Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

meso-Alkylidenyl-thia-(*p*-benzi)porphyrins and their unusual protonation selectivity

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Experimental Section

Proton NMR spectra (300 MHz, Bruker Avance™ and 400 MHz, Bruker DPX-400) were recorded using TMS as the internal standard. High resolution mass spectra were obtained on an Voyager-DE STR MALDI-TOF mass spectrometer. Column chromatography was performed over silica gel (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2. All other reagents were obtained from Aldrich and used as received unless noted otherwise.

1,4-bis(2,2-diethoxycarbonylvinyl)benzene(5)

Terephthalaldehyde (0.20 g, 1.49 mmole), sodium acetate (0.15 g, 1.79 mmole) and methylamine hydrochloride (0.12 g, 1.79 mmole) dissolved in MeOH (5 mL) and then diethyl malonate (0.54 mL, 3.58 mmole) was added. The mixture was stirred for 25 hr at room temperature. Then, the mixture was combined with brine (15 mL) and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo*. The remaining solid was purified by recrystallization from hexanes/EtOAc to obtain pure product. Yield: 0.44 g (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H, CH), 7.47 (s, 4H, benzene-H), 4.37-4.29 (m, 8H, $\underline{CH_2}CH_3$), 1.34 (t, J = 7.13 Hz, 6H, $CH_2\underline{CH_3}$), 1.29 (t, J = 7.13 Hz, 6H, $CH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.72, 164.22, 141.05, 135.19, 130.12, 127.97, 62.26, 62.22, 14.51, 14.27

1,4-Bis[(α-diethoxycarbonylmethyl-α-(pyrrol-2-yl))methyl]benzene (6)

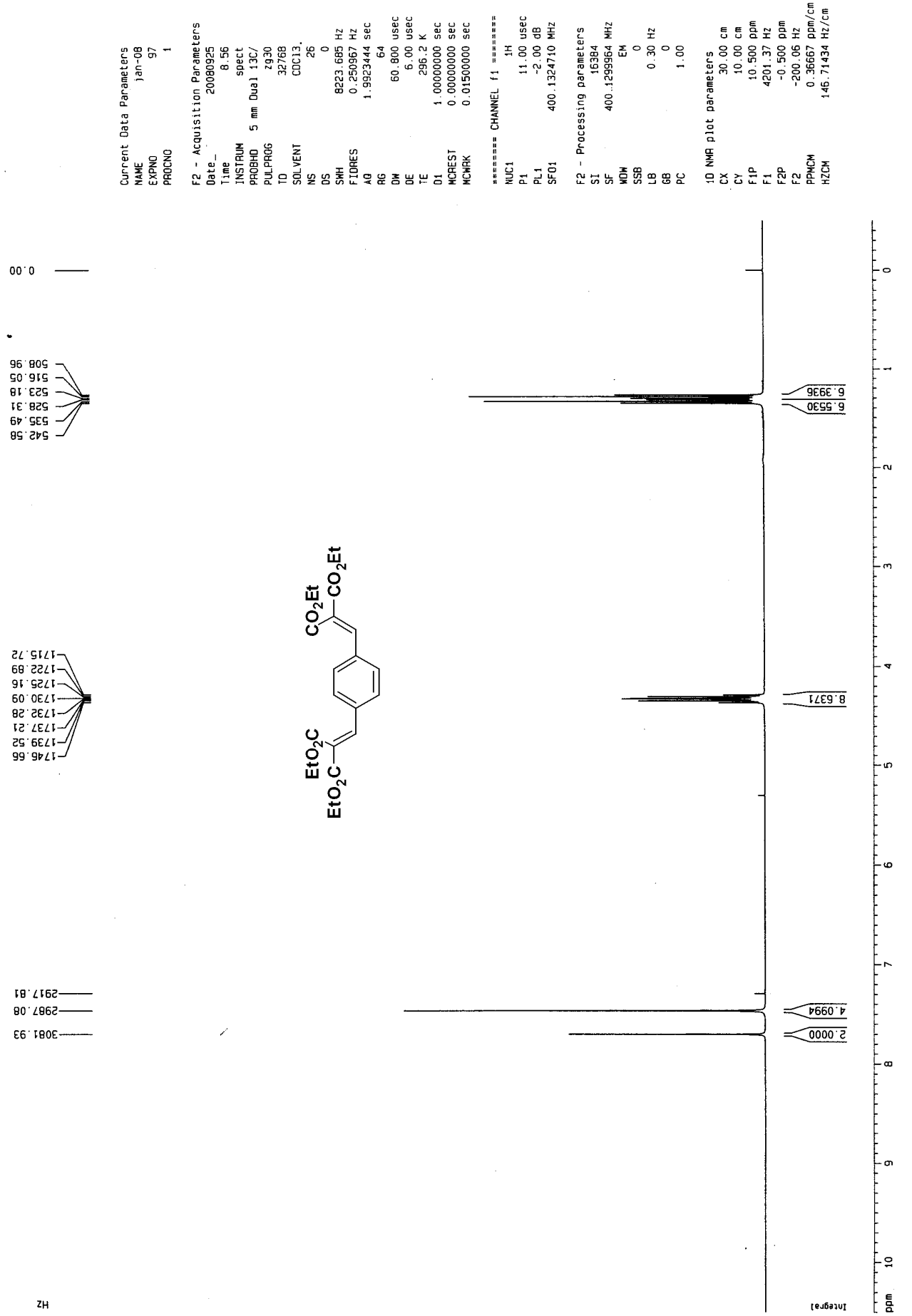
Compound **1** (0.20 g, 0.48 mmole) and Indium(III) chloride (0.03 g, 0.15 mmole)was dissolved in neat pyrrole (3 mL, 43 mmole). The mixture was stirred for 1 hr at room temperature. Then, the mixture was combined with brine (20 mL) and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and the solvent was removed *in vacuo*. The remaining solid was purified by column chromatography on silica ($CHCl_3$/EtOAc/Hexanes = 7/2/1) to obtain pure product. Yield 0.22 g (84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (br s, 2H, NH), 7.18 (s, 4H, benzene-H), 6.63-6.61 (m, 2H, pyrrole-H), 6.05-6.03 (m, 2H, pyrrole-H),

5.89 (s, 2H, pyrrole-H), 4.75 (d, *J* = 10.36 Hz, 2H, CH), 4.15-4.08 (m, 6H, CH, $\underline{CH_2}CH_3$), 3.96-3.87 (m, 4H, $\underline{CH_2}CH_3$), 1.16 (t, *J* = 7.13 Hz, 6H, $CH_2\underline{CH_3}$), 0.97 (t, *J* = 7.13 Hz, 6H, $CH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.67, 167.46, 167.15, 138.79, 130.79, 130.75, 128.37, 117.50, 108.03, 106.60, 106.56, 61.82, 61.52, 57.85, 43.87, 13.91, 13.76

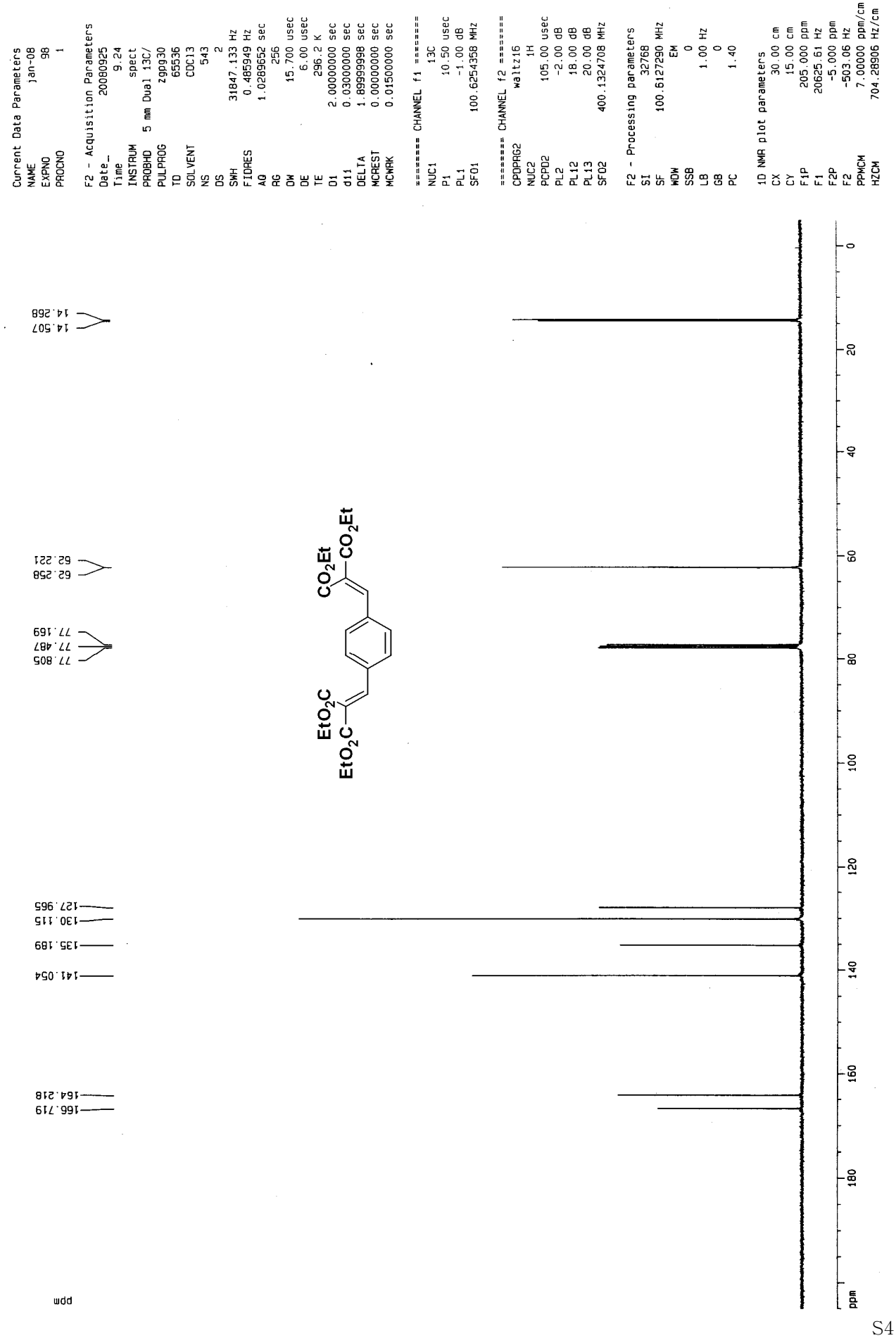
5,20-Bis(diethoxycarbonylmethylidene)-10,15-di(*p*-tolyl)-24-thia(*p*-benzi)porphyrin (1), and expanded macrocycle (7)

Compound **2** (0.22 g, 0.40 mmol) and compoud **3 (**0.15 g, 0.46 mmol) were dissolved in $CHCl_3$ (40 mL) and TFA (0.055 mL, 0.72 mmol) was added. The mixture was stirred for 45 min at room temperature. Then DDQ (0.34 g, 0.15 mmol) was added and stirred additional 1 hr. The reaction was stopped by adding saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and solvent was removed *in vacuo*. The remaining solid was purified by column chromatography on silica ($CHCl_3$/EtOAc = 40/1) to obtain two different products **4** and **5**. For compound (**4**); Yield: 0.079 g (23%); UV-Vis. (CH_2Cl_2) λ_{max} (log ε) 396 (4.54), 563 (4.31), 600 (4.29); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (br s, 2H, NH), 7.52 (s, 4H, benzene-H), 7.18 (d, *J* = 8.29 Hz, 4H, tolyl-H), 7.14 (d, *J* = 8.29 Hz, 4H, tolyl-H), 6.76-6.74 (m, 2H, pyrrole-H), 6.33 (s, 2H, thiophene-H), 5.96-5.94 (m, 2H, pyrrole-H), 4.38 (q, J = 7.13 Hz, 4H, $\underline{CH_2}CH_3$), 4.07 (q, J = 7.12 Hz, 4H, $\underline{CH_2}CH_3$), 2.38 (s, 6H, tolyl-CH_3), 1.36 (t, *J* = 7.13 Hz, 6H, $CH_2\underline{CH_3}$), 1.15 (t, *J* = 7.12 Hz, 6H, $CH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 164.32, 142.61, 139.29, 137.96, 136.46, 136.33, 135.73, 132.39, 131.65, 130.58, 129.37, 128.97, 122.85, 119.64, 117.48, 115.49, 61.72, 60.96, 21.28, 13.99, 13.89; MALDI-TOF MS Calcd. for $C_{50}H_{46}N_2O_8S$ exact mass 834.30, Found 834.28 For (**5**); Yield: 0.027 g (4%); UV-Vis. (CH_2Cl_2) λ_{max} (log ε) 420 (4.16), 540 (4.95), 583 (4.78); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 11.75 (br s, 4H, NH), 7.34 (d, *J* = 7.97 Hz, 8H, tolyl-H), 7.27 (d, *J* = 7.97 Hz, 8H, tolyl-H), 7.23 (s, 4H, benzene-H), 7.00-6.98 (m, 4H, pyrrole-H), 6.52 (s, 4H, thiophene-H), 6.07-6.05 (m, 4H, pyrrole-H), 4.02 (q, J = 7.10 Hz, 8H, $\underline{CH_2}CH_3$), 3.80 (q, J = 7.11 Hz, 8H, $\underline{CH_2}CH_3$), 2.45 (s, 12H, tolyl-CH_3), 1.19 (t, *J* = 7.10 Hz, 12H, $CH_2\underline{CH_3}$), 1.10 (t, *J* = 7.11 Hz, 12H, $CH_2\underline{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.84, 165.77, 144.40, 141.54, 138.46, 138.19, 137.74, 135.10, 132.87, 130.48, 130.19, 129.49, 128.48, 123.92, 123.15, 116.41, 112.79, 61.21, 60.95, 21.30, 13.94, 13.87; MALDI-TOF MS Calcd. for $C_{100}H_{92}N_4O_{16}S_2$ exact mass 1668.59, Found 1669.58.

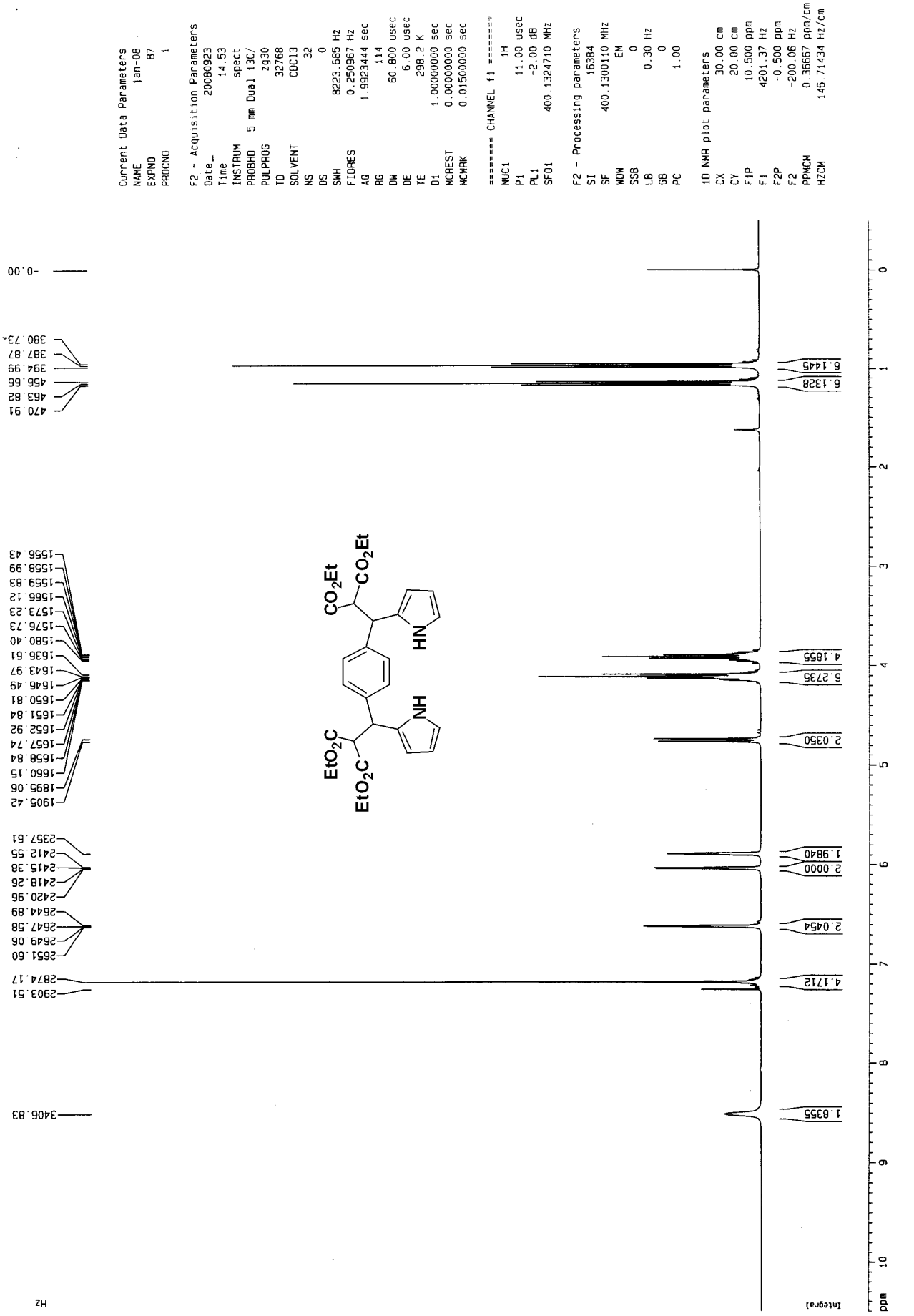
^{1}H NMR spectrum of 1,4-bis(2,2-diethoxycarbonylvinyl)benzene **1** in $CDCl_3$



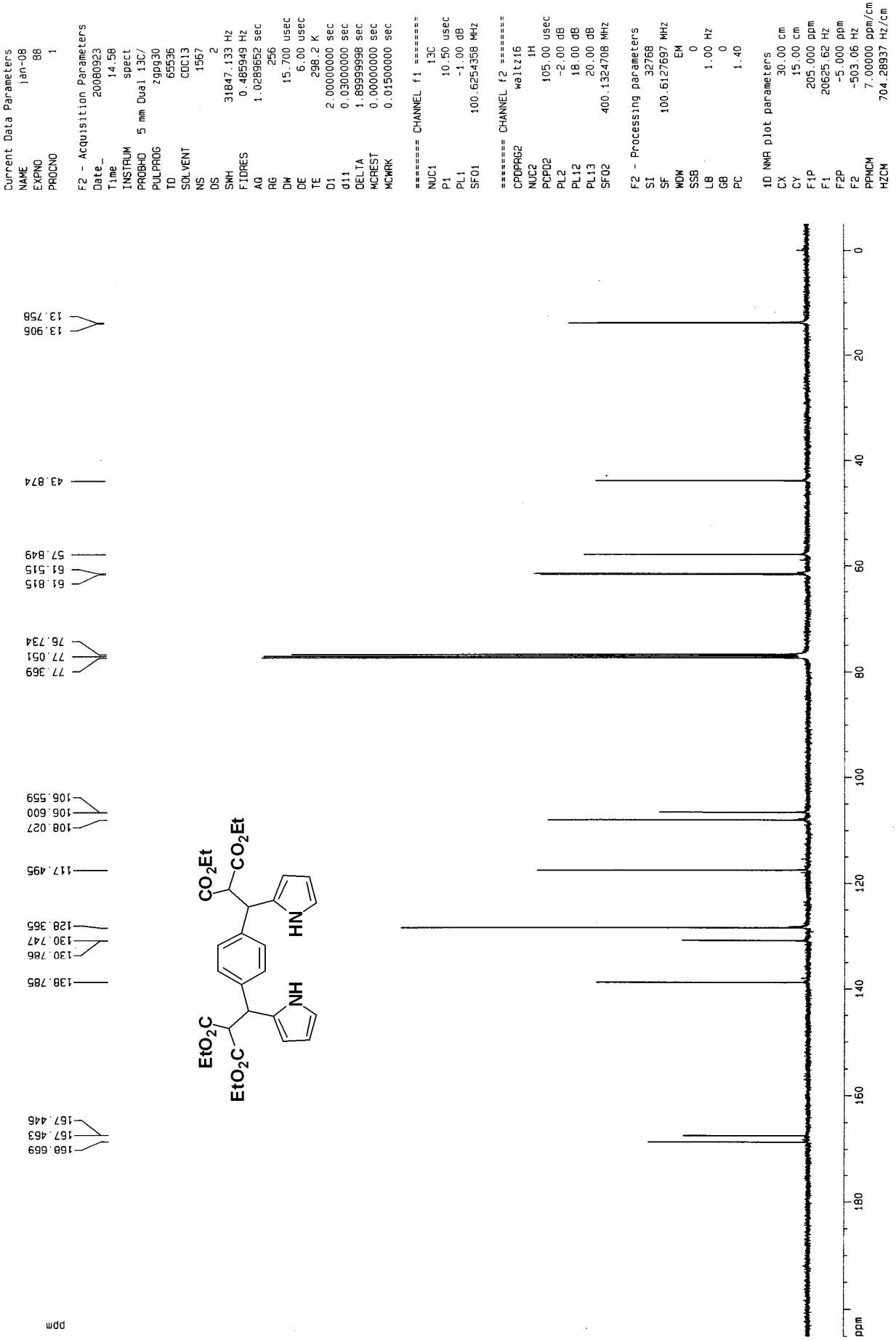
^{13}C NMR spectrum of 1,4-bis(2,2-diethoxycarbonylvinyl)benzene **1** in $CDCl_3$



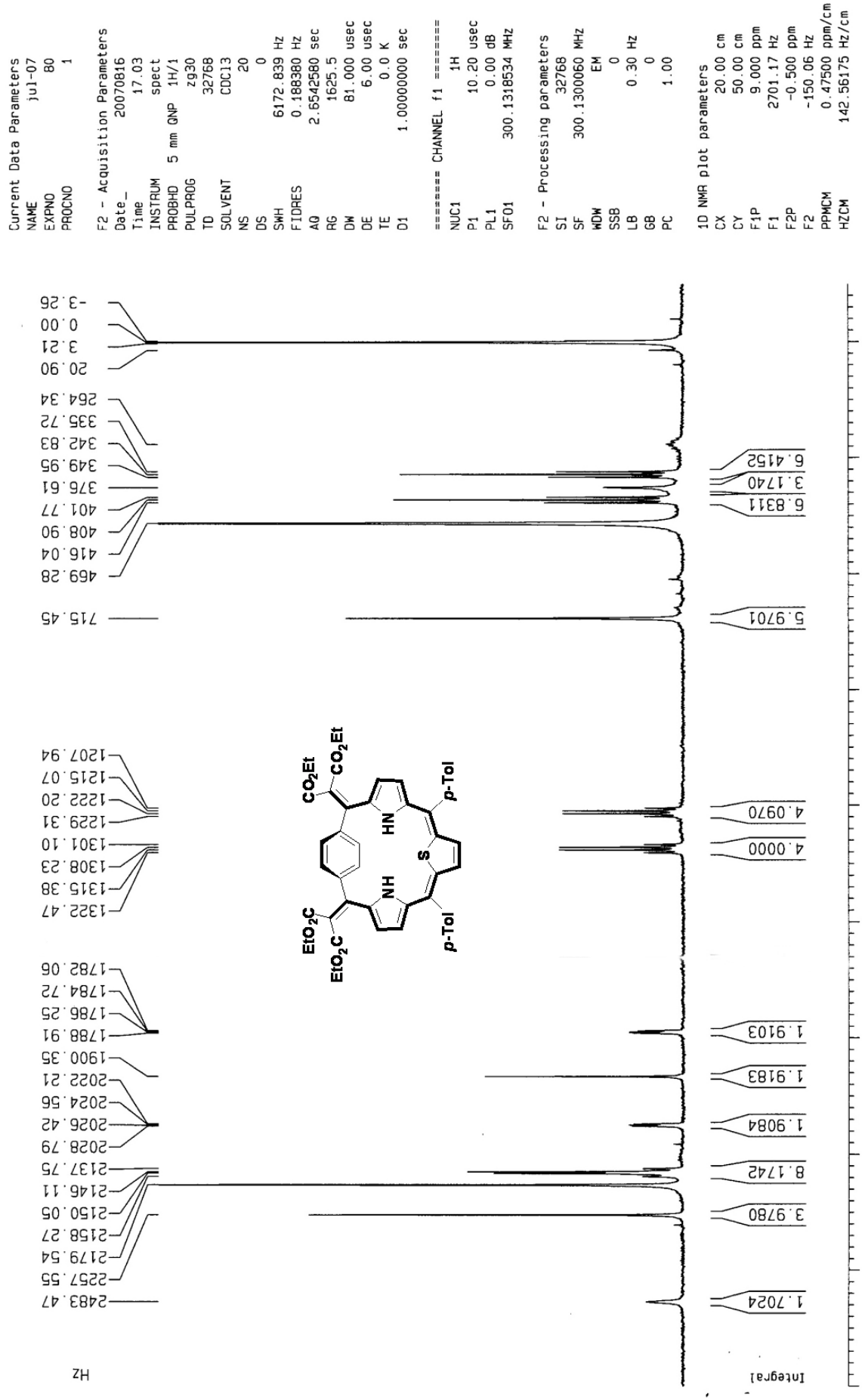
^{1}H NMR spectrum of 1,4-Bis[(α-diethoxycarbonylmethyl-α-(pyrrol-2-yl))methyl]benzene **2** in $CDCl_3$



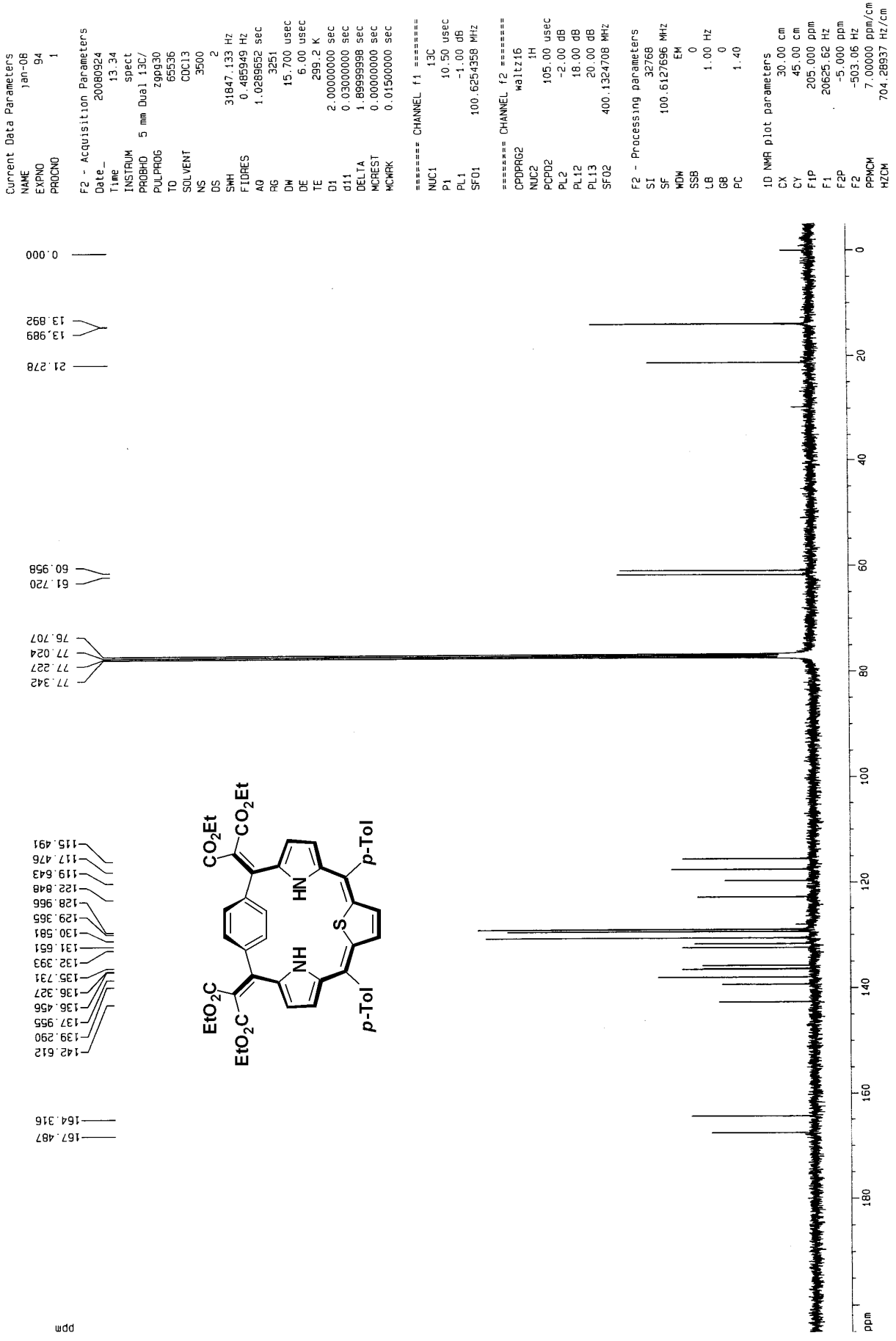
^{13}C NMR spectrum of 1,4-Bis[(α-diethoxycarbonylmethyl-α-(pyrrol-2-yl))methyl]benzene **2** in $CDCl_3$



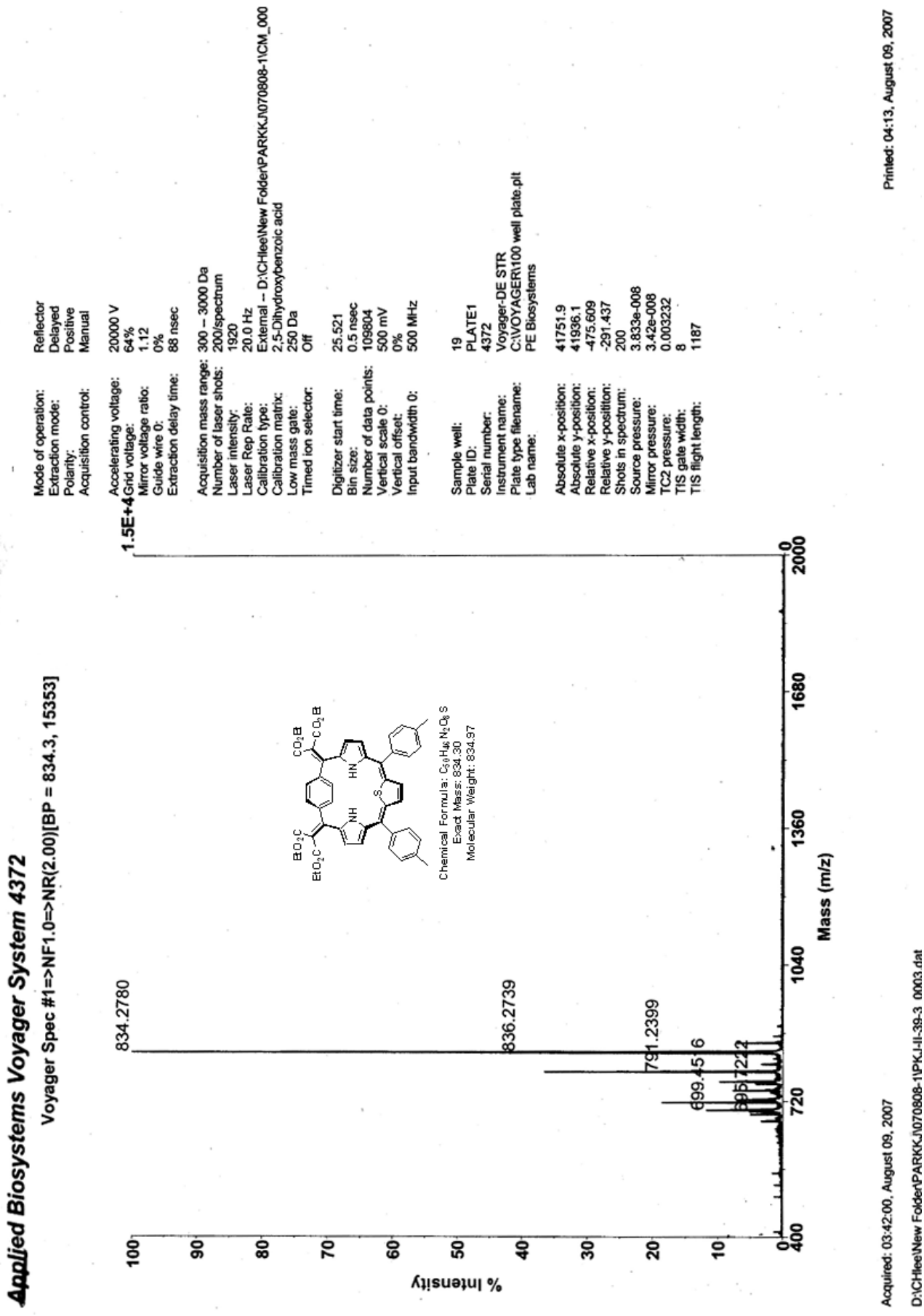
^{1}H NMR spectrum of 5,20-Bis(diethoxycarbonylmethylidene)-10,15-di(*p*-tolyl)-24-thia(*p*-benzi)porphyrin **4** in $CDCl_3$



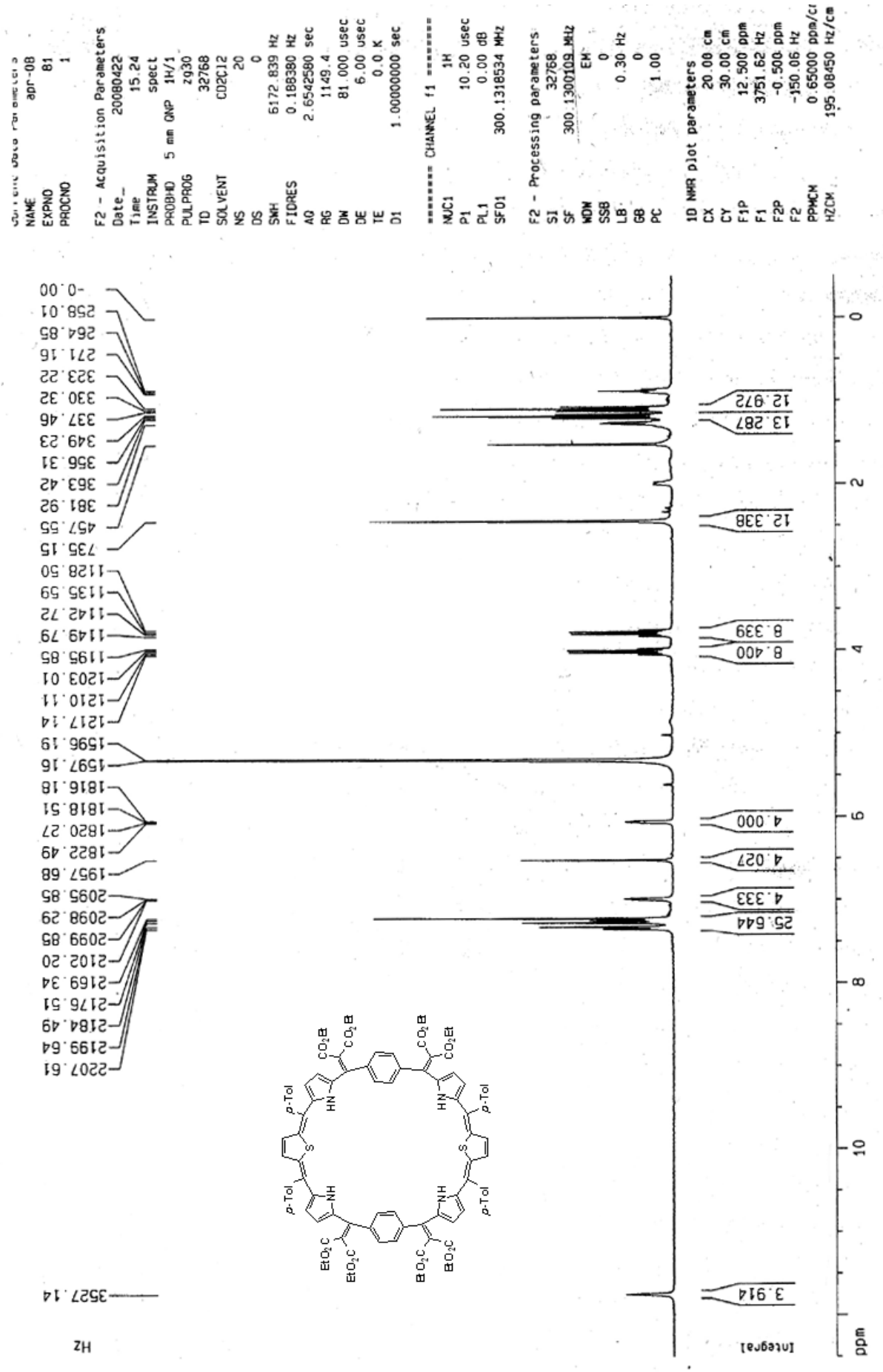
^{13}C NMR spectrum of 5,20-Bis(diethoxycarbonylmethylidene)-10,15-di(*p*-tolyl)-24-thia(*p*-benzi)porphyrin **4** in $CDCl_3$



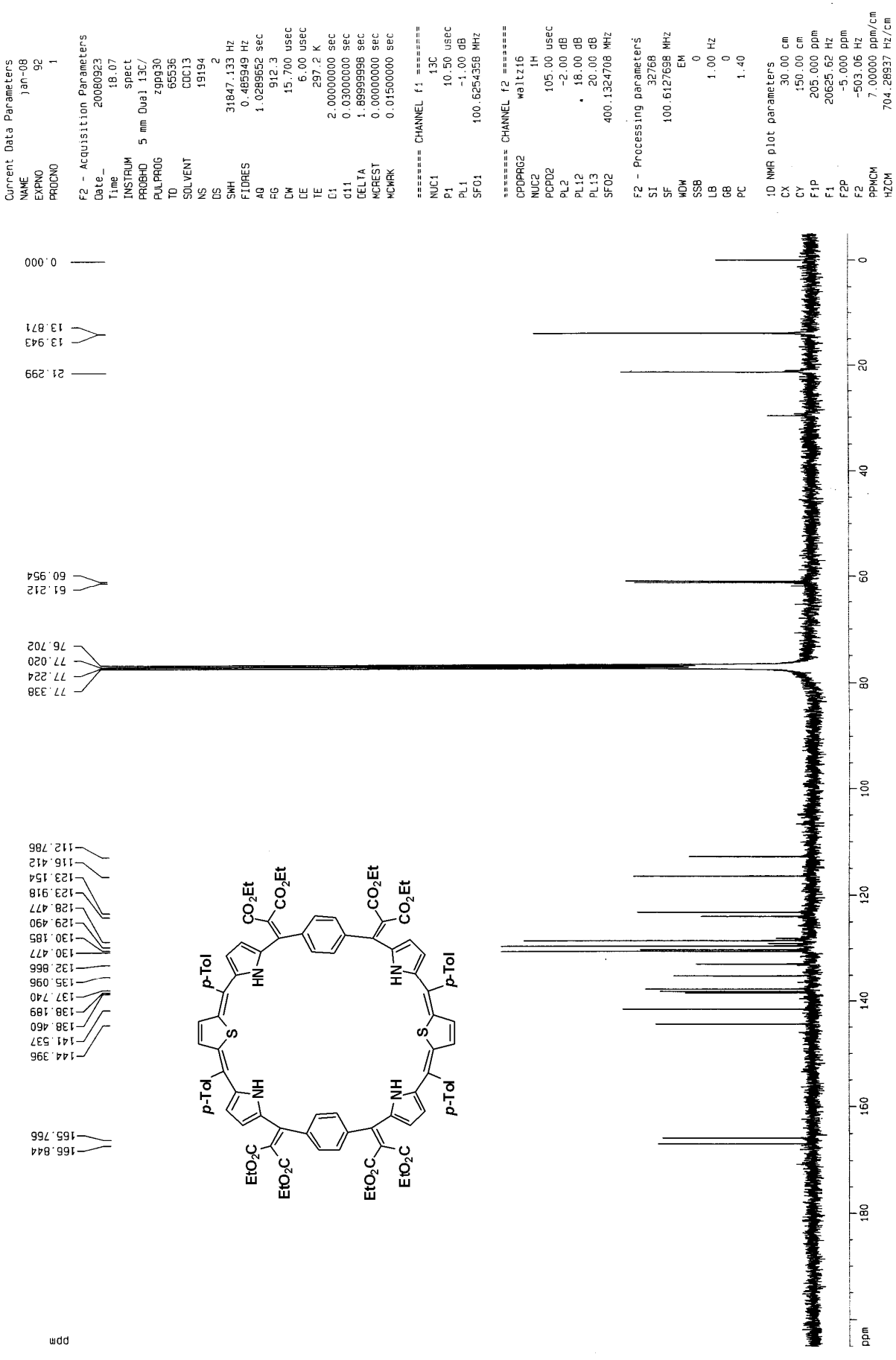
MALDI-TOF Mass spectrum of 5,20-Bis(diethoxycarbonylmethylidene)-10,15-di(*p*-tolyl)-24-thia(*p*-benzi)porphyrin **4** in CH_2Cl_2



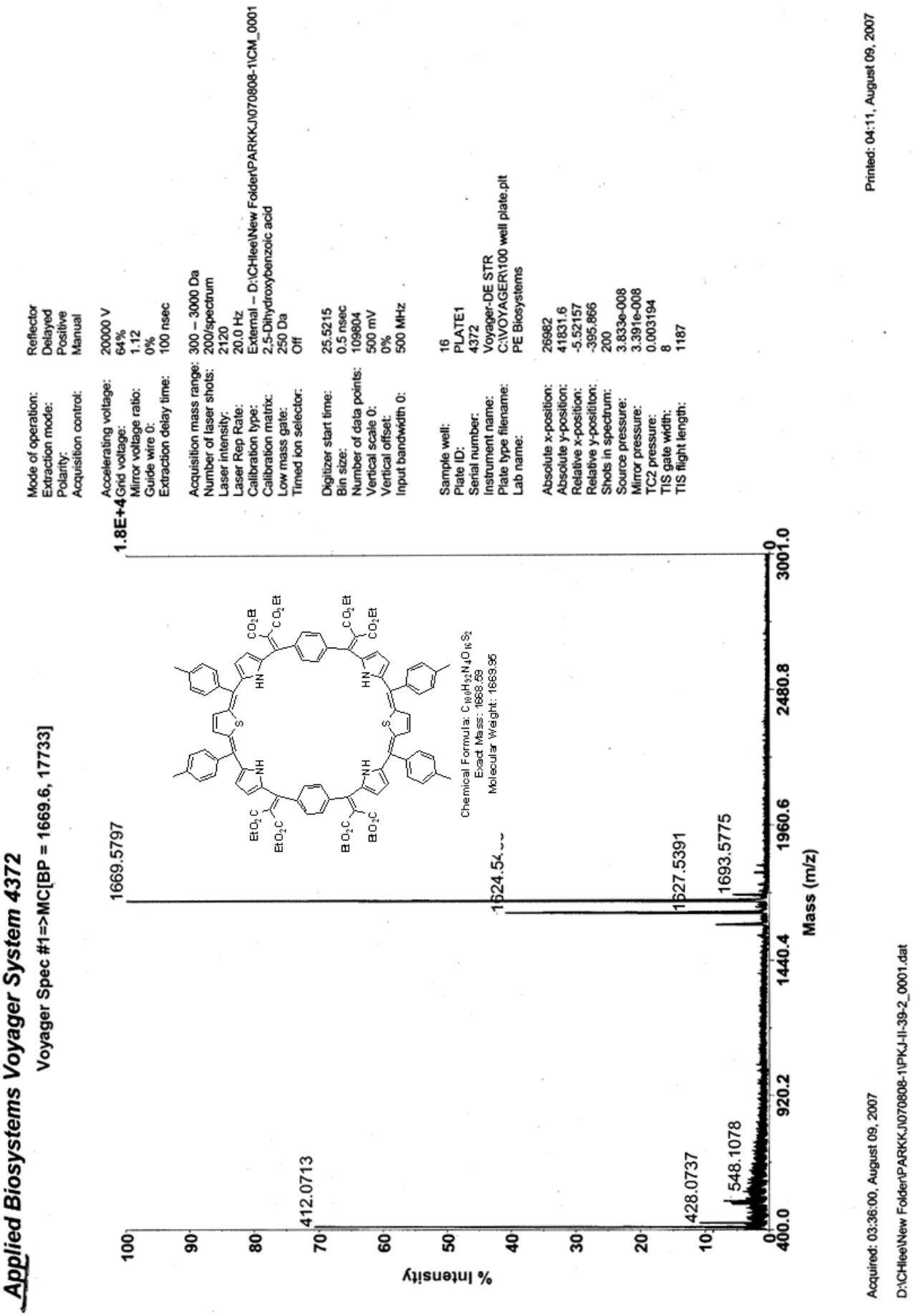
^{1}H NMR spectrum of expanded macrocycle **5** in CD_2Cl_2



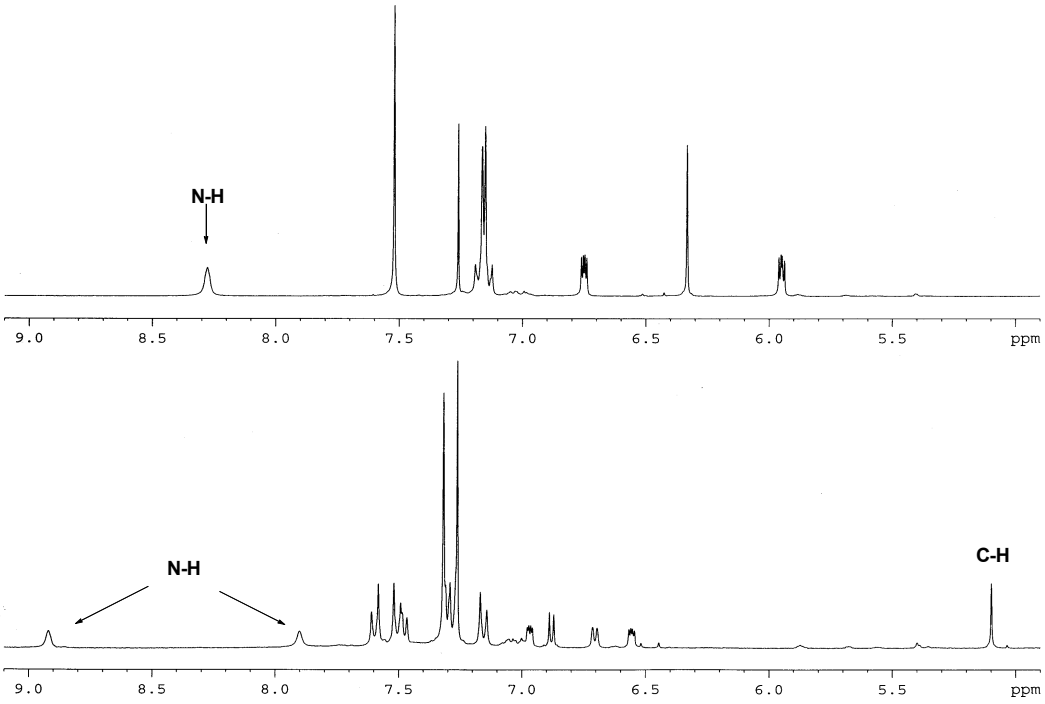
^{13}C NMR spectrum of expanded macrocycle **5** in $CDCl_3$



MALDI-TOF Mass spectrum of expanded macrocycle **5** in CH_2Cl_2

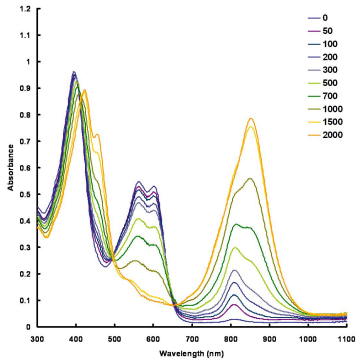


^{1}H NMR spectral changes of thia(p-benzi)porphyrin in $CDCl_3$ upon the addition of trifluoroacetic acid (10.0 equiv.)

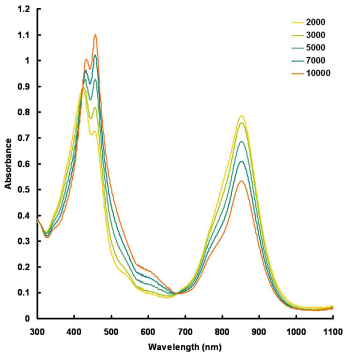


UV-vis absorption spectral changes of thia(p-benzi)porphyrin (2.1 x 10-5 M in CH2Cl2) upon the addition of trifluoroacetic acid A) 0-2000 equiv. B) 2000-10000 equiv. C) original absorption spectrum was fully recovered by subsequent addition of base.

A)



B)



C)