

# Supporting Information

## A General Method for the Synthesis of Functionalized Tetrabenzo[8]circulenes

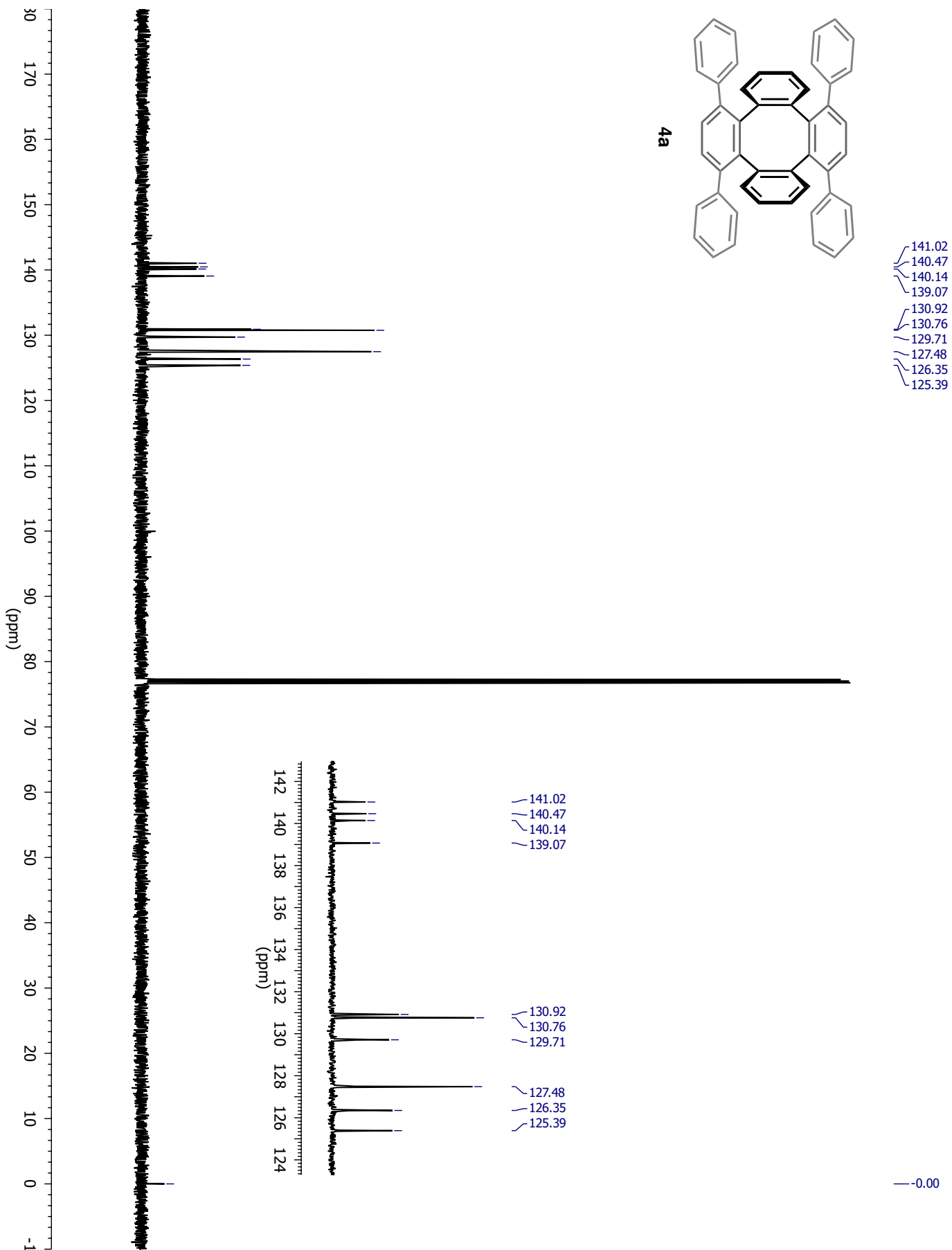
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**Figure S2:**  $^{13}\text{C}$  NMR Spectrum of 1,4,9,12-tetraphenyltetraphenylene (**4a**) in  $\text{CDCl}_3$ .

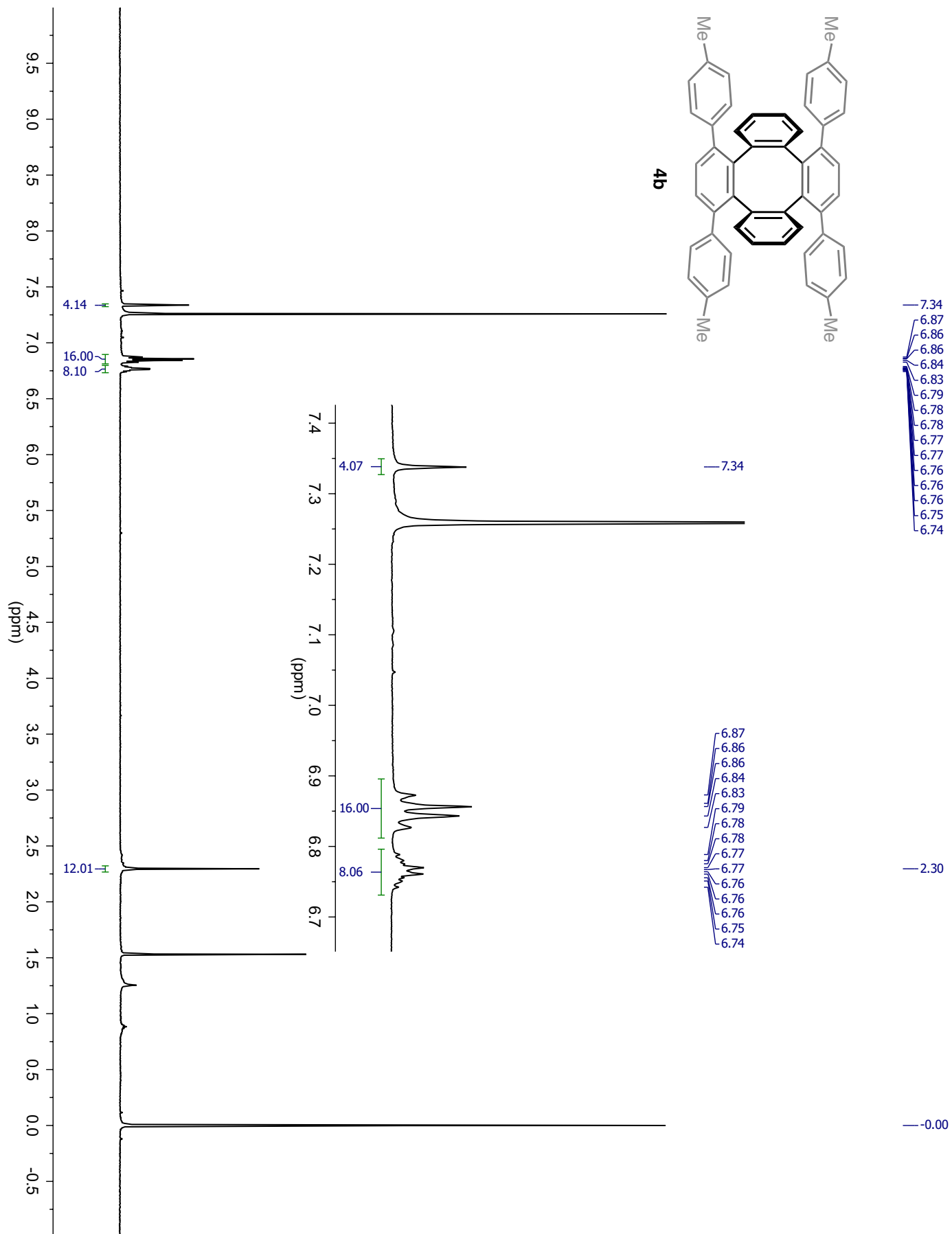
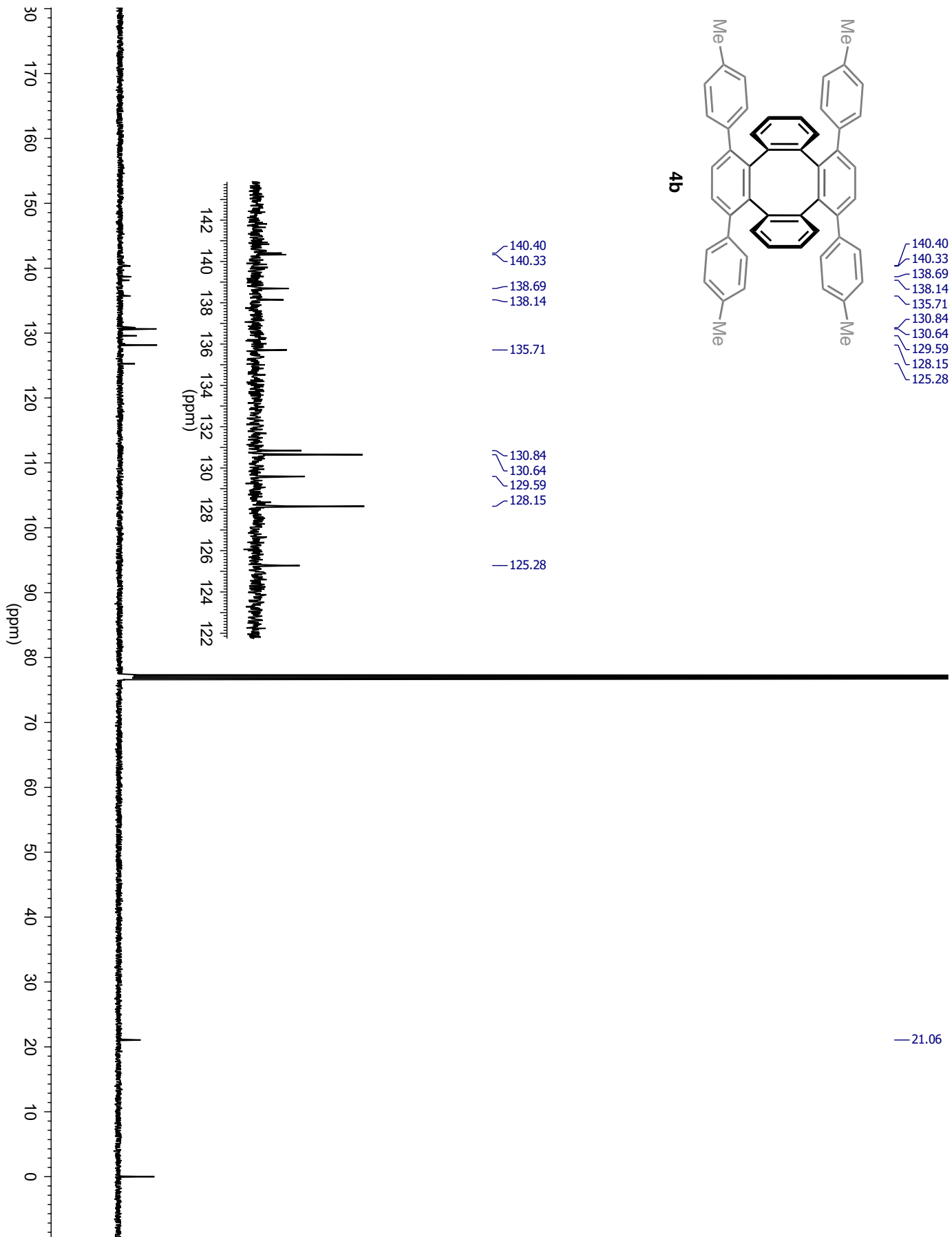
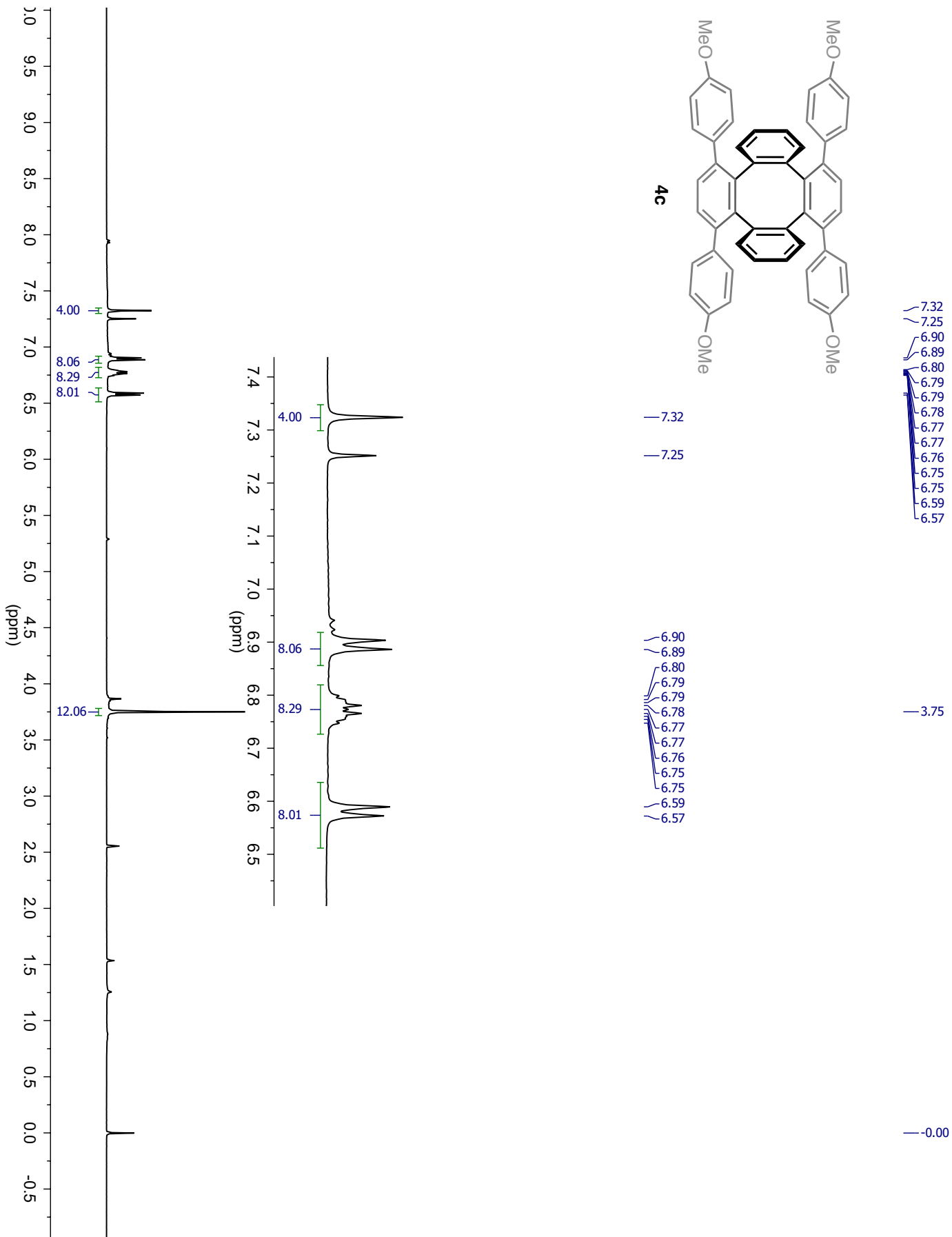


Figure S3:  $^1\text{H}$  NMR Spectrum of 1,4,9,12-tetra-*p*-tolyltetraphenylene (**4b**) in CDCl<sub>3</sub>.



**Figure S4:**  $^{13}\text{C}$  NMR Spectrum of 1,4,9,12-tetra-*p*-tolyltetraphenylene (**4b**) in CDCl<sub>3</sub>.



**Figure S5:** <sup>1</sup>H NMR Spectrum of 1,4,9,12-tetrakis(4-methoxyphenyl)tetraphenylene (**4c**) in CDCl<sub>3</sub>.

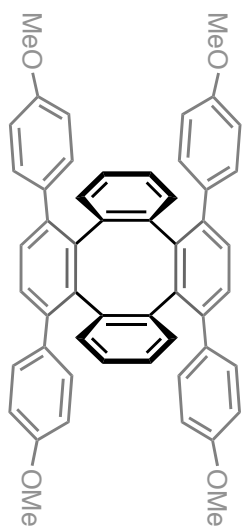
— 158.26

140.68  
140.60  
138.39  
133.69  
132.04  
131.06  
129.75  
125.56

— 113.05

77.48  
77.22  
76.97

— 55.23



**4c**

— 158.26

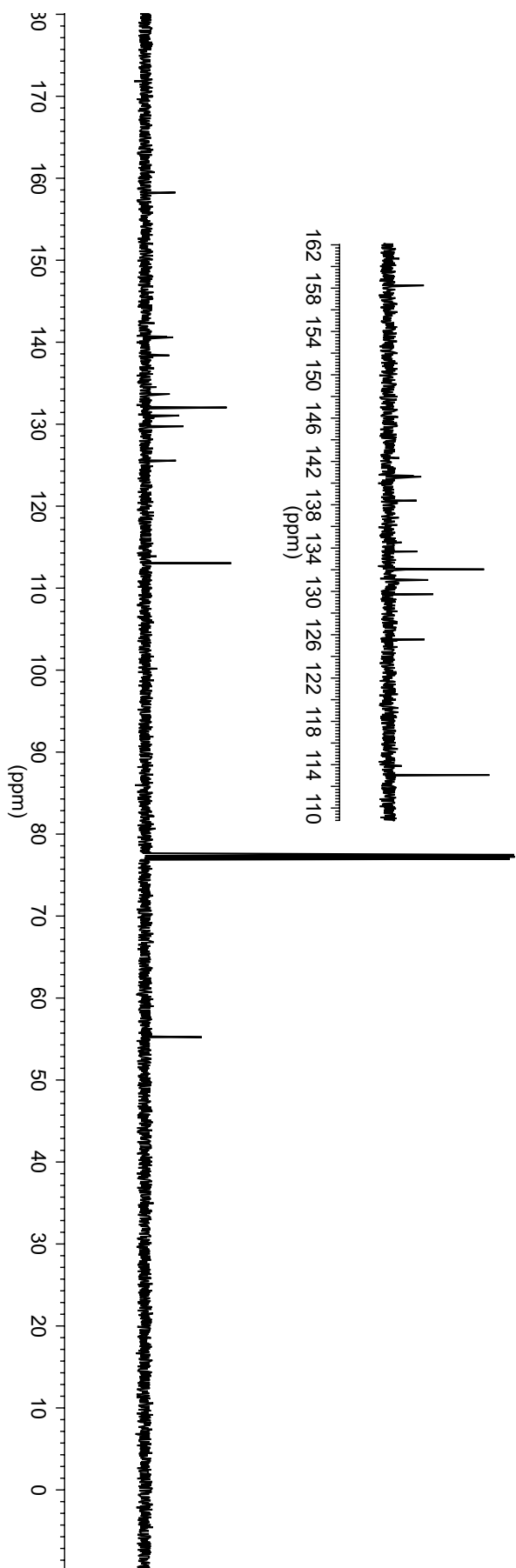
140.68  
140.60  
138.39

133.69  
132.04  
131.06  
129.75

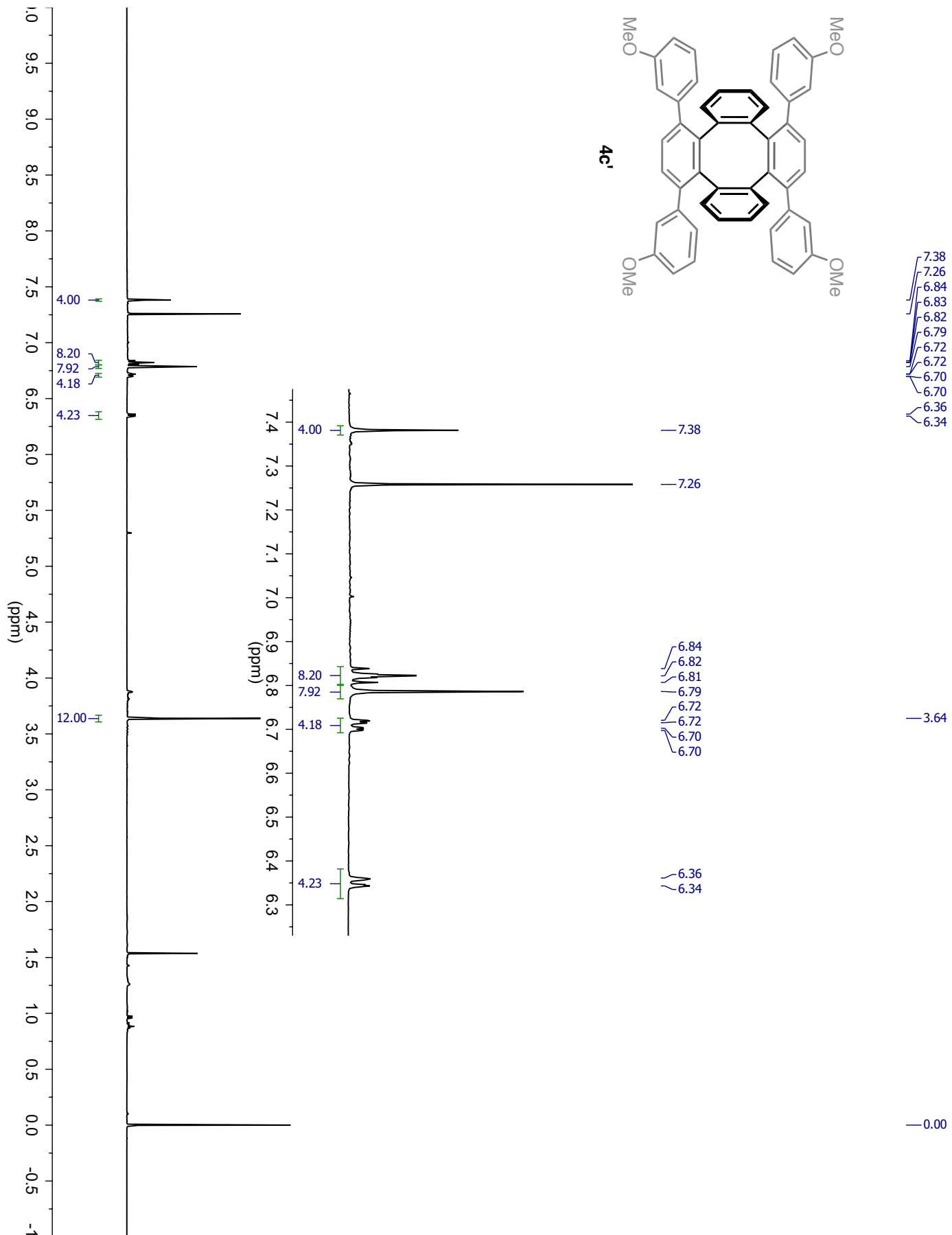
— 125.56

— 113.05

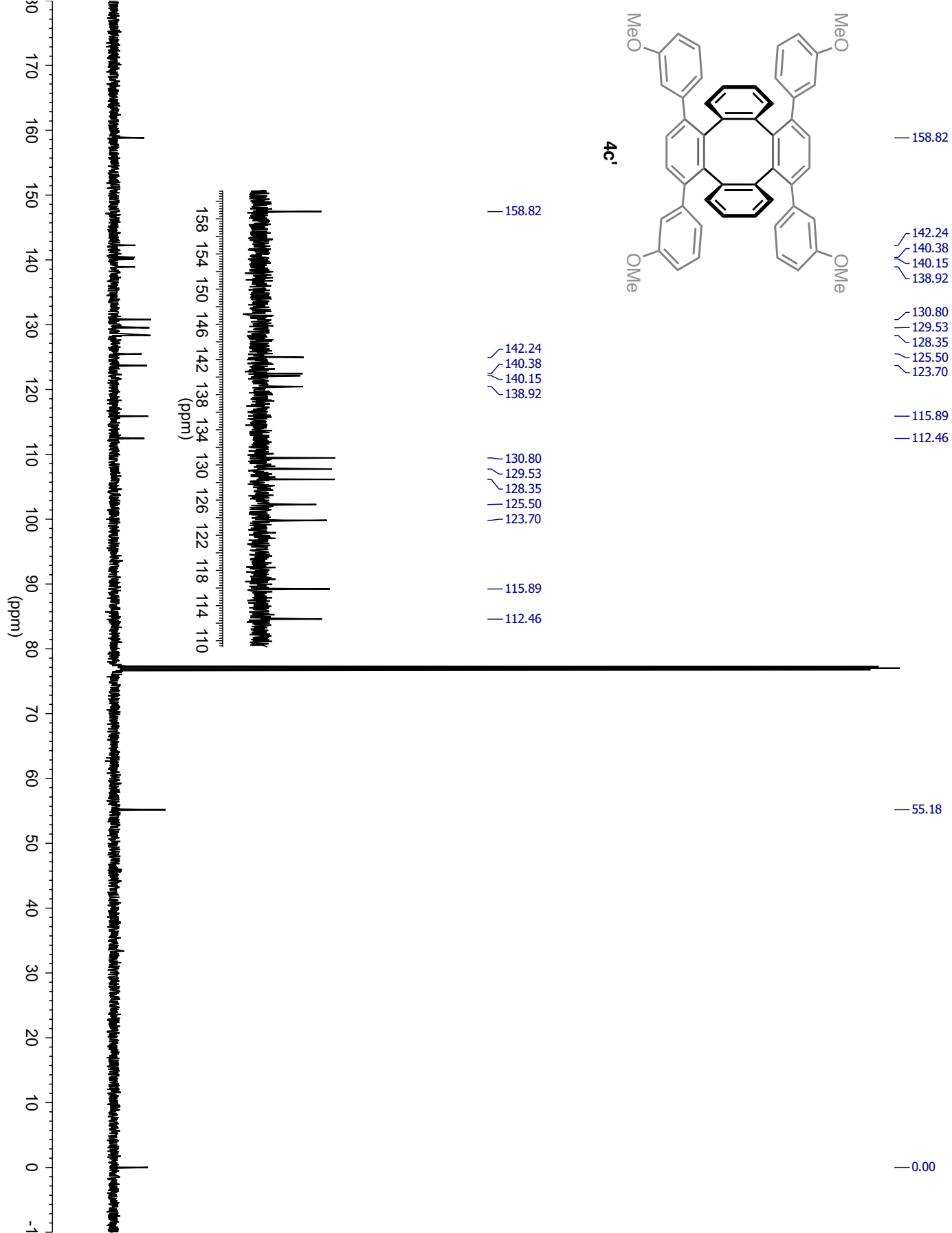
162 158 154 150 146 142 138 134 130 126 122 118 114 110  
(ppm)



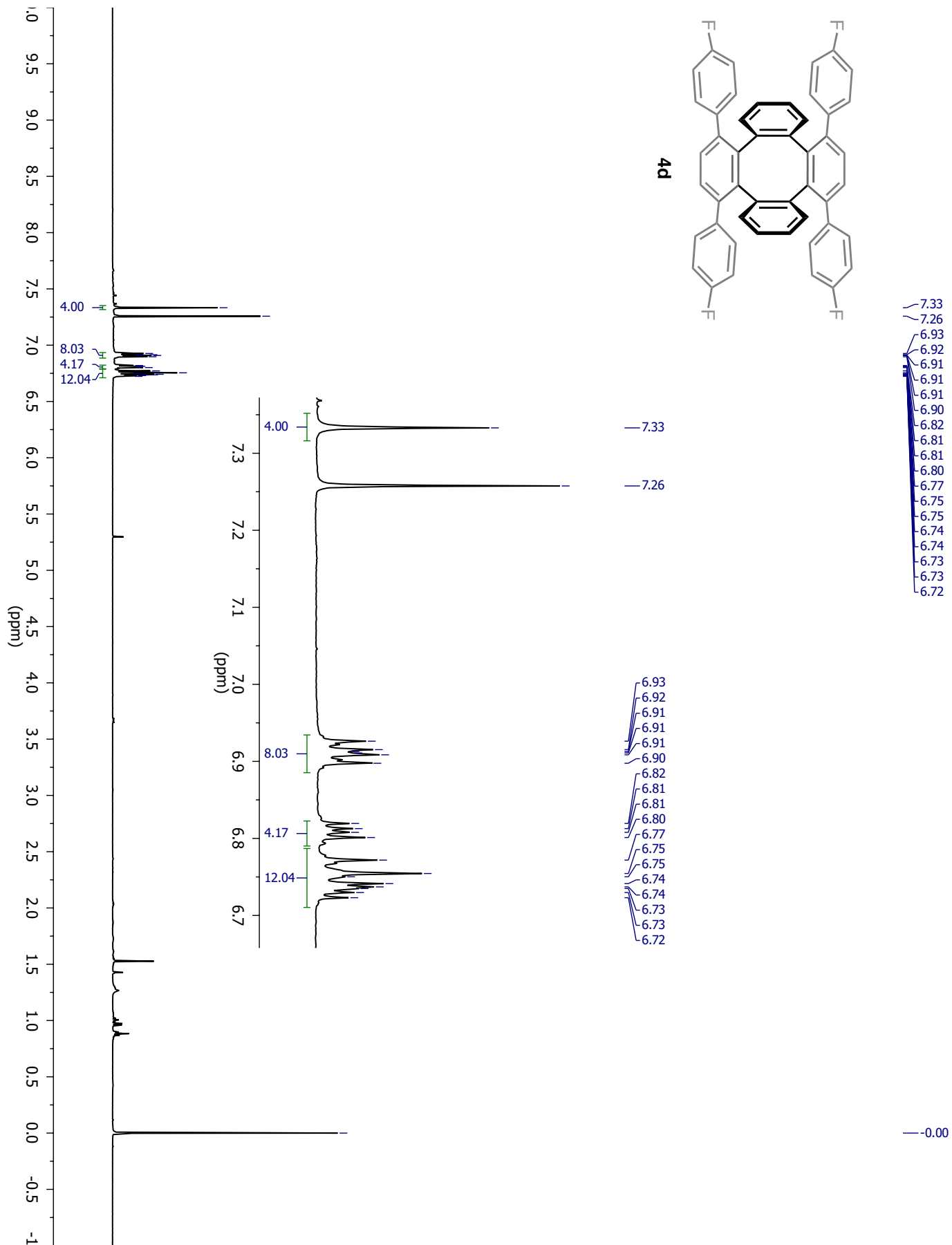
**Figure S6:**  $^{13}\text{C}$  NMR Spectrum of 1,4,9,12-tetrakis(4-methoxyphenyl)tetraphenylene (**4c**) in  $\text{CDCl}_3$ .



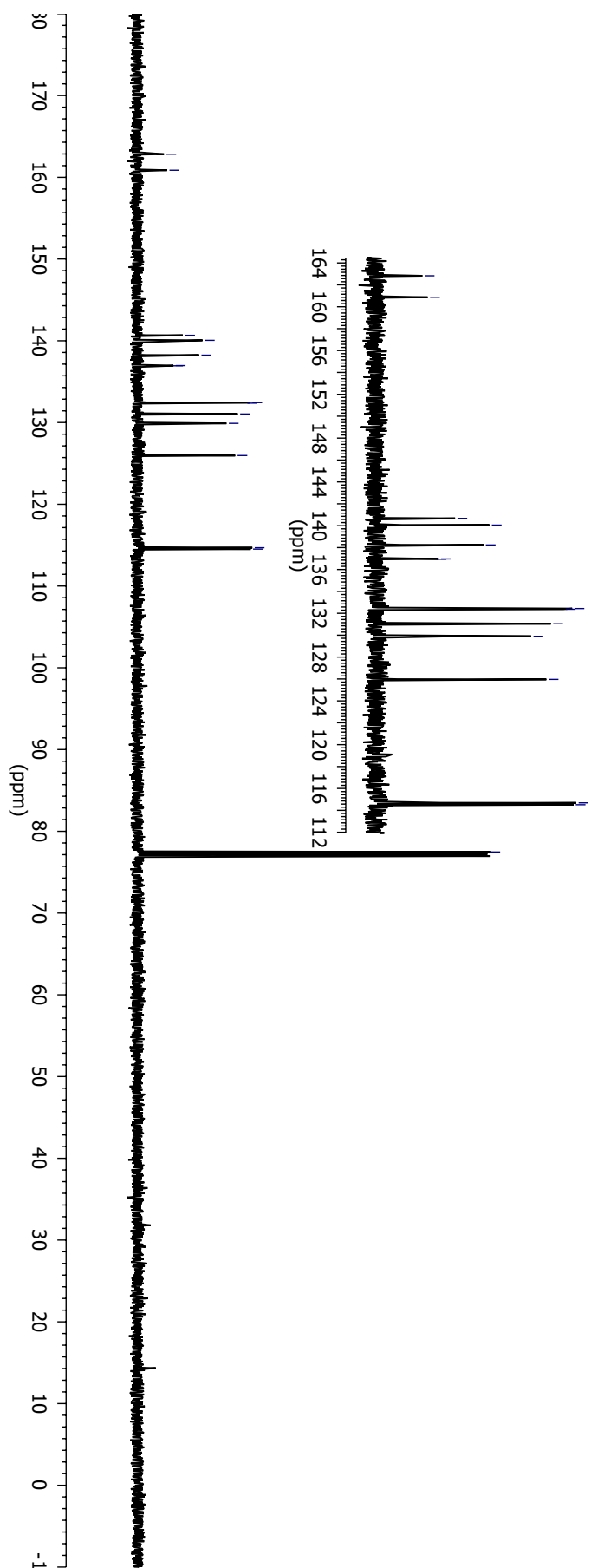
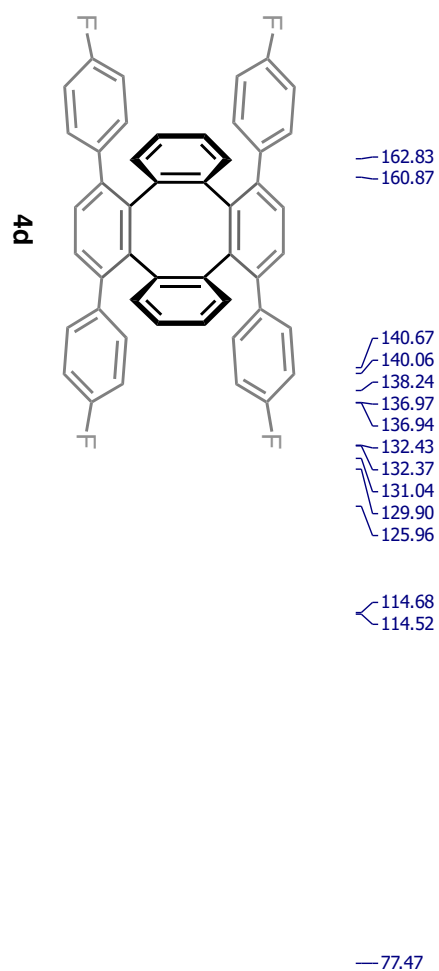
**Figure S7:** <sup>1</sup>H NMR Spectrum of 1,4,9,12-tetrakis(3-methoxyphenyl)tetraphenylene (**4c'**) in CDCl<sub>3</sub>.



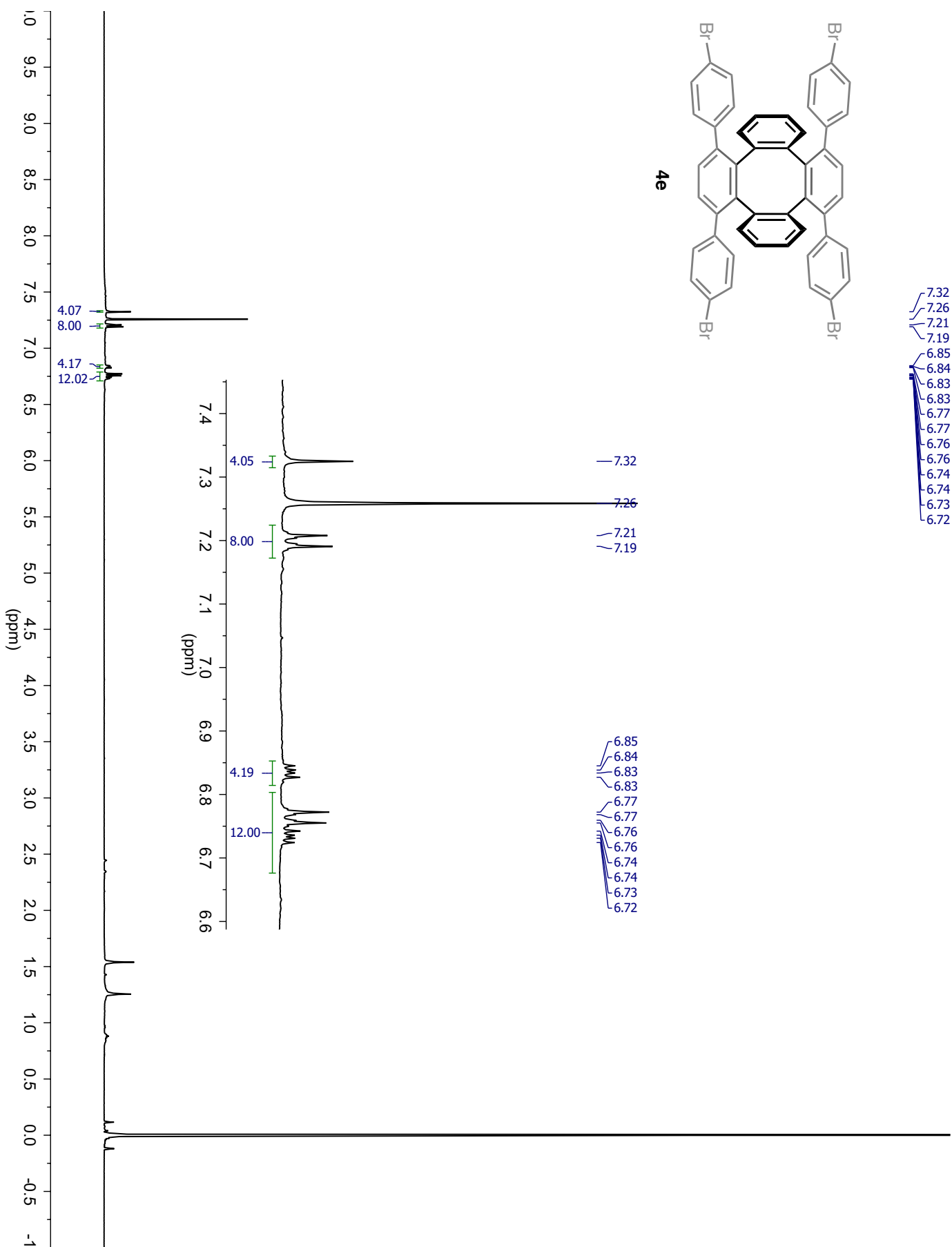
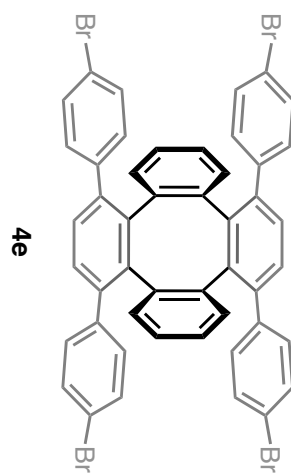
**Figure S8:**  $^{13}\text{C}$  NMR Spectrum of 1,4,9,12-tetrakis(3-methoxyphenyl)tetraphenylene (**4c'**) in  $\text{CDCl}_3$ .



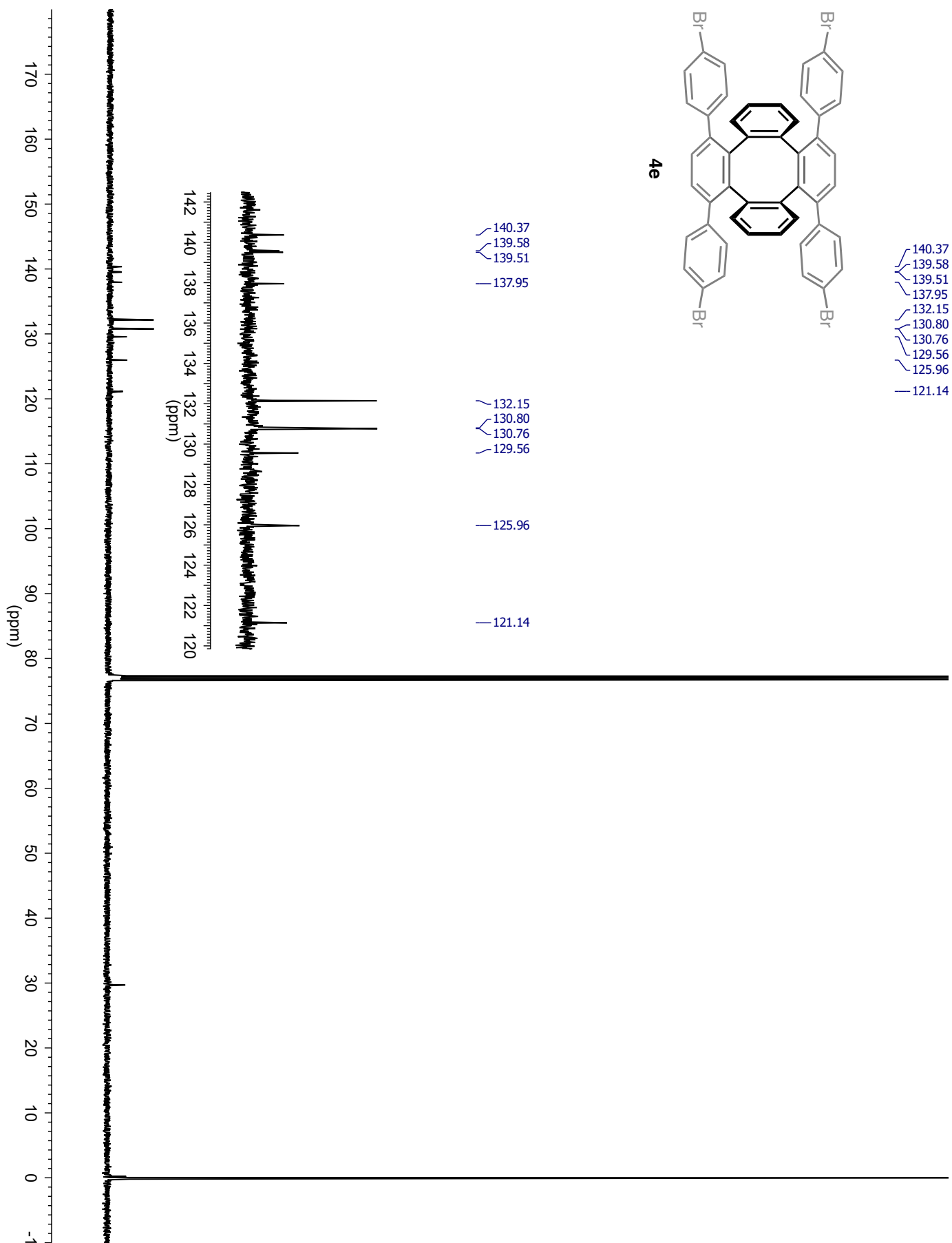
**Figure S9:** <sup>1</sup>H NMR Spectrum of 1,4,9,12-tetrakis(4-fluorophenyl)tetraphenylene (**4d**) in CDCl<sub>3</sub>.



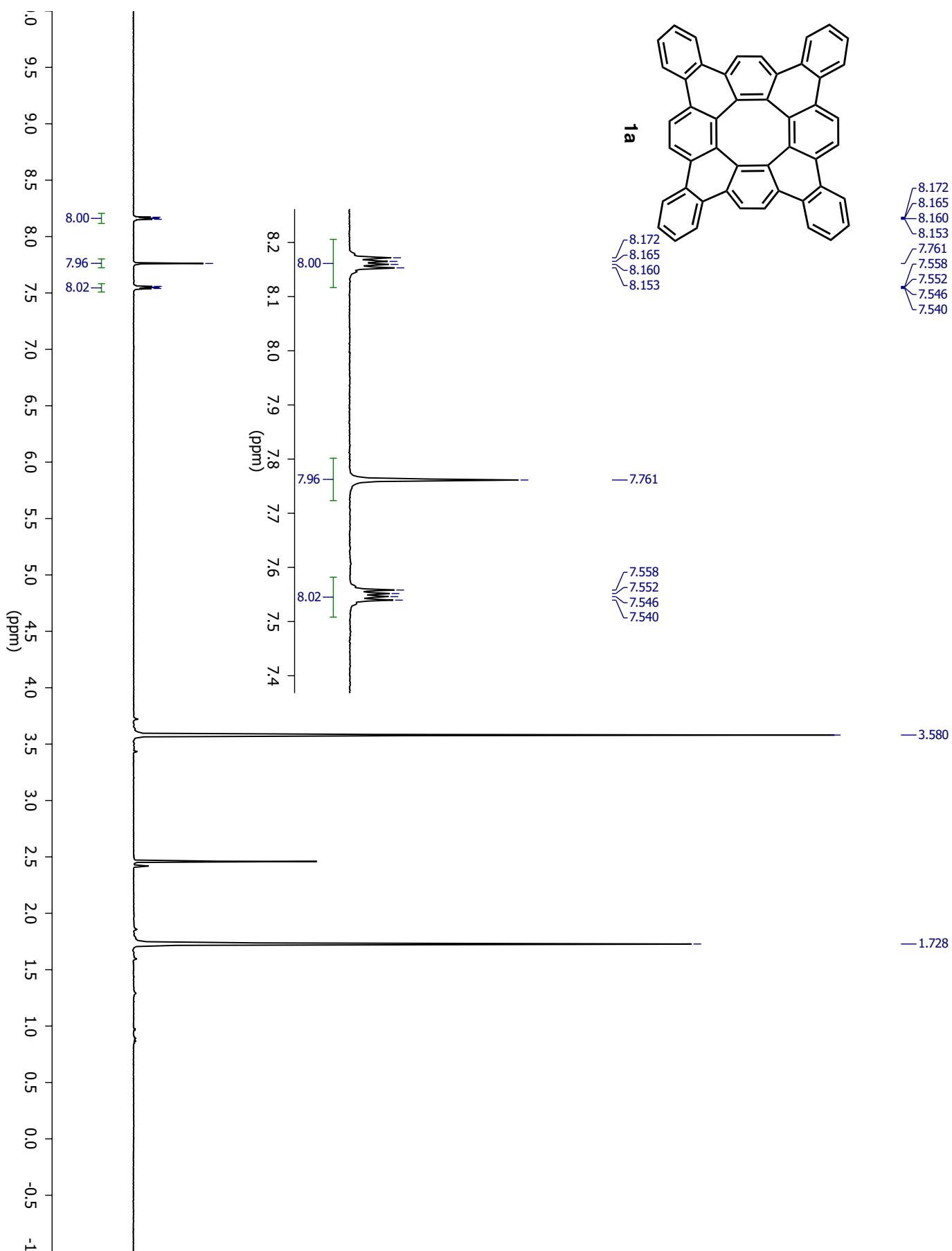
**Figure S10:** <sup>13</sup>C NMR Spectrum of 1,4,9,12-tetrakis(4-fluorophenyl)tetraphenylene (**4d**) in CDCl<sub>3</sub>.



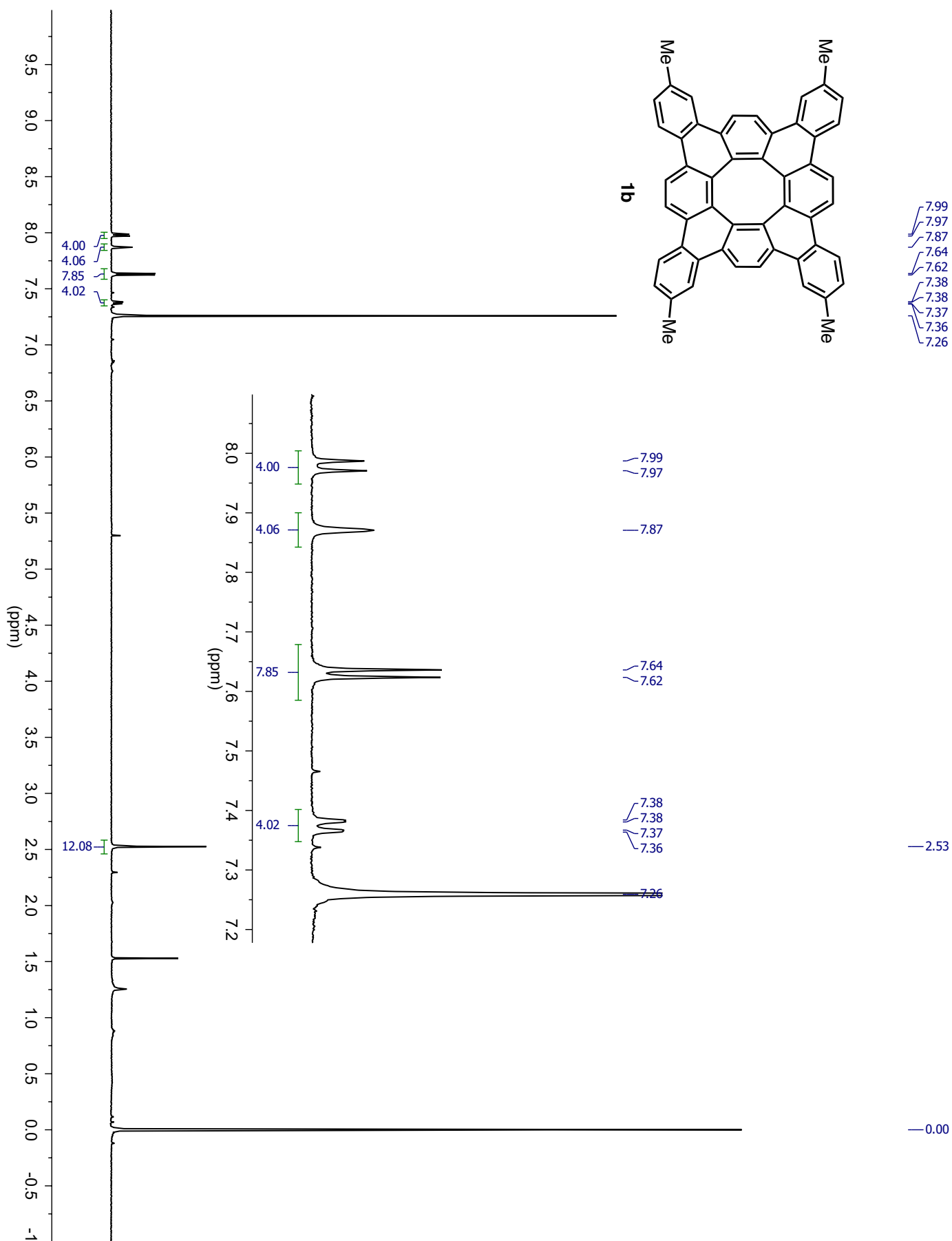
**Figure S11:**  $^1\text{H}$  NMR Spectrum of 1,4,9,12-tetrakis(4-bromophenyl)tetraphylene (**4e**) in  $\text{CDCl}_3$ .



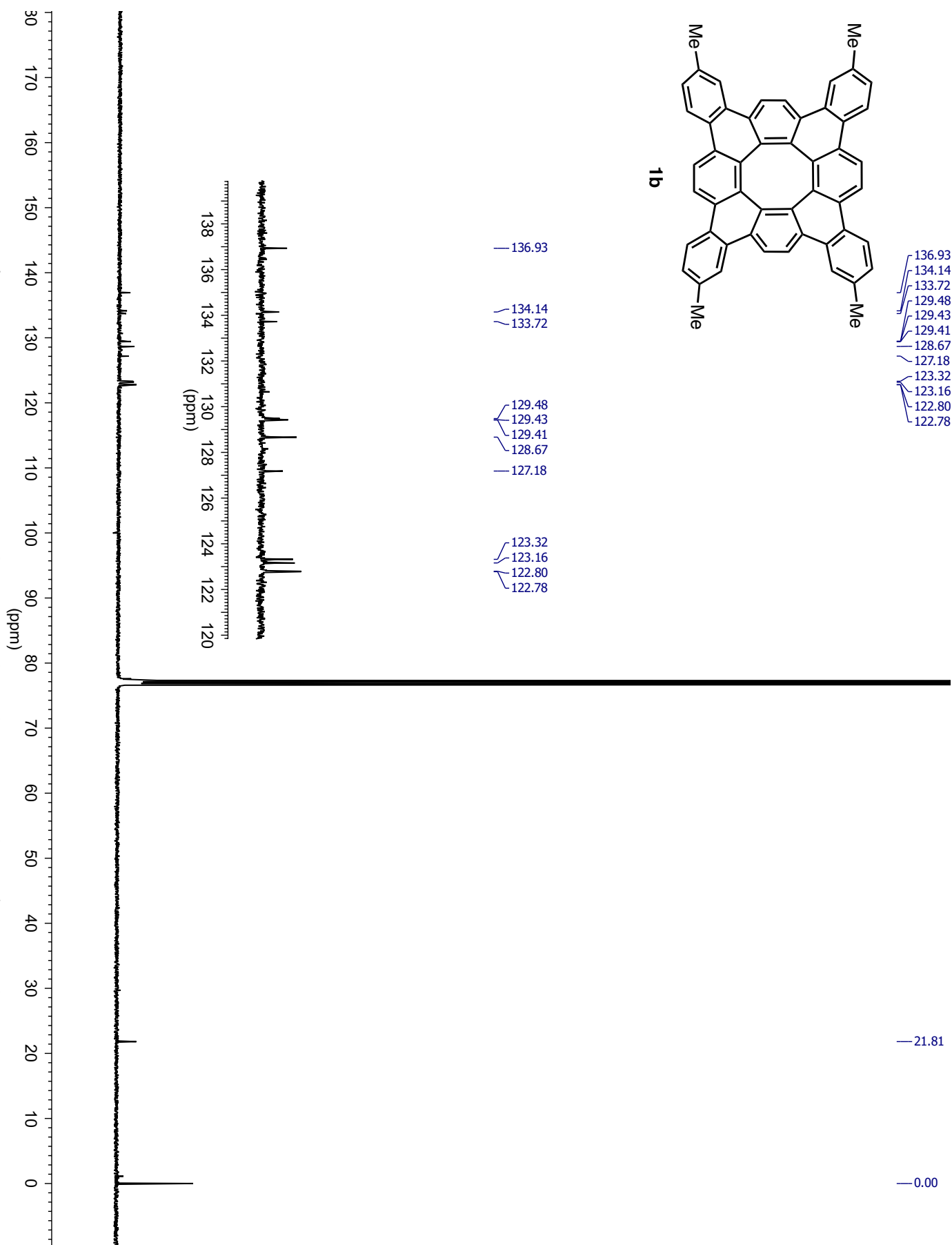
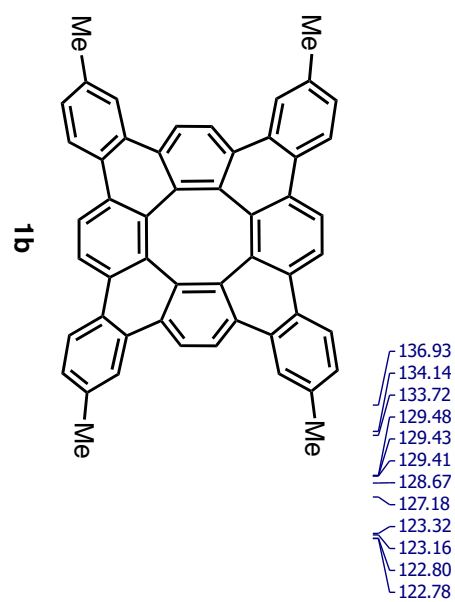
**Figure S12:** <sup>13</sup>C NMR Spectrum of 1,4,9,12-tetrakis(4-bromophenyl)tetraphenylene (**4e**) in CDCl<sub>3</sub>.

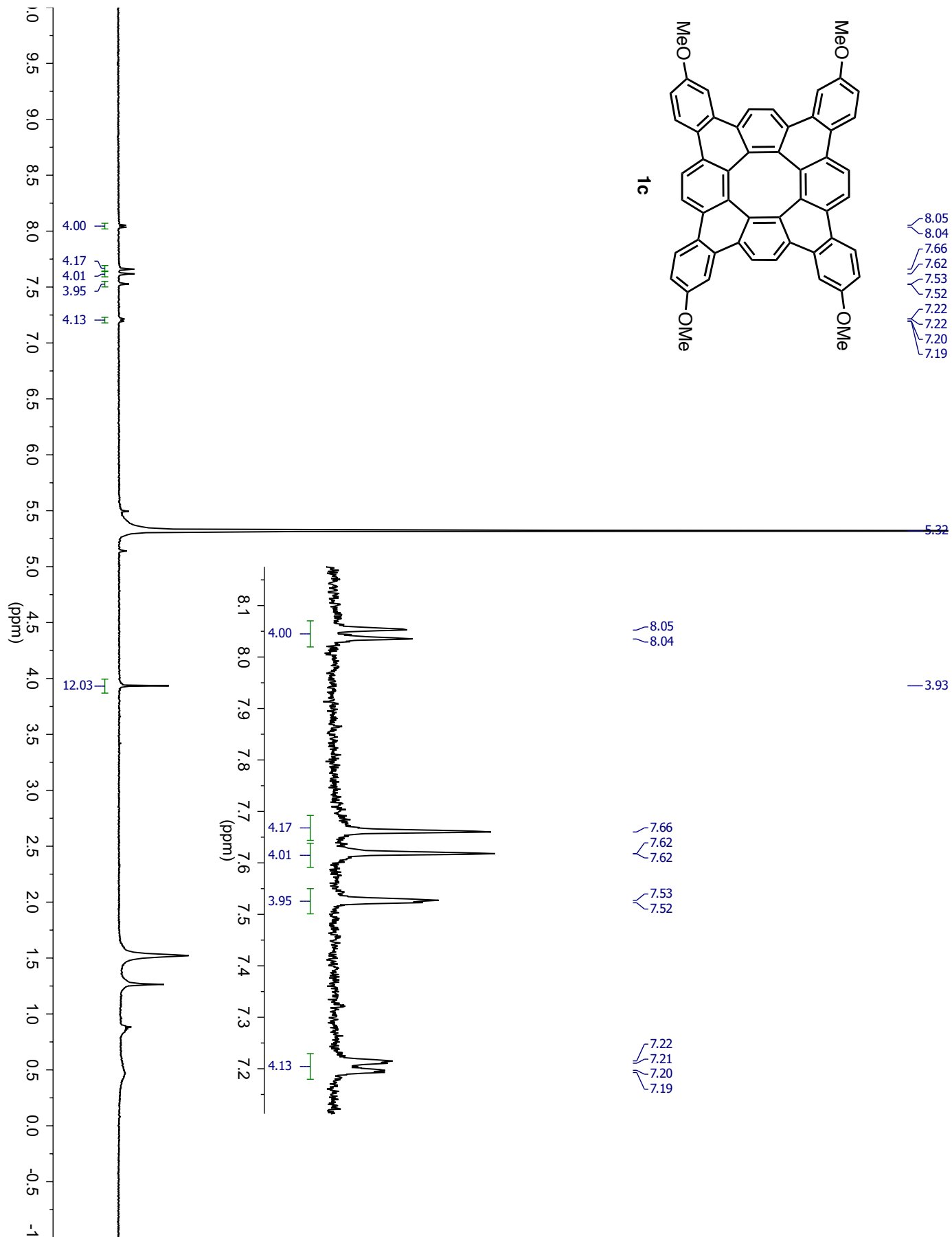


**Figure S13:**  $^1\text{H}$  NMR Spectrum of tetrabenzo[8]circulene (**1a**) in  $\text{THF-d}_8$ .



**Figure S14:**  $^1\text{H}$  NMR Spectrum of tetramethyl-tetrabenzo[8]circulene (**1b**) in  $\text{CDCl}_3$ .





**Figure S16:** <sup>1</sup>H NMR Spectrum of tetramethoxy-tetrabenzo[8]circulene (**1c**) in CD<sub>2</sub>Cl<sub>2</sub>.

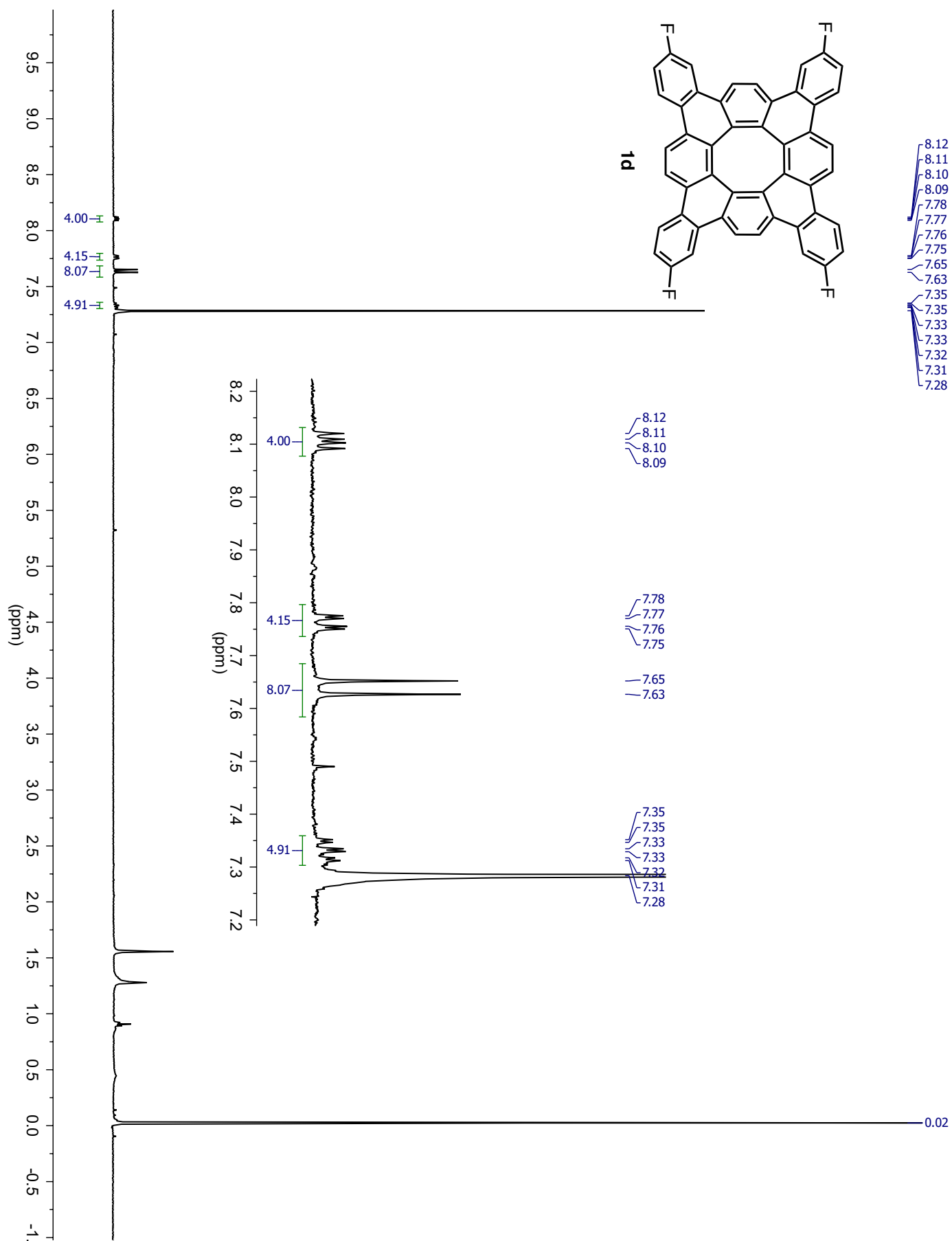
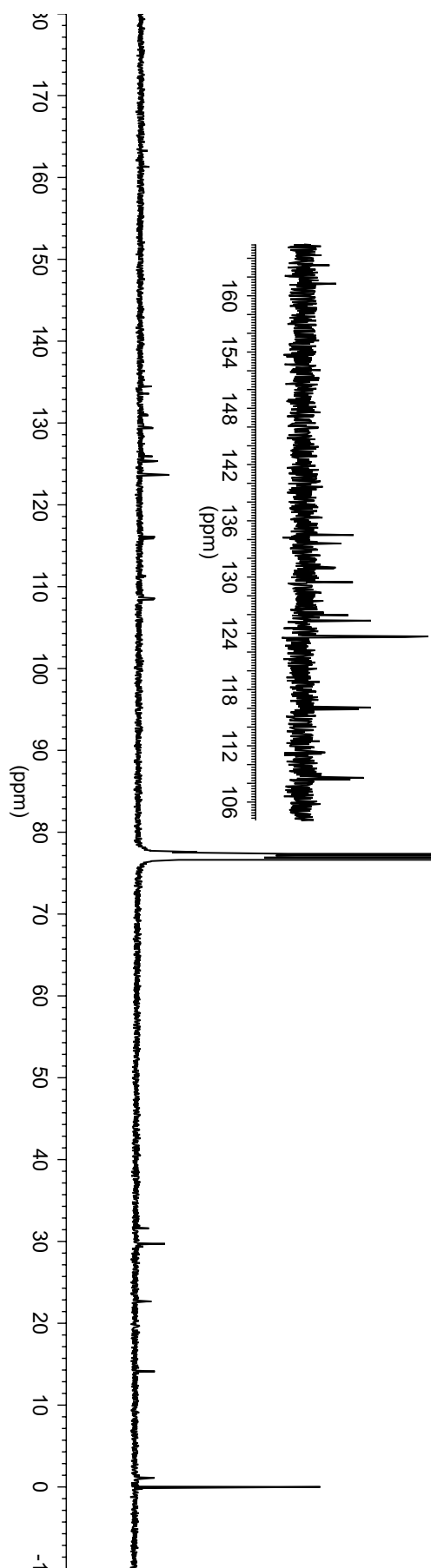
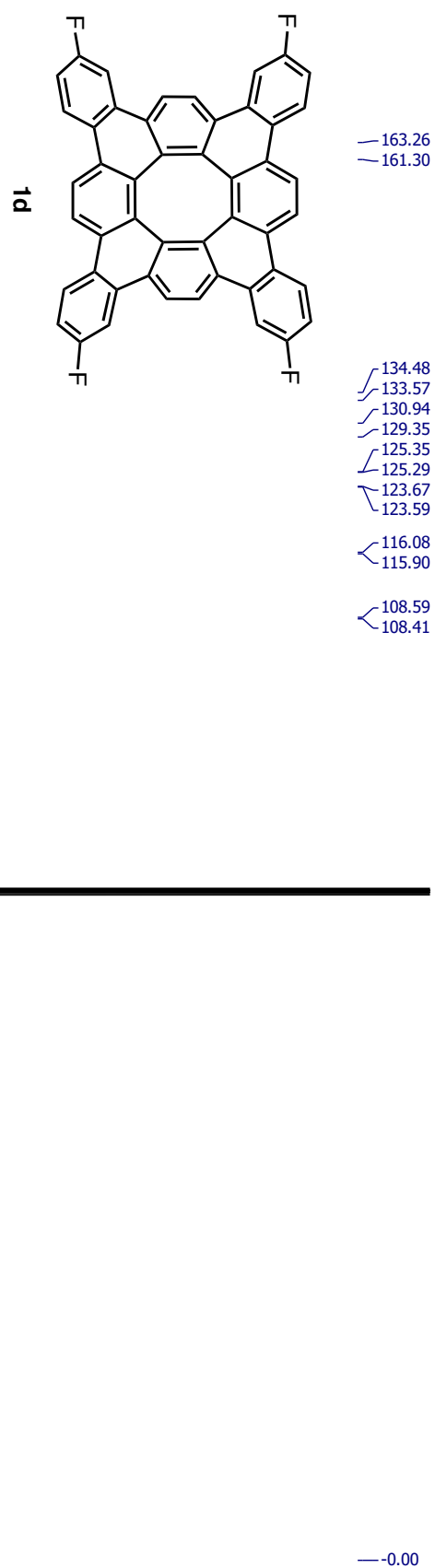
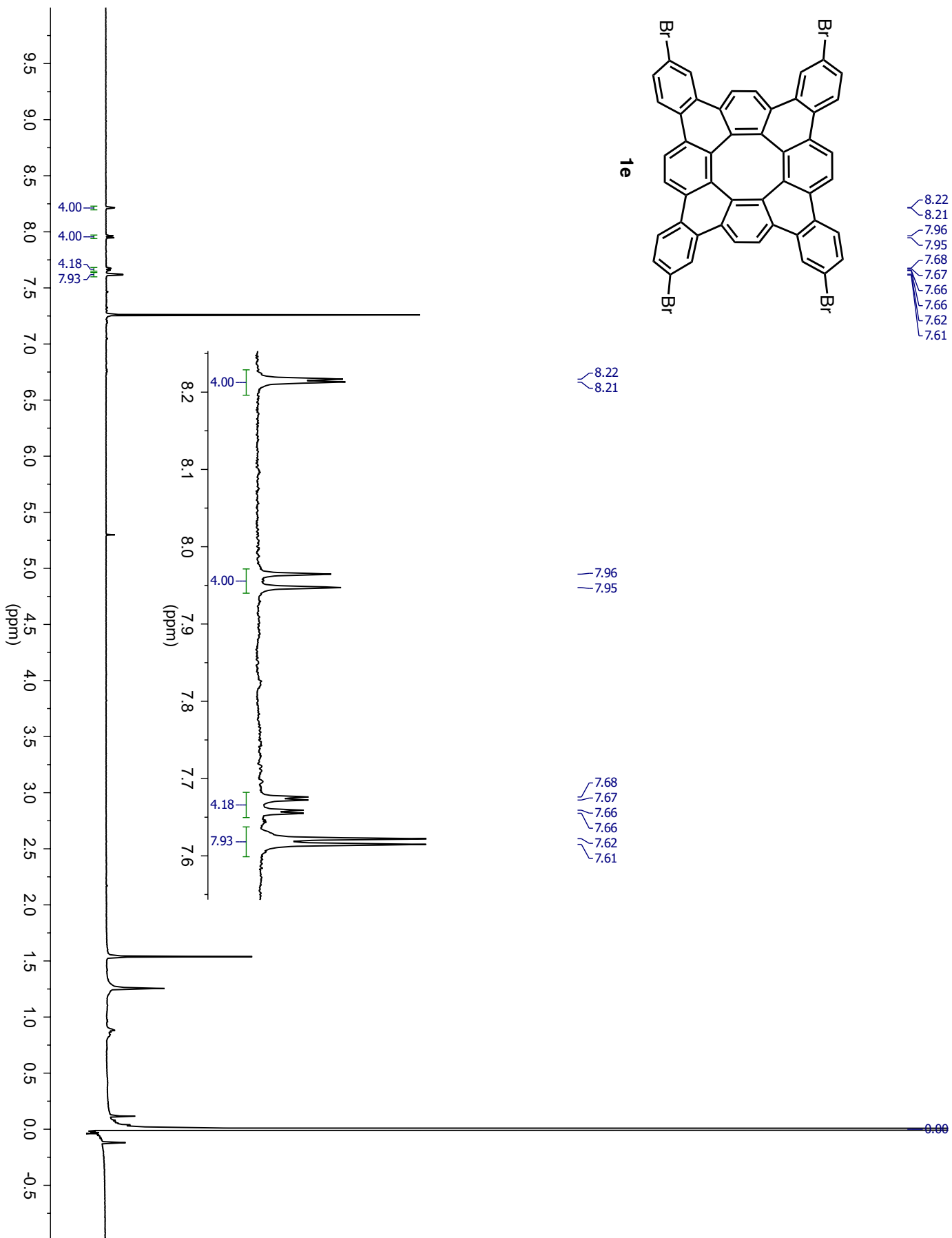


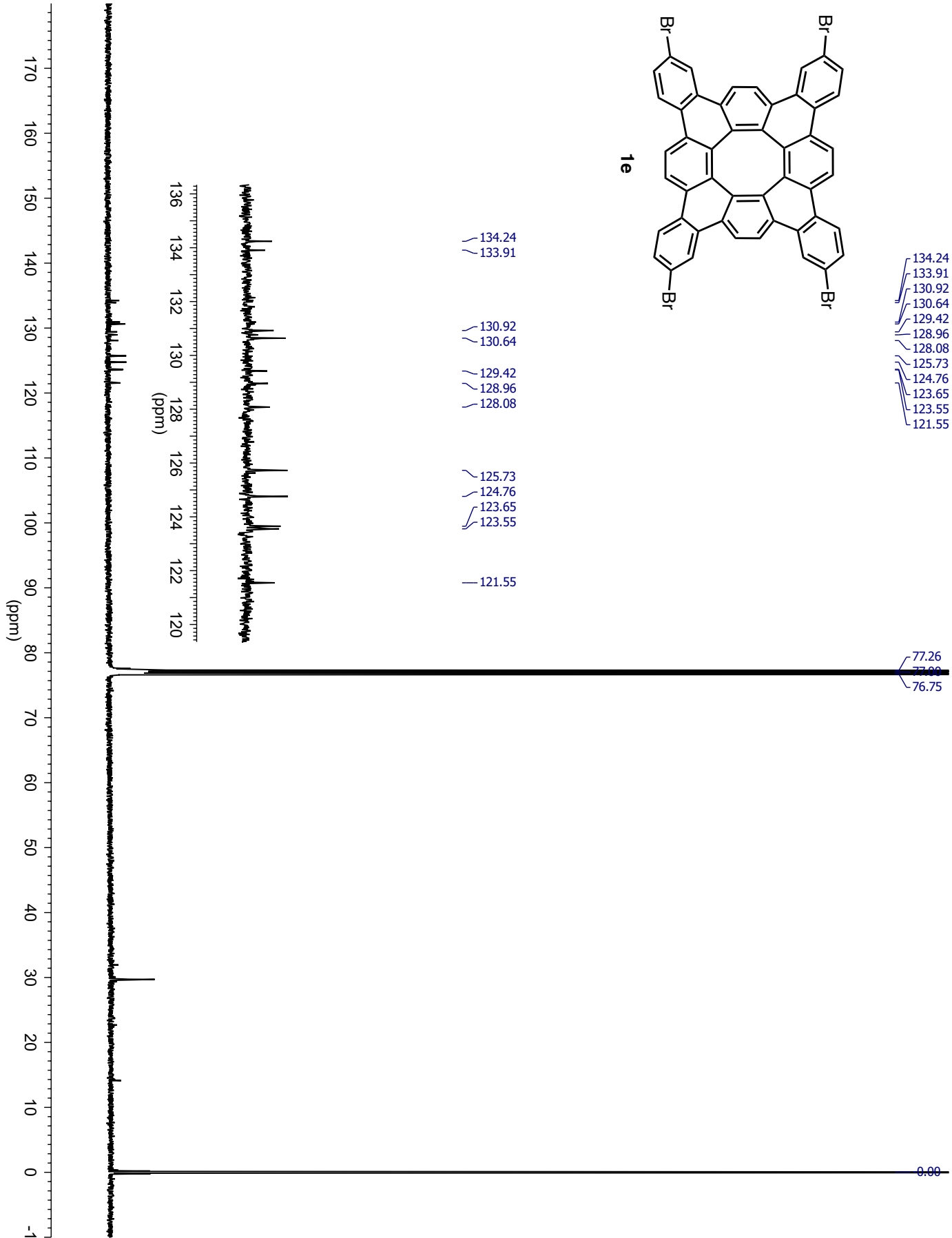
Figure S17: <sup>1</sup>H NMR Spectrum of tetrafluoro-tetrabenzo[8]circulene (**1d**) in CDCl<sub>3</sub>.



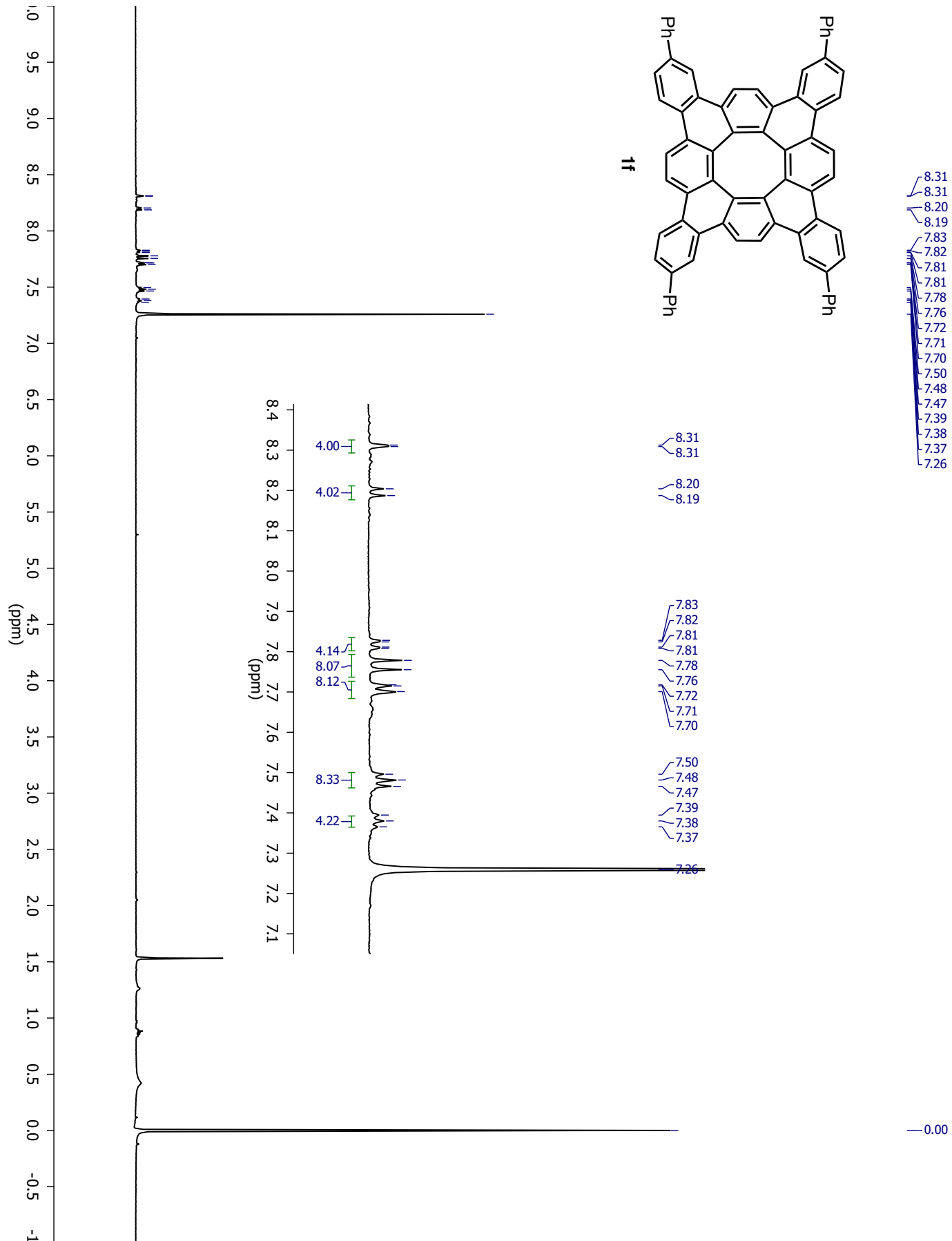
**Figure S18:** <sup>13</sup>C NMR Spectrum of tetrafluoro-tetrabenzo[8]circulene (**1d**) in CDCl<sub>3</sub>.



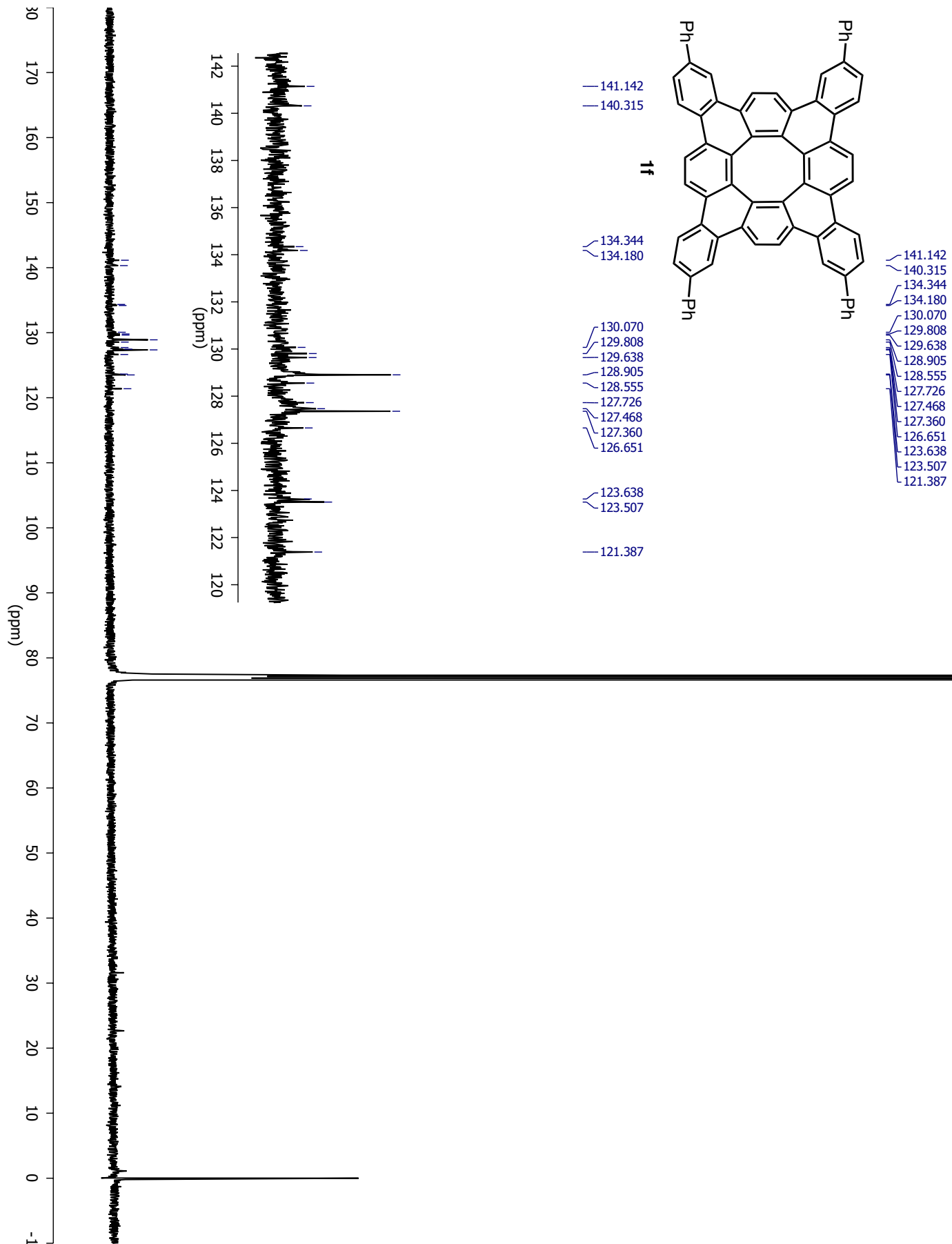
**Figure S19:** <sup>1</sup>H NMR Spectrum of tetrabromo-tetrabenzo[8]circulene (**1e**) in CDCl<sub>3</sub>.



**Figure S20:** <sup>13</sup>C NMR Spectrum of tetrabromo-tetrabenzzo[8]circulene (**1e**) in CDCl<sub>3</sub>.



**Figure S21:**  $^1\text{H}$  NMR Spectrum of tetraphenyl-tetrabenzocyclopentadiene (**1f**) in  $\text{CDCl}_3$ .



**Figure S22:** <sup>13</sup>C NMR Spectrum of tetraphenyl-tetrabenzo[8]circulene (**1f**) in CDCl<sub>3</sub>.

## II. Electrochemistry

**General Methods:** Electrochemical potentials were determined using cyclic voltammetry (CV) and square wave voltammetry (SWV). SWV was used when the concentration of the analyte was too low for CV. Electrochemistry was performed in CH<sub>2</sub>Cl<sub>2</sub>, except in cases where access to more negative potential was required; the electrochemistry was performed in THF. Anhydrous solvents were obtained from an alumina-based solvent system. Tetrabutylammonium tetrakis(pentafluorophenyl)borate ([NBu<sub>4</sub>][TFAB]) was used as the supporting electrolyte, in concentrations of 0.05 M. Ag/AgCl was used as the experimental reference electrode. Reference potentials of the ferrocene/ferrocium couple were determined *in situ* by measuring the potential of the decamethylferrocene/decamethylferrocium couple and subtracting 0.61 V. Glassy carbon disk electrodes of 2 mm diameter were prepared by polishing with diamond paste. Platinum wire was used as the auxiliary electrode.

|                                        | 1 (-H) <sup>a</sup>                 | 2 (-F) <sup>b</sup>      | 3 (-OMe) <sup>b</sup>    | 4 (-Ph) <sup>b</sup>     | 5 (-Me) <sup>b</sup>                | 6 (-Br) <sup>b</sup>     |
|----------------------------------------|-------------------------------------|--------------------------|--------------------------|--------------------------|-------------------------------------|--------------------------|
| 3 <sup>rd</sup> Oxidation              | E <sub>pa</sub> <sup>c</sup> 1.19 V |                          |                          |                          |                                     |                          |
| 2 <sup>nd</sup> Oxidation              | E <sub>1/2</sub> 0.82 V             | E <sub>1/2</sub> 0.91 V  | E <sub>1/2</sub> 0.72 V  | E <sub>1/2</sub> 0.85 V  | E <sub>pa</sub> <sup>c</sup> 0.74 V |                          |
| 1 <sup>st</sup> Oxidation              | E <sub>1/2</sub> 0.44 V             | E <sub>1/2</sub> 0.54 V  | E <sub>1/2</sub> 0.38 V  | E <sub>1/2</sub> 0.45 V  | E <sub>1/2</sub> 0.39 V             | E <sub>1/2</sub> 0.39 V  |
| 1 <sup>st</sup> Reduction              | E <sub>1/2</sub> -1.79 V            | E <sub>1/2</sub> -1.75 V | E <sub>1/2</sub> -1.83 V | E <sub>1/2</sub> -1.77 V | E <sub>1/2</sub> -1.83 V            | E <sub>1/2</sub> -1.83 V |
| 2 <sup>nd</sup> Reduction              | E <sub>1/2</sub> -1.89 V            |                          | E <sub>1/2</sub> -2.02 V | E <sub>1/2</sub> -1.92 V |                                     |                          |
| 1 <sup>st</sup> Reduction <sup>d</sup> | E <sub>1/2</sub> -1.92 V            |                          |                          |                          | E <sub>1/2</sub> -1.95 V            |                          |
| 2 <sup>nd</sup> Reduction <sup>d</sup> | E <sub>1/2</sub> -2.09 V            |                          |                          |                          | E <sub>1/2</sub> -2.12 V            |                          |
| HOMO-LUMO Gap                          | 2.23 V                              | 2.29 V                   | 2.21 V                   | 2.22 V                   | 2.22 V                              | 2.22 V                   |

**Table S1:** The potential versus ferrocene of the various redox processes for each compound. Unless otherwise noted, the measurements were made in CH<sub>2</sub>Cl<sub>2</sub>/ 0.05 M [NBu<sub>4</sub>][TFAB]. **a:** CV measurement, scan rate 0.2 V s<sup>-1</sup>. **b:** SWV measurement 5 Hz frequency. **c:** Anodic peak potential by CV, 0.2 V s<sup>-1</sup>. **d:** Measurement in THF/ 0.05 M [NBu<sub>4</sub>][TFAB].