# Supporting Information

# Distorted Fused Porphyrin-Phthalocyanine Conjugates: Synthesis and Photophysics of Supramolecular Assembled Systems with a Pyridylfullerene

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**General:** $^{1}$H NMR spectra were recorded at 300 or 500 MHz and $^{13}$C NMR spectra were recorded at 75.5 or 125.8 MHz with Bruker Avance 300 and Bruker DRX 500 spectrometers. $CDCl_3$ was used as solvent (except when indicated) and TMS as internal reference. The chemical shifts are expressed in δ (ppm) and the coupling constants (*J*) in Hertz (Hz). Unequivocal $^{1}$H assignments were made using 2D COSY and NOESY experiments (mixing time of 800 ms), while $^{13}$C assignments were made on the basis of 2D HSQC and HMBC experiments (delay for long-range *J* C/H couplings were optimized for 7 Hz). The HRMS (MALDI-TOF) were determined with a Bruker Reflex III spectrometer using dithranol as matrix. The UV-Vis spectra were recorded with a Shimadzu UV-250 Pc spectrophotometer using $CH_2Cl_2$ or toluene as solvent. Column chromatography was carried out with silica gel (Merck, 230-400 mesh). Preparative thin-layer chromatography was carried out on 20x20 cm glass plates coated with silica gel (1 mm thick). Analytical TLC was carried out on precoated sheets with silica gel (0.2 mm thick, Merck). Toluene and tetrahydrofuran were distilled from benzophenone and sodium metal, all other solvents and reagents were used without further purification.

**Synthetic Procedures**

Porphyrin-phthalocyanine dyads **1a** and **1b** were synthesized according to the following scheme:

i) TFA, $CH_2Cl_2$, r.t., 10 min; ii) fumaronitrile, toluene, reflux, 24 h; iii) DDQ, toluene, reflux, 48 h; iv) 4-*tert*-butylphthalonitrile, $Zn(OAc)_2$, DMAE/*o*-$Cl_2C_6H_4$, 145 ºC, 18 h; v) TFA/$CH_2Cl_2$, r.t.

Compound **3a** was prepared according to the literature.[1]

**Compounds 4 and 5**

A solution of porphyrin **3b** (52.7 mg, 82.3 μmol) and fumaronitrile (77 mg, 986 μmol, 12 equiv) in toluene (6 mL) was refluxed under inert atmosphere for 24 h. The solvent was removed and the crude was submitted to column chromatography (silica gel) using a mixture of light petroleum and $CHCl_3$ (4:1) as the eluent. Two new compounds, **4** (34.2 mg, 58%) and **5** (7.4 mg, 13%), were separated by preparative thin-layer chromatography and crystallized from $CH_2Cl_2$/light petroleum.

Compound **4**: $^1$H NMR (300 MHz, $CDCl_3$): δ -1.61 (s, 1 H, NH), -1.55 (s, 1 H, NH), 2.54-2.61 (m, 1 H, $2^3$-H), 2.71-2.76 (m, 1 H, $2^3$-H), 2.80-2.85 (m, 1 H, $2^1$-H), 3.17-3.21 (m, 1 H, $2^2$-H), 5.42-5.45 (m, 1 H, $2^4$-H), 6.09-6.13 (m, 1 H, 2-H), 7.69-7.94 (m, 12 H, Ph-*m*,*p*-H), 8.00-8.22 (m, 7 H, Ph-*o*-H),

8.34 (d, *J* = 5.0 Hz, 1 H, *β*-H), 8.38 (d, *J* = 7.9 Hz, 1 H, Ph-*o*-H), 8.42-8.45 (m, 3 H, *β*-H), 8.59 (d, *J* = 5.0 Hz, 1 H, *β*-H), 8.62 (d, *J* = 5.0 Hz, 1 H, *β*-H). $^{13}$C NMR (125 MHz; $CDCl_3$): δ 27.0, 29.6, 49.3, 111.5, 112.4, 116.2, 121.6, 123.2, 123.3, 124.5, 125.2, 126.8, 126.9, 127.1, 127.5, 127.8, 127.95, 127.98, 128.07, 128.12, 128.2, 128.27, 128.34, 128.6, 128.8, 128.9, 129.0, 129.3, 129.4, 131.5, 132.6, 132.7, 133.1, 133.8, 133.9, 134.1, 134.2, 134.26, 134.30, 134.5, 134.6, 134.8, 135.8, 136.1, 140.0, 140.1, 140.9, 141.1, 141.6, 141.7, 142.0, 153.5, 155.7, 156.5. UV-Vis $\lambda_{max}(CH_2Cl_2)$/nm: 421 (log ε 5.4), 520 (4.2), 550 (3.9), 611 (3.7), 667 (4.3). HRMS (MALDI-TOF): *m/z* calculated for $C_{50}H_{34}N_6$ $(M)^{+\bullet}$ 718.2840, found 718.2844.

Compound **5**: $^1$H NMR (500 MHz, $CDCl_3$): δ -2.68 (s, 2 H, NH), 2.24-2.27 (m, 2 H, $2^3$-H), 2.90-2.98 (m, 1 H, $2^4$-H), 3.08-3.20 (m, 1 H, $2^4$-H), 3.42-3.44 (m, 1 H, $2^2$-H), 4.07 (br s, 1 H, $2^1$-H), 7.71-7.80 (m, 10 H, Ph-*m*,*p*-H), 7.87-7.90 (m, 2 H, Ph-*m*,*p*-H), 7.96 (d, *J* = 7.5 Hz, 1 H, Ph-*o*-H), 8.03 (d, *J* = 7.9 Hz, 1 H, Ph-*o*-H), 8.17-8.20 (m, 5 H, Ph-*o*-H), 8.61-8.63 (m, 1 H, Ph-*o*-H), 8.66-8.73 and 8.78-8.81 (2m, 6 H, *β*-H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 22.6, 23.0, 29.2, 30.6, 117.8, 118.3, 118.8, 120.1, 120.6, 120.9; 127.4, 127.5, 127.8, 127.9, 128.0, 128.6, 128.9, 129.1, 133.0, 134.3, 134.4, 134.6, 134.7, 134.8, 141.2, 141.6, 141.7, 142.0. UV-Vis $\lambda_{max}$ $(CH_2Cl_2)$/nm: 418 (log ε 5.6), 515 (4.3), 549 (3.7), 594 (3.6), 653 (3.4). HRMS (MALDI-TOF): *m/z* calculated for $C_{50}H_{34}N_6$ $(M)^{+\bullet}$ 718.2840, found 718.2844.

**Benzo[*b*]porphyrin-$2^1$,$2^2$-dicarbonitrile 6**

A mixture of adducts **4** and **5** (50 mg, 69.6 μmol) and DDQ (174.4 mg, 768 μmol, 11 equiv) was refluxed in toluene (5 mL) for 48h. The reaction mixture was filtered through a short plug column of Celite®-545, washed with a saturated solution of $NaHCO_3$ and dried ($Na_2SO_4$). The solvent was removed and the crude was submitted to flash chromatography (silica gel) with a mixture of light petroleum and $CH_2Cl_2$ (1:2) as the eluent. After crystallization from $CH_2Cl_2$/light petroleum, the desired compound **6** was obtained in 71% yield (35.1 mg). $^1$H NMR (300 MHz, $CDCl_3$): δ -2.31 (s, 2 H, NH), 7.41 (d, *J* = 8.4 Hz, 1 H, $2^3$-H or $2^4$-H), 7.68 (d, *J* = 8.4 Hz, 1 H, $2^3$-H or $2^4$-H), 7.76-7.95 (m, 12 H, Ph-*m*,*p*-H), 8.20-8.23 (m, 2 H, Ph-*o*-H), 8.26-8.29 (m, 4 H, Ph-*o*-H), 8.38-8.40 (m, 2 H, Ph-*o*-H), 8.65 (AB, *J* = 5.0 Hz, 2 H, 12,13-H), 8.77 (d, *J* = 5.0 Hz, 1 H, *β*-H), 8.82 (d, *J* = 5.0 Hz, 1 H, *β*-H), 8.89 (d, *J* = 5.0 Hz, 1 H, *β*-H), 8.96 (d, *J* = 5.0 Hz, 1 H, *β*-H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 114.3, 114.8, 117.1, 118.5, 119.9, 120.8, 121.7; 127.0, 127.1, 127.9, 128.0, 128.09, 128.13, 128.2, 128.4, 128.7, 128.8, 128.9, 129.1, 129.2, 129.3, 129.4, 137.9, 134.3, 134.5, 134.6, 134.8, 135.3, 138.5, 138.7, 139.1, 139.5, 139.7, 140.5, 141.1, 141.26, 141.32, 144.0, 145.9, 155.7, 156.3. UV-Vis

$\lambda_{max}(CH_2Cl_2)$/nm: 441 (log ε 5.6), 536 (4.3), 614 (3.8), 677 (3.7). HRMS (MALDI-TOF): *m/z* calculated for $C_{50}H_{30}N_6$ $(M)^{+\bullet}$ 714.2527, found 714.2532.

**Dyad 1a**

A mixture of benzo[*b*]porphyrin-2[1],2[2]-dicarbonitrile **6** (26.7 mg, 37.4 μmol), 4-*tert*-butylphthalonitrile (82.4 mg, 447 μmol, 12 equiv) and $ZnCl_2$ (55.6 mg, 303 μmol, 9 equiv) was stirred at 145 ºC in a mixture of *o*-dichlorobenzene and DMAE (1:1, 2 mL) under inert atmosphere for 18h. After precipitation of the reaction mixture with MeOH/$H_2O$ (3:1), the obtained solid was filtered through a short plug column of Celite®-545, washed with water and MeOH, dried under reduced pressure and the crude was taken up in $CH_2Cl_2$. The desired dyad **1a** was then separated from the symmetrical phthalocyanine, tetra-*tert*-butylphthalocyaninatozinc(II) (**Zn$^t$Bu$_4$Pc**),[2] by flash chromatography (silica gel) with a mixture of light petroleum and THF (4:1) as the eluent. After purification by preparative thin-layer chromatography, using the same eluent, and crystallization from $CH_2Cl_2$/light petroleum, the expected dyad **1a** was obtained in 32% yield (16.7 mg) and **Zn$^t$Bu$_4$Pc** in 45% yield (40.3 mg). Data for dyad **1a**: $^1$H NMR (300 MHz, THF-$d_8$): δ 1.06-1.72 (m, 27 H, $C(CH_3)_3$), 6.06-6.20 (m, 2 H, 20-Ph-*o*-H), 6.44-6.54 (m, 3 H, 20-Ph-*m*,*p*-H), 7.53-8.31 (m, 14 H, 1'-H, 2'-H, 3 Pc-*β*-H and 9 5,10,15-Ph-*m*,*p*-H), 8.40-8.49 and 8.62-8.79 (2m, 6 H, 20-Ph-*o*-H), 8.87 (d, *J* = 4.6 Hz, 1 H, Por-*β*-H), 8.92 (d, *J* = 4.6 Hz, 1 H, Por-*β*-H), 9.12 (d, *J* = 4.6 Hz, 1 H, Por-*β*-H), 9.14-9.55 (m, 9 H, 3 Por-*β*-H and 6 Pc-*α*-H). UV-Vis $\lambda_{max}$(toluene)/nm: 354 (log ε 4.3), 442 (5.1), 621 (4.1), 649 (4.3), 685 (4.8), 709 (5.0). HRMS (MALDI-TOF): *m/z* calculated for $C_{86}H_{64}N_{12}Zn_2$ $(M)^{+\bullet}$ 1392.3954, found 1392.3960.

**Dyad 1b**

Trifluoroacetic acid (0.6 mL) was added dropwise to a vigorously stirred solution of dyad **1a** (10 mg, 7.18 μmol) in $CH_2Cl_2$ (2.4 mL) at room temperature (10 min.). The reaction mixture was then neutralized with diluted $NaHCO_3$, washed with water and dried ($Na_2SO_4$). Dyad **1b** was obtained in 97% yield (9.2 mg) after crystallization from $CH_2Cl_2$/light petroleum. UV-Vis $\lambda_{max}$(toluene)/nm: 356 (log ε 4.5), 441 (5.1), 538 (4.0), 626 (4.1), 704 (4.8). HRMS (MALDI-TOF): *m/z* calculated for $C_{86}H_{66}N_{12}Zn$ $(M)^{+\bullet}$ 1330.4819, found 1330.4824.

References:

1. H. J. Callot, *Tetrahedron*, 1973, **29**, 899-901.
2. S. Gaspard, Ph. Maillard, *Tetrahedron*, 1987, **43**, 1083-1090.

**Adduct 4**

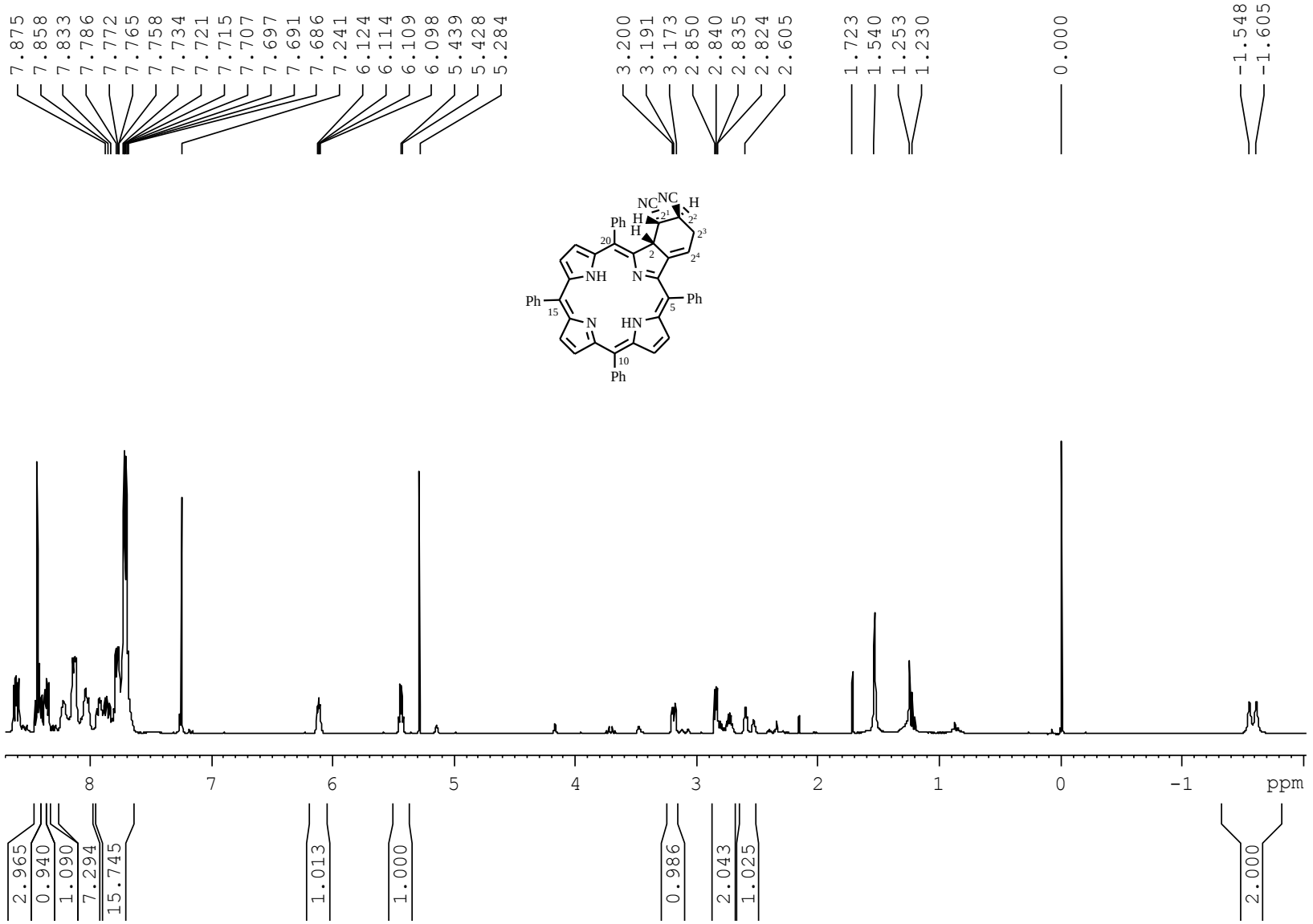


**Chart S1** – $^{1}$H NMR spectrum of compound **4** in $CDCl_3$

**Adduct 4**

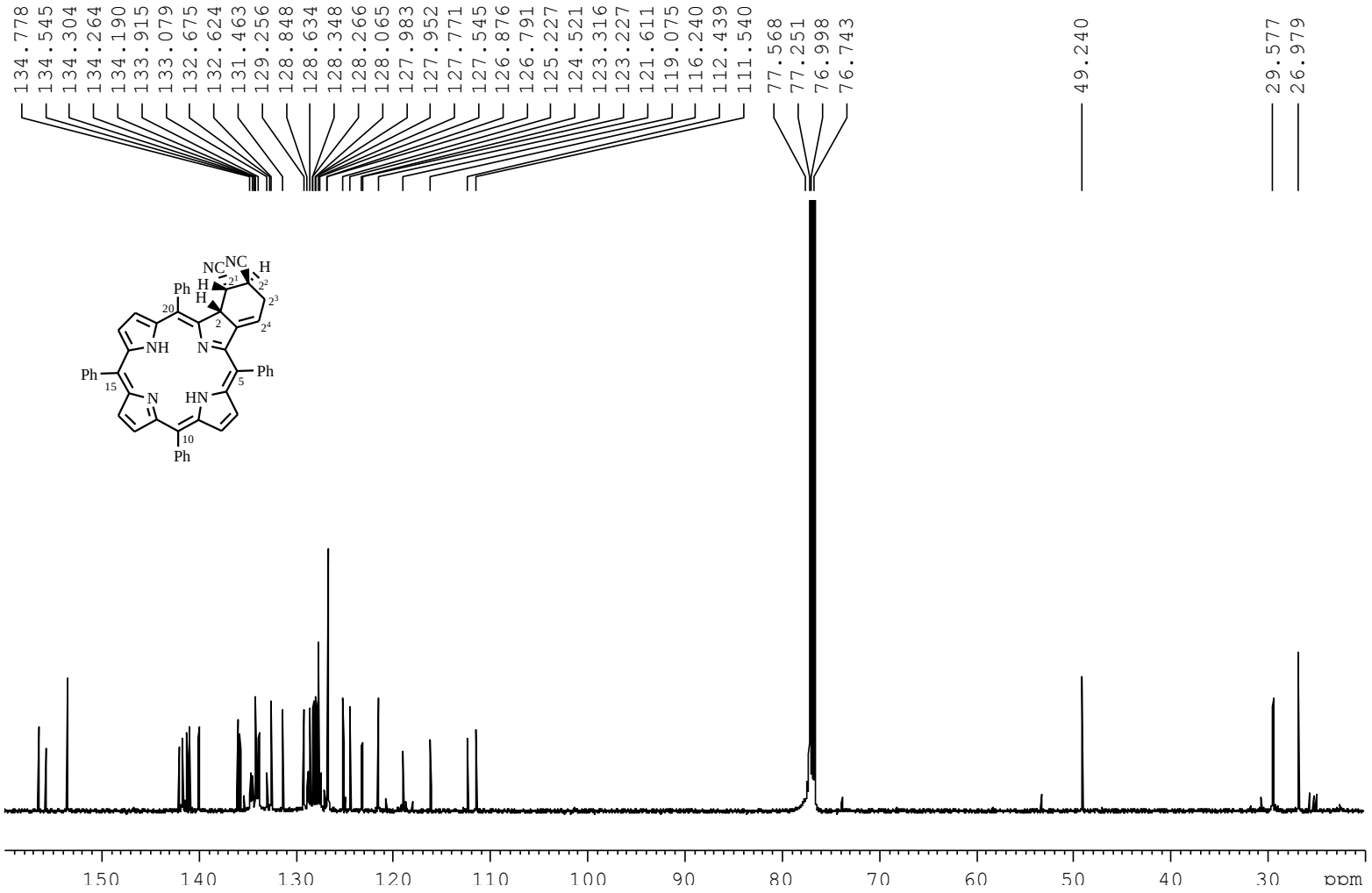


**Chart S2** – $^{13}C$ NMR spectrum of compound **4** in $CDCl_3$.

**Adduct 4**

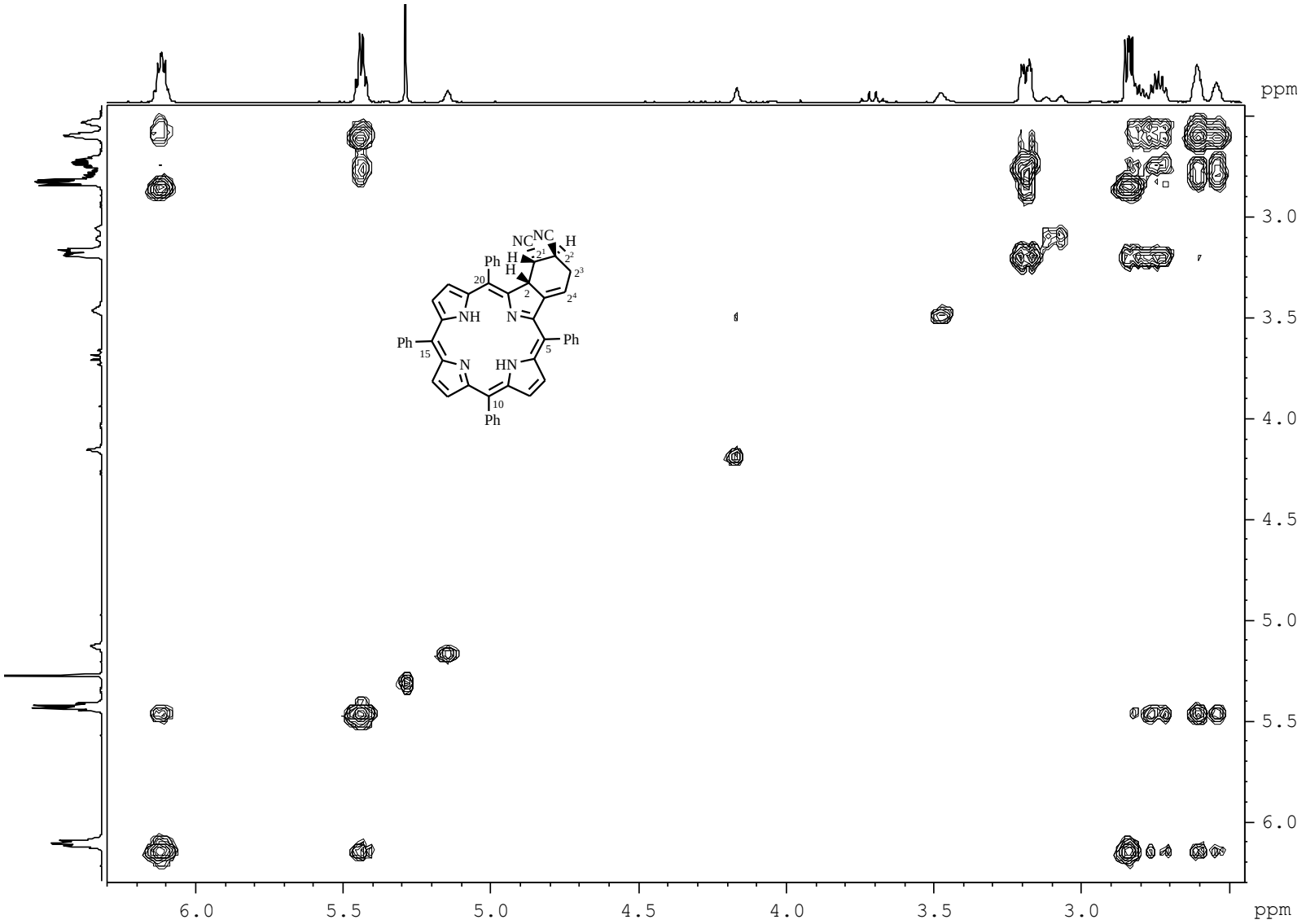


**Chart S3** – COSY spectrum of compound **4** in $CDCl_3$.

**Adduct 4**

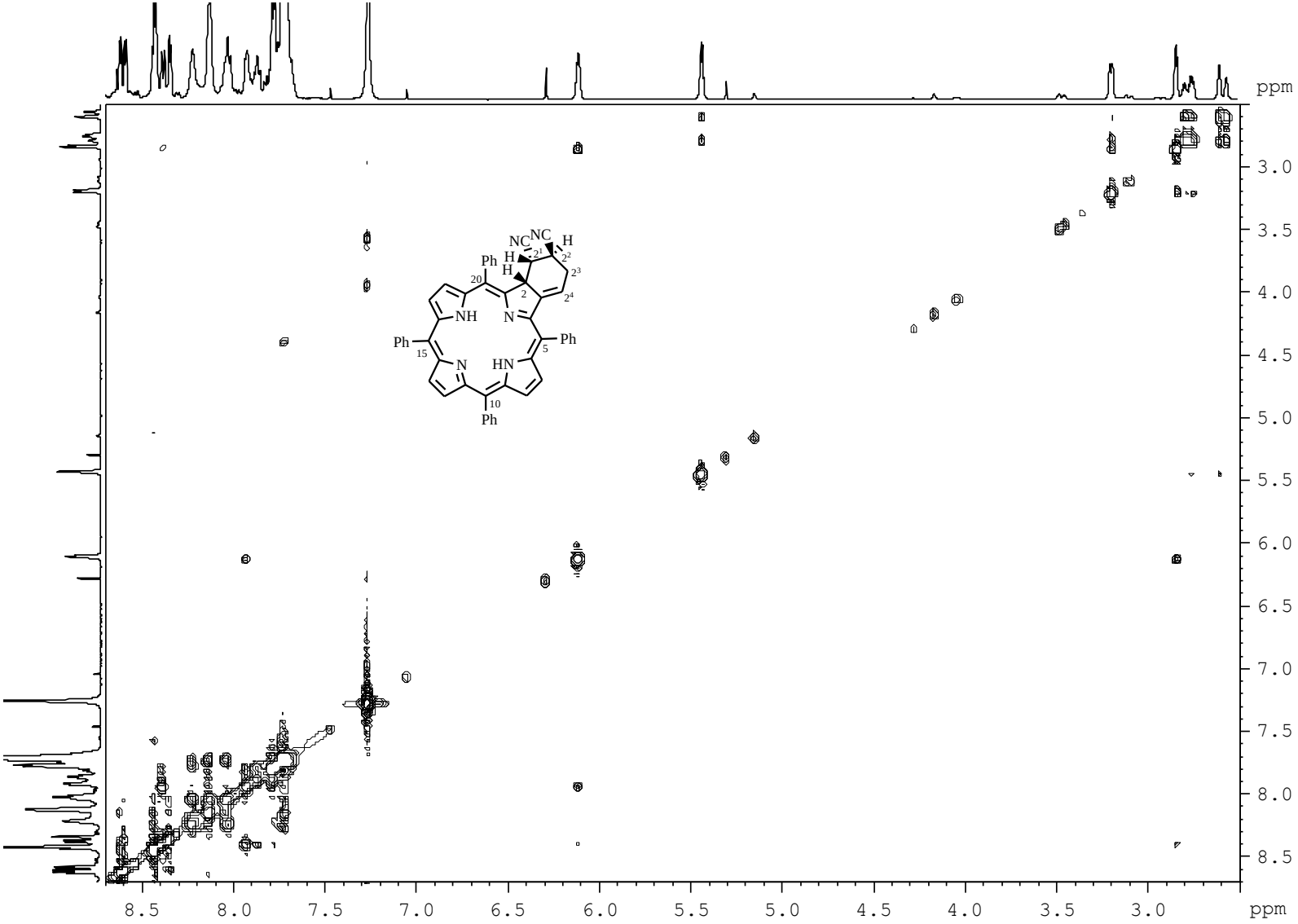


**Chart S4**– NOESY spectrum of compound **4** in $CDCl_3$.

**Adduct 4**

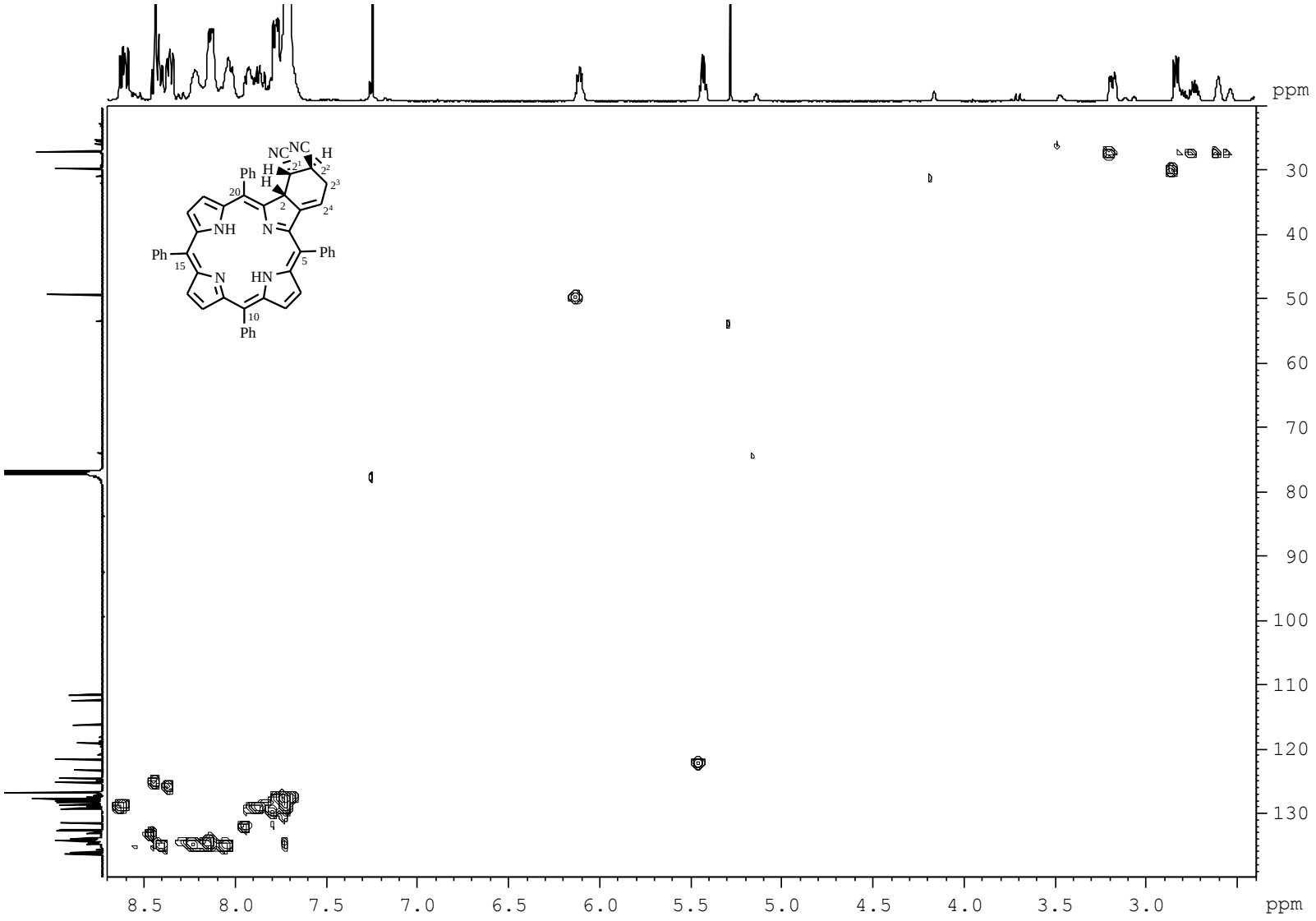


**Chart S5** – HSQC spectrum of compound **4** in $CDCl_3$.

**Adduct 4**

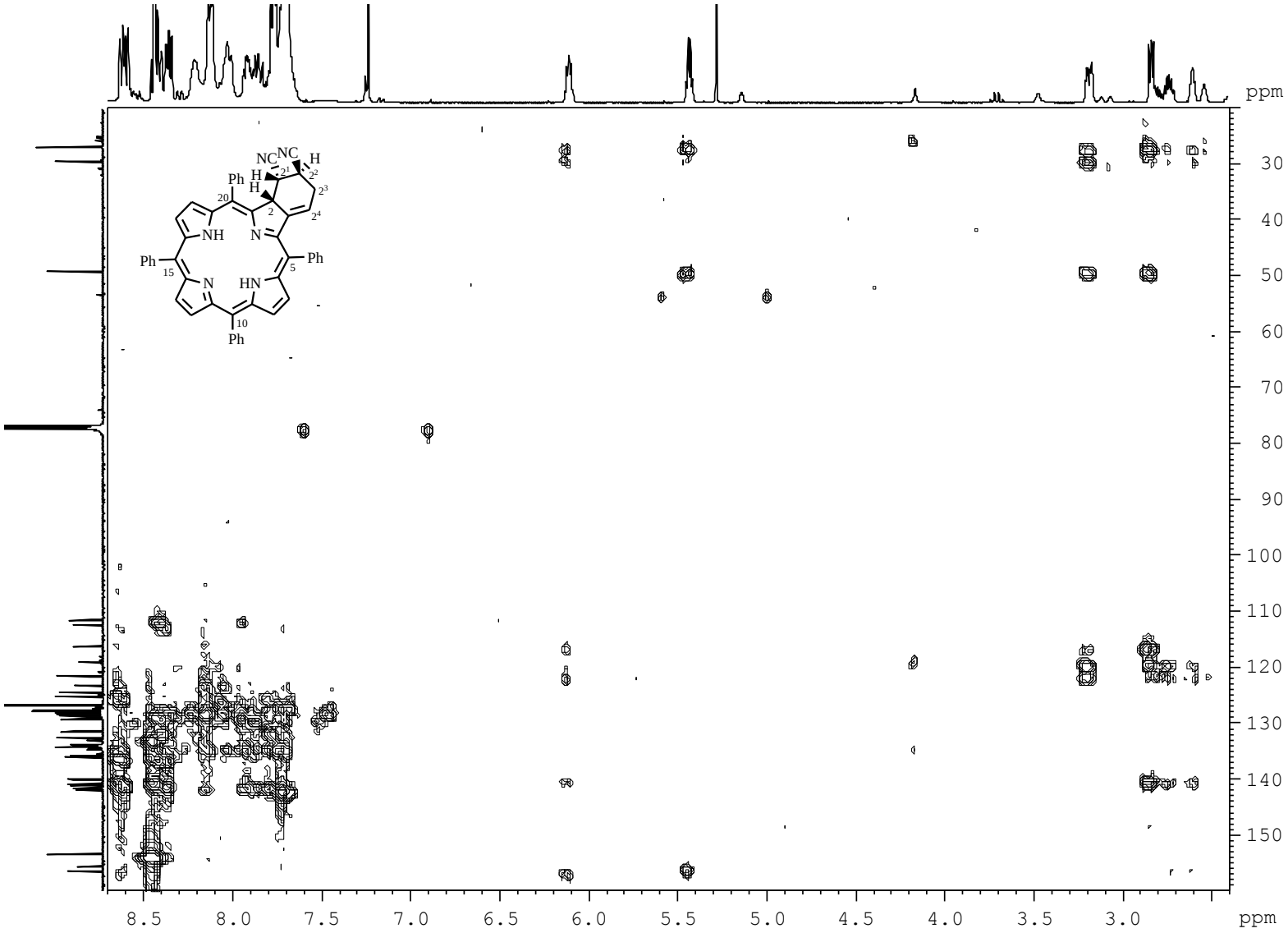


**Chart S6** – HMBC spectrum of compound **4** in $CDCl_3$.

**Adduct 4**

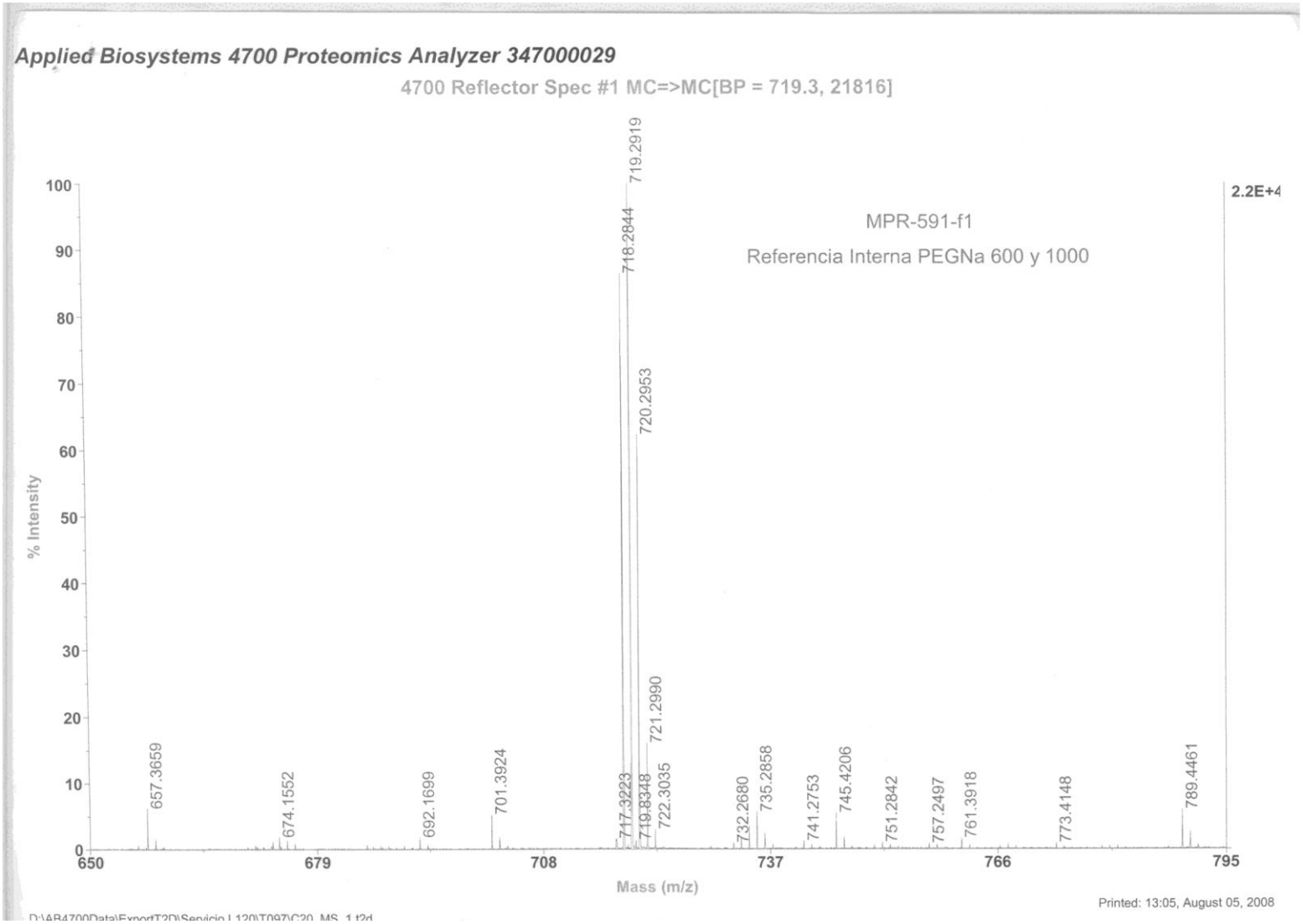


**Chart S7** – HRMS (MALDI-TOF) of adduct **4**.

**Adduct 5**

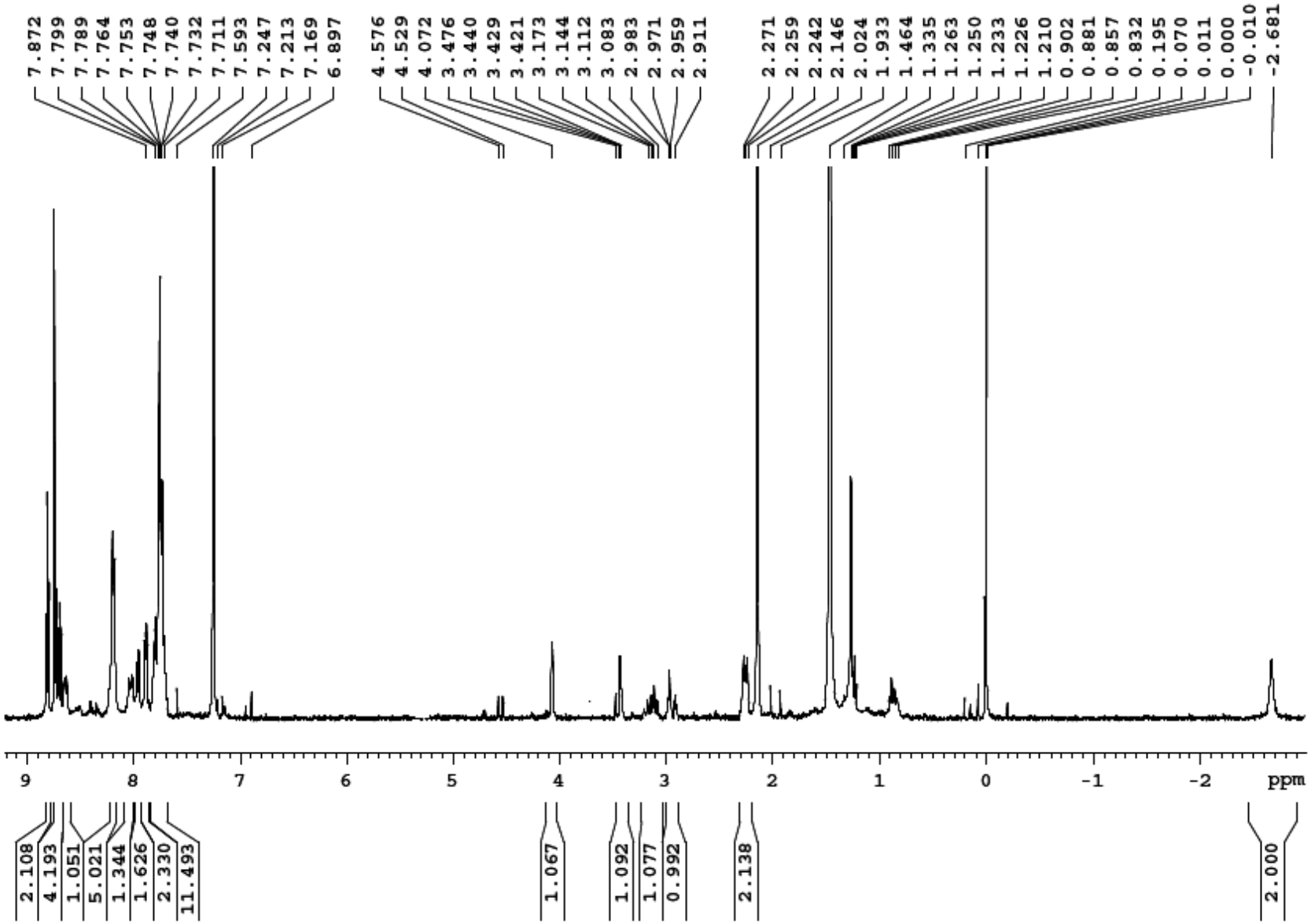


**Chart S2** – $^{1}$H NMR spectrum of compound **5** in $CDCl_3$.

**Adduct 5**

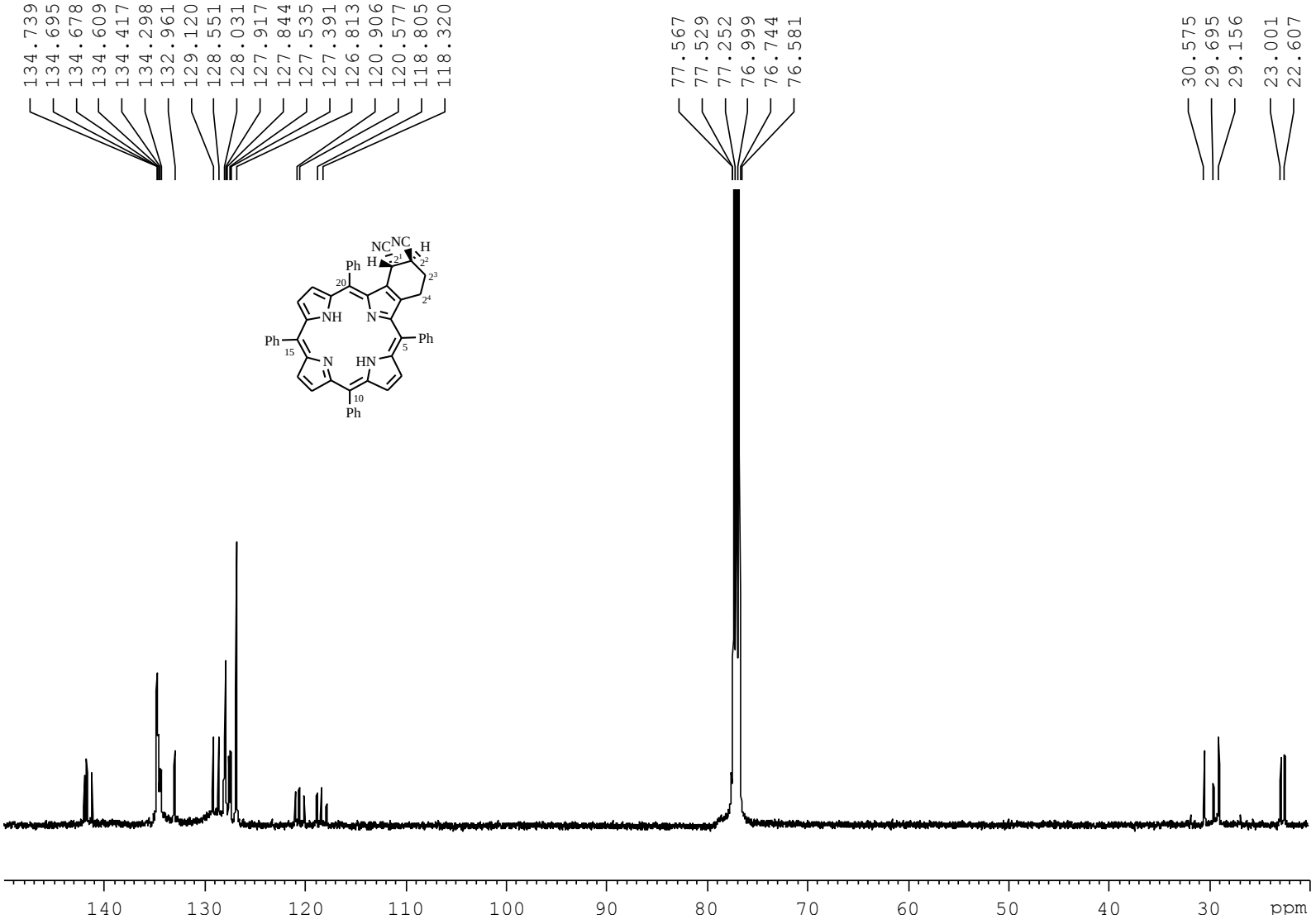


**Chart S9** – $^{13}C$ NMR spectrum of compound **5** in $CDCl_3$.

**Adduct 5**

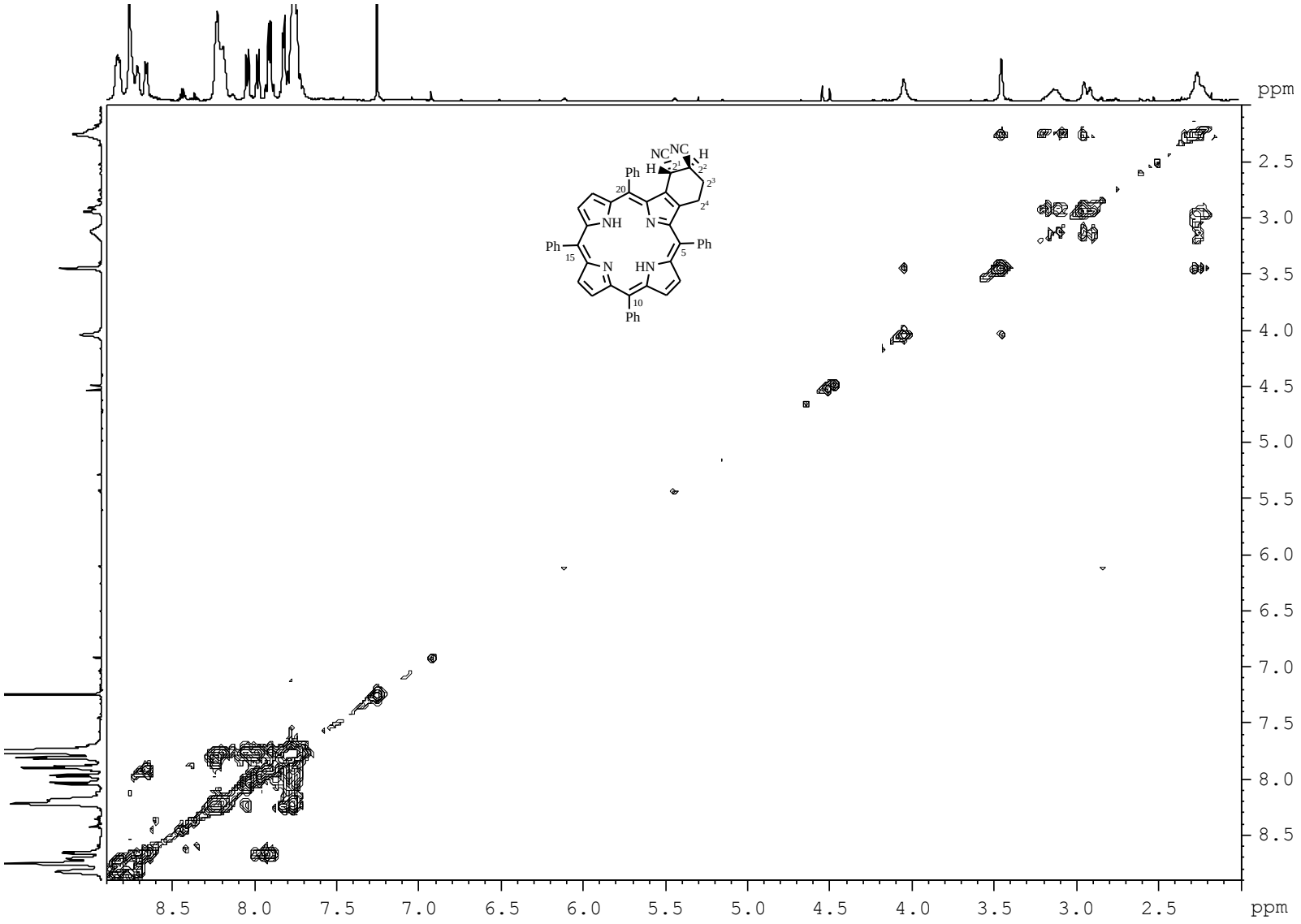


**Chart S30** – COSY spectrum of compound **5** in $CDCl_3$.

**Adduct 5**

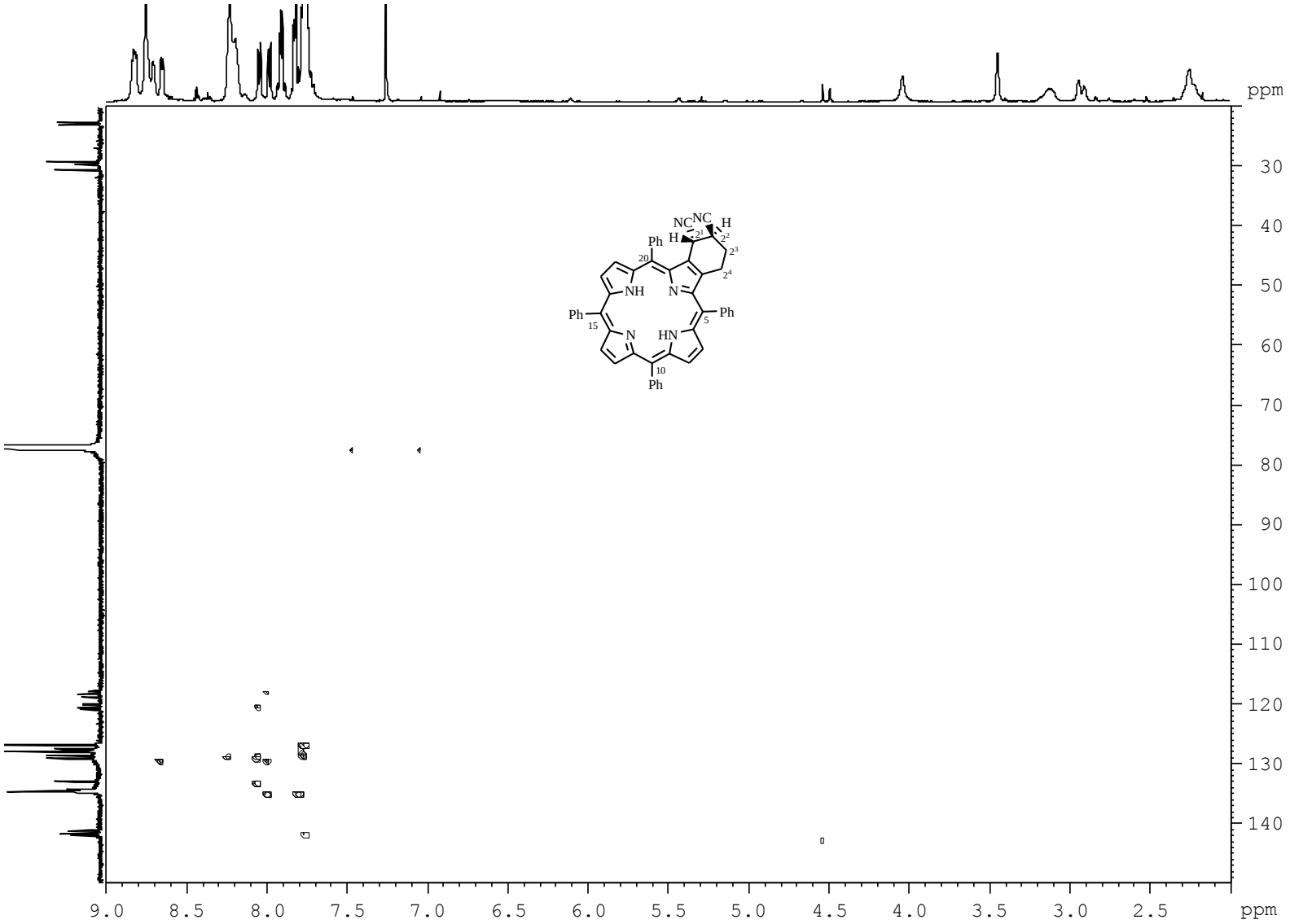


**Chart S41** – HSQC spectrum of compound **5** in $CDCl_3$.

**Adduct 5**

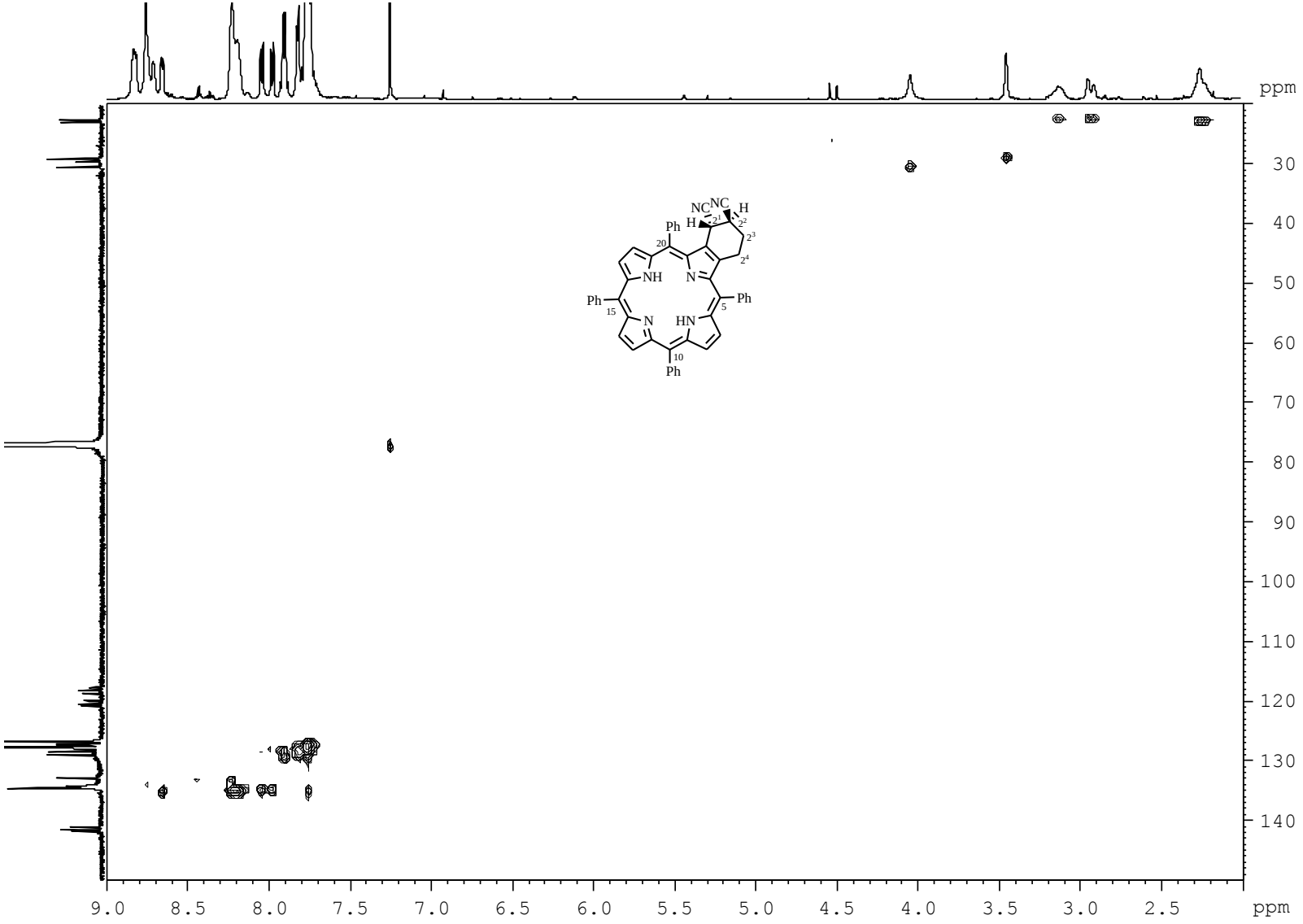


**Chart S52** – HMBC spectrum of compound **5** in $CDCl_3$.

**Adduct 5**

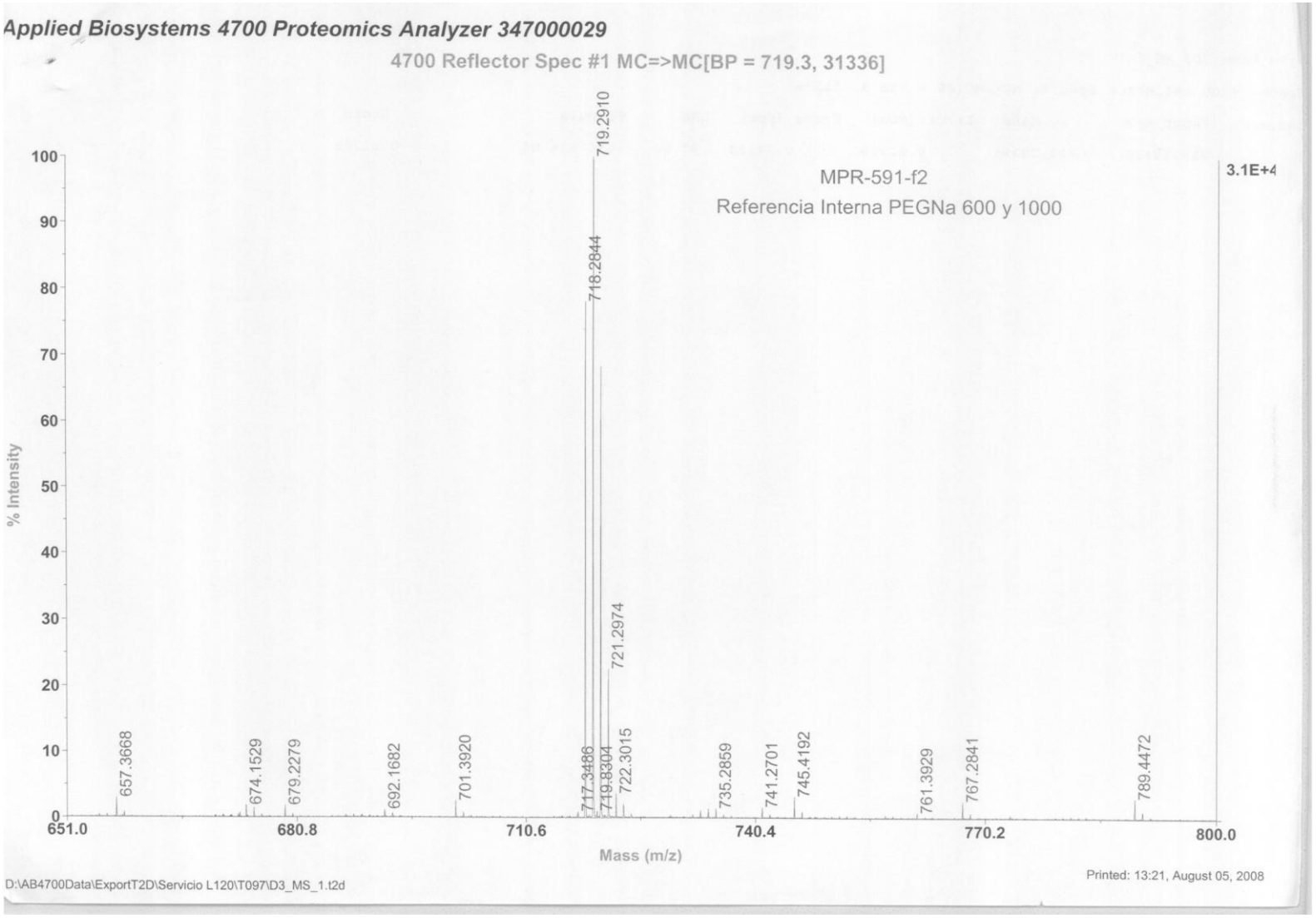


**Chart S63** – HRMS (MALDI-TOF) of adduct **5**.

**Benzo[*b*]porphyrin-2$^{1}$,2$^{2}$-dicarbonitrile 6**

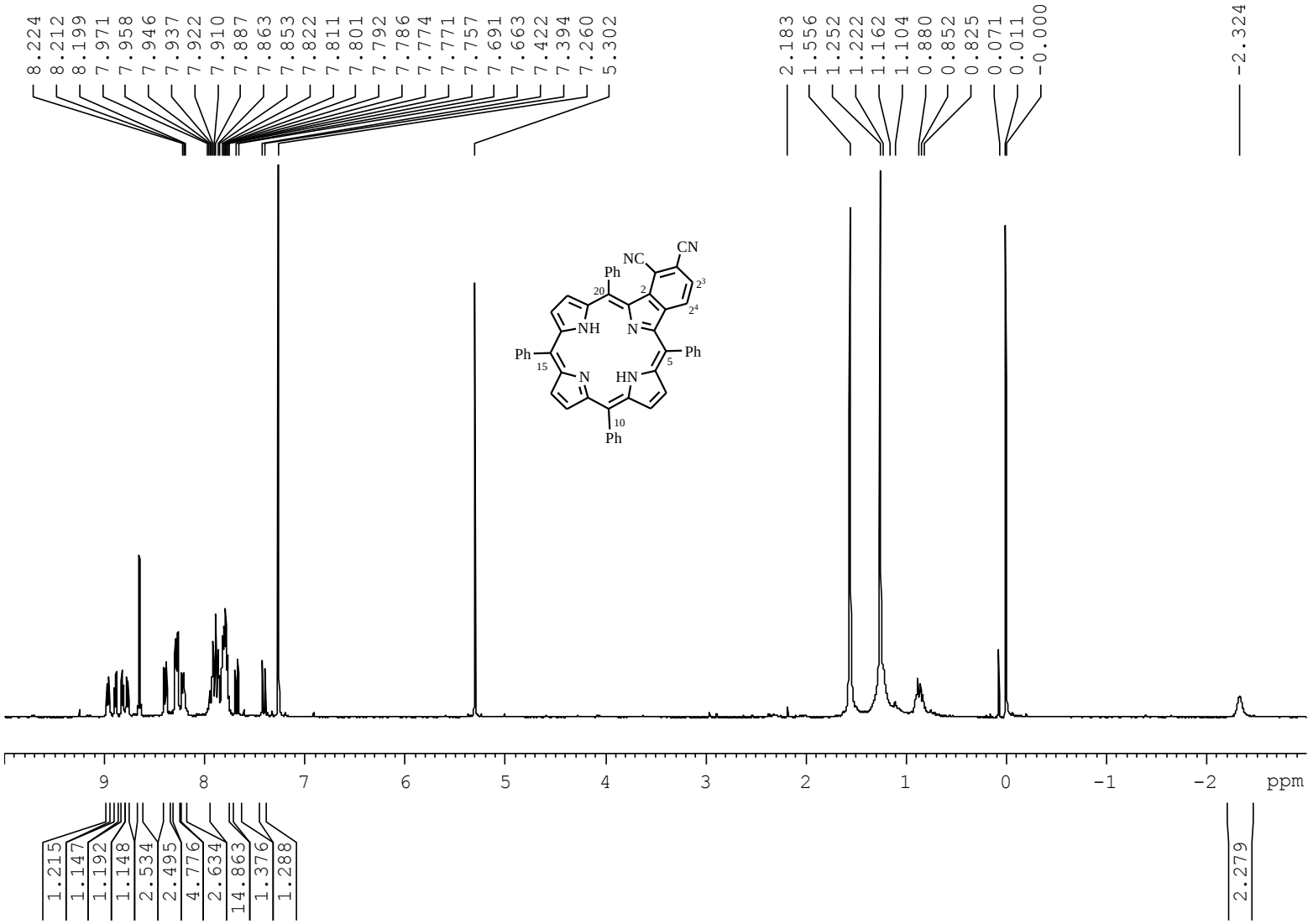


**Chart S74** – $^{1}$H NMR spectrum of compound **6** in $CDCl_3$.

**Benzo[*b*]porphyrin-2$^{1}$,2$^{2}$-dicarbonitrile 6**

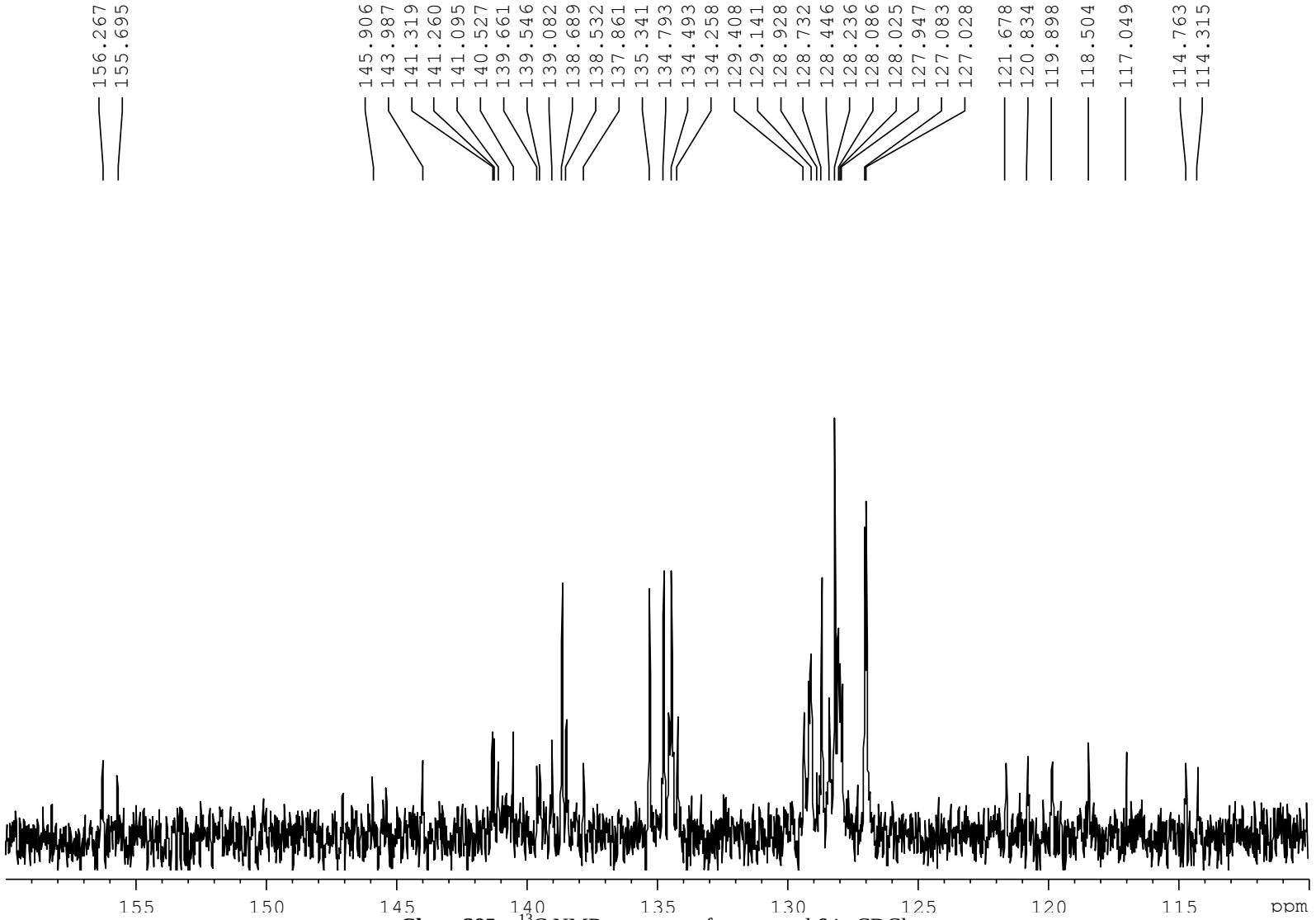


**Chart S85** – $^{13}$C NMR spectrum of compound **6** in $CDCl_3$.

**Benzo[*b*]porphyrin-$2^1$,$2^2$-dicarbonitrile 6**

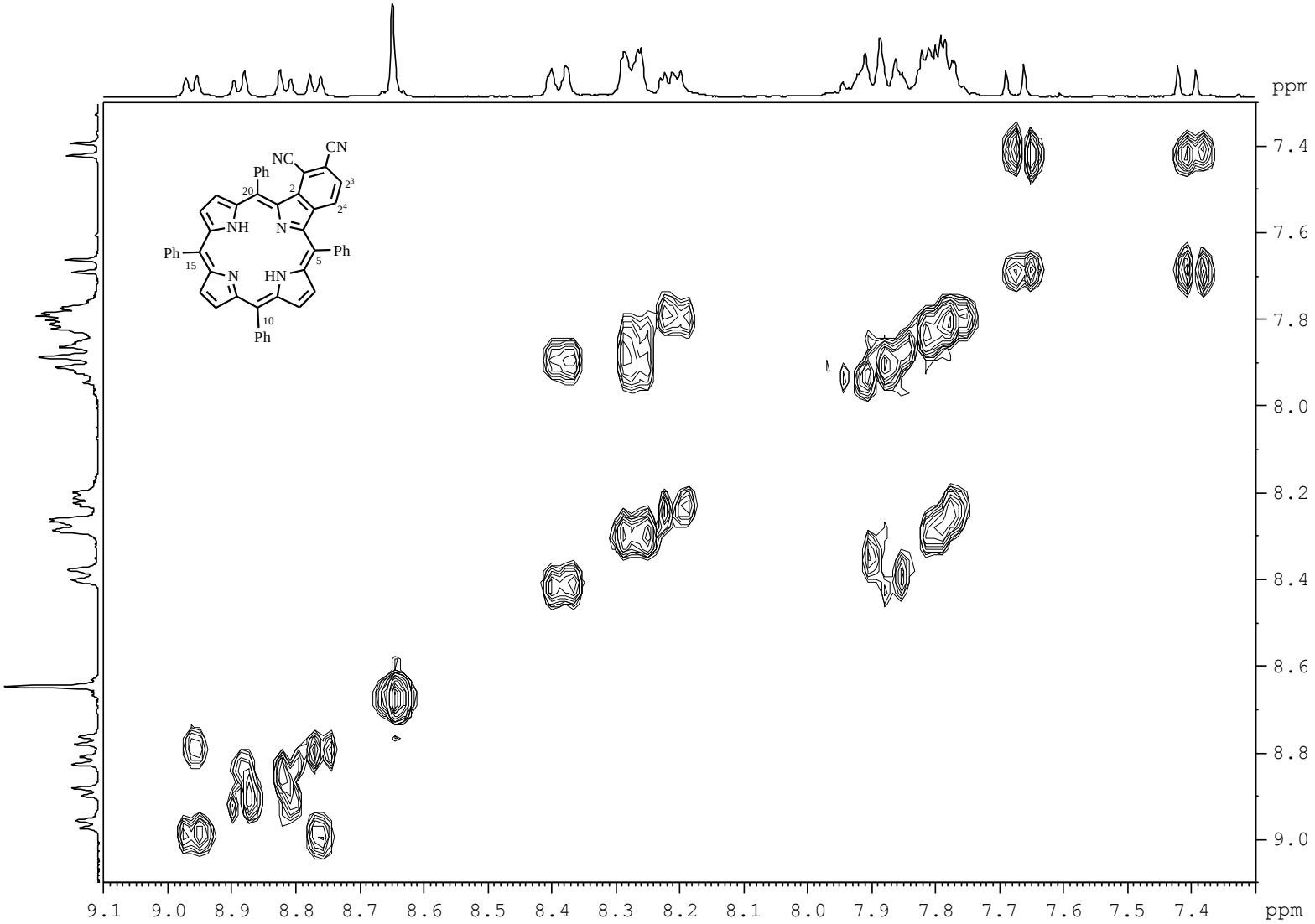


**Chart S96** – COSY spectrum of compound **6** in $CDCl_3$.

**Benzo[*b*]porphyrin-$2^1$,$2^2$-dicarbonitrile 6**

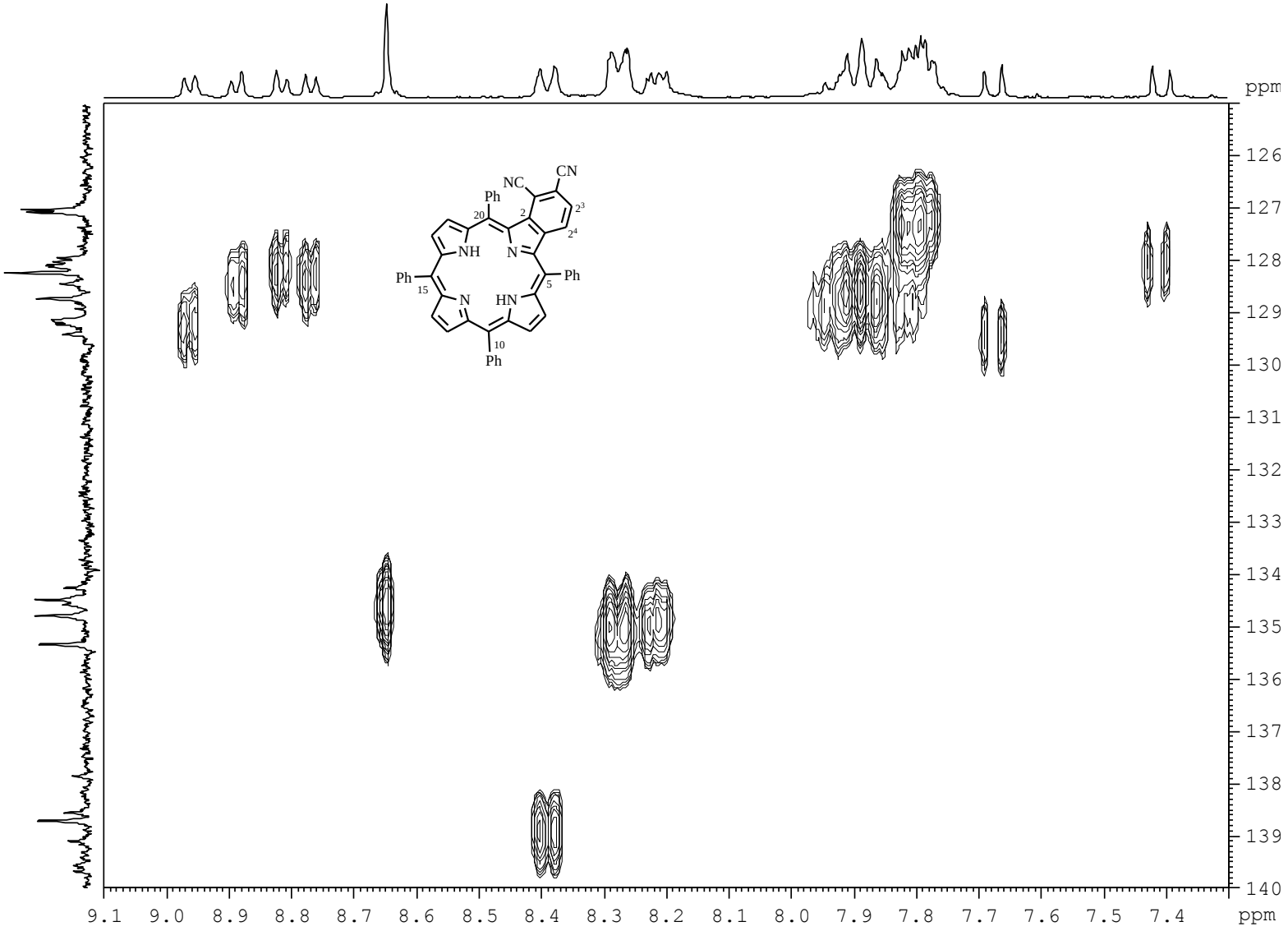


**Chart S107** – HSQC spectrum of compound **6** in $CDCl_3$.

**Benzo[*b*]porphyrin-2$^1$,2$^2$-dicarbonitrile 6**

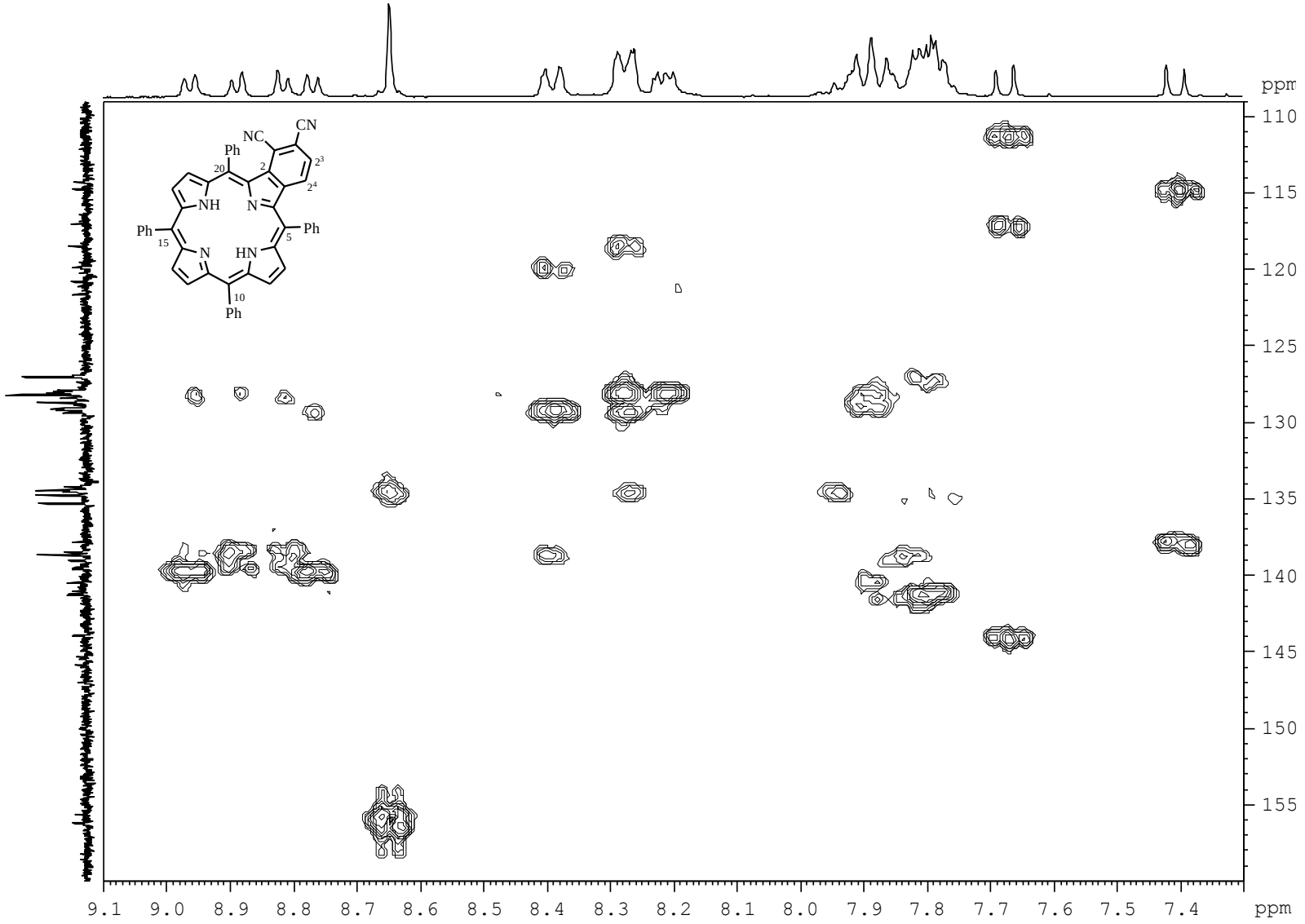


**Chart S118** – HMBC spectrum of compound **6** in $CDCl_3$.

**Benzo[*b*]porphyrin-2[1],2[2]-dicarbonitrile 6**

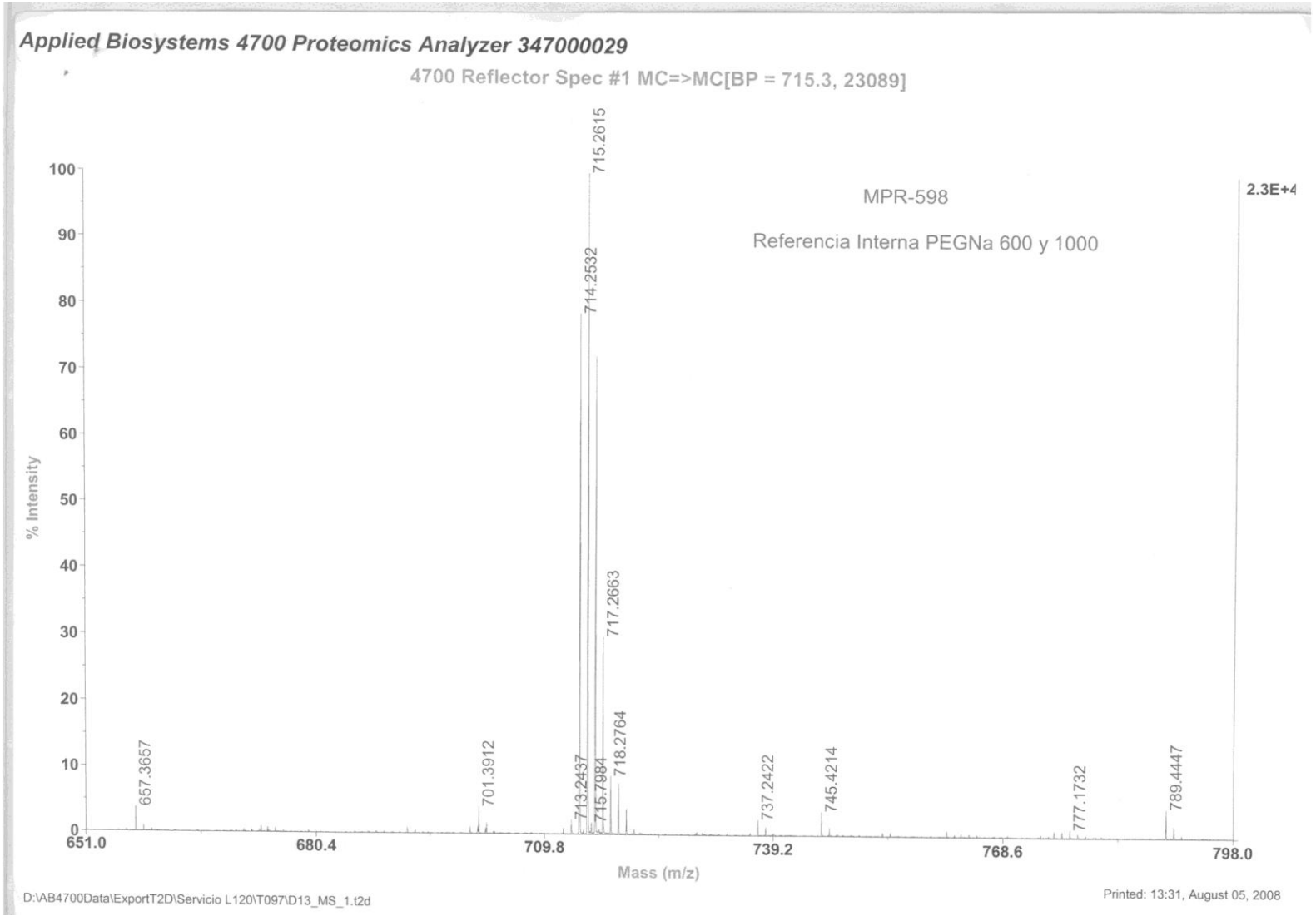


**Chart S129** – HRMS (MALDI-TOF) of fused-porphyrinylphthalonitrile **6**.

**Dyad 1a**

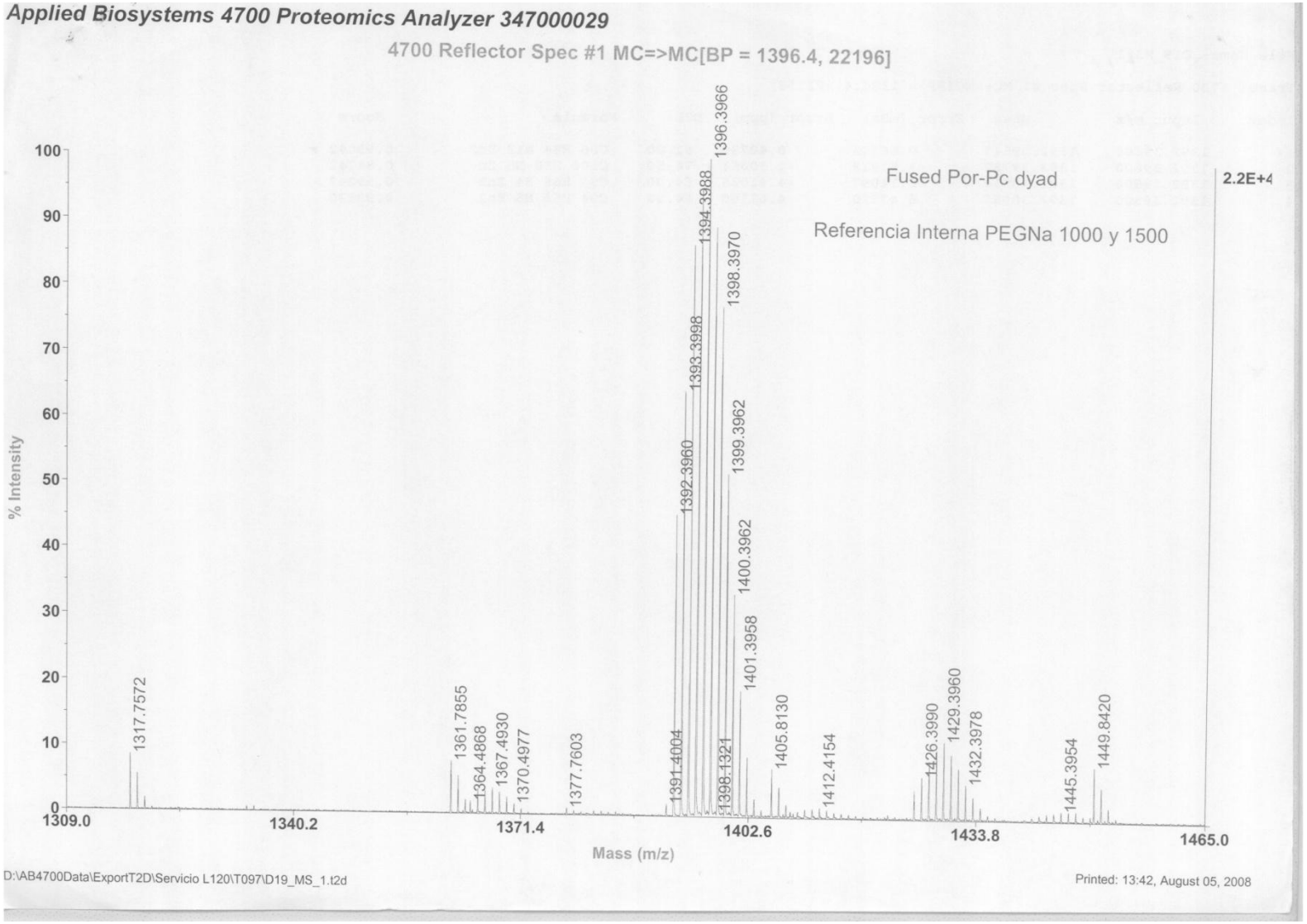


**Chart S20** – HRMS (MALDI-TOF) of dyad **1a**.

## Dyad 1b

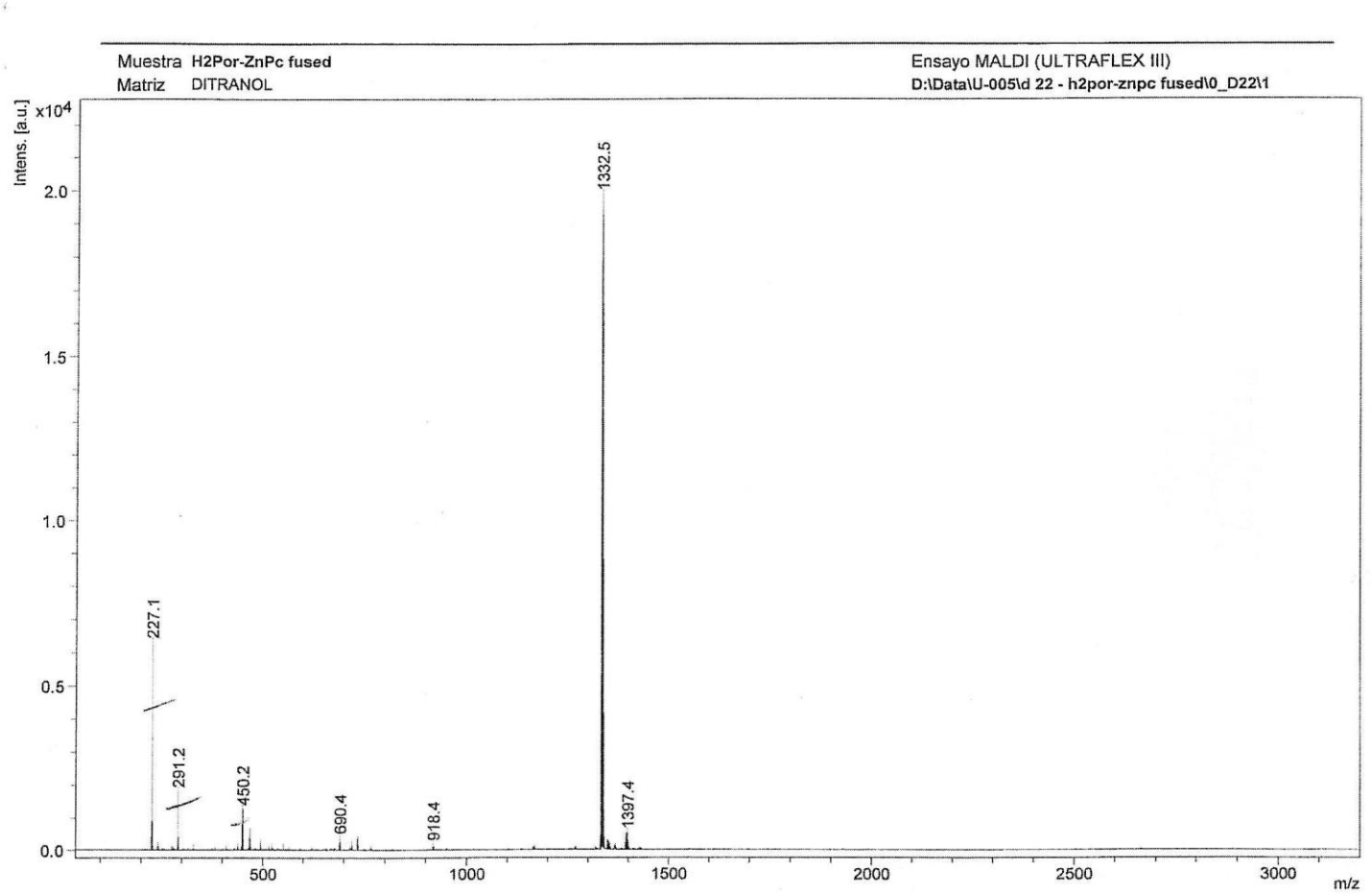


**Chart S21** – HRMS (MALDI-TOF) of dyad **1b**.

**UV-Vis spectra of dyads 1a and 1b and references**

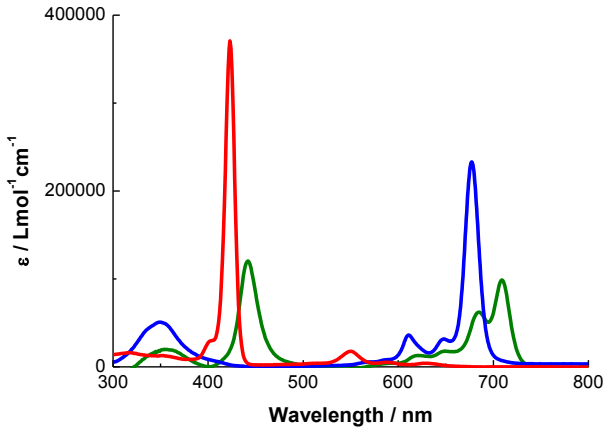


**Chart S22-** UV-Vis spectra of dyad **1a** (green), **ZnTPP** (red) and **Zn*t*Bu$_4$Pc** (blue), all in toluene.

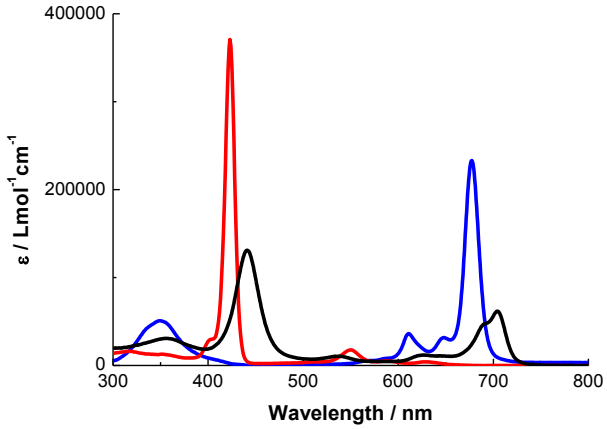


**Chart S23-** UV-Vis spectra of dyad **1b** (black), **ZnTPP** (red) and **Zn*t*Bu$_4$Pc** (blue), all in toluene.

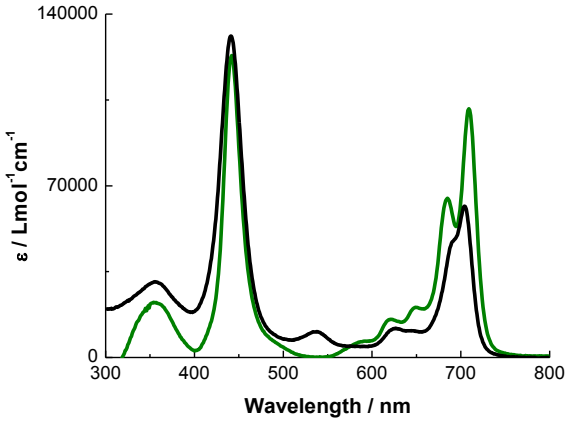


**Chart 24 -** UV-Vis spectra of dyad **1a** (green) and **1b** (back) in toluene.

## Photophysical data

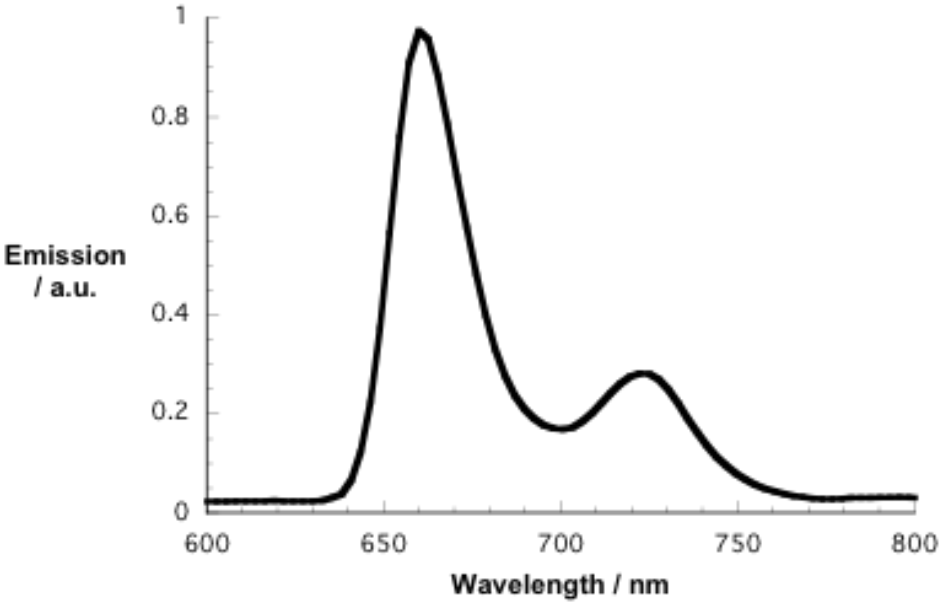


Figure S1: Room temperature fluorescence spectrum of **$H_2$TPP** in toluene – 420 nm excitation wavelength.

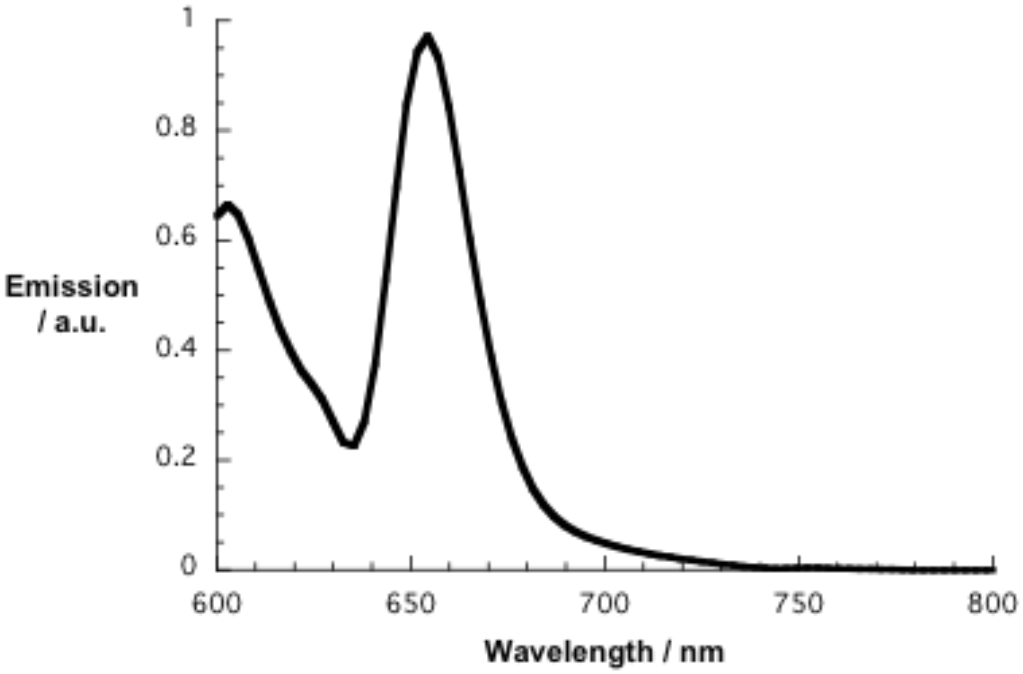


Figure S2: Room temperature fluorescence spectrum of **ZnTPP** in toluene – 420 nm excitation wavelength.

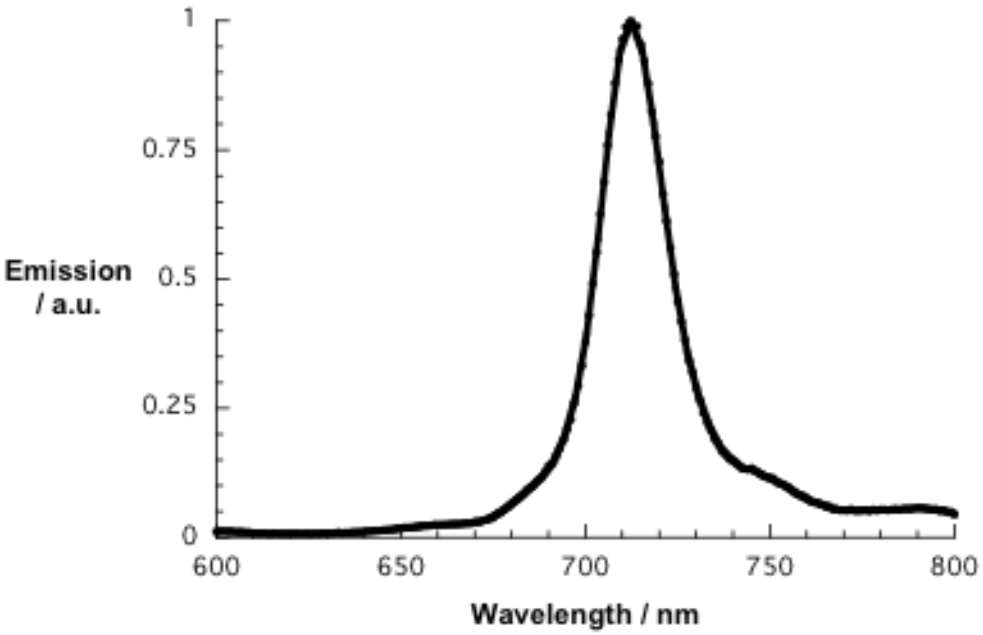


Figure S3: Room temperature fluorescence spectrum of **Zn$^{t}$Bu$_4$Pc** in toluene – 600 nm excitation wavelength.

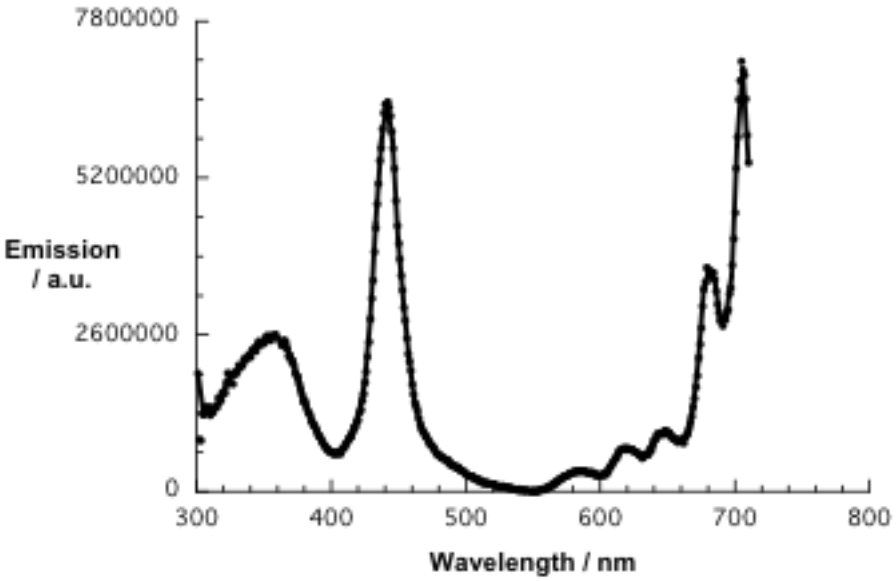


Figure S4: Excitation spectrum of **1a** in toluene with emission wavelength of 720 nm.

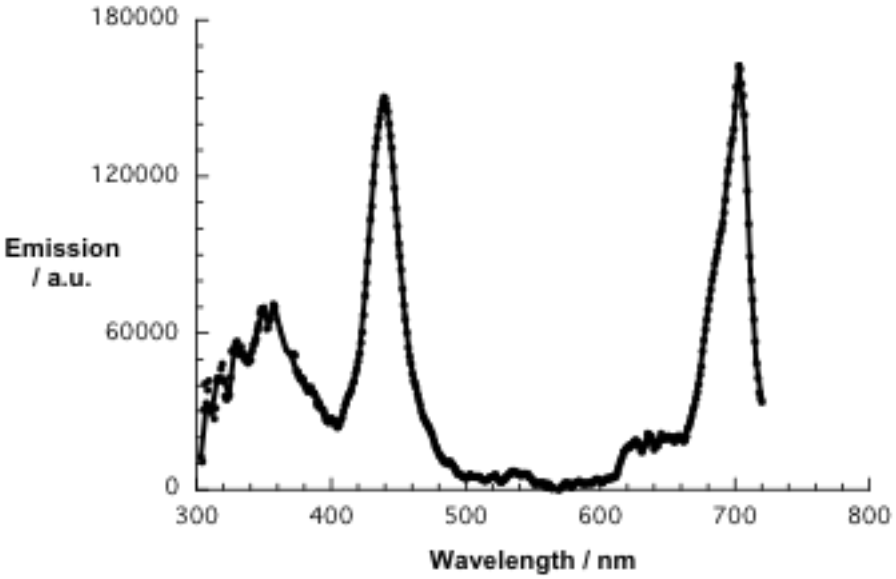


Figure S5: Excitation spectrum of **1b** in toluene with emission wavelength of 720 nm.

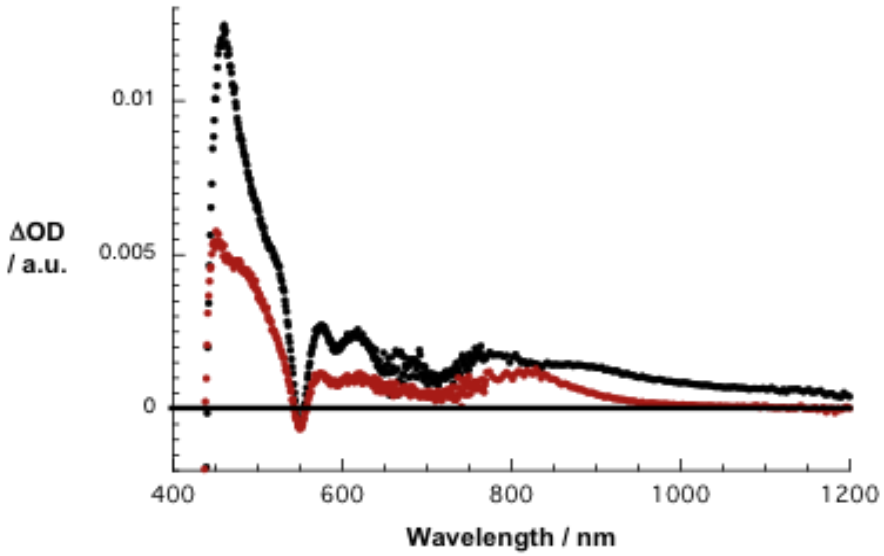


Figure S6: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (420 nm) of **ZnTPP** in toluene with 2 (black spectrum) and 3000 ps (red spectrum) time delay.

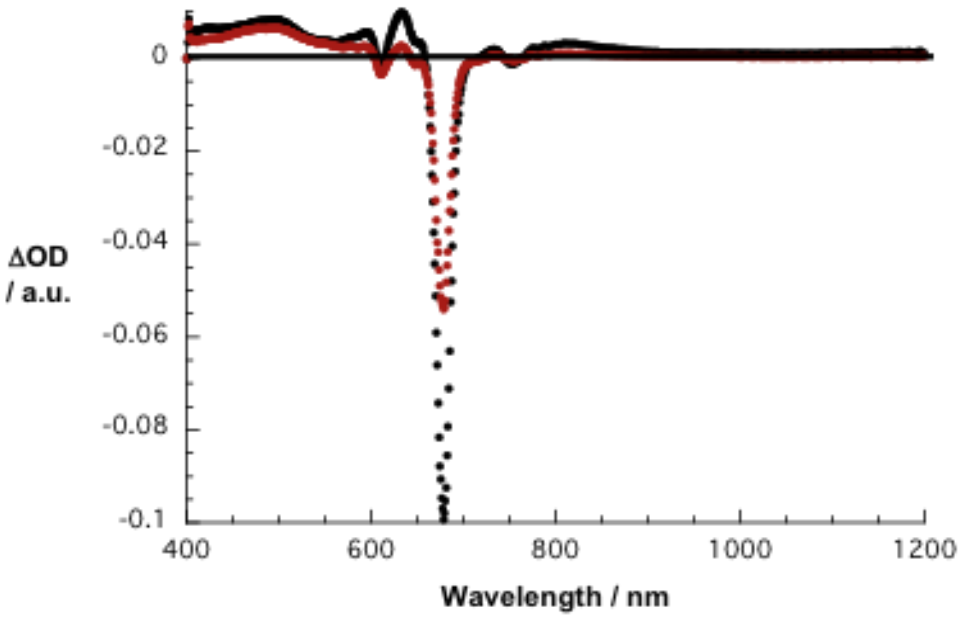


Figure S7: Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **Zn$^t$Bu$_4$Pc** in toluene with 2 (black spectrum) and 3000 ps (red spectrum) time delay.

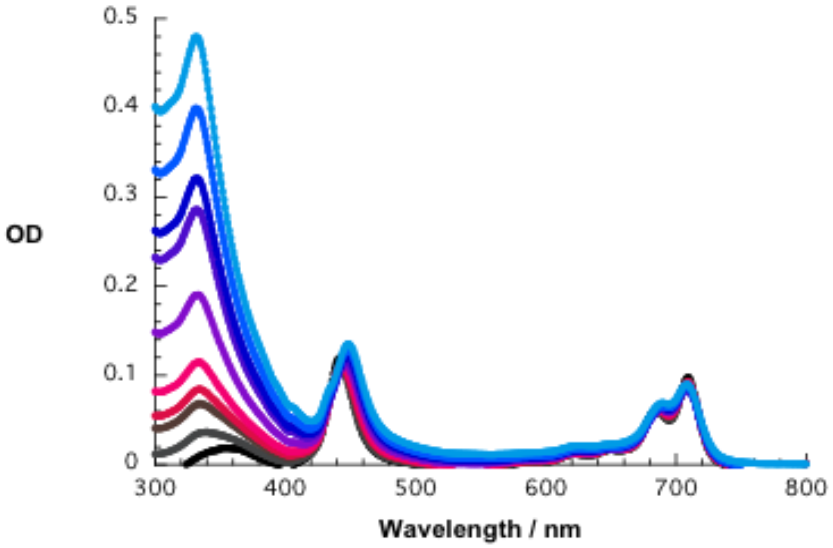


Figure S8: Absorption spectra of **1a** (1 x $10^{-6}$ M) in toluene with variable concentrations of **2** (0; 6.9 x $10^{-7}$ M; 1.4 x $10^{-6}$ M; 1.7 x $10^{-6}$ M; 2.4 x $10^{-6}$ M; 4.1 x $10^{-6}$ M; 6.2 x $10^{-6}$ M; 6.9 x $10^{-6}$ M; 8.6 x $10^{-6}$ M; 1.0 x $10^{-5}$ M).

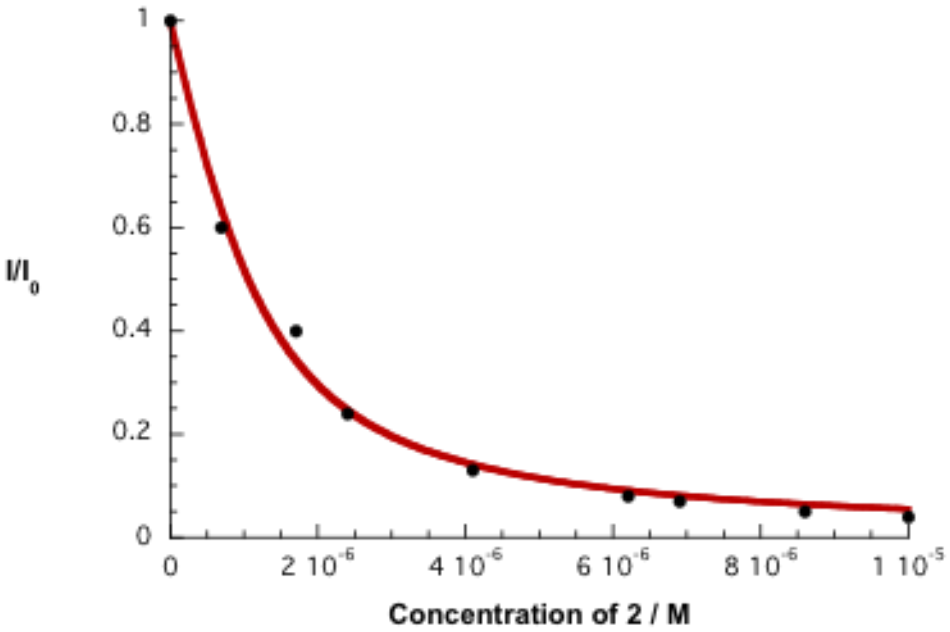


Figure S9: Plot of the normalized intensity $I/I_0$ at 715 nm versus concentration of **2** used to determine the association constant.