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**Unusually high SCLC hole mobility in solution-processed thin films of a polycyclic thiophene-based small-molecule semiconductor**

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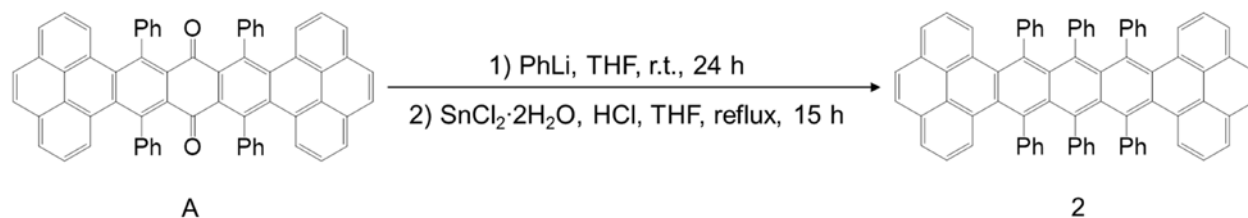
## Experimental

*General.* All reagents and solvents were used as received without further purification unless otherwise noted. Indium tin oxide (ITO) coated glass slides with a sheet resistance of 8–12  $\Omega$ /square was purchased from Delta Technologies. UV-vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Fluorescence spectra were recorded with a Shimadzu RF-5301PC spectrofluorophotometer. Crystal structure characterization was carried out by X-ray diffraction measurements on a Rigaku Miniflex automated powder X-ray diffractometer (Cu K $\alpha$ , 35 kV 15 mA, Ni filter). DSC thermograms were recorded on a PerkinElmer DSC 8000 differential scanning calorimeter.

### *Synthesis and Spectral Characteristics of Compound 1*

Compound **1** was prepared according to previously published procedures resulting in a bright orange solid.<sup>1,2</sup> 4,7-Di-*tert*-butylcenaphthylene (8.45 g, 32.0 mmol) and sulfur (Calcd. as S<sub>8</sub>, 4.15 g, 16.2 mmol) were refluxed in DMF (130 mL) for 22 h. The reaction contents were cooled to r.t. and vacuum filtered. The solid was washed with methanol to give the product as an orange solid, which was recrystallized from DMF (6.58 g, 11.8 mmol, 73.8%). mp: 375-376 °C dec; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 1.51 (s, 18 H), 1.58 (s, 18 H), 7.73 (d,  $J$  = 1.0 Hz, 2 H), 7.77 (d,  $J$  = 1.0 Hz, 2 H), 7.83 (d,  $J$  = 1.0 Hz, 2 H), 8.17 (d,  $J$  = 1.0 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 31.7, 35.5, 35.6, 118.6, 120.3, 121.5, 121.6, 128.7, 130.7, 132.6, 133.9, 138.7, 144.5, 150.9, 151.4 (15 of 16 expected resonances; but  $\delta$  31.7 resonance may contain two lines); HRMS (APPI-TOF): 556.3166 (Calcd. for C<sub>40</sub>H<sub>44</sub>S 556.3158). NMR spectra are attached below:

### Synthesis and Spectral Characterization of Compound 2.



Compound **2** was prepared by addition of eight equivalents of Ph-Li to the appropriate quinone, followed by the reductive elimination resulting in Compound **2**. Using an adapted approach of previously published procedures, the quinone was prepared where the appropriate cyclone was added to the corresponding dienone.<sup>3</sup> Phenyllithium (2 M in dibutyl ether, 1.0 mL, 2.0 mmol) was added to a suspension of quinone **A** (215 mg, 0.250 mmol) in dry THF (10 mL), and the contents were stirred for 24 h at r.t. under argon. The reaction was quenched by the addition of water (10 mL), acidified with acetic acid, poured into water (20 mL), and steam distilled to remove the organic solvents. The precipitate was collected *via* vacuum filtration and rinsed with ethanol. The crude diol, SnCl<sub>2</sub>·2H<sub>2</sub>O (2.07 g, 9.17 mmol), and HCl (0.5 mL) were placed into a screw-capped vial and refluxed in THF (8 mL) for 15 h. The THF was removed under reduced pressure, and the residue was triturated with ethanol. Recrystallization from CHCl<sub>3</sub>-MeOH gave **2** as a red solid (142 mg, 0.144 mmol, 67.8%). mp >400 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 6.40 (t, *J* = 7.5 Hz, 4 H), 6.52 (t, *J* = 7.5 Hz, 2 H), 6.59-6.60 (m, 8 H), 6.63-6.65 (m, 4 H), 6.82 (d, *J* = 7.5 Hz, 2 H), 6.85 (dd, *J* = 8.0, 1.0 Hz, 4 H), 6.86-6.90 (m, 6 H), 7.00 (t, *J* = 7.5 Hz, 4 H), 7.08 (t, *J* = 8.0 Hz, 4 H), 7.71 (dd, *J* = 7.5, 1.0 Hz, 4 H), 7.79 (s, 4 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ/ppm = 124.3, 125.4, 125.7, 126.1, 126.2, 126.6, 127.7, 127.9, 128.0, 128.2, 130.6, 130.7, 132.8, 133.1, 133.3, 134.1, 134.9, 135.3, 140.1, 141.5 (19 expected but 20 of a theoretically possible 23 resonances observed; but the δ 126.6 resonance may contain two lines); HRMS (APPI-TOF): 982.3595 (Calcd. for C<sub>78</sub>H<sub>46</sub> 982.3594). NMR spectra are attached below:

*Cyclic Voltammetry (CV) Measurements.* CV studies were carried out under argon atmosphere using BAS Epsilon EC electrochemical station employing a platinum working electrode (MF-2013) of 1.6 mm in diameter, a silver wire as the reference electrode, and a Pt wire as the counter electrode. For a solution measurement, a 0.1 M tetra-*n*-butylammonium hexafluorophosphate solution in CH<sub>2</sub>Cl<sub>2</sub> was used as supporting electrolyte. For a thin film measurement, a 0.1 M tetra-*n*-butylammonium hexafluorophosphate solution in acetonitrile was used as the supporting electrolyte. The scan rate was 20 mV s<sup>-1</sup>. The measured potentials were calibrated using a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated by HOMO = -( $E_{ox}^{onset} + 4.80$ ) (eV) and LUMO = -( $E_{red}^{onset} + 4.80$ ) (eV), respectively.

*Devices Preparation and SCLC Measurements:* ITO glass slides were used as the substrates. Under the protection of Magic tape, the ITO films were patterned by etching with aqua regia vapor. The patterned ITO glass substrates were cleaned in an ultrasonic bath sequentially by hot detergent, water, deionized water, toluene, acetone, and isopropyl alcohol, and then dried by compressed air. The cleaned ITO substrates were treated with UV ozone for 45 min before use. A highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Heraeus Precious Metals; Clevious P VP AI4083) thin layer was spin-coated (4000 RPM, 30 s) onto the ITO substrates from an aqueous solution. The PEDOT:PSS thin films were dried at 120 °C for 45 min on a hotplate in air. The solutions of **1** and **2** were prepared in chloroform with concentration of 20 mg mL<sup>-1</sup>. The above solutions were spin-coated (once) on top of the PEDOT:PSS layers at 600 RPM for 30 s. The devices were transferred to glove box, and half of them were thermally annealed (once) one by one at 120 °C for 10 min in the dark. Subsequently,

electrodes composed of 10 nm thick MoO<sub>3</sub> and 100 nm thick Au were deposited on the top by thermal evaporation under high vacuum ( $< 2 \times 10^{-6}$  mb) through a shadow mask. The active area of 0.14 cm<sup>2</sup> of the devices was defined by the overlap area of the ITO and the deposited MoO<sub>3</sub>/Au electrodes. Current–voltage characteristics of the devices were measured using a Keithley 2400 source meter in the dark. The thickness of the films was measured with a Tencor Alphastep 200 automatic step profiler.

For each condition, at least 10 individual devices were fabricated. The SCLC mobilities of 10 devices for each condition are listed below (from highest to lowest):

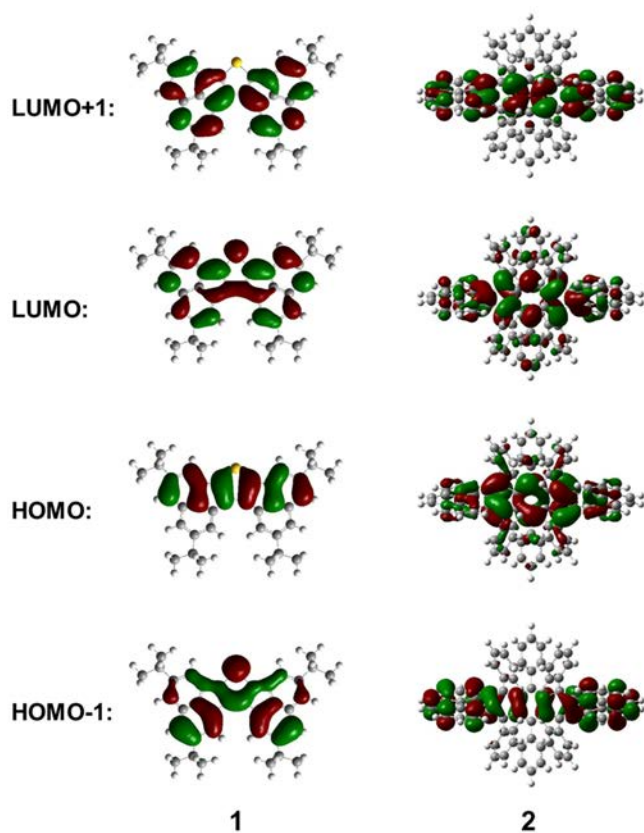
For **1**, unannealed: 1.10E-4, 8.58E-5, 5.28E-5, 4.32E-5, 2.83E-5, 2.61E-5, 2.47E-5, 2.20E-5, 2.16E-5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

For **1**, annealed: 0.08716, 0.08283, 0.07968, 0.07714, 0.06979, 0.06826, 0.06507, 0.06311, 0.05984, 0.05836 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

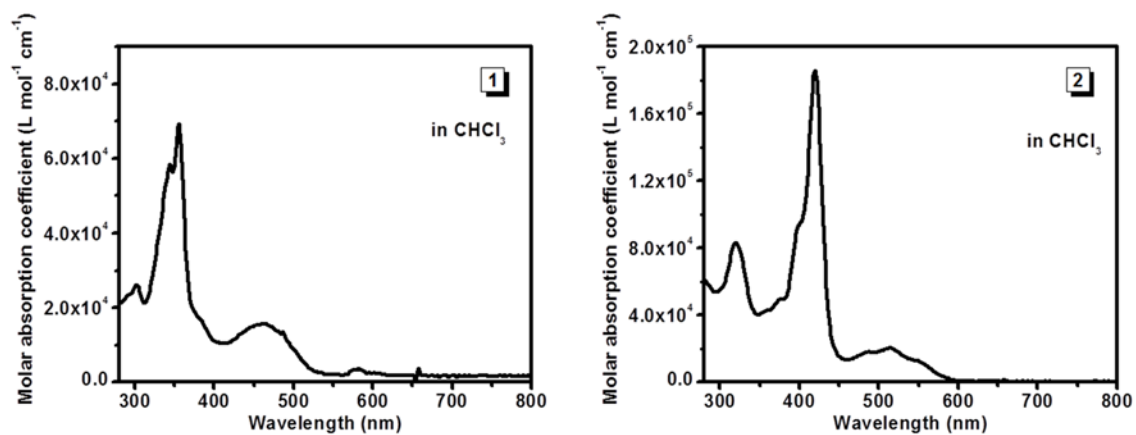
For **2**, unannealed: 2.41E-4, 2.06E-4, 1.64E-4, 1.10E-4, 8.35E-5, 7.31E-5, 5.86E-5, 5.45E-5, 4.66E-5, 4.44E-5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

For **2**, annealed: 8.89E-4, 6.57E-4, 5.46E-4, 5.26E-4, 5.10E-4, 4.77E-4, 2.59E-4, 2.56E-4, 2.09E-4, 2.01E-4 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.

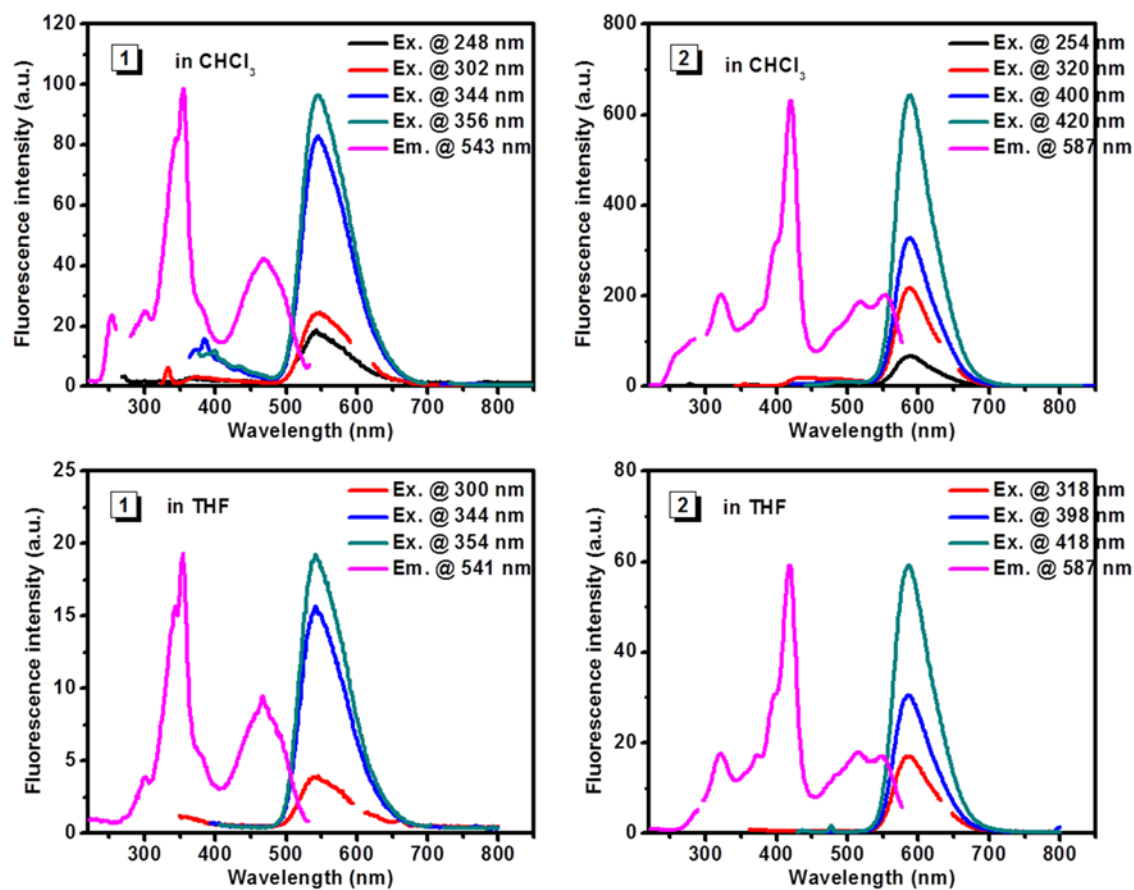
- 1 J. A. Watson Jr., R. A. Pascal Jr., D. M. Ho and K. V. Kilway, *Tetrahedron Lett.*, 2000, **41**, 5005.
- 2 K. V. Kilway, K. A. Lindgren, J. A. Watson Jr., R. G. Clevenger, R. D. Ingalls, D. M. Ho and R. A. Pascal Jr., *Tetrahedron*, 2004, **60**, 2433.
- 3 S. Mondal, A. J. Bhattacharya, *Curr. Sci.*, 1984, **53**, 1229.



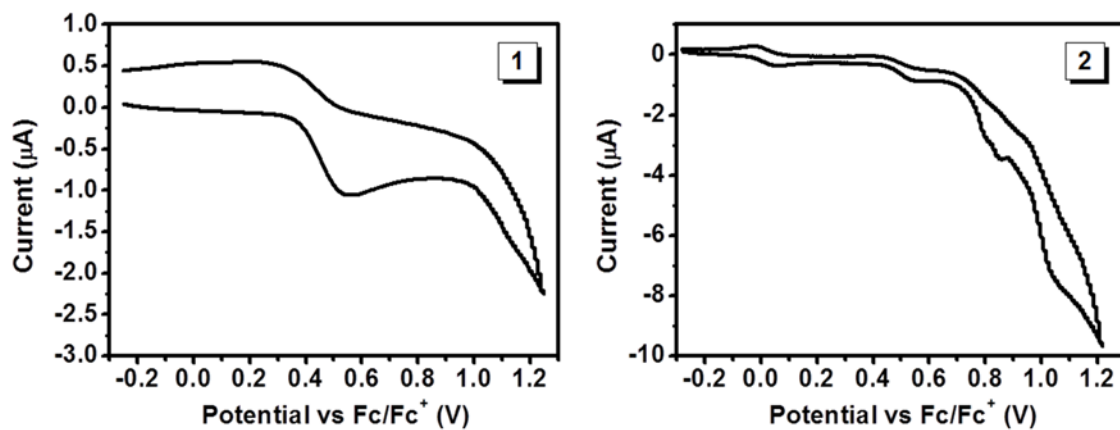
**Fig. S1.** LUMO+1, LUMO, HOMO and HOMO-1 orbitals (top to bottom) of **1** and **2** obtained using DFT calculations at the B3LYP/6-31G(d) level.



**Fig. S2.** UV-vis absorption spectra of **1** (5.24  $\mu\text{M}$ ) and **2** (4.92  $\mu\text{M}$ ) in  $\text{CHCl}_3$ .



**Fig. S3.** Fluorescence spectra of **1** and **2** in  $\text{CHCl}_3$  and THF, respectively.



**Fig. S4.** Oxidative cyclic voltammograms of **1** and **2** measured in  $\text{CH}_2\text{Cl}_2/\text{TBAPF}_6$  (0.1 M).

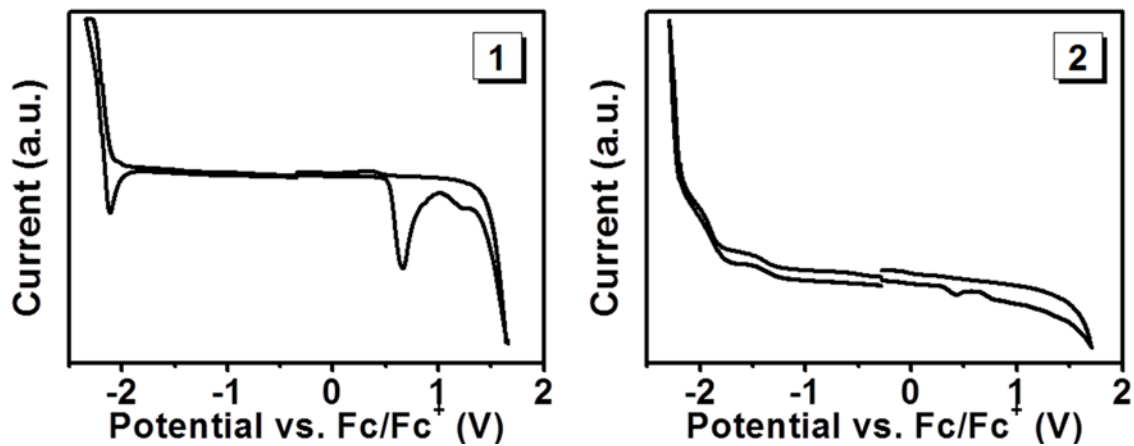


Fig. S5. Cyclic voltammograms of thin films 1 and 2.

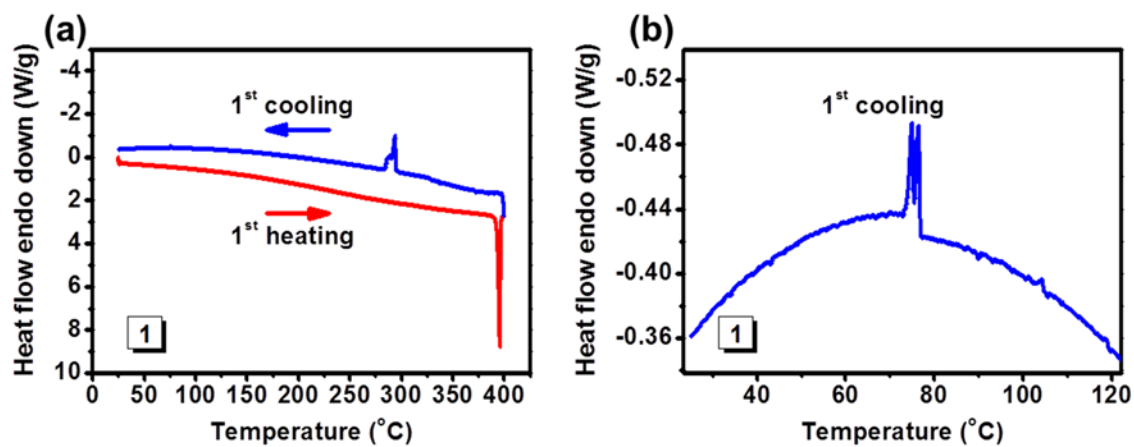


Fig. S6. (a) DSC thermograms of 1 with a heating and cooling rate of 10 °C/min. (b) A zoomed area of (a).



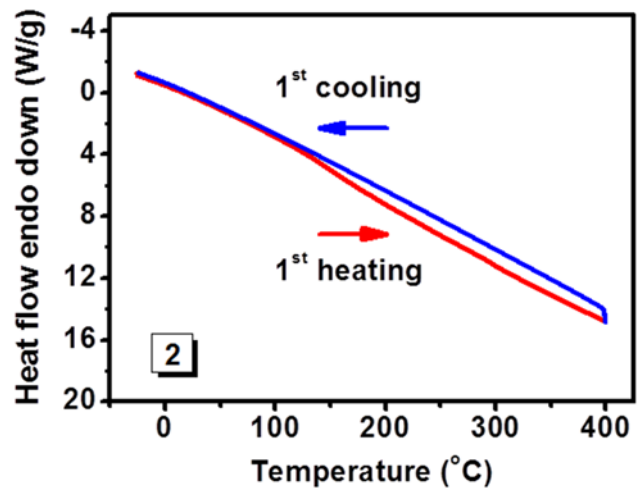
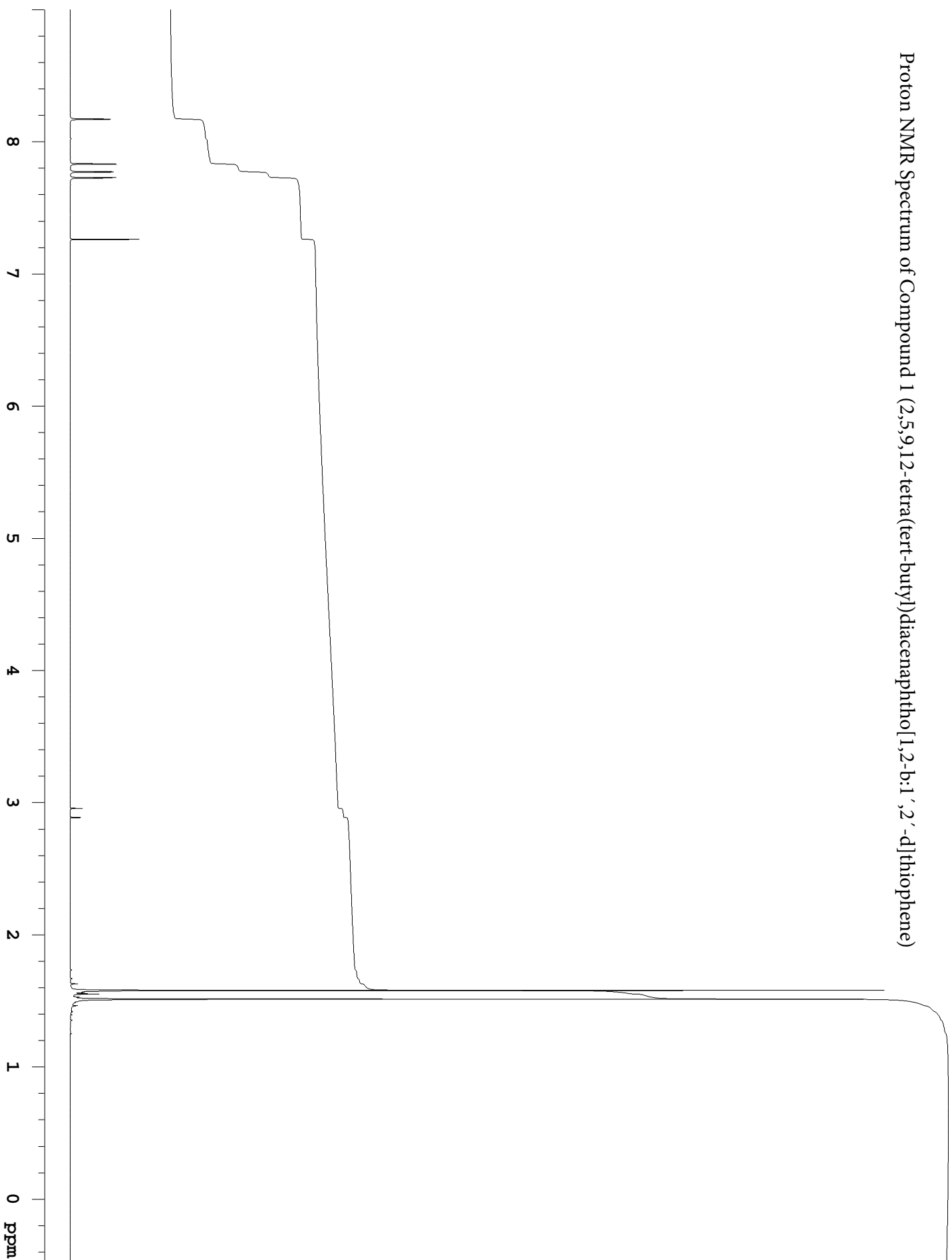
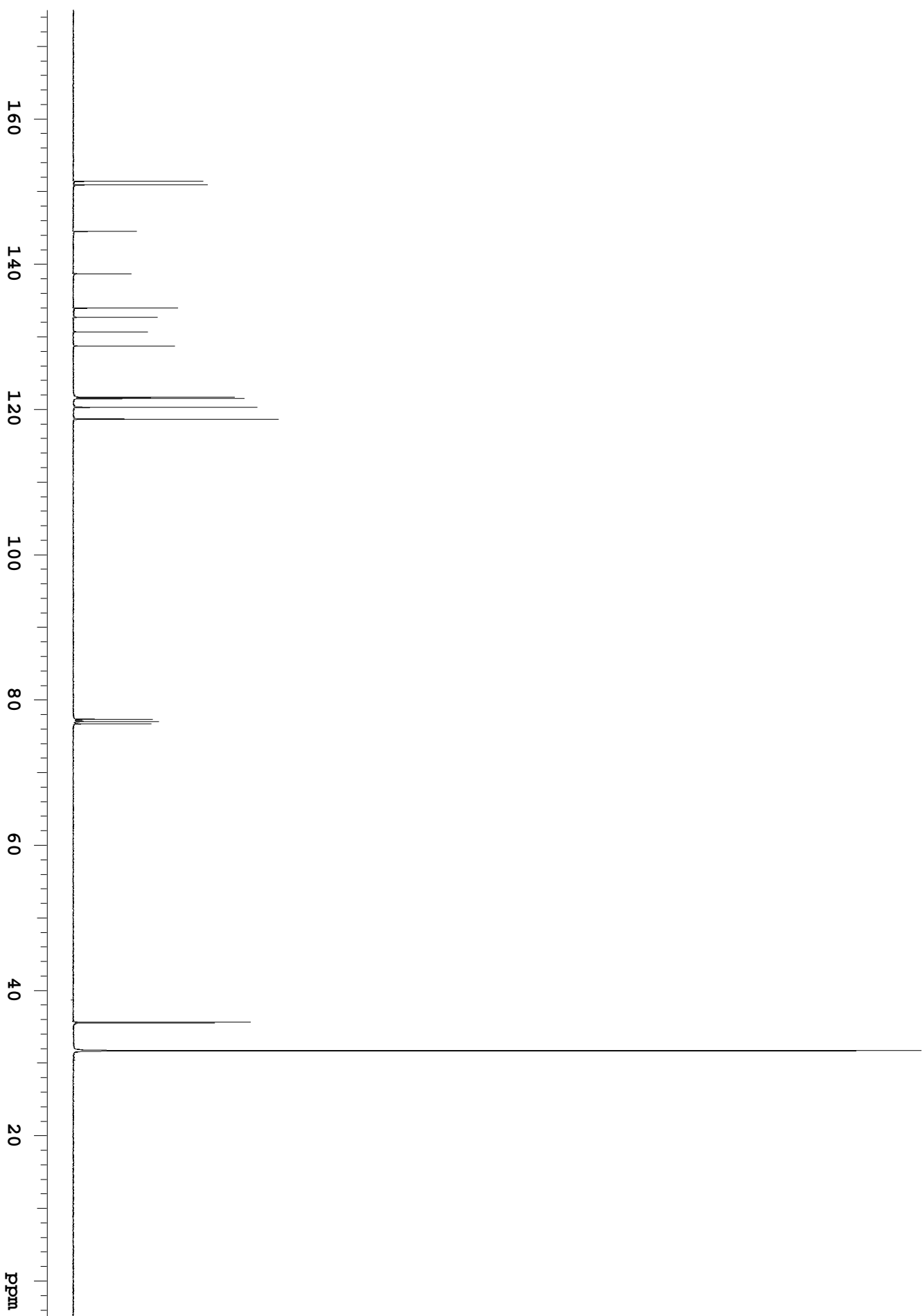


Fig. S7. DSC thermograms of **2** with a heating and cooling rate of 10 °C/min.

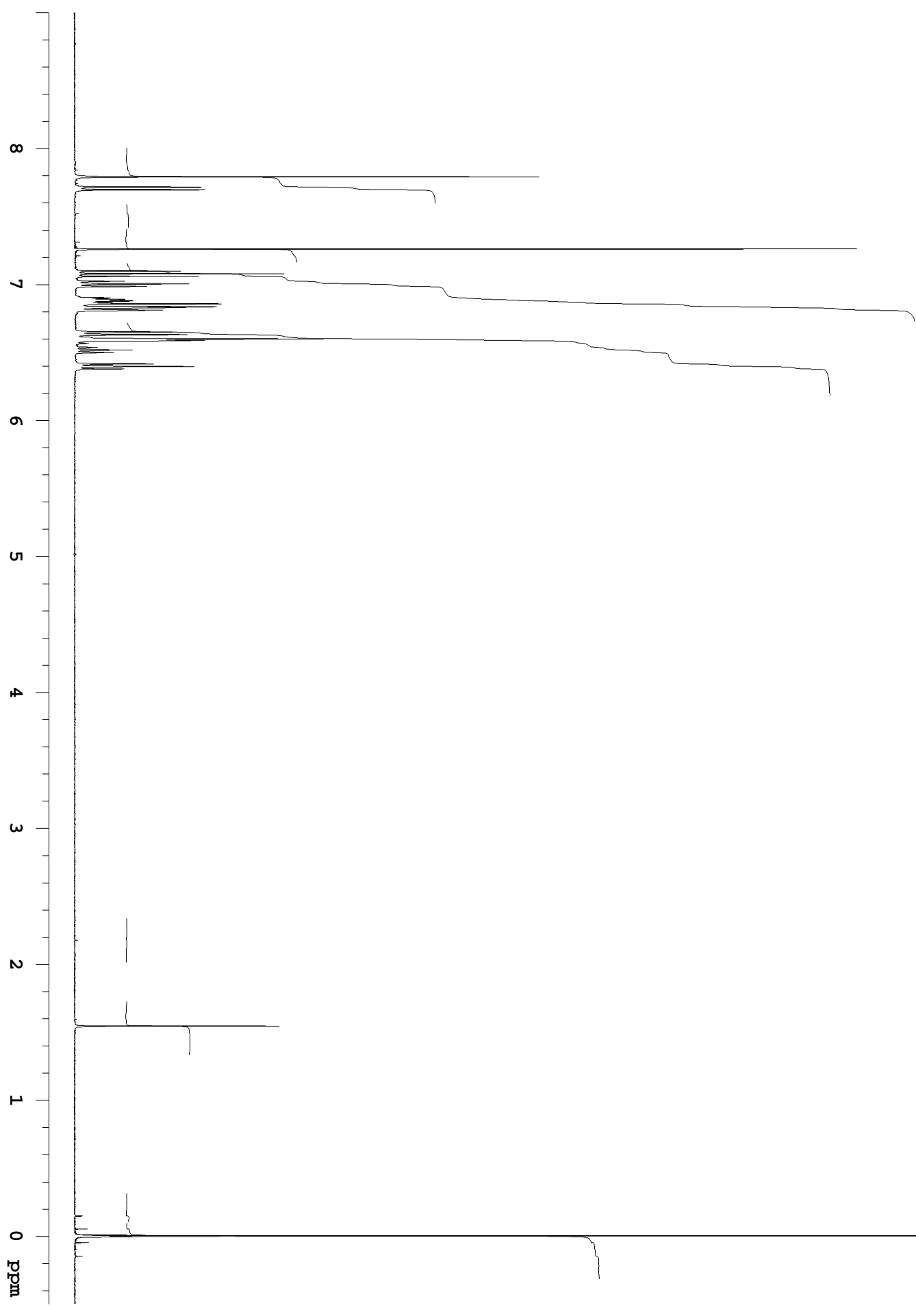
Proton NMR Spectrum of Compound 1 (2,5,9,12-tetra(tert-butyl)diacenaphtho[1,2-b:1',2'-d]thiophene)



Carbon NMR Spectrum of Compound 1 (2,5,9,12-tetra(tert-butyl)diacenaphtho[1,2-b:1',2'-d]thiophene)



Proton NMR Spectrum of Compound 2 (6,7,8,15,16,17-hexaphenyl-1,18,4,5,9,10,13,14-tetraazobenzheptacene)



Carbon NMR Spectrum of Compound 2 (6,7,8,15,16,17-hexaphenyl-1,18,4,5,9,10,13,14-tetrabenzozheptacene)

