

## Synthesis and Properties of a Fluorene-Capped Isotruxene: A New Unsymmetrical Star-Shaped $\pi$ -System

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### Supporting Information (19 pages)

Experimental methods, synthetic procedures, characterization data, a proposed mechanism for isotruxene formation, and <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds, and DSC and TGA scans for compound **1**. (PDF).

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**General Methods.** Electronic spectra were recorded at room temperature ( $23 \pm 1$  °C). UV-visible spectra were measured on a Cary300 double beam spectrophotometer. Fluorescence spectra were recorded on a PTI QuantaMaster C-60 spectrometer and corrected for the response of the detector. The optical density (OD) of the toluene solution of **1** was about 0.1 at the wavelength of excitation. A N<sub>2</sub>-bubbled solution of anthracence ( $\Phi_f = 0.27$  in hexane)<sup>S1</sup> was used as a standard for the fluorescence quantum yield determination of compound **1** under N<sub>2</sub>-bubbled toluene solutions with solvent refractive index correction. An error of  $\pm 10\%$  is estimated for the fluorescence quantum yields. Electrochemical data of compound **1** were determined by cyclic voltammetry (CV) in 0.1M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> on a platinum button electrode or 0.1M Bu<sub>4</sub>NPF<sub>6</sub>/THF solutions on a glassy carbon electrode with a platinum coil auxiliary electrode and an isolated silver/silver nitrate reference electrode using an CHI 611A Electrochemical Analyzer. The data were corrected by the CV of ferrocene under the same condition. DSC thermographs were carried out on a Mettler DSC 822 and calibrated by a pure indium sample. All phase transitions were determined by a scan rate of 5.0 °C/min. Thermogravimetric analysis (TGA) was performed with a perkin Elmer TGA-7 thermal analysis system using dry nitrogen as a carrier gas at a flow rate of 100 mL min<sup>-1</sup>. The TGA experiments were conducted from room temperature to 900 °C with a linear heating rate of 10 °C min<sup>-1</sup>.

**Materials.** Solvent for organic synthesis were reagent grade or HPLC grade but all were HPLC grade for electronic spectra, CV, and fluorescence quantum yield measurements. Compound **6** was previously reported,<sup>S2</sup> and our melting points and <sup>1</sup>H NMR spectrum for **6** conform to the literature values. The synthesis of compound **3** was also previously

reported,<sup>S3</sup> but, as described in the following, we employed a new synthetic method for the preparation of **3**.

**Compound 3.** A mixture of indene (1.30 mL, 10.00 mmol), Cs<sub>2</sub>CO<sub>3</sub> (3.25 g, 10.00 mmol) and I<sub>2</sub> (1.00 g, 3.94 mmol) in 5 mL of anhydrous DMF was refluxed at 160 °C for 24 h. After cooling to rt, 40~50 mL of CH<sub>2</sub>Cl<sub>2</sub> was added. The insoluble residue was filtered off and the filtrate was concentrated under reduced pressure to afford the crude product. Further purification was performed by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) as the eluent to provide the white solid of **3** with a yield of 18%. mp: 218-220 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 3.87 (s, 4H), 4.13 (s, 2H), 7.32-7.39 (m, 3H), 7.42-7.50 (m, 3H), 7.56-7.60 (m, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.84 (d, *J* = 7.4 Hz, 1H), 8.54 (t, *J* = 8.8 Hz, 2H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 35.7, 35.9, 36.6, 122.1, 123.3, 123.5, 125.0, 125.1, 125.2, 126.1, 126.2, 126.3, 126.4, 126.5, 126.9, 135.7, 136.1, 136.5, 136.8, 137.5, 139.1, 141.8, 142.0, 142.4, 143.9, 144.1 (2C) ppm; IR (KBr): 1557, 1651 cm<sup>-1</sup>; Anal. Calcd for C<sub>27</sub>H<sub>18</sub>: C, 94.70, H, 5.30. Found: C, 94.64, H, 5.27.

**Compound 4.** To a stirred solution of isotruxene **3** (0.17 g, 0.50 mmol) in THF (3 mL) under argon, 1.6 mL of *n*-butyllithium in hexane (1.60 M, 2.56 mmol) was added dropwise at rt. The solution turned to deep red. The solution was stirred for an additional 30 min at rt and bromoethane (0.15 mL, 2.00 mmol) was added over a period of 5 min period. After stirring for 4 h, the second portion of BuLi (1.6 mL, 2.56 mmol) was added and in 30 min the second portion of bromoethane (2 mmol, 0.15 mL) was added. After stirring the mixture for 12 h, it was quenched with a few drops of water. The mixture was subjected to a EtOAc/H<sub>2</sub>O workup. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the filtrate was passed through a thin-layer of silica gel to remove some impurities

and then concentrated under reduced pressure to afford the crude product. Further purification was performed by column chromatography to provide the white solid of **4** with a yield of 90%: mp: 180-181 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 0.23-0.30 (m, 18H), 2.04-2.18 (m, 6H), 2.62-2.67 (m, 4H), 2.94-2.96 (m, 2H), 7.33-7.37 (m, 8H), 7.44 (d, *J* = 7.1 Hz, 1H), 8.27 (d, *J* = 7.3 Hz, 1H), 8.45 (t, *J* = 3.4 Hz, 1H), 8.51 (d, *J* = 7.3 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 8.7, 8.9, 29.5, 33.0, 33.1, 57.6, 58.3, 59.4, 121.5, 121.7, 122.3, 122.9, 124.4, 125.6, 125.8, 126.0, 126.5, 126.9, 137.5, 137.9, 139.4, 140.7, 141.3, 141.4, 143.9, 144.8, 145.1, 151.2, 151.5, 152.3 ppm; IR (KBr): 1459, 1559, 1653, 2967 cm<sup>-1</sup>; Anal. Calcd for C<sub>39</sub>H<sub>42</sub>: C, 91.71, H, 8.29. Found: C, 91.60, H, 8.31; FAB-HRMS calcd for C<sub>39</sub>H<sub>42</sub>: 510.3287, found 510.3272.

**Compound 5.** To a stirred solution of **4** (0.26 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), Br<sub>2</sub> (0.1 mL, 2 mmol) was slowly added at rt under the protection from light by covering the round-bottom flask with aluminum foil. After 16 h excess bromine was removed by bubbling argon through the solution. The mixture was washed with Na<sub>2</sub>S<sub>2</sub>O<sub>4(aq)</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the filtrate was concentrated under reduced pressure to afford the crude product. The crude product was recrystallized from MeOH to afford the solid of **5** with a yield of 86%: mp: 133-134 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 0.24-0.30 (m, 18H), 2.00-2.13 (m, 6H), 2.59-2.62 (m, 4H), 2.84-3.01 (m, 2H), 7.44-7.56 (m, 6H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 8.5, 8.7, 8.8, 29.4 (2C), 29.7, 32.8, 32.9, 33.0, 58.0, 58.7, 59.8, 121.2, 121.2, 121.3, 123.5, 124.0, 124.9, 125.1, 125.7, 125.8, 129.0, 129.2, 129.4, 136.6, 137.2, 138.8, 139.2, 139.7, 139.9, 143.8, 145.1, 145.2, 153.7, 153.9, 154.6 ppm; IR (KBr): 1459, 1559, 1653, 2967 cm<sup>-1</sup>;

FAB-HRMS calcd for  $C_{39}H_{39}Br_3$ : 744.0602, found 744.0588.

**Compound 7.** To a solution of **6** (3.01 g, 10.00 mmol) in THF (30 mL) at  $-78\text{ }^{\circ}\text{C}$  under argon, *n*-BuLi in hexane (2.50 M, 10.0 mL, 25.00 mmol) was added dropwise. The mixture was stirred at this temperature for 1 h and then (*i*-PrO)<sub>3</sub>B was added dropwise. The mixture was allowed to warm to rt for 12 h. The solution was poured to ice water and acidified with HCl<sub>(aq)</sub> until pH was between 2 and 3. The pH of the mixture was then adjusted to pH 14 with 6 M aqueous KOH. The mixture was washed with ether, and the organic layer was dried over anhydrous MgSO<sub>4</sub>. Further purification was performed by column chromatography with EtOAc/hexane (1:3) to provide the white solid of **7** with a yield of 71%: mp: 118-120  $^{\circ}\text{C}$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 0.20 (t, *J* = 7.1 Hz, 6H), 2.01 (q, *J* = 7.1 Hz, 4H), 7.32-7.34 (m, 2H), 7.41-7.42 (m, 1H), 7.77-7.83 (m, 4H), 8.03 (s, 2H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 8.4, 31.9, 55.4, 118.8, 120.1, 122.9, 126.9, 127.4, 128.4, 133.0, 140.9, 142.7, 148.1, 149.8 ppm.

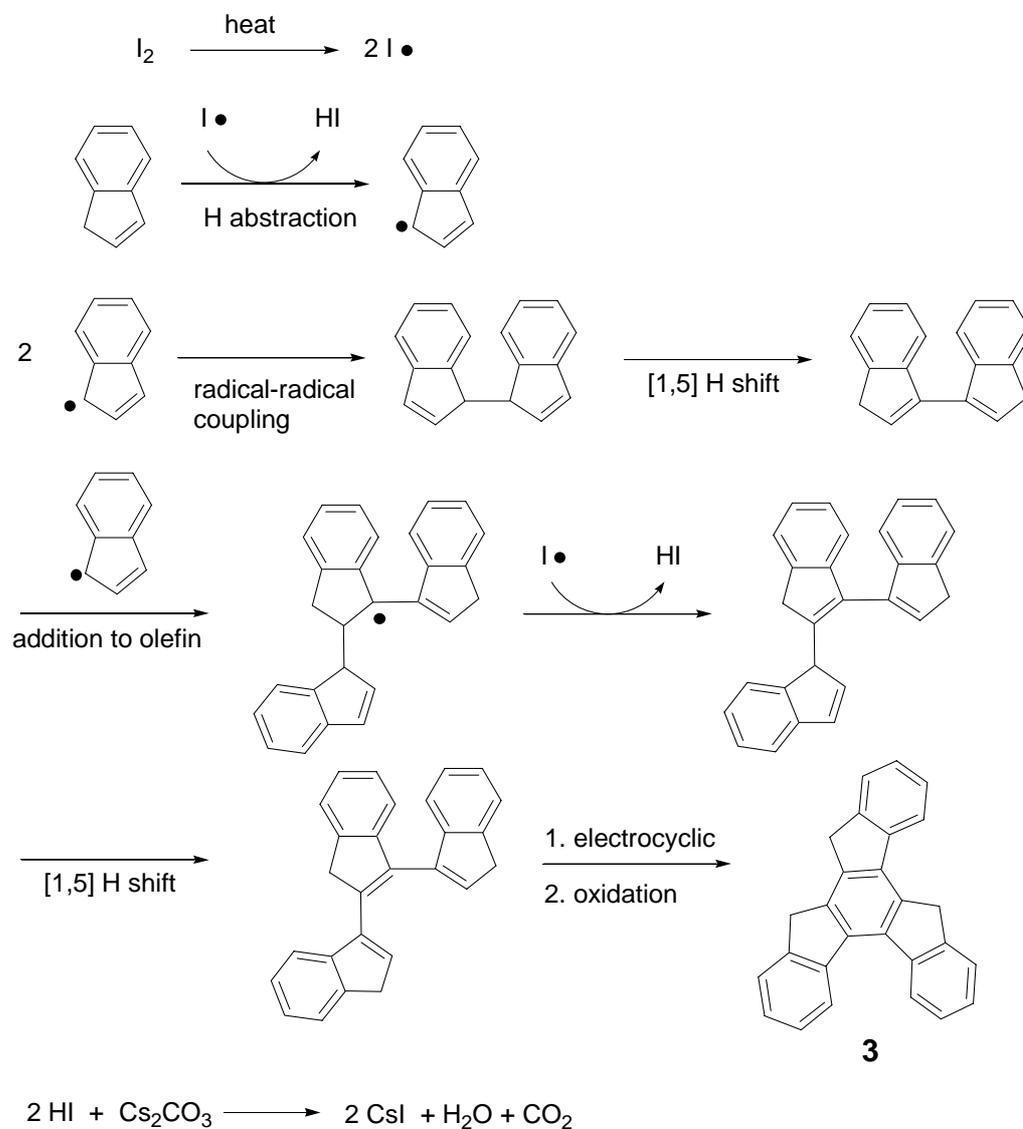
### Compound 1

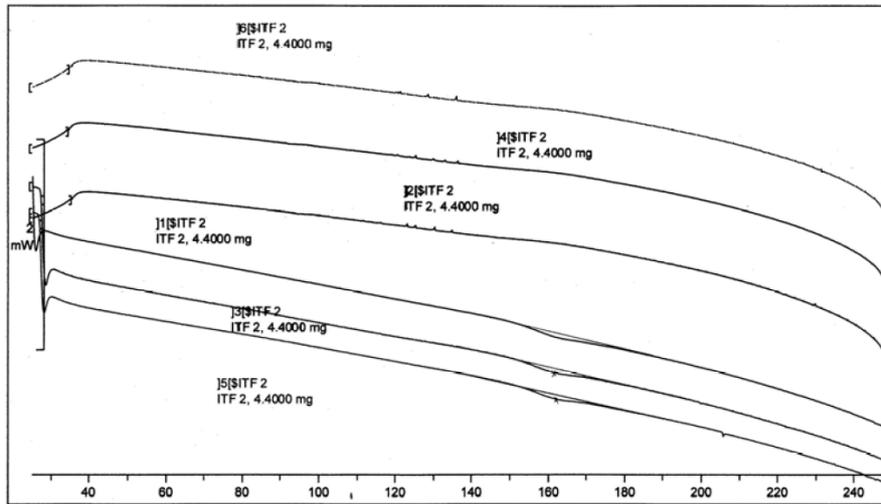
A mixture of **5** (0.37 g, 0.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.11 g, 0.093 mmol), K<sub>2</sub>CO<sub>3</sub> (0.69 g, 5.00 mmol) in H<sub>2</sub>O (2.5 mL), and **7** (0.53 g, 2.0 mmol) in toluene (30 mL) was heated to 90  $^{\circ}\text{C}$  for 24 h under argon. After cooling, the solution was diluted with CH<sub>2</sub>Cl<sub>2</sub>. The insoluble portion was filtered off and the filtrate was concentrated under reduced pressure. Column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) as eluent afforded the crude product. The crude product was recrystallized from CHCl<sub>3</sub>/MeOH to afford the solid of **1** with a yield of 58%: mp > 300  $^{\circ}\text{C}$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 0.42-0.44 (m, 36H), 2.75-2.77 (m, 4H), 3.06-3.10 (m, 2H), 7.34-7.38 (m, 9H), 7.65-7.84 (m, 18H), 8.42 (d, *J* = 7.9 Hz, 1H),

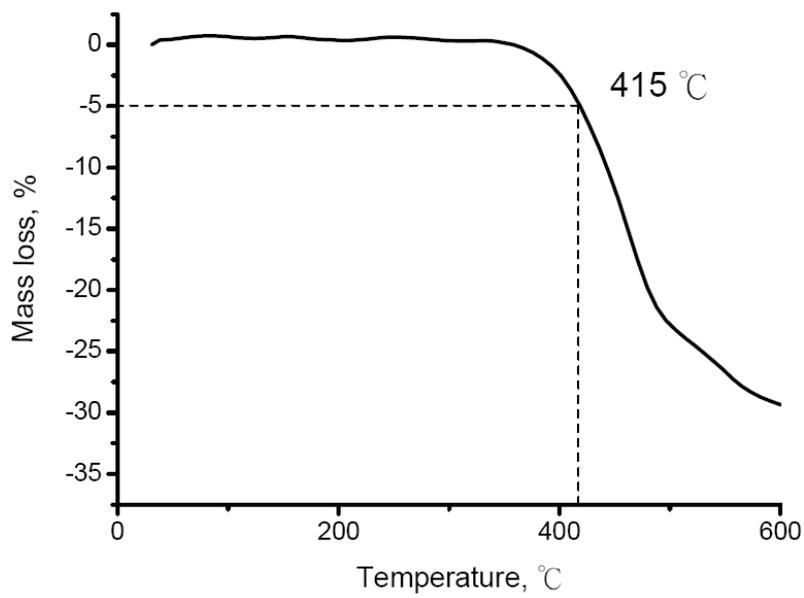
8.59 (d,  $J = 7.9$  Hz, 1H), 8.65 (d,  $J = 7.9$  Hz, 1H) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 8.6 (2C), 9.0 (2C), 9.1, 29.7, 32.9, 33.1, 33.2, 56.3, 57.8, 58.5, 59.7, 119.7, 119.8, 119.9, 120.0, 120.7, 121.4 (2C), 122.6, 123.0, 123.2, 124.7, 125.0, 125.1, 125.3, 126.0, 126.9, 127.0, 137.2, 137.7, 139.1, 139.9, 140.2, 140.3, 140.4 (2C), 140.6, 140.7, 140.8 (2C), 141.3, 144.2, 145.2, 145.6, 150.2 (2C), 150.7, 152.0, 152.3, 153.1 ppm; IR (KBr): 1461, 1559, 1653, 2965  $\text{cm}^{-1}$ ; FAB-HRMS calcd for  $\text{C}_{90}\text{H}_{90}$ : 1170.7043, found 1170.7031.

**Reference:**

- S1. Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251-3260.
- S2. Sonntag, M.; Kreger, K.; Hanft, D.; Strohmriegl, P.; Setayesh, S.; de Leeuw, D. *Chem. Mater.* **2005**, *17*, 3031-3039.
- S3. Lang, K. F.; Zander, M.; Theiling, E. A. *Chem. Ber.* **1960**, *93*, 321-325.

**Scheme S1.** A proposed mechanism for the formation of isotxuene.

**Figure S1.** The DSC scan of compound **1**

**Figure 2.** The TGA scan of compound **1**.

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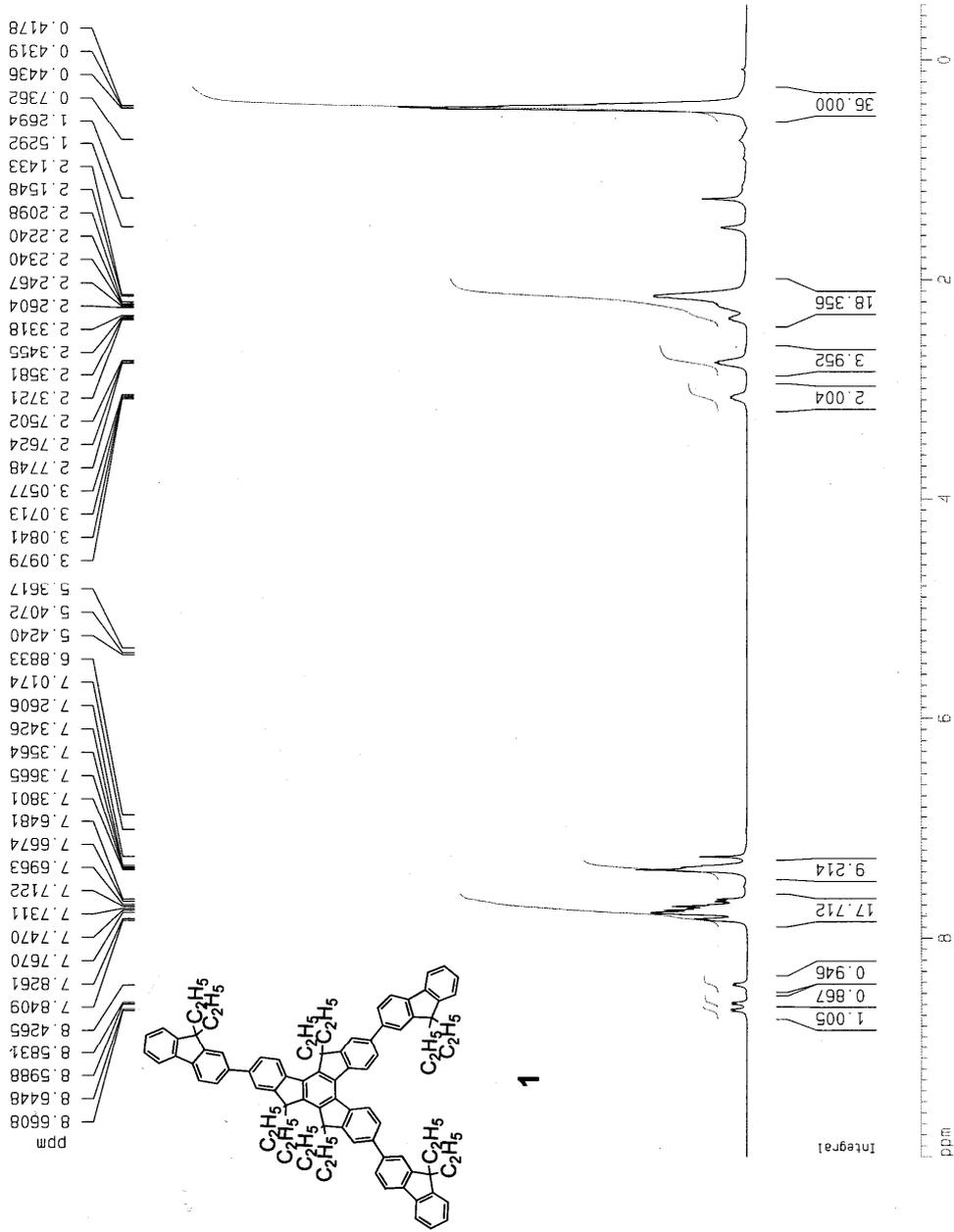
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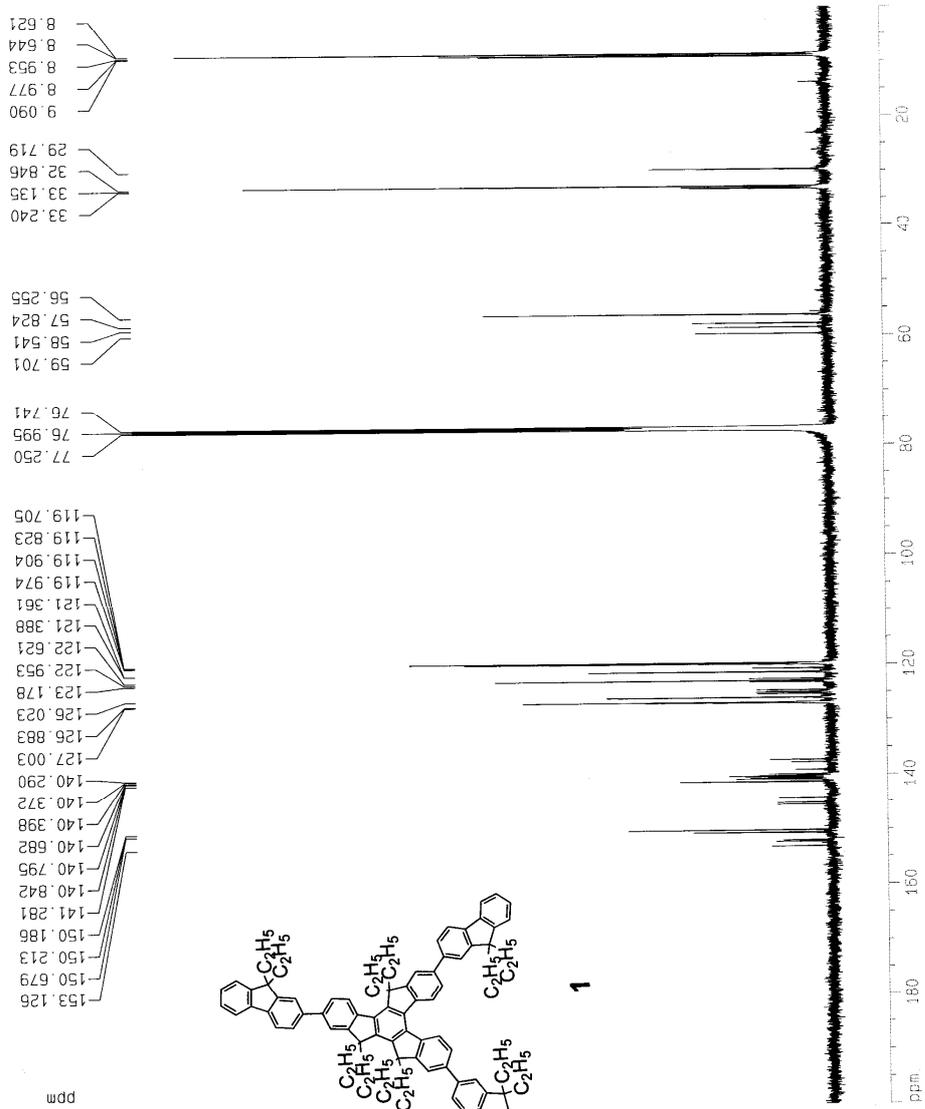
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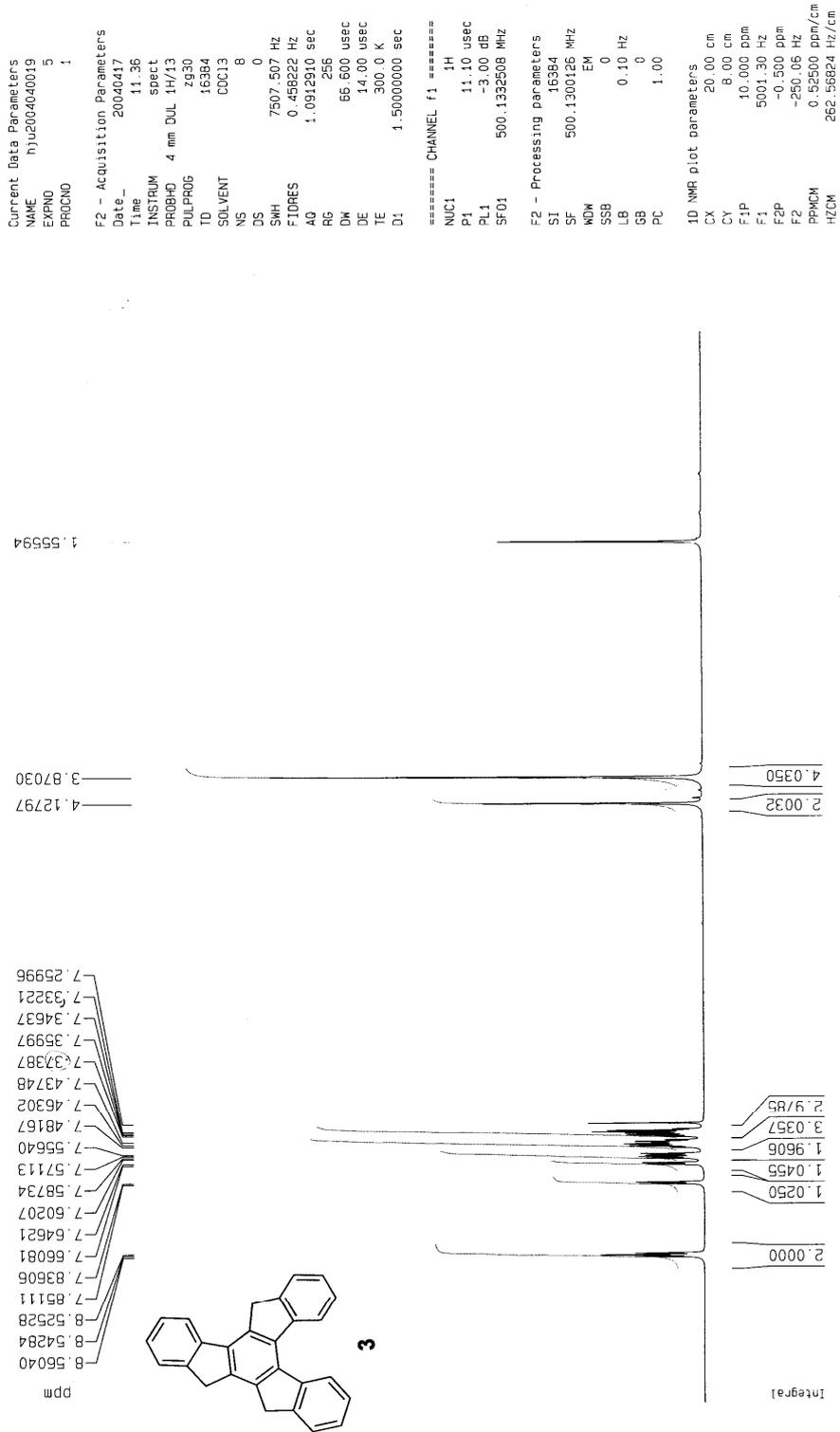
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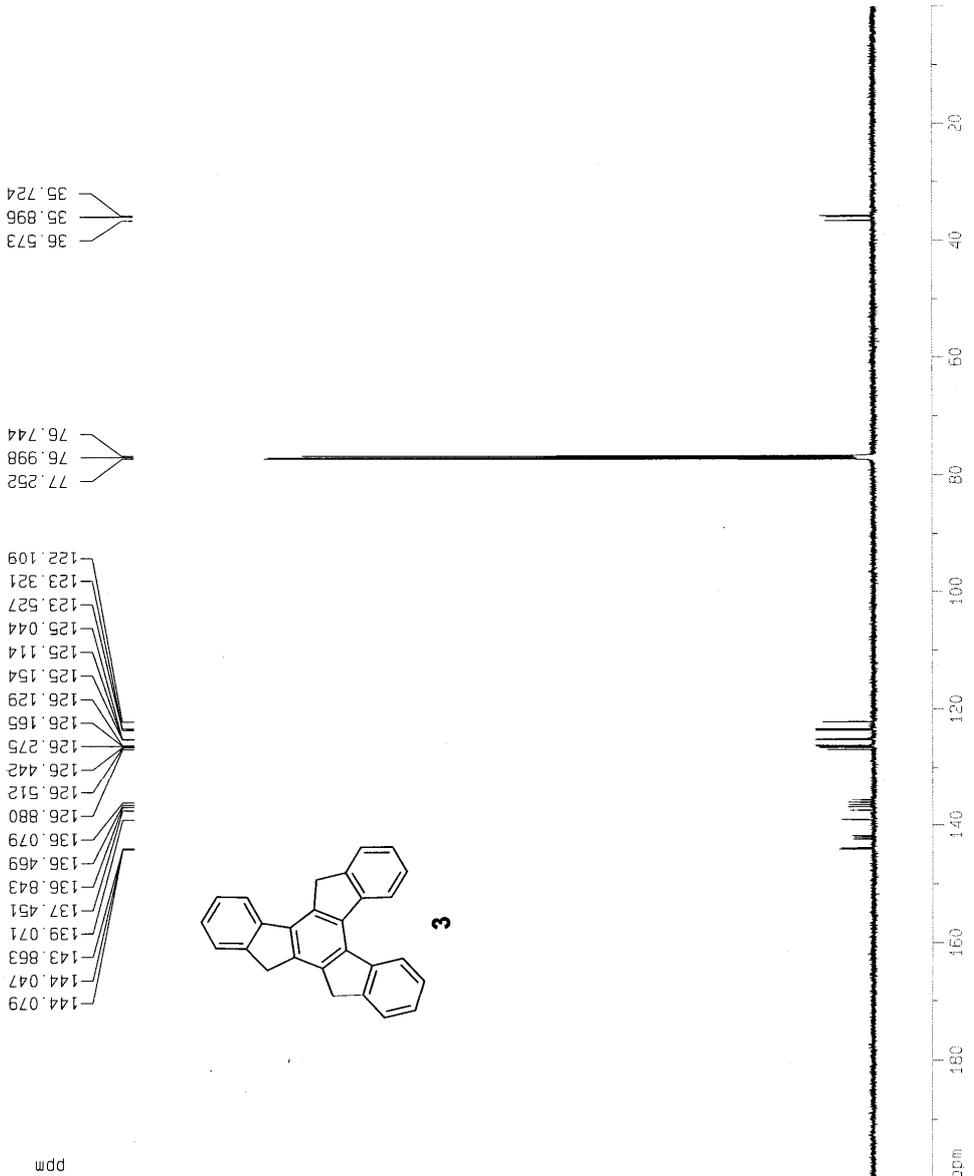
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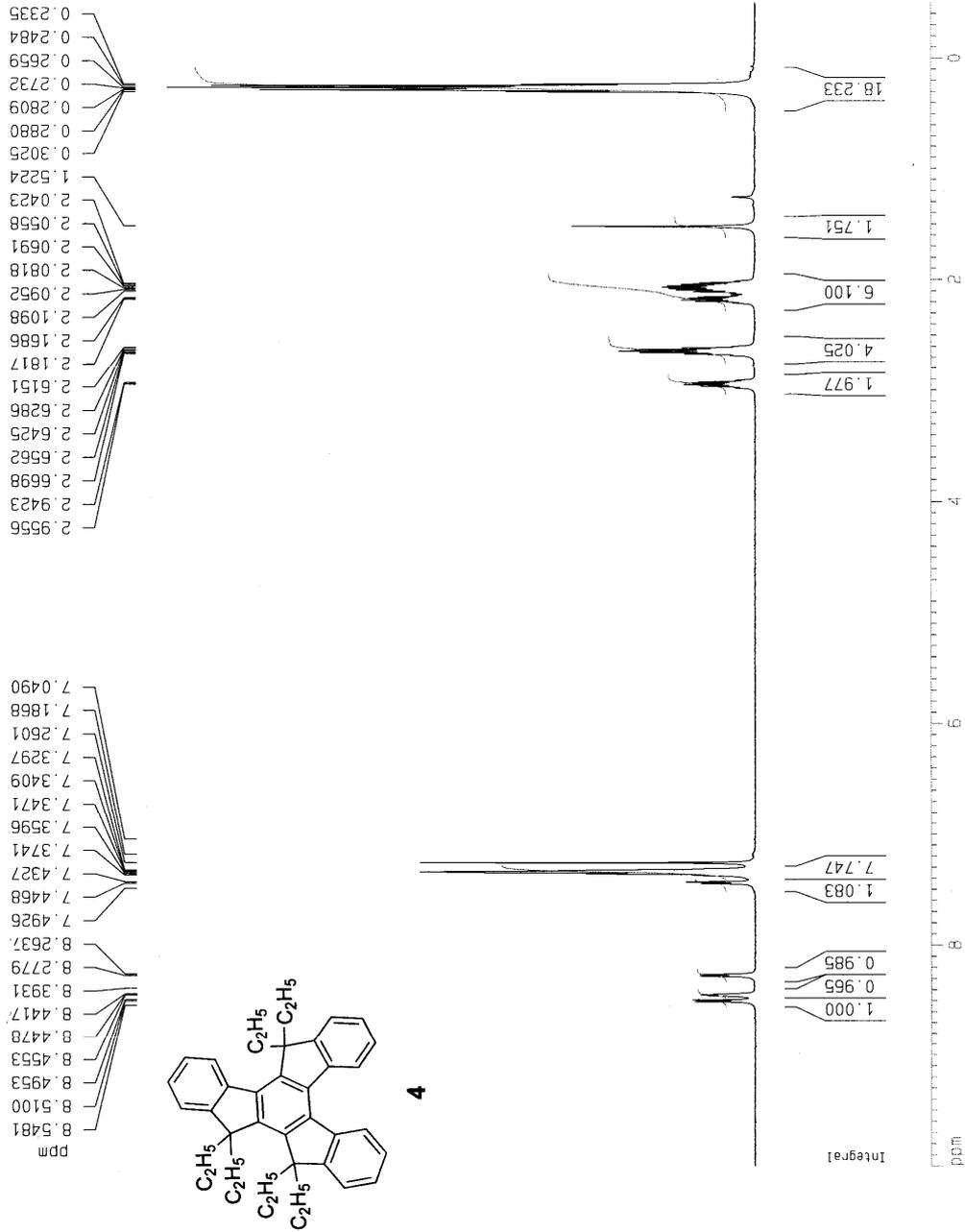
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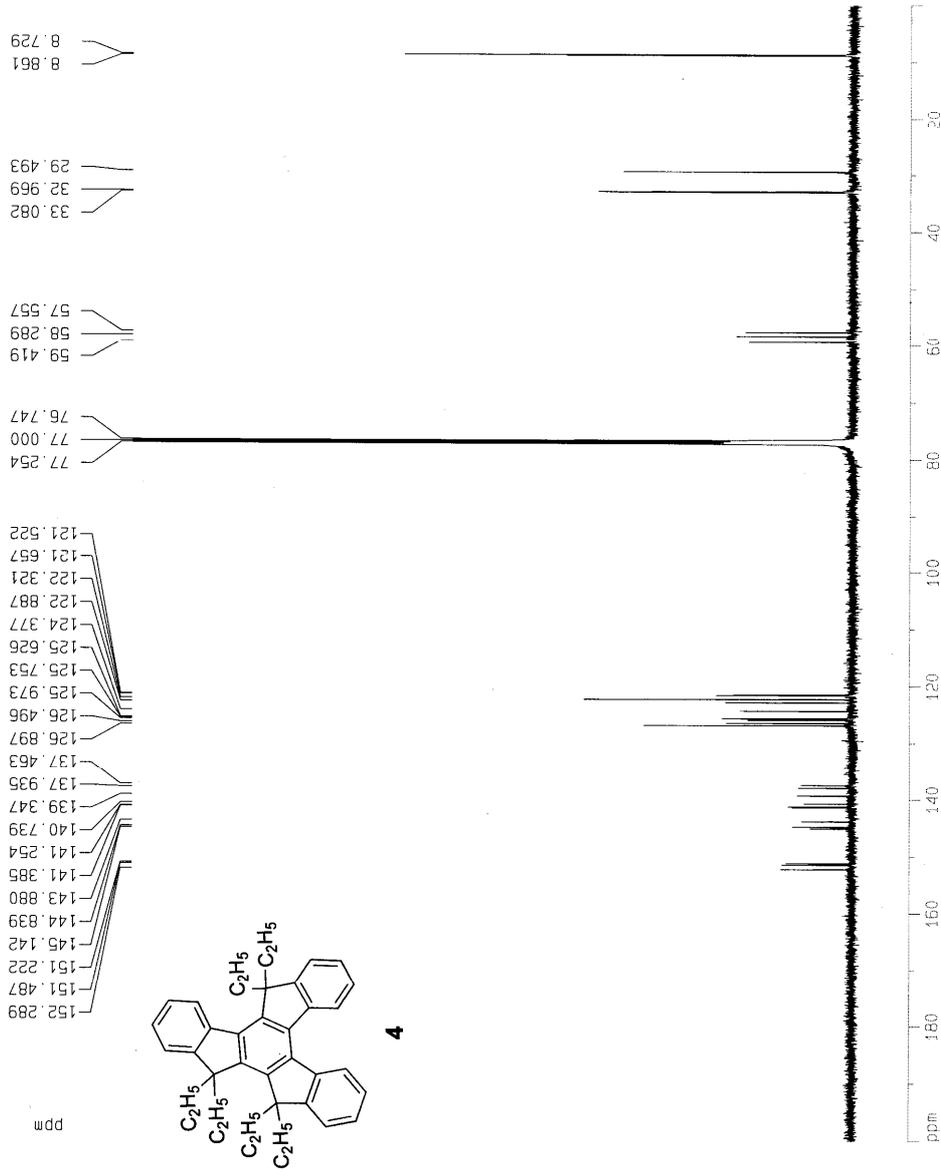
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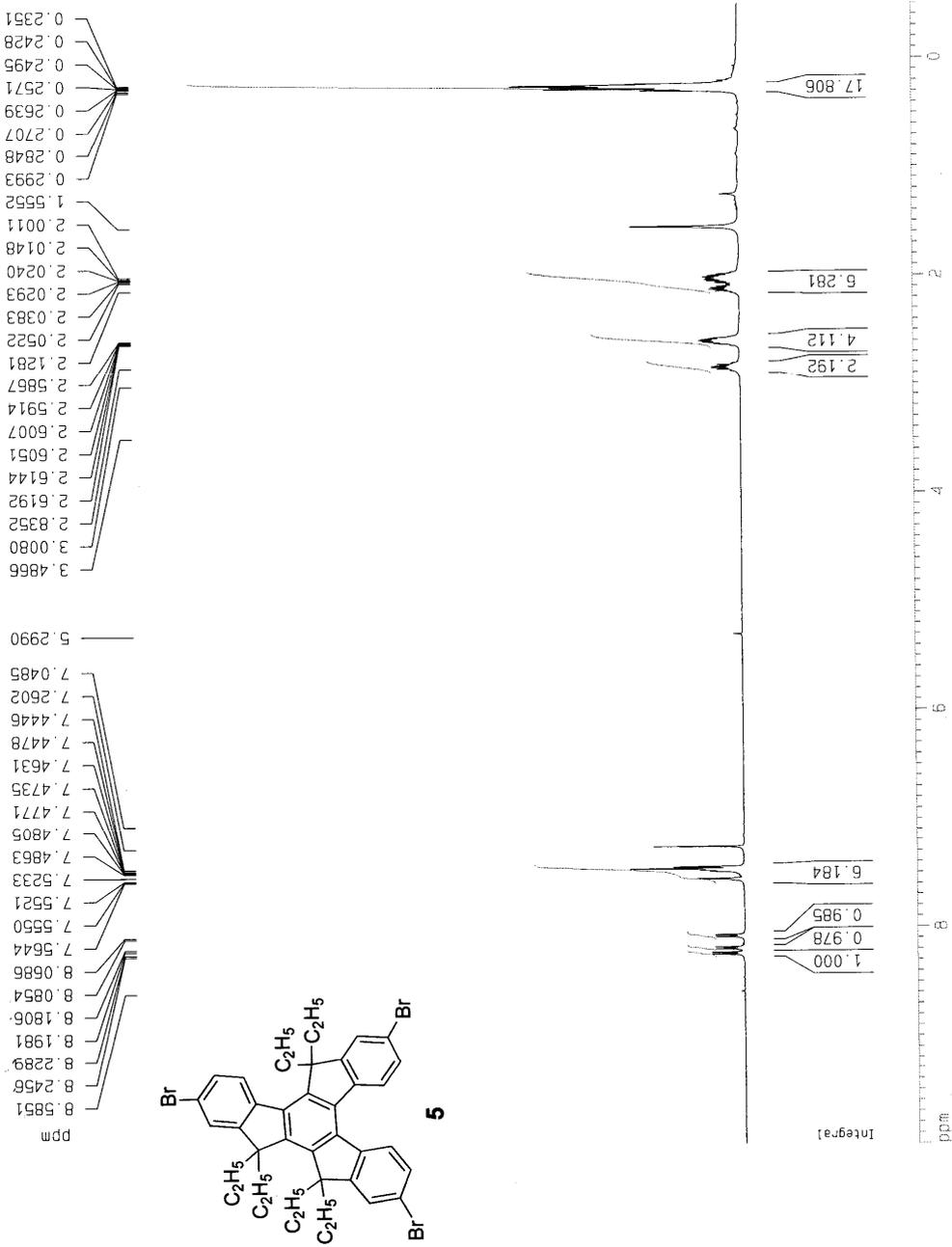
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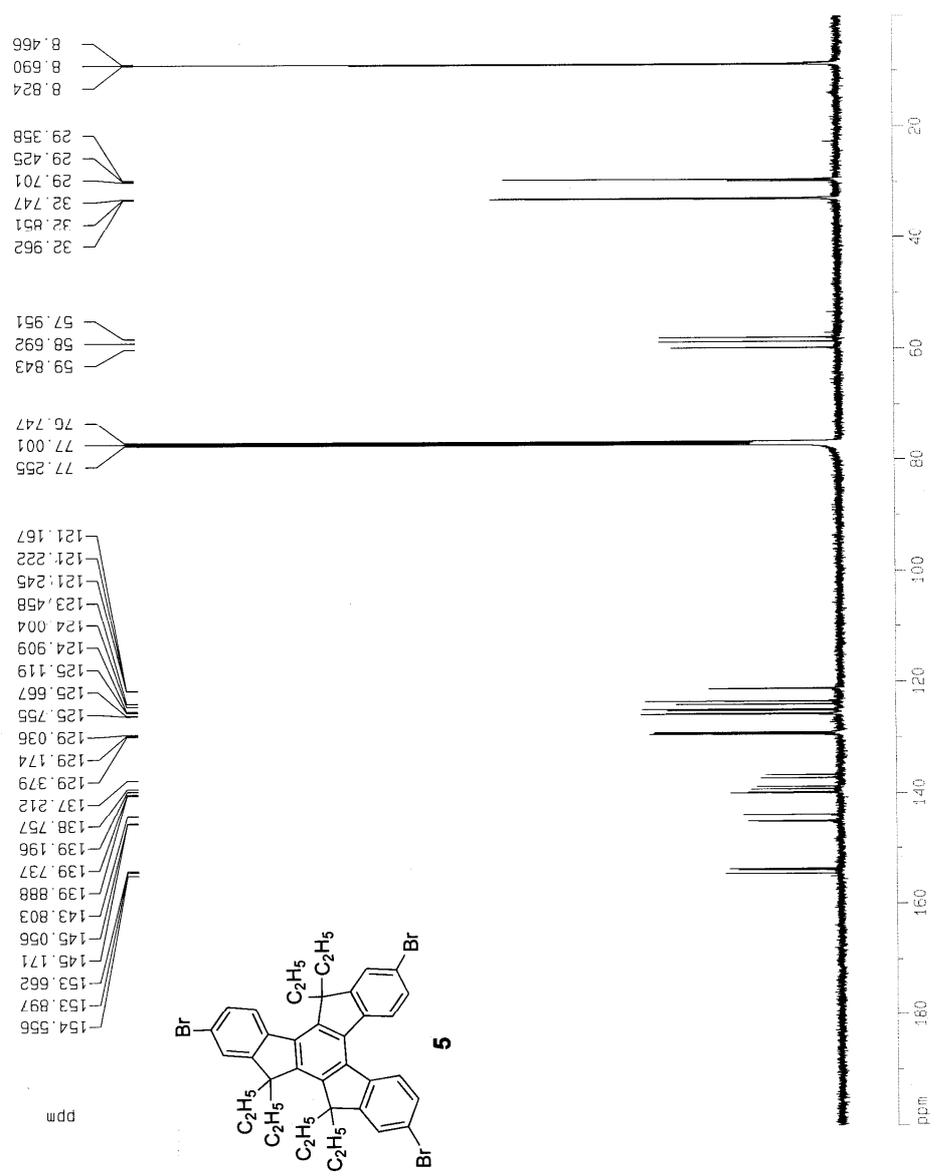
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 F2 -0.000 ppm  
 PPMCM 10.00000 ppm/cm  
 HZCM 1257.57788 Hz/cm



STANDARD 1H OBSERVE  
Pulse Sequence: s2pr1

