SUPPLEMENTARY MATERIAL

Porphyrin 3

Di-ter-butyl-3,5-benzaldehyde 2 (8.05 g, 36.9 mmol), dipyrrylmethane 1 (900 mg, 6.15 mmol) and sodium chloride (220 mg, 3.7 mmol) were added in 380 ml of distilled dichloromethane in a round bottom flask. The solution was sonicated under a nitrogen stream for 20 min. Then pyrrole (2.14 ml, 31 mmol) and BF_3,OEt_2 (390 µl, 3.1 µmol) were injected and the mixture was stirred at room temperature for 10 minutes. A solution of DDQ (13 g in 100 ml of toluene) was added and the reaction mixture was refluxed for 30 min with an oil bath preheated at 60°C. Separation of the three different porphyrins was accomplished by flash chromatography eluted with hexane/CH_2Cl_2 : 80/20 and yielded to 582 mg of the desired porphyrin 3 (12%). TLC analysis on silica with hexane/AcOEt : 9.5/0.5, Rf=0.52.

^1H NMR ($CDCl_3$) 10,27 (1H, s), 9.34 (2H, d, J=4.8 Hz), 9.05 (2H, d, J=4.8 Hz), 8.93 (4H, AB system), 8.12 (4H, d, J=1.8 Hz), 8.07 (2H, d, J=1.8 Hz), 7.81 (2H, t, J=1.8 Hz), 7.79 (1H, t, J=1.8 Hz), 1.6 (36H, s), 1.55 (18H, s), -2.42 (2H, s).

FAB-MS : calculated for $C_{62}H_{74}N_4$: 874.6 found : 875.6 ($M+H^+$).

Iodo-porphyrins 5 and 6

A round bottom flask of 50 ml was charged with porphyrin 3 (65 mg, 7.43 10^{-2} mmol), iodine (17 mg, 6.69 10^{-2} mmol), $PhI(CF_3CO_2)_2$ (35 mg, 8.02 10^{-2} mmol) and with 10 ml of chloroform. The mixture was stirred at room temperature in the dark for 30 min. The crude was washed with an aqueous solution sodium carbonate solution and with a sodium thiosulfate solution. The organic phase was dried over $MgSO_4$ and the crude was purified by flash column chromatography on silica gel using hexane/CH_2Cl_2 : 80/20 as eluent. 65 mg (87% yield) of porphyrin 5 were obtained as a dark purple solid.

Zinc insertion in iodo porphyrin 5 was carried out as usual with $Zn(OAc)_2$, $2H_2O$ in a mixture CH_3OH/CH_2Cl_2 : 5/5. The zinc iodoporphyrin 6 was obtained in 98 % yield.

^1H NMR ($CDCl_3$) 9.81 (2H, d, J=4.8 Hz), 9.04 (2H, d, J=4.8 Hz), 9.00 (4H, AB system), 8.10 (4H, d, J=1.8 Hz), 8.08 (2H, d, J=1.8 Hz), 7.85 (2H, t, J=1.8 Hz), 7.81 (1H, t, J=1.8 Hz), 1.6 (36H, s), 1.55 (18 H, s). FAB-MS : calculated for $C_{62}H_{71}N_4ZnI$: 1062.4 found : 1062.4 ($M^{\cdot +}$)

Stille cross-coupling : porphyrin 8.

In a Schlenk tube, zinc iodo-porphyrin 6 (200 mg, 0.19 mmol), dienyltin 7 (90 mg, 0.22 mmol) and $Pd(PPh_3)_4$ (11 mg, 0.9 10^{-2} mmol) were heated under argon in dry and degased DMF (5 ml) at 80°C for 6 hours. The crude reaction mixture was then quenched with water, extracted with dichloromethane and dried over $MgSO_4$. After evaporation of the solvents, purification by flash column chromatography over silica gel using hexane/CH_2Cl_2/Et_3N : 83/15/2 as eluent gave the pure coupled product 8 in 86% yield.

^1H NMR ($CDCl_3$) 9.53 (2H, d, J=4.8 Hz), 9.20 (1H, d, J=15.1 Hz), 9.05 (2H, d, J=4.8 Hz), 8.97 (4H, AB system), 8.10 (4H, d, J=1.8 Hz), 8.06 (2H, d, J=1.8 Hz), 7.81 (2H, t, J=1.8 Hz), 7.78 (1H, t, J=1.8 Hz), 6.95 (1H, dd, J=15.1, Hz J=11.0 Hz), 6.69 (1H, dd, J=15.0 Hz J=11.0 Hz), 5.23 (1H, dd, J=15.0 Hz, J=6 Hz), 4.42 (1H, d , J=6 Hz), 3.38 (2H, m), 3.09 (2H, m), 1.6 (36H, s), 1.55 (18H, s). FAB-MS : calculated for $C_{69}H_{80}N_4ZnO_2$: 1060.5 : found : 1060.5 ($M^{\cdot+}$)

Deprotection of the acetal group and demetallation of the zinc porphyrin

Zinc demetallation without hydrolysis of the acetal group : compound **9**.

In a round bottom flask, 106 mg of zinc porphyrin **8** and 0.2 ml of trifluoroacetic acid were stirred under argon for one hour in 20 ml of dry CH_2Cl_2. The mixture was washed with a sodium carbonate solution, dried over $MgSO_4$ and purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2 : 5/5). 93 mg of porphyrin **9** were obtained (93% yield).

^1H NMR ($CDCl_3$), 9.43 (2H, d, J=4.8 Hz), 9.24 (1H, d, J=15.0 Hz), 8.98 (2H, d, J=4.8 Hz), 8.87 (4H, AB system), 8.10 (4H, d, J=1.8 Hz), 8.08 (2H, d, J=1.8 Hz), 7.83 (2H, t, J=1.8 Hz), 7.80 (1H, t, J=1.8 Hz), 7.27 (1H, dd, J=15 Hz J=11 Hz), 7.16 (1H, dd, J=15 Hz J=11 Hz), 6.10 (1H, dd, J=15 Hz J=6 Hz), 5.62 (1H, d, J=6.0 Hz), 4.17 (2H, m), 4.07 (2H, m), 1.6 (36H, s), 1.55 (18 H, s), -2.47 (2H, s). ESI-MS : calculated for $C_{69}H_{82}N_4O_2$: 998.6 found : 999.6 ($M + H^+$).

Hydrolysis of the acetal group without demetallation of the zinc porphyrin : compound **10**.

In a round bottom flask, 100 mg of zinc porphyrin **8**, 0.5 g of silica gel and 0.2 ml of aqueous HCl solution (1M) were stirred under argon overnight at room temperature with 20 ml of CH_2Cl_2. The mixture was filtered over alumina and dried with $MgSO_4$. Compound **10** was obtained sufficiently pure to be used in the next step without further purification (92% yield).

^1H NMR ($CDCl_3$), 9.80 (1H, d, J=7.9 Hz), 9.72 (1H, d, J=15.2 Hz), 9.55 (2H, d, J=4.8 Hz), 9.09 (2H, d, J=4.8 Hz), 8.97 (4H, AB system), 8.08 (4H, d, J=1.8 Hz), 8.05 (2H, d, J=1.8 Hz), 7.96 (1H, dd, J=15.1 Hz J=11.1 Hz), 7.88 (2H, t, J=1.8 Hz), 7.86 (1H, t, J=1.8 Hz), 7.40 (1H, dd, J=15.2 Hz J=11.1 Hz), 6.48 (1H, dd, J=15.1 Hz J=7.9 Hz), 1.6 (36H, s), 1.55 (18 H, s). FAB-MS : calculated for $C_{67}H_{76}N_4ZnO$: 1016.5 found : 1016.5 ($M^{\cdot+}$)

Zinc dematallation with hydrolysis of the acetal group : compound **11**.

In a round bottom flask, 106 mg of zinc porphyrin **8** was dissolved in 20 ml of CH_2Cl_2, then 0.5 ml of acetic acid, 4 drops of conc. HCl and 0.1 ml of water were added and the mixture was stirred under argon for one hour. The mixture was washed with a sodium carbonate solution, dried over $MgSO_4$ and purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2 : 1/1). 90 mg of porphyrin **11** were obtained (94% yield).

^{1}H NMR (CD_2Cl_2), 9.90 (1H, d, J=7.9 Hz), 9.68 (1H, d, J=15.4 Hz), 9.50 (2H, d, J=4.8 Hz), 8.98 (2H, d, J=4.8 Hz), 8.85 (4H, AB system), 8.10 (4H, d, J=1.8 Hz), 8.06 (2H, d, J=1.8 Hz), 7.95 (1H, dd, J=15.3 Hz J=11.0 Hz), 7.83 (2H, t, J=1.8 Hz), 7.80 (1H, t, J=1.8 Hz), 7.45 (1H, dd, J=15.4 Hz J=11 Hz), 6.57 (1H, dd, J=15.3 Hz J=7.9 Hz), 1.6 (36H, s), 1.55 (18H, s), -2.4 (2H, s). ESI-MS : calculated for $C_{67}H_{78}N_4O$: 954.6 found : 955.6 (M + H^+).

Wittig-Horner reaction : compound **13**.

^{t}BuOK (25 mg, 0.22 mmol) was added to a solution of aldehyde **11** (90 mg, 94 μmol) and bipyridine bis phosphonate **12** (18 mg, 40.3 μmol) in 10 ml of dry THF. After 1 hour of stirring under argon at room temperature, the reaction mixture was quenched with a sodium carbonate solution, extracted with CH_2Cl_2 and dried over $MgSO_4$. The crude purified by flash column chromatography (eluted with CH_2Cl_2/CH_3OH: 98/2) afforded 70 mg of pure dyad **13** (72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) 9.59 (4H, d, J=4.7 Hz) ; 9.31 (2H, d, J= 14.2 Hz) ; 9.01 (4H, d, J=4.7 Hz) ; 8.92 (8H, AB system) ; 8.85 (2H, s) ; 8.44 (2H, d, J=8.3 Hz) ; 8.11 (8H, d, J=1.8 Hz) ; 8.09 (4H, d, J=1.8 Hz) ; 8.05 (2H, d, J=8.3 Hz) ; 7.87 (4H, t, J=1.8 Hz) ; 7.85 (2H, t, J=1.8 Hz) ; 7.31 (2H, dd, J = 15.4 Hz, J = 11 Hz) ; 7.21 (2H, dd, J = 14.2 Hz, J = 10.7 Hz) ; 7.16 (2H, broad triplet, J ≈ 11 Hz) ; 6.73 (2H, d, J = 15.4 Hz) ; 6.68 (2H, broad triplet, J ≈ 11 Hz) 1.6 (72H, s, ^{t}Bu) ; 1.55 (36H, s, ^{t}Bu), -2.42 (4H, s). ESI-MS : calculated for $C_{146}H_{164}N_{10}$: 2057.3 found : 2058.3 (M + H^+).

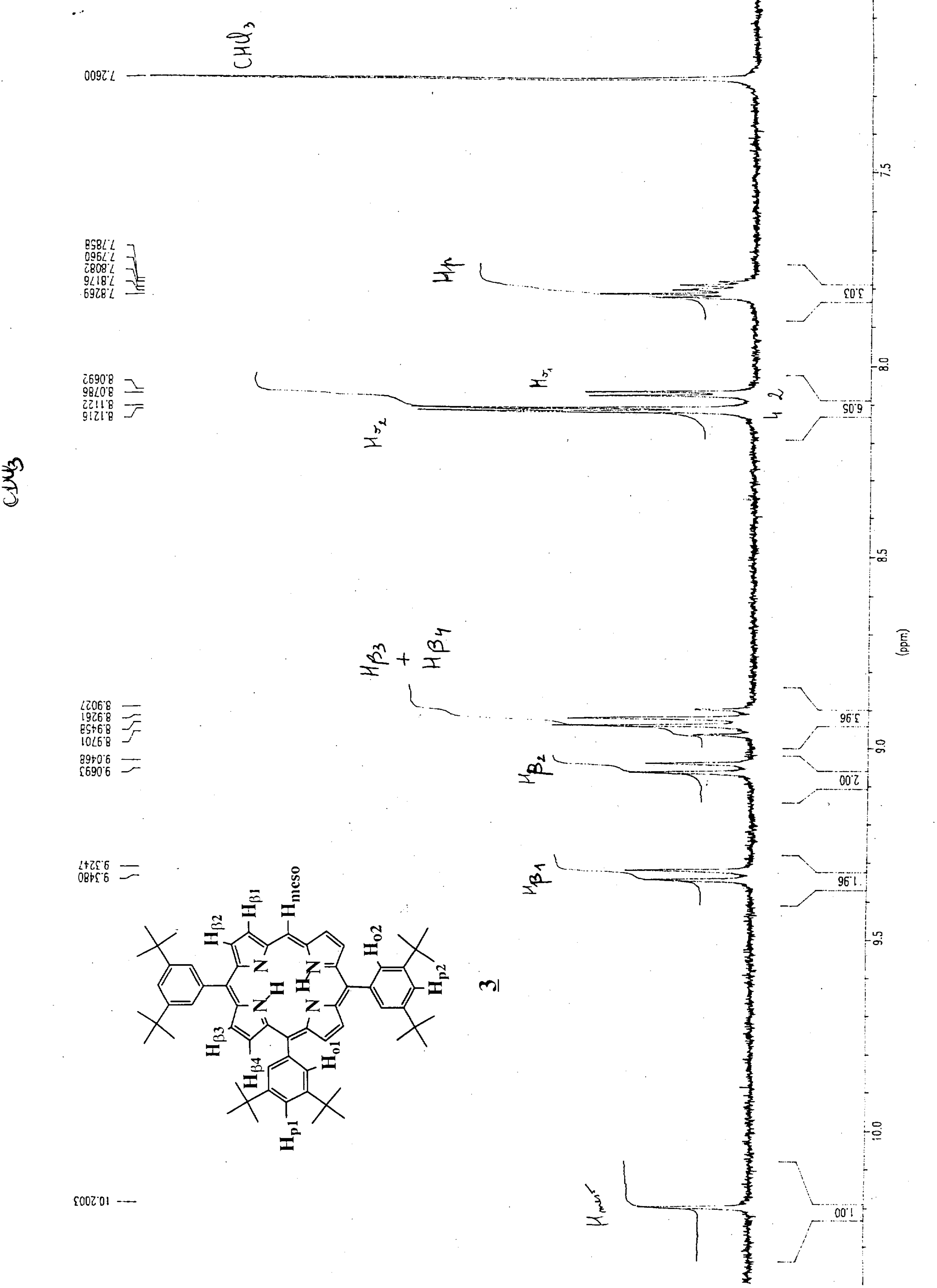
UV-Vis (CH_2Cl_2) λ max (nm): 424, 586, 673.

Compound **14**.

Dyad **13** was metalated with zinc acetate in a mixture CH_3OH/CH_2Cl_2 : 1/1 in a quantitative yield as usual or by Wittig-Horner reaction between aldehyde **10** and bis phosphonate **12** according the above procedure (17 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) 9.51 (4H, d, J=4.7 Hz) ; 9.30 (2H, d, J= 14.1 Hz) ; 9.01 (4H, d, J=4.7 Hz) ; 8.90 (8H, AB system) ; 8.86 (2H, s) ; 8.44 (2H, d, J=8.3 Hz) ; 8.12 (8H, d, J=1.8 Hz) ; 8.09 (4H, d, J=1.8 Hz) ; 8.05 (2H, d, J=8.3 Hz) ; 7.87 (4H, t, J=1.8 Hz) ; 7.85 (2H, t, J=1.8 Hz) ; 7.3 (2H, dd, J=15.6 Hz, J = 11 Hz) ; 7.2 (4H, bqt, J ≈ 11 Hz) ; 6.7 (4H, m) 1.6 (72H, s, ^{t}Bu) ; 1.55 (36H, s, ^{t}Bu). FAB-MS using 15-crown-5 as matrix: calculated for $C_{146}H_{160}N_{10}Zn_2 + H^+$: 2186 ; found : 2187 indicative of the occurrence of an hydride transfer to a doubly charged cation as already observed in FAB ionization mode (*cf.* Cabildo P. ; Claramunt R. ; Sanz D. ; Elguero J. ; Enjalbal C. ; Aubagnac J. L. *Rapid. Commun. Mass. Spectr.* , 1996, 10, 1071-1075 and references therein).

UV-Vis (CH_2Cl_2) λ max (nm): 428, 561, 622 (cf. fig 1).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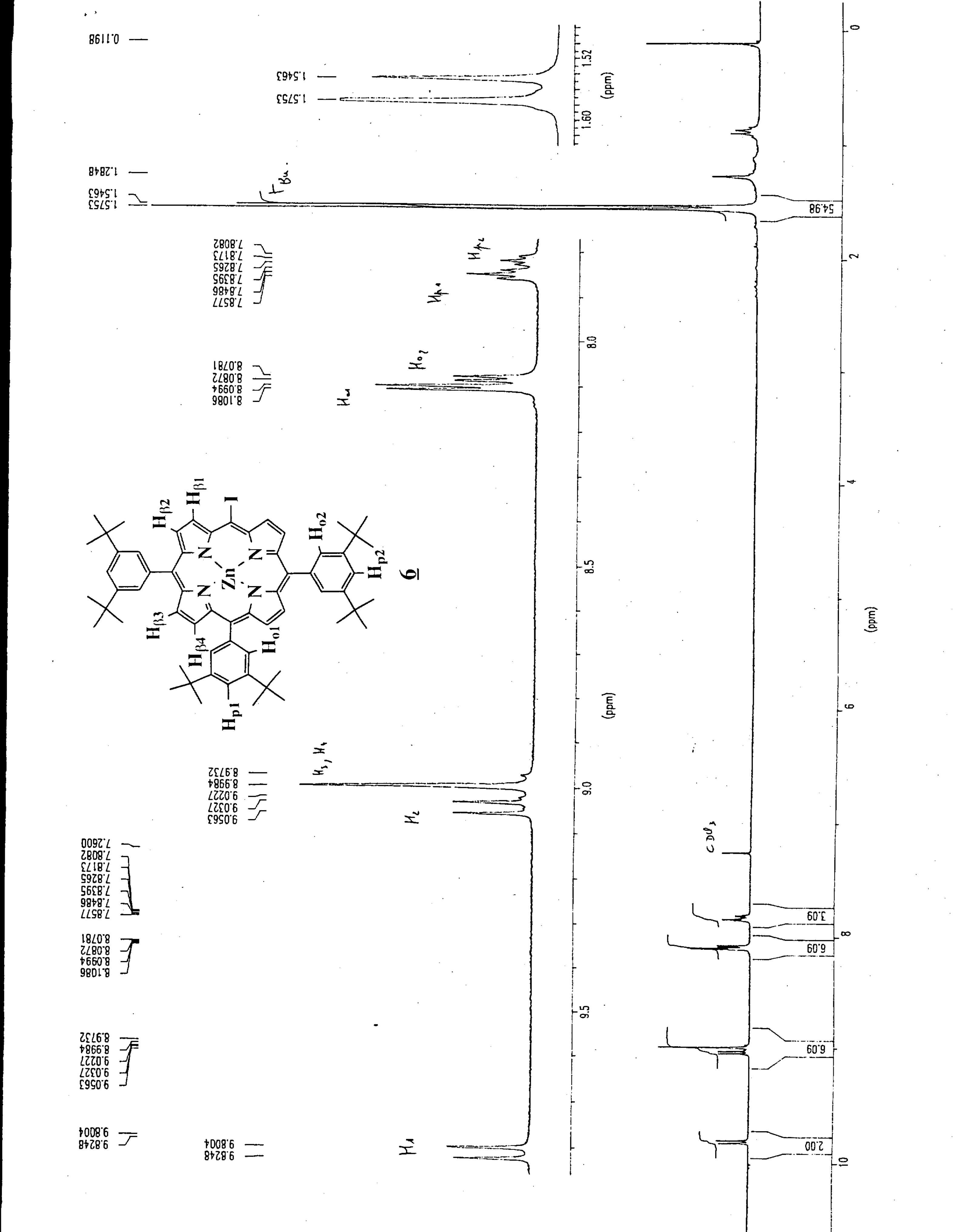
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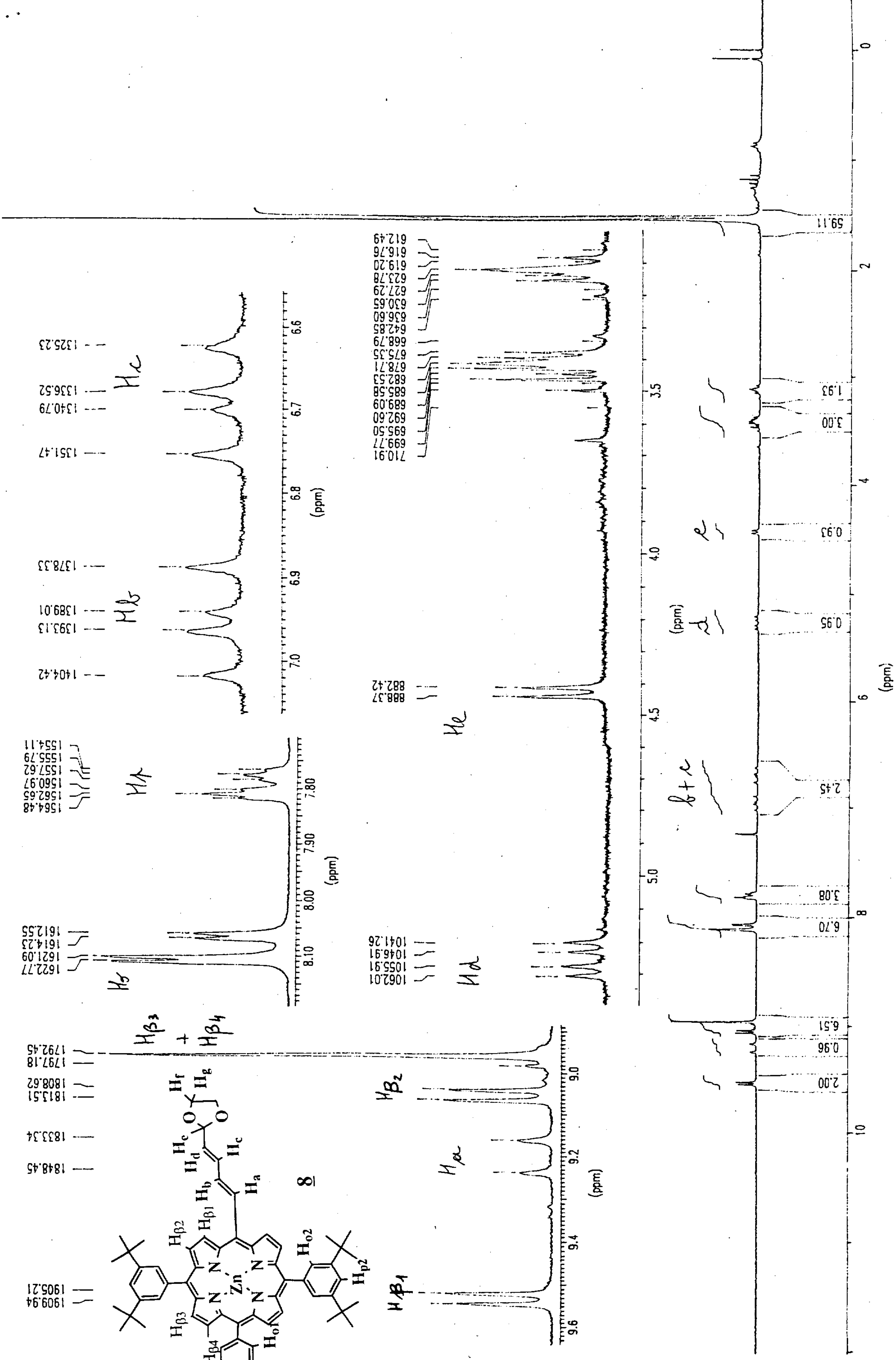
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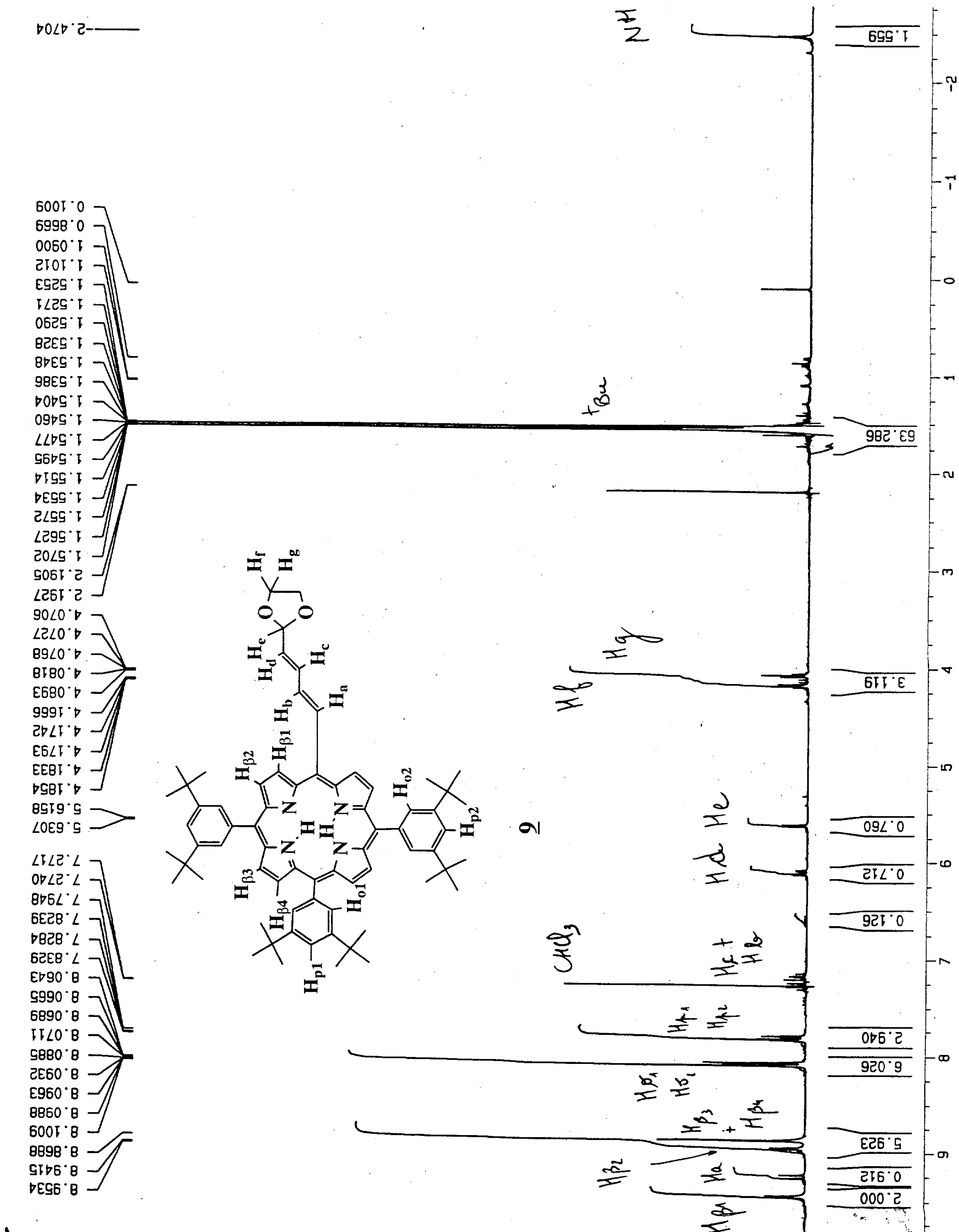
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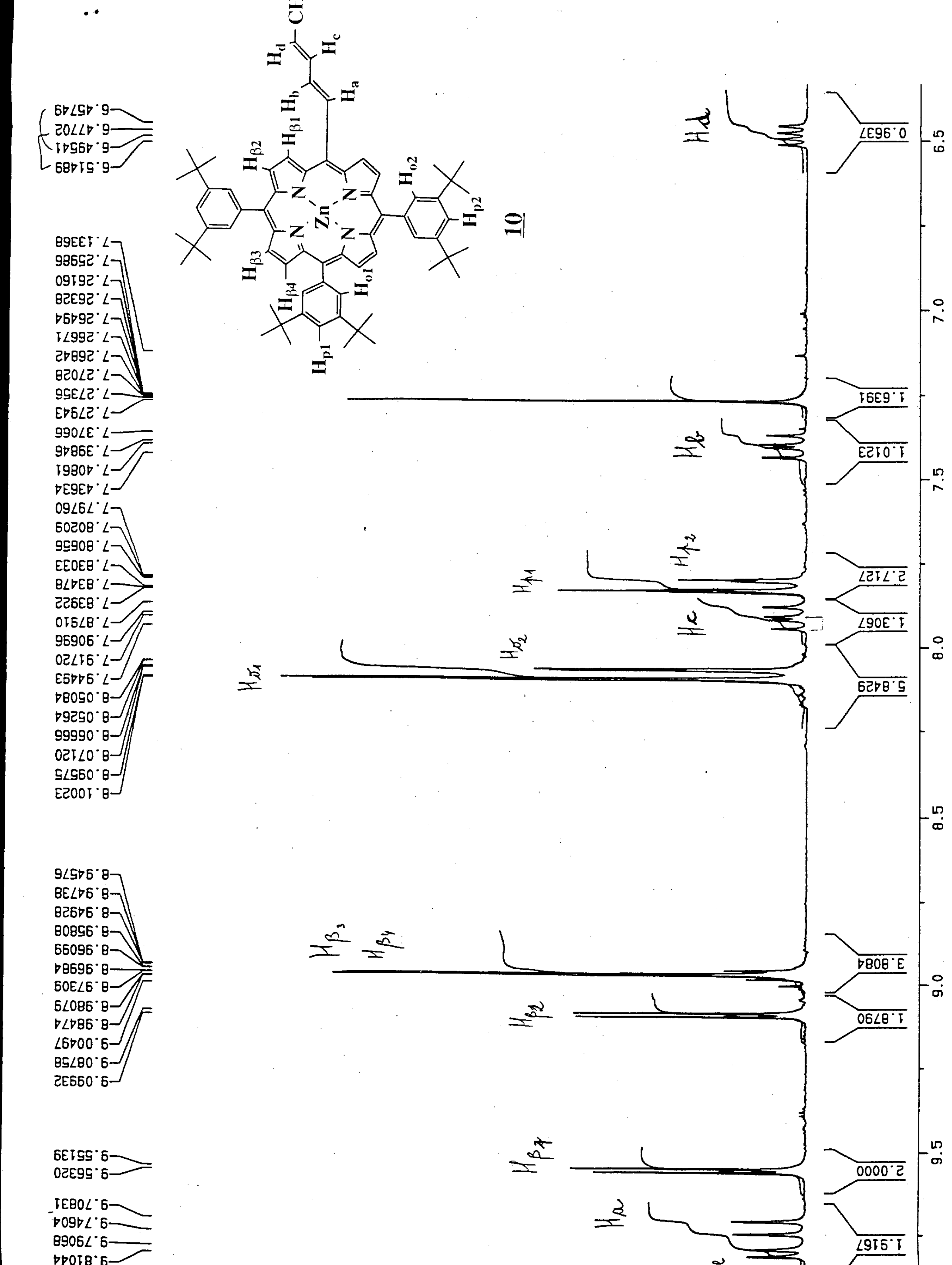

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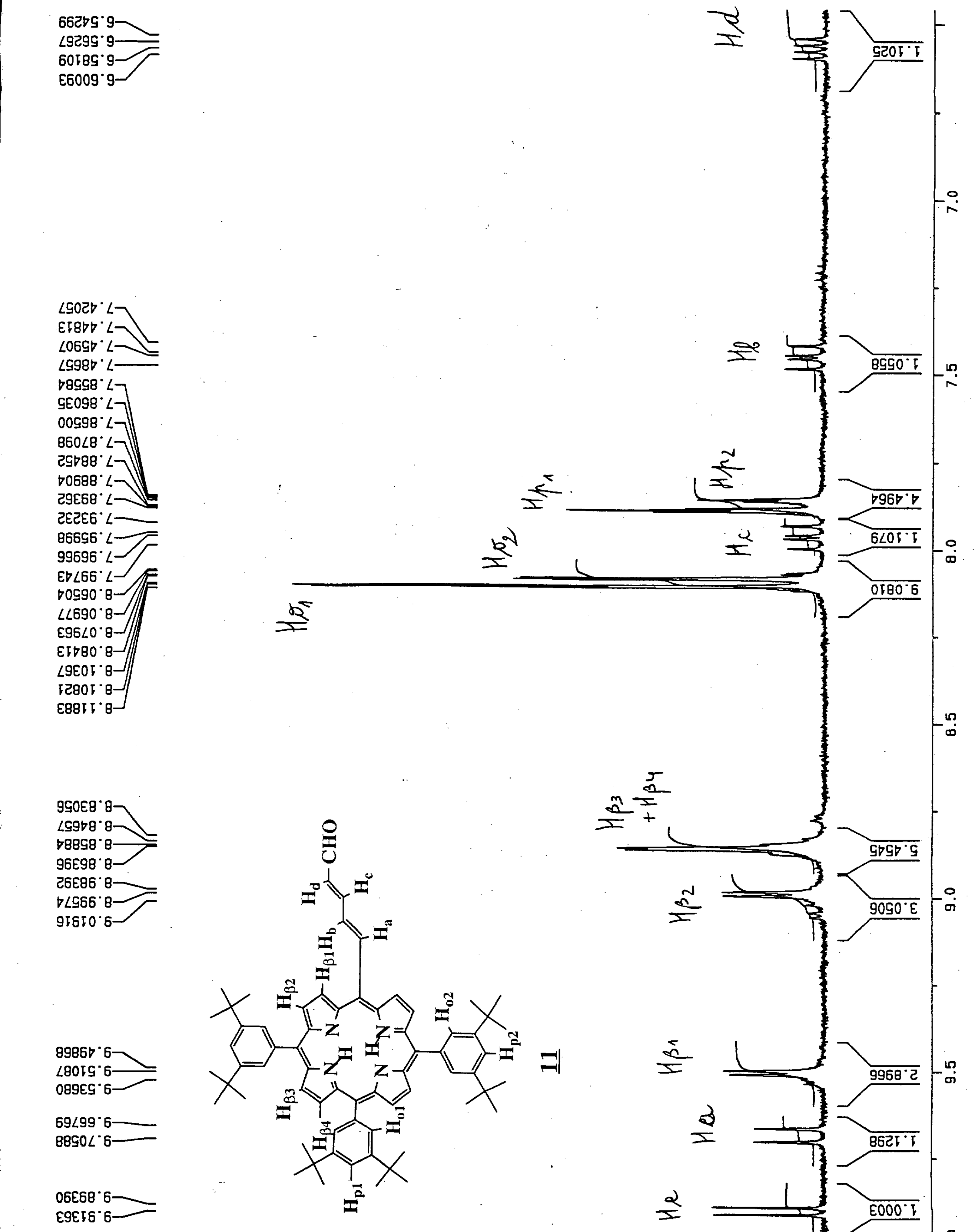
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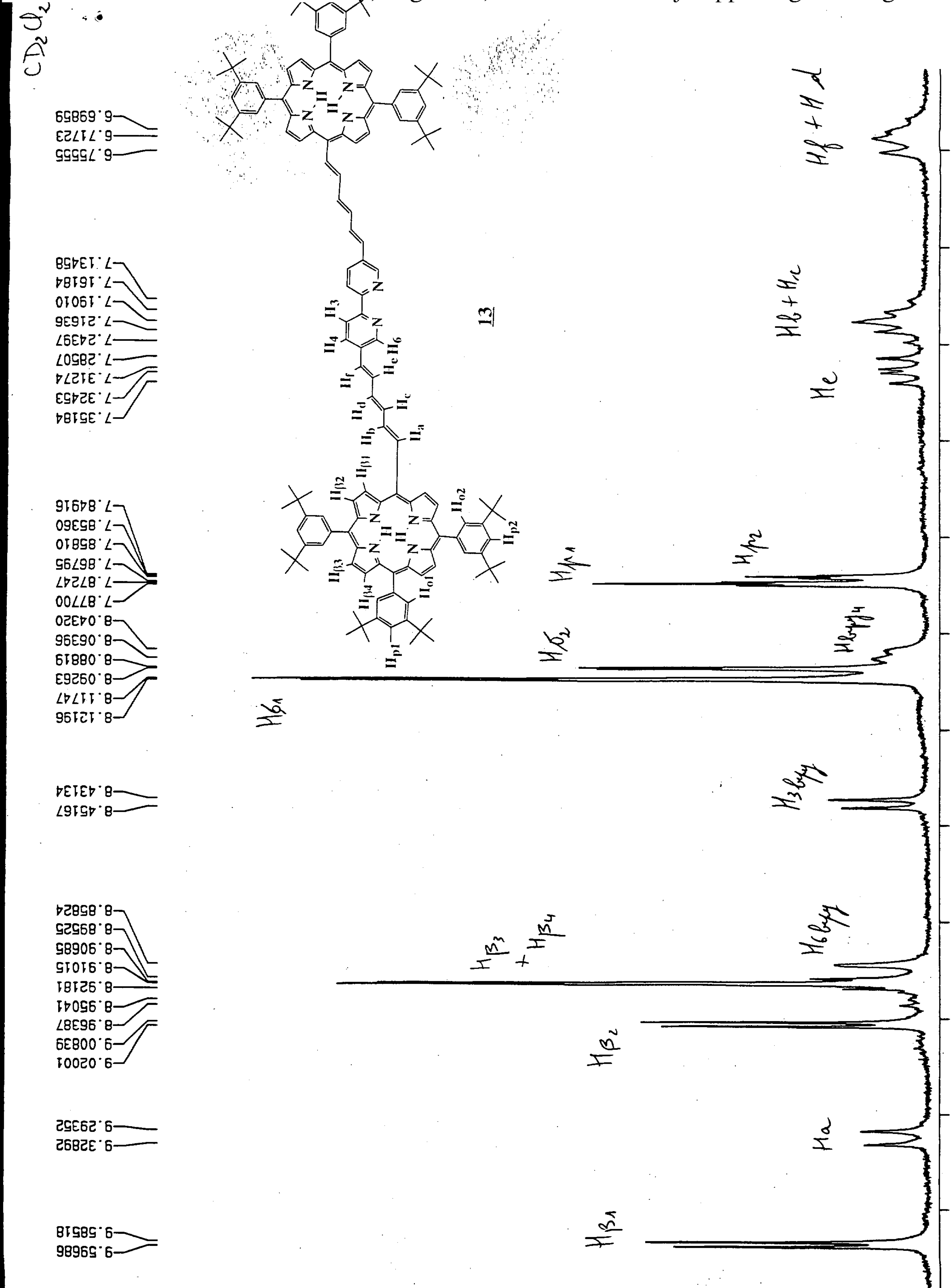
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