Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

A Tongs-like Fluorescence Sensor for Metal Ions: Perfect Conformational Switch of Hinge Sugar by a Pyrene Stacking

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Table of contents

General experimental procedures.

All solvents and reagents used were reagent grade and, in cases where further purification was required, standard procedures (Perrin, D.D.; Armarego, W.L.; Perrin, D.R. Purification of Laboratory Compounds. 2nd ed. Pergamon Press, London. 1980.) were followed. Solution transfers where anhydrous conditions were required were done under dry argon using syringes. Thin-layer chromatograms (TLC) were performed on precoated silica gel Merck 60-F254 plates (Art 5715) and visualized by quenching of fluorescence and/or by charring after spraying with 1 % $CeSO_4$-1.5 % $(NH_4)6Mo_7O_{24}\cdot 4H_2O$-10 % H_2SO_4. Column chromatography was performed on Merck Kieselges 60 (Art 7734), Wako gel C-300, or Kanto Silica gel 60N (spherical, neutral) with the solvent systems specified

Optical rotations were determined with a Horiba SEPA-200 or JASCO DIP-4 polarimeter using 1 dm or 0.1 dm length cell. ^{1}H NMR (1D, COSY, HMQC, and HMBC) spectra were recorded at 400 MHz (Varian Unity-400) or 270 MHz (JEOL EX-270). Internal tetramethylsilane (δ 0 ppm) was used as a standard in $CDCl_3$ or solvents peaks were used as standards (δ 2.05 ppm in acetone-d_6, δ 2.50 ppm in DMSO-d_6 or δ 2.75 in DMF-d_7). Chemical shifts are expressed in ppm referenced to the solvent, as an internal standard. The multiplicity of signals is abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, ddd = doublet of doublets of doublets, br = broad signal, m = multiplet. ^{13}C NMR spectra were recorded at 67.8 MHz (JEOL JNM-EX-270) or 100.6 MHz (Varian Unity-400) and solvents peaks were used as standards (δ 77.0 ppm in $CDCl_3$, δ 29.8 ppm in acetone-d_6 or δ 29.76 in DMF-d_7). High resolution mass spectra (HRMS) were recorded on Mariner Biospectrometry Workstation ESI-TOF MS. Fourier transform infrared spectrum was obtained with Shimadzu FTIR-8400S, in which a 10 mM solution in CCl_4 was measured in a cell with 0.5 mm length.

General fluorescence experiments.

Fluorescence spectra were recorded at 35°C on Shimadzu RF-5300PC fluorophotometer with exitation at 355 nm for **2** (1 μM) and 347 nm for **1** (1 μM), sampling intervals of 2 nm for **2** and 1 nm for **1**, excitation band widths of 3 nm for **2** and 1.5 nm for **1**, and an emission band width of 5.0 nm for both compounds. A cell with 10 mm width and 3 mm depth was used.

1) Titration: To a thermostated (35°C) solution of **1** (1 μM, 1 mL) were dropped appropriate amounts of the solution of a metal ion and **1** (1 μM), and fluorescence spectrum was recorded each at specified amounts of the metal ion. The titration results with $ZnCl_2$ and $CdCl_2 \cdot 4H_2O$ are shown in Figure 1 of the main text. The results with $Mg(ClO_4)_2$ and $MnCl_2 \cdot 4H_2O$ were shown in Figure S34-35.

2) Time course: To a thermostated (35°C) solution of **1** (2 μM) in DMSO (500 μL) was added the solution of $K_2[PtCl_4]$ (2 μM) in DMSO (500 μL), and fluorescence spectrum was recorded at appropriate time intervals. The result is shown in Figure 1 of the main text.

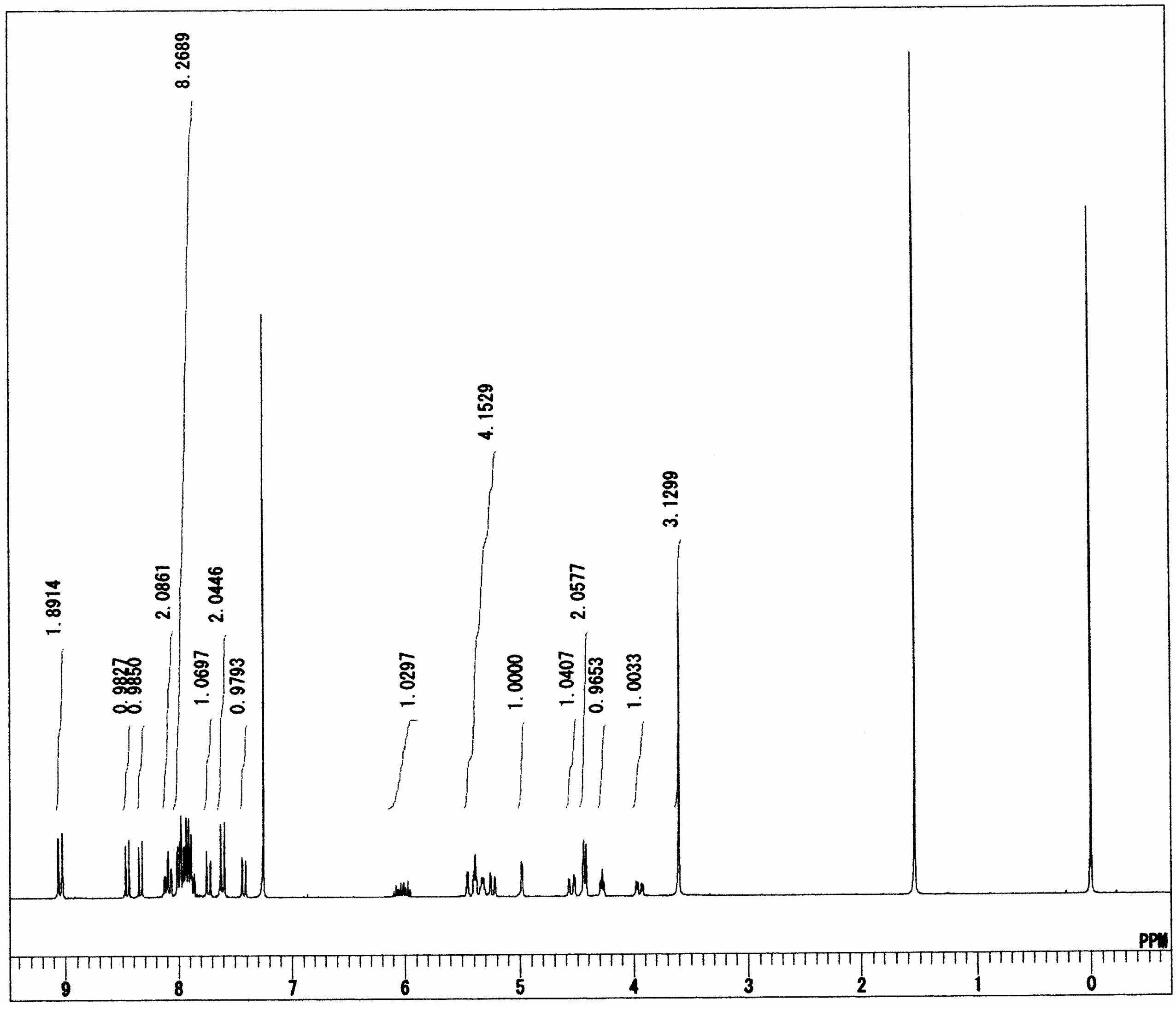

Figure S1. ^{1}H NMR of **5**.

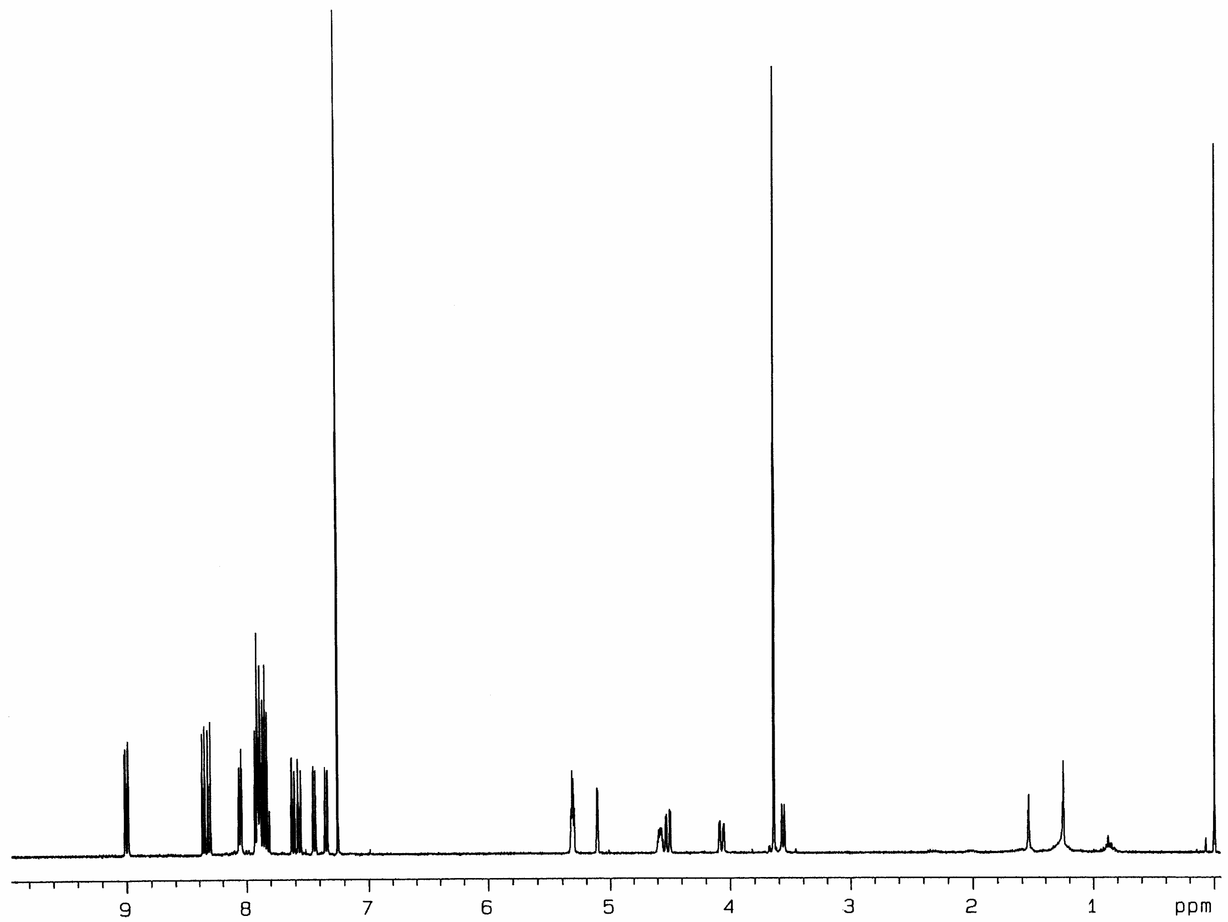

Figure S3. ^{1}H NMR of **2** in $CDCl_3$.

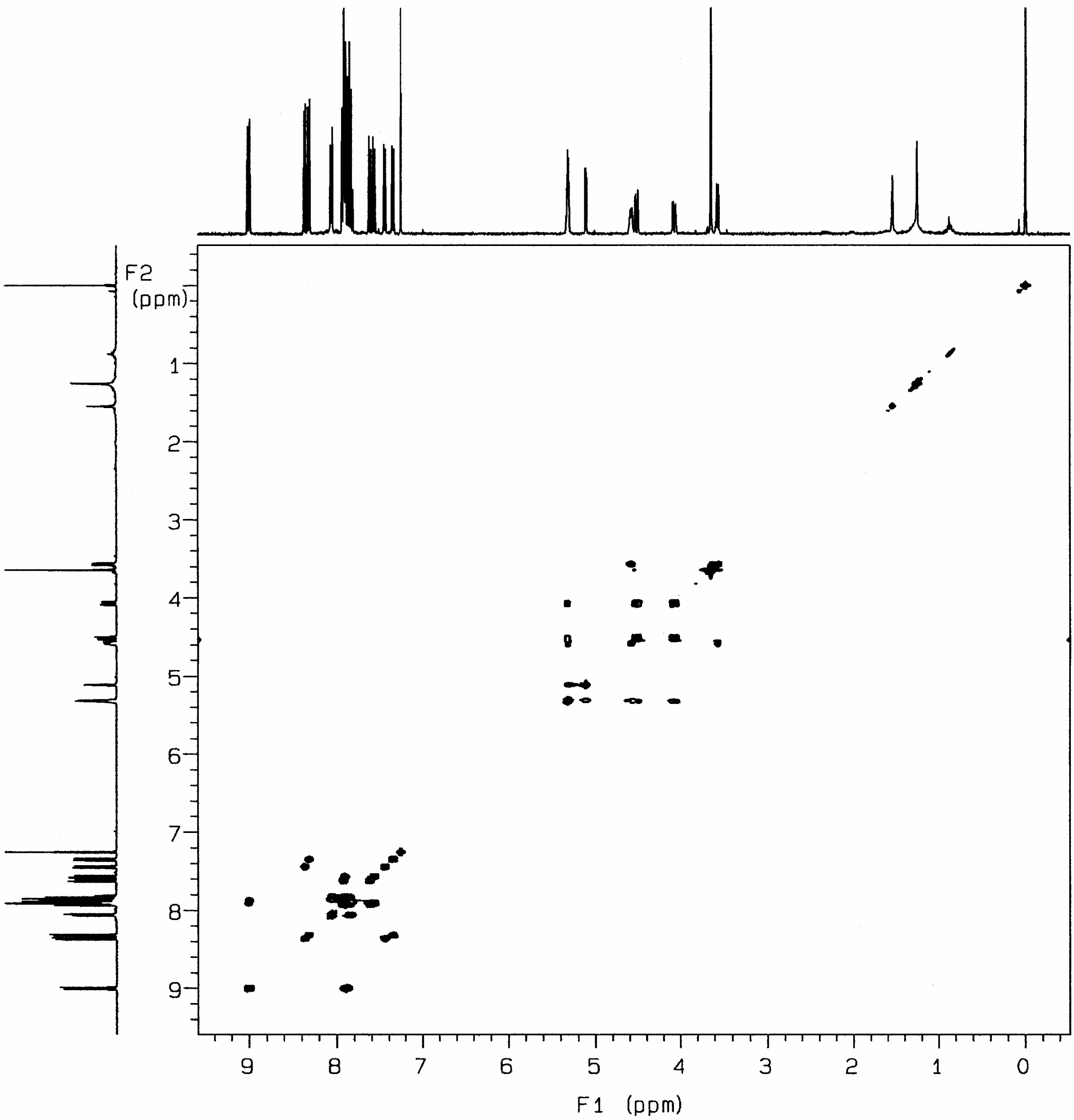

Figure S4. COSY spectrum of **2** in $CDCl_3$.

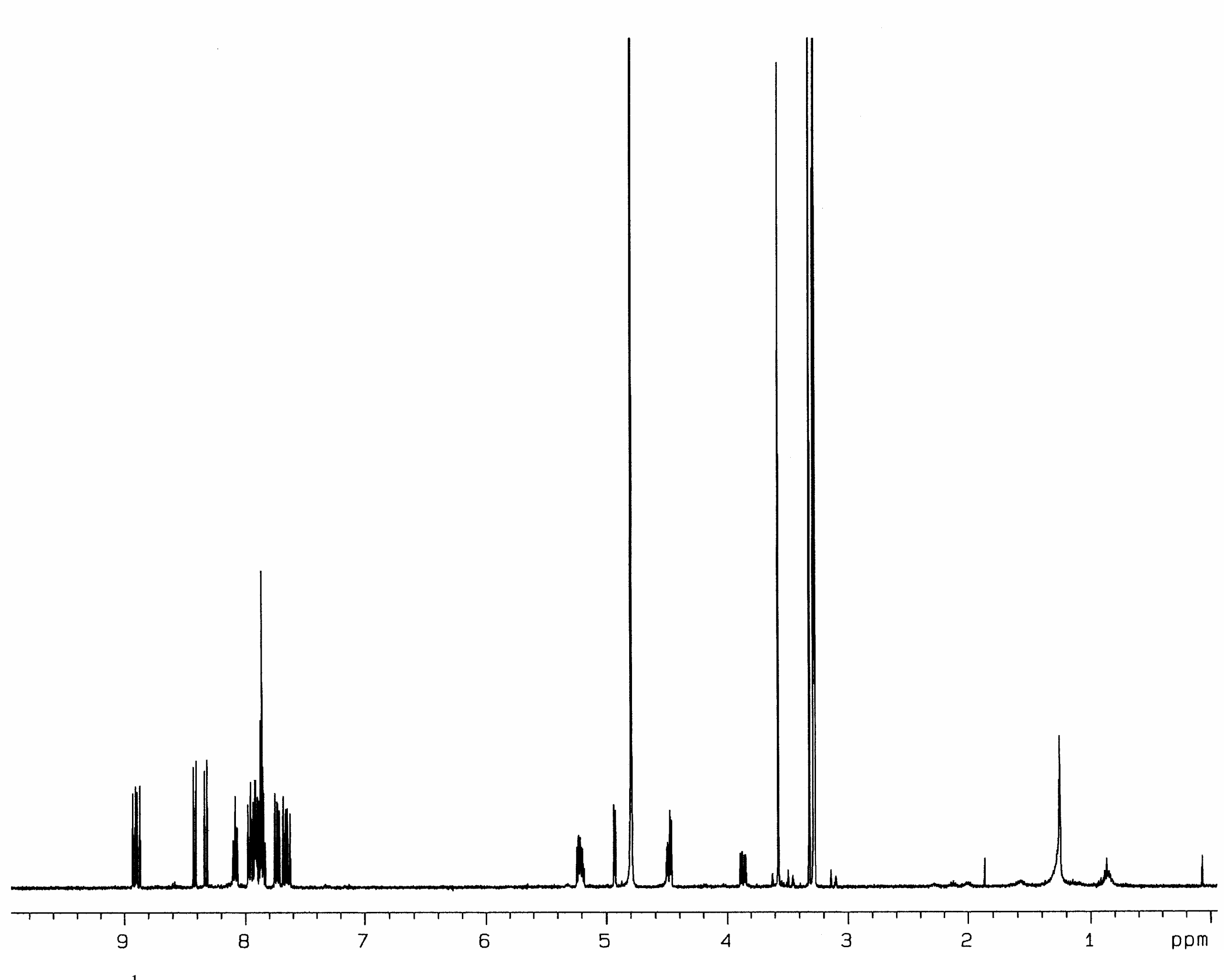

Figure S5. ^{1}H NMR of **2** in CD_3OD.

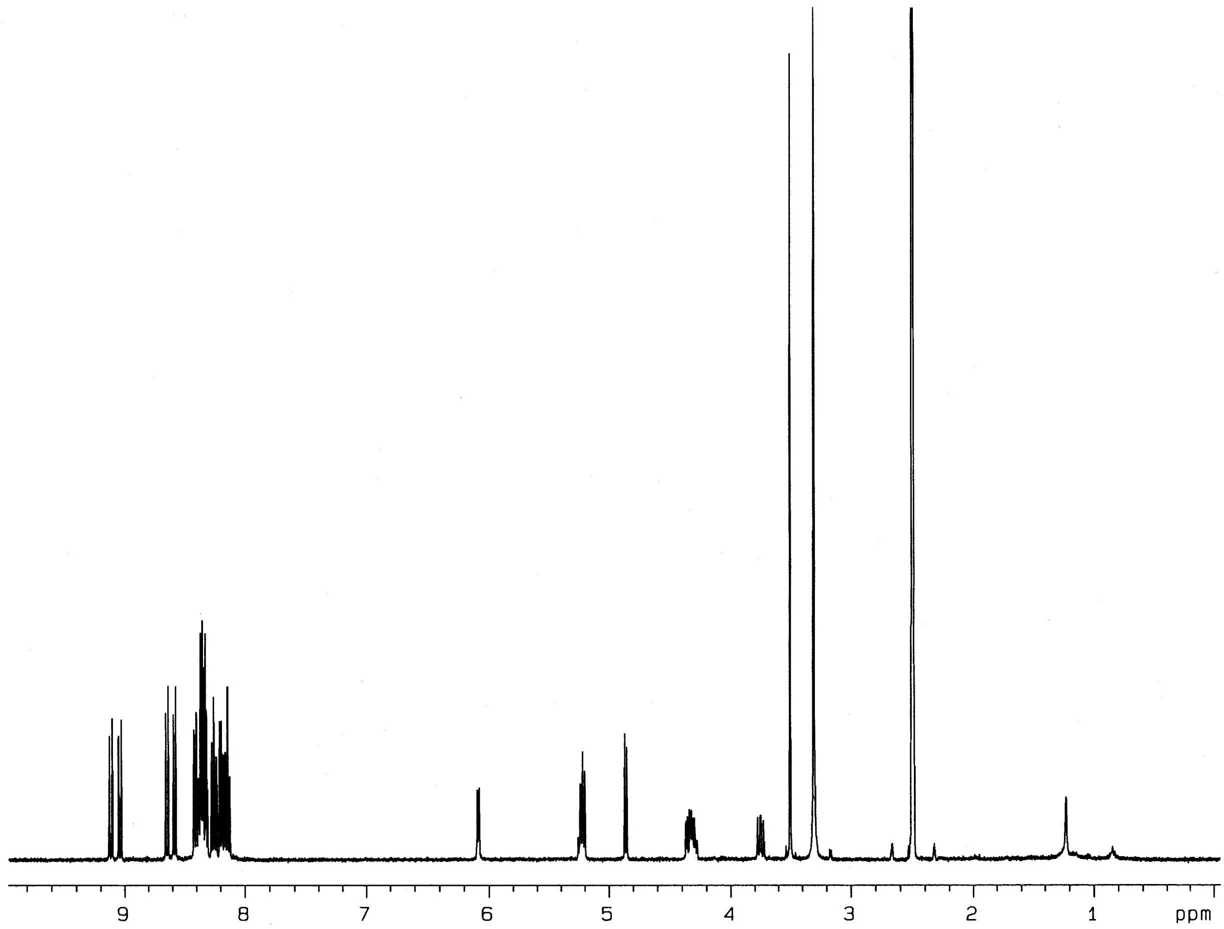

Figure S6. ^{1}H NMR of **2** in DMSO.

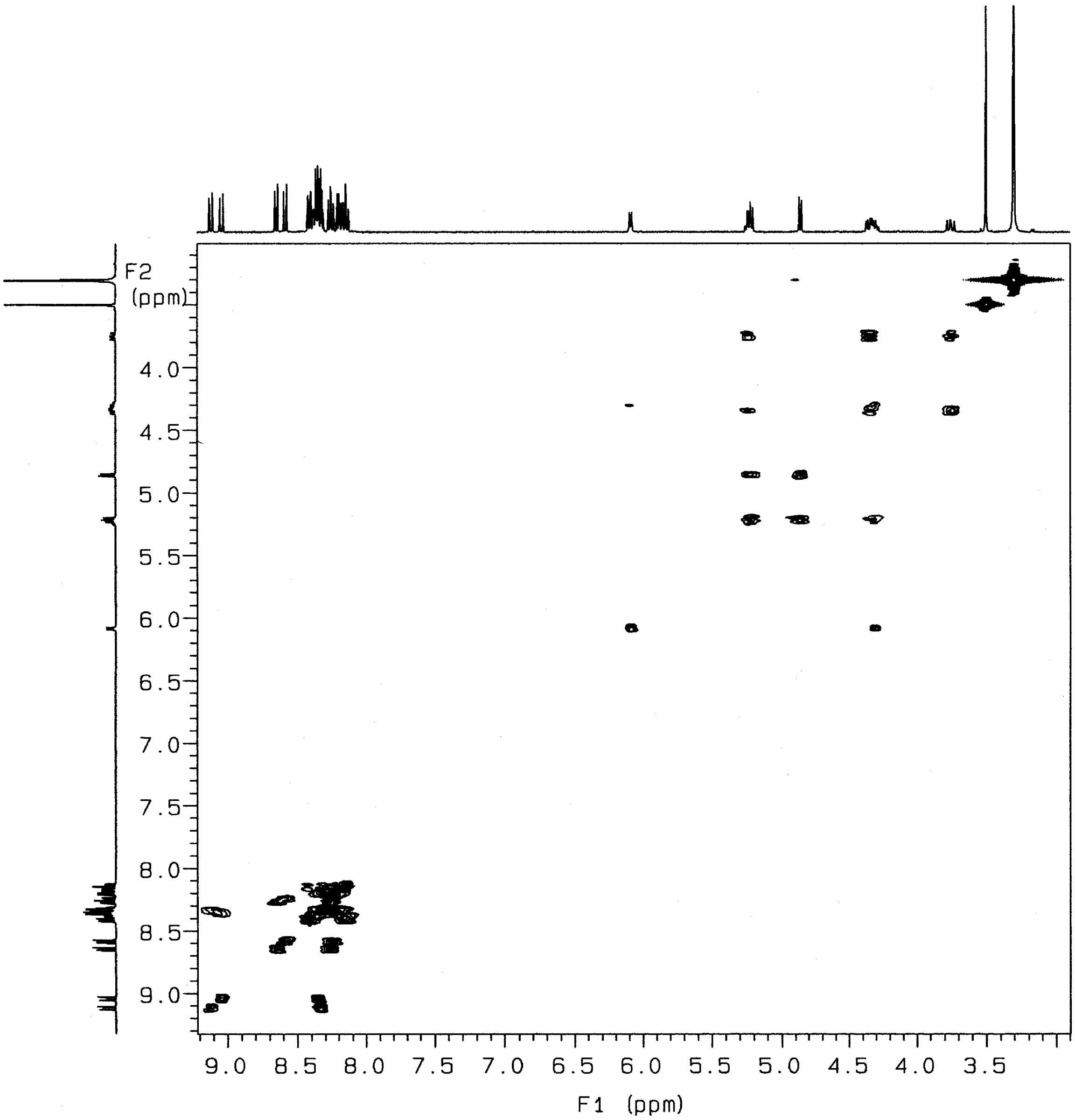

Figure S7. COSY spectrum of **2** in DMSO.

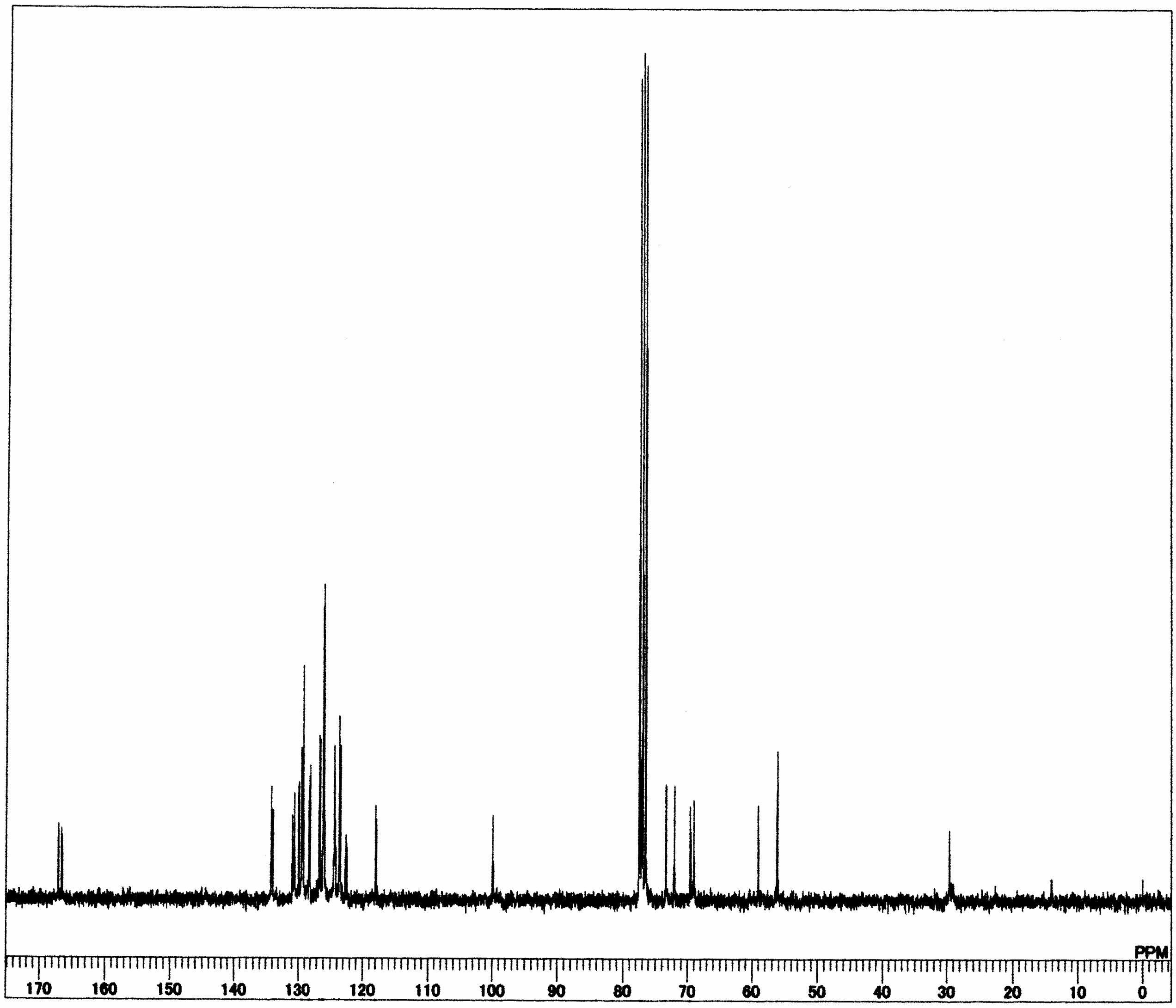

Figure S2. ^{13}C NMR of **5**.

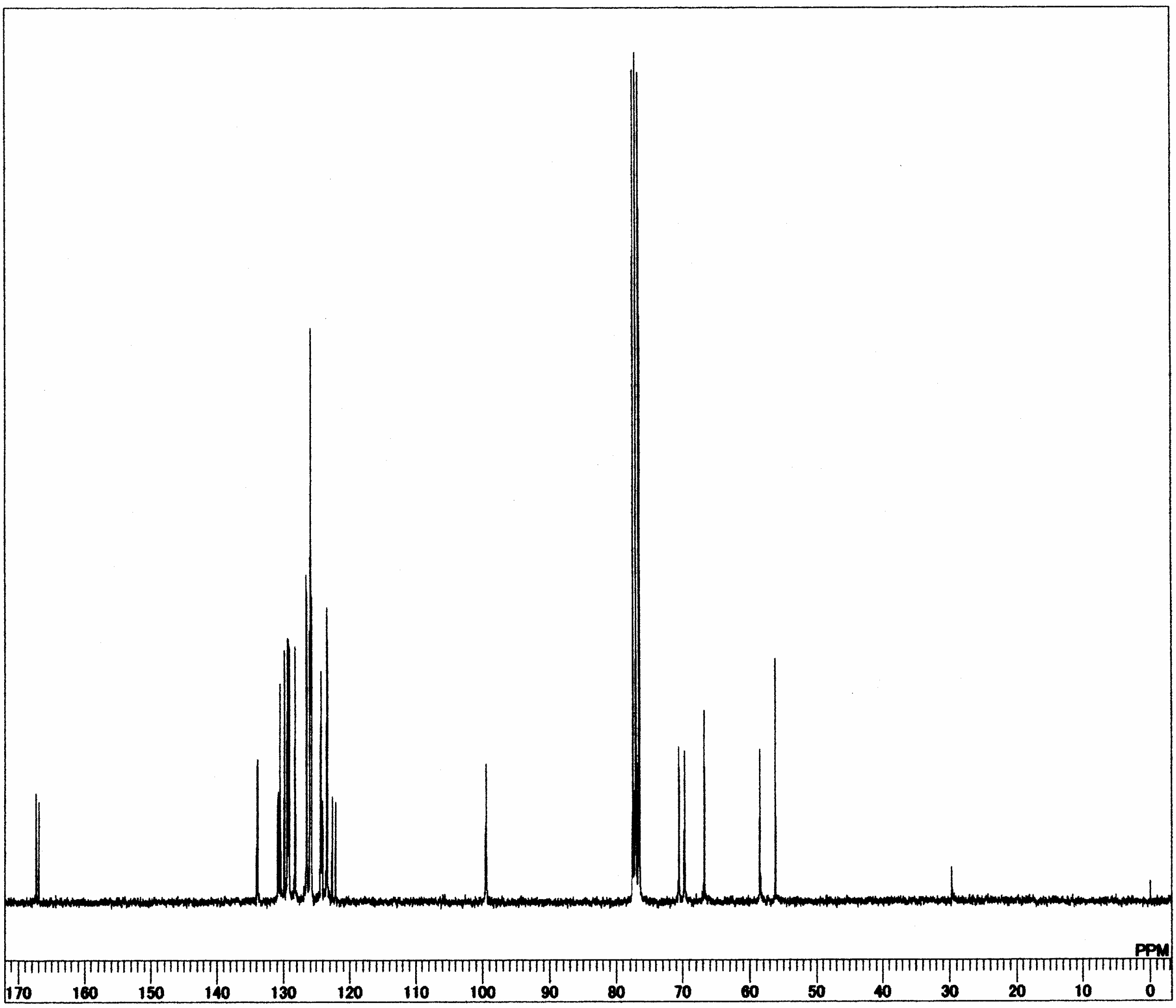

Figure S8. ^{13}C NMR of **2**.

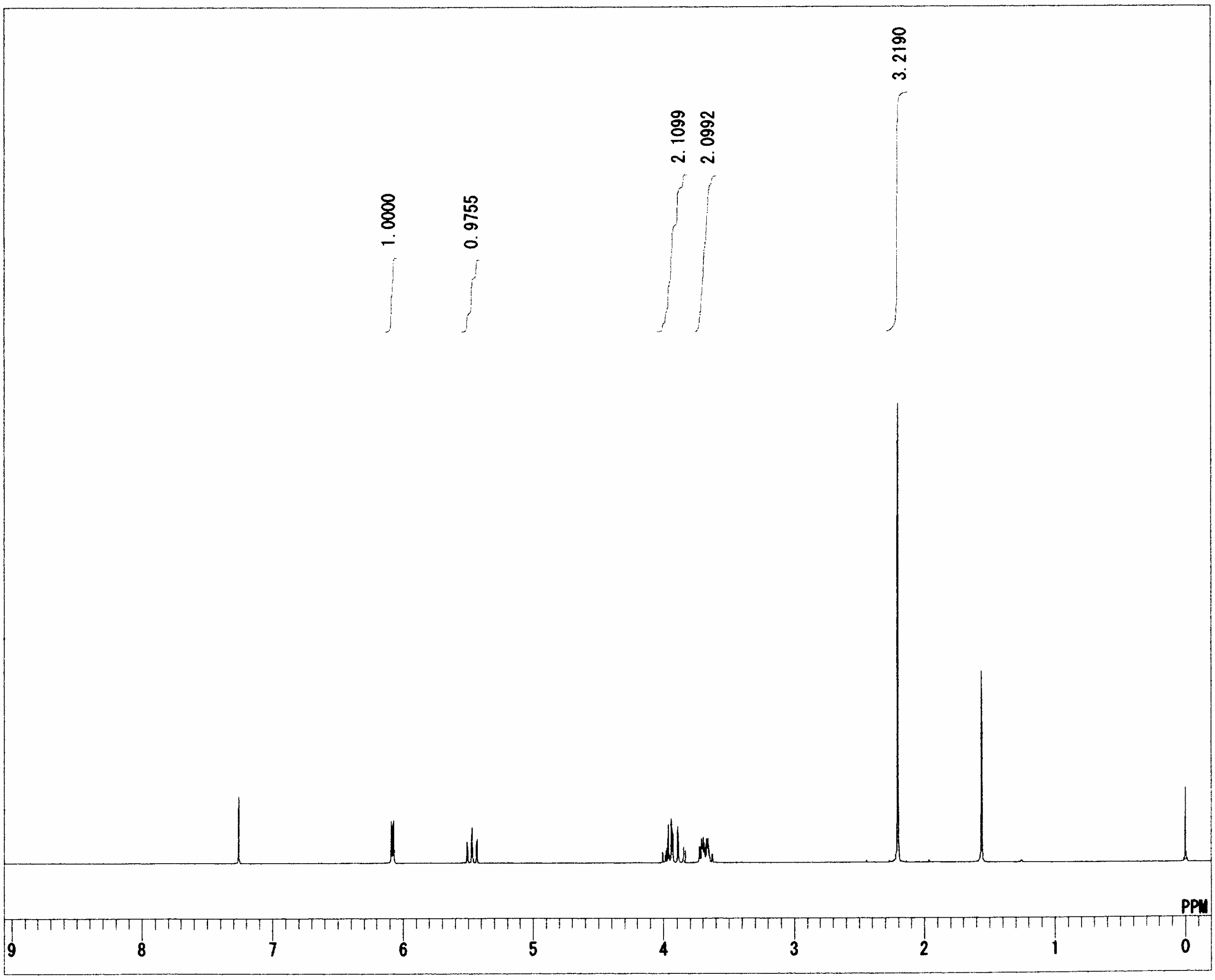

Figure S9. [1]H NMR of **7** in $CDCl_3$.

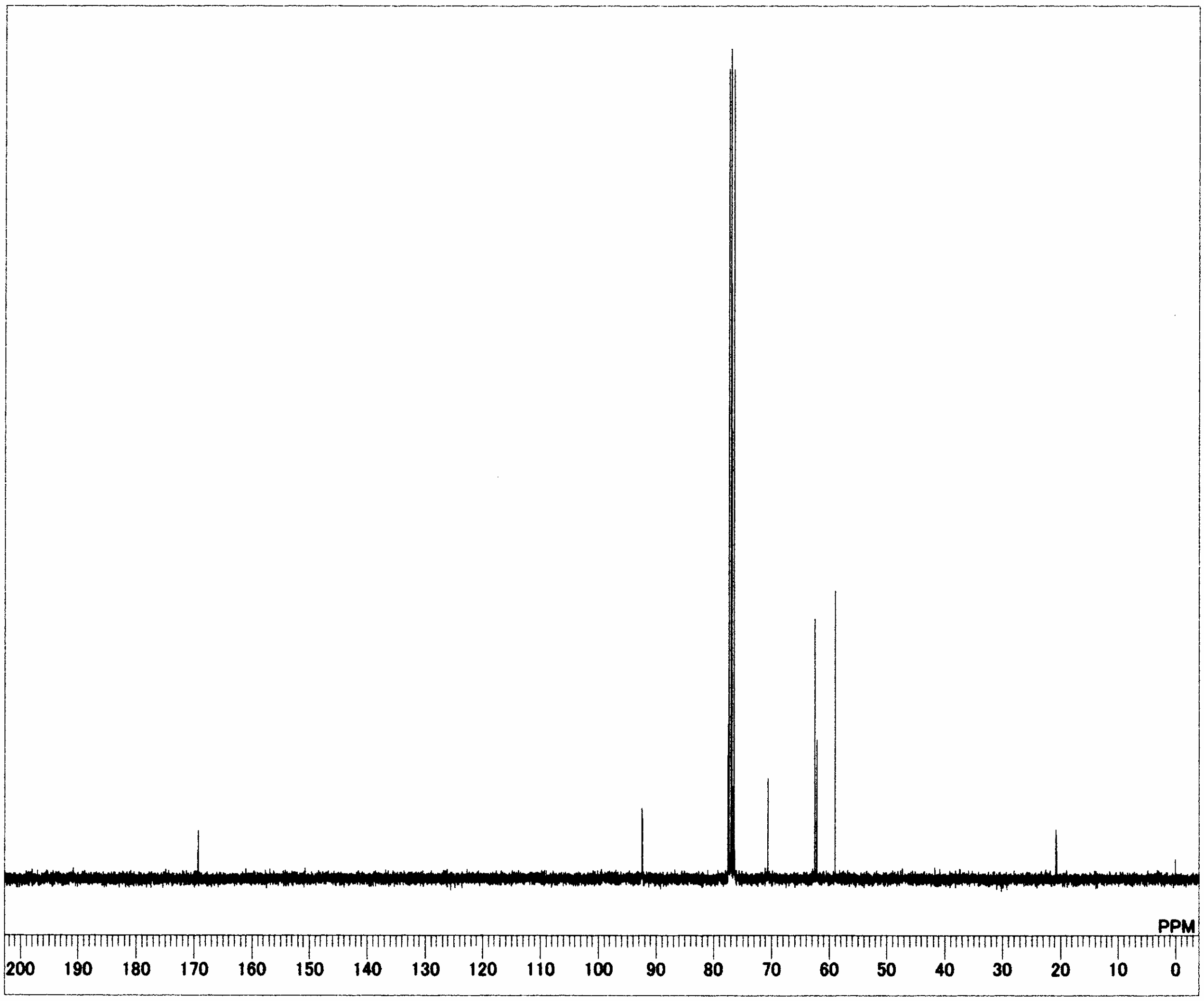

Figure S10. ^{13}C NMR of **7** in $CDCl_3$.

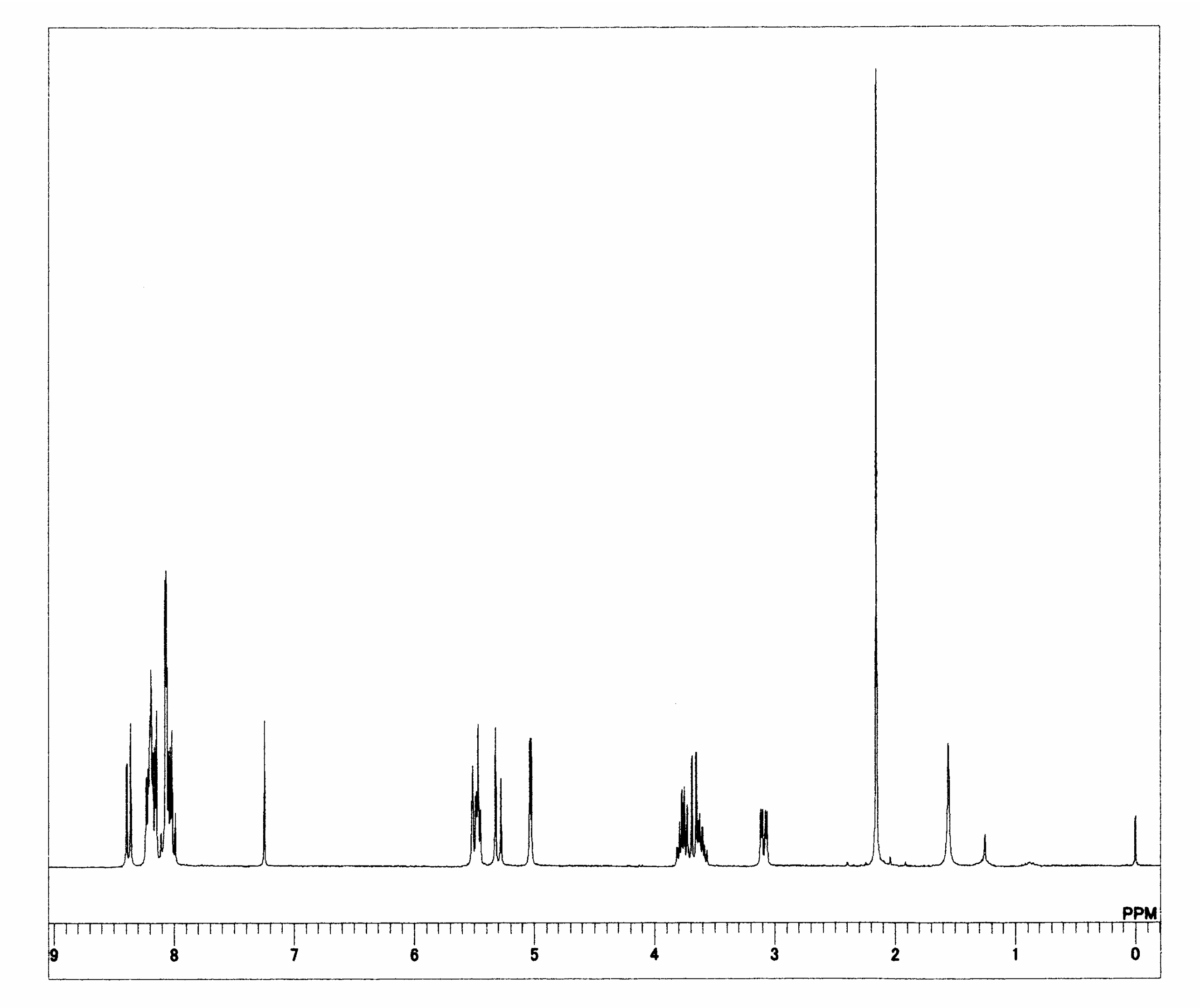

Figure S11. ^{1}H NMR of **8**α in $CDCl_3$.

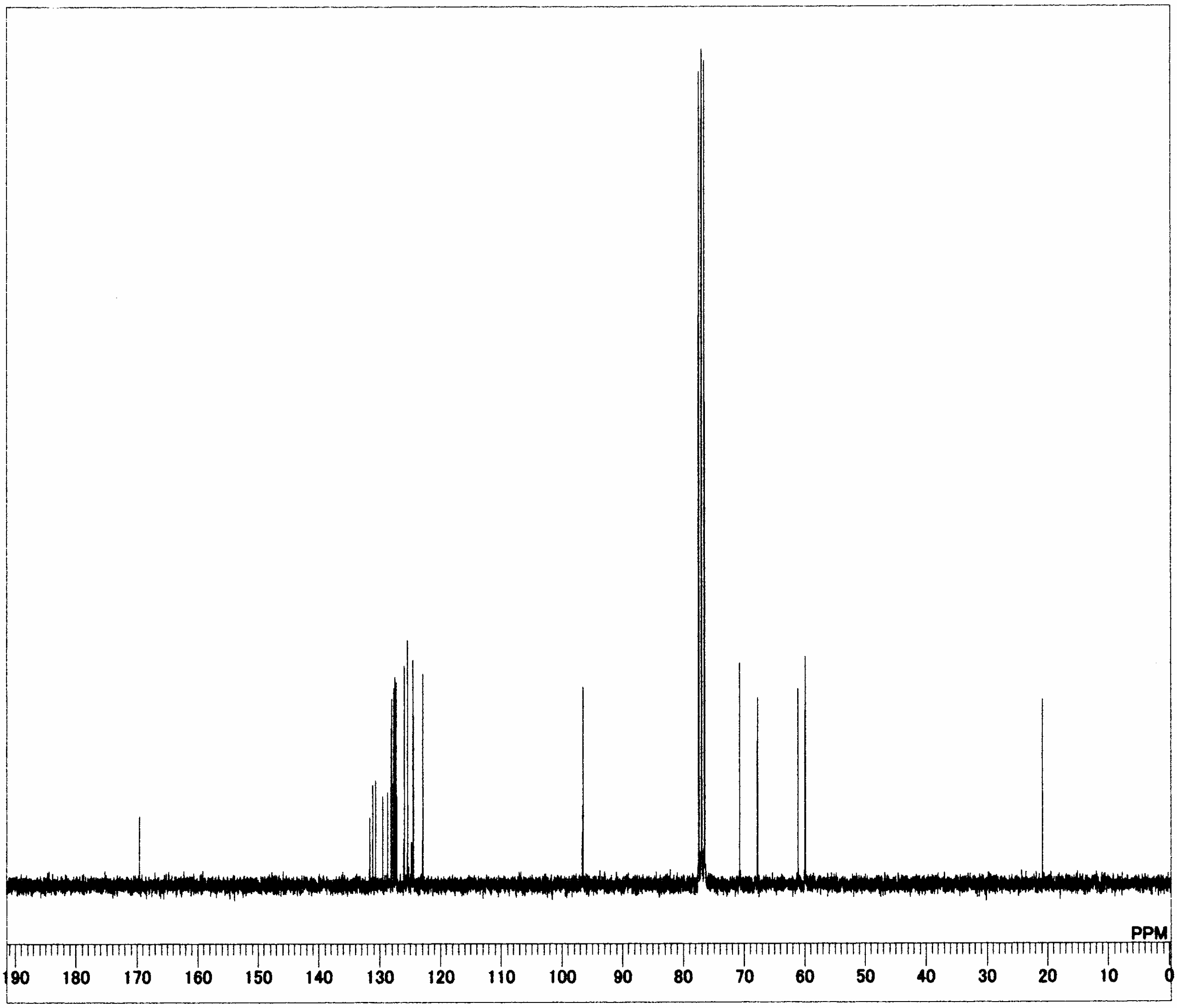

Figure S12. ^{13}C NMR of **8α** in $CDCl_3$.

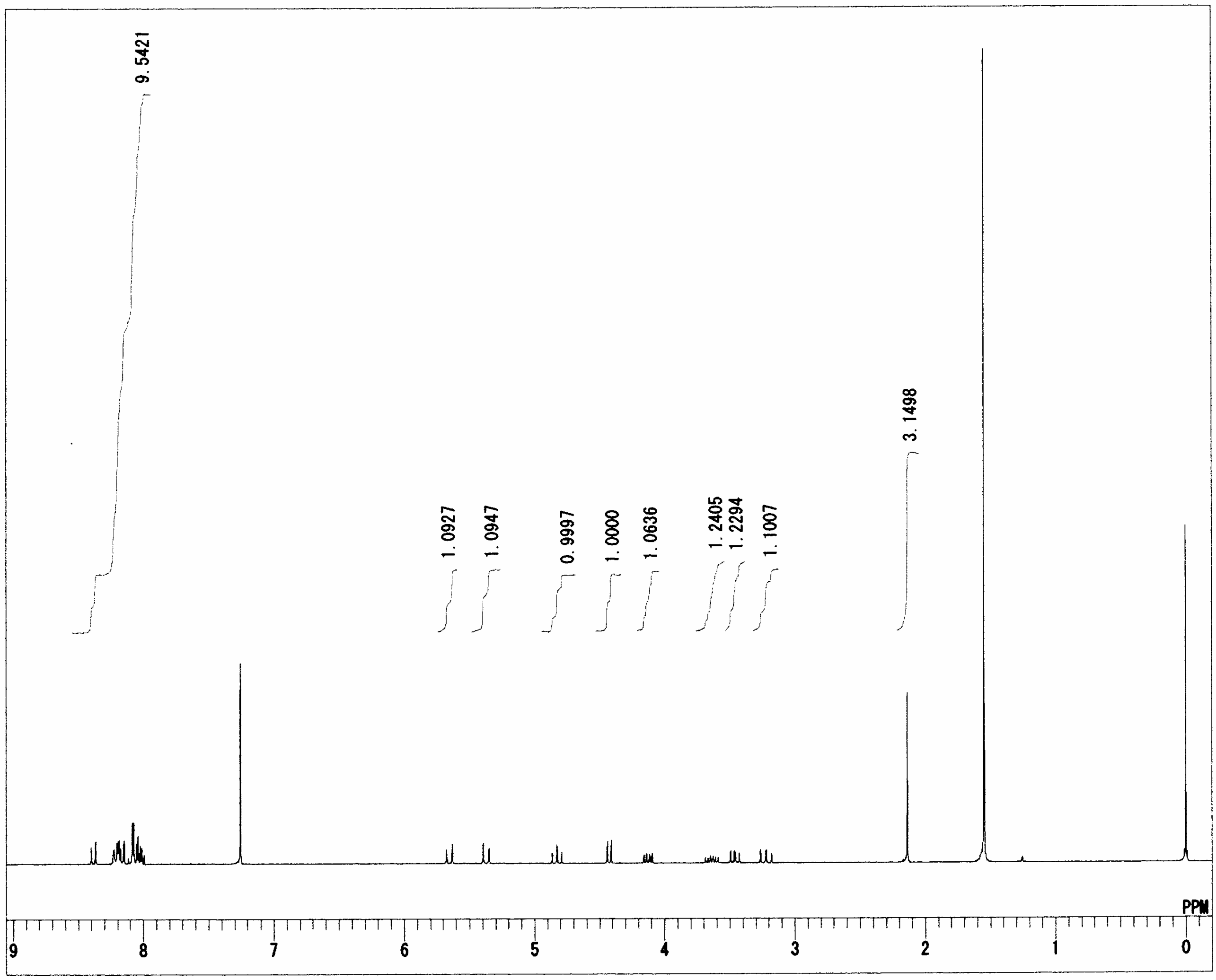

Figure S13. ^{1}H NMR of **8**β in $CDCl_3$.

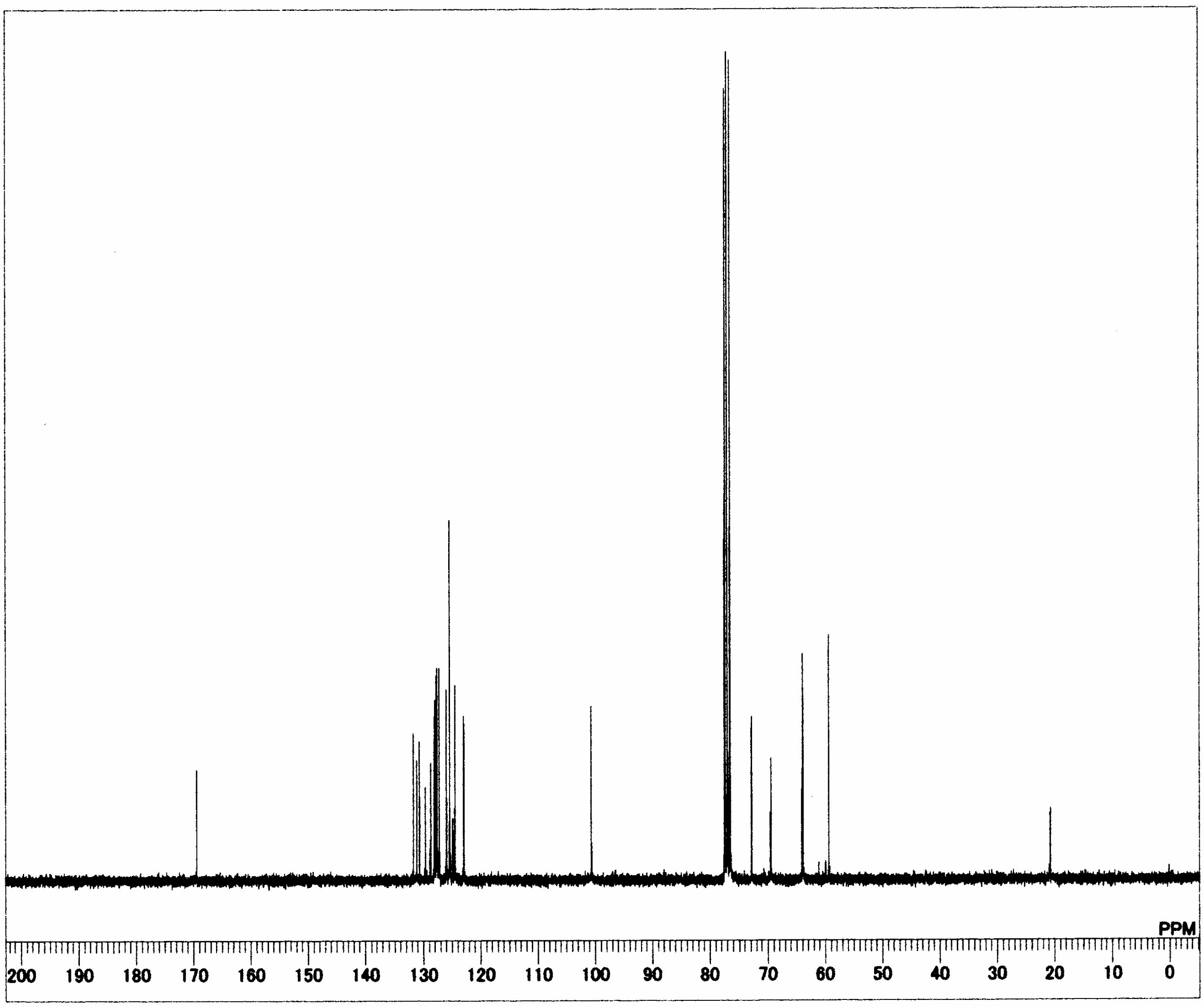

Figure S14. ^{13}C NMR of **8β** in $CDCl_3$.

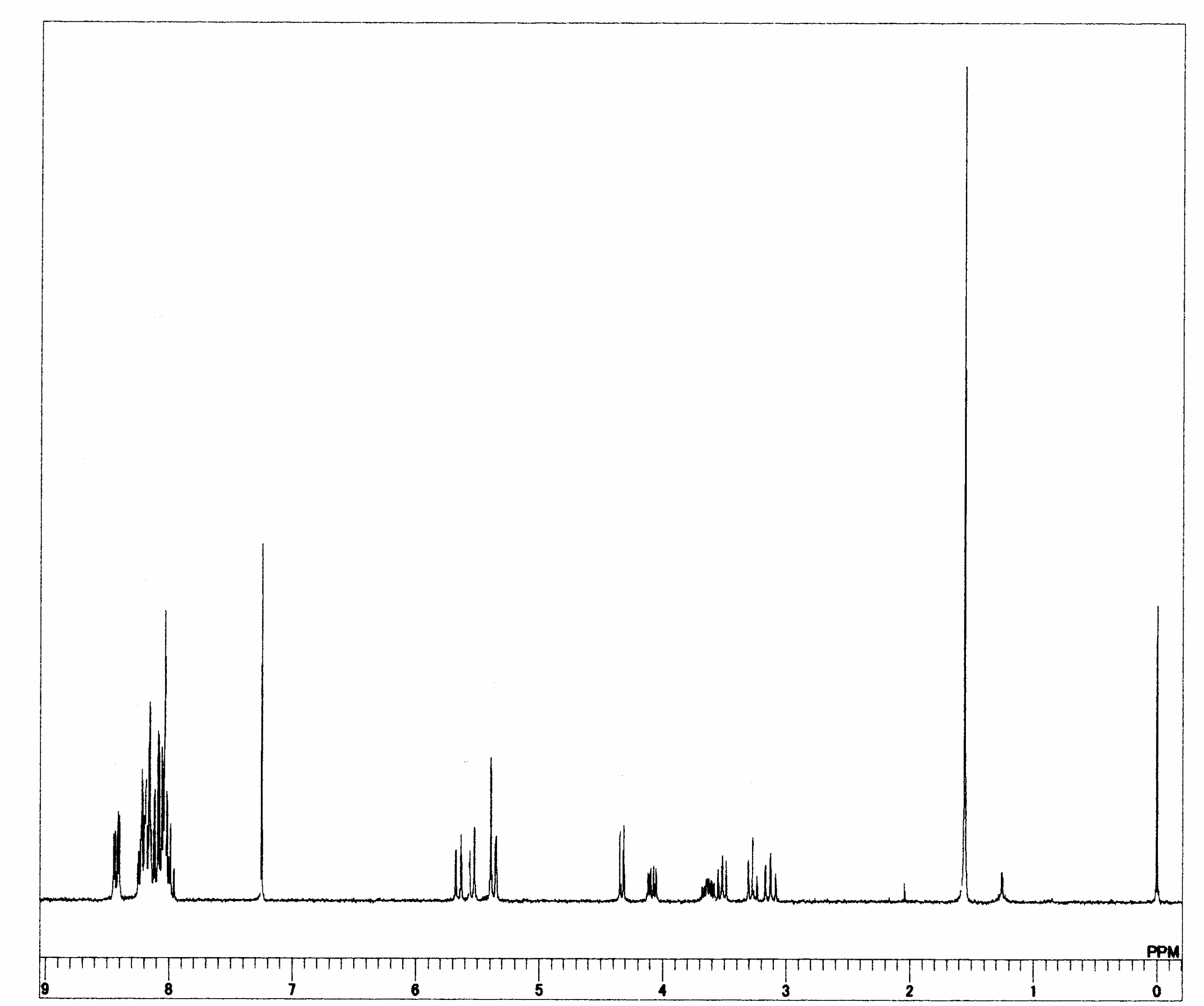

Figure S15. ^{1}H NMR of **9** in $CDCl_3$.

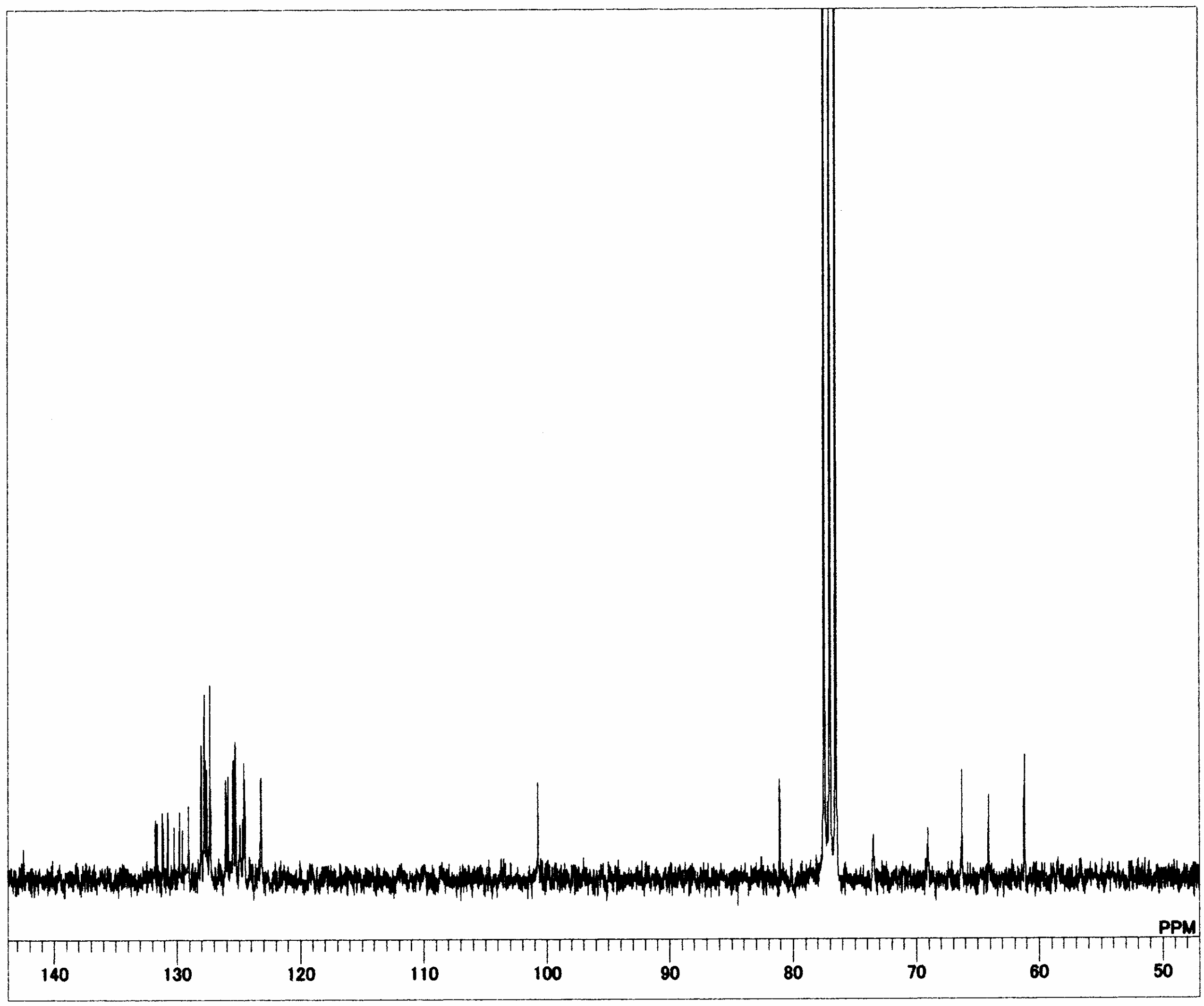

Figure S16. ^{13}C NMR of **9** in $CDCl_3$.

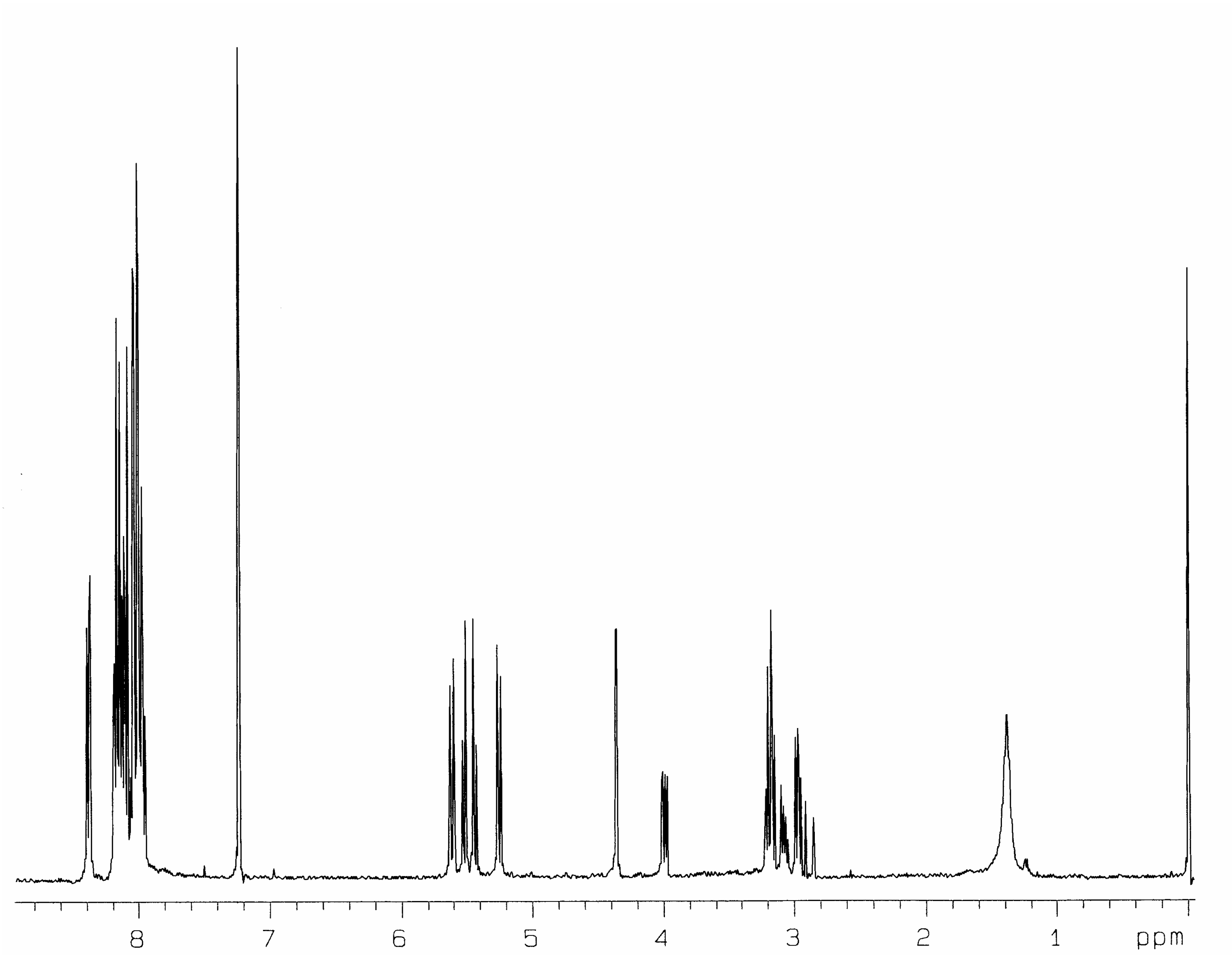

Figure S17. ^{1}H NMR of **1** in $CDCl_3$.

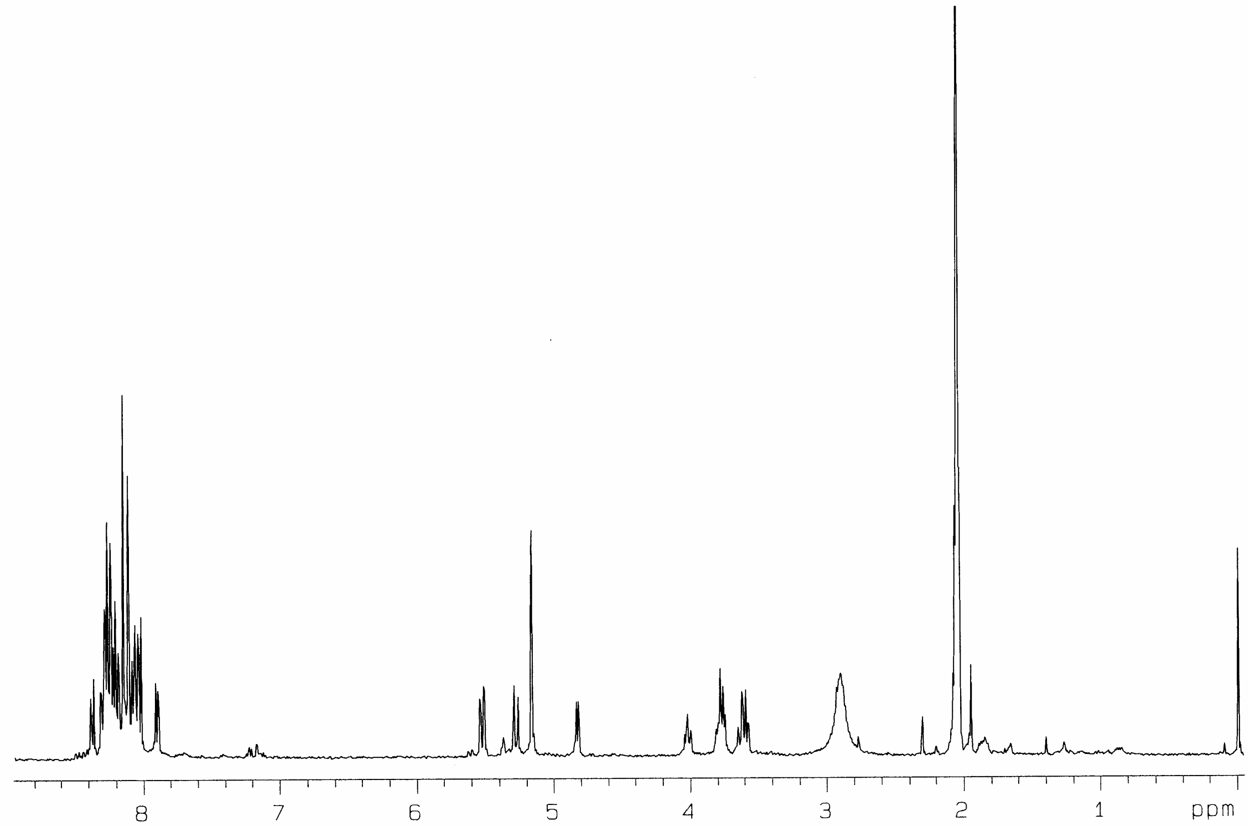

Figure S18. ^{1}H NMR of **1** in acetone-d_6.

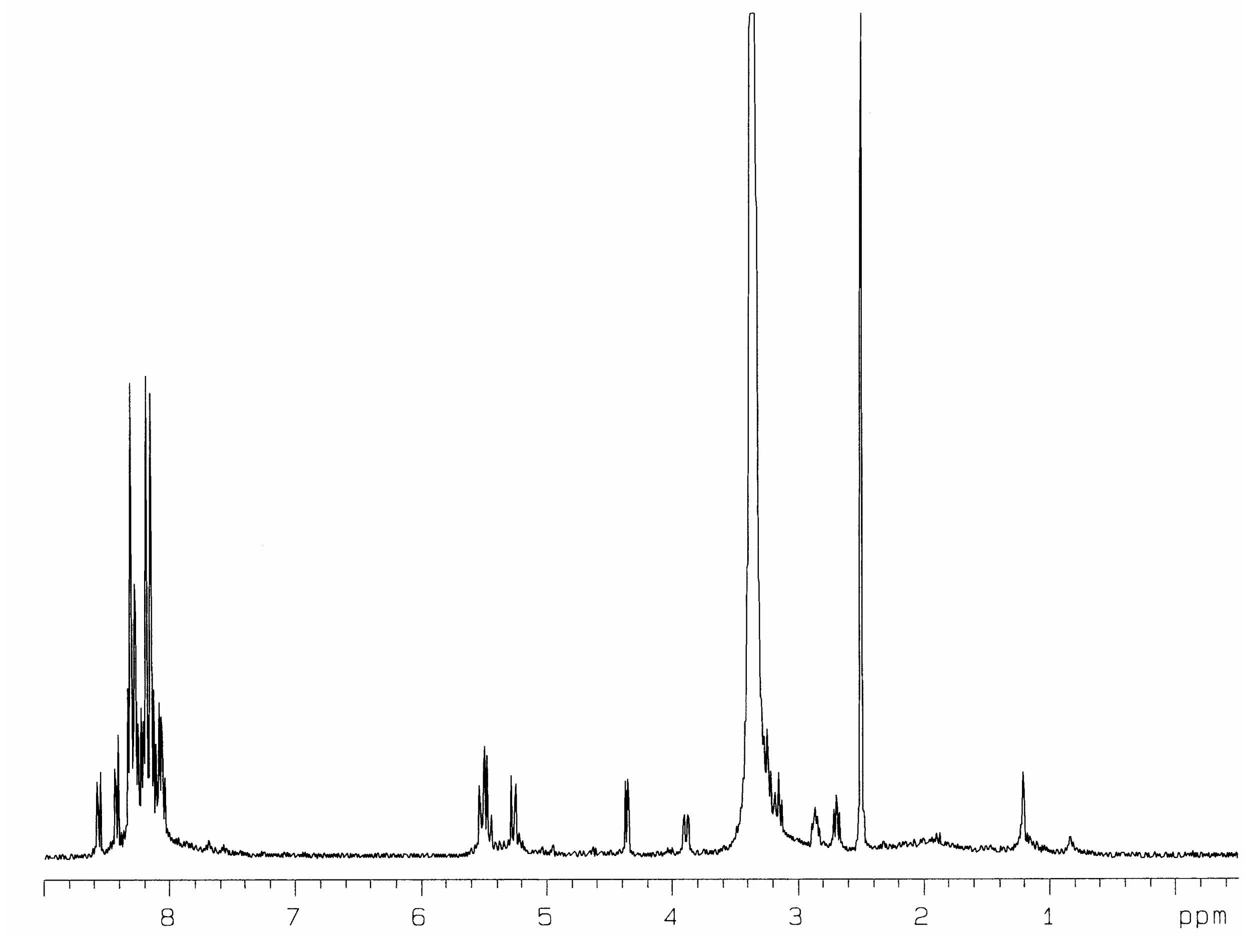

Figure S19. ^{1}H NMR of **1** in DMSO-d_6.

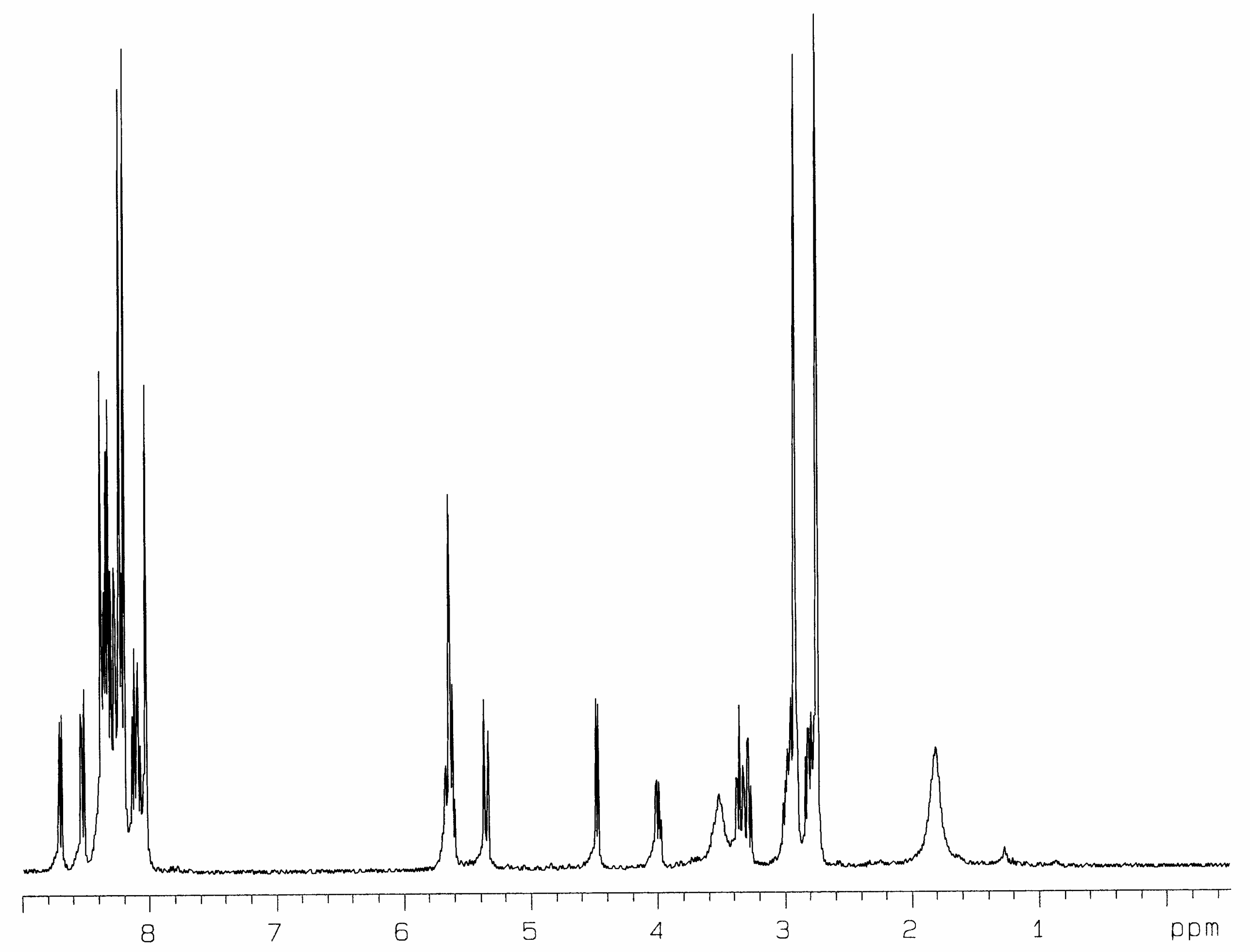

Figure S20. ^{1}H NMR of **1** in DMF-d_7.

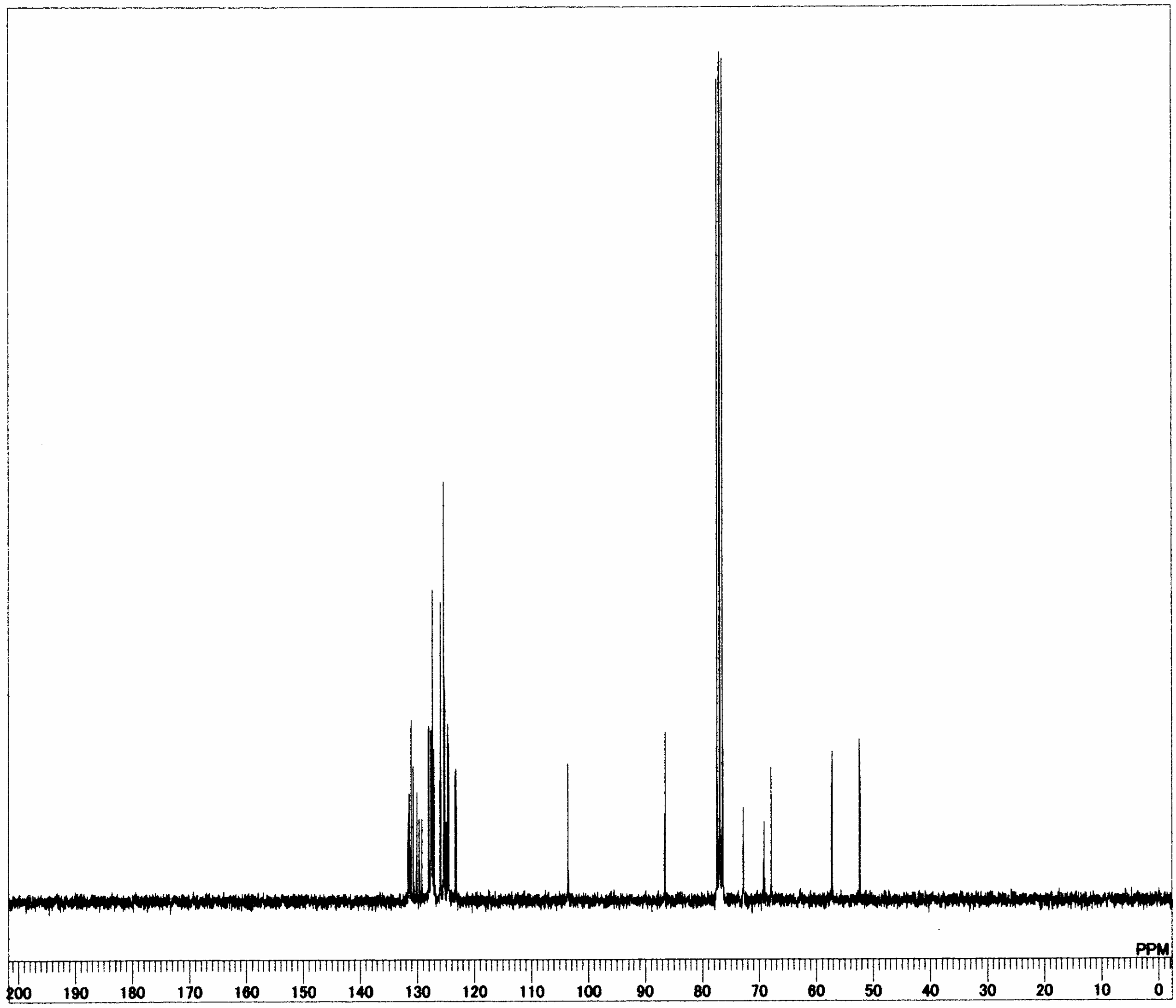

Figure S21. ^{13}C NMR of **1** in $CDCl_3$.

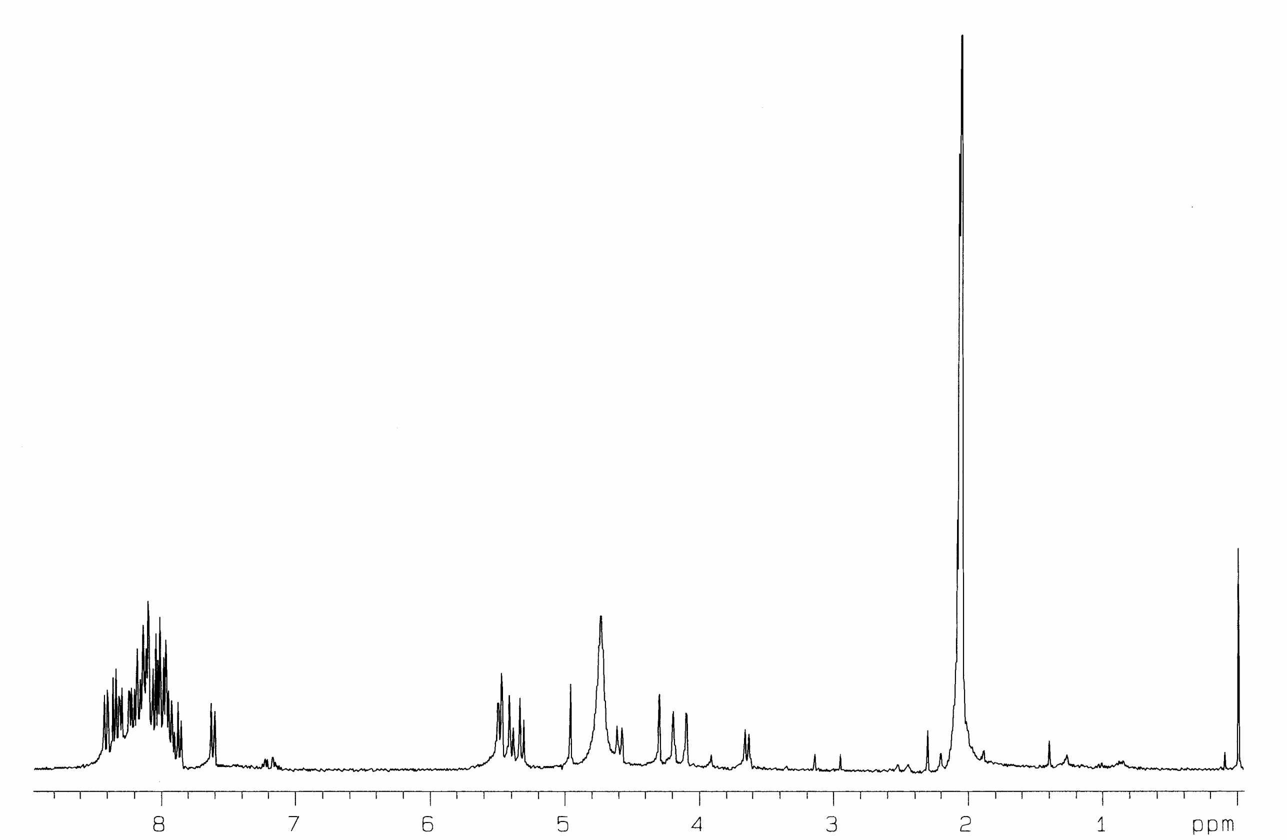

Figure S22. ^{1}H NMR of **1** with $ZnCl_2$ in acetone-d_6.

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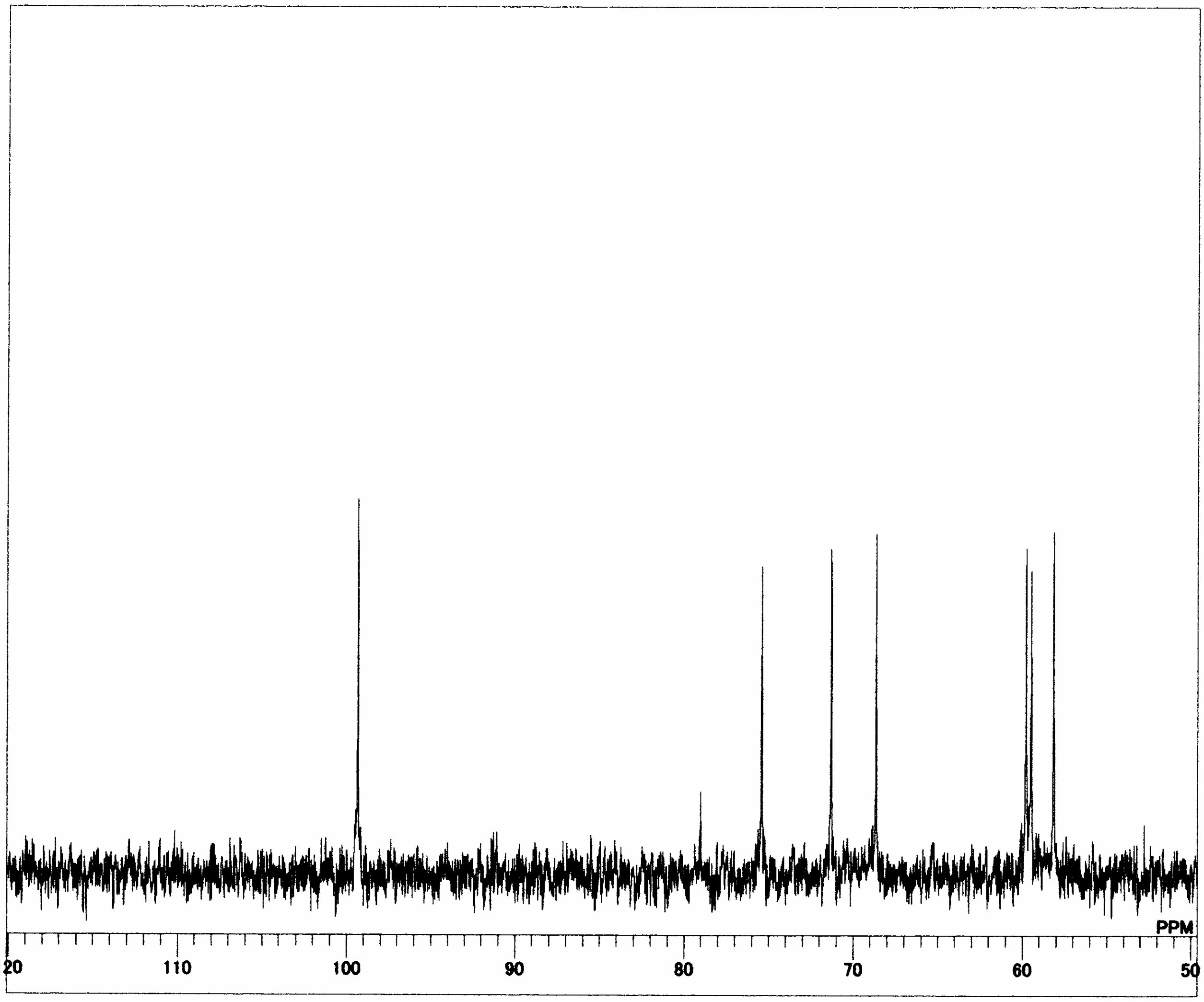

Figure S23. ^{13}C NMR of **1** with $ZnCl_2$ in acetone-d_6.

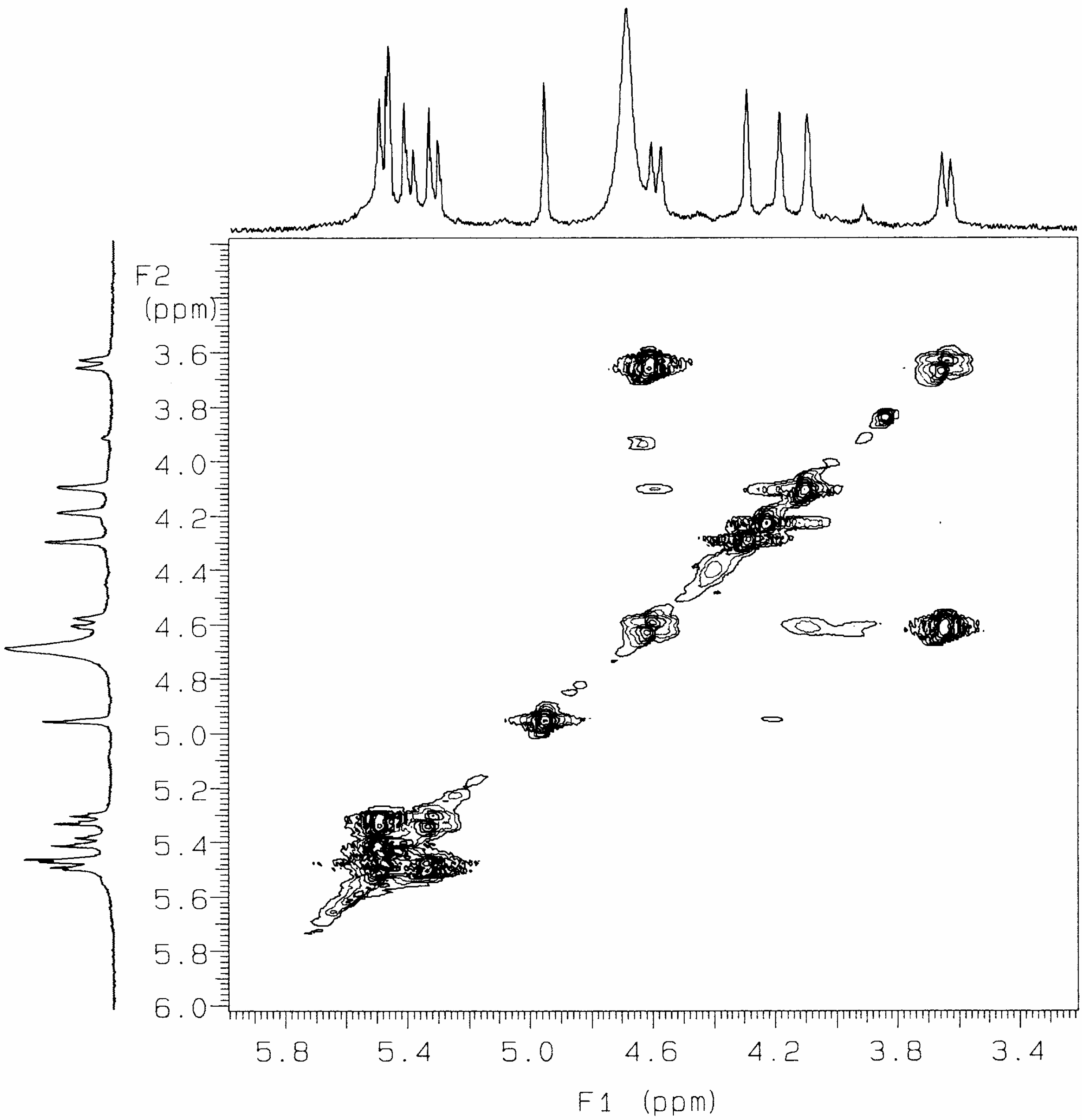

Figure S24. COSY spectrum of **1** with $ZnCl_2$ in acetone-d_6.

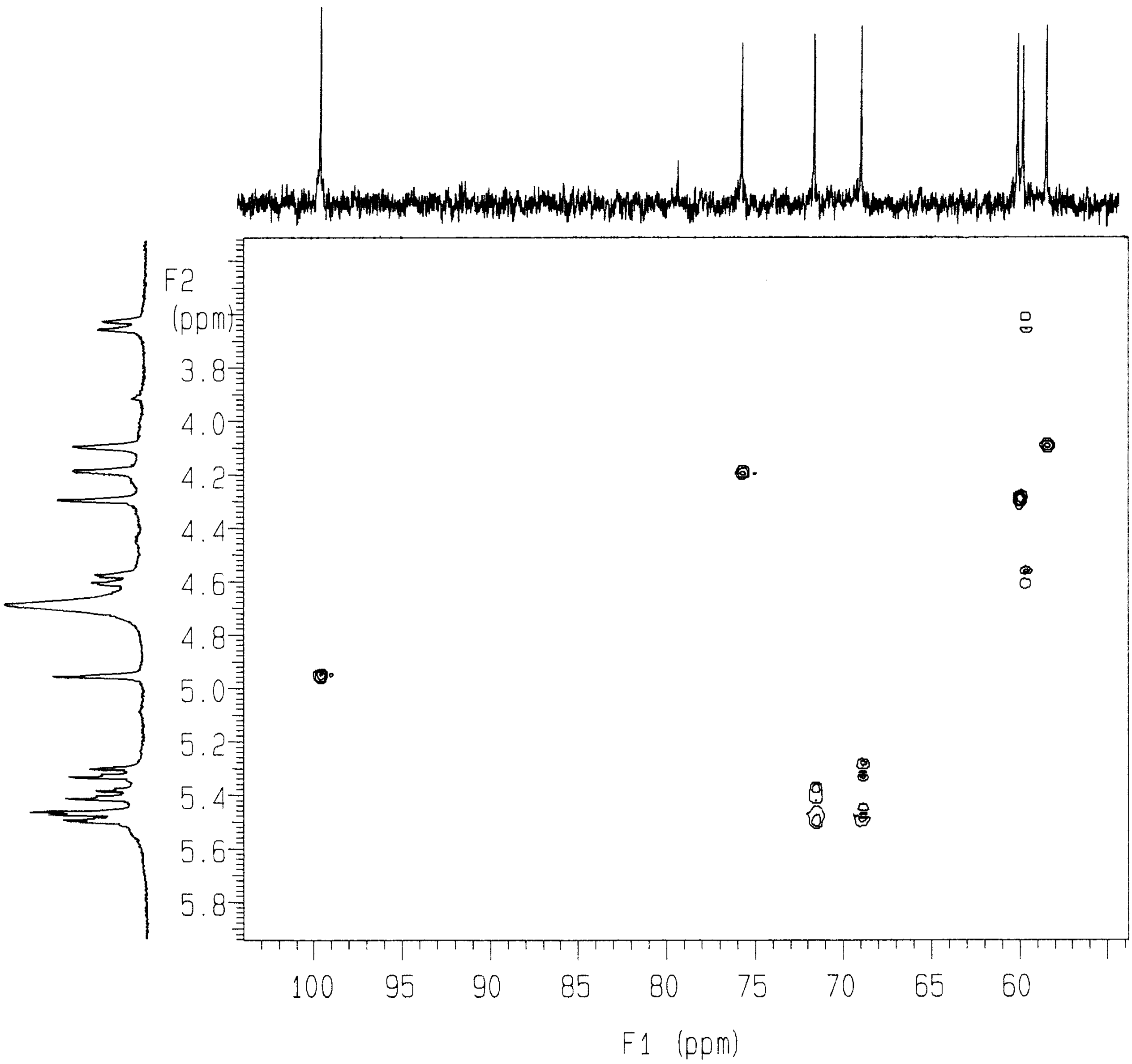

Figure S25. HMQC spectrum of **1** with $ZnCl_2$ in acetone-d_6.

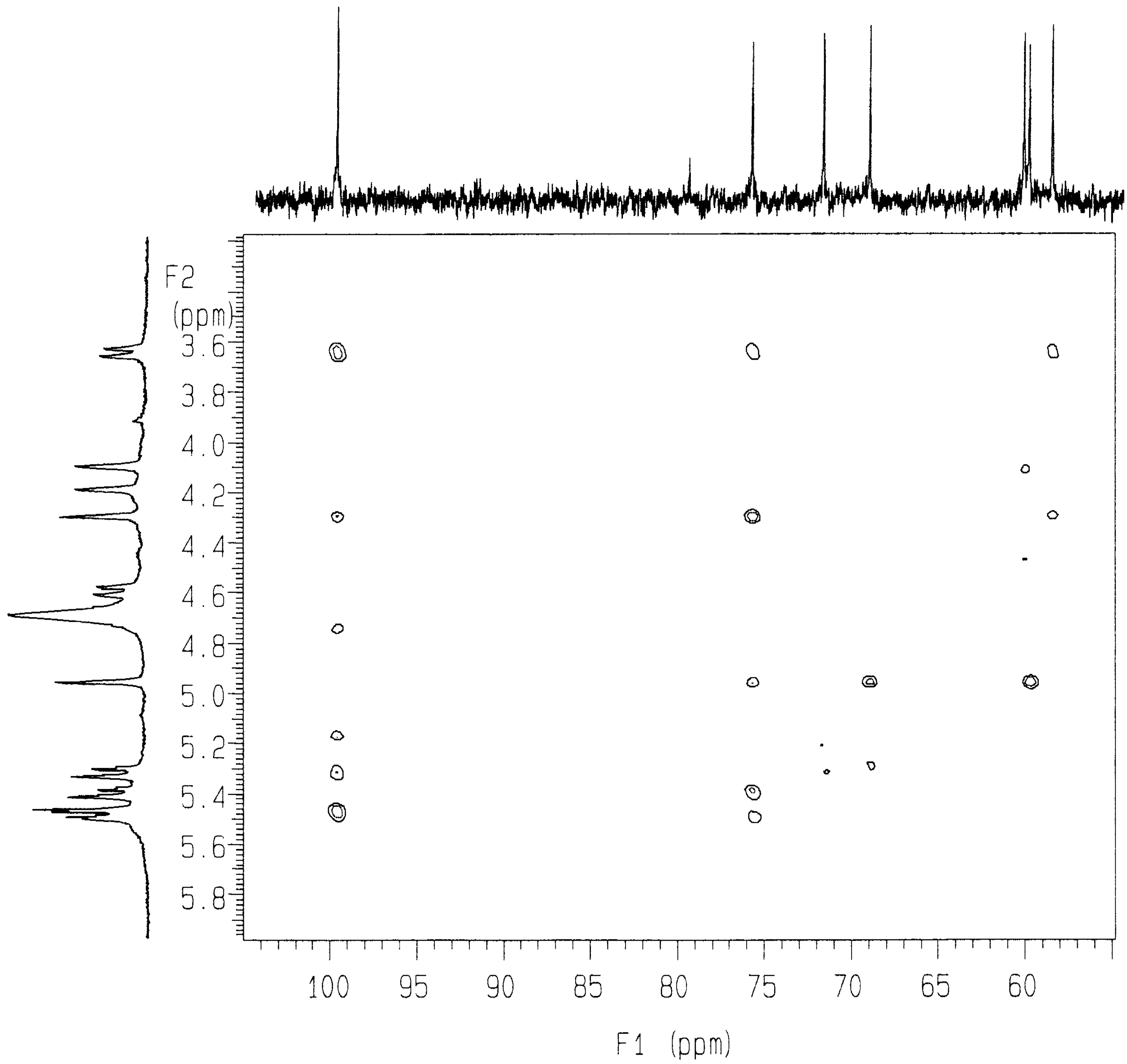

Figure S26. HMBC spectrum of **1** with $ZnCl_2$ in acetone-d_6.

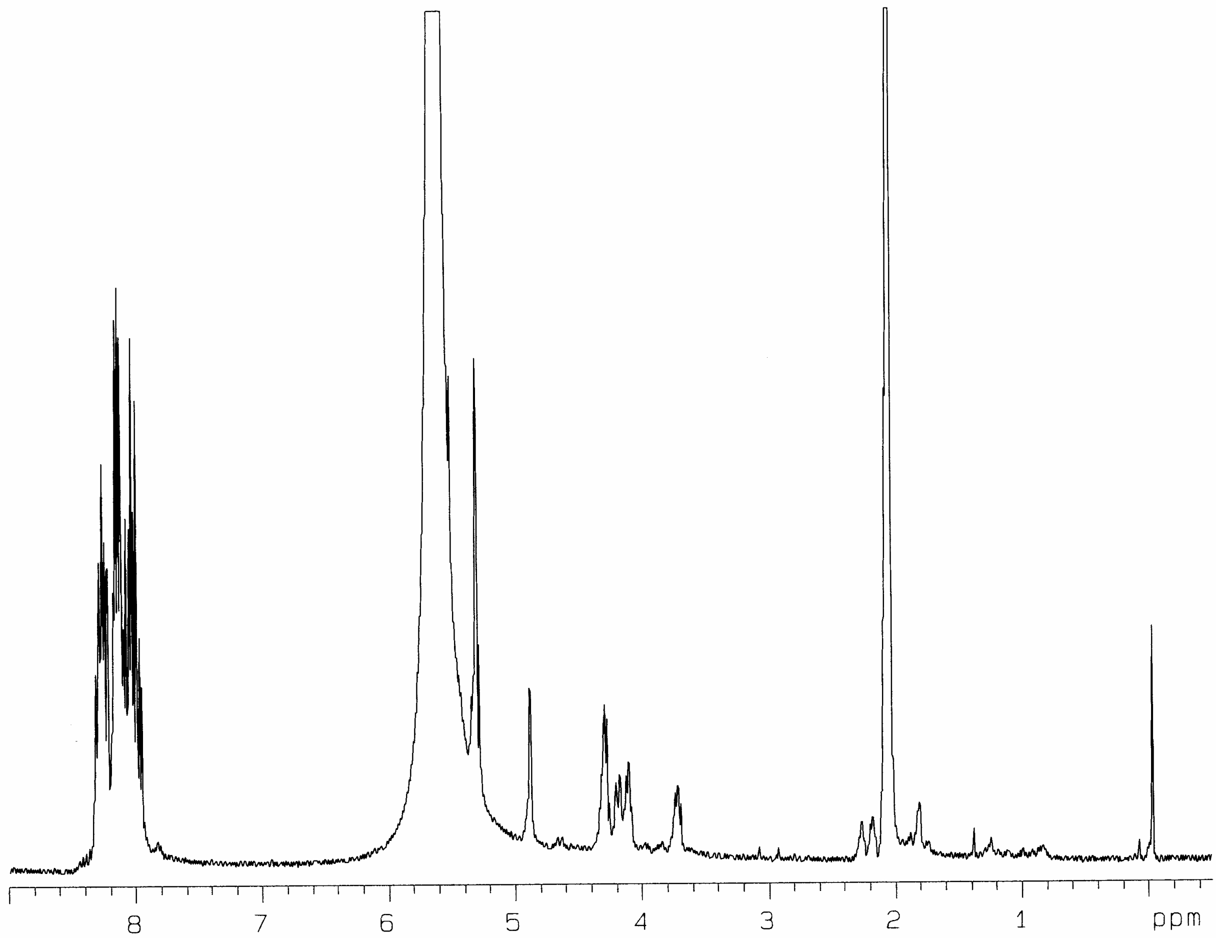

Figure S27. ^{1}H NMR of **1** with $Mg(ClO_4)_2$ in acetone-d_6.

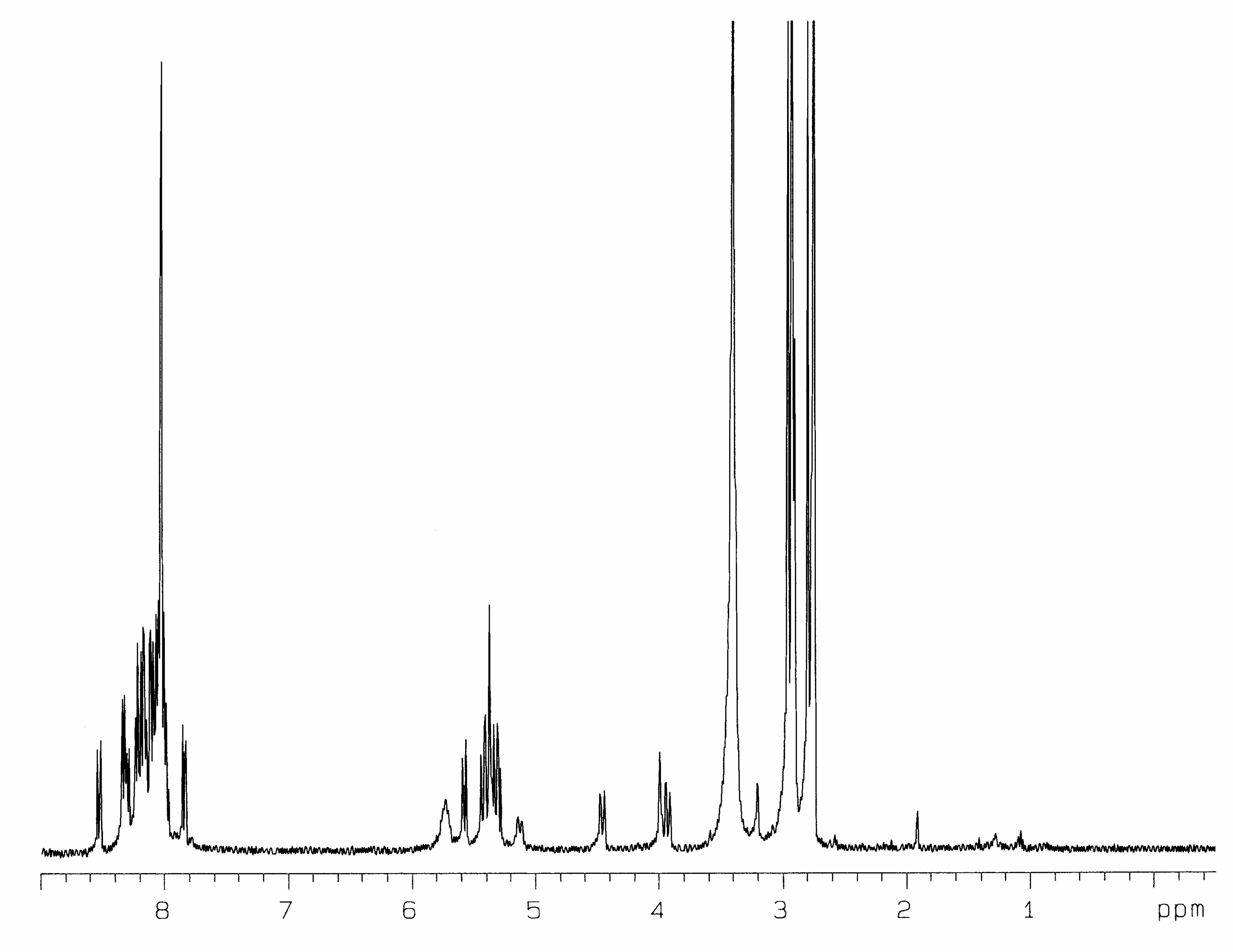

Figure S28. ^{1}H NMR of **1-Pt** in DMF-d_7.

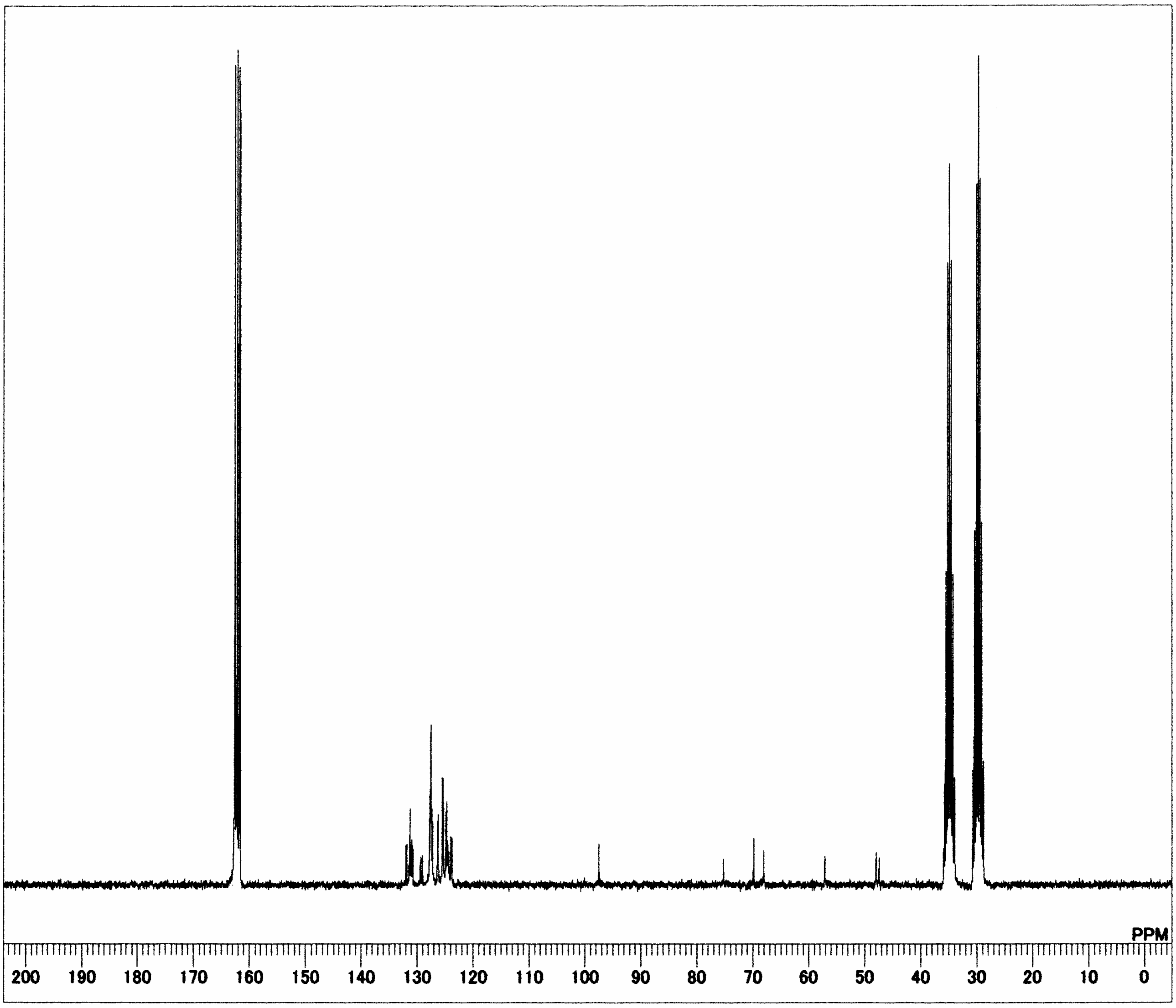

Figure S29. ^{13}C NMR of **1-Pt** in DMF-d_7.

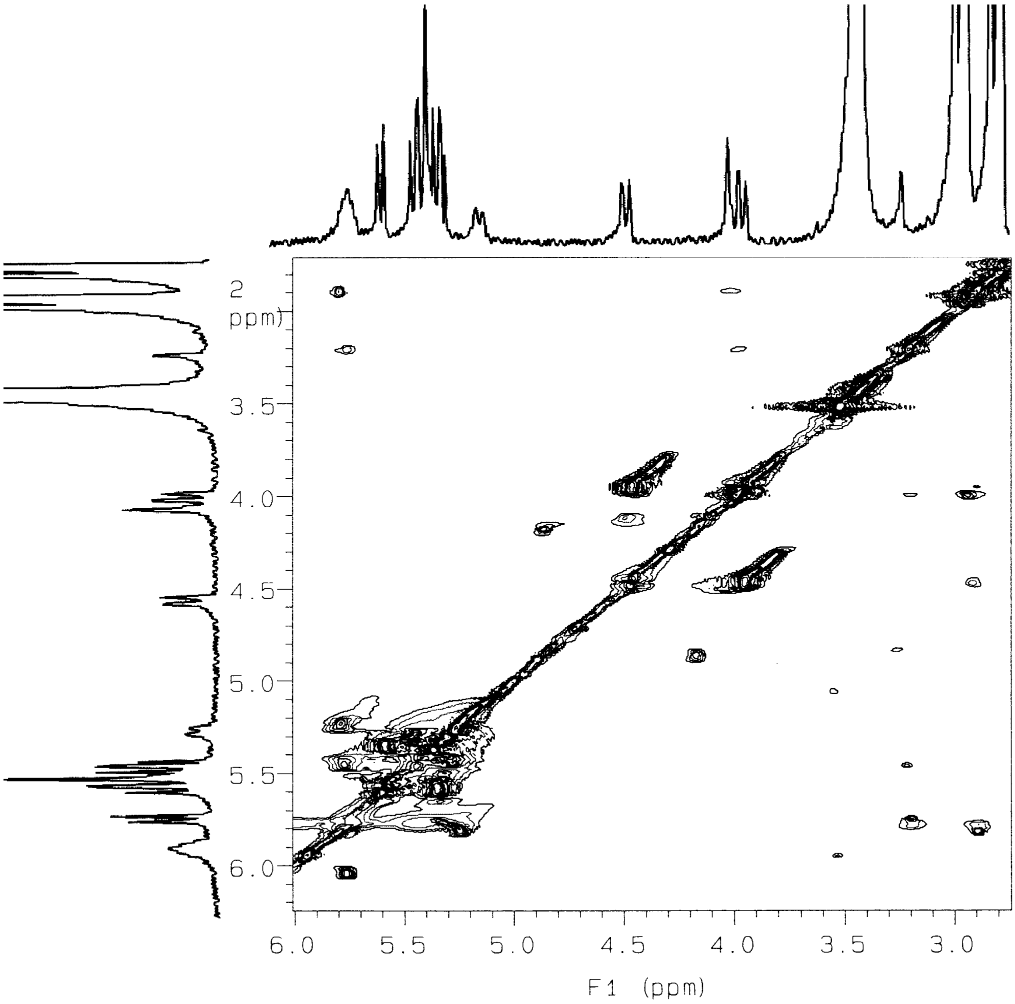

Figure S30. COSY spectrum of **1-Pt** in DMF-d_7.

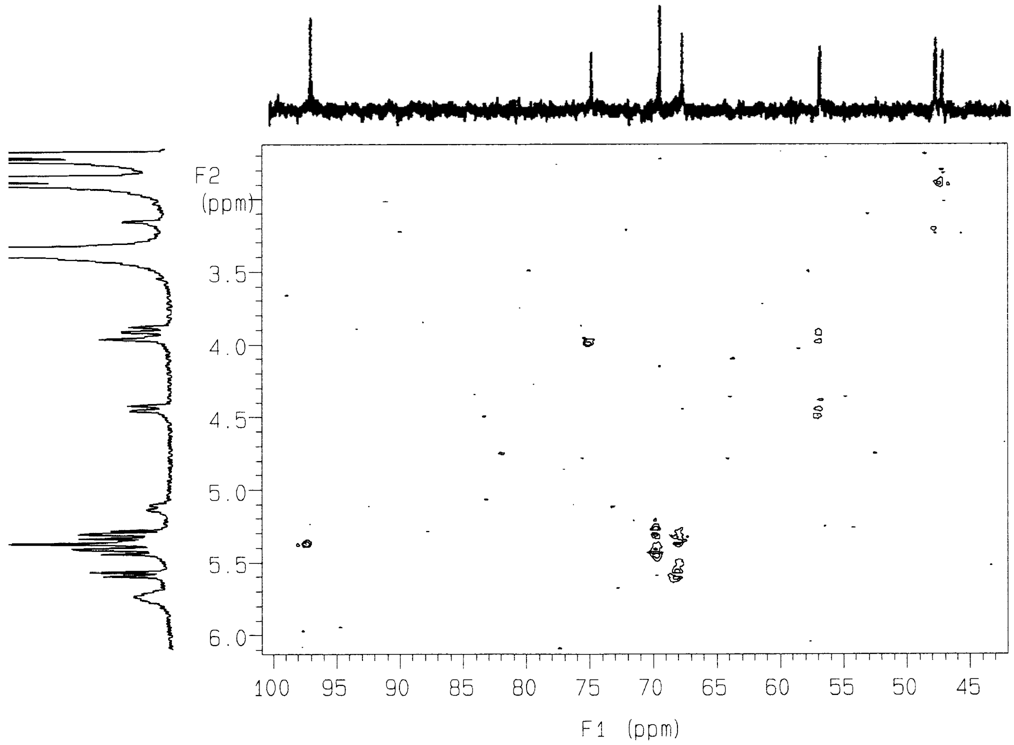

Figure S31. HMQC spectrum of **1-Pt** in DMF-d_7.

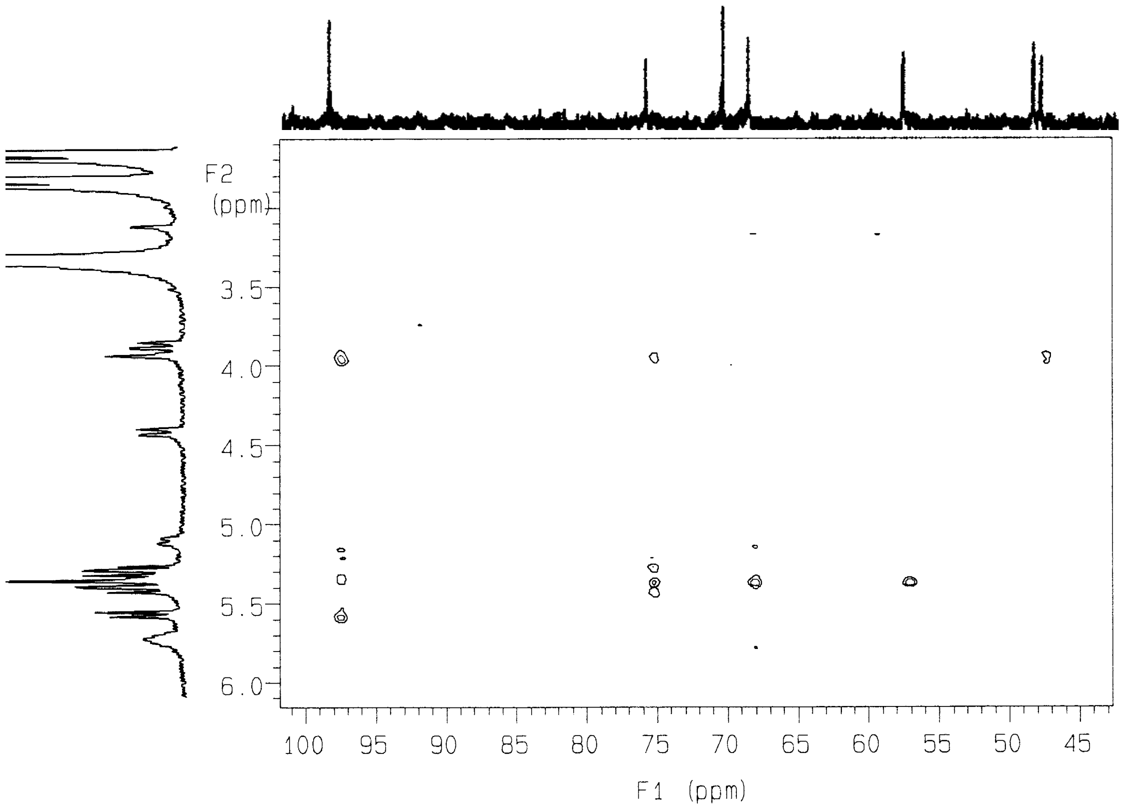

Figure S32. HMBC spectrum of **1-Pt** in DMF-d_7.