

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 AvanceTM 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 CaH₂. 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 CH₂Cl₂. The organic layer was dried (Na₂SO₄) 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%); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 2H, CH), 7.47 (s, 4H, benzene-H), 4.37-4.29 (m, 8H, CH₂CH₃), 1.34 (t, *J* = 7.13 Hz, 6H, CH₂CH₃), 1.29 (t, *J* = 7.13 Hz, 6H, CH₂CH₃); ¹³C NMR (100 MHz, CDCl₃) 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)

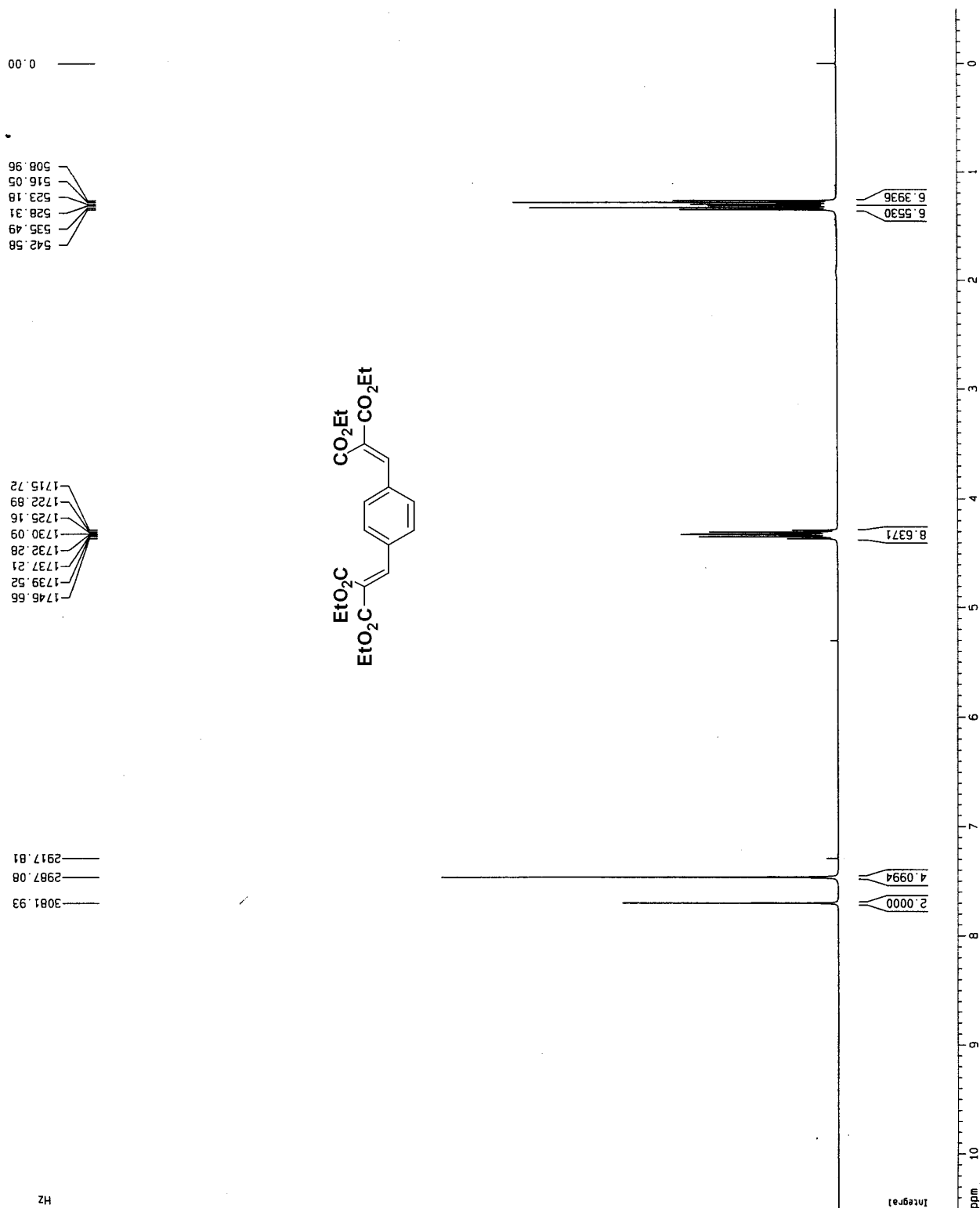
Compound **1** (0.20 g, 0.48 mmole) and Indium(III) chloride (0.03 g, 0.15 mmole) was dissolved in neat pyrrole (3 mL, 43 mmole). The mixture was stirred for 1 hr at room temperature. Then, the mixture was combined with brine (20 mL) and extracted with CH₂Cl₂. The organic layer was dried (Na₂SO₄) and the solvent was removed *in vacuo*. The remaining solid was purified by column chromatography on silica (CHCl₃/EtOAc/Hexanes = 7/2/1) to obtain pure product. Yield 0.22 g (84%); ¹H NMR (400 MHz, CDCl₃) 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, $\underline{\text{CH}_2\text{CH}_3}$), 3.96-3.87 (m, 4H, $\underline{\text{CH}_2\text{CH}_3}$), 1.16 (t, $J = 7.13$ Hz, 6H, $\text{CH}_2\underline{\text{CH}_3}$), 0.97 (t, $J = 7.13$ Hz, 6H, $\text{CH}_2\underline{\text{CH}_3}$); ^{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 compound **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 ($\text{CHCl}_3/\text{EtOAc} = 40/1$) 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); ^1H 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, $\underline{\text{CH}_2\text{CH}_3}$), 4.07 (q, $J = 7.12$ Hz, 4H, $\underline{\text{CH}_2\text{CH}_3}$), 2.38 (s, 6H, tolyl- CH_3), 1.36 (t, $J = 7.13$ Hz, 6H, $\text{CH}_2\underline{\text{CH}_3}$), 1.15 (t, $J = 7.12$ Hz, 6H, $\text{CH}_2\underline{\text{CH}_3}$); ^{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 $\text{C}_{50}\text{H}_{46}\text{N}_2\text{O}_8\text{S}$ 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); ^1H 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, $\underline{\text{CH}_2\text{CH}_3}$), 3.80 (q, $J = 7.11$ Hz, 8H, $\underline{\text{CH}_2\text{CH}_3}$), 2.45 (s, 12H, tolyl- CH_3), 1.19 (t, $J = 7.10$ Hz, 12H, $\text{CH}_2\underline{\text{CH}_3}$), 1.10 (t, $J = 7.11$ Hz, 12H, $\text{CH}_2\underline{\text{CH}_3}$); ^{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 $\text{C}_{100}\text{H}_{92}\text{N}_4\text{O}_{16}\text{S}_2$ exact mass 1668.59, Found 1669.58.

¹H NMR spectrum of 1,4-bis(2,2-diethoxycarbonylvinyl)benzene **1** in CDCl₃



¹³C NMR spectrum of 1,4-bis(2,2-diethoxycarbonylvinyl)benzene **1** in CDCl₃

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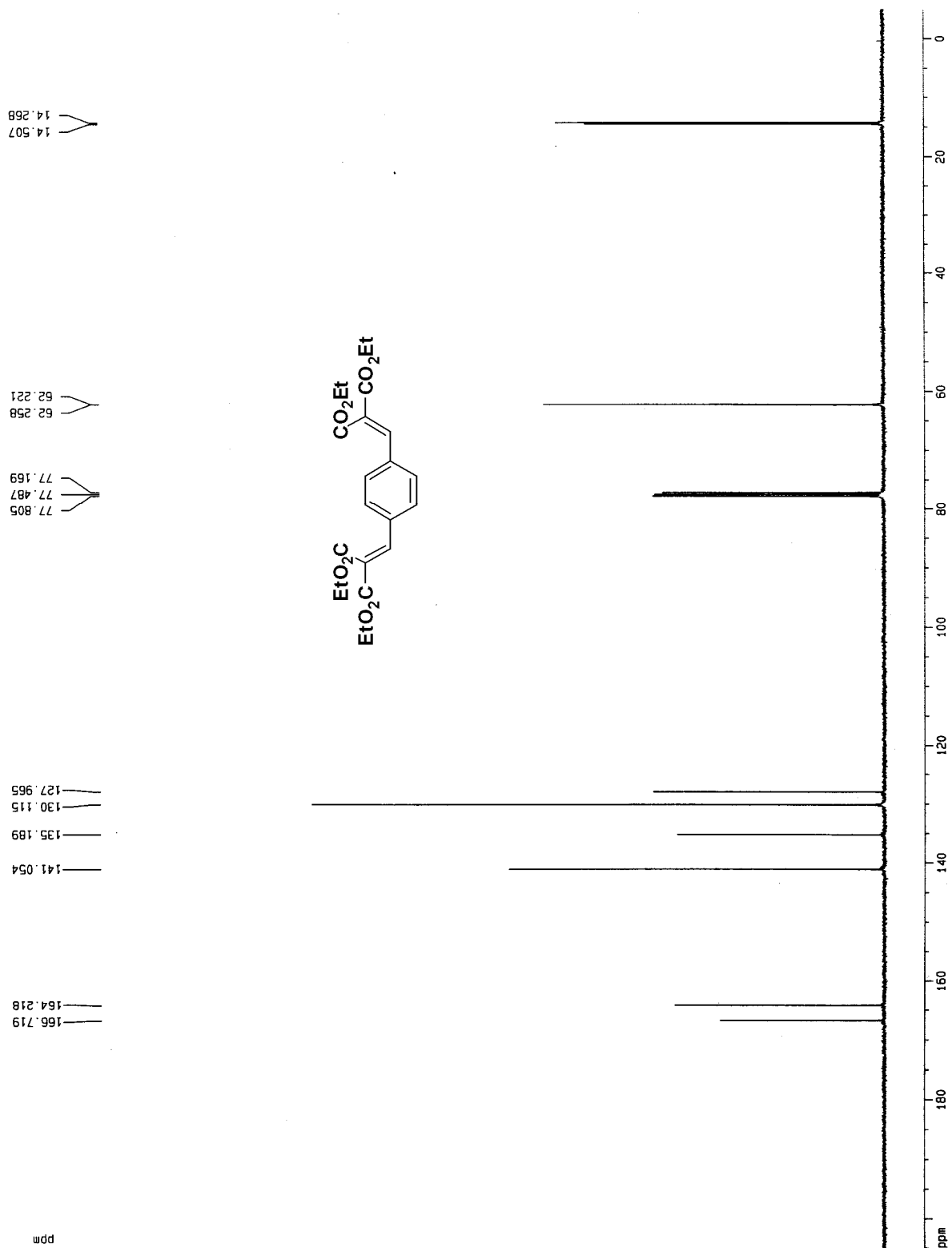
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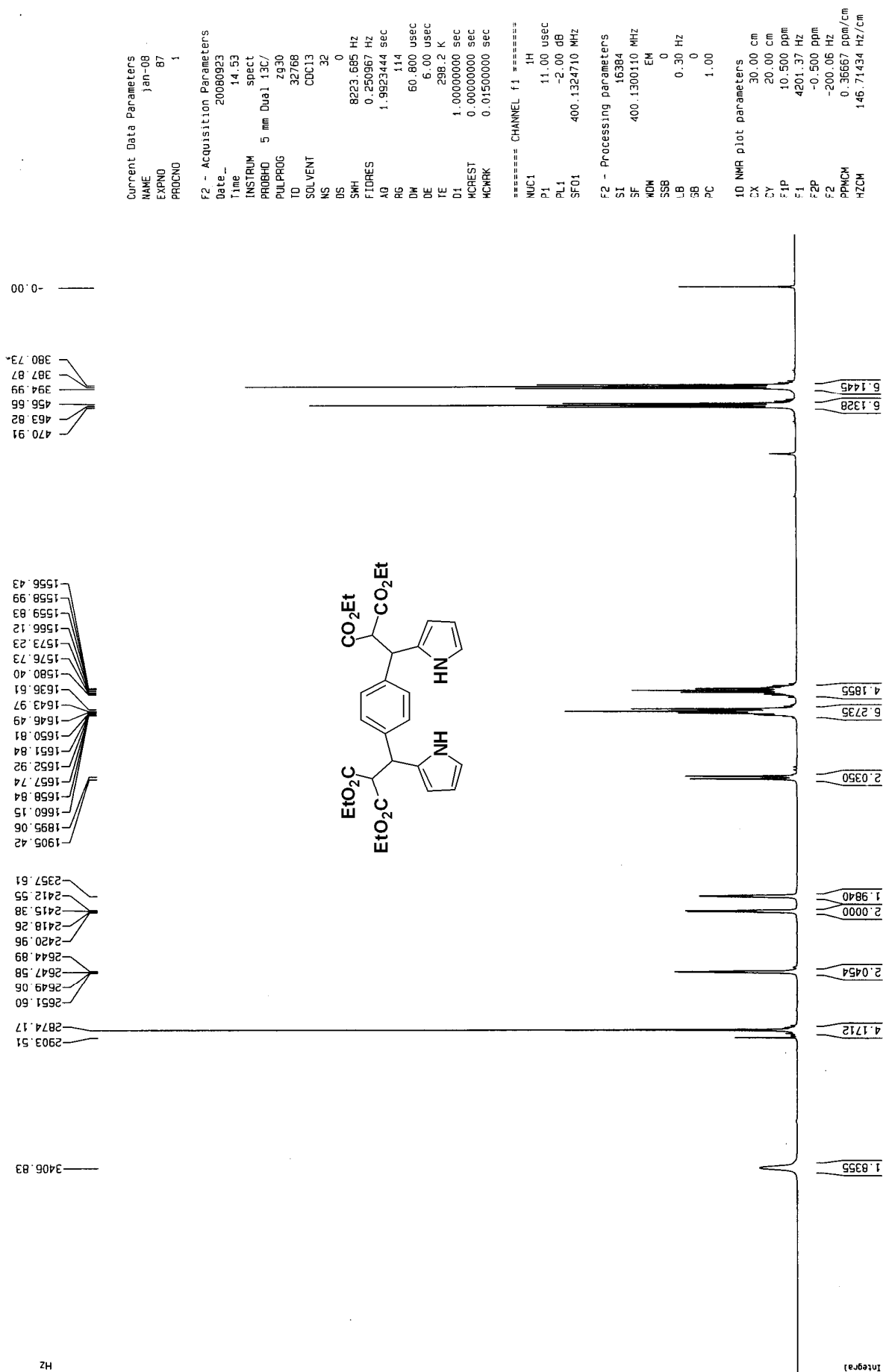
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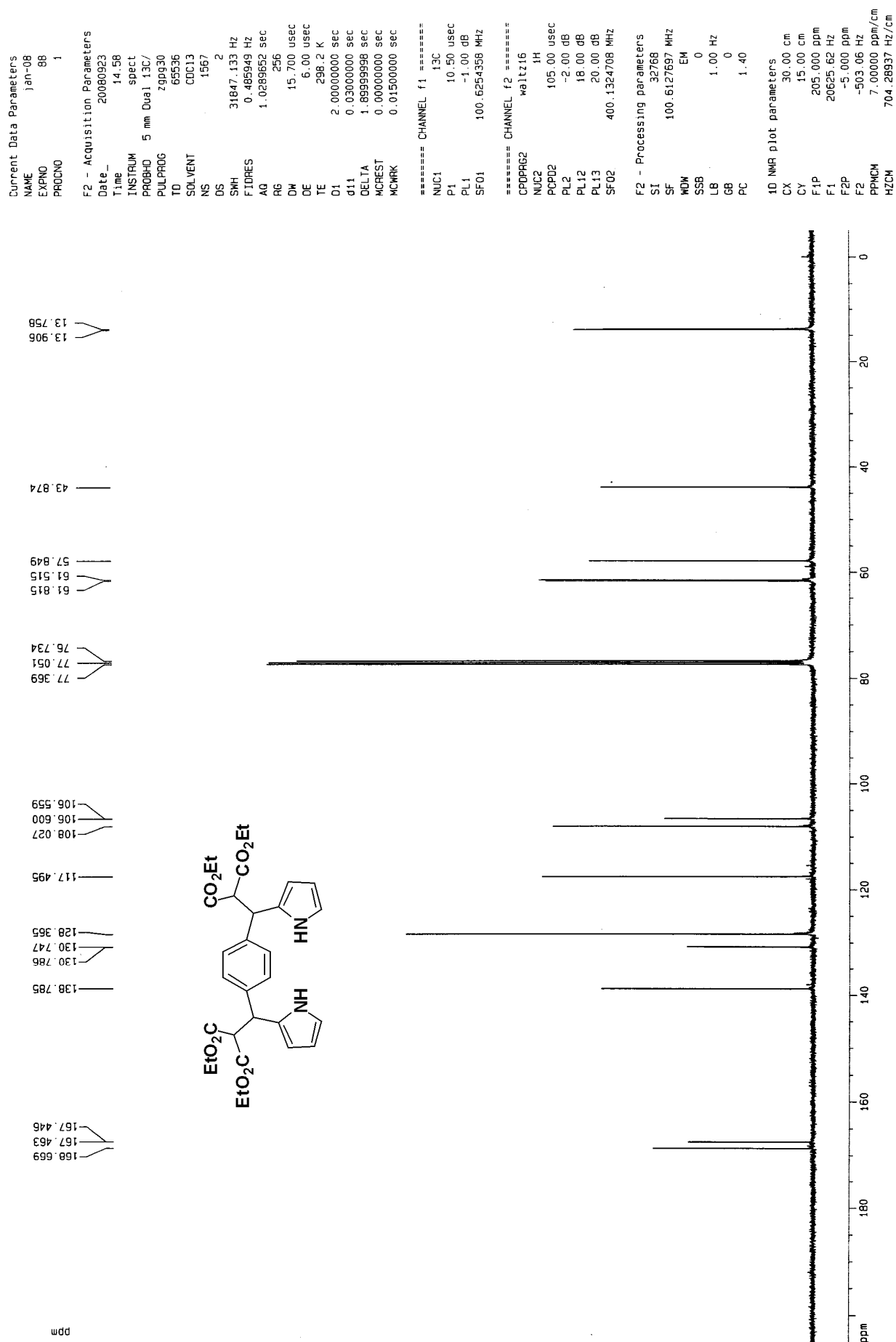
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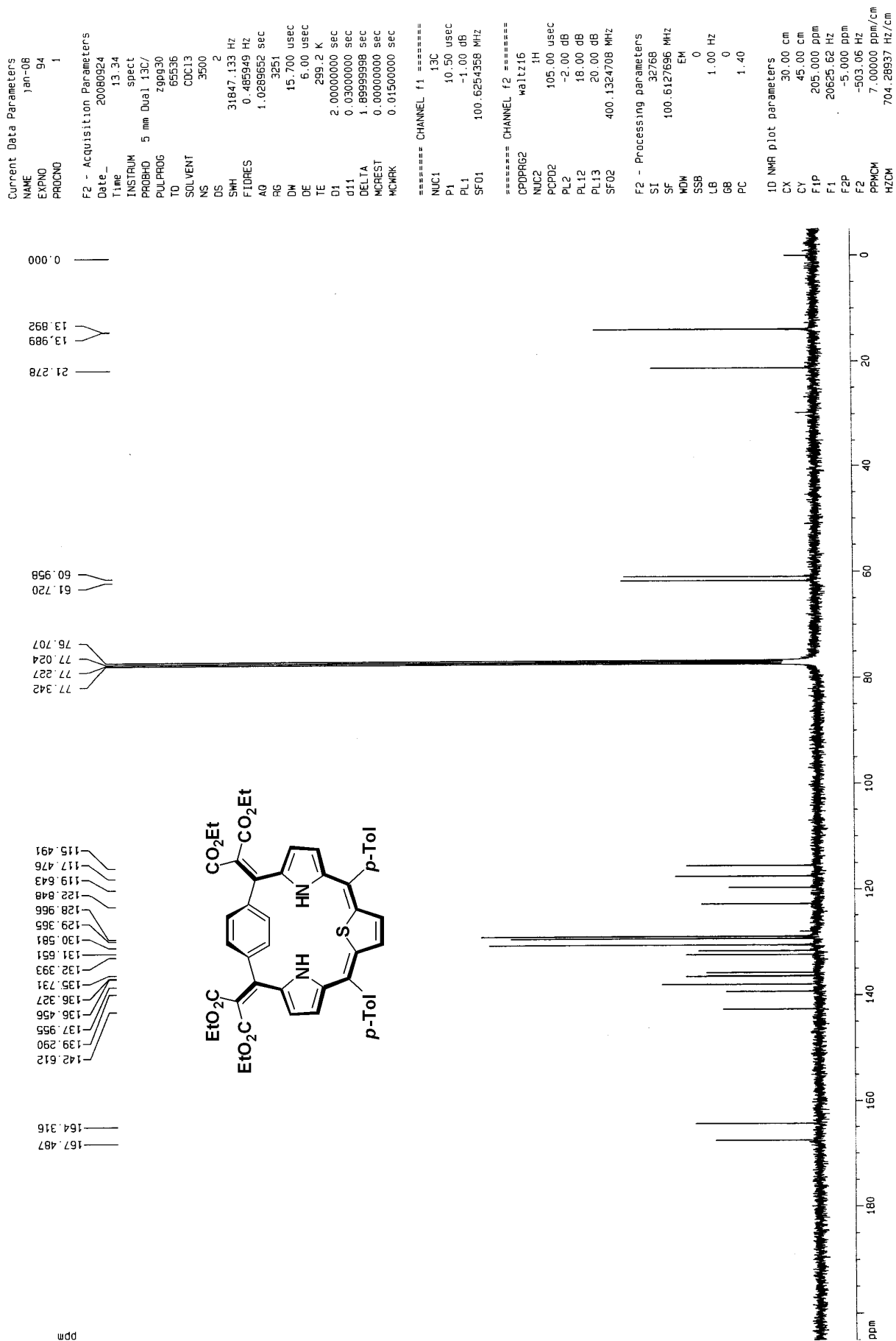
¹H NMR spectrum of 1,4-Bis[(α -diethoxycarbonylmethyl- α -(pyrrol-2-yl))methyl]benzene **2** in CDCl₃



¹³C NMR spectrum of 1,4-Bis[(α -diethoxycarbonylmethyl- α -(pyrrol-2-yl)methyl]benzene **2** in CDCl₃

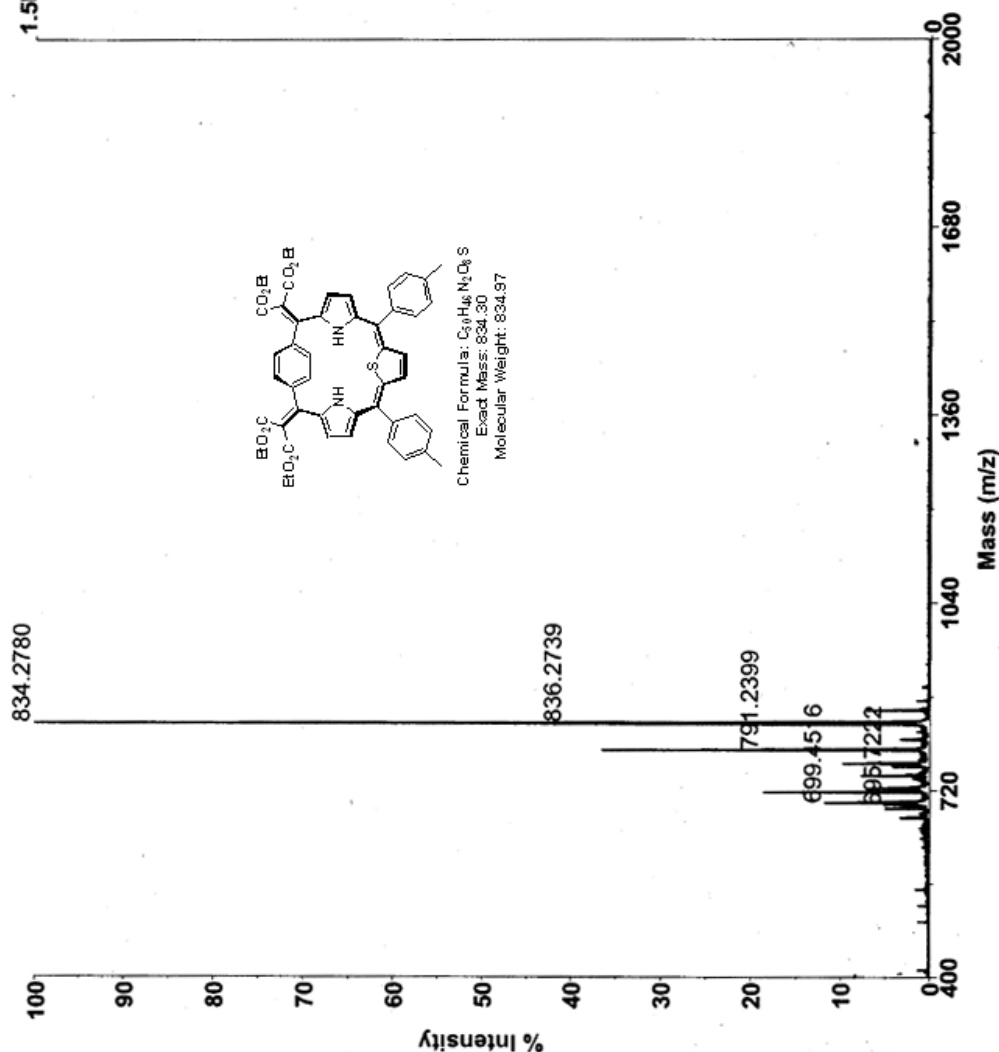


¹³C NMR spectrum of 5,20-Bis(diethoxycarbonylmethylidene)-10,15-di(*p*-tolyl)-24-thia(*p*-benzi)porphyrin **4** in CDCl₃



Applied Biosystems Voyager System 4372

Voyager Spec #1=>NF1.0=>NR(2.00)[BP = 834.3, 15353]



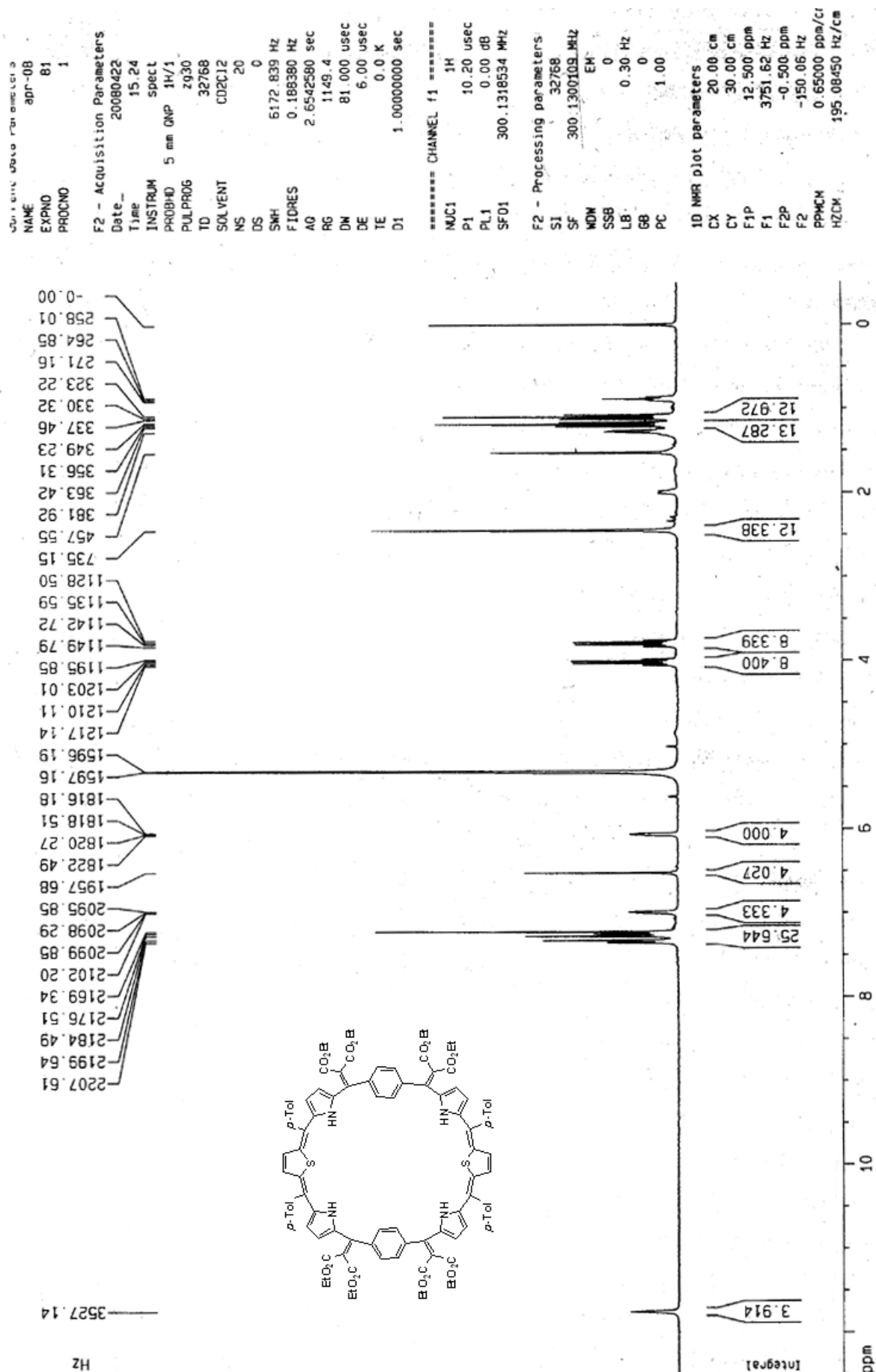
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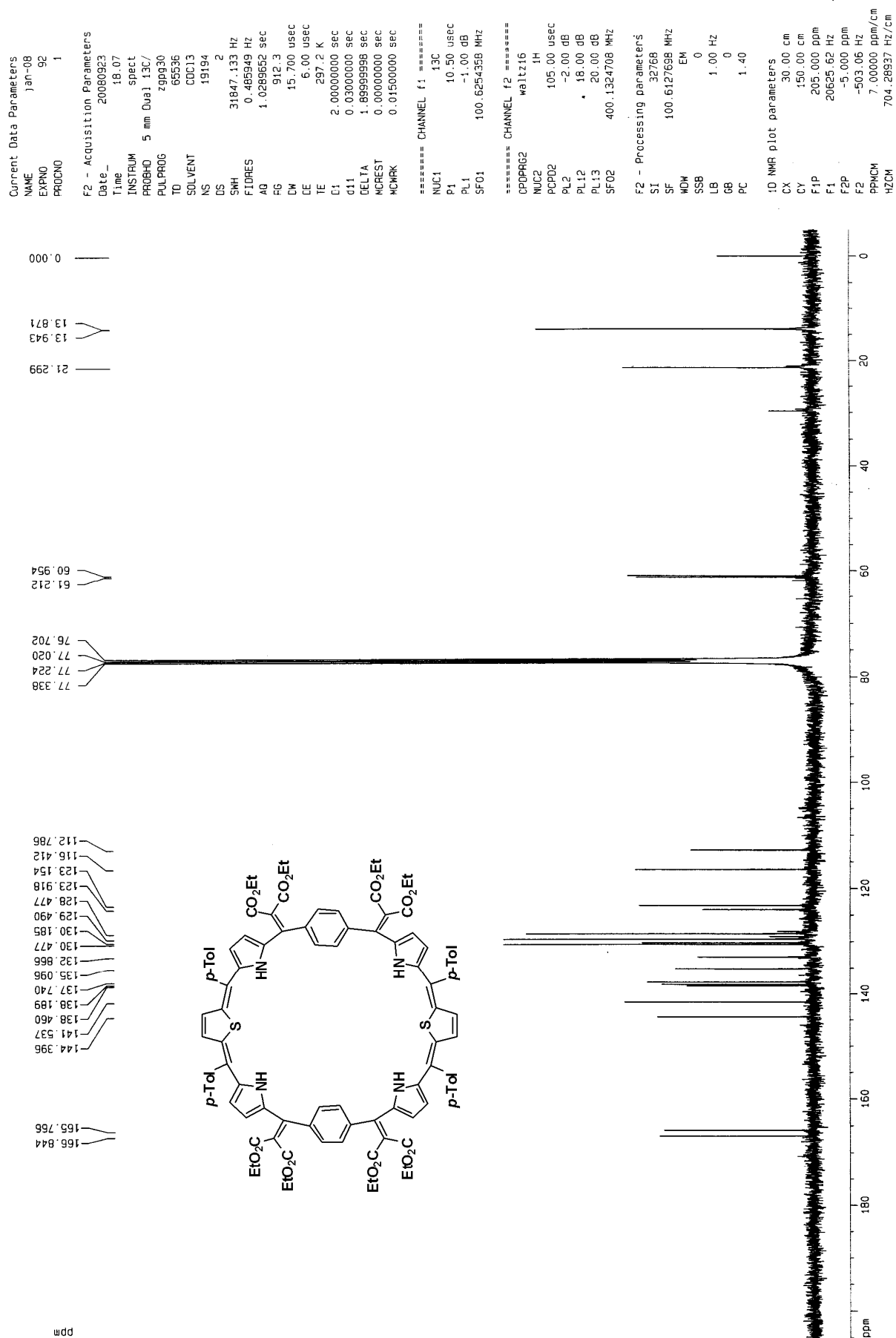
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^1H NMR spectrum of expanded macrocycle **5** in CD_2Cl_2



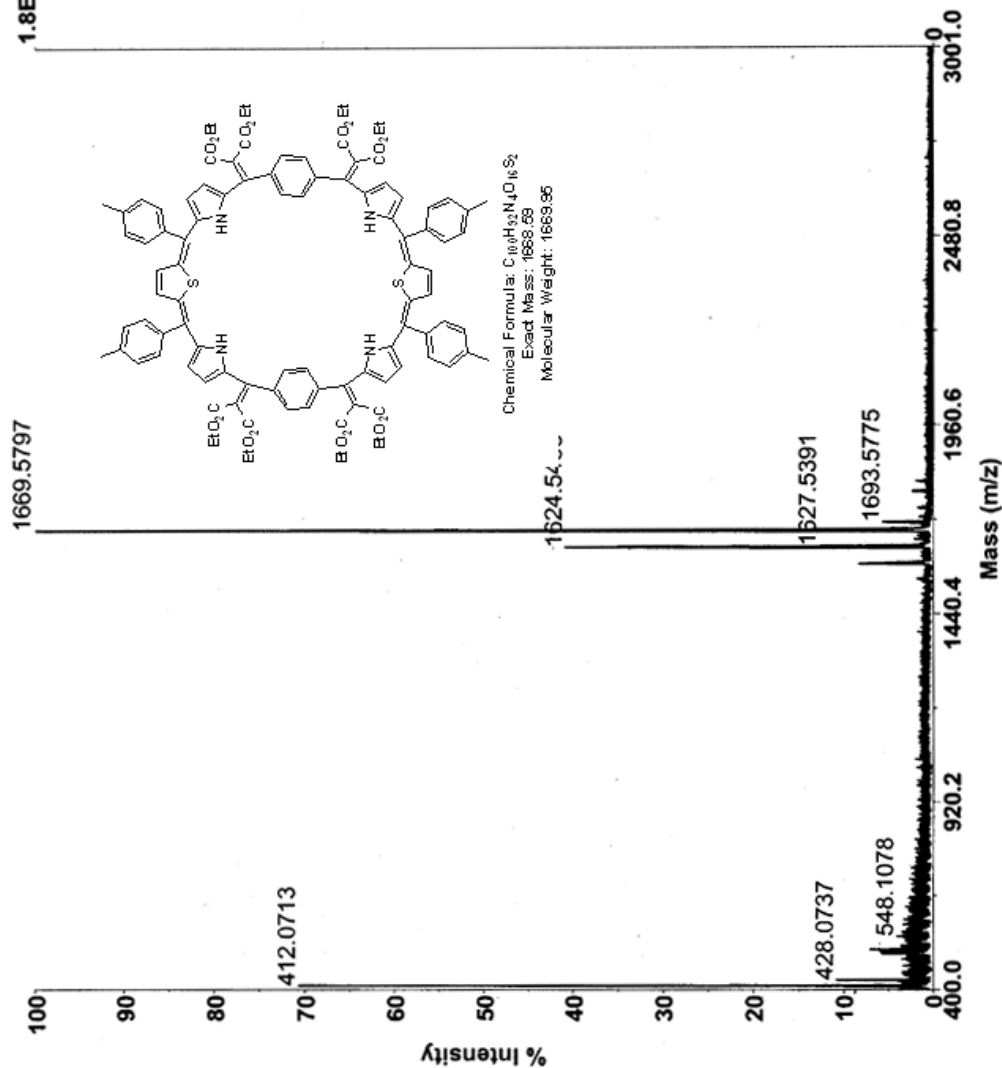
¹³C NMR spectrum of expanded macrocycle **5** in CDCl₃



Applied Biosystems Voyager System 4372

Voyager Spec #1=>MC[BP = 1669.6, 17733]

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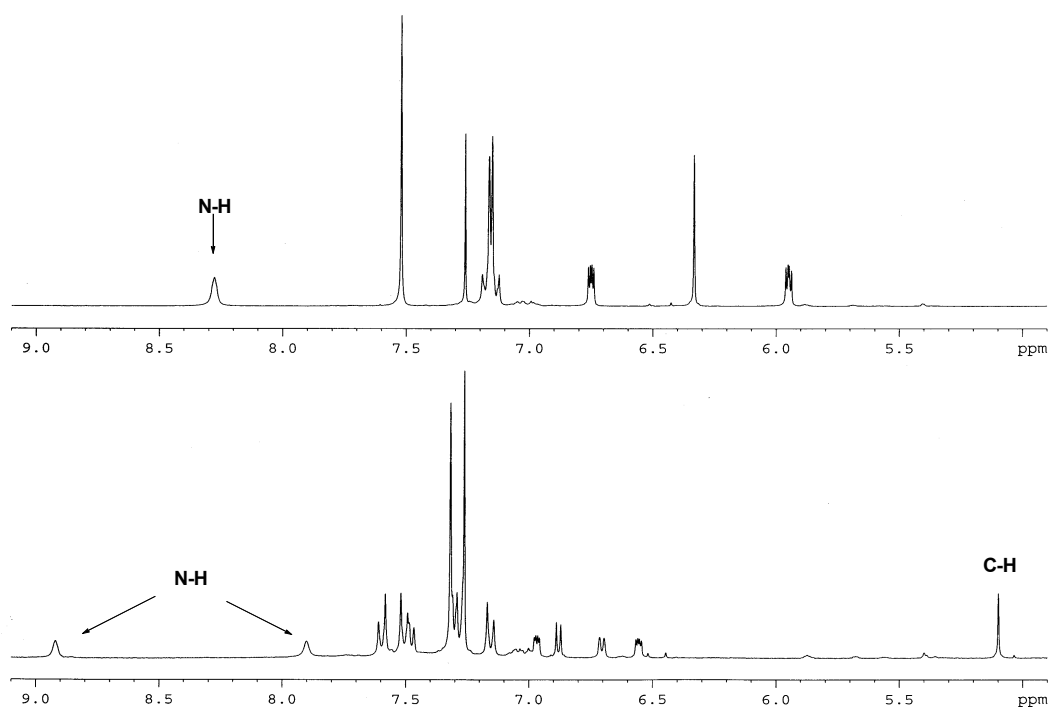


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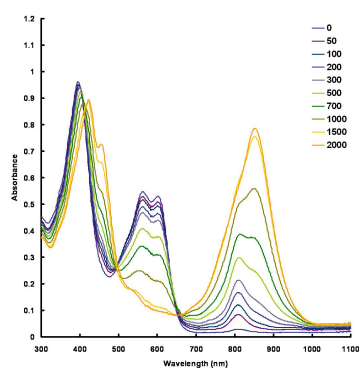
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^1H NMR spectral changes of thia(p-benzi)porphyrin in CDCl_3 upon the addition of trifluoroacetic acid (10.0 equiv.)

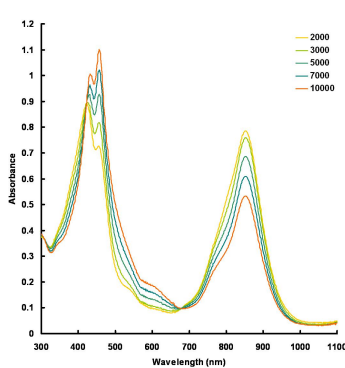


UV-vis absorption spectral changes of thia(p-benzi)porphyrin (2.1×10^{-5} M in CH_2Cl_2) upon the addition of trifluoroacetic acid A) 0-2000 equiv. B) 2000-10000 equiv. C) original absorption spectrum was fully recovered by subsequent addition of base.

A)



B)



C)

