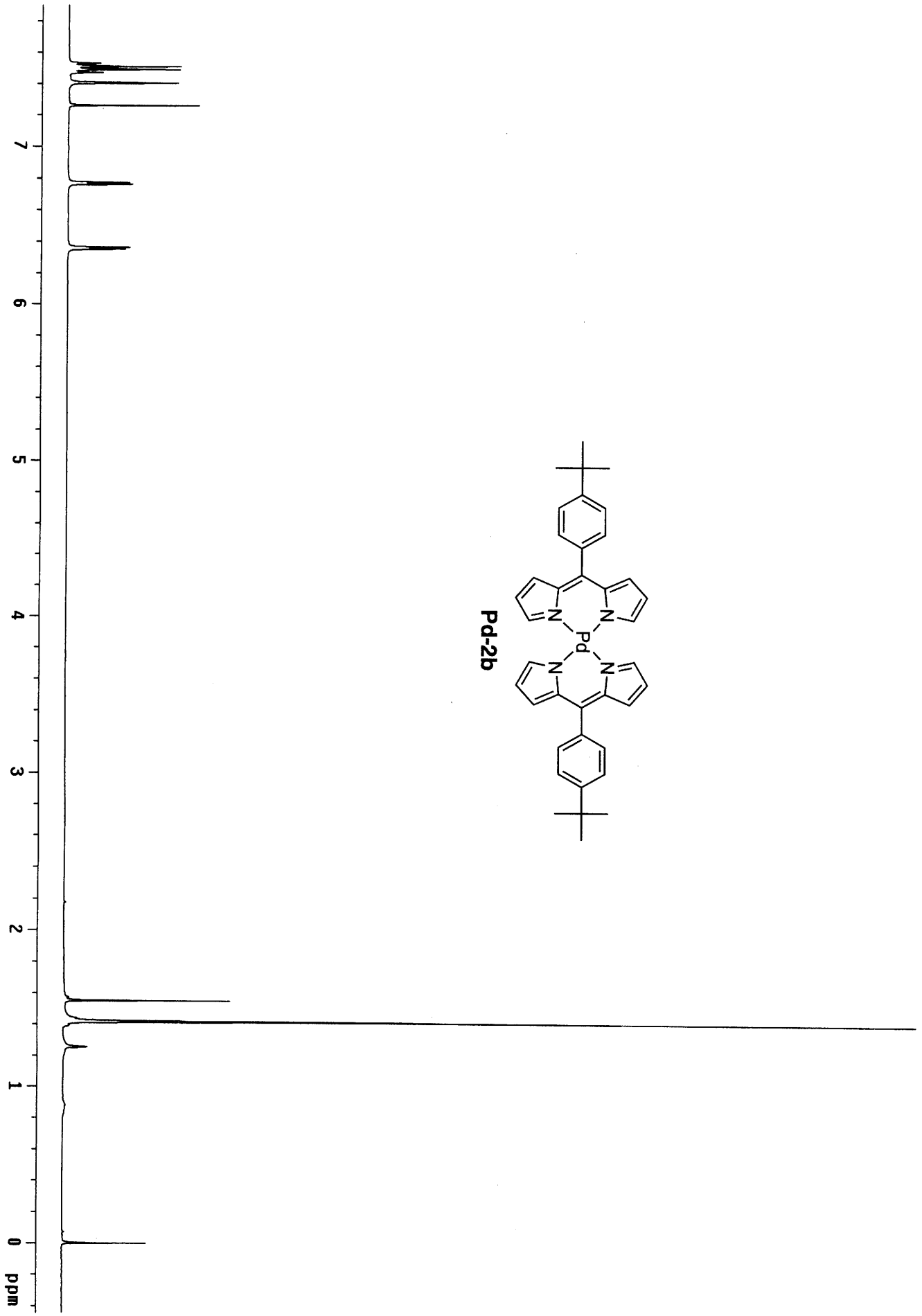
Zn-2a



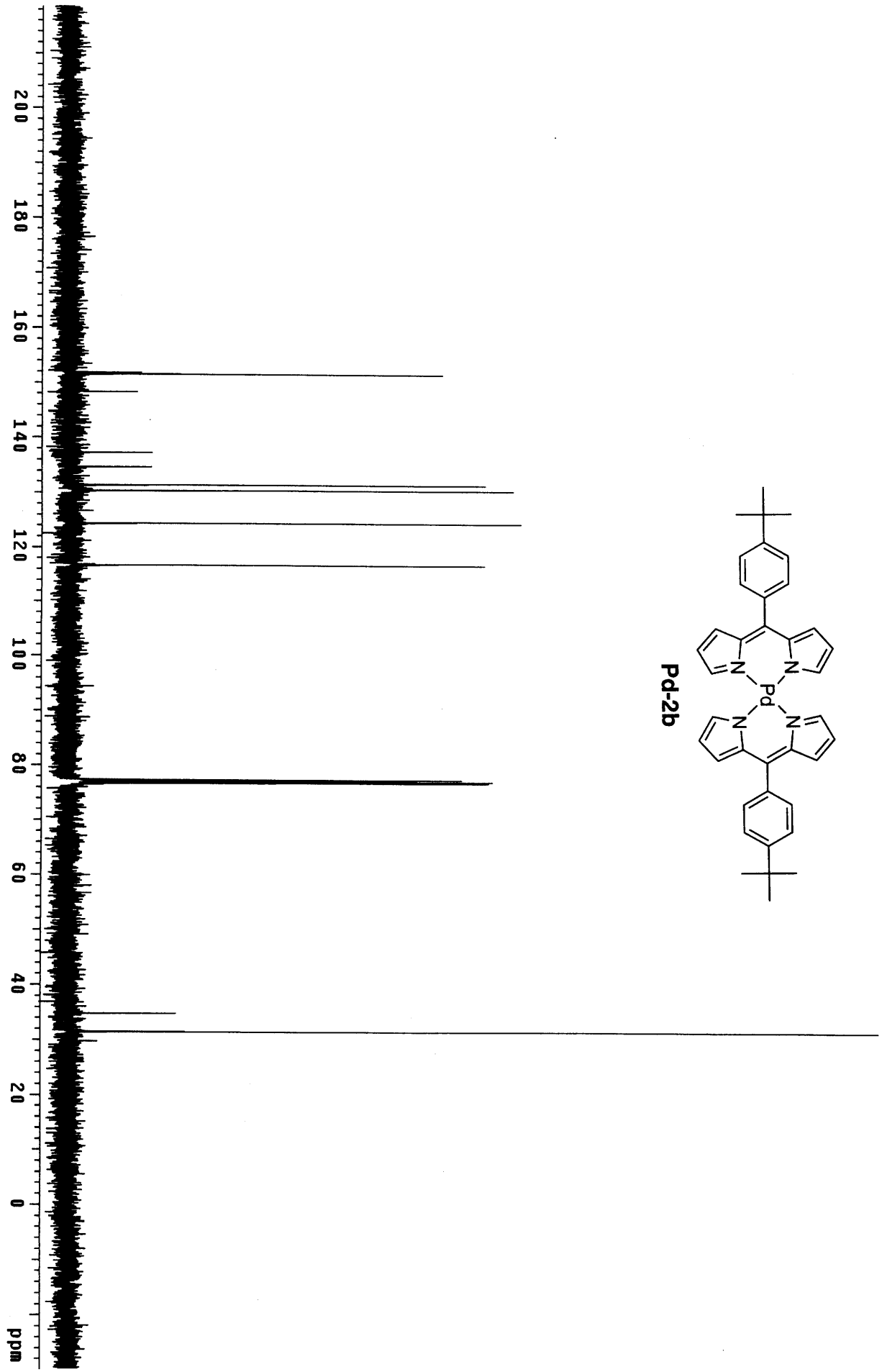
Zn-2b



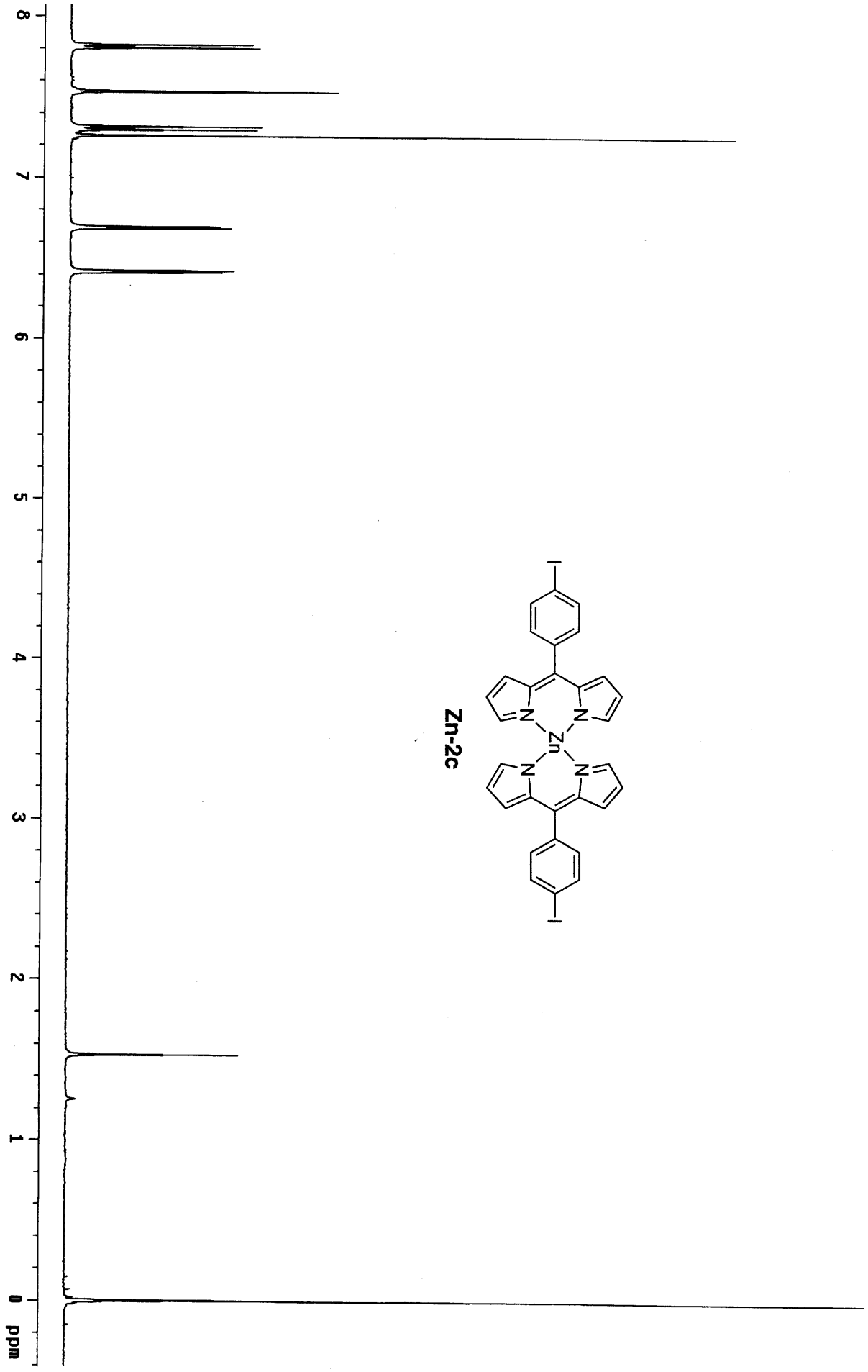
Zn-2b



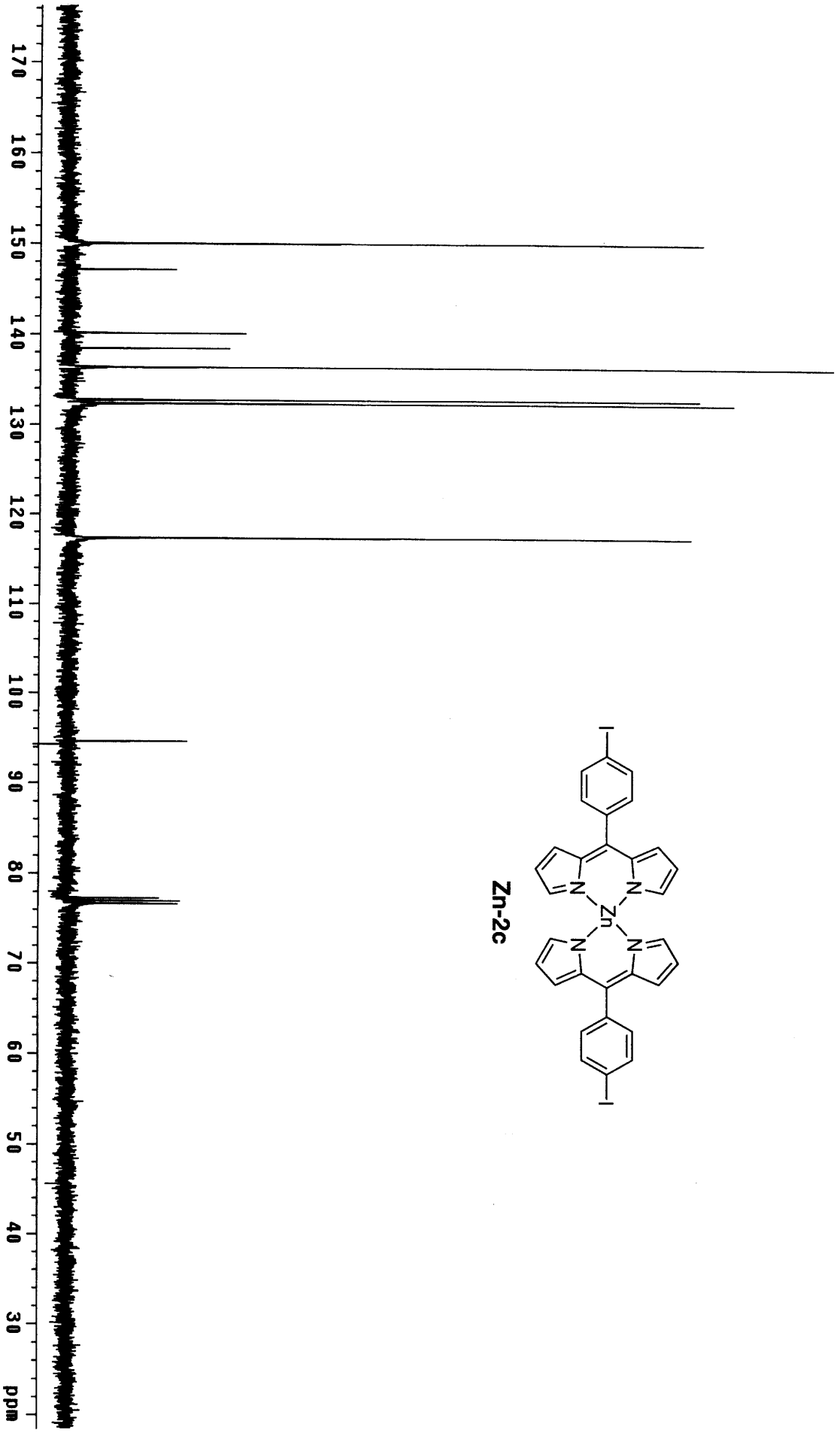
Pd-2b



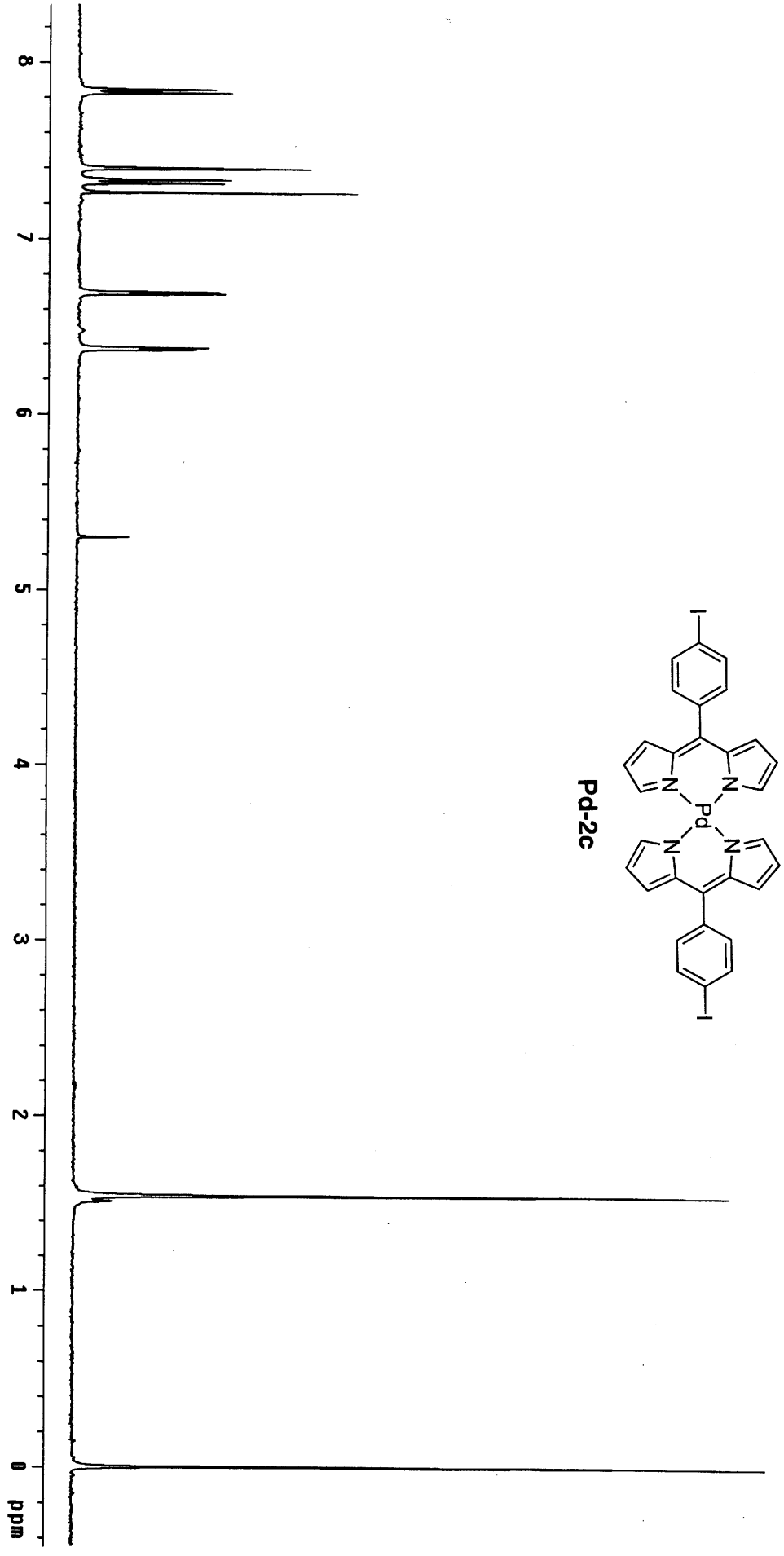
Pd-2b



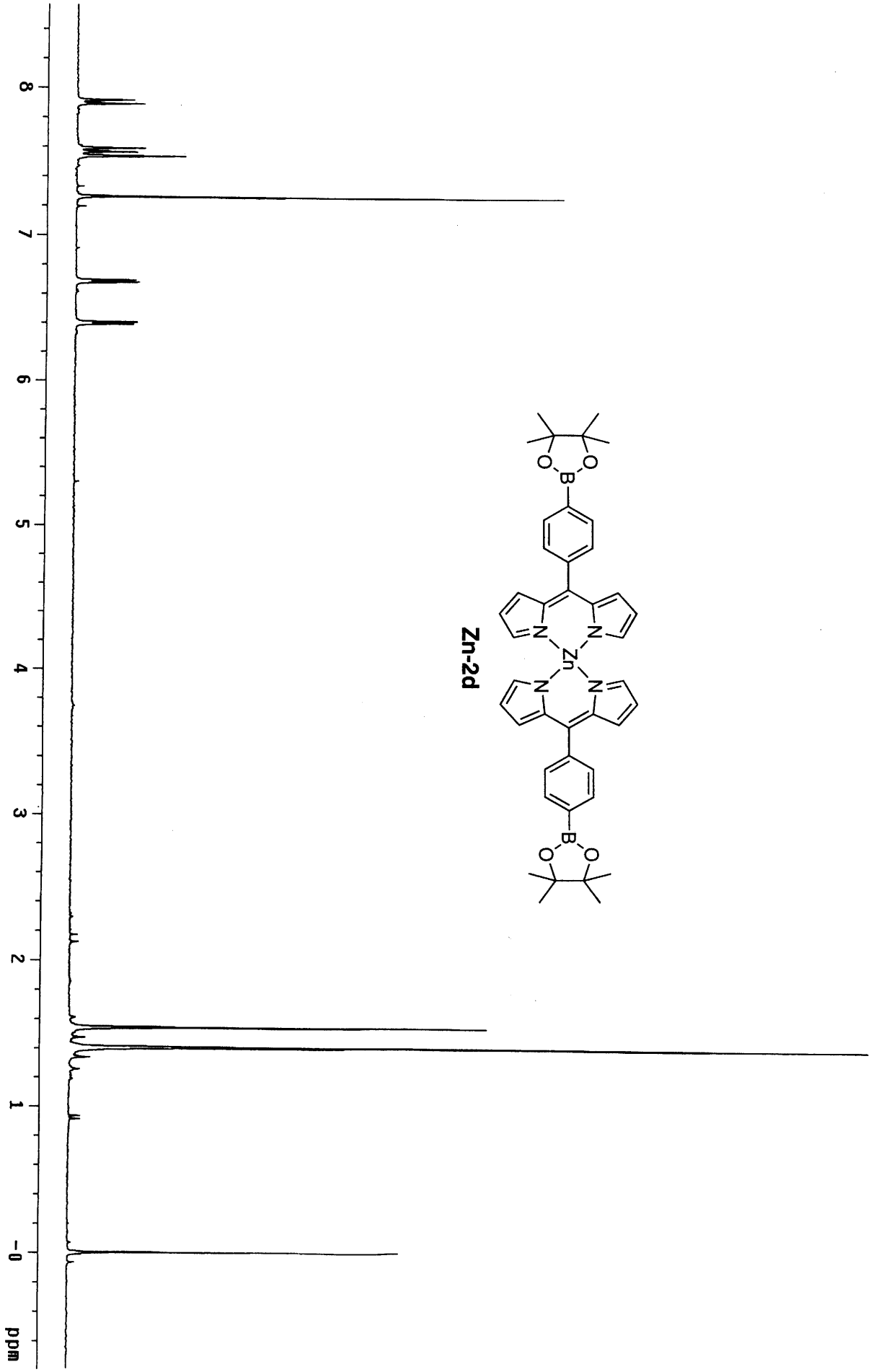
Zn-2c



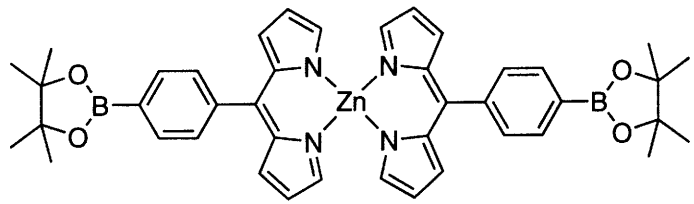
Zn-2c



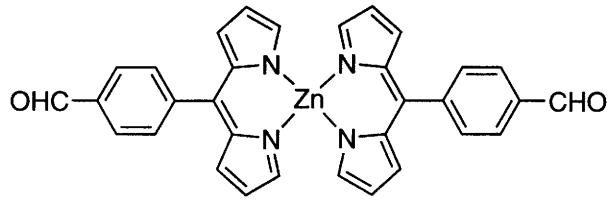
Pd-2c



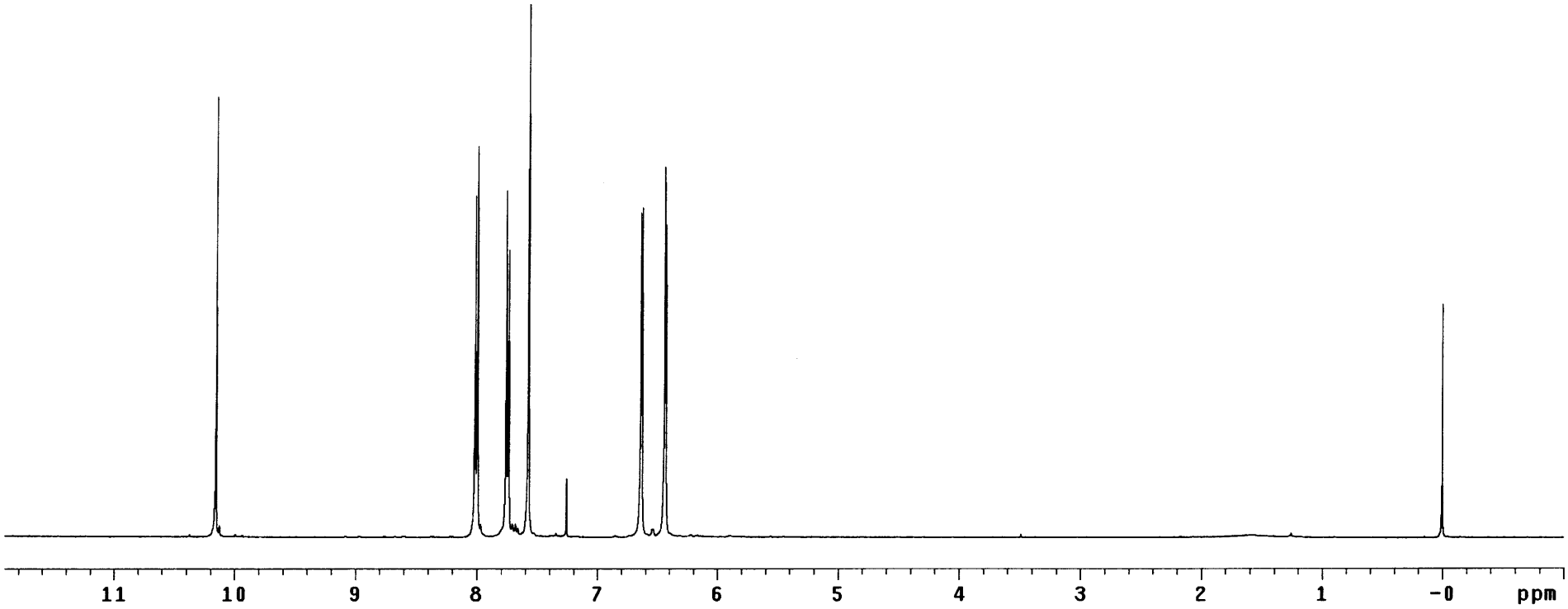
Zn-2d

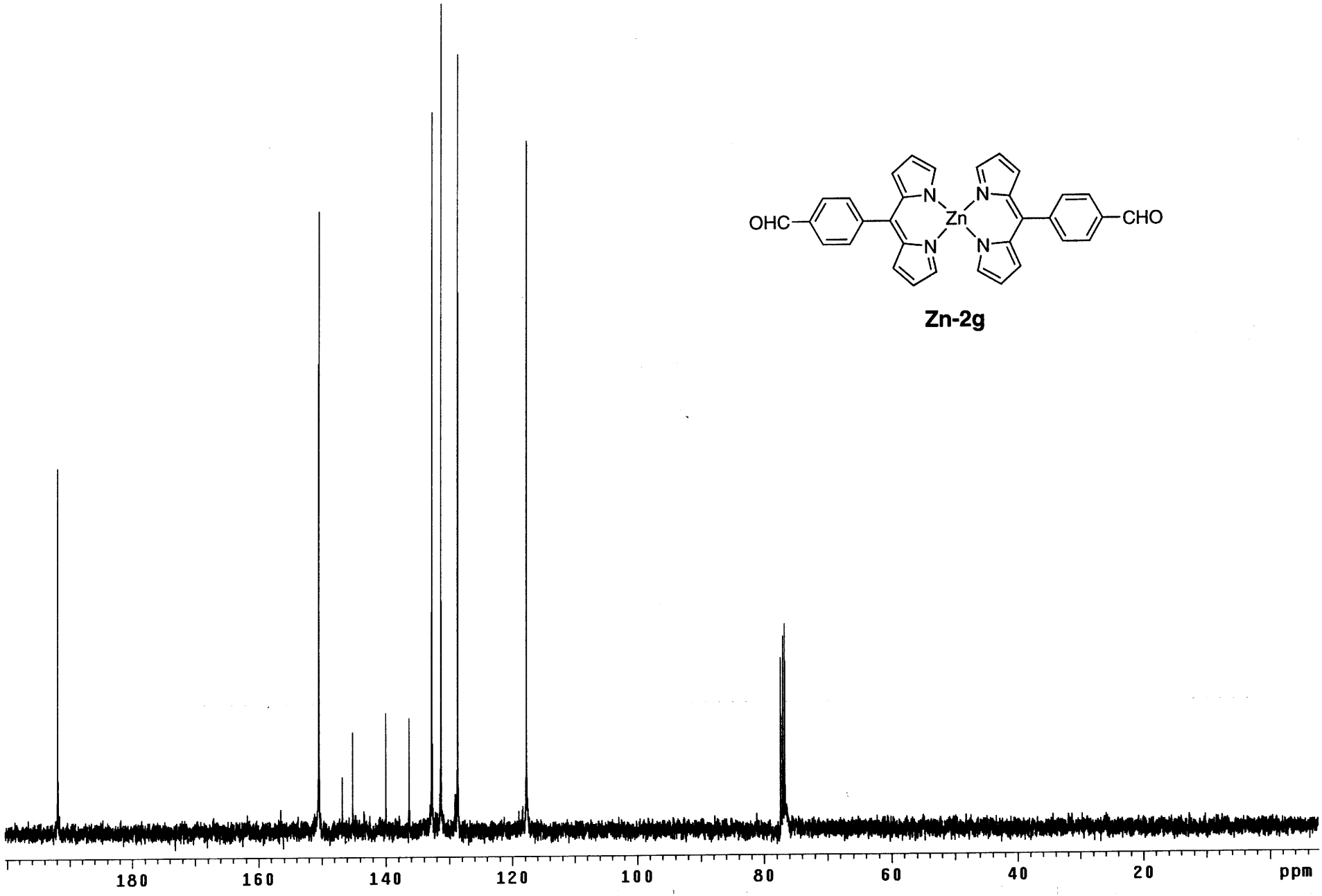


Zn-2d

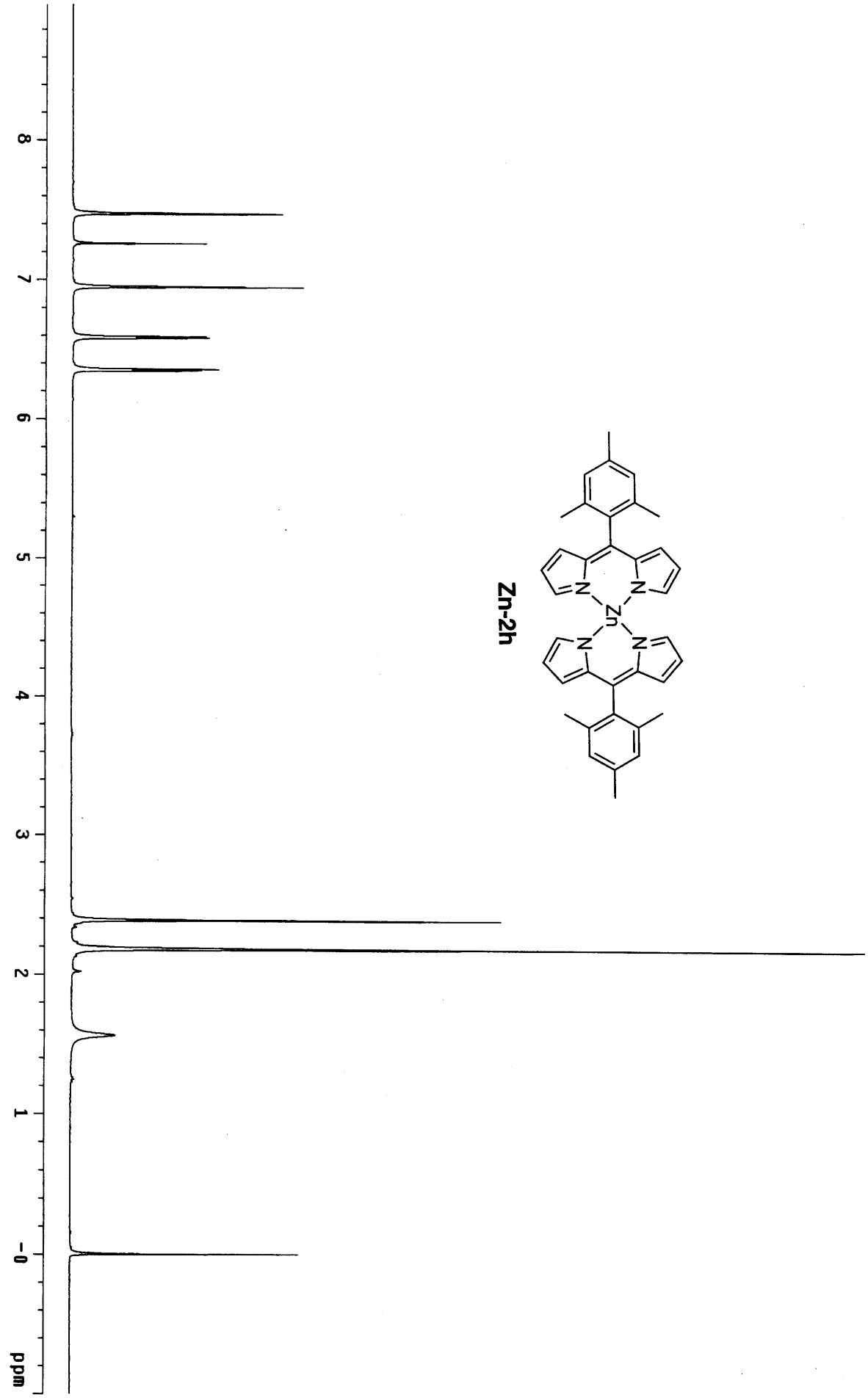


Zn-2g

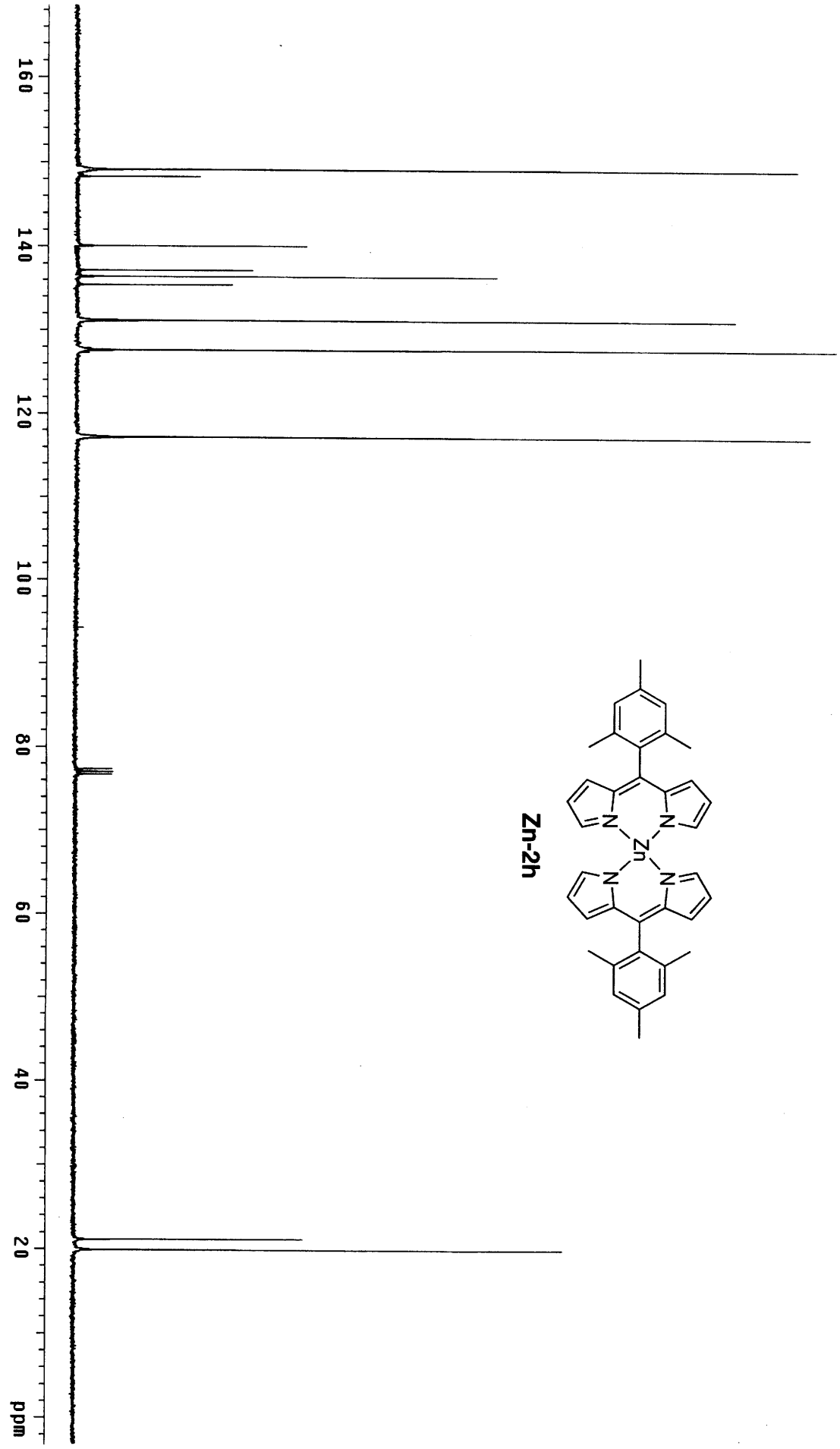




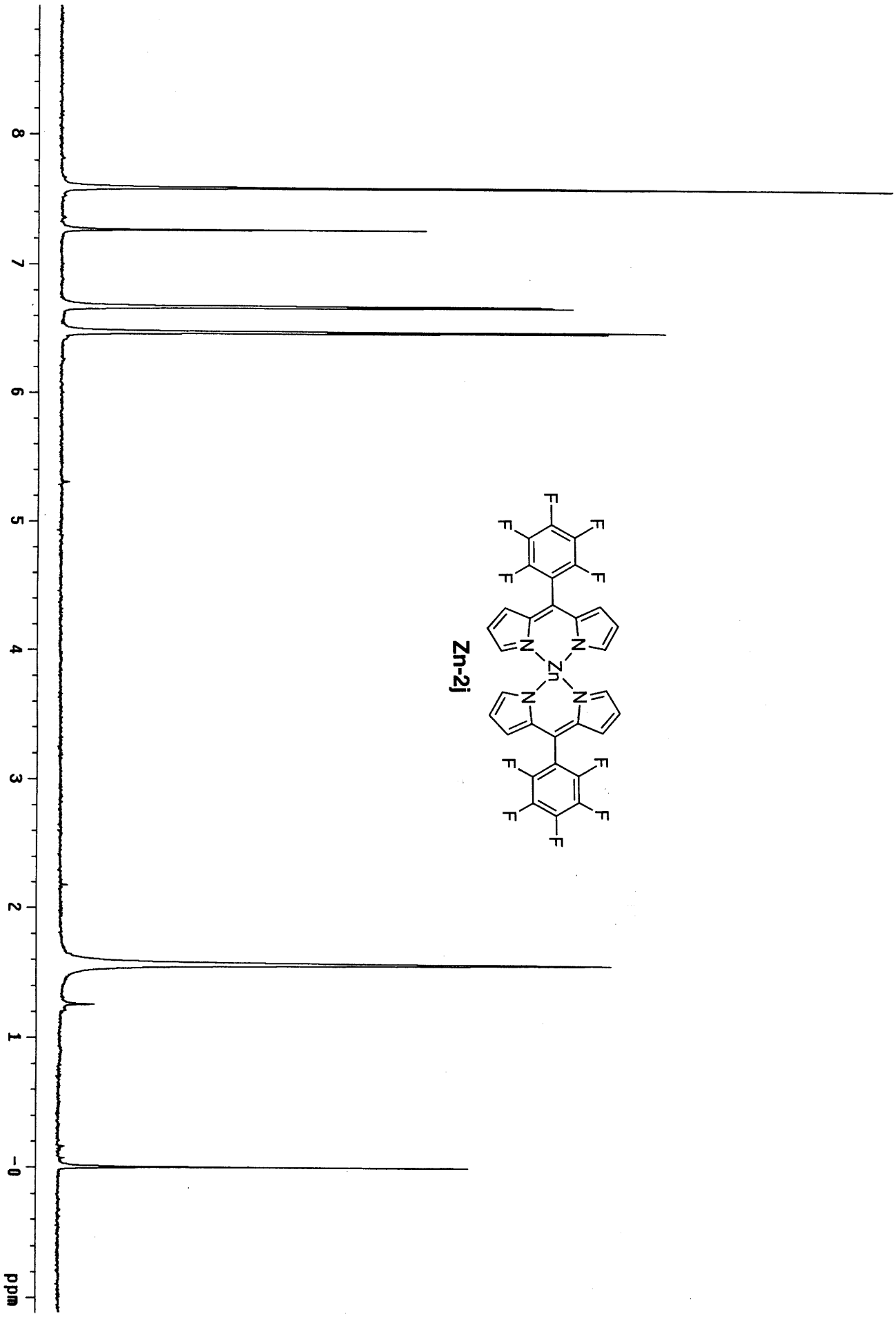
Zn-2g



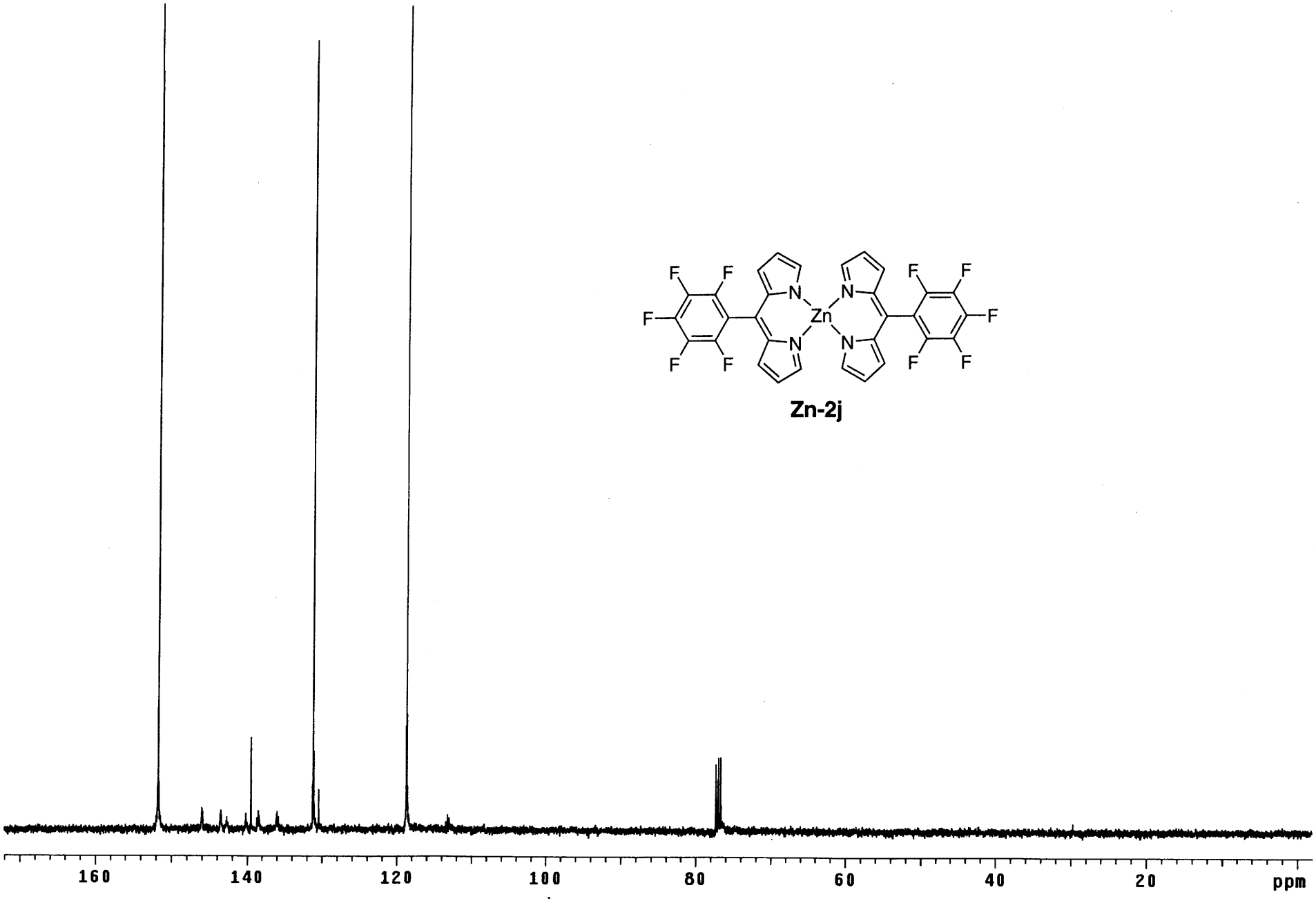
Zn-2h



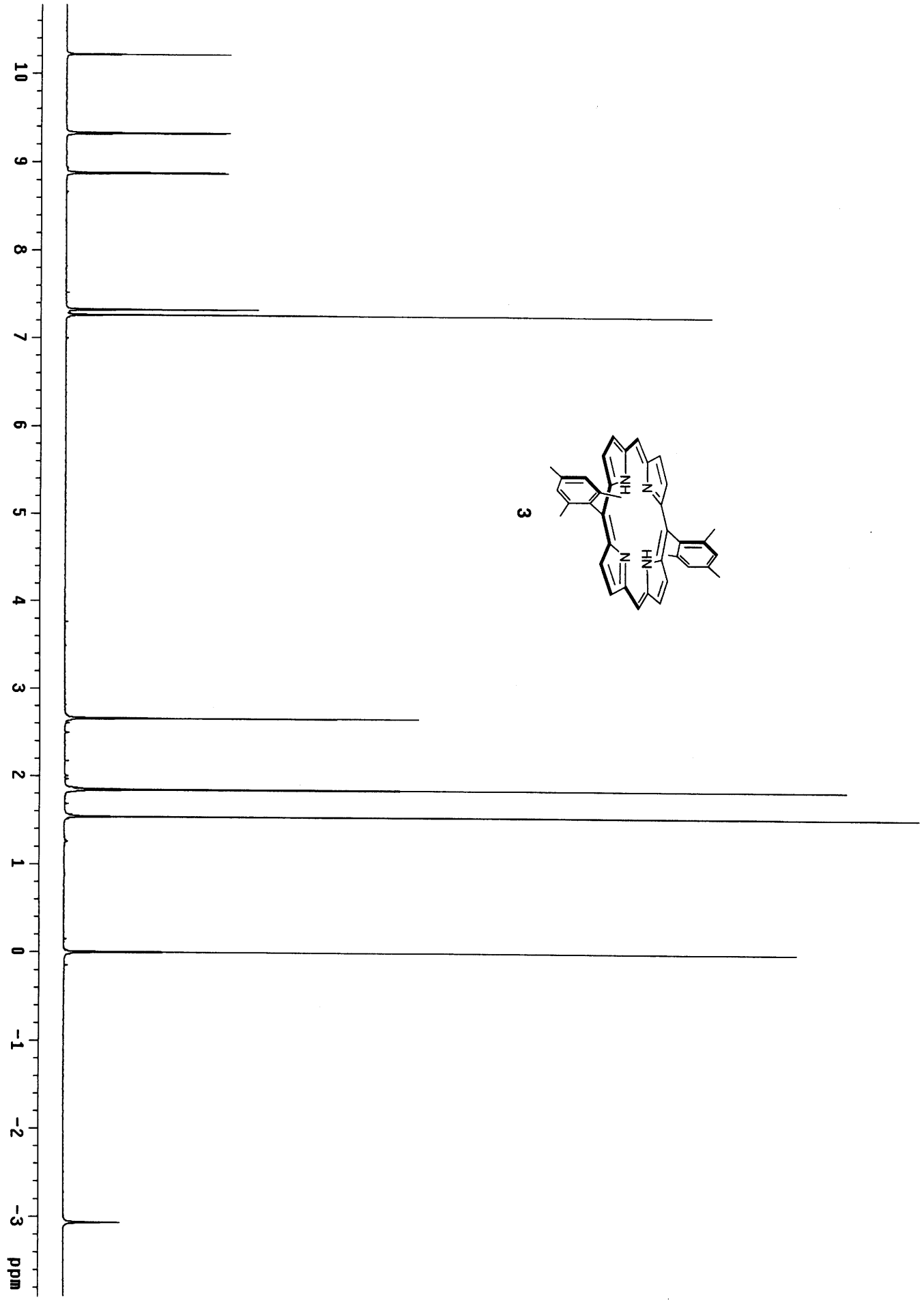
Zn-2h



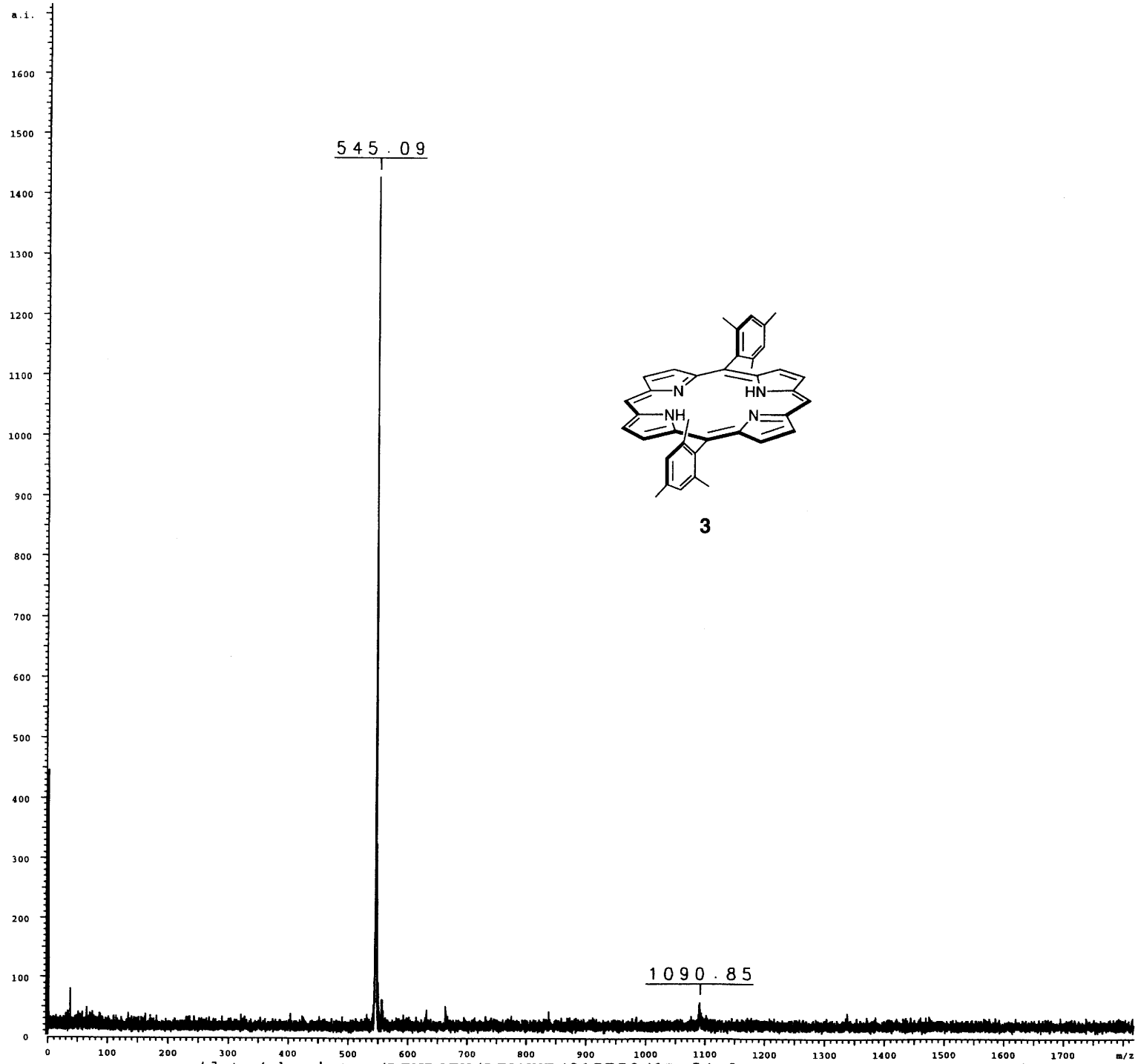
Zn-2j



Zn-2j



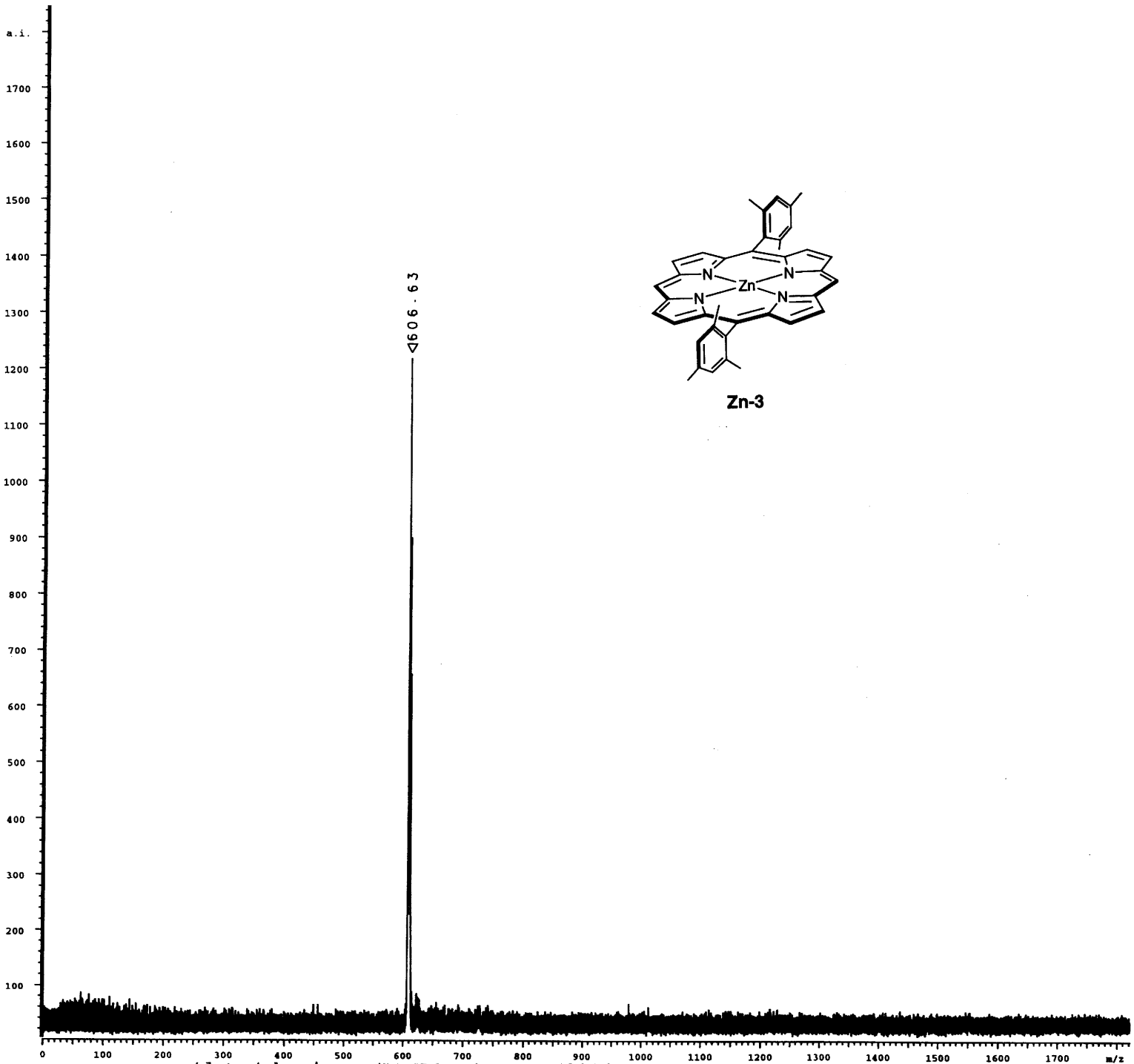
3



3

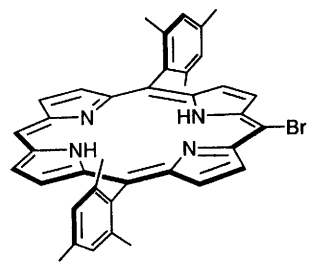
```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015759
AQ_DATE Tue Oct 16 11:31:40 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              30000
NoSHOTS            71
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFull             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udefl               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              48.0
ML1          2067125.193
ML2              333.982
ML3                0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1           510.84
DPMASS           700.00  [Da]
RENDVAL            0.33
LENDVAL            0.28
IS2ENDV            0.91
CMT1    2Ms-2H-PBB (Fb), purified
CMT2    attn = 48, shot = 70
```

GE NMR Instruments
/home/general/data/lindsey/Lianhe/2Ms-2H-Zn-FBBn 5 08:48:07 2001
Page 1
ppm
0
2
4
6
8
10
Zn-3
N
N
N
N
Zn

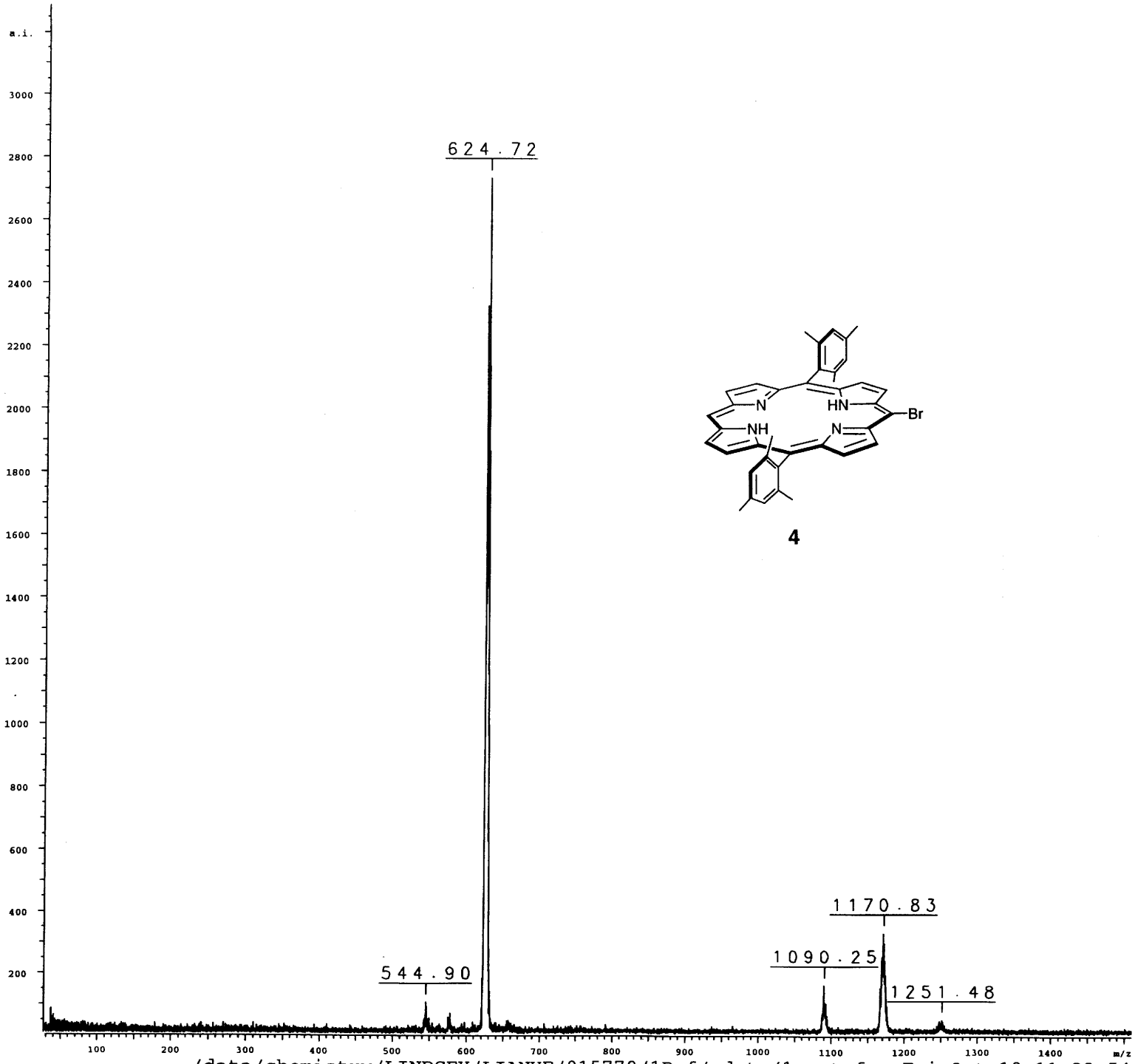


Zn-3

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  004624
AQ_DATE Thu Jan  4 16:12:50 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              30000
NoSHOTS            72
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00   [ns]
DELAY               0 [ns]
Uis1               20.00   [kV]
Uis2               18.70   [kV]
Urefl               0.00   [kV]
Ulens               7.50   [kV]
Uhimass            10.00   [kV]
RefFull             0.00   [kV]
UdetL               1.50   [kV]
UdetR               0.00   [kV]
Udefl               2.00   [kV]
REPHZ               1.00   [Hz]
ATTEN              28.0
ML1          2071592.159
ML2              333.982
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    2Ms-2H-Zn-PBB
CMT2    attn = 28, shot = 72
```

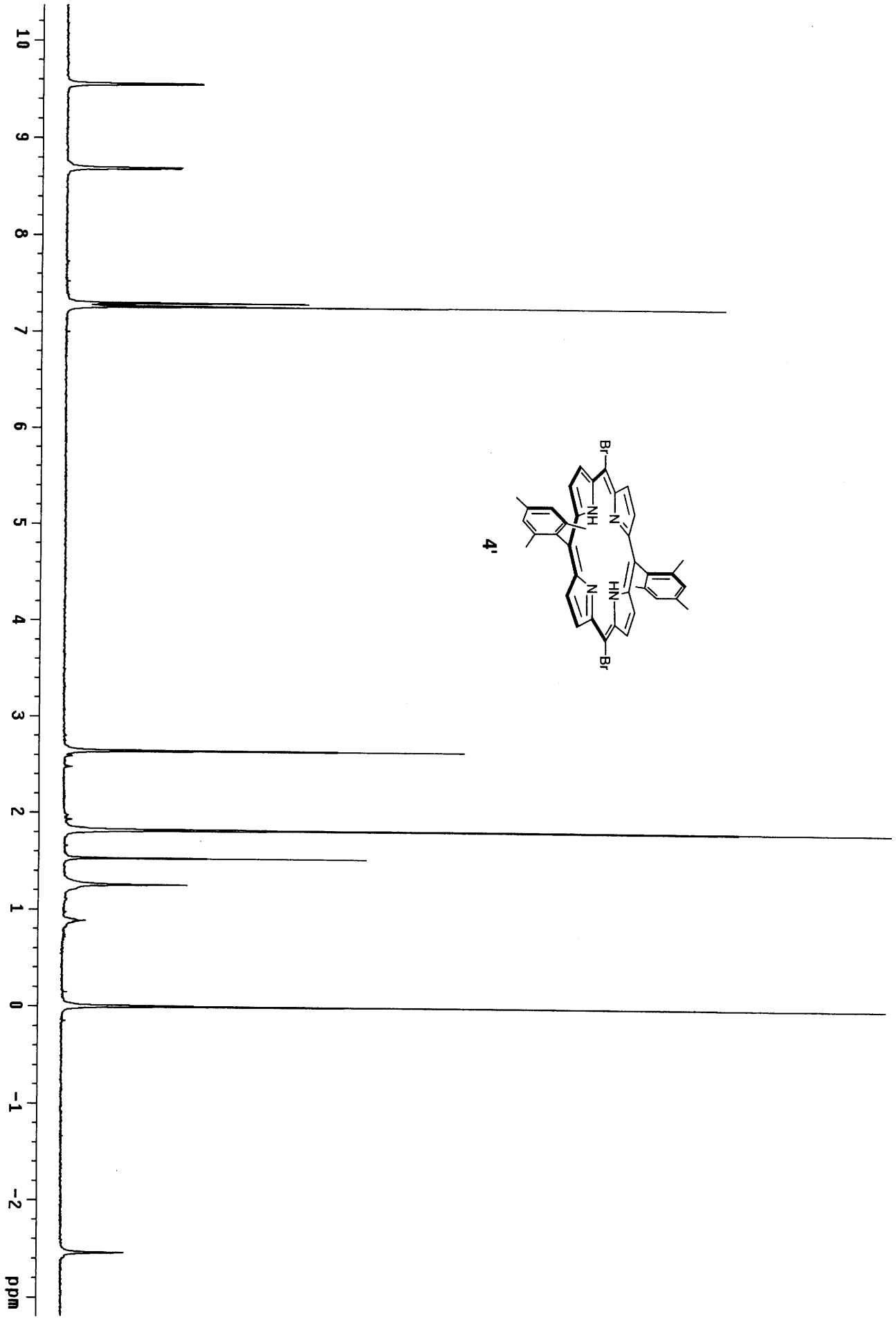


4

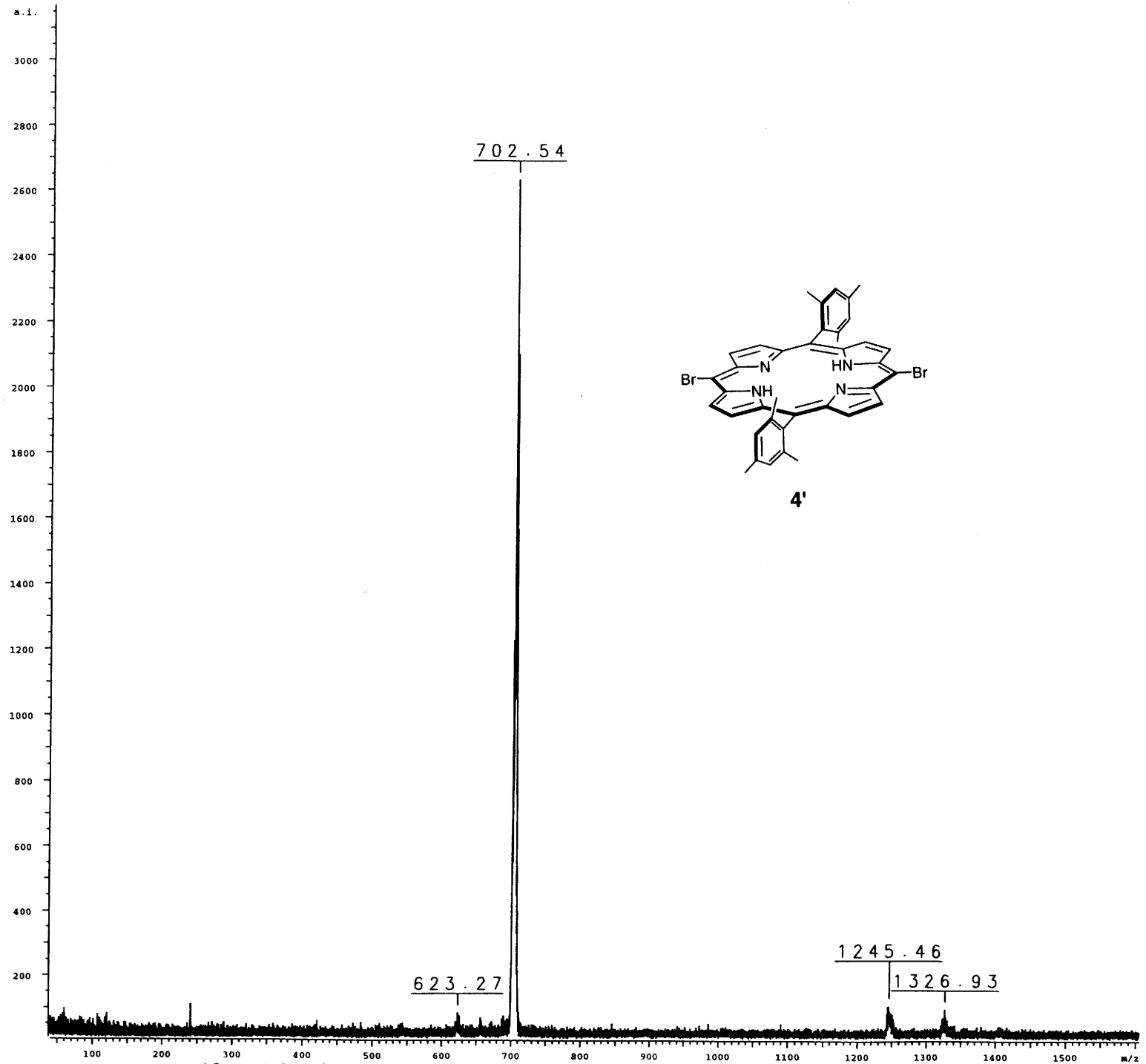


4

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015770
AQ_DATE Fri Oct 19 11:16:53 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              30000
NoSHOTS            61
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [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           2067125.193
ML2               333.982
ML3                 0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSEND no
LLNSEND no
UIS2END no
DPCAL1            510.84
DPMASS            700.00  [Da]
RENDVAL             0.33
LENDVAL             0.28
IS2ENDV             0.91
CMT1    2Ms-1Br-1H-Fb-PBB
CMT2    attn = 35, shot = 60
```



4'



4'

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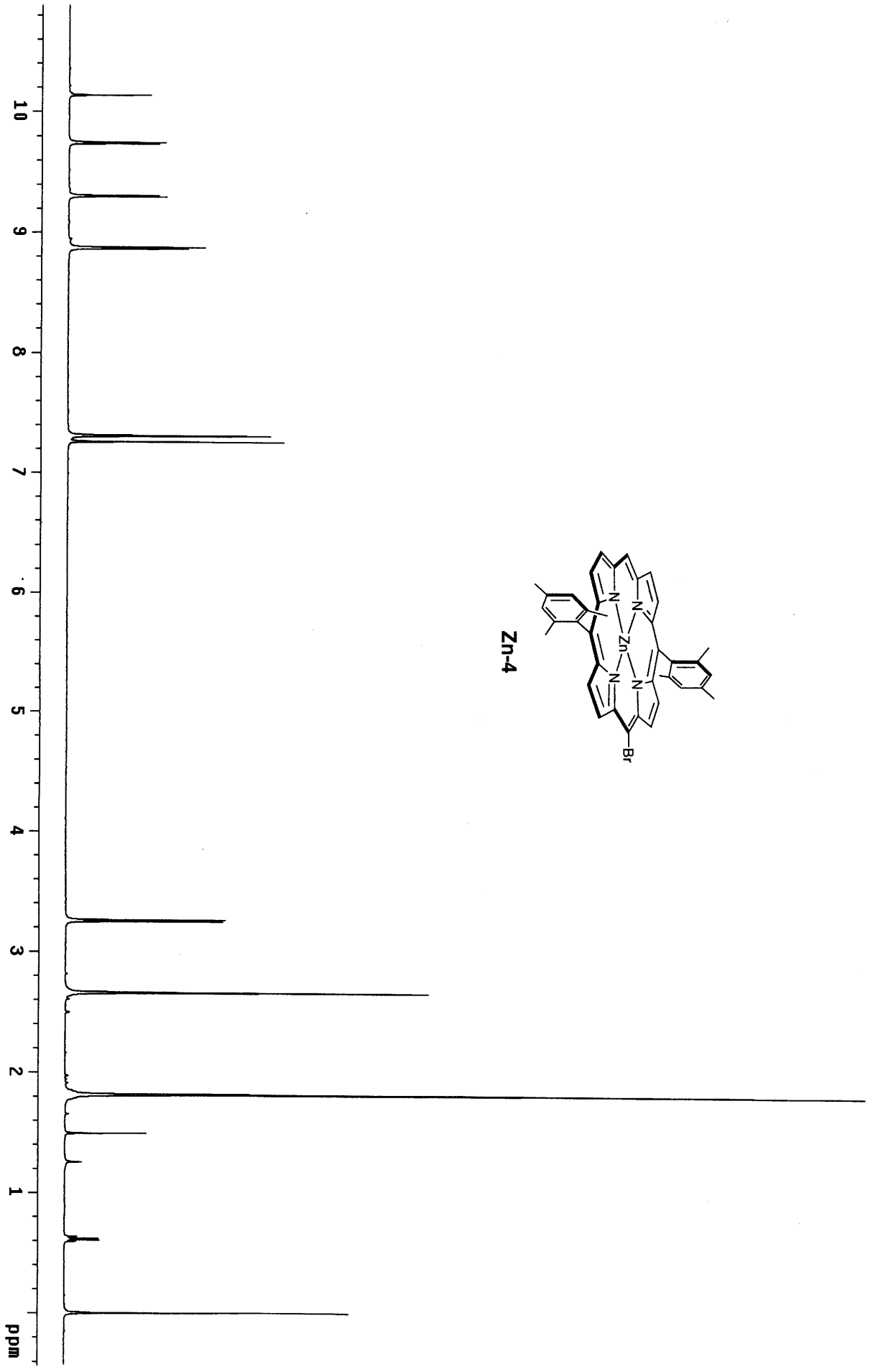
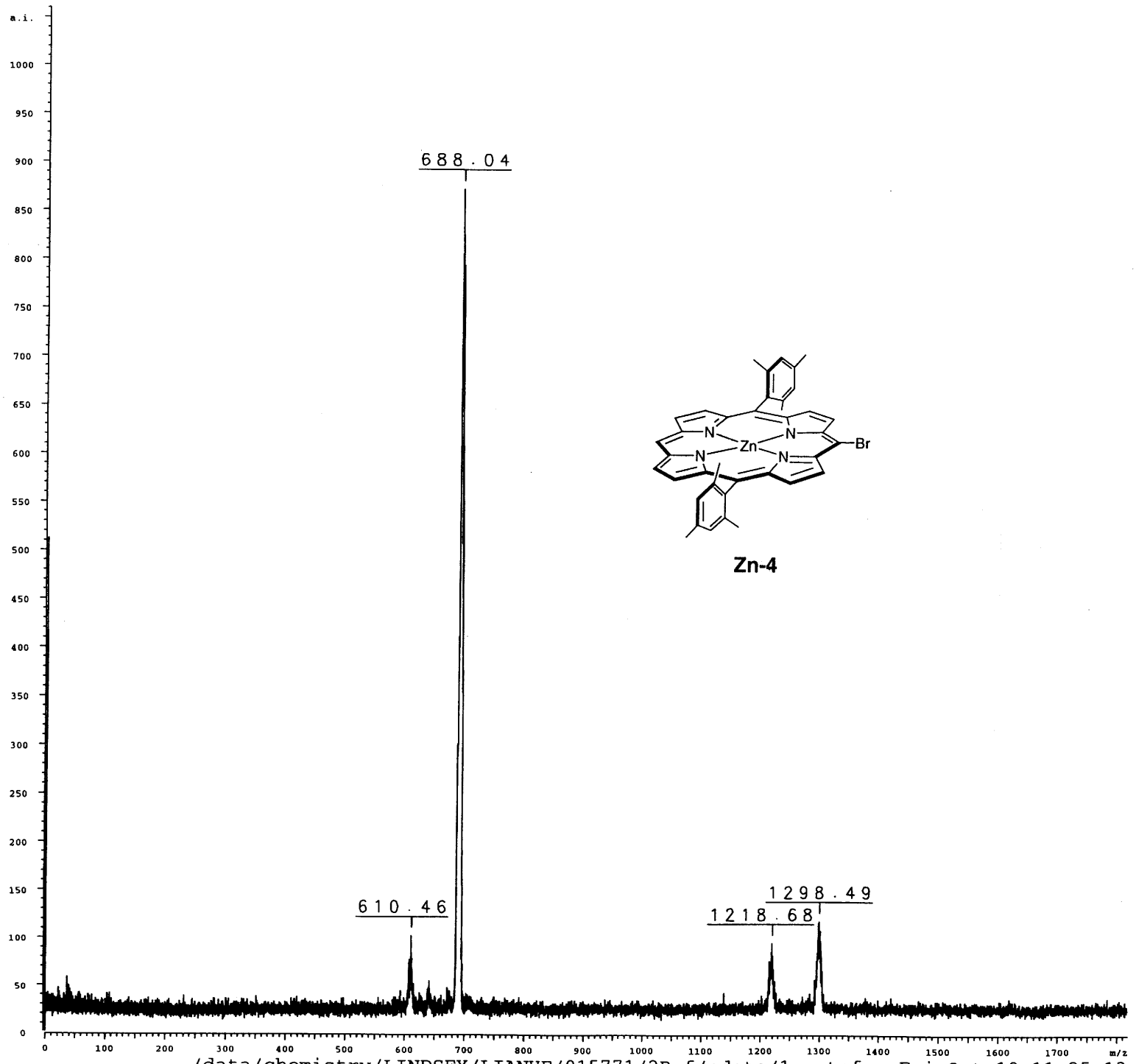
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015769
AQ_DATE Fri Oct 19 11:15:14 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              30000
NoSHOTS            71
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Uref1               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFull             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udef1               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              35.0
ML1          2067125.193
ML2              333.982
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    2Ms-2Br-Fb-PBB
CMT2    attn = 35, shot = 70
```

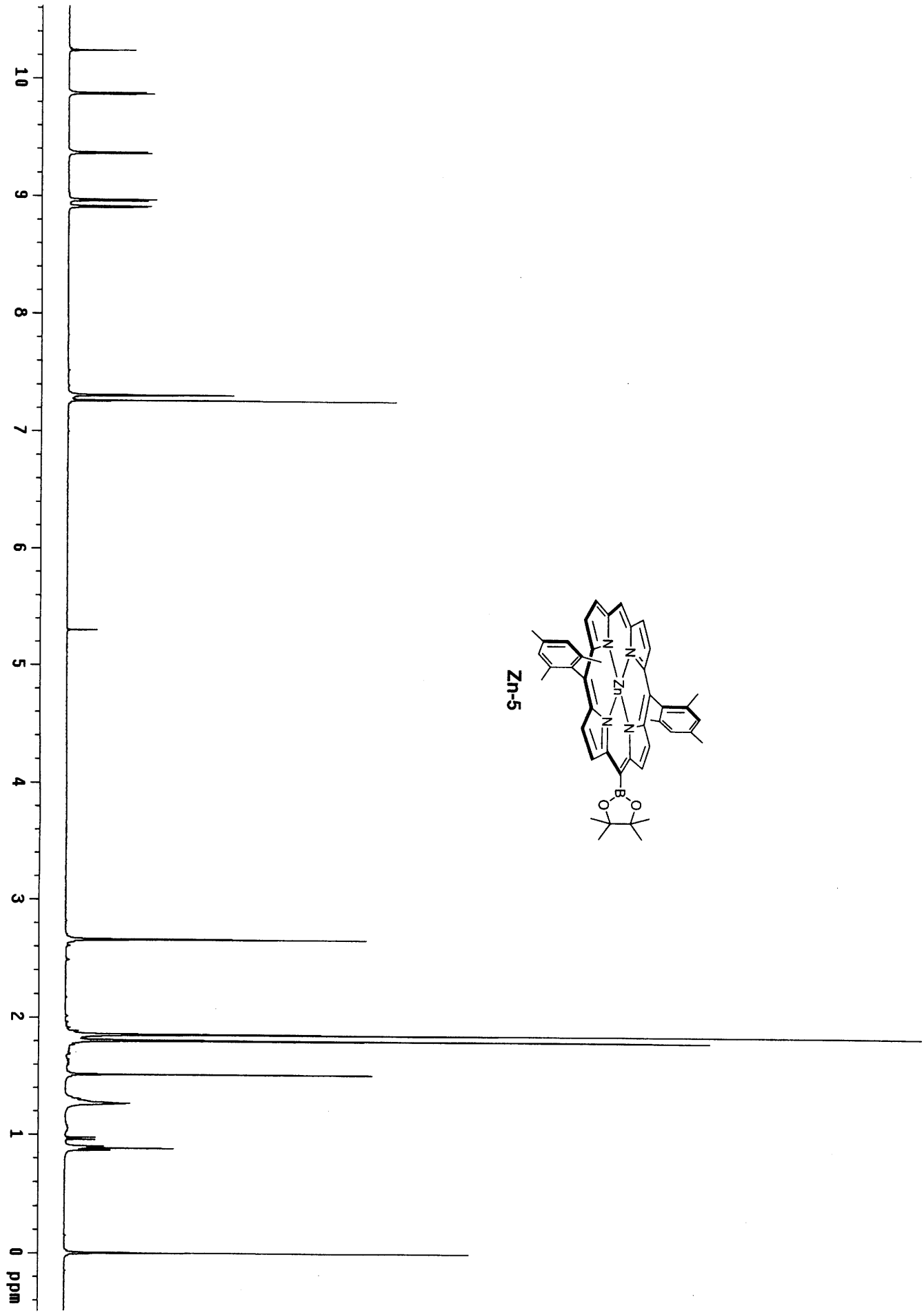


Zn-4

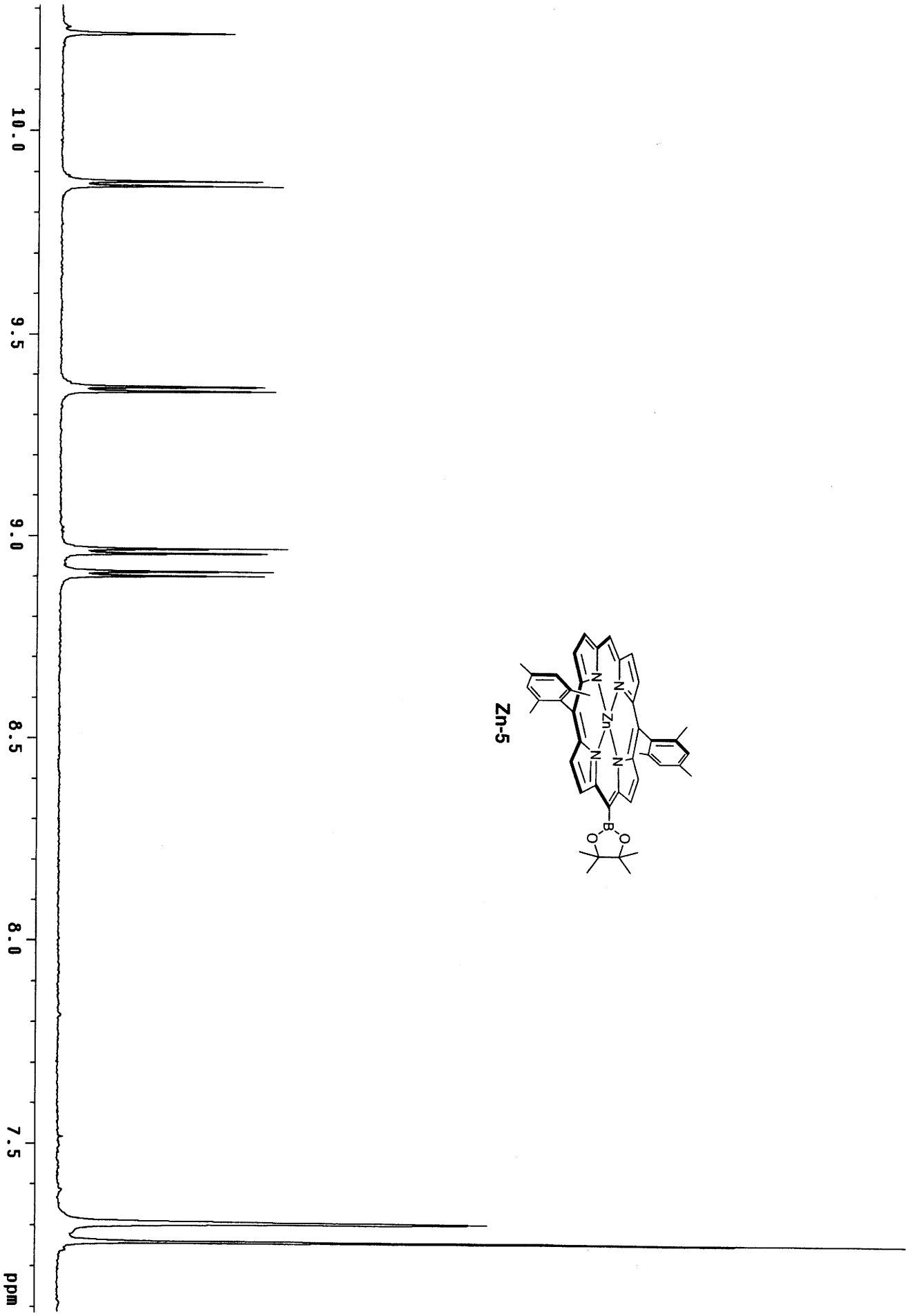


Zn-4

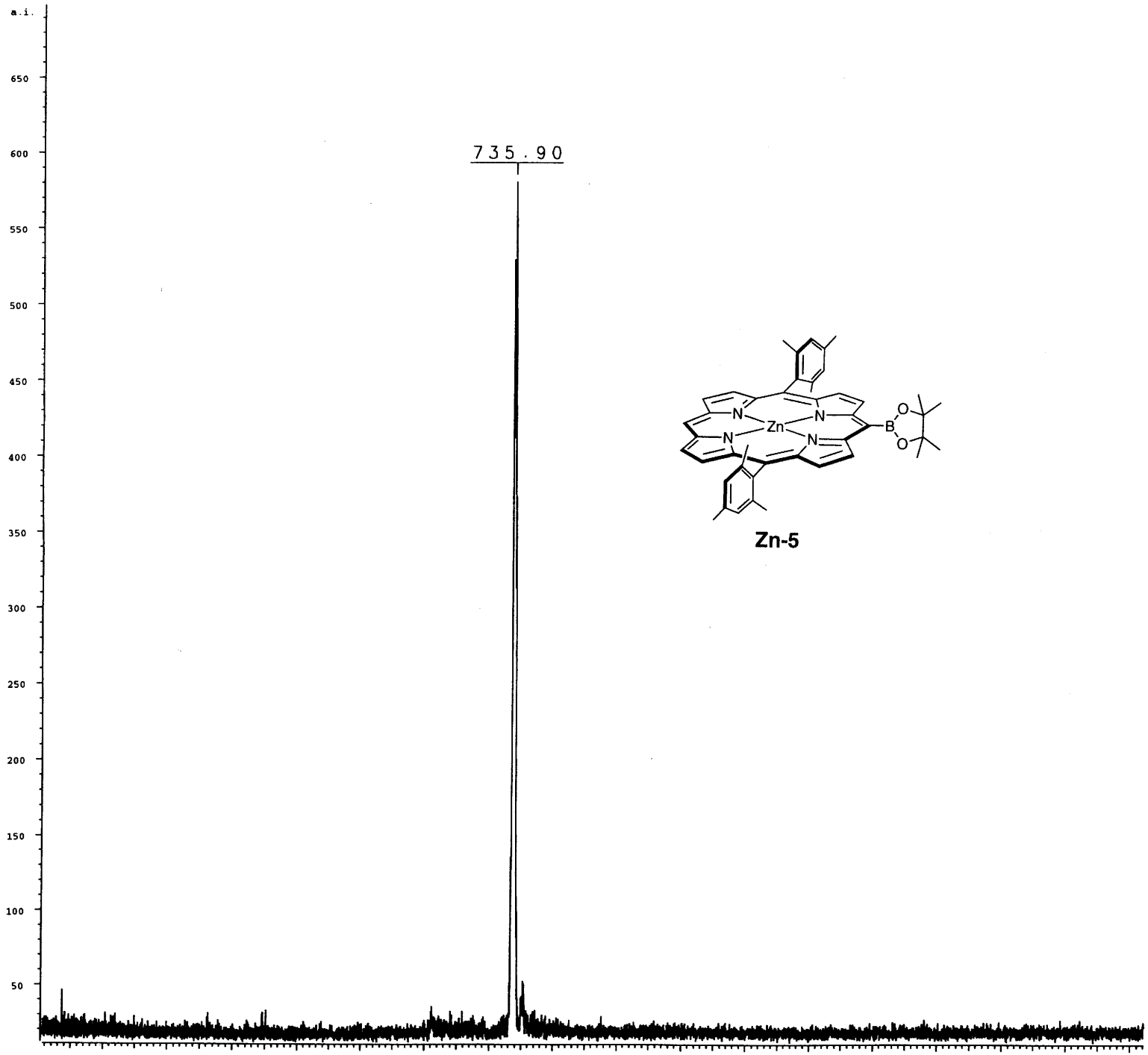
```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015771
AQ_DATE Fri Oct 19 11:21:02 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              30000
NoSHOTS            90
SMONUM              1
SMOPTS1             2
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFull             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udefl               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              43.0
ML1          2067125.193
ML2              333.982
ML3                0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1            510.84
DPMASS            700.00  [Da]
RENDVAL             0.33
LENDVAL             0.28
IS2BNDV             0.91
CMT1    2Ms-1Br-1H-Zn-PBB
CMT2    attn = 43, shot = 90
```



Zn-5



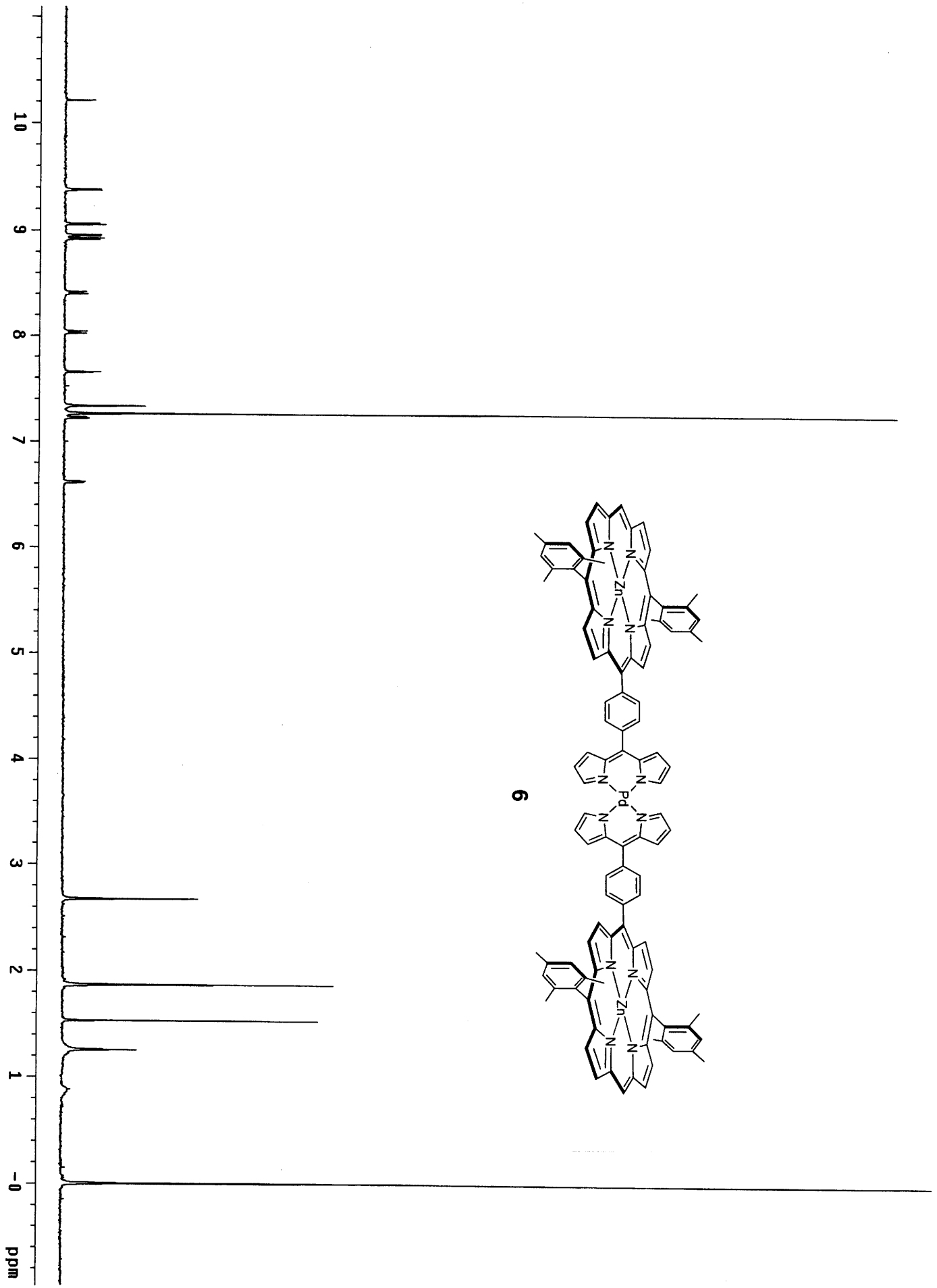
Zn-5



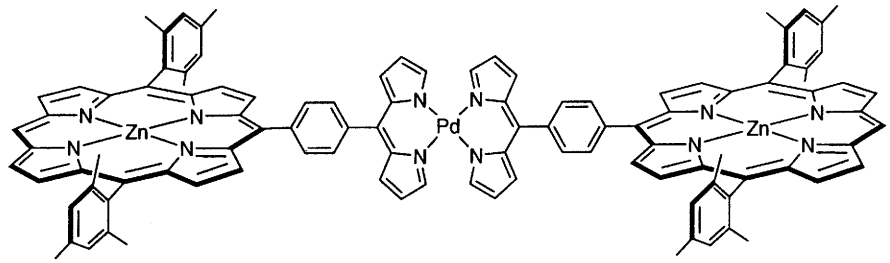
Zn-5

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015781
AQ_DATE Wed Oct 24 17:38:10 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              30000
NoSHOTS            62
SMONUM              1
SMOPTS1             4
SMOPTS2             0
SMOPTS3             0
DW                  1.00   [ns]
DELAY               0 [ns]
Uis1               20.00   [kV]
Uis2               18.70   [kV]
Uref1               0.00   [kV]
Ulens               7.50   [kV]
Uhimass            10.00   [kV]
RefFull             0.00   [kV]
UdetL               1.50   [kV]
UdetR               0.00   [kV]
Udef1               2.00   [kV]
REPHZ               1.00   [Hz]
ATTEN              42.0
ML1          2067125.193
ML2              333.982
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    2Ms-1H-1B-PBB
CMT2    attn = 42, shot = 60
```

/data/chemistry/LINDSEY/LIANHE/015781/2Ref/pdata/1 tof Wed Oct 24 17:43:26 2001



6

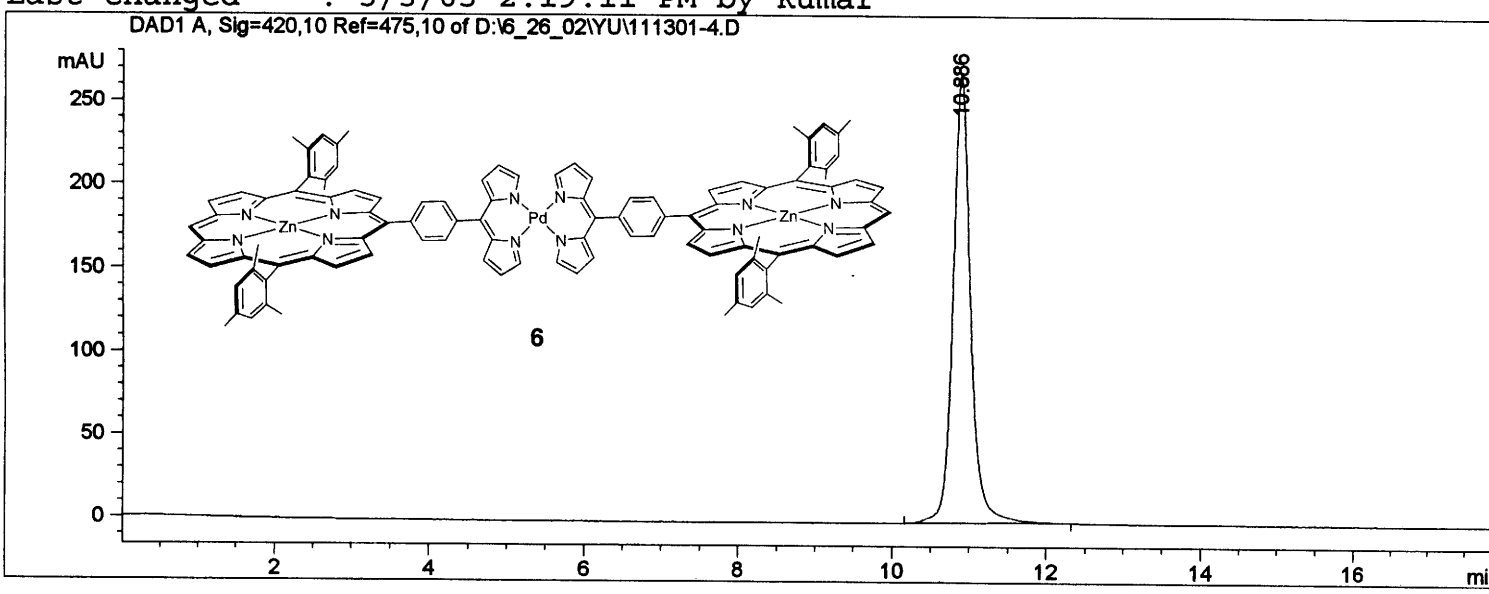


6

Suzuki coupling, Ba(OH)2, DME/H2O, 80 oC 15 h
After short silica column
SEC, 2nd F (Product)

```
==========================================================================
Injection Date  : 11/13/01 1:11:02 PM          Seq. Line :   -
Sample Name     : Suzuki-BaOH                      Vial : 100
Acq. Operator   : LHY                              Inj :   -
                                               Inj Volume : 20 µl

Acq. Method     : C:\HPCHEM\1\METHODS\YLH.M
Last changed    : 11/13/01 8:55:56 AM by LHY
Analysis Method : C:\HPCHEM\1\METHODS\YU-DP.M
Last changed    : 3/3/03 2:19:11 PM by Kumar
```




```
==========================================================================
                        Area Percent Report
==========================================================================

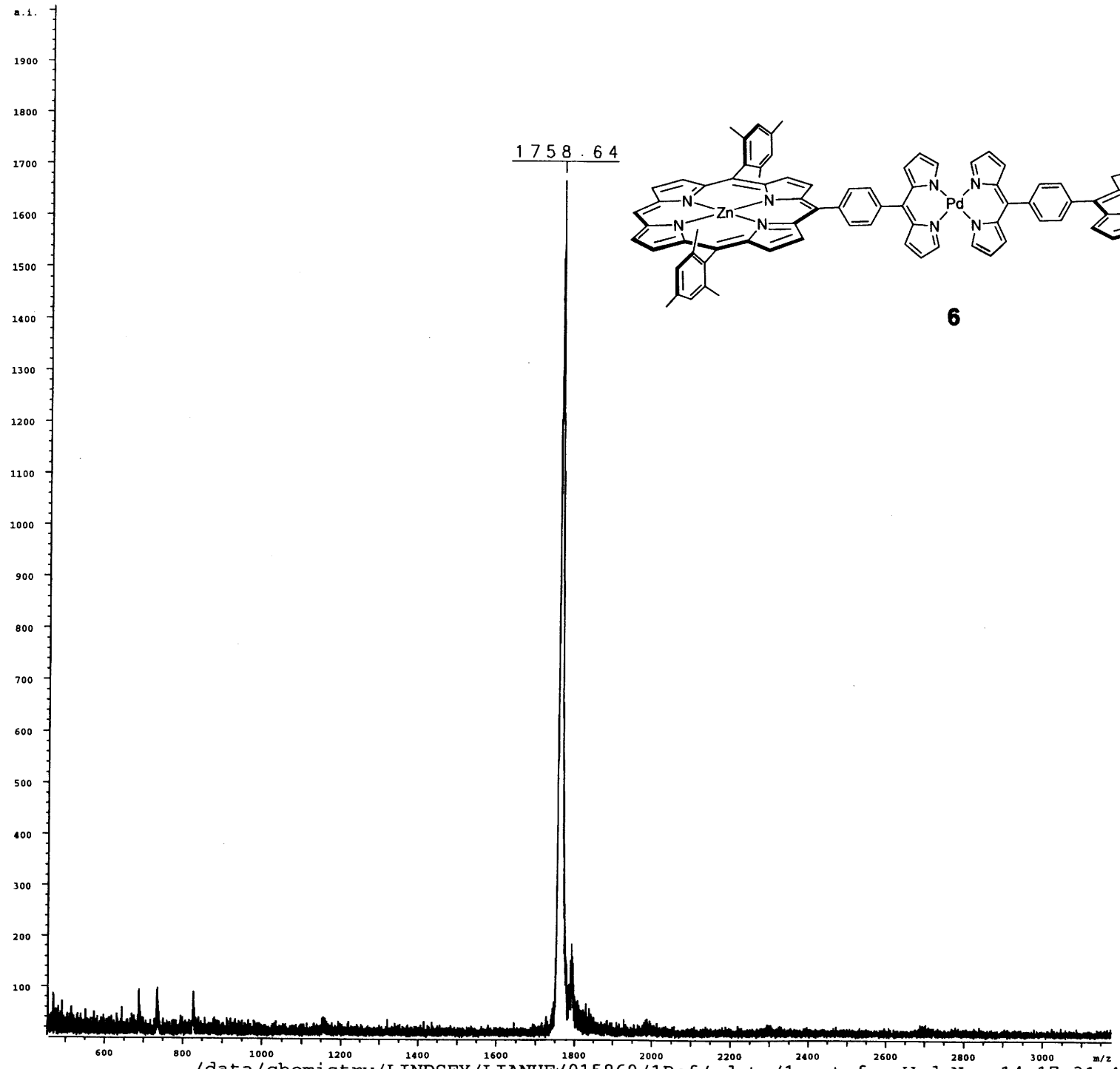
Sorted by Signal
Multiplier                :      1.000000
Dilution                  :      1.000000

Signal 1: DAD1 A, Sig=420,10 Ref=475,10
```

Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.886	BB	0.242	4294.34668	268.53076	100.0000
Totals :				4294.34668	268.53076	

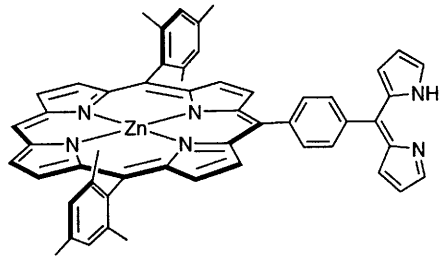
```
==========================================================================
                        *** End of Report ***
```

Analytical SEC trace of **triad-6**



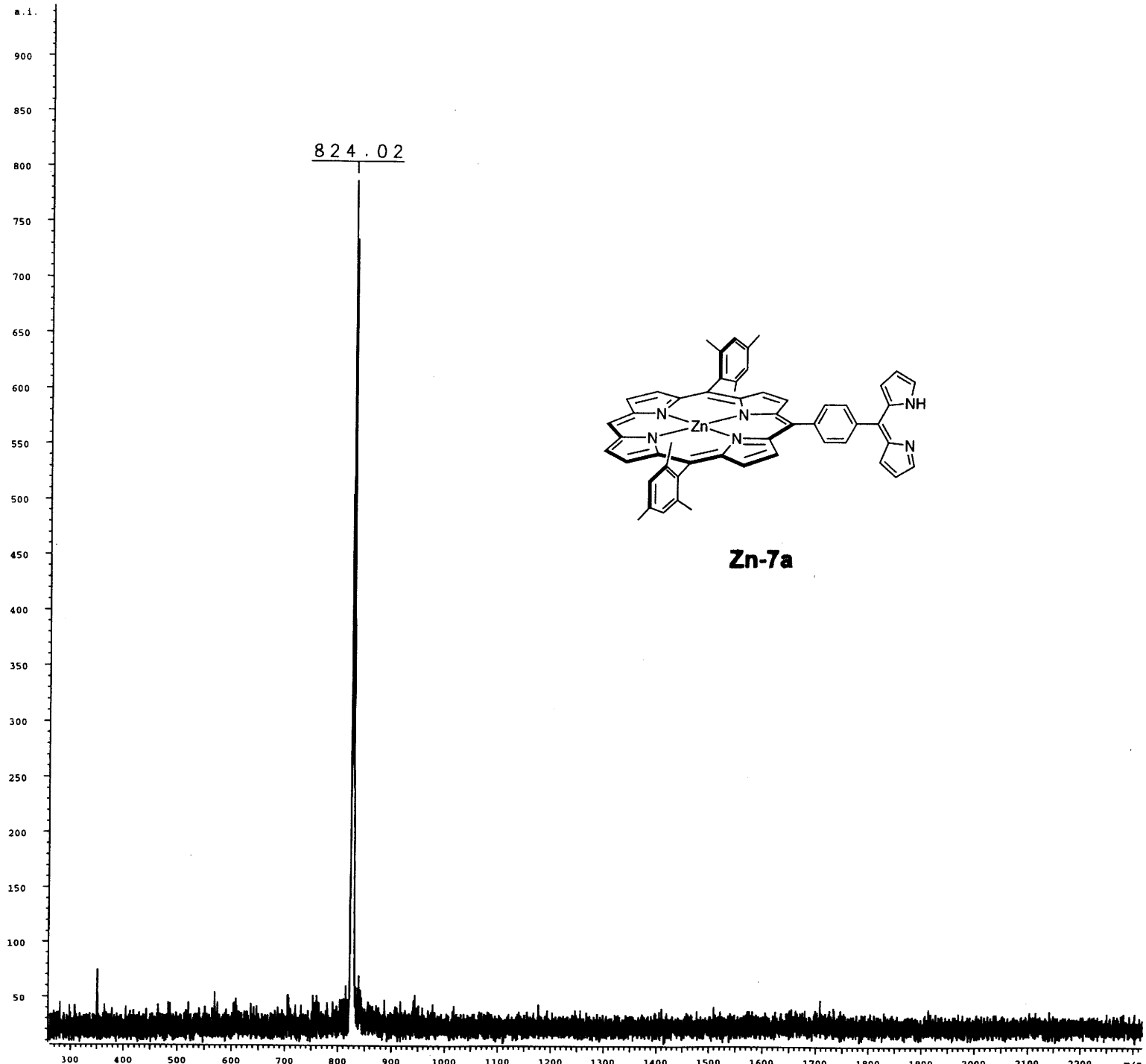
6

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015869
AQ_DATE Wed Nov 14 17:24:12 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS            71
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFull             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udefl               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              37.0
ML1           2071659.729
ML2               333.982
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    Zn-Pd-Zn, final, matrix = dithanol
CMT2    atten. = 37, shots = 71
```



Zn-7a

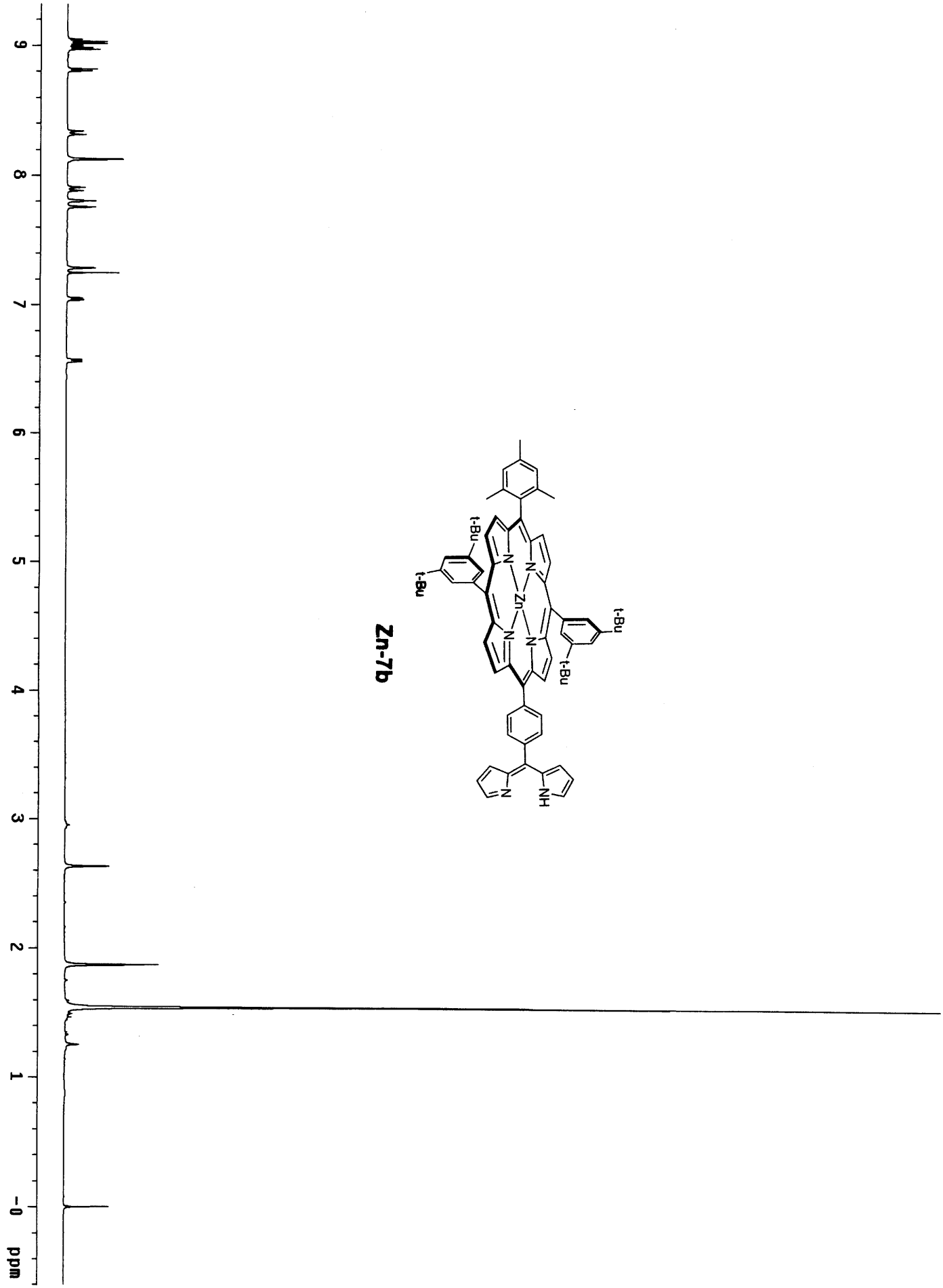
Zn-7a



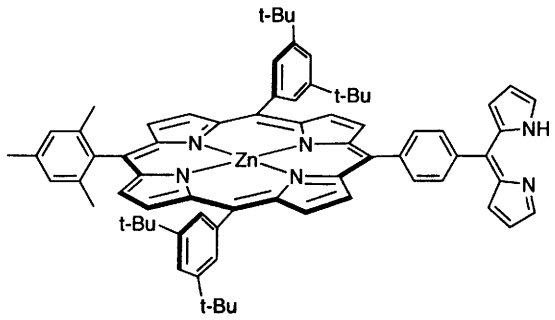
Zn-7a

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015898
AQ_DATE Tue Nov 27 16:55:30 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS           100
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                1.00  [ns]
DELAY             0 [ns]
Uis1             20.00  [kV]
Uis2             18.70  [kV]
Uref1             0.00  [kV]
Ulens             7.50  [kV]
Uhimass          10.00  [kV]
RefFull           0.00  [kV]
UdetL             1.50  [kV]
UdetR             0.00  [kV]
Udef1             2.00  [kV]
REPHZ             1.00  [Hz]
ATTEN             45.0
ML1         2067125.193
ML2             333.982
ML3               0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1          510.84
DPMASS          700.00  [Da]
RENDVAL           0.33
LENDVAL           0.28
IS2ENDV           0.91
CMT1    ZnPdZn+DTT, CC, pure
CMT2    attn = 45, shot = 100
```


/data/chemistry/LINDSEY/LIANHE/015898/6Ref/pdata/1 tof Tue Nov 27 16:55:49 2001

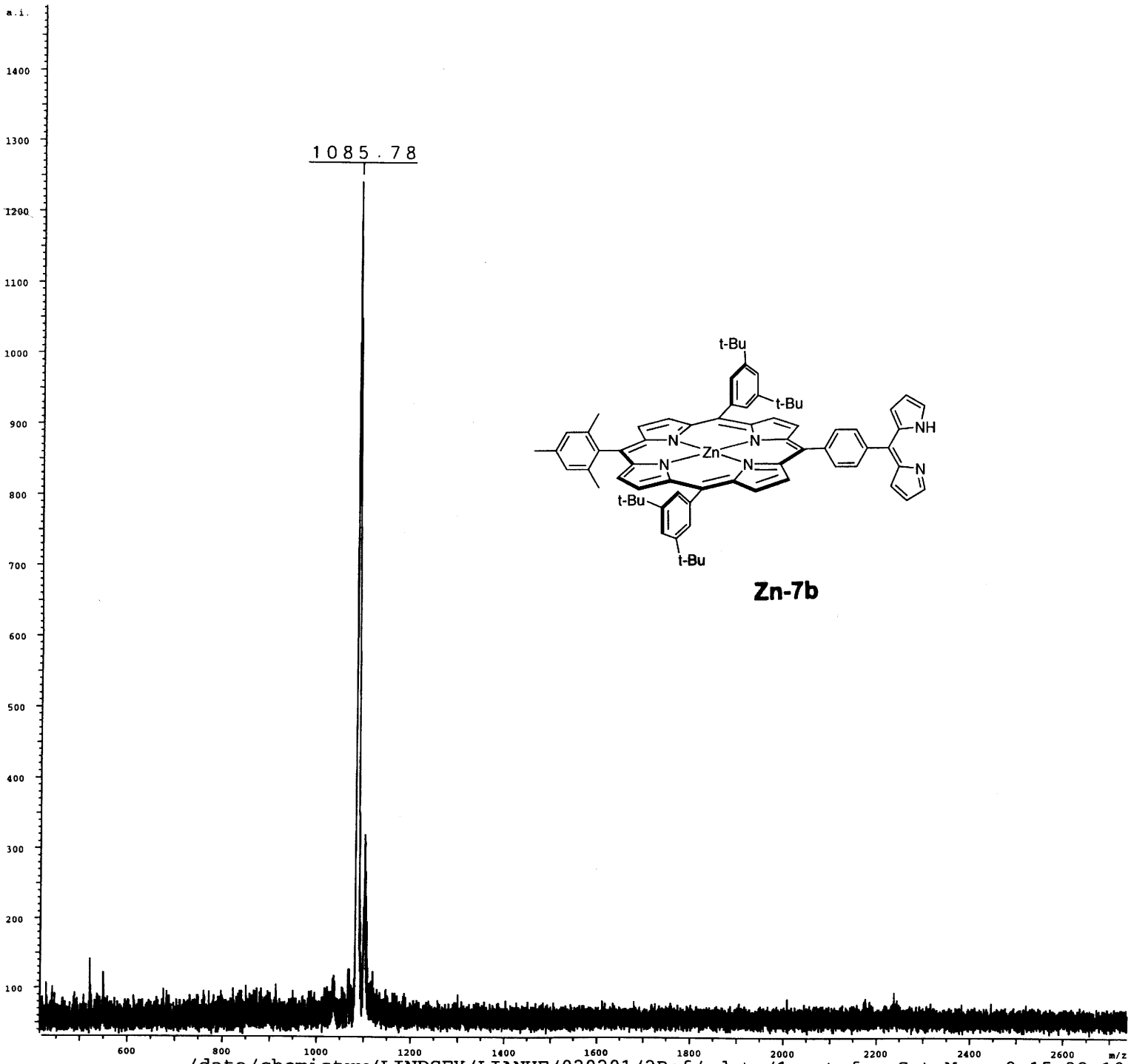


Zn-7b


t-Bu
t-Bu
NH
N
Zn
N
N
N
t-Bu
t-Bu

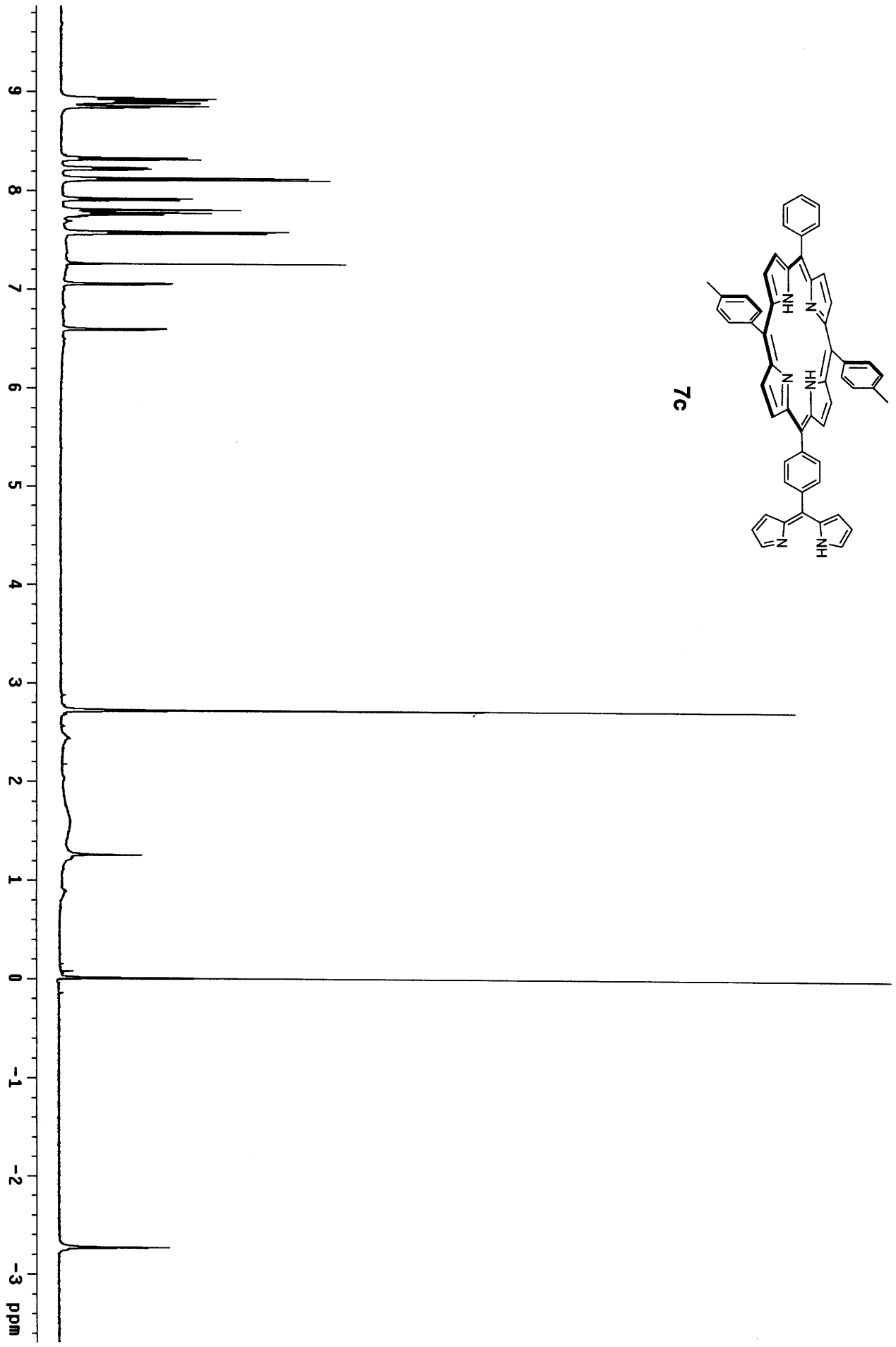
Zn-7b

9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm

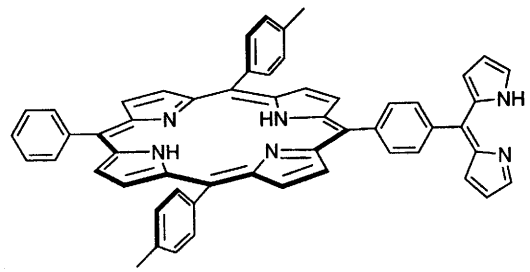


Zn-7b

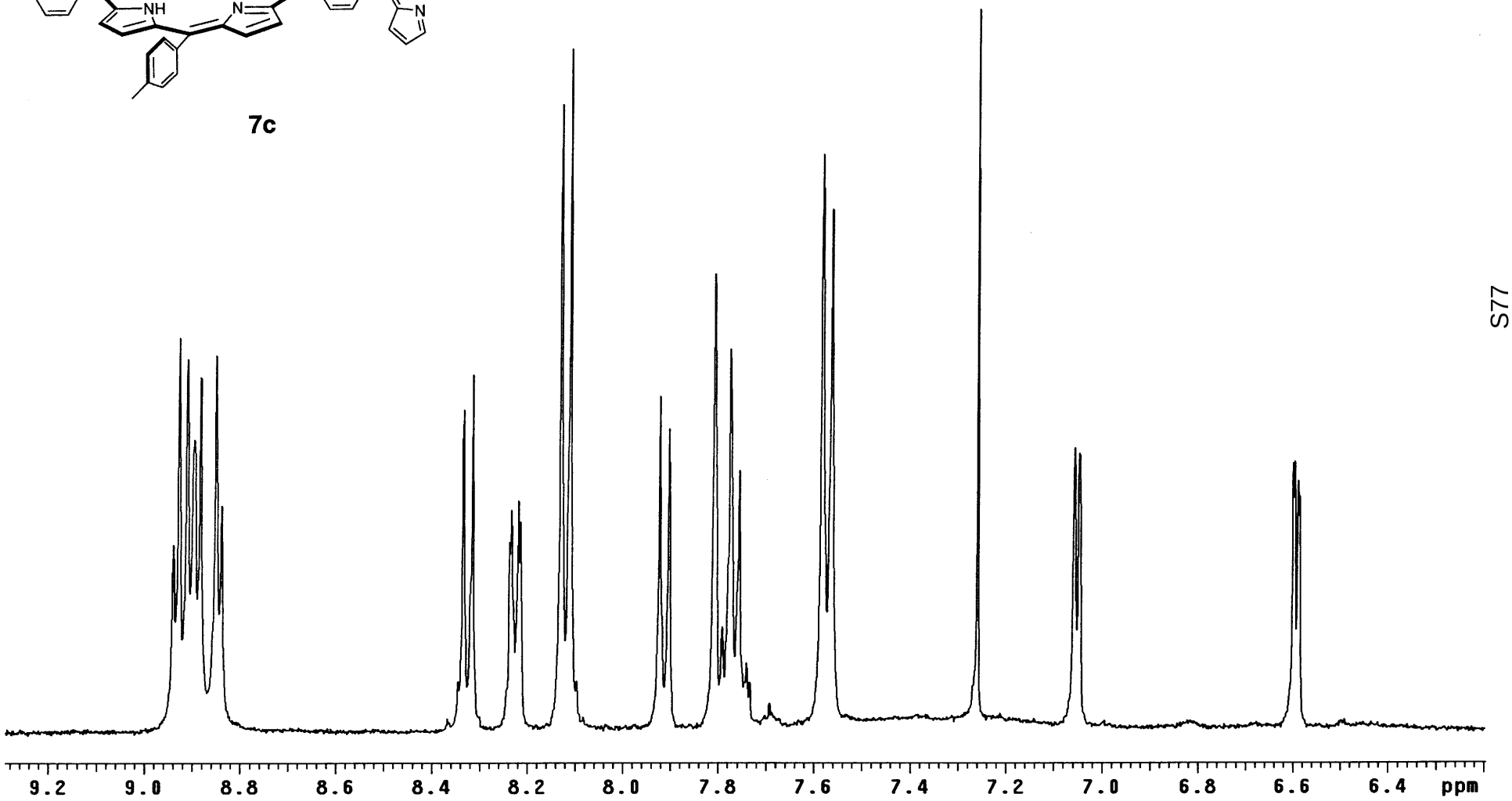
```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  020201
AQ_DATE Sat Mar  9 15:29:15 2002
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD          40000
NoSHOTS        87
SMONUM          0
SMOPTS1         0
SMOPTS2         0
SMOPTS3         0
DW              1.00  [ns]
DELAY           0 [ns]
Uis1           20.00  [kV]
Uis2           18.70  [kV]
Urefl           0.00  [kV]
Ulens           7.50  [kV]
Uhimass        10.00  [kV]
RefFull         0.00  [kV]
UdetL           1.50  [kV]
UdetR           0.00  [kV]
Udefl           2.00  [kV]
REPHZ           1.00  [Hz]
ATTEN          34.0
ML1        2067125.193
ML2            333.982
ML3              0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSEND no
LLNSEND no
UIS2END no
DPCAL1         510.84
DPMASS         700.00  [Da]
RENDVAL          0.33
LENDVAL          0.28
IS2ENDV          0.91
CMT1    Ms-2-t-Bu-Ph-Dp, pure
CMT2    Attn=36, shots = 87
```

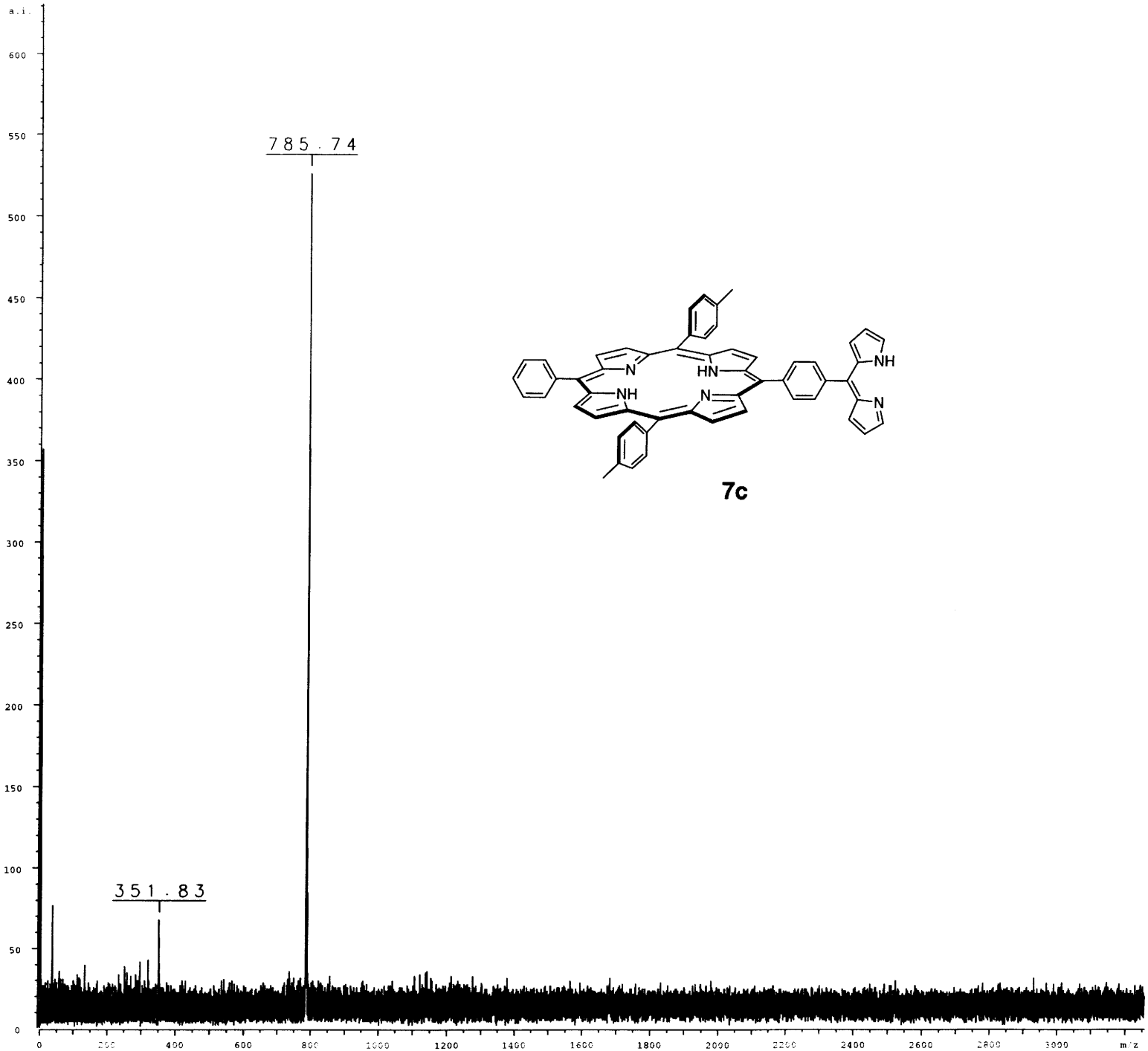


7c



7c

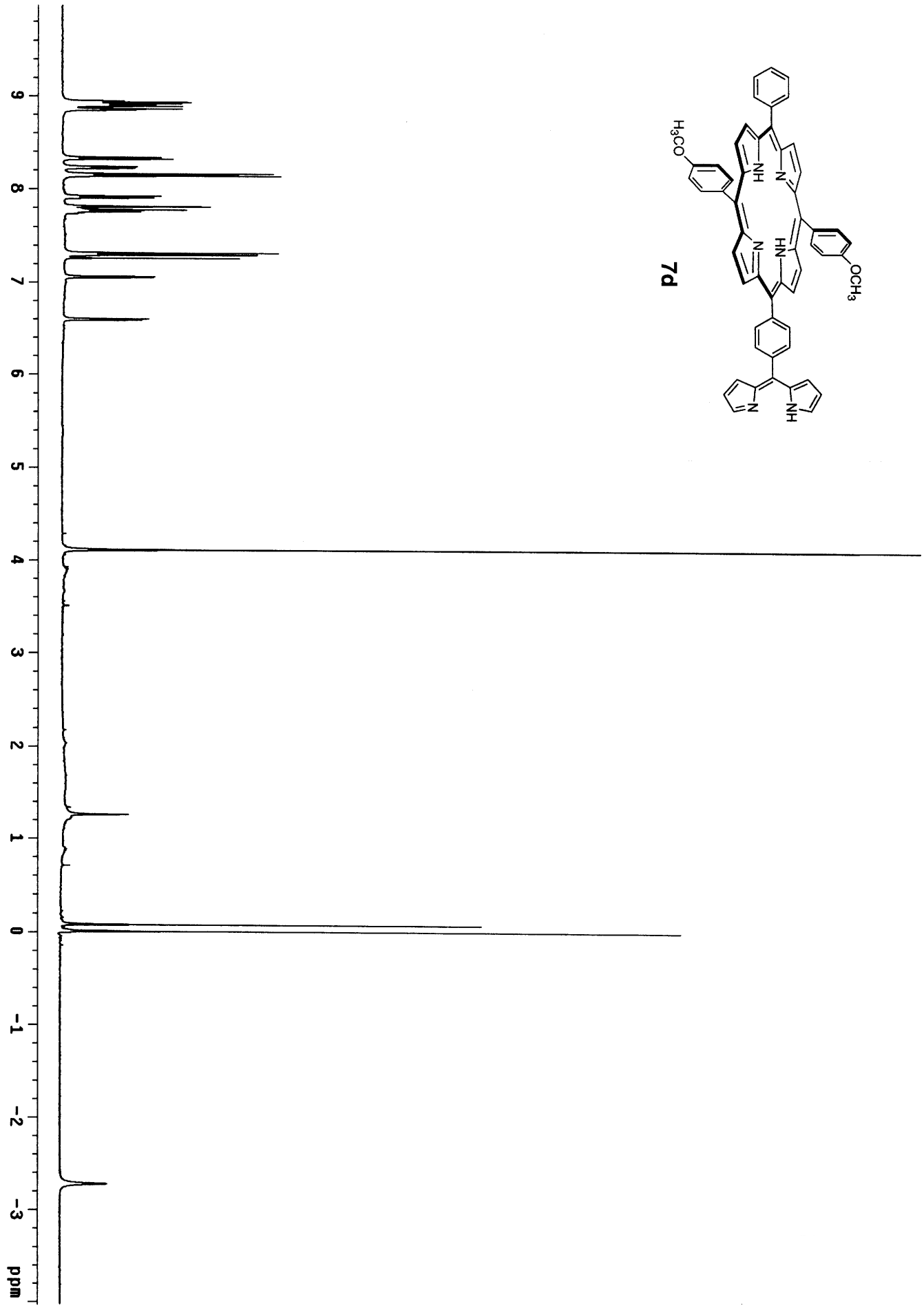




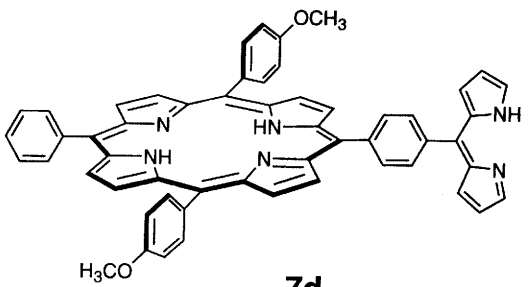
7c

```
INSTRUM TOF
OpId     N. Srinivasan
SMPNAM   030101
AQ_DATE  Mon Jul 29 11:11:04 2002
PATH     /data/chemistry/LINDSEY/KUMAR
POLARI   POS
AQOP_m   Reflector
TD              40000
NoSHOTS            50
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Uref1               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFul1             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udef1               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              28.0
ML1          2071692.944
ML2              333.982
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     kmk-319   7/29/02
CMT2     att 28
```

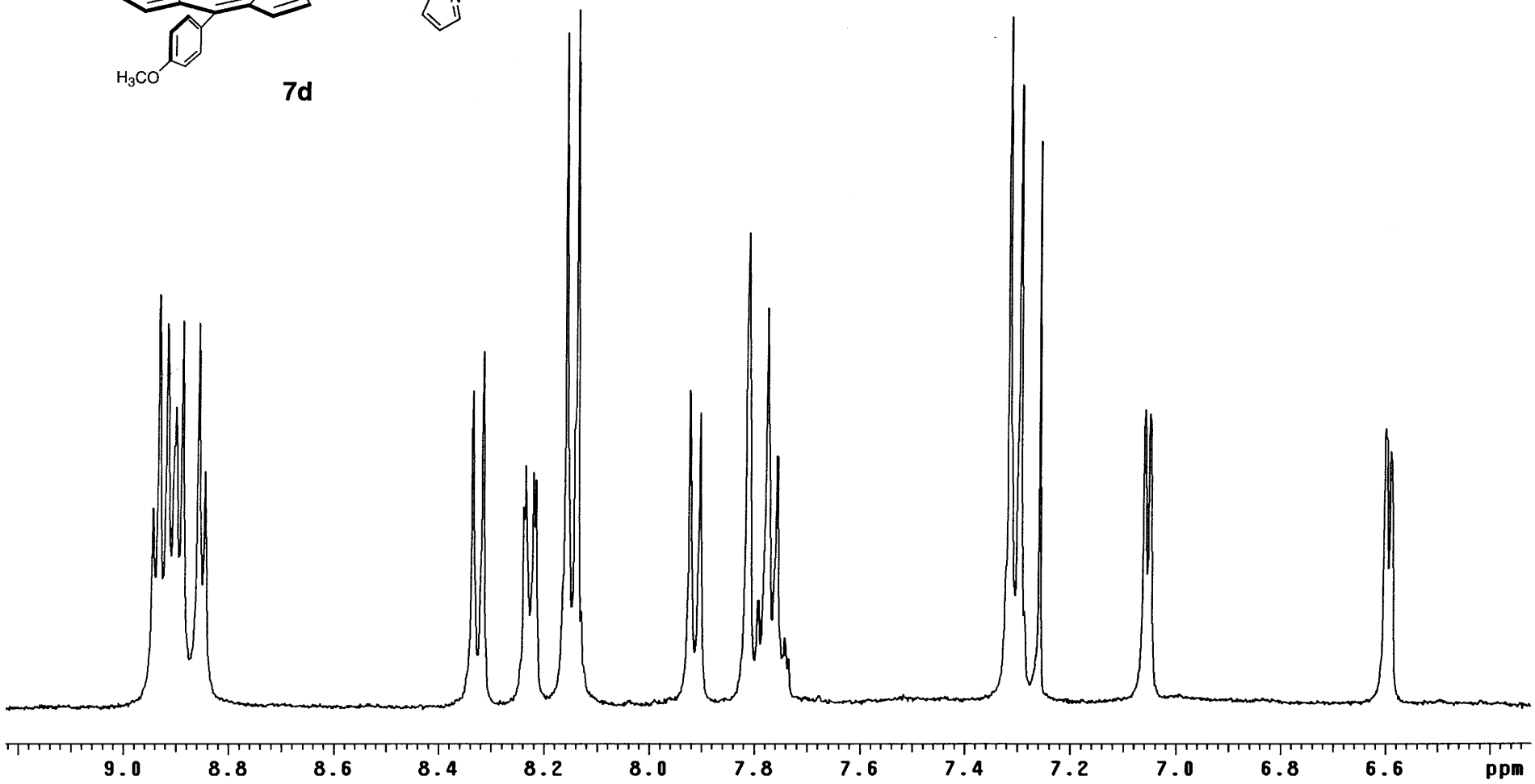
/data/chemistry/LINDSEY/KUMAR/030101/2Ref/pdata/1 tof Mon Jul 29 11:18:49 2002

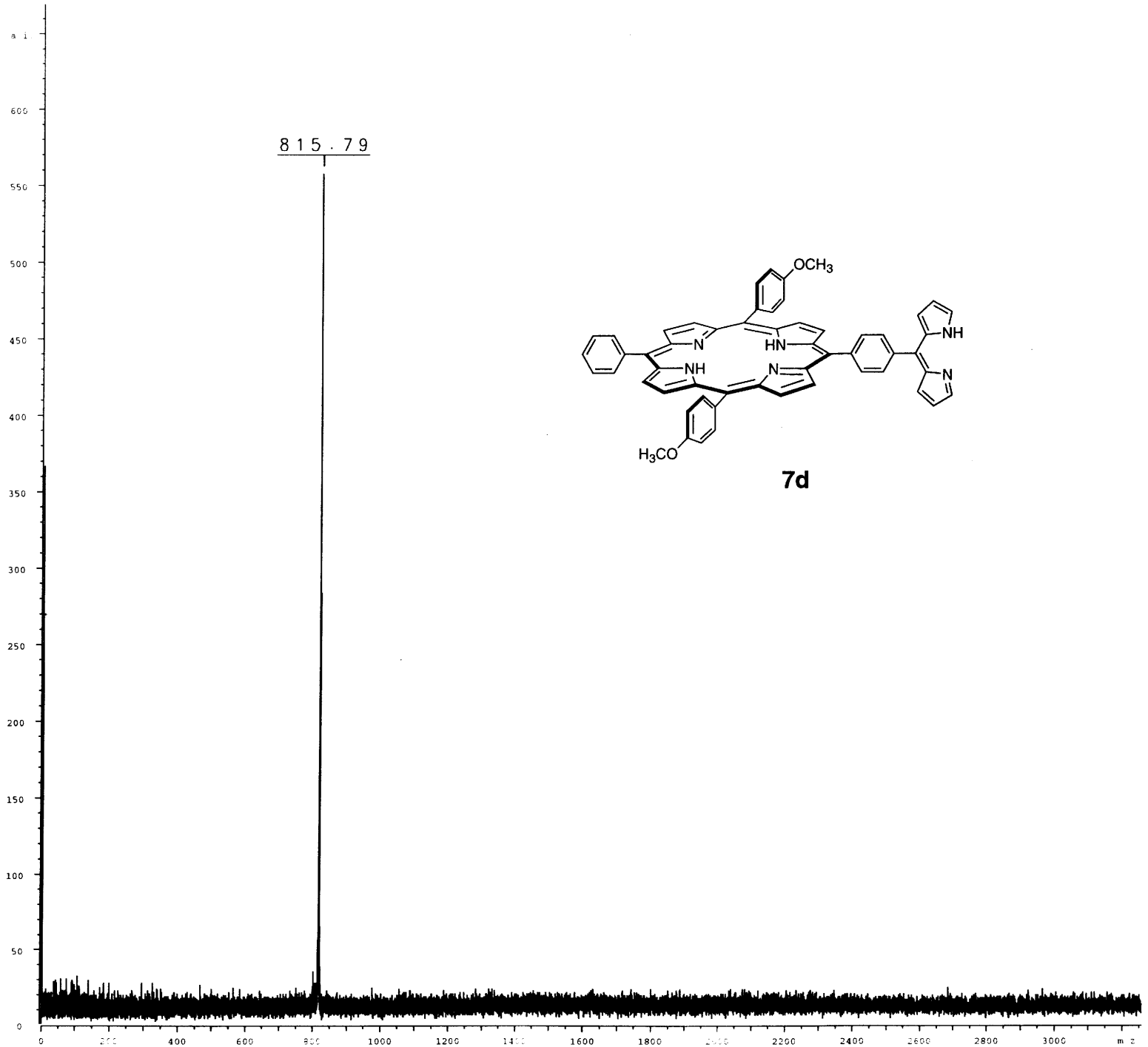


7d



7d

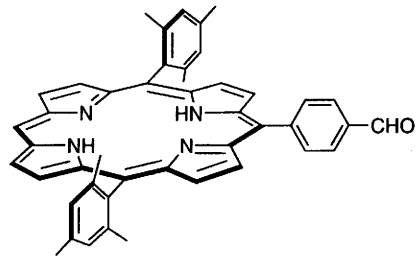




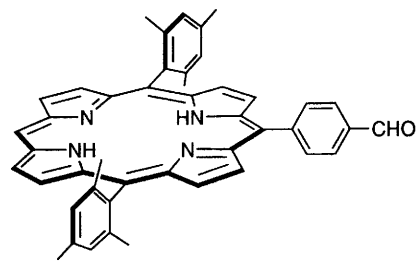
7d

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  030102
AQ_DATE Mon Jul 29 11:14:41 2002
PATH    /data/chemistry/LINDSEY/KUMAR
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS            50
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFull             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udefl               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              29.0
ML1           2071692.944
ML2               333.982
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    kmk-318   7/29/02
CMT2    att 28
```

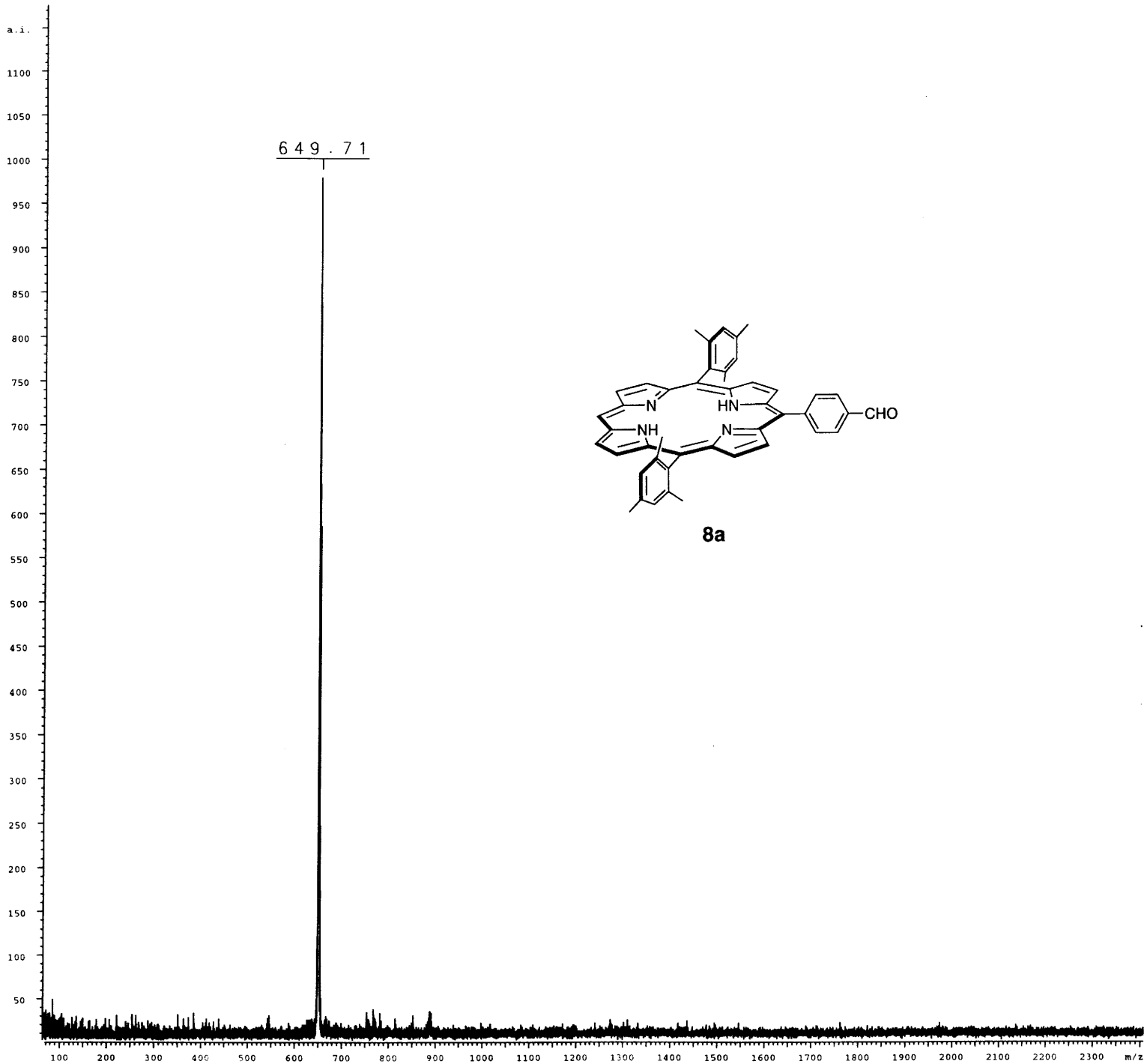
/data/chemistry/LINDSEY/KUMAR/030102/1SRef/pdata/1 tof Mon Jul 29 11:19:24 2002



8a



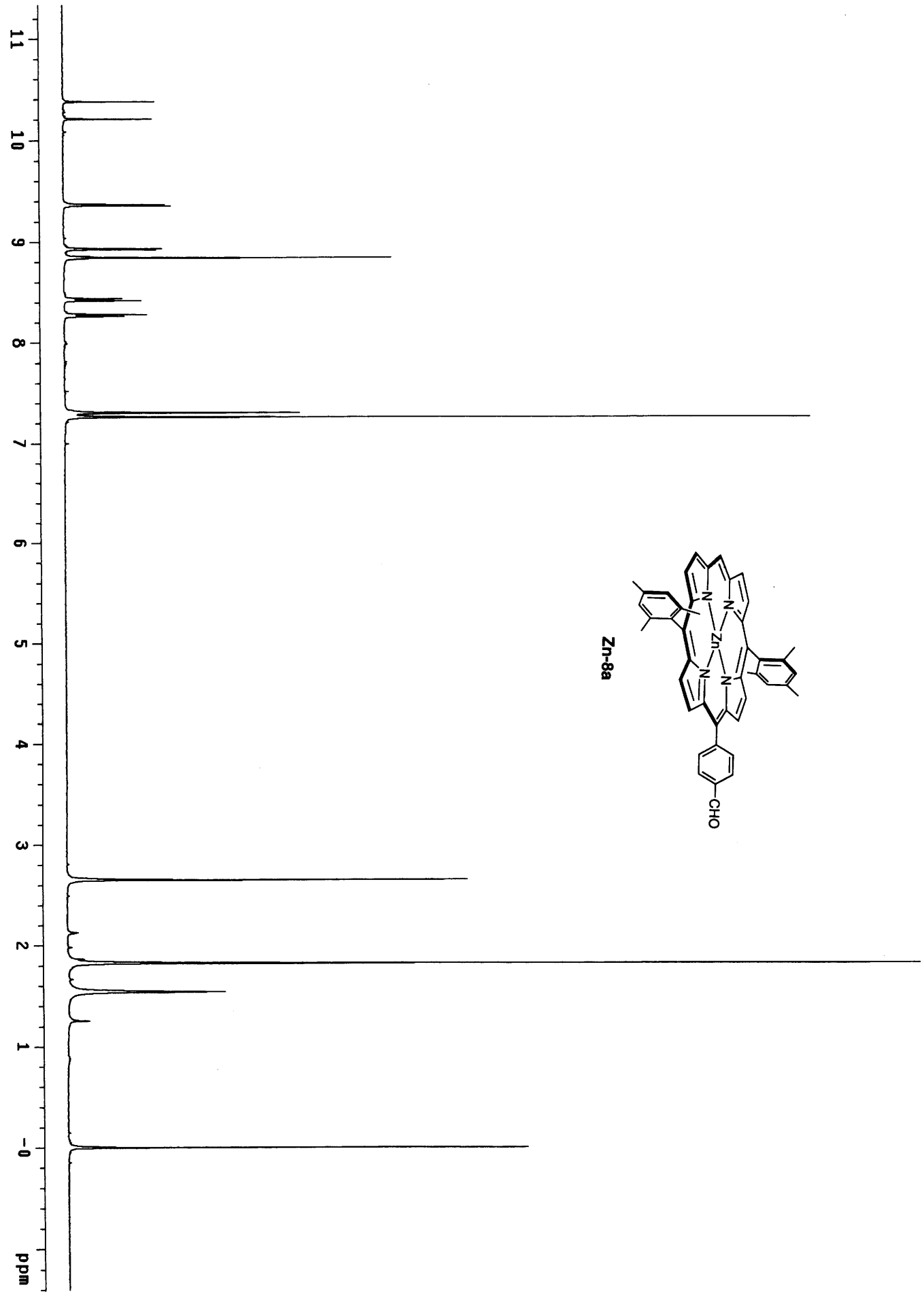
8a

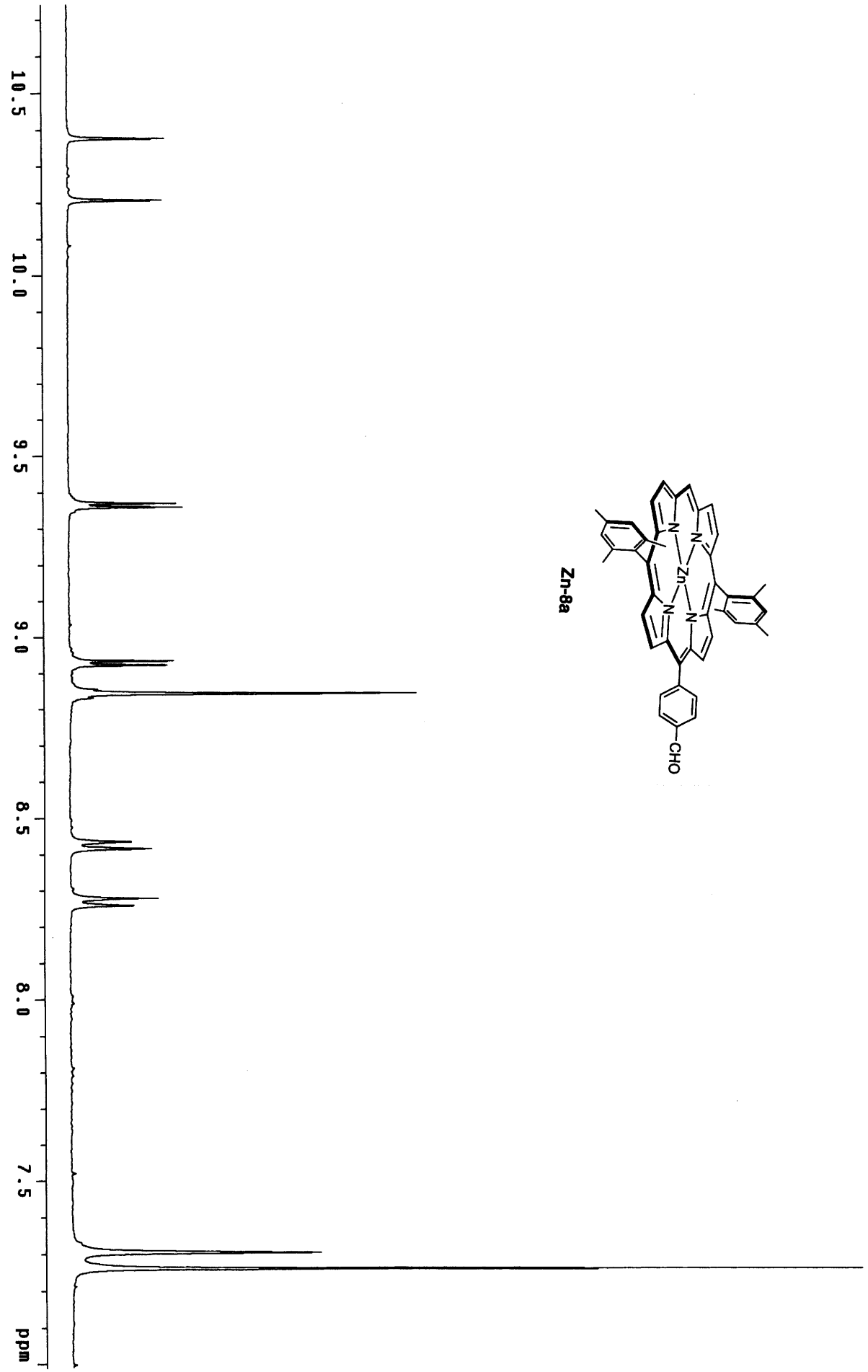


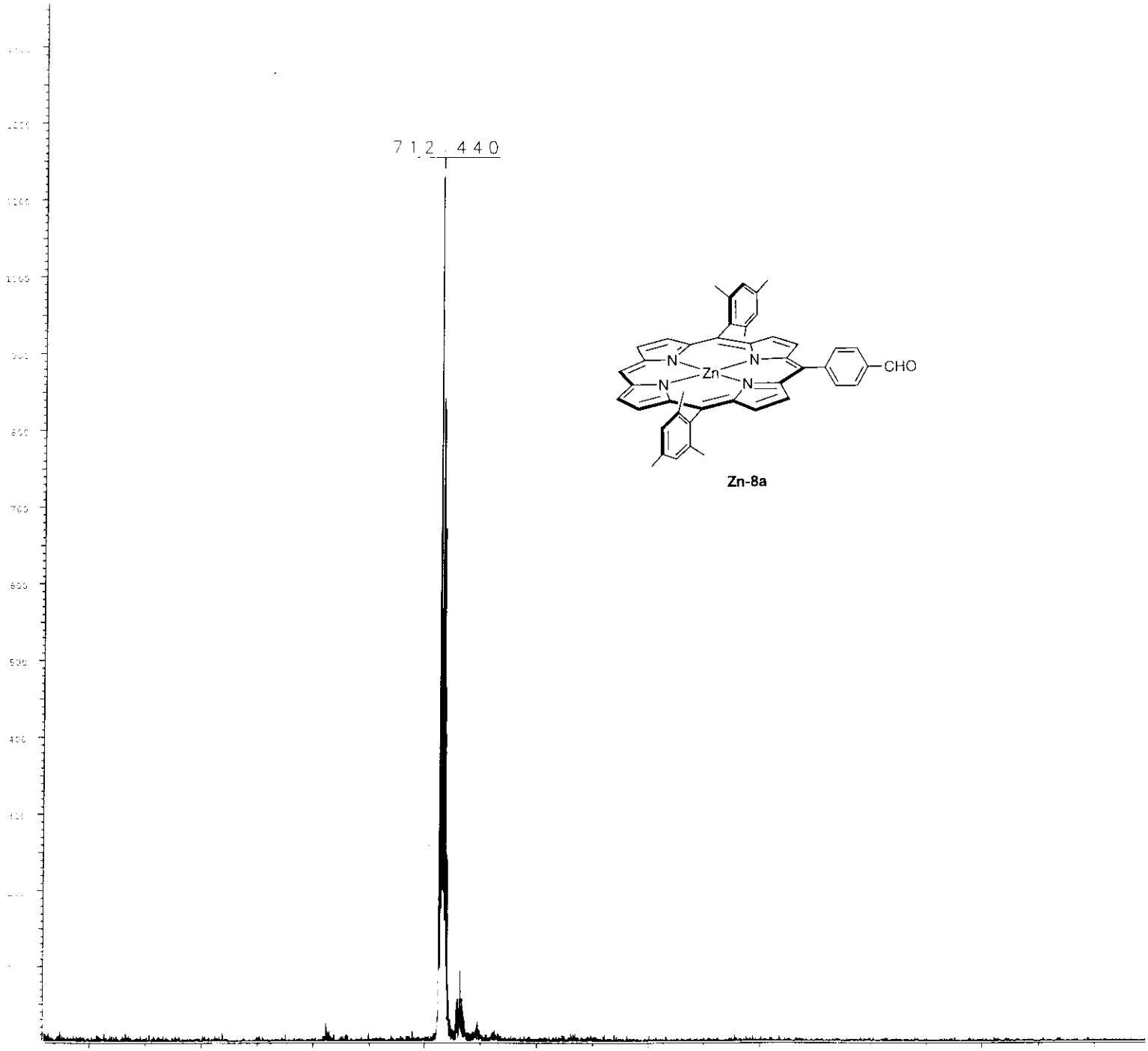
8a

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  020140
AQ_DATE Wed Feb 27 10:44:00 2002
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS            51
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00   [ns]
DELAY               0 [ns]
Uis1               20.00   [kV]
Uis2               18.70   [kV]
Urefl               0.00   [kV]
Ulens               7.50   [kV]
Uhimass            10.00   [kV]
RefFull             0.00   [kV]
UdetL               1.50   [kV]
UdetR               0.00   [kV]
Udefl               2.00   [kV]
REPHZ               1.00   [Hz]
ATTEN              43.0
ML1           2067125.193
ML2               333.982
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    1H-2Ms-Benzene-CHO-Fb, pure
CMT2    attn =40, shot = 50
```

/data/chemistry/LINDSEY/LIANHE/020140/1Ref/pdata/1 tof Wed Feb 27 10:51:24 2002


11
10
9
8
7
6
5
4
3
2
1
0
ppm
Zn-8a
N
N
Zn
N
N
CHO

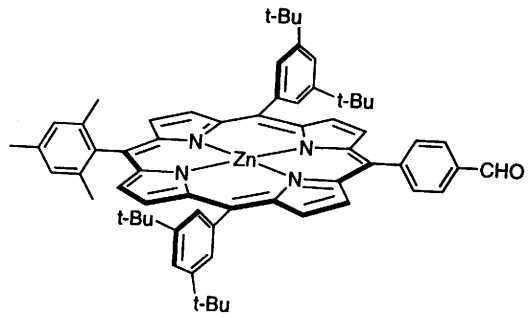

10.5
10.0
9.5
9.0
8.5
8.0
7.5
ppm
Zn-8a
N
N
Zn
N
N
CHO



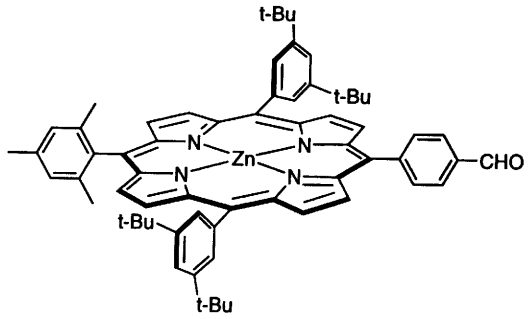
Zn-8a

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  030313
AQ_DATE Tue Jun  3 10:16:10 2003
PATH    data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQSEQ.m Reflect
TD              32768
NoSHOTS            50
SMONUM              1
SMOPTS1             1
SMOPTS2             1
SMOPTS3             1
DW                 1.00  [ns]
DELAY              0.00  [ns]
Uis1              20.00  [kV]
Uis2              18.75  [kV]
Uref1              1.00  [kV]
Ulens              7.50  [kV]
Uhlmass           19.00  [kV]
RefFull            1.00  [kV]
UdetL              1.50  [kV]
UdetR              2.00  [kV]
Udef1              2.00  [kV]
REPHZ              1.00  [Hz]
ATTEN             16.0
ML1          2063721.151
ML2           329.709
ML3             0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1          529.84
DPMASS          700.00  [Da]
RBNDVAL           0.35
LBNDVAL           0.26
IS2BNDV           1.91
CMT1    Zn-8a + SE 152
CMT2    no matrix
```

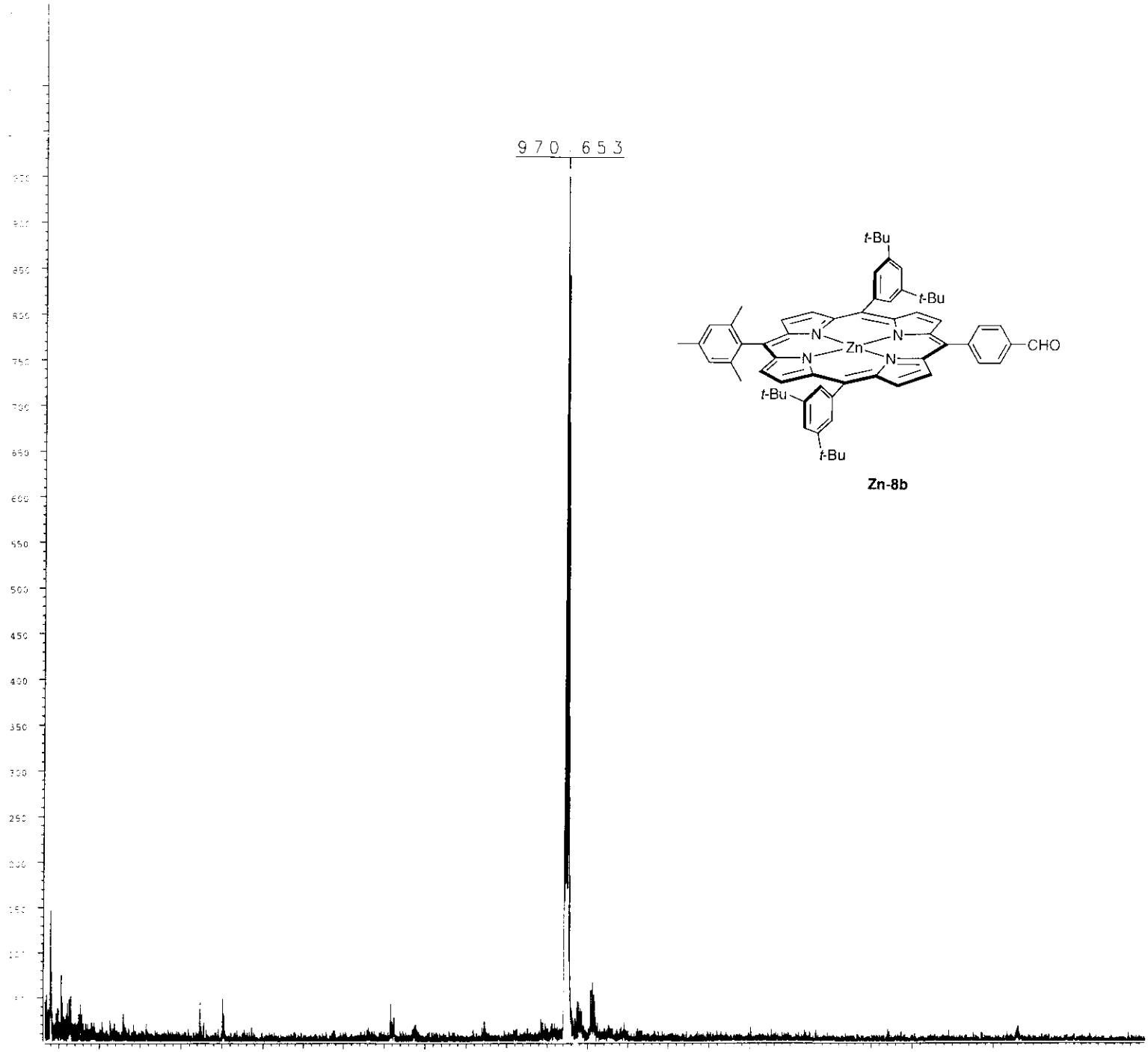
/data/chemistry/LINDSEY/LIANHE/030313/2Ref/pdata/1 tof Tue Jun 3 10:19:18 2003



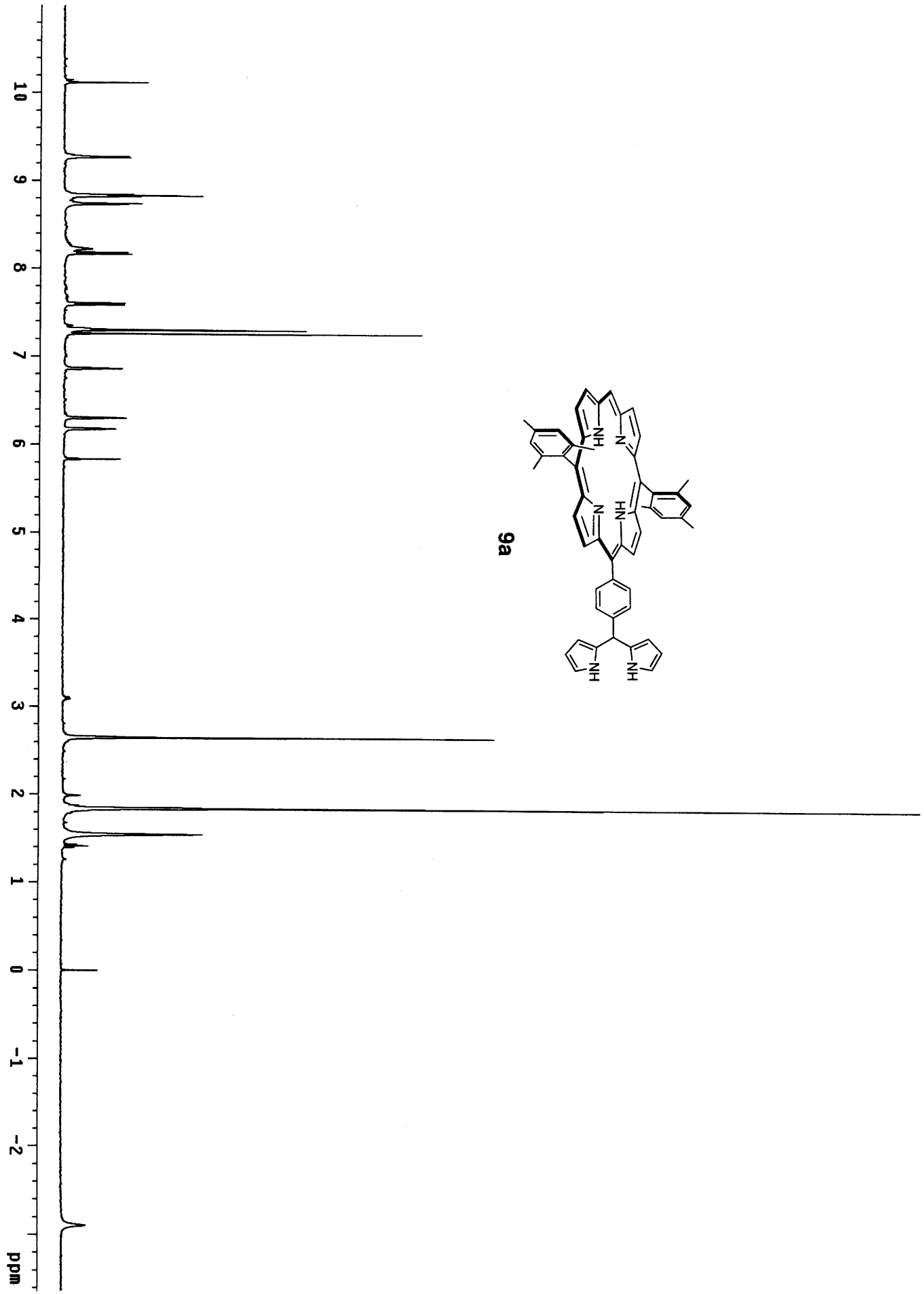
Zn-8b



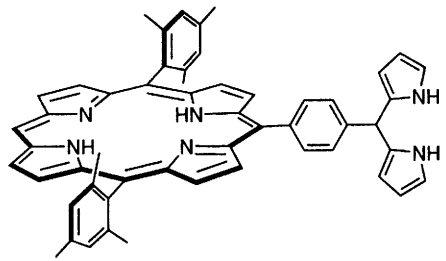
Zn-8b



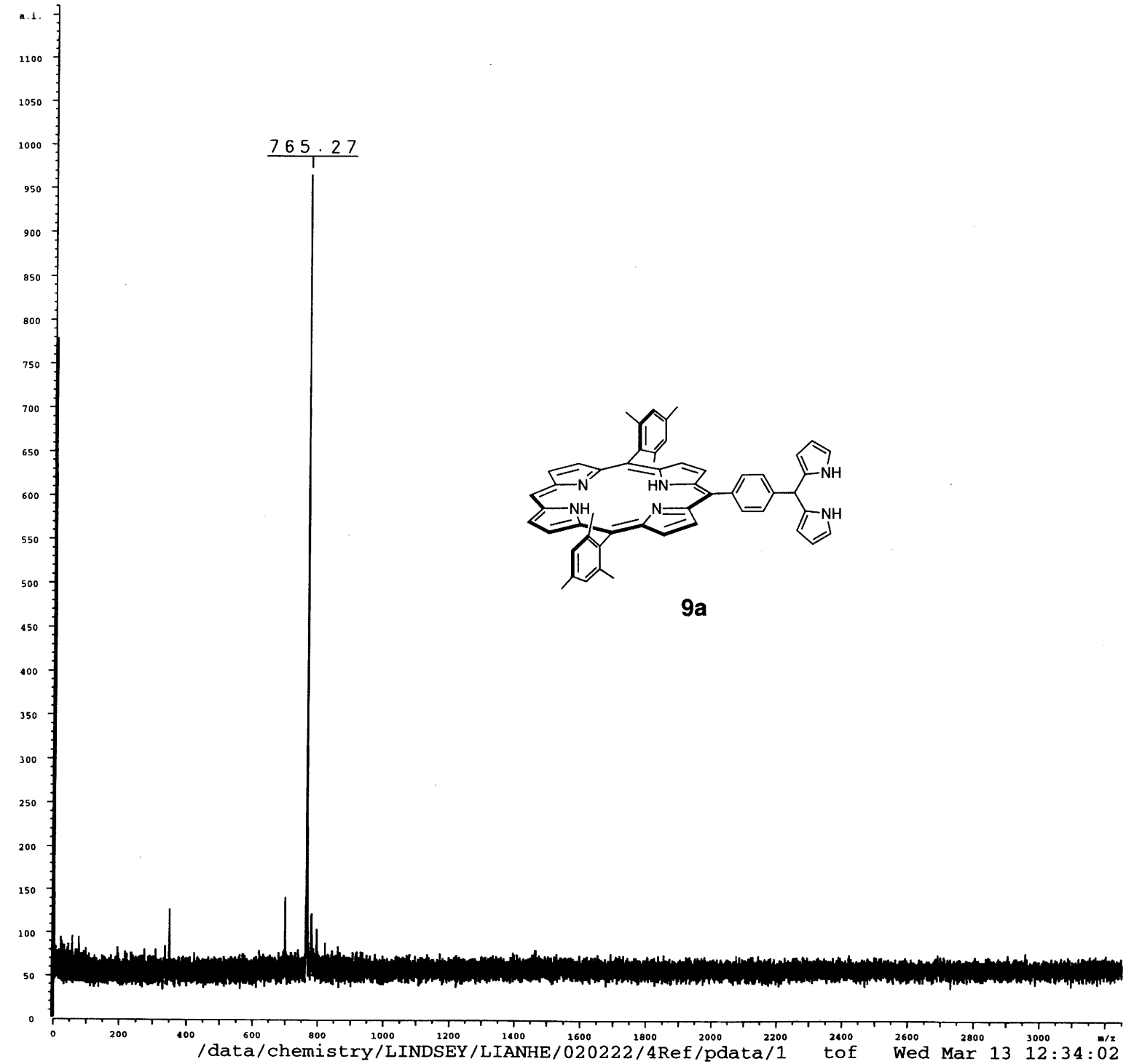

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  030314
AQ_DATE Tue Jun  3 10:24:46 2003
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
ANSP_M  Reflector
                  35000
NoSHOTS             65
SMCNUM               0
SMCPTS1              0
SMCPTS2              0
SMCPTS3              0
DU                1.00  [ns]
DELAY            0 [ns]
Uis1            20.00  [kV]
Uis2            18.70  [kV]
Uref1            0.00  [kV]
Ulens            7.50  [kV]
Uhimass         10.00  [kV]
RefPul1          0.00  [kV]
UdetL            1.50  [kV]
UdetR            0.00  [kV]
Udef1            2.00  [kV]
PEPHZ            1.00  [Hz]
ATTEN            30.0
ML1         2063321.150
ML2             326.709
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           0.53
LBNDVAL           0.28
IS2BNDV           0.91
CMT1    Zn-8b = SE 153
CMT2    no matrix
```



9a

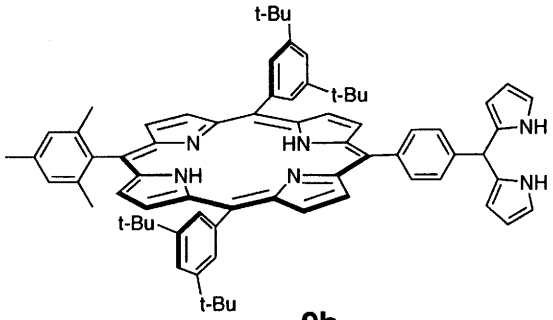


9a



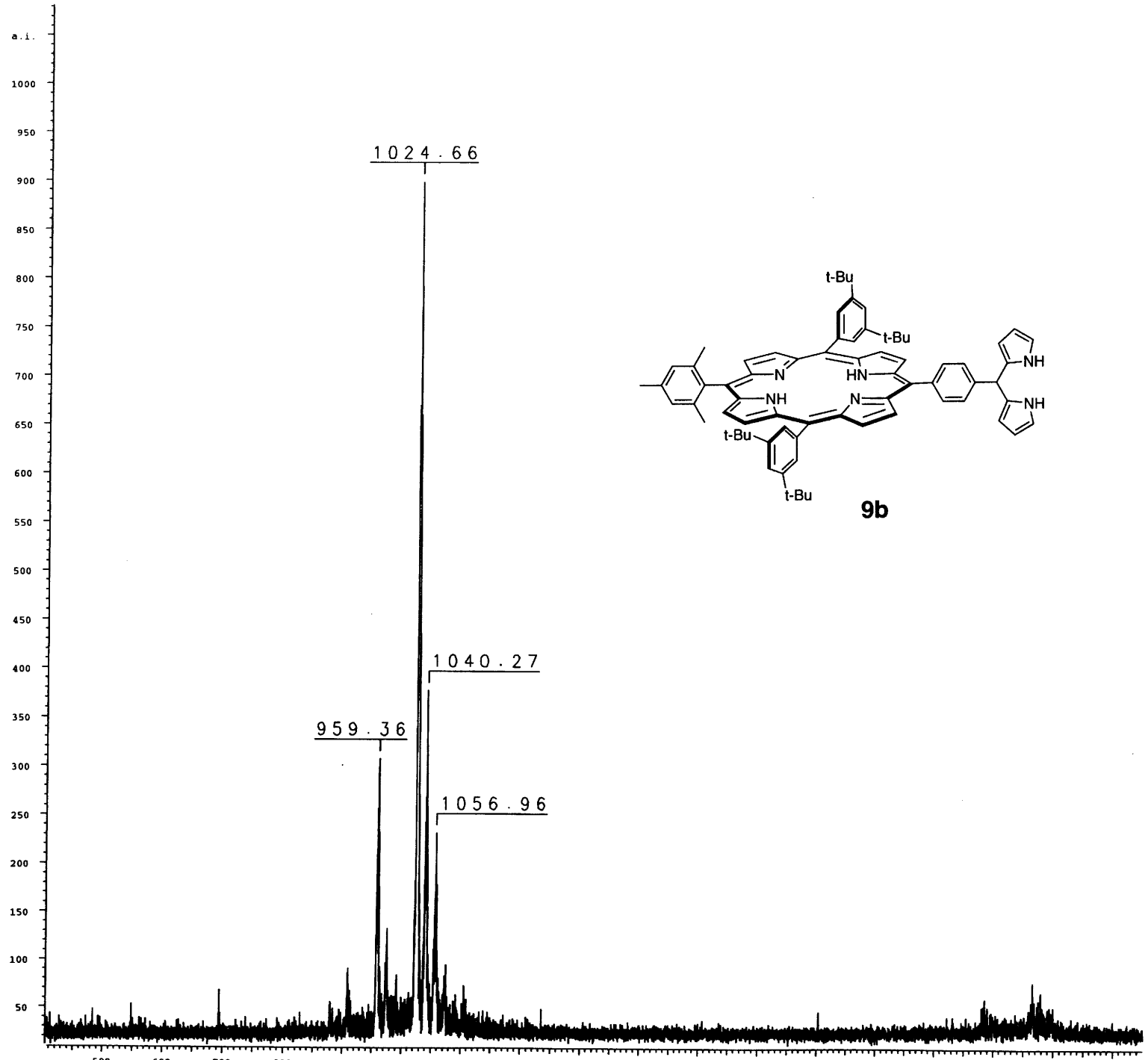
9a

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  020222
AQ_DATE Wed Mar 13 12:33:28 2002
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS           100
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [kV]
RefFull             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udefl               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN              40.0
ML1          2067125.193
ML2              333.982
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    1H-2Ms-Ph-DPM-Fb, pure
CMT2    Attn= 40 shots = 100
```



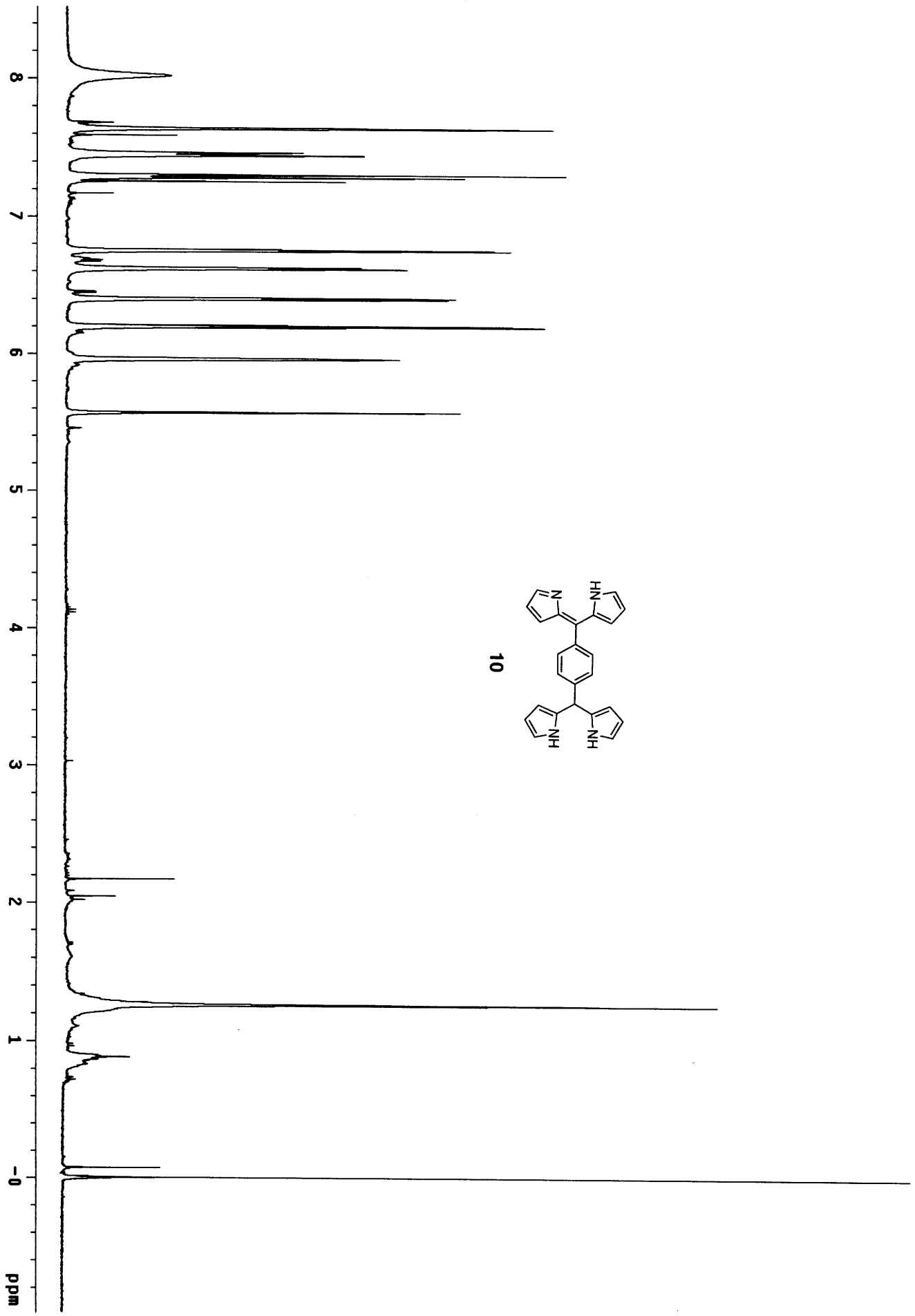
9b

9b



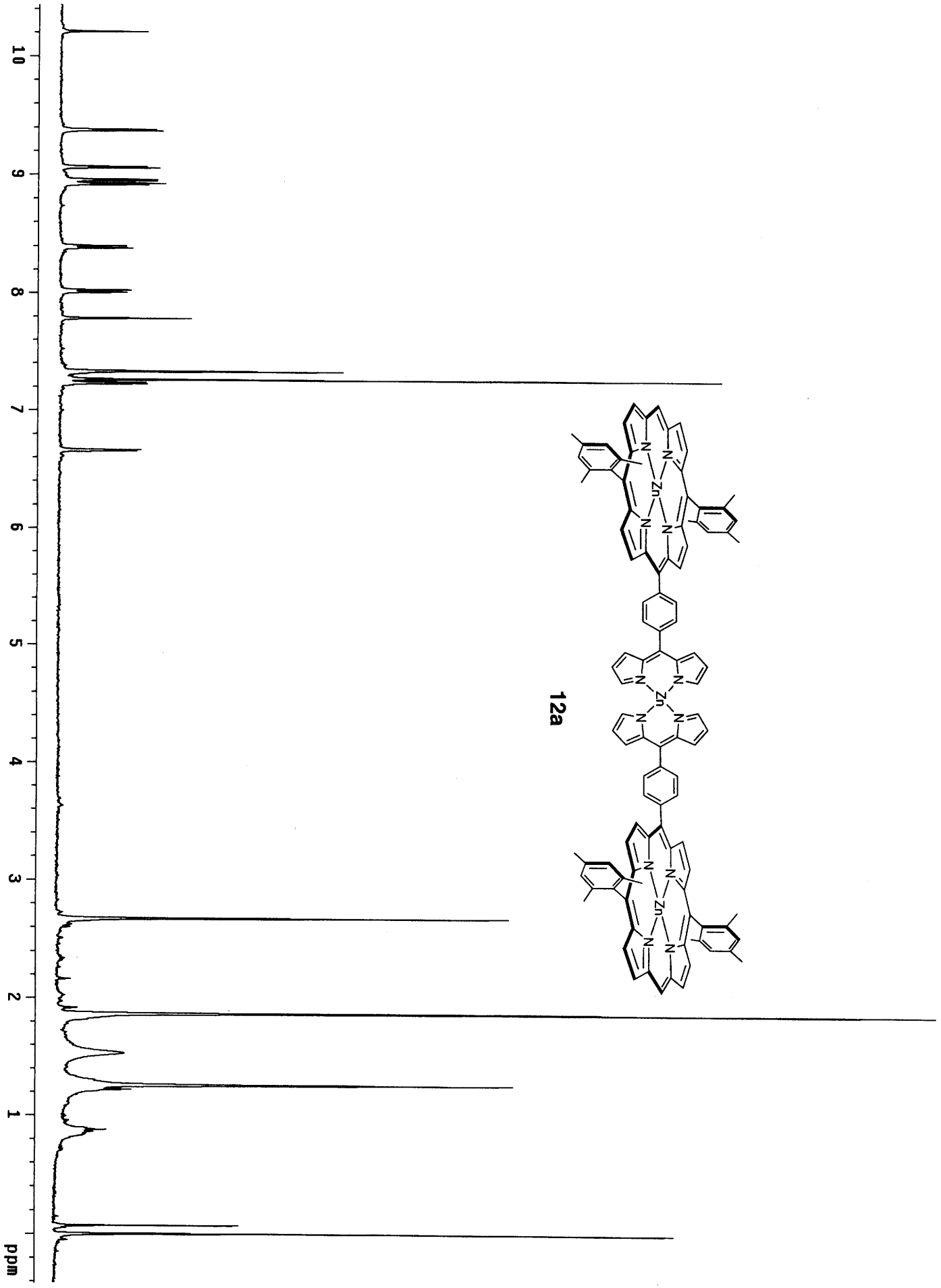
9b

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  020198
AQ_DATE Fri Mar  8 16:15:57 2002
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD          40000
NoSHOTS        39
SMONUM          0
SMOPTS1         0
SMOPTS2         0
SMOPTS3         0
DW              1.00   [ns]
DELAY           0 [ns]
Uis1           20.00   [kV]
Uis2           18.70   [kV]
Urefl           0.00   [kV]
Ulens           7.50   [kV]
Uhimass        10.00   [kV]
RefPull         0.00   [kV]
UdetL           1.50   [kV]
UdetR           0.00   [kV]
Udefl           2.00   [kV]
REPHZ           1.00   [Hz]
ATTEN           35.0
ML1        2067125.193
ML2         333.982
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    Ms-2-t-Bu-Ph-DPm. Pure
CMT2    Attn=35, shots = 40
```

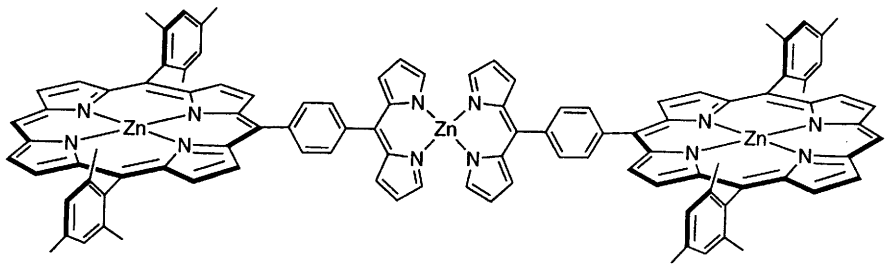


10

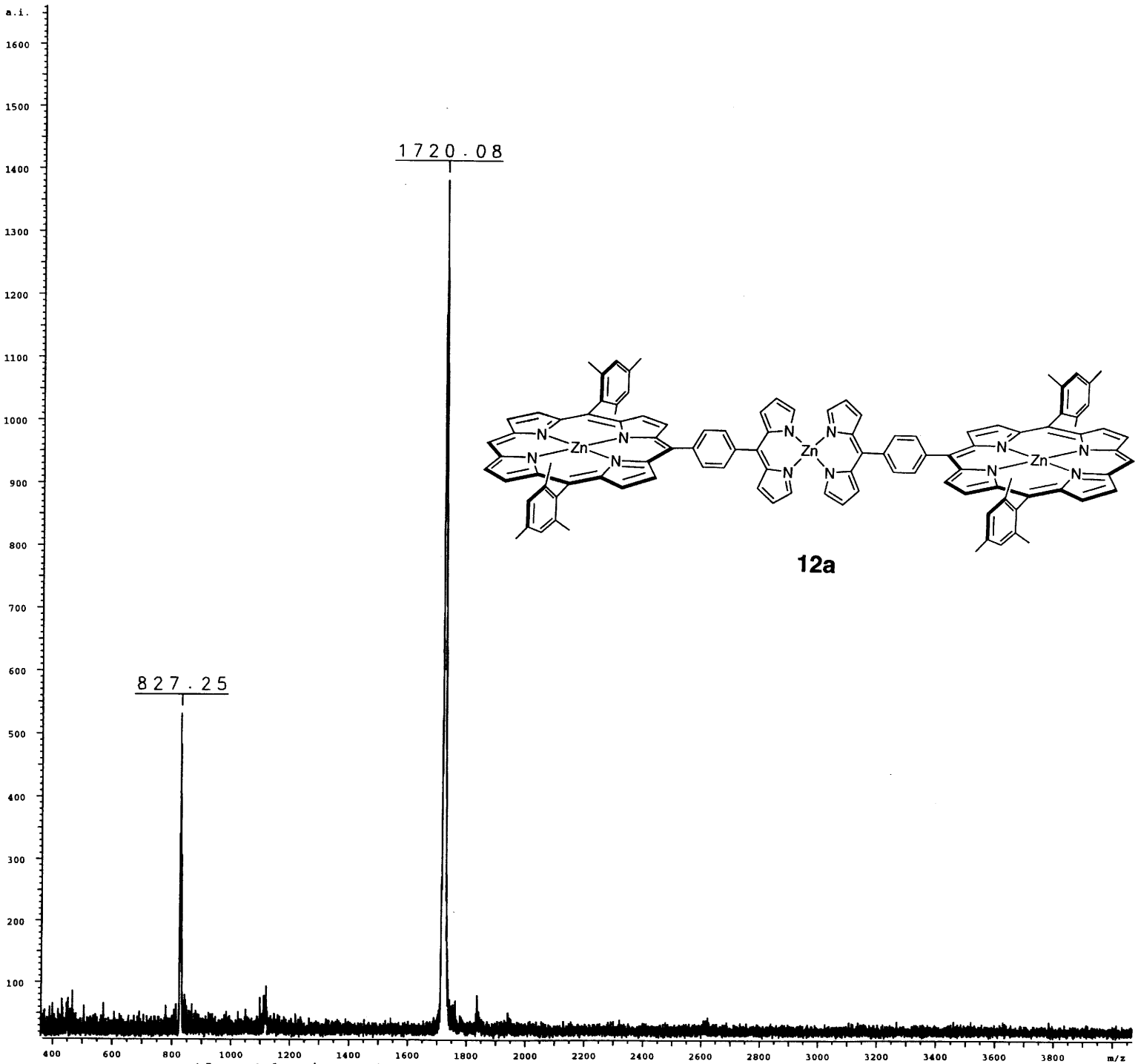
10



12a

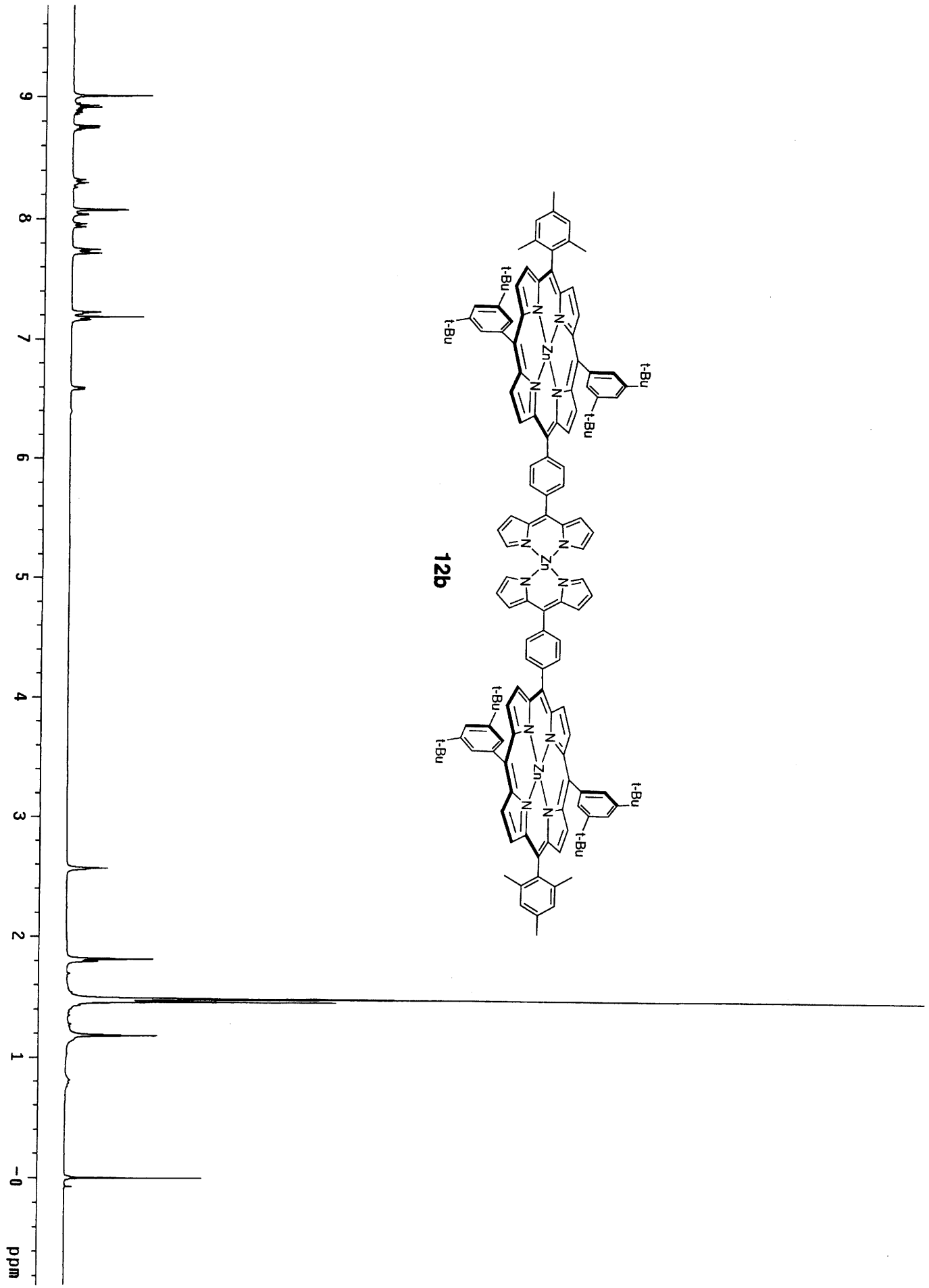


12a

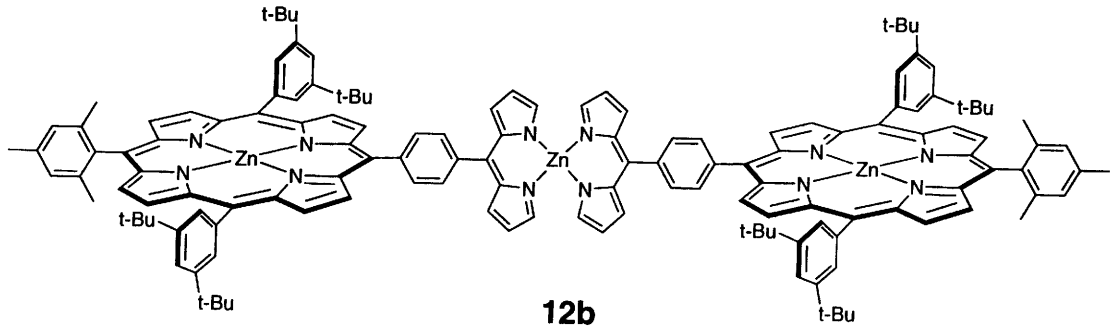


12a

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015900
AQ_DATE Wed Nov 28 10:13:53 2001
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              50000
NoSHOTS           100
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                1.00  [ns]
DELAY             0 [ns]
Uis1             20.00  [kV]
Uis2             18.70  [kV]
Urefl             0.00  [kV]
Ulens             7.50  [kV]
Uhimass          10.00  [kV]
RefFull           0.00  [kV]
UdetL             1.50  [kV]
UdetR             0.00  [kV]
Udefl             2.00  [kV]
REPHZ             1.00  [Hz]
ATTEN             40.0
ML1          2067125.193
ML2              333.982
ML3                0.000
MITURBO no
GOBSCN  yes
GDBDLY  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    Zn-Por-dp + Zn(OAc)2, final
CMT2    attn = 40, shot = 100
```

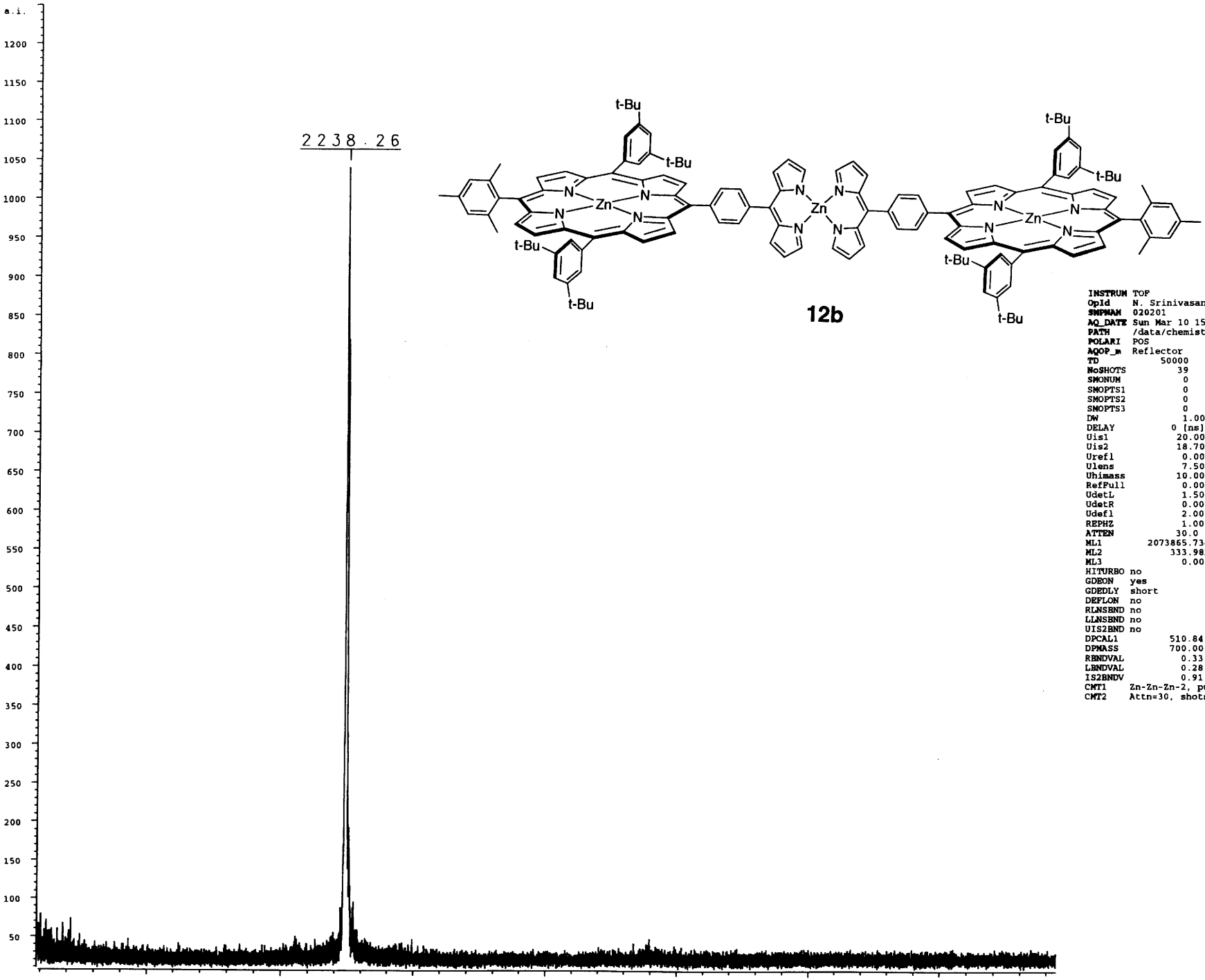


12b


t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
N
Zn
N
N
N
N
Zn
N
N
N
N
Zn
N
N
N
N
Zn
N
N

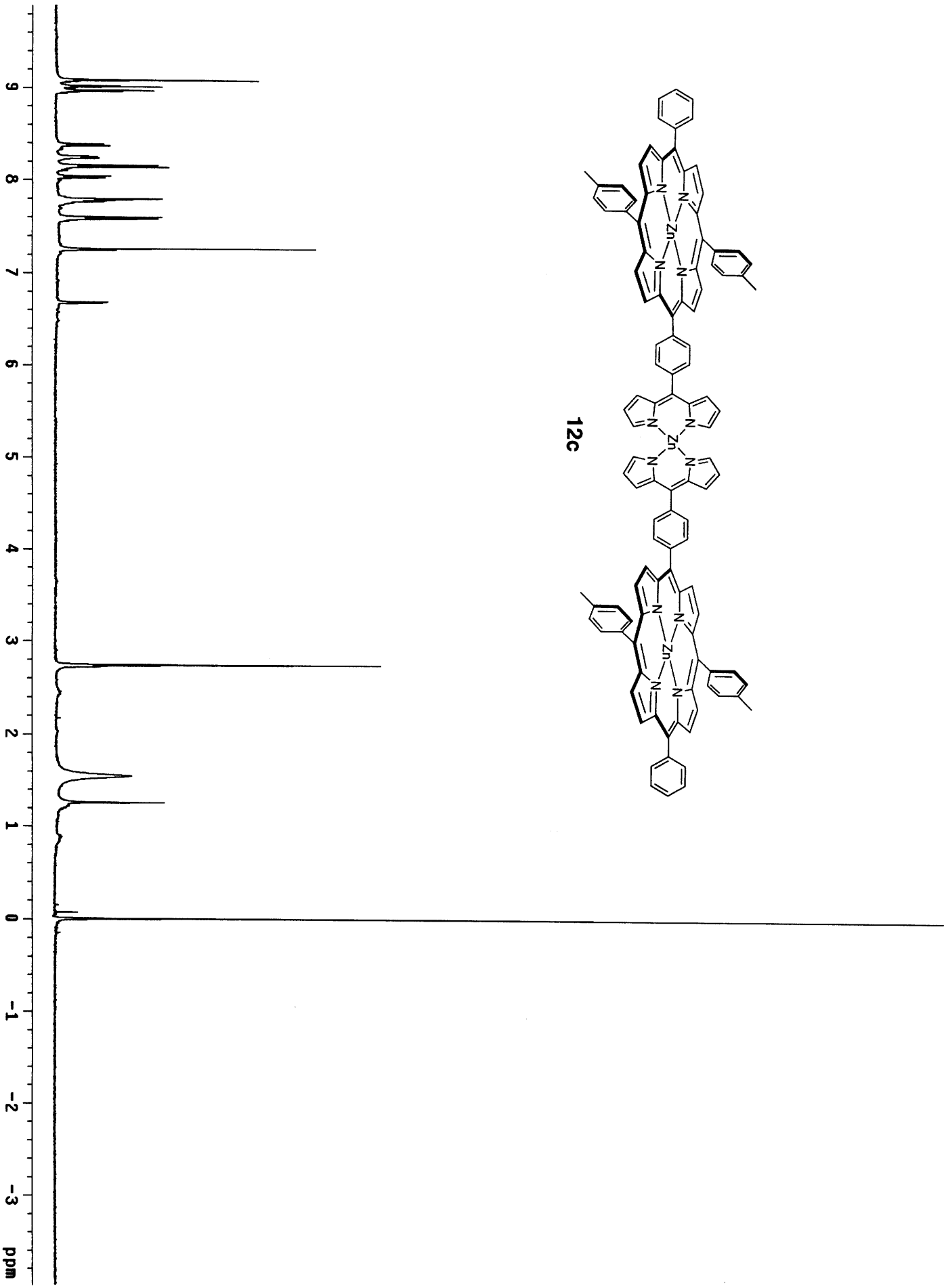
12b

9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm

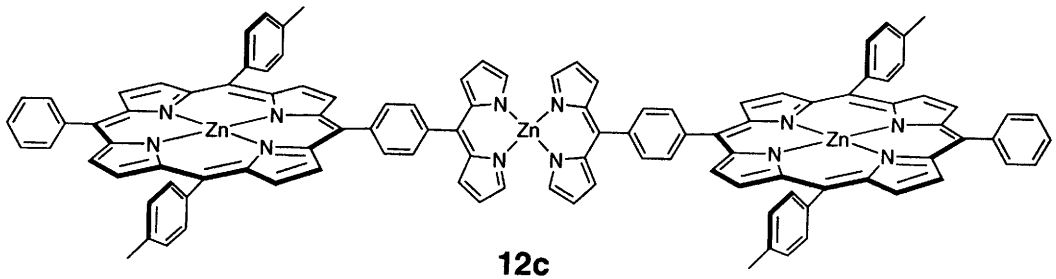


12b

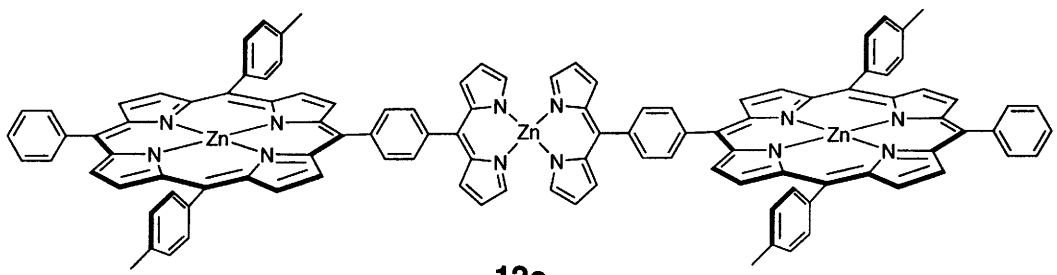
```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  020201
AQ_DATE Sun Mar 10 15:44:34 2002
PATH    /data/chemistry/LINDSEY/LIANHE
POLARI  POS
AQOP_m  Reflector
TD              50000
NoSHOTS            39
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00  [ns]
DELAY               0 [ns]
Uis1               20.00  [kV]
Uis2               18.70  [kV]
Urefl               0.00  [kV]
Ulens               7.50  [kV]
Uhimass            10.00  [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           2073865.734
ML2               333.982
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    Zn-Zn-Zn-2, pure
CMT2    Attn=30, shots = 40
```



12c



12c



12c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INSTRUM TOF
OpId     N. Srinivasan
SMPNAM   030103
AQ_DATE  Mon Jul 29 14:14:08 2002
PATH     /data/chemistry/LINDSEY/KUMAR
POLARI   POS
AQOP_m   Reflector
TD            40000
NoSHOTS          50
SMONUM            0
SMOPTS1           0
SMOPTS2           0
SMOPTS3           0
DW                1.00  [ns]
DELAY           0 [ns]
Uis1             20.00  [kV]
Uis2             18.70  [kV]
Uref1             0.00  [kV]
Ulens             7.50  [kV]
Uhimass          10.00  [kV]
RefFull           0.00  [kV]
UdetL             1.50  [kV]
UdetR             0.00  [kV]
Udef1             2.00  [kV]
REPHZ             1.00  [Hz]
ATTEN            25.0
ML1         2071978.755
ML2             333.982
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    kmk-321   7/29/02
CMT2    att 28
```

Spectrum/Peak Report Date 07/24/02 Time 10:43:04 Page 1 of 1

Method file : <untitled>
Information : Default Method
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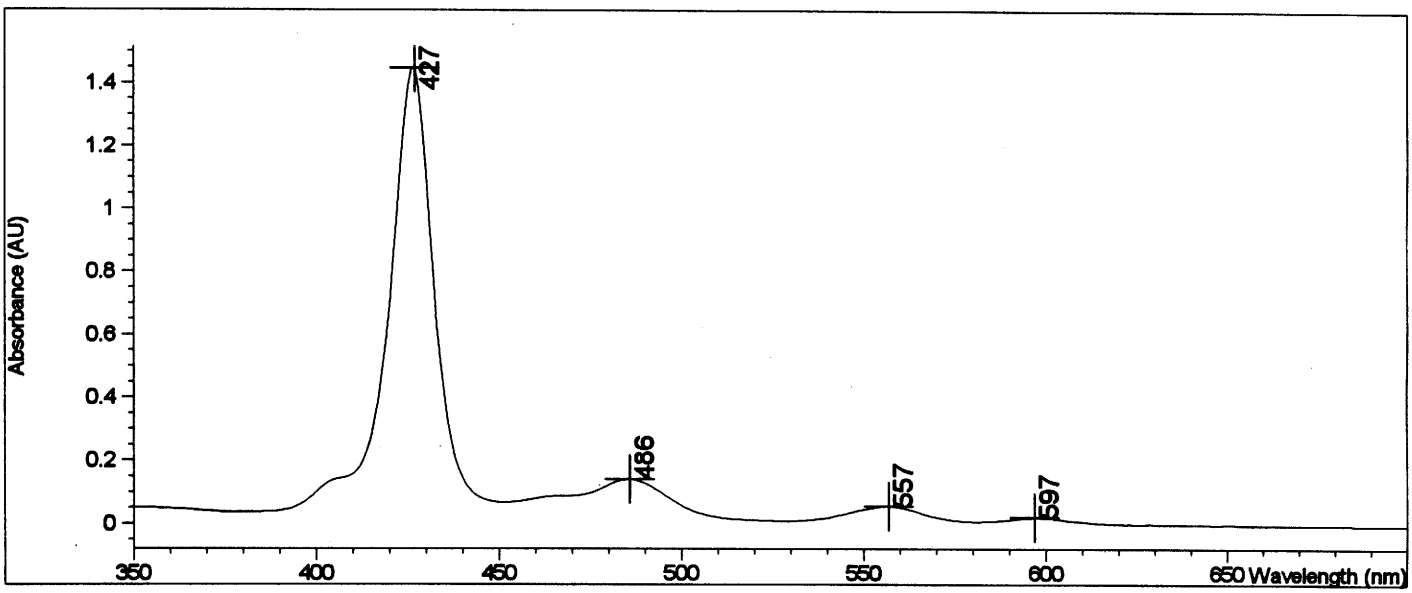
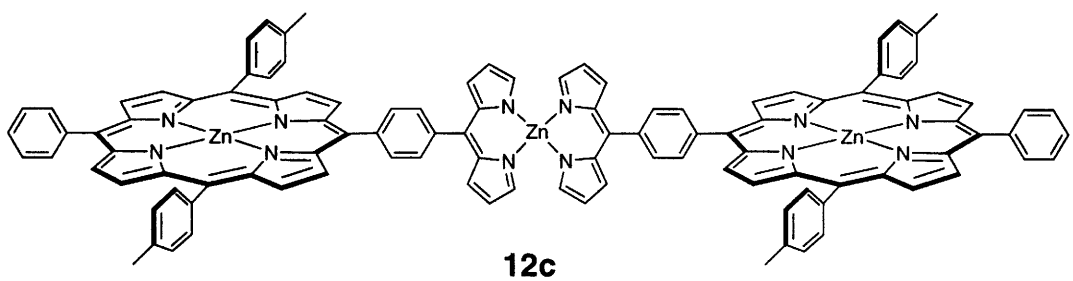
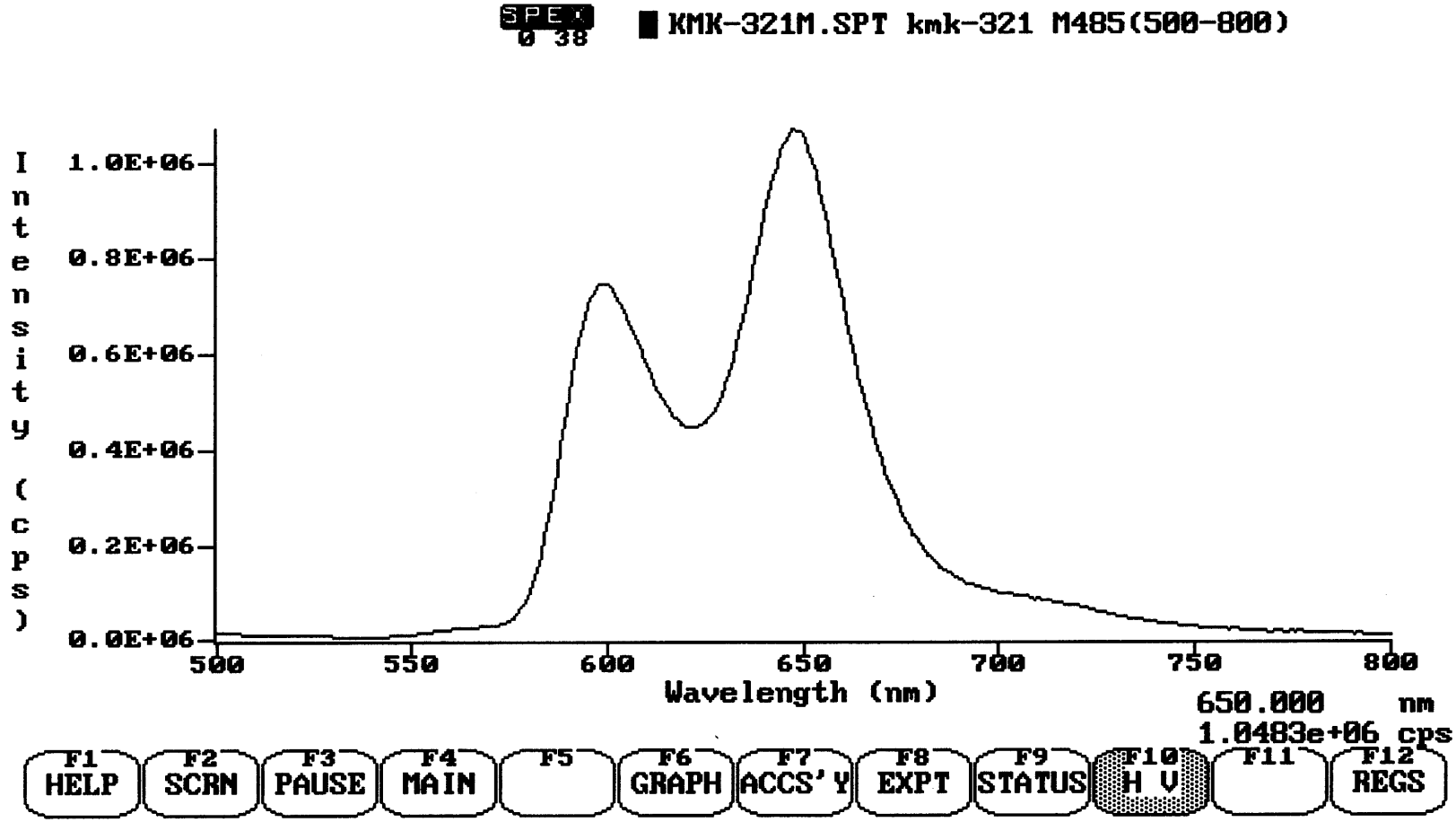


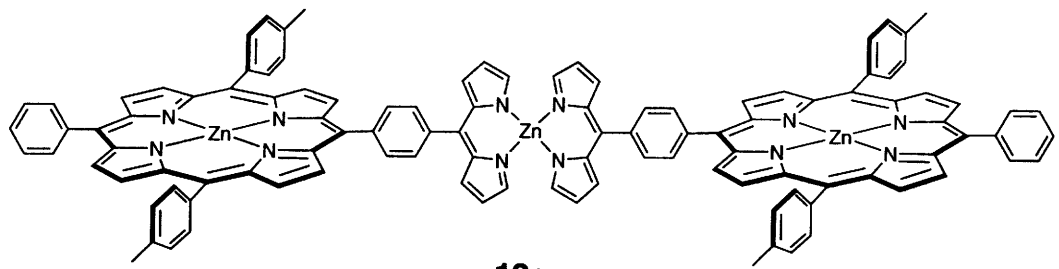
#	Name	Peaks (nm)	Abs (AU)
1		427.0	1.44550
1		486.0	0.14018
1		557.0	5.4822E-2
1		597.0	1.8900E-2

Report generated by : Signature: .....

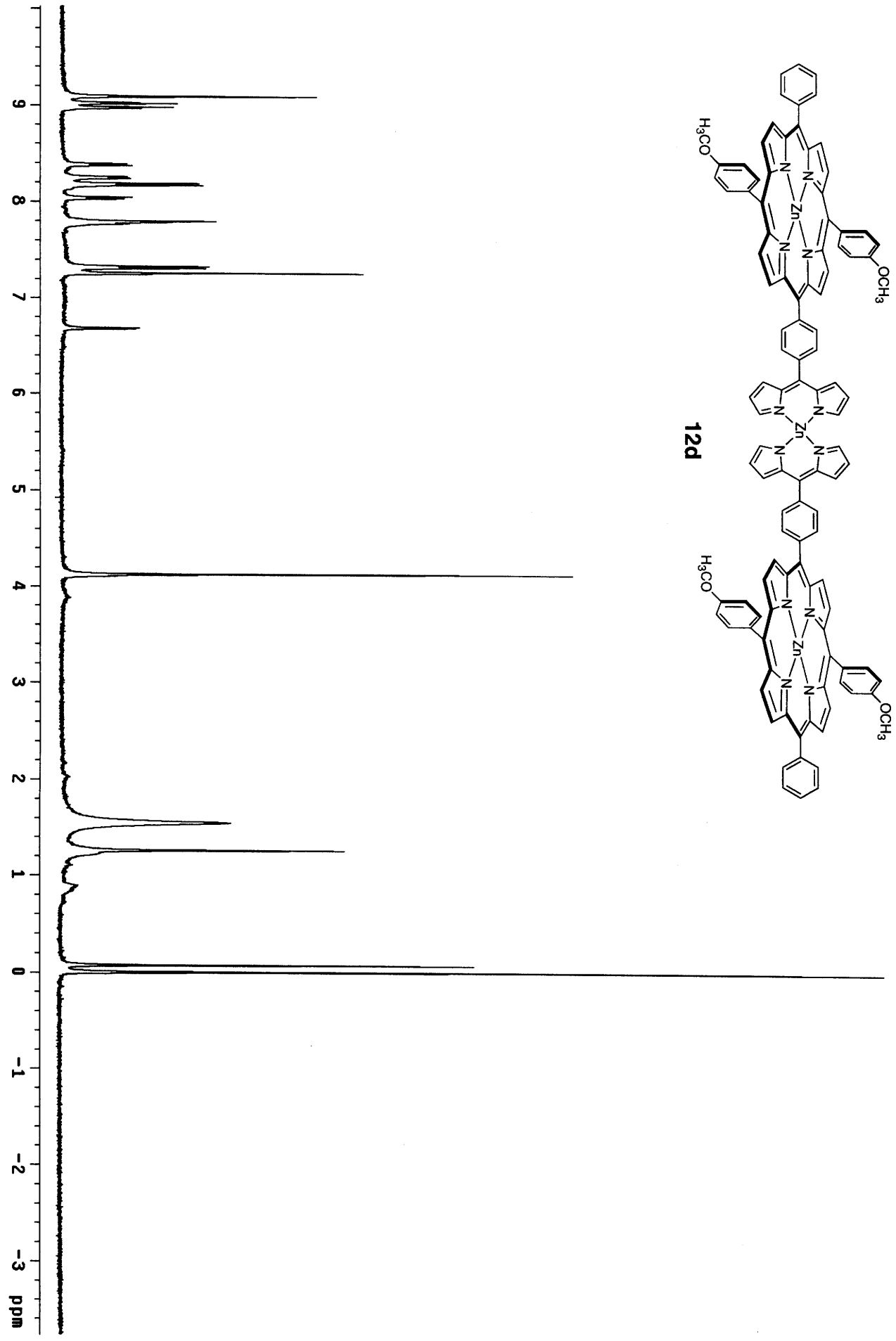


12c

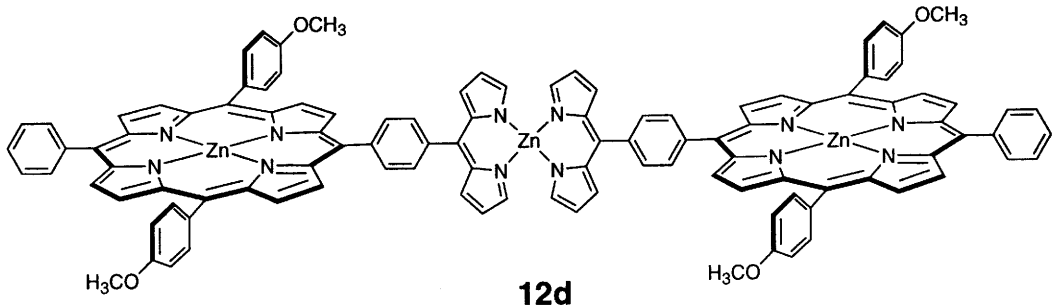

SPEC
0 38
KMK-321M.SPT kmk-321 M485(500-800)
Intensity (cps)
1.0E+06
0.8E+06
0.6E+06
0.4E+06
0.2E+06
0.0E+06
500
550
600
650
700
750
800
Wavelength (nm)
650.000 nm
1.0483e+06 cps
F1 HELP
F2 SCRN
F3 PAUSE
F4 MAIN
F5
F6 GRAPH
F7 ACCS'Y
F8 EXPT
F9 STATUS
F10 H V
F11
F12 REGS


N
Zn

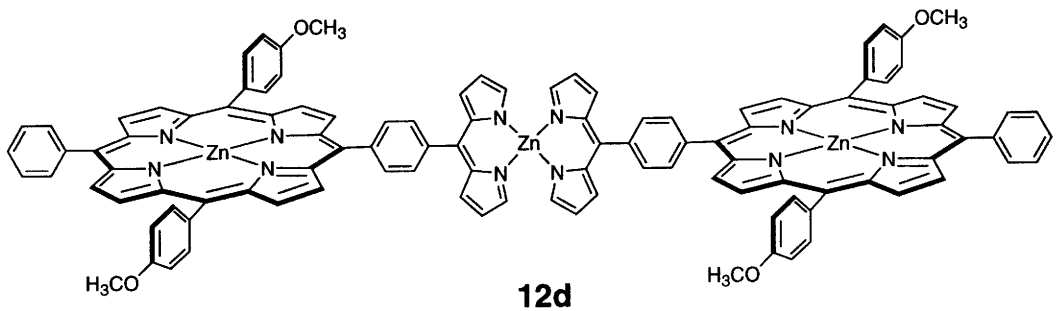
12c



12d



12d



12d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INSTRUM TOF
OpId     N. Srinivasan
SMPNAM   030103
AQ_DATE  Mon Jul 29 14:23:35 2002
PATH     /data/chemistry/LINDSEY/KUMAR
POLARI   POS
AQOP_m   Reflector
TD            40000
NoSHOTS          50
SMONUM            0
SMOPTS1           0
SMOPTS2           0
SMOPTS3           0
DW                1.00  [ns]
DELAY           0 [ns]
Uis1             20.00  [kV]
Uis2             18.70  [kV]
Uref1             0.00  [kV]
Ulens             7.50  [kV]
Uhimass          10.00  [kV]
RefFul1           0.00  [kV]
UdetL             1.50  [kV]
UdetR             0.00  [kV]
Udef1             2.00  [kV]
REPHZ             1.00  [Hz]
ATTEN            25.0
ML1         2071978.755
ML2              333.982
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     kmk-323   7/29/02
CMT2     att 28
```

Spectrum/Peak Report Date 07/29/02 Time 11:51:38 Page 1 of 1

Method file : <untitled>
Information : Default Method
Data File : <untitled>

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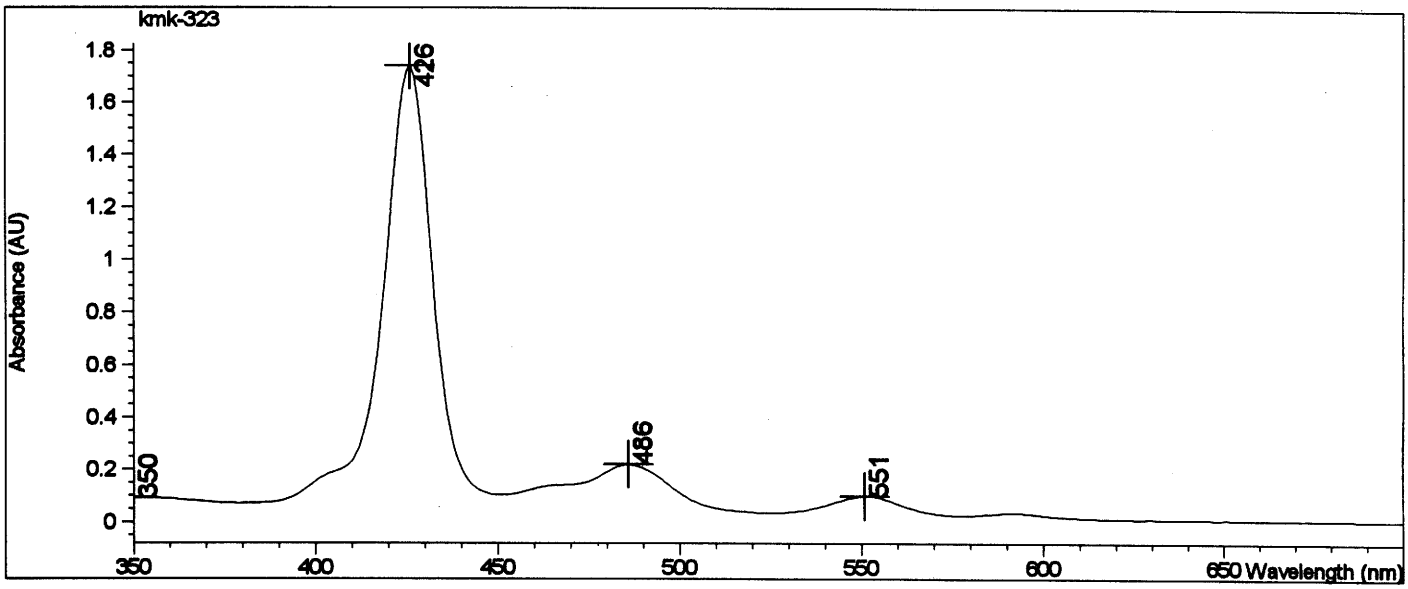
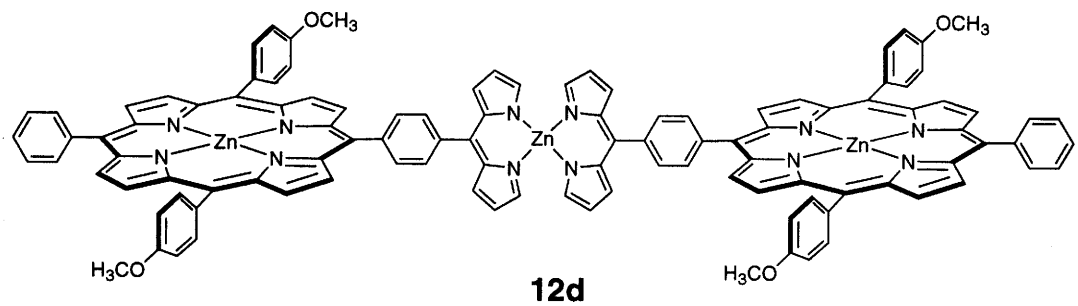
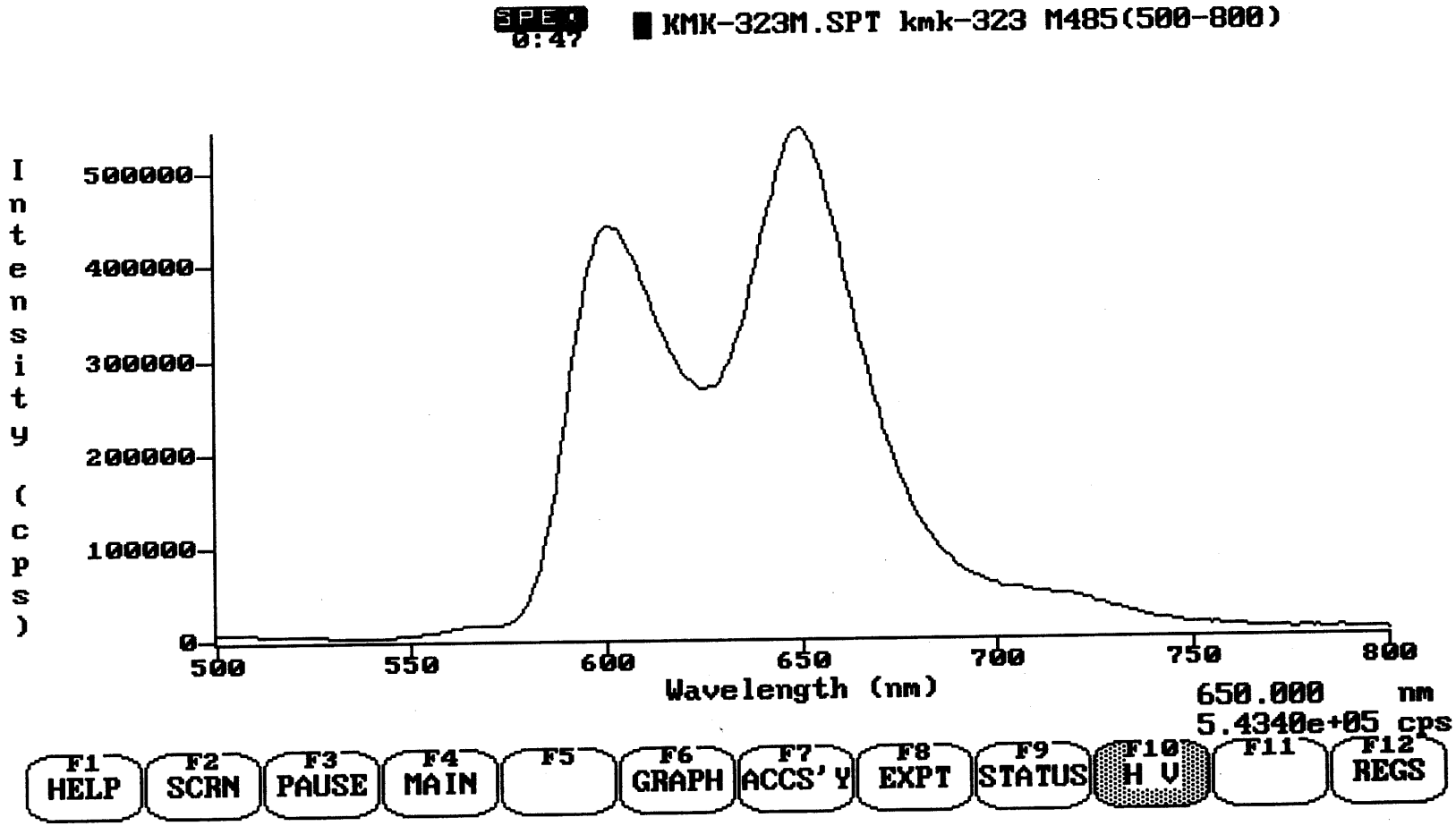


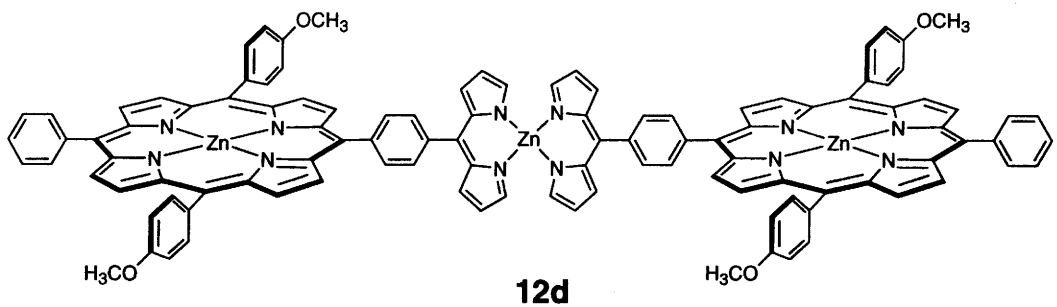
#	Name	Peaks (nm)	Abs (AU)
1	kmk-323	426.0	1.74090
1		486.0	0.22075
1		551.0	9.9855E-2
1		350.0	9.2105E-2

Report generated by : Signature: .....



12d


SPEC
0:47
KMK-323M.SPT kmk-323 M485(500-800)
Intensity (cps)
500000
400000
300000
200000
100000
0
500
550
600
650
700
750
800
Wavelength (nm)
650.000 nm
5.4340e+05 cps
F1 HELP
F2 SCRN
F3 PAUSE
F4 MAIN
F5
F6 GRAPH
F7 ACCS'Y
F8 EXPT
F9 STATUS
F10 H V
F11
F12 REGS


OCH3
H3CO
Zn
N

12d