Appending a tris-Imidazole Ligand with a Tyr^{244} Mimic on the distal Face of Bromo-acetamidoporphyrin

(Supplementary Material)

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Materials and Methods. All reagents were used as supplied commercially unless otherwise noted. α,β,α,β- and α,α,α,α-Tetrakis-aminophenylporphyrin **25a,c** [1a] , α,α,α,-tris-(*o*-aminophenyl)-β-(*o*-N-triphenylmethylaminophenyl)porphyrin **25b**, [1b-c] α,α,α,-tris-(*o*-chloroacetamidophenyl)-β-(*o*-N-triphenylmethylaminophenyl)porphyrin **24d**,[1b] *N*-(2-cyanoethyl)imidazole **28**,[1b] dipodal ligand bis-(5-methylaminomethyl-1-methyl-1H-2-imidazolyl)(1'-(2''-methoxyphenyl)-1'H-2'-imidazolyl) Methyl Methyl Ether **22**[2] and tripodal ligand tris(5-methylaminomethyl-1-methyl-*1H*-2-imidazolyl)-methyl methyl ether **27**[2] were prepared according to previously published procedures. Spectral data of pyridine-3,5-biscarbinol [5a-b] pyridine-3,5-diester [5c], pyridine-3,5-bis-carbaldehyde,[3c-e] α_3-imidazole-β-trityl porphyrin **11**,[1b] were as previously published. Routine mass spectra were obtained from the Stanford University Mass Spectrometry laboratory and from the University of California, San Francisco Mass Spectrometry Facility of the Stanford PAN facility. All compounds showed up together with their sodium adduct or sometimes with their solvates. ^{1}H-NMR spectra were recorded at 400 MHz and 500 MHz on Mercury-400 and Inova-500 respectively, in the solvent specified, and referenced to the residual proton signals. UV/Vis spectra were recorded on a HP8452 diode array spectrophotometer.

Synthesis and Characterization

Pyridine-3,5-bis-carbaldehyde (18)

Route A. Following reported procedure [5f] and modified as follows. A suspension of pyridine-3,5-dicarboxylic acid (1g, 5.983 mmol) in toluene (11 mL) was put under nitrogen atmosphere then thionyl chloride (30 mL) was added followed by DMF (2 drops, 10 μL). The mixture was refluxed under agitation for 1 hour until it became a yellow solution. Thionyl chloride and toluene were evaporated and the oily residue containing 3,5-bis(acyl chloride)pyridine **3** crystallized at room temperature, and was immediately re-dissolved in dry THF (100 mL) under N_2 atmosphere by sonication. The solution was cooled to –78 °C under agitation then 2.2 equiv. of lithium tri-*tert*-butoxyaluminumhydride (0.5 M in diglyme) were added over 20 minutes. The mixture was stirred at – 78 °C for 1 h, then the cool bath was removed and the mixture was stirred for an additional 30 min. The mixture was cooled again and water (0.3 mL) was added and the mixture was stirred for 15 min. The mixture was filtered and the cake was copiously washed with ethanol (50 mL). 1**8** (0.226 g, 28%).

Route B: 3,5-bis(*p*-toluenesulphonpyridoylhydrazide (1g, 1.992 mmol) was dissolved in glycol (100 mL), heated at 150 °C and while stirring, a large excess of anhydrous K_2CO_3 (*ca* 20 g) was added in one portion, causing effervescence. After 5 min, the reaction was stopped by addition of hot water (50 mL) and allowed to cool at room temperature. The reaction mixture was washed with diethyl ether (2 x 100 mL), dried and the solvent evaporated under reduced pressure to afford a mixture which was chromatographed as described in Route A. **18** (0.067 g, 25 %).

Route C: An adaptation of the procedure described for 2,6-lutidine[3g] was applied here. A mixture of 3,5-dimethylpyridine (0.617 mL, 5.761 mmol) and selenium dioxide (3.0 g,

27.079 mmol) in dioxane-water (96:4 vol., 100 mL) was refluxed for 12 h and filtered through celite while hot. The filtrate was evaporated and the residue was purified by two sets of chromatography (SiO_2, 20 x 2 cm, CH_2Cl_2 / Ethyl acetate 5:1 vol. as eluent, gradient elution). After evaporation of solvents **4** was obtained as a pale yellow solid (194 mg, 25 %). **18** (0.155 g, 20%).
Route D: Pyridine-3,5-dicarbinol (0.150 g, 1.079 mmol) was dissolved in CH_2Cl_2 (20 mL) and manganese oxide tunings (0.100 g) were introduced. Then the mixture was allowed to stir for 2h at room temperature and was filtered. Evaporation of the solvent afforded a yellowish oily solid chromatographed under conditions as described in route A. **18** (0.046 g, 32 %).
Mp 89-93 °C, lit.[3c-e] mp 95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) was as described in the literature.[3c-e] M.S.: m/e = 136.0 $M+H^+$ for $C_7H_5NO_2$ ($LSIMS^+$); Rf 0.30 (SiO_2, CH_2Cl_2 / ethyl acetate 7:3 vol.).

Pyridine-3,5-bis-tosylhydrazide (19)
Following McFayden-Stevens method,[3h-j] a solution of pyridine-3,5-bisacylchloride **3** (1.2 g, 5.9 mmol) in dichloromethane-pyridine mixture (2:1 vol. 10 mL) was slowly introduced to a solution of *p*-toluenesulfonylhydrazine (2.7 g, 14.2 mmol) and the reaction mixture was stirred at 40 °C for 4 h. The mixture was poured in a water-hexanes mixture (1:1 vol., 50 mL) and vigorously shaken until a white precipitate appears. The solid is filtered off and recrystallized from methanol. 2.485 g (82 %). Mp (methanol): 135-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 2H), 8.24 (s, 1H), 7.81 (d, 4H, J = 8.2 Hz), 7.32 (d, 4H, J = 7.32 Hz), 2.38 (s, 6H). M.S.: m/e = 471 $M+H^+$ for $C_{21}H_{21}N_5O_6S_2$ (ESI^+); Rf 0.2 (SiO_2, $CHCl_3$ / methanol 95:5 vol.).

Pyridine-3,5-bis(hydroxymethylene) (20)
Route A: Following reported procedures from the di-ester (methyl or ethyl), [3b-e] **4** was obtained in 5% and 10 % yield respectively.
Route B: Beads of polymer supported borohydride [3k] (0.8 g, 2 mmol/ g of bead) are loaded in a dry round-bottom flask with dry CH_2Cl_2 (25 mL). The flask was plunged in an ice bath and N_2 was bubbled for 10 min. Then a solution of **17** (0.6 g, 3.1 mmol) in CH_2Cl_2 (10 mL) was introduced dropwise (1 mL / min), and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was filtered, the cake washed with CH_2Cl_2 (10 mL) and the solvent evaporated under reduced pressure to yield **6** as a pale yellow solid. (0.185 g, 43%). Mp (methanol) 80-83 °C; lit.[3a] mp 84-85 °C; Rf 0.2 (CH_2Cl_2 / ethyl acetate 7:3 vol.). Rf 0.3 (Al_2O_3, CH_2Cl_2 / methanol 7:3 vol.).

Pyridine-3,5-Bis-*N*-methyl-methylamine (16)
A solution of compound **18** (0.150 g, 1.1 mmol) in CH_3NH_2 (20mL, 40% in water) and methanol (40 mL) was stirred at room temperature for 16h, and then $NaBH_4$ was cautiously added to the solution. The resulting mixture was cooled to room temperature and evaporated to dryness *in vacuo*. The resulting solid was extracted with hot chloroform, and the extract was dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by column chromatography (SiO_2, eluent CH_2Cl_2/CH_3OH 95:5 vol.) to give an oil identified as **7d** (0.090 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 2H); 7.65 (s, 1H); 3.80 (s, 4H); 2.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ

148.57, 135.59, 135.14, 53.15, 36.00; M.S.: m/e = 165.1 $M+H^+$ for $C_9H_{15}N_3$ (EI^+), 136.0 (MH^+ - $2CH_3$), 106.6 (MH^+ - $2CH_3NH$); Rf 0.3 (SiO_2, NH_3 saturated CH_2Cl_2 / CH_3OH 95:5 vol.)

(*N*-Allyl-*N*-methyl-aminomethyl-1-methyl-1H-2-imidazolyl)-bis(5-methylaminomethyl-1-methyl-*1H*-2-imidazolyl)-methyl Methyl ether (23)

A mixture of Tris-(*N*-Allyl-*N*-methyl-aminomethyl-1-methyl-1H-2-imidazolyl)-methyl Methyl ether[2] (0.345 g, 0.643 mmol), $Pd(PPh_3)_4$ (0.151 g, 0.131 mmol) and *p*-tolylsulfinic acid (0.376 g, 2.114 mmol) in dry CH_2Cl_2 (30 mL) was stirred at room temperature for 29h under N_2. Na_2CO_3 (0.438 g, 4.141 mmol) was added to the mixture and stirring was carried on for 3h. The solid was filtered off, washed with dry CH_2Cl_2 (10 mL) and the filtrate was concentrated. The residue was purified by preparative silica gel thin-layer chromatography (SiO_2, 1000 μm, eluent NH_3-saturated $CHCl_3$/MeOH (19:1 vol.). Compound **23** was isolated as a yellowish semi-solid compound (0.090 g, 31 %).
^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 2H), 6.87 (s, 1H); 5.81 (m, 1H); 5.16 (m, 2H), 3.74 (s, 4H); 3.41 (m, 12H), 2.99 (d, 1H, J = 6.46 Hz), 2.92 (m, 6H), 2.47 (s, 5H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.22, 135.30, 131.35, 131.23, 131.23, 131.01, 127.16, 126.43, 118.19, 117.87, 78.75, 60.17, 55.0, 50.64, 44.60, 41.74; M.S.: m/e = 456.6 (M-H) for $C_{23}H_{37}N_9O$ (ESI^-); Rf 0.3 (SiO_2, NH_3 saturated $CHCl_3$)

General acylation procedure

0.4 mmol porphyrin **25a,c** (0.300 g) or **25b** (0.407 g) was dissolved in dry THF (60-70 mL) and 12 eq. diethylaniline (855 μl) were added. N_2 was flushed for 10 min and the vessel was plunged in an ice-bath until the temperature of the solution reached O °C (15 min). 8 equiv. bromoacetylbromide (3.5 mmol, 309 μL) in solution in dichloromethane (5 mL) were introduced dropwise over 30 s to the stirred mixture at O °C. After stirring for 2 min at O °C the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and chromatographed (silica gel 60 μm, 35 x 3 cm) washed with CH_2Cl_2 and eluted with a dichloromethane/ethyl acetate (95:5 vol.) mixture to afford first a yellow and a pink unidentified fraction followed by the desired fraction. **24a** (0.400 g, 86 %), **24e** (0.412 g, 89 %), **24c** (0.281 g, 55 %).

α,β,α,β-Tetra-(*o*-bromoacetamidophenyl)porphyrin (24a)

^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (m, 8H), 8.63 (d, 4H, J = 8.3 Hz), 8.05 (d, 4H, J = 7.5 Hz), 7.83 (m, 8H), 7.59 (t, 4H, J = 7.33Hz), 3.20 (s, 8H), -2.60 (s, 2H); M.S.: m/e = 1158.9 $M+H^+$ for $C_{52}H_{38}Br_4N_8O_4$ (ESI^+); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 421 (395), 512 (28.3), 546 (6.6), 588 (8.4), 648 (1.8) nm; Rf 0.6 (SiO_2, CH_2Cl_2 / ethyl acetate 95:5 vol.).

α_4-Tetra-(*o*-bromoacetamidophenyl)porphyrin (24e)

^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (m, 8H), 8.63 (d, 4H, J = 8.30 Hz), 8.05 Hz (d, 4H, J = 7.50 Hz), 7.82 (m, 8H), 7.59 (t, 4H, J = 7.30 Hz), 3.20 (s, 8H), -2.60 (s, 2H); M.S.: m/e = 1158.9 $M+H^+$ for $C_{52}H_{38}Br_4N_8O_4$ (ESI^+); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 421 (381), 512 (27.8), 545 (6.5), 589 (8.4), 648 (1.8) nm; Rf 0.41 (SiO_2, CH_2Cl_2 / ethyl acetate 80:20 vol.)

α_3–Tris-(*o*-bromoacetamidophenyl)-β-(*o*-N-triphenylmethylaminophenyl)porphyrin (24c):

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (d, 2H, J = 4.67 Hz), 8.76 (m, 6H), 8.67 (d, 2H, J = 8.3 Hz), 8.06 (d, 2H, J = 7.48 Hz), 7.94 (d, 1H, J = 7.50 Hz), 7.88 (m, 6H), 7.60 (m, 6H), 7.18 (m, 2H), 6.95 (m, 15H), 6.64 (d, 1H, J = 8.57 Hz), 3.24 (s, 2H), 3.22 (s, 4H), -2.67 (s, 2H); M.S.: m/e = 1279.1 $M+H^+$ for $C_{69}H_{51}Br_3N_8O_3$ (ESI^+); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 418 (329.1), 516 (26.6), 548 (6.6), 590 (8.6), 648 (3.4) nm; Rf 0.6 (SiO_2, CH_2Cl_2 / ethyl acetate 90:10 vol.)

Pyridine- and tris-imidazoles-strap binding procedures ($\alpha\beta\alpha\beta$ porphyrins)

Using bromoacetamido porphyrins.

A 500-mL two neck round bottom flask equipped with a stir bar was charged with tetrabromoacetamidoporphyrin **24a** (0.312 g, 0.269 mmol) or pyridine-strapped-dibromoacetamido porphyrin **26a** (60 mg, 0.051 mmol) in dry THF (360 mL (**24a**) or 70 mL (**26a**)) with 20 equiv. diethyl aniline (0.786 mL (**24a**) or 0.171 mL (**24e**)). The mixture was bubbled with N_2 for 10 min, then diamine **16** (0.044 g, 0.268 mmol), or **22**[2] (0.024 g, 0.051 mmol), or **23** (0.023 g, 0.051 mmol) in solution in THF (81.5 mL (**16**)) or in MeCN (15 mL (**22,23**) was introduced over 1h. The solution was allowed to stir for 48 h, then the solvent was evaporated and the residue was dissolved in CH_2Cl_2 (50 mL). The solution was poured on top of a silica gel (20 x 2 cm) for chromatography. For **26a**: Eluents: dichloromethane 100 %, then a mixture dichloromethane/ethyl acetate 9/1 vol allows the separation of the unreacted porphyrin **24a**, then a mixture dichloromethane/ethyl acetate 7/3 vol allows the obtention of the desired product. Two unidentified fractions were noticed: one moving close to **26a**, the other may be isolated at 100 % ethyl acetate. They were obtained in low amount under the conditions described and in higher yield when working at higher concentration.
Yields: **26a**: 0.140 g (45 %).
For **8-9**: dichloromethane/ethyl acetate 3:1 vol. allows the obtention of unreacted **26a-b**, followed by dichloromethane and dichloromethane-methanol (97:3 vol.) to get **8-9**. (10 %), **8**: 0.030 g (40 %), **9** 0.026 g (35 %).

Using chloroacetamido porphyrins
Same procedure as for bromoacetamidoporphyrins.
1- **24b** (0.250 g, 0.254 mmol) and **16** (0.042g , 0.254 mmol) stirred for several weeks at room temperature to get **26b:** 38 mg (14 %).
2- At 60 °C, **26b** was obtained in 25% yield.
3- Halogen exchange: **26b** (0.038 g, 0.035 mmol) was mixed with NaI in acetone at 50 °C for 2h, **23** (0.016 g, 0.035 mmol) was added dropwise. **9** (8%, 0.004 g).

α,β,α,β– Pyridine-strapped-dibromoacetamidophenyl porphyrin (26a)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 2H), 8.83 (d, 2H, J = 8.63 Hz), 8.74 (m, 7H), 8.65 (d, 2H, J = 8.3 Hz), 7.93 (brs, 4H), 7.83 (m, 8H), 7.48 (t, 4H, J = 7.49 Hz), 4.87 (s, 2H), 3.21 (s, 4H), 2.72 (s, 4H), 2.14 (brs, 4H), -0.17 (s, 6H), -3.03 (s, 2H); M.S.: m/e = 1162.3 $M+H^+$ for $C_{61}H_{51}Br_2N_{11}O_4$ (LCQ-ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 404 (sh), 422 (347), 516 (58.9), 552 (9.7), 592 (45), 656 (12) nm; Rf 0.3 (SiO_2, CH_2Cl_2 / ethyl acetate 70:30 vol.).

α,β,α,β– Pyridine-strapped-dichloroacetamidophenyl porphyrin (26b)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 2H), 8.82 (d, 2H, J = 8.19 Hz), 8.74 (m, 7H), 8.68 (d, 2H, J = 8.41 Hz), 8.19 (s, 4H), 7.83 (m, 8H), 7.48 (t, 4H, J = 7.33 Hz), 4.86 (s, 2H), 3.45 (s, 4H), 2.72 (s, 4H), 2.13 (brs, 4H), -0.17 (s, 6H), -3.03 (s, 2H); M.S.: m/e = 1072.3 $M+H^+$ for $C_{61}H_{51}Cl_2N_{11}O_4$ (LCQ-ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 402 (sh), 422 (410), 514 (75), 544 (52), 586 (49.8), 648 (20) nm; Rf 0.3 (SiO_2, CH_2Cl_2 / ethyl acetate 70:30 vol.)

α,β,α,β– Methoxyphenyl-containing-tris-imidazole- strapped / pyridine-strapped porphyrin (8a)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.40 (s, 2H), 8.97 (s, 2H), 8.87 (d, 2H, J = 8.57 Hz), 8.70 (m, 8H), 8.42 (brs, 1H), 7.91 (brs, 1H), 7.80 (m, 5H), 7.49 (s, 2H), 7.45 (t, 2H, J = 7.82 Hz), 7.32 (t, 3H, J = 6.84 Hz), 6.97 (t, 1H), 6.91 (brs, 1H), 6.86 (s, 1H), 6.81 (s, 1H), 6.58 (d, 1H), 6.40 (t, 1H, J = 8.2 Hz), 5.20 (s, 1H), 4.76 (s, 2H, *o*-Py), 3.61 (s, 3H), 2.70 (s, 6H), 2.50 (brm, 8H), 2.32 (brm, 2H), 2.06 (brs, 6H), 1.38 (brm, 6H), 1.12 (s, 6H), -0.17 (s, 6H), -3.03 (s, 2H); M.S.: m/e = 1464.6 $M+H^+$ for $C_{85}H_{81}N_{19}O_6$ (ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 423 (312.8), 518 (16.7), 550 (2.5), 592 (2.6), 658 (0.4) nm; Rf 0.5 (SiO_2, CH_2Cl_2 / MeOH 98:2 vol.).

α,β,α,β– allyl-protected-containing-tris-imidazole-strapped / pyridine-strapped porphyrin (9)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 2H), 8.97 (d, 2H, J = 7.0 Hz), 8.70 (m, 6H), 7.97 (brs, 1H), 7.85 (t, 1H, J = 9.0 Hz), 7.79 (m, 4H), 7.58 (brs, 2H), 7.46 (t, 2H, J = 7.82 Hz), 7.40 (t, 1H, J = 7.5 Hz), 7.34 (m, 2H), 7.20 (m, 5H), 6.58 (s, 1H), 5.76 (m, 2H), 5.21 (s, 1H), 5.15 (s, 1H), 5.09 (m, 2H), 4.83 (s, 1H, *o*-Py), 4.81 (s, 1H, *o*-Py), 3.44 (s, 3H), 3.25 (brs, 4H), 3.11 (s, 1H), 2.97 (s, 4H), 2.75 (brm, 8H), 2.40 (brs, 2H), 2.31 (brs, 2H), 2.05 (s, 8H), 1.68 (s, 6H), 1.22 (brs, 4H), -0.21 (s, 6H), -3.14 (s, 2H); M.S.: m/e = 1455.7 for $C_{84}H_{86}N_{20}O_5$ (ESIλ$_{abs}$ (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 422 (357), 516 (21), 546 (6.4), 592 (6.9), 650 (7.7) nm; Rf 0.55 (SiO_2, CH_2Cl_2/MeOH 89:11 vol.).

Tripodal triimidazole ligand attachement (α,α,α,β porphyrins)

Using chloroacetamido porphyrin.

Under N_2 atmosphere, a solution of tripodal triamine **27**[2] (0.090 g, 0.216 mmol) and NaI (156 mg, 1 mmol) in dry THF (10 mL) was added to a solution of chloroacetamidoporphyrin **24d** (0.200 g, 0.174 mmol) in THF (150 mL) with a syringe pump (1 mL/h) and the solution is stirred at 50 °C for 3 days (1.08 mM porphyrin). The

solvent is evaporated off and the residue is purified by preparative TLC (SiO_2, 500 μm, CH_2Cl_2 / MeOH 9:1 vol. then CH_2Cl_2/isopropanol 85:15 vol. Yield **10** (0.016 g, 6.3 %).

Using bromoacetamido porphyrin.

In a typical reaction, a 1.0 mM solution of α_3-tribromoacetamido-β-trityl-porphyrin **24c** (0.050 g, 0.039 mmol) in THF (40 mL) under nitrogen atmosphere was added a solution of tripodal triamine **27** (0.016 g, 0.039 mmol), and diethylaniline (25 μL, 0.156 mmol) in THF (10 mL) at a rate of 40 mL/h using syringe pump. After the addition was completed, the solution was allowed to stir for an additional 36-72 h at room temperature. After removing the solvent, the resulting solid was dissolved in CH_2Cl_2 (10 mL) and loaded on top of a silica gel column (25 x 3 cm). Elution with CH_2Cl_2 , CH_2Cl_2 / ethyl acetate 7:3 vol to remove **24c** left, and then as described above. **10** (0.015 g, 28 %).

α_3-Triimidazole-capped-β -trityl-porphyrin (10)

^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 9.32 (brs, 1H), 8.92 (brs, 1H), 8.83 (m, 4H), 8.70 (s, 4H), 8.65 (d, 1H, J = 8.3 Hz), 8.22 (d, 2H, J = 7.5 Hz), 7.80 (m, 5H), 7.65 (d, 1H, J = 7.80 Hz), 7.51 (t, 1H, J = 7.49 Hz), 7.45 (m, 4H), 7.20 (t, 1H, J = 6.80 Hz), 7.05 (m, 2H), 6.90 (m, 15H), 6.53 (d, 1H, J = 8.5 Hz), 5.10 (s,1H), 4.85 (s, 2H), 3.20 (d, 2H), 3.05 (m, 9H), 2.82 (s, 3H), 2.75 (d, 3H), 2.60 (s, 2H), 2.55 (s, 3H), 2.50 (m, 4H), 2.10 (brs, 9H), -2.75 (s, 2H); M.S.: m/e = 1453.3 $M+H^+$ for $C_{89}H_{81}N_{17}O_4$ (LCQ-ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 424 (264.4), 520 (17.7), 558 (4.5), 598 (4.5), 650 (1.5) nm; Rf 0.7 (SiO_2, NH_3-saturated $CHCl_3$ / isopropanol 8:2 vol.)

TACN and cyclen capping procedures (α,α,α,β and α,α,α,α porphyrins)

In a typical reaction, a 3.1 mM solution of α_3-tribromoacetamido-β-trityl-porphyrin **24c** (0.200 g, 0.156 mmol) or α_4-tetrabromoacetamidoporphyrin **24d** (0.100 g, 0.0861 mmol) in THF (50 mL) under nitrogen atmosphere was added a solution of 1,4,7-triazacyclononane (0.021 g, 0.1640 mmol) or cyclen (0.015 g, 0.086 mmol), and diethylaniline (751 μL, 4.68 mmol) in THF (20 mL) at a rate of 40 mL/h using syringe pump. After the addition was completed, the solution was allowed to stir for an additional 36 h at room temperature. The solvent was removed *in vacuo*. The resulting solid was dissolved in CH_2Cl_2 (100 mL), washed with $NaHCO_3$ (2 x 100 mL), water (100 mL), dried over Na_2SO_4 and loaded on top of a silica gel column (20 x 3 cm). Washings with CH_2Cl_2 followed by dichloromethane/ethylacetate (7:3 vol.) to remove unreacted **24c**, and dichloromethane:methanol. (9:1 vol. For **12**, 8:2 vol. For **13**) afforded the desired products. **12** (0.080 g, 44 %); **13**[1c] (0.043 g, 50 %).

α_3-Triazacyclononane-capped-β-(*o*-N-triphenylmethylaminophenyl)porphyrin (12):
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (brs, 1H), 9.12 (brs, 1H), 8.91 (d, 2H, J = 4.89 Hz), 8.82 (2H, d, J = 4.5 Hz), 8.77 (m, 8H), 8.58 (d, 2H, J = 4.51 Hz), 7.80 (t, 2H, J = 8.19 Hz), 7.75 (d, 2H, J = 7.33 Hz), 7.68 (t, 2H, J = 7.6 Hz), 7.38 (t, 1H, J = 6.45 Hz), 7.15 (m, 2H), 6.88-6.99 (m, 15H), 6.60 (d, 1H, J = 8.35 Hz), 6.31 (brs, 1H), 4.65 (s, 1H), 2.64 (m, 2H), 2.03 - 1.75 (m, 4H), 1.73 (m, 2H), 1.34 (m, 4H), 0.61 (brs, 2H), -0.20 (brs, 1H), -

1.95 (brs, 1H), -2.34 (s, 2H), -2.60 (brs, 2H). M.S.: m/e = 1167.4 M+H$^+$ for $C_{75}H_{63}N_{11}O_3$ (ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 418 (345), 516 (24.9), 546 (4.5), 590 (7.2) nm; Rf 0.30 (SiO_2, CH_2Cl_2 / MeOH 96:4 vol.).

α_4-Tetrazacyclododecane-capped porphyrin (13):
^{I}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 8H), 8.60 (d, 4H, J = 8.5 Hz), 8.57 (s, 4H), 8.18 (d, 4H, J = 6 Hz), 7.86 (t, 4H, J = 8.0 Hz), 7.56 (t, 4H, J = 8.0 Hz), 2.31 (s, 8H), 0.33 (brs, 8H), -0.90 (brs, 8H), -2.73 (brs, 2H). M.S.: m/e = 1005.1 M-H$^+$ for $C_{60}H_{54}N_{12}O_4$ (ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 418 (360), 510 (25.2), 544 (3.4), 586 (6.6) nm; Rf 0.30 (SiO_2, CH_2Cl_2 / MeOH 96:4 vol.).

Dimethylethylenediamine-strap binding procedures (α,α,α,α porphyrins)

To a 0.7 mM solution of α_4-tetrabromoacetamidoporphyrin **24d** (0.040 g, 0.034 mmol) in THF (50 mL) under nitrogen atmosphere was added a solution of *N*,*N*-dimethylethylenediamine (3.6 μL, 0.0144 g, 0.070 mmol) and diethylaniline (100 μL, 4.68 mmol) in THF (5 mL) at a rate of 10 mL/min using syringe pump. After the addition was completed, the solution was allowed to stir for an additional 36 h at room temperature. The solvent was removed *in vacuo*. The resulting solid was dissolved in CH_2Cl_2 (100 mL), and loaded on top of a short silica pad (10 x 3 cm), washed with CH_2Cl_2 then CH_2Cl_2 / ethyl acetate (7:3 vol.) to remove diethylaniline and unreacted **24e**. Elution with dichloromethane-methanol (80:20 vol.) followed by evaporation of the solvent led to a residue which was chromatographed over preparative TLC (SiO_2, 500 A, eluent CH_2Cl_2 / methanol 94:6 vol.) afforded the mono-strapped porphyrin **15** (0.018 g, 47 %) and the desired product **14** (0.009 g, 25 %) moving very closely.

α_4-*Cis,cis*-bis-dimethylethylenediamine-straped (14):
^{I}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 4H), 8.80 (4H, s), 8.75 (s, 4H), 8.66 (d, 4H, J = 8.03 Hz), 7.83 (m, 8H), 7.47 (t, 4H, J = 7.60 Hz), 2.65-2.42 (m, 8H), 1.23 (m, 4H), 0.49 (s, 12H), 0.29 (s, 4H), -2.56 (s, 2H). M.S.: m/e = 1011.7 M+H$^+$ for $C_{60}H_{58}N_{12}O_4$ (ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 422 (374), 514 (27.1), 548 (6.1), 590 (7.7), 646 (1.5) nm; Rf 0.5 (SiO_2, CH_2Cl_2 / MeOH 9:1 vol.)

α_2–*Cis*-dimethylethylenediamine-straped-α_2-dibromoacetamido-porphyrin (15):
^{I}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 2H), 8.80 (m, 2H), 8.76 (s, 4H), 8.67 (d, 2H, J = 8.19 Hz), 8.62 (d, 2H, J = 8.30 Hz), 8.06 (s, 2H), 7.97 (m, 4H), 7.84 (m, 4H), 7.56 (t, 2H, J = 7.59 Hz), 7.50 (t, 2H, J = 7.44 Hz), 3.29 (m, 4H), 2.49-2.29 (m, 4H), 1.20 (brs, 4H), 0.21 (brs, 6H), 0.10 (m, 2H), -2.60 (s, 2H). M.S.: m/e = 1082.2 M+H$^+$ for $C_{56}H_{48}Br_2N_{10}O_4$ (ESI$^+$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 420 (288.6), 514 (16.4), 546 (2.5), 588 (4.2) nm; Rf 0.6 (SiO_2, CH_2Cl_2 / MeOH 9:1 vol.)

Distal Imidazoles Attachment (αααβ porphyrin)

Following a procedure earlier reported and modified as follows. To a mixture of cyanoethyl-protected imidazole **28**[1b] (0.141 g, 1.17 mmol) and diethylaniline (1.17 mmol, 186 μL) in THF (20 mL) was added a solution of porphyrin **24c** (0.050 g, 0.039 mmol) in

THF (30 mL) under nitrogen atmosphere and the mixture was stirred at room temperature for 16 hrs. The imidazole nitrogen deprotection and porphyrin workup was as previously described by mixing the porphyrin with sodium methoxide in CH_2Cl_2 for 30 min. **11**[1b] (0.0155 g, 40%).

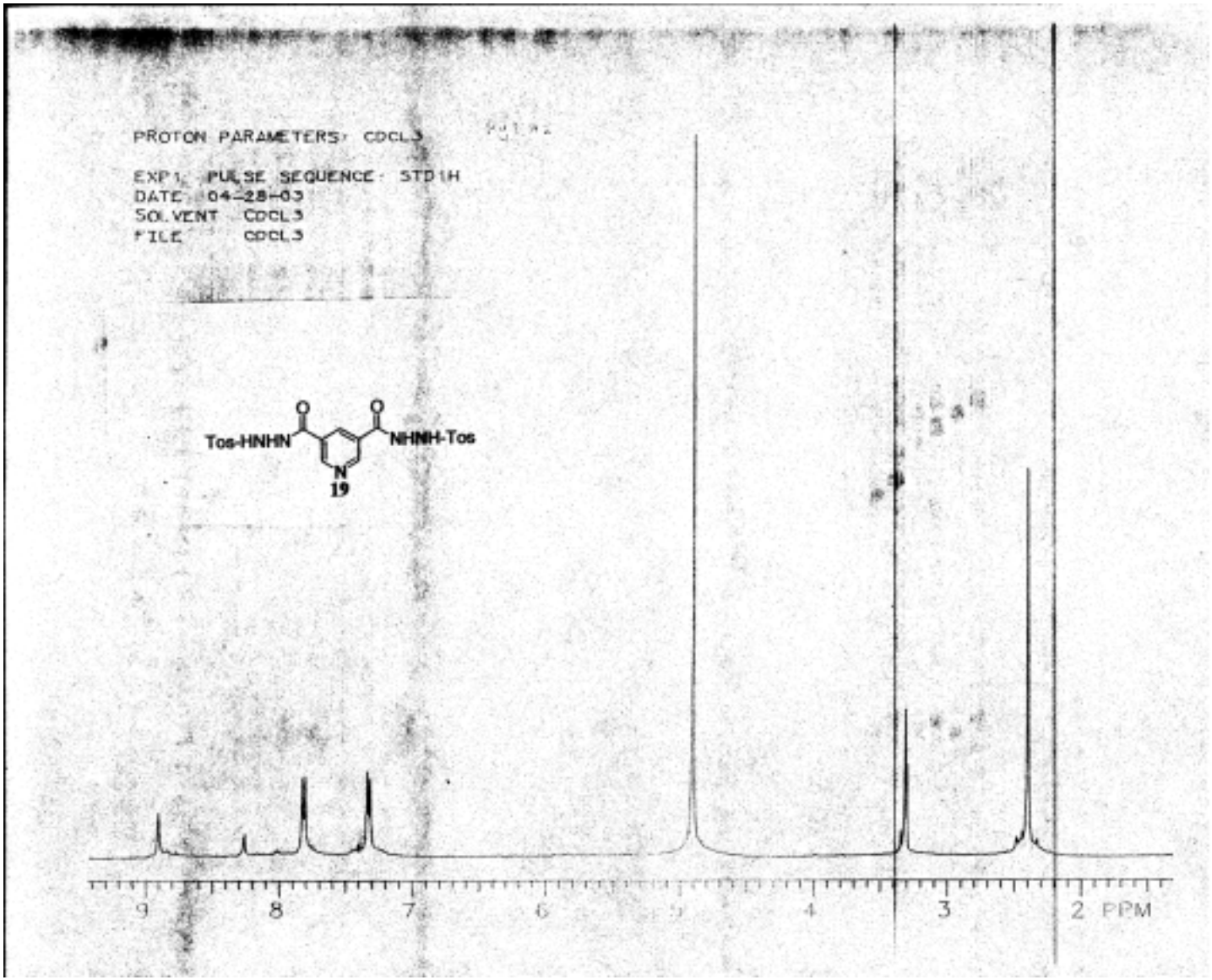
Phenol deprotection reaction: To a solution of **8a** (10 mg, 6.8 μmol) in dry dichloromethane (8 mL) cooled at –78 °C was introduced a 1.0 *M* solution of BBr_3 in dichloromethane (0.136 mL, *ca* 25 eq., 0.8 eq. per heteroatom present in **8a**). The mixture was stirred at –78 °C for 30 min and at 0 °C for 1h. The reaction was quenched with methanol (100 μL) and stirred for 10 min at 0 °C. The mixture was washed with 50 %-saturated aqueous $NaHCO_3$ solution (2 x 50 mL), H_2O (50 mL), then dried and the solvent was evaporated under reduced pressure. The crude was chromatographied on preparative silica plates (eluent CH_2Cl_2/MeOH 90/10 vol.). **8b** 4 mg, 40 %.

α,β,α,β–phenol-containing-tris-imidazole- strapped / pyridine-strapped porphyrin (8b)

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.40 (s, 2H), 9.10 (brs, 1H), 9.00 (s, 2H), 8.86 (d, 2H, J = 8.57 Hz), 8.70 (m, 7H), 8.62 (brs, 1H), 8.06 (brs, 1H), 7.80 (m, 5H), 7.49 (s, 2H), 7.45 (t, 2H, J = 7.82 Hz), 7.32 (t, 3H, J = 6.84 Hz), 7.03 (t, 1H), 6.91 (brs, 1H), 6.86 (s, 1H), 6.81 (s, 1H), 6.58 (d, 1H), 6.40 (t, 1H, J = 8.2 Hz), 5.05 (s, 1H), 4.76 (s, 2H, *o*-Py), 2.70 (s, 6H), 2.50 (brm, 8H), 2.32 (brm, 2H), 2.06 (brs, 6H), 1.38 (brm, 6H), 1.12 (s, 6H), -0.17 (s, 6H), -3.03 (s, 2H); M.S.(ESI+): m/e = 1483.4 $M+CH_3OH+H^+$ for $C_{84}H_{79}N_{19}O_6$; M.S.(ESI+, 30eV): m/e = 1450.6 $M+H^+$ for $C_{84}H_{79}N_{19}O_6$, 1361.5 ($MH^+ - 6CH_3$); λ_{abs} (CH_2Cl_2)(ε, mM^{-1} cm^{-1}) 422 (387.7), 516 (29.4), 548 (9.6), 592 (10.1), 654 (4.7) nm; Rf 0.4 (SiO_2, CH_2Cl_2 / MeOH 9:1 vol.).

References

1. (a) Collman, J.P.; Gagne, R. R.; Reed, C. A.; Halbert, T. R.; Lang, G.; Robinson, W. T.; *J. Am. Chem. Soc.* **1975**, *97*, 1427. (b) Collman, J.P.; Broring, M.; Fu, L.; Rapta, M.; Schwenniger, R. *J. Org. Chem.* **1998**, *63*, 8084. (c) Collman, J.P.; Broring, M.; Fu, L.; Rapta, M.; Schwenniger, R.; Straumanis, A. *J. Org. Chem.* **1998**, *63*, 8082. (d) Collman, J. P.; Boitrel, B.; Fu, L.; Galanter, J.; Straumanis, A.; Rapta, M. *J. Org. Chem.* **1997**, *62*, 2308.
2. (a)Collman, J. P.; Zhong, M.; Costanzo, S.; Zhang, C. *J. Org. Chem.* **2001**, *66*, 8252.
3. (a) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc. Perkin Trans I* **1983**, 189. (b) Palecek, J.; Ptackova, L.; Kuthan, J. *Coll. Czechosl. Chem. Commun.* **1969**, *34*, 427. (c) Queguiner, G.; Pastour, P. *C. R. Acad. Sci. Paris (C)* **1966**, *262*, 1335 (d) Queguiner, G.; Pastour, P. *Bull. Soc. Chim. Fr.* **1968**, 4117. (e) (f) Choma, C. T.; Kaeslte, K.; Akerfeldt, K. S.; Kim, R. M.; Groves, J. T.; DeGrado, W. F. *Tetrahedron Letters*, **1994**, *35*, 6191. (g) Luenig, U.; Baumstark, R.; Peters, K.; Van Schnering, H. G. *Liebigs Annalen der Chemie* **1990**, *2*, 129. (h) Jaisankar, P.; Pal, B. Giri, V. S. *Synth. Commun.* **2002**, *32*, 2569. (i) *Org. React.* **1954**, VIII, 232; (j) McFayden, J.S.; Stevens, T.S. *J. Chem. Soc.* **1936**, 584. (k) Habermann, J.; Ley, S. V.; Scott, J. S. *Perkin 1* **1999**, 1253.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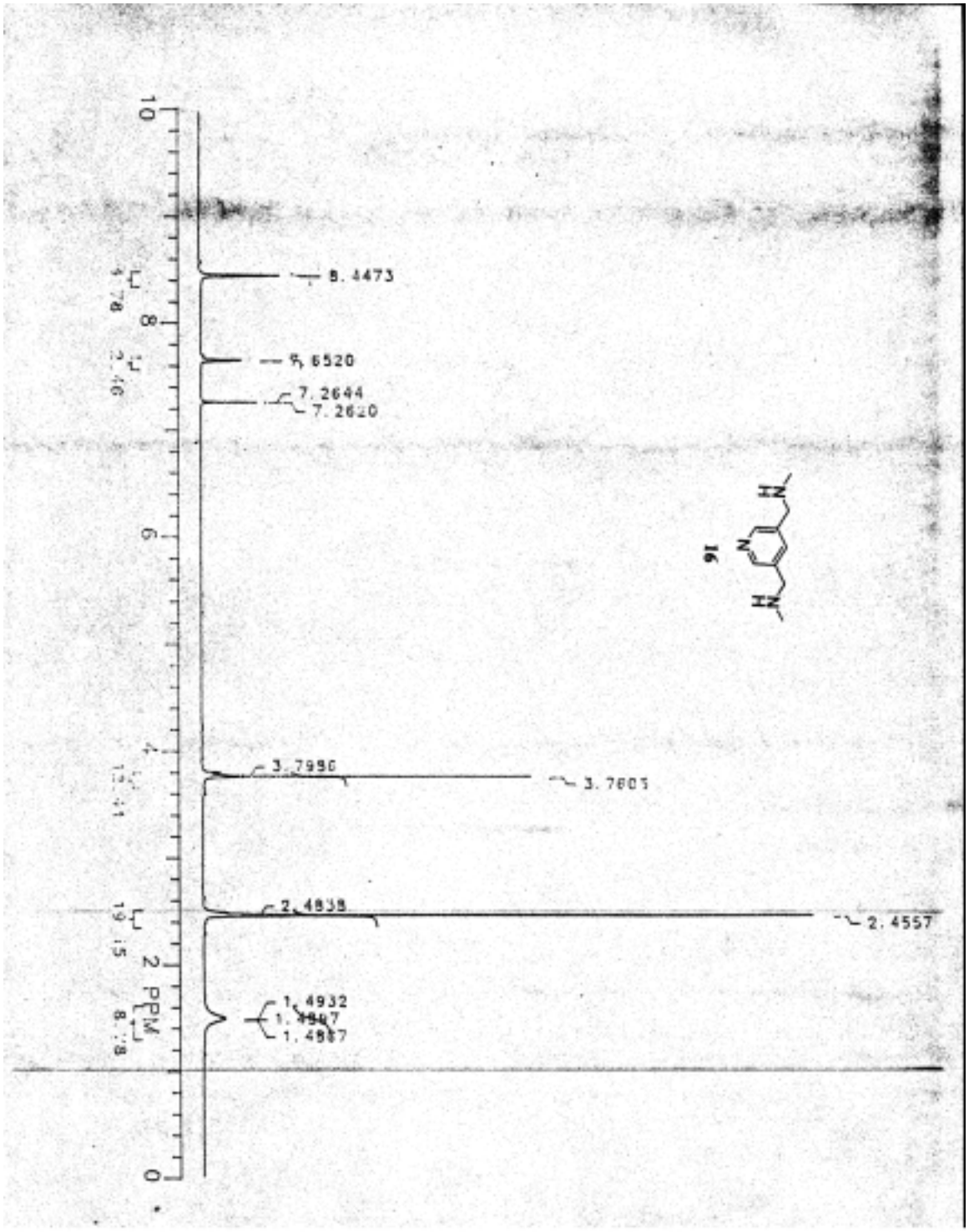
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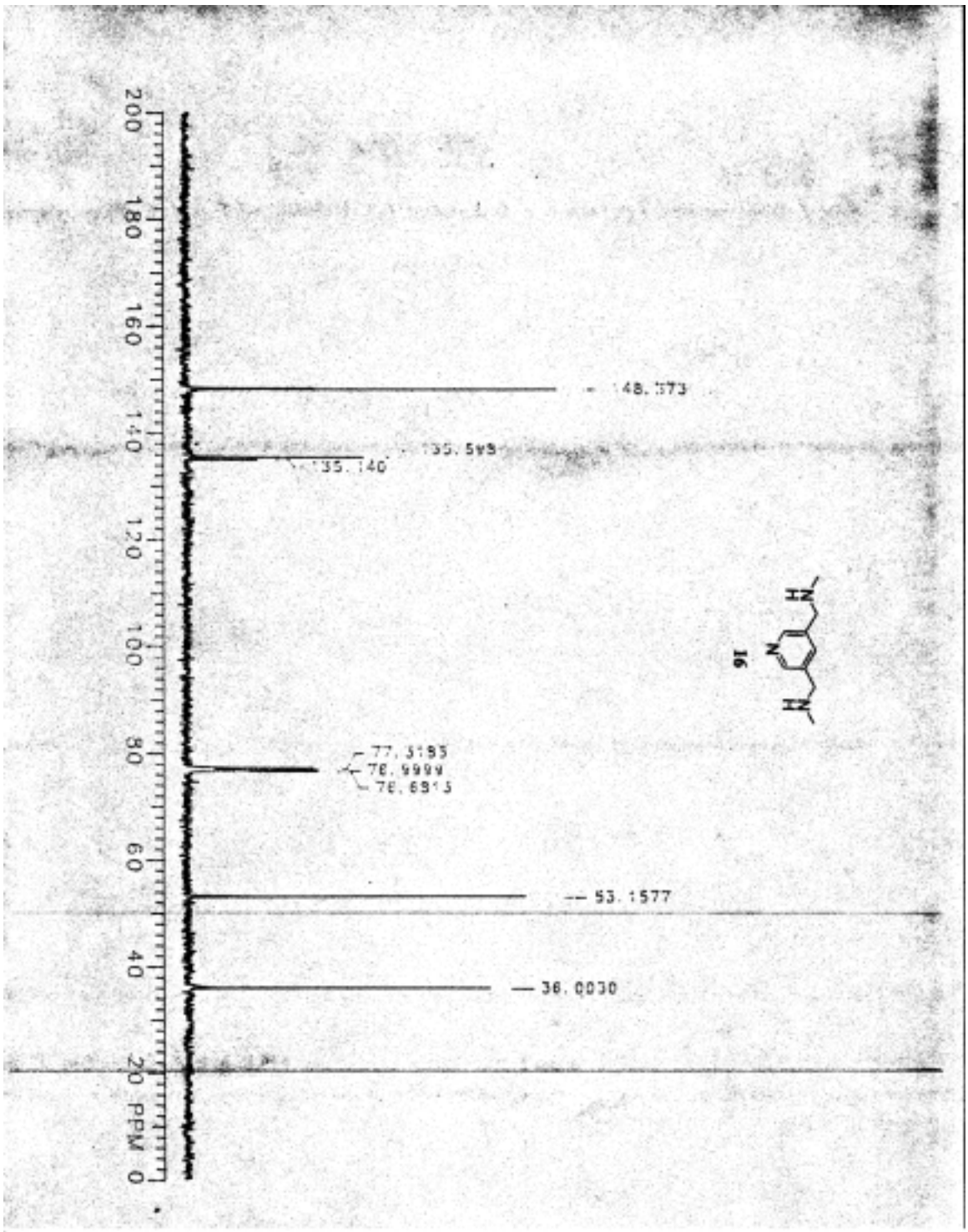
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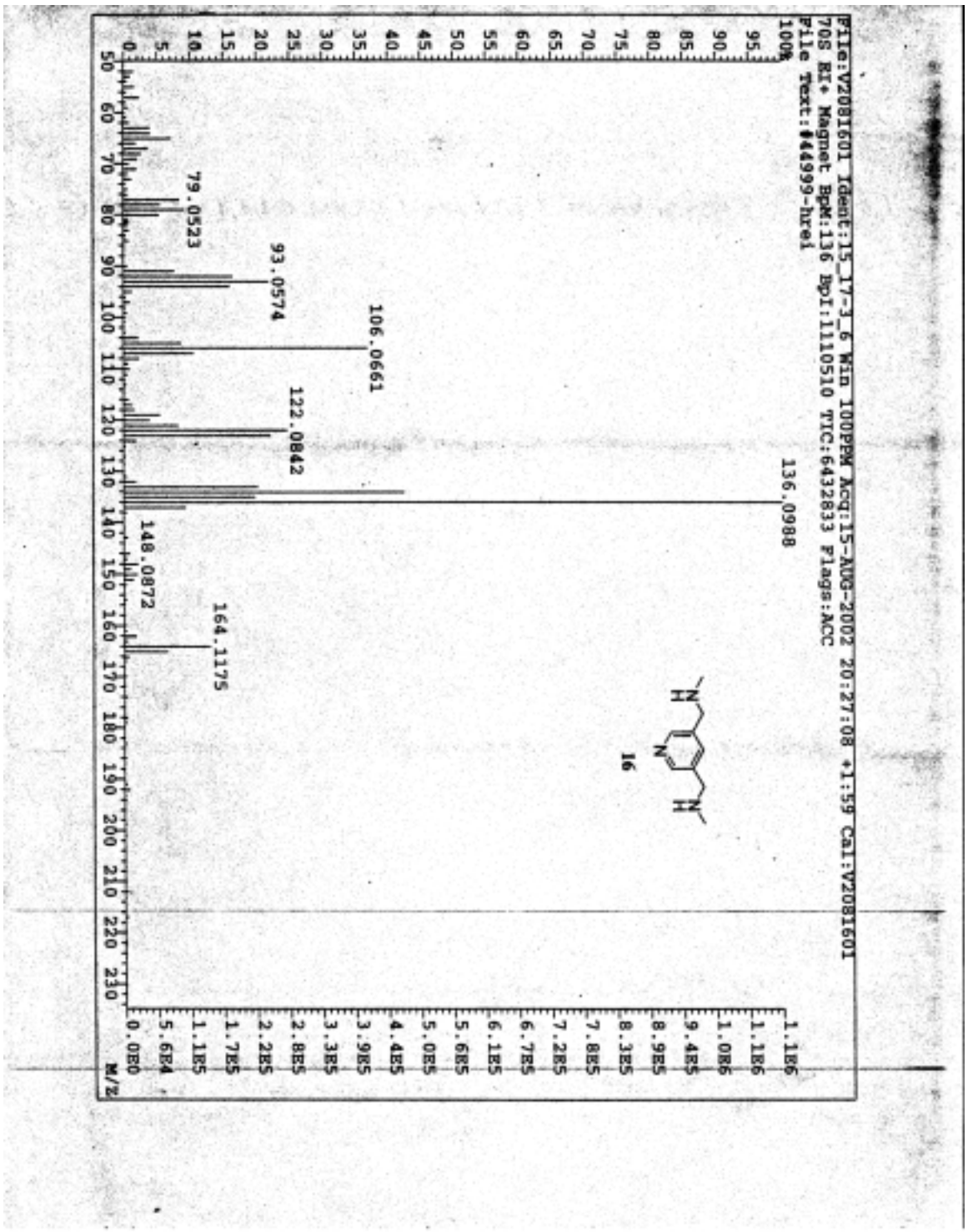
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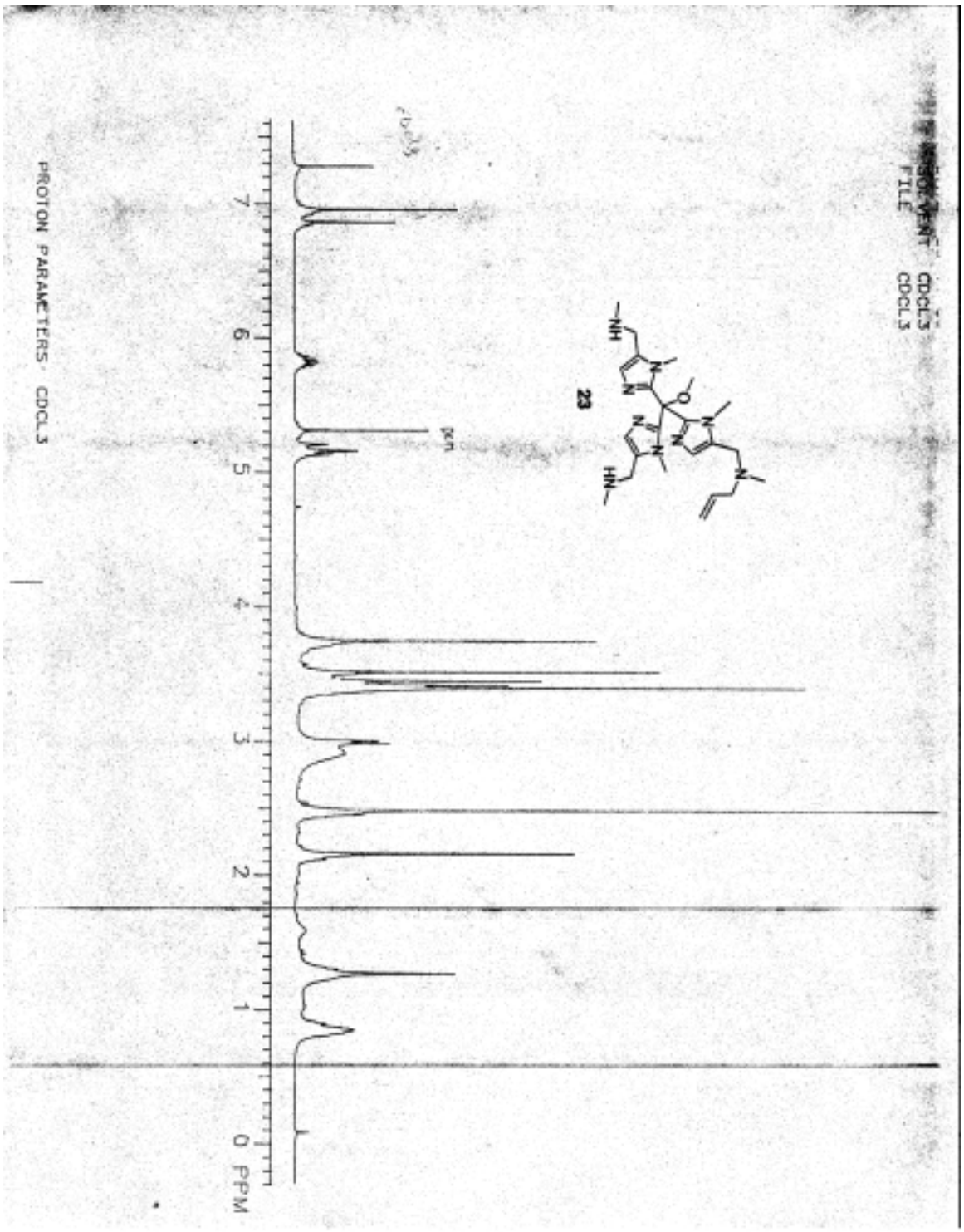
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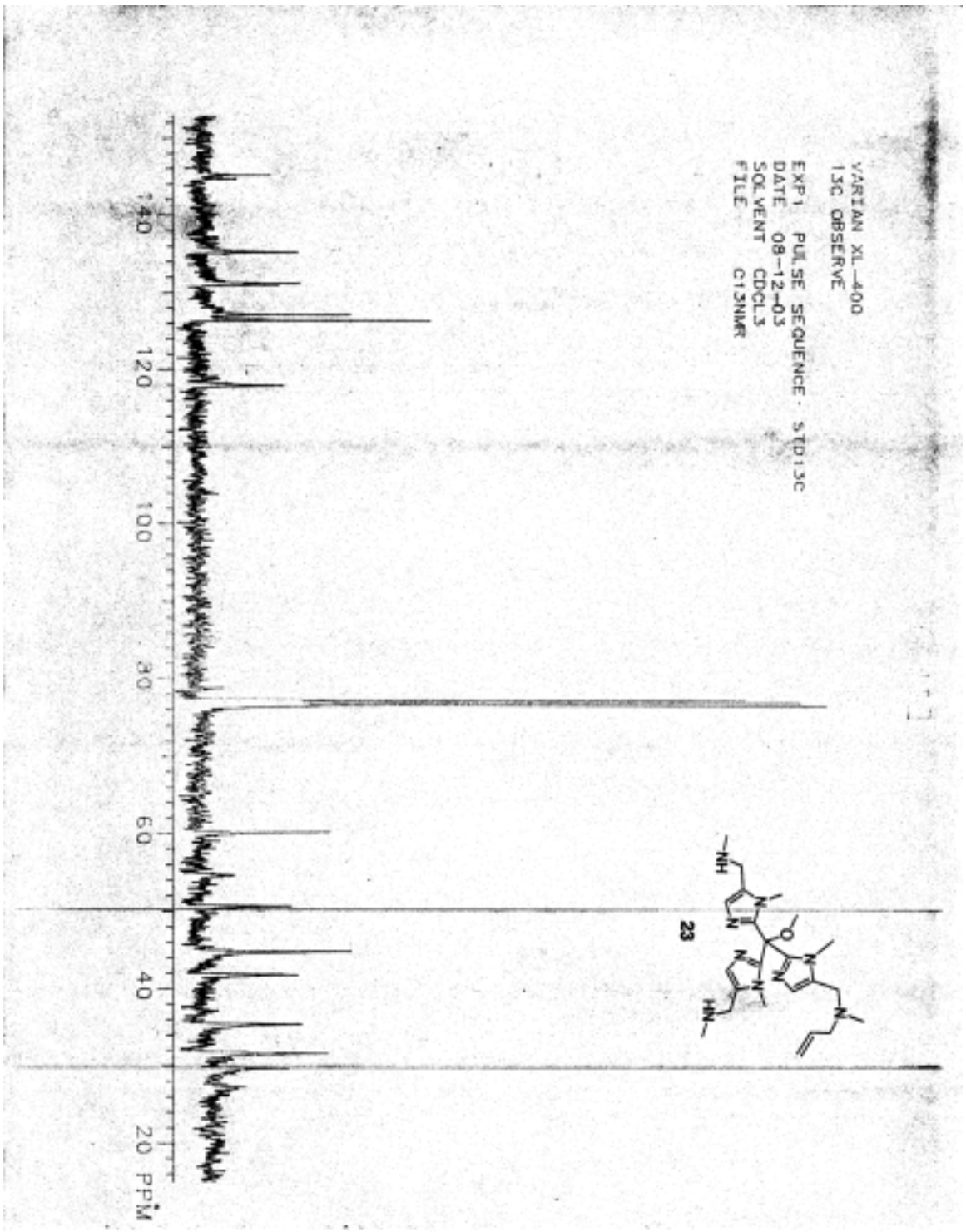
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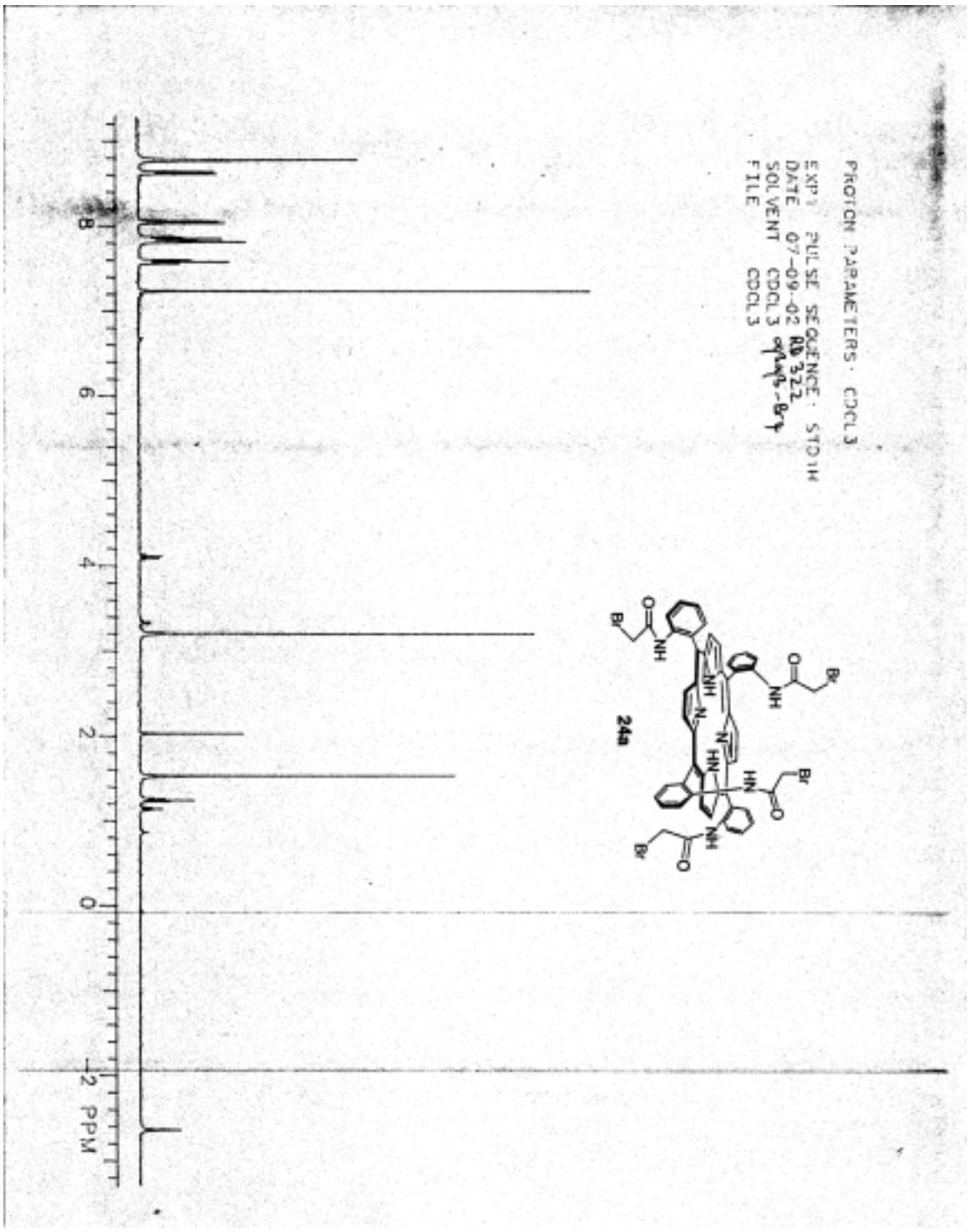
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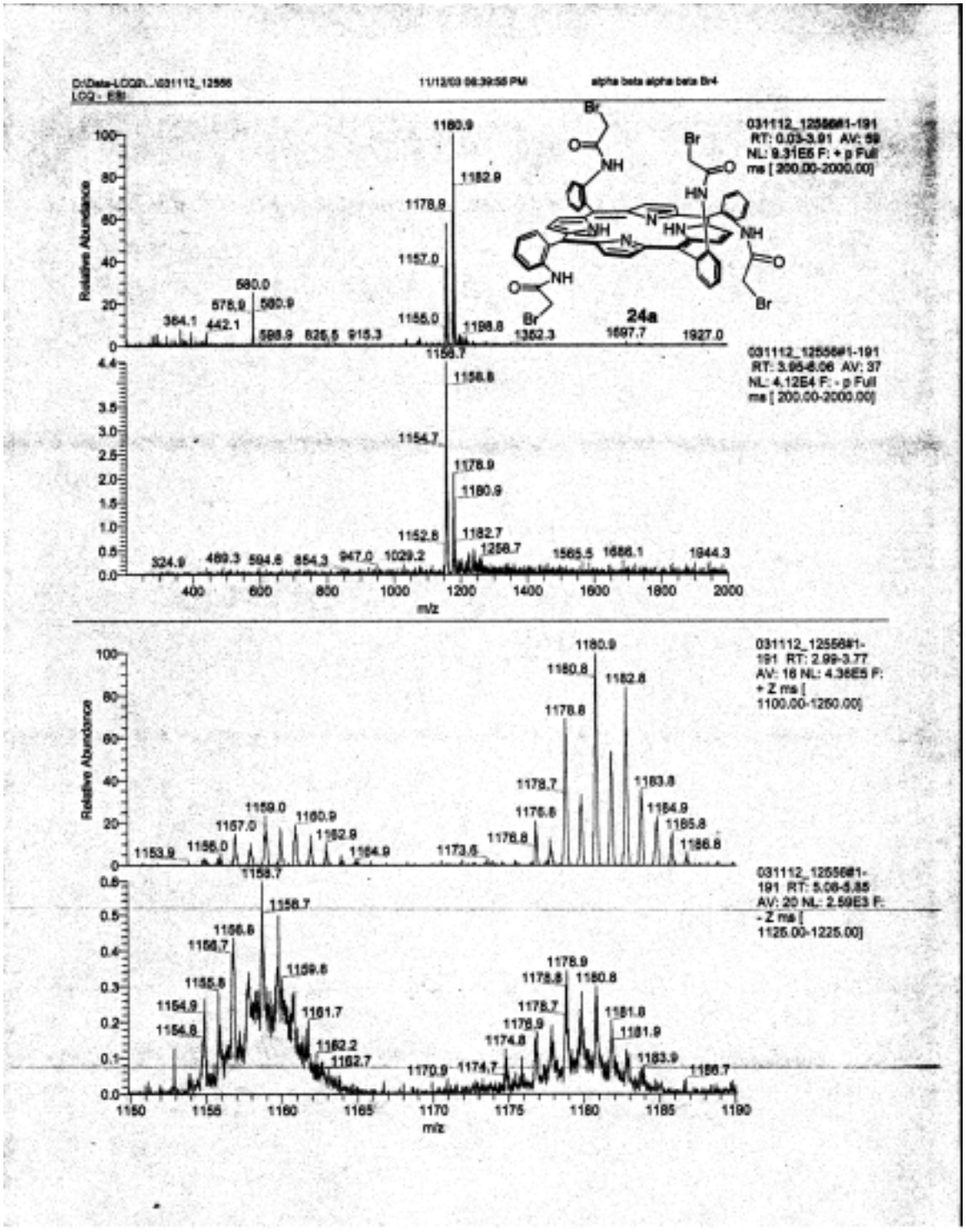
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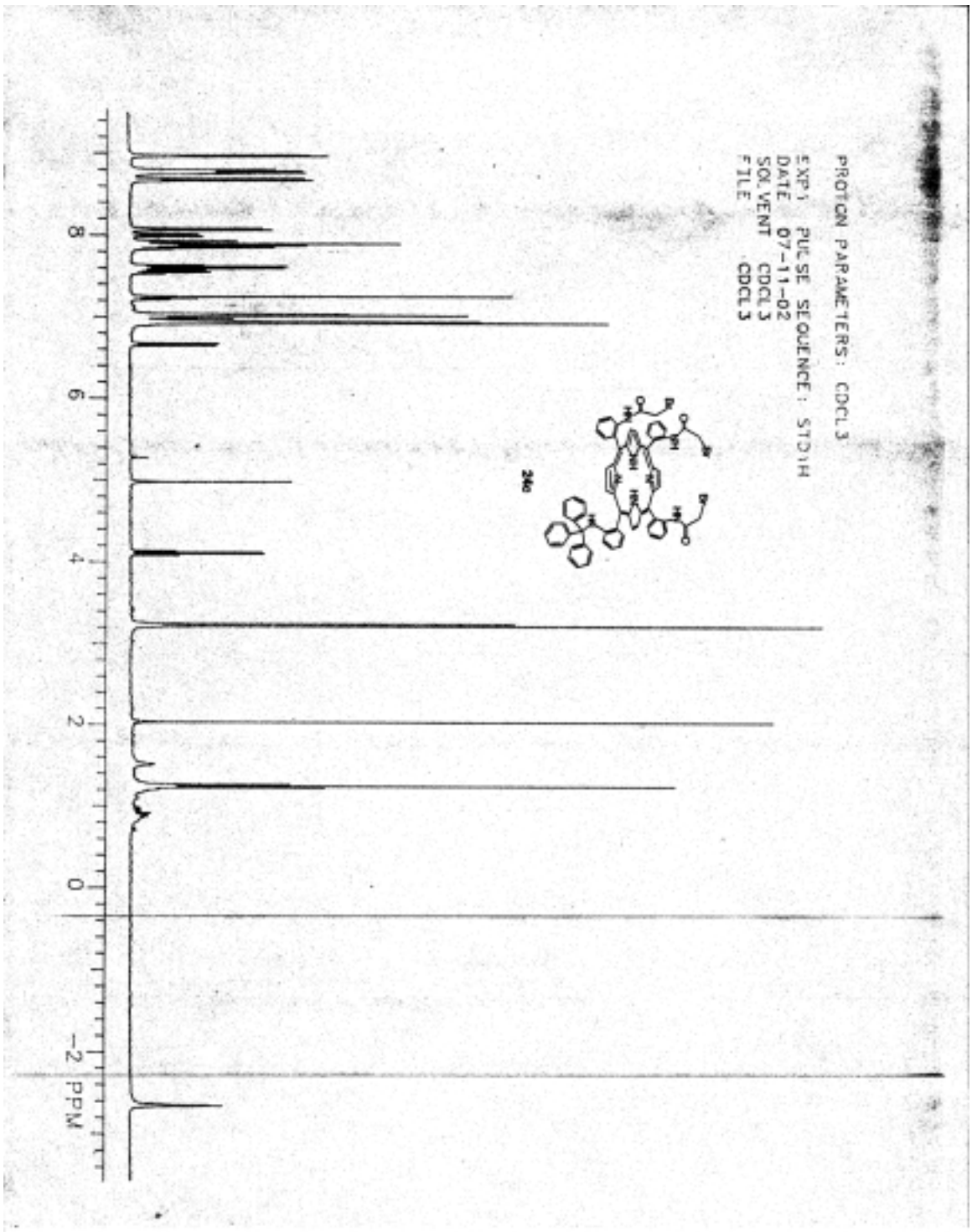
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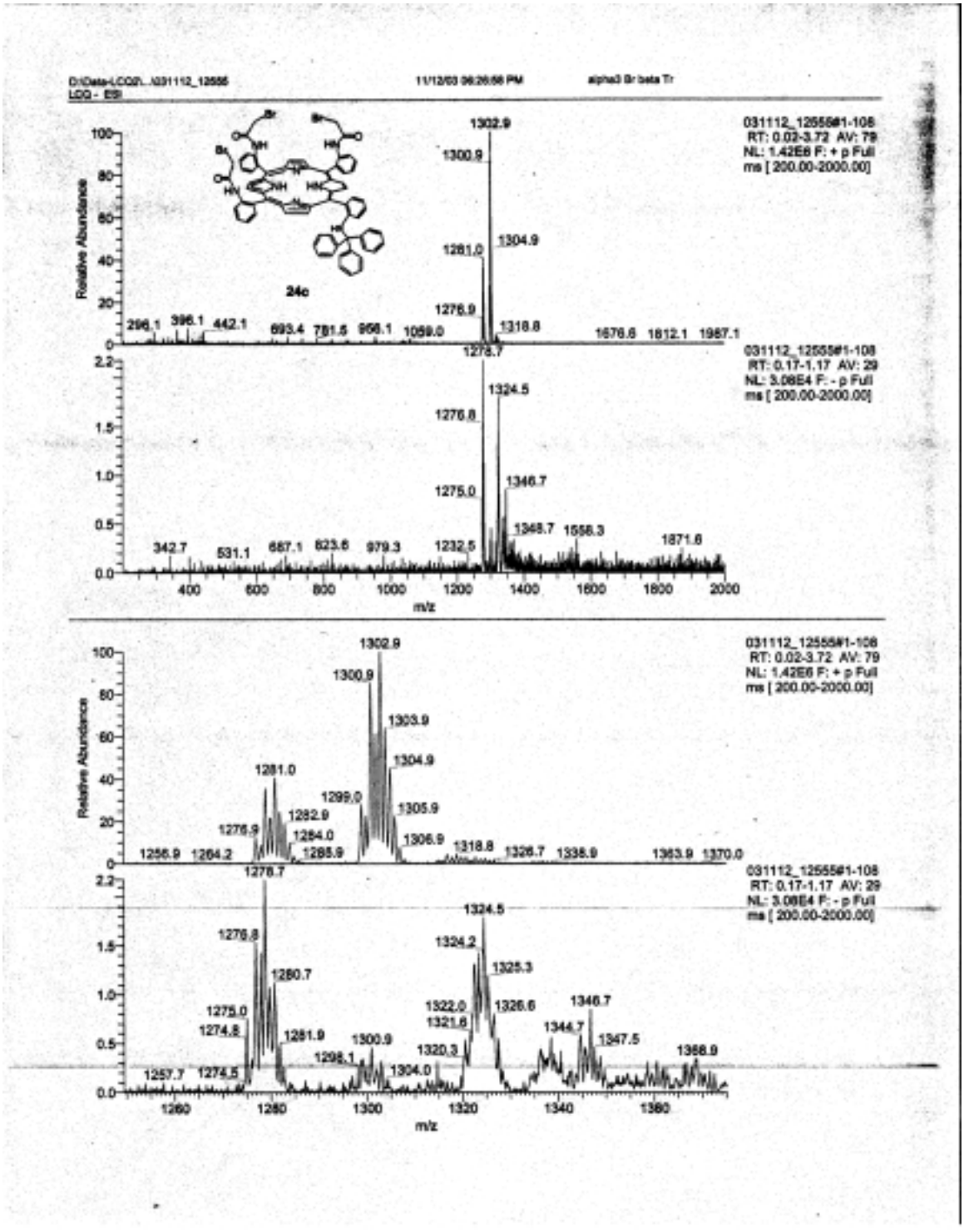
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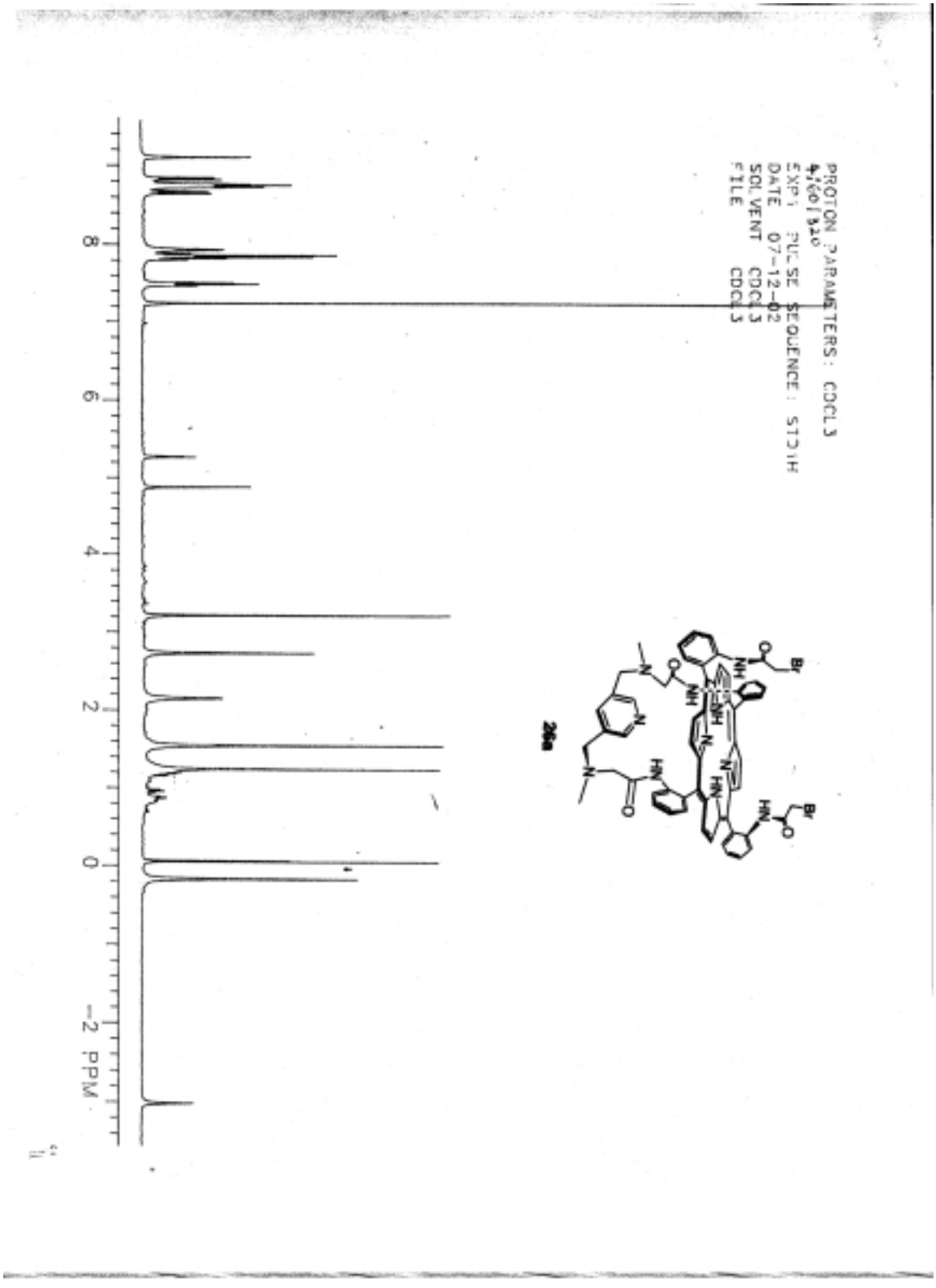
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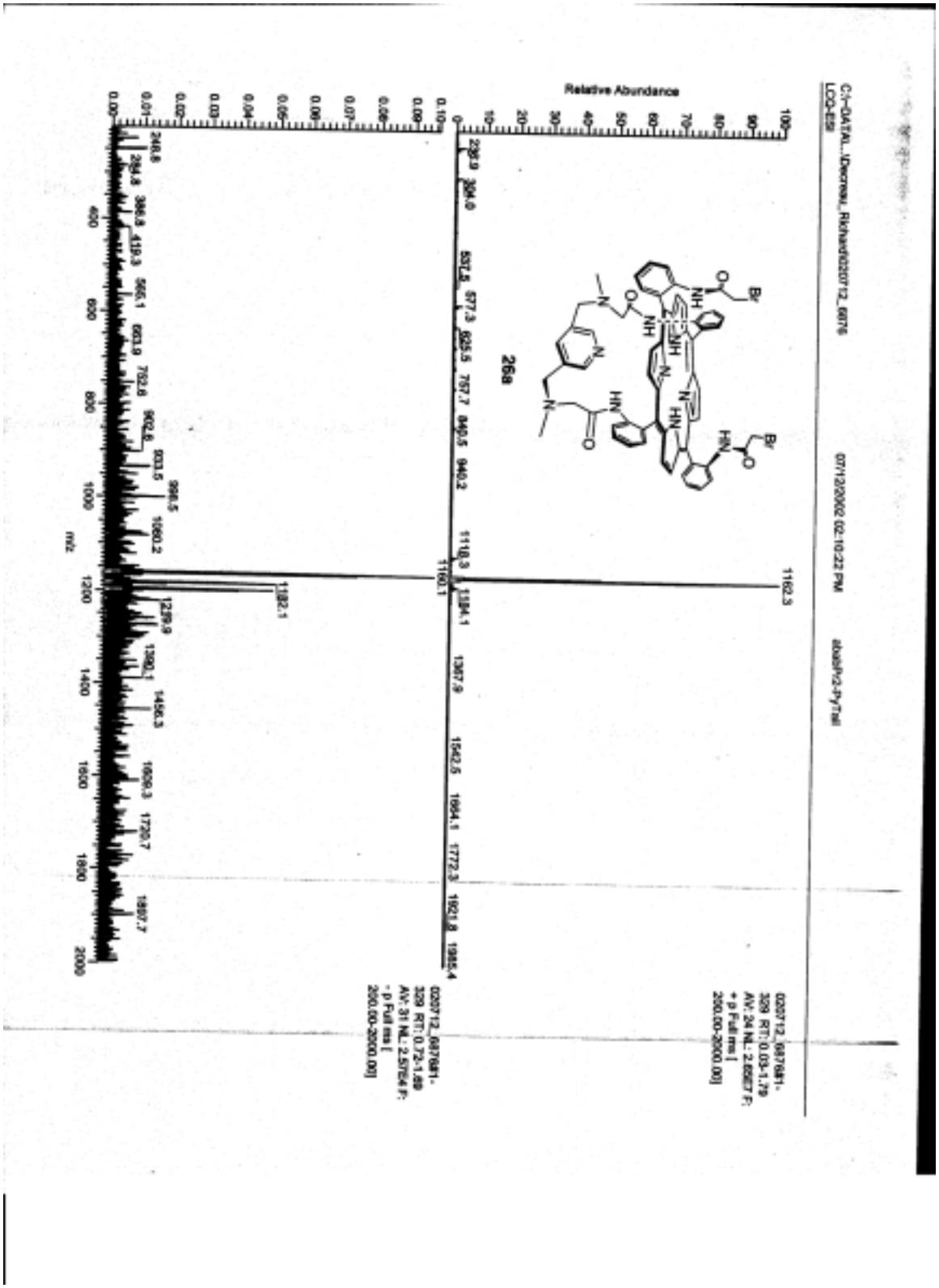
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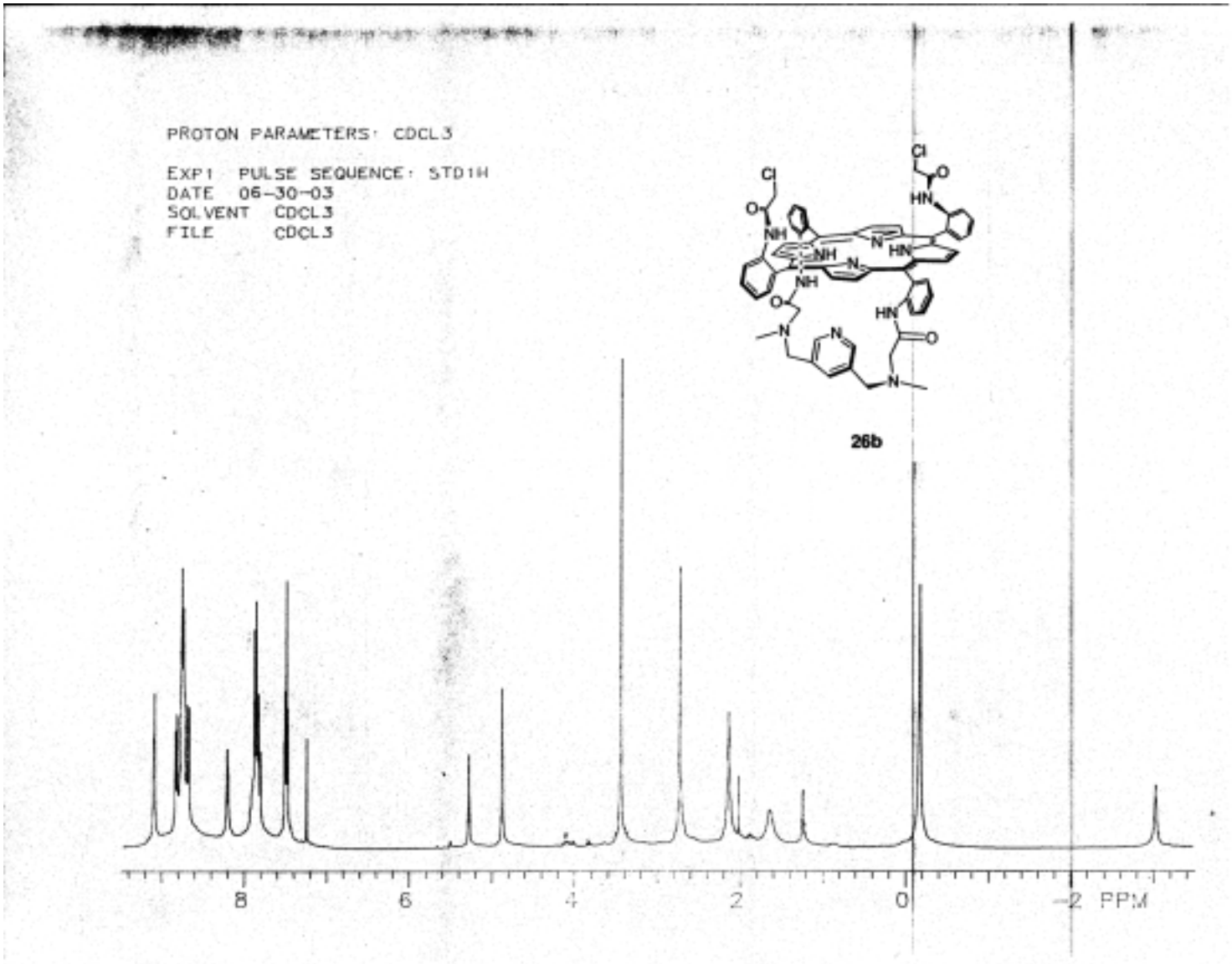
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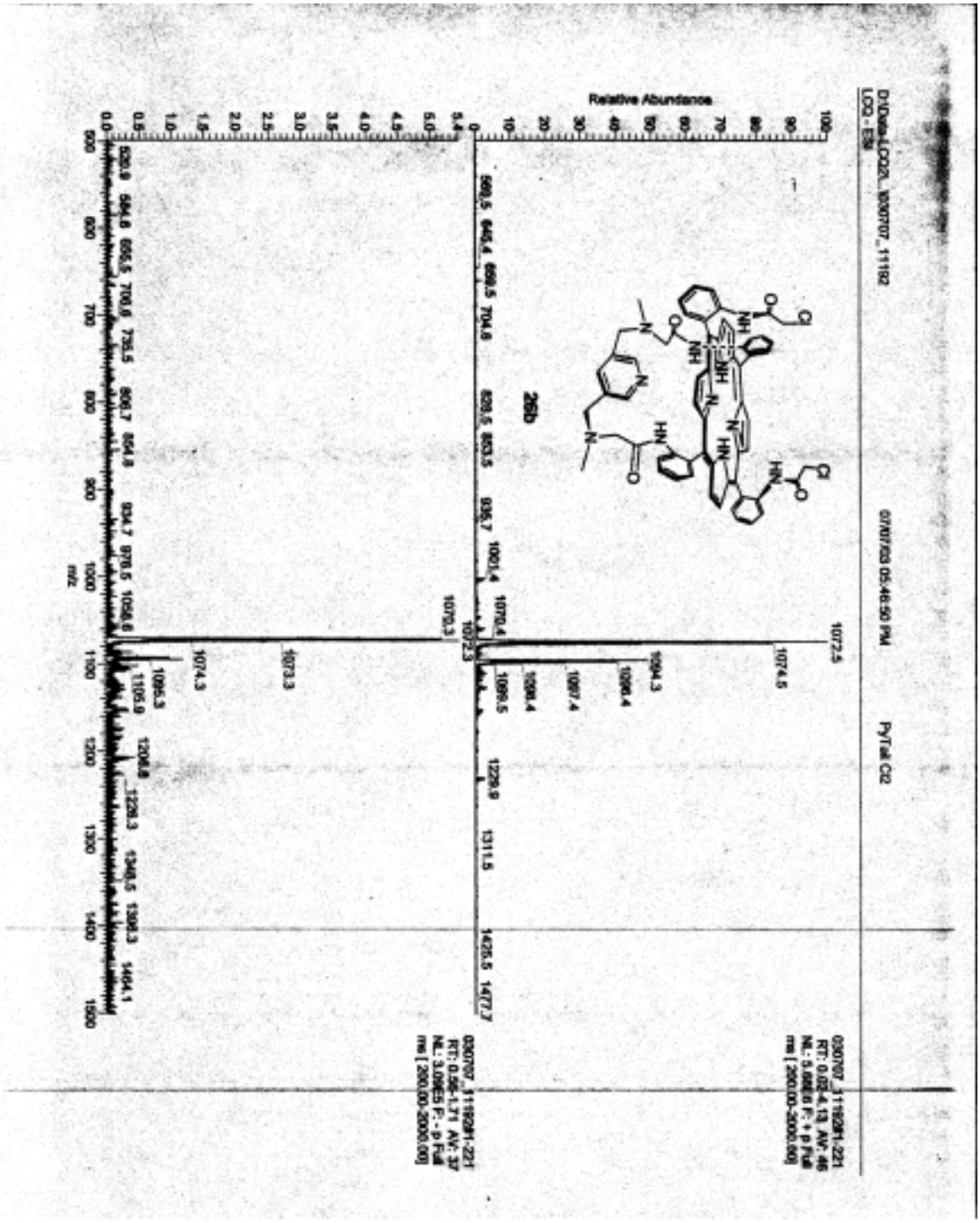
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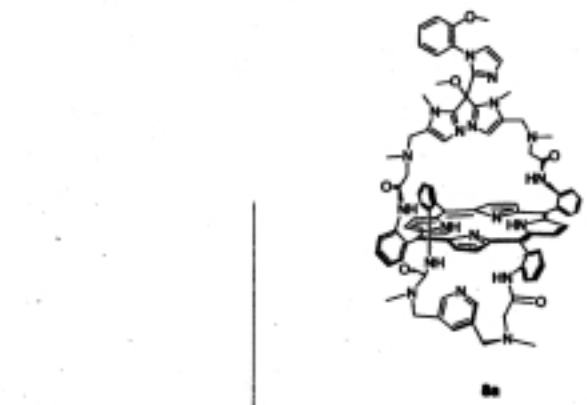

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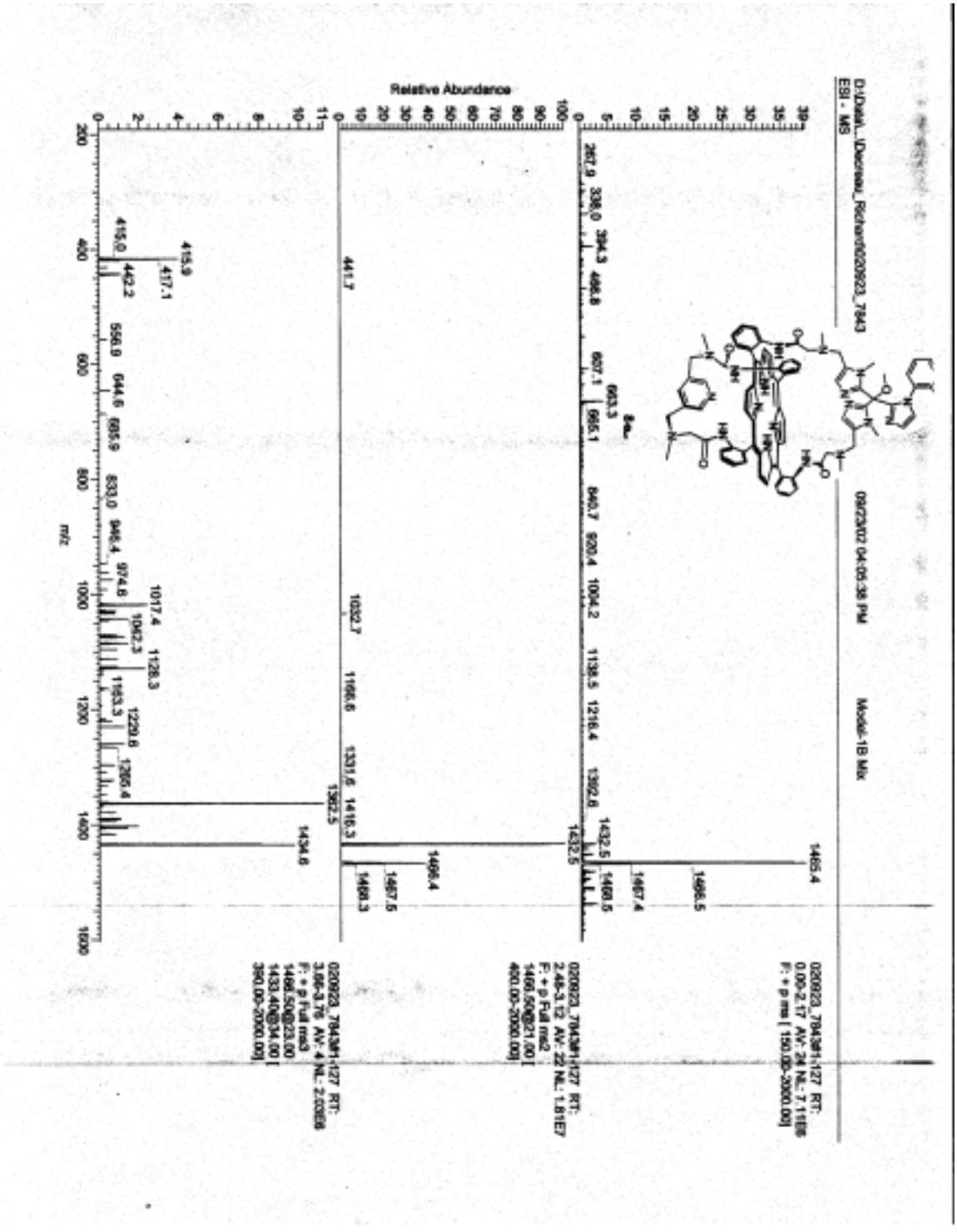
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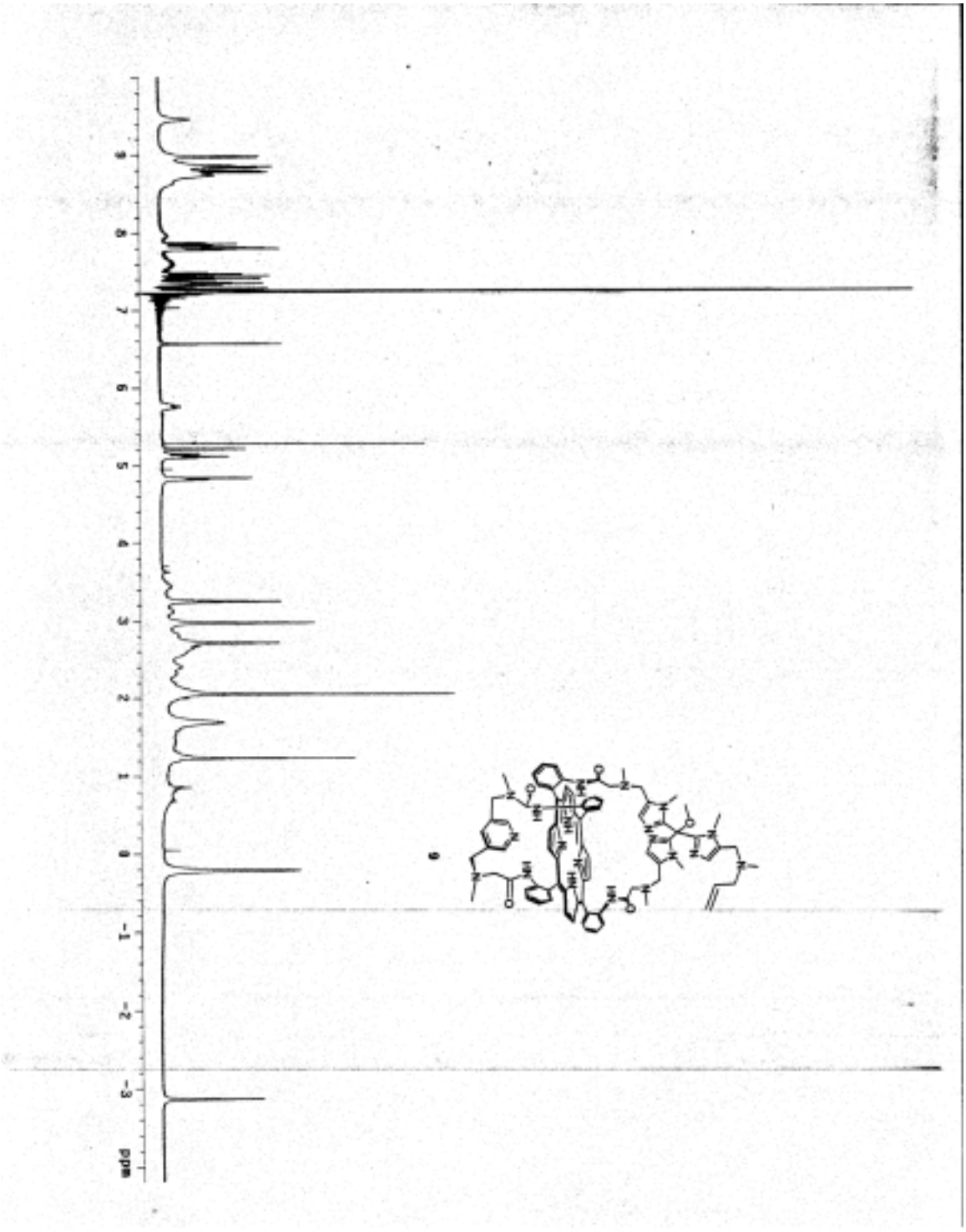
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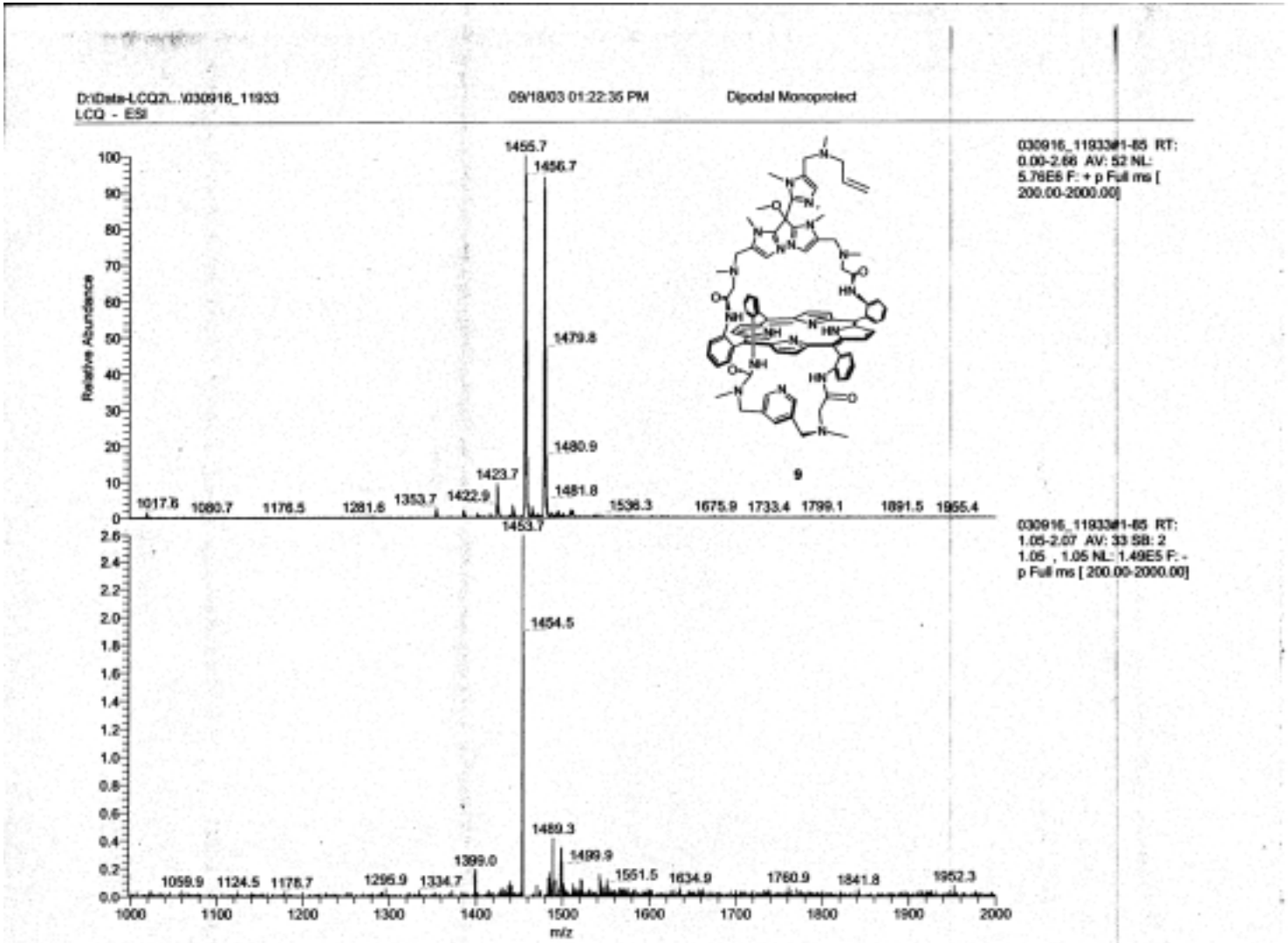
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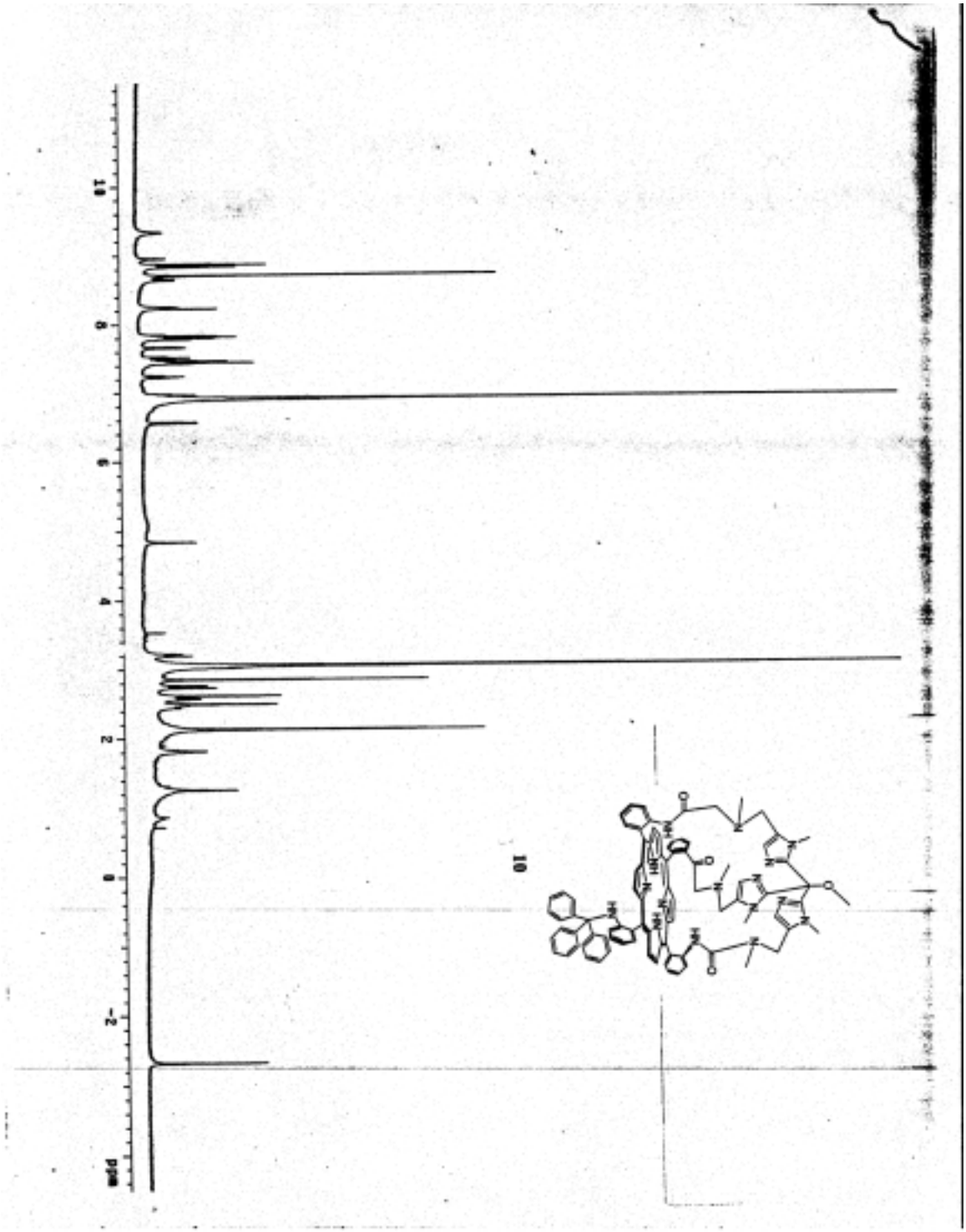
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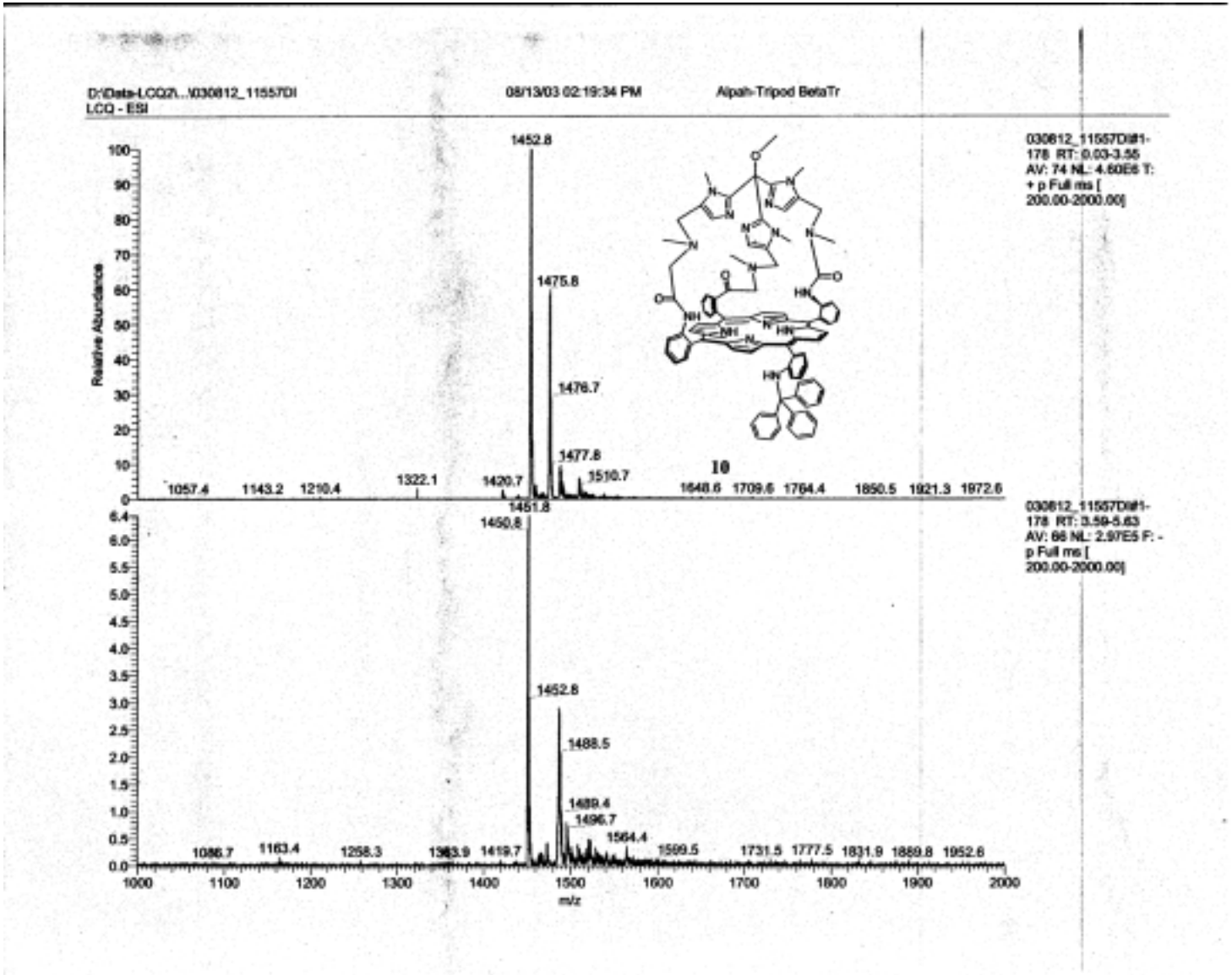
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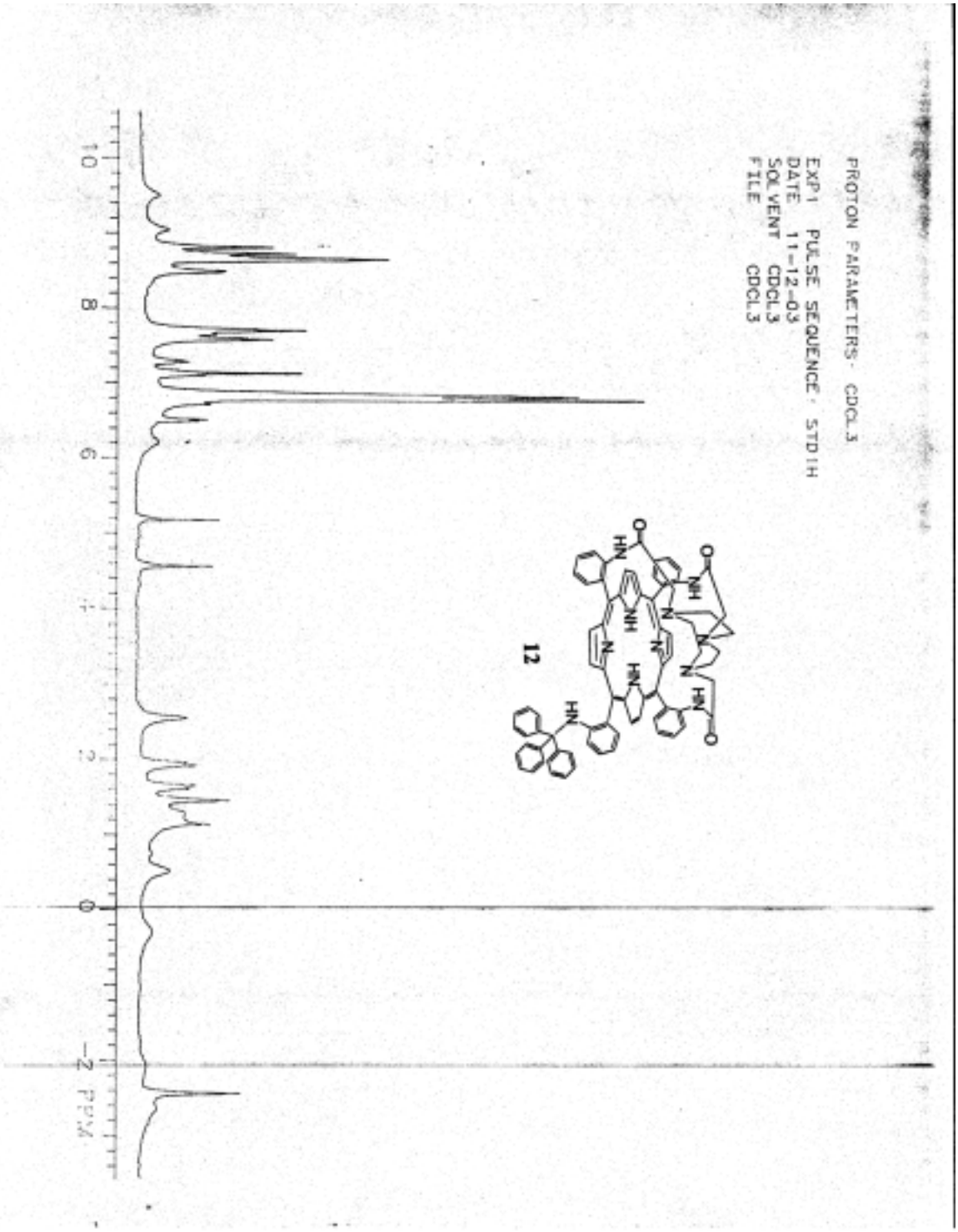
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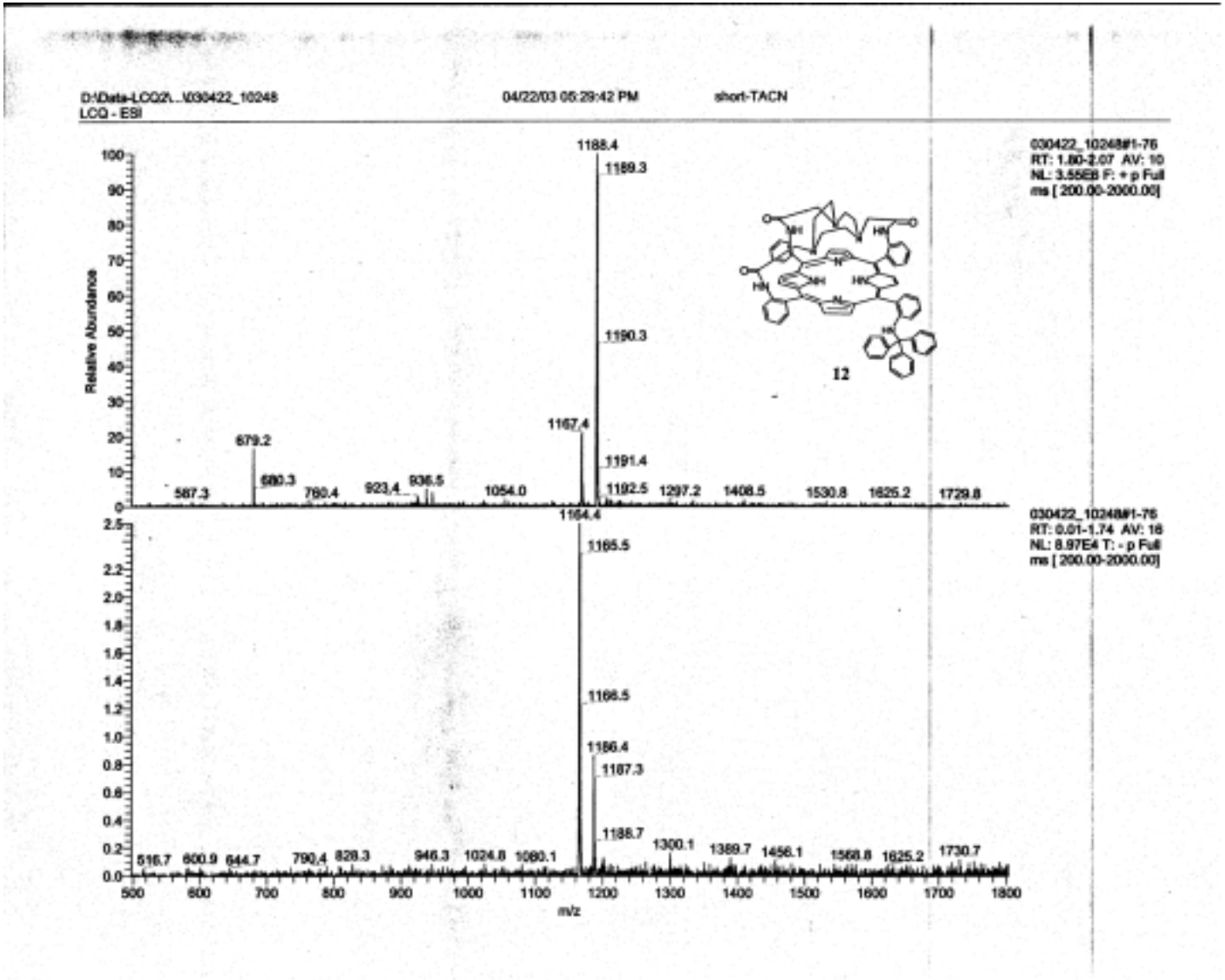
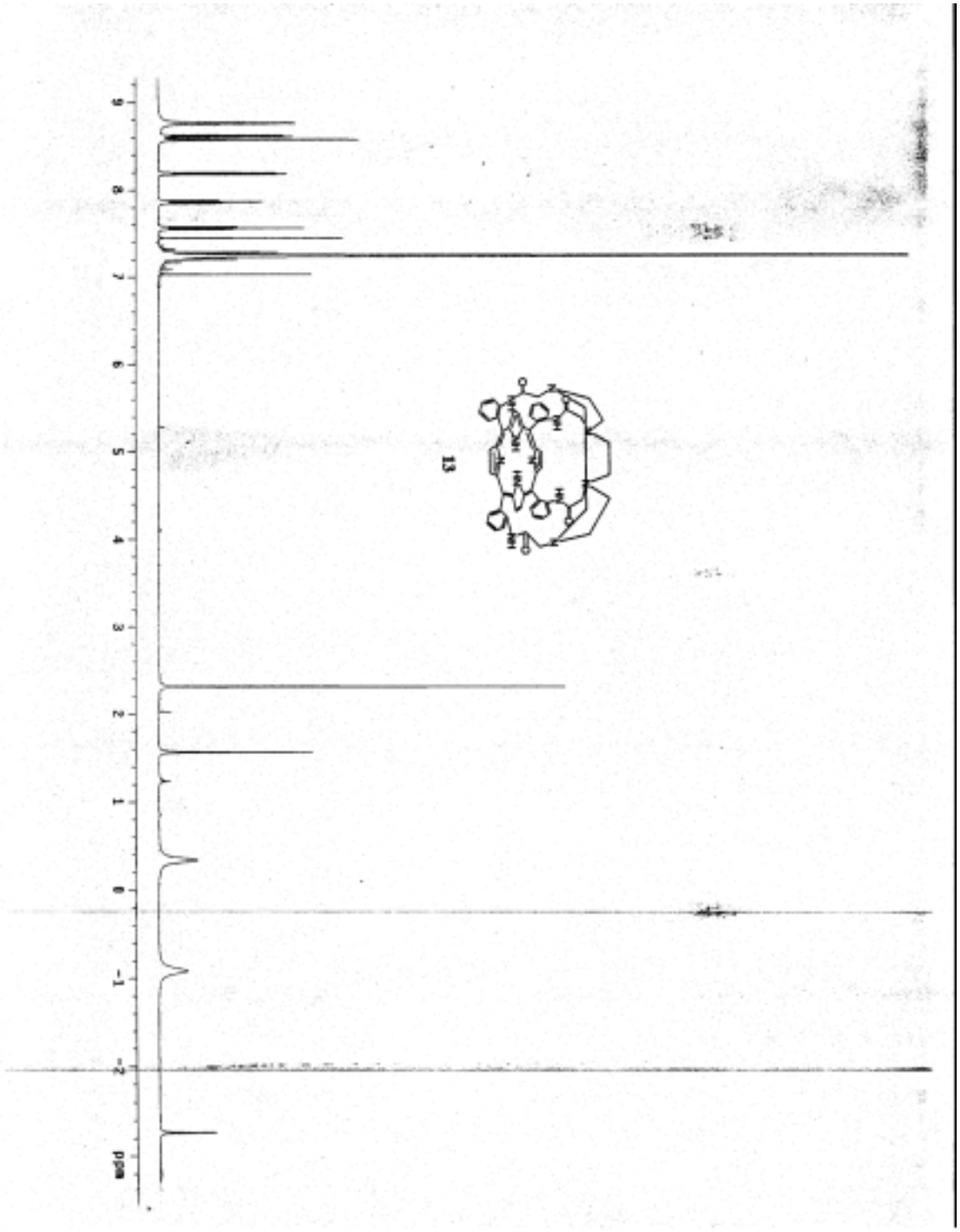
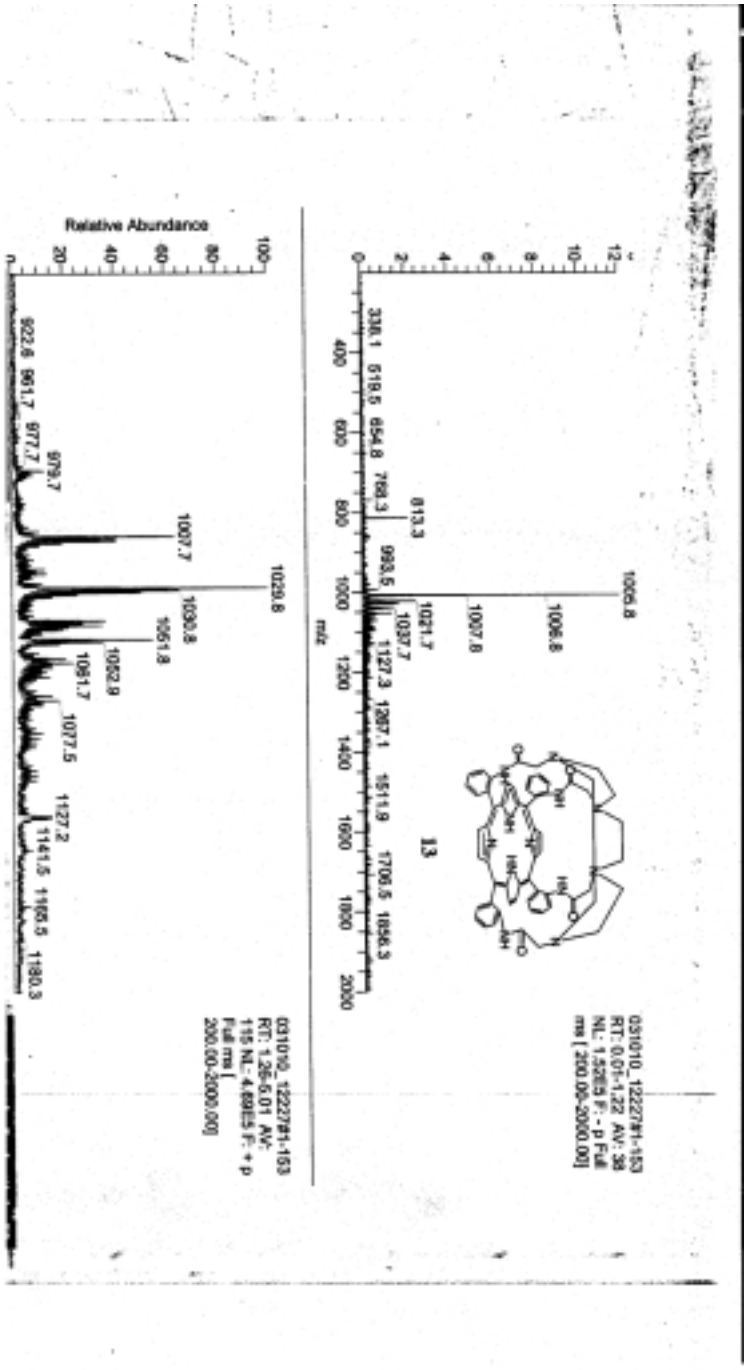
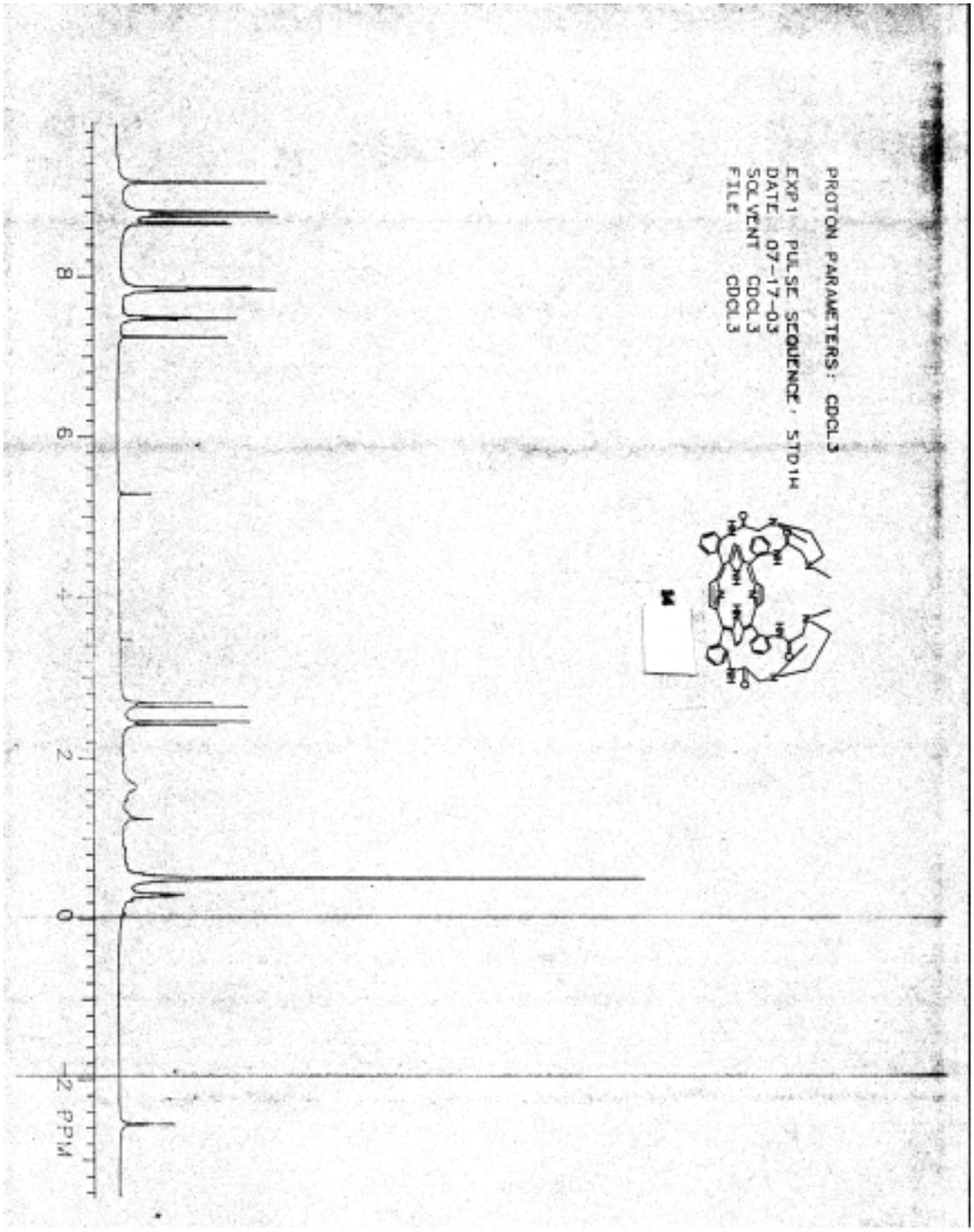
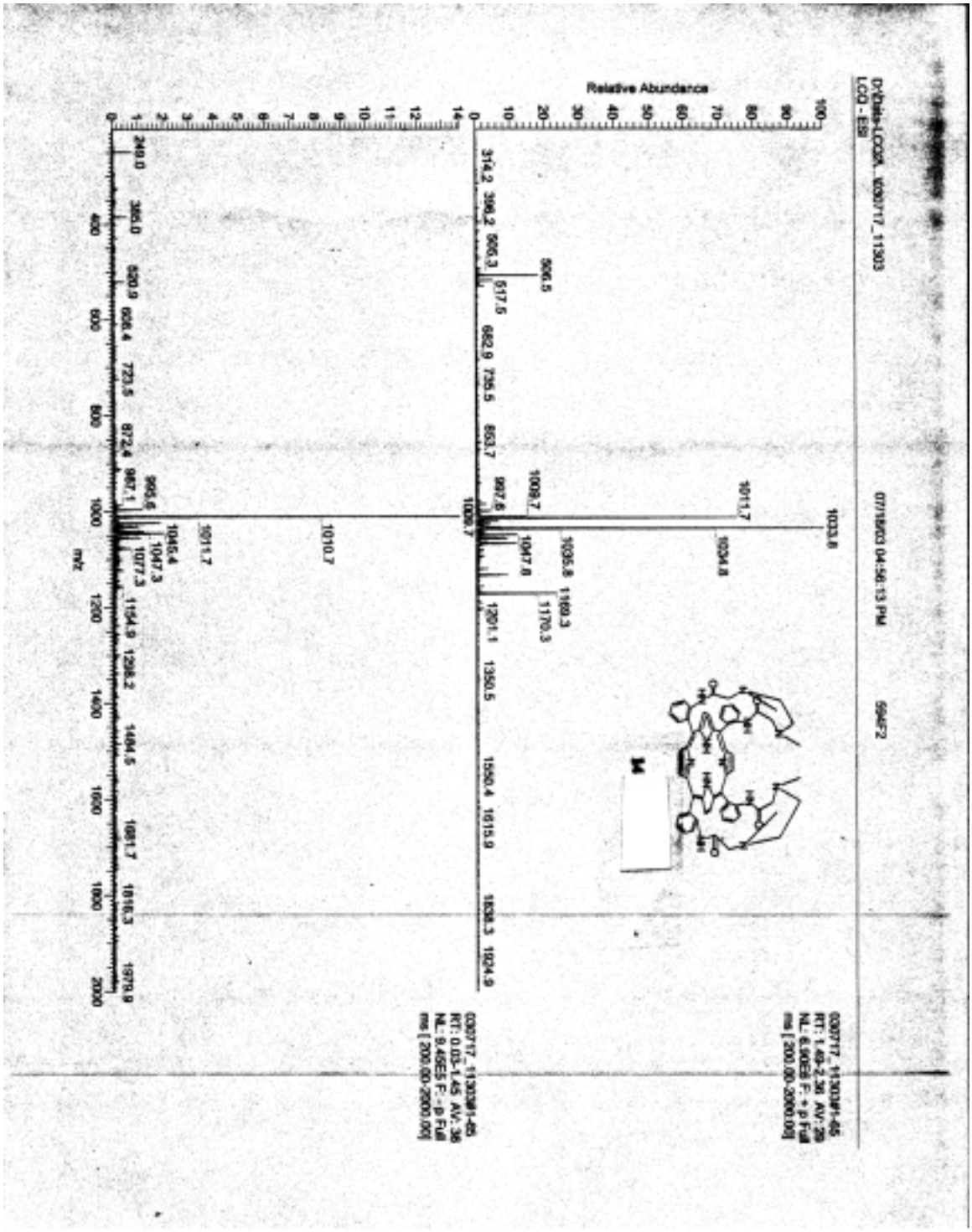
PPM

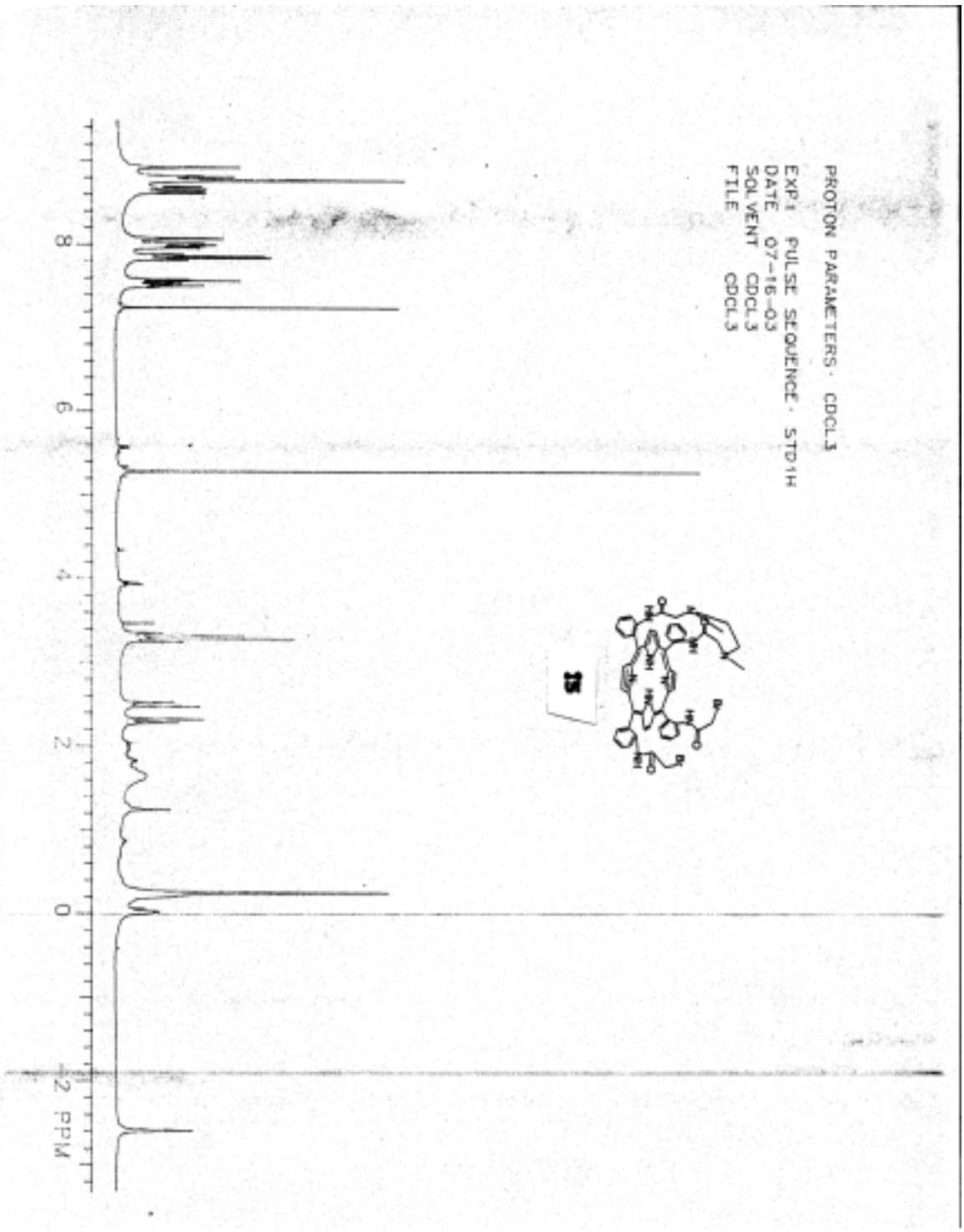

D:\Data-LCQ2\...\030422_10248
LCQ - ESI
04/22/03 05:29:42 PM
short-TACN
030422_10248#1-76
RT: 1.80-2.07 AV: 10
NL: 3.55E8 F: + p Full
ms [200.00-2000.00]
Relative Abundance
1188.4
1189.3
1190.3
1167.4
679.2
680.3
1191.4
1192.5
587.3
760.4
923.4
936.5
1054.0
1297.2
1408.5
1530.8
1625.2
1729.8
12
030422_10248#1-76
RT: 0.01-1.74 AV: 16
NL: 8.97E4 T: - p Full
ms [200.00-2000.00]
1164.4
1165.5
1166.5
1186.4
1187.3
1188.7
516.7
600.9
644.7
790.4
828.3
946.3
1024.8
1080.1
1300.1
1389.7
1456.1
1568.8
1625.2
1730.7
m/z

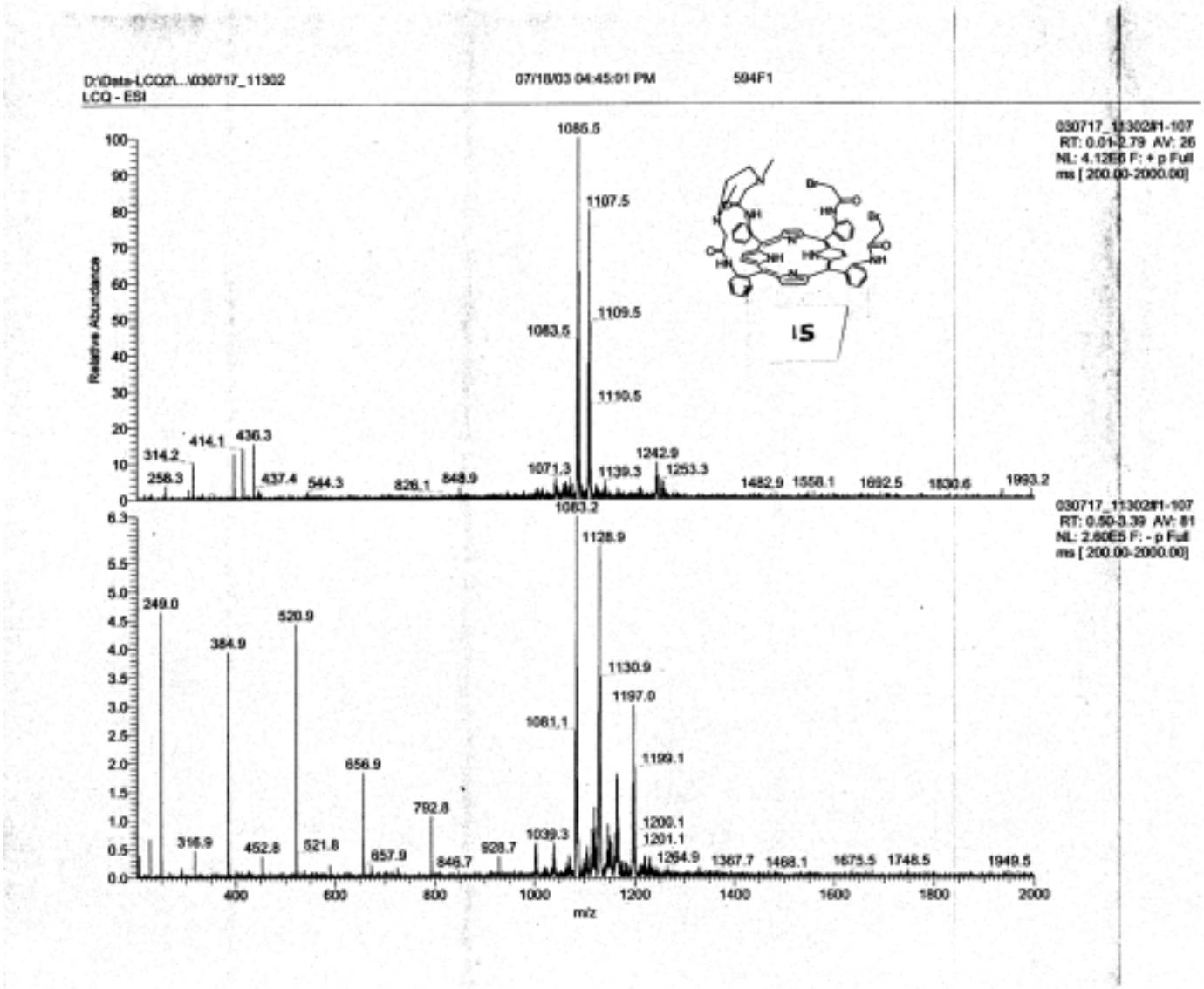

13
ppm

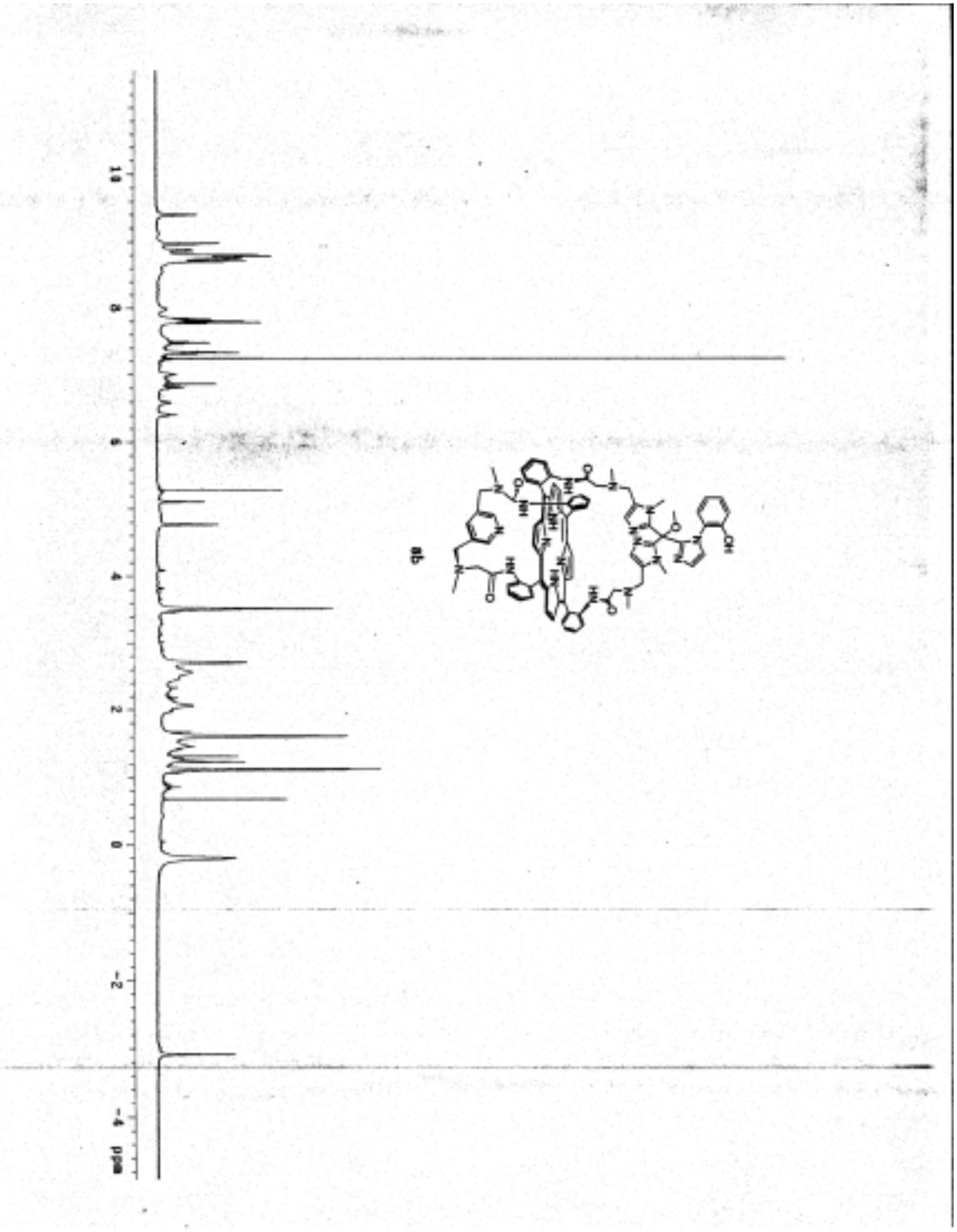

031010_122278#1-153
RT: 0.01-1.22 AV: 38
NL: 1.52E5 F: - p Full
ms [200.00-2000.00]
1005.8
1006.8
1007.8
1021.7
1037.7
1127.3
1287.1
1511.9
1706.5
1856.3
813.3
993.5
338.1
619.5
654.8
769.3
m/z
13
031010_122278#1-153
RT: 1.26-5.01 AV:
115 NL: 4.69E5 F: + p
Full ms [
200.00-2000.00]
1029.6
1007.7
1030.8
1051.8
1052.9
1051.7
1077.5
1127.2
1141.5
1165.5
1180.3
922.6
961.7
977.7
979.7
Relative Abundance

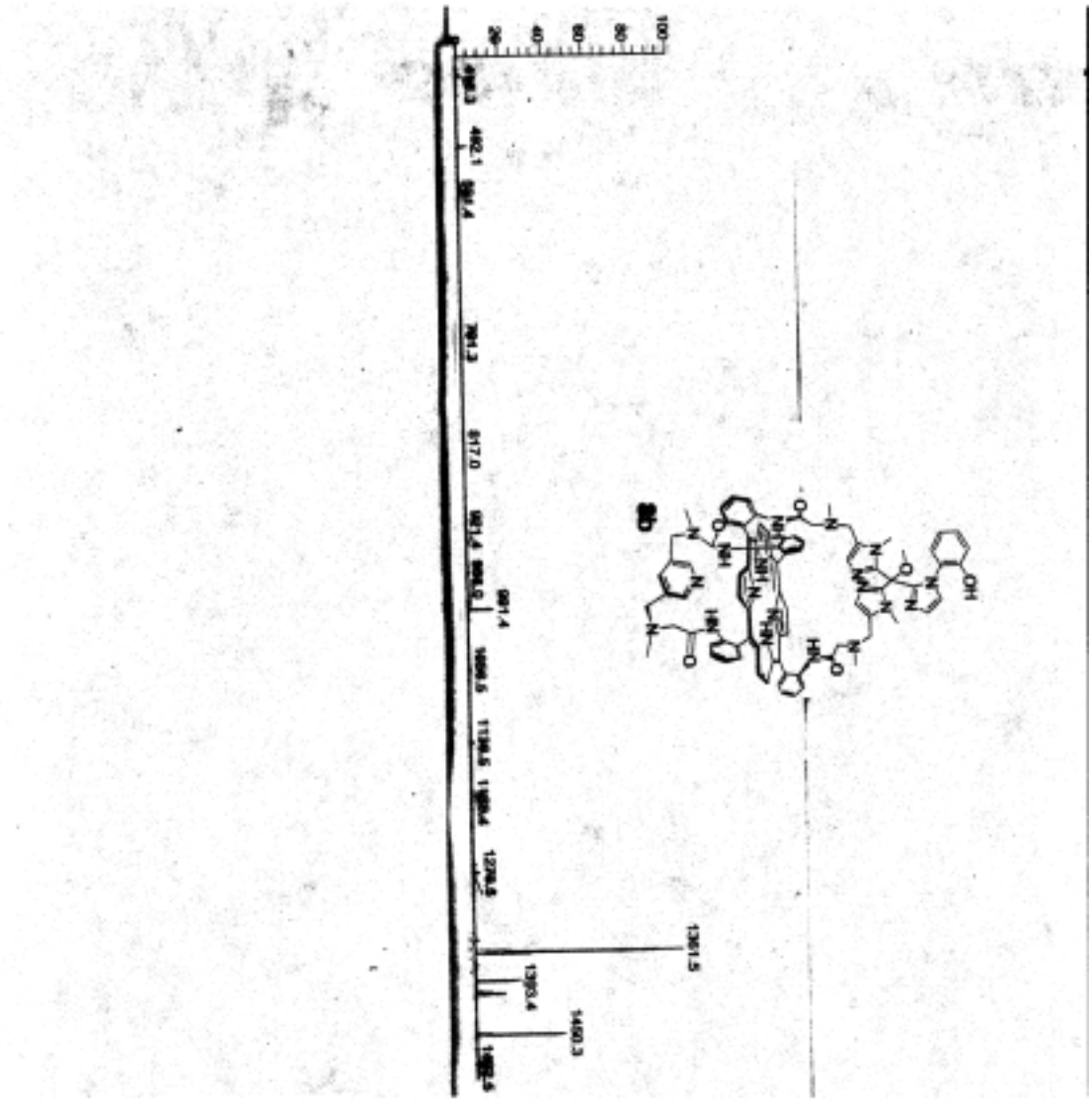

PROTON PARAMETERS: CDCL3
EXP1 PULSE SEQUENCE: STD1H
DATE 07-17-03
SOLVENT CDCL3
FILE CDCL3
8
6
4
2
0
-2 PPM

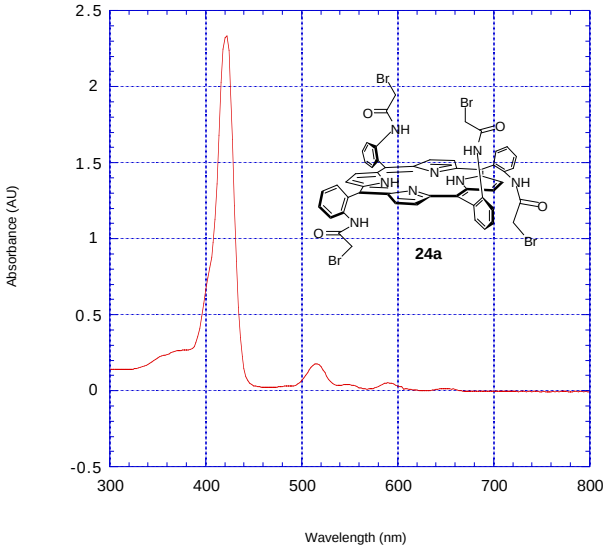

D:\Data-LCQ\X_030717_11303
LCQ - ESI
07/18/03 04:56:13 PM
594F2
Relative Abundance
m/z
1033.8
1011.7
1034.8
1009.7
1035.8
1169.3
1047.8
1170.3
1010.7
1011.7
030717_11303#1-45
RT: 1.49-2.36 AV: 29
NL: 6.90E6 F: + p Full
ms [200.00-2000.00]
030717_11303#1-45
RT: 0.03-1.45 AV: 36
NL: 9.45E5 F: - p Full
ms [200.00-2000.00]

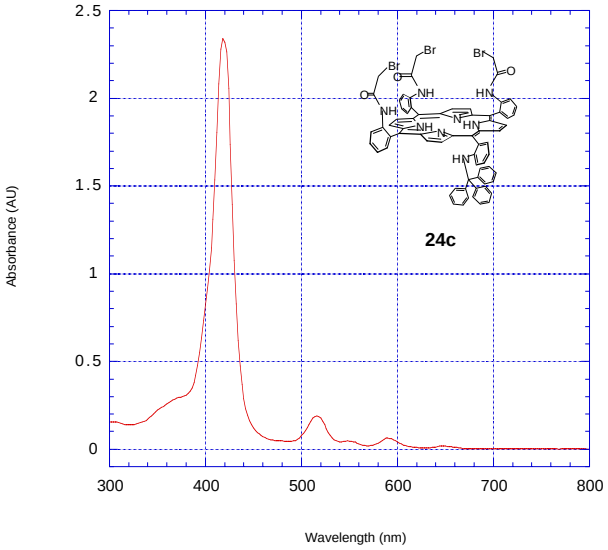

PROTON PARAMETERS- CDCL3
EXP:1 PULSE SEQUENCE- STD1H
DATE 07-16-03
SOLVENT CDCL3
FILE CDCL3
8
6
4
2
0
-2 PPM

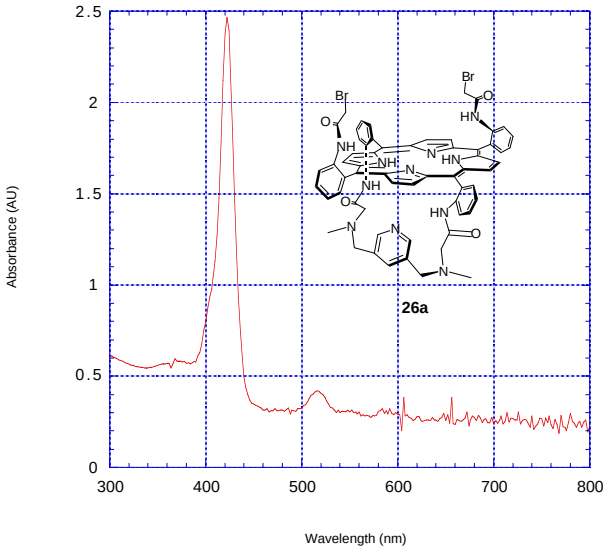

D:\Data-LCQ2\...\030717_11302
07/18/03 04:45:01 PM
594F1
LCQ - ESI
030717_11302#1-107
RT: 0.01-2.79 AV: 26
NL: 4.12E6 F: + p Full
ms [200.00-2000.00]
Relative Abundance
1086.5
1107.5
1109.5
1083.5
1110.5
414.1
436.3
314.2
258.3
437.4
544.3
826.1
848.9
1071.3
1139.3
1242.9
1253.3
1482.9
1556.1
1692.5
1830.6
1993.2
030717_11302#1-107
RT: 0.50-3.39 AV: 81
NL: 2.60E5 F: - p Full
ms [200.00-2000.00]
1083.2
1128.9
249.0
520.9
384.9
1130.9
1197.0
1081.1
1199.1
656.9
792.8
1200.1
1201.1
316.9
452.8
521.8
657.9
846.7
928.7
1039.3
1264.9
1367.7
1468.1
1675.5
1748.5
1949.5
m/z

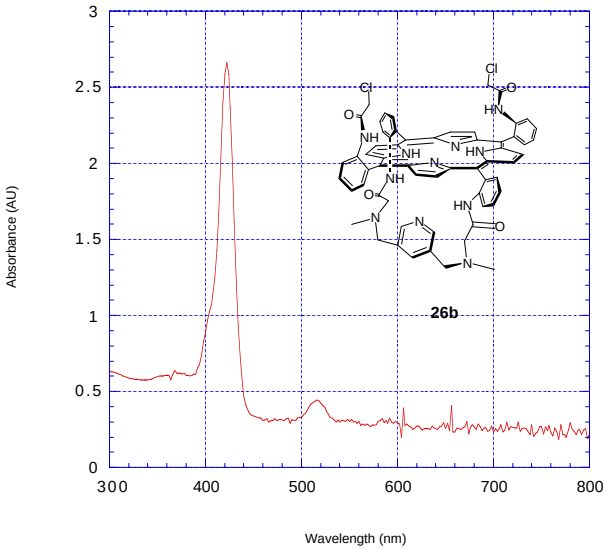

ppm
10
8
6
4
2
0
-2
-4

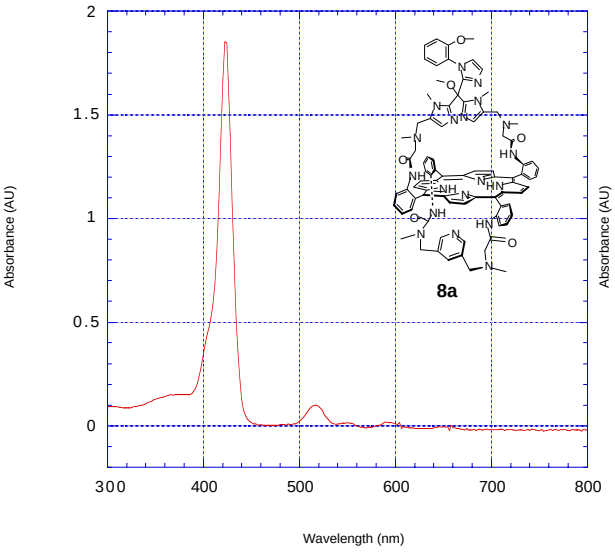


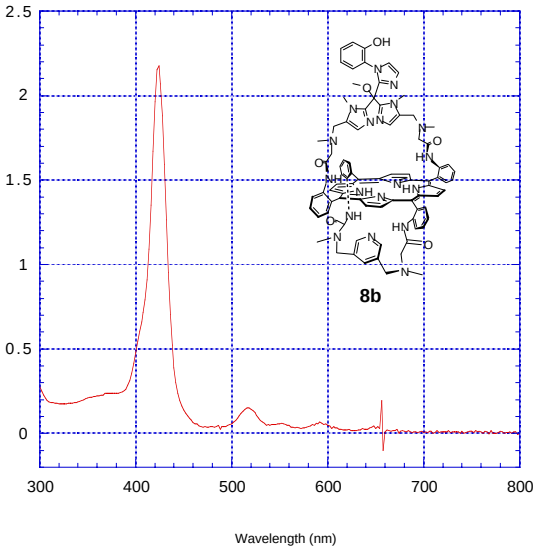

Absorbance (AU)
Wavelength (nm)
24a

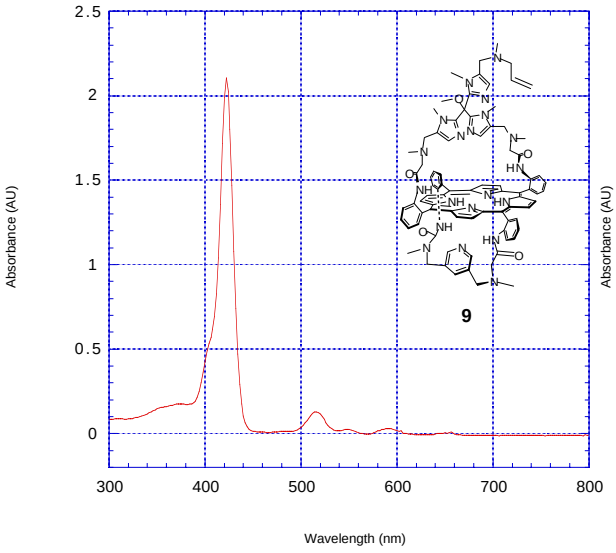

Absorbance (AU)
Wavelength (nm)
24c

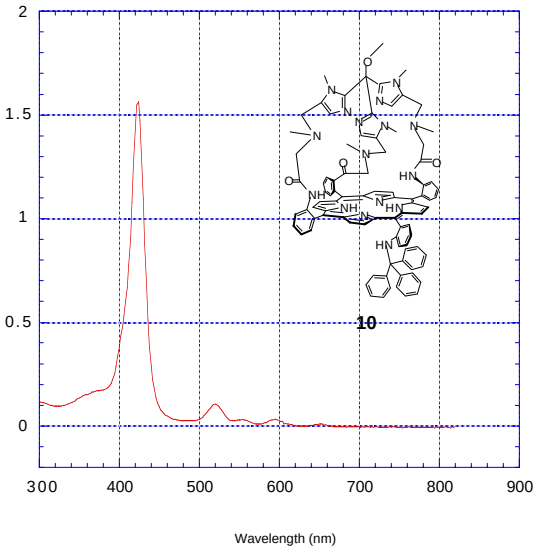

Absorbance (AU)
Wavelength (nm)
26a

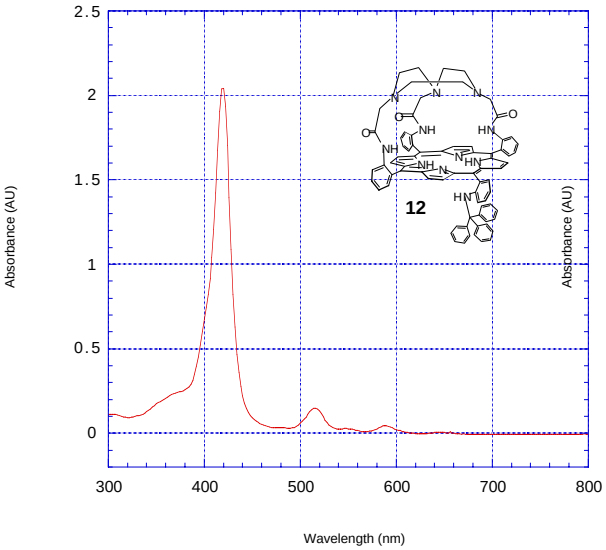

Absorbance (AU)
Wavelength (nm)
26b

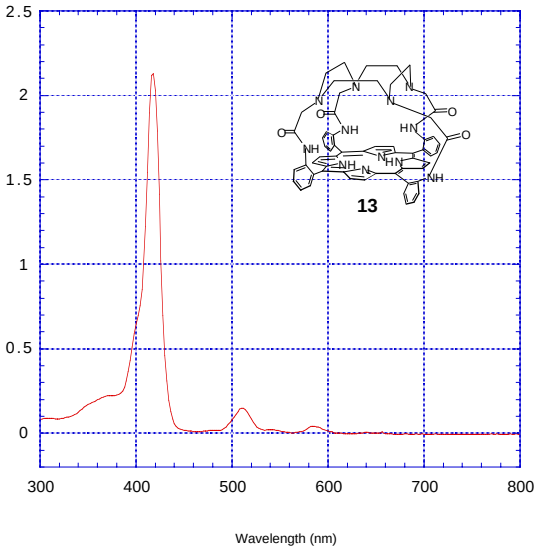

Absorbance (AU)
Wavelength (nm)
8a

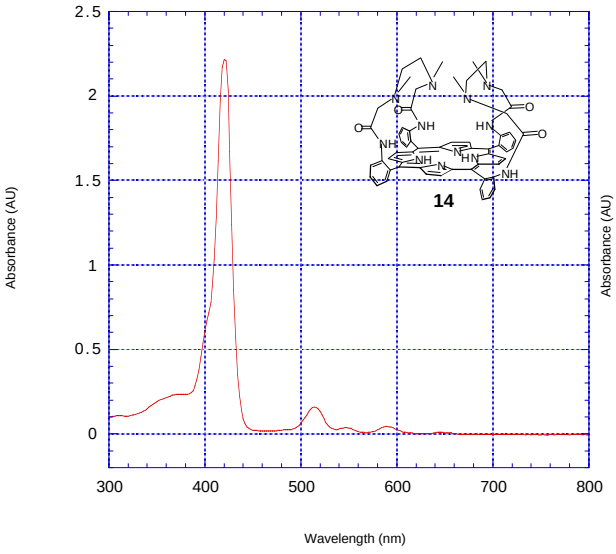

Absorbance (AU)
Wavelength (nm)
8b

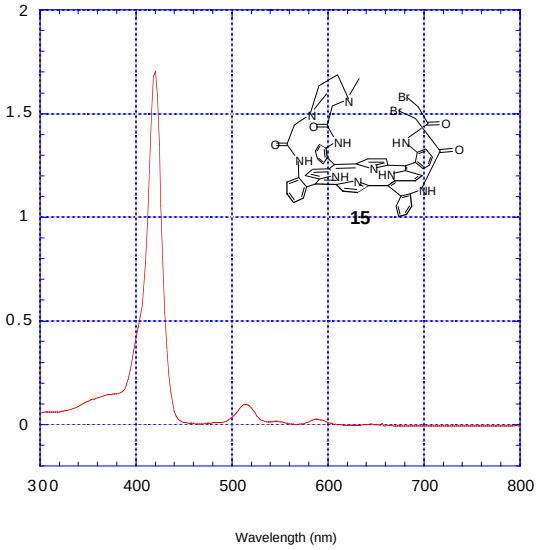

Absorbance (AU)
Wavelength (nm)
9


Absorbance (AU)
Wavelength (nm)
10


Absorbance (AU)
Wavelength (nm)
12


Absorbance (AU)
Wavelength (nm)
13


Absorbance (AU)
Wavelength (nm)
14


Absorbance (AU)
Wavelength (nm)
15