Dynamic Supramolecular Complexation by Shapeshifting Organic Molecules

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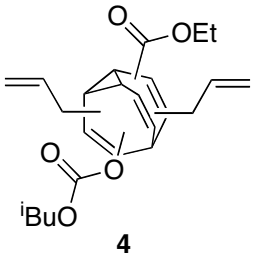
Supporting Information

General Methods. All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry N_2. THF and CH_2Cl_2 were distilled over CaH_2. Hexamethyldisilazane was distilled from KOH. *iso*-Butyl chloroformate was distilled under N_2. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254, Art 5715, 0.25 mm) and were visualized by fluorescence quenching under UV light or by staining with phosphomolybdic acid. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck Kieselgel 60 PF254 (Art 7747). Column chromatography was performed on E. Merck Silica Gel 60 (230–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were measured on a Bruker Avance 500 spectrometer. Chemical shifts are expressed in parts per million (PPM) downfield from residual solvent peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrophotometer and are reported as wavenumber (cm^{-1}).

A. Synthetic Protocols and Tabulated Spectra



4

Bisallyl Bullvalene 4: Hexamethyldisilazane (0.55 mL, 0.26 mmol, 3.1 equiv) was added to a solution of 2.5M *n*-butyl lithium in hexane (0.10 mL, 0.25 mmol, 3.0 equiv) in THF at –78 °C and allowed to warm to 0 °C. After stirring for 20 min at 0 °C, the reaction was cooled to –78 °C and bullvalone **3**[1] (25.0 mg, 0.0838 mmol, 1.0 equiv) was added as a solution in 3 x 0.8 mL THF and stirred for 15 min. *iso*-Butyl chloroformate (110 μL, 0.840 mmol, 10 equiv) was added and the reaction was allowed to warm to rt. After 2 h 45 min, the reaction was poured into 10 mL sat NH_4Cl and extracted with 3 x 10 mL CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Isolation of three major bands by silica chromatography (20:1 hexanes:EtOAc → 10:1 hexanes:EtOAc) yielded bisallyl bullvalene **4** (16.2 mg, 49%) as a clear oil. ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 120 °C) δ 5.90–5.70 (m, 2H), 5.10–5.00 (m, 4H), 4.16 (q, 2H, *J* = 7.5 Hz), 3.95 (d, 2H, *J* = 6.5 Hz), 2.75–2.60 (m, 3H), 1.95 (quintet, 1H, *J* = 6.5 Hz), 1.25 (t, 3H, *J* = 6.5 Hz), 0.93 (d, 6H, *J* = 6.5 Hz); ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 30 °C)* δ 7.05 (m, 1H), 5.85–5.68 (m, 3H), 5.2–5.0 (m, 4H), 4.12–4.09 (m, 2H), 3.91 (d, 2H, *J* = 6.0 Hz), 2.90–2.70 (m, 4H), 2.50–2.30 (m, 2H), 1.91 (quintet, 1H, *J* = 6.5 Hz), 1.24–1.19 (m, 1H), 0.89 (d, 6H, *J* = 7 Hz); ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C)* δ 7.27 (m, 1H), 5.79–5.67 (m, 3H), 5.11–5.04 (m, 4H), 4.20–4.16 (m, 2H), 3.97 (d, 2H, *J* = 9.5 Hz), 3.40 (m, 1H), 2.93–2.80 (m, 4H), 2.70–2.35 (m, 3H), 1.98 (quintet, 1H, *J* = 6.5 Hz), 1.30–1.24 (m, 1H), 0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 153.6, 153.4, 137.4, 136.0, 135.9, 135.8, 135.6, 135.5, 134.9, 134.6, 134.5, 120.8, 120.6, 117.5, 117.4, 117.3, 117.2, 116.9, 116.8, 116.8, 116.7, 116.6, 116.4, 116.3, 74.5, 60.8, 60.7, 60.7, 45.6, 45.2, 44.8, 44.6, 44.4, 43.9, 43.8, 43.7, 43.6, 43.5, 38.8, 38.3, 37.1, 36.8, 36.0, 35.9, 31.9, 29.7, 29.4, 29.2, 29.0, 28.0, 27.8, 27.7, 27.4, 27.3, 25.8, 25.7, 22.7, 22.1, 21.0, 19.7, 18.9, 18.8, 14.3, 14.2, 14.1; IR (thin film) ν 2958.3, 2919.7, 2849.3, 1756.8, 1707.6, 1463.2, 1238.6 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{30}O_5$ $[M+H]^+$ 399.2171, found 399.2176.

* Only major peaks are reported. See variable temperature spectra in Figure S12 on page S15 (in $(CD_3)_2SO$) and spectra on page S21 (in $CDCl_3$).

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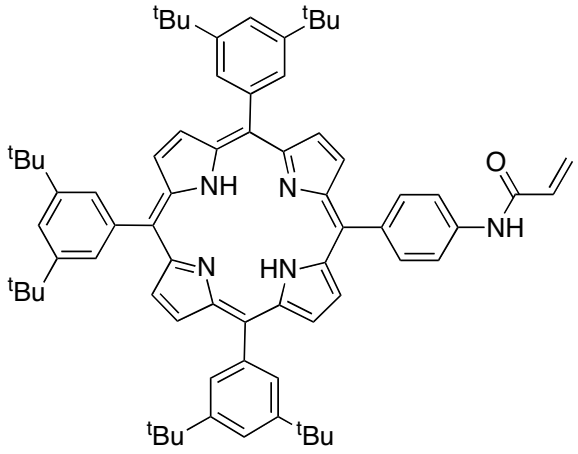
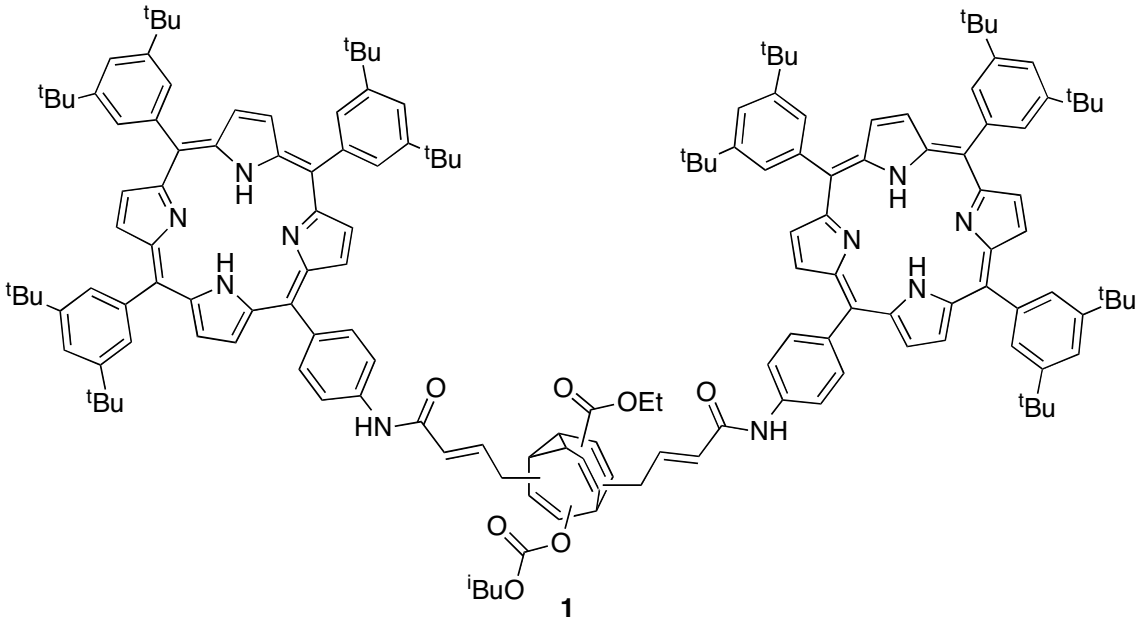
[1] A. R. Lippert, J. Kaeobamrung, J. W. Bode, *J. Am. Chem. Soc.* **2006**, *128*, 14738–14739.



6

Acrylamide Porphyrin 6: Acrylic acid (0.57 mL, 0.83 mmol, 6.9 equiv) was added to a solution of thionyl chloride (57 μL, 0.79 mmol, 6.6 equiv) in 0.50 mL of dimethylacetamide at –10 °C. After stirring for 5 min, a solution of amino porphyrin **5**[2] (119.8 mg, 0.1202 mmol, 1.0 equiv) in 4 mL dimethylacetamide was added to the reaction mixture over 10 min, giving a green solution. Upon complete addition, the reaction mixture was allowed to warm and stirred at rt. After 1 h, the reaction was quenched by the addition of 10 mL of distilled water causing a purple solid to precipitate, which was filtered and washed with water. The solid was dissolved in CH_2Cl_2, washed through the filter, poured onto brine, and extracted into 3 x 15 mL CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel chromatography (hexane → 5:1 hexane:EtOAc) to yield the acrylamide porphyrin **6** (94.0 mg, 77%) as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (m, 6H), 8.87 (d, 2H, J = 4.5 Hz), 8.21 (d, 2H, J = 8 Hz), 8.10 (dd, 6H, J = 4 Hz, 1.5 Hz), 7.95 (d, 2H, J = 7.5 Hz), 7.81 (m, 3H), 7.54 (s, 1H), 6.60 (d, 1H, J = 17 Hz), 6.41 (m, 1H), 5.90 (d, 1H, J = 10.5 Hz), 1.54 (s, 54H), –2.68 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 141.3, 138.7, 137.3, 135.0, 131.2, 129.8, 129.7, 128.2, 121.5, 121.4, 121.0, 119.0, 118.0, 35.0, 31.7; IR (thin film) ν 3318.4, 2951.2, 2869.1, 2910.1, 1586.0, 1592.9 cm^{-1}; HRMS (ESI) calcd for $C_{71}H_{81}N_5O$ $[M+H]^+$ 1020.6520, found 1020.6490.

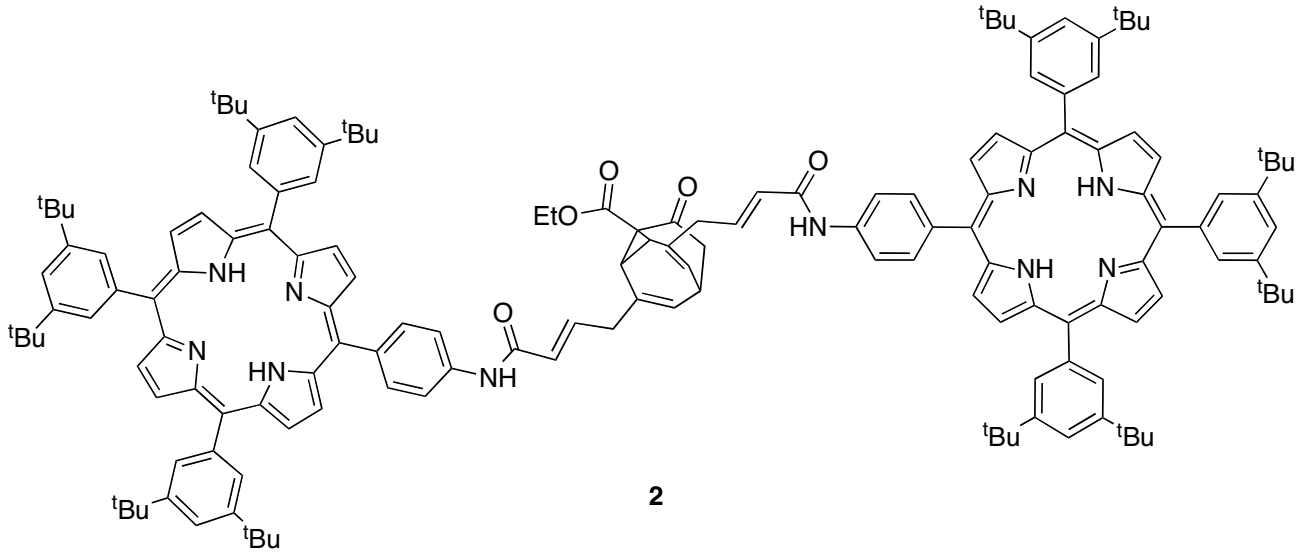
[2] H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, Y. Sakata, *J. Am. Chem. Soc.* **1996**, *118*, 11771–11782.



1

Bisporphyrin Bullvalene 1: Acrylamide porphyrin **6** (21.3 mg, 0.0209 mmol, 2.5 equiv) and bisallyl bullvalene **4** (3.3 mg, 0.0084 mmol, 1.0 equiv) were dissolved in 0.42 mL CH_2Cl_2. Grubbs' 2nd generation catalyst[3] (4.3 mg, 0.0051 mmol, 0.61 equiv) was added, the flask was sealed, and the reaction was heated at 40 °C for 16 h. The reaction mixture was concentrated and purified by PTLC (11:1 toluene:EtOAc) to yield the bisporphyrin bullvalene **1** (3.8 mg, 19%) as a red oil. ^{1}H NMR (500 MHz, $C_6D_5CD_3$) δ 9.0–8.85 (m, 14H), 8.24–8.16 (m, 12H), 8.14–8.00 (m, 6H), 7.93–7.85 (m, 8H), 6.53–6.49 (m, 2H), 6.15–5.80 (m, 2H), 5.65–5.41 (m, 3H), 4.30–3.75 (m, 6H), 3.38–2.70 (m, 6H), 1.49–1.43 (m, 108H), 1.14 (t, 3H, J = 7.5 Hz), 0.84 (d, 6H, J = 22 Hz), –2.02 (br s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 148.6, 141.3, 141.2, 137.9, 135.1, 130.0, 129.8, 128.2, 125.3, 121.4, 120.9, 119.0 (br), 118.0 (br), 61.5 (br), 39.4 (br), 37.4 (br), 37.1, 35.9, 35.0, 34.4, 32.7, 31.9, 31.7, 30.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.0, 27.8, 27.2, 27.1, 25.5, 24.5, 22.7, 21.5, 19.7 (br), 19.3, 18.9, 14.4, 14.1 cm^{-1}; IR (thin film) ν 3315.5, 2954.9, 2923.6, 2853.2, 1753.9, 1665.7, 1592.4, 1525.4, 1475.3, 1466.6, 1362.9, 1260.3, 1362.9, 1260.3, 1246.8 cm^{-1}; HRMS (MALDI) calcd for $(C_{162}H_{185}N_{10}O_7)^+$, 2382.44; found 2382.83.

[3] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.



2

Bisporphyrin Bullvalone 2: Acrylamide porphyrin **6** (65.3 mg, 0.0640 mmol, 2.3 equiv) and bisallyl bullvalone **3**[1] (8.2 mg, 0.028 mmol, 1.0 equiv) were dissolved in 0.20 mL of CH_2Cl_2. Grubbs' 2nd generation catalyst[3] (11.8 mg, 0.0138 mmol, 0.50 equiv) was added, the flask was sealed, and the reaction was heated at 40 °C for 16 h. The reaction mixture was concentrated and purified by PTLC (6:1 toluene:EtOAc) to yield bisporphyrin bullvalone **2** (12.8 mg, 20%) as a red oil. ^{1}H NMR (500 MHz, $C_6D_5CD_3$) δ 9.02 (m, 10H), 9.00 (m, 4H), 8.21 (d, 10H, J = 18 Hz), 8.06 (d, 6H, J = 1.7 Hz), 7.92–7.89 (m, 6H), 5.81 (dd, 2H, J = 15.6, 3.5 Hz), 5.62–5.41 (m, 2H), 4.19 (q, 2H, J = 7.1 Hz), 3.48 (m, 2H), 2.75 (m, 4H), 2.53 (br s, 2H), 2.43 (br s, 2H), 1.57–1.39 (m, 108H), 1.19 (t, 3H, J = 7.2 Hz), –2.03 (s, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 175.4, 148.6, 141.2, 137.6, 135.0, 130.0, 129.7, 129.7, 128.8, 128.6, 128.4, 127.9, 127.7, 127.5, 125.0, 124.6, 121.4, 120.9, 116.4, 60.4, 53.4, 35.9, 35.3, 35.0, 32.8, 31.9, 31.7, 31.4, 30.2, 30.0, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 27.2, 27.1, 25.5, 22.7, 21.0, 20.7, 19.7, 14.2; IR (thin film) ν 3317.5, 2959.2, 2924.5, 2854.1, 1722.1, 1666.2, 1592.4, 1529.3, 1475.8, 1462.7, 1363.4, 1260.3, 1247.7 cm^{-1}; HRMS (MALDI) calcd for $(C_{157}H_{176}N_{10}O_5)^+$, 2281.38; found 2282.19.

B. UV Experiments (Job's Plots and Spectrophotometric Titrations):

Concentrations of bisporphyrin compounds were calculated according to the extinction coefficient for the acrylamide porphyrin **6** which was determined to be 405000 ± 8000 $M^{-1}cm^{-1}$ by measuring the absorbance at 422 nm for a series of solutions of the acrylamide porphyrin ranging from 9.53 X 10^{-7} M to 4.76 X 10^{-6} M. The extinction coefficients of the bisporphyrin compounds **1** and **2** were taken to be twice the value calculated for the acrylamide porphyrin **6** due to the presence of two porphyrin groups. Concentrations of C_{60} were calculated based on a literature value[4] for the extinction coefficient of 65000 ± 5000 $M^{-1}cm^{-1}$.

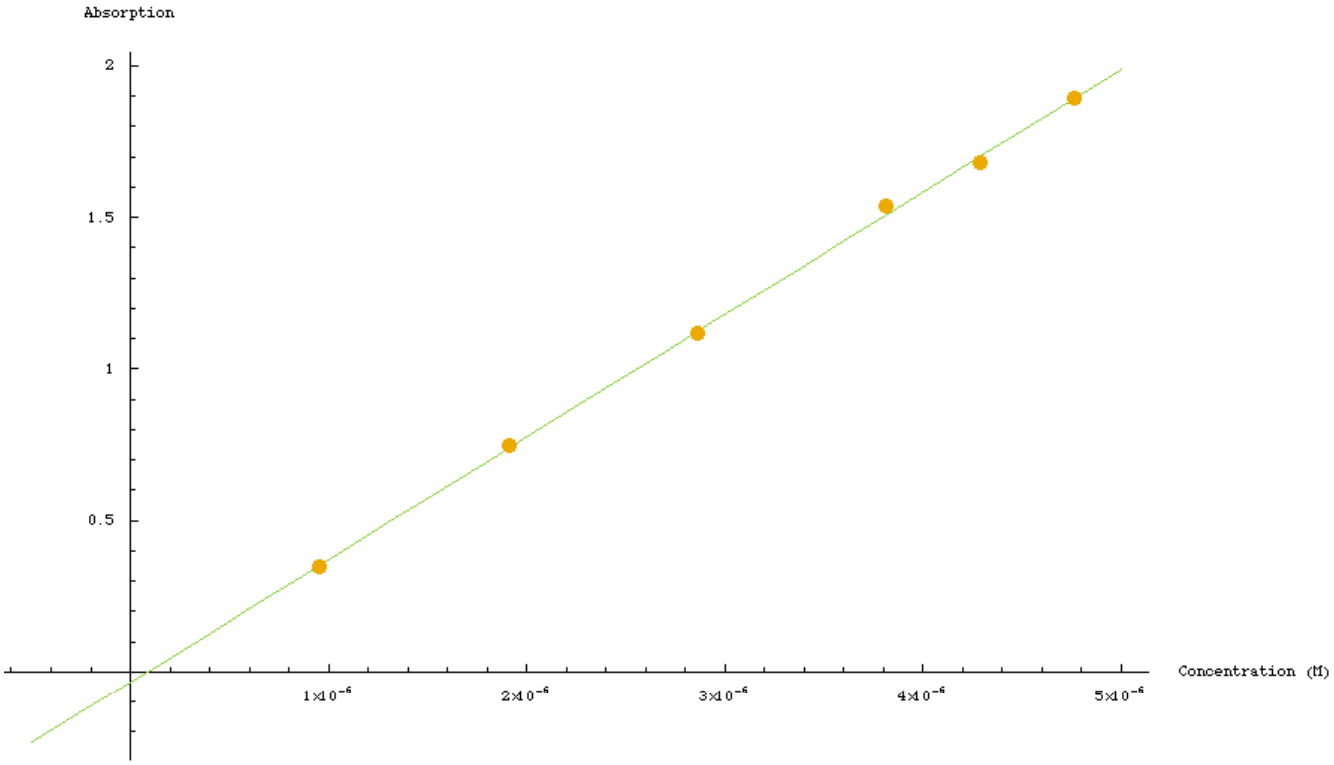


Figure S1. Calculation of the extinction coefficient of acrylamide porphyrin **6** at 422 nm in toluene.

[4] The extinction coefficient for C_{60} in toluene at 334 nm was taken to be 65000 ± 5000 $M^{-1}cm^{-1}$: H. Hungerühler, D. M. Guldi, K.-D. Asmus, *J. Am. Chem. Soc.* **1993**, *115*, 3386–3387.

Job's Plots:

Bisporphyrin Bullvalene 1: Stock solutions of bisporphyrin bullvalene **1** at 1.36 x 10^{-4} M and C_{60} at 1.37 x 10^{-4} M (calculated based on the extinction coefficients) were prepared in spectral grade toluene. Multiples of 12 μL of these solutions were added into a 3.5 mL cuvette at ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 **1**:C_{60} for a total volume of added solution of 48 μL. The cuvette was diluted to a constant total volume and the absorbance was measured at 418 nm, 422 nm, and 427 nm.

Bisporphyrin Bullvalone 2: Stock solutions of bisporphyrin bullvalone **2** at 1.56 x 10^{-4} M and C_{60} at 1.82 x 10^{-4} M (calculated based on the extinction coefficients) were prepared in spectral grade toluene. Multiples of 12 μL of these solutions were added into a 3.5 mL cuvette at ratios of 3:1, 2:1, 1:1, 1:2, and 1:3 **2**:C_{60} for a total volume of added solution of 48 μL. The cuvette was diluted to a constant total volume and the absorbance was measured at 422 nm.

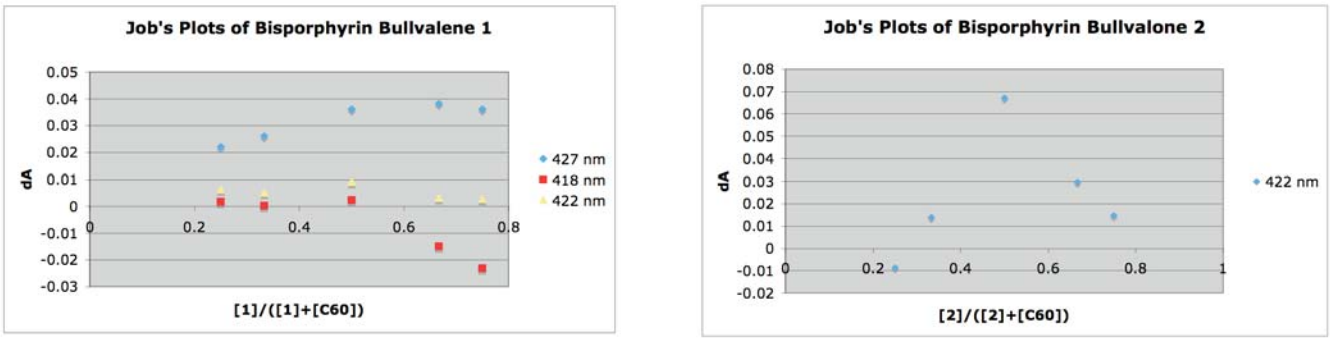


Figure S2. Job's plots for bisporphyrin bullvalene **1** and C_{60} at 418 nm, 422 nm, and 427 nm in toluene with a total concentration of [**1**] + [C_{60}] = 1.88 μM and bisporphyrin bullvalone **2** at 422 nm in toluene with a total concentration [**2**] + [C_{60}] = 2.32 μM.

Spectrophotometric Titrations:

Bisporphyrin Bullvalene 1: A solution of bisporphyrin bullvalene **1** (2500 μL, 2.1 X 10^{-6} M) in spectral grade toluene was added to a quartz cuvette and the absorbance was measured upon the addition of 2 to 100 μL (1000 μL total) aliquots of a stock solution of C_{60} (3.4 X 10^{-3} M) in toluene to both the sample and the reference cuvette. Plots of ΔA at 421 nm and 434 nm versus [C_{60}] were analyzed after dilution corrections and the binding constants (K_b) and the absorbance at maximum saturation of binding sites (ΔA_{max}) were evaluated by a least-squares non linear fitting approach using the equation:[5]

$$\Delta A = \frac{\Delta A_{max}(1 + K_b[C_{60}] + [BP]K_b) - ((1 + K_b[C_{60}] + [BP]K_b)^2 - 4K_b^2[C_{60}][BP])^{1/2}}{2K_b[BP]}$$

where $\Delta A = A_{obs} - A_o$, [C_{60}] is the total concentration of C_{60} in solution, and [BP] is the total concentration of the bisporphyrin in solution. The inconsistency of the equilibrium constant at different wavelengths is indicative of multiple complexes.

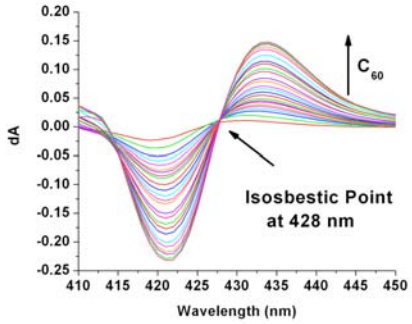


Figure S3. Differential absorbance plots of 2.1 μM bisporphyrin bullvalene **1** with 10–1000 equivalents of C_{60} in toluene.

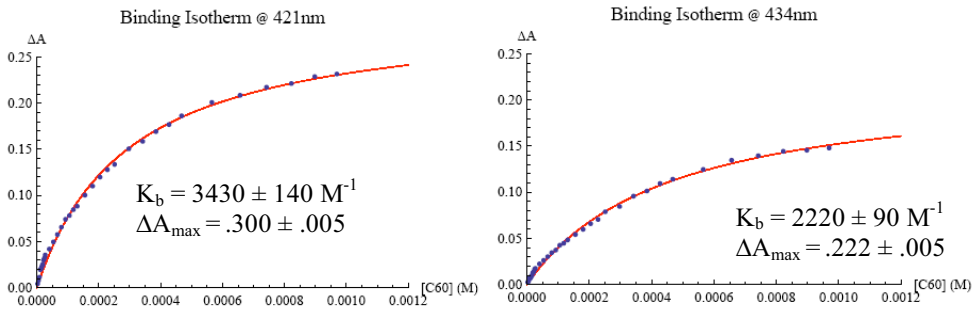


Figure S4. Binding isotherms for the spectrophotometric titration of 2.1 μM bisporphyrin bullvalene **1** at 421 nm and 434 nm in toluene.

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[5] J.-S. Marois, K. Cantin, A. Desmarais, J.-F. Morin, *Org. Lett.* **2008**, *10*, 33–36.

Bisporphyrin Bullvalone 2: A solution of bisporphyrin bullvalone **2** (2500 μL, 2.9 X 10^{-6} M) in spectral grade toluene was added to a quartz cuvette and the absorbance was measured upon the addition of 2 to 100 μL (1000 μL total) aliquots of a stock solution of C_{60} (3.7 X 10^{-3} M) in toluene to both the sample and the reference cuvette. Plots of ΔA at 421 nm and 434 nm versus [C_{60}] were analyzed after dilution corrections and the binding constants (K_b) and the absorbance at maximum saturation of binding sites (ΔA_{max}) were evaluated by a least-squares non linear fitting approach using the equation:[5]

$$\Delta A = \frac{\Delta A_{max}(1 + K_b[C_{60}] + [BP]K_b) - ((1 + K_b[C_{60}] + [BP]K_b)^2 - 4K_b^2[C_{60}][BP])^{1/2}}{2K_b[BP]}$$

where $\Delta A = A_{obs} - A_o$, [C_{60}] is the total concentration of C_{60} in solution, and [BP] is the total concentration of the bisporphyrin in solution. The consistency of the binding constant at different wavelengths is indicative of a single binding complex.

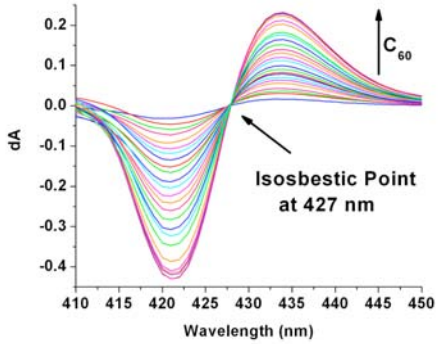


Figure S5. Differential absorbance plots of 2.9 μM bisporphyrin bullvalone **2** with 10–1000 equivalents of C_{60} in toluene.

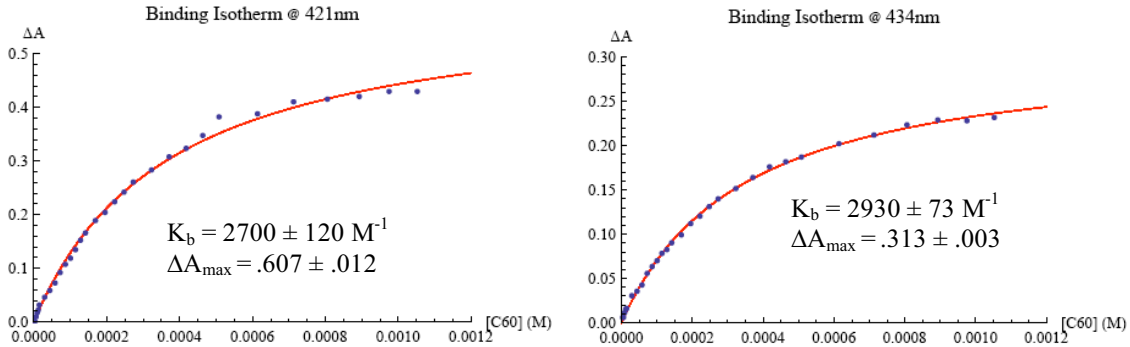


Figure S6. Binding isotherms for the spectrophotometric titration of 2.9 μM bisporphyrin bullvalone **2** at 421 nm and 434 nm in toluene.

C. ^{1}H NMR Titrations:

Bisporphyrin Bullvalene 1: A 1.3 X 10^{-3} M stock solution of bisporphyrin bullvalene **1** in $C_6D_5CD_3$ was prepared and 100 µL aliquots (1.3 X 10^{-7} mol) were added to 7 NMR tubes (10 mm). Appropriate aliquots of a stock solution of C_{60} (3.7 X 10^{-3} M) in $C_6D_5CD_3$ were added to each NMR tube to obtain mixtures with 0, 0.5, 1, 1.5, 2, 2.5, and 3 equivalents of C_{60}. All NMR tubes were diluted with additional $C_6D_5CD_3$ to a final volume of 300 µL. The chemical shift of the upfield N-H proton of the porphyrin was monitored. Plots of Δδ versus $[C_{60}]/[BP]$ were plotted and the binding constant (K_b) and the chemical shift at saturation of binding sites ($\Delta\delta_{max}$) were evaluated by a least-squares non linear fitting approach using the equation:[6]

$$\Delta\delta = \frac{\Delta\delta_{max}}{2}\left(\frac{[C_{60}]}{[BP]} + 1 + \frac{1}{K_b[BP]} \pm \left(\left(\frac{[C_{60}]}{[BP]} + 1 + \frac{1}{K_b[BP]}\right)^2 - 4\,\frac{[C_{60}]}{[BP]}\right)^{1/2}\right)$$

where $\Delta\delta = \delta_{obs} - \delta_o$, $[C_{60}]$ is the total concentration of C_{60} in solution, and [BP] is the total concentration of the bisporphyrin in solution. The appearance of multiple peaks upon the addition of C_{60} indicates multiple complexes that are in fast exchange with their respective unbound isomer. The binding constant at 25 °C was calculated monitoring the shift of two separate complexes that appear as separated distinct peaks. The titration was also performed at 90 °C and coalescence of the peaks was observed.

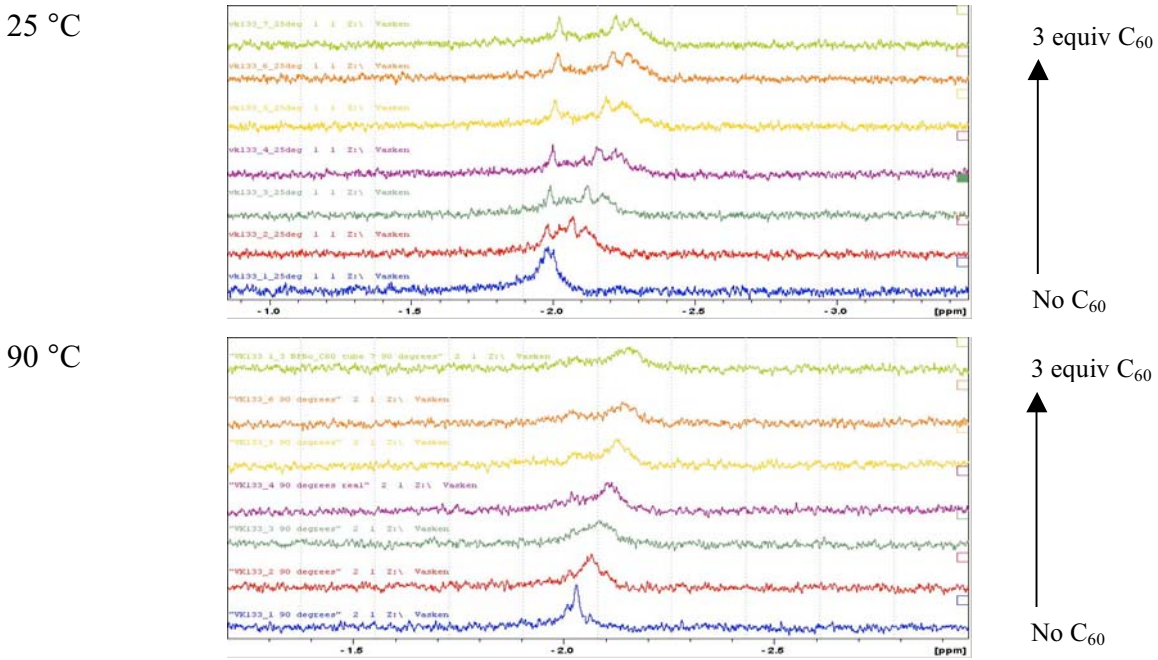


Figure S7. NMR titrations of 0.43 mM bisporphyrin bullvalene **1** at 25 °C and 90 °C in $C_6D_5CD_3$.

[6] Y. Cao, X. Xiao, R. Lu, Q. Guo, *J. Mol. Struct.* **2003**, *660*, 73–80.

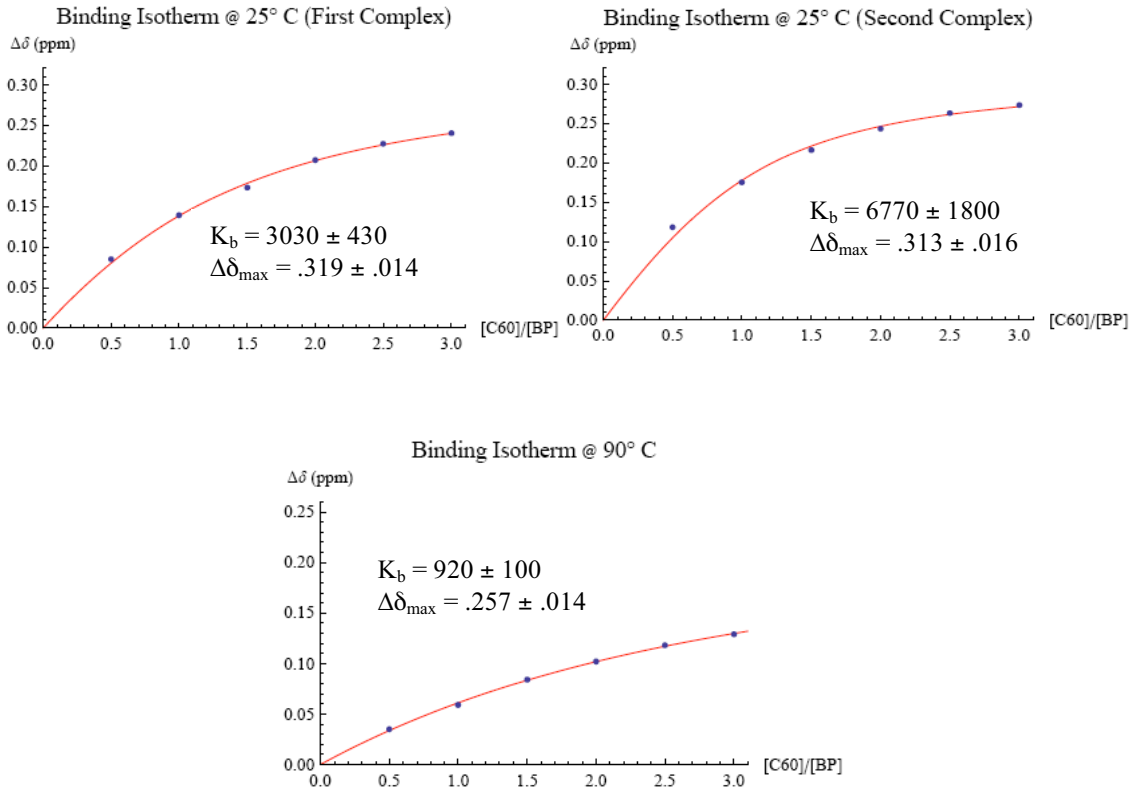


Figure S8. Binding isotherms of the NMR titration of 0.43 mM bisporphyrin bullvalene **1** at 25 °C and 90 °C in $C_6D_5CD_3$.

Stated Assumptions: Our calculation of the binding constants for bisporphyrin bullvalene **1** requires two key assumptions. The first assumption is that the observed Δδ upon addition of C_{60} is predominately due to the change in the ratio of bound and unbound bisporphyrin compounds and not due to any change in the relative ratio of valence isomers. We believe this assumption is valid because (1) the rate of exchange of valence isomers (which coalesce at 90 °C) is much slower than the rate of exchange of the bound and unbound bisporphyrin compounds (which coalesce at –50 °C) and (2) the observed difference in the chemical shift between the observed peaks (Δδ ~ 0.05 ppm, see peak d and e in Figure 3b) at 25 °C changes very little (< 0.009 ppm) as increasing amounts of C_{60} are added. The second assumption is that the concentrations of each binding isomer are 100% of the total concentration of bisporphyrin bullvalene **1** used in the experiment. In actuality, the population of each binding isomer is a difficult to measure fraction of this value, which would lead to higher calculated affinities. For example, the binding affinities for the complex giving rise to peak d in Figure 3b would be 4037 ± 578 M^{-1}, 6056 ± 867 M^{-1}, and 12111 ± 1734 M^{-1} if we assume that the concentration, [BP], of this binding isomer is 75%, 50%, and 25%, respectively, of the amount of bisporphyrin bullvalene **1** added.

The same analysis for peak e in Figure 3b yields values of 9033 ± 2425 M^{-1}, 13550 ± 3637 M^{-1}, and 27099 ± 7274 M^{-1} if we assume that the concentration, [BP], of this binding isomer is 75%, 50%, and 25%, respectively, of the amount of bisporphyrin bullvalene **1** added. Our best estimates for these relative populations based on ^1H NMR integrations of the N-H peak indicate that the two isomers are in approximately a 1:1 ratio, which would give binding constants of 6056 ± 867 M^{-1} for peak d and 13550 ± 3637 M^{-1} for peak e.

Bisporphyrin Bullvalone 2: A 1.5 X 10^{-3} M stock solution of bisporphyrin bullvalone **2** in $C_6D_5CD_3$ was prepared and 100 µL aliquots (1.5 X 10^{-7} mol) were added to 7 NMR tubes (10 mm). Appropriate aliquots of a stock solution of C_{60} (2.6 X 10^{-3} M) in $C_6D_5CD_3$ were added to each NMR tube to obtain mixtures with 0, 0.5, 1, 1.5, 2, 2.5, and 3 equivalents of C_{60}. All NMR tubes were diluted with additional $C_6D_5CD_3$ to a final volume of 300 µL. The chemical shift of the upfield N-H proton of the porphyrin was monitored. Plots of Δδ versus $[C_{60}]/[BP]$ were plotted and the binding constant (K_b) and the chemical shift at saturation of binding sites ($\Delta\delta_{max}$) were evaluated by a least-squares non linear fitting approach using the equation:[6]

$$\Delta\delta = \frac{\Delta\delta_{max}}{2}\left(\frac{[C_{60}]}{[BP]} + 1 + \frac{1}{K_b[BP]} \pm \left(\left(\frac{[C_{60}]}{[BP]} + 1 + \frac{1}{K_b[BP]}\right)^2 - 4\,\frac{[C_{60}]}{[BP]}\right)^{1/2}\right)$$

where $\Delta\delta = \delta_{obs} - \delta_o$, $[C_{60}]$ is the total concentration of C_{60} in solution, and [BP] is the total concentration of the bisporphyrin in solution. The appearance of one peak that shifts upon the addition of C_{60} indicates the formation of a single complex that is in fast exchange with the unbound bisporphyrin.

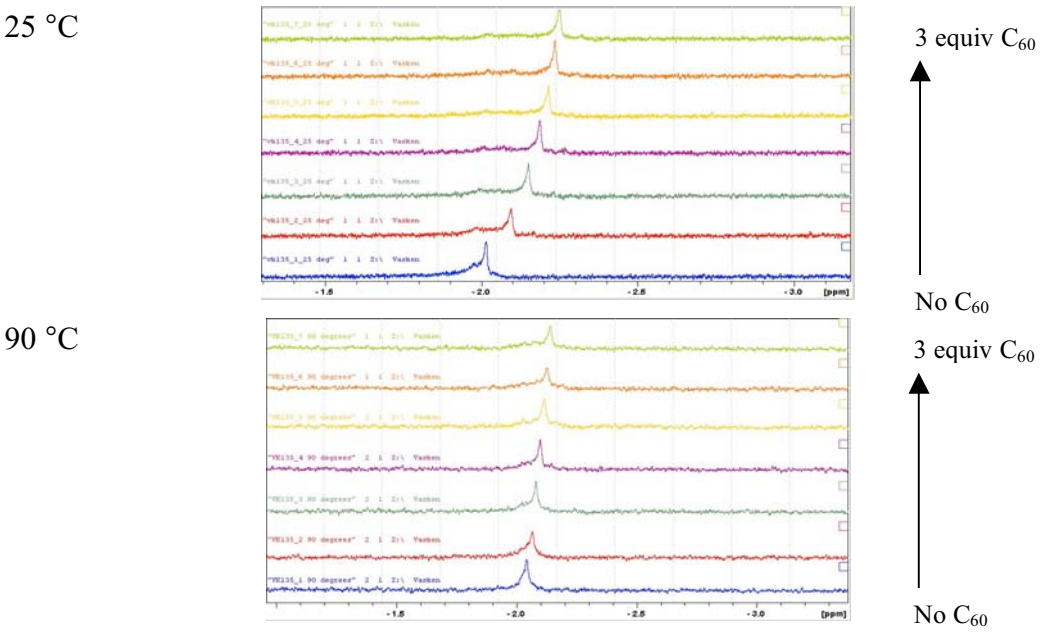


Figure S9. NMR titrations of 0.5 mM bisporphyrin bullvalone **2** at 25 °C and 90 °C in $C_6D_5CD_3$.

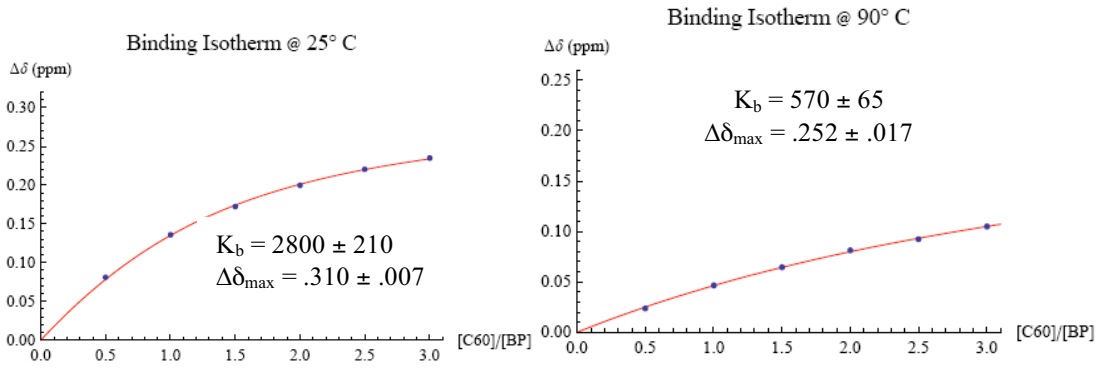
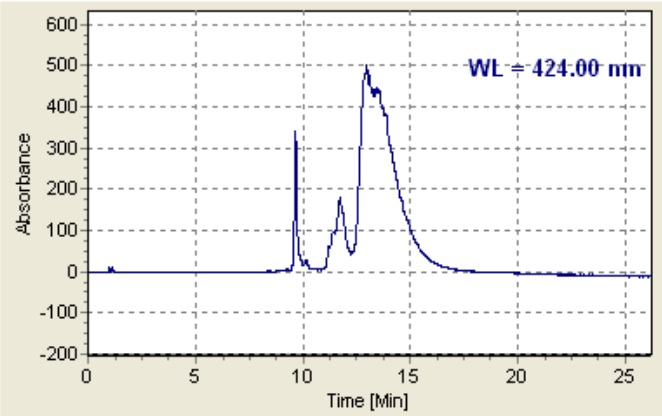


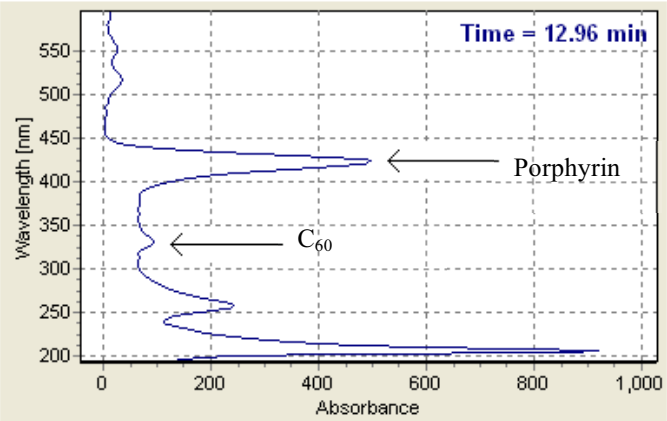
Figure S10. Binding isotherms of the NMR titration of 0.5 mM bisporphyrin bullvalone **2** at 25 °C and 90 °C in $C_6D_5CD_3$.

D. SFC–UV Traces:

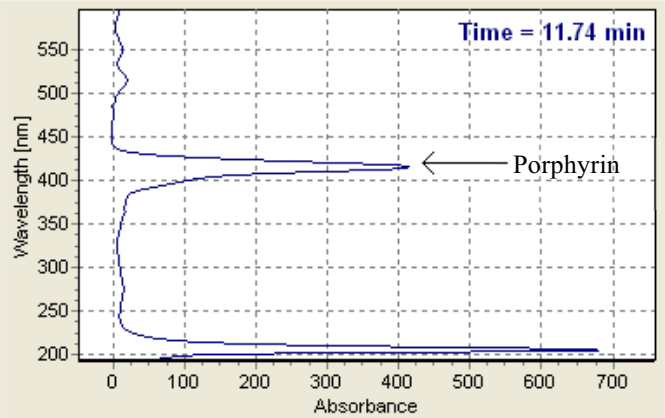
SFC (Supercritical CO_2 Fluid Chromatography) Conditions. Columns: Silica (4.6 x 250 mm). Eluents: gradient 5%–80% *i*-PrOH in CO_2, rate 3%/min, Flow rate 2.0 ml/min. Detection: 424 nm.

Figure S11. SFC-UV trace of bisporphyrin bullvalene **1** and C_{60}. Comparison of the absorbances of the porphyrin and C_{60} peaks in the UV spectra of the isolated complex yields an estimate of a 1:1 ratio of bisporphyrin bullvalene **1** to C_{60}.





Time = 9.8 min: Residual Acrylamide Porphyrin
Time = 11.7 min: Bisporphyrin Bullvalene
Time = 13 min: Bisporphyrin Bullvalene–C_{60}



E. UV Spectra

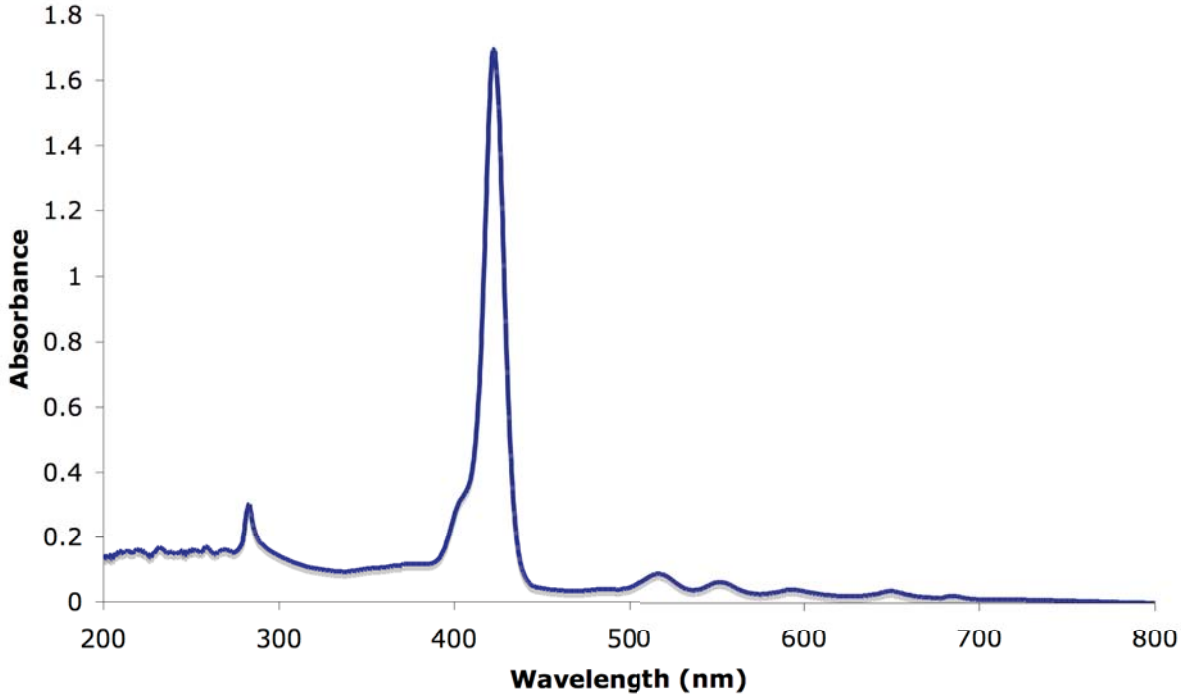


Figure S12. UV spectra of 2.1 μM bisporphyrin bullvalene **1** in spectral grade toluene.

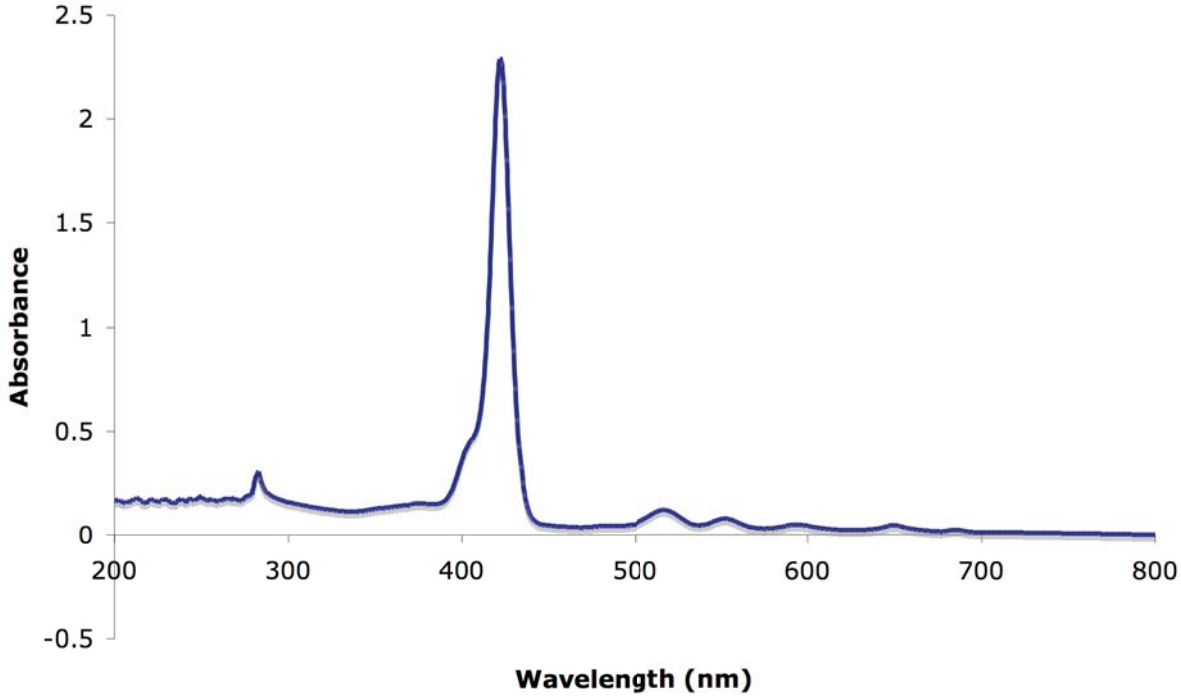
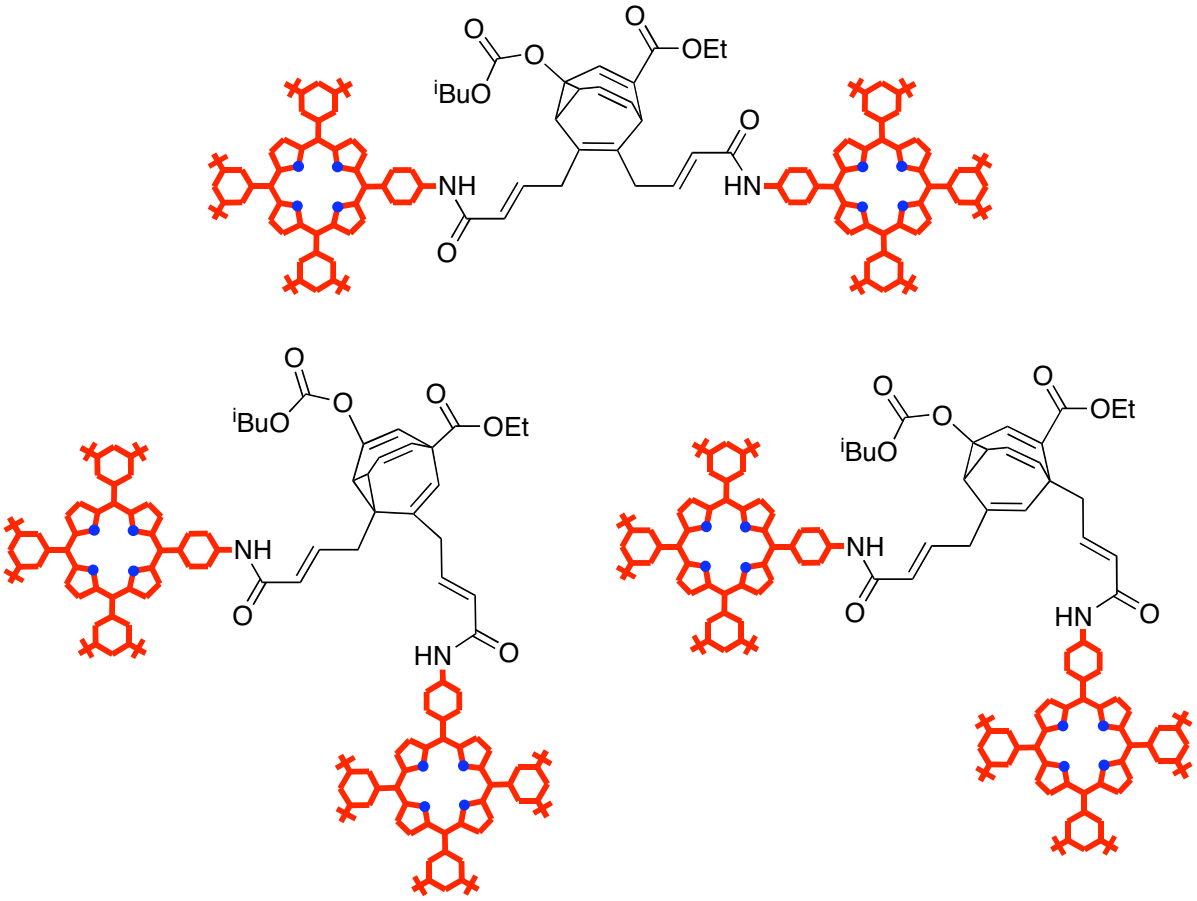


Figure S13. UV spectra of 2.9 μM bisporphyrin bullvalene **2** in spectral grade toluene.

F. Potential High-Binding Isomers of Bisporphyrin Bullvalene 1



G. NMR Spectra

Figure S14. VTNMR of bisallyl bullvalene **4** in $(CD_3)_2SO$.

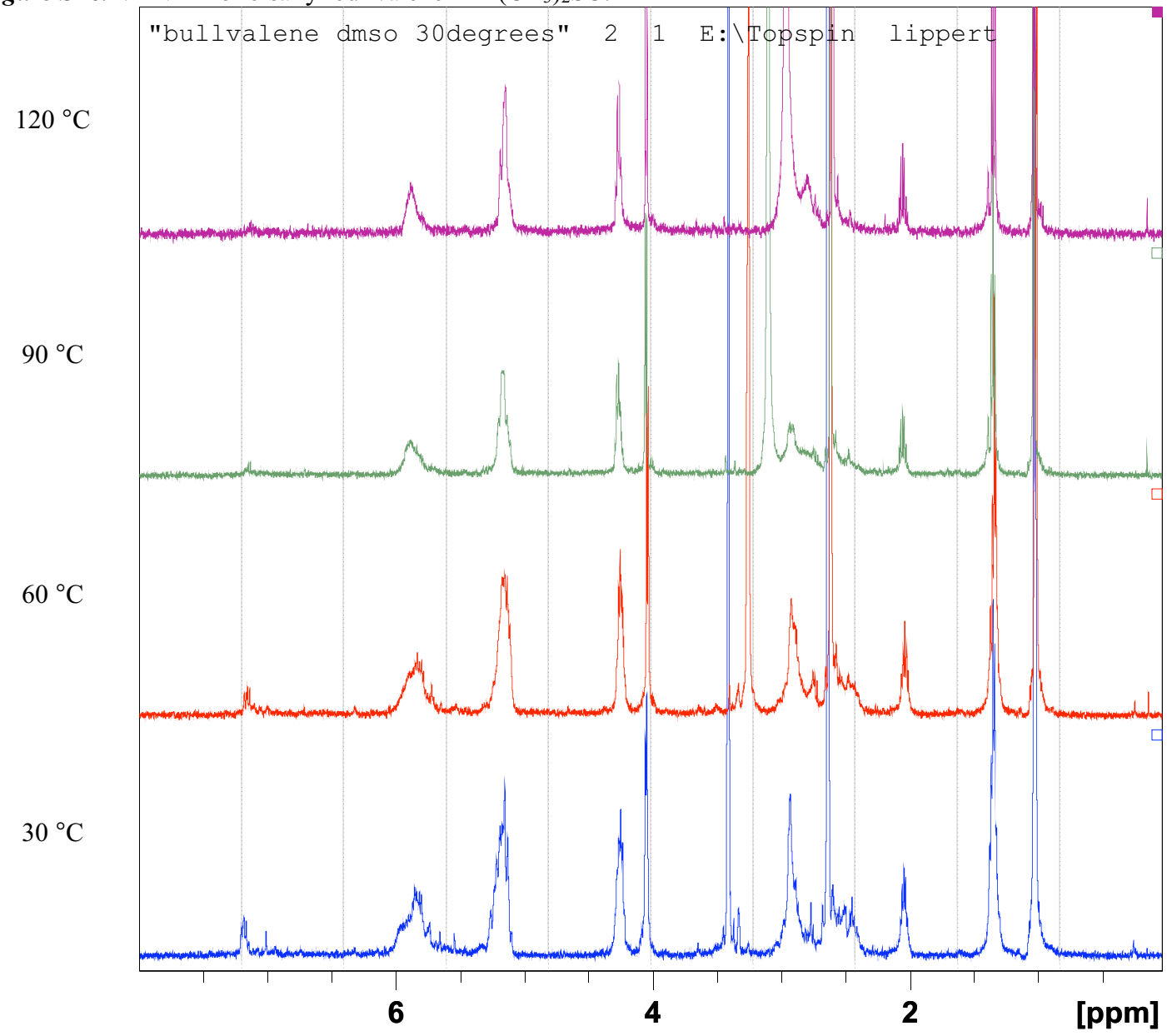


Figure S15. VTNMR of bisporphyrin bullvalene **1** in $C_6D_5CD_3$.

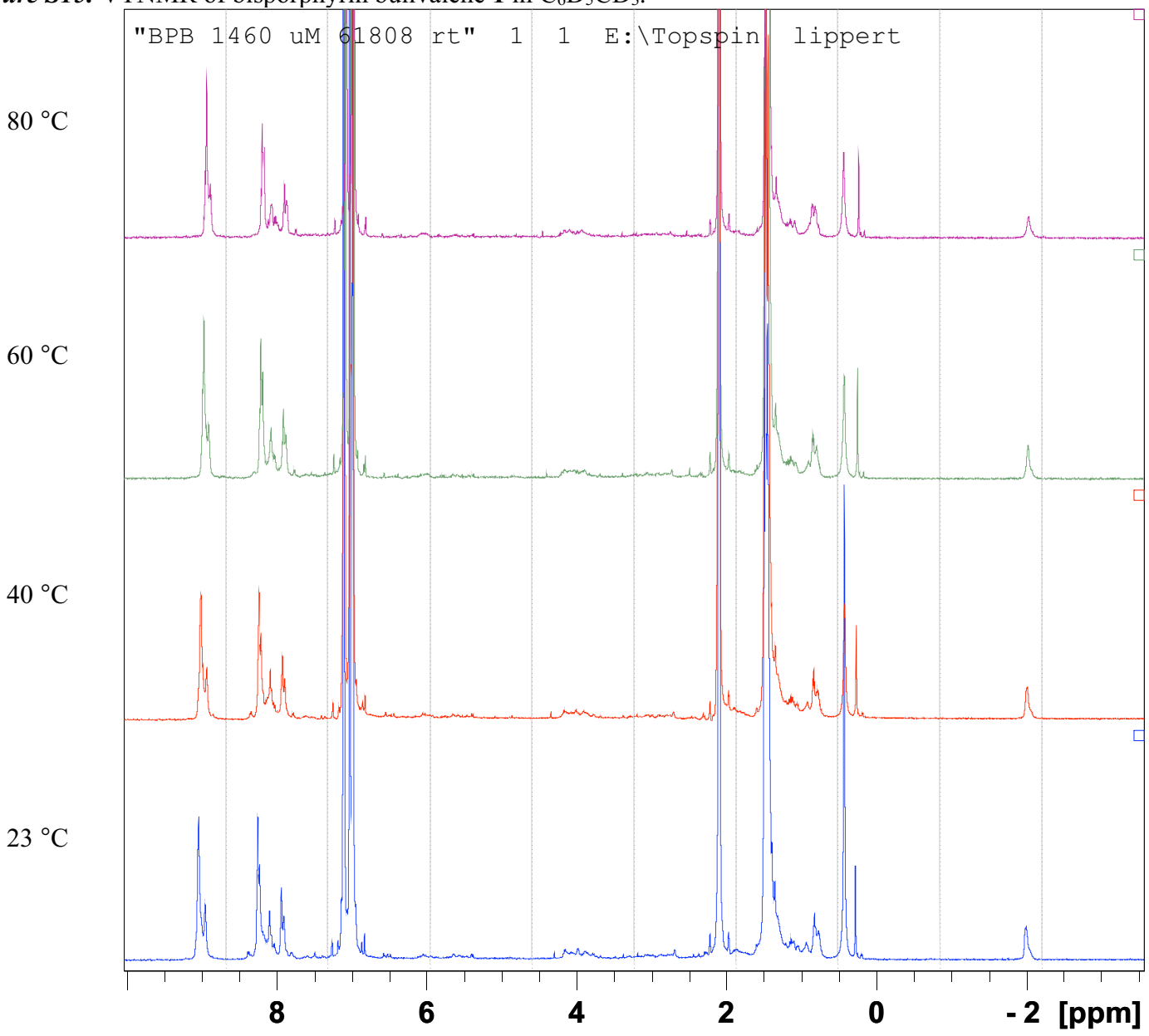


Figure S16. VTNMR of bisporphyrin bullvalene **1** and C_{60} $C_6D_5CD_3$.

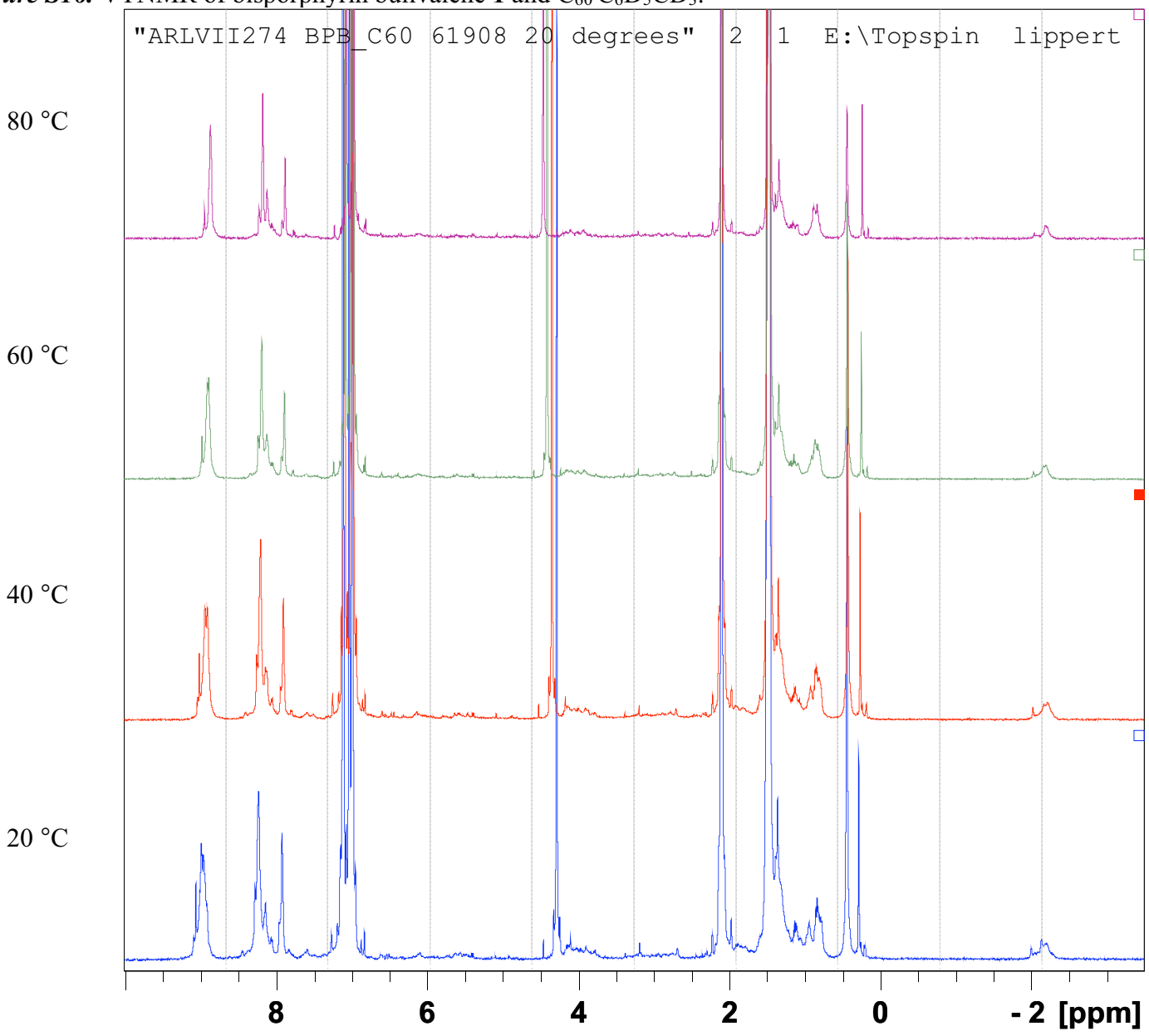


Figure S17. ^{13}C VTNMR of bisporphyrin bullvalene **1** and C_{60} in $C_6D_5CD_3$.

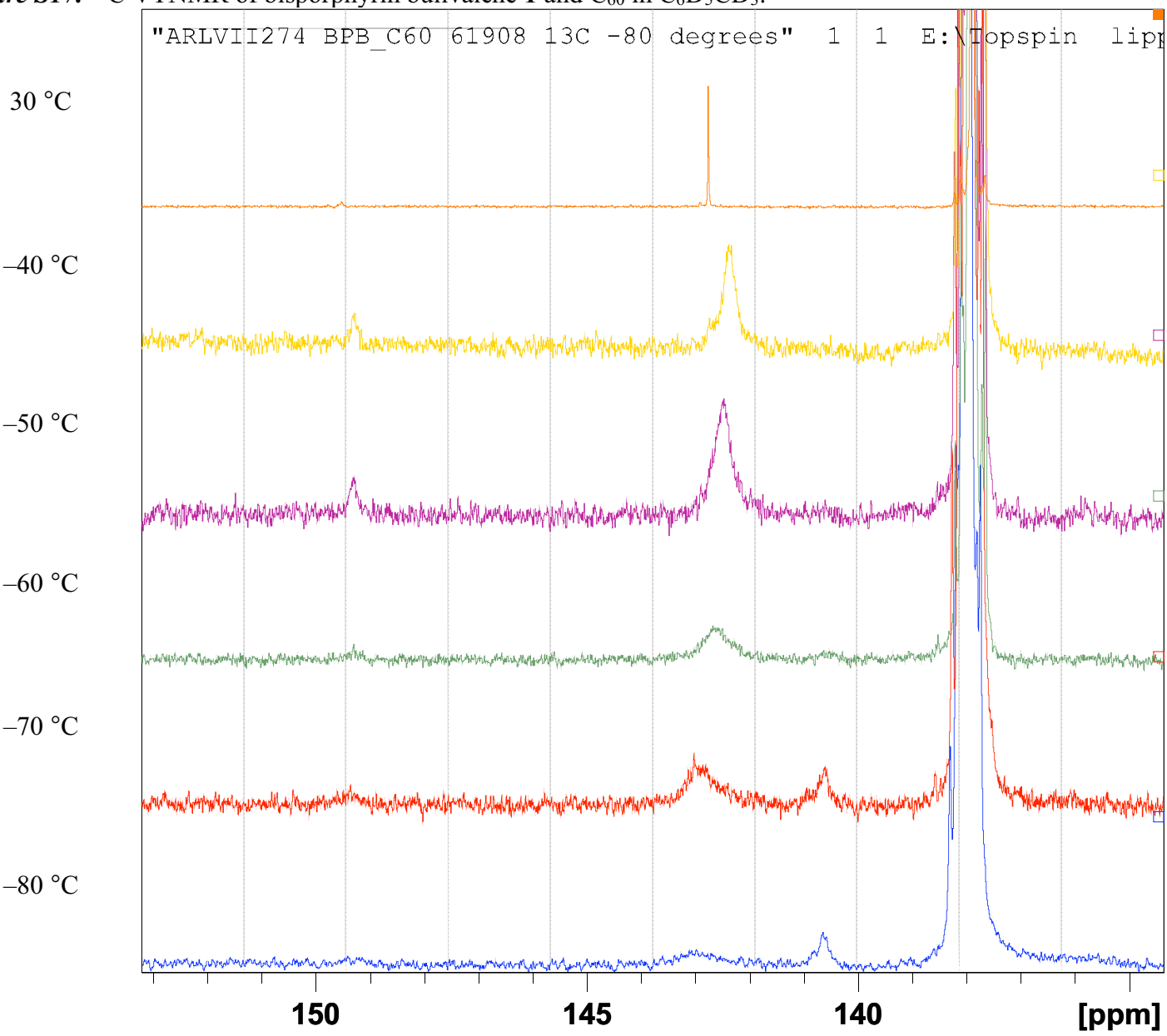


Figure S18. VTMR of bisporphyrin bullvalone **2** and C_{60} in $C_6D_5CD_3$.

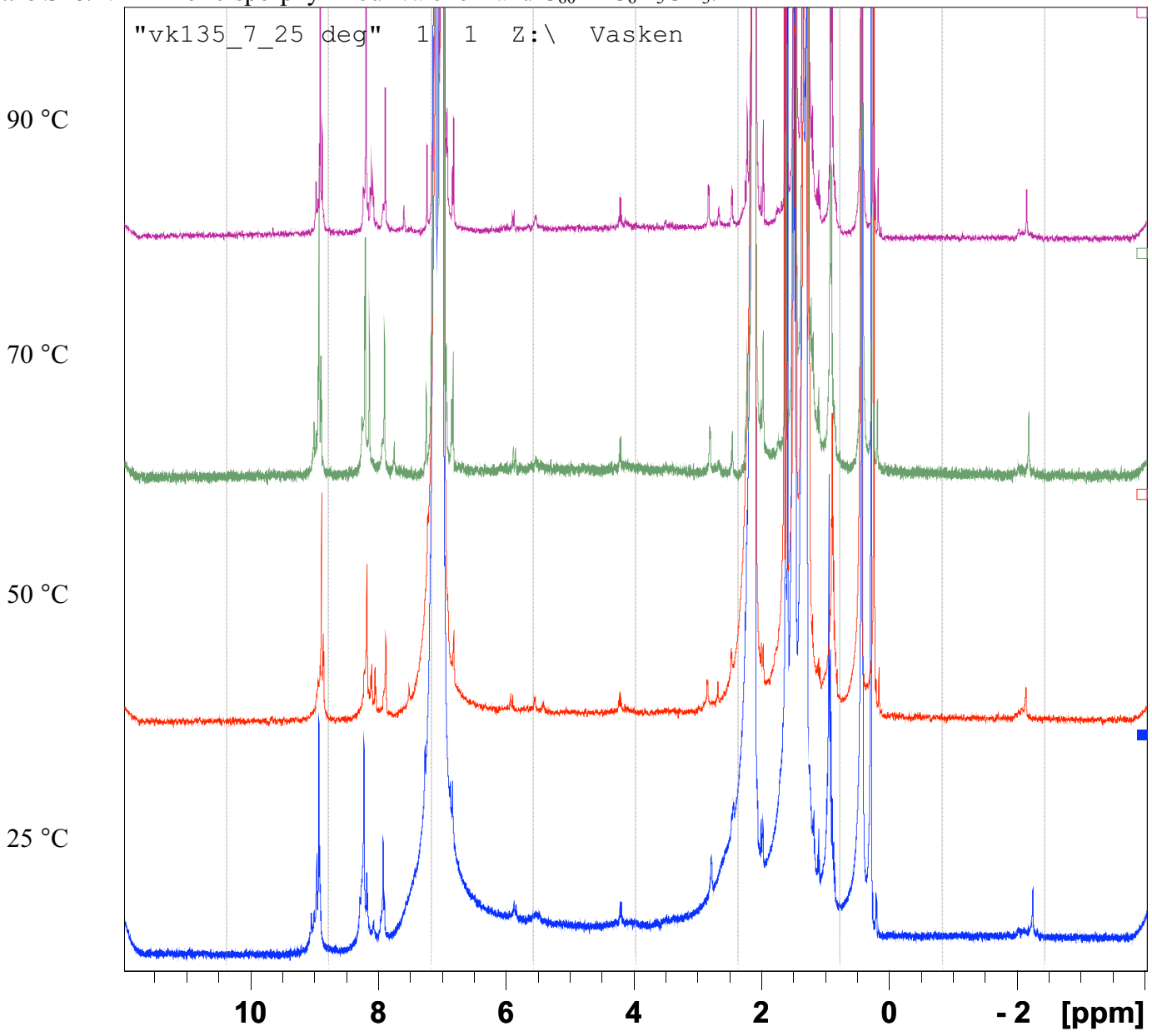
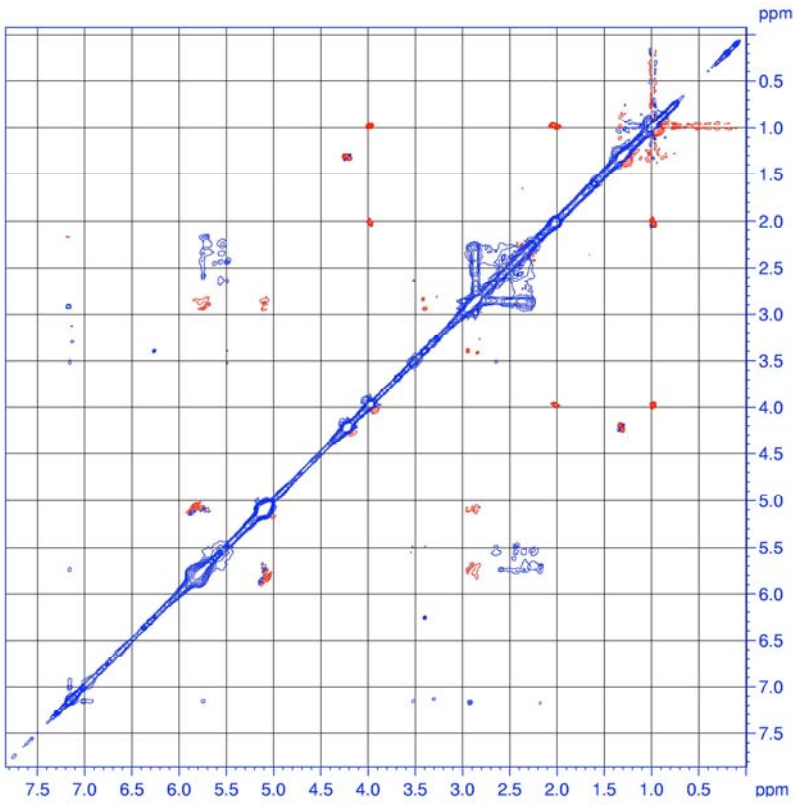


Figure S19. 2D-EXSY of bisallyl bullvalene **4** in $CDCl_3$.

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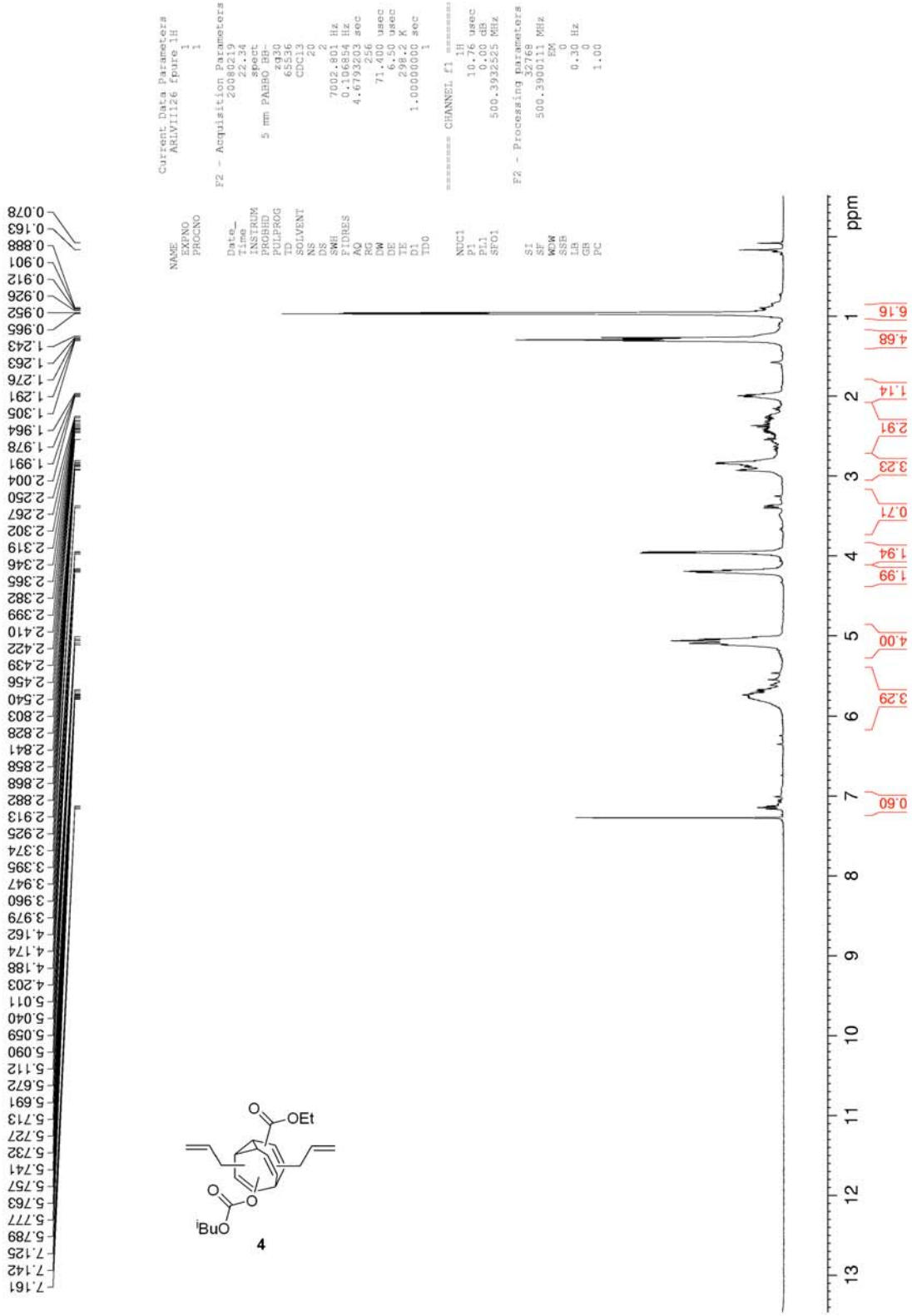
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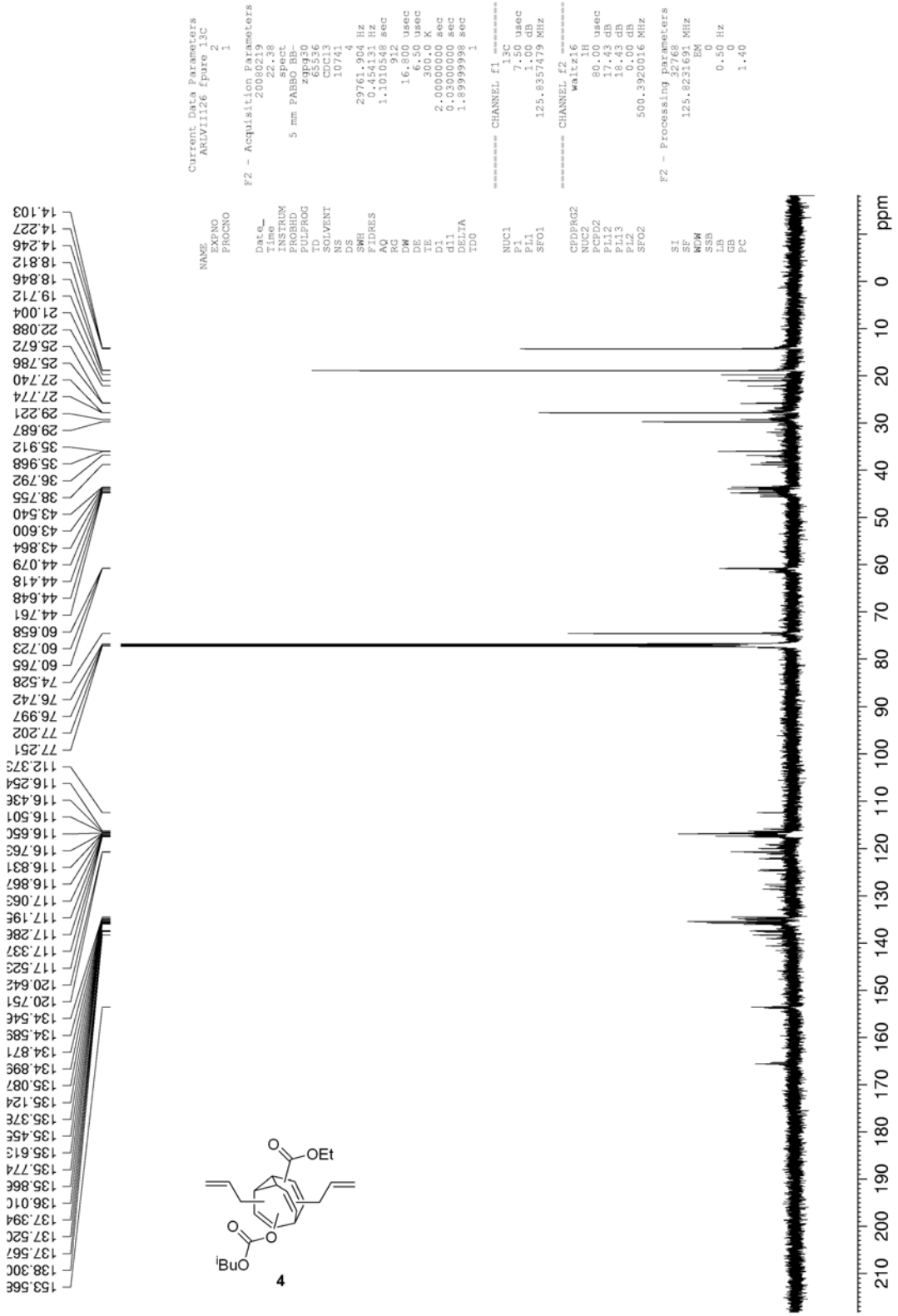
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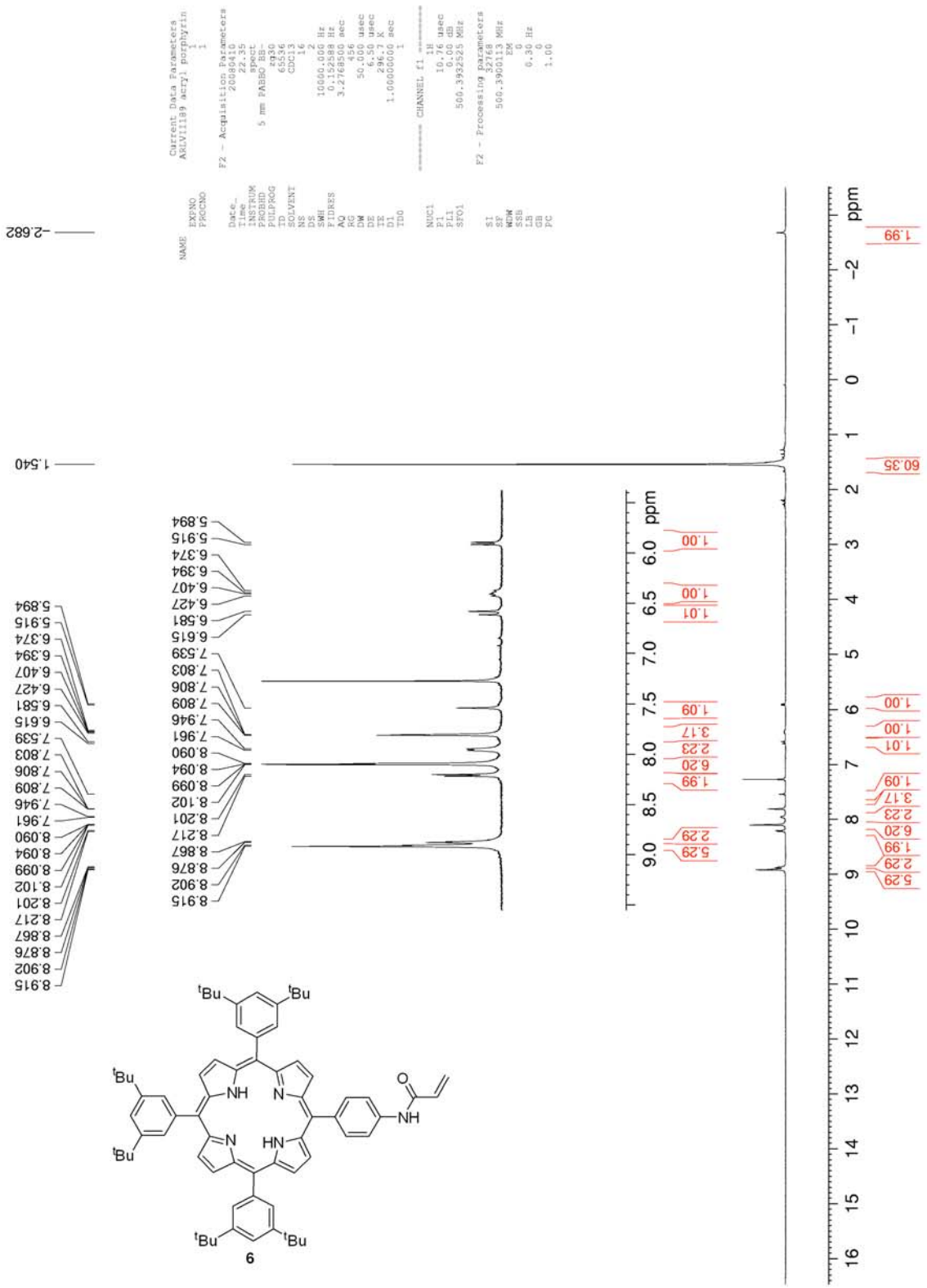
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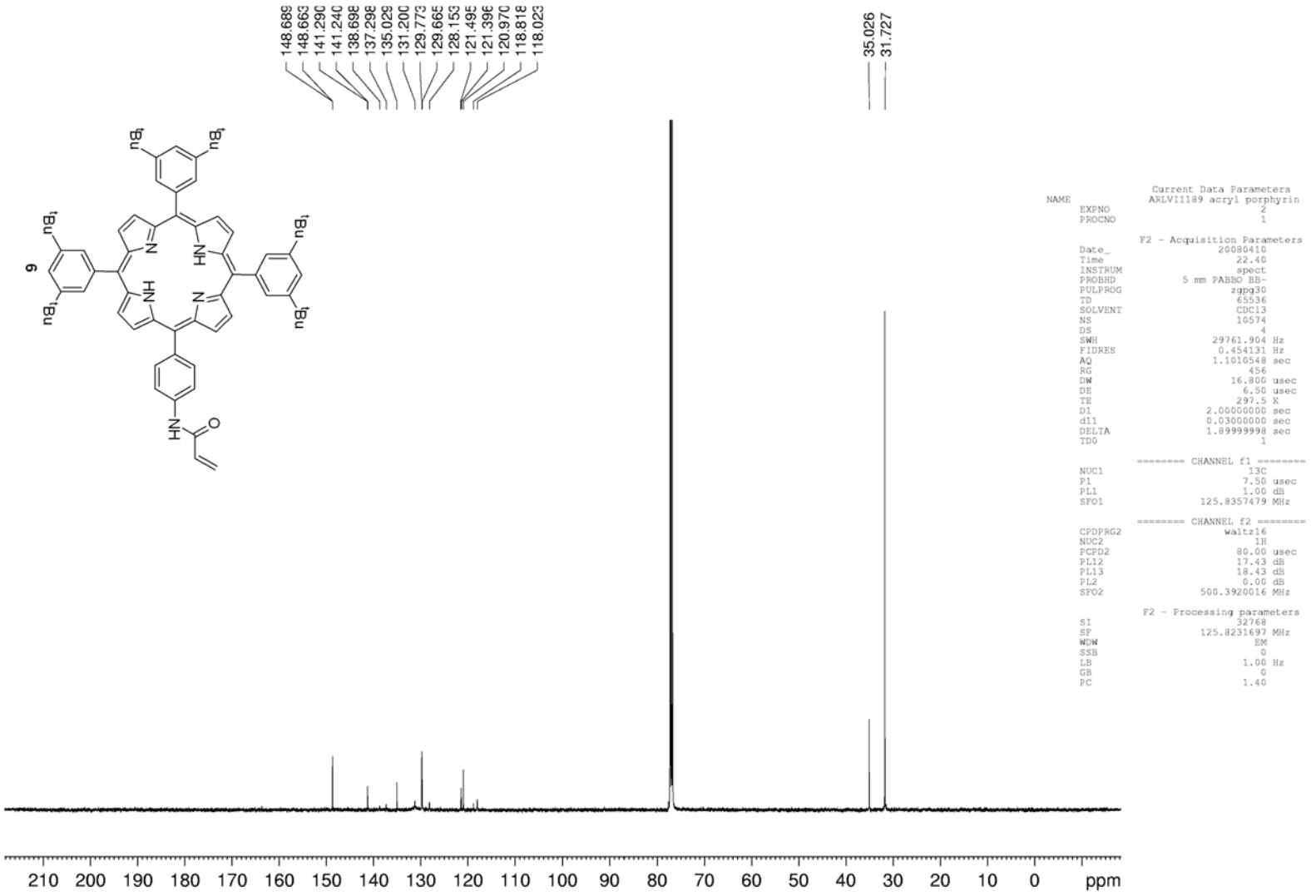
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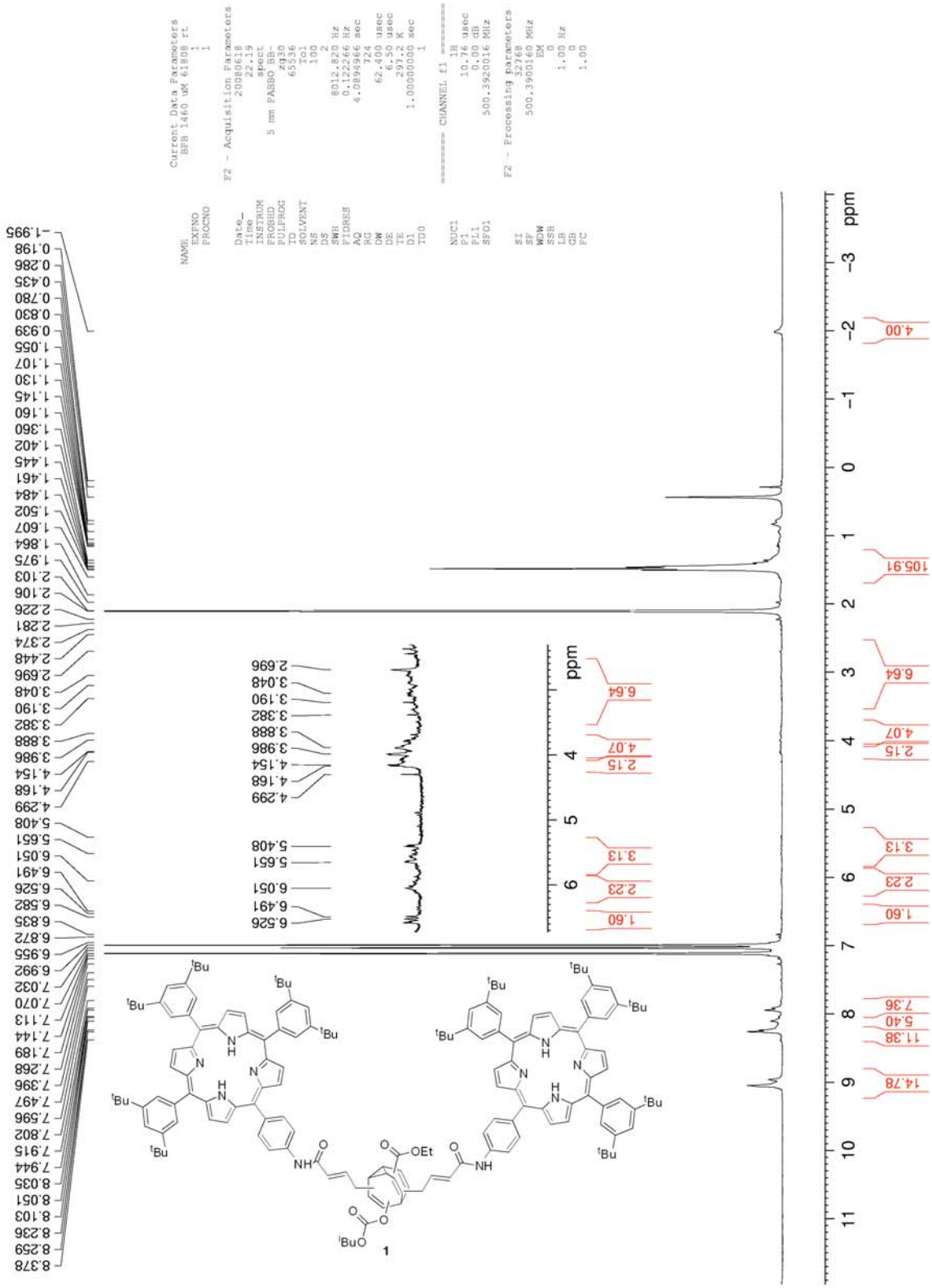
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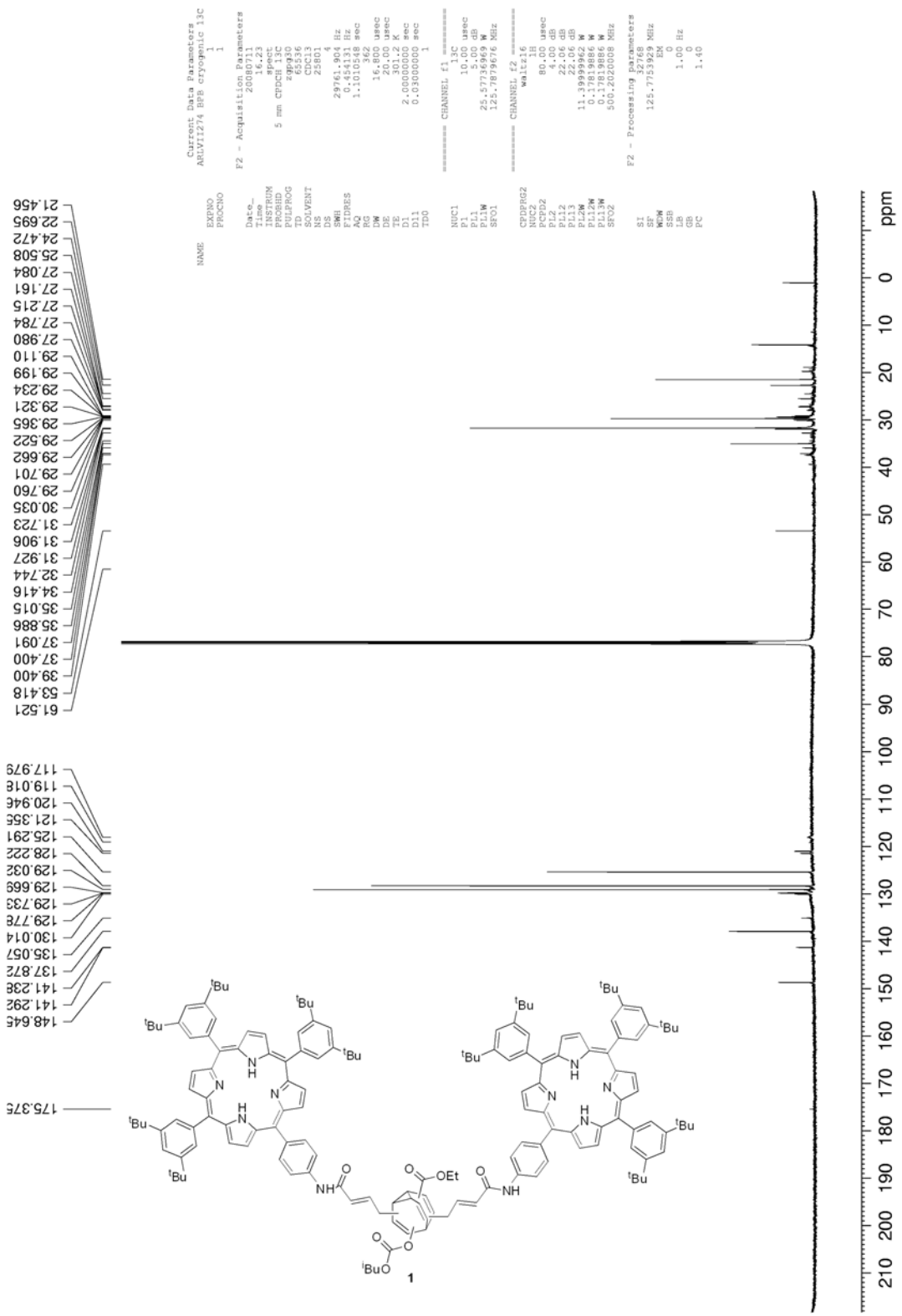
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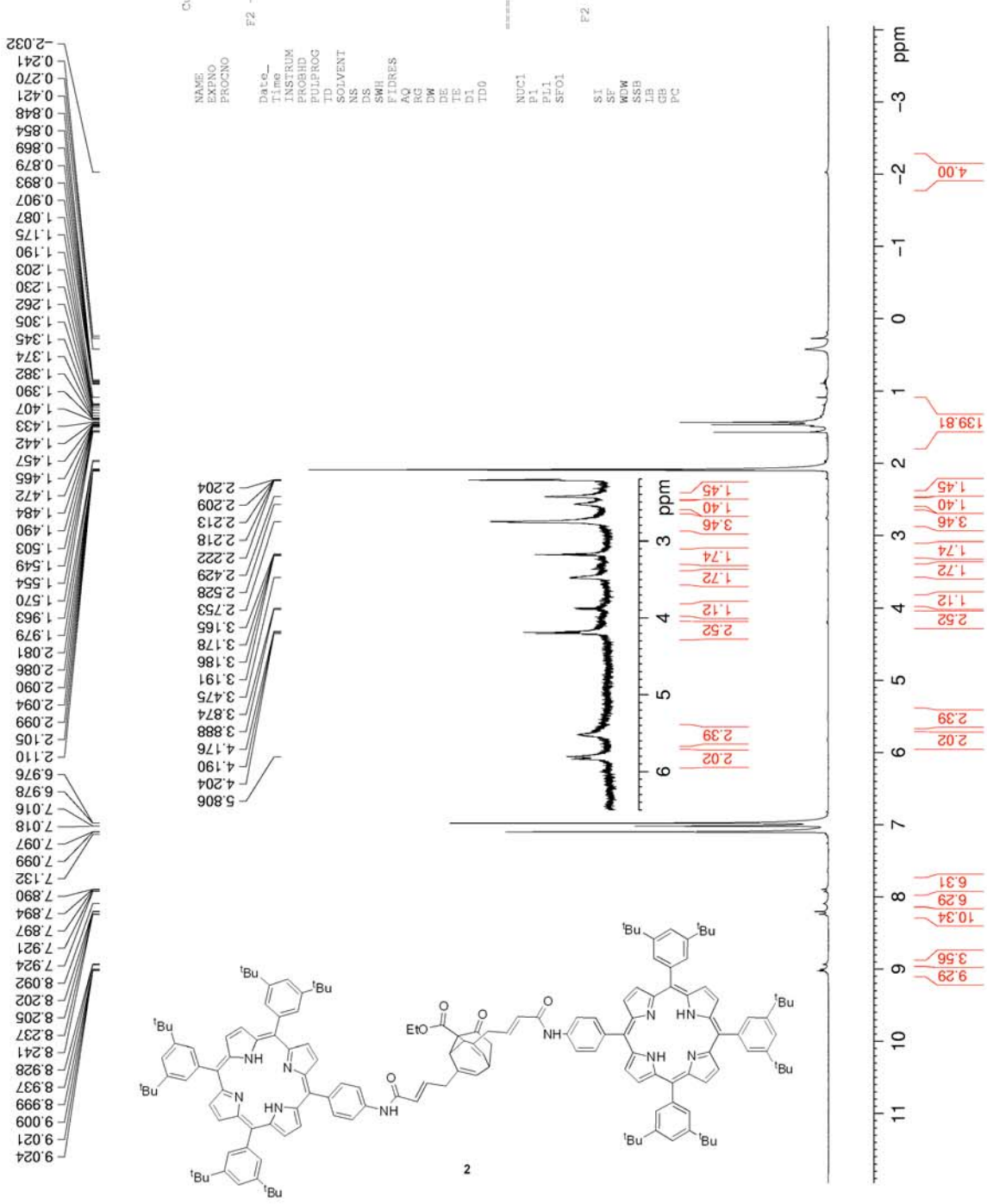
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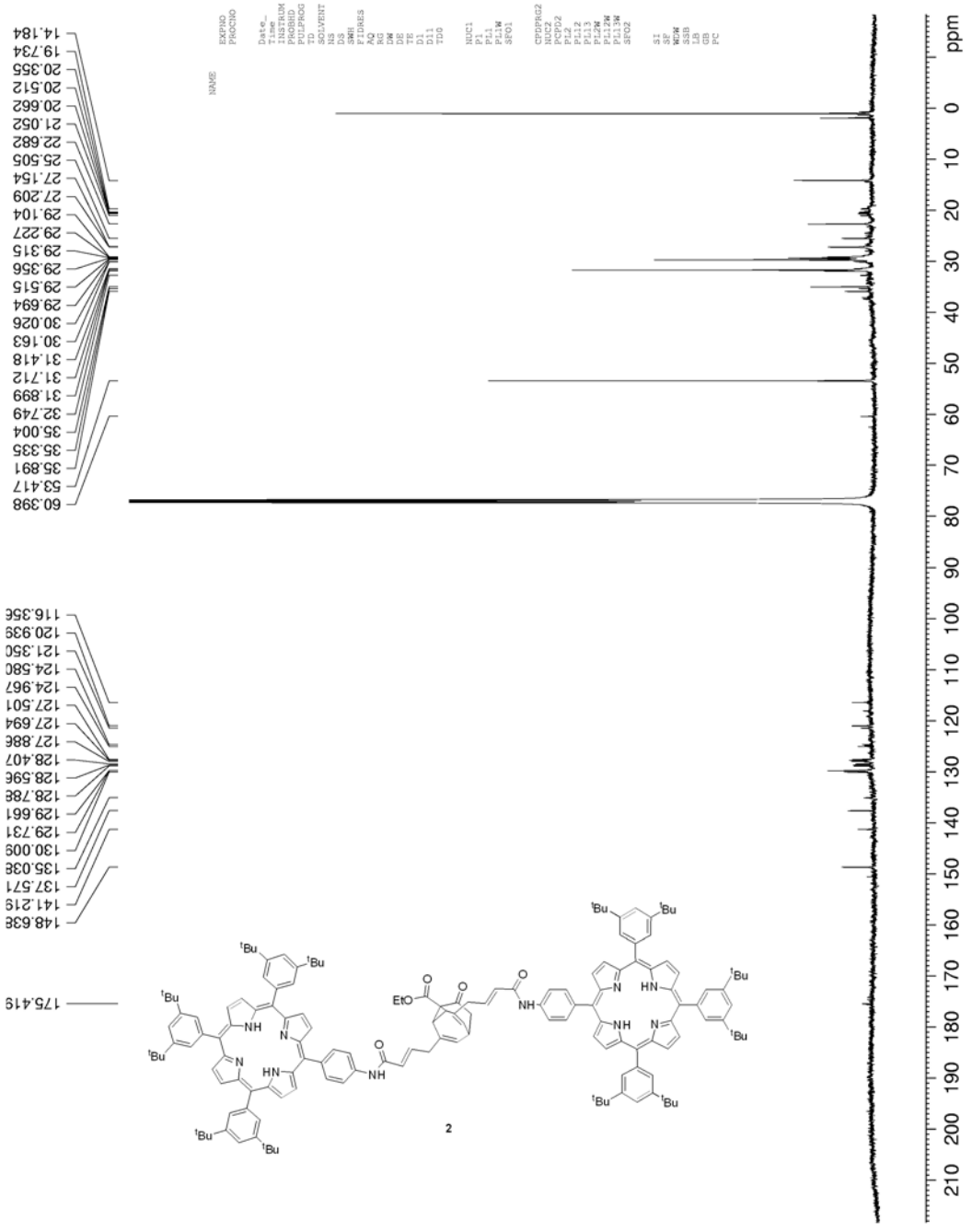
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