

# Supporting Information for

## Absolute Stereochemistry of Citrinadins A and B from Marine-Derived Fungus

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**General Experimental methods.** All NMR spectra except for NOESY spectrum (500 MHz) of **3** were recorded on a 600 MHz spectrometer using 2.5 mm micro cells for CDCl<sub>3</sub> (Shigemi Co., Ltd.). The 7.26 ppm resonance of residual CHCl<sub>3</sub> and 77.0 ppm of CDCl<sub>3</sub> were used as internal references for <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. NOESY spectra were measured with spectral widths of both dimensions of 4800 Hz, and 32 scans with two dummy scans were accumulated into 1K data points for each of 256 *t*<sub>1</sub> increments. The mixing time was set to 0.6 sec, and measuring time was ca. 6 h. For the HMBC measurements, the constant times for <sup>1</sup>J<sub>CH</sub> and <sup>2,3</sup>J<sub>CH</sub> evaluation were 3.57 and 50 msec, respectively. FAB mass spectra were obtained using nitrobenzylamine as a matrix. ESIMS were measured as a MeOH solution (flow rate 0.2 mL/min). For compounds **4a** and **4b**, VCD spectra were measured as a CCl<sub>4</sub> solution without data correction. The VCD spectrum for citrinadin A (**2**) was recorded in CHCl<sub>3</sub>, and was obtained by reduction of effect of the solvent. Integration times, spectral resolution, and modulation were set to 8000 times, 8 cm<sup>-1</sup>, and 1250 cm<sup>-1</sup>, respectively.

**Extraction and Separation.** The fungus *Penicillium citrinum* (N059 strain) was grown in PYG seawater medium (peptone, 1 %; D-glucose, 2 %; yeast extract, 0.5 %; pH 7.5) for 14 days at 25 °C. The culture broth (12 L) was filtered. The mycelium (258 g) of the culture broth was extracted with MeOH (1 L x 2). The MeOH extracts were partitioned between 90% aqueous MeOH (1 L) and hexane

(1 L x 3), and then the aqueous layer was extracted with *n*-BuOH (1 L x 3). The *n*-BuOH-soluble portions (3.12g, wet weight) were subjected to SiO<sub>2</sub> (CHCl<sub>3</sub>/MeOH, 100:0 → 85:15) and then LH-20 (CHCl<sub>3</sub>/MeOH, 1:1) column chromatographies to afford citrinadins B (**1**, 4.1 mg, 0.0015 %, wet weight) and A (**2**, 6.7 mg, 0.0026 %).

Figure S1. <sup>1</sup>H NMR spectrum of citrinadin B (1) in CDCl<sub>3</sub>.

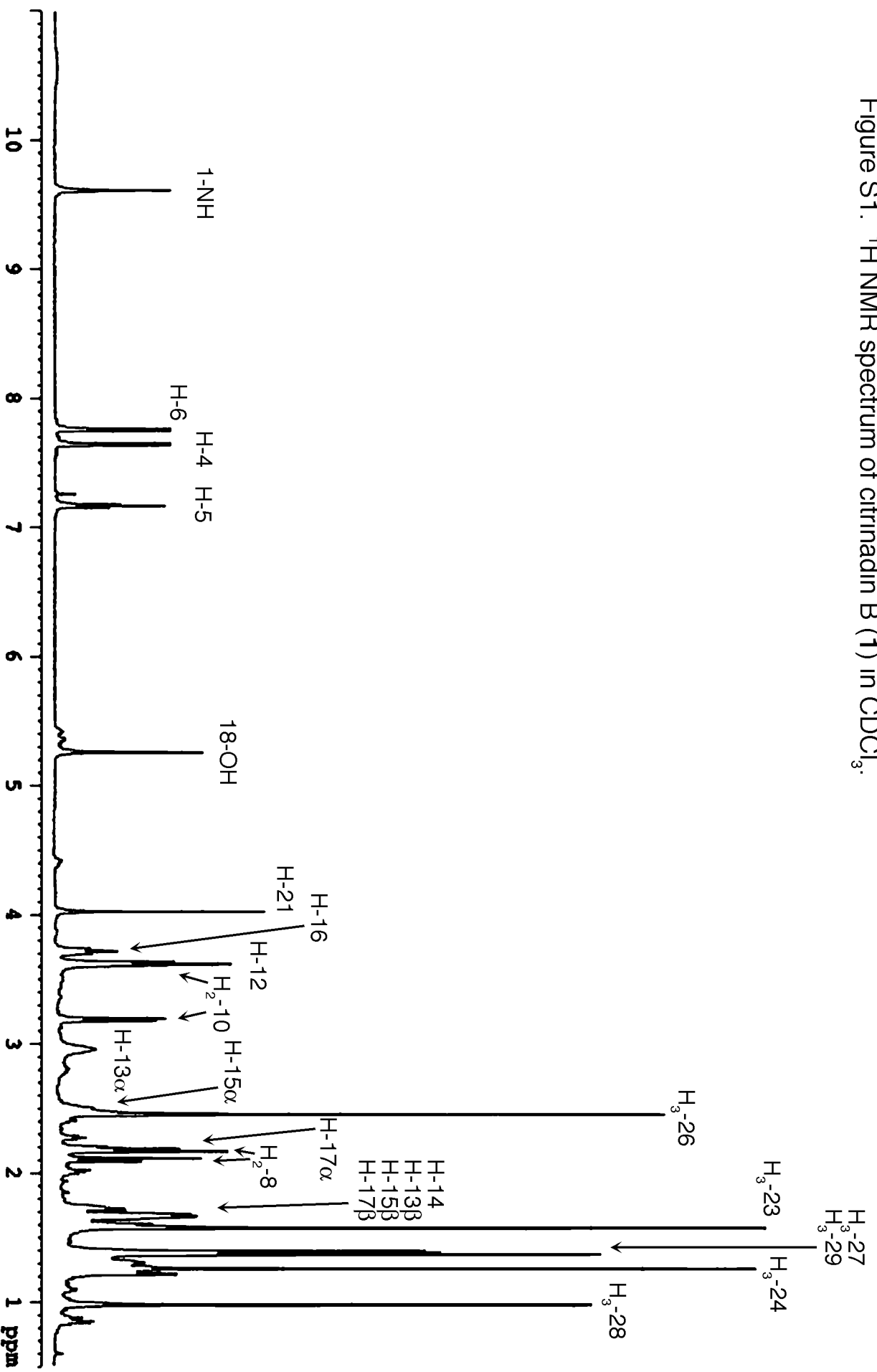


Figure S2.  $^{13}\text{C}$  NMR spectrum of citrinadin B (**1**) in  $\text{CDCl}_3$ .

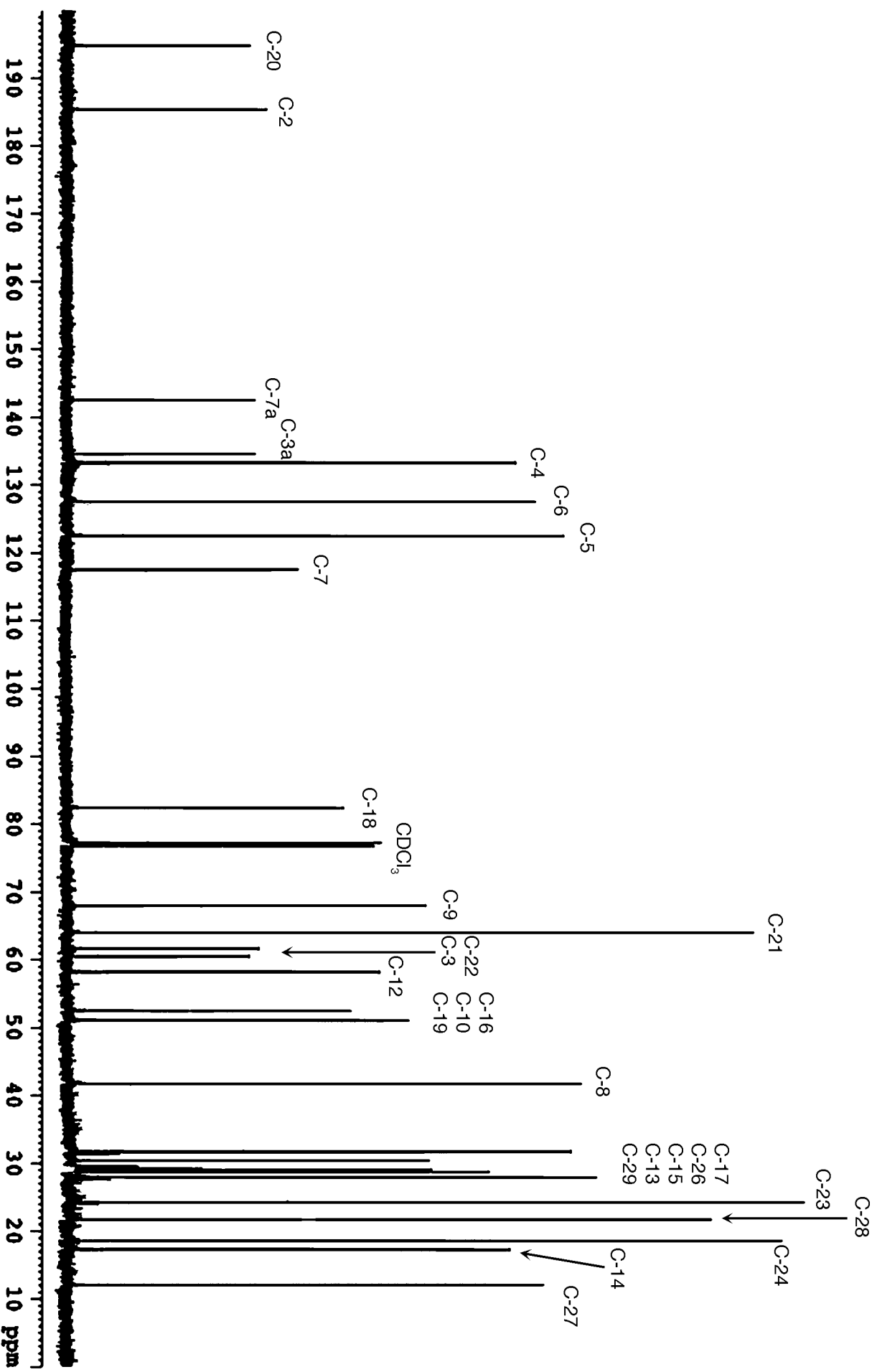


Figure S3.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of citrinadin B (1) in  $\text{CDCl}_3$ .

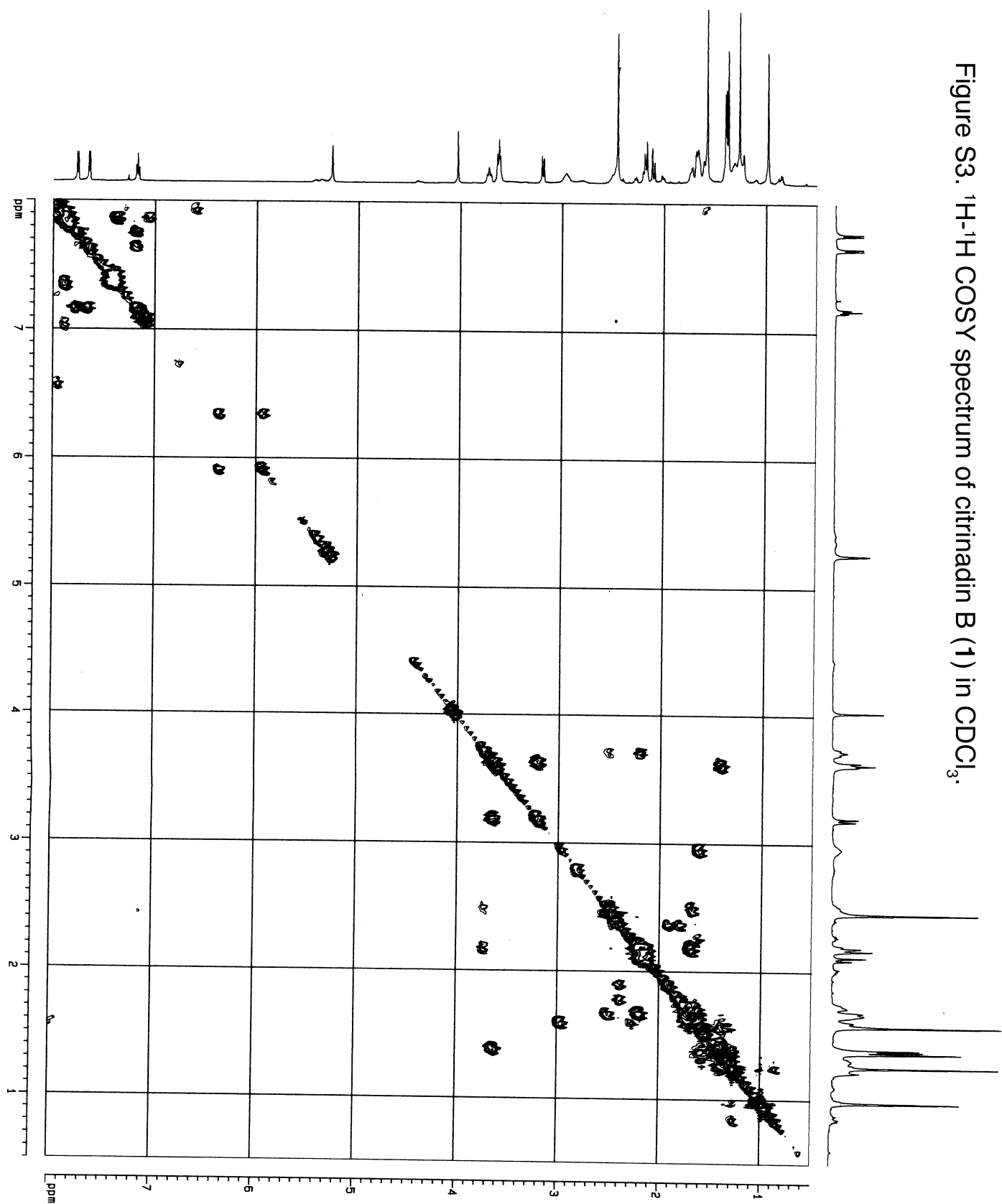


Figure S4. TOCSY spectrum of citrinadin B (1) in CDCl<sub>3</sub>.

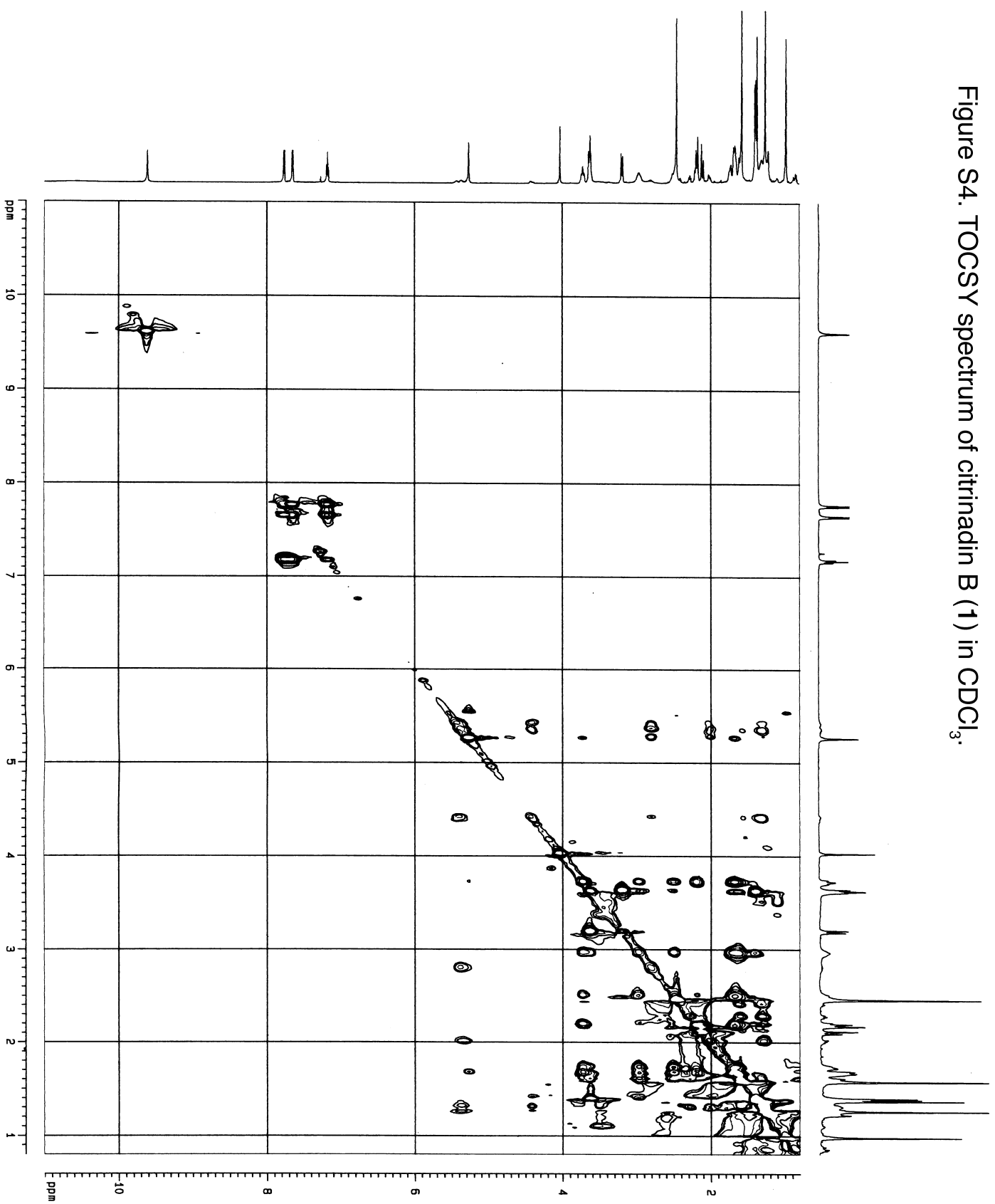




Figure S5. HMQC spectrum of citrinadin B (1) in CDCl<sub>3</sub>.

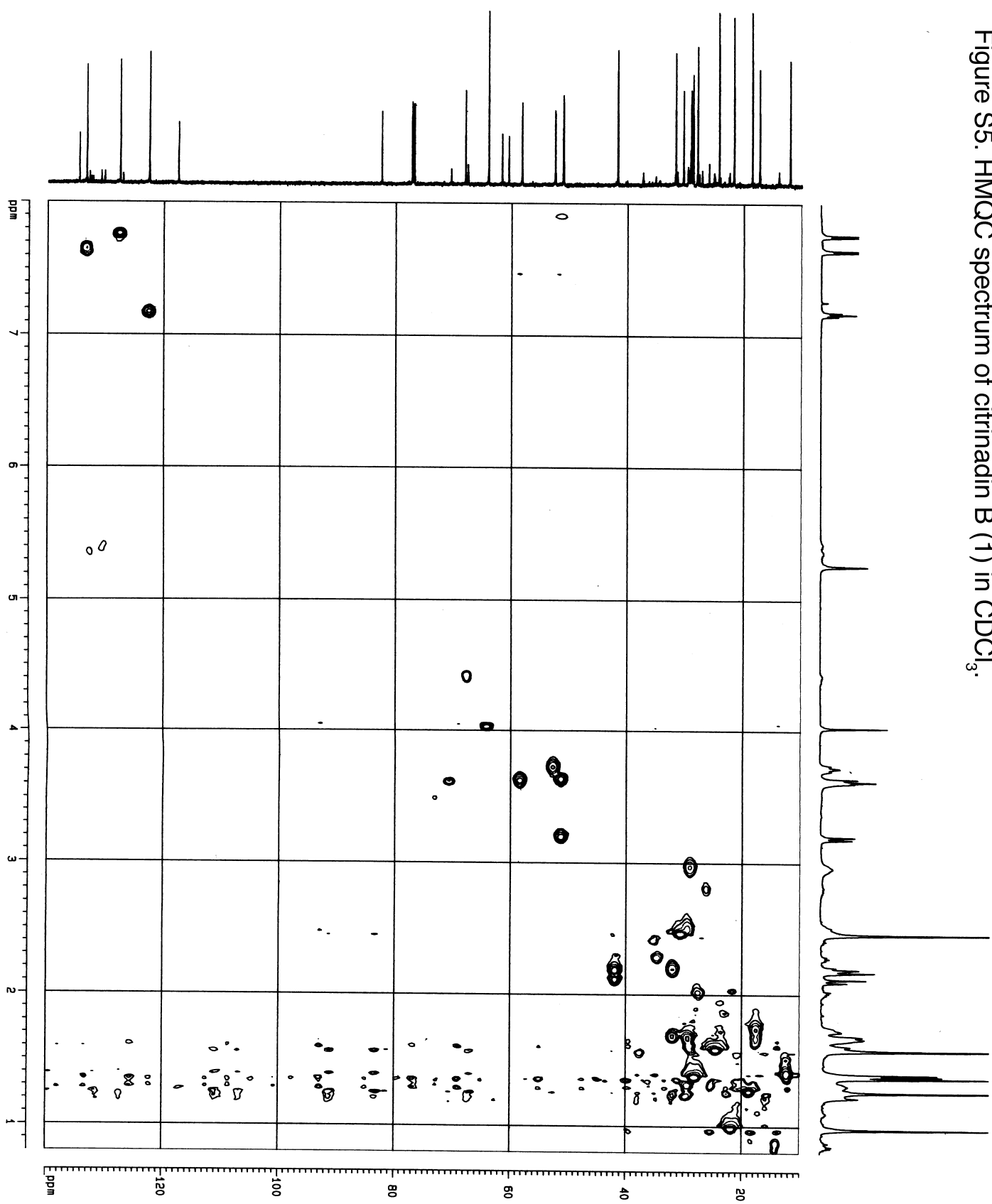


Figure S6. HMBC spectrum of citrinadin B (1) in CDCl<sub>3</sub>.

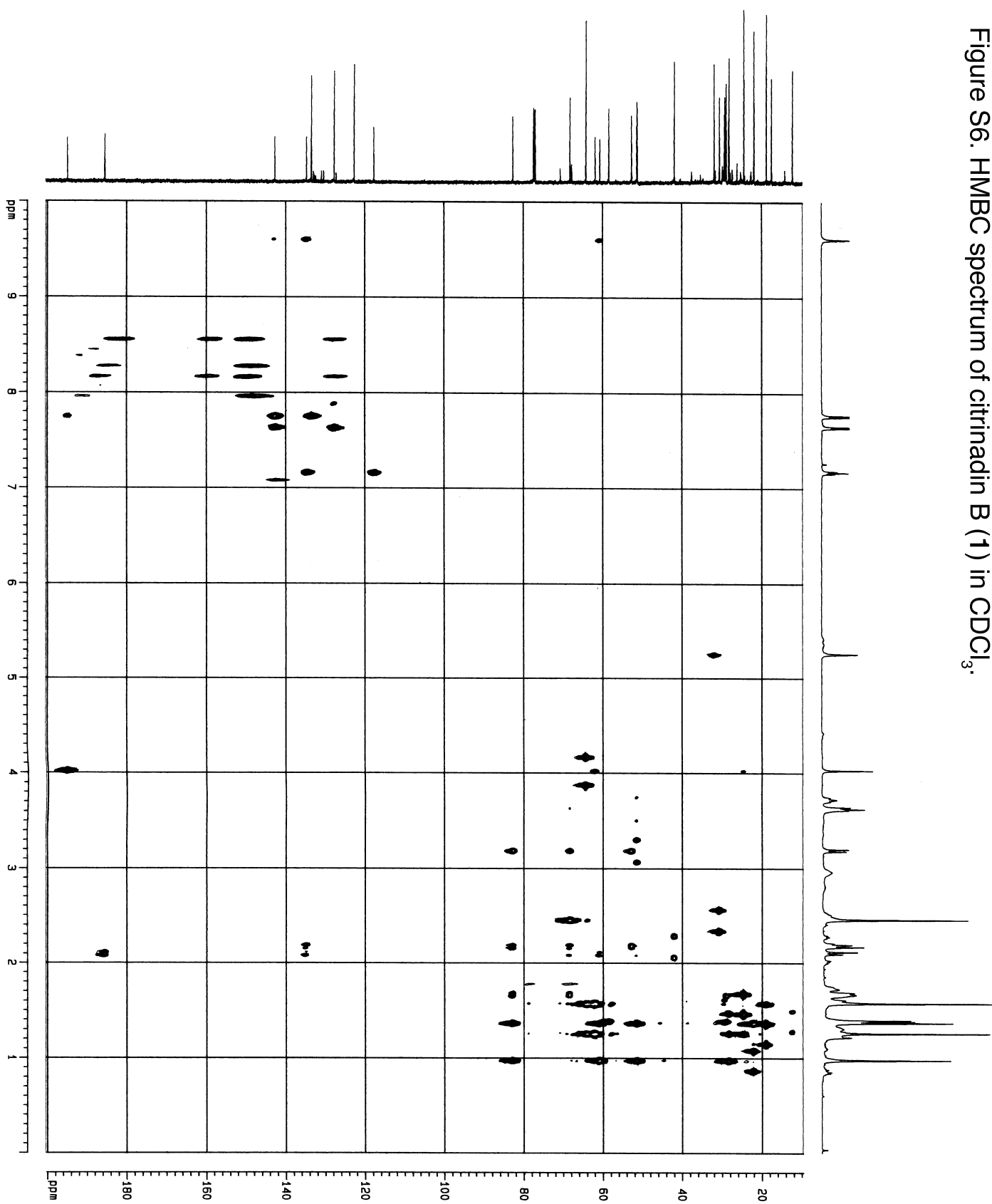


Figure S7. ROESY spectrum of citrinadin B (1) in CDCl<sub>3</sub>.

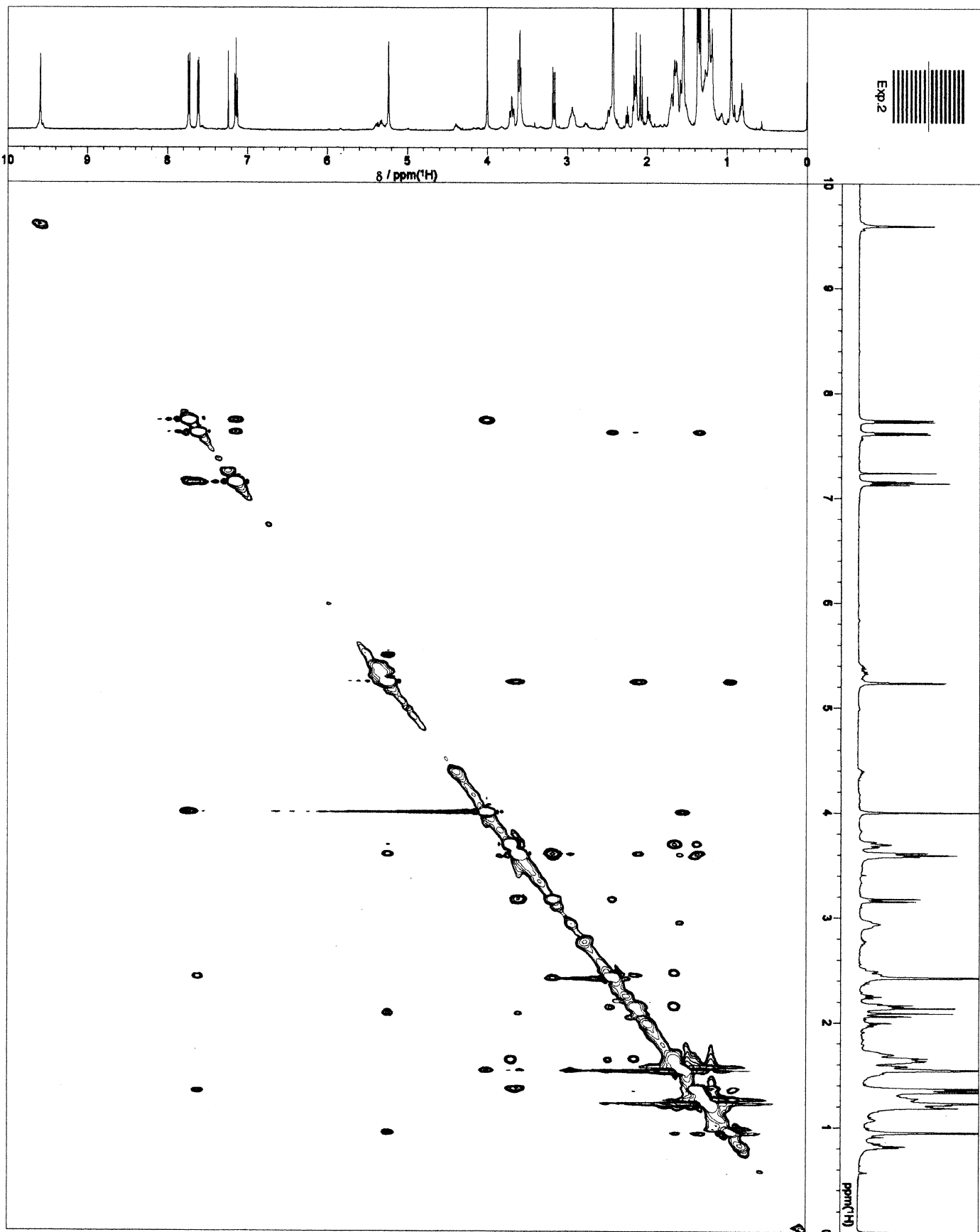
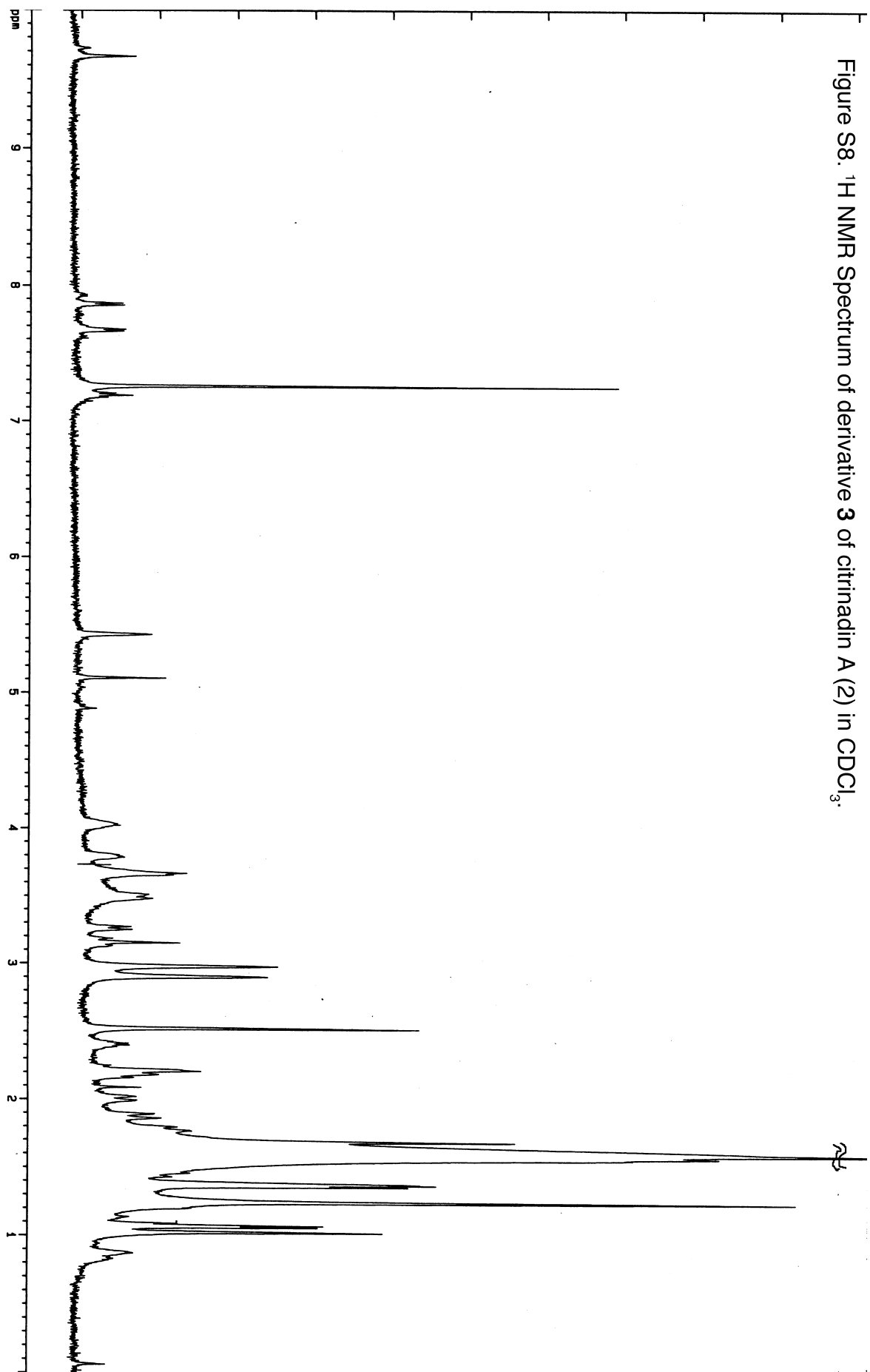


Figure S8.  $^1\text{H}$  NMR Spectrum of derivative **3** of citrinadin A (**2**) in  $\text{CDCl}_3$ .



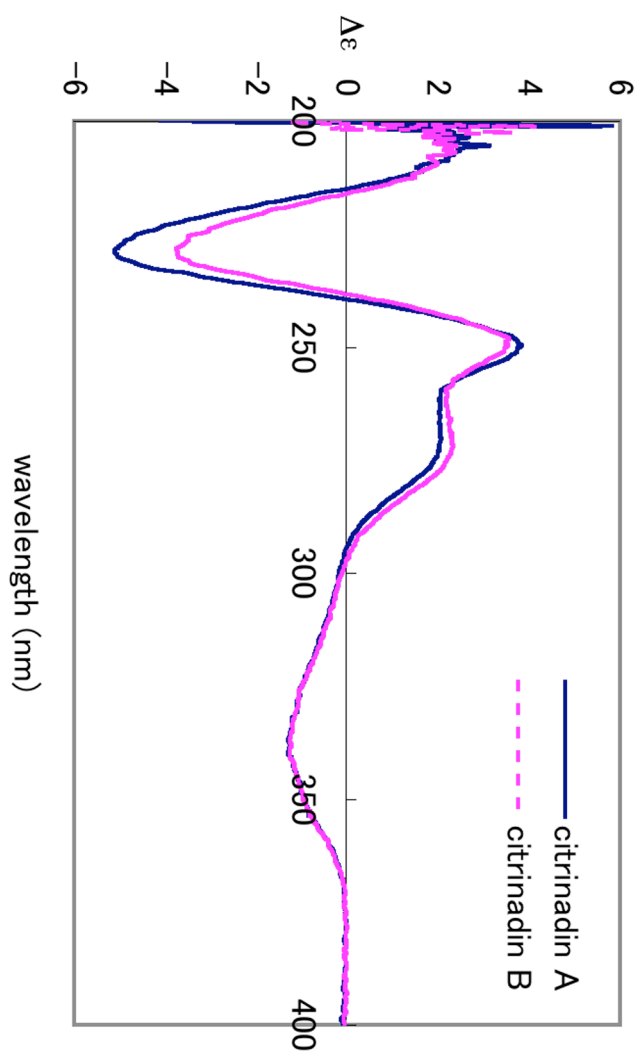


Figure S10. <sup>1</sup>H NMR spectrum of compound **6** in CDCl<sub>3</sub>.

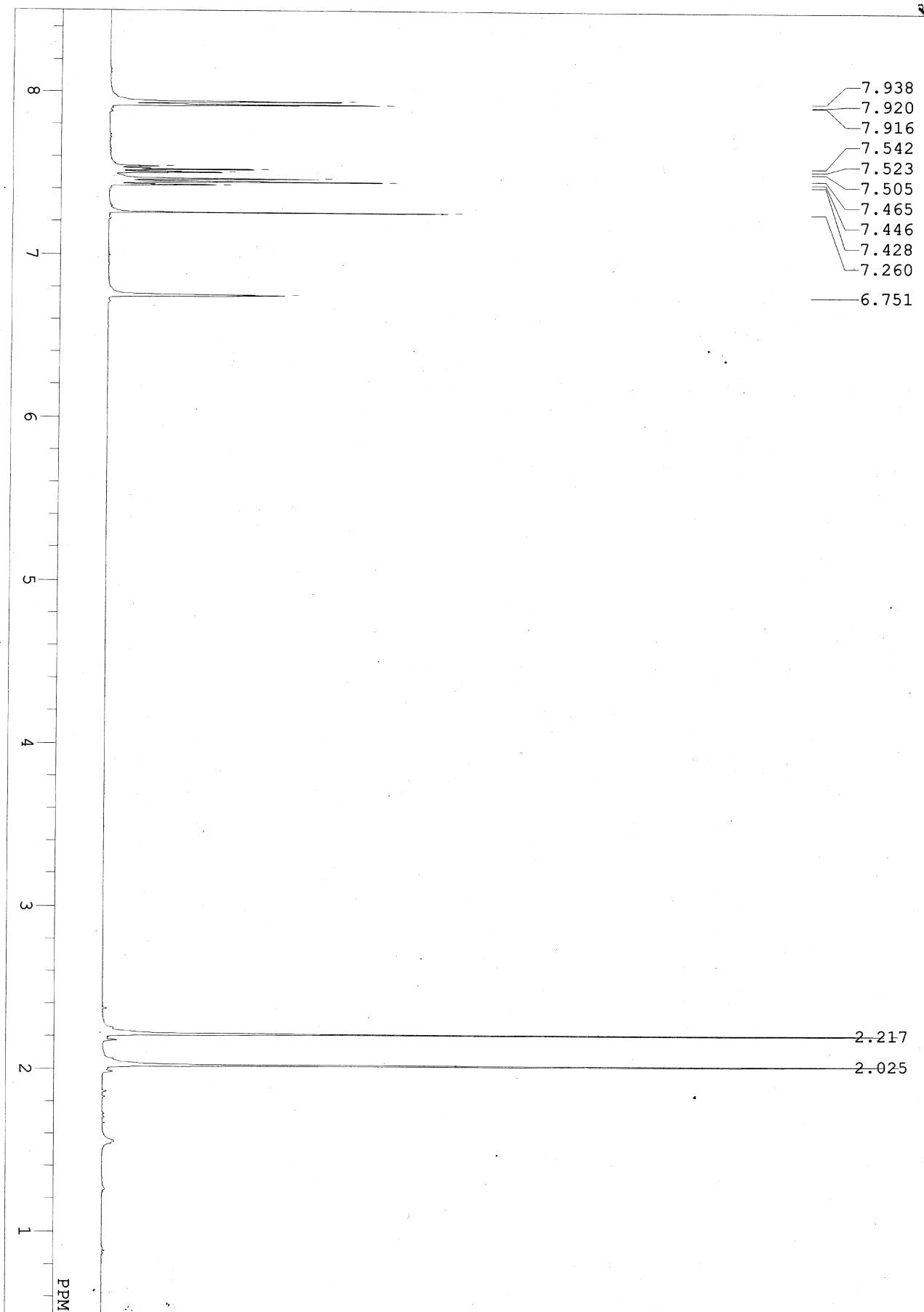


Figure S11.  $^{13}\text{C}$  NMR spectrum of compound **6** in  $\text{CDCl}_3$ .

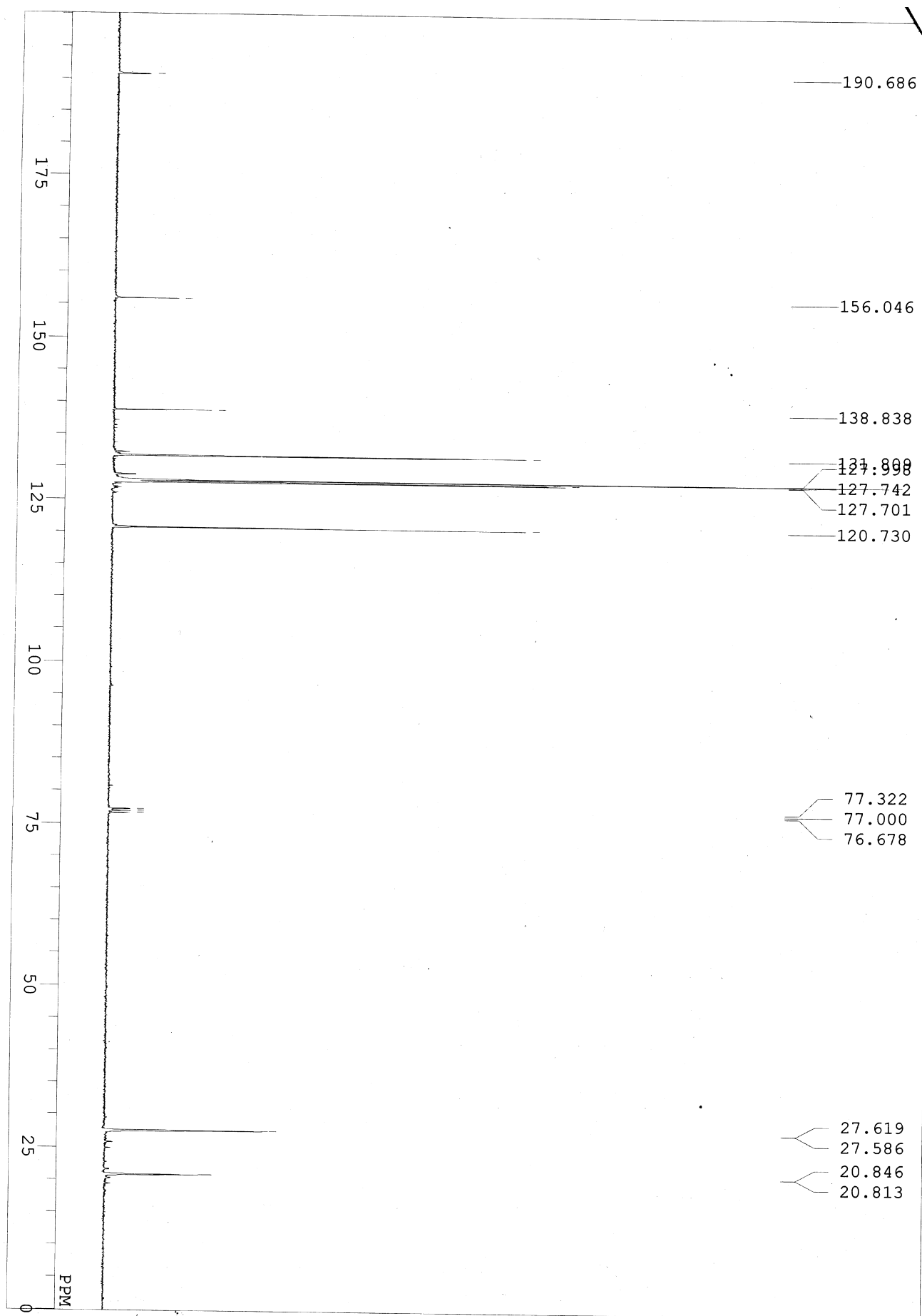


Figure S12. <sup>1</sup>H NMR spectrum of compound 7a in CDCl<sub>3</sub>.

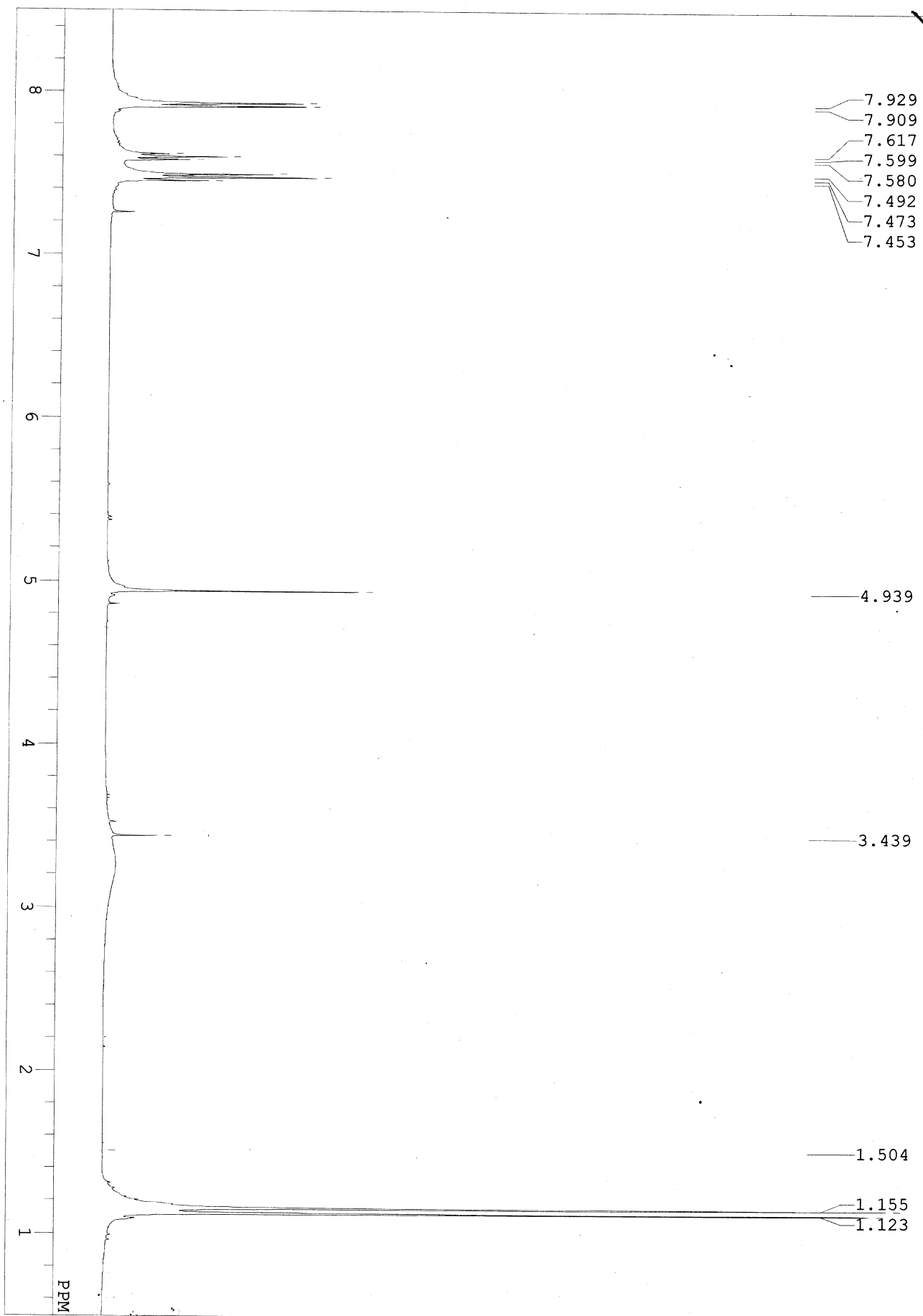




Figure S13.  $^{13}\text{C}$  NMR spectrum of compound **7a** in  $\text{CDCl}_3$ .

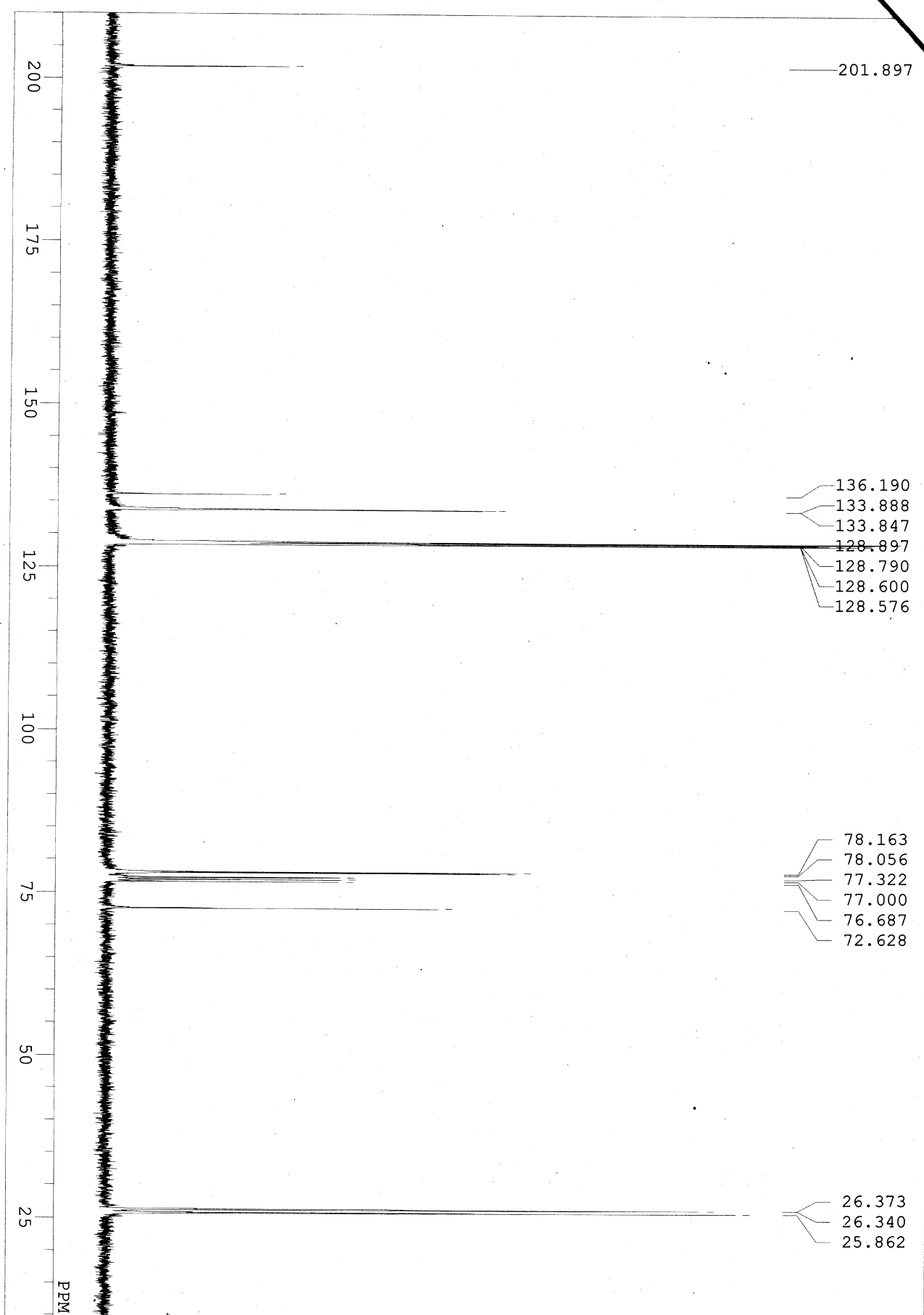


Figure S14.  $^1\text{H}$  NMR spectrum of compound 7b in  $\text{CDCl}_3$ .

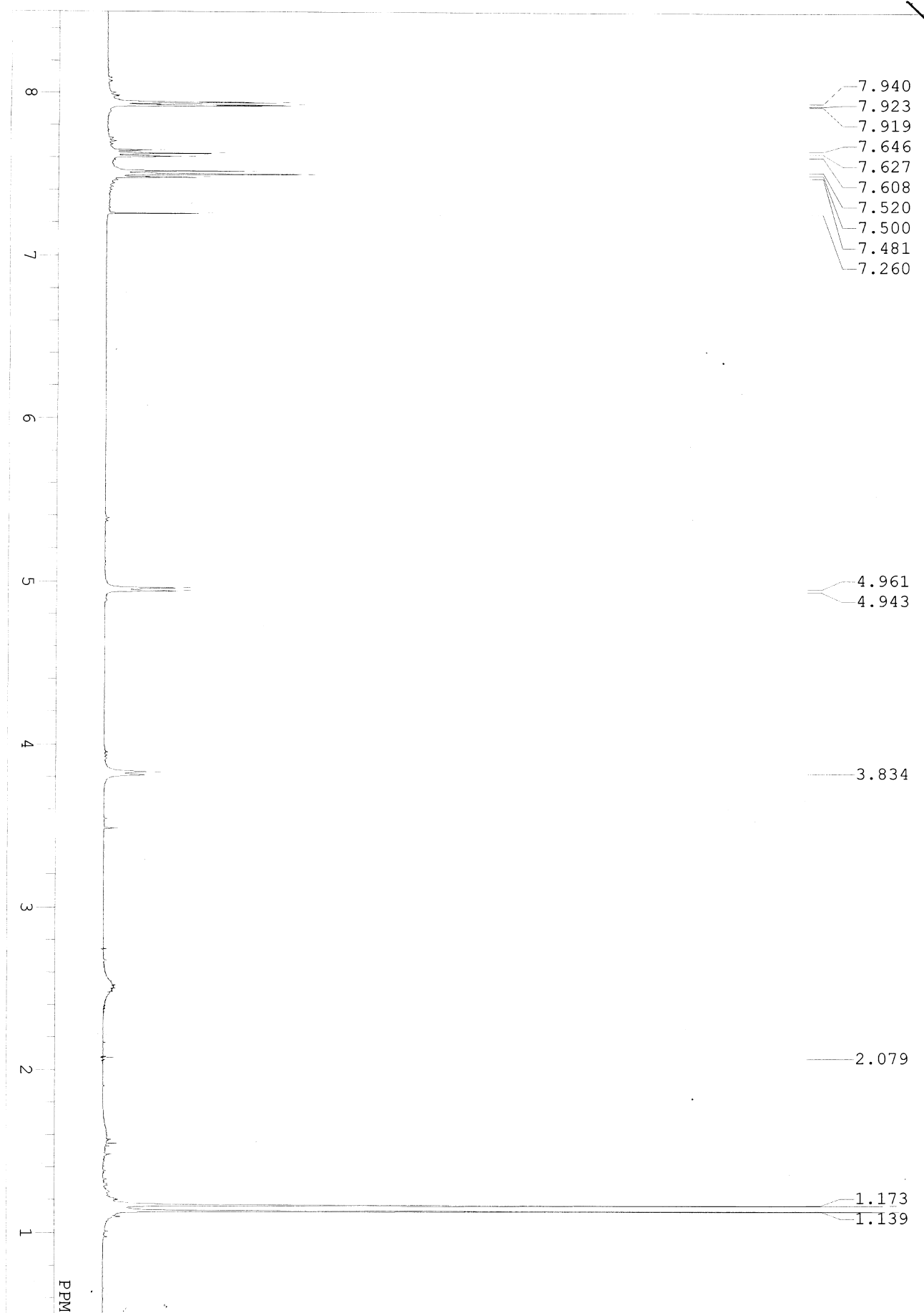


Figure S15.  $^{13}\text{C}$  NMR spectrum of compound 7b in  $\text{CDCl}_3$ .

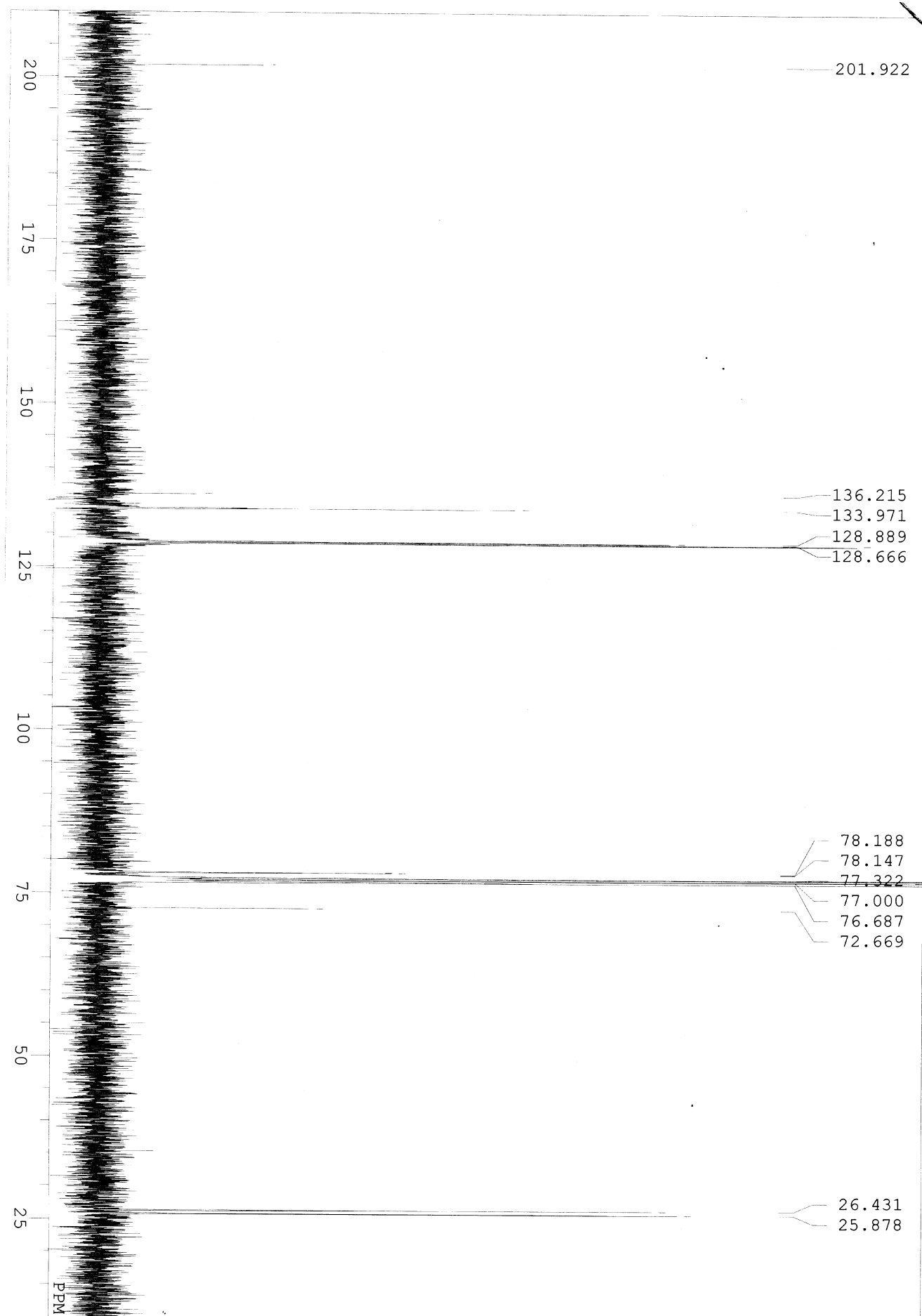


Figure S16. <sup>1</sup>H NMR spectrum of compound **8a** in CDCl<sub>3</sub>.

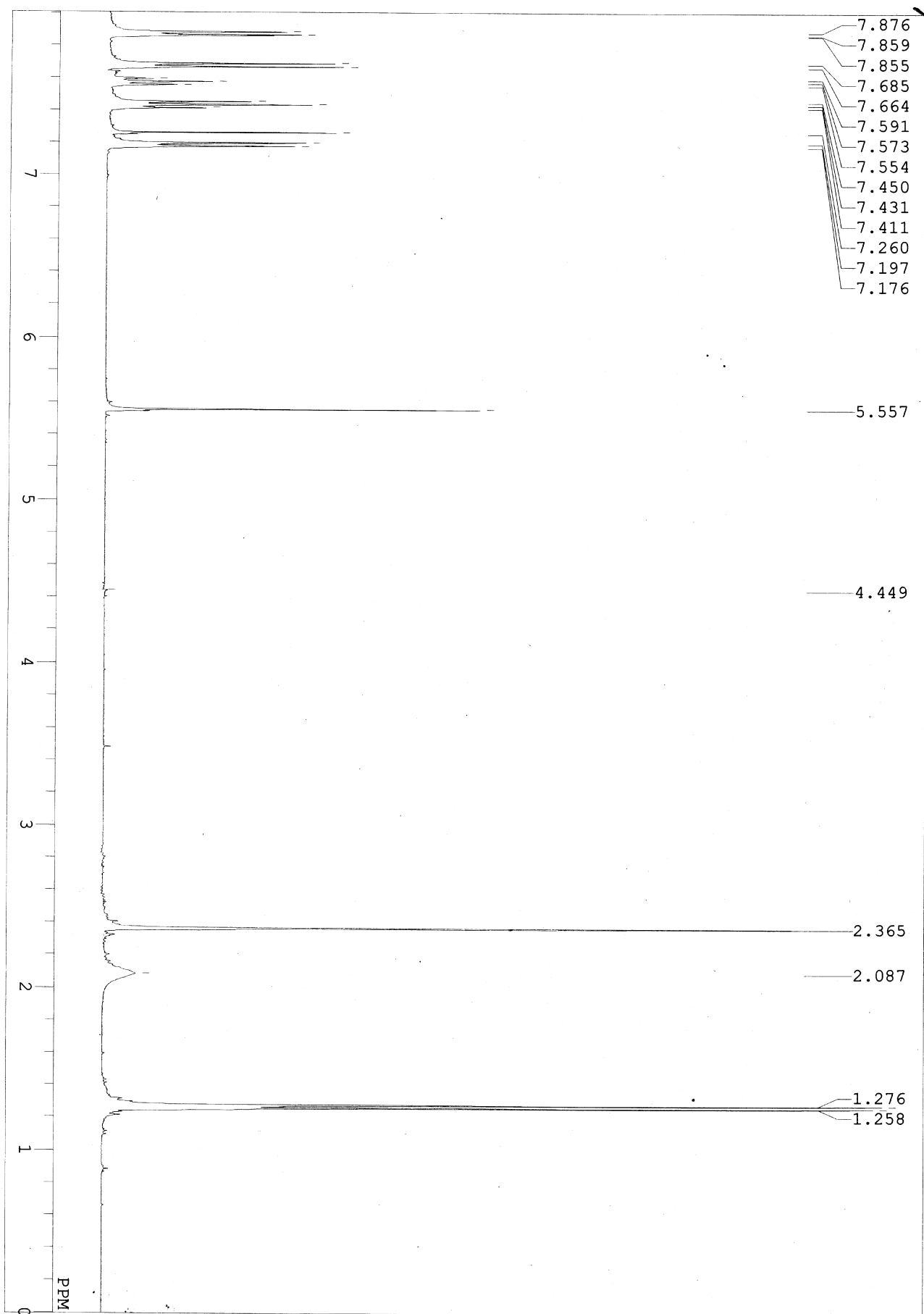


Figure S17.  $^{13}\text{C}$  NMR spectrum of compound **8a** in  $\text{CDCl}_3$ .

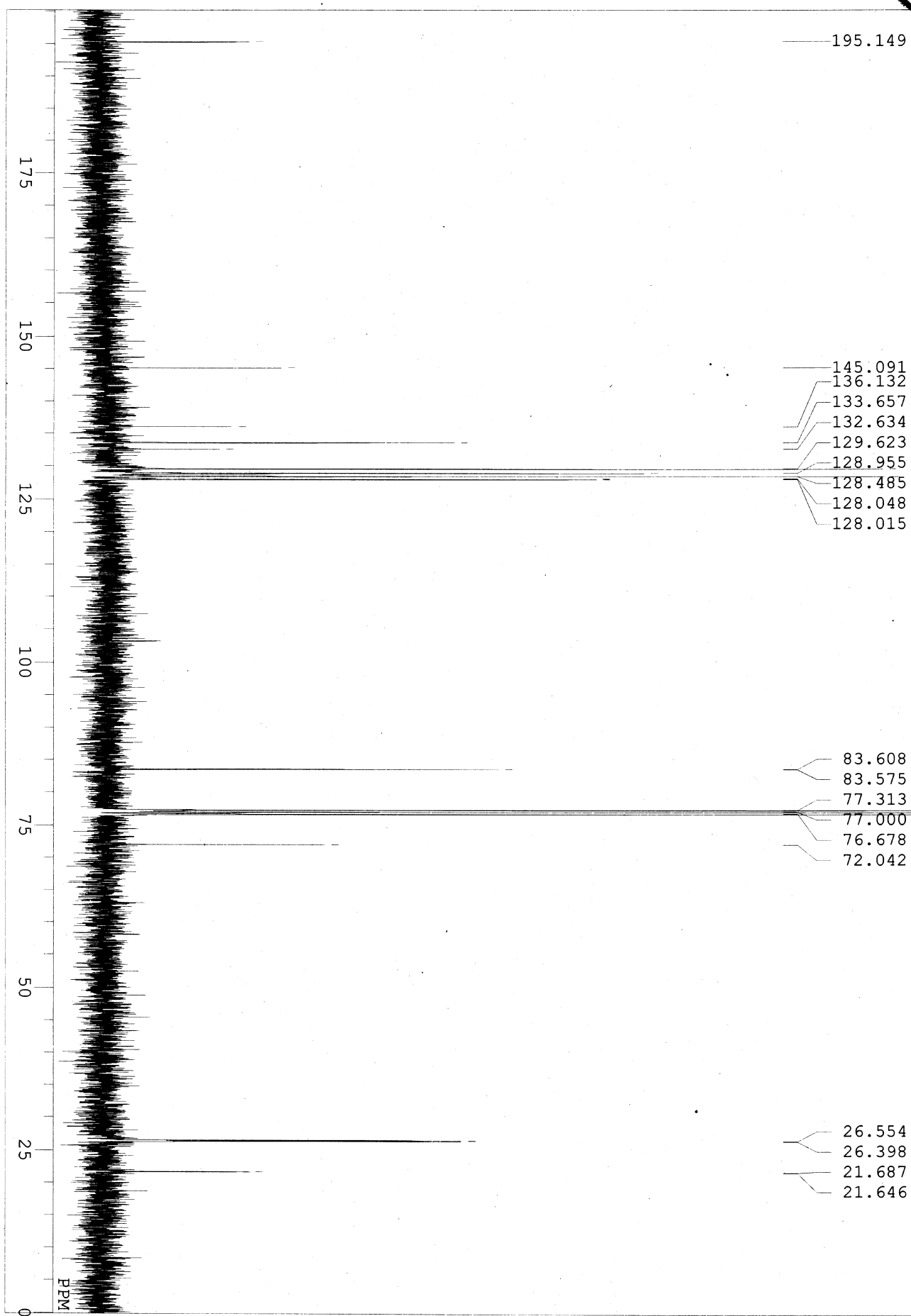


Figure S18.  $^1\text{H}$  NMR spectrum of compound **8b** in  $\text{CDCl}_3$ .

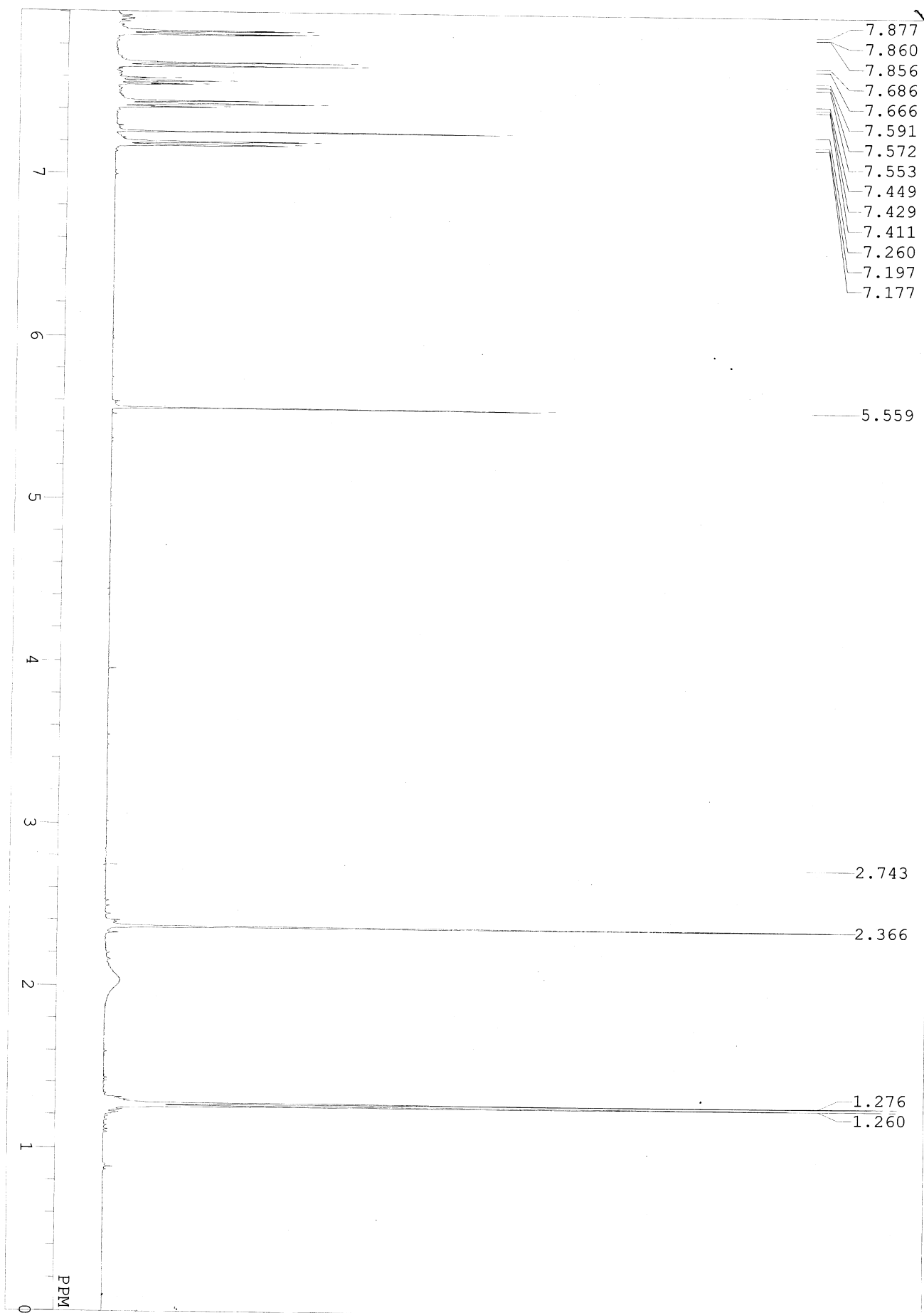


Figure S19.  $^{13}\text{C}$  NMR spectrum of compound **8b** in  $\text{CDCl}_3$ .

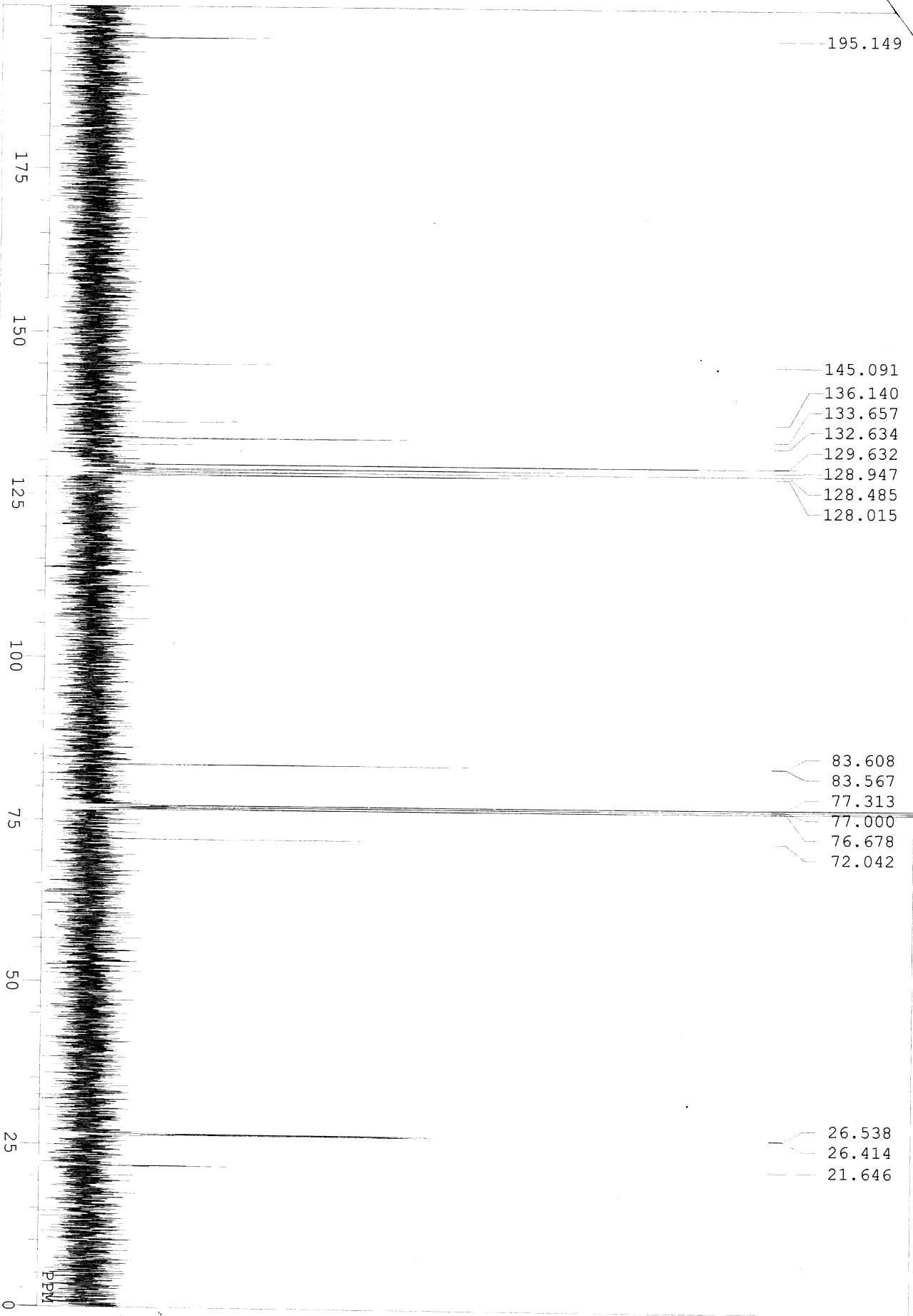


Figure S20.  $^1\text{H}$  NMR spectrum of compound **4a** in  $\text{CDCl}_3$ .

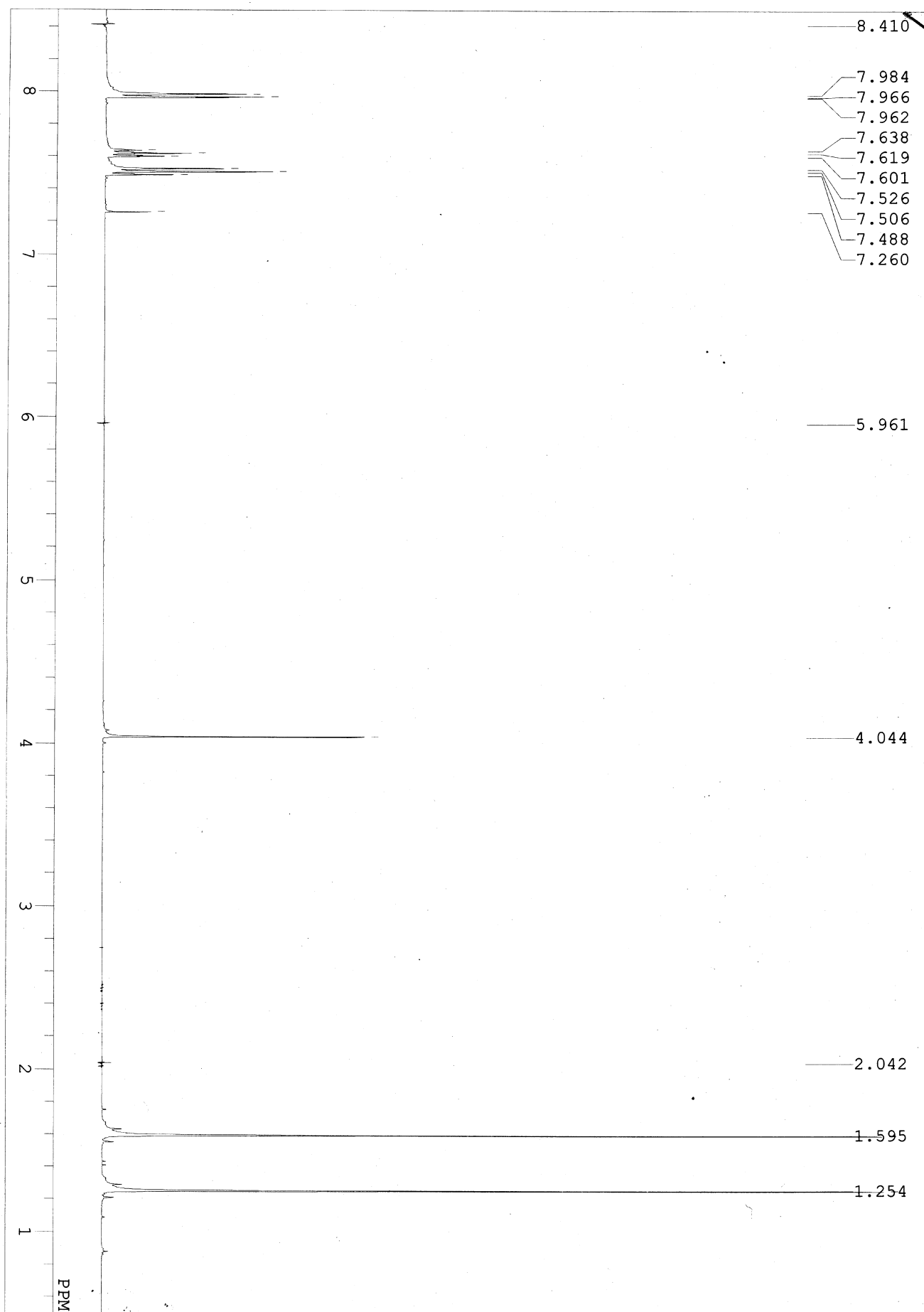




Figure S21.  $^{13}\text{C}$  NMR spectrum of compound 4a in  $\text{CDCl}_3$ .

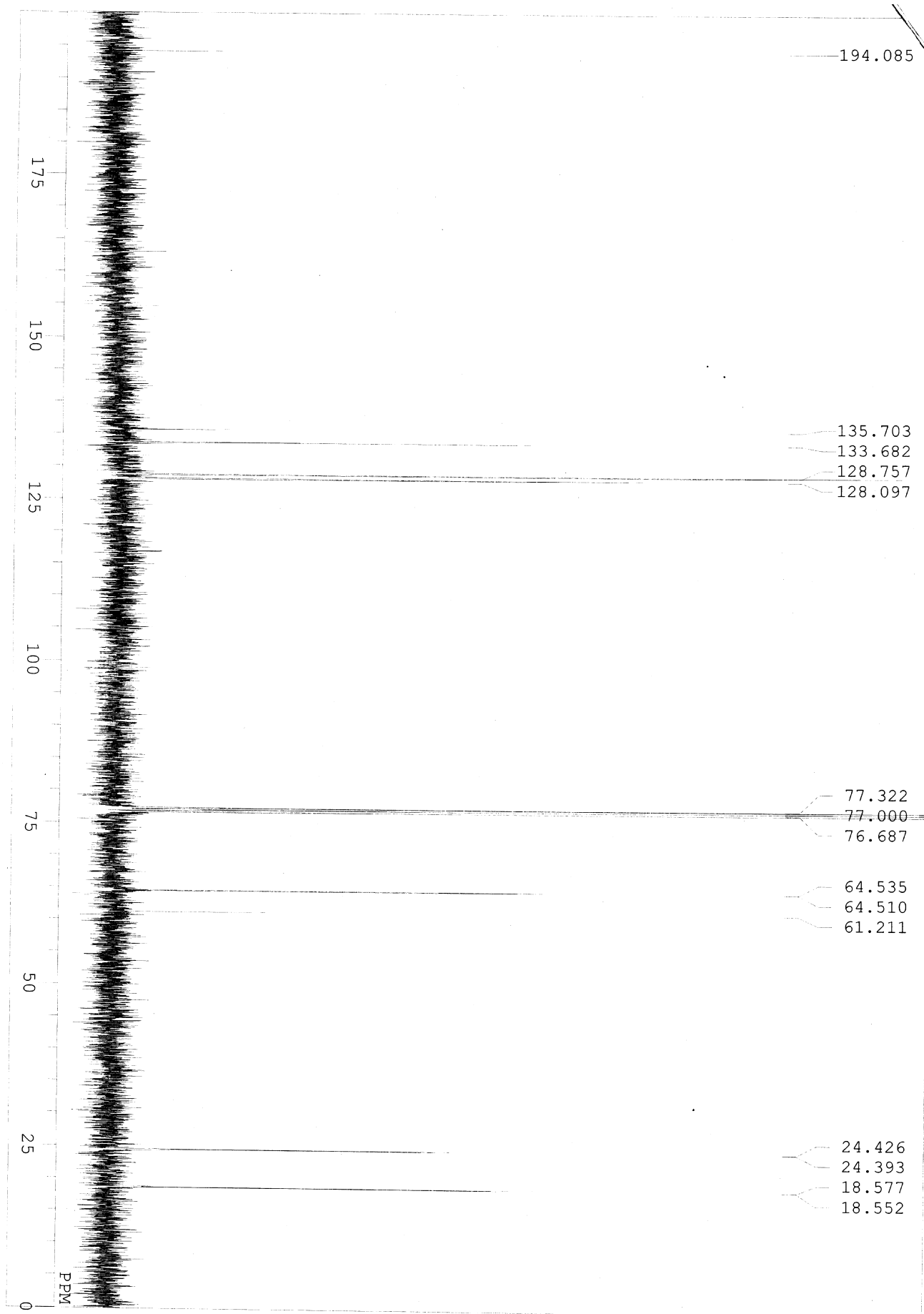


Figure S22. <sup>1</sup>H NMR spectrum of compound 4b in CDCl<sub>3</sub>.

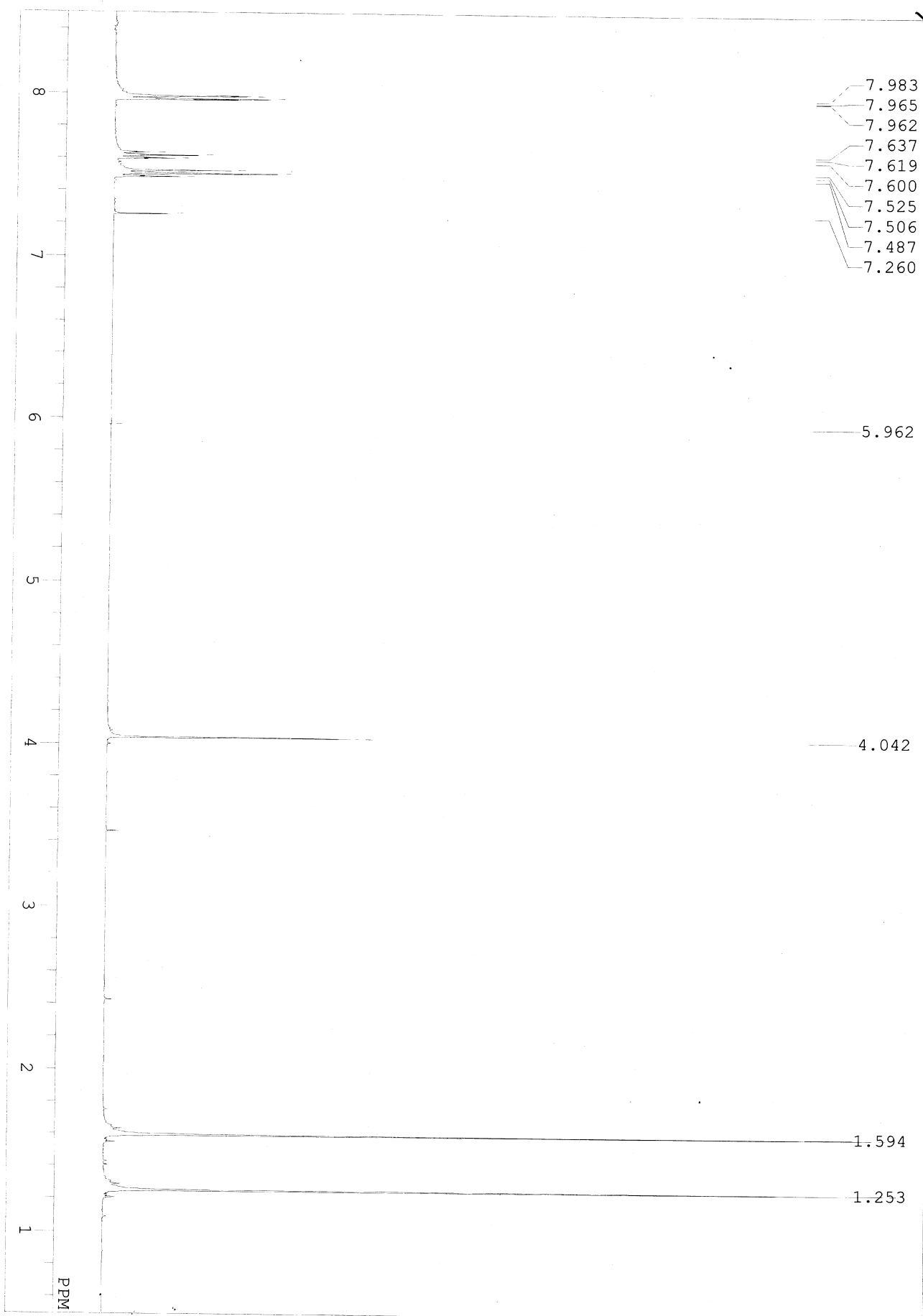


Figure S23.  $^{13}\text{C}$  NMR spectrum of compound **4b** in  $\text{CDCl}_3$ .

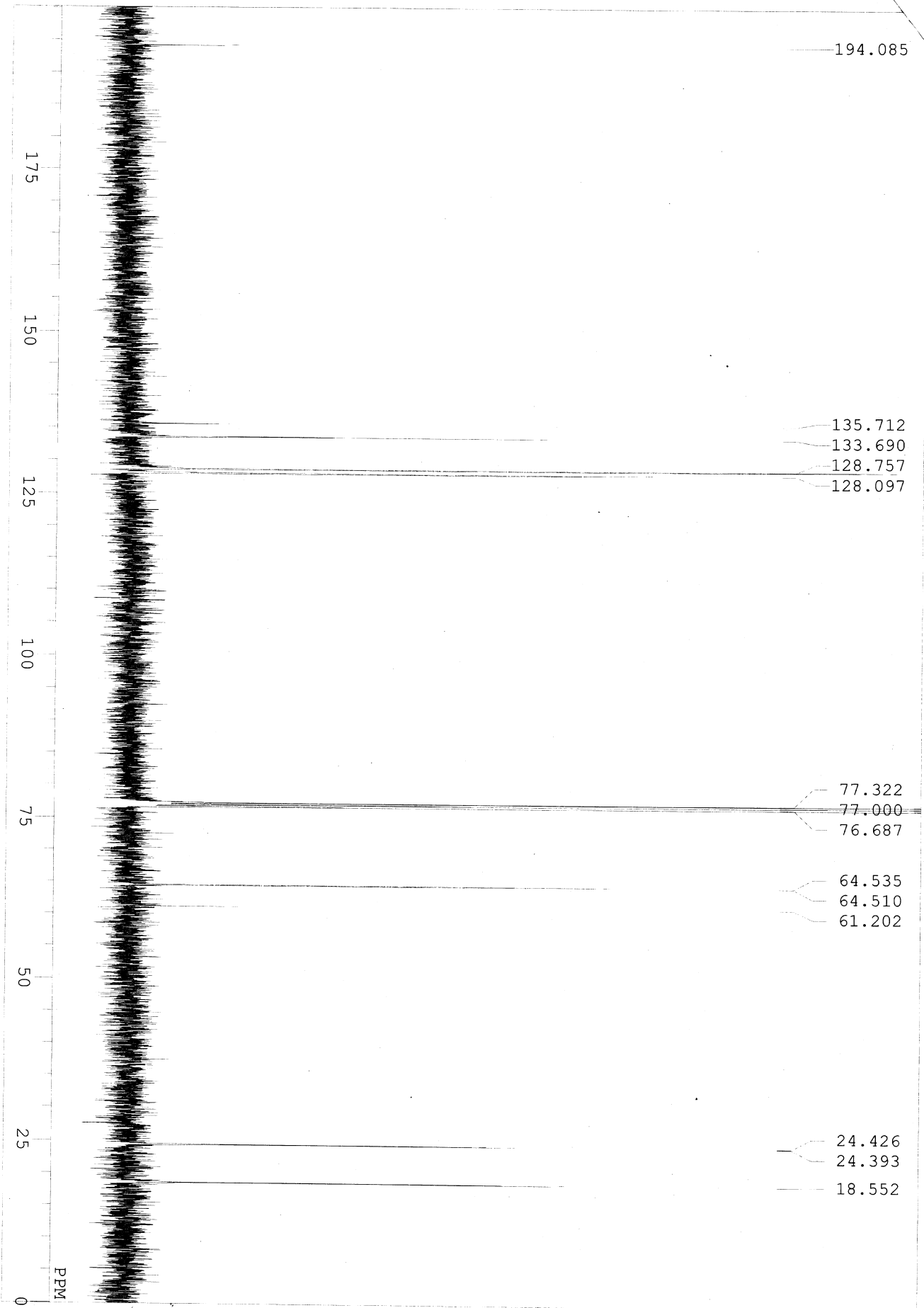
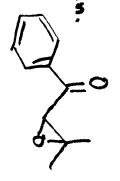
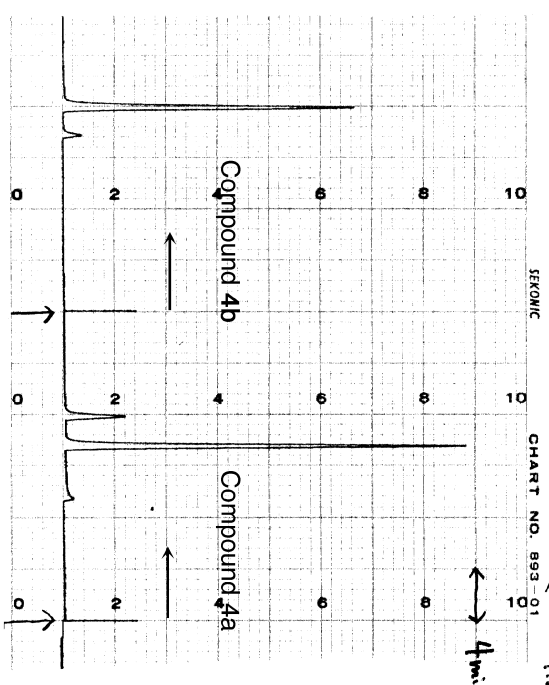
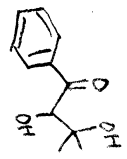
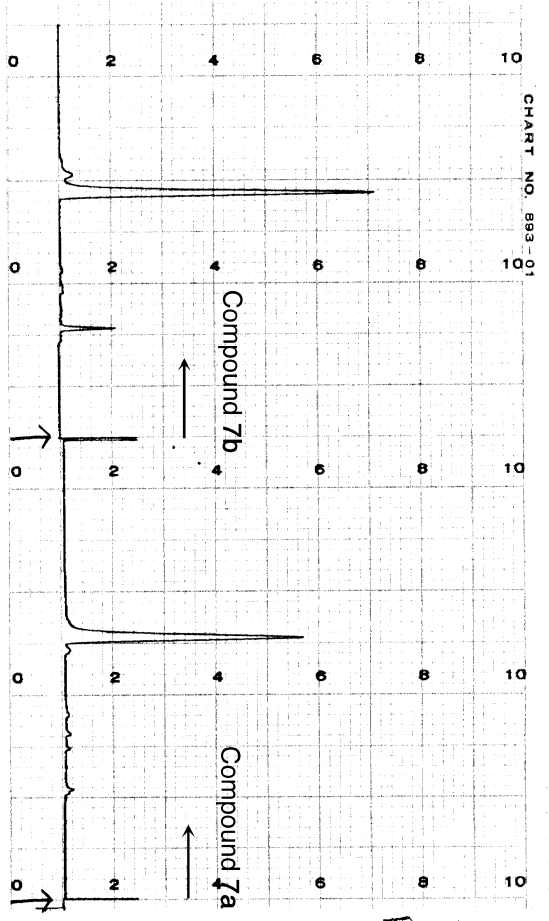


Figure S24. Chiral HPLC chromatographies of compounds 4a, 4b, 7a, 7b, 8a, and 8b.



column : CHIRALCEL OD  $\phi$  4.6 x 250  
 elu. : n-Hexane : iPrOH = 9 : 1  
 detect : UV 270nm (0.16)  
 flow : 0.5 mL/min.  
 inject it 5  $\mu$ g.

