

## Supporting Information

### Exploring different designs in thieno[3,4-*b*]pyrazine-based dyes to enhance divergent optical properties in Dye-Sensitized Solar Cells

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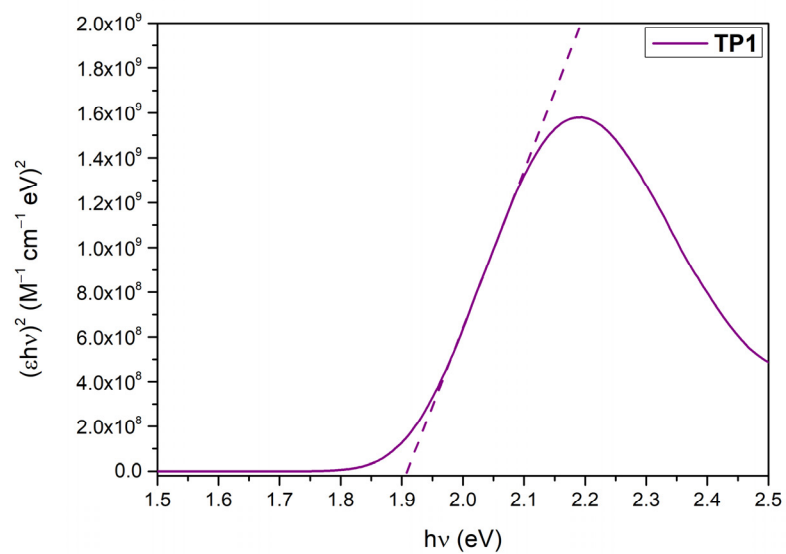
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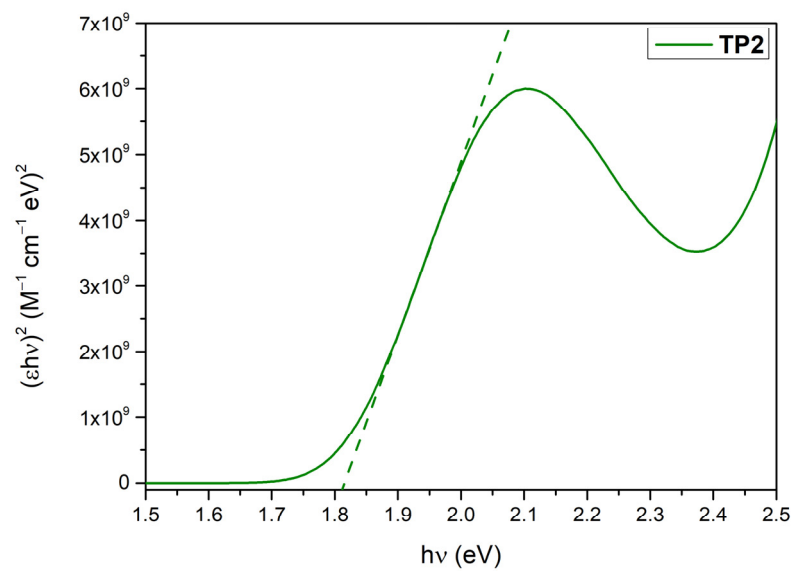
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### S1. Tauc plots for TP1-2



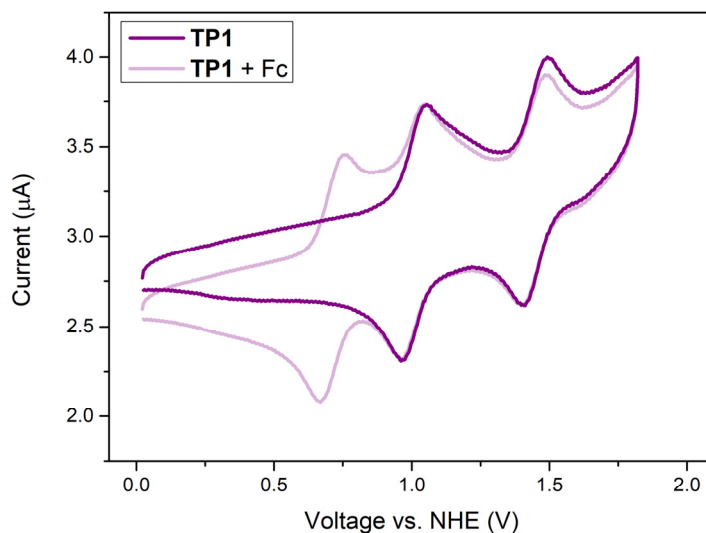
**Figure S1.** Tauc plot of the dye **TP1** in  $\text{CHCl}_3$  solution.



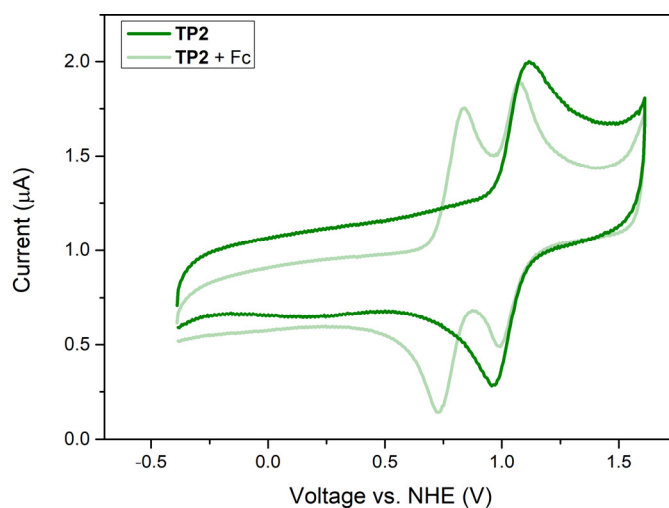
**Figure S2.** Tauc plot of the dye **TP2** in  $\text{CHCl}_3$  solution.

## S2. Cyclic voltammetry for TP1-2

Cyclic voltammograms were recorded using a glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and an Ag/AgNO<sub>3</sub> 0.01 M in CH<sub>3</sub>CN pseudo reference electrode. 0.1 M TBAPF<sub>6</sub> in the chosen solvent was used as the supporting electrolyte. The lighter curves displayed in the background correspond to the measurements carried out with ferrocene as the internal standard. Ferrocene was used to set the potential scale assuming its redox potential to be equal to 0.715 V vs NHE in CH<sub>2</sub>Cl<sub>2</sub> and 0.787 V vs NHE in THF.[1]

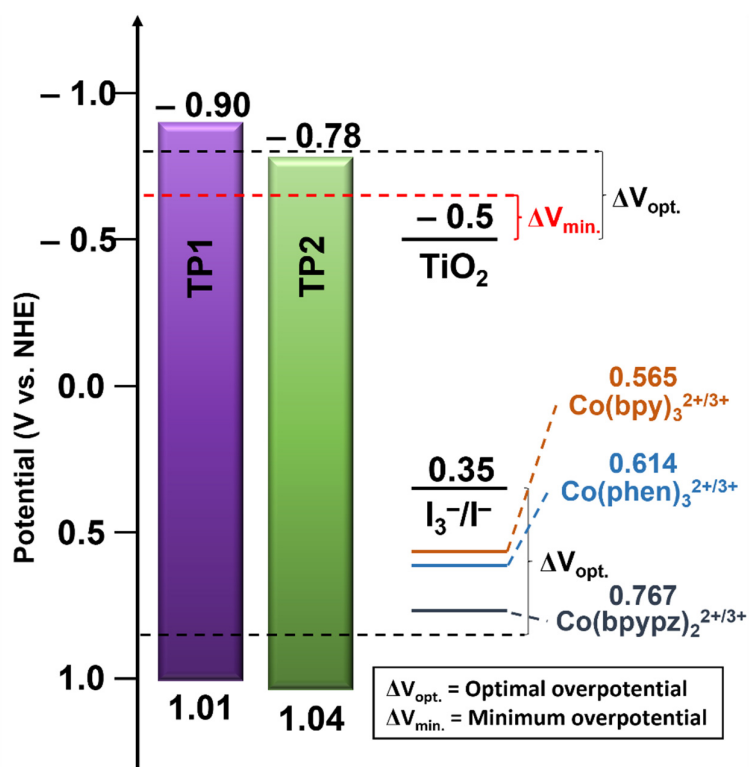


**Figure S3.** Cyclic Voltammetry of dye **TP1** in CH<sub>2</sub>Cl<sub>2</sub> solution.

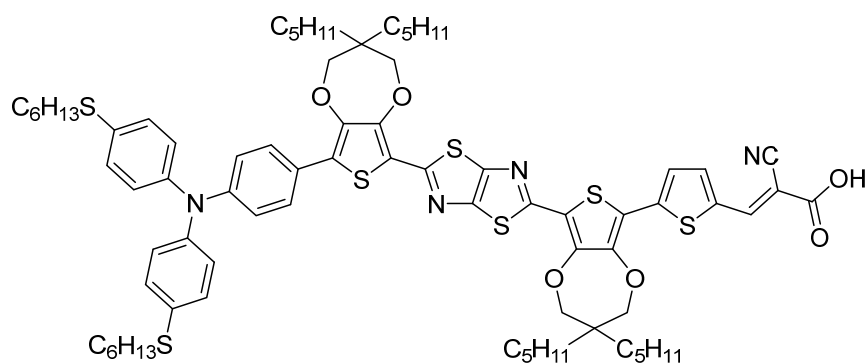


**Figure S4.** Cyclic Voltammetry of dye **TP2** in THF solution.

### S3. TP1-2 energy levels



**Figure S5.** Energy level diagram of ground-state and excited-state oxidation potentials of dyes **TP1-2** compared with TiO<sub>2</sub> CB (-0.50 V), iodide/triiodide redox couple (0.35 V) potentials, and Co-based electrolytes (0.565, 0.614, and 0.767 V vs. NHE respectively for Co(bpy)<sub>3</sub>, Co(phen)<sub>3</sub> and Co(bppz)<sub>2</sub>). Black dotted lines mark the optimal E<sub>S+/S</sub> (0.85 V) and E<sub>S+/S\*</sub> (-0.80 V) values for a sensitizer with fast electron transfer kinetics. The red dotted line defines the limit potential (-0.65 V) to guarantee electron injection.



**Figure S6.** Molecular structure of the reference dye **TTZ5**.

## ***S4. DSSC assembly and efficiency measurements***

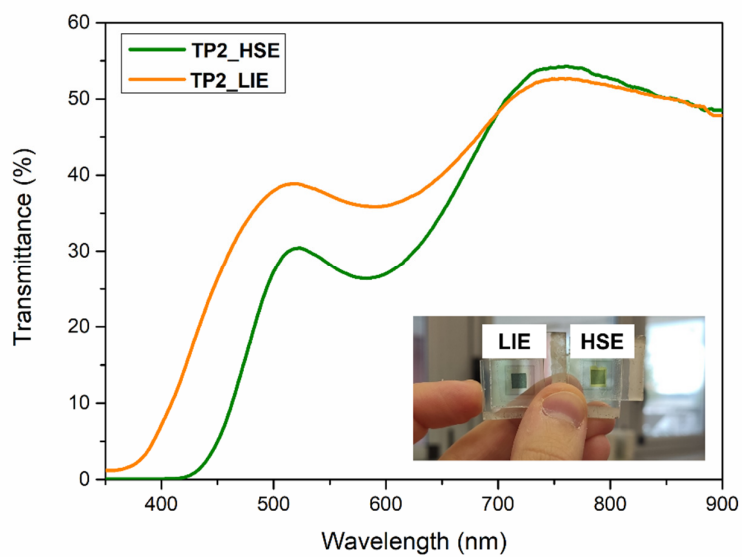
### ***S4.1. Photovoltaic devices: fabrication and characterization***

10×10 cm FTO-coated conducting glass ( $\text{TEC } 8 \, \Omega \, \text{sq}^{-1}$ , GreatCell solar) was cleaned in an ultrasonic bath by subsequent immersion in soapy water, distilled water, and acetone for 15 min each, followed by immersion in boiling *i*PrOH and drying. A  $\text{TiO}_2$  compact layer was deposited on the glass substrate heated at 450 °C in a 1.5 cm large bands-pattern by spray pyrolysis of a freshly prepared  $\text{Ti}(\text{iPrO})_2(\text{acac})_2$  0.2M solution in absolute EtOH. After sintering the compact layer at 450 °C for 1 h and letting it cool down slowly, a single layer of a commercially available nanocrystalline  $\text{TiO}_2$  paste (DyeSol  $\text{TiO}_2$  Paste DSL 18NR-T) was screen-printed in 0.5×0.5 cm<sup>2</sup> spots. The plates were left to sit in an EtOH-fumes-filled chamber for 30" before drying at 120 °C for 30 min, then sintered once again according to the following programmed ramp: 15 min at 350 °C, 30 min at 375 °C, 1 h at 450 °C, and 1 h at 500 °C. The active area of the resulting mesoporous semi-transparent  $\text{TiO}_2$  films was 0.25 cm<sup>2</sup> and the plate was cut into 2×2 cm<sup>2</sup> slides. The coated glass slides were heated at 80 °C and immersed in a  $1 \times 10^{-4}$  M solution of the appropriate dye in a 1:4 (v/v) THF:EtOH mixture for at least 10 h. The electrodes were rinsed with ethanol and dried under airflow. For the preparation of the counter electrodes, a commercial platinum-based paint (PT1 Platinum Paste, GreatCell solar) was screen printed in 1×1 cm<sup>2</sup> spots on an FTO conducting glass cleaned as described above, followed by drying at 120 °C for 15 min and sintering at 450 °C for 1 h. The cooled-down plate was cut into 2×2 cm counter-electrode slides. The two electrodes were held into a sandwich-type cell with small spring clamps gluing the edges of the slides together with a commercially available UV curing resin (ThreeBond 3035B).[2] A drop of the appropriate electrolyte solution was placed on a few-millimeters-long gap in the sealing frame and generally would intercalate into the cell by itself or else it was driven into the cell by vacuum backfilling. The hole was finally sealed by using additional UV-curing resin.

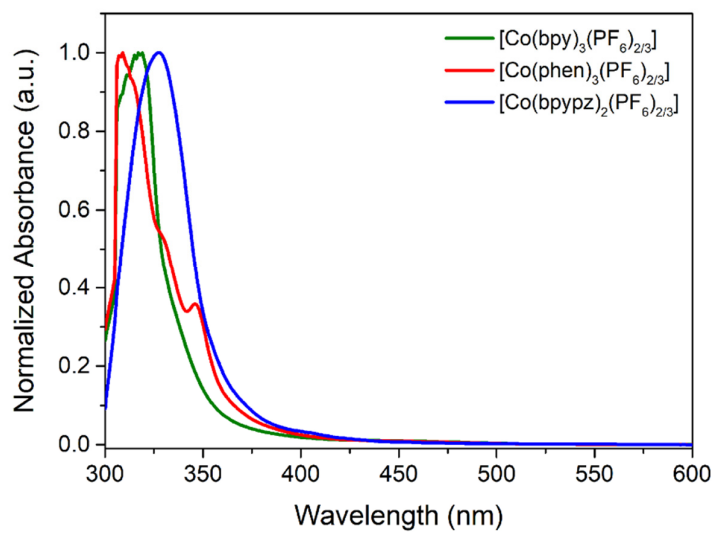
The photoelectrochemical characterization of the solar cells was performed by using an Abet Technologies Sun 2000 class AAA solar simulator under global AM 1.5G sunlight. The power of the incoming radiation was calibrated to 100 mW cm<sup>-2</sup> using a Reference solar cell. *J/V* curves were obtained with a Source Meter Unit Agilent (Keysight) SMU B2901A. Samples were stored in the dark and measured under the simulated light for approximately 5 minutes.

### ***S4.2. Electrolytes formulation***

The devices were filled with a commercially available iodine-based electrolyte solution (EL-HSE electrolyte, GreatCell solar) or with one of the following in-house prepared compositions. The "Low Iodine" electrolyte solution (EL-LIE) was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M LiI, and 0.5 M 4-*tert*-butylpyridine (4-TBP) in acetonitrile. The cobalt complexes were synthesized as described elsewhere.[3–5] The electrolyte based on the cobalt/2,2'-bipyridine complex  $\text{Co}(\text{bpy})_3$  (II/III) was composed of 0.22 M  $\text{Co}(\text{bpy})_3(\text{PF}_6)_2$ , 0.033 M  $\text{Co}(\text{bpy})_3(\text{PF}_6)_3$ , 0.1 M  $\text{LiClO}_4$ , and 0.2 M 4-TBP in acetonitrile. That based on the cobalt phenanthroline complex  $\text{Co}(\text{phen})_3$  (II/III) was composed of 0.22 M  $\text{Co}(\text{phen})_3(\text{PF}_6)_2$ , 0.033 M  $\text{Co}(\text{phen})_3(\text{PF}_6)_3$ , 0.1 M  $\text{LiClO}_4$ , and 0.2 M 4-TBP in acetonitrile. Finally, the electrolyte containing the cobalt 6-(3,5-dimethylpyrazol-1-yl)-2,2'-bipyridine complex  $\text{Co}(\text{bpypz})_2$  (II/III) was composed of 0.22 M  $\text{Co}(\text{bpypz})_2(\text{PF}_6)_2$ , 0.033 M  $\text{Co}(\text{bpypz})_2(\text{PF}_6)_3$ , 0.1 M  $\text{LiClO}_4$ , and 0.2 M 4-TBP in acetonitrile.

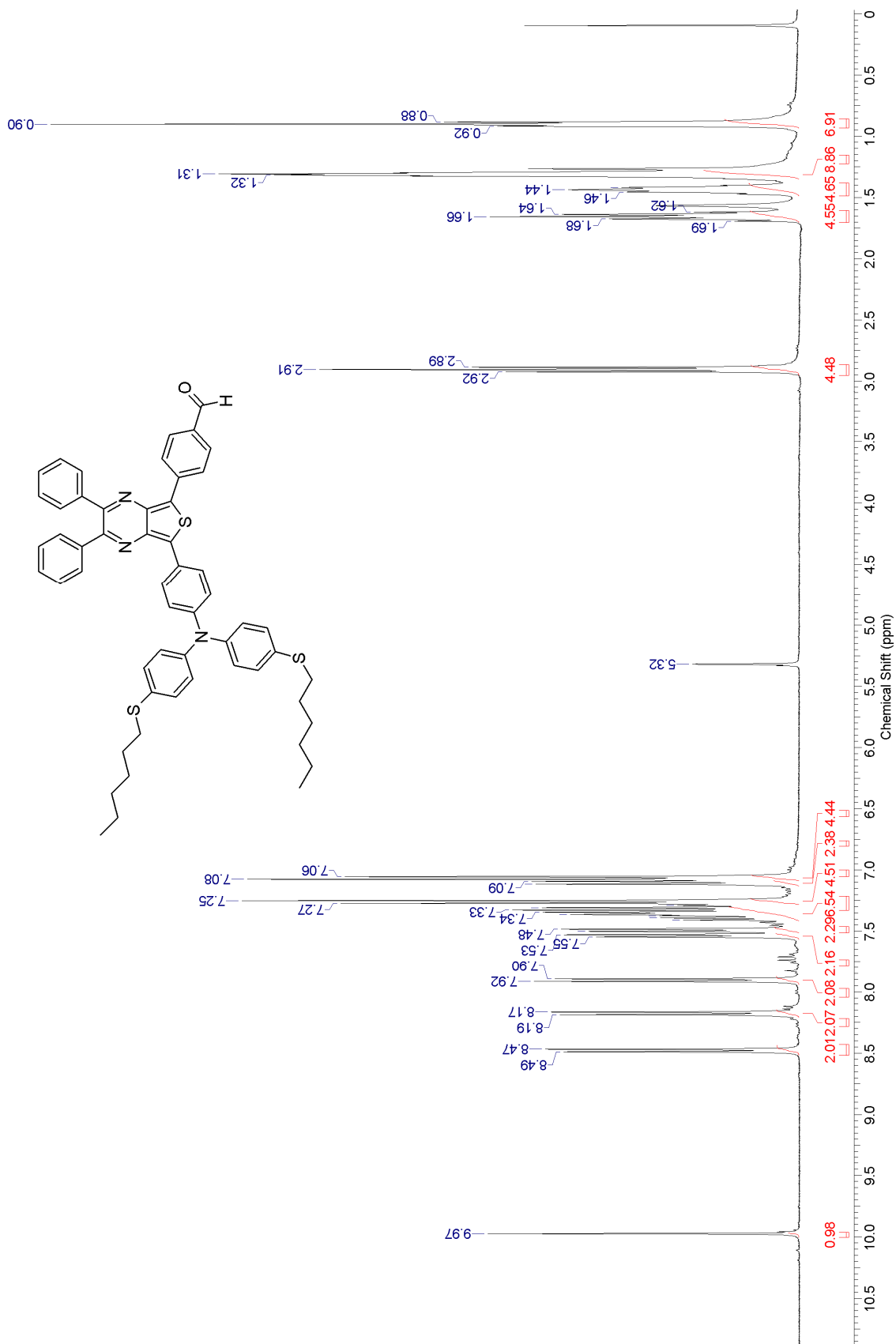


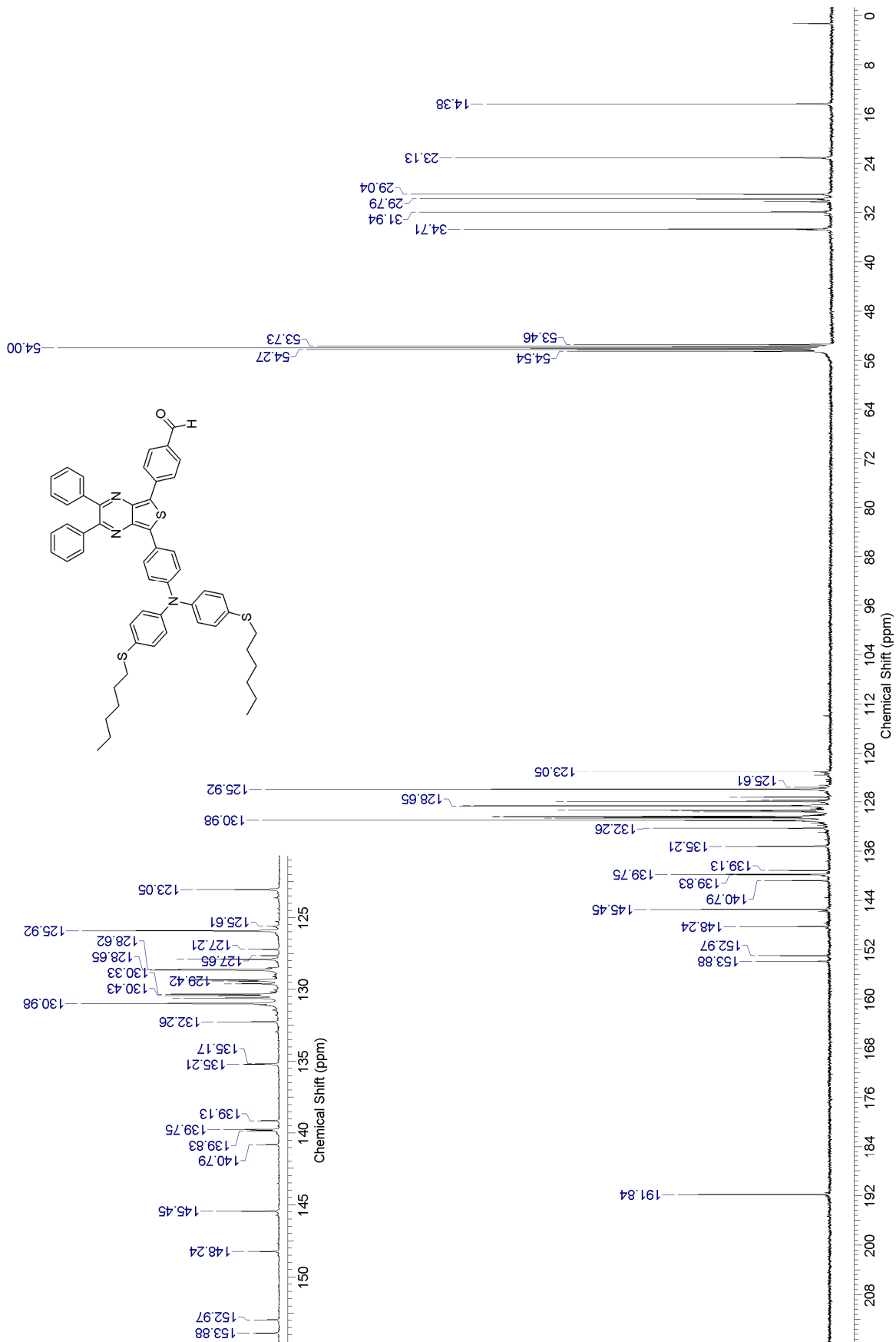
**Figure S7.** Transmittance spectra of the whole semi-transparent cells containing **TP-2** and different electrolytes (HSE and LIE).



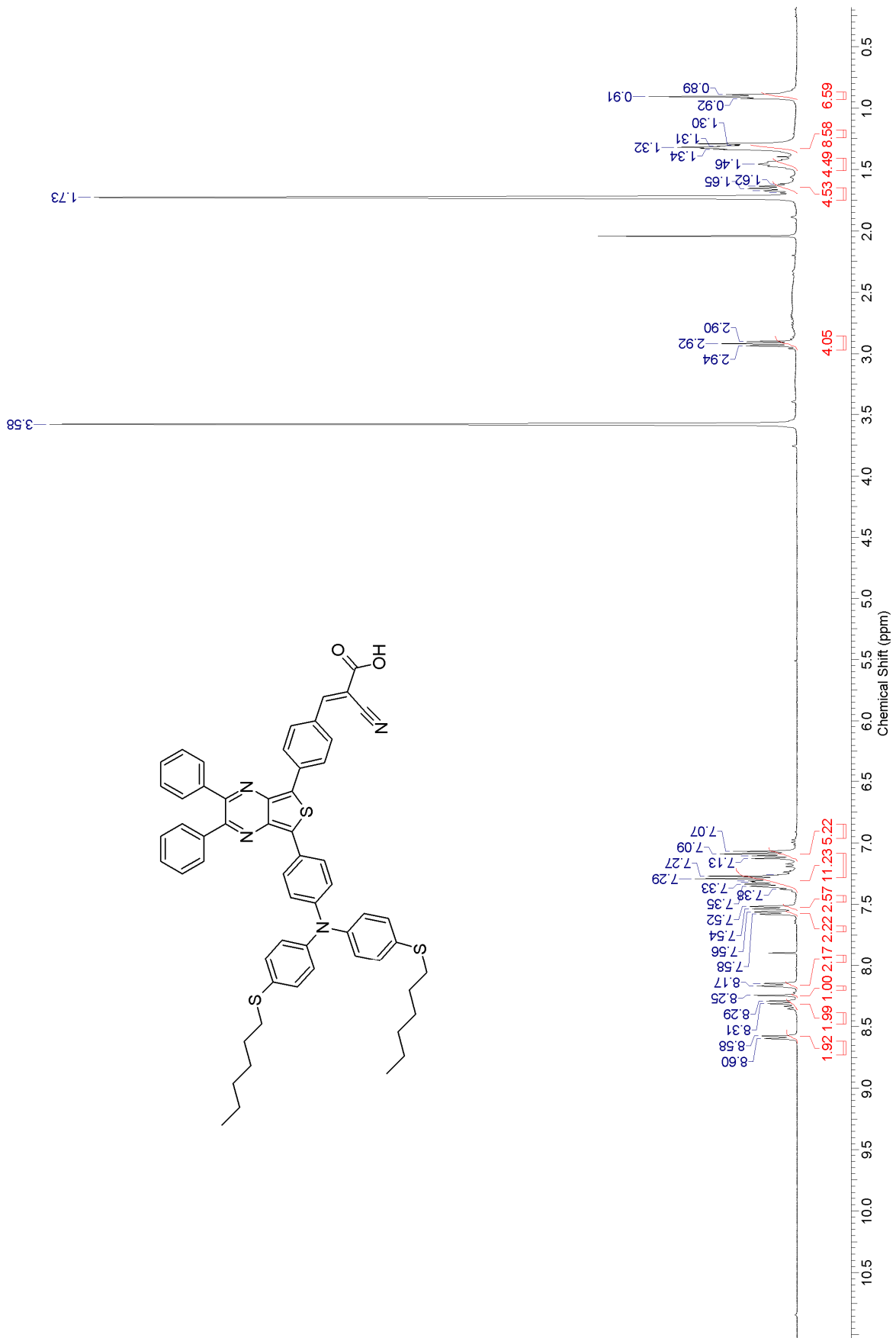
**Figure S8.** UV-Vis light absorption spectra of the three cobalt-based electrolyte solutions  $\text{Co}(\text{bpy})_3$ ,  $\text{Co}(\text{phen})_3$ , and  $\text{Co}(\text{bpy})_2(\text{bpyz})_2$ .

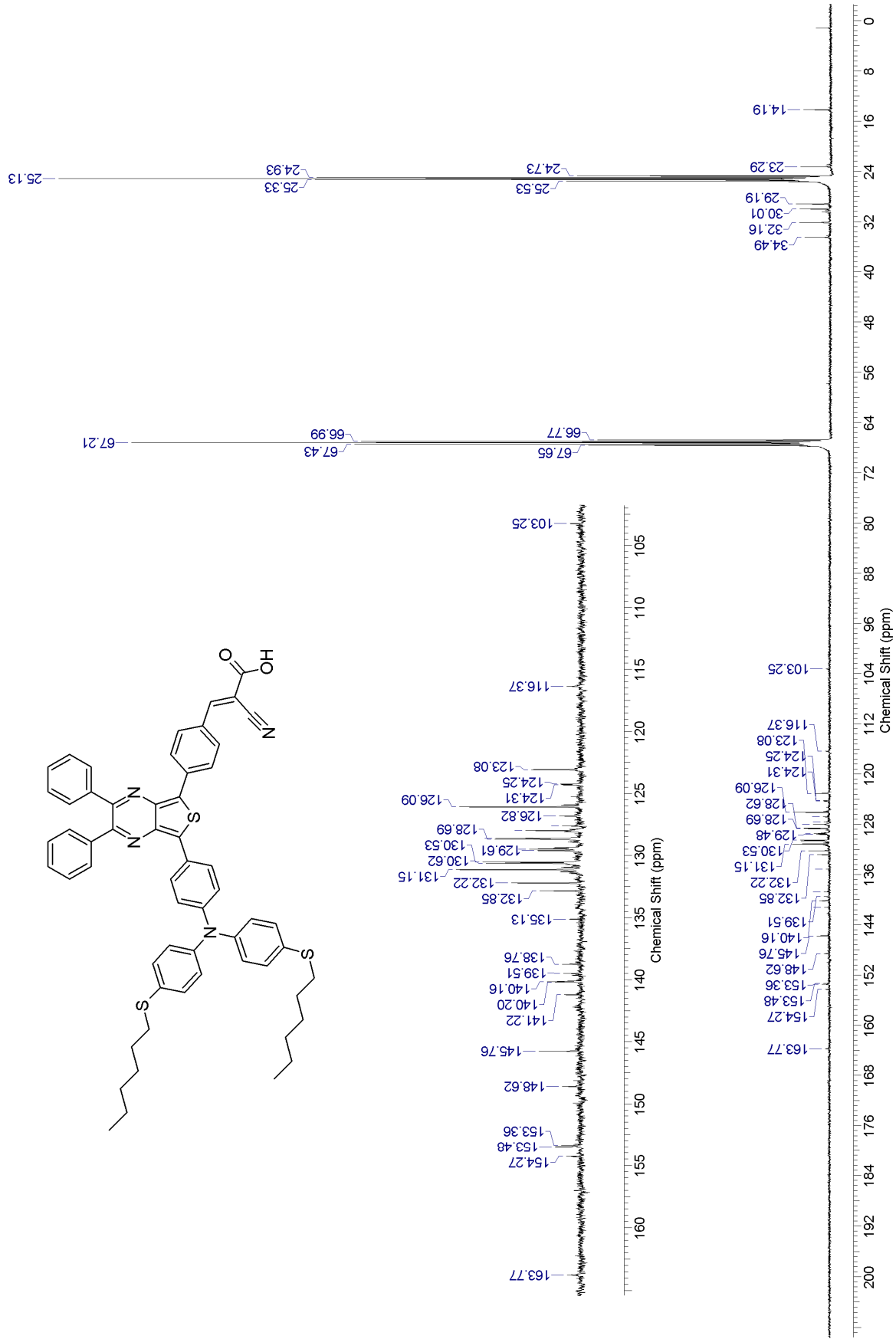
***S5. Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra***

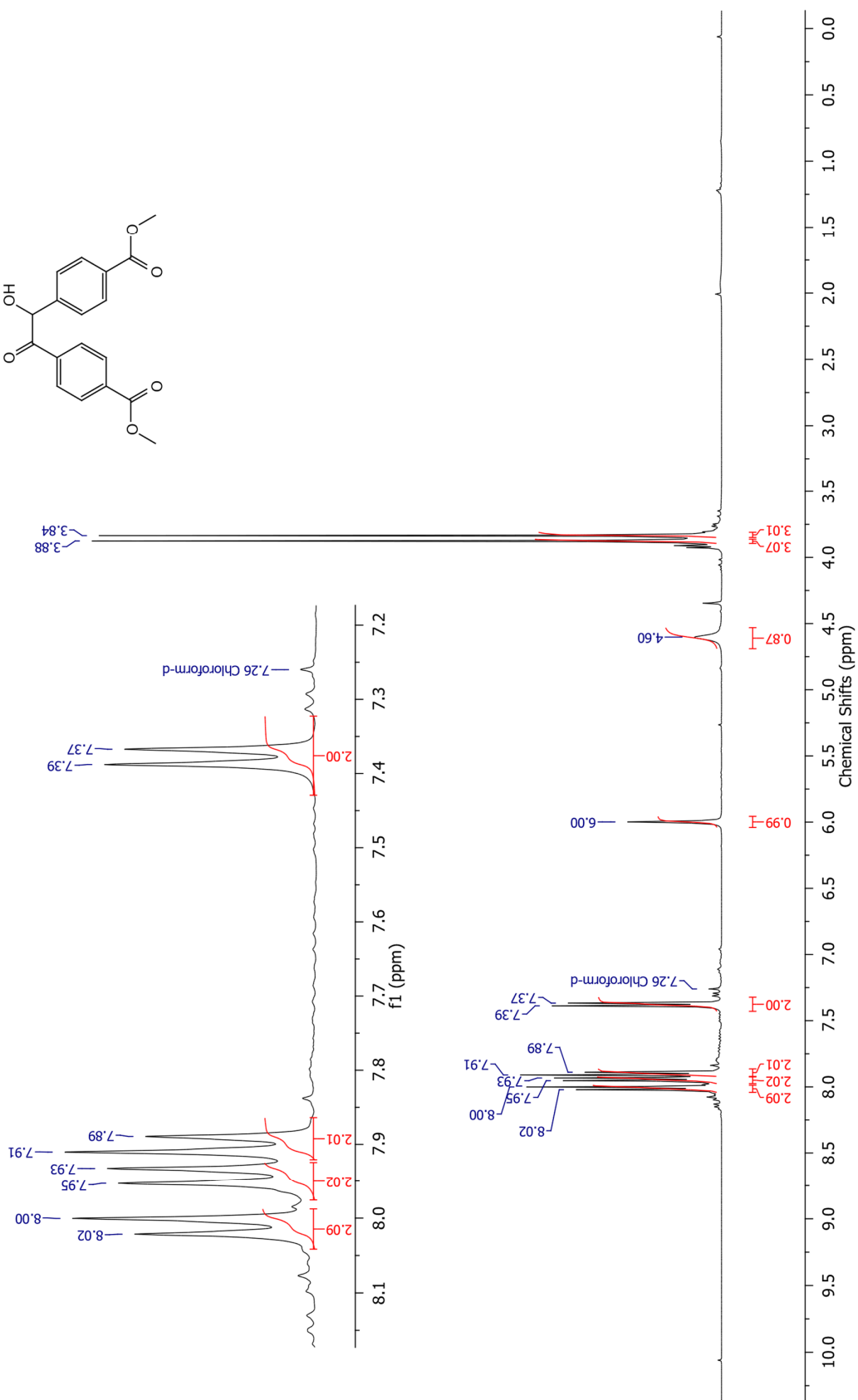
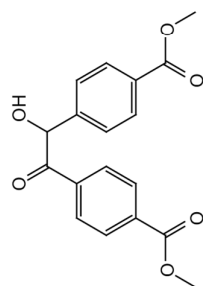


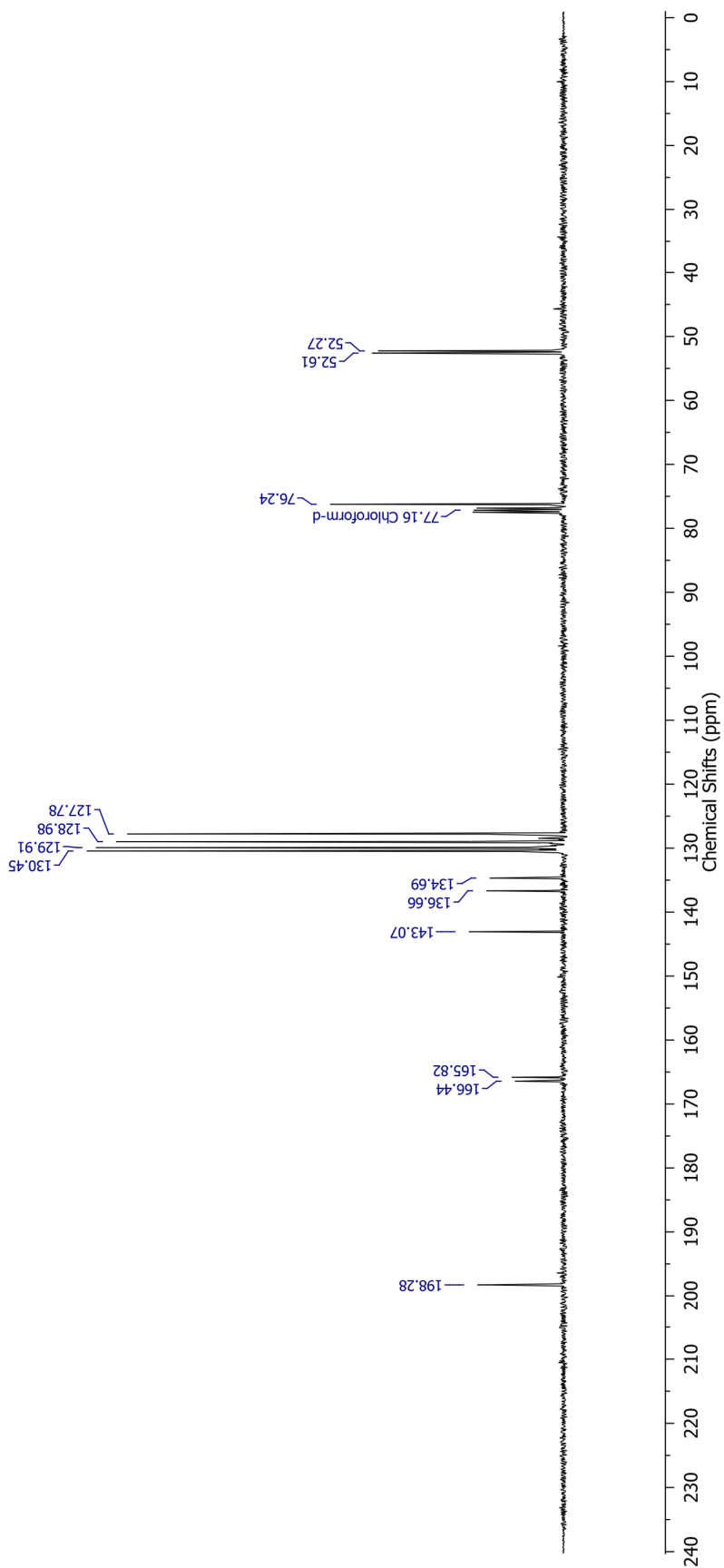
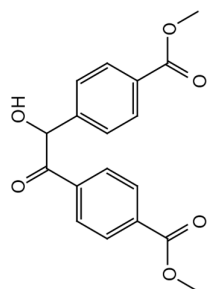


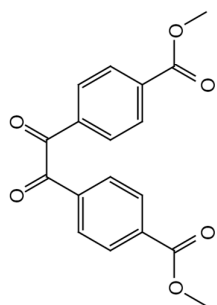












3.96

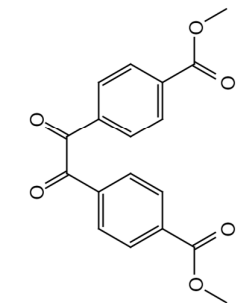
8.19  
8.17  
8.06  
8.04

7.26 Chloroform-d

1.98  
2.00

3.15

Chemical Shifts (ppm)



— 77.16 Chloroform-d

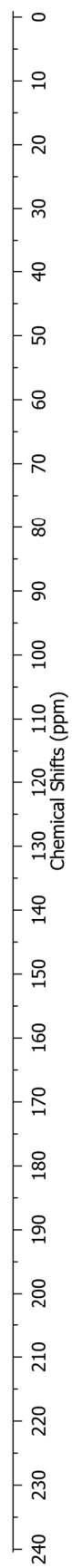
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135.66  
130.31  
130.03

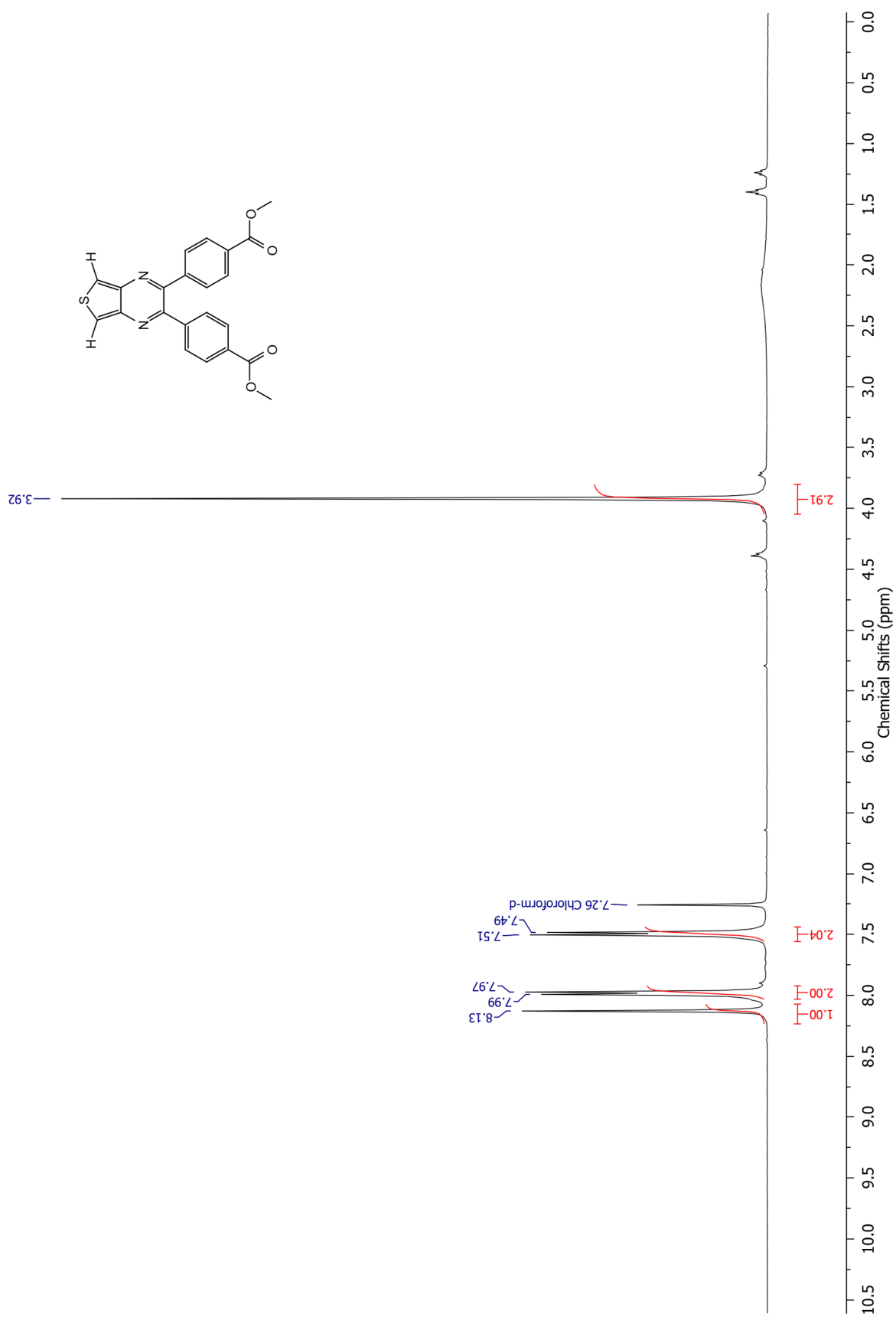
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135.66

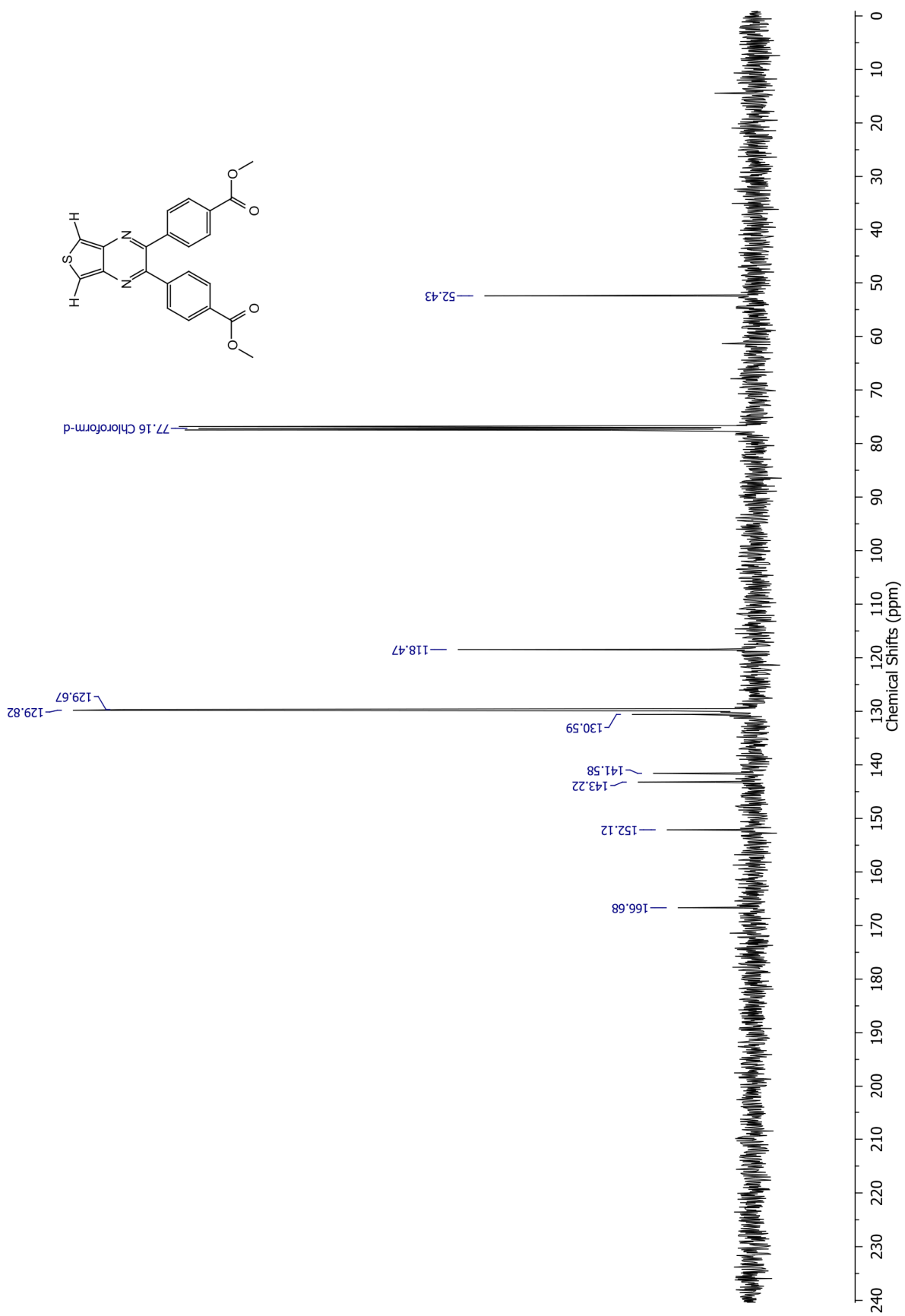
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193.03

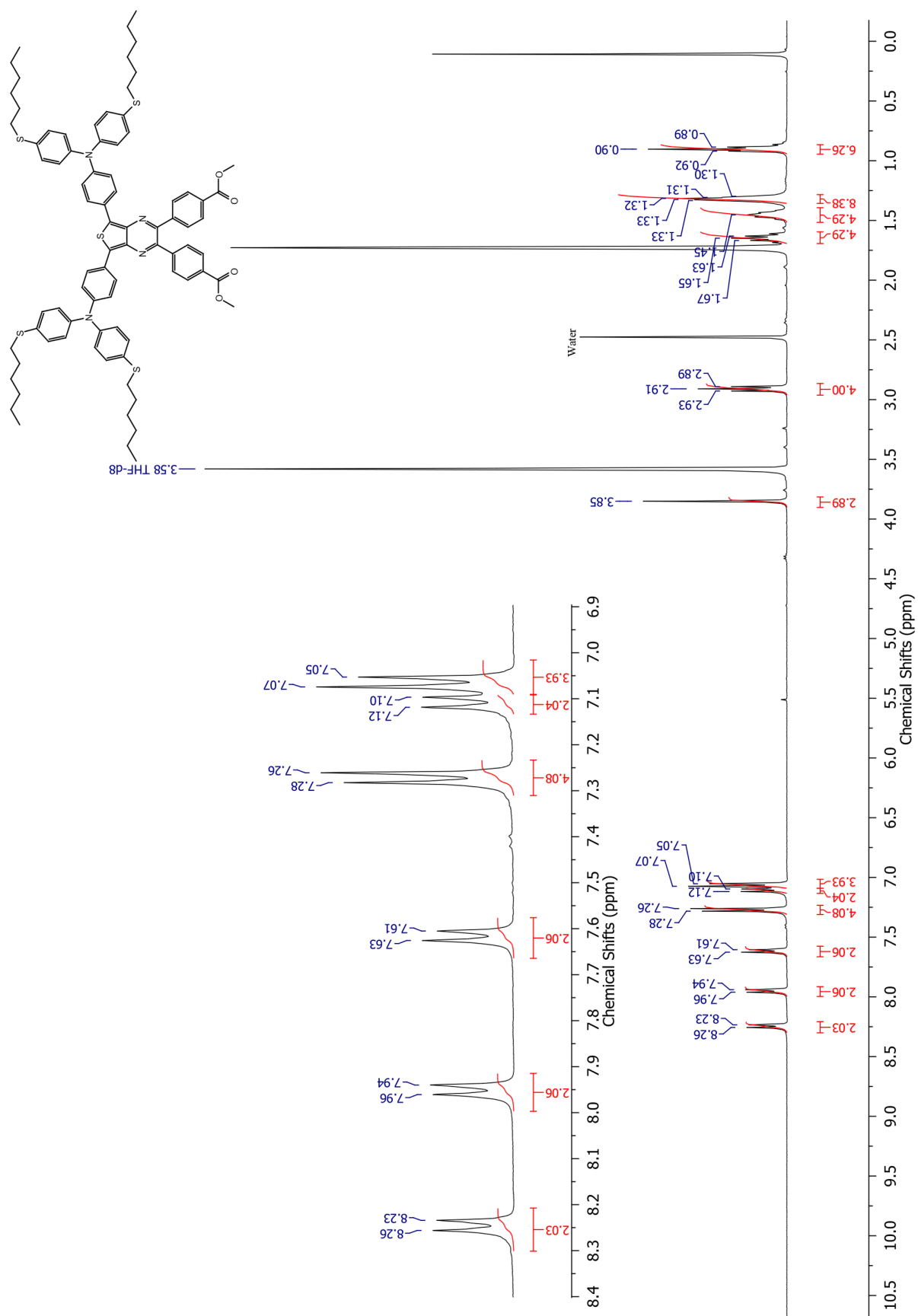
52.84

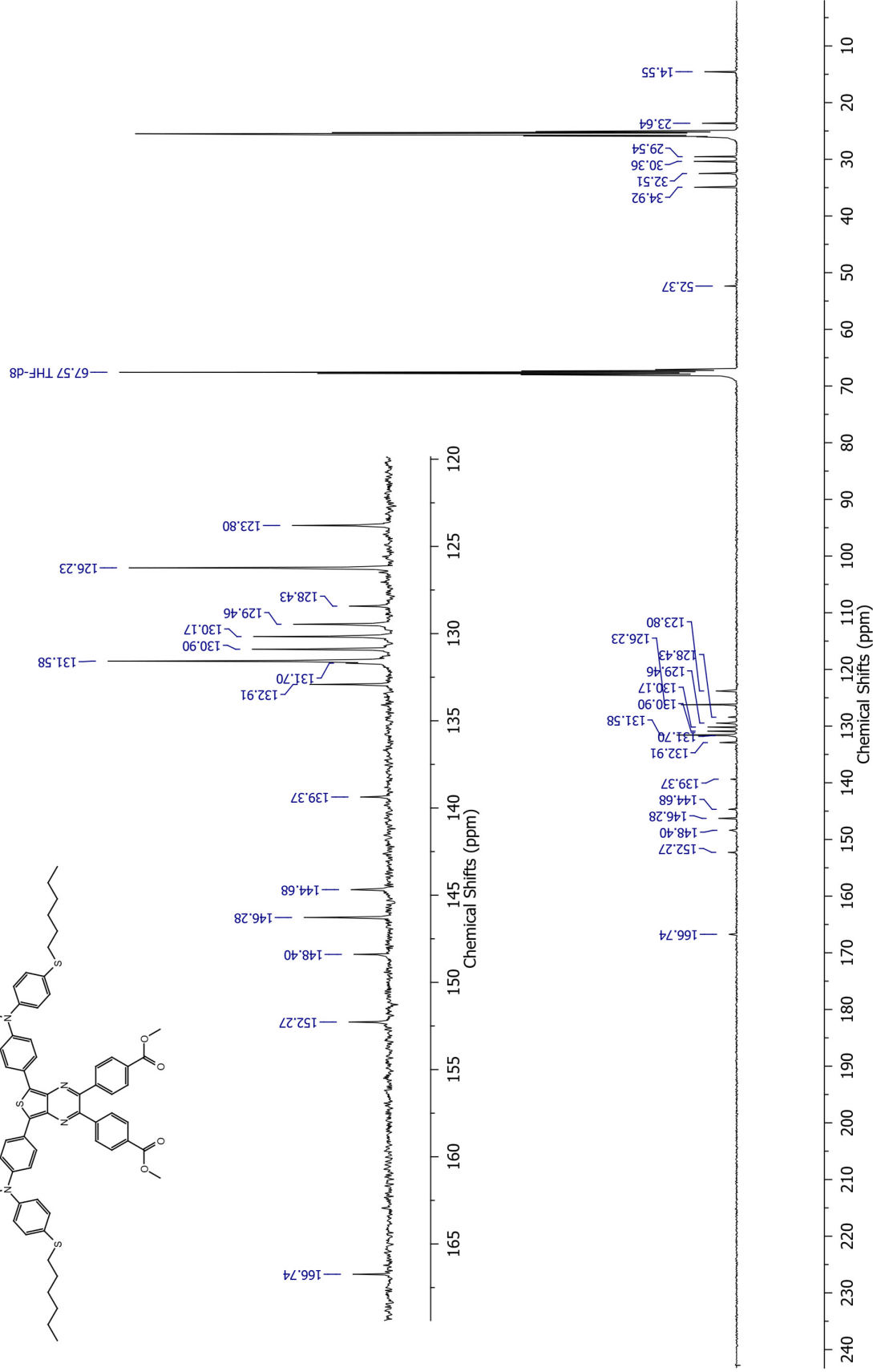
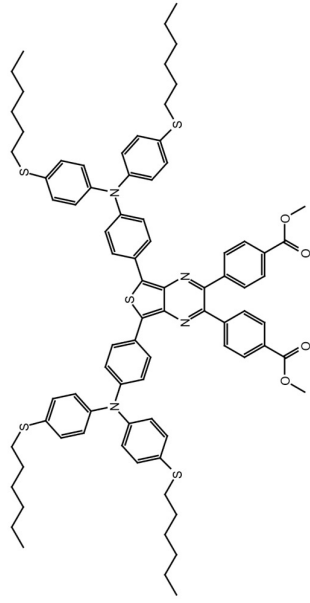


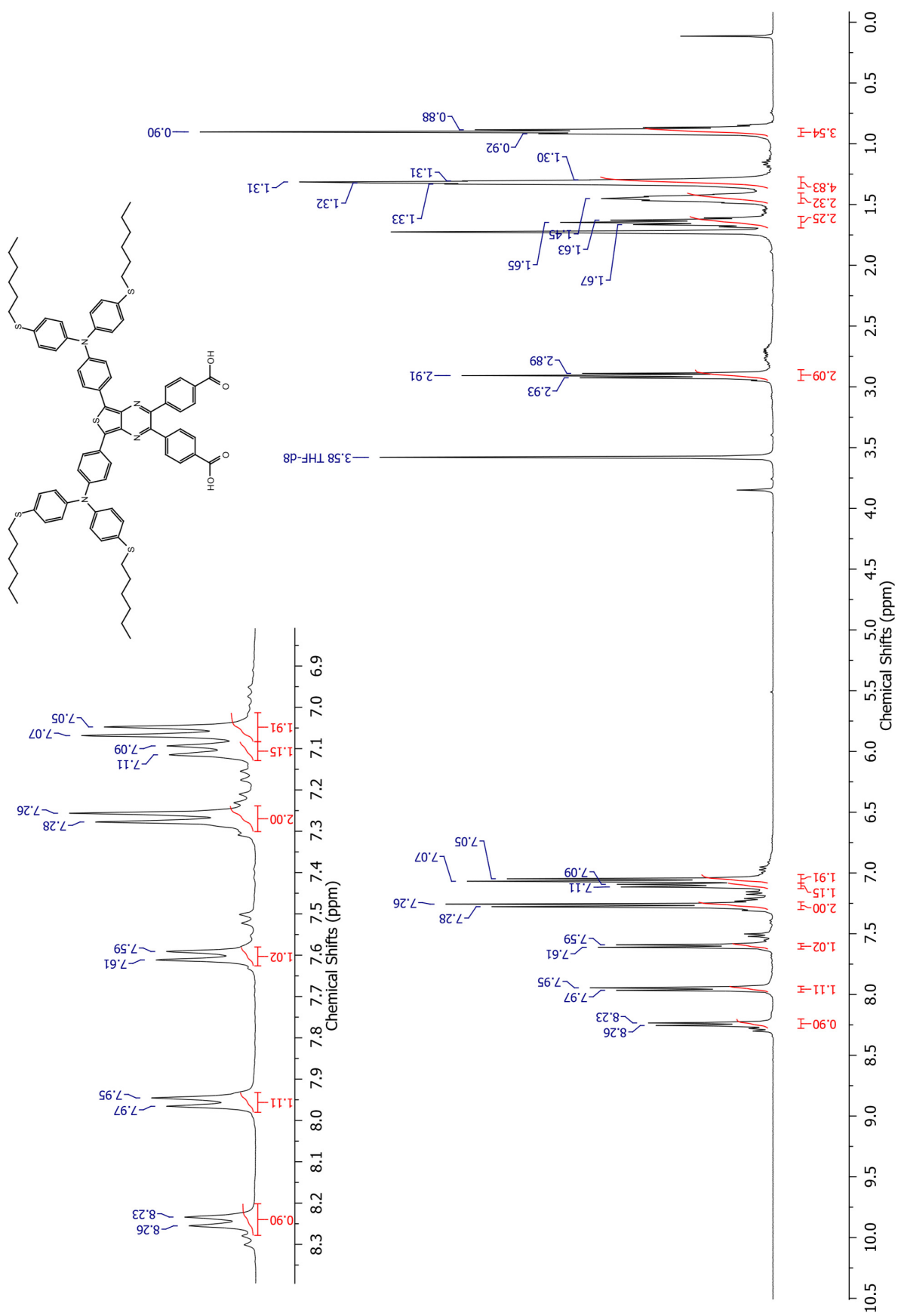


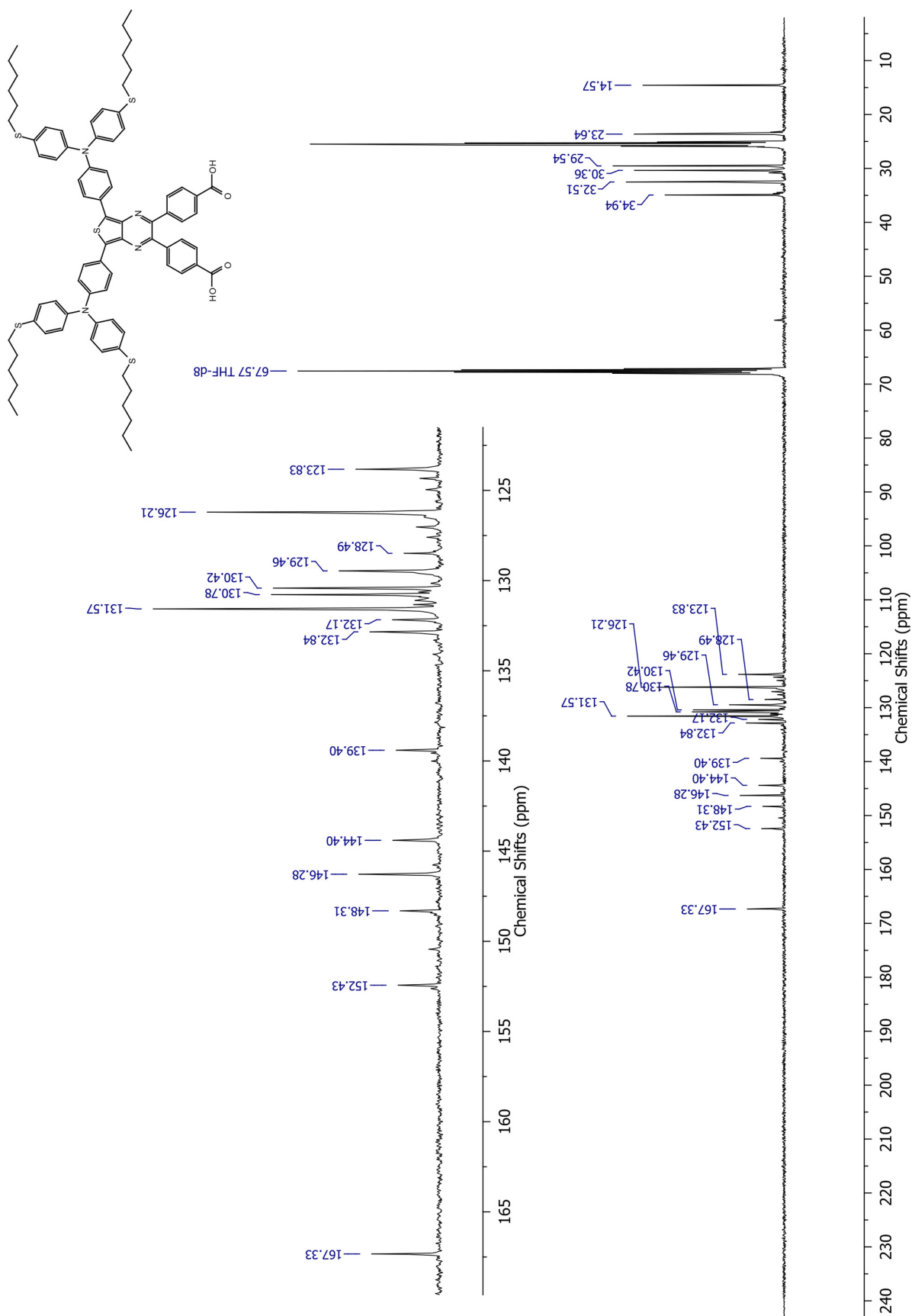












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