

Supporting Information

Oligopyridine Ligands Derived from Amino Acid Precursors: Their Zn²⁺ Complexation and Effects on Hepatic Stellate Cell Functions

Hiroshi Tsukube,^{*a} Yuki Noda,^a Yumiko Kataoka,^a Hiroyuki Miyake,^a Satoshi Shinoda,^a Akiko Kojima-Yuasa,^{*b} Yoshitake Nishida,^b and Isao Matsui-Yuasa^b

^a *Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan. Fax: +81-6-6605-2560; Tel: +81-6-6605-2560; E-mail: tsukube@sci.osaka-cu.ac.jp*

^b *Department of Food and Human Health Sciences, Graduate School of Human Life Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan Fax: +81-6-6605-2810; Tel: +81-6-6605-2865; E-mail: kojima@life.osaka-cu.ac.jp*

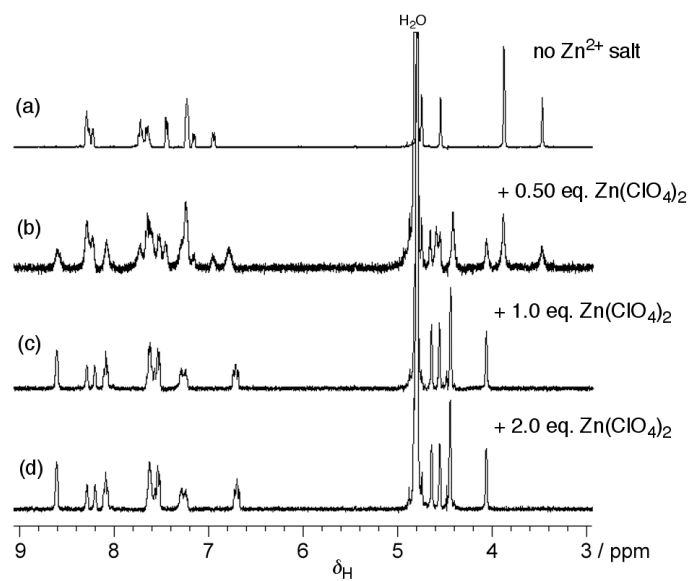


Fig. S1 ^1H NMR spectral changes of ligand **3a** upon Zn^{2+} complexation.

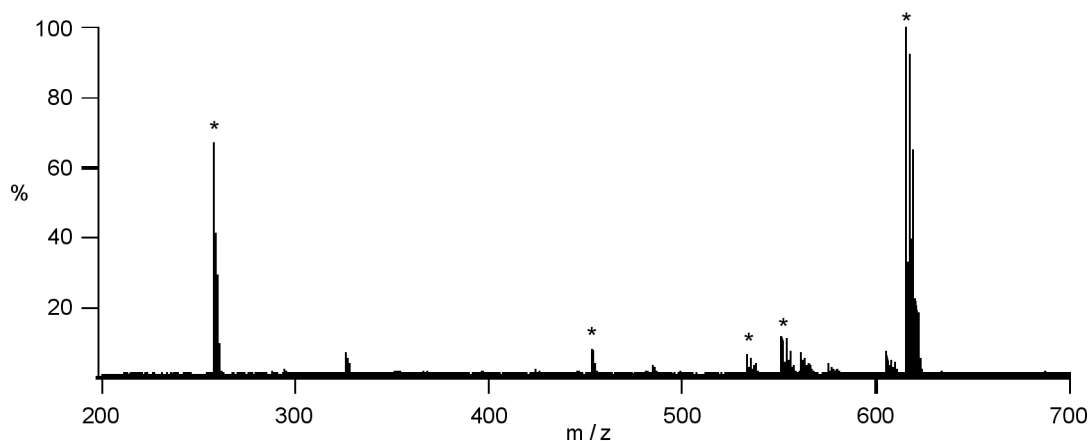


Fig. S2. ESI-MS spectrum of an equimolar mixture of **3b** and $\text{Zn}(\text{ClO}_4)_2$ in H_2O . $[\mathbf{3b}] = [\text{Zn}^{2+}] = 2.2 \times 10^{-4}$ mol/L.

$[\mathbf{3b} + \text{Zn}^{2+}]^{2+}$: $m/z = 258.2$; $[\mathbf{3b} + \text{H}^+]^+$: $m/z = 453.4$; $[\mathbf{3b} + \text{Zn}^{2+} + \text{OH}^-]^+$: $m/z = 533.2$;

$[\mathbf{3b} + \text{Zn}^{2+} + \text{OH}^- + \text{H}_2\text{O}]^+$: $m/z = 551.3$; $[\mathbf{3b} + \text{Zn}^{2+} + \text{ClO}_4^-]^+$: $m/z = 615.3$.

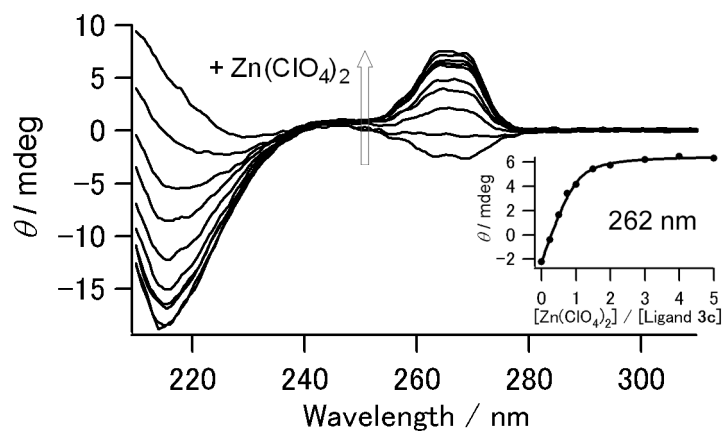


Fig. S3. CD spectral changes and titration curve for $\log K'$ determination of **3c**- $\text{Zn}(\text{ClO}_4)_2$ complex in aqueous solutions. $[\mathbf{3c}] = 4.0 \times 10^{-5}$ mol/L.

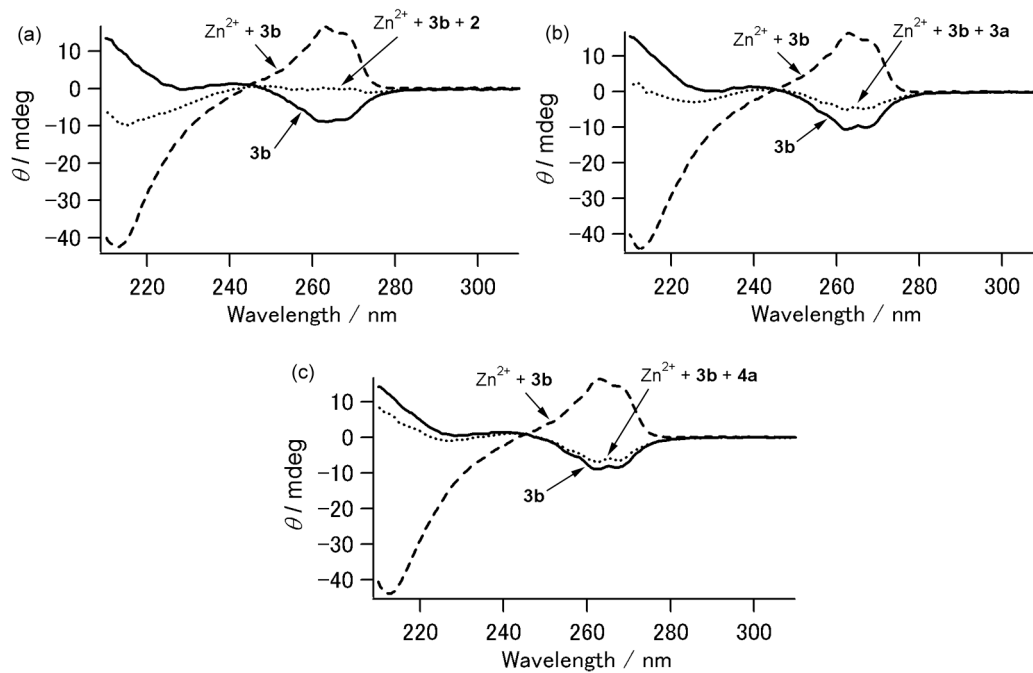


Fig. S4. Competitive $\text{Zn}(\text{ClO}_4)_2$ complexation experiments of ligands **2**, **3a** and **4a** with chiral ligand **3b** in H_2O . (—): $[\mathbf{3b}] = 6.0 \times 10^{-5} \text{ mol/L}$, ($\cdot \cdot \cdot$): $[\mathbf{3b}] = [\mathbf{2}, \mathbf{3a}, \text{ or } \mathbf{4a}] = [\text{Zn}^{2+}] = 6.0 \times 10^{-5} \text{ mol/L}$, (---): $[\mathbf{3b}] = 6.0 \times 10^{-5} \text{ mol/L}$, $[\text{Zn}^{2+}] = 1.8 \times 10^{-4} \text{ mol/L}$.

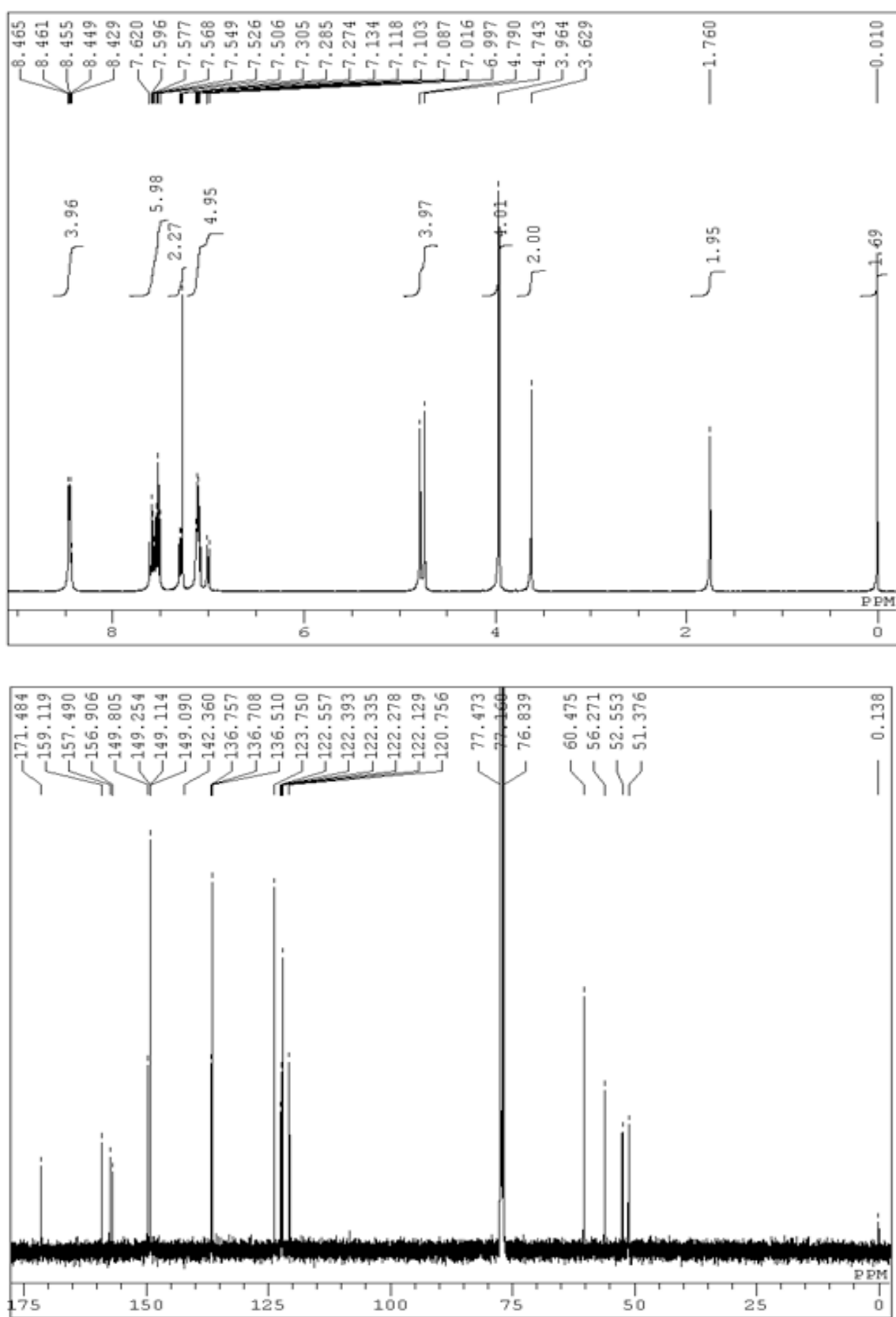


Fig. S5. ^1H and ^{13}C NMR spectra of ligand 3a.

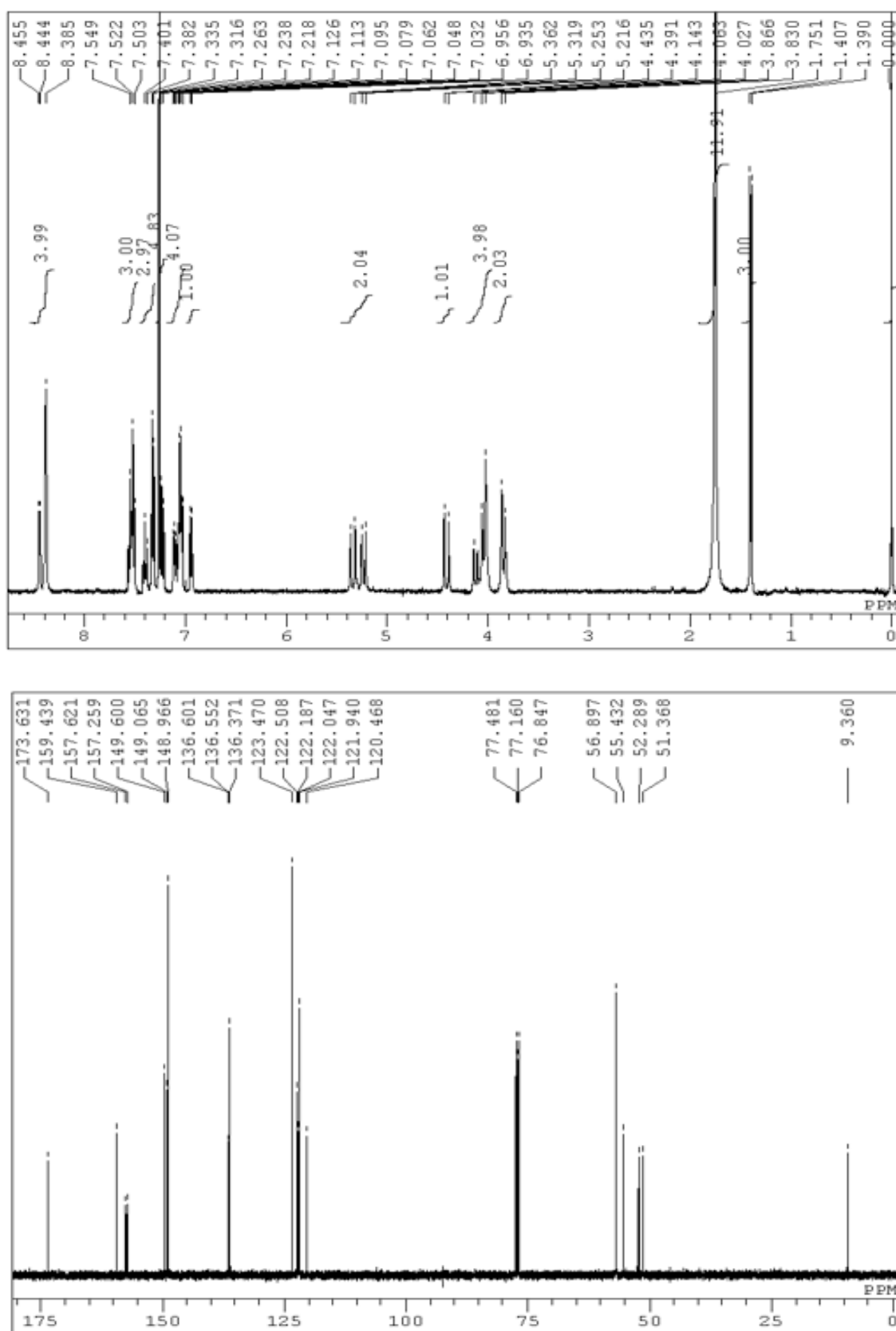


Fig. S6. ^1H and ^{13}C NMR spectra of ligand **3b**.

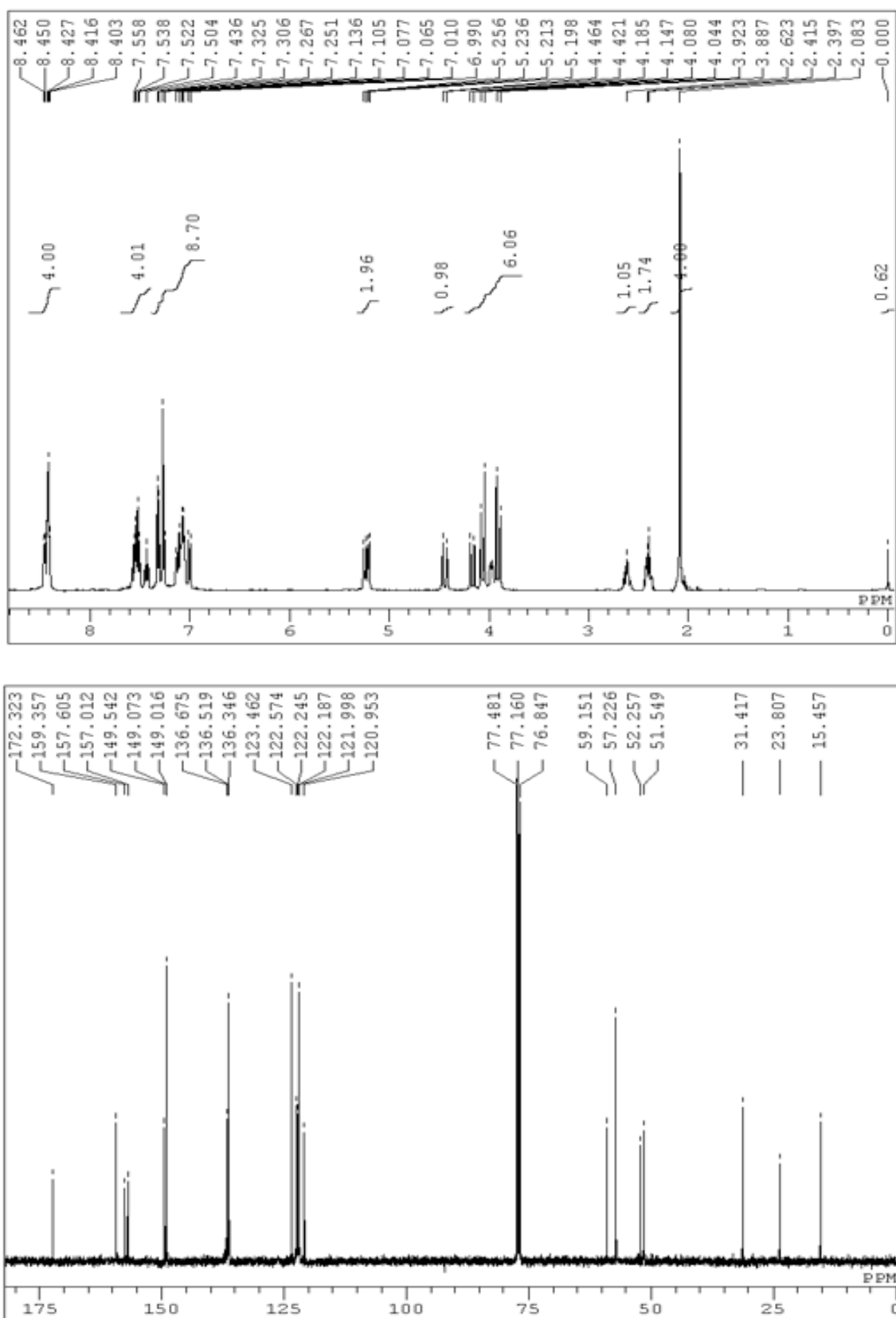


Fig. S7. ^1H and ^{13}C NMR spectra of ligand 3c.

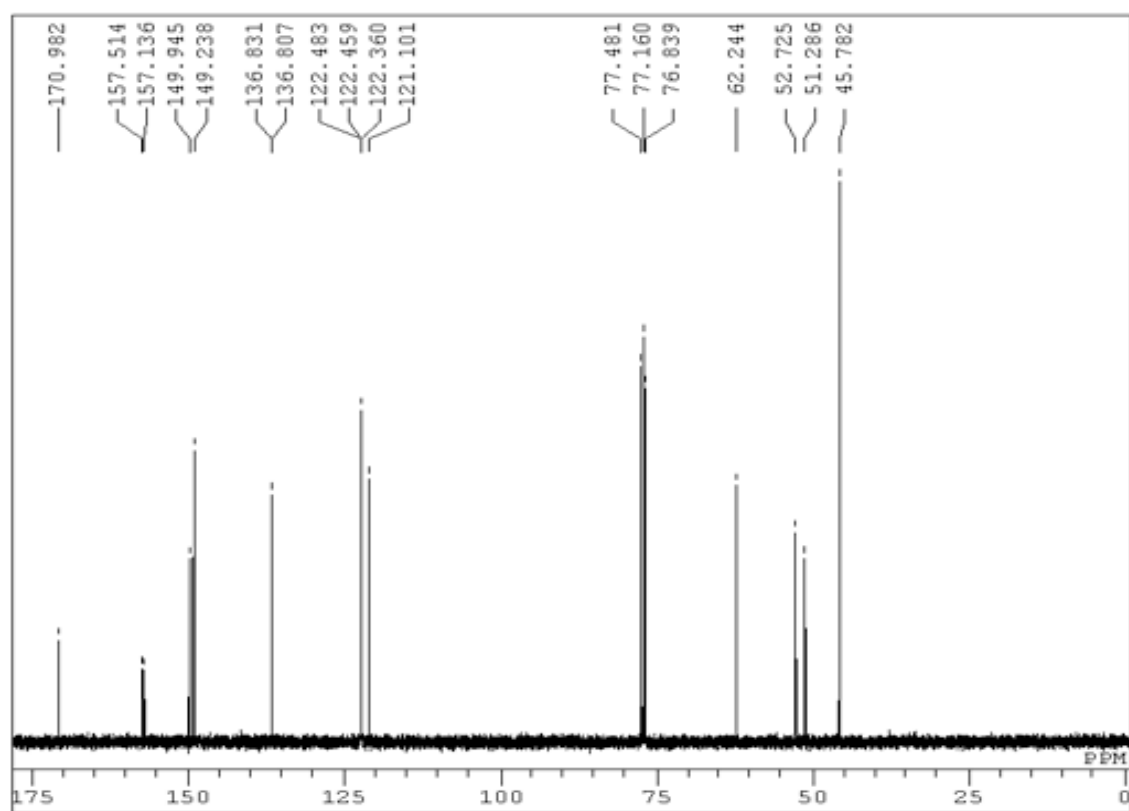
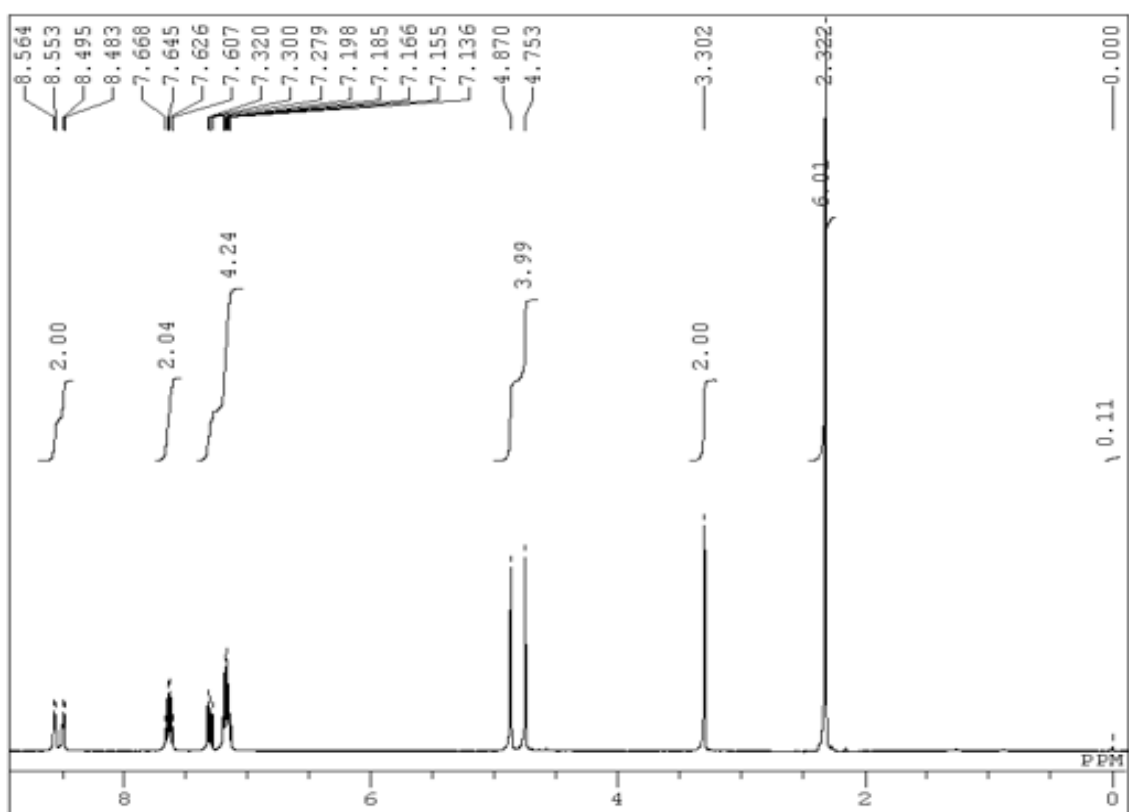


Fig. S8. ¹H and ¹³C NMR spectra of ligand 4b.