

Electronic supplementary information

**Synthesis of aluminum complexes supported by
2-(1,10-phenanthrolin-2-yl)phenolate ligands and their catalysis in
the ring-opening polymerization of cyclic esters**

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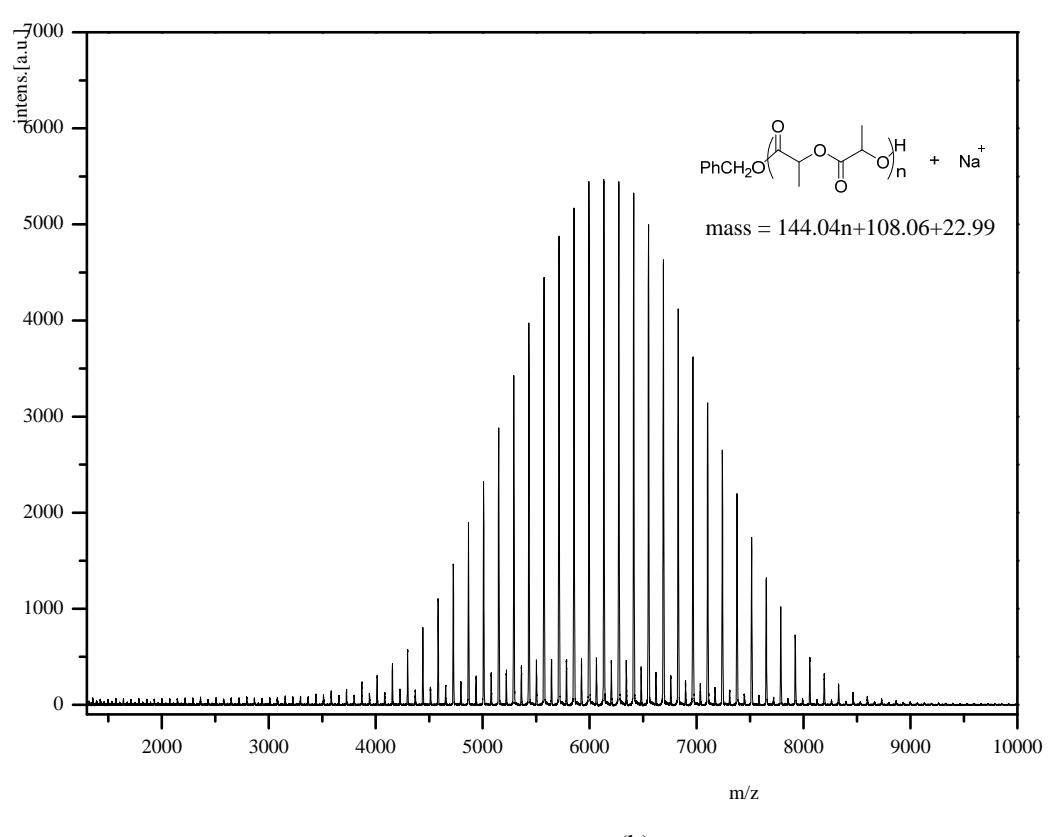
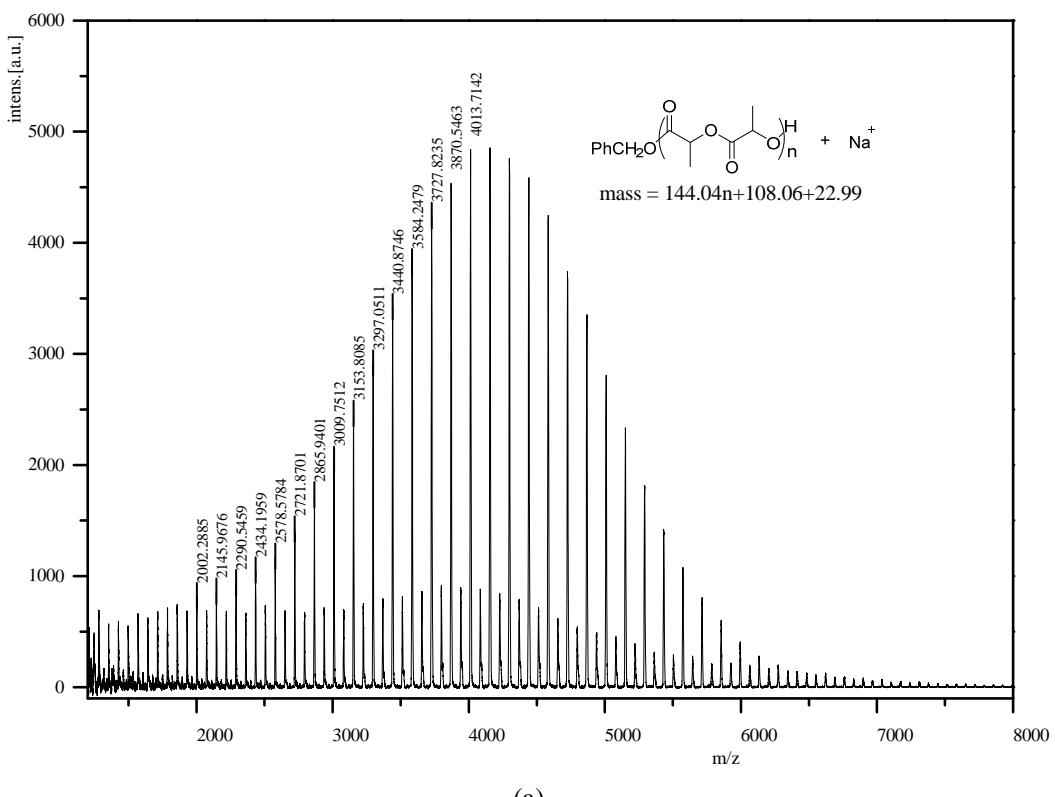


Figure S1. MALDI-TOF mass spectrum (matrix: DCTB) of PLA catalyzed by **2b**/BnOH (a, Table 2, entry 7) and **2f** (b, Table 2, entry 12).

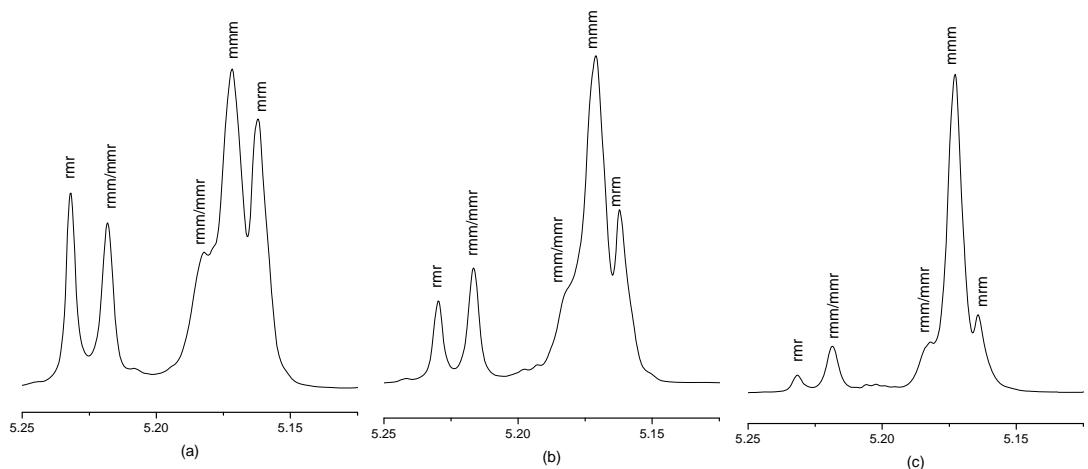


Figure S2. Homonuclear decoupled ¹H NMR spectra (CDCl₃, 25°C) of the methine range of PLA obtained from *rac*-LA, (a) (Table 2, entry 1) $P_m = 0.48$; (b) (Table 2, entry 3) $P_m = 0.62$; (c) (Table 2, entry 14) $P_m = 0.77$.

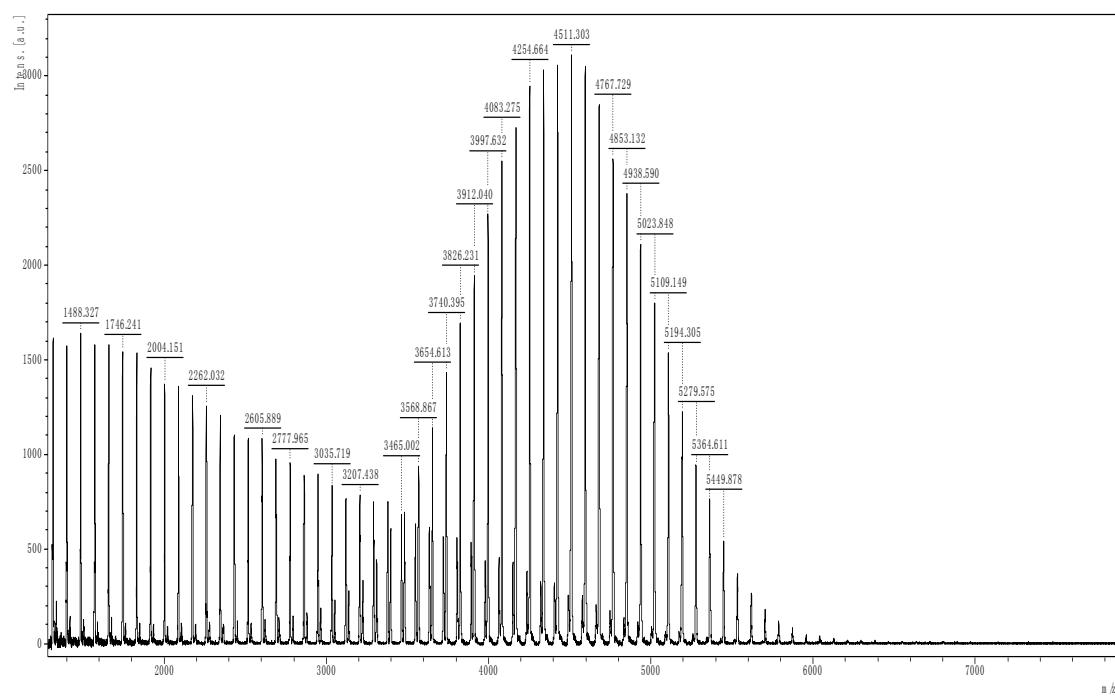


Figure S3. MALDI-TOF mass spectrum (matrix: DCTB) of the polymer isolated from *rac*- β -BL polymerization (Table 3, entry 3).

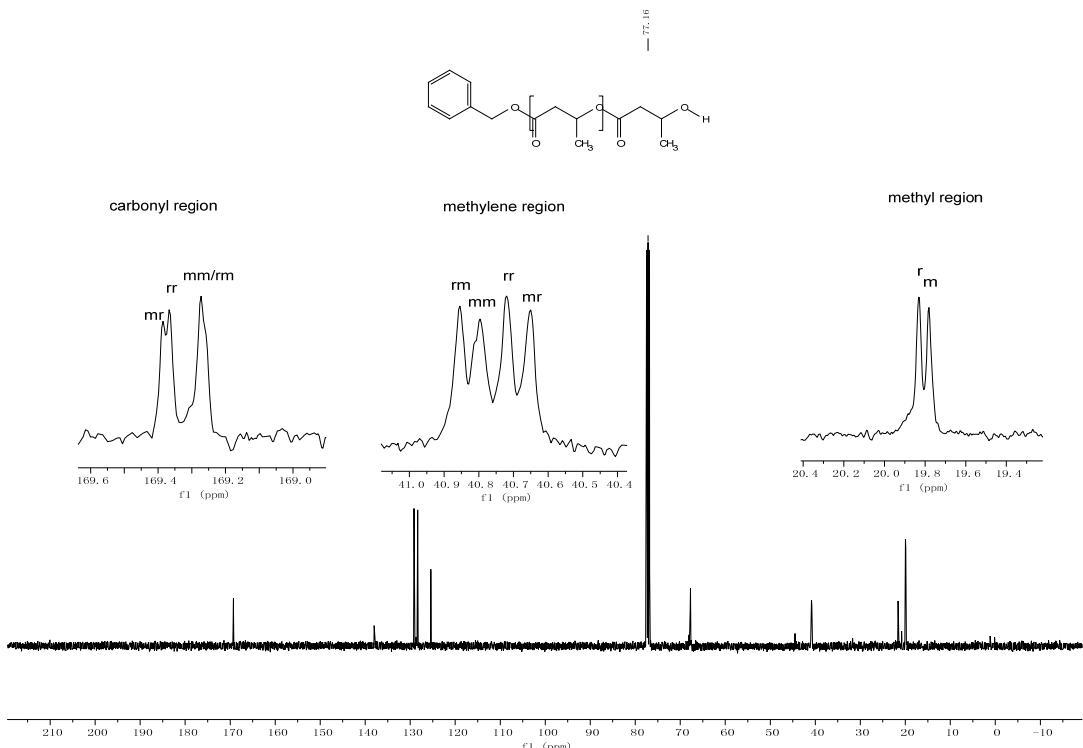


Figure S4. ^{13}C NMR spectrum (CDCl_3 , 101 MHz, 25 °C) of PHB.

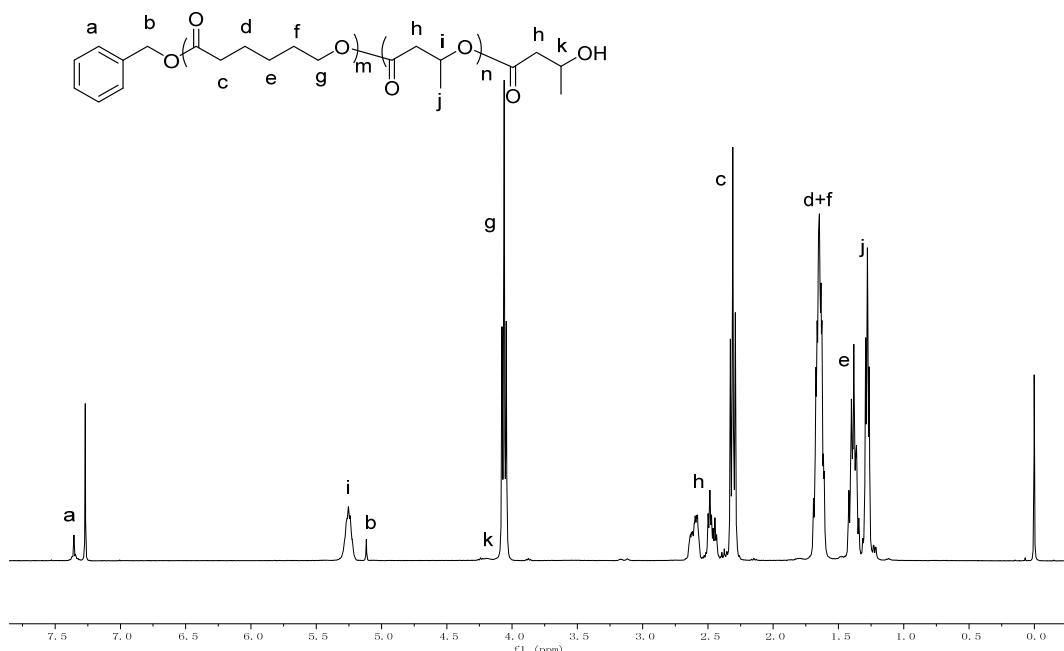


Figure S5. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of the PCL-b-PHB copolymer.

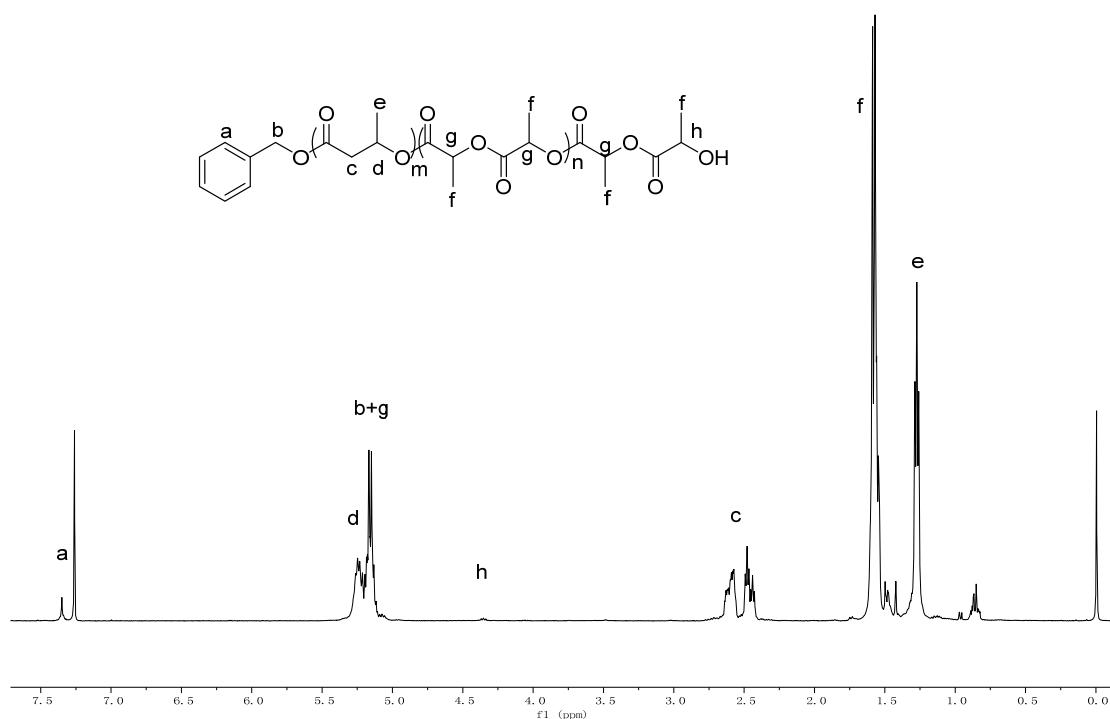


Figure S6. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of PHB-b-PLA

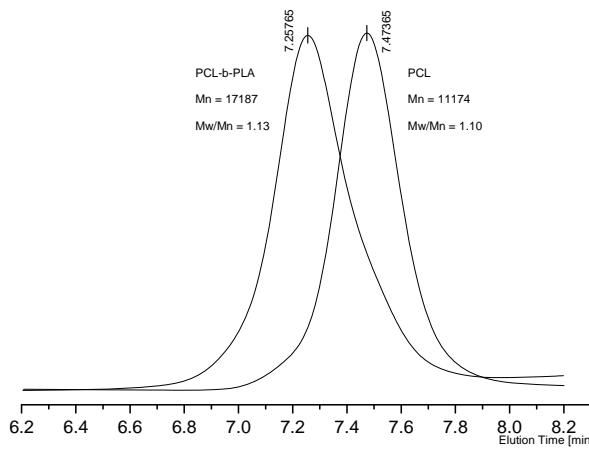


Figure S7. The GPC curves of PCL and PCL-b-PLA copolymer catalyzed by **2f**. Conditions: $[\text{Cat.}]_0$: $[\varepsilon\text{-CL}]_0$: $[\text{rac-LA}]_0$ = 1:100:100; $[\text{Cat.}]_0$ = 0.01 mol/L; solvent: toluene. When $\varepsilon\text{-CL}$ monomer conversion approached to 99%, a 1/8 volume of sample was taken from the polymerization system for GPC test and rac-LA monomer was sequentially added into the reaction system to generate the block copolymer of PCL-b-PLA with 84.7% rac-LA conversion.

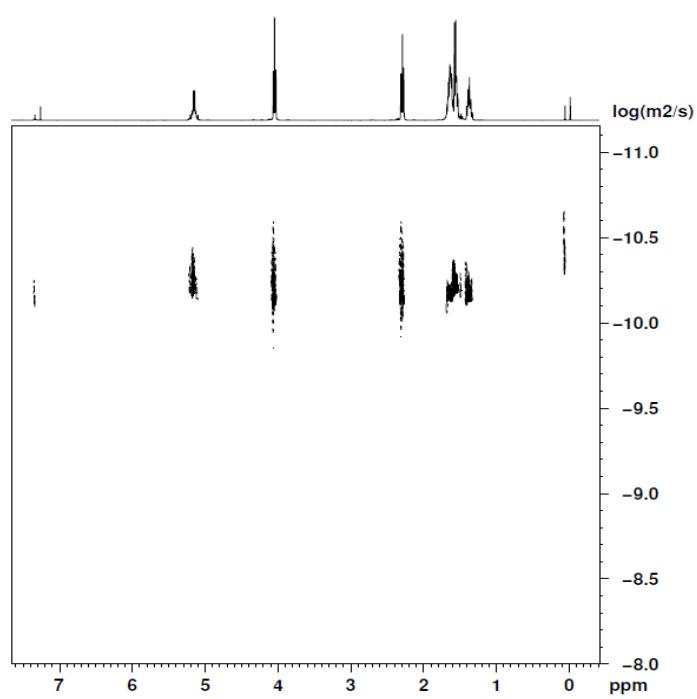


Figure S8. 2D DOSY NMR (CDCl_3 , 25 °C) of PCL-b-PLA.

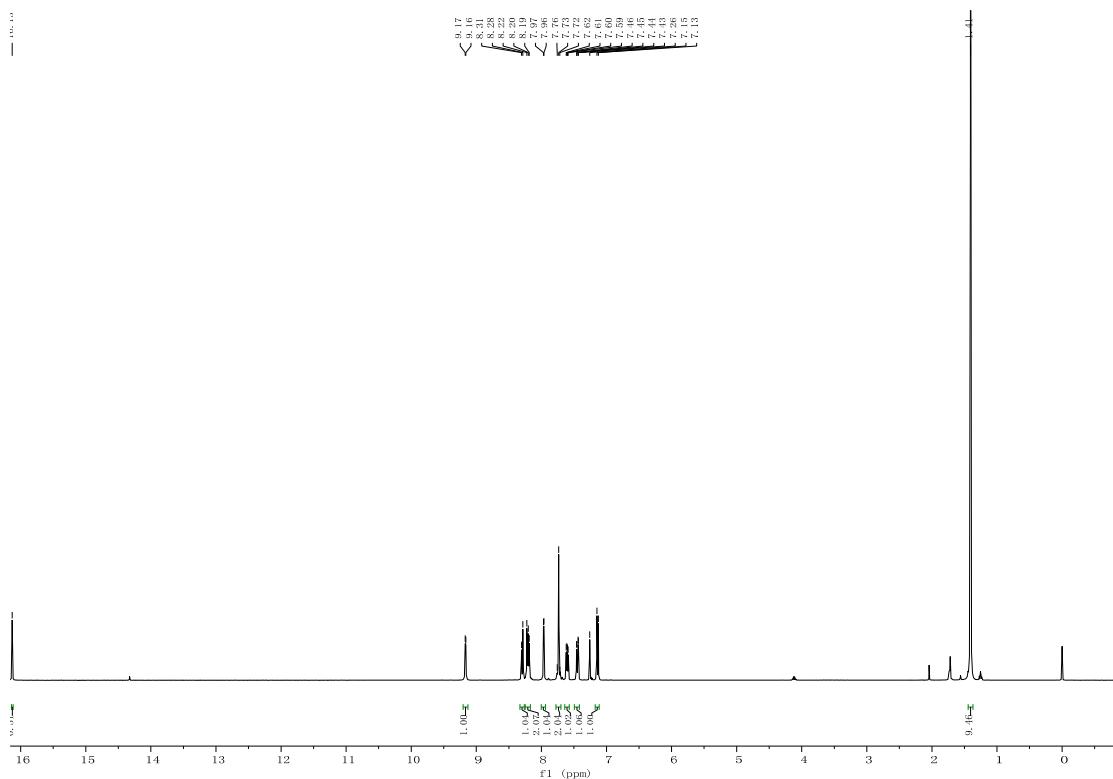


Figure S9. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of complex **1a**.

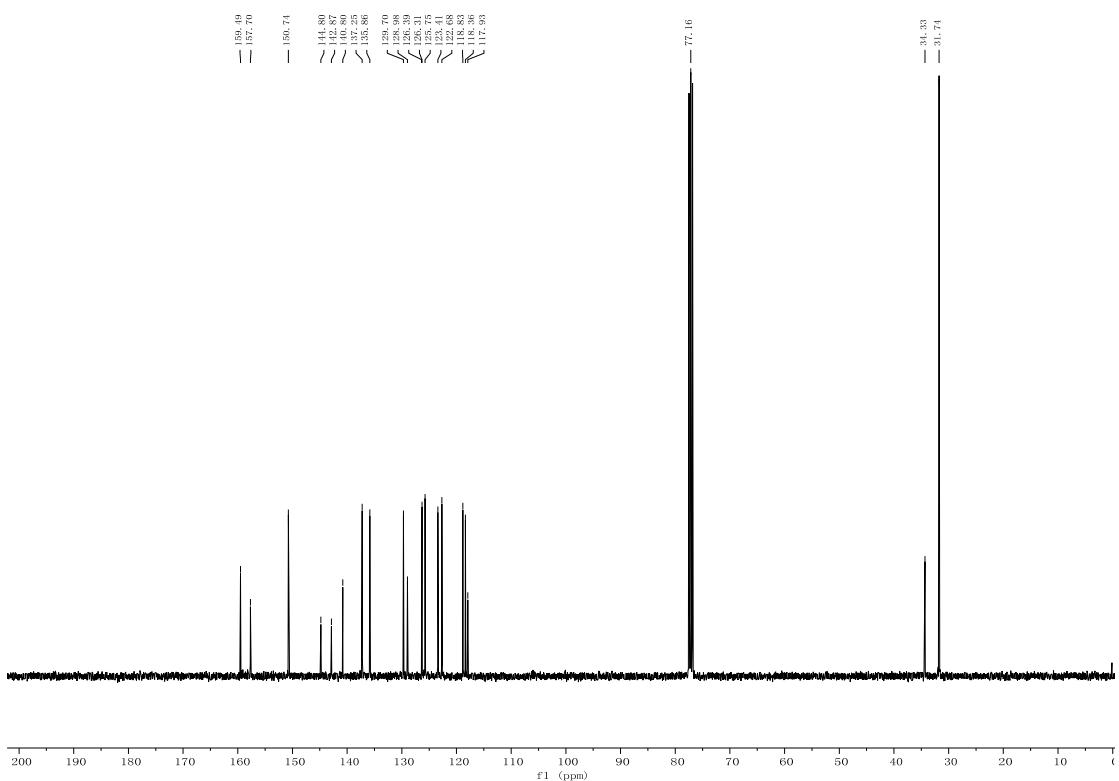


Figure S10. ¹³C NMR spectrum (CDCl₃, 101 MHz, 25 °C) of complex **1a**.

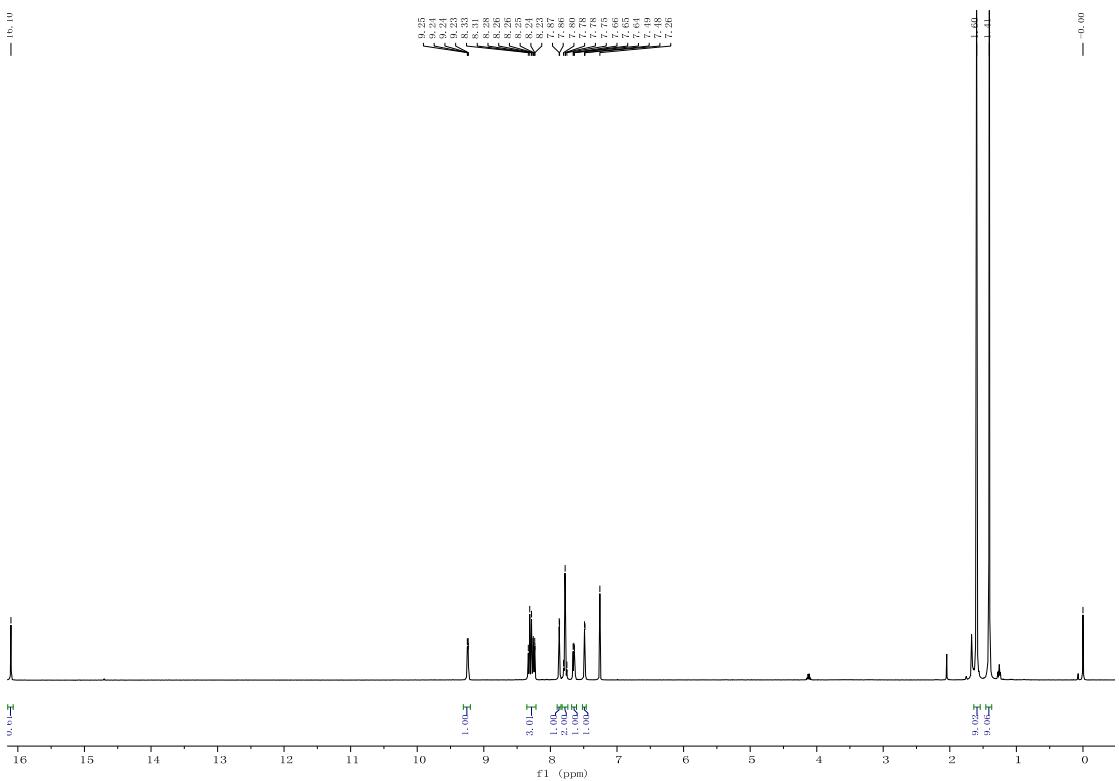


Figure S11. ¹H NMR spectrum (CDCl₃, 400 MHz, 25 °C) of complex **1b**.

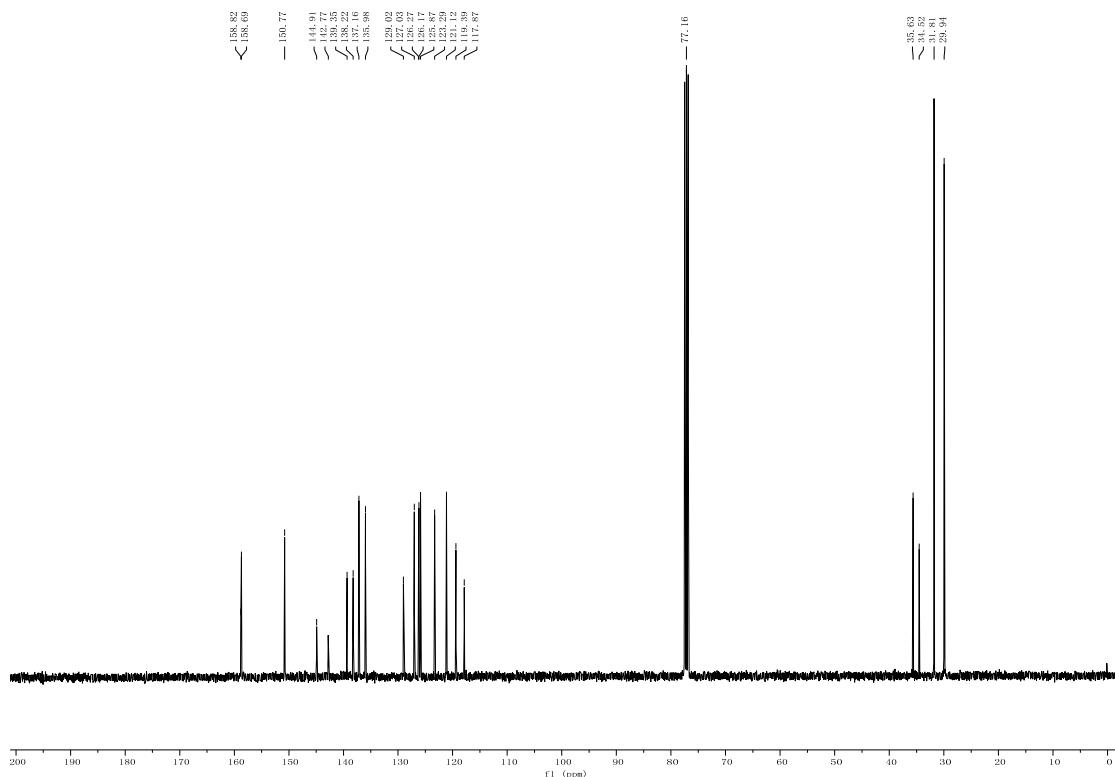


Figure S12. ^{13}C NMR spectrum (CDCl_3 , 101 MHz, 25 °C) of complex **1b**.

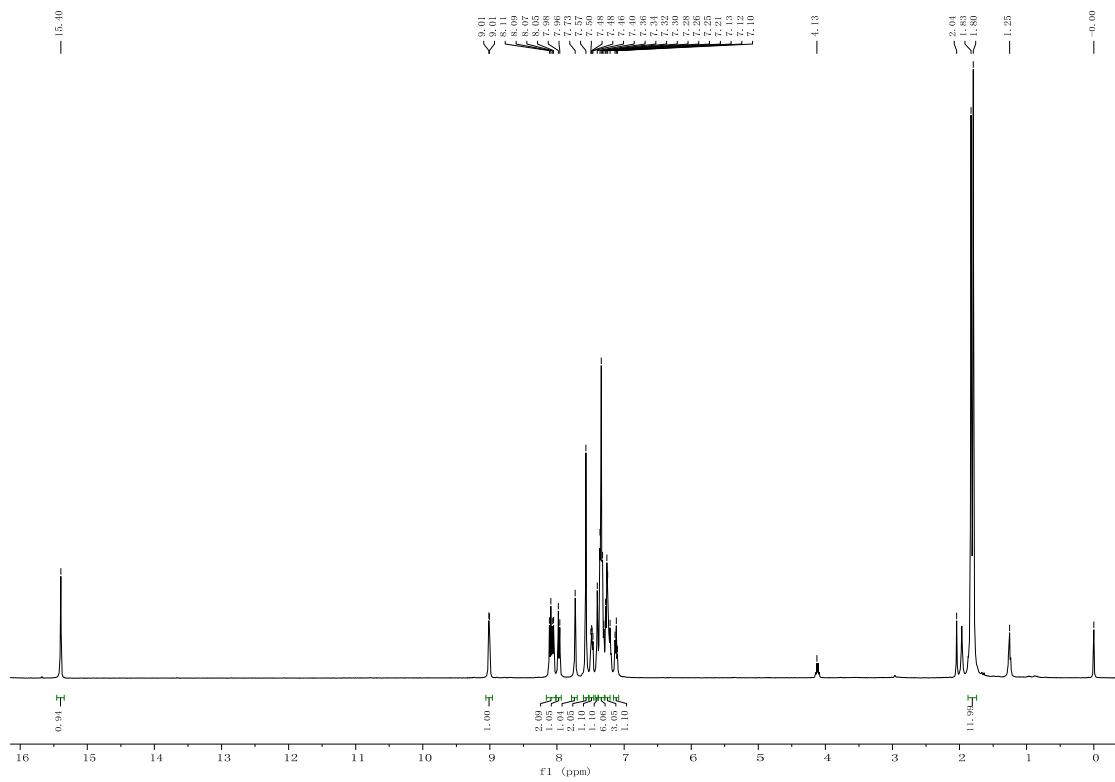


Figure S13. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of complex **1c**.

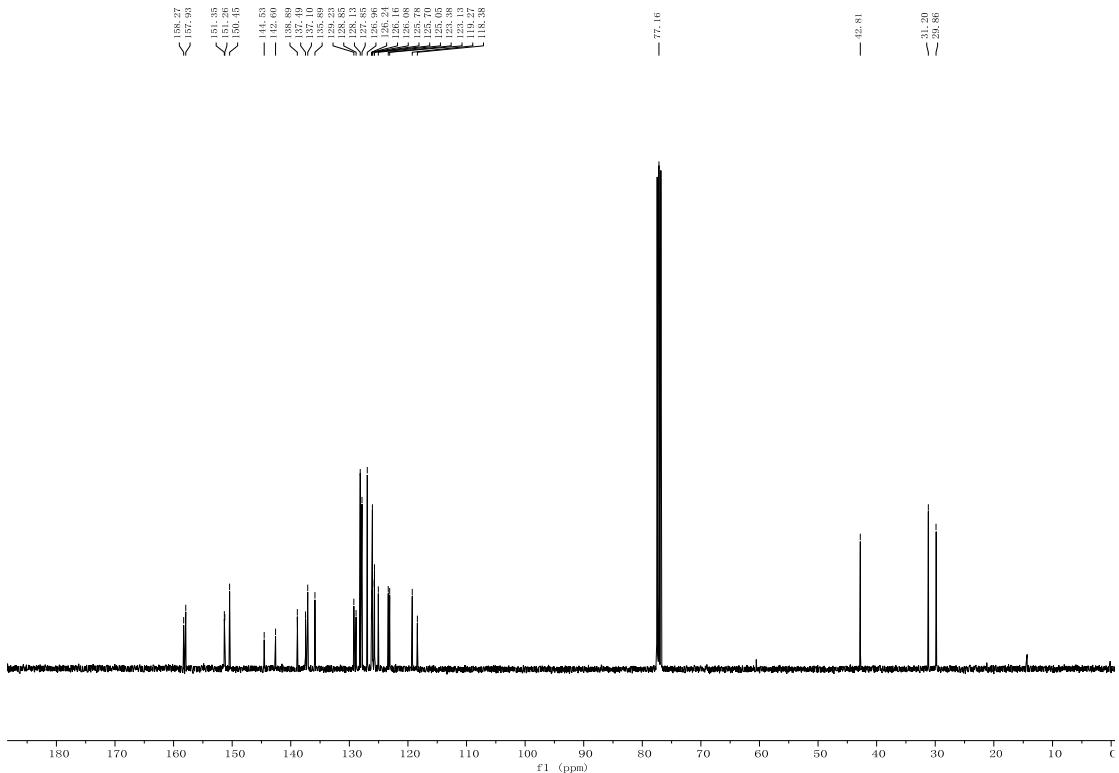


Figure S14. ^{13}C NMR spectrum (CDCl_3 , 101 MHz, 25 °C) of complex **1c**.

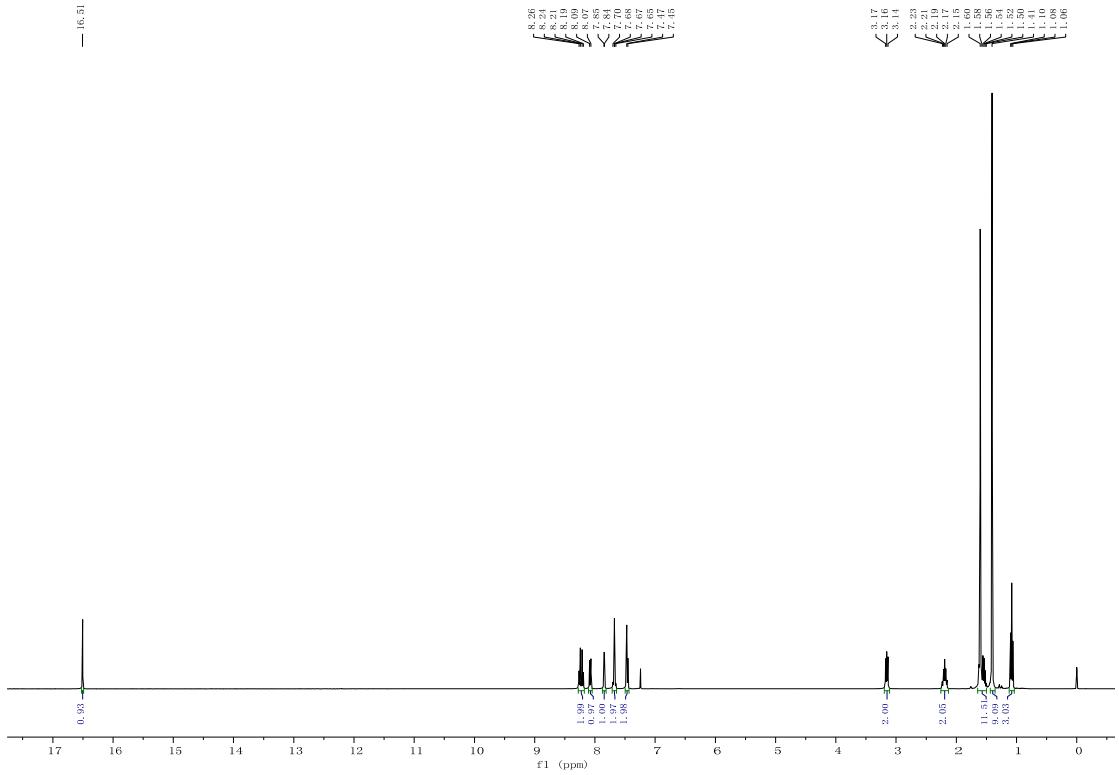


Figure S15. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of complex **1d**.

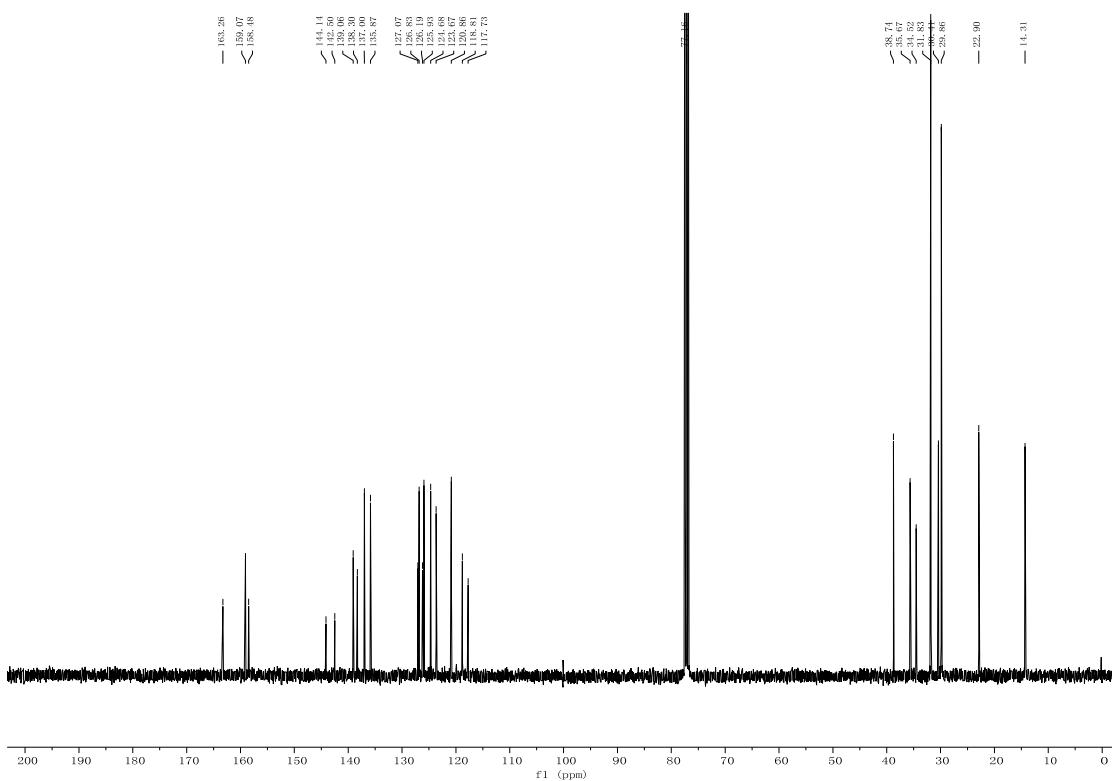


Figure S16. ^{13}C NMR spectrum (CDCl_3 , 101 MHz, 25 °C) of complex **1d**.

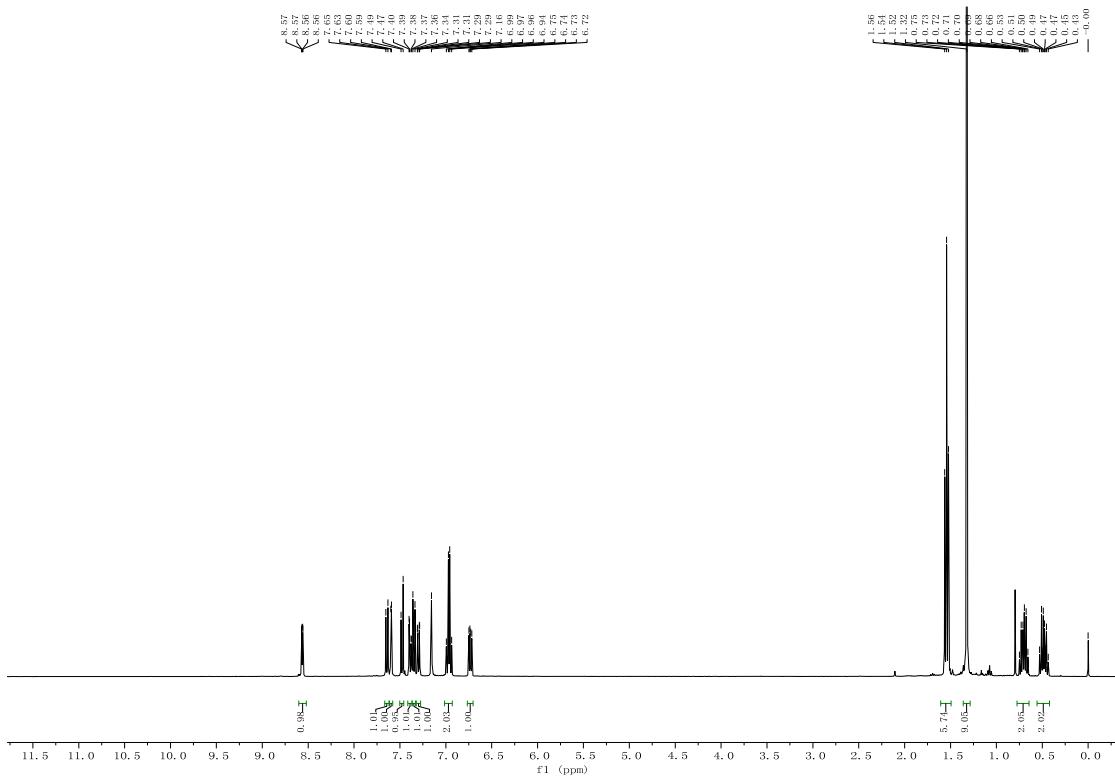


Figure S17. ^1H NMR spectrum (C_6D_6 , 400 MHz, 25 °C) of complex **2a**.

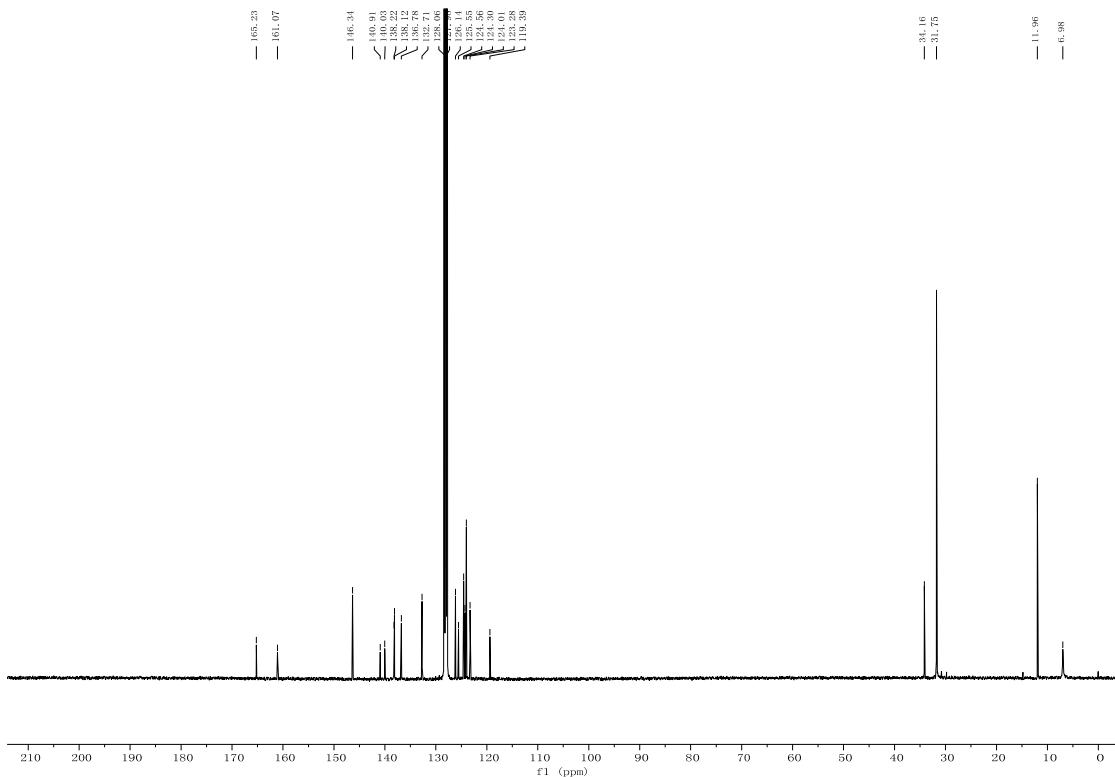


Figure S18. ^{13}C NMR spectrum (C_6D_6 , 101 MHz, 25 °C) of complex **2a**.

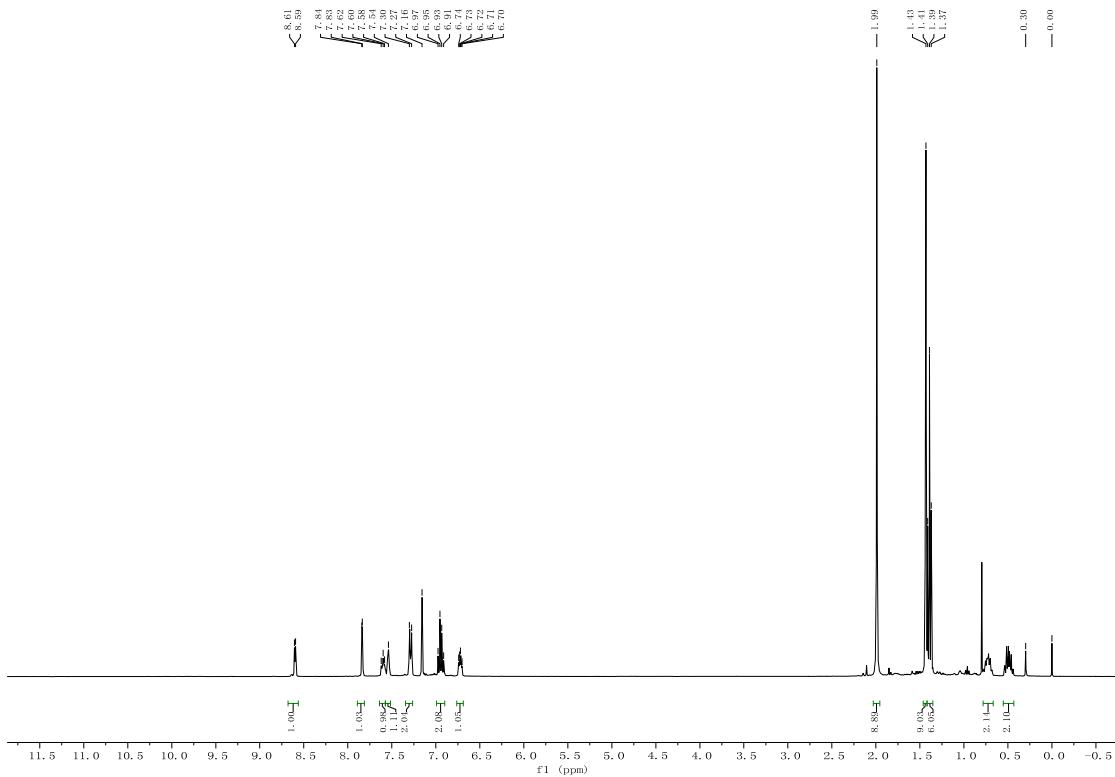


Figure S19. ^1H NMR spectrum (C_6D_6 , 400 MHz, 25 °C) of complex **2b**.

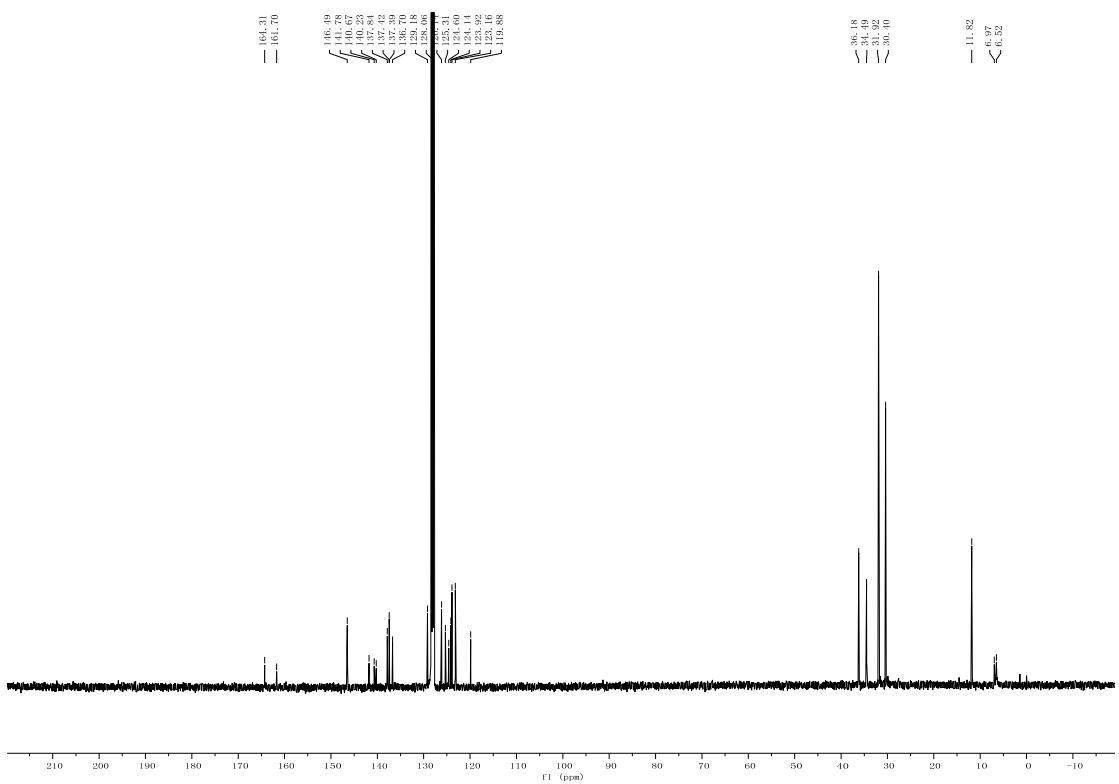


Figure S20. ^{13}C NMR spectrum (C_6D_6 , 101 MHz, 25 °C) of complex **2b**.

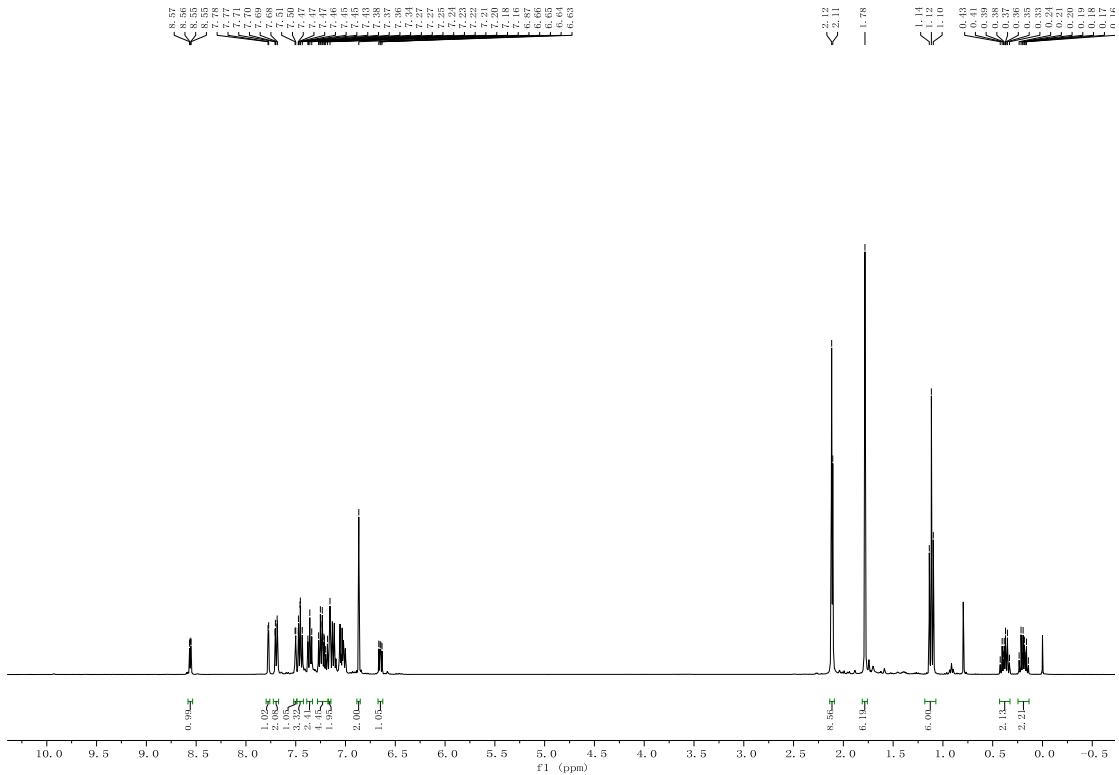


Figure S21. ^1H NMR spectrum (C_6D_6 , 400 MHz, 25 °C) of complex **2c**.

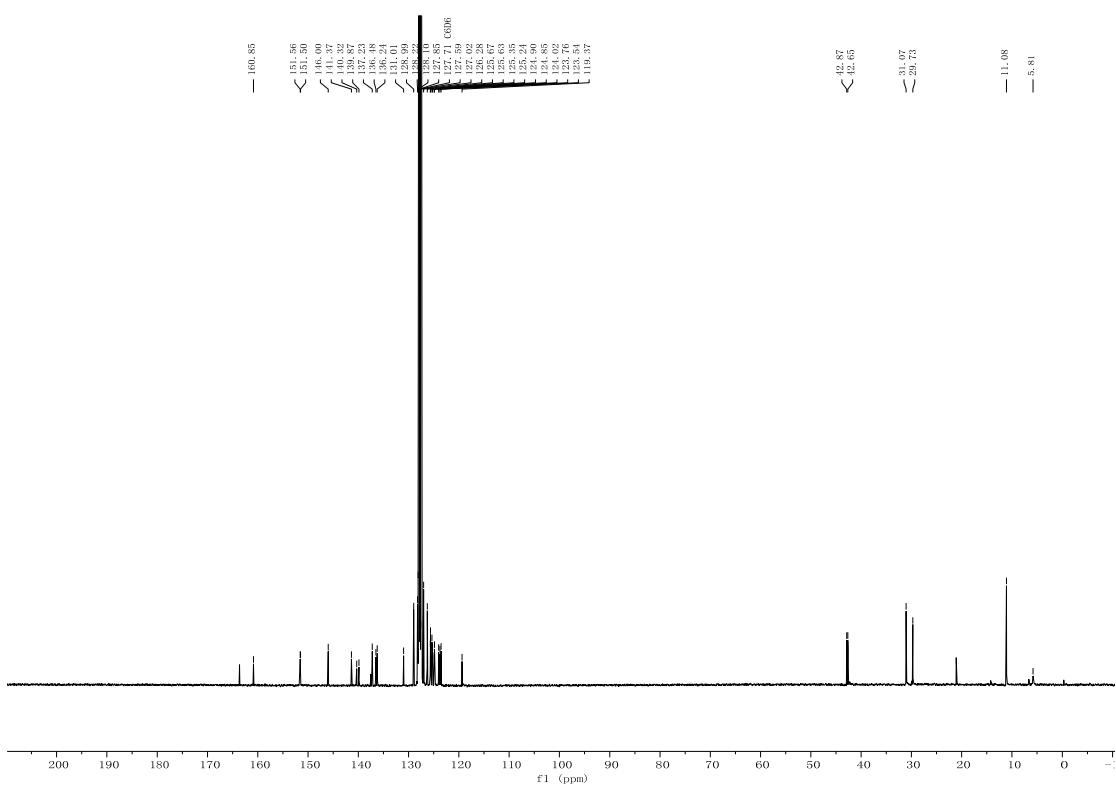


Figure S22. ^{13}C NMR spectrum (C_6D_6 , 101 MHz, 25 °C) of complex **2c**.

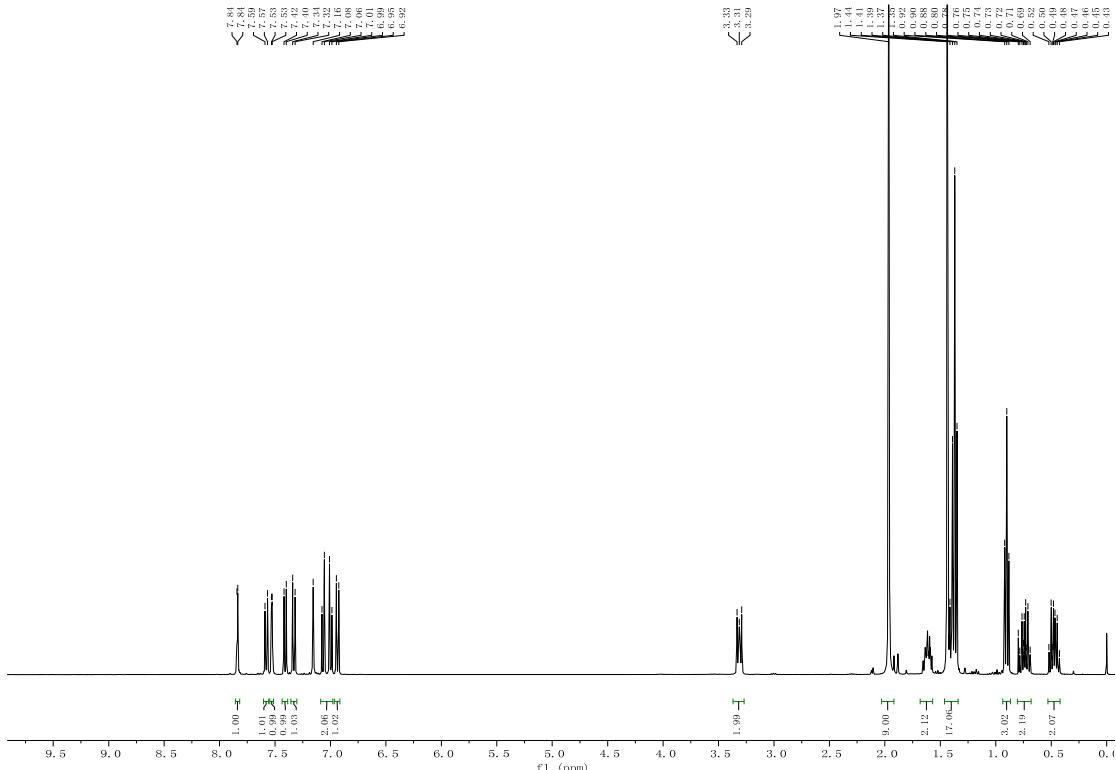


Figure S23. ^1H NMR spectrum (C_6D_6 , 400 MHz, 25 °C) of complex **2d**.

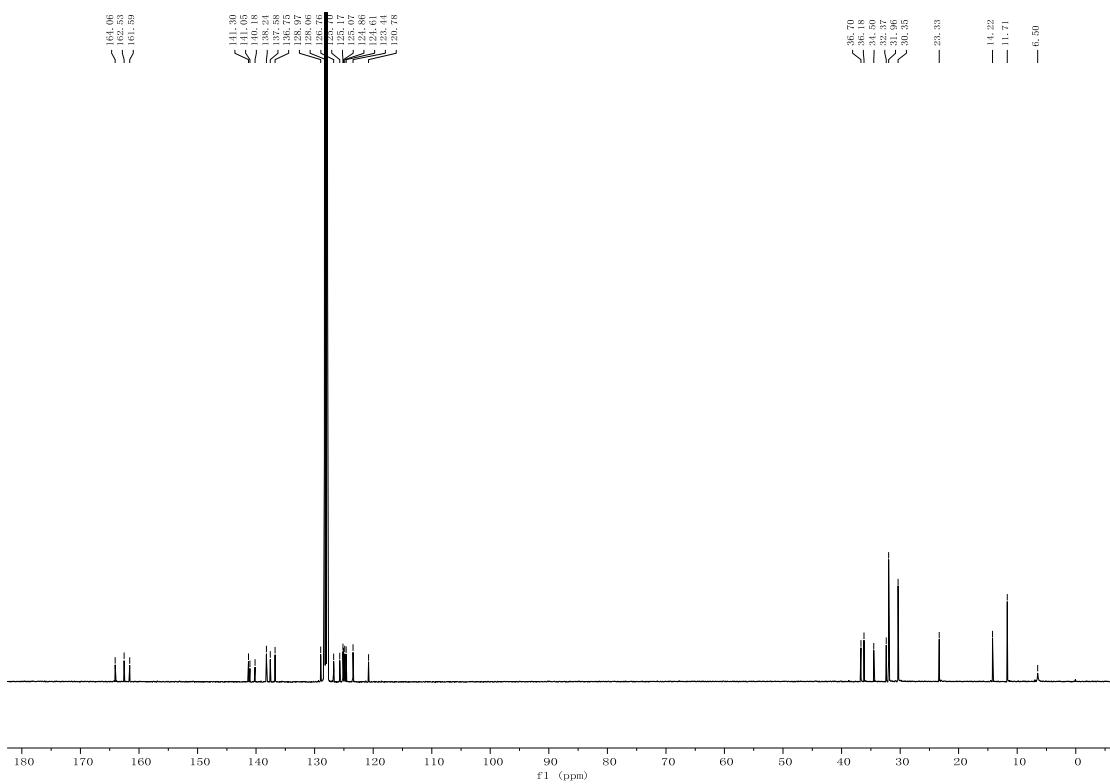


Figure S24. ^{13}C NMR spectrum (C_6D_6 , 101 MHz, 25 °C) of complex **2d**.

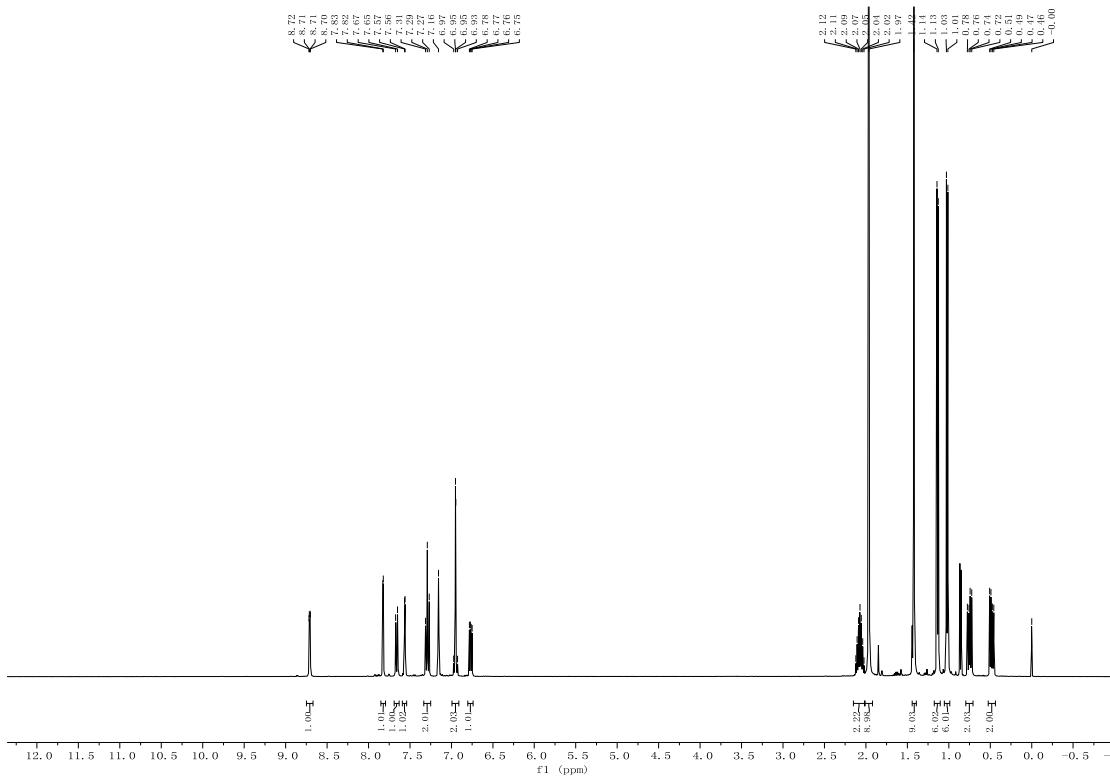


Figure S25. ^1H NMR spectrum (C_6D_6 , 400 MHz, 25 °C) of complex **2e**.

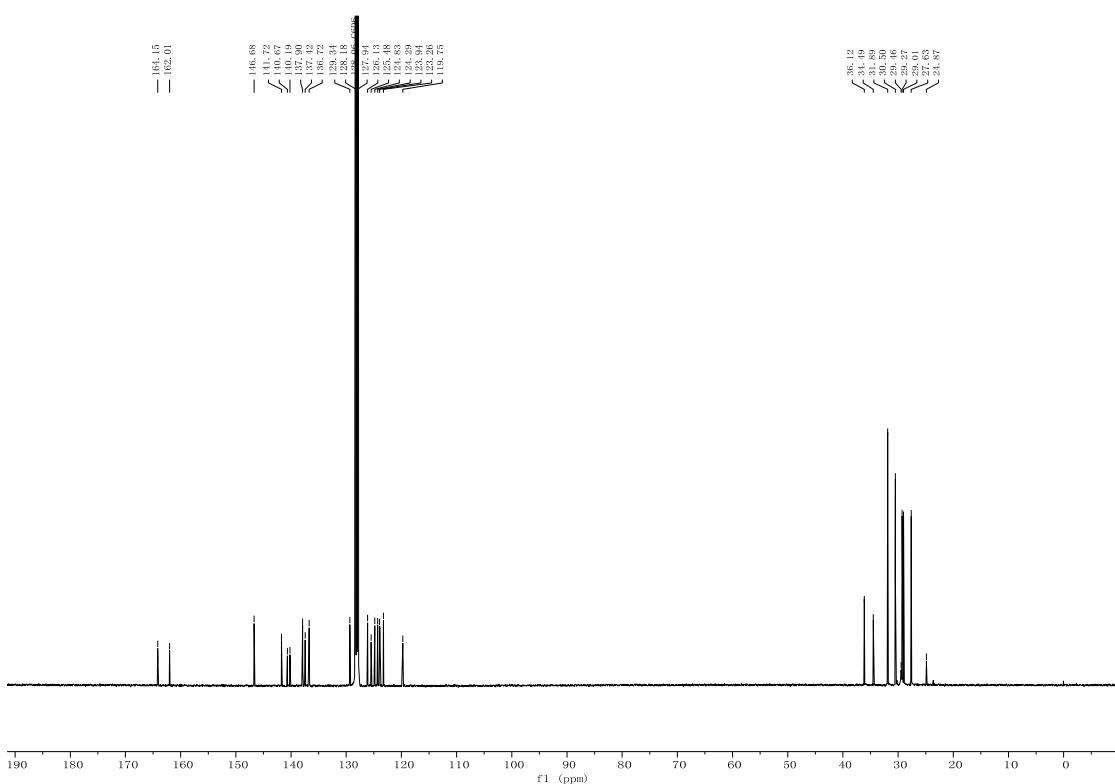


Figure S26. ^{13}C NMR spectrum (C_6D_6 , 101 MHz, 25 °C) of complex **2e**.

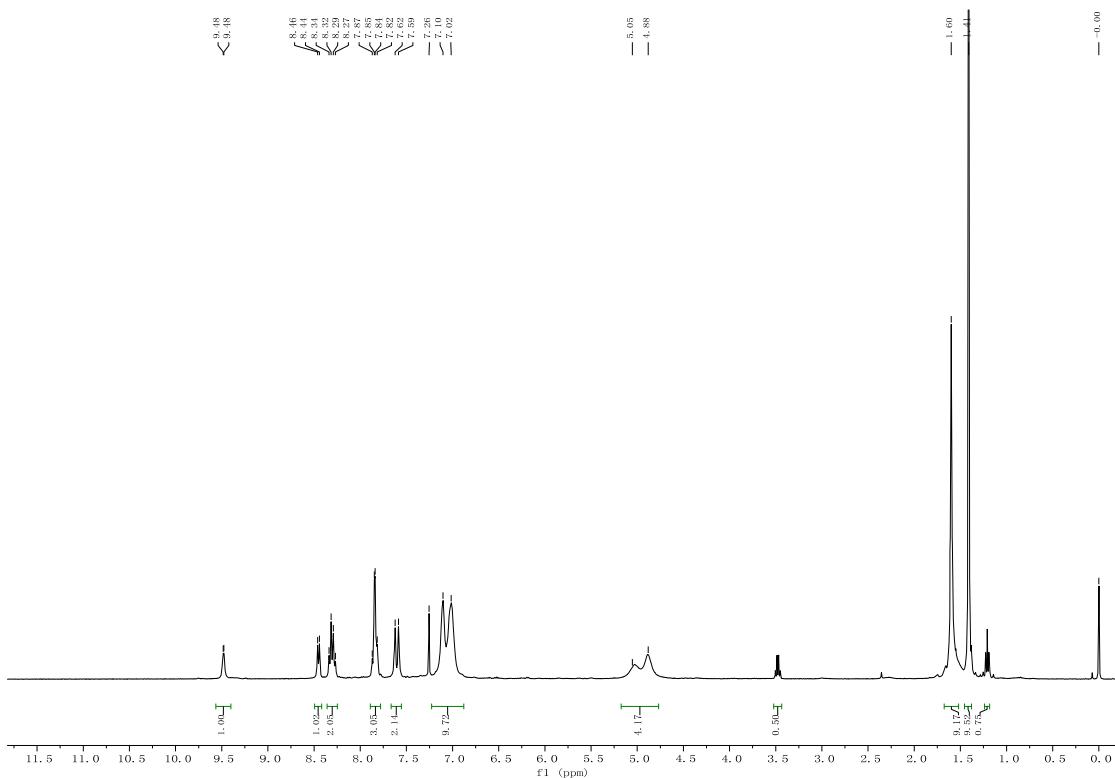


Figure S27. ^1H NMR spectrum (CDCl_3 , 400 MHz, 25 °C) of complex **2f**.

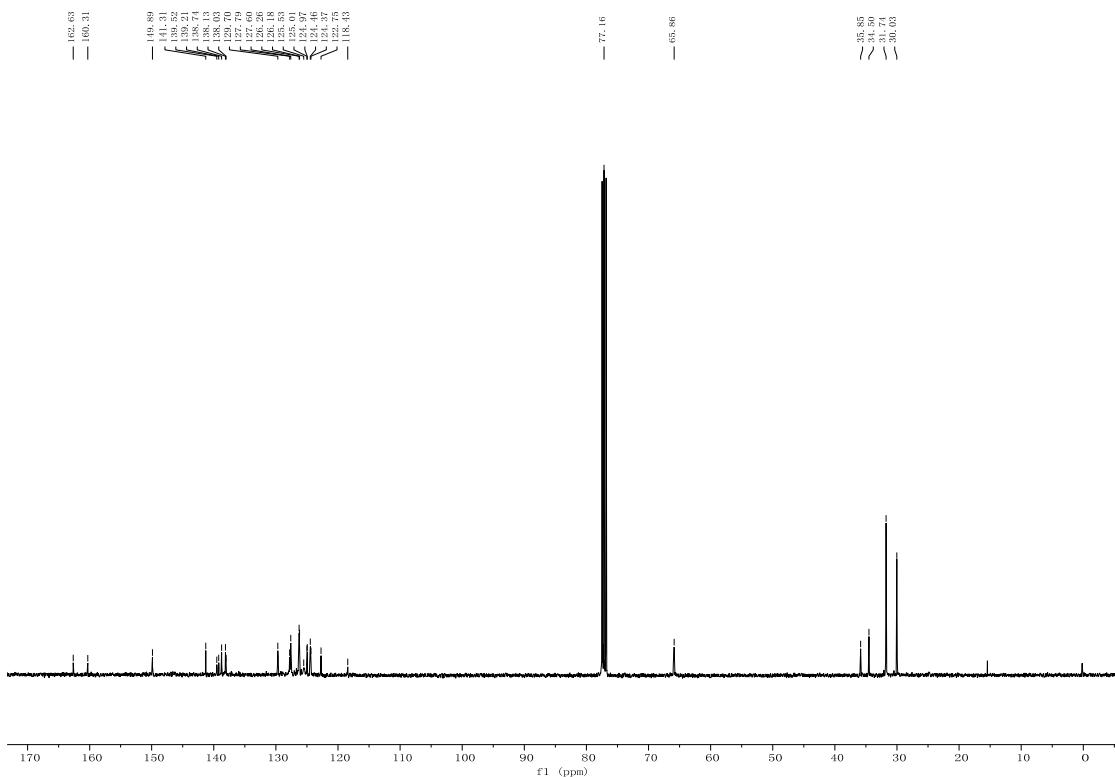


Figure S28. ^{13}C NMR spectrum (CDCl_3 , 101 MHz, 25 °C) of complex **2f**.