Supporting Information for:

Synthesis of Perylene–Porphyrin Building Blocks and Rod-Like Oligomers for Light-Harvesting Applications

Robert S. Loewe, Kin-ya Tomizaki, W. Justin Youngblood, Zhishan Bo, and Jonathan S. Lindsey*

Note: Compounds **1-6** as found in the main text are hereby referred to as compounds **S1-S6**, respectively.

Synthesis of porphyrin model compounds and porphyrin building blocks. We sought to prepare porphyrin building blocks that exhibit high solubility in organic solvents such as toluene, THF, $CHCl_3$ or CH_2Cl_2. High solubility of porphyrin monomeric building blocks is critical in order to achieve soluble oligomers. Many of the porphyrin building blocks we have prepared previously have incorporated mesityl substituents attached at the meso-position of the porphyrin macrocycle (e.g., *meso*-tetramesitylporphyrin, TMP).[1] The mesityl group suppresses cofacial aggregation between porphyrins; thus, TMP has a higher degree of solubility compared to *meso*-tetraphenylporphyrin (TPP). However, the solubility of multiporphyrin arrays is typically much less than that of the corresponding monomeric building blocks. Indeed, our first attempts at preparing porphyrin light-harvesting oligomers utilized the porphyrin building block **S1**.[2] However, we were unable to obtain soluble oligomers of sufficient length (>6 porphyrins).

We therefore decided to prepare a porphyrin bearing ethyl substituents at the 2,4,6-positions of the meso-aryl ring rather than methyl substituents (as in the mesityl group) in order to determine whether the increased steric bulk of the ethyl groups would further suppress cofacial aggregation and afford increased solubility. Thus, commercially available 1-bromo-2,4,6-triethylbenzene (**S7**) was treated with *n*-BuLi and DMF to yield 2,4,6-triethylbenzaldehyde

(**S8**), which has been prepared by a different route.[3] The reaction of aldehyde **S8** and pyrrole following the same conditions employed for mesitaldehyde ($BF_3{\cdot}O(Et)_2$-ethanol cocatalysis[4] in $CHCl_3$ followed by oxidation with DDQ) at elevated concentration[5] afforded the desired *meso*-tetrakis(2,4,6-triethylphenyl)porphyrin **S2** in 9.1% yield (Scheme S1). No effort was made to optimize the yield of porphyrin.

Studies were performed to assess the solubility of porphyrin **S2**, particularly in comparison to that of TMP (see Experimental Section). The solubility of **S2** in toluene (~50-70 mM) is nearly identical to that of TMP. In THF, the solubility of **S2** (~5 mM) is approximately 10-times that of TMP. In $CHCl_3$, the solubility of **S2** (~23 mM) is approximately twice that of TMP. In CH_2Cl_2, roughly comparable solubilities were observed for **S2** and TMP though the data by the two measurements varied somewhat. Given the lack of a substantial solubility increase, we did not attempt to prepare porphyrin building blocks using the 2,4,6-triethylphenyl substituent.

We have also prepared several porphyrin building blocks containing the 2,4,6-tris(2,3,4,5,6-pentafluorobenzyloxy)phenyl substituent[6] in the hopes that this bulky group may impart the solubility needed to prepare porphyrin light-harvesting oligomers. Scheme S2 shows the synthesis of porphyrin building block **S3**. The first step in the synthesis of this building block is reduction of diacyldipyrromethane **S9**[7] with $NaBH_4$ in THF/MeOH (10:1). The resulting dipyrromethane-dicarbinol was condensed with dipyrromethane **S10**[8] under TFA catalysis, then oxidized with DDQ to furnish porphyrin **S11** in 20% yield. Metalation using $Zn(OAc)_2{\cdot}2H_2O$ followed by removal of the trimethylsilyl group using TBAF in CH_2Cl_2 afforded zinc porphyrin **S3** in 92% yield.

The synthesis of porphyrin building block **S4** is shown in Scheme S3. The sterically hindered dipyrromethane **S10** was reacted with 4-[2-(trimethylsilyl)ethynyl]benzaldehyde under

non-scrambling conditions[9] (condensation in CH_2Cl_2 containing a catalytic amount of TFA followed by oxidation with DDQ), affording porphyrin **S12** in 26% yield. Treatment of **S12** with $Zn(OAc)_2 \cdot 2H_2O$ afforded the zinc chelate **S13** in 98% yield. Removal of the two trimethylsilyl groups was achieved using TBAF in CH_2Cl_2, giving **S4** in 91% yield.

A magnesium porphyrin bearing one carboxylic acid and one ethyne group was prepared as a potential capping unit for the light-harvesting oligomers.[10] The carboxylic acid provides a site for attachment to an electroactive surface. The porphyrin bears two pentafluorophenyl groups at the non-linking meso-positions in order to increase the oxidation potential, as is desired for the terminal unit in the light-harvesting rods. The synthesis of porphyrin **S5** is outlined in Scheme S4. Following a procedure for preparing *trans*-AB_2C porphyrins,[7] dipyrromethane **S14**[11] was treated with phenylmagnesium bromide followed by pentafluorobenzoyl chloride to yield diacyldipyrromethane **S15** in 43% yield. Reduction of **S15** with excess $NaBH_4$ afforded the dipyrromethane-dicarbinol, which was condensed with dipyrromethane **S16**[7] under TFA catalysis. Oxidation with DDQ afforded porphyrin **S17** in 15% yield. Metalation of **S17** using $MgBr \cdot O(Et)_2$ and TEA in CH_2Cl_2[12] gave magnesium porphyrin **S18** in 99% yield. Deprotection of both trimethylsilyl groups was achieved by employing a slight excess (3 eq) of TBAF in DMF to yield porphyrin **S5** in 71% yield.

The first step in the synthesis of a perylene–porphyrin dyad building block is the preparation of 5-(2-ethynylphenyl)dipyrromethane (**S19**) as shown in Scheme S5. Room temperature condensation between 2-ethynylbenzaldehyde and excess pyrrole (25 eq)[13] under TFA catalysis afforded dipyrromethane **S19** in 40% yield after column chromatography. Purification by Kugelrohr distillation was not attempted given the reactive nature of the ethyne group.

The synthesis of ethynylporphyrin building block **S21** was attempted under new conditions for the dipyrromethane + dipyrromethane-dicarbinol condensation, which employ a Lewis acid [$InCl_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, or $Dy(OTf)_3$] in CH_2Cl_2 at room temperature.[14] Compared to TFA catalysis (30 mM in CH_3CN at room temperature),[7] these conditions can provide increased yields of porphyrin accompanied by a simplified purification procedure. We initially chose $Yb(OTf)_3$ to promote condensation.

Standard reduction of diacyldipyrromethane **S20**[15] with excess $NaBH_4$ yielded the dipyrromethane-dicarbinol as a foam-like solid. The dicarbinol (2.5 mM) was immediately dissolved in reagent-grade CH_2Cl_2 along with dipyrromethane **S19** (2.5 mM). A sample of $Yb(OTf)_3$ (3.2 mM)[14] was then added. Aliquots were removed at 5 and 10 min intervals, treated with DDQ to cause oxidative conversion of the porphyrinogen to the porphyrin, and then analyzed by absorption spectroscopy. A broad and intense peak centered at 489 nm (fwhm ~50 nm) was observed but no Soret peak could be detected. After 15 min, DDQ was added but only traces of porphyrin were detected by TLC.

Attempts to use the standard condensation conditions (30 mM TFA in acetonitrile[7]) were not successful because the dicarbinol was only sparingly soluble in acetonitrile at 2.5 mM. However, the addition of CH_2Cl_2 in small portions to the suspension of **S19** and **S20-diol** in acetonitrile resulted in a homogeneous solution with a 9:1 mixture of acetonitrile/CH_2Cl_2. The addition of TFA (26 mM, due to the dilution factor of the additional CH_2Cl_2) caused an immediate color change. Aliquots were removed after 1 and 2 min, oxidized with DDQ, and analyzed by absorption spectroscopy. The spectroscopic yield of porphyrin at both timepoints was only 8%. After 3 min, DDQ was added to the mixture. LD-MS analysis did not show the formation of any products due to acidolysis and undesired recombination (i.e., scrambling). The absence of scrambling is important given that the dipyrromethane + dipyrromethane-dicarbinol

condensation using TFA in neat CH_2Cl_2 typically affords significant scrambling after 1 min.[7] The solubility of the porphyrin in acetonitrile was poor. After workup, a 23% yield of porphyrin was obtained; nearly three times that calculated by absorption spectroscopy. This discrepancy is likely due to the poor solubility of the porphyrinogen intermediate in the polar reaction medium. The free base porphyrin was then treated with $Zn(OAc)_2 \cdot 2H_2O$ in $CHCl_3$/MeOH to afford the zinc chelate **S22** in 98% yield (Scheme S6).

Porphyrin **S22** and bromoperylene **S23**[16] were coupled in a Sonogashira reaction (Scheme S6). The reaction was performed at 2.5 mM using $Pd_2(dba)_3$/P(*o*-tol)$_3$[17] at 60 °C in toluene/TEA (5:1) for 21 h, which are conditions similar to those used with bromo- and ethynyl-substituted porphyrins.[10,16,18] Perylene–porphyrin **S24** was obtained in 66% yield. This porphyrin was treated with TBAF in THF at room temperature for 2 h to furnish the perylene–porphyrin building block **S6** in 60% yield. This compound proved to be quite soluble in organic solvents. ^{1}H NMR spectroscopy revealed upfield resonances of the isopropyl and *N*-aryl hydrogens of the perylene, as expected given that the perylene projects over the face of the porphyrin macrocycle.

Experimental

General. ^{1}H NMR (300 MHz or 400 MHz) and ^{13}C NMR (75 MHz) spectra were taken in $CDCl_3$ unless noted otherwise. Mass spectra of porphyrins were obtained by high-resolution fast atom bombardment (FAB) and by laser desorption mass spectrometry (LD-MS). Absorption spectra were collected in toluene at room temperature. Elemental analyses were performed by Atlantic Microlab, Inc. Melting points are uncorrected. Silica gel (Baker 32-63 μm particle size) and alumina (Fisher, 80-200 mesh) were used for column chromatography. Chloroform contained 0.75% ethanol as stabilizer.

Solubility experiments. For each porphyrin, a sample of at least 50 mg was measured into each of four 4-mL vials. Four solvents (toluene, THF, $CHCl_3$, and CH_2Cl_2) were chosen to test the solubility of the porphyrin. An aliquot of each solvent (1.00 mL) was added to each sample at room temperature. The samples were sonicated for 30 min, protected from ambient light, and allowed to stand overnight at room temperature. The samples were then centrifuged (~3000 rpm). The solubility was assessed in two ways, by absorption spectrophotometric analysis of the supernatant and by gravimetric analysis of the evaporated solvent. For absorption spectrophotometric analysis, 2.0 μL of each supernatant (10.0 μL in the case of TMP in THF) was added to 3.00 mL of the corresponding solvent. Subsequent serial dilution was performed until the absorbance of the Soret band (ε_{420} = 427,000 $M^{-1}cm^{-1}$) was around 1 (1-cm pathlength cell). The concentration of the supernatant was extrapolated from this measurement. For gravimetric analysis, 250 μL of the supernatant was transferred to a pre-weighed vial. The sample was concentrated to dryness and weighed.

Non-commercial compounds: Dipyrromethanes **S10**,[8] **S14**,[11] and **S16**;[7] diacyl dipyrromethane **S9**;[7] and bromoperylene **S23**[16] were prepared as described in the literature.

***Meso*-Tetrakis(2,4,6-triethylphenyl)porphyrin (S2).** Following a standard procedure,[4,5] a solution containing **S8** (1.91 g, 10.0 mmol) and pyrrole (0.692 mL, 10.0 mmol) in $CHCl_3$ (137 mL) under argon was treated with $BF_3{\cdot}O(Et)_2$ (0.309 mL, 2.44 mmol) at room temperature. After stirring for 1 h, a sample of DDQ (1.70 g, 7.52 mmol) was added and stirring was continued for 1 h. A sample of TEA (0.340 mL, 2.44 mmol) was added and the crude reaction mixture was passed over a pad of alumina over silica and eluted with $CHCl_3$. The filtrate was concentrated and chromatographed [silica, hexanes/$CHCl_3$ (3:1)]. The crude porphyrin sample was concentrated and redissolved in CH_2Cl_2 to which methanol was added. The solution was concentrated and the resulting porphyrin precipitate was collected and washed

with methanol, yielding a purple solid (216 mg, 9.1%); ^{1}H NMR δ –2.43 (s, 2H), 0.71 (t, *J* = 7.2 Hz, 24H), 1.53 (t, *J* = 7.2 Hz, 12H), 2.16 (q, *J* = 7.2 Hz, 16H), 2.97 (q, *J* = 7.2 Hz, 8H), 7.31 (s, 8H), 8.58 (s, 8H); LD-MS obsd 954.7, calcd avg mass 951.37 ($C_{68}H_{78}N_4$); λ_{abs} 421, 516, 549, 593, 650 nm.

5-(4-Iodophenyl)-10-[2,4,6-tris(pentafluorobenzyloxy)phenyl]-15-mesityl-20-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (S11). Following a general procedure,[7] reduction of **S9** (416 mg, 0.60 mmol), followed by treatment of the resulting dipyrromethane-dicarbinol with dipyrromethane **S10** (486 mg, 0.60 mmol) and TFA (0.580 mL, 7.24 mmol) in CH_3CN (240 mL) for 3.5 min, oxidation with DDQ (408 mg, 1.80 mmol), and standard workup furnished a purple solid (174 mg, 20%): ^{1}H NMR (300 MHz) δ –2.86 (s, 2H), 0.39 (s, 9H), 1.82 (s, 6H), 2.63 (s, 3H), 4.88 (s, 4H), 5.45 (s, 2H), 6.84 (s, 2H), 7.28 (s, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 2H), 8.11 (d, *J* = 8.1 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 2H), 8.63–8.77 (m, 8H); LD-MS obsd 1463.08, calcd avg mass 1467.14 ($C_{73}H_{46}F_{15}IN_4O_3Si$); λ_{abs} 422, 483, 515, 550, 593, 648 nm.

Zn(II)-5-(4-Ethynylphenyl)-10-[2,4,6-tris(2,3,4,5,6-pentafluorobenzyloxy)phenyl]-15-mesityl-20-(4-iodophenyl)porphyrin (S3). A solution of **S11** (174 mg, 120 μmol) in $CHCl_3$ (50 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (266 mg, 1.20 mmol) in methanol (5 mL) for 2 h under reflux. The reaction mixture was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a purple solid (177 mg, 98%): ^{1}H NMR (300 MHz) δ 0.47 (s, 9H), 1.90 (s, 6H), 2.68 (s, 3H), 4.87 (s, 4H), 5.45 (s, 2H), 6.90 (s, 2H), 7.34 (s, 2H), 7.96 (d, *J* = 8.1 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 8.15 (d, *J* = 8.1 Hz, 2H), 8.23 (d, *J* = 8.1 Hz, 2H), 8.70–8.95 (m, 8H); LD-MS obsd 1524.7; calcd avg mass 1530.51 ($C_{73}H_{44}F_{15}IN_4O_3SiZn$). The solid (128 mg, 84 μmol) in CH_2Cl_2 (20 mL) was then treated with TBAF (125 μL, 125 μmol, 1.0 M in THF) and stirred at room temperature overnight. The solvent was removed and the residue was chromatographed (silica, CH_2Cl_2)

yielding a purple solid (113 mg, 92%): ^{1}H NMR (300 MHz) δ 1.83 (s, 6H), 2.64 (s, 3H), 4.86 (s, 4H), 5.45 (s, 2H), 6.87 (s, 2H), 7.28 (s, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 2H), 8.65–8.86 (m, 8H); LD-MS obsd 1454.3; calcd avg mass 1456.09 ($C_{70}H_{36}F_{15}IN_4O_3Zn$); λ_{abs} 423, 512, 551, 590 nm.

5,15-Bis[2,4,6-tris(pentafluorobenzyloxy)phenyl]-10,20-bis[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (S12). Following a general procedure,[9] a solution of 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (143 mg, 0.70 mmol) and dipyrromethane **S10** (571 mg, 0.70 mmol) in CH_2Cl_2 (175 mL) was purged with argon for 10 min, then TFA (52.5 μL, 0.70 mmol) was added. The mixture was stirred at room temperature for 50 min then DDQ (238 mg, 1.05 mmol) was added. After 2 h the mixture was neutralized with TEA. Two chromatography procedures [silica, CH_2Cl_2 followed by CH_2Cl_2/hexanes (2:1)] afforded a purple solid (178 mg, 26%): ^{1}H NMR (300 MHz) δ –3.03 (s, 2H), 0.41 (s, 18H), 4.89 (s, 8H), 5.46 (s, 4H), 6.85 (s, 4H), 7.90 (d, *J* = 8.1 Hz, 4H), 8.11 (d, *J* = 8.1 Hz, 4H), 8.63 (m, 4H), 8.66 (m, 4H); LD-MS obsd 1981.3, calcd avg mass 1983.58 ($C_{96}H_{52}F_{30}N_4O_6Si_2$); λ_{abs} 424, 517, 551, 593, 650 nm; λ_{em} (λ_{ex} 517 nm) 653, 721 nm.

Zn(II)-5,15-Bis[2,4,6-tris(2,3,4,5,6-pentafluorobenzyloxy)phenyl]-10,20-bis[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (S13). A solution of **S12** (177 mg, 89 μmol) in $CHCl_3$ (50 mL) was treated with a solution of $Zn(OAc)_2{\cdot}2H_2O$ (38 mg, 173 μmol) in methanol (5 mL) for 2 h under reflux. The reaction mixture was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/hexanes (5:2)] afforded a purple solid (179 mg, 98%): ^{1}H NMR (300 MHz) δ 0.40 (s, 18H), 4.86 (s, 8H), 5.45 (s, 4H), 6.86 (s, 4H), 7.88 (d, *J* = 8.1 Hz, 4H), 8.13 (d, *J* = 8.1 Hz, 4H), 8.63 (d, *J* = 5.1 Hz, 4H), 8.73 (d, *J* = 4.2 Hz, 4H); LD-MS obsd 2044.7, calcd avg mass 2046.96 ($C_{96}H_{50}F_{30}N_4O_6Si_2Zn$); λ_{abs} 428, 514, 552, 591 nm; λ_{em} (λ_{ex} 552 nm) 600, 649 nm.

Zn(II)-5,15-Bis[2,4,6-tris(pentafluorobenzyloxy)phenyl]-10,20-bis[4-ethynylphenyl]porphyrin (S4). A mixture of **S13** (120 mg, 58 μmol) and TBAF (200 μL, 200 μmol, 1.0 M in THF) in CH_2Cl_2 (100 mL) was stirred at room temperature for 20 min. The solvent was removed and the residue was chromatographed (silica, CH_2Cl_2) yielding a purple solid (100 mg, 91%): ^{1}H NMR (300 MHz) δ 3.33 (s, 2H), 4.87 (s, 8H), 5.45 (s, 4H), 6.87 (s, 4H), 7.91 (d, *J* = 8.1 Hz, 4H), 8.15 (d, *J* = 8.1 Hz, 4H), 8.65 (d, *J* = 5.1 Hz, 4H), 8.75 (d, *J* = 4.2 Hz, 4H); LD-MS obsd 1900.9, calcd avg mass 1902.60 ($C_{90}H_{34}F_{30}N_4O_6Zn$); λ_{abs} 427, 514, 552, 591 nm; λ_{em} (λ_{ex} 552 nm) 599, 649 nm.

1,9-Bis(2,3,4,5,6-pentafluorobenzoyl)-5-[4-(2-trimethylsilyl)ethynyl]dipyrromethane (S15). To a solution of dipyrromethane **S14** (2.00 g, 6.28 mmol) in toluene (100 mL) was added PhMgBr (31.3 mL, 31.3 mmol, 1.0 M in THF). The solution was stirred for 30 min at room temperature. Then a solution of pentafluorobenzoyl chloride (2.26 mL, 15.7 mmol) in toluene (15 mL) was added dropwise over 5 min. After stirring for 30 min, saturated aqueous ammonium chloride (100 mL) was added followed by ethyl acetate (100 mL). The aqueous layer was washed with ethyl acetate (50 mL). The organic layers were combined, dried (Na_2SO_4), filtered, and concentrated. Column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] followed by precipitation (twice) from CH_2Cl_2/hexanes afforded a white solid (1.92 g, 43%): mp >260 °C (dec.) ^{1}H NMR (300 MHz) δ 0.25 (s, 9H), 5.67 (s, 1H), 6.11 (m, 2H), 6.67 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 10.02 (brs, 2H); ^{13}C NMR δ –0.2, 44.1, 95.3, 103.9, 112.1, 113.6, 122.6, 123.0, 128.2, 131.3, 131.5, 132.5, 135.6, 135.8, 135.9, 136.0, 138.6, 139.1, 139.2, 140.6, 142.0, 142.2, 145.5, 172.3; Anal Calcd for $C_{34}H_{20}N_2O_2F_{10}Si$: C, 57.79; H, 2.85; N, 3.96. Found: C, 57.75; H, 3.00; N, 3.90.

5,15-Bis(2,3,4,5,6-pentafluorophenyl)-10-[4-[2-(trimethylsilyl)ethynyl]phenyl]-20-[4-[2-(trimethylsilyl)ethoxycarbonyl]phenyl]porphyrin (S17). Following a general procedure,[7]

reduction of **S15** (1.80 g, 2.55 mmol) followed by treatment of the resulting dipyrromethane-dicarbinol with dipyrromethane **S16** (0.93 g, 2.55 mmol) and TFA (2.47 mL, 30.8 mmol) in CH_3CN (1.02 L) for 3.5 min, oxidation with DDQ (1.73 g, 7.62 mmol), and standard workup afforded a purple solid. Two additional silica columns [CH_2Cl_2/hexanes, (1:1)] afforded a purple solid (401 mg, 15%); ^{1}H NMR (300 MHz) δ 0.20 (s, 9H), 0.39 (s, 9H), 1.32 (t, 2H), 4.64 (t, 2H), 7.91 (d, *J* = 8.1 Hz, 2H), 8.17 (d, *J* = 8.1 Hz, 2H), 8.31 (d, *J* = 8.1 Hz, 2H), 8.47 (d, *J* = 7.8 Hz, 2H), 8.83–8.95 (m, 8H); LD-MS obsd 1033.8; HR-MS (FAB) obsd 1034.2527, calcd 1034.2530 ($C_{55}H_{40}F_{10}N_4O_2Si_2$); λ_{abs} 420, 512, 546, 590, 645 nm; λ_{em} (λ_{ex} 512 nm) 647, 715 nm.

Mg(II)-5,15-Bis(2,3,4,5,6-pentafluorophenyl)-10-[4-[2-(trimethylsilyl)ethynyl]phenyl]-20-[4-[2-(trimethylsilyl)ethoxycarbonyl]phenyl]porphyrin (S18). Following a general procedure,[12] a solution of **S17** (229 mg, 221 μmol) in CH_2Cl_2 (30 mL) was treated with triethylamine (1.24 mL, 8.84 mmol) followed by $MgBr_2{\cdot}O(Et)_2$ (1.15 g, 4.42 mmol). The mixture was stirred at room temperature under argon for 30 min. Water was then added and the organic layer was washed with brine. Column chromatography (alumina, $CHCl_3$) afforded a purple solid (230 mg, 99%): ^{1}H NMR (400 MHz, THF-d_8) δ 0.20 (s, 9H), 0.36 (s, 9H), 1.31 (t, 2H), 4.61 (t, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 8.18 (d, *J* = 7.6 Hz, 2H), 8.30 (d, *J* = 8.4 Hz, 2H), 8.41 (d, *J* = 7.6 Hz, 2H), 8.82–8.85 (m, 4H), 8.88 (m, 4H); LD-MS obsd 1059.0; HR-MS (FAB) obsd 1056.2220, calcd 1056.2224 ($C_{55}H_{38}F_{10}MgN_4O_2Si_2$); λ_{abs} 427, 523, 562, 604 nm; λ_{em} (λ_{ex} 562 nm) 609, 663 nm.

Mg(II)-5,15-Bis(pentafluorophenyl)-10-(4-ethynylphenyl)-20-(4-carboxyphenyl]porphyrin (S5). A sample of **S18** (122 mg, 115 μmol) in DMF (30 mL) was treated with TBAF (300 μL, 300 μmol, 1.0 M in THF). The mixture was stirred at room temperature for 3 h. The solvent was removed and CH_2Cl_2 (50 mL) was added. The organic layer was washed with 5% aqueous $NaHCO_3$ (2 x 50 mL), water (2 x 50 mL), dried (Na_2SO_4),

filtered, and concentrated to dryness. Column chromatography [silica, CH_2Cl_2/MeOH (4:1)] afforded a purple solid (72 mg, 71%): ^{1}H NMR (400 MHz) δ 3.33 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 8.31 (brs, 4H), 8.83 (m, 4H), 8.90 (d, *J* = 4.4 Hz, 2H), 8.95 (d, *J* = 4.4 Hz, 2H); LD-MS obsd 885.0; HR-MS (FAB) obsd 884.1143, calcd 884.1121 ($C_{47}H_{18}F_{10}MgN_4O_2$); λ_{abs} 427, 521, 562, 605 nm; λ_{em} (λ_{ex} 562 nm) 609, 663 nm.

5-(2-Ethynylphenyl)dipyrromethane (S19). Following a general procedure,[13] a mixture of pyrrole (43 mL, 0.62 mol) and 2-ethynylbenzaldehyde (2.00 g, 15.4 mmol) was treated with TFA (0.119 mL, 1.54 mmol). The mixture was stirred at room temperature for 10 min. A solution of 0.1 M aqueous NaOH (40 mL) and ethyl acetate (40 mL) were added. The layers were separated. The aqueous layer was washed with additional ethyl acetate (50 mL). The organic layers were combined, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2 followed by silica, CH_2Cl_2/hexanes, (3:2)] afforded a light brown solid (1.51 g, 40%): mp 95–97 °C; ^{1}H NMR (400 MHz) δ 3.27 (s, 1H), 5.92 (m, 2H), 6.03 (s, 1H), 6.16 (m, 2H), 6.70 (m, 2H), 7.18–7.32 (m, 3H), 7.52 (d, *J* = 7.6 Hz, 1H), 8.03 (brs, 2H); ^{13}C NMR δ 41.6, 81.8, 81.9, 107.2, 108.4, 117.1, 121.4, 126.7, 128.2, 129.3, 131.9, 133.1, 144.8; FAB-MS obsd 246.1153, calcd 246.1157; Anal. Calcd for ($C_{17}H_{14}N_2$): C, 82.90; H, 5.73 N, 11.37. Found: C, 82.84; H, 5.75; N, 11.18.

5-(2-Ethynylphenyl)-15-mesityl-10,20-bis[4-[2-(triisopropylsilyl)ethynyl]phenyl]porphyrin (S21). Following a general procedure,[7] a solution of diacyl dipyrromethane **S20**[15] (715 mg, 0.858 mmol) in THF/methanol [33 mL (10:1)] was reduced by portion-wise addition of $NaBH_4$ (650 mg, 17.2 mmol). After standard workup, the dipyrromethane-dicarbinol and dipyrromethane **S19** (211 mg, 0.858 mmol) were dissolved in acetonitrile/CH_2Cl_2 [383 mL (9:1)]. The concentration of each reactant was 2.2 mM. A sample of TFA (794 μL, 10.3 mmol, 27 mM) was added dropwise over a period of 30 s. After 3 min,

DDQ (584 mg, 2.57 mmol) was added. After 1 h, TEA (1 mL) was added and the entire reaction mixture was filtered through a pad of alumina using CH_2Cl_2 as eluent. The porphyrin-containing fractions were concentrated. Column chromatography (silica, CH_2Cl_2) afforded a purple solid (195 mg, 23%): ^{1}H NMR (400 MHz) δ –2.70 (brs, 2H), 1.26 (s, 42H), 1.84 (m, 6H), 2.15 (s, 1H), 2.64 (s, 3H), 7.29 (s, 2H), 7.70–7.74 (m, 1H), 7.76–7.80 (m, 1H), 7.87 (d, *J* = 7.6 Hz, 4H), 7.95 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 8.14 (d, *J* = 7.2 Hz, 2H), 8.19 (d, *J* = 7.6 Hz, 2H), 8.71 (d, *J* = 4.4 Hz, 2H), 8.72 (d, *J* = 5.2 Hz, 2H), 8.79 (d, *J* = 5.2 Hz, 2H), 8.82 (d, *J* = 4.8 Hz, 2H); LD-MS obsd 1041.0; FAB-MS obsd 1041.57, calcd 1041.57 ($C_{71}H_{76}N_4Si_2$); λ_{abs} 422, 480, 515, 550, 592, 648 nm.

Zn(II)-5-(2-Ethynylphenyl)-15-mesityl-10,20-bis[4-[2-(triisopropylsilyl)ethynyl]phenyl]porphyrin (S22). To a solution of porphyrin **S21** (190 mg, 182 μmol) in $CHCl_3$ (75 mL) was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (400 mg, 1.82 mmol) in methanol (10 mL). After 2 h, the reaction mixture was concentrated. Column chromatography (silica, $CHCl_3$) afforded a purple solid (197 mg, 98%): ^{1}H NMR δ 1.26 (s, 42H), 1.79 (s, 3H), 1.88 (s, 3H), 2.10 (s, 1H), 2.64 (s, 3H), 7.28 (s, 1H), 7.30 (s, 1H), 7.71–7.79 (m, 2H), 7.86–7.89 (m, 4H), 7.94–7.96 (m, 1H), 8.13–8.17 (m, 3H), 8.21–8.24 (m, 2H), 8.80 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 4.8 Hz, 2H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.93 (d, *J* = 4.4 Hz, 2H); LD-MS obsd 1105.2; FAB-MS obsd 1102.47, calcd 1102.47 ($C_{71}H_{74}N_4Si_2Zn$); λ_{abs} 426, 551, 590 nm; λ_{em} (λ_{ex} = 551 nm) 598, 647 nm.

Zn(II)-5-[2-[2-[4-[9-(4-*tert*-Butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl]ethynyl]phenyl]-15-mesityl-10,20-bis[4-[2-(triisopropylsilyl)ethynyl]phenyl]porphyrin (S24). A mixture of **S22** (100 mg, 90.5 μmol), **S23** (70.0 mg, 98.8 μmol), $Pd_2(dba)_3$ (12.4 mg, 13.6 μmol), and P(*o*-tol)$_3$ (33.0 mg, 109 μmol) in

toluene/triethylamine [36 mL (5:1)] was stirred at 60 °C for 21 h. The reaction mixture was then concentrated and passed over a silica column ($CHCl_3$). Preparative SEC (THF) followed by column chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a purple solid (103 mg, 66%): ^{1}H NMR δ –0.39 (d, *J* = 6.9 Hz, 12H), 1.26 (s, 42H), 1.36 (s, 9H), 1.71 (m, 2H), 1.75 (s, 3H), 1.82 (s, 3H), 2.60 (s, 3H), 5.11 (s, 2H), 6.88 (d, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 7.21 (s, 1H), 7.26 (s, 1H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.74–7.86 (m, 6H), 7.96 (d, *J* = 6.6 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.15–8.29 (m, 9H), 8.38–8.44 (m, 2H), 8.73 (d, *J* = 5.1 Hz, 2H), 8.84 (d, *J* = 4.8 Hz, 2H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.95 (d, *J* = 4.5 Hz, 2H); LD-MS obsd 1731.0, calcd avg mass 1732.70 ($C_{115}H_{111}N_5O_3Si_2Zn$); λ_{abs} 426, 510, 547, 591 nm; λ_{em} (λ_{ex} = 510 nm) 599, 647 nm.

Zn(II)-5-[2-[2-[4-[9-(4-*tert*-Butylphenoxy)perylene-3,4-dicarboximido]-3,5-diisopropylphenyl]ethynyl]phenyl]-15-mesityl-10,20-bis(4-ethynylphenyl)porphyrin (S6). A sample of **S24** (100 mg, 57.7 μmol) in THF (15 mL) was treated with TBAF (127 μL, 127 μmol, 1.0 M in THF) for 2 h at room temperature. The reaction mixture was concentrated and then passed through a silica column ($CHCl_3$) to afford a purple solid (49 mg, 60%): ^{1}H NMR δ ; –0.38 (d, *J* = 6.9 Hz, 12H), 1.35 (s, 9H), 1.72 (m, 2H), 1.75 (s, 3H), 1.80 (s, 3H), 2.59 (s, 3H), 3.29 (s, 2H), 5.15 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.20 (s, 1H), 7.26 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.72–7.87 (m, 6H), 7.96 (d, *J* = 7.2 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.16–8.27 (m, 9H), 8.36–8.42 (m, 2H), 8.73 (d, *J* = 4.8 Hz, 2H), 8.81 (d, *J* = 4.5 Hz, 2H), 8.90–8.94 (m, 4H); LD-MS obsd 1421.0, calcd avg mass 1420.02 ($C_{97}H_{71}N_5O_3Zn$); λ_{abs} 426, 511, 546, 589 nm; λ_{em} (λ_{ex} = 511 nm) 598, 647 nm.

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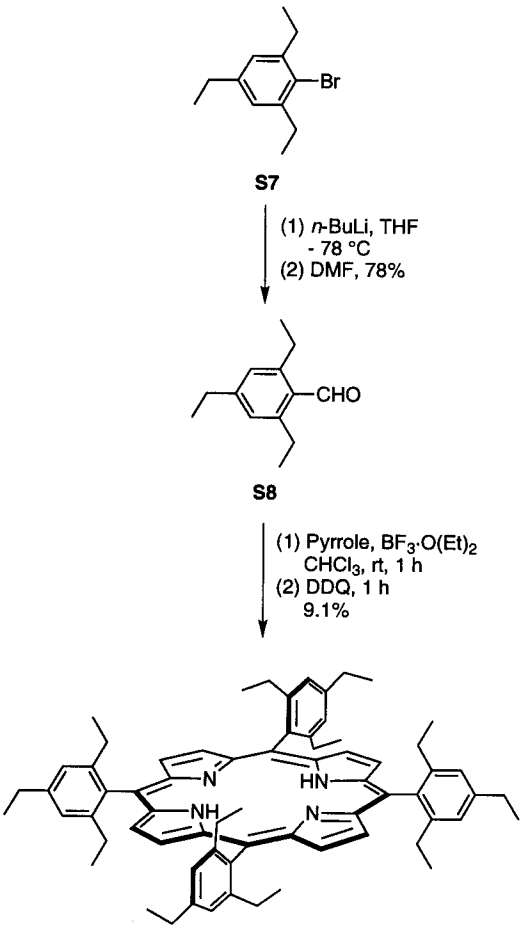
Scheme S1.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S7
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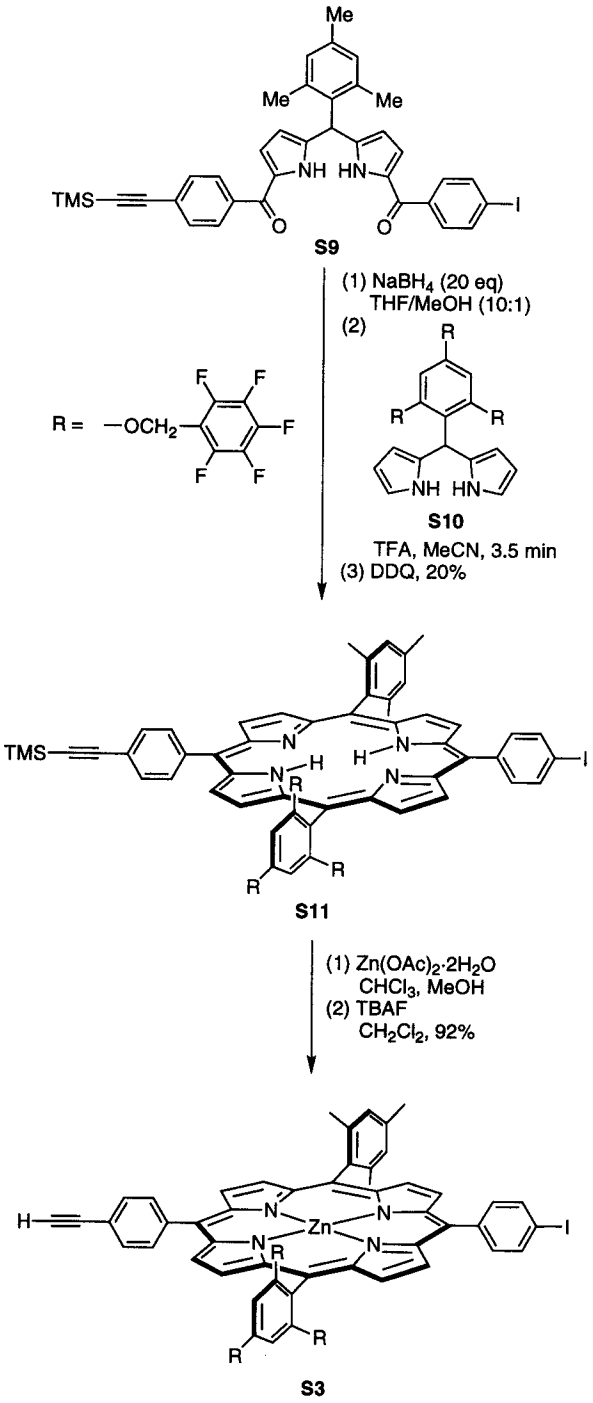
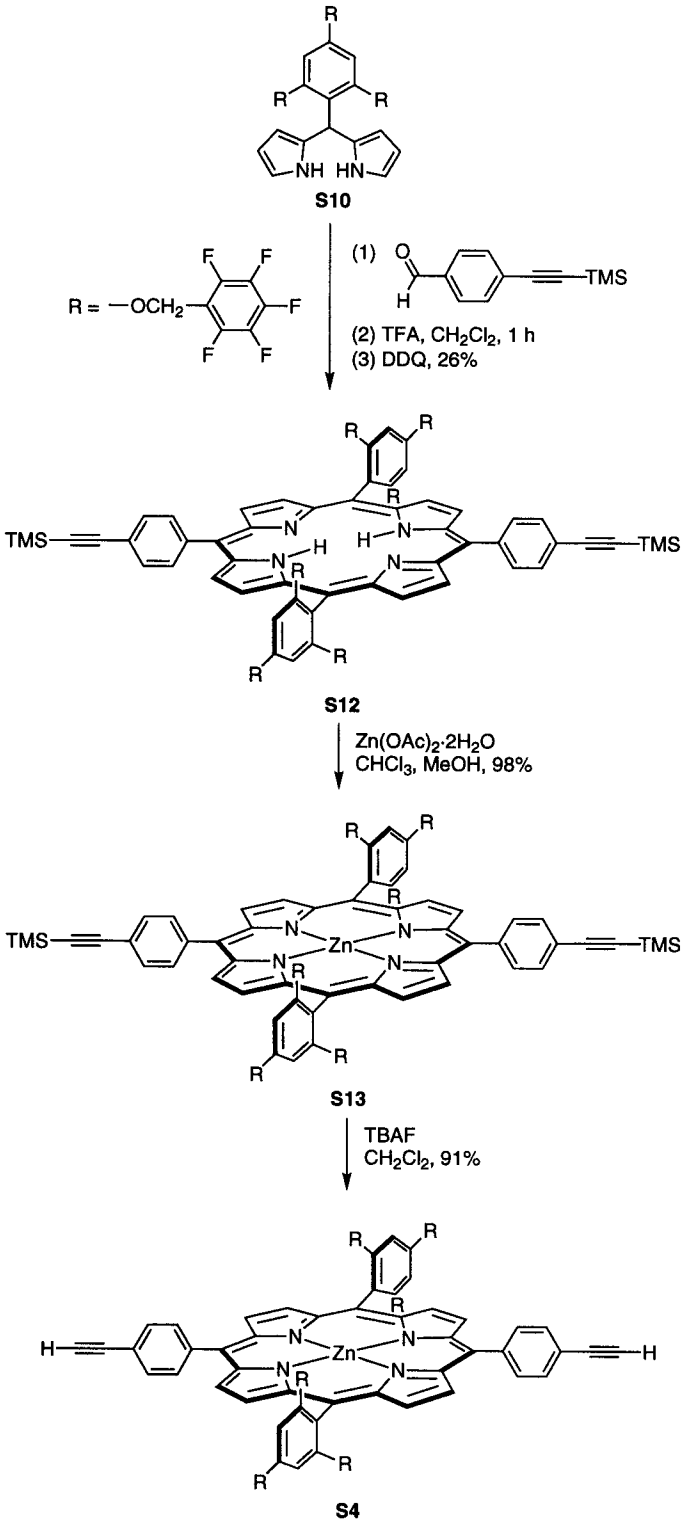
- 78 °C
(2) DMF, 78%
CHO
S8
(1) Pyrrole, BF3·O(Et)2
CHCl3, rt, 1 h
(2) DDQ, 1 h
9.1%
N
HN
NH
N
S2

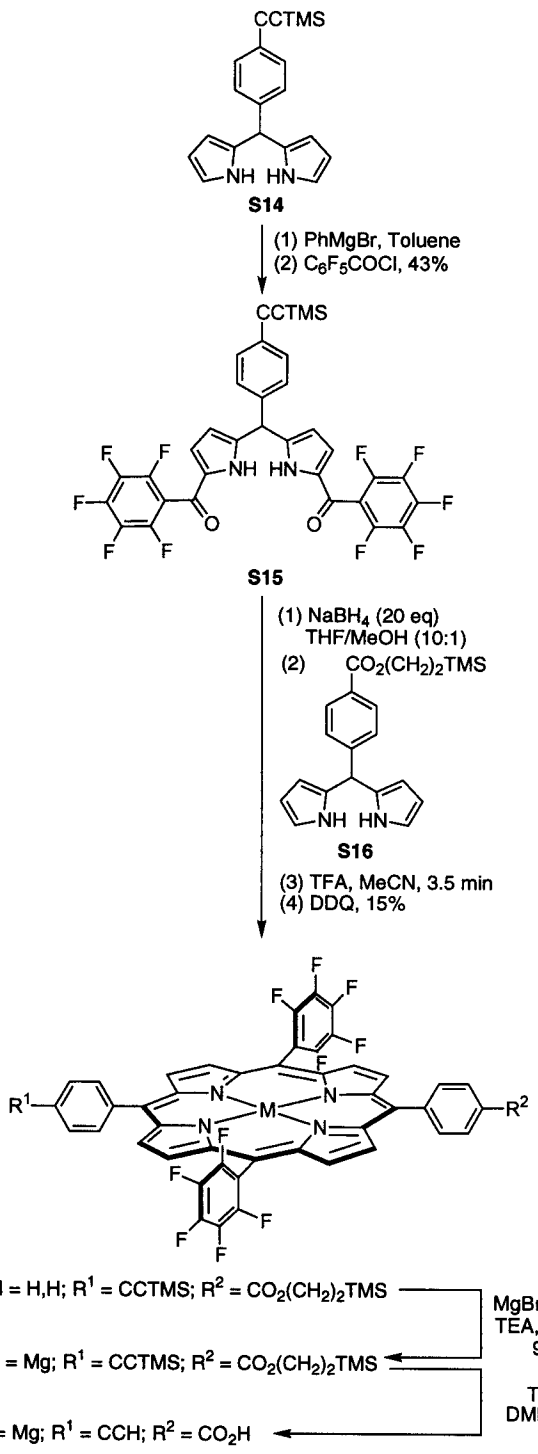
Scheme S2.


Me
Me
Me
NH
HN
TMS
I
O
O
S9
(1) NaBH4 (20 eq)
THF/MeOH (10:1)
(2)
R
R
R
NH
HN
S10
R =
OCH2
F
F
F
F
F
TFA, MeCN, 3.5 min
(3) DDQ, 20%
TMS
I
N
H
N
H
N
N
R
R
R
S11
(1) Zn(OAc)2·2H2O
CHCl3, MeOH
(2) TBAF
CH2Cl2, 92%
H
I
N
N
Zn
N
N
R
R
R
S3

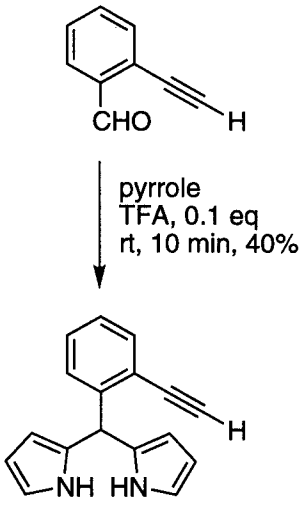
Scheme S3.


R
R
R
NH HN
S10
R = —OCH2
F
F
F
F
F
(1)
O
H
TMS
(2) TFA, CH2Cl2, 1 h
(3) DDQ, 26%
TMS
TMS
S12
Zn(OAc)2·2H2O
CHCl3, MeOH, 98%
Zn
S13
TBAF
CH2Cl2, 91%
H
H
S4

Scheme S4.

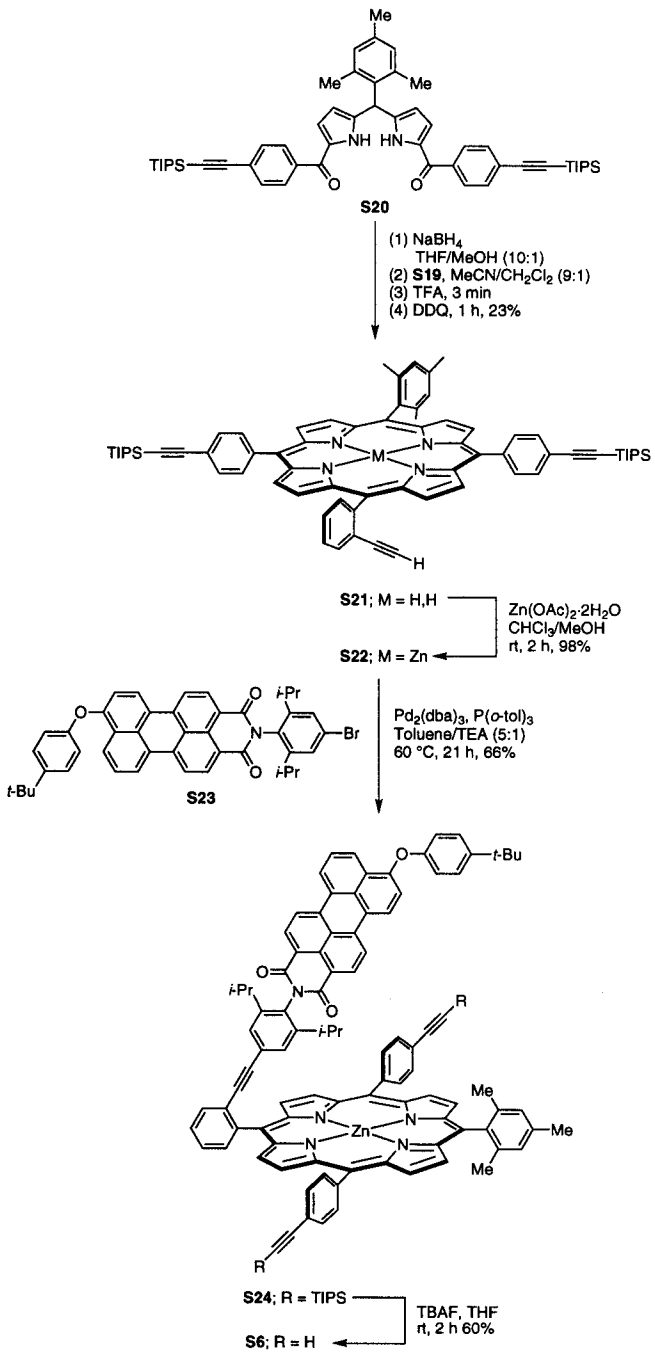

CCTMS
NH HN
S14
(1) PhMgBr, Toluene
(2) C_6F_5COCl, 43%
CCTMS
F
NH HN
O
S15
(1) $NaBH_4$ (20 eq)
THF/MeOH (10:1)
(2) $CO_2(CH_2)_2TMS$
NH HN
S16
(3) TFA, MeCN, 3.5 min
(4) DDQ, 15%
R^1
R^2
M
N
F
S17, M = H,H; R^1 = CCTMS; R^2 = $CO_2(CH_2)_2TMS$
$MgBr_2 \cdot O(Et)_2$
TEA, CH_2Cl_2
99%
S18, M = Mg; R^1 = CCTMS; R^2 = $CO_2(CH_2)_2TMS$
TBAF
DMF, 71%
S5, M = Mg; R^1 = CCH; R^2 = CO_2H

Scheme S5.



S19

Scheme S6.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Me
Me
NH HN
TIPS
TIPS
O
O
S20
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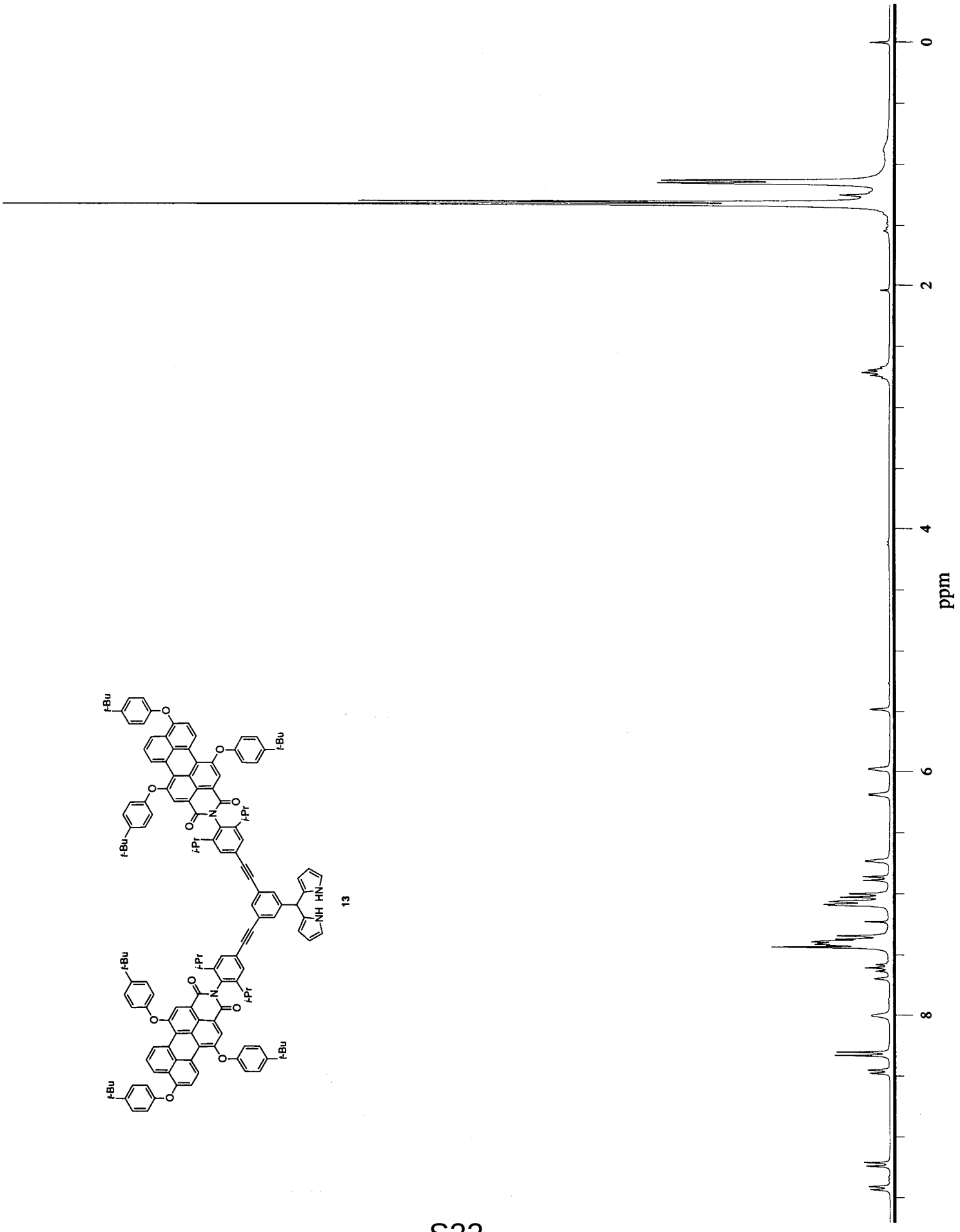
THF/MeOH (10:1)
(2) S19, MeCN/CH2Cl2 (9:1)
(3) TFA, 3 min
(4) DDQ, 1 h, 23%
TIPS
TIPS
N
M
N
N
N
H
S21; M = H,H
Zn(OAc)2·2H2O
CHCl3/MeOH
rt, 2 h, 98%
S22; M = Zn
O
i-Pr
N
Br
O
i-Pr
O
t-Bu
S23
Pd2(dba)3, P(o-tol)3
Toluene/TEA (5:1)
60 °C, 21 h, 66%
t-Bu
O
O
N
O
i-Pr
i-Pr
R
Me
Me
Me
N
N
Zn
N
N
R
S24; R = TIPS
S6; R = H
TBAF, THF
rt, 2 h 60%



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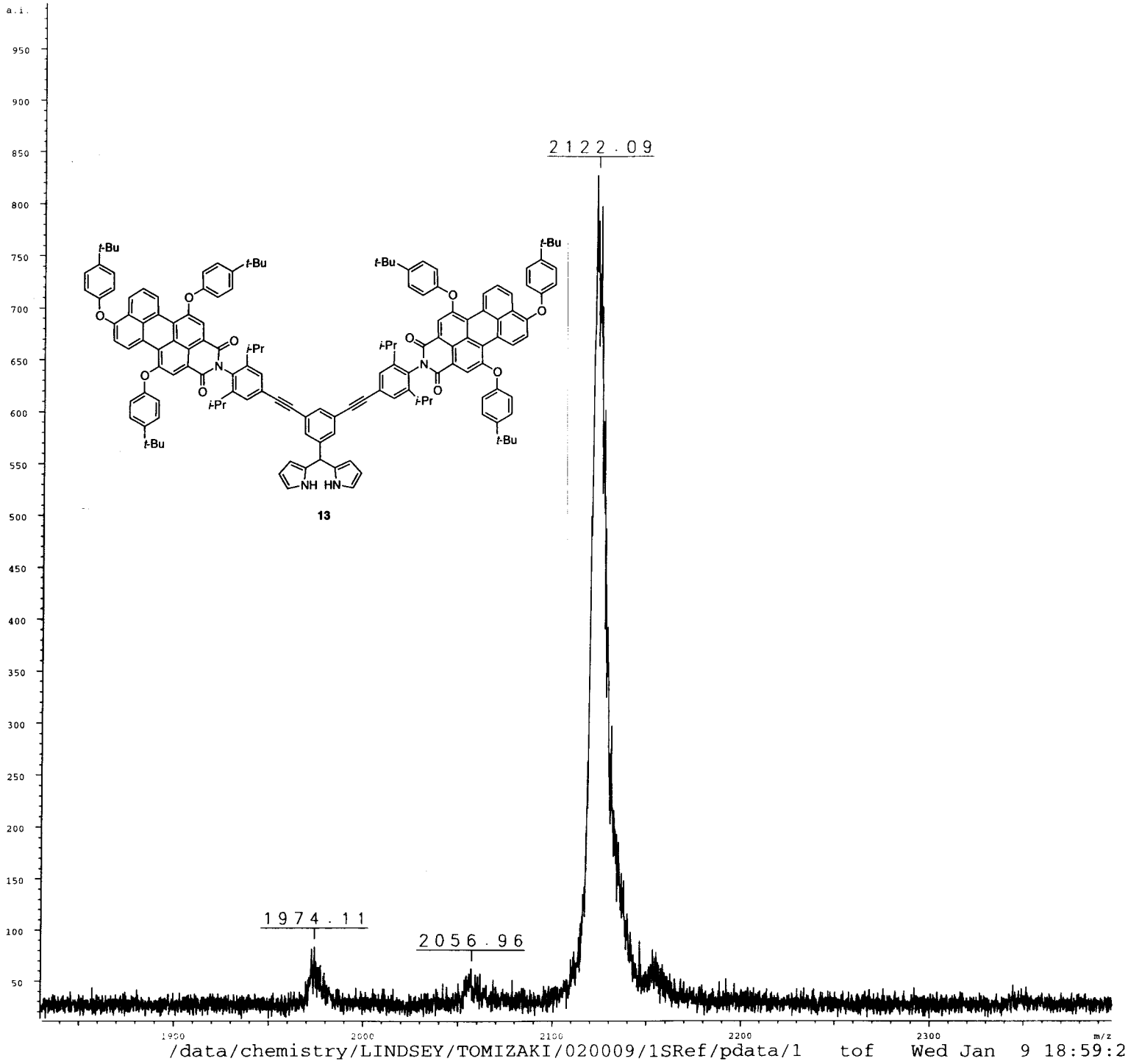


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LLNSBND nc
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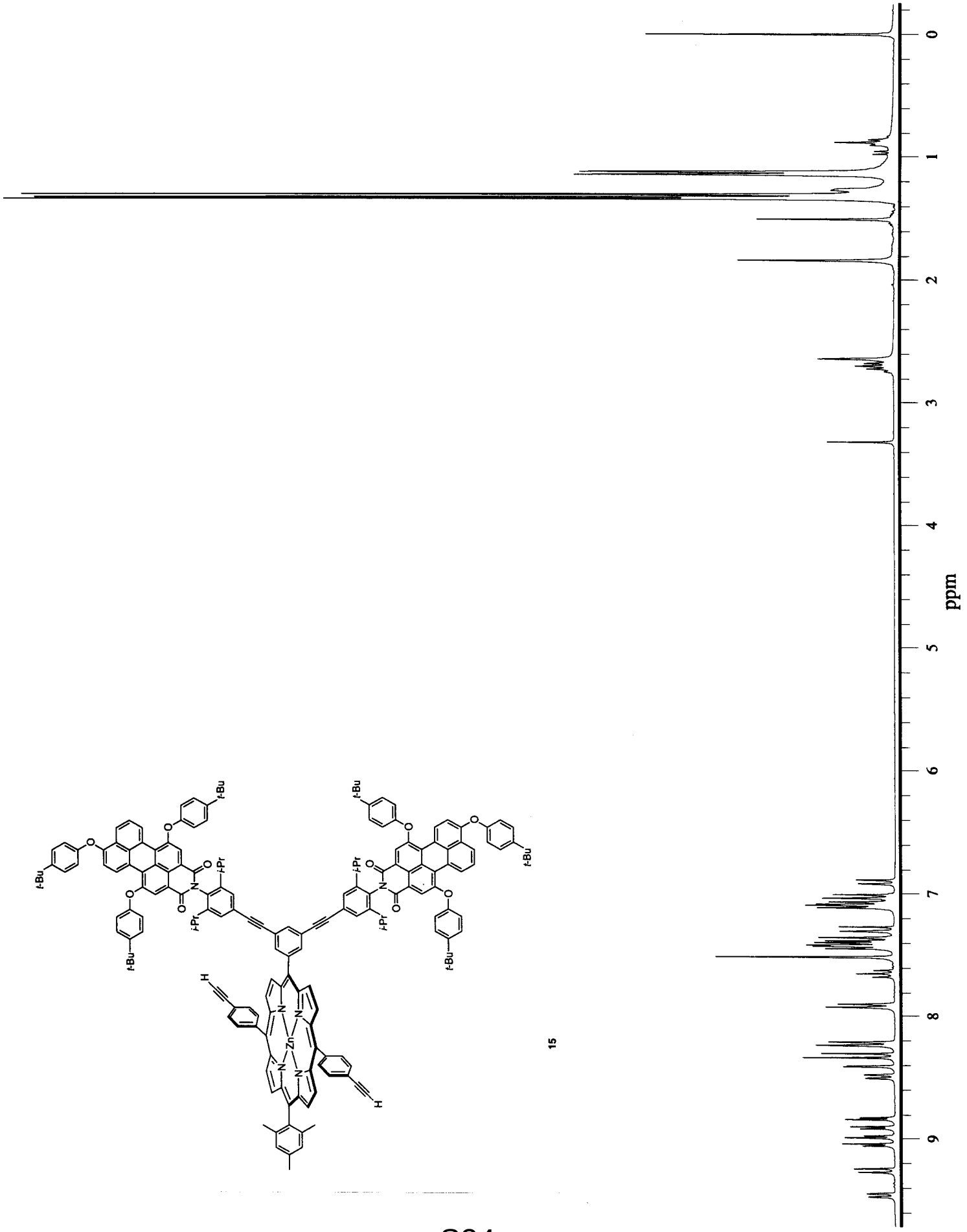
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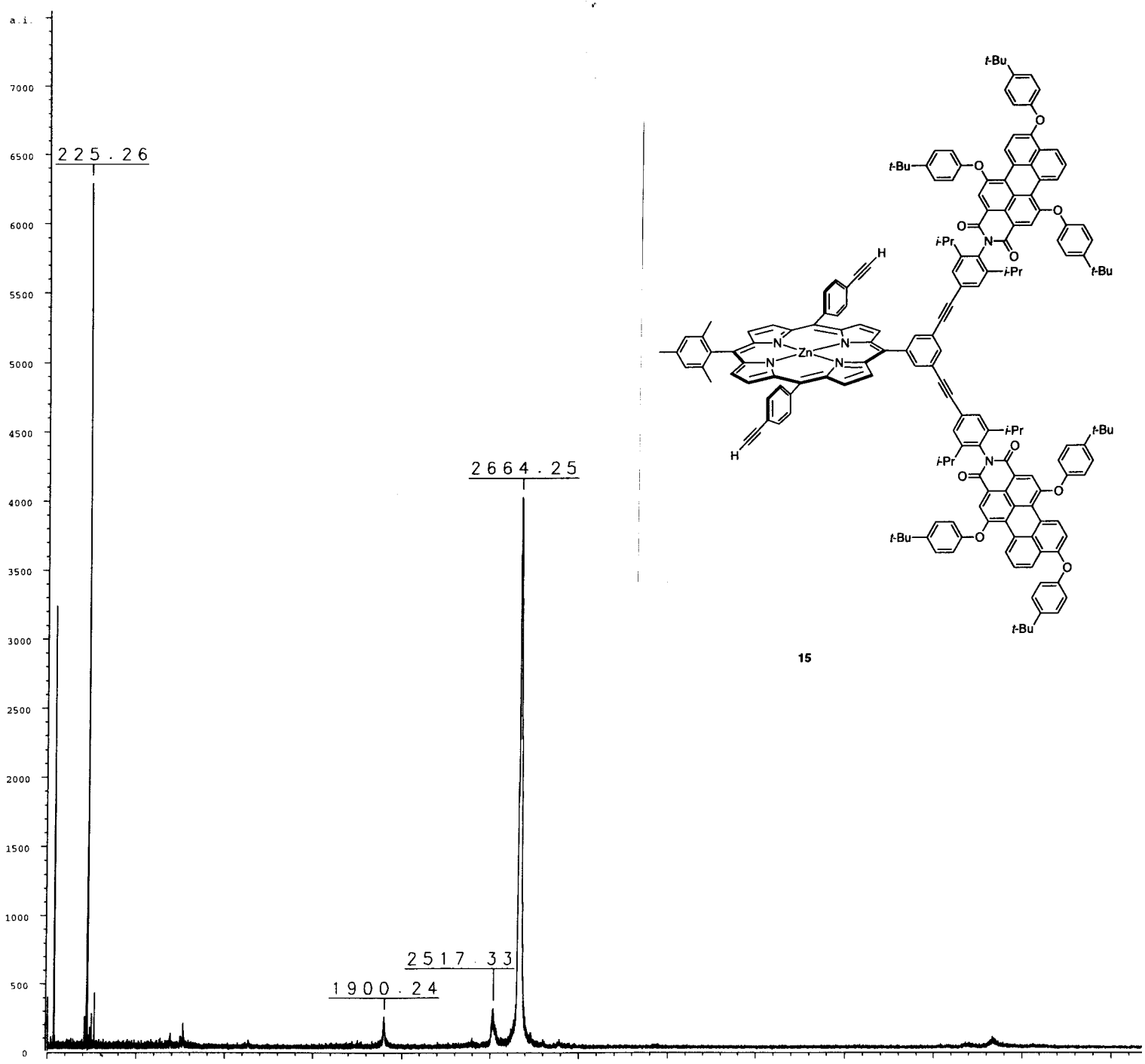
9



15

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ML2              333.982
ML3                0.000
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DEFLON  no
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LLNSBND no
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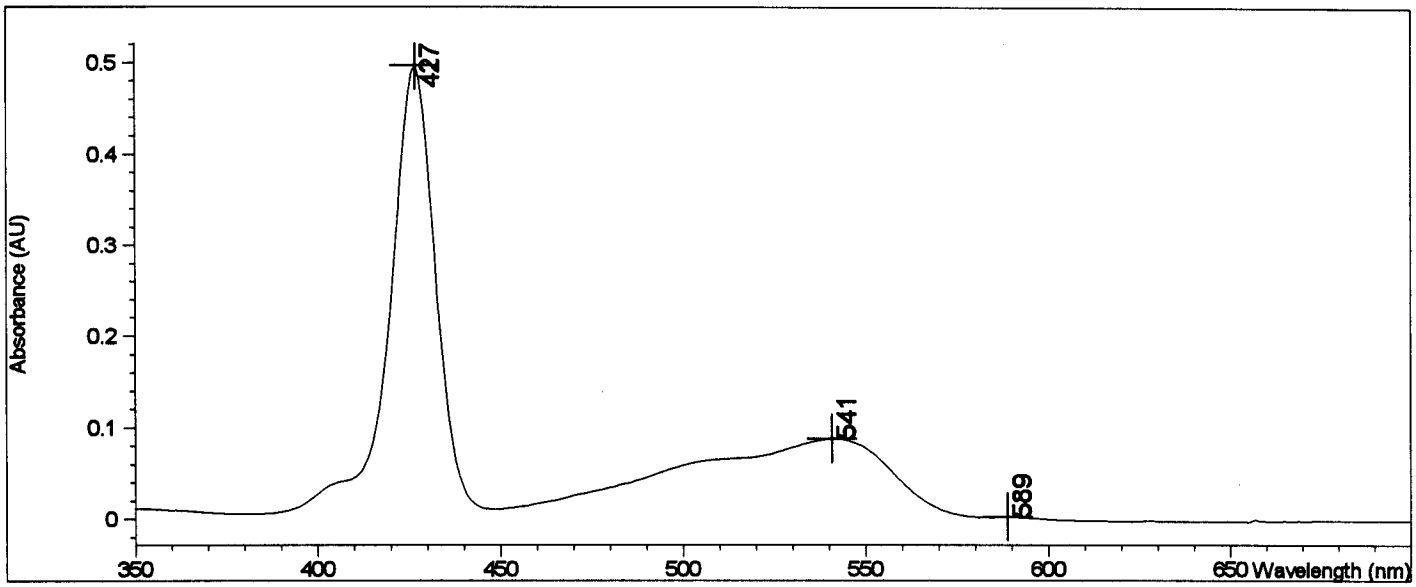

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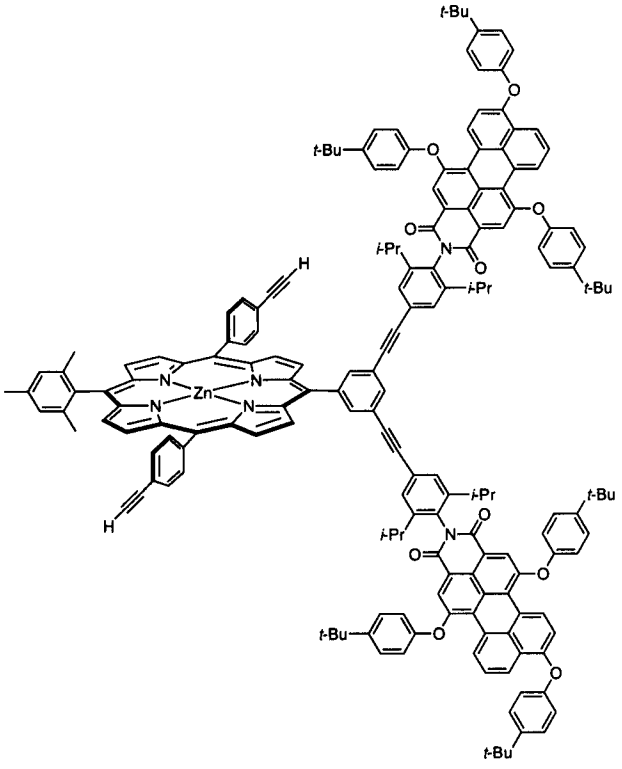
1		589.0	2.3108E-3



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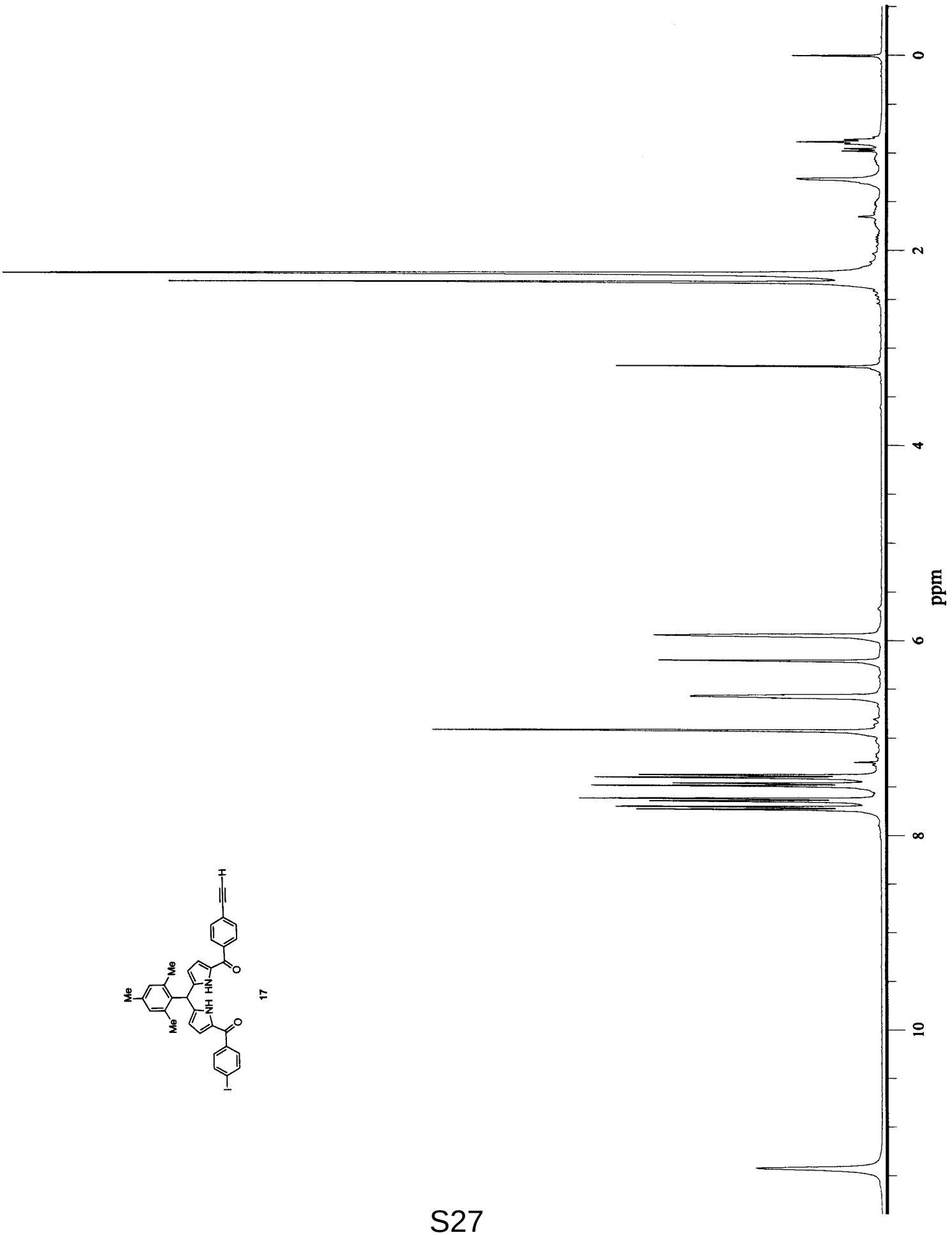

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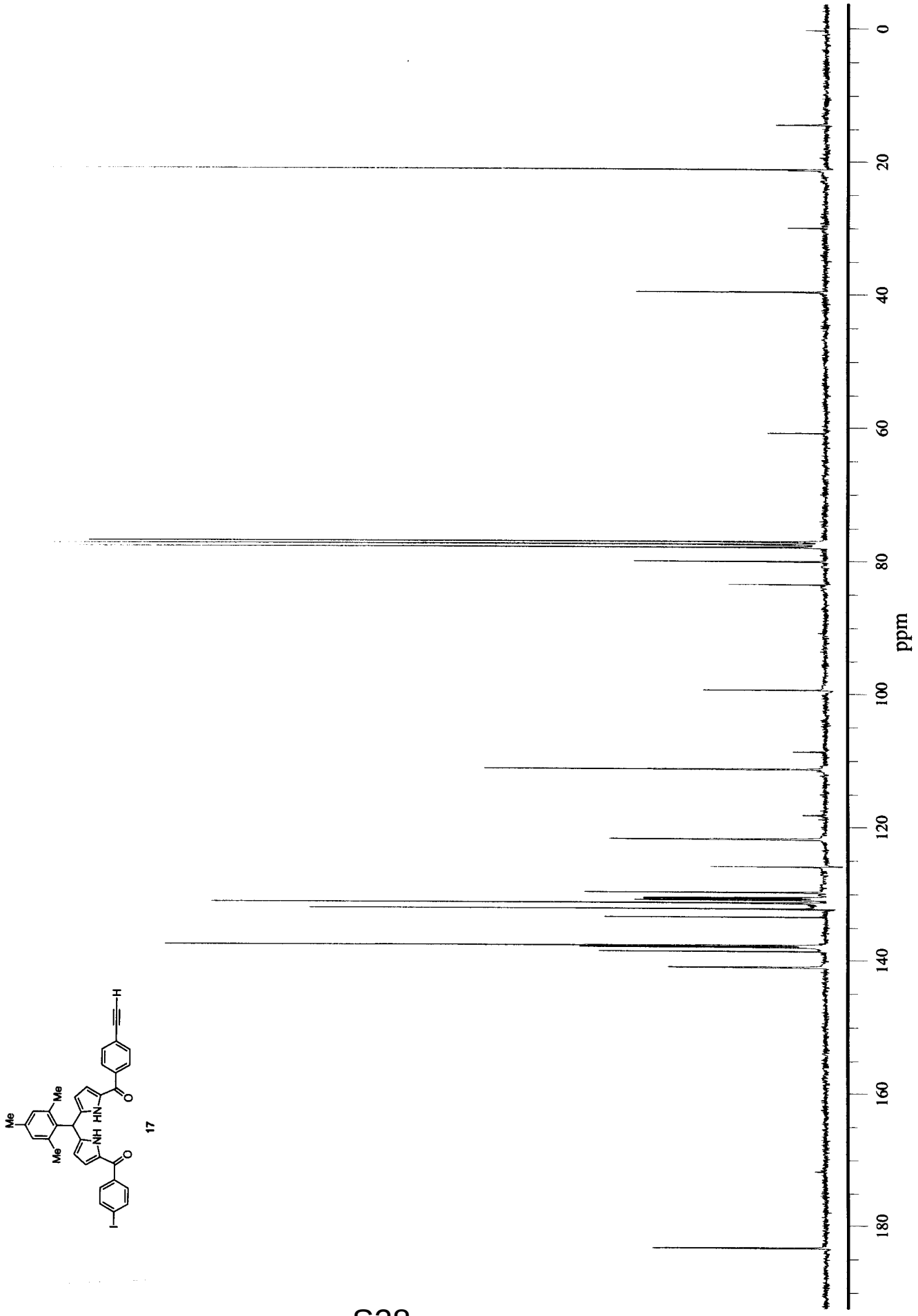
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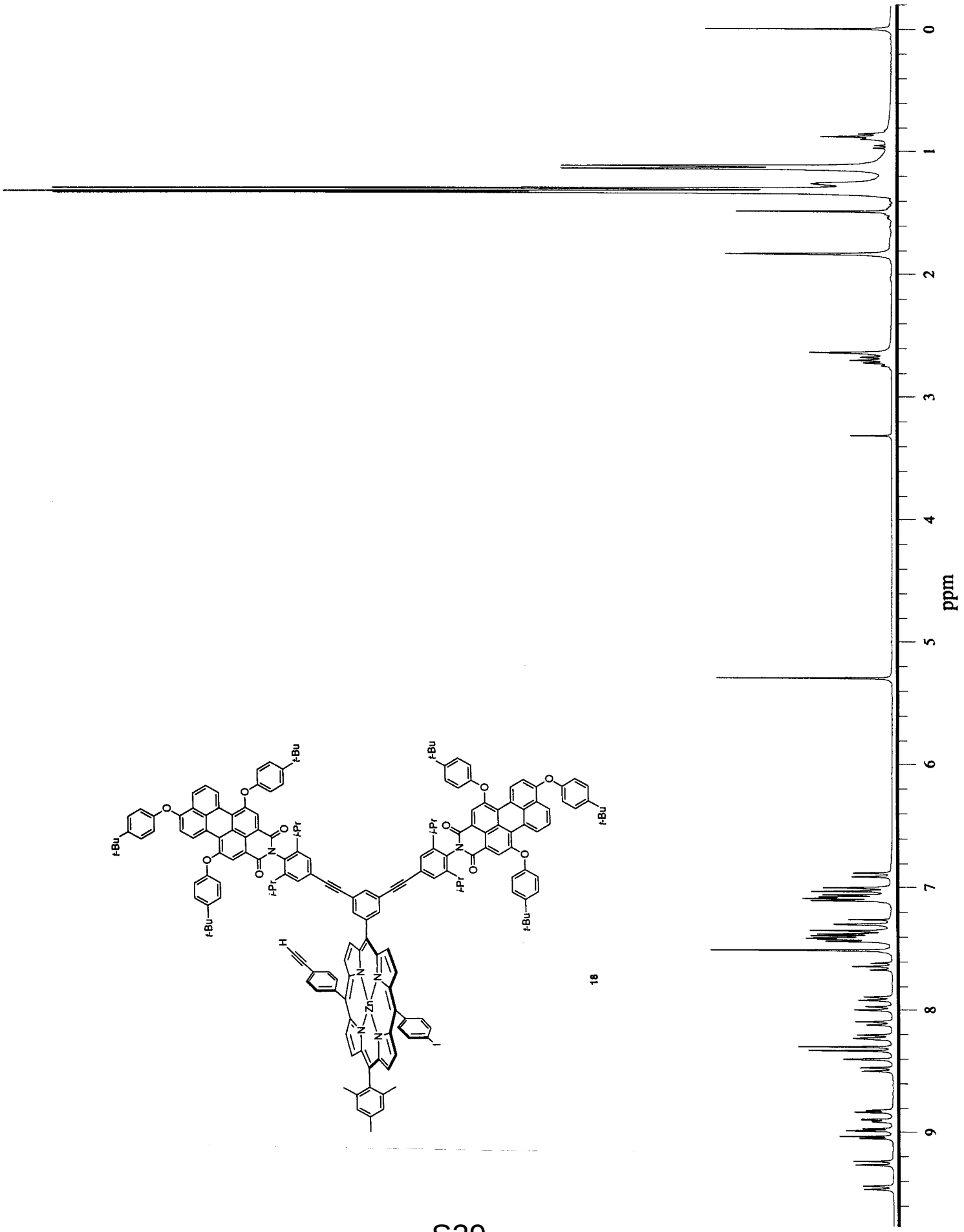
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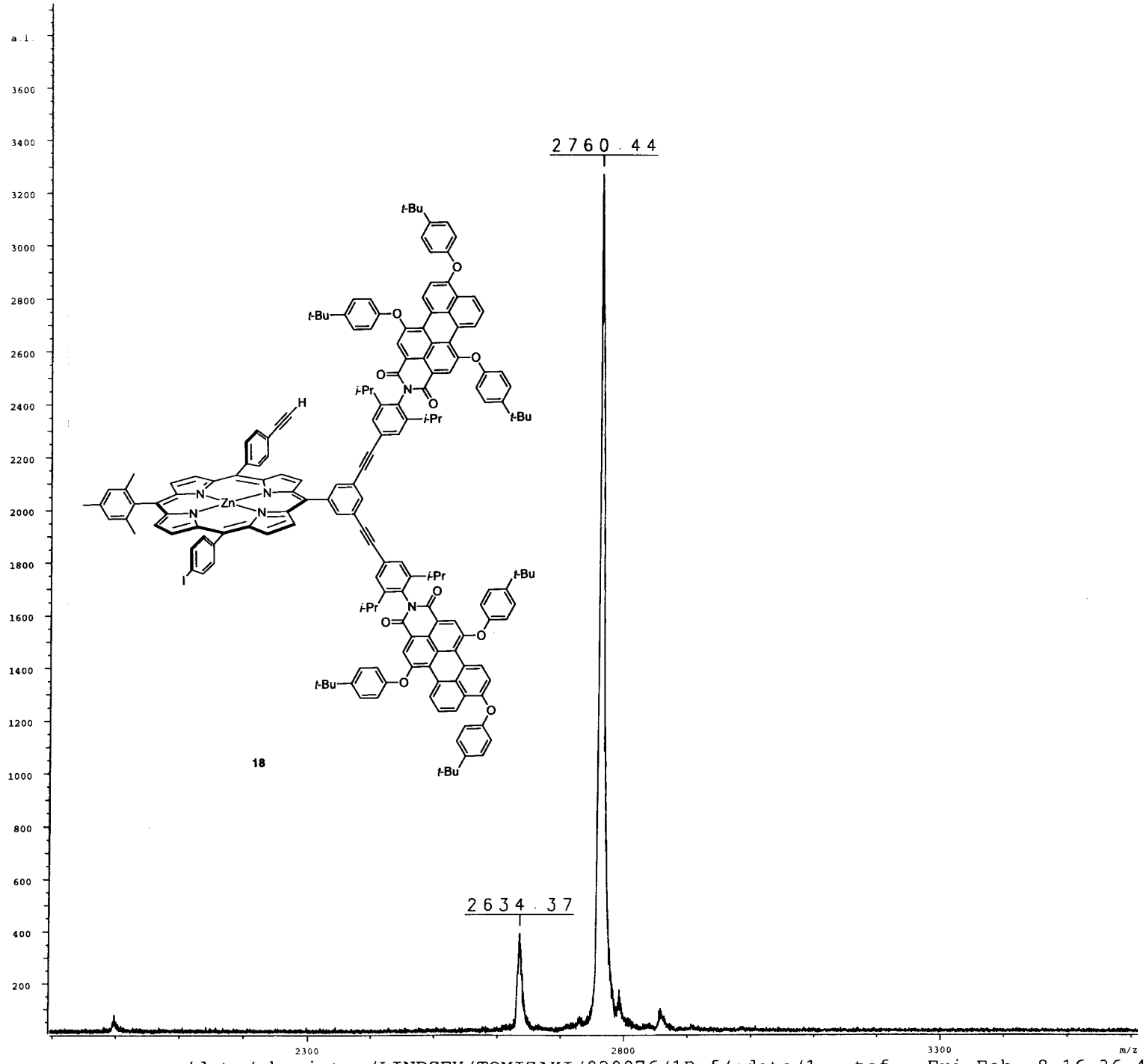
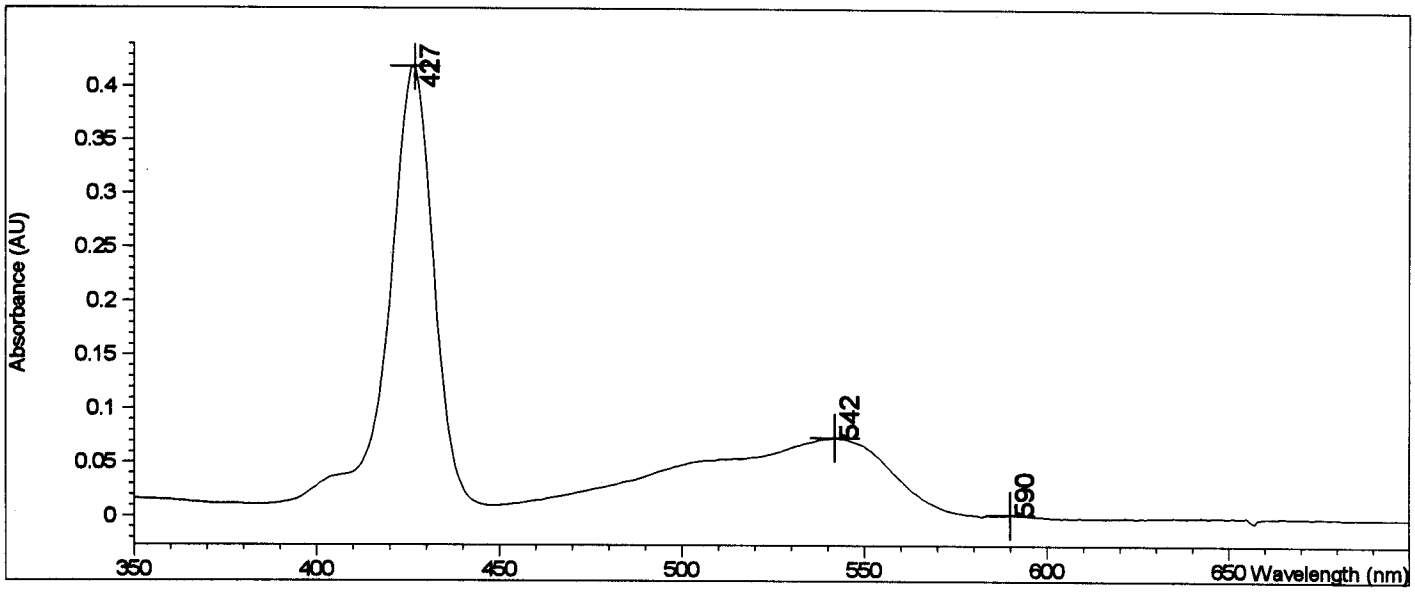
H
18

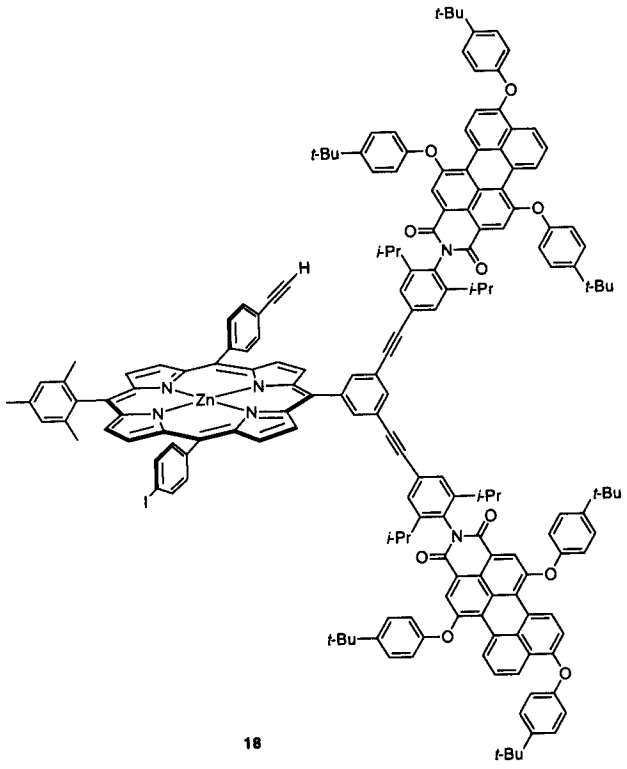


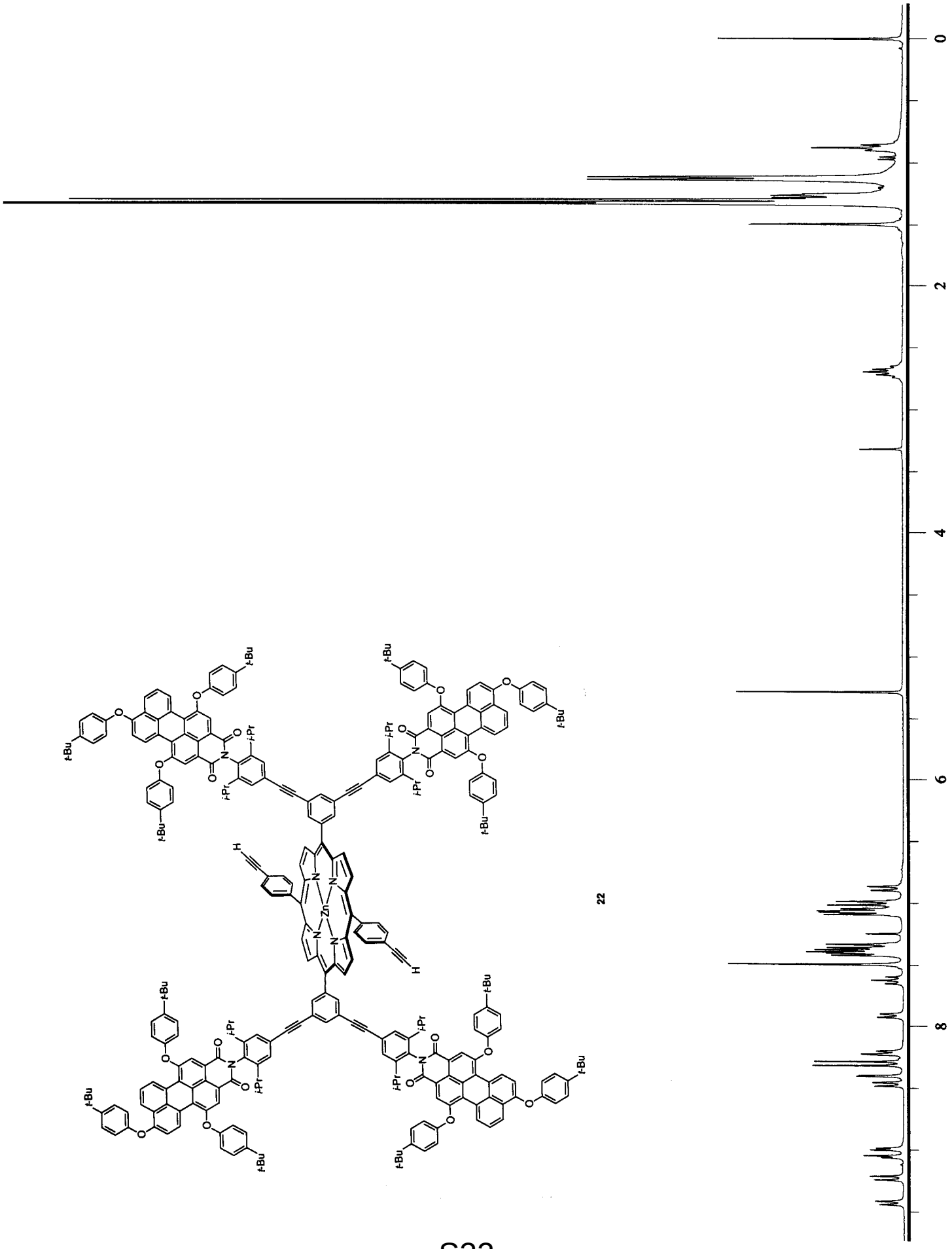

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  020076
AQ_DATE Fri Feb  8 16:35:05 2002
PATH    /data/chemistry/LINDSEY/TOMIZAKI
POLARI  POS
AQOP_m  Reflector
TD              50000
NoSHOTS            50
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  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               30.0
ML1          2070399.914
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    kt270y w/ dithranol
CMT2    attn =30, shot = 50
```

/data/chemistry/LINDSEY/TOMIZAKI/020076/1Ref/pdata/1 tof Fri Feb 8 16:36:49 2002

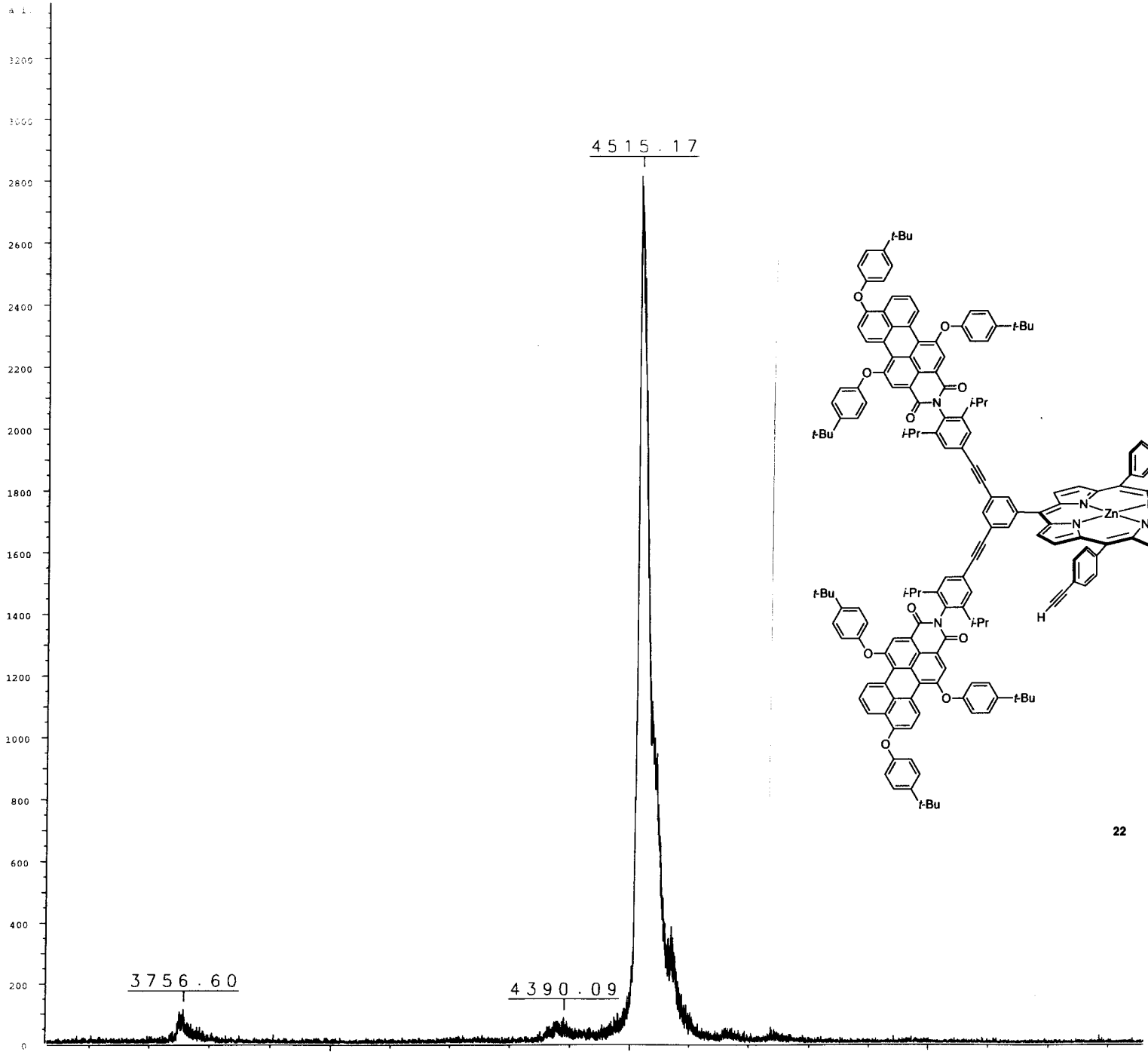


#	Name	Peaks (nm)	Abs (AU)
1		427.0	0.41900
1		542.0	7.3269E-2
1		590.0	1.4849E-3



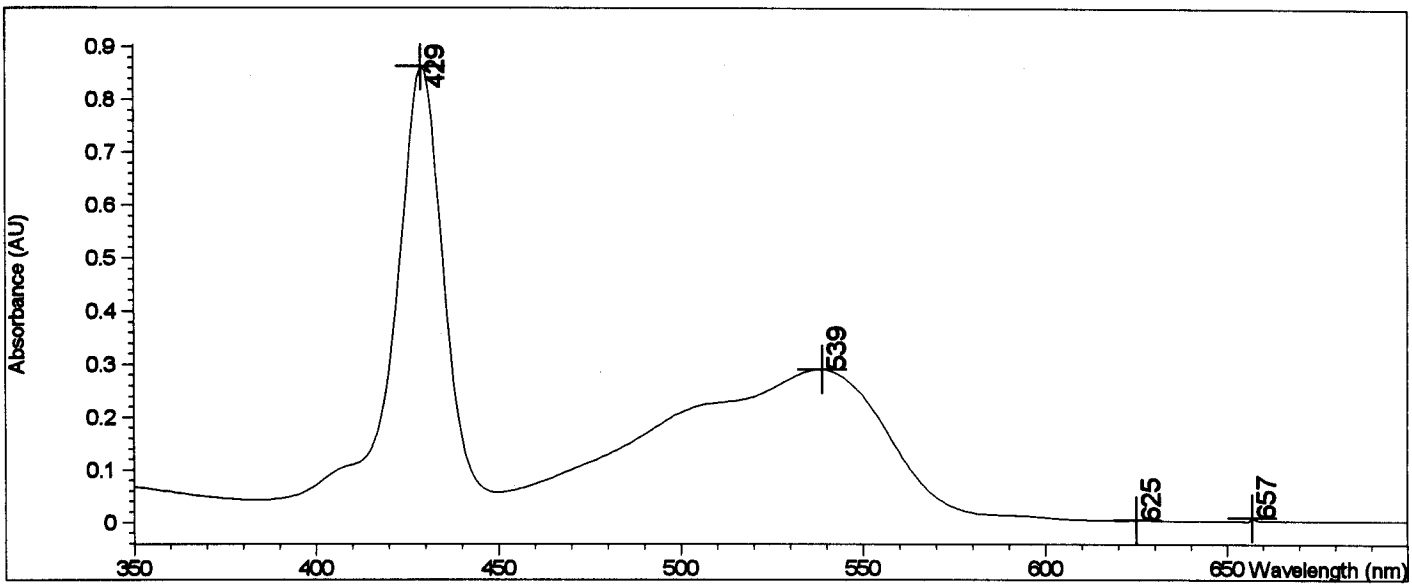


22

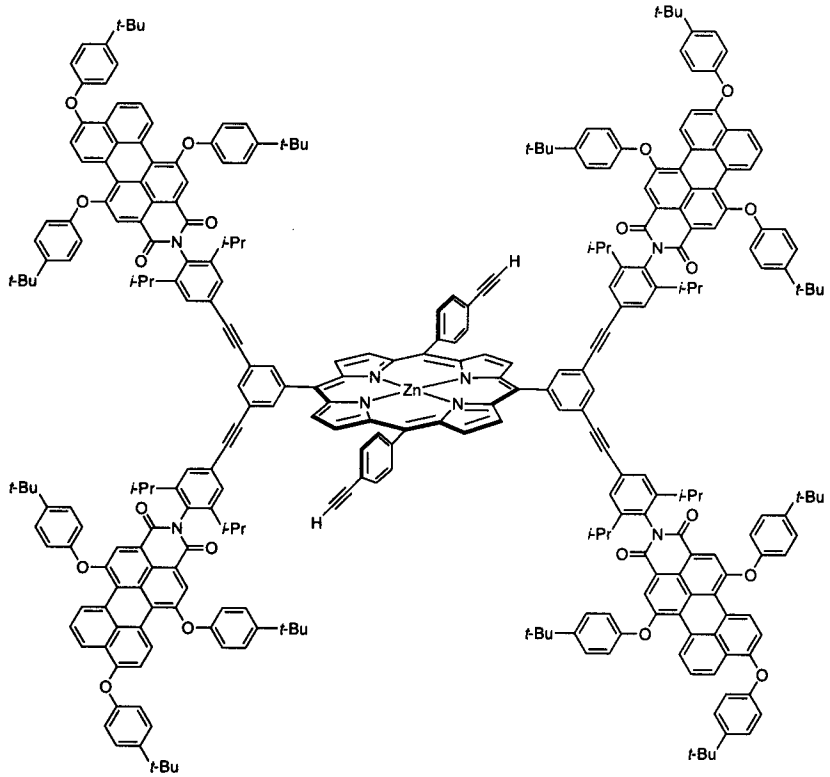


/data/chemistry/LINDSEY/TOMIZAKI/020044/1SRef/pdata/1 tof Mon Feb 4 12:49:34 2002

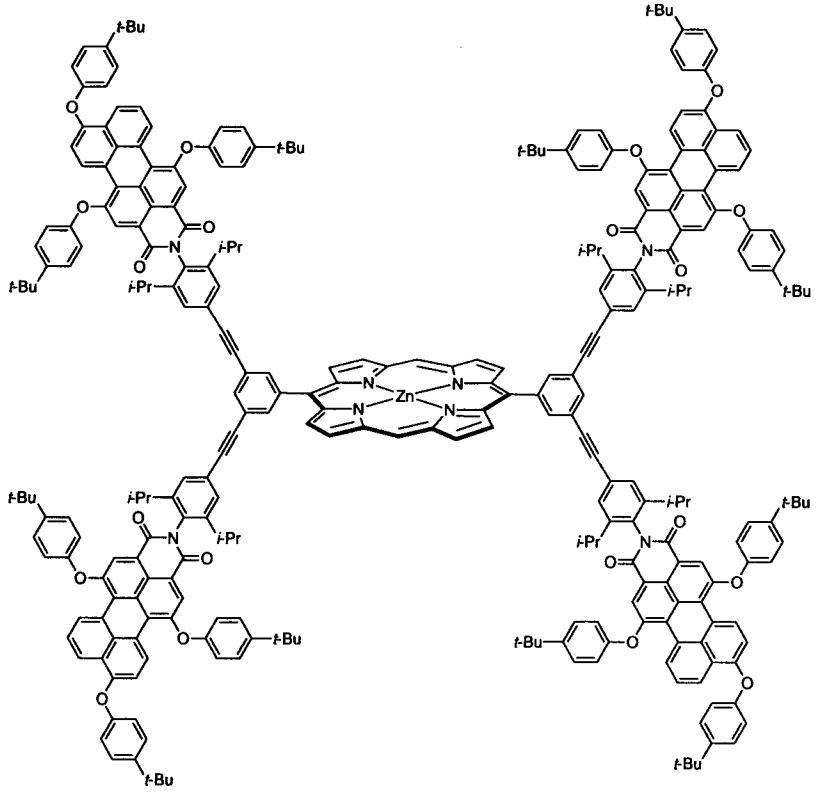
22



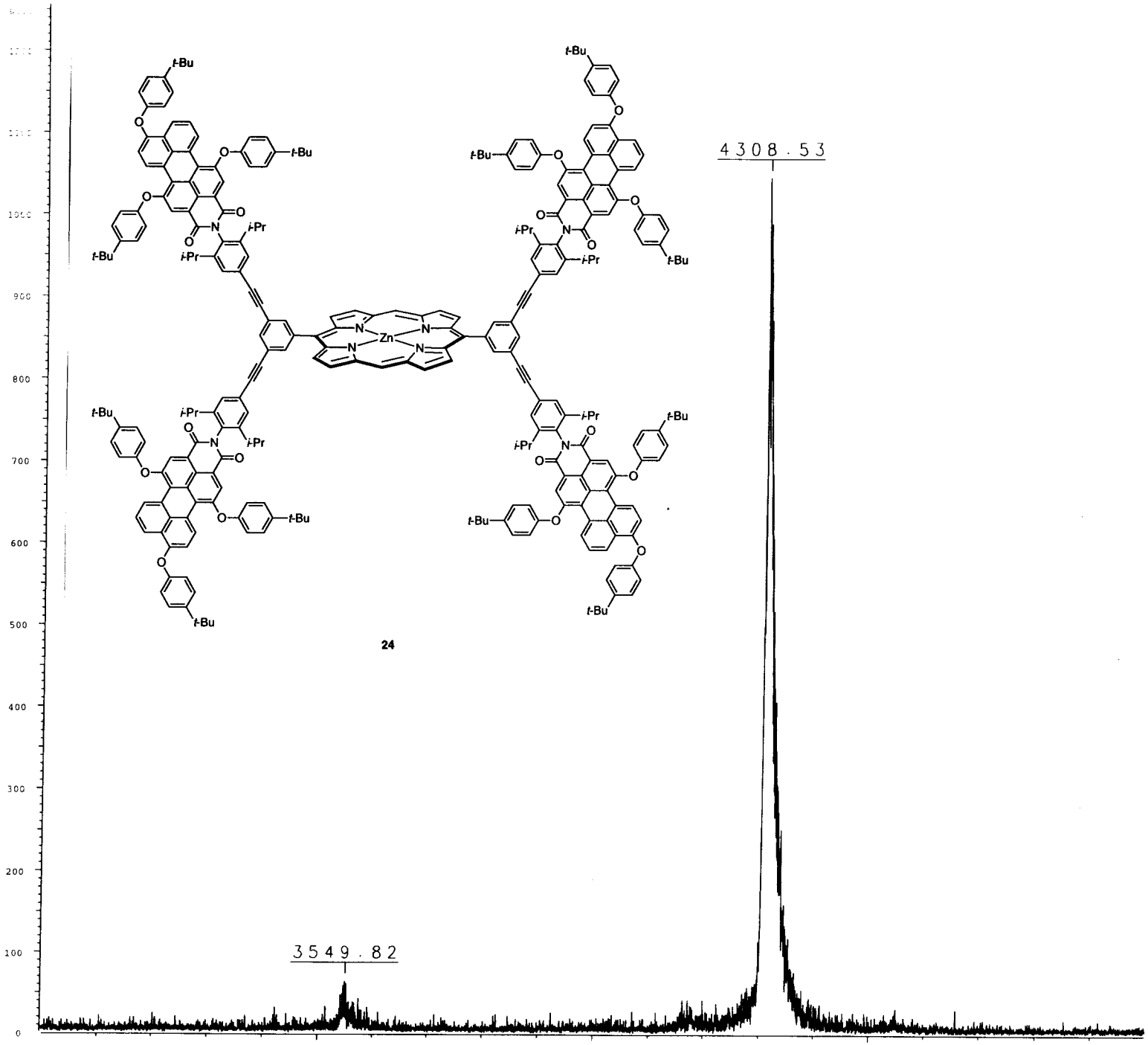
#	Name	Peaks (nm)	Abs (AU)
1		429.0	0.86269
1		539.0	0.29049
1		657.0	9.5491E-3
1		625.0	4.0197E-3
1		***	***



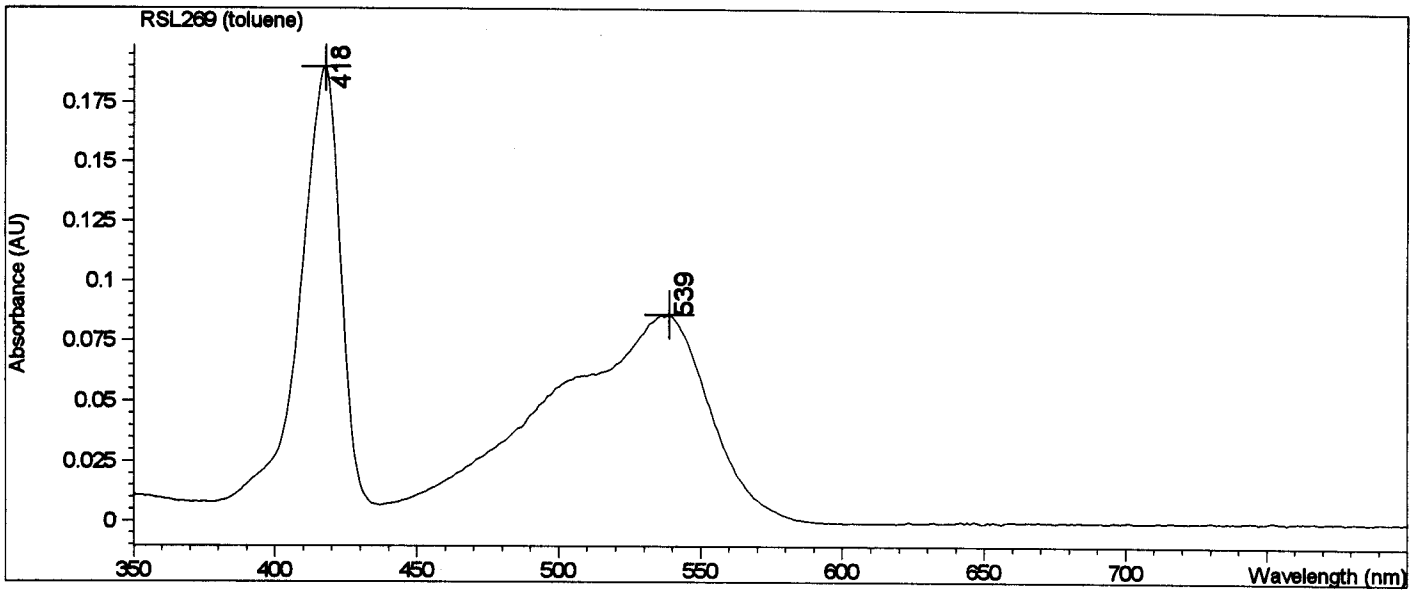
22



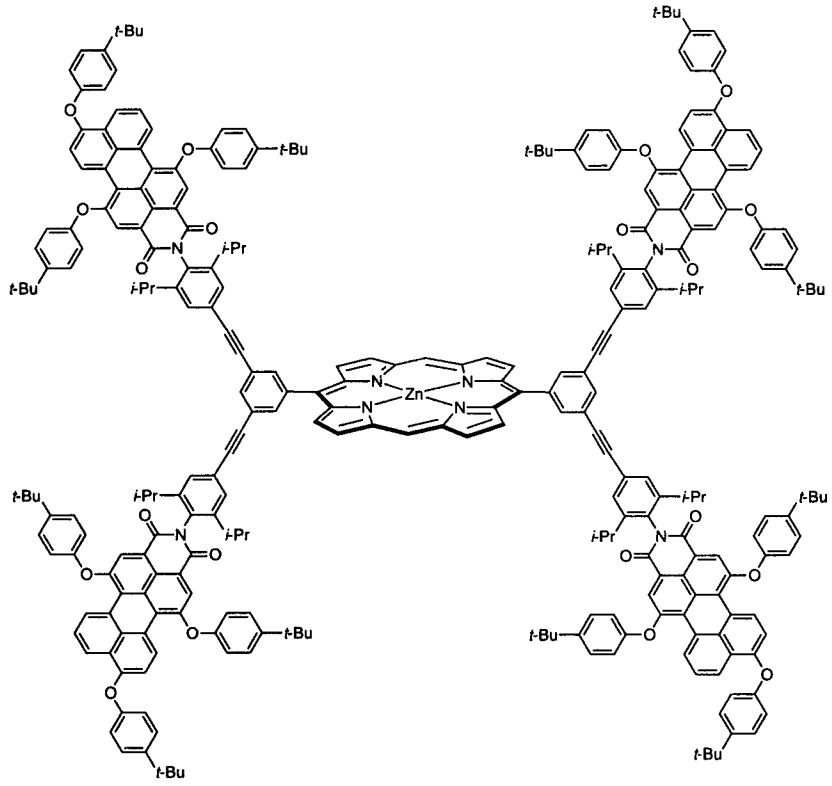
24



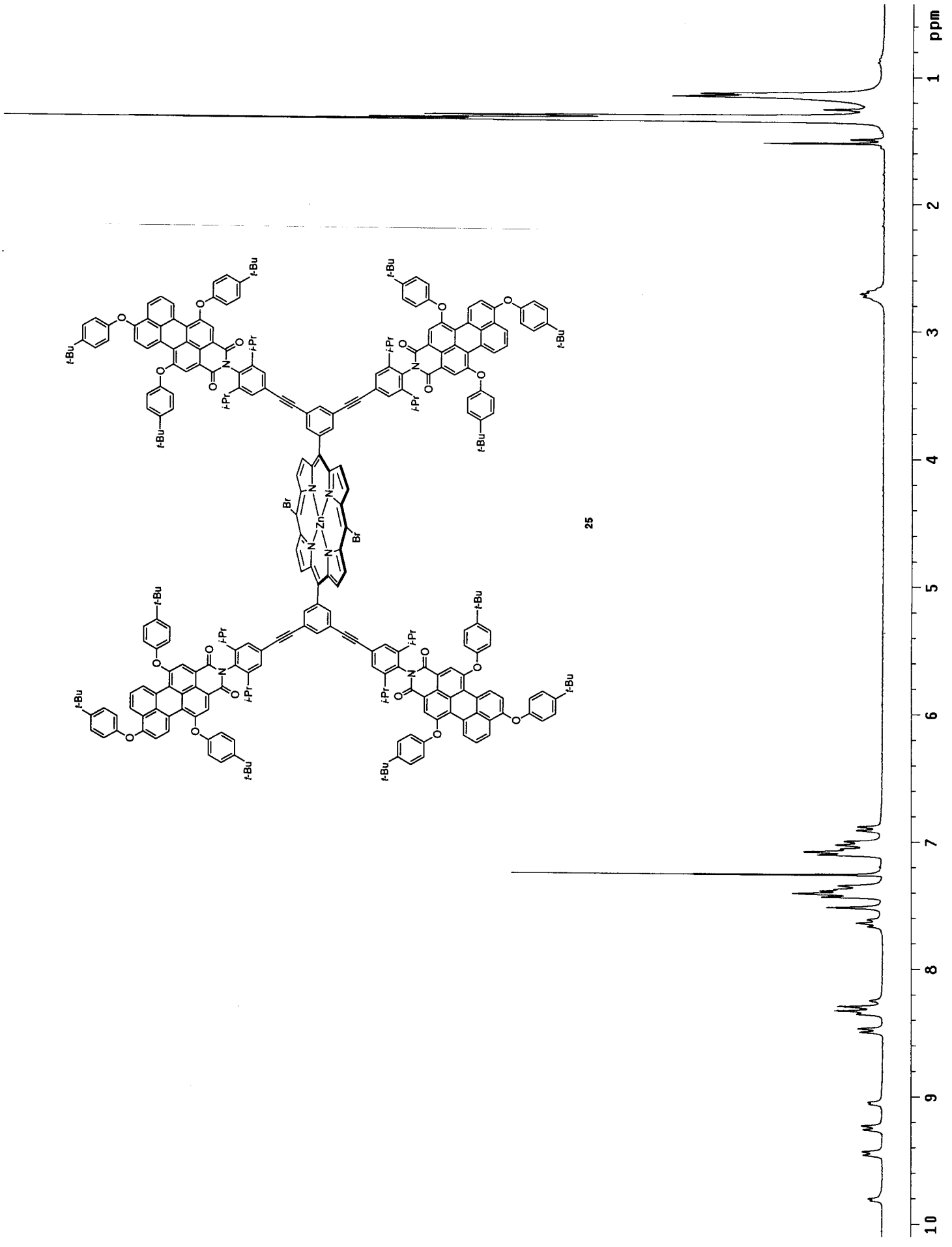

```
INSTRUM TOF
OpId    Unknown
SMPNAM  020160
AQ_DATE Tue Mar  5 11:53:58 2002
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD              60000
NoSHOTS            21
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  1.00   [ns]
DELAY             0 [ns]
Uis1               20.00   [kV]
Uis2               18.50   [kV]
Uref1               0.00   [kV]
Ulens               7.50   [kV]
Uhimass            10.00   [kV]
RefFull1            0.00   [kV]
UdetL               1.55   [kV]
UdetR               0.00   [kV]
Udef1               2.00   [kV]
REPHZ               1.00   [Hz]
ATTEN              30.0
ML1          2070371.899
ML2              333.982
ML3                0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1           510.84
DPMASS           200.00   [Da]
RBNDVAL            0.33
LBNDVAL            0.28
IS2BNDV            0.91
CMT1    RSL269
CMT2    Dithranol matrix
```

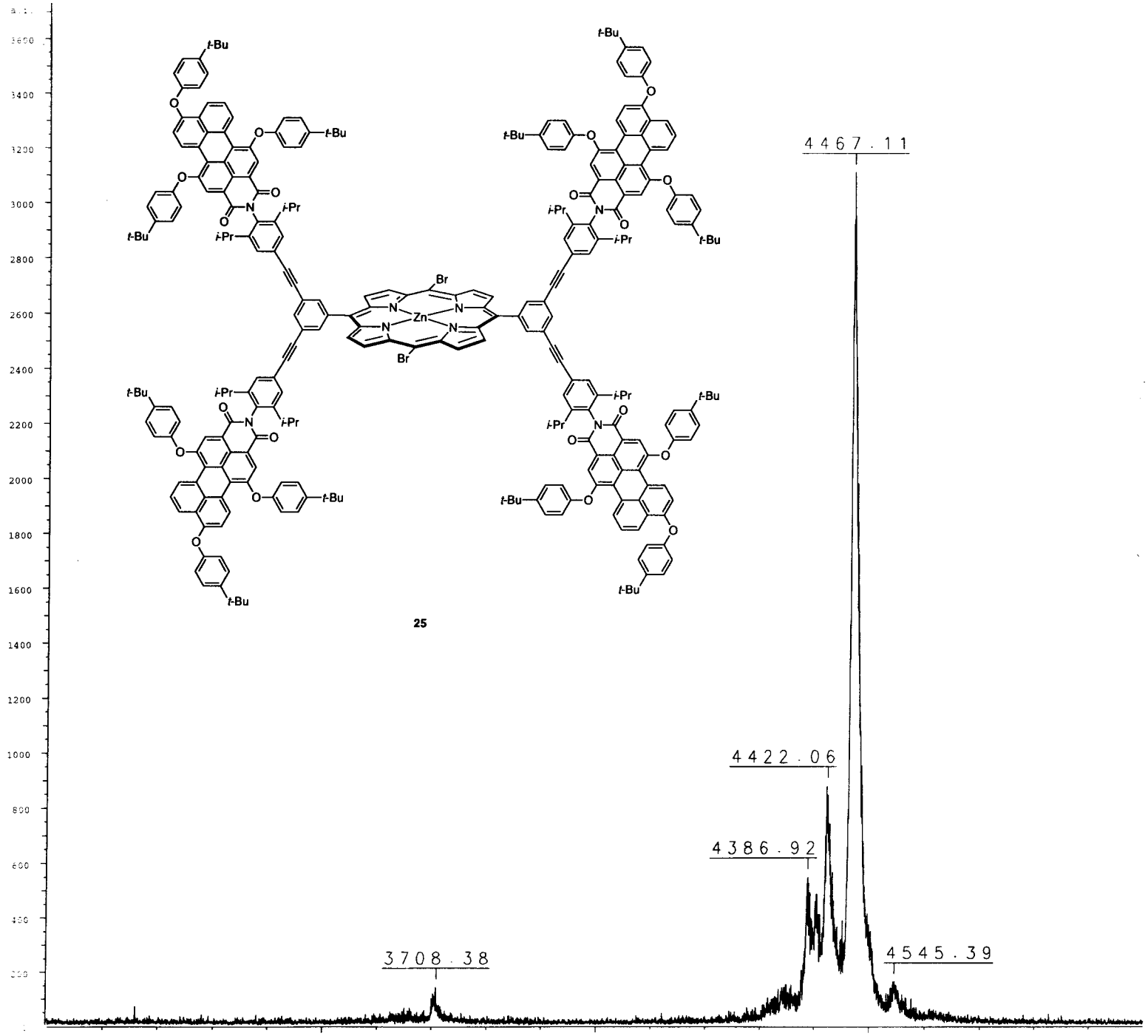


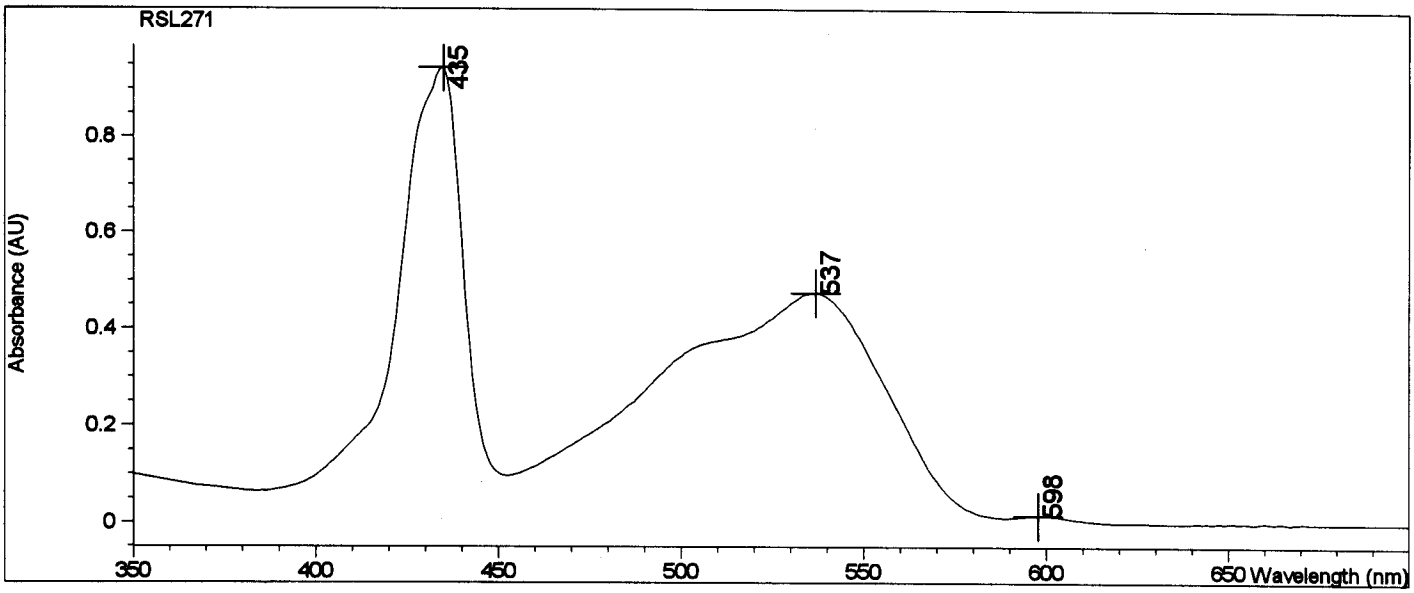
#	Name	Peaks (nm)	Abs (AU)
1	RSL269 (toluene)	418.0	0.18953
1		539.0	8.5990E-2
1		***	***
1		***	***
1		***	***



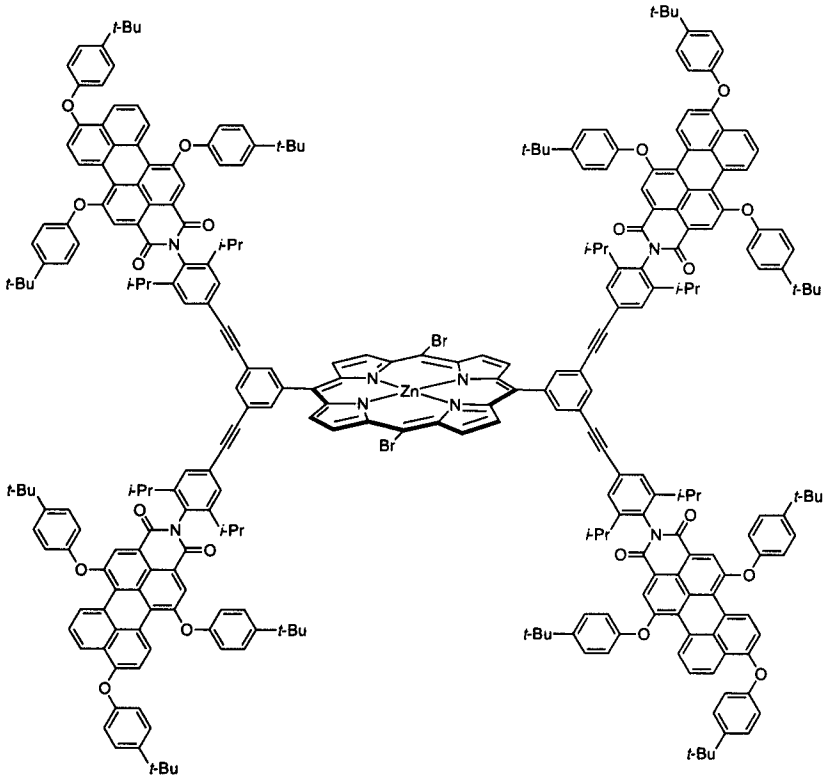
24


25
ppm
1
2
3
4
5
6
7
8
9
10

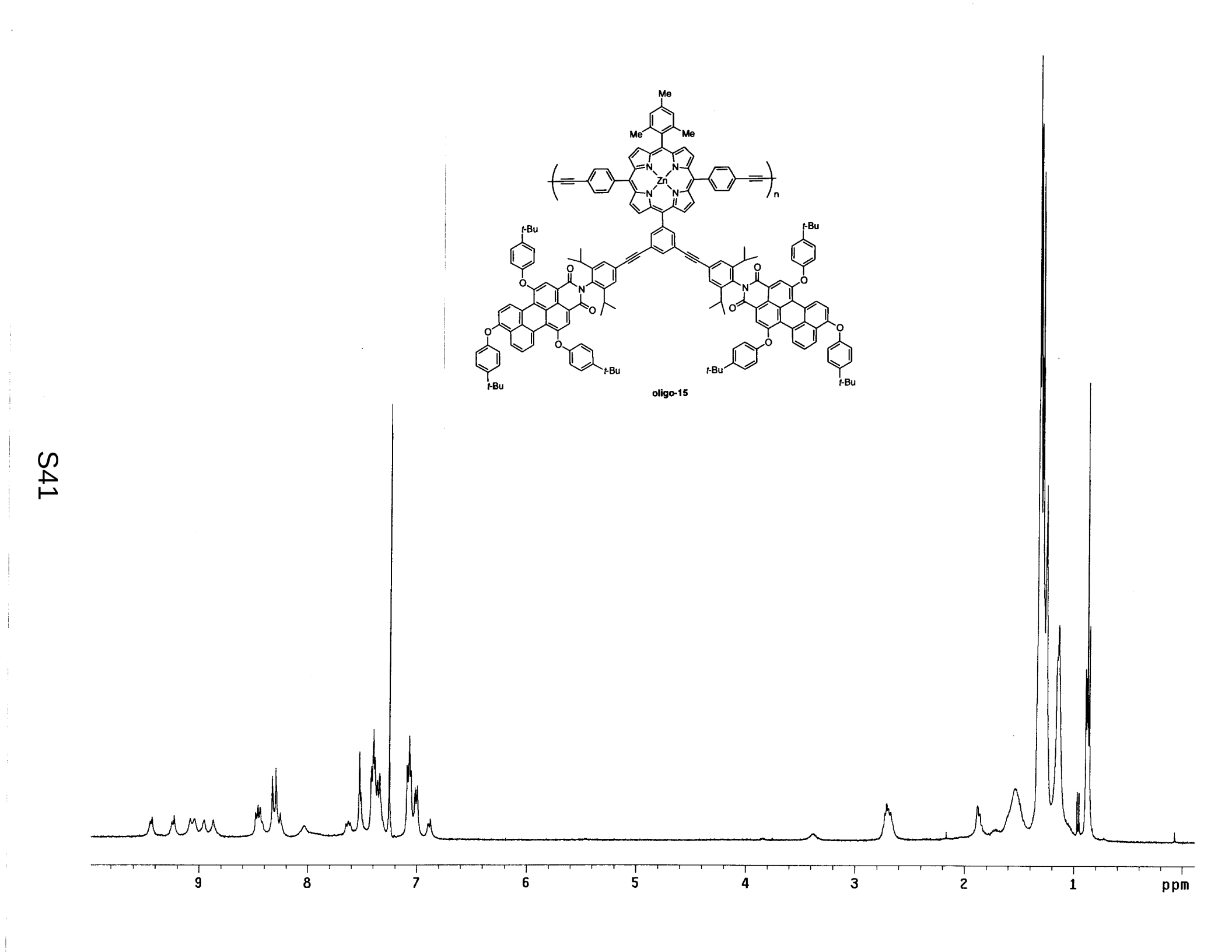

4467.11
4422.06
4386.92
3708.38
4545.39
25
INSTRUM TOF
OpId Unknown
SMPNAM 020161
AQ_DATE Tue Mar 5 11:57:52 2002
PATH /data/chemistry/LINDSEY/LOEWE
POLARI POS
AQOP_m Reflector
TD 60000
NoSHOTS 32
SMONUM 0
SMOPTS1 0
SMOPTS2 0
SMOPTS3 0
DW 1.00 [ns]
DELAY 0 [ns]
Uis1 20.00 [kV]
Uis2 18.50 [kV]
Urefl 0.00 [kV]
Ulens 7.50 [kV]
Uhimass 10.00 [kV]
RefFull 0.00 [kV]
UdetL 1.55 [kV]
UdetR 0.00 [kV]
Udefl 2.00 [kV]
REPHZ 1.00 [Hz]
ATTEN 31.0
ML1 2070371.899
ML2 333.982
ML3 0.000
HITURBO no
GDEON yes
GDEDLY short
DEFLON no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1 510.84
DPMASS 200.00 [Da]
RBNDVAL 0.33
LBNDVAL 0.28
IS2BNDV 0.91
CMT1 RSL271
CMT2 Dithranol matrix
/data/chemistry/LINDSEY/LOEWE/020161/1Ref/pdata/1 tof Tue Mar 5 11:59:24 2002

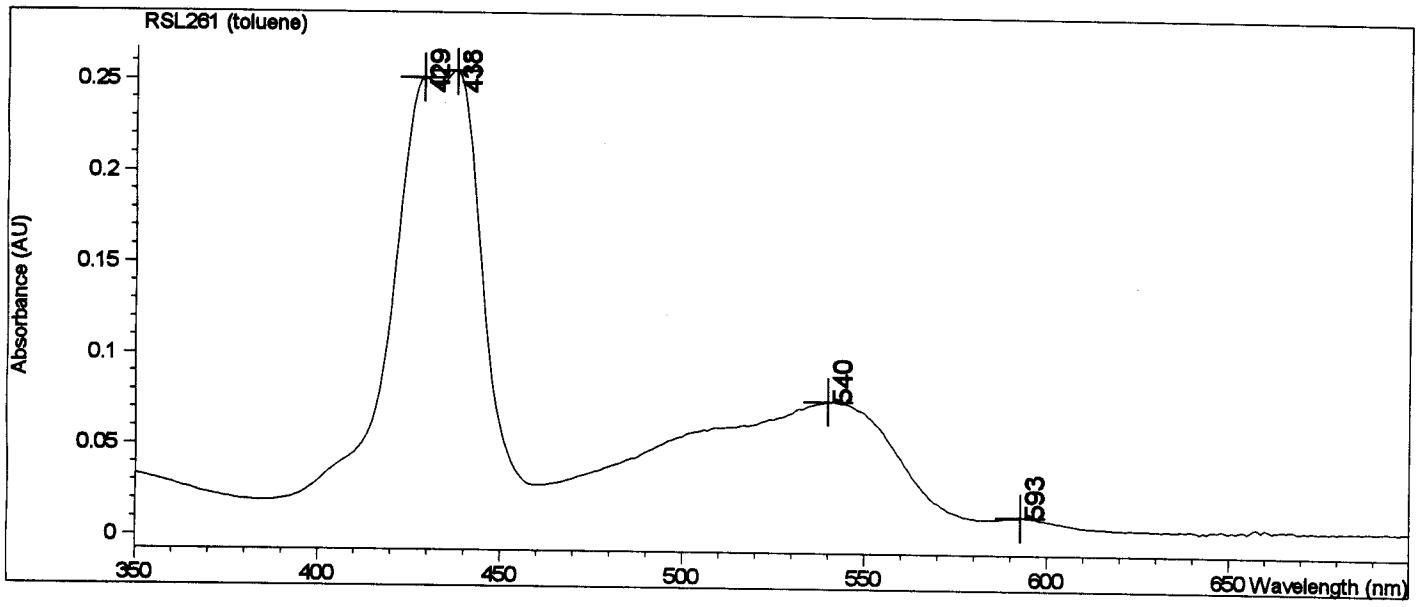


#	Name	Peaks (nm)	Abs (AU)
1	RSL271	435.0	0.94328
1		537.0	0.47447
1		598.0	1.4730E-2

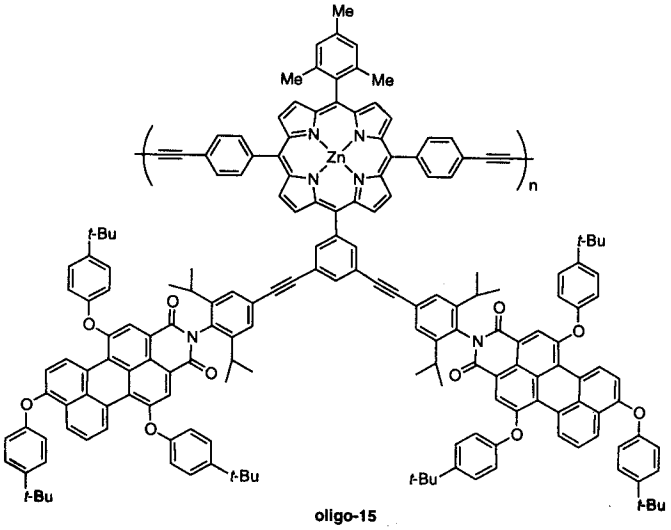


25

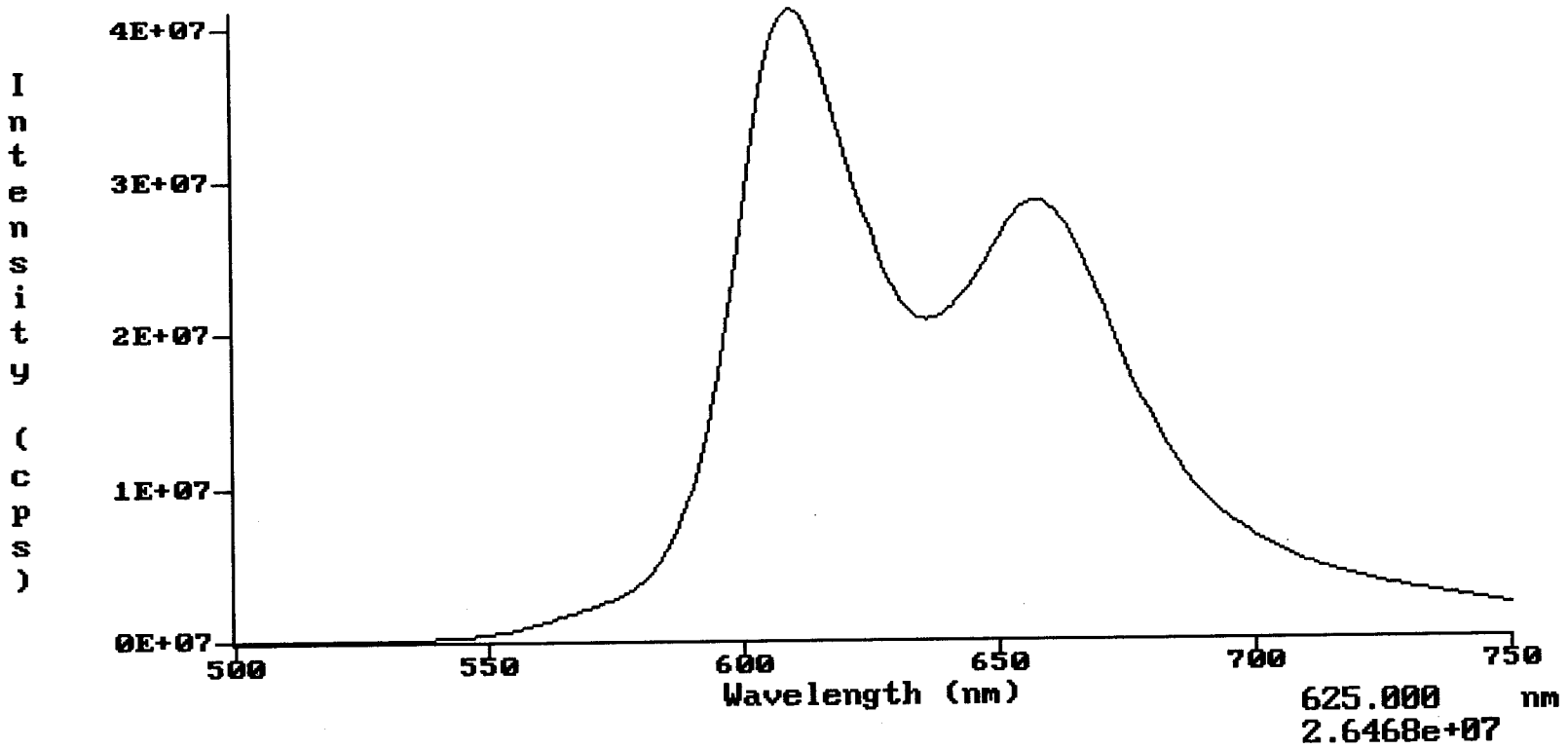

Me
Me
Me
Zn
n
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu
oligo-15
9
8
7
6
5
4
3
2
1
ppm

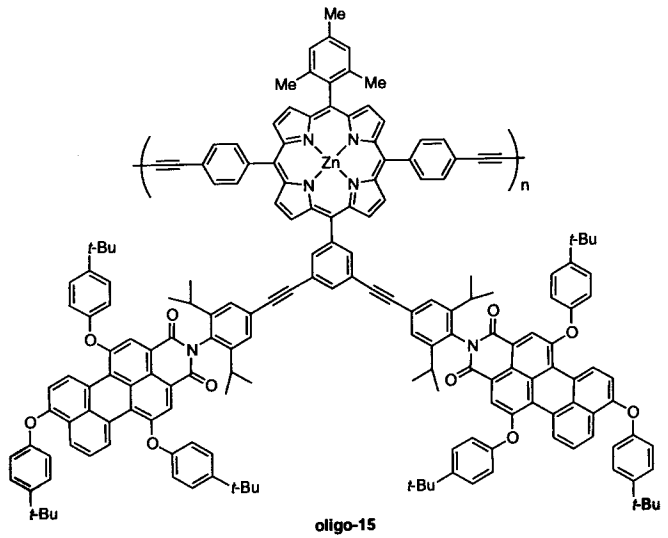


#	Name	Peaks (nm)	Abs (AU)
1	RSL261 (toluene)	438.0	0.25517
1		429.0	0.25125
1		540.0	7.5670E-2
1		593.0	1.2918E-2

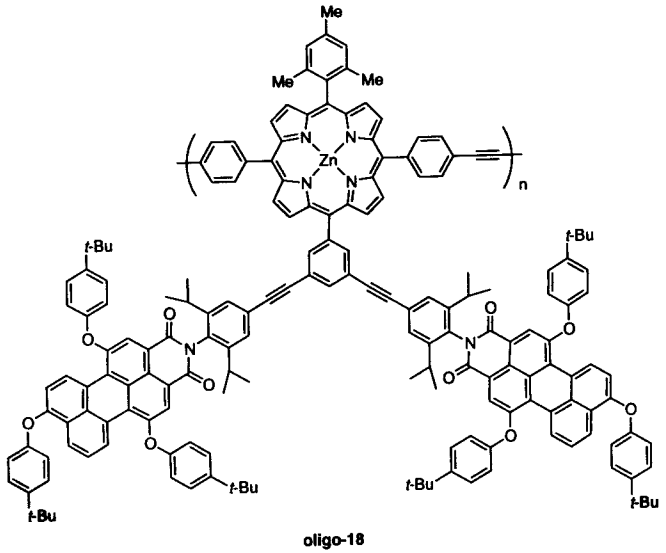


oligo-15


Intensity (cps)
4E+07
3E+07
2E+07
1E+07
0E+07
500
550
600
650
700
750
Wavelength (nm)
625.000 nm
2.6468e+07

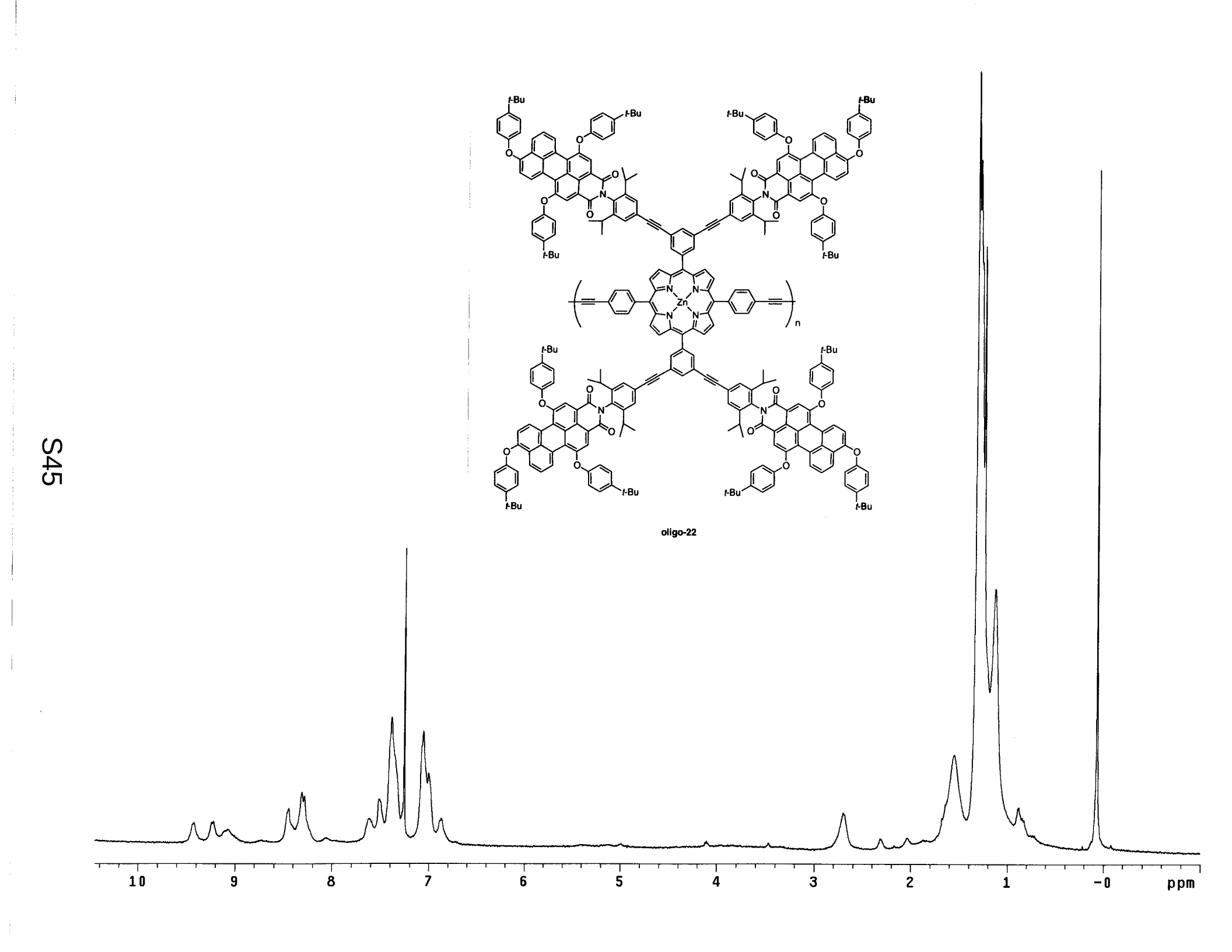

Me
Me
Me
Zn
n
t-Bu
O
N

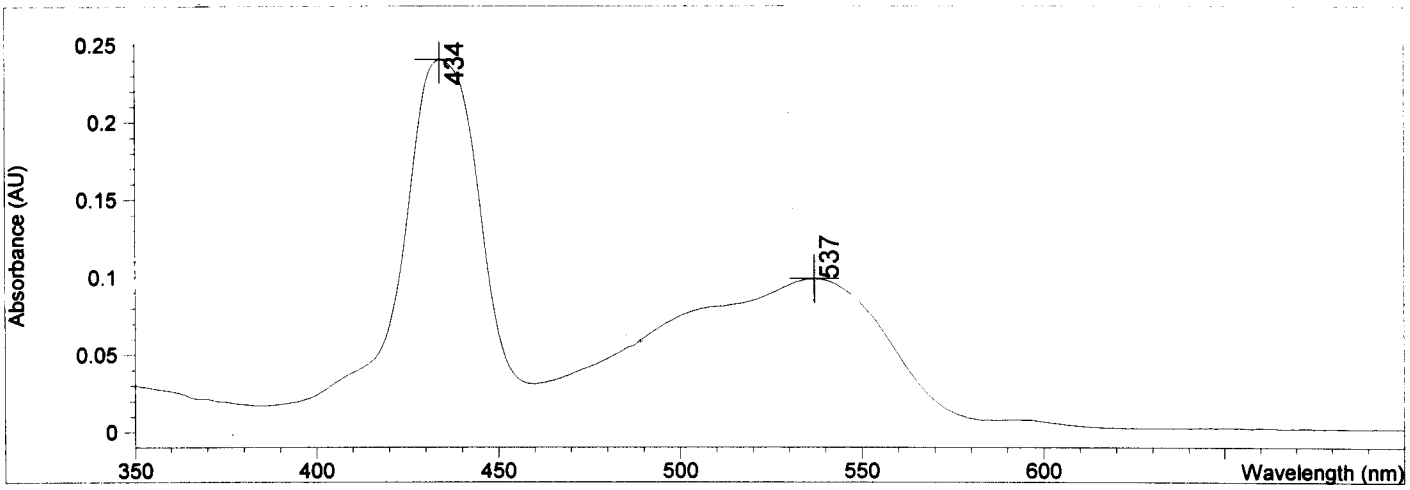
oligo-15


Me
Me
Me
N
N
Zn
N
N
n
t-Bu
t-Bu
O
O
N
O
O
O
O
t-Bu
t-Bu
t-Bu
t-Bu
t-Bu

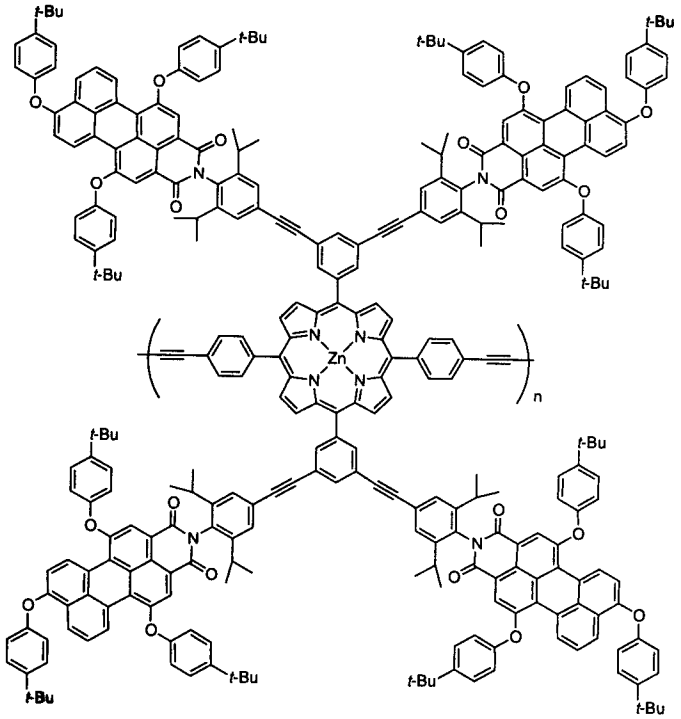
oligo-18

10
9
8
7
6
5
4
3
2
1
-0
ppm

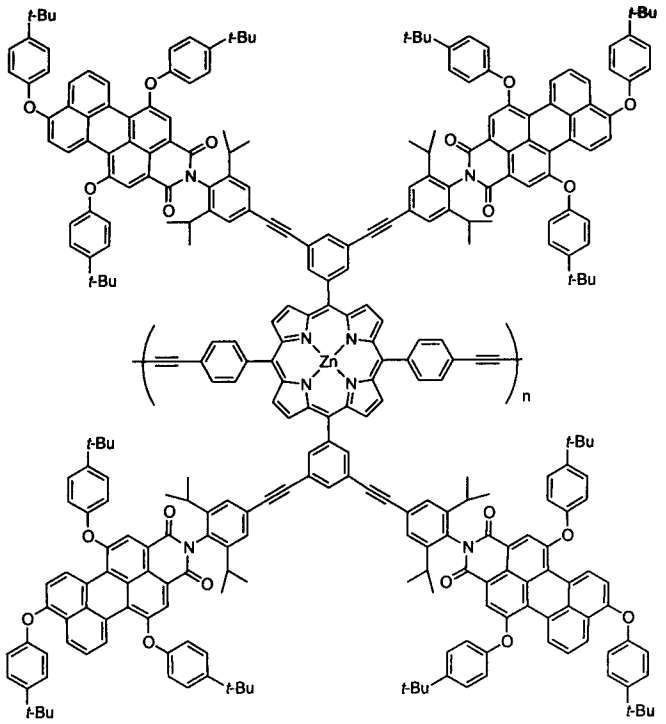

t-Bu
Zn
n
oligo-22
10
9
8
7
6
5
4
3
2
1
-0
ppm



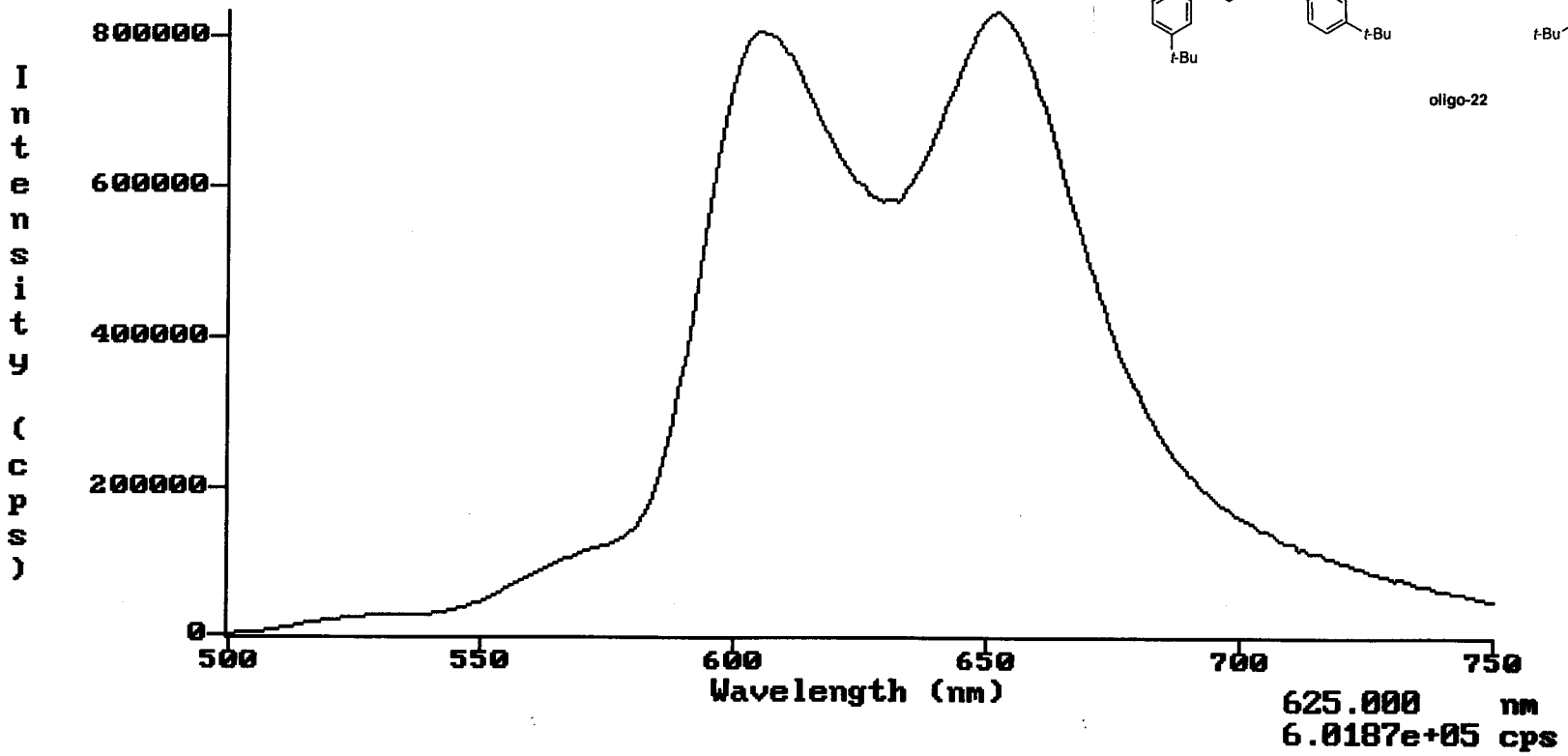
#	Name	Peaks(nm)	Abs(AU)
1	RSL298	434.0	0.24049
1		537.0	9.8961E-2
1		***	***
1		***	***
1		***	***

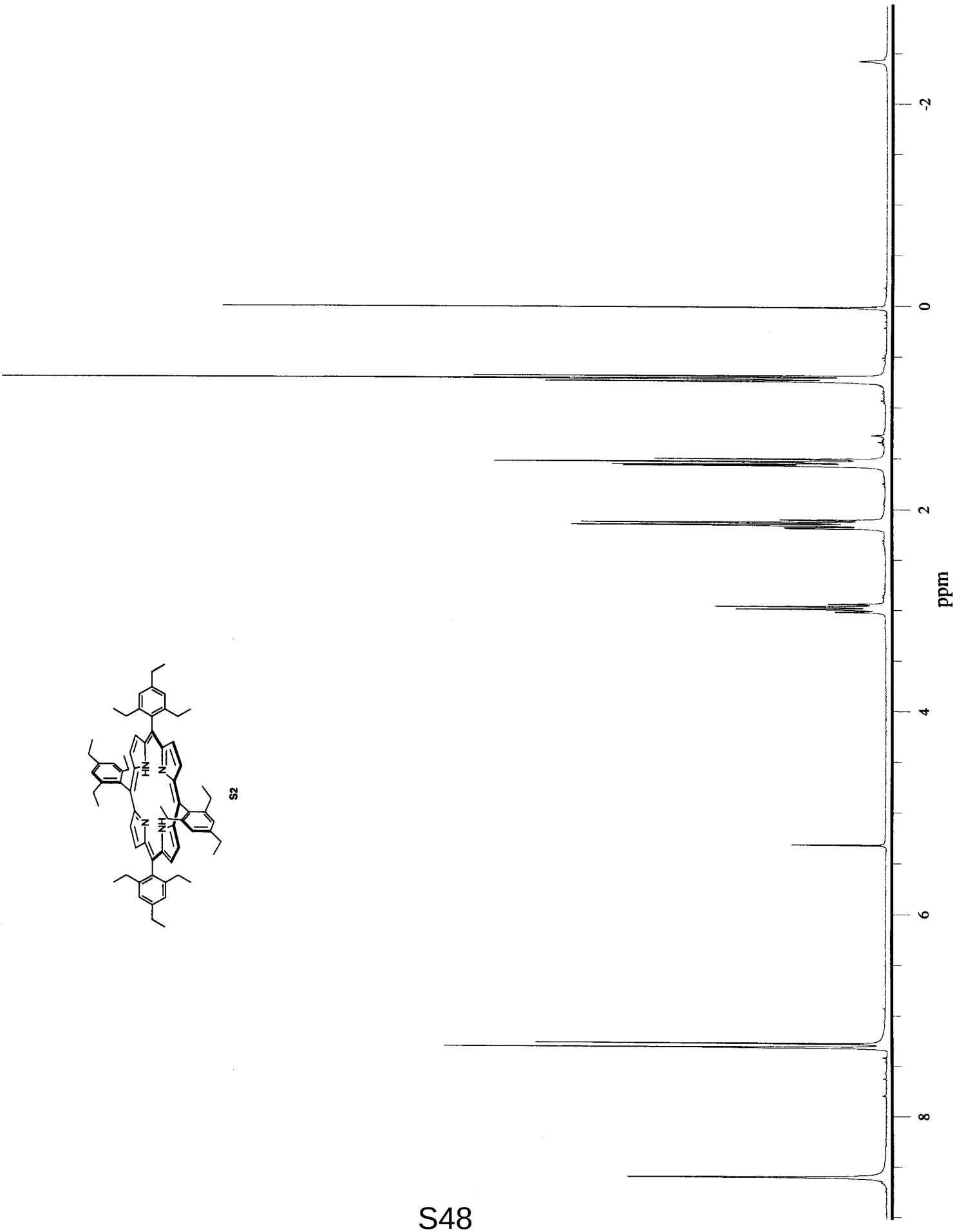


oligo-22

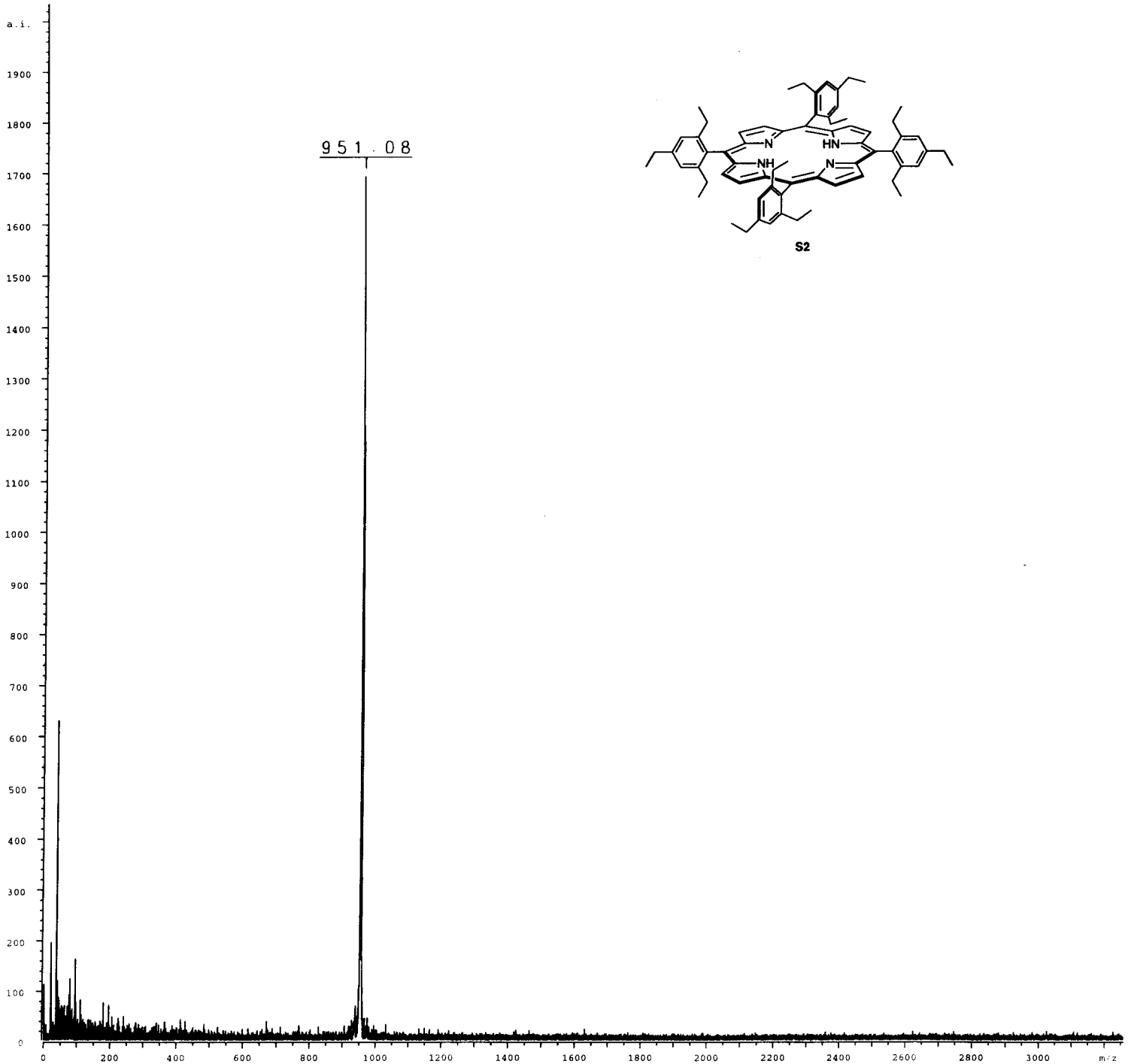

t-Bu
O
N
Zn
n

oligo-22


800000
600000
400000
200000
0
Intensity (cps)
500
550
600
650
700
750
Wavelength (nm)
625.000 nm
6.0187e+05 cps

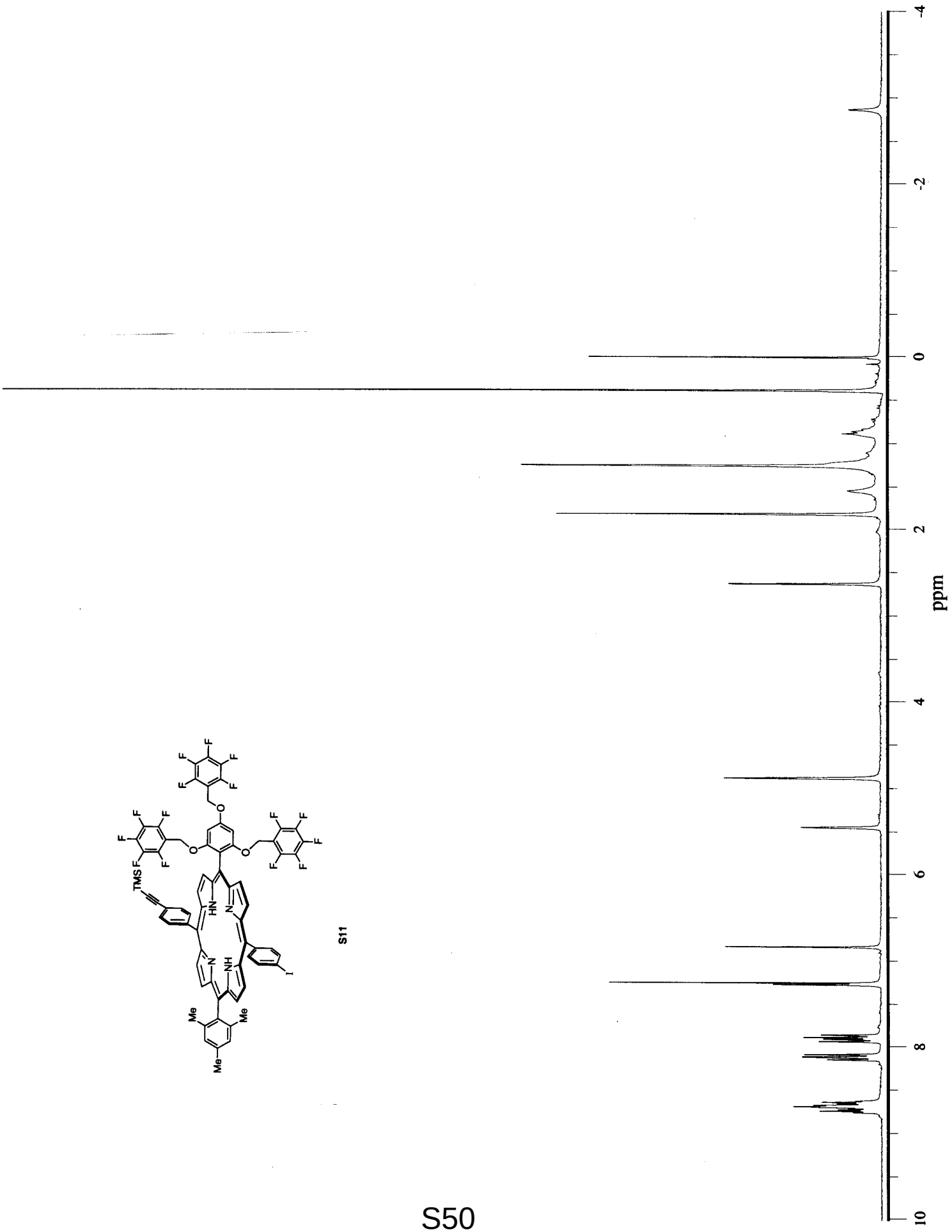


S2

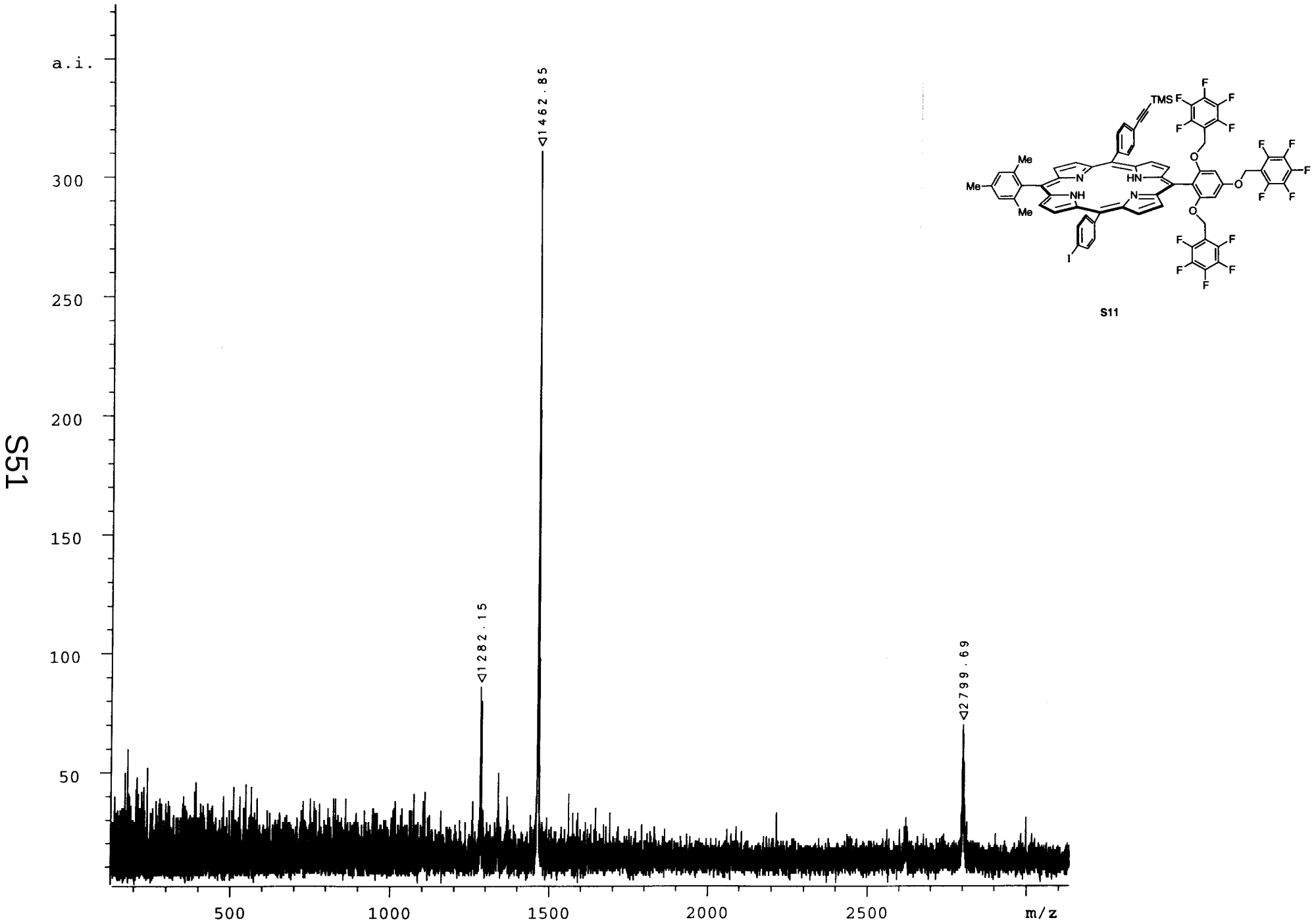


S2

```
INSTRUM TOF
OpId     N. Srinivasan
SMPNAM   020664
AQ_DATE  Thu Jun  6 16:11:28 2002
PATH     /data/chemistry/LINDSEY/YOUNGBLOOD
POLARI   POS
AQOP_m   Reflector
TD            40000
NoSHOTS          22
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         2071938.026
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     triethylphenylporphyrin
CMT2     atten. = 33 shots = 22
```

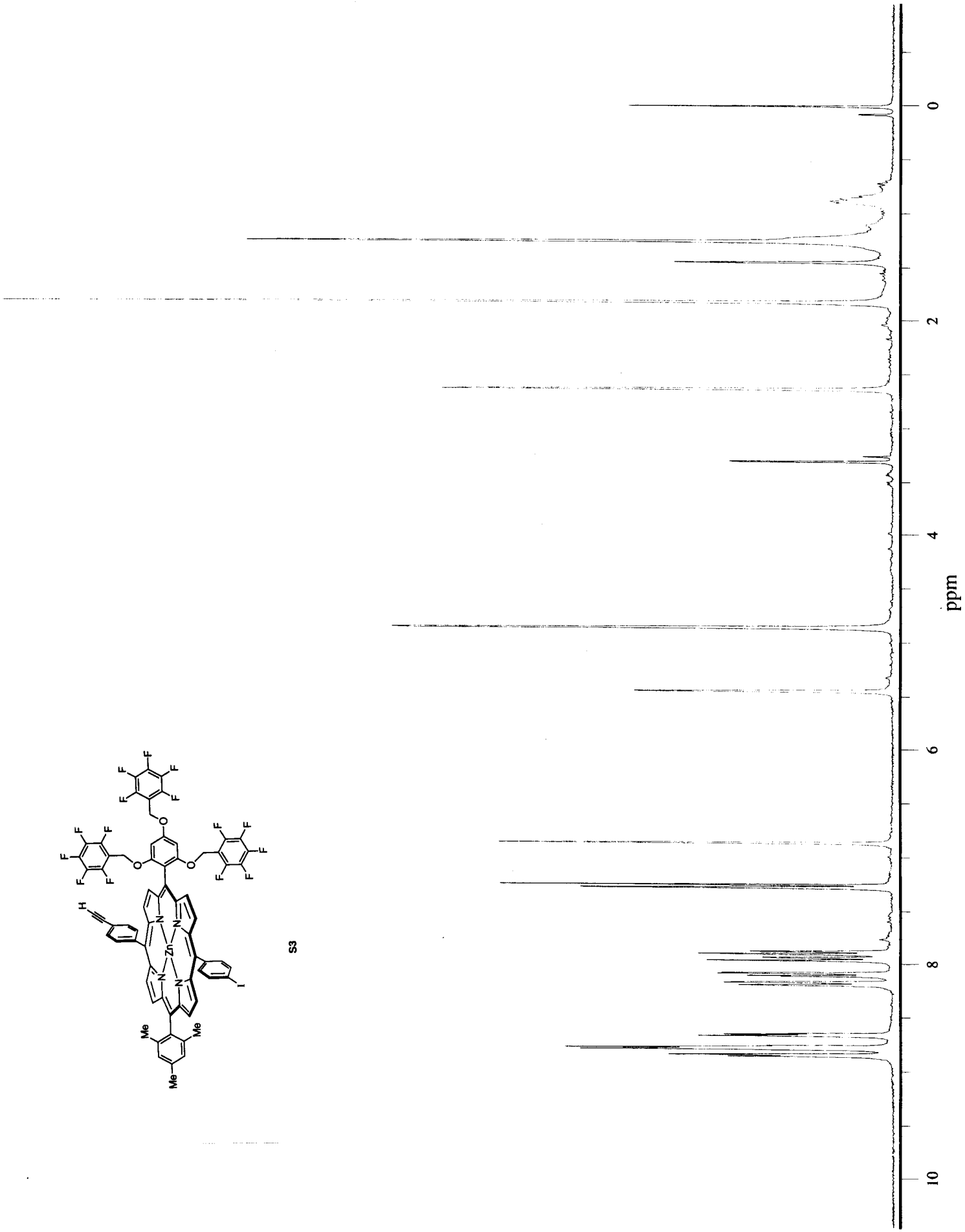


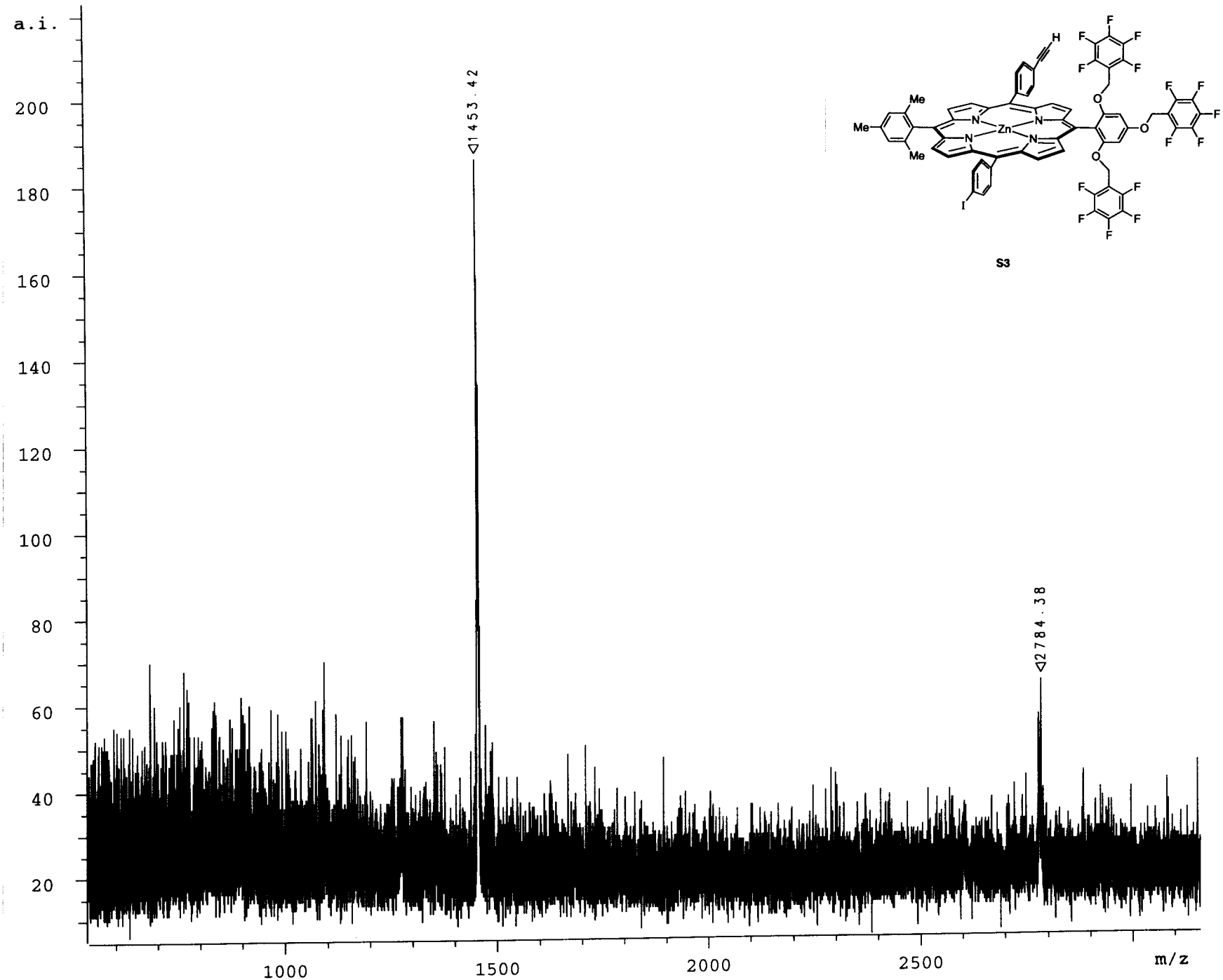
S11


a.i.
300
250
200
150
100
50
1462.85
1282.15
2799.69
500
1000
1500
2000
2500
m/z

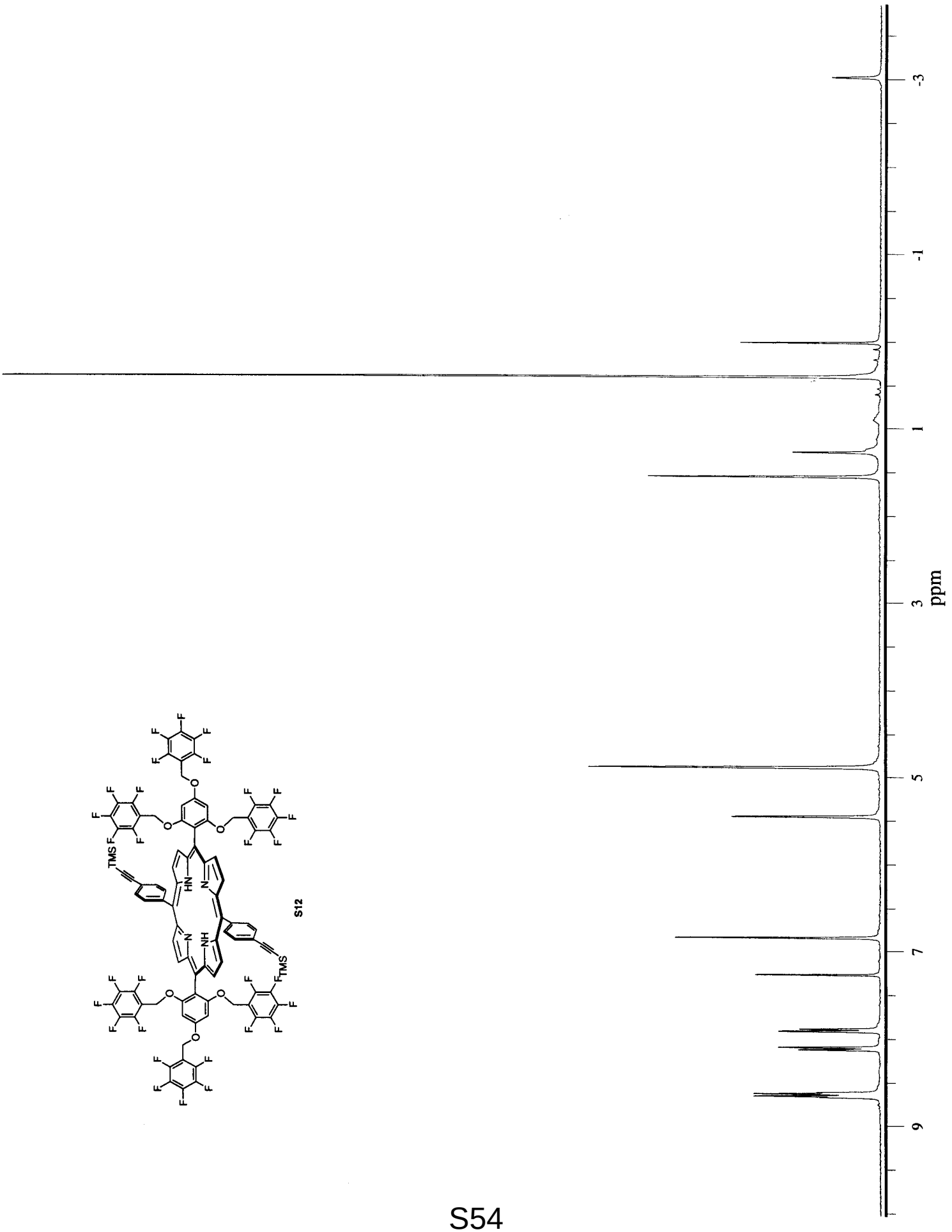
TMS
F
Me
N
HN
NH
O
I

S11

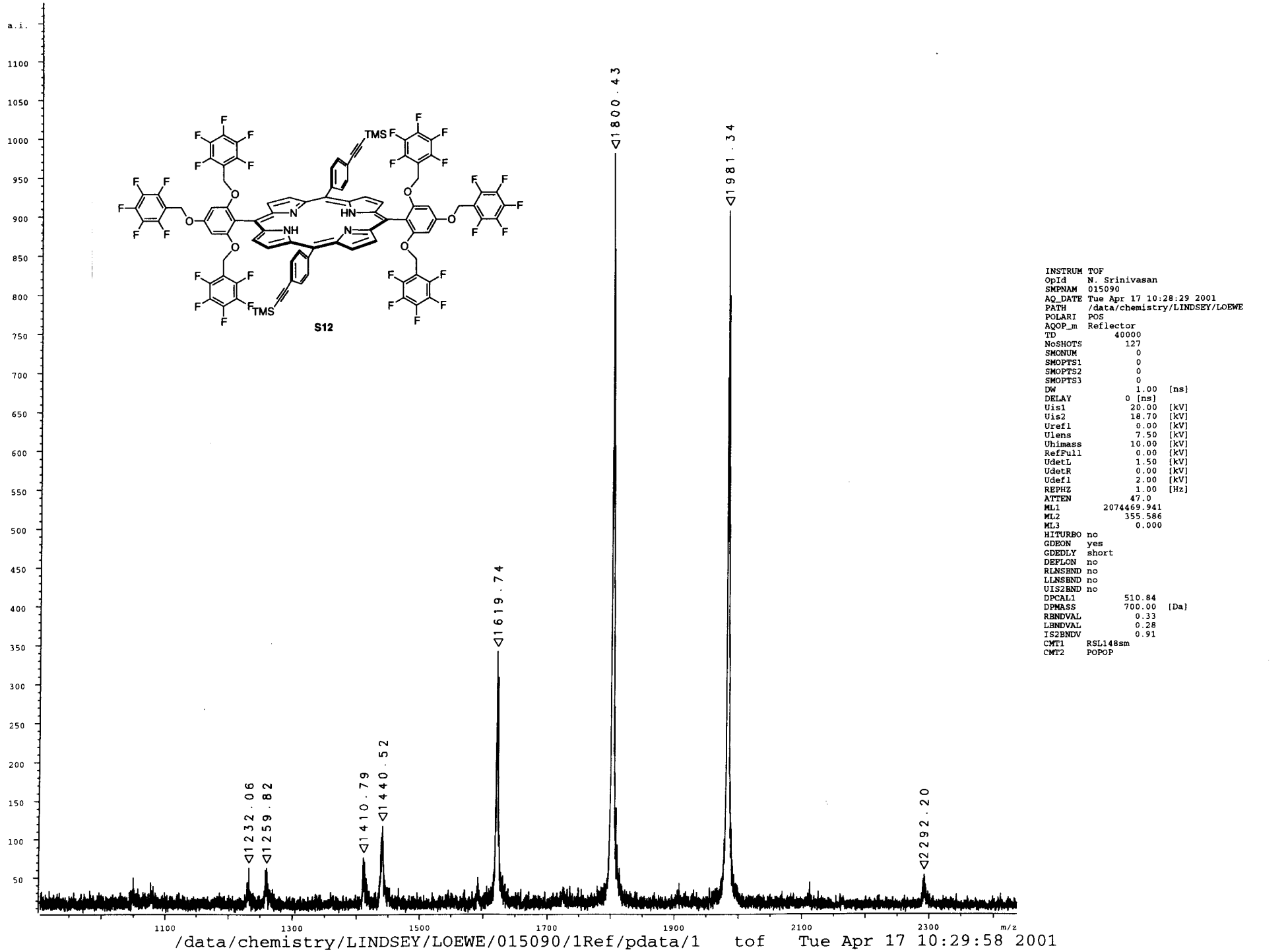

F
O
N
Zn
H
I
Me
S3
0
2
4
6
8
10
ppm

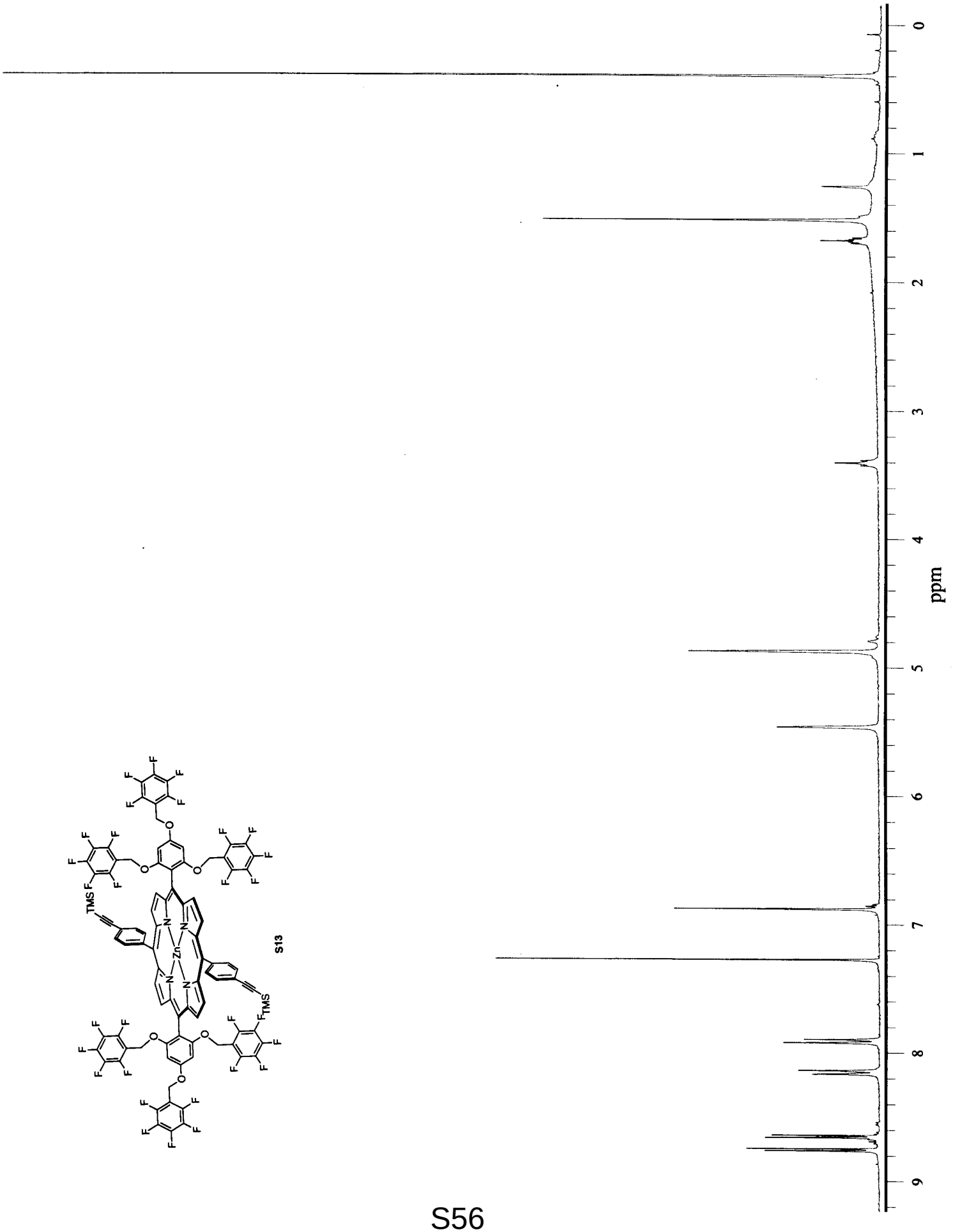

a.i.
200
180
160
140
120
100
80
60
40
20
1453.42
2784.38
1000
1500
2000
2500
m/z
Me
Me
Me
N
Zn
N
N
N
H
I
O
O
O
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F

S3

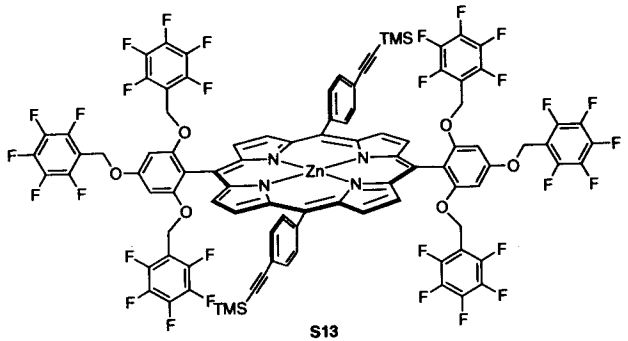


S12


a.i.
1100
1050
1000
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
1232.06
1259.82
1410.79
1440.52
1619.74
1800.43
1981.34
2292.20
1100
1300
1500
1700
1900
2100
2300
m/z
/data/chemistry/LINDSEY/LOEWE/015090/1Ref/pdata/1 tof Tue Apr 17 10:29:58 2001
TMS
TMS
S12
INSTRUM TOF
OpId N. Srinivasan
SMPNAM 015090
AQ_DATE Tue Apr 17 10:28:29 2001
PATH /data/chemistry/LINDSEY/LOEWE
POLARI POS
AQOP_m Reflector
TD 40000
NoSHOTS 127
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 47.0
ML1 2074469.941
ML2 355.586
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 RSL148sm
CMT2 POPOP

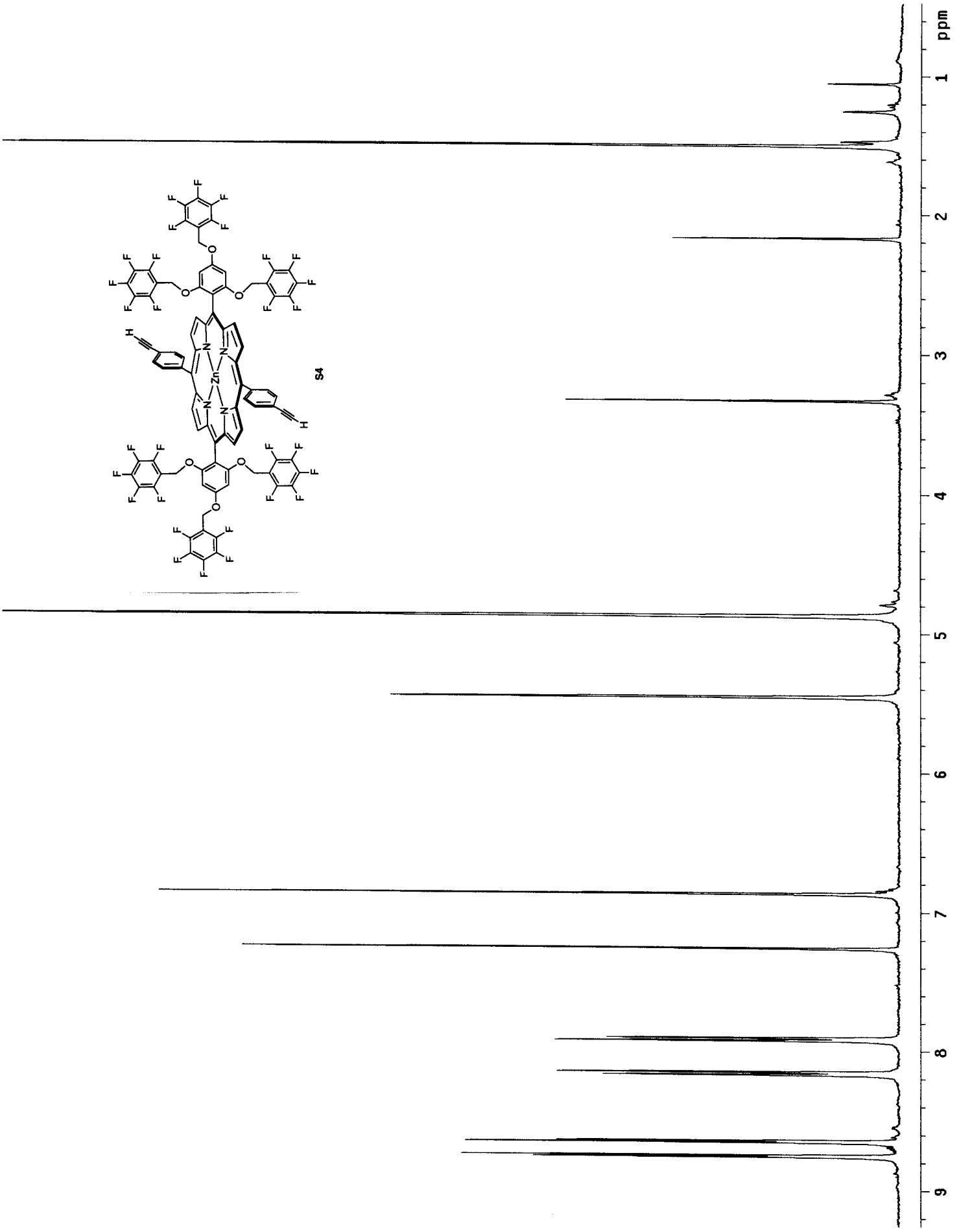

0
1
2
3
4
5
6
7
8
9
ppm

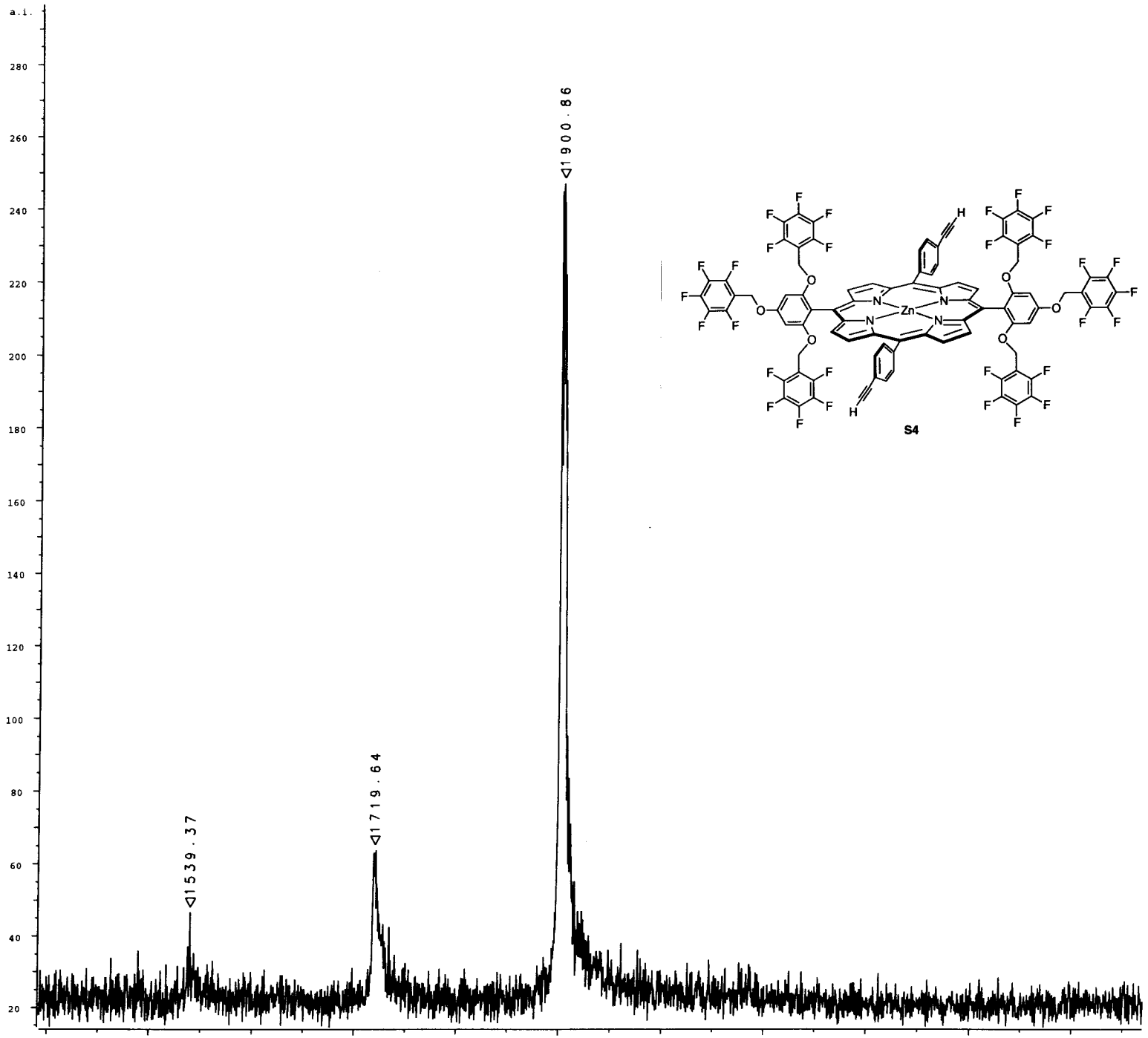
TMS
TMS
Zn
S13



S13

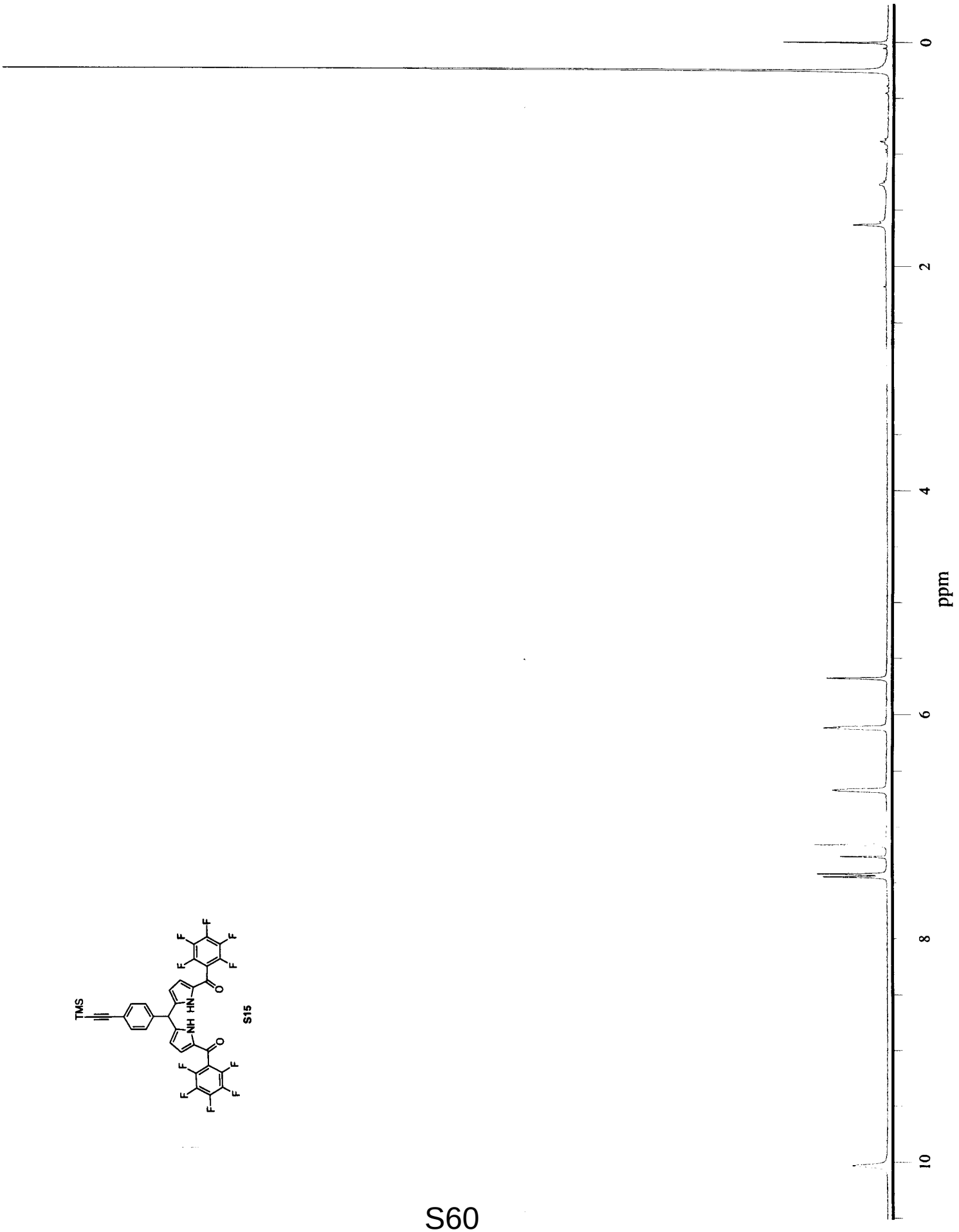

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015092
AQ_DATE Tue Apr 17 10:35:59 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD          40000
NoSHOTS       124
SMONUM          0
SMOPTS1         0
SMOPTS2         0
SMOPTS3         0
DW              1.00  [ns]
DELAY           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           27.0
ML1       2074469.941
ML2           355.586
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    RSL148
CMT2    no matrix
```


S4
ppm
1
2
3
4
5
6
7
8
9

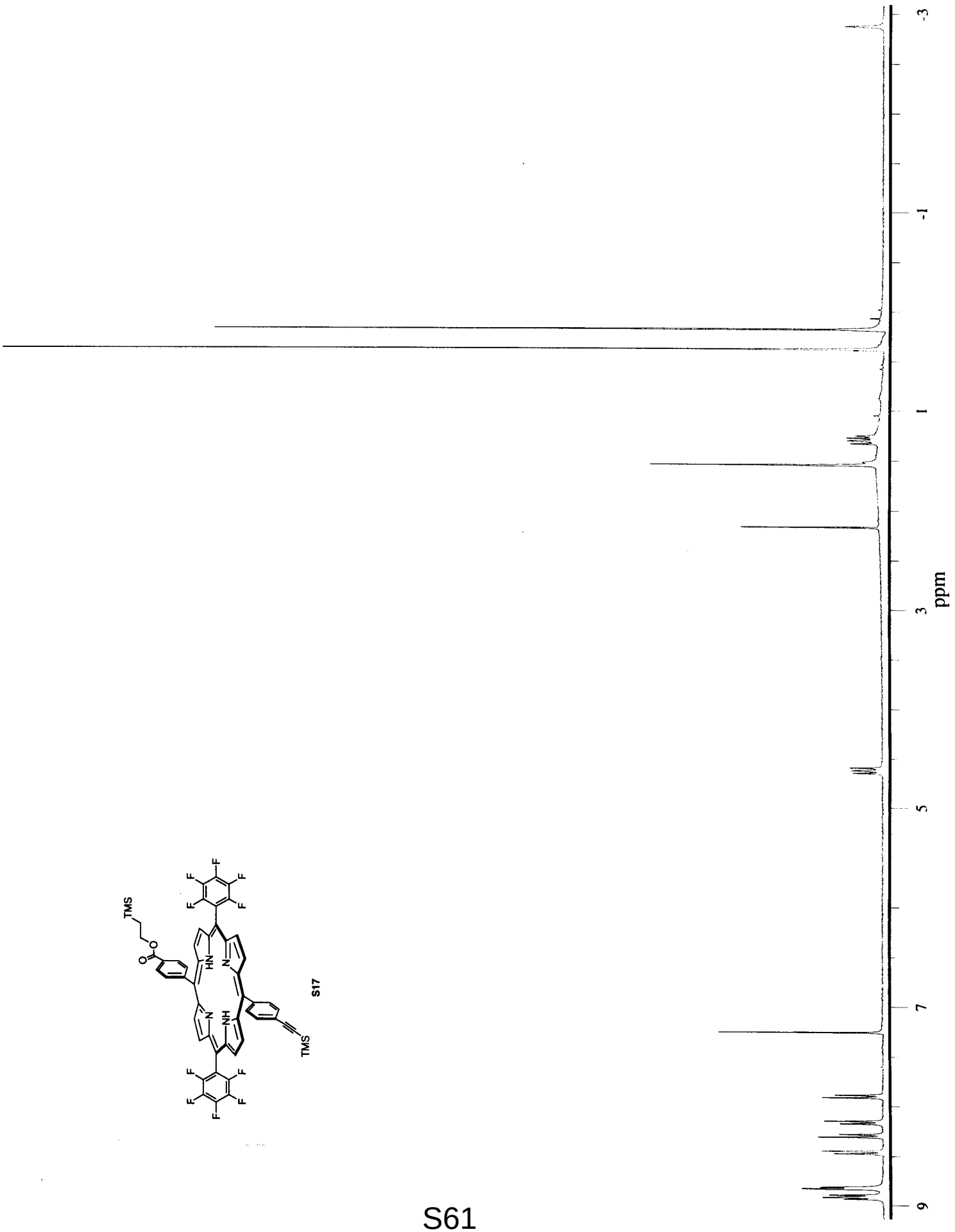


S4

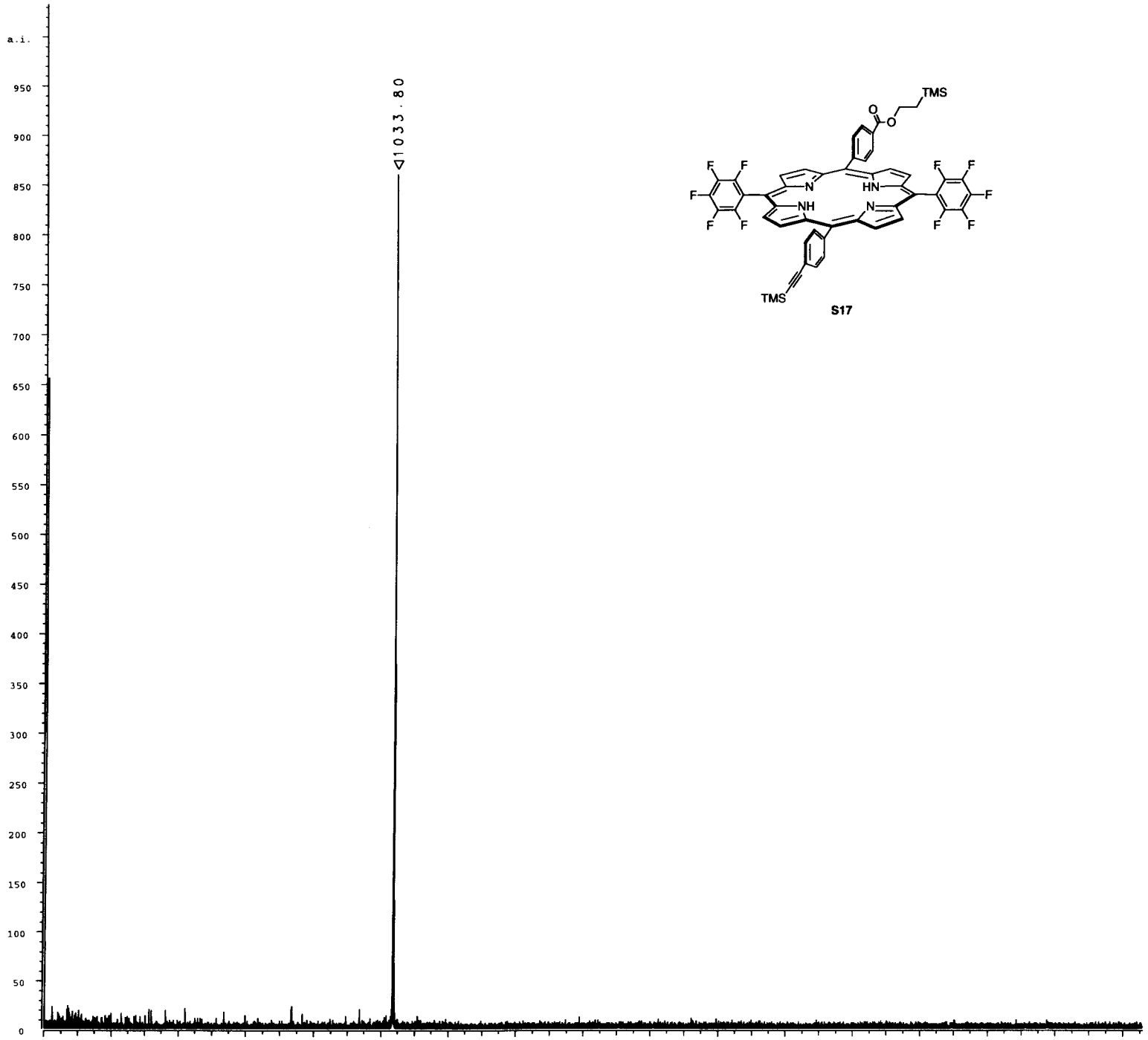
```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015070
AQ_DATE Tue Apr 10 15:13:45 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS           185
SMONUM              1
SMOPTS1             5
SMOPTS2             0
SMOPTS3             0
DW                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         2068474.776
ML2             302.397
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    RSLMonomer1
CMT2    no matrix
```



S15

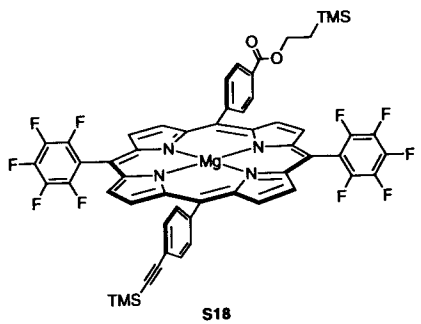


S17



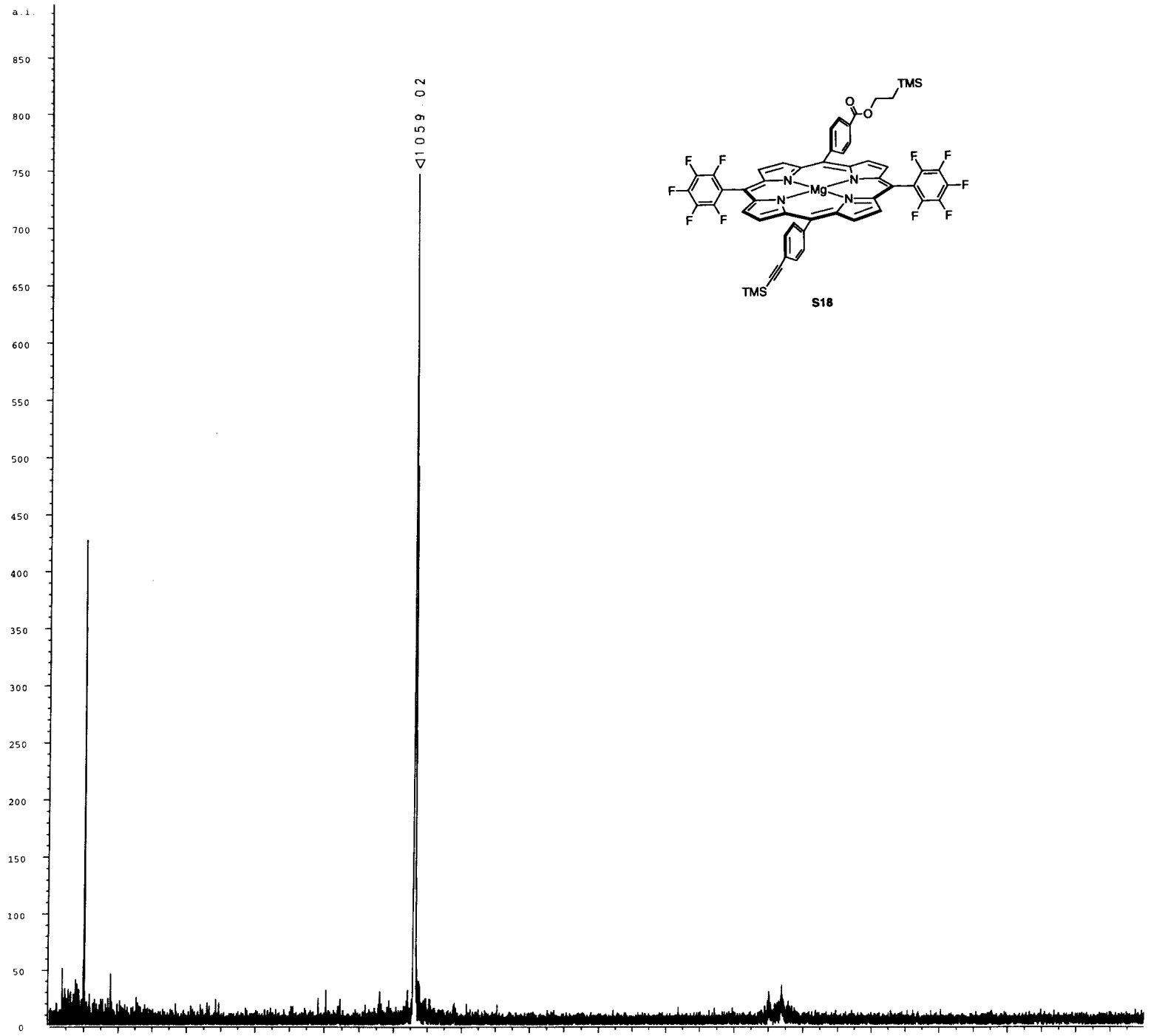
S17

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015115
AQ_DATE Wed Apr 25 16:00:28 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS            28
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          2074469.941
ML2              355.586
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    RSL152
CMT2    no matrix
```



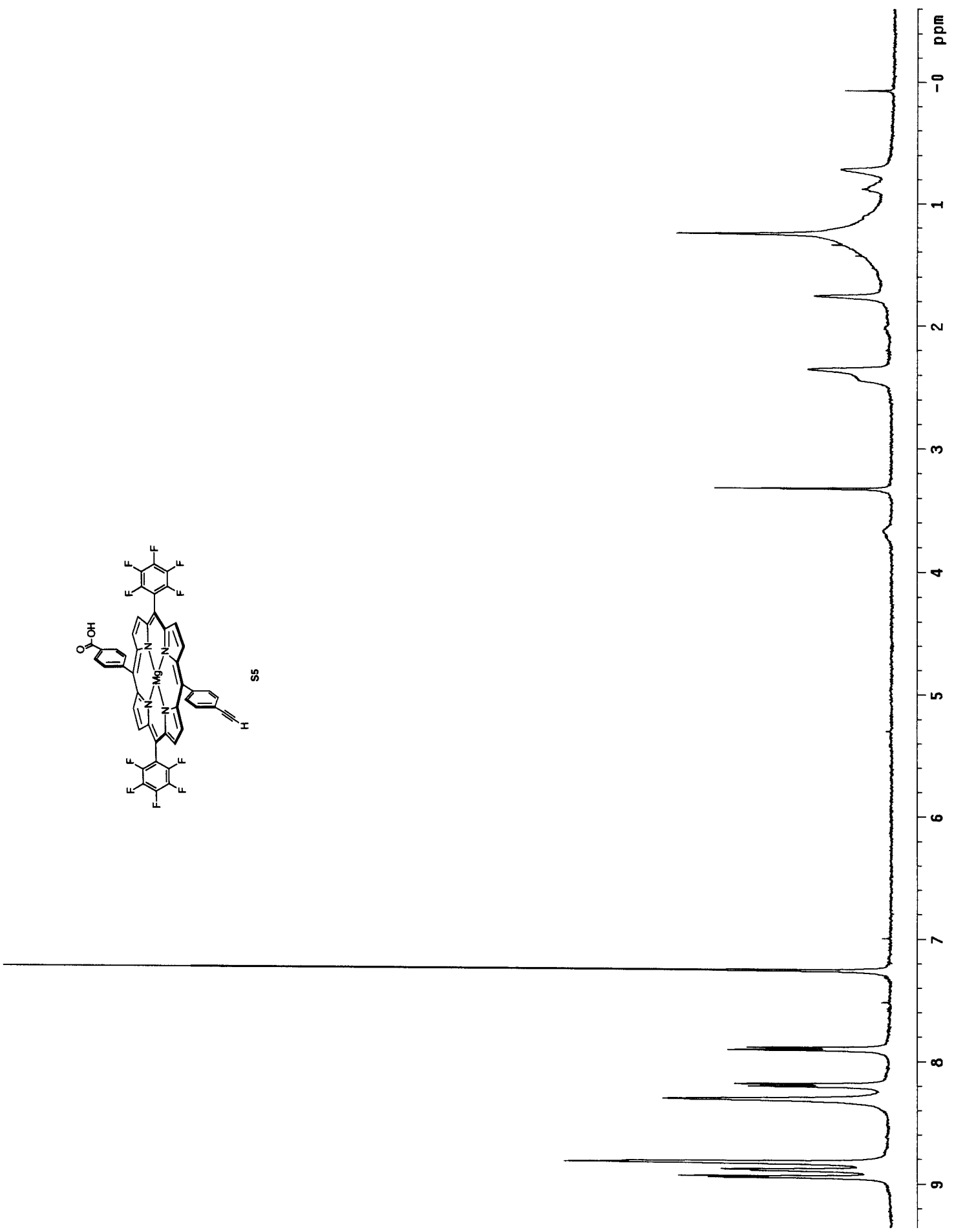
S18

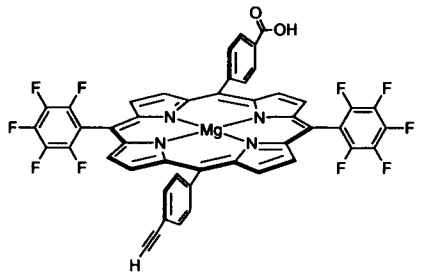
9 8 7 6 5 4 3 2 1 ppm



S18

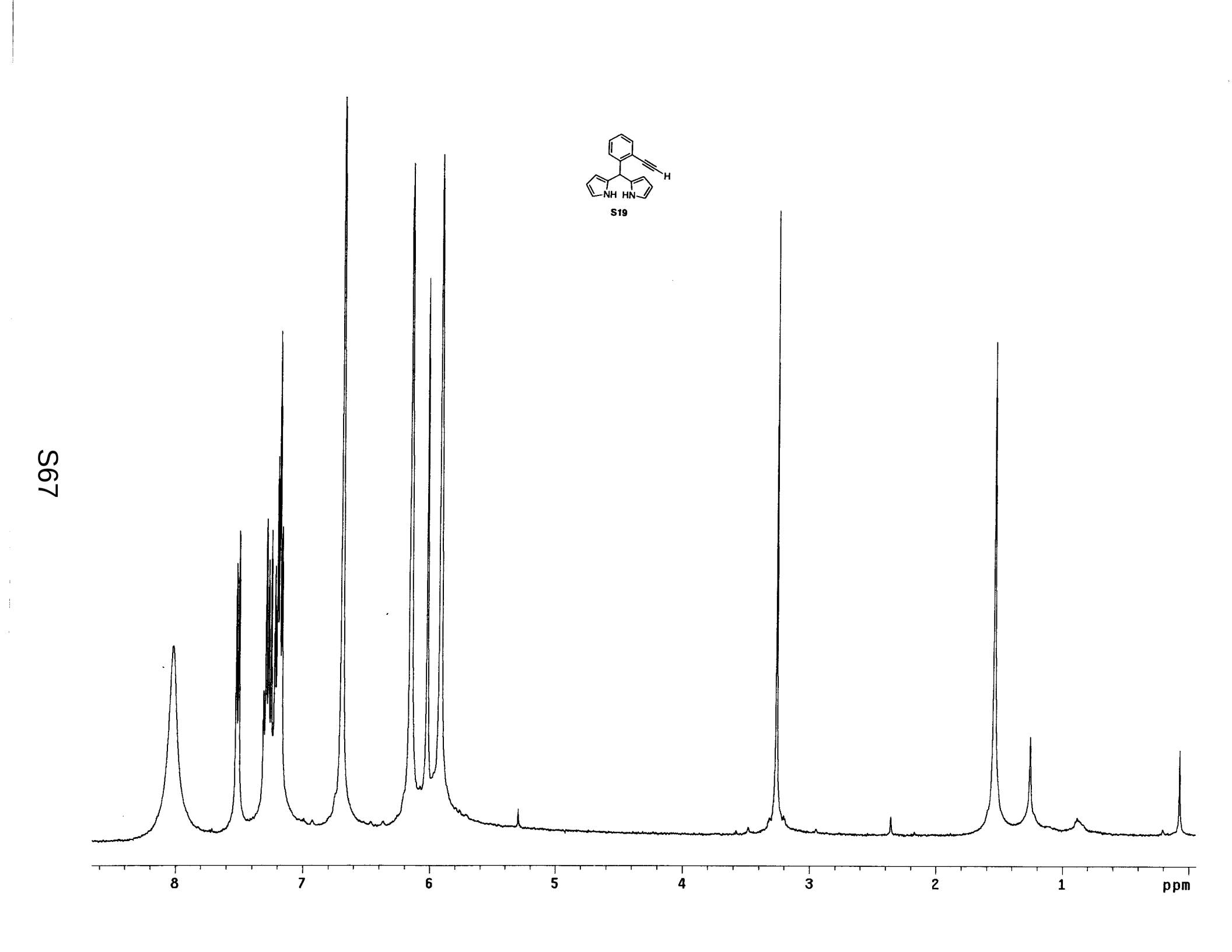
```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015125
AQ_DATE Thu Apr 26 13:42:59 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS            59
SMONUM              0
SMOPTS1             0
SMOPTS2             0
SMOPTS3             0
DW                  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]
RefPul1             0.00  [kV]
UdetL               1.50  [kV]
UdetR               0.00  [kV]
Udef1               2.00  [kV]
REPHZ               1.00  [Hz]
ATTEN               31.0
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    RSL153
CMT2    no matrix
```

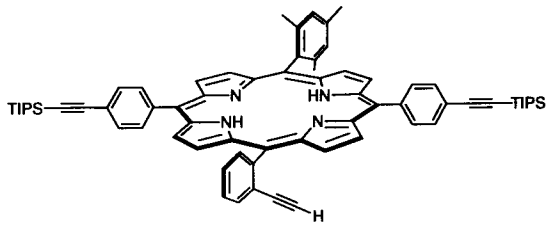

F
F
F
F
F
OH
O
N
N
Mg
N
N
F
F
F
F
F
H
S5
9
8
7
6
5
4
3
2
1
0
ppm



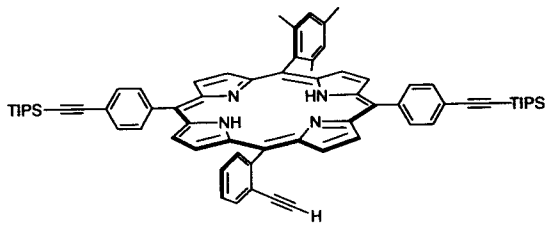
S5


```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015143
AQ_DATE Tue May  1 11:34:21 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD              40000
NoSHOTS           176
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               33.0
ML1           2076511.811
ML2               348.244
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    RSL155
CMT2    no matrix
```


NH HN
H
S19
8
7
6
5
4
3
2
1
ppm

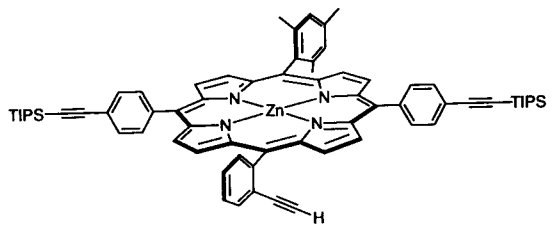


S21


TIPS
TIPS
N
HN
NH
N
H

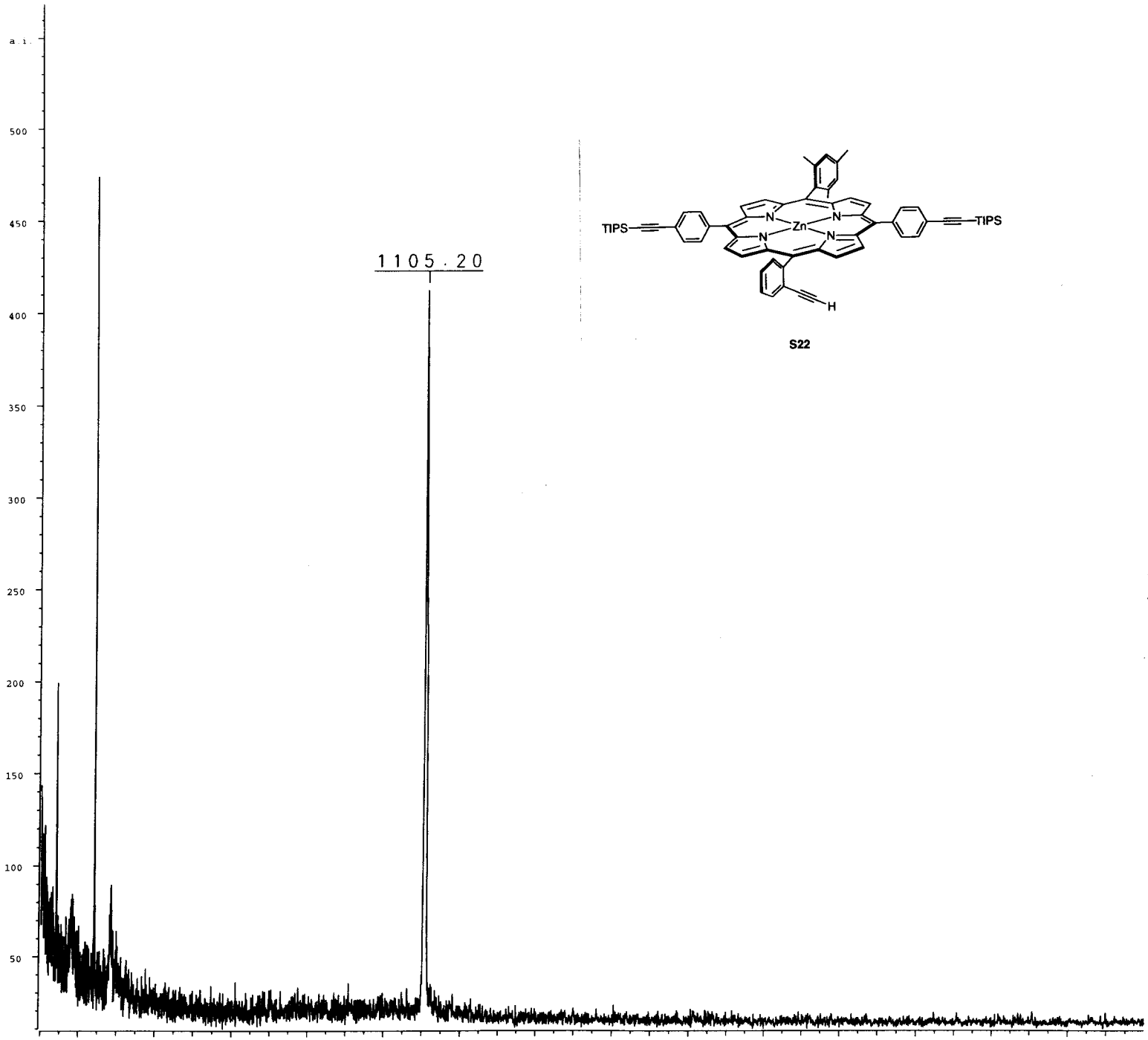
S21

1040.95
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
900
1000
1100
1200
m/z
/data/chemistry/LINDSEY/LOEWE/015885/1Ref/pdata/1 unknown Wed Nov 21 16:15:53 2001



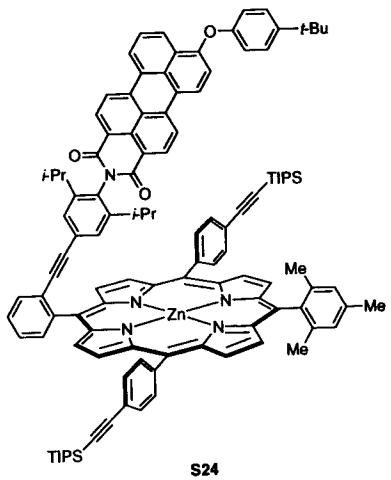
S22

S70

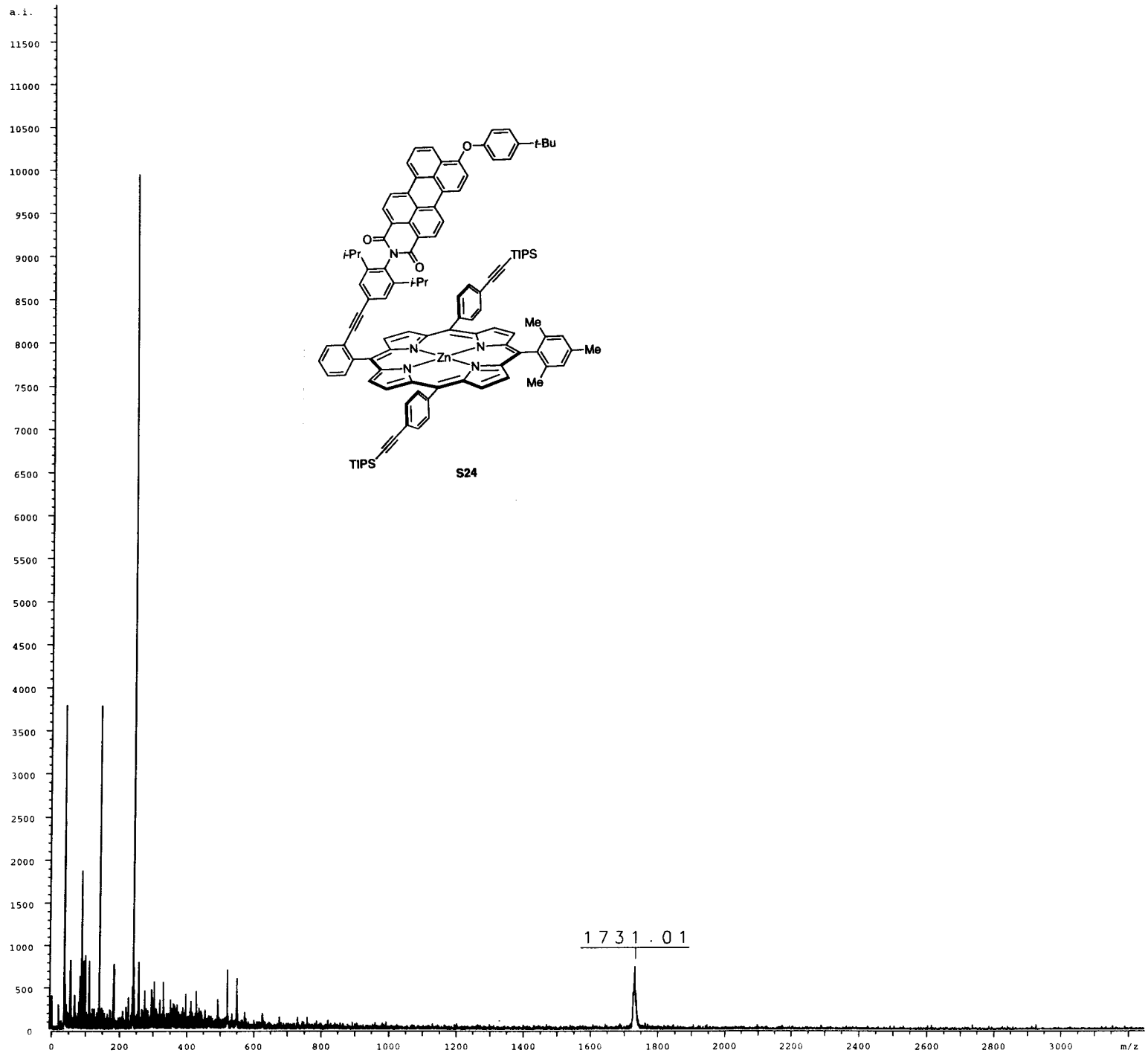


S22

```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015893
AQ_DATE Mon Nov 26 15:33:43 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD          40000
NoSHOTS        60
SMONUM          1
SMOPTS1        10
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          25.0
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    RSL246
CMT2    no matrix
```

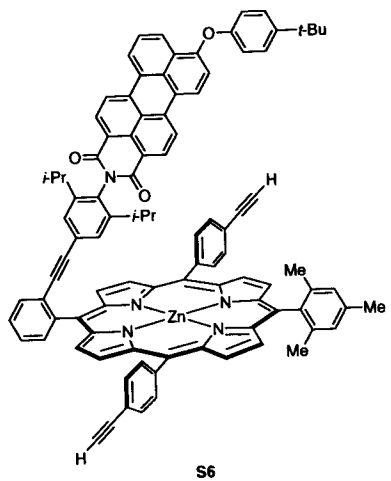


S24

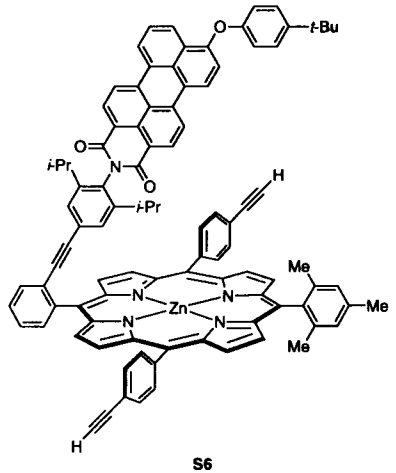


S24

```
INSTRUM TOF
OpId    Unknown
SMPNAM  015907
AQ_DATE Fri Nov 30 14:21:32 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD          40000
NoSHOTS        61
SMONUM          0
SMOPTS1         0
SMOPTS2         0
SMOPTS3         0
DW              1.00  [ns]
DELAY         0 [ns]
Uis1           20.00  [kV]
Uis2           18.50  [kV]
Uref1           0.00  [kV]
Ulens           7.50  [kV]
Uhimass        10.00  [kV]
RefFull         0.00  [kV]
UdetL           1.55  [kV]
UdetR           0.00  [kV]
Udef1           2.00  [kV]
REPHZ           1.00  [Hz]
ATTEN          26.0
ML1       2067510.748
ML2           353.368
ML3             0.000
HITURBO no
GDEON   yes
GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1        510.84
DPMASS        200.00  [Da]
RBNDVAL         0.33
LBNDVAL         0.28
IS2BNDV         0.91
CMT1    RSL248
CMT2    no matrix
```



S6



S6


```
INSTRUM TOF
OpId    N. Srinivasan
SMPNAM  015921
AQ_DATE Wed Dec  5 11:05:53 2001
PATH    /data/chemistry/LINDSEY/LOEWE
POLARI  POS
AQOP_m  Reflector
TD          40000
NoSHOTS        33
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          31.0
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    RSL249
CMT2    no matrix
```