

**Electronic Supplementary Information for:**

**Synthesis and Characterization of Novel  
Dibenz[a,c]anthracenedicarboxythioimides: The Effect of  
Thionation on Self-Assembly**

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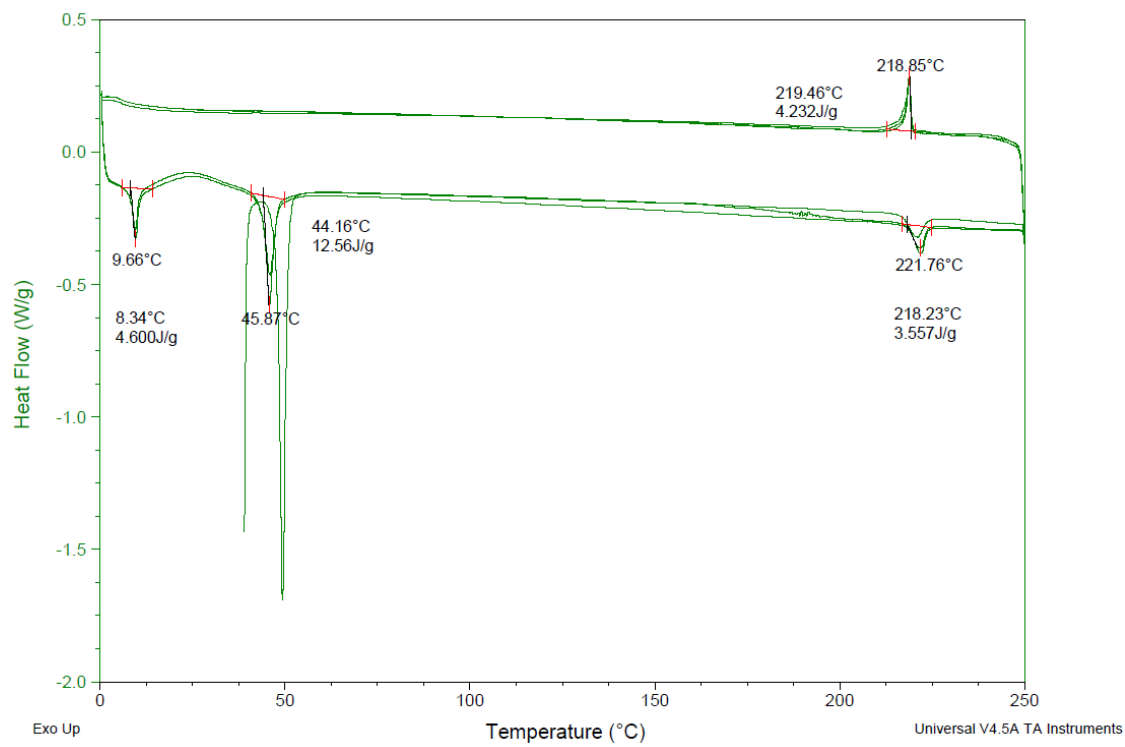
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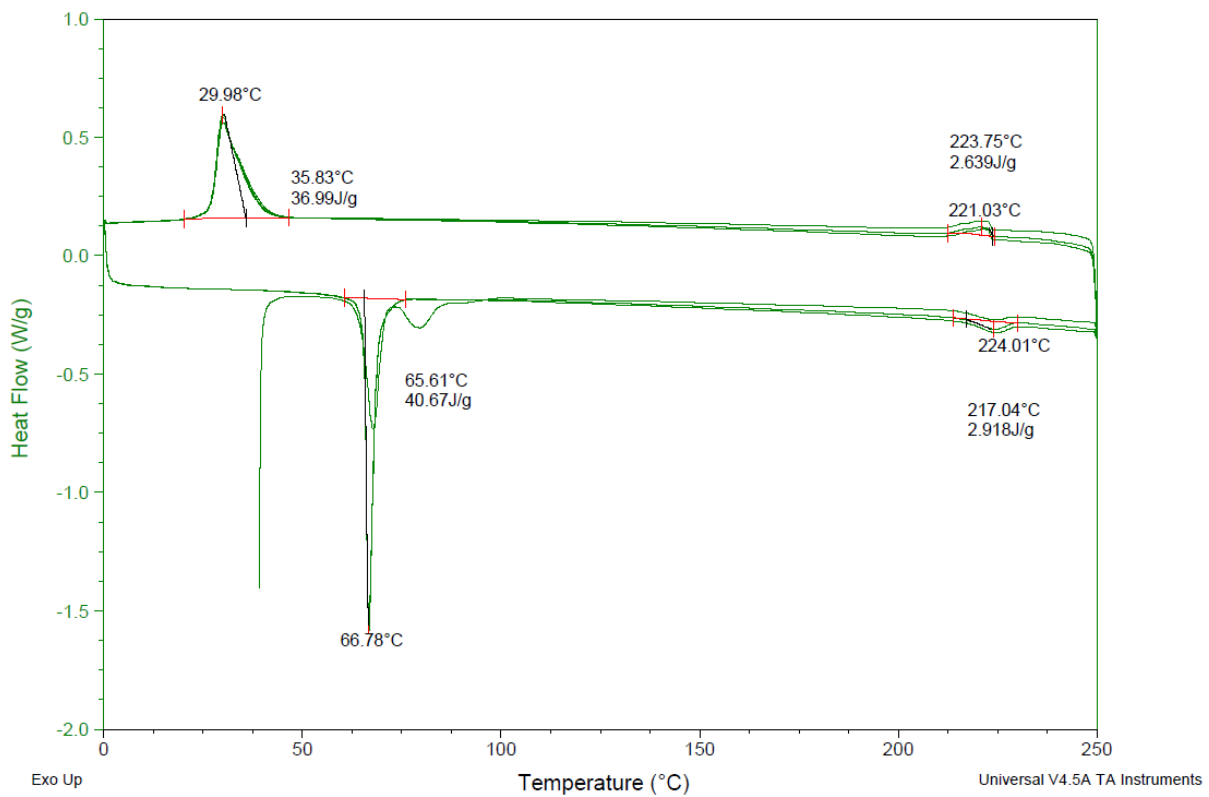
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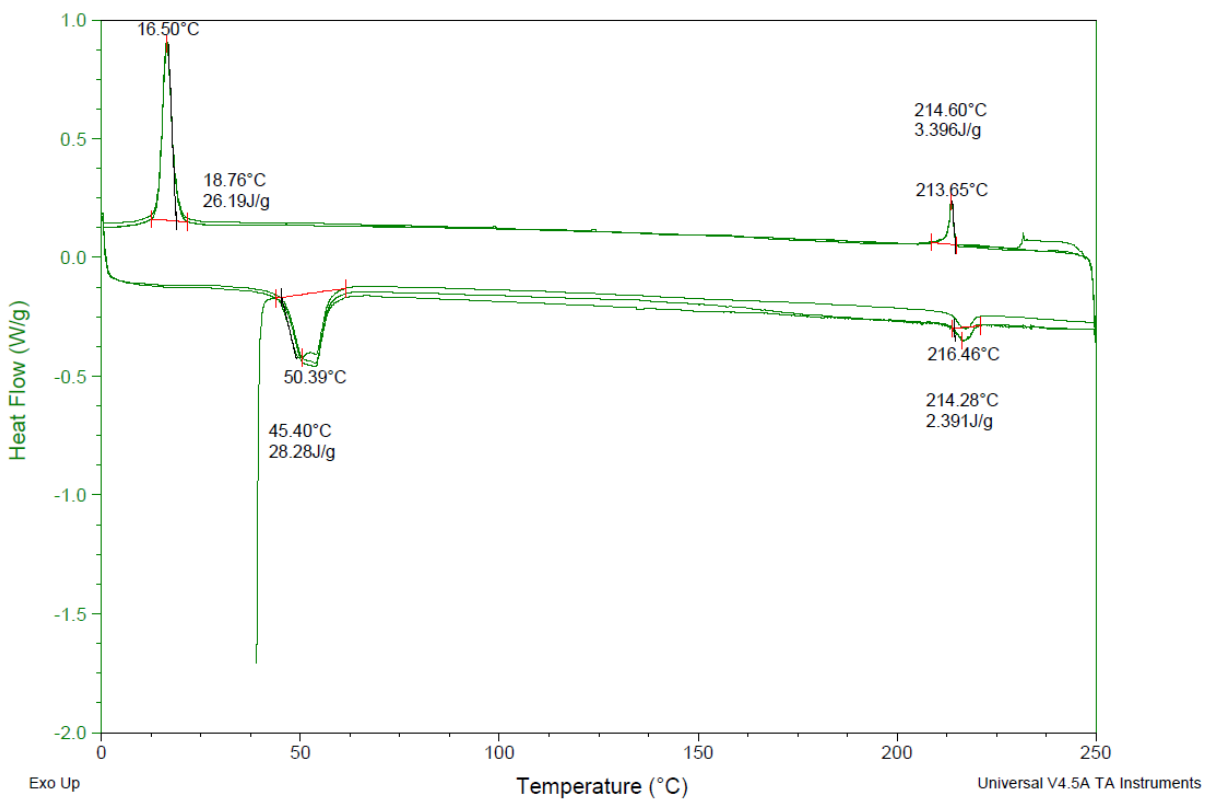
## Representative DSC Traces



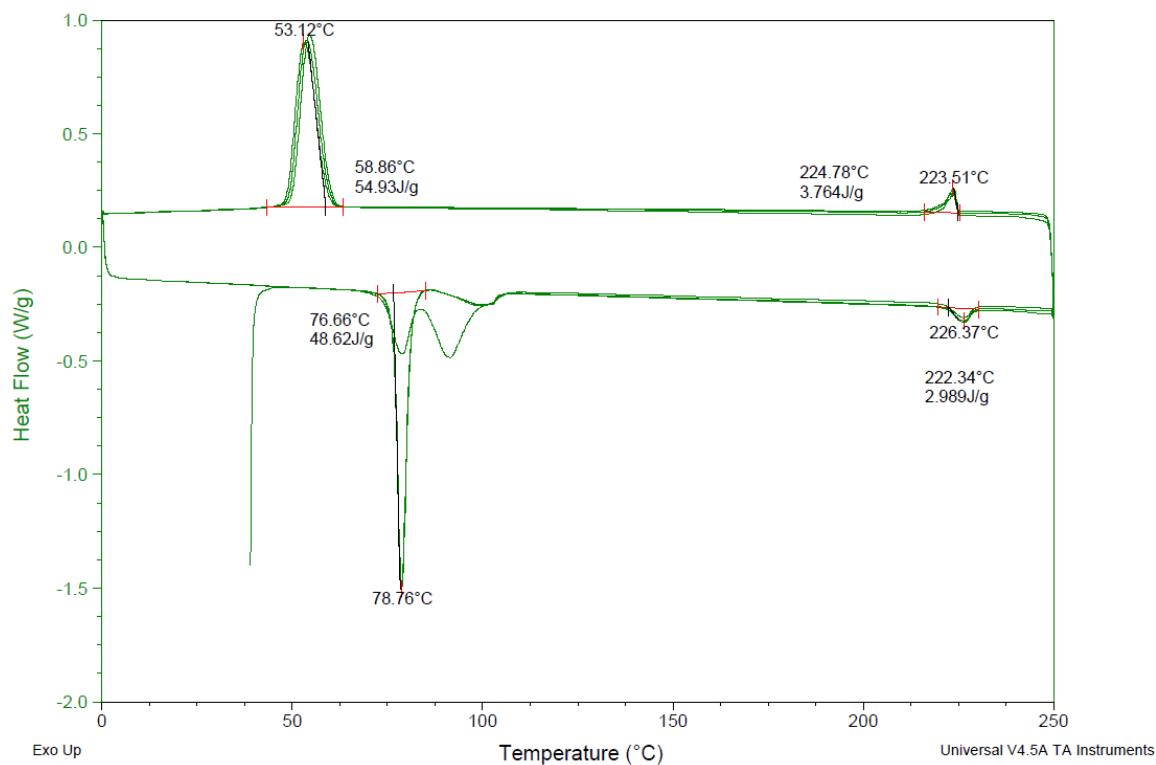
**Figure S1:** DSC trace of **2a**



**Figure S2: DSC trace of 2b**



**Figure S3: DSC trace of 3a**



**Figure S4:** DSC trace of **3b**

## Concentration Dependent $^1\text{H}$ NMR Studies and Dimer Model

### *Concentration Dependent $^1\text{H}$ NMR Experiments*

Dilution experiments were performed on compounds **1a,b**, **2a,b**, and **3a,b**. A 0.05 M stock solution of the desired derivative was prepared in chloroform- $d_6$ . The stock solution was subsequently diluted until a concentration of  $2.59 \times 10^{-4}$  M had been reached. An  $^1\text{H}$  NMR spectrum was recorded after each dilution. The chemical shifts of the aromatic protons were plotted as a function of concentration.

### *Dimer Model*

The data for the six derivatives was analyzed using the following model<sup>1</sup>:

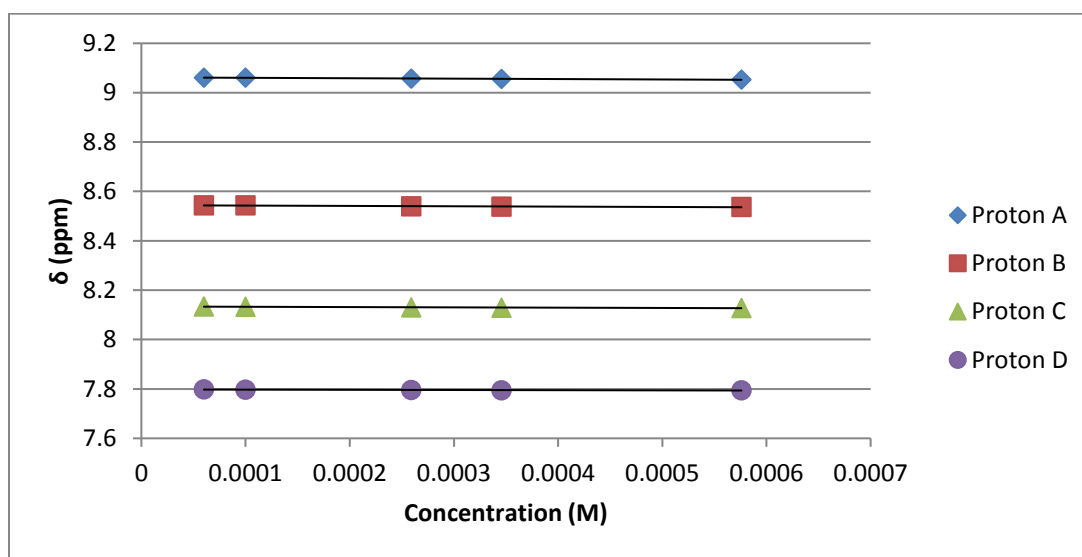
$$(\delta - \delta_A) = \frac{1 + 4K_{dim}[A]_0 - \sqrt{1 + 8K_{dim}[A]_0}}{4K_{dim}[A]_0} (\delta_{dim} - \delta_A) \quad (\text{S1})$$

<sup>1</sup> Lavigueur, C.; Foster, E.J.; Williams, V.E. *J. Am. Chem. Soc.* **2008**, *130*, 11791-11800.

This model defines the relationship between the change in chemical shift ( $\delta - \delta_A$ ) and the total concentration of compound in solution  $[A]_0$  based on two parameters, the dimerisation constant  $K_{dim}$  and the chemical shift of the dimer  $\delta_{dim}$ .

#### *Fitting with the Dimer Model*

In order to fit the data to the dimer model, the chemical shift of the monomer had to be estimated. This was done by linear regression on the first data points for each curve (between  $2.59 \times 10^{-4}$  and  $5.76 \times 10^{-4}$  M). Figure S5 shows the fit for **1a**.



**Figure S5:** Change in chemical shifts with concentration for **1a** at low concentrations. Lines show linear fit extrapolated to zero to evaluate the chemical shifts of the monomer.

Once the chemical shifts of the monomers were obtained for each of the six compounds, the difference in chemical shift ( $\delta - \delta_A$ ) was plotted against concentration and the plots were fitted to equation S1 using a non-linear two parameter fit performed with the Levenberg-Marquadt least squares routine in the Non Linear Curve Fitting Tool of Origin 6.1. This gave both the chemical shift for the dimer and a dimerisation constant for each proton. The dimerisation constant constants for each molecule were obtained by averaging the values obtained for each proton. The results can be seen in Table S1.

**Table S1:** Dimerization constants and reduced chi-squared values obtained with each proton.

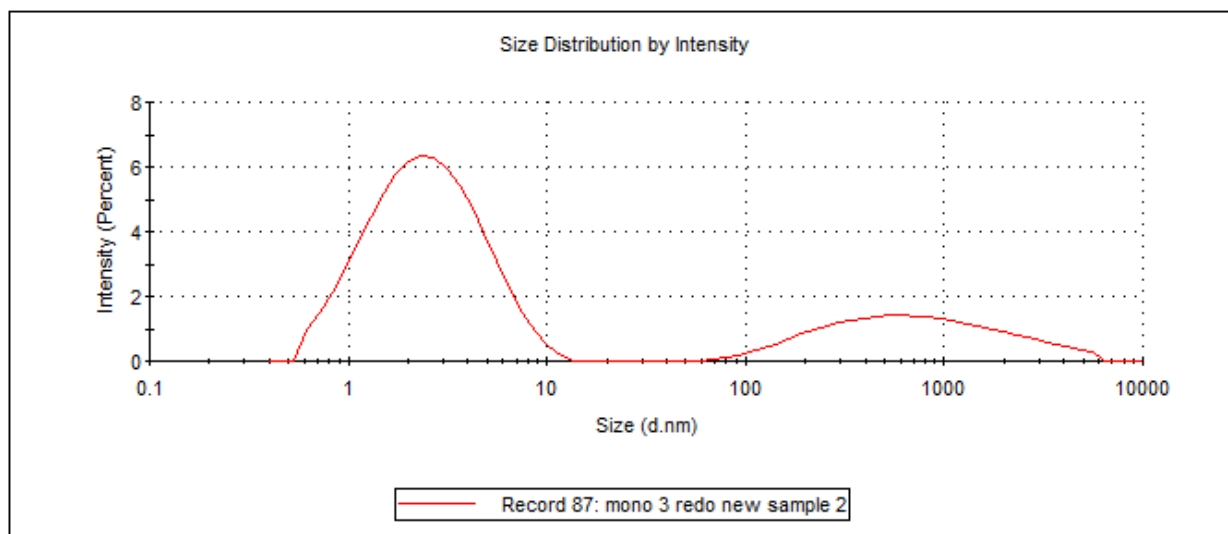
	Proton A	Proton B	Proton C	Proton D	Proton E	Proton F	Average	Std. Dev.
<b>1a</b> K <sub>dim</sub> (M <sup>-1</sup> ) Reduced chi-squared	1.39 1.00E-3	1.00 2.71E-4	1.06 3.05E-4	0.42 2.21E-4			1.07	0.31
<b>2a</b> K <sub>dim</sub> (M <sup>-1</sup> ) Reduced chi-squared	4.82 2.47E-4	4.55 2.07E-4	5.03 1.85E-4	5.06 1.91E-4	4.36 1.47E-4	3.58 4.72E-5	4.61	0.43
<b>3a</b> K <sub>dim</sub> (M <sup>-1</sup> ) Reduced chi-squared	10.92 4.59E-4	11.58 4.62E-4	10.19 1.90E-4	8.48 9.60E-5			10.29	1.33
<b>1b</b> K <sub>dim</sub> (M <sup>-1</sup> ) Reduced chi-squared	2.28 9.44E-5	2.47 1.08E-4	2.18 1.20E-4	1.57 2.57E-5			2.15	0.24
<b>2b</b> K <sub>dim</sub> (M <sup>-1</sup> ) Reduced chi-squared	6.42 5.59E-4	6.59 6.19E-4	6.08 1.81E-4	6.06 2.04E-4	5.69 1.79E-4	5.17 4.73E-5	6.07	0.44
<b>3b</b> K <sub>dim</sub> (M <sup>-1</sup> ) Reduced chi-squared	16.38 8.47E-4	16.08 5.40E-4	14.92 3.60E-4	14.00 1.19E-4			15.43	1.31

### Dynamic Light Scattering Experiments

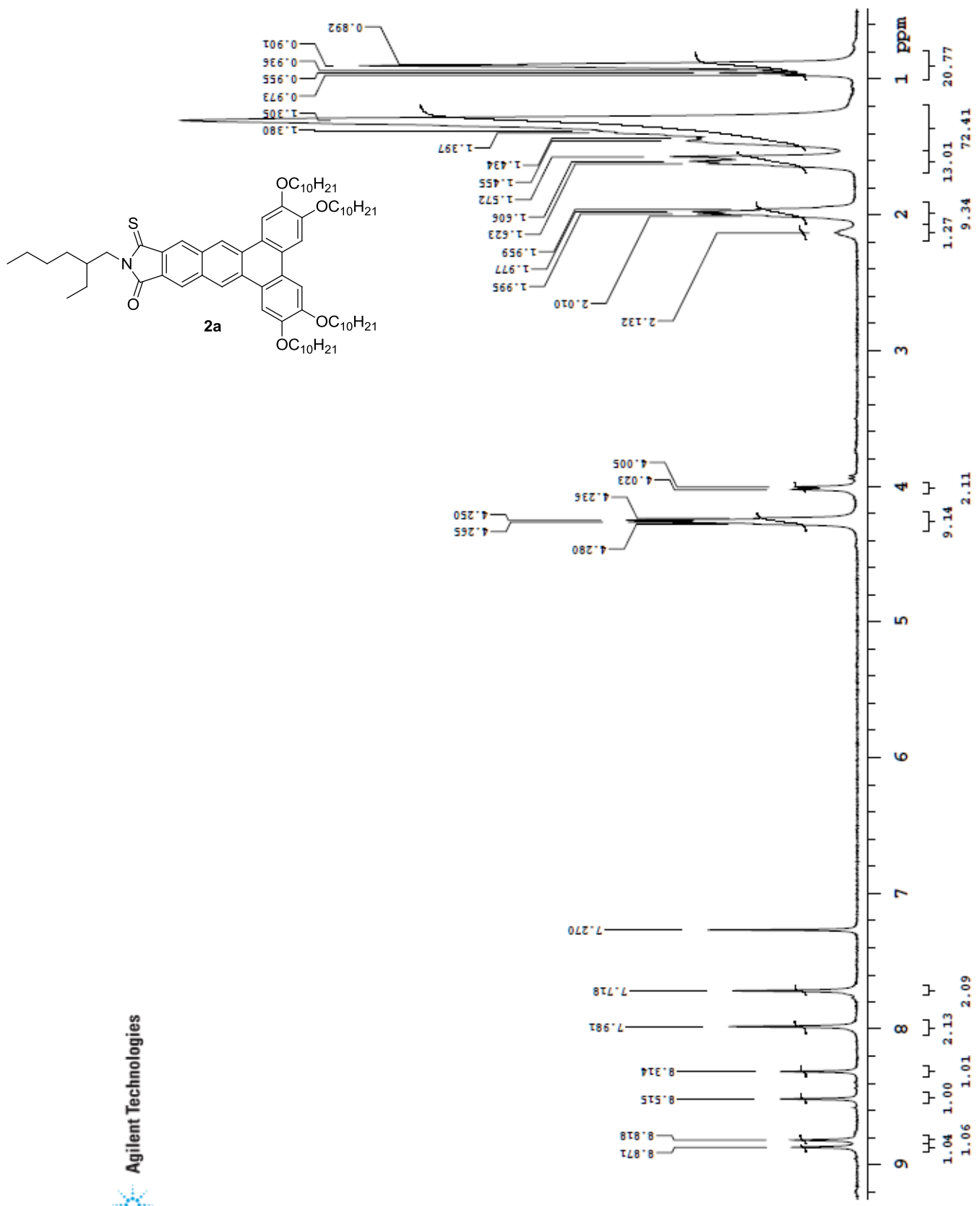
Hydrodynamic diameter measurements were carried out by dynamic light scattering on **1a** and **2a** at various concentrations. All measurements were performed at 25 °C in chloroform (viscosity: 0.5370 cP, refractive index: 1.445) in a glass cuvette. Sample volumes of 2 mL were used. Prepared solutions were filtered through 0.45 μm polytetrafluoroethylene membranes made by VWR International before being measured.

For each compound at each concentration, 3 trials of 17 measurements were performed and averaged. Individual results were analyzed using an intensity size distribution. Often, two peaks were observed in the intensity size distribution, as exemplified in Figure S6. Only the peak corresponding to a smaller particle size (10 to 30 Å) was considered while the larger peak was attributed to trace impurities present at minute concentrations.<sup>1,2</sup>

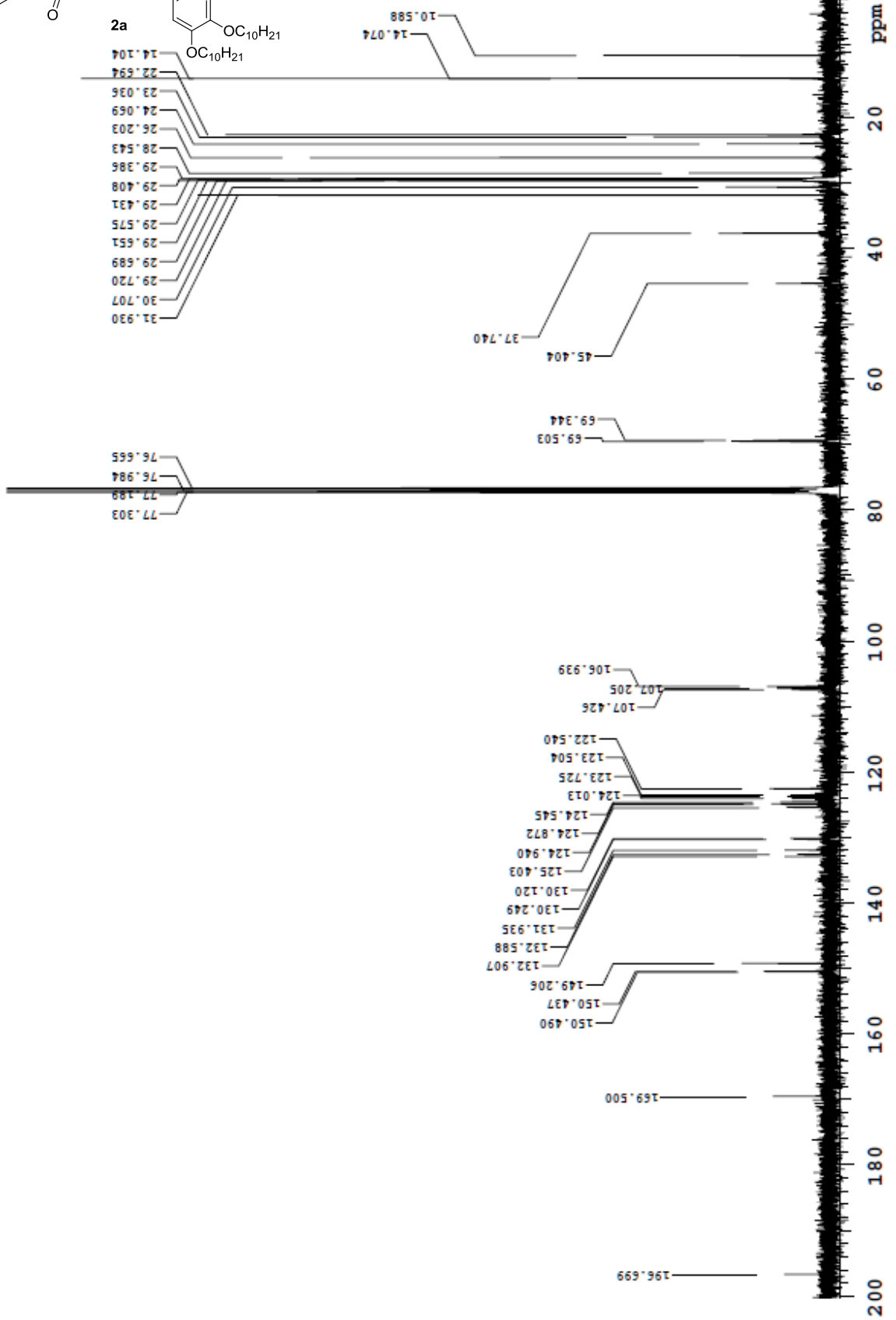
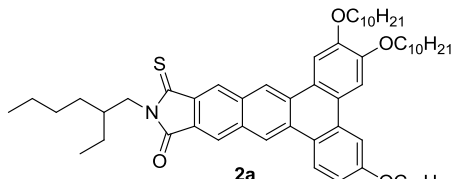
<sup>2</sup> (a) Pecora, R.J. *Nanopart. Res.* 2000, **2**, 123. (b) Schmitz, K.S. *In Introduction to Dynamic Light Scattering by Macromolecules.* Academic Press Inc. Boston: MA, 2003.

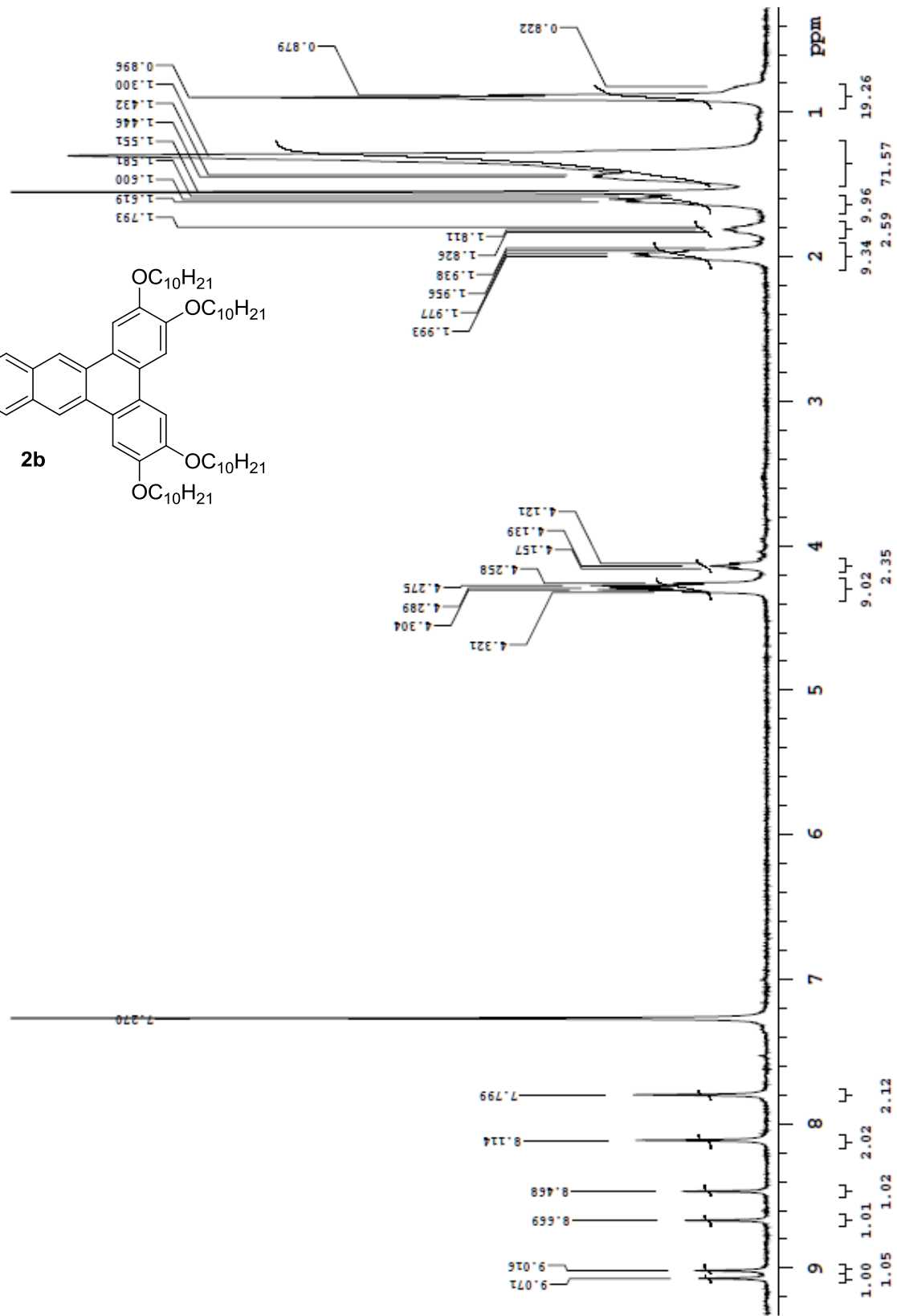
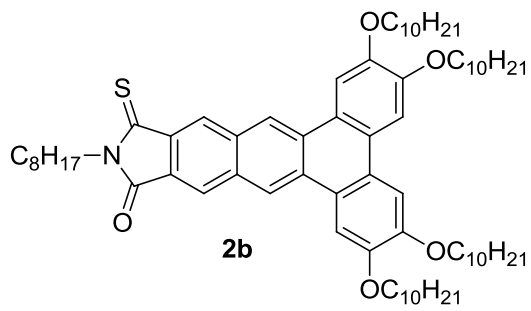


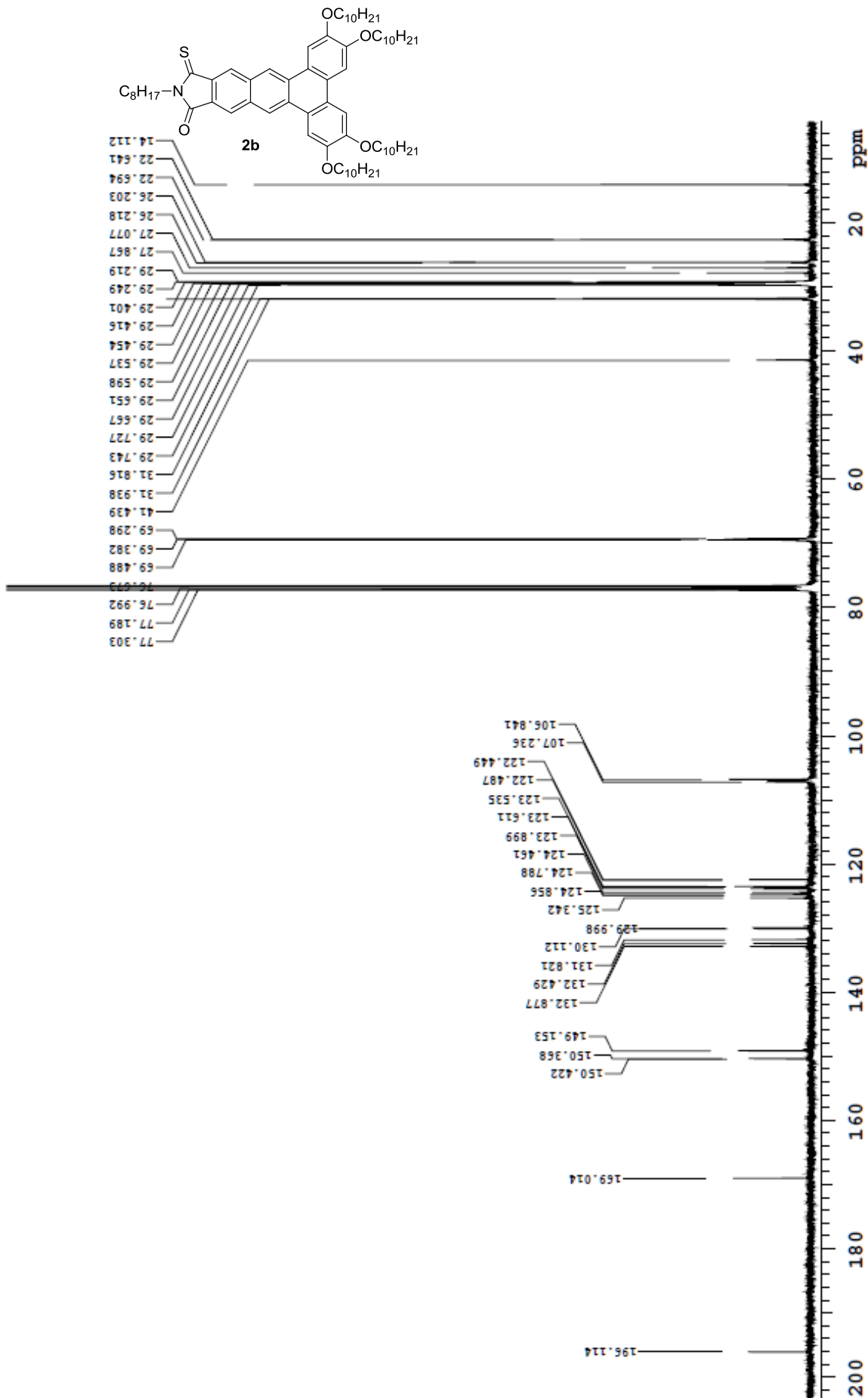
**Figure S6:** Example of results obtained for **2a** at 0.01 M. In this case, peaks were observed at 2.882 nm and 1089 nm corresponding to 73.7% and 26.3% of the scattered light intensity, respectively. Only the 2.882 nm peak was used when calculating the average size.

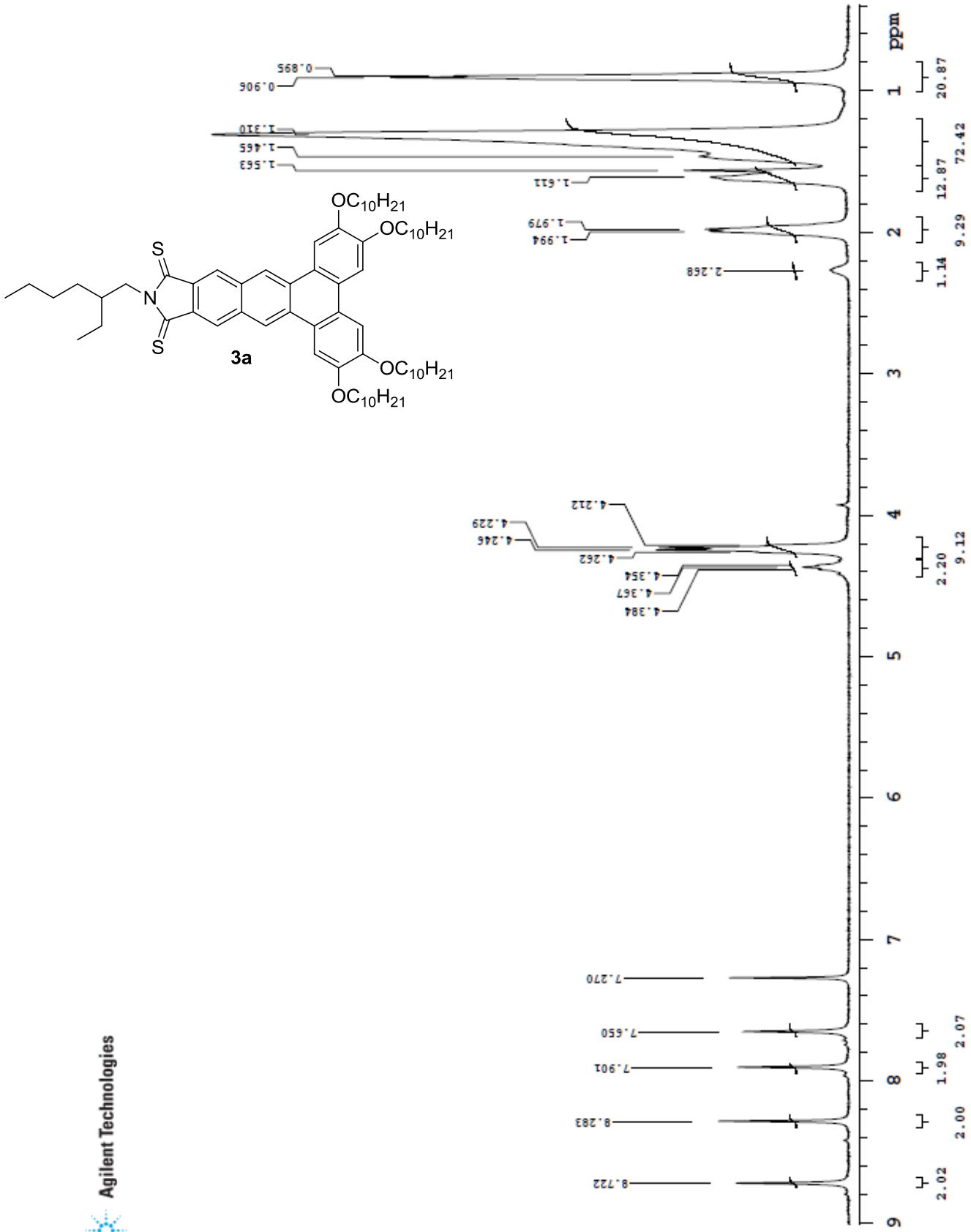


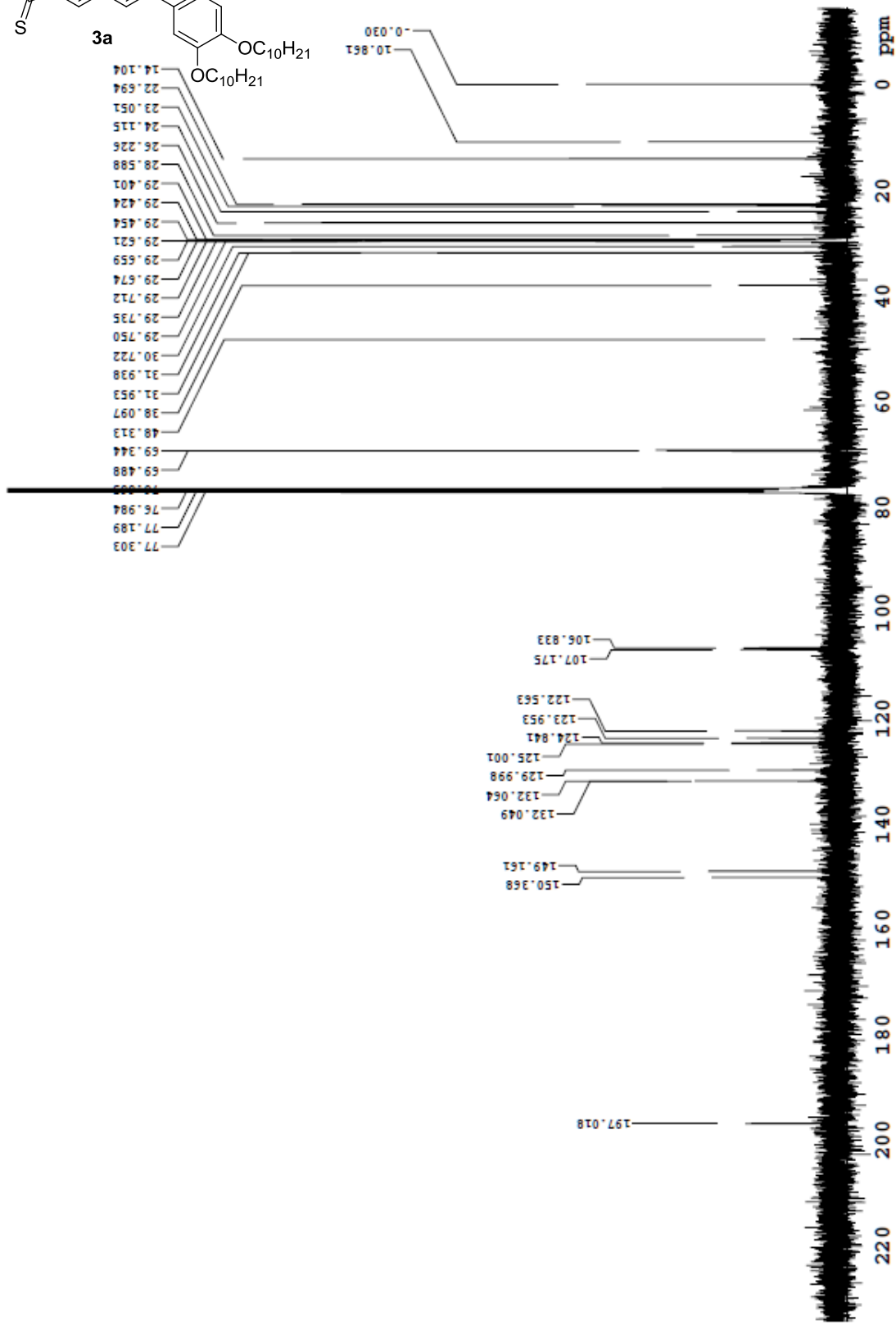
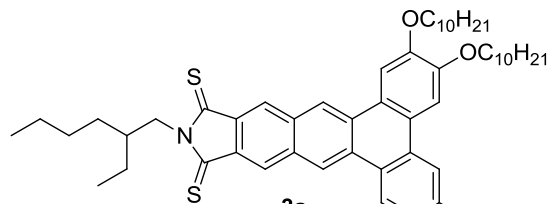


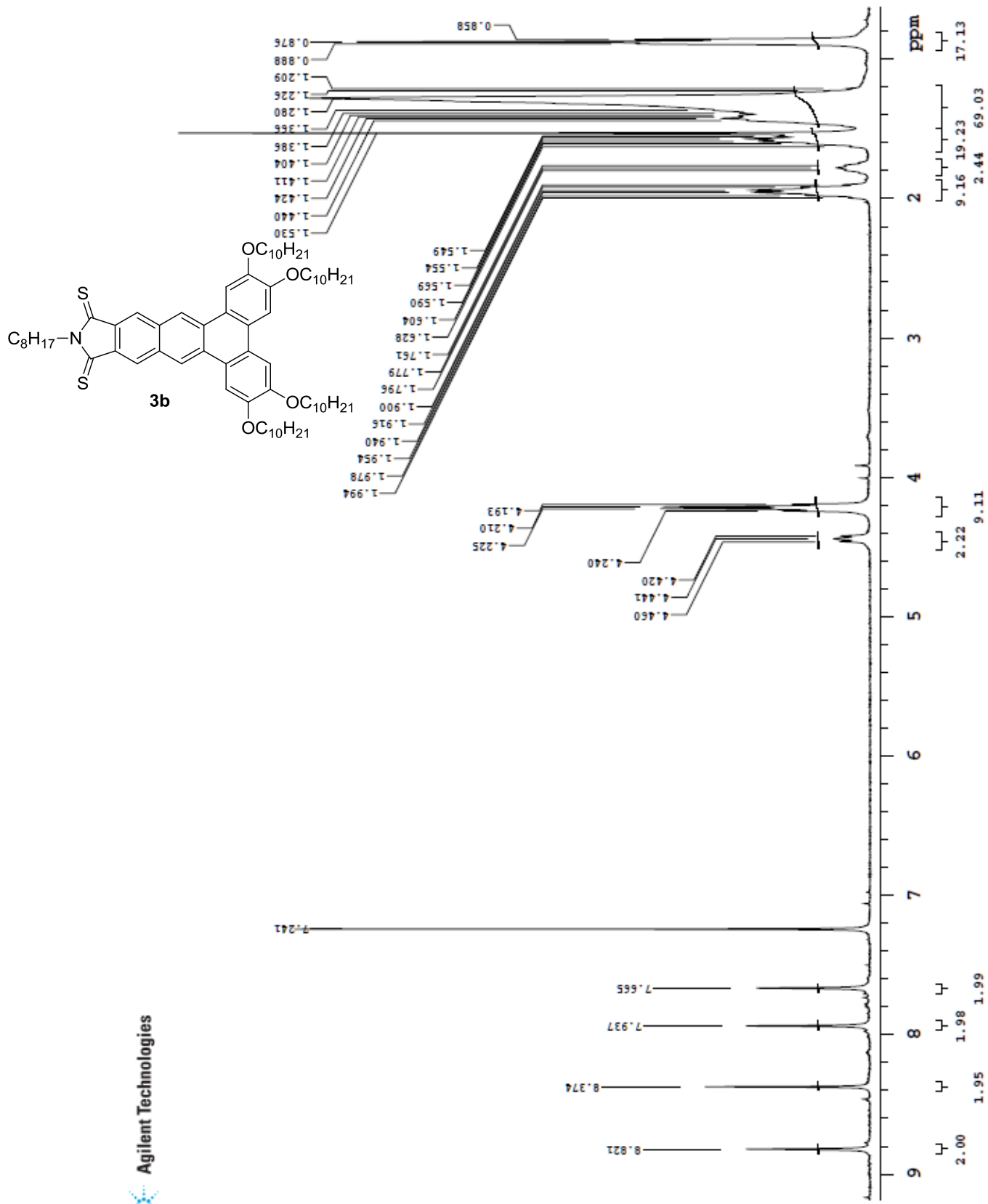


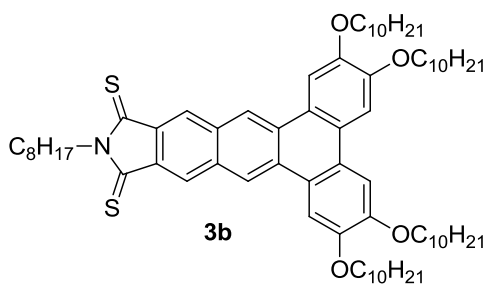












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