

Supporting Information

Mn(OAc)₃-Promoted Oxidative C_{sp3}-P Bond Formation through C_{sp2}-C_{sp2} and P-H Bond Cleavage: Access to β -Ketophosphonates.

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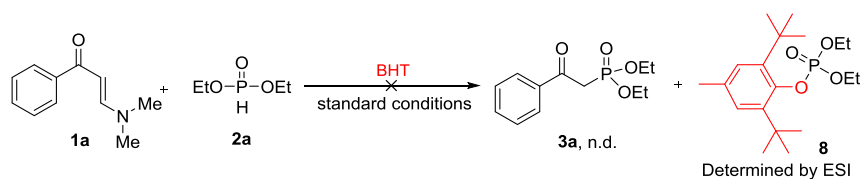
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1. Control Experiments.

1.1 Trapping and detecting the intermediate.



Scheme S1 BHT-radical scavenging experiment.

N,N-Dimethylenaminone **1a** (0.1 mmol, 1.0 equiv), H-phosphonate **2a** (0.2 mmol, 2.0 equiv), butylated hydroxytoluene (BHT, 0.3 mmol, 3.0 equiv), $\text{Mn}(\text{OAc})_3$ (0.3 mmol, 3.0 equiv), AcOH (0.2 ml) 1,4-dioxane (1 ml) were charged into a 15 ml ace glass pressure tub, and the mixture was stirred at 80 °C for 1.0 h. The mixture in situ HRMS study of the crude reaction mixture revealed the formation of adduct **8**.

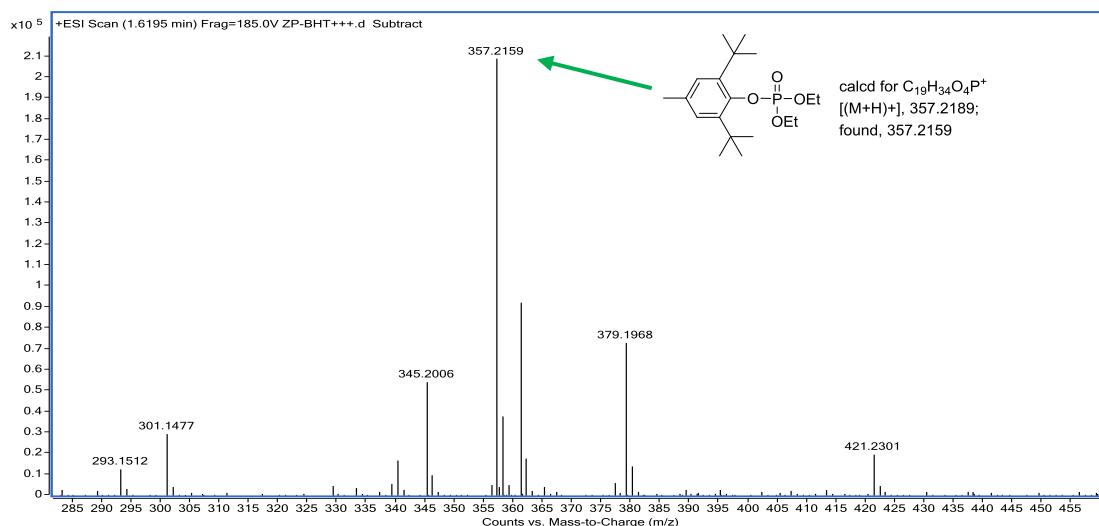
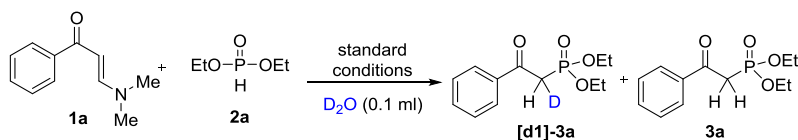


Fig. S1 The BHT intermediate was detected by ESI.

1.2 Isotope-labeling studies



Scheme S2 Deuterium exchange.

N,N-Dimethylenaminone **1a** (1 mmol, 1.0 equiv), H-phosphonate **2a** (2.0 mmol, 2.0 equiv), $\text{Mn}(\text{OAc})_3$ (3 mmol, 3.0 equiv), AcOH (2 ml) 1,4-dioxane (4 ml) were charged into a 15 ml ace glass pressure tub, and the mixture was stirred at 80 °C for 12 h until *N,N*-dimethylenaminone **1a** were completely consumed. The mixture was cooled to room temperature, the reaction mixture was concentrated and purified by flash column chromatography to afford the β -ketophosphonate **3a** (51%), the desired product **[d₁]-3a** was observed in ^1H -NMR.

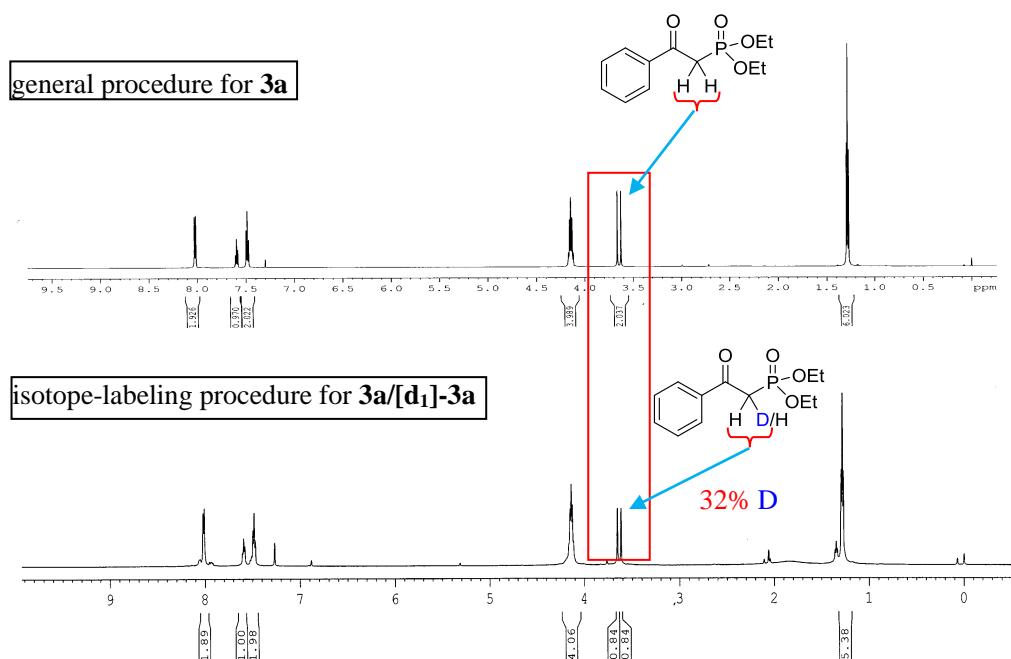


Fig. S2 The deuterium-incorporated product **[d₁]-3a** was determined by ¹H-NMR.

2. NMR spectra (^1H NMR and ^{13}C NMR)

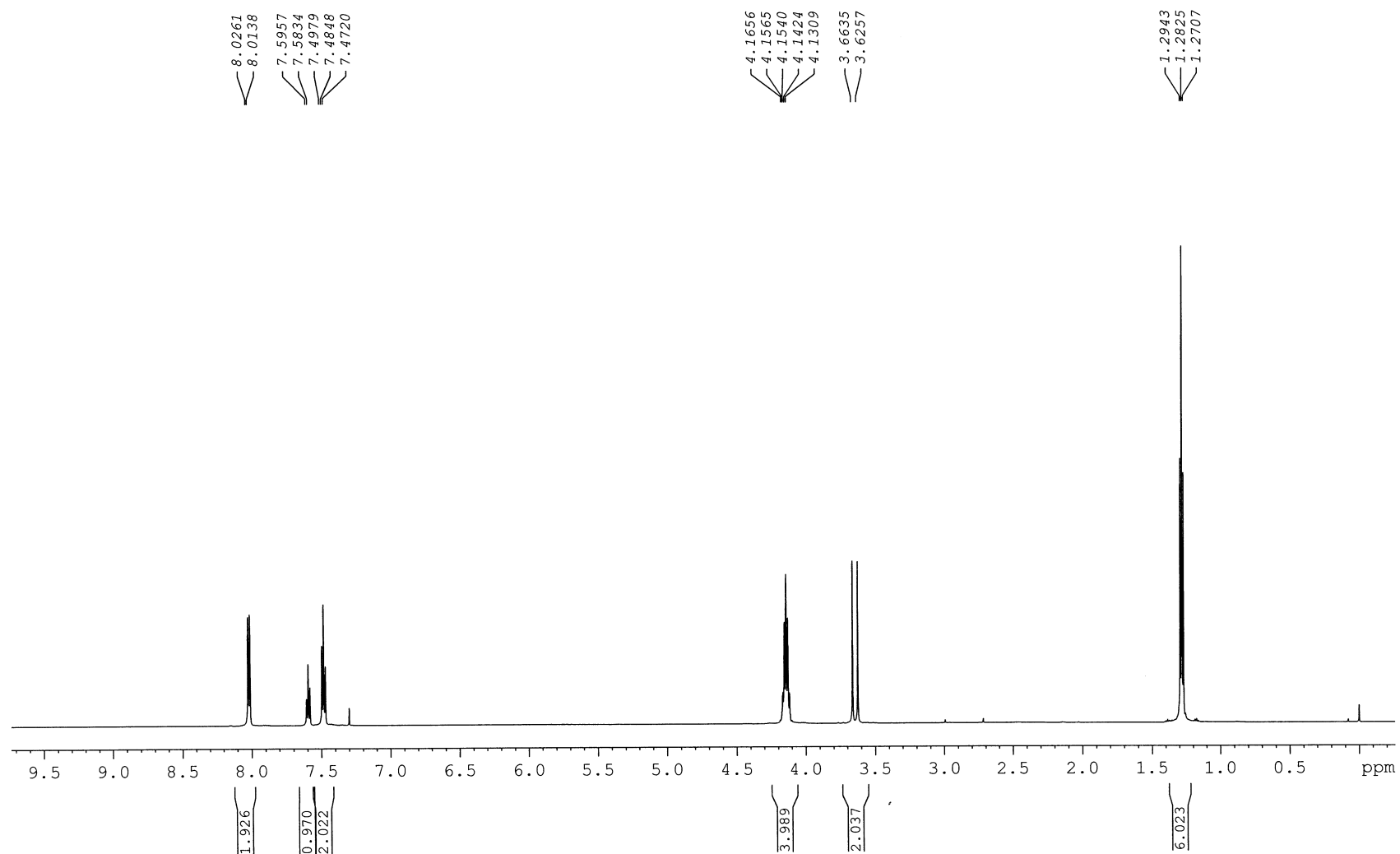


Figure S3. ^1H NMR (600 MHz, CDCl_3) spectra of compound **3a**

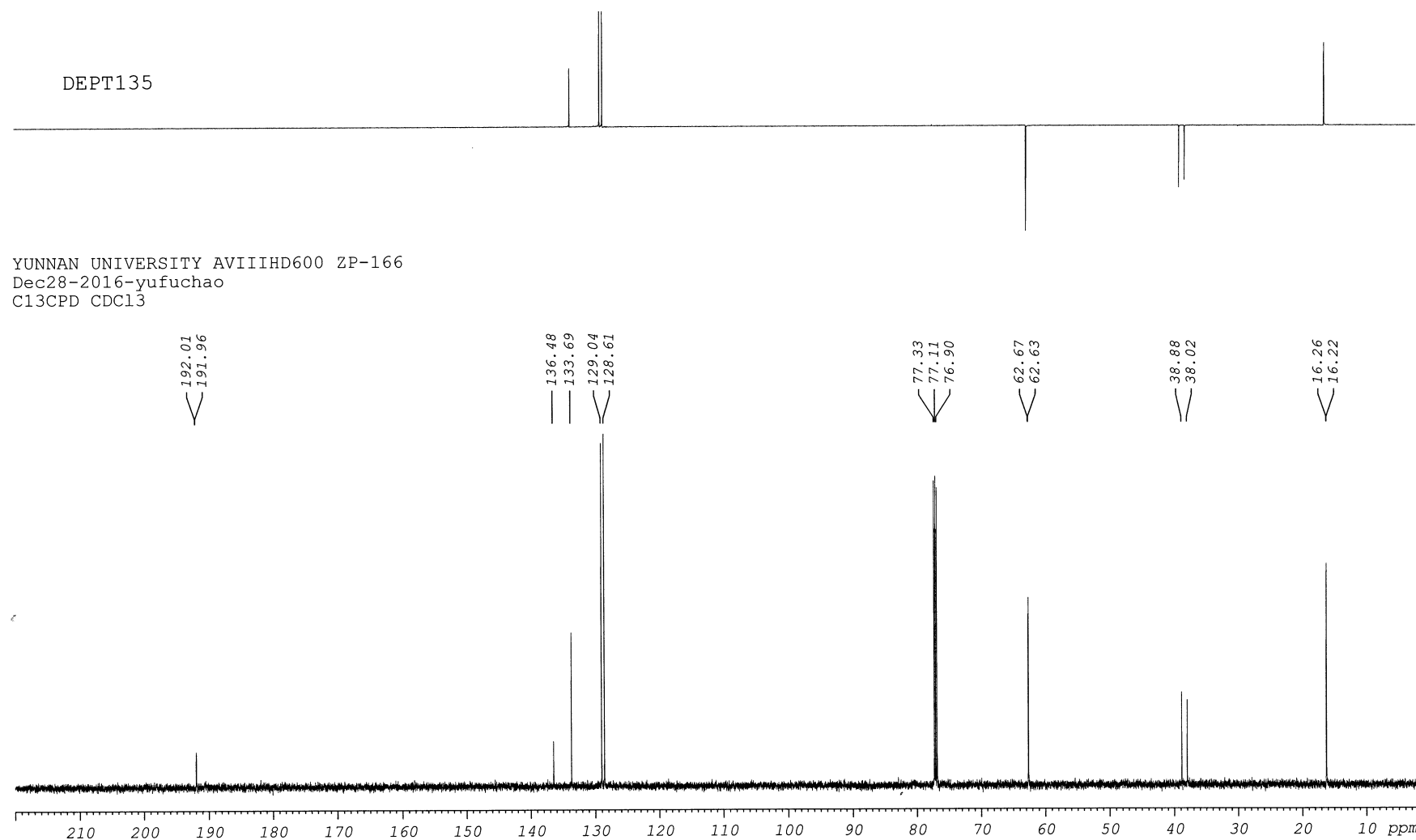


Figure S4. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3a**

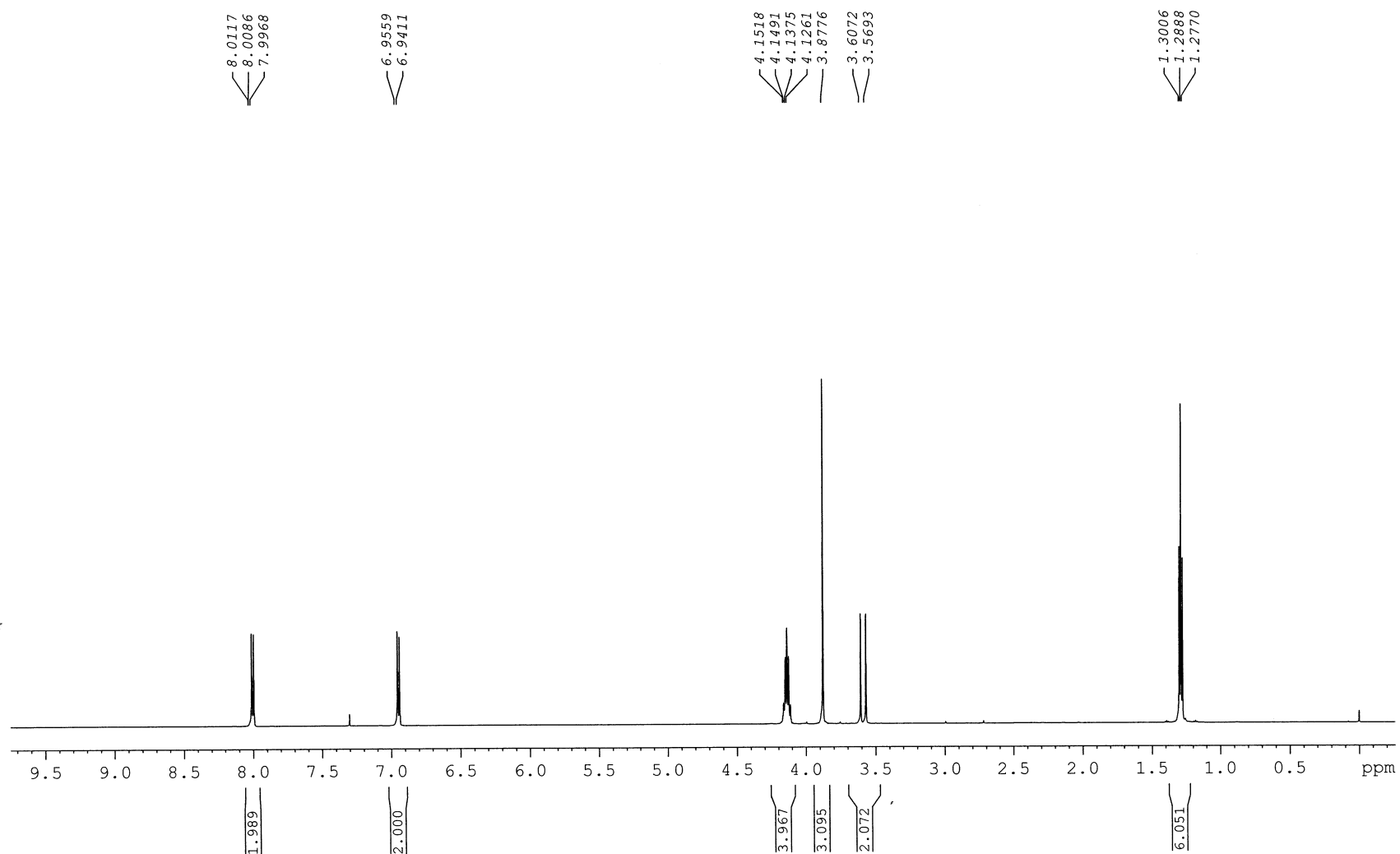


Figure S5. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3b**

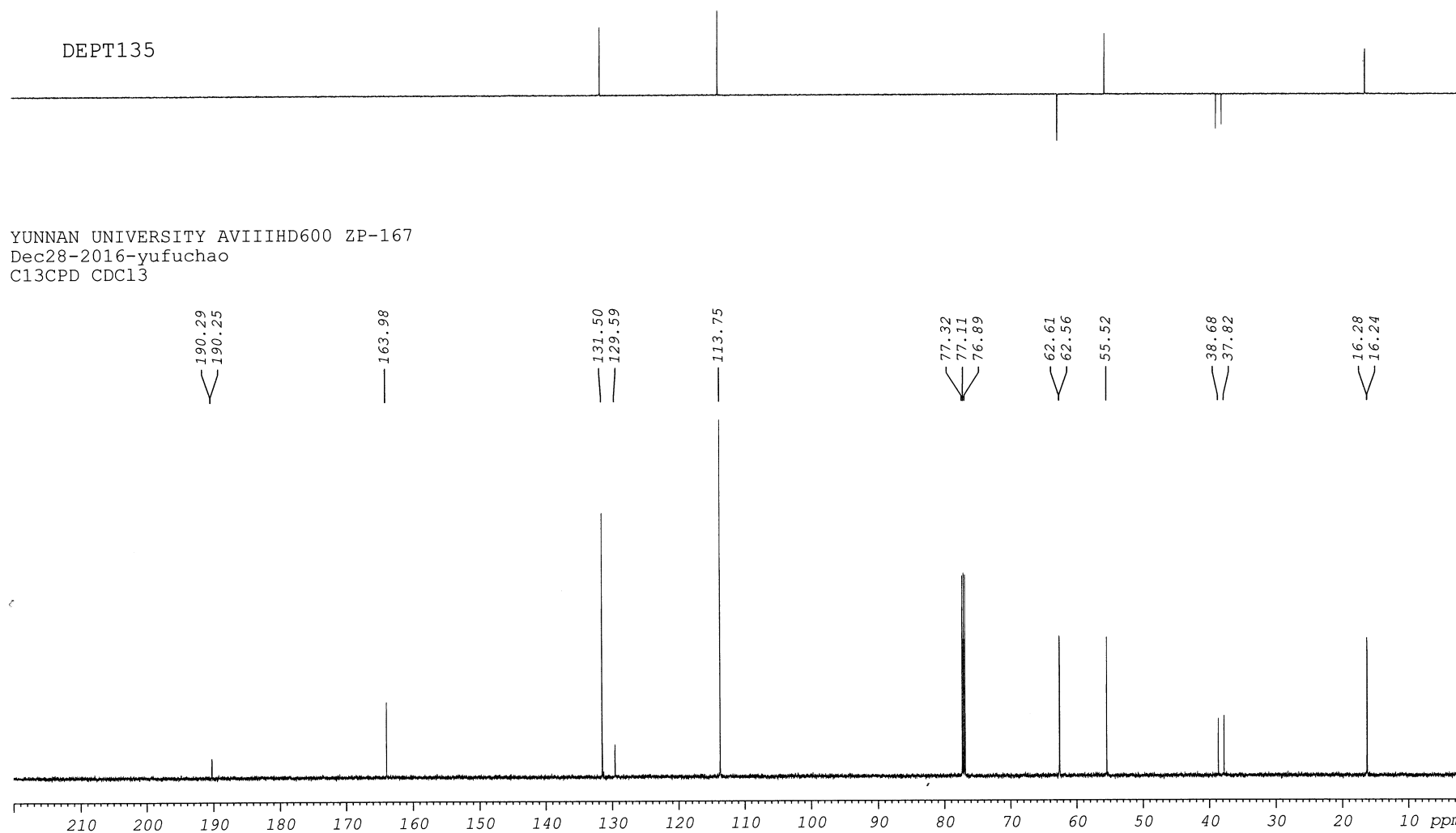


Figure S6. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3b**

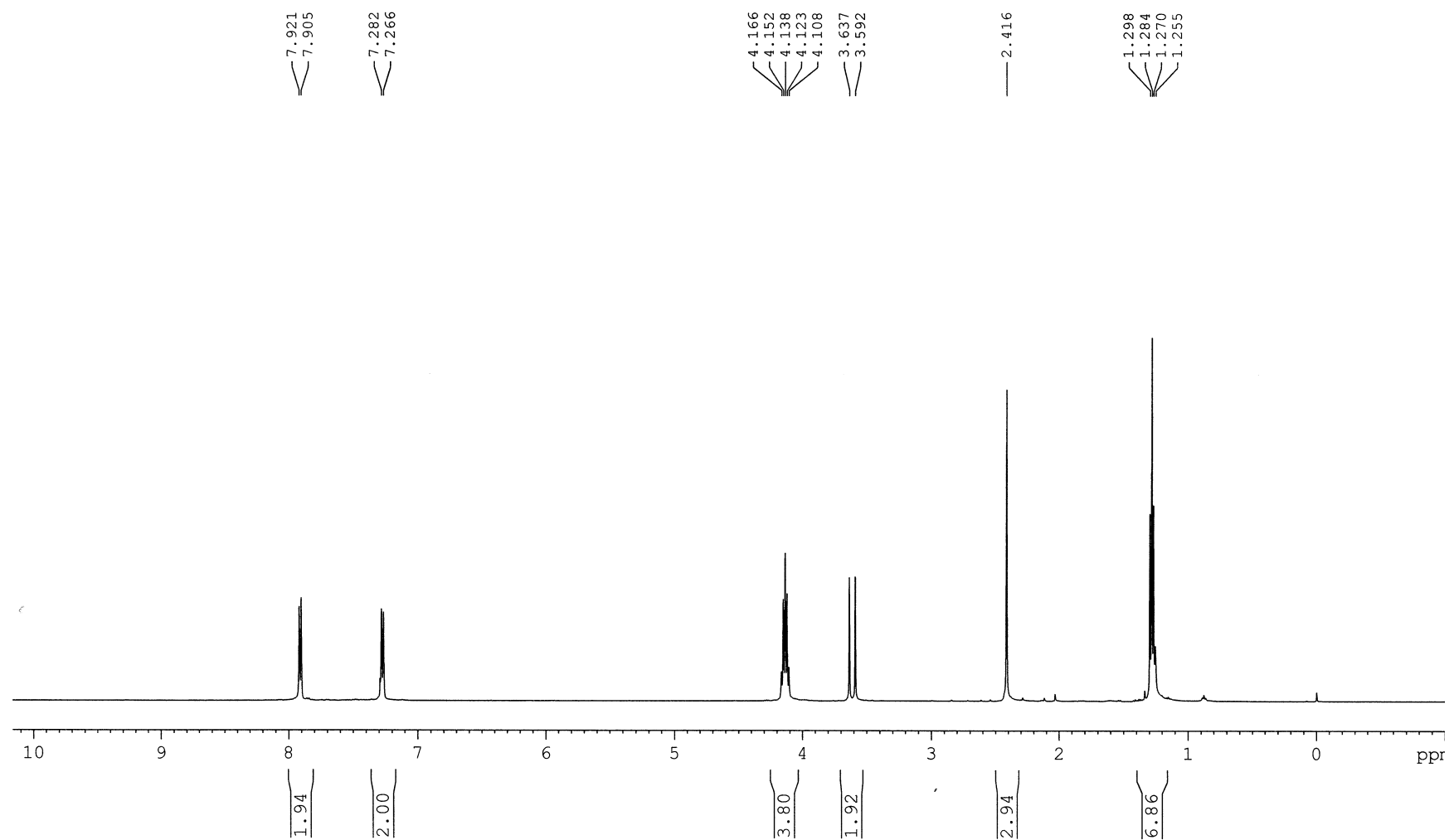


Figure S7. ¹H NMR (500 MHz, CDCl₃) spectra of compound **3c**

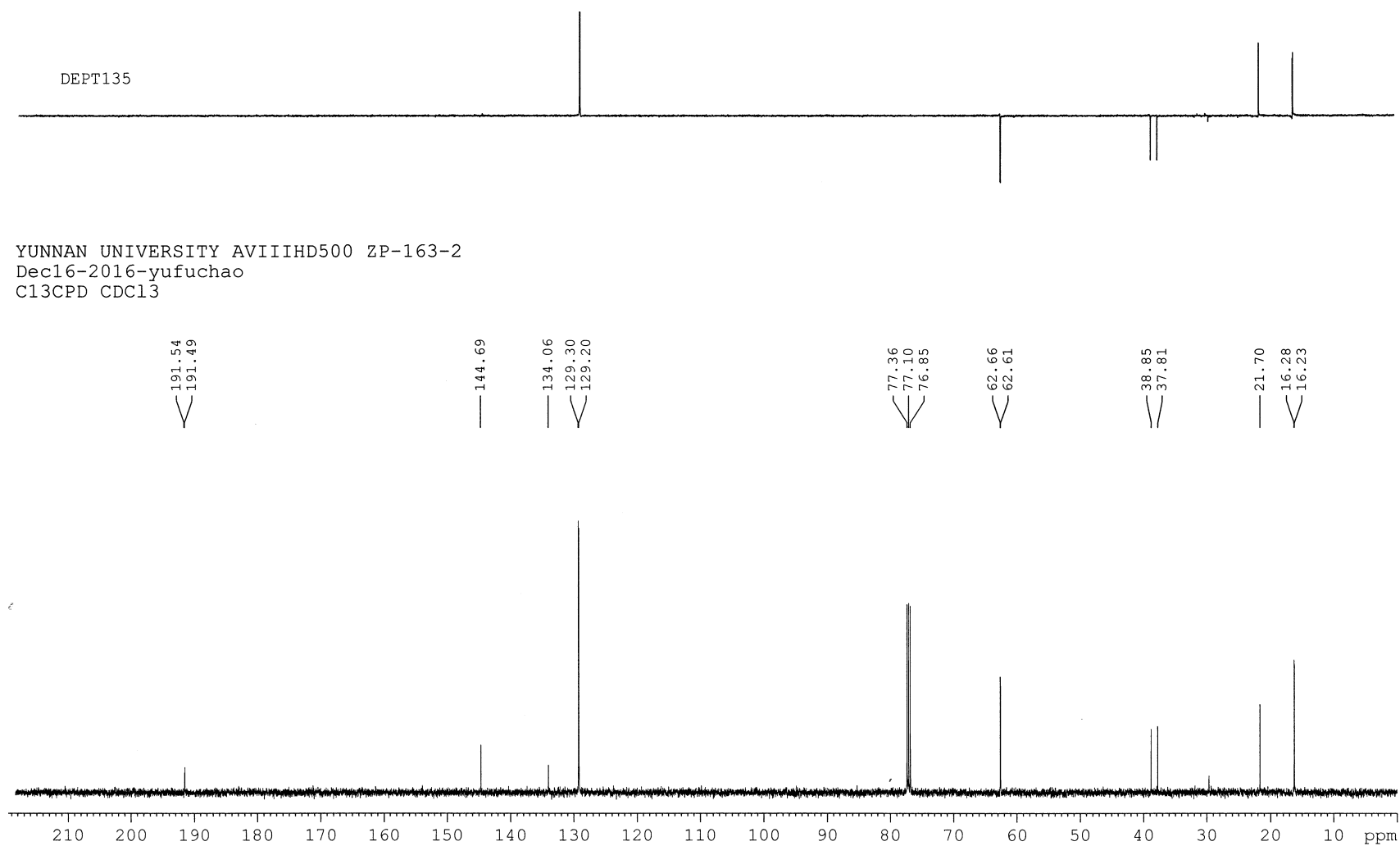


Figure S8. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3c**

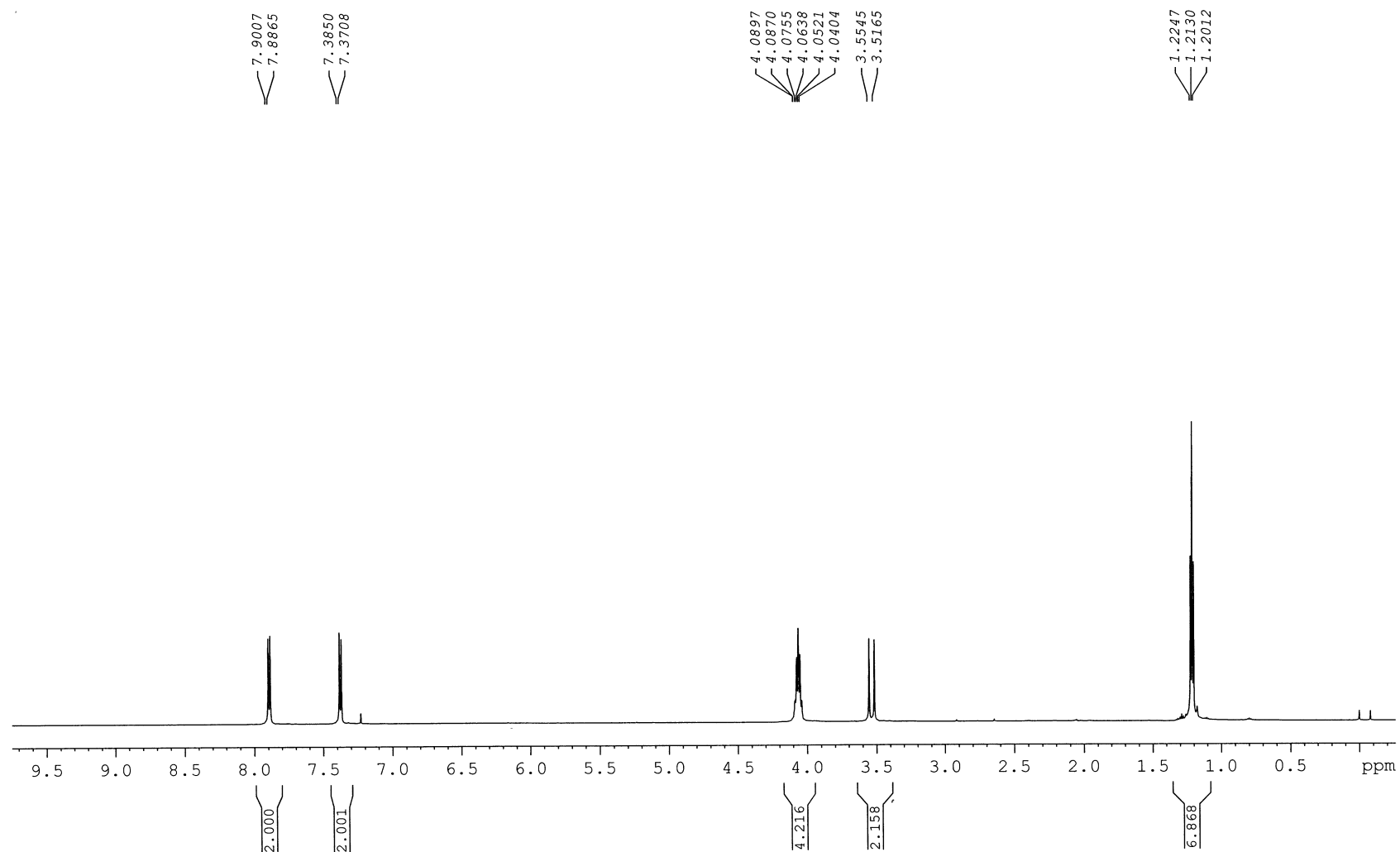


Figure S9. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3d**

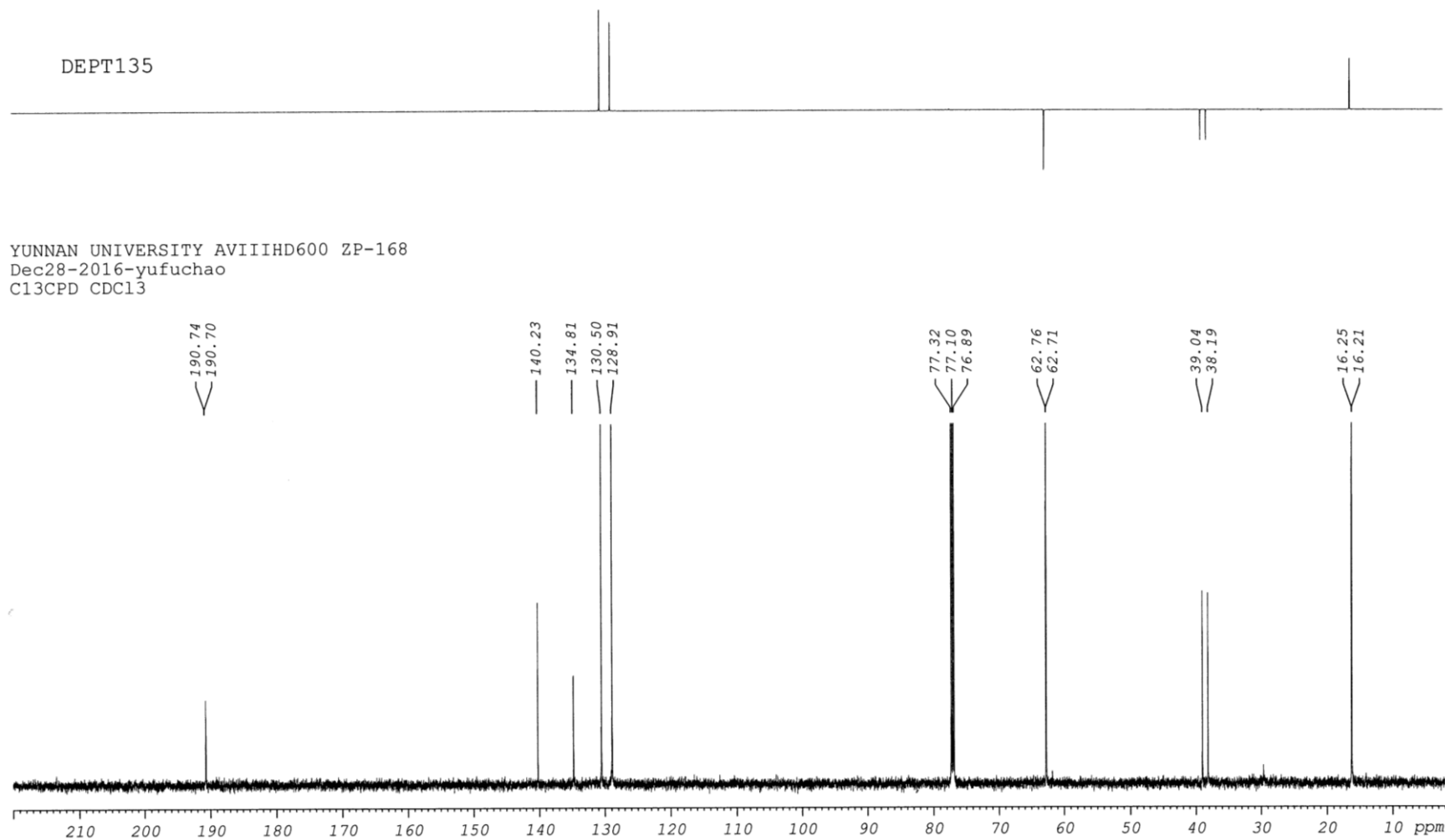


Figure S10. ¹³C NMR (150 MHz, CDCl₃) spectra of compound **3d**

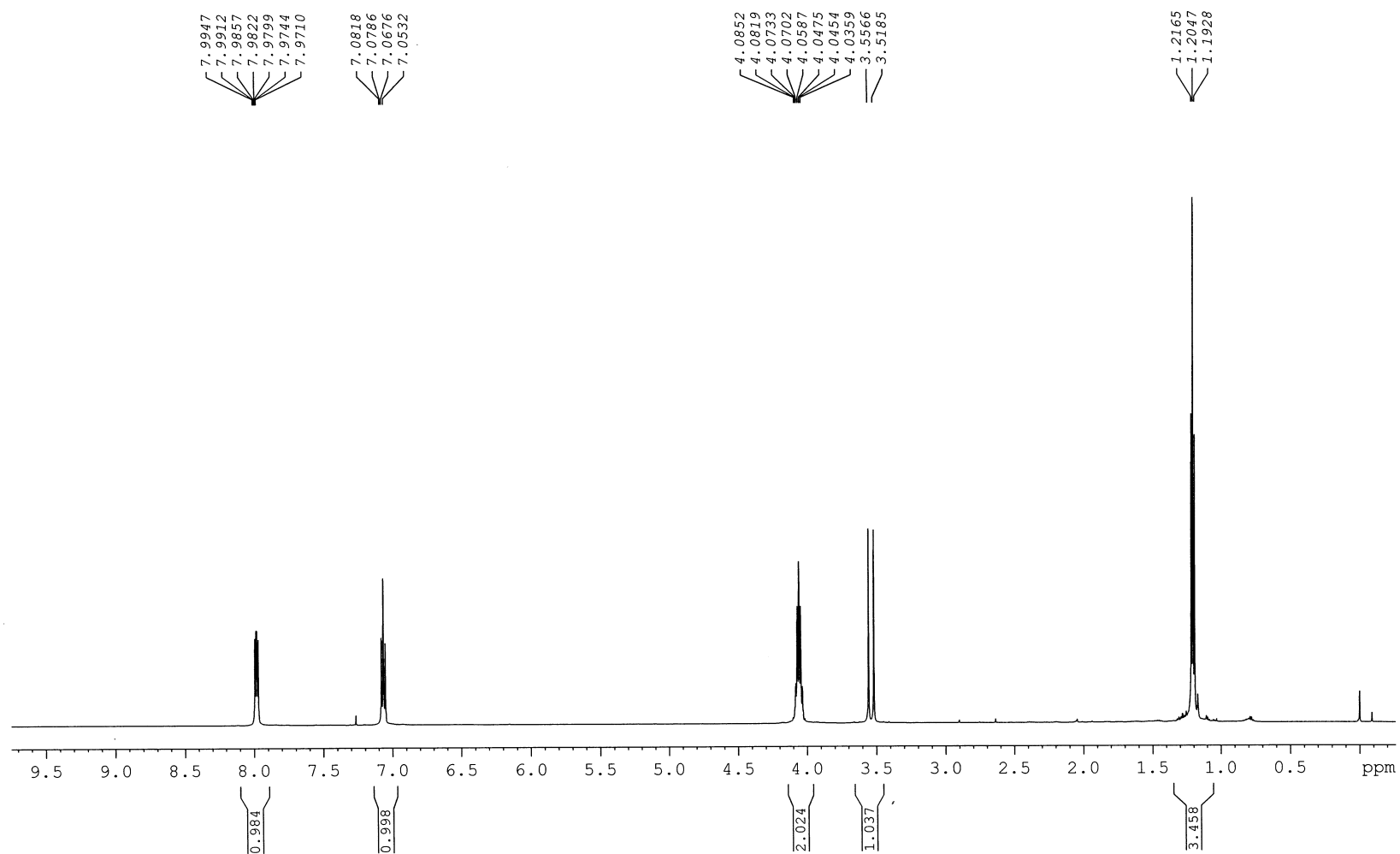


Figure S11. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3e**

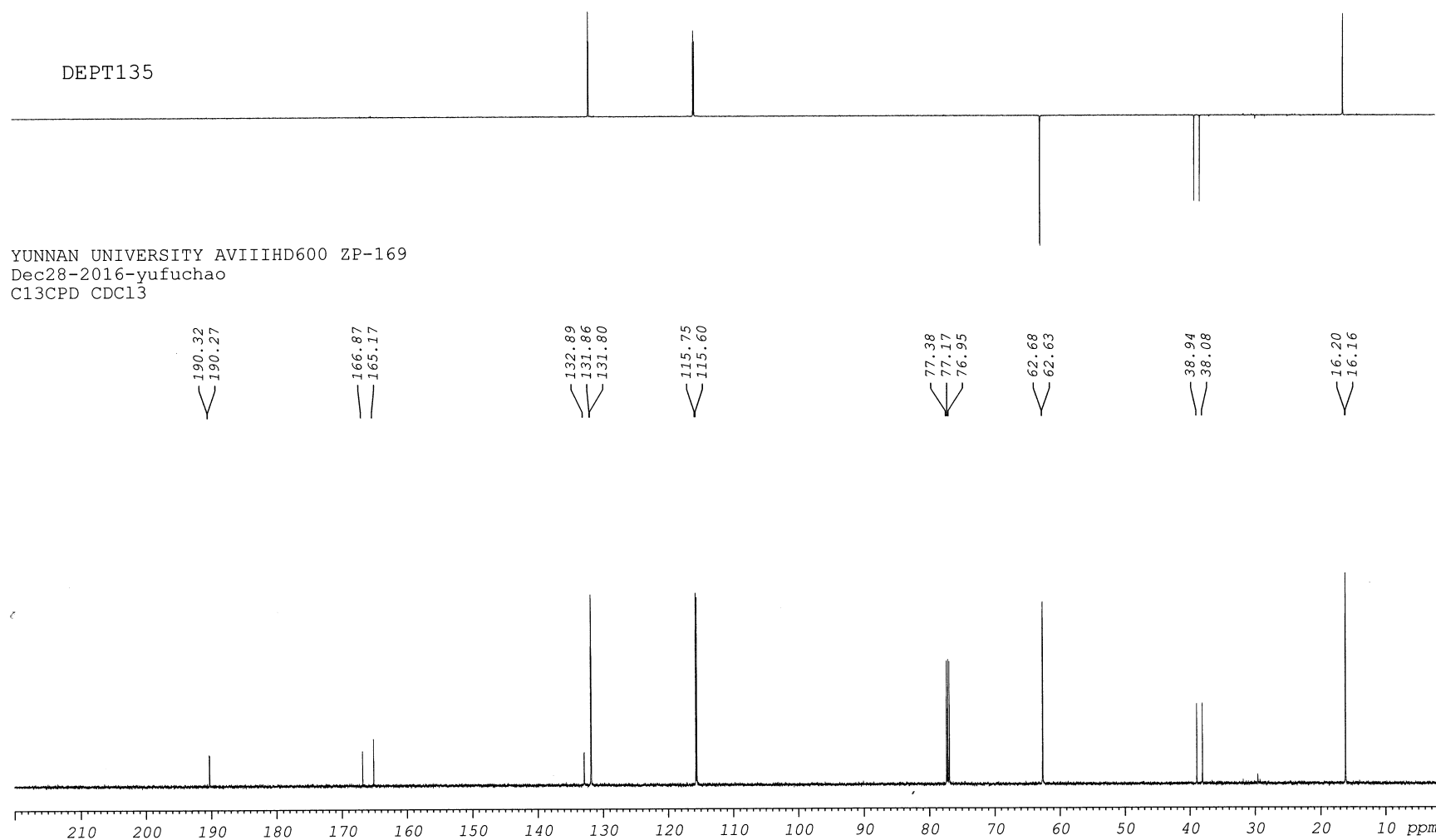


Figure S12 ¹³C NMR (150 MHz, CDCl₃) spectra of compound **3e**

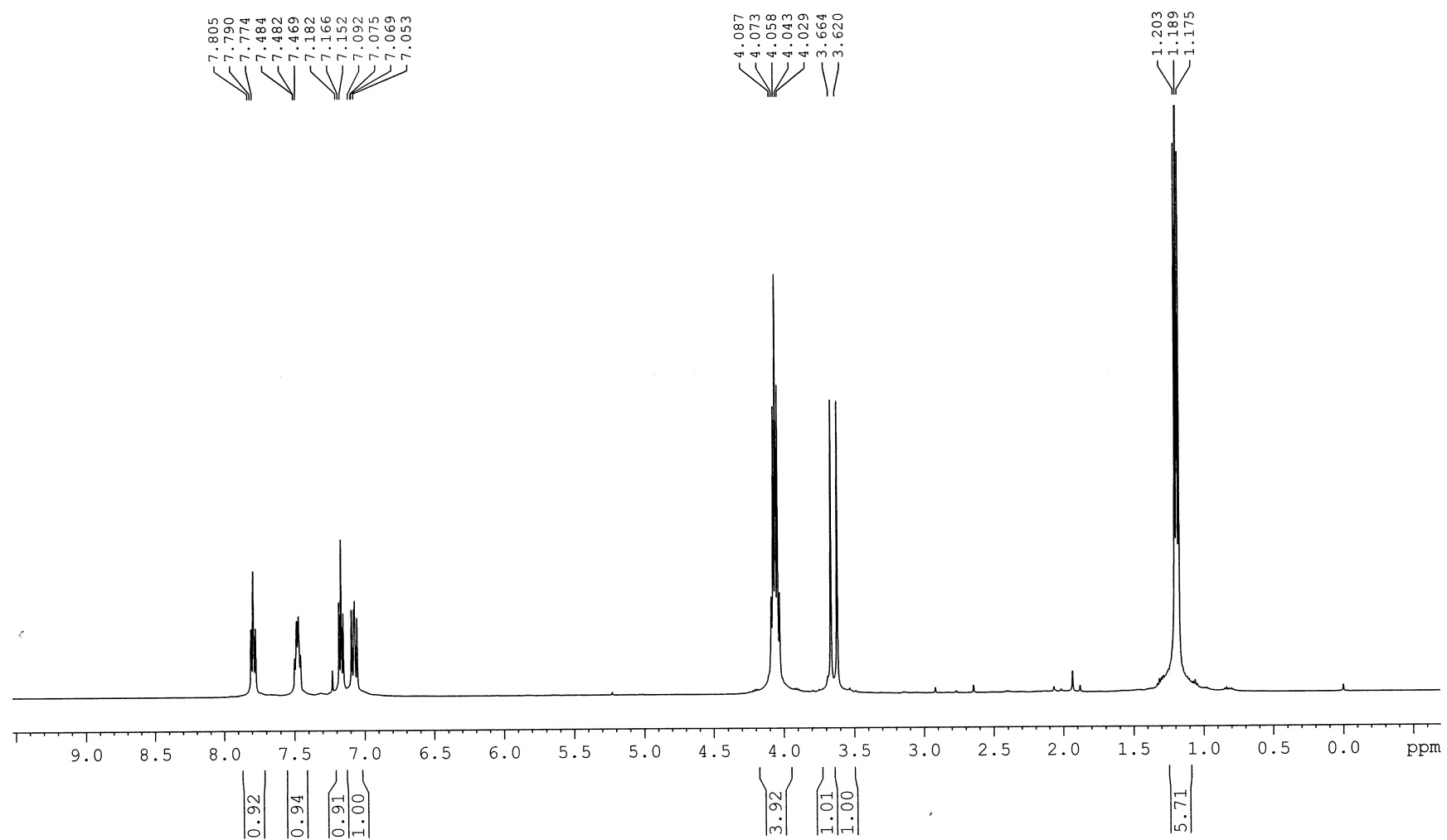


Figure S13. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3f**

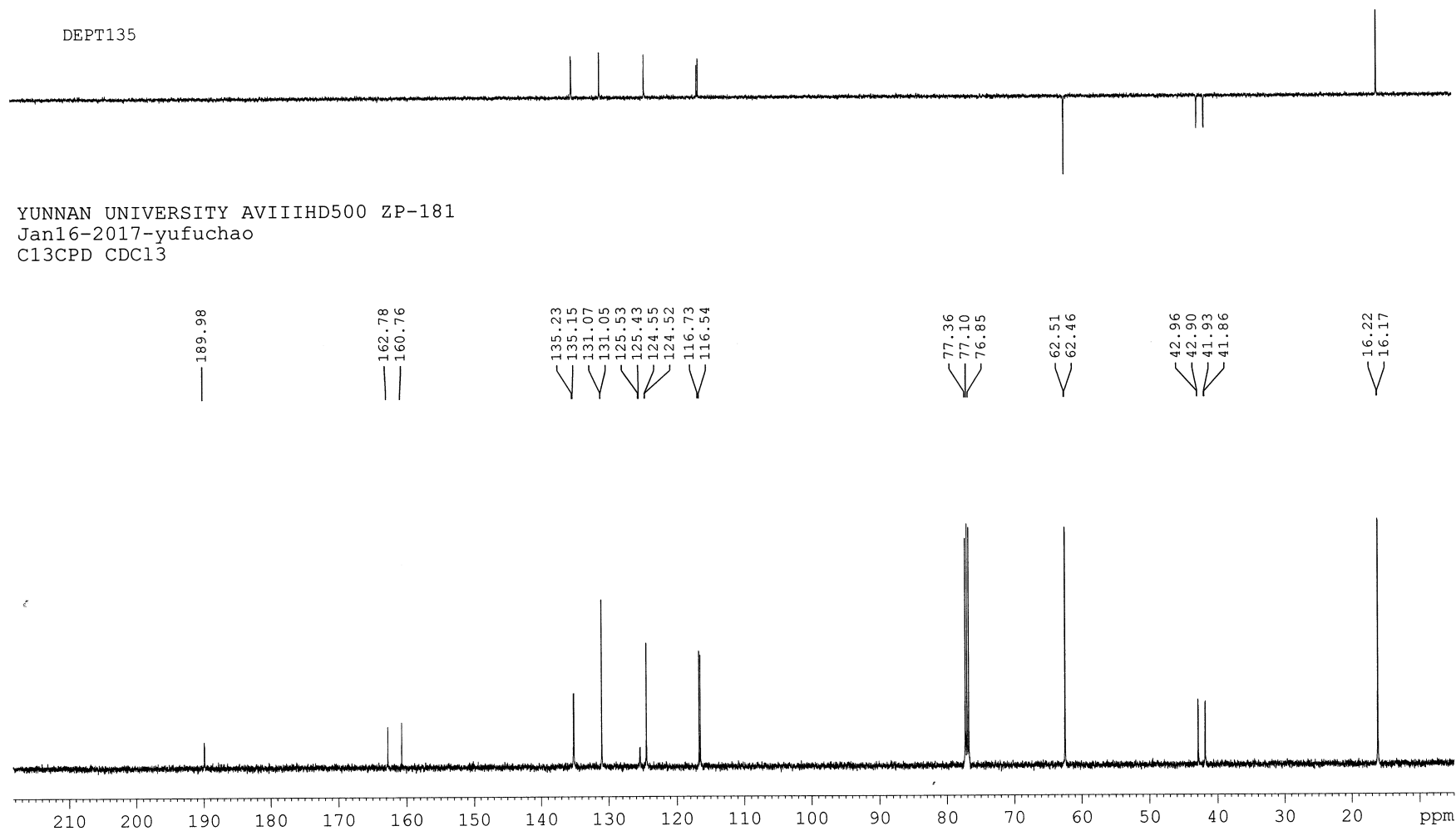


Figure S14. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3f**

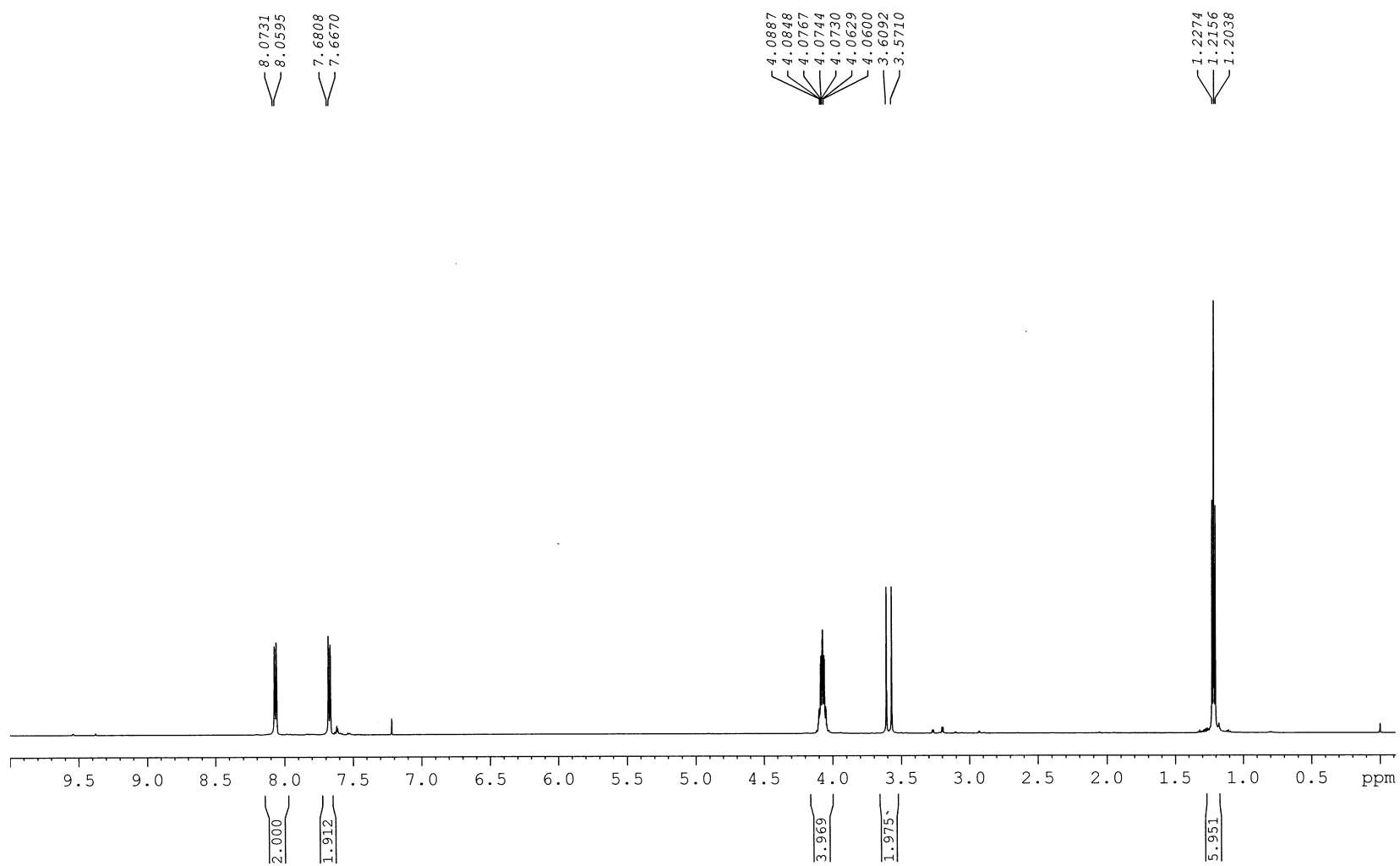


Figure S15. ^1H NMR (600 MHz, CDCl_3) spectra of compound **3g**

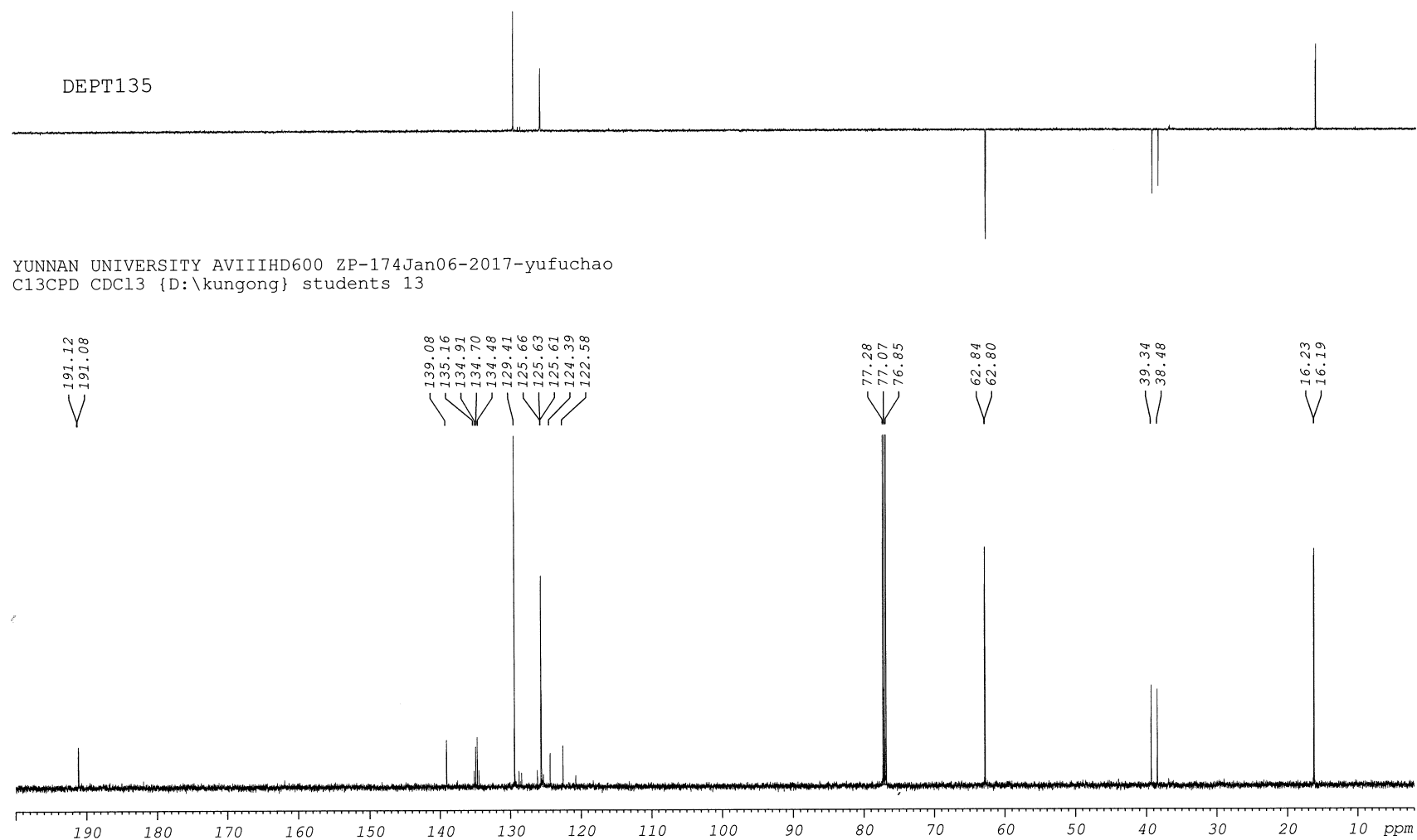


Figure S16. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3g**

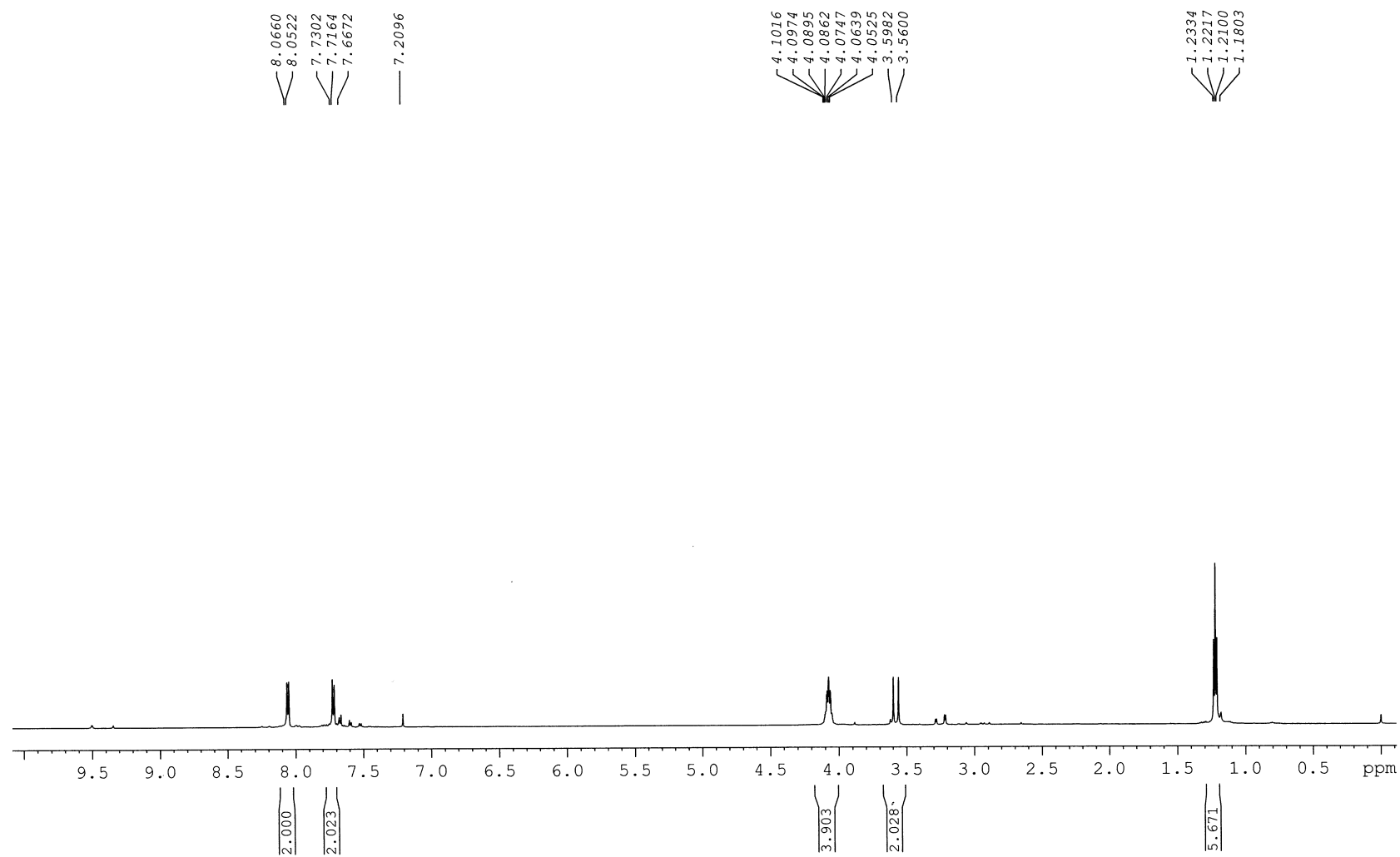


Figure S17. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3h**

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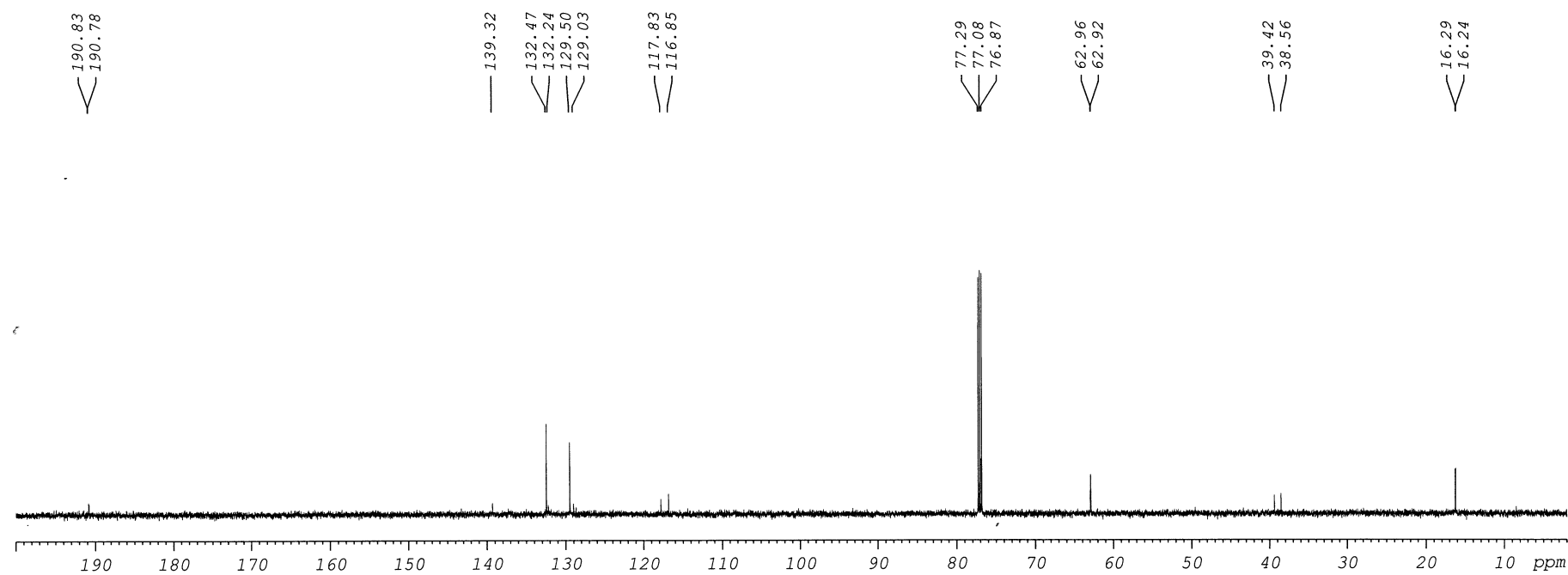


Figure S18. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3h**

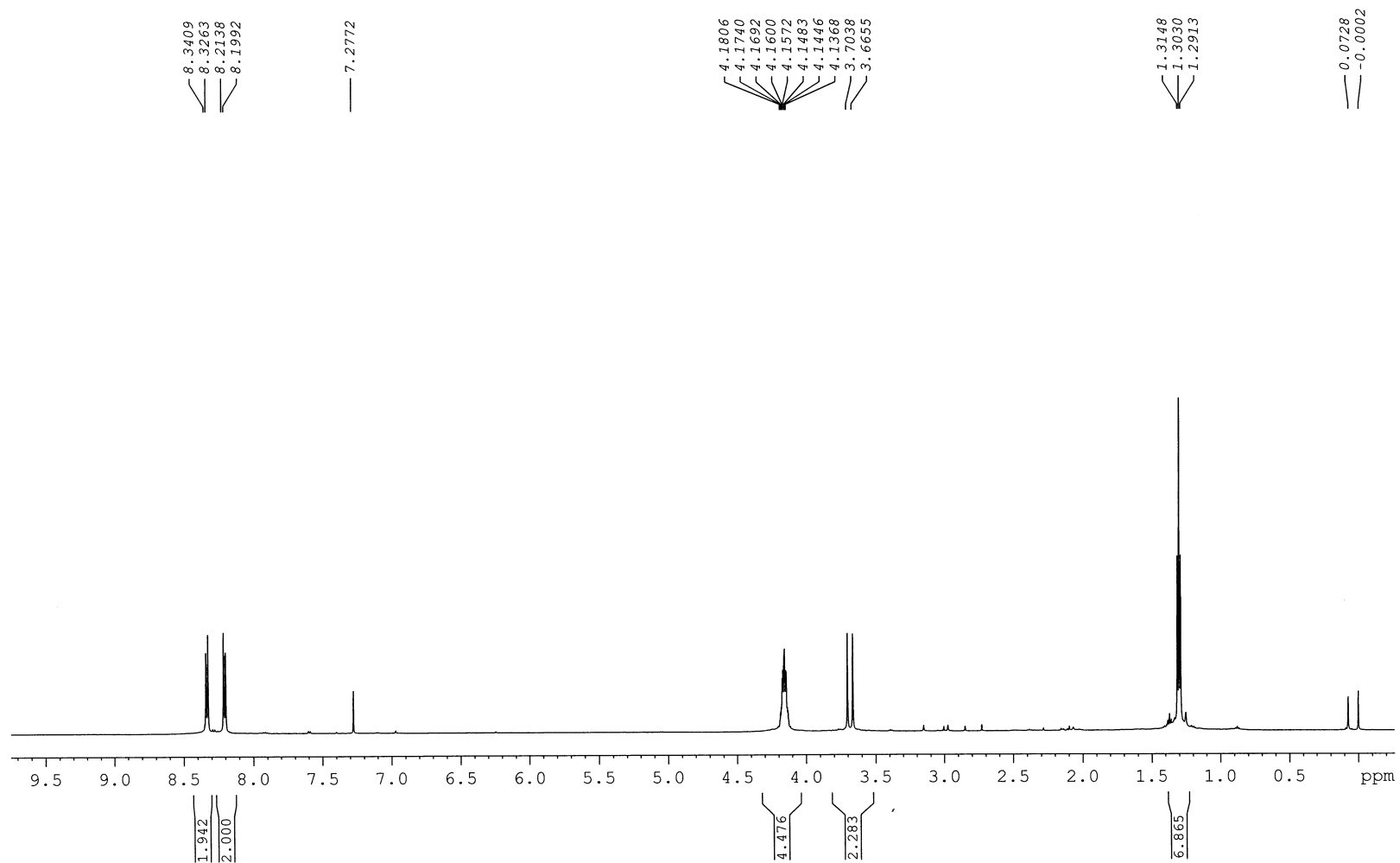


Figure S19. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3i**

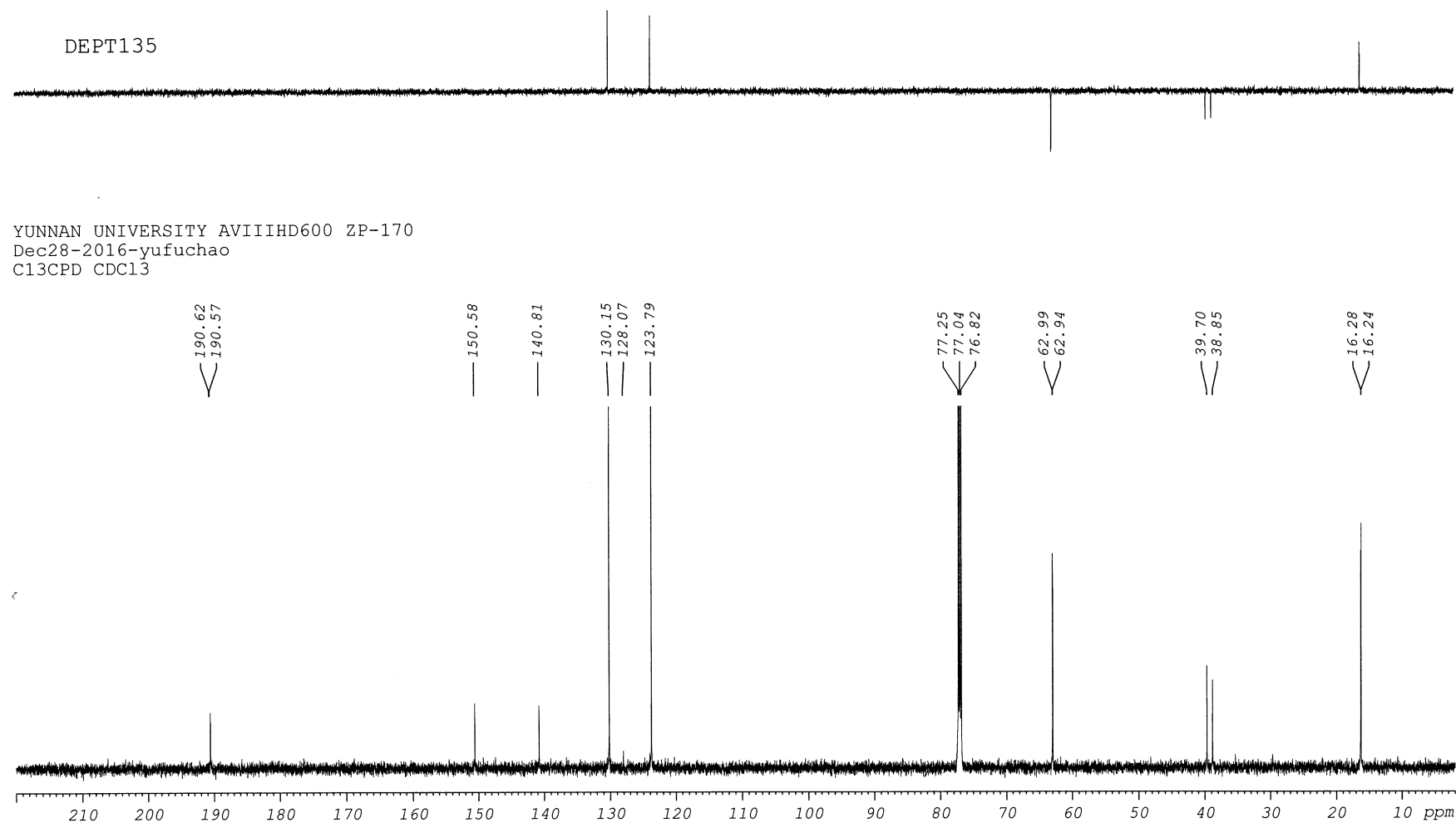


Figure S20. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3i**

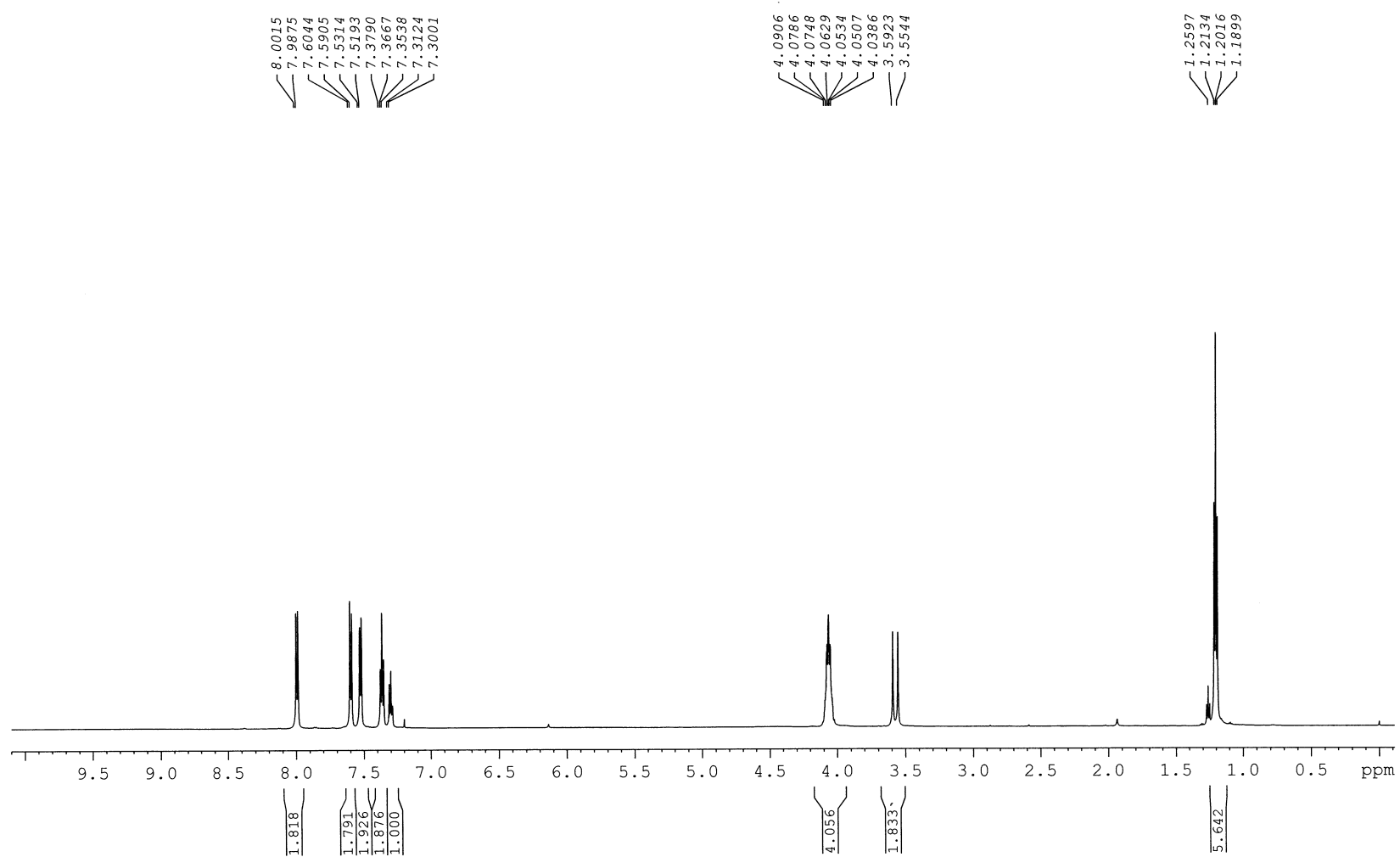


Figure S21. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3j**

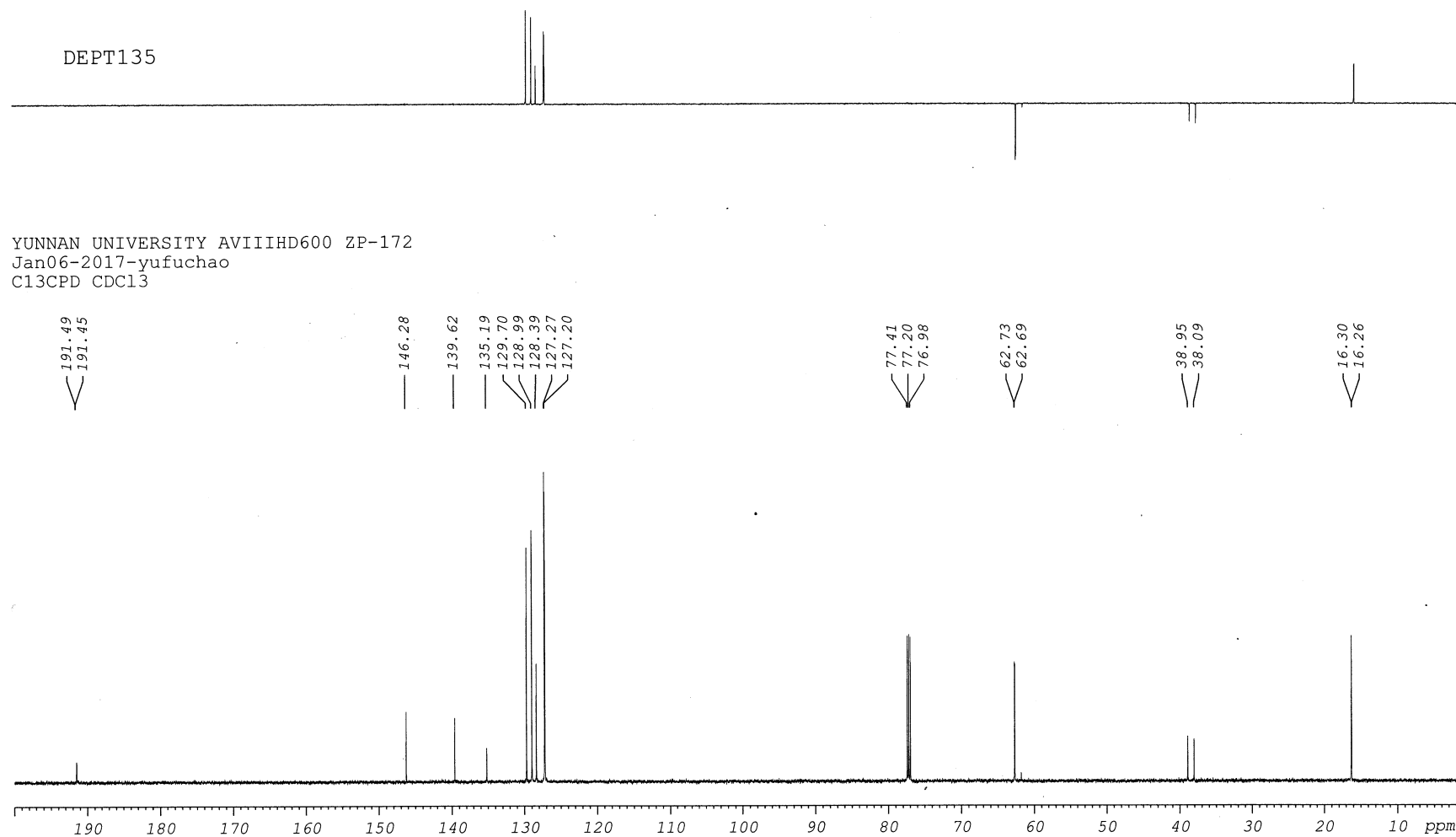


Figure S22. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3j**

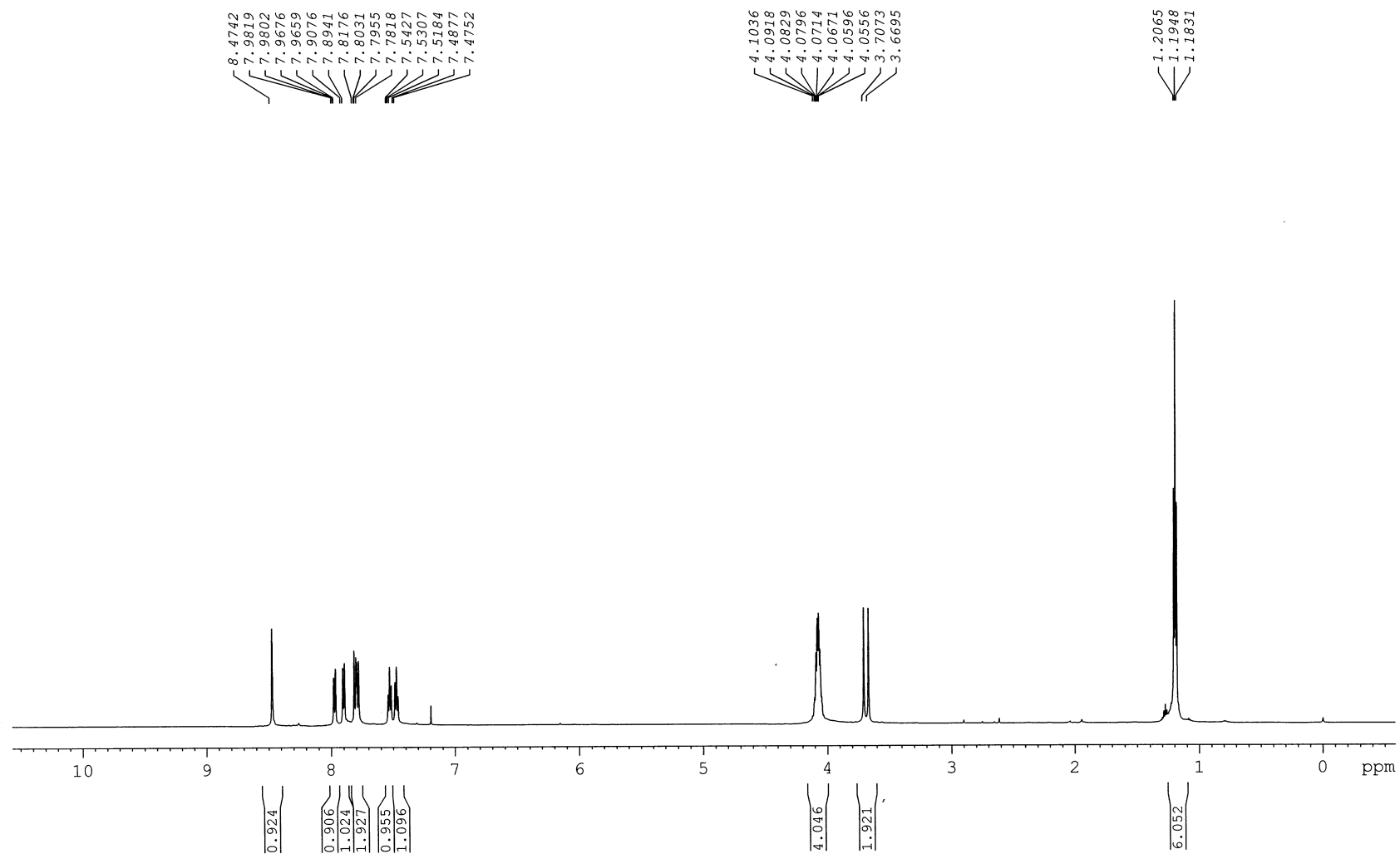


Figure S23. ¹H NMR (600 MHz, CDCl₃) spectra of compound **3k**

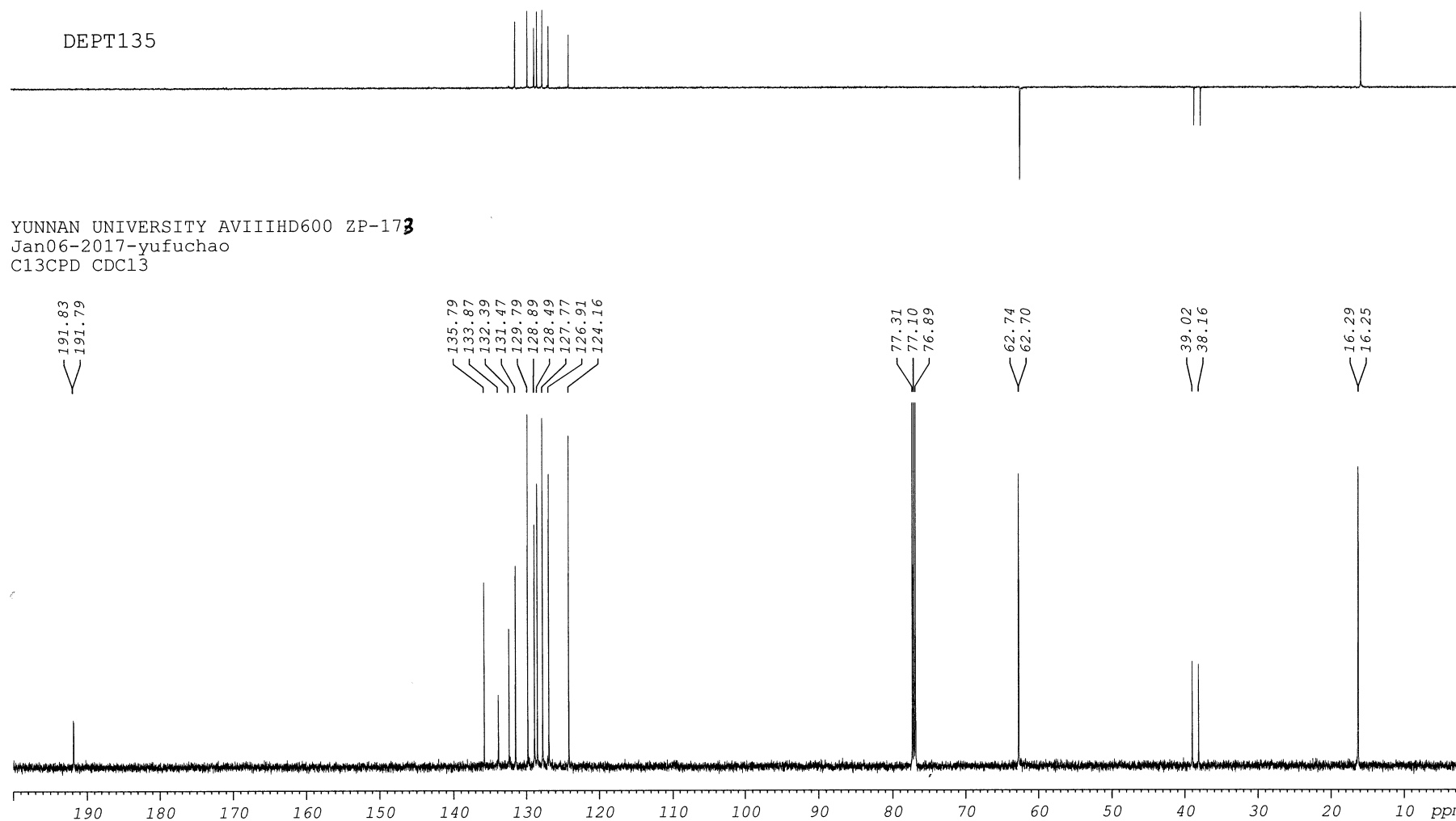


Figure S24. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3k**

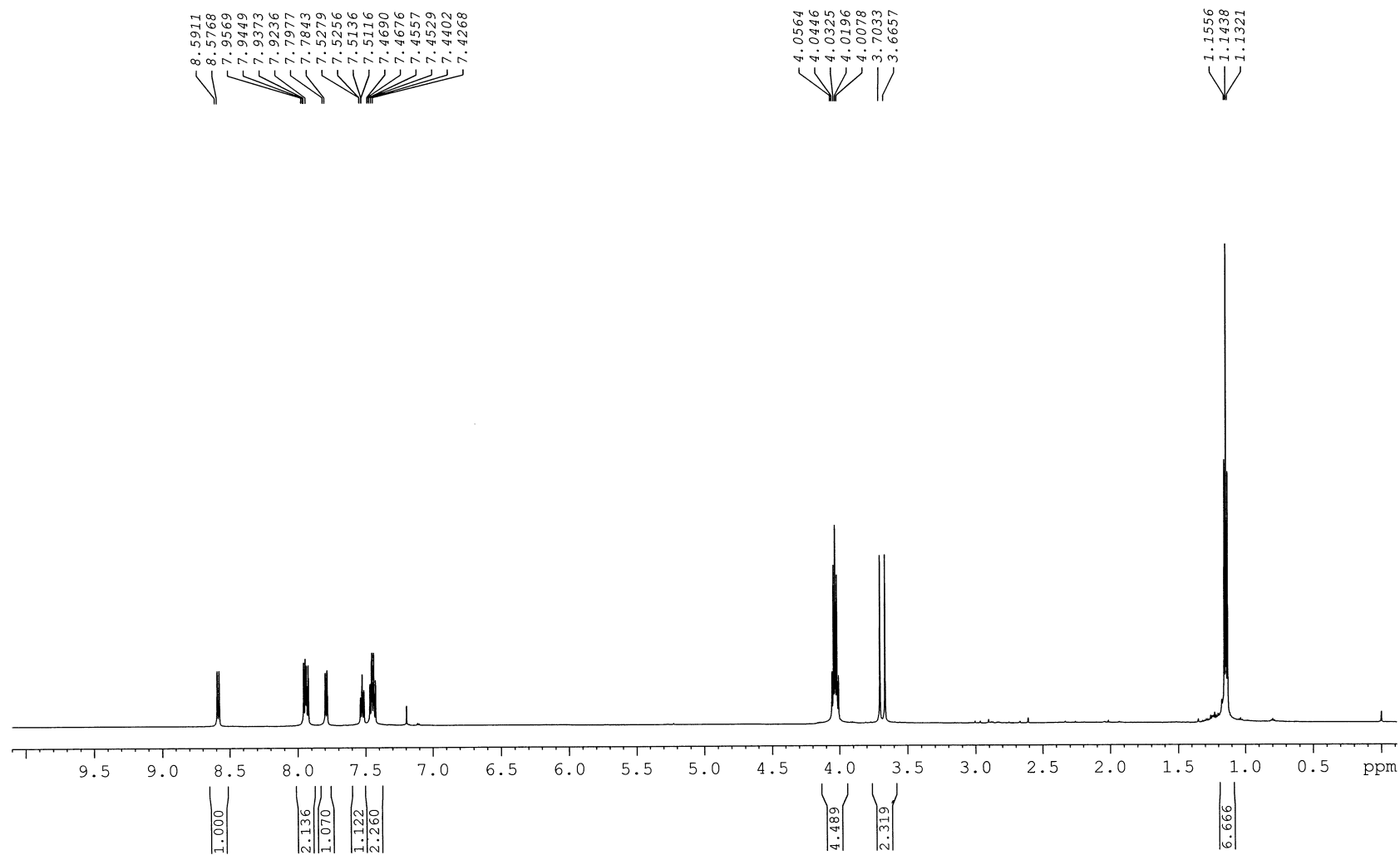


Figure S25. ^1H NMR (600 MHz, CDCl_3) spectra of compound **3l**

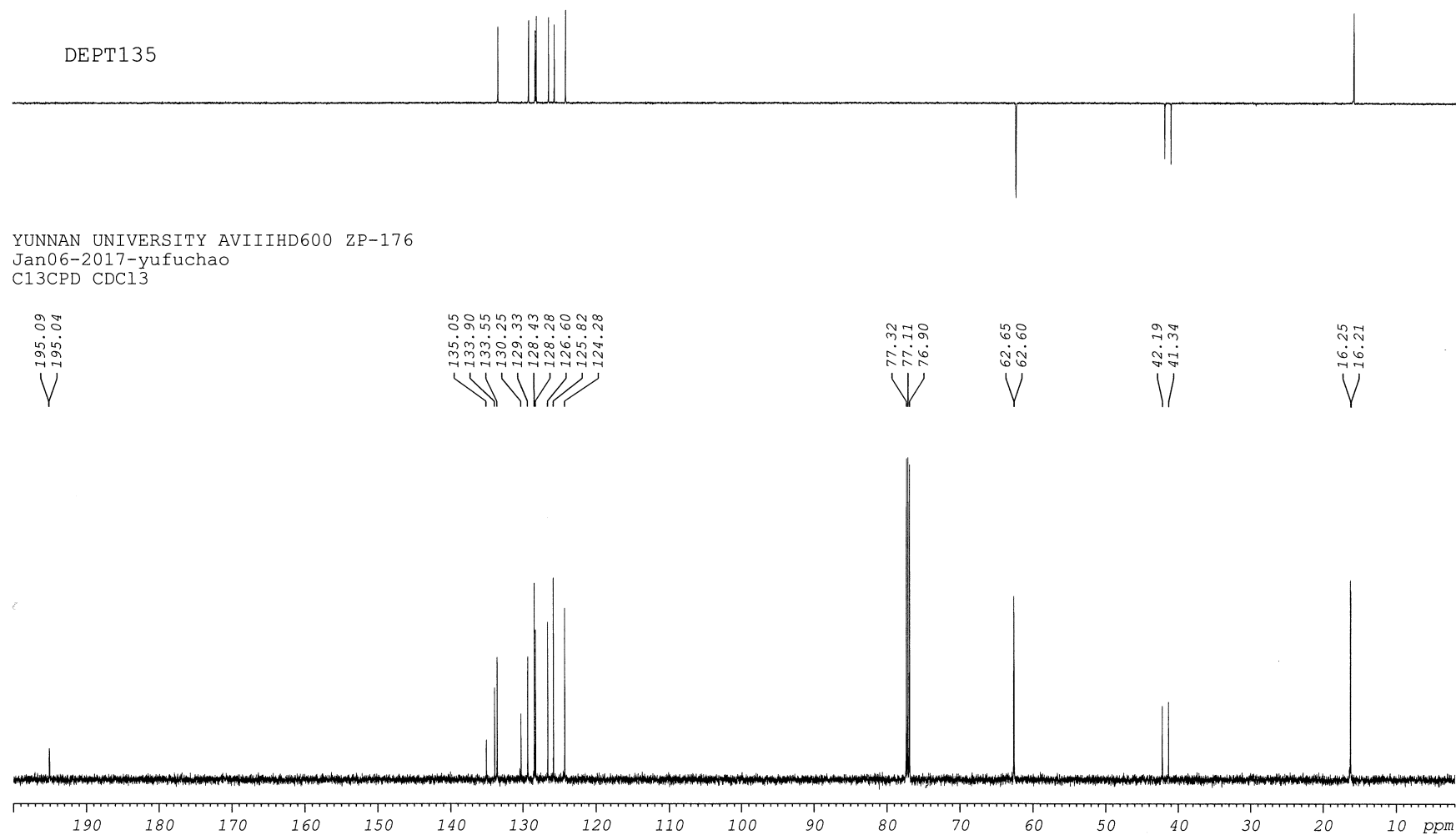


Figure S26. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **31**

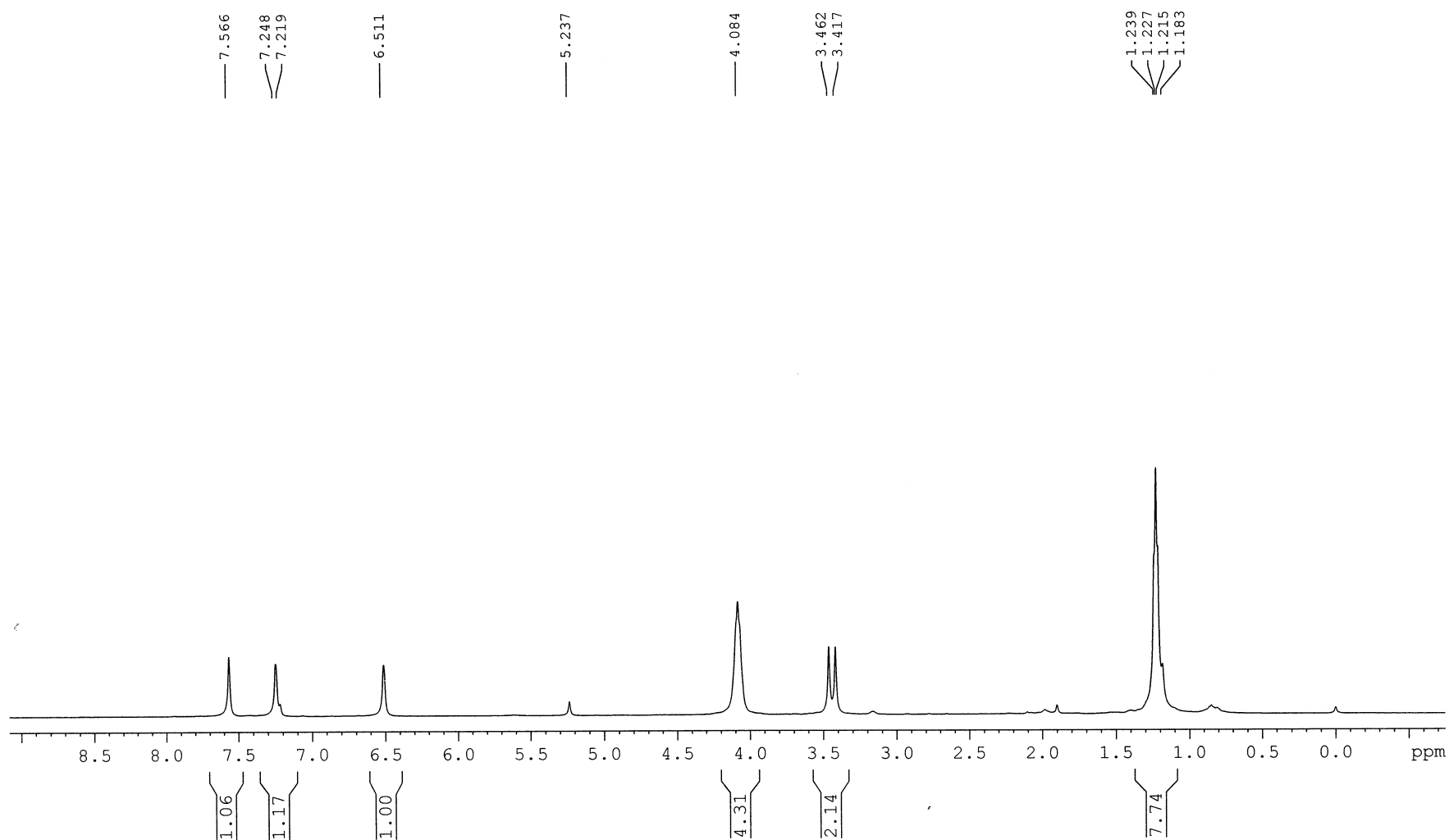


Figure S27. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3m**

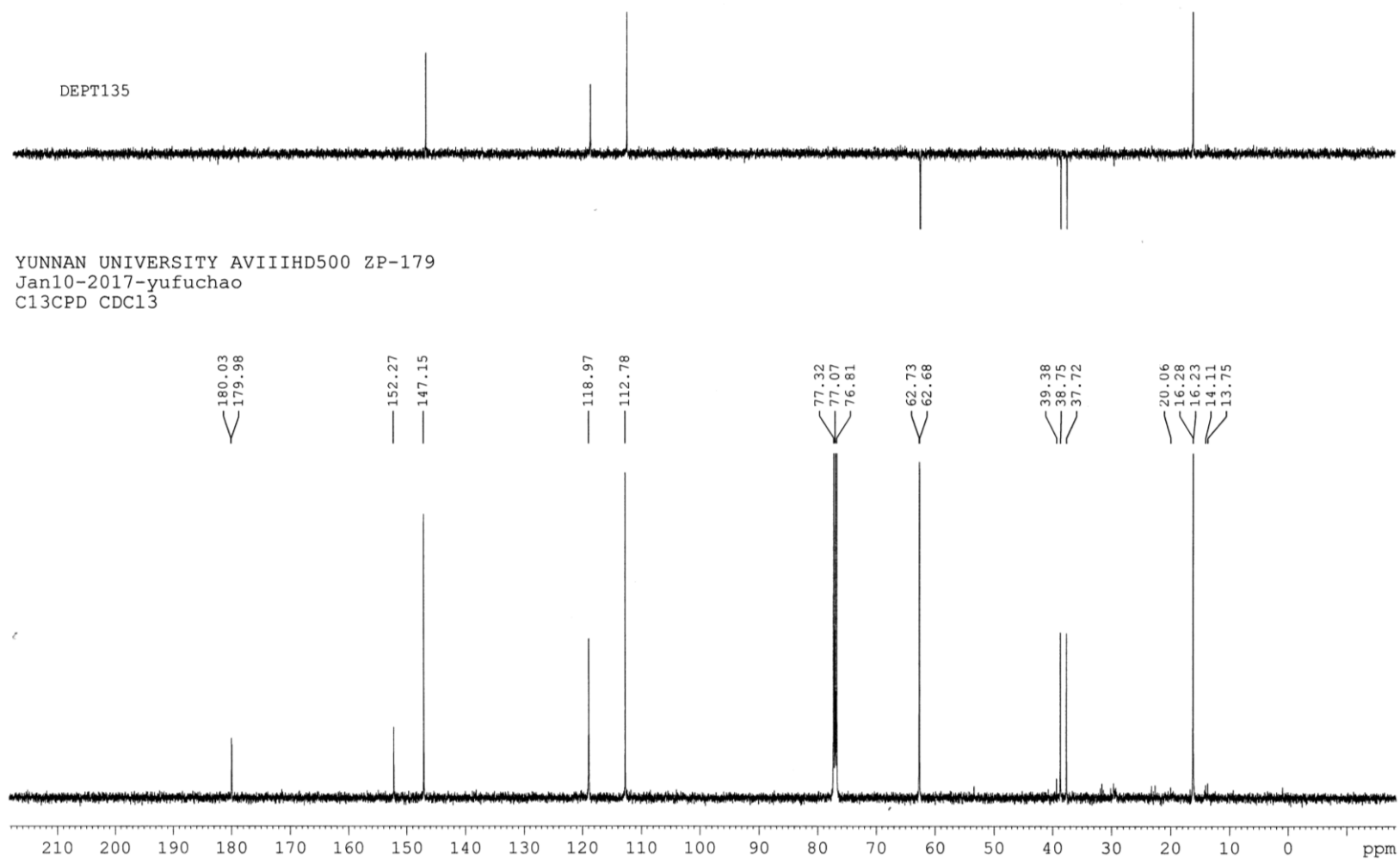


Figure S28. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3m**

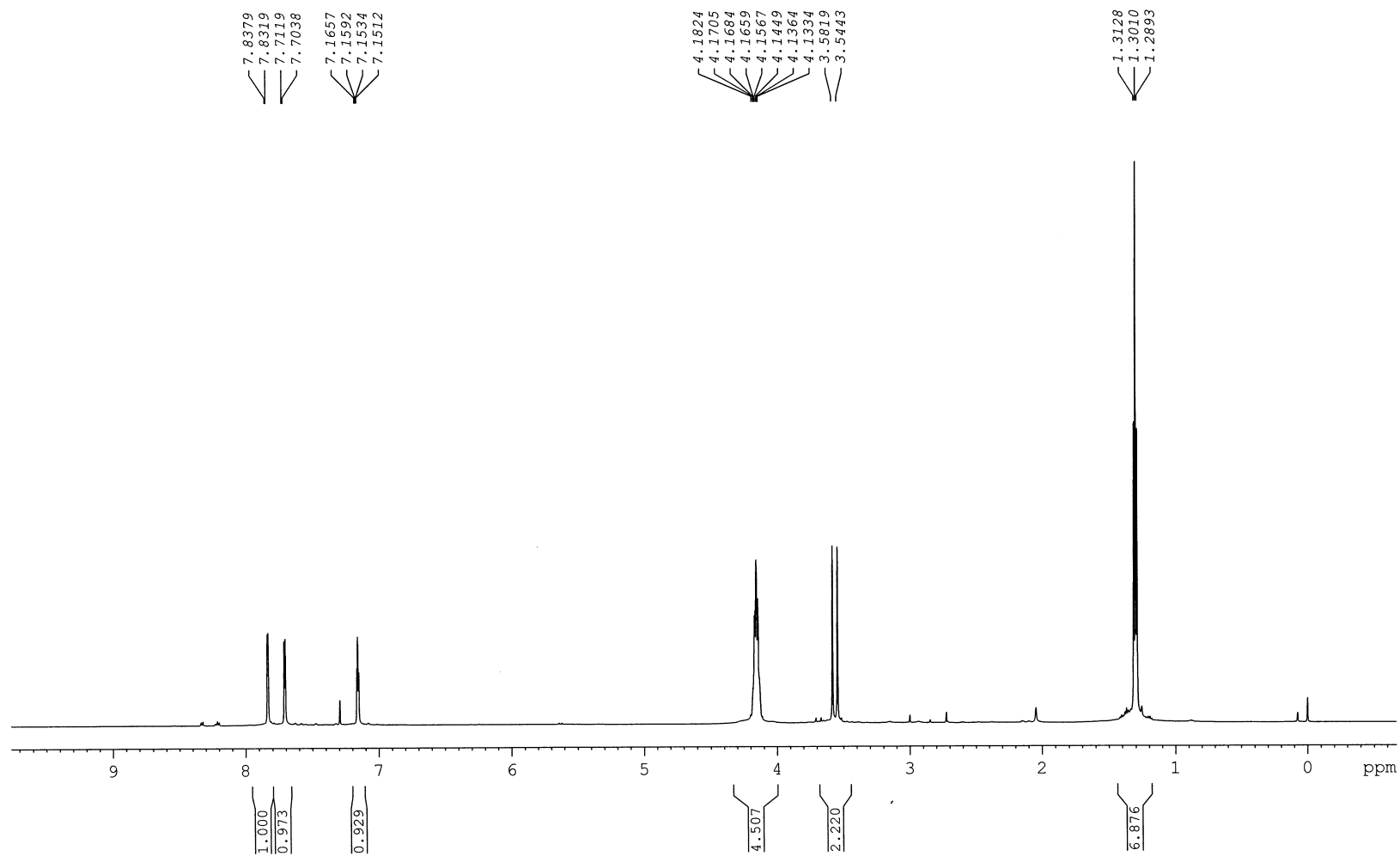


Figure S29. ^1H NMR (600 MHz, CDCl_3) spectra of compound **3n**

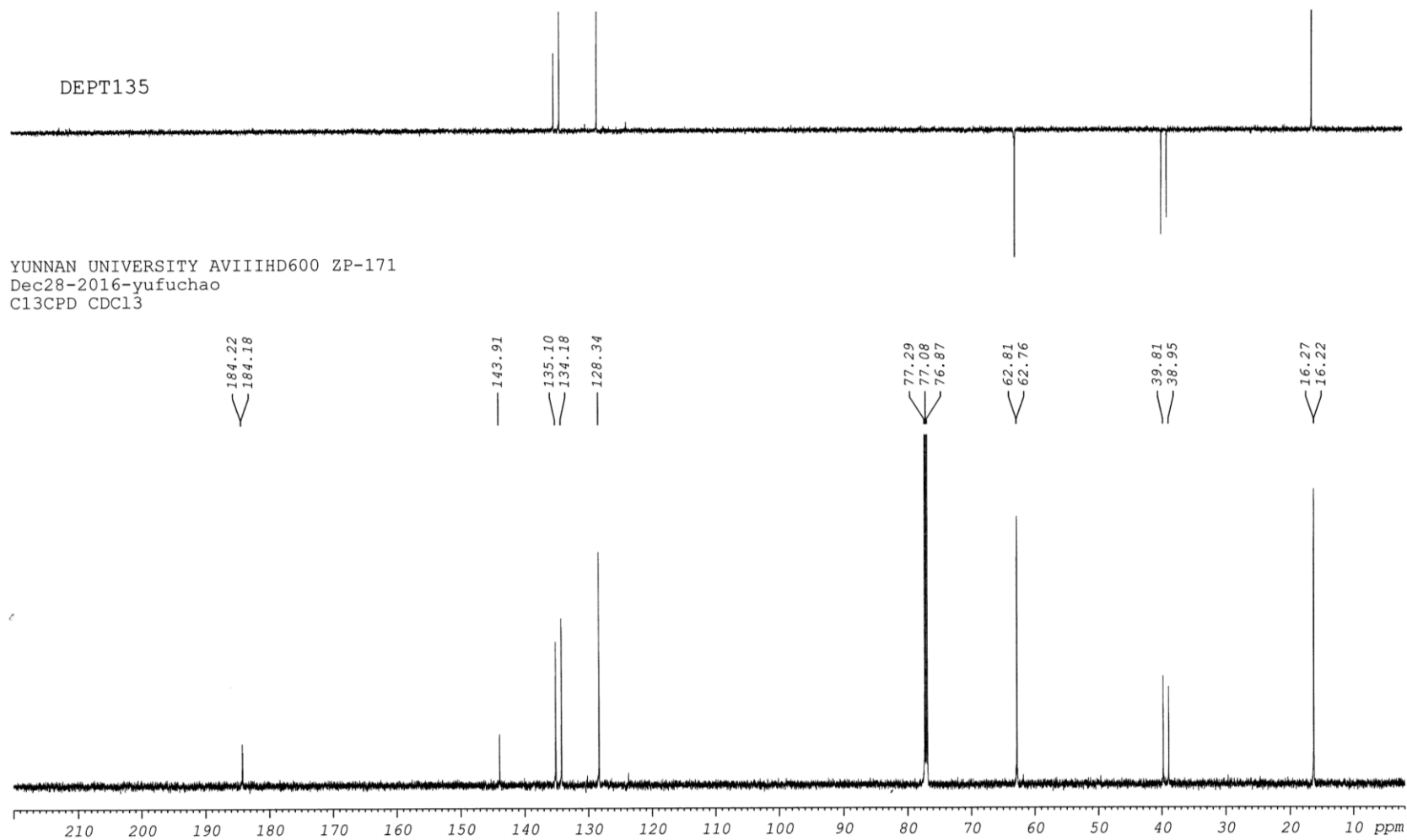


Figure S30. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3n**

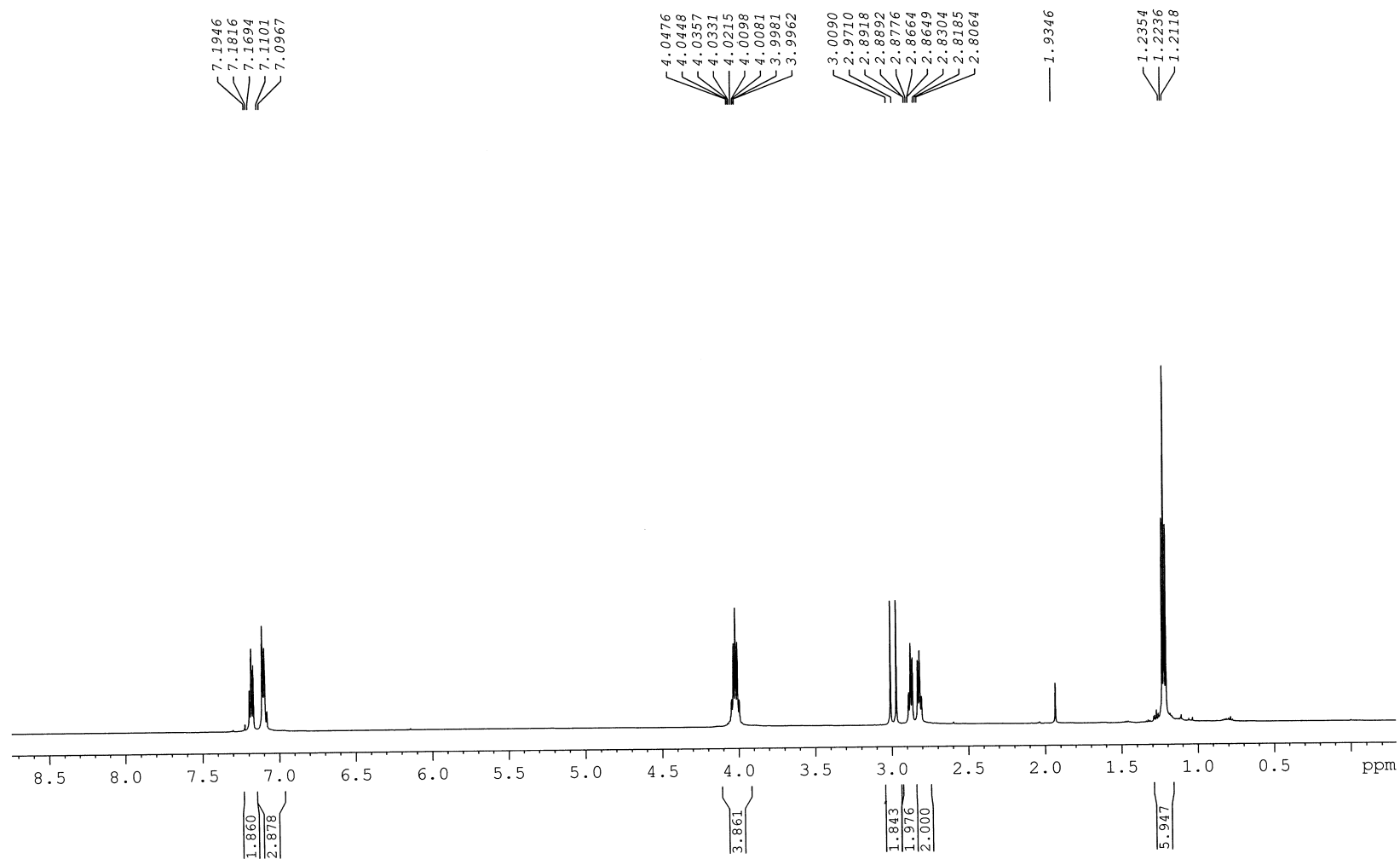


Figure S31. ^1H NMR (600 MHz, CDCl_3) spectra of compound **3q**

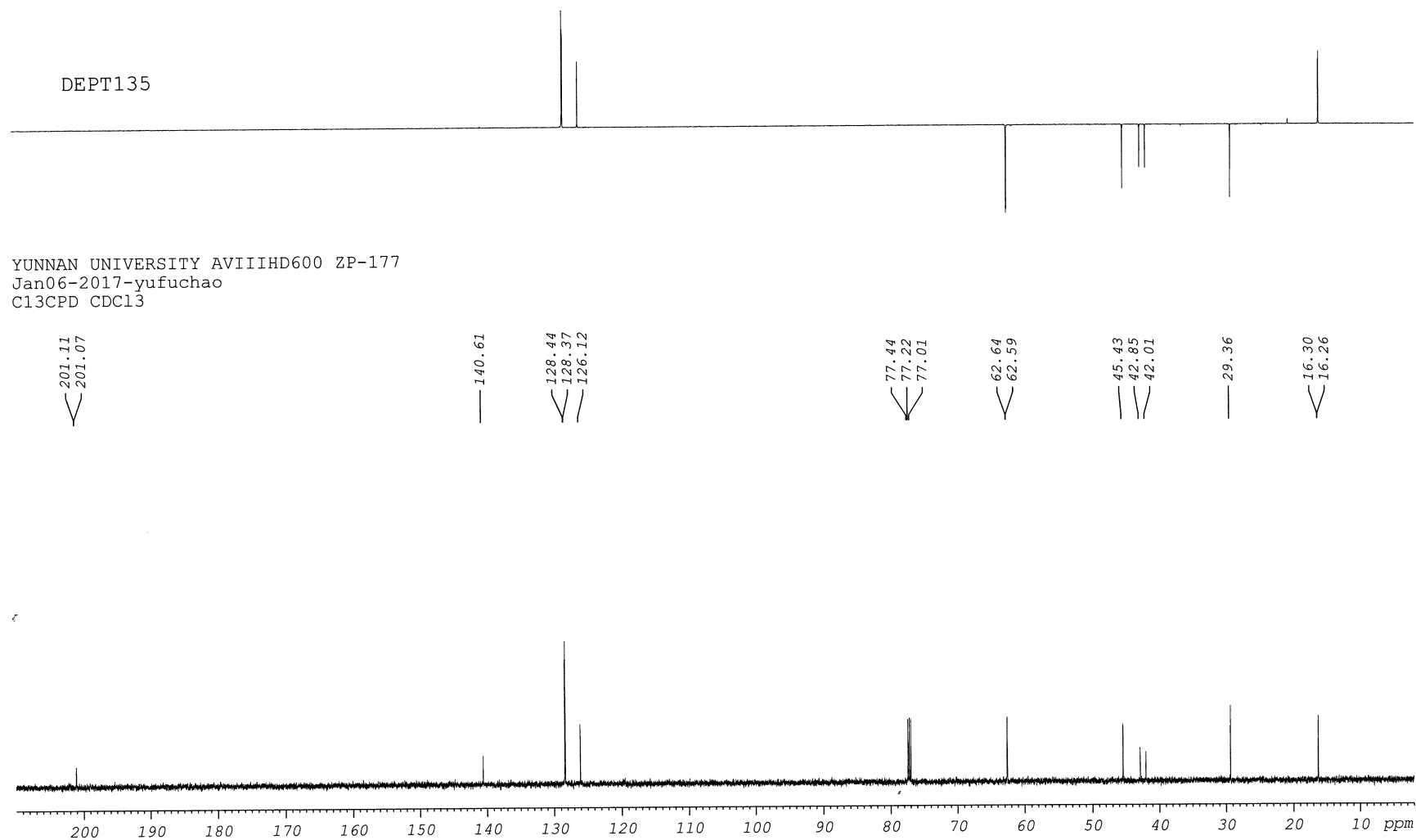


Figure S32. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **3q**

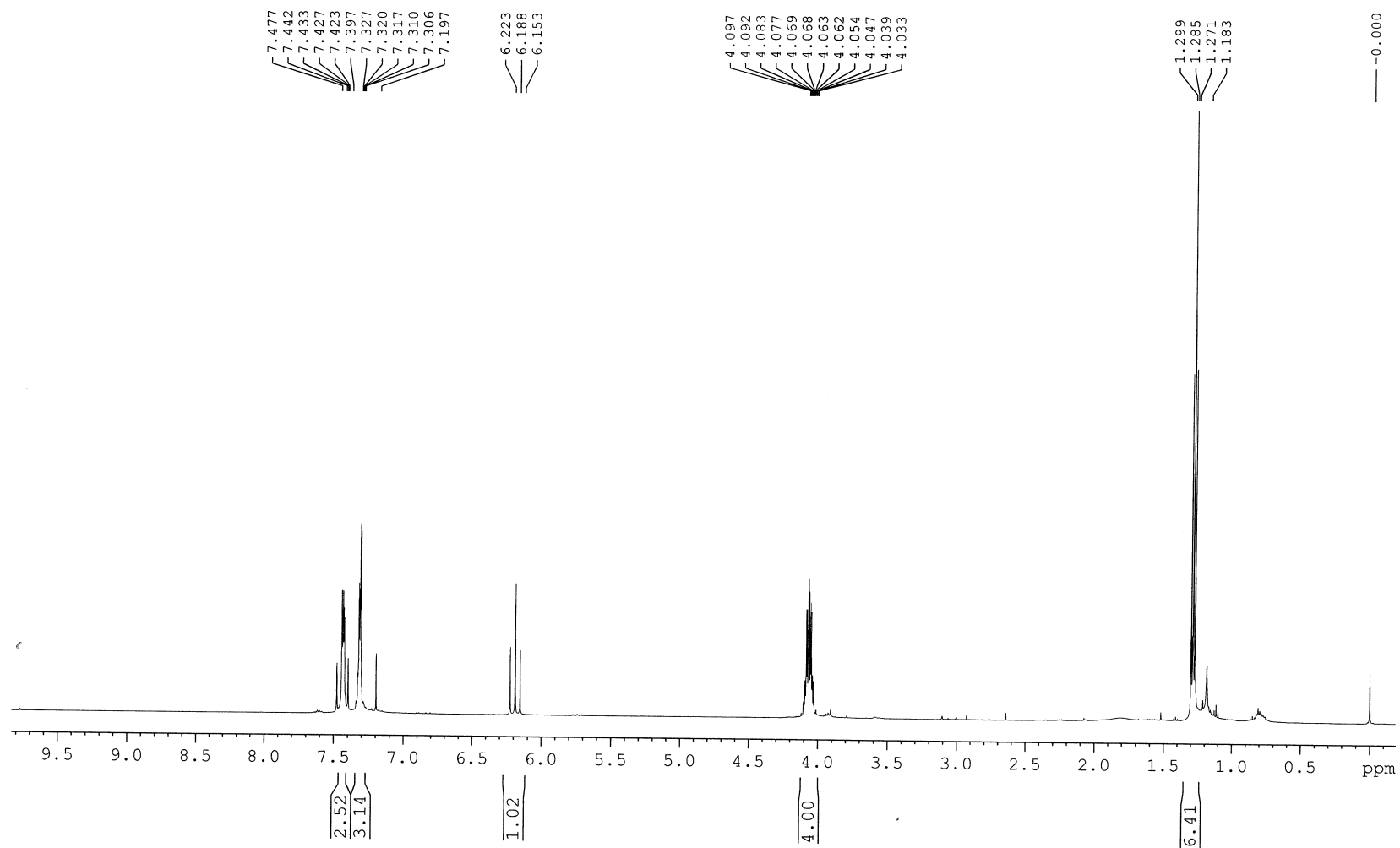


Figure S33. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3r**

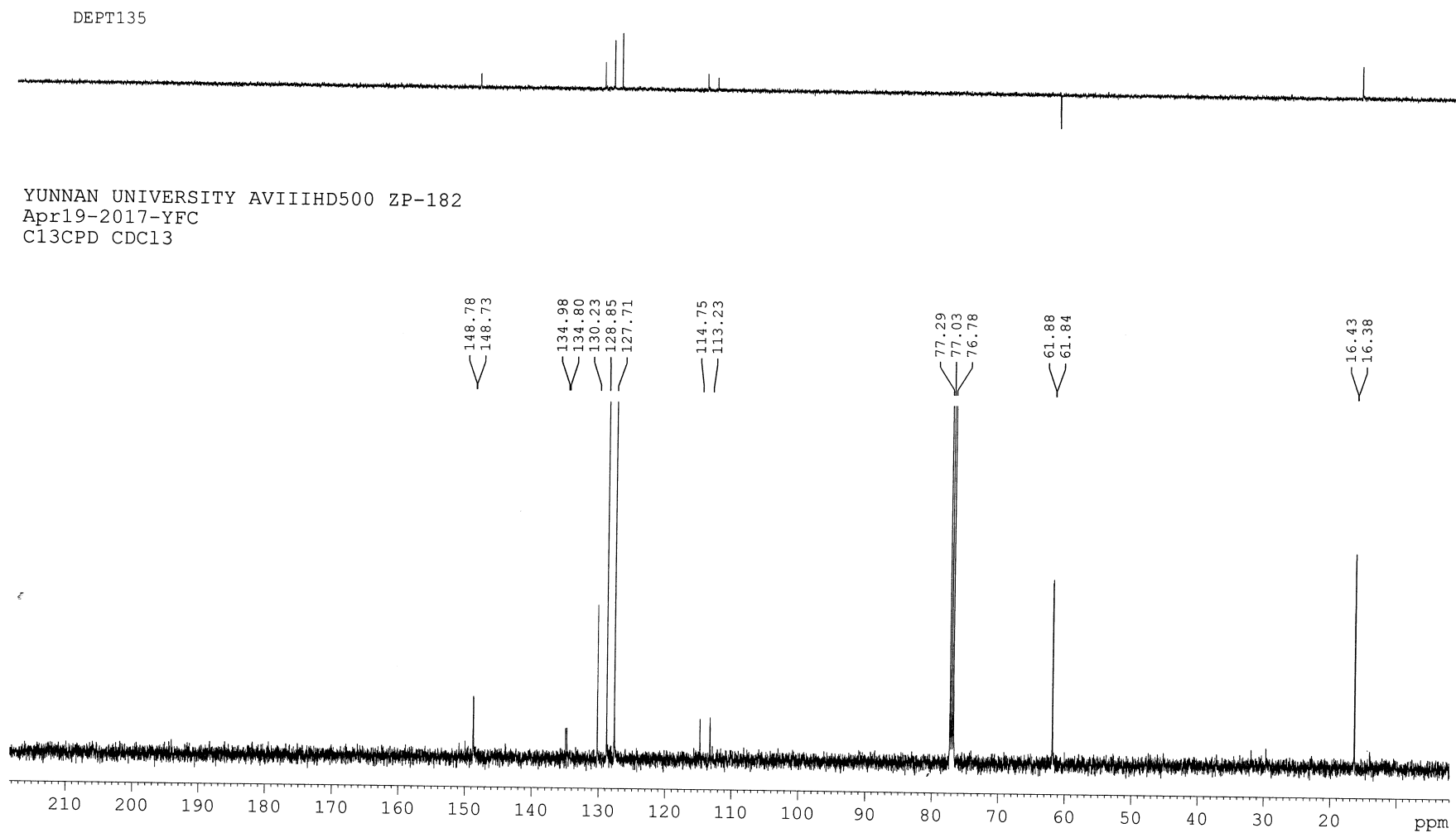


Figure S34. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3r**

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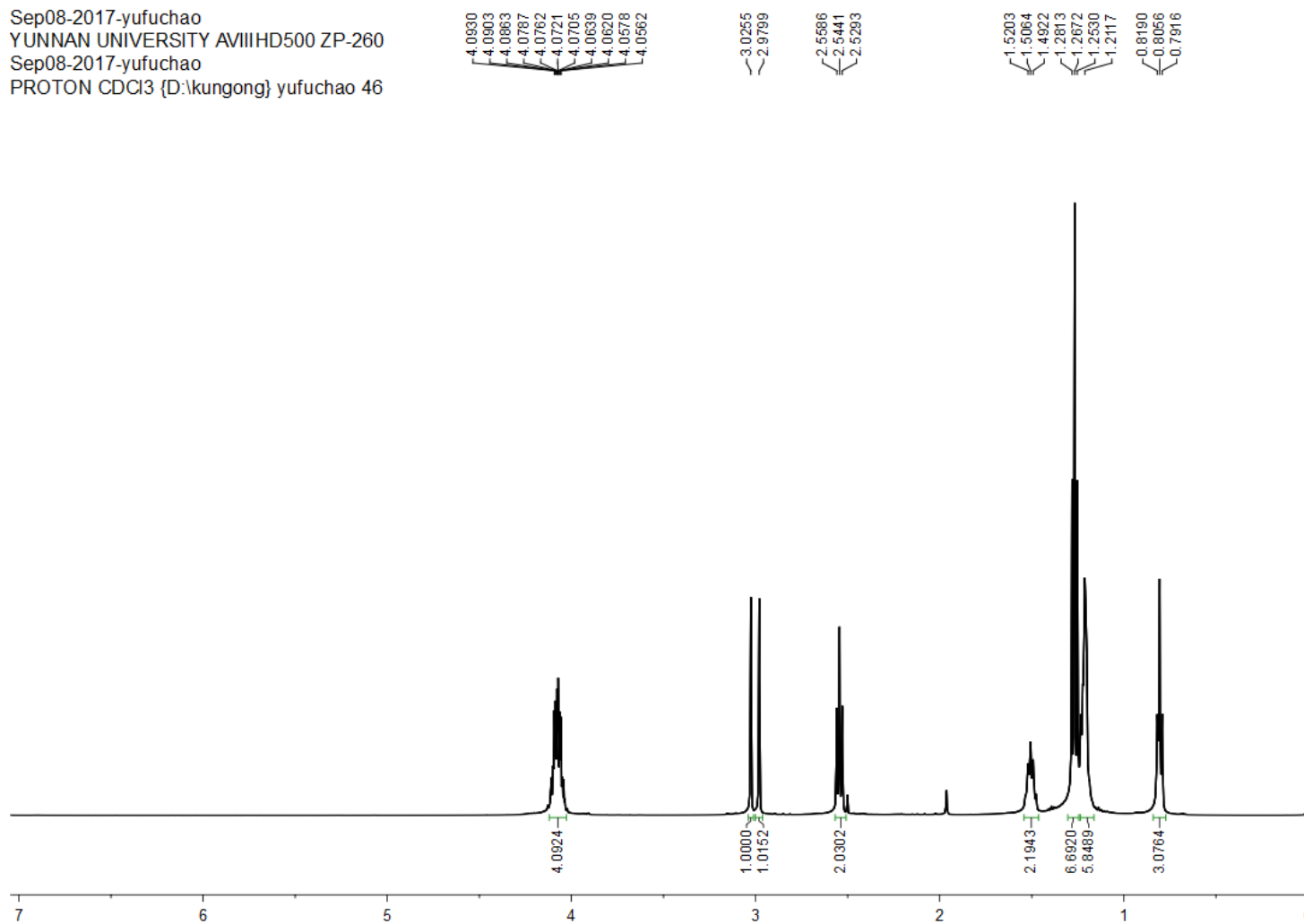


Figure S35. ¹H NMR (500 MHz, CDCl₃) spectra of compound **3s**

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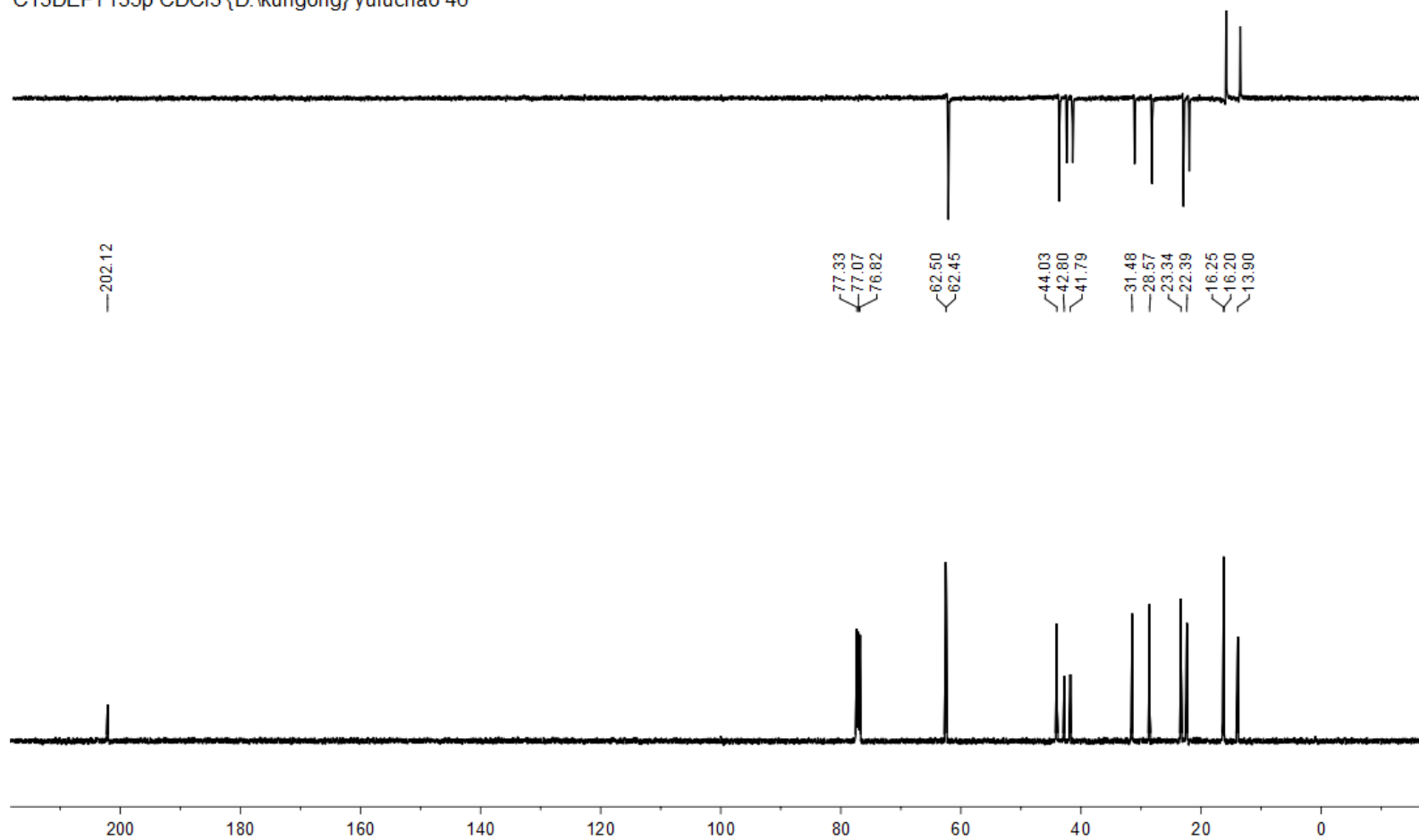


Figure S36. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3s**

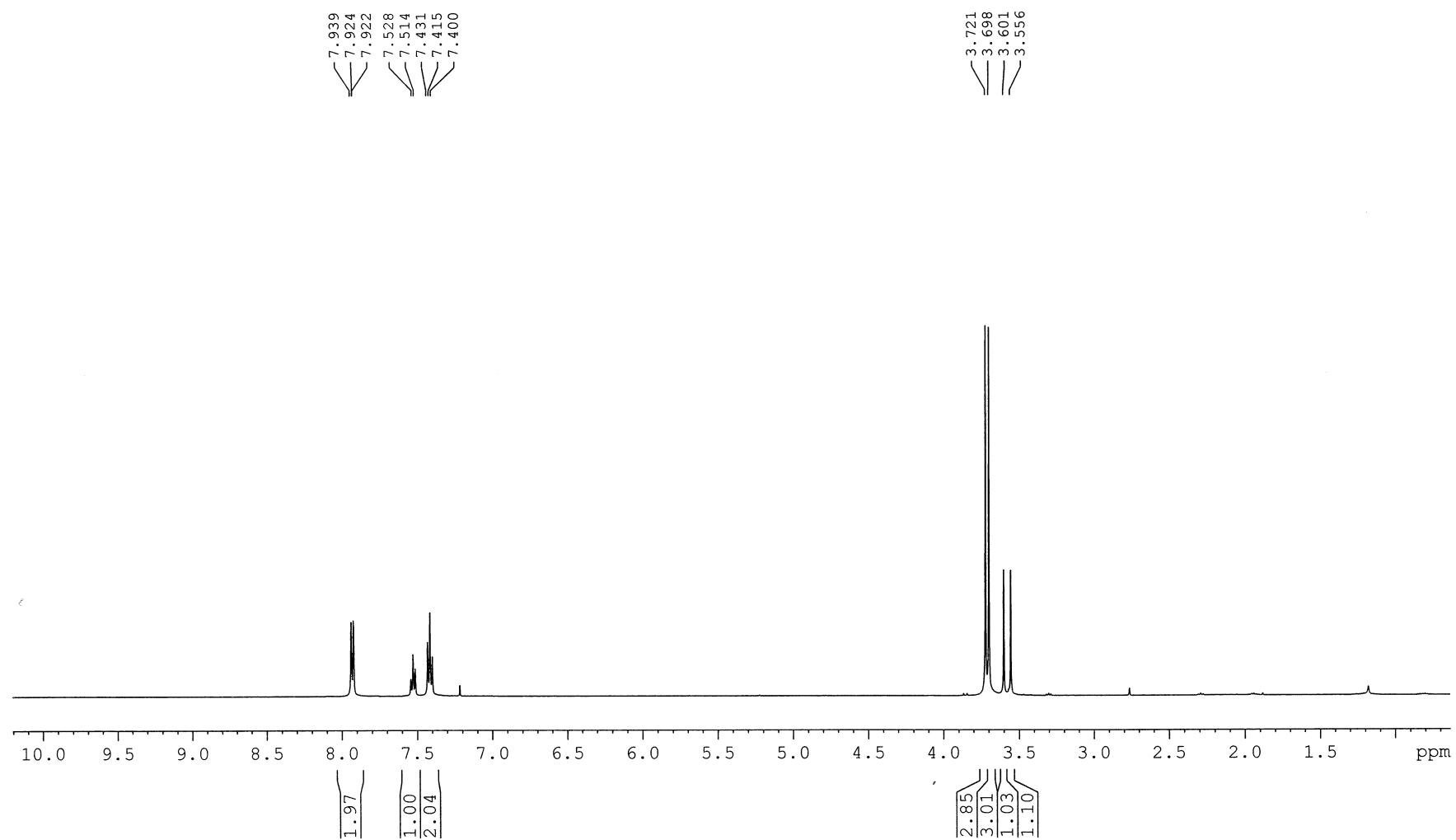
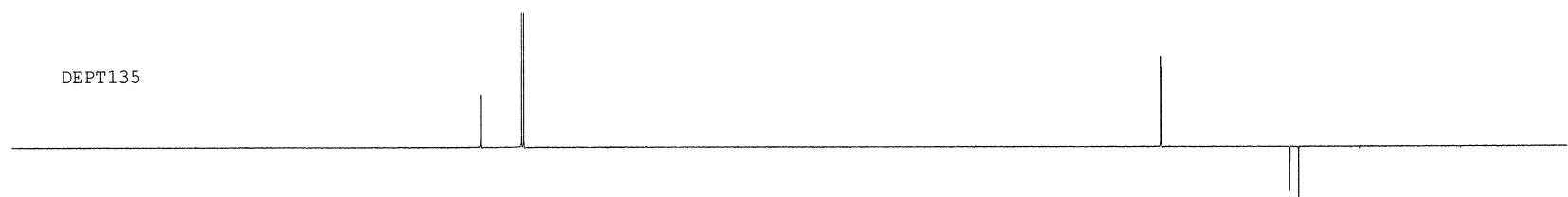


Figure S37. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3t**



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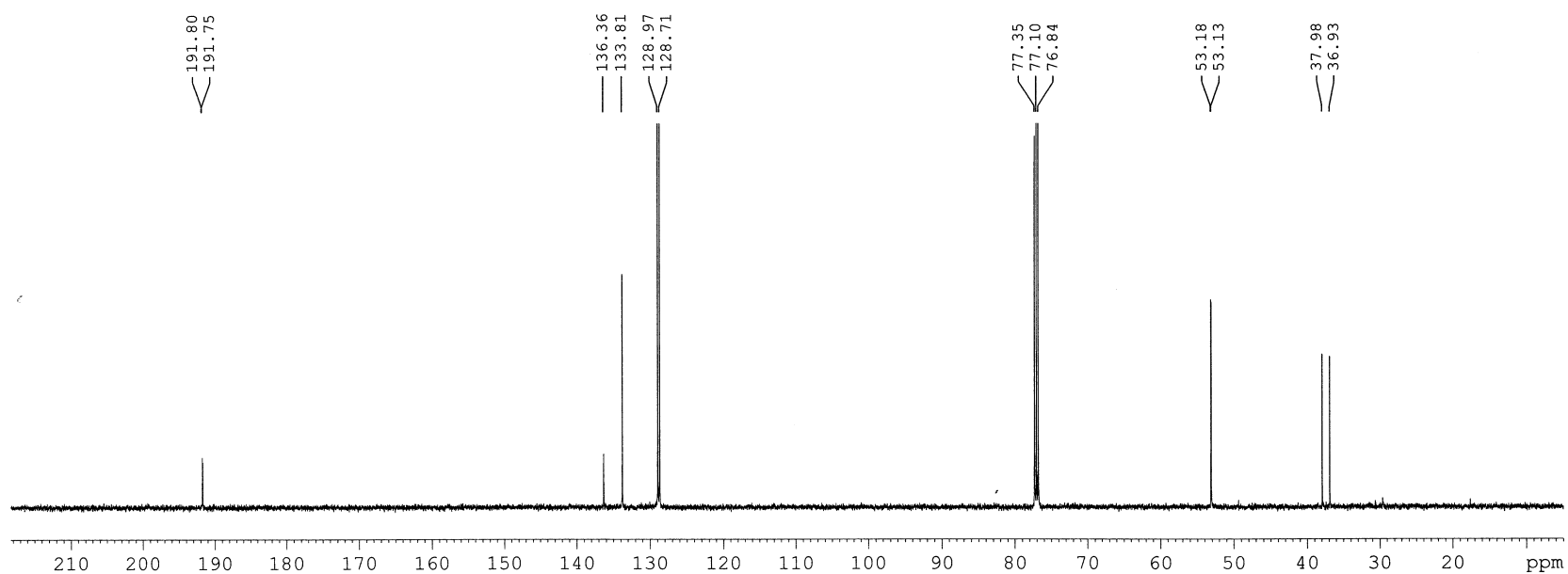


Figure S38. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3t**

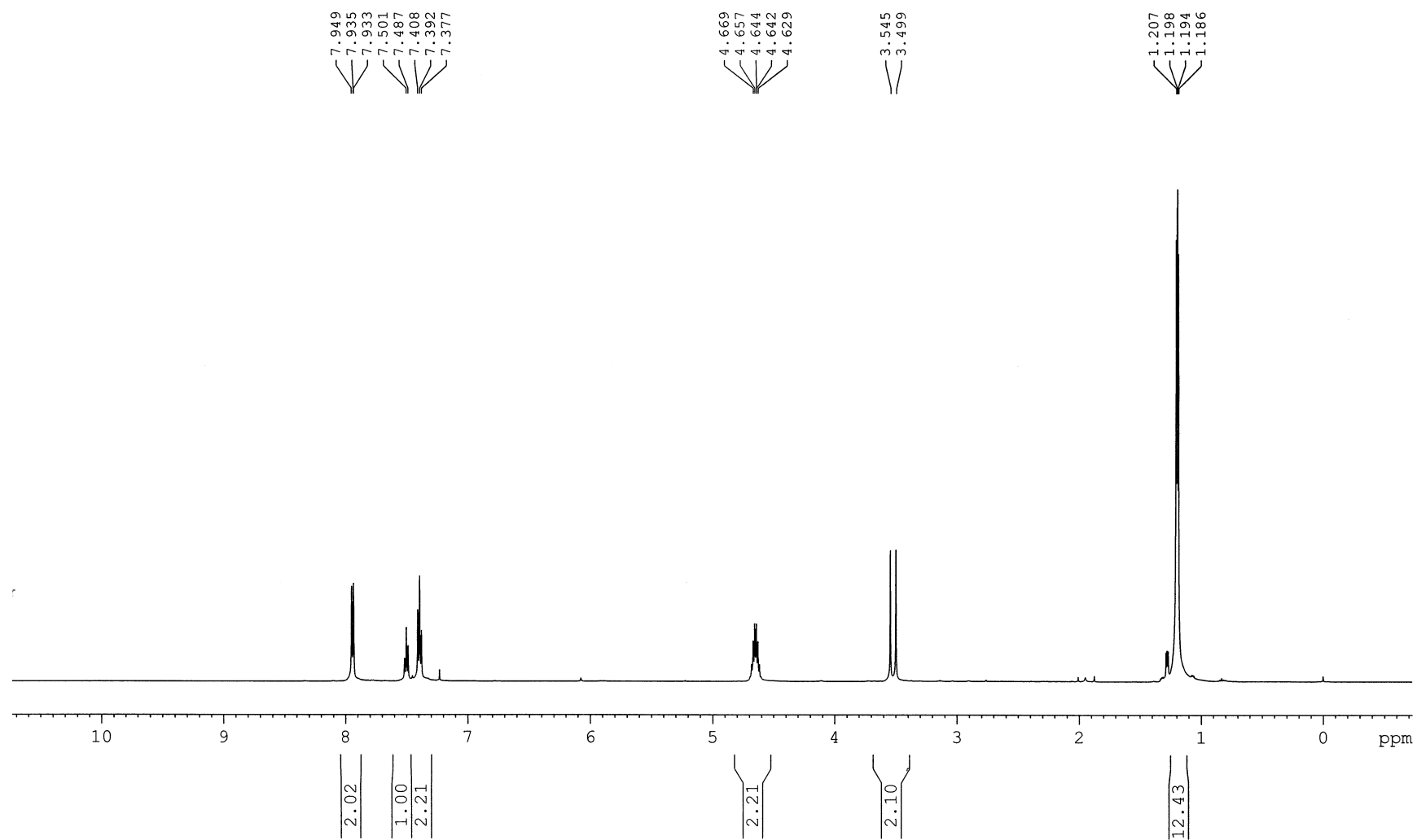


Figure S39. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3u**

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C13CPD CDCl3

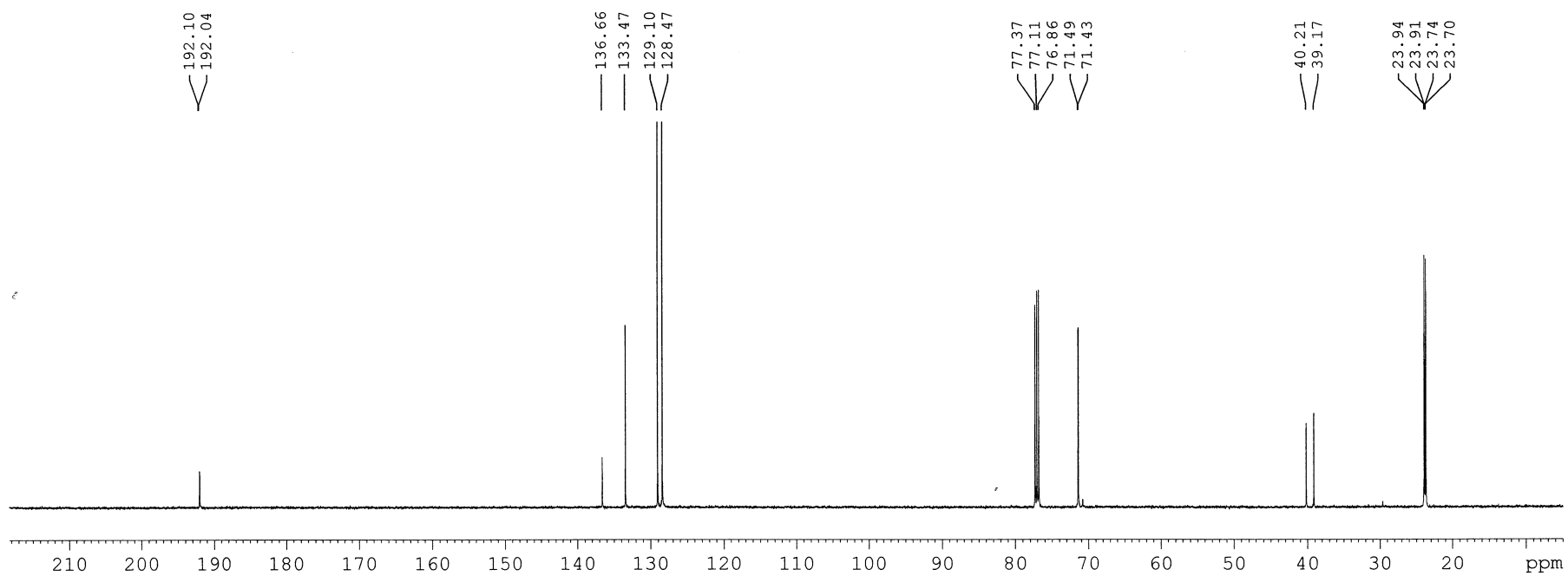


Figure S40. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3u**

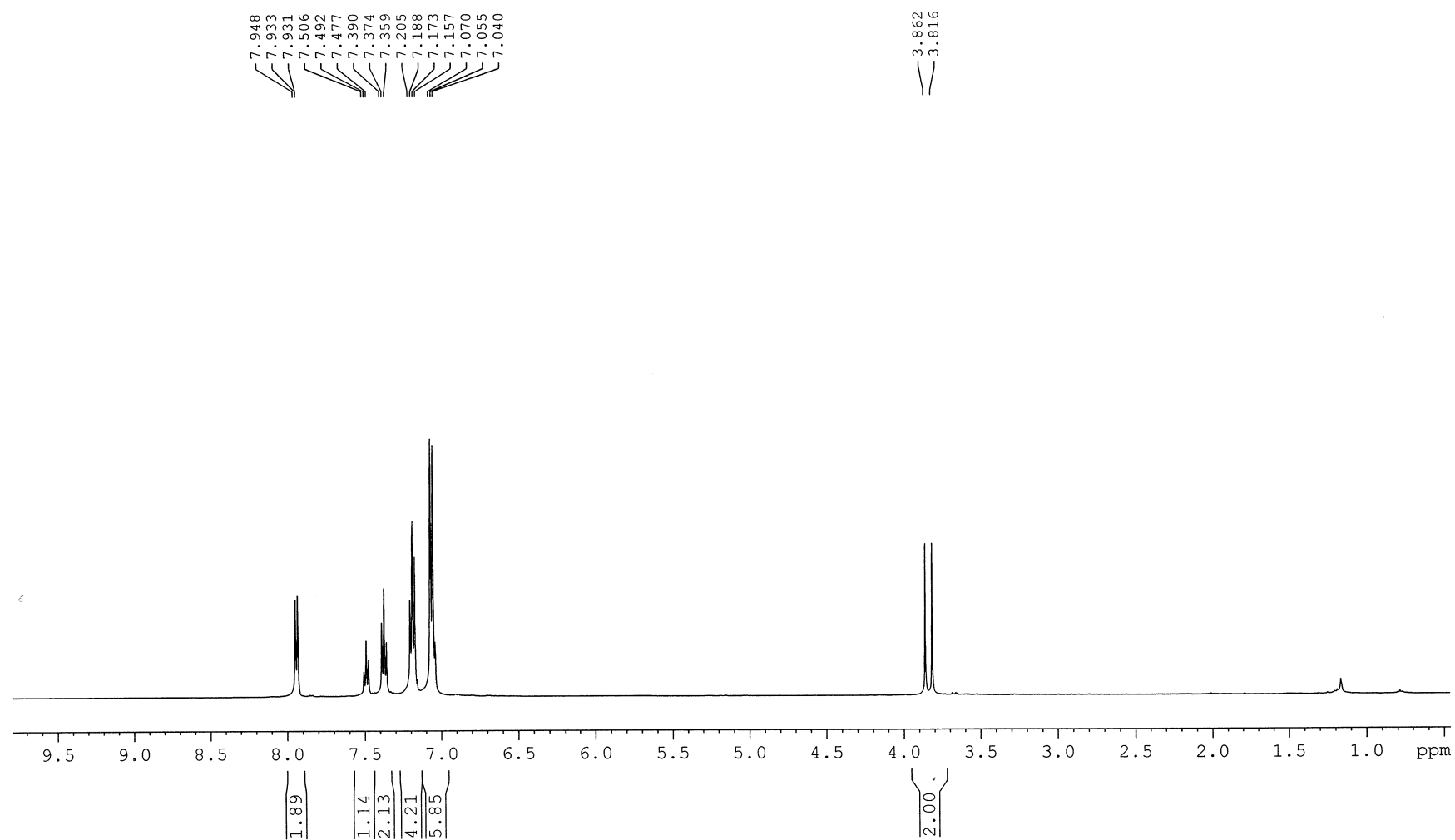
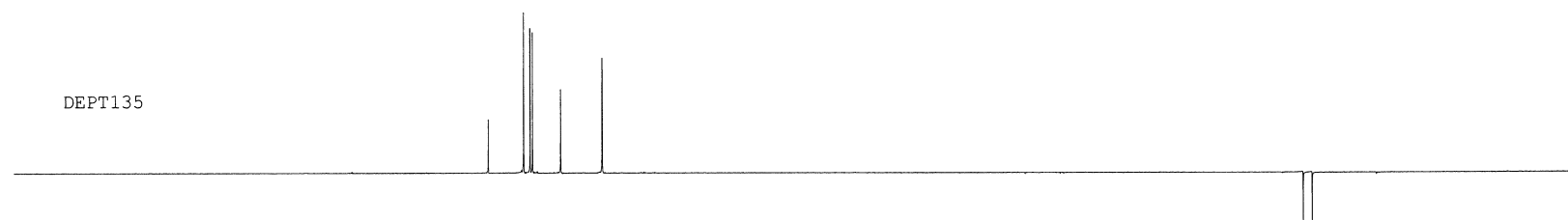


Figure S41. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3v**



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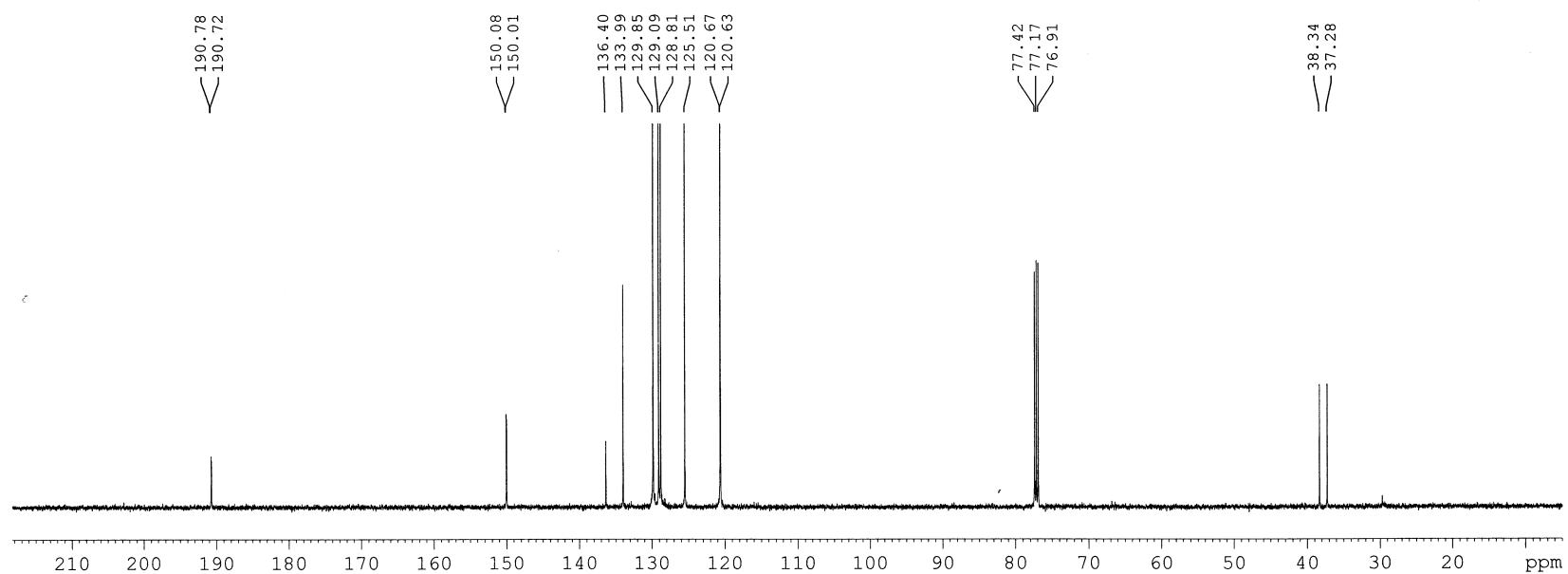


Figure S42. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3v**

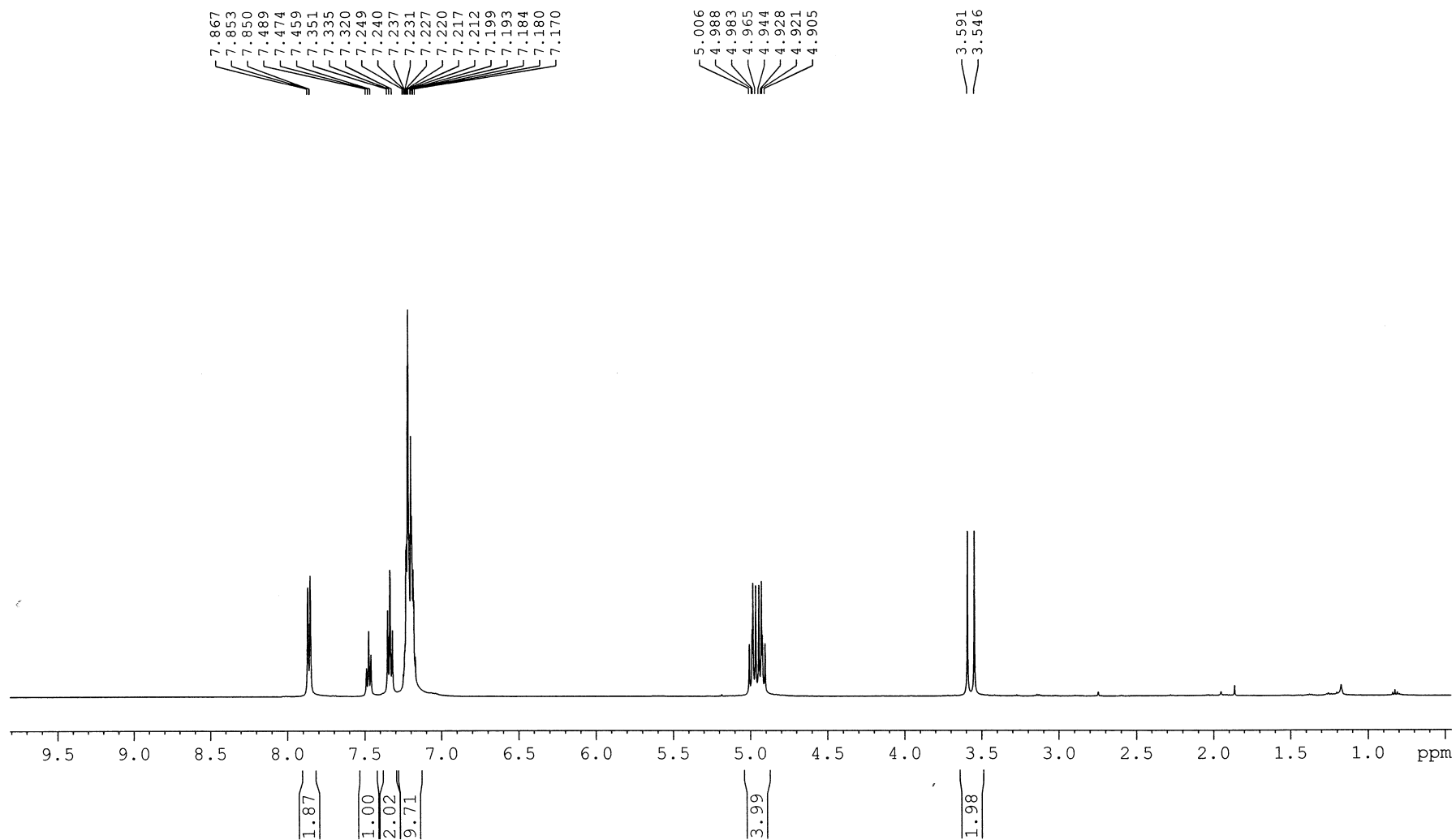


Figure S43. ^1H NMR (500 MHz, CDCl_3) spectra of compound **3w**

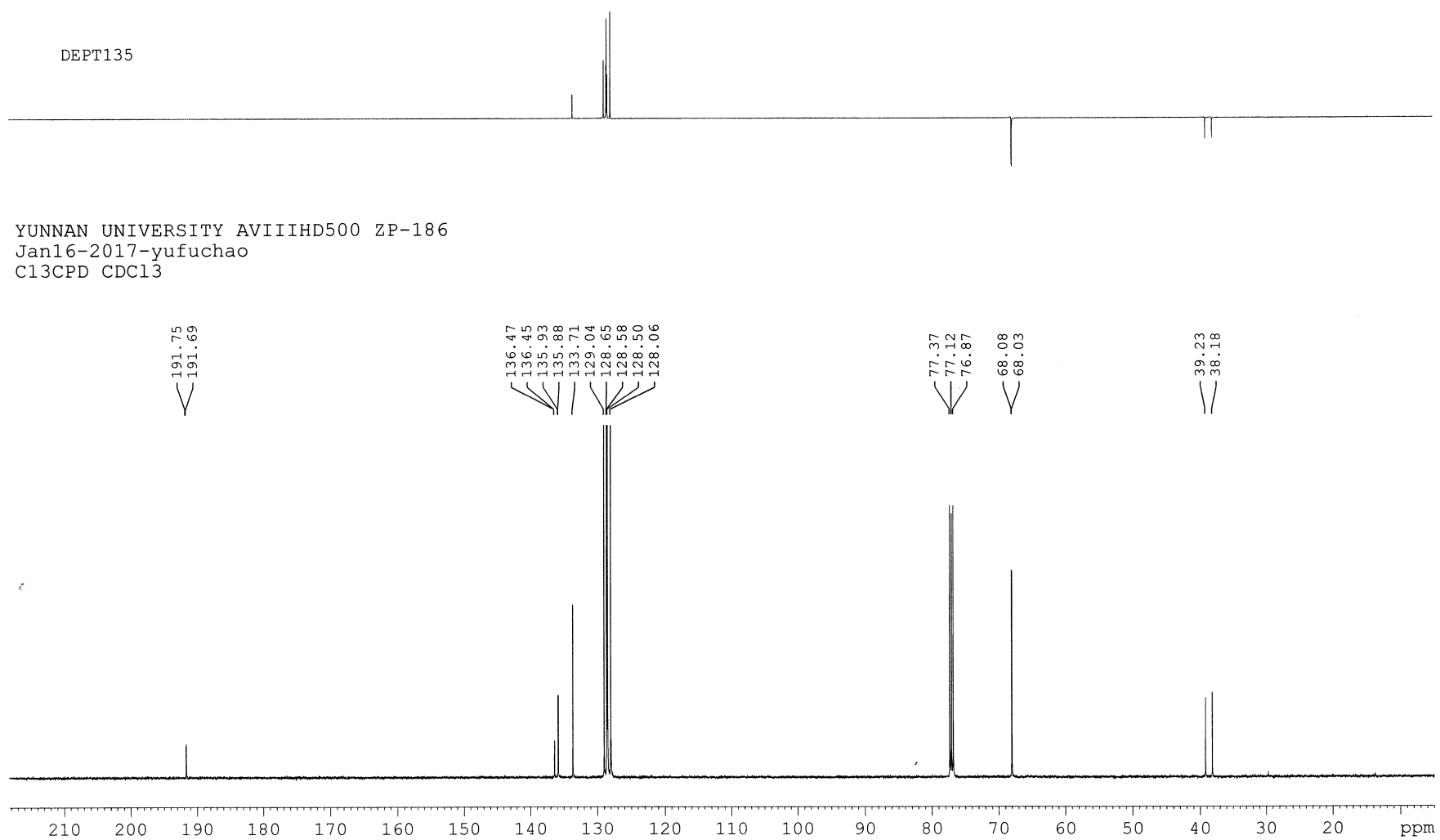


Figure S44. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **3w**

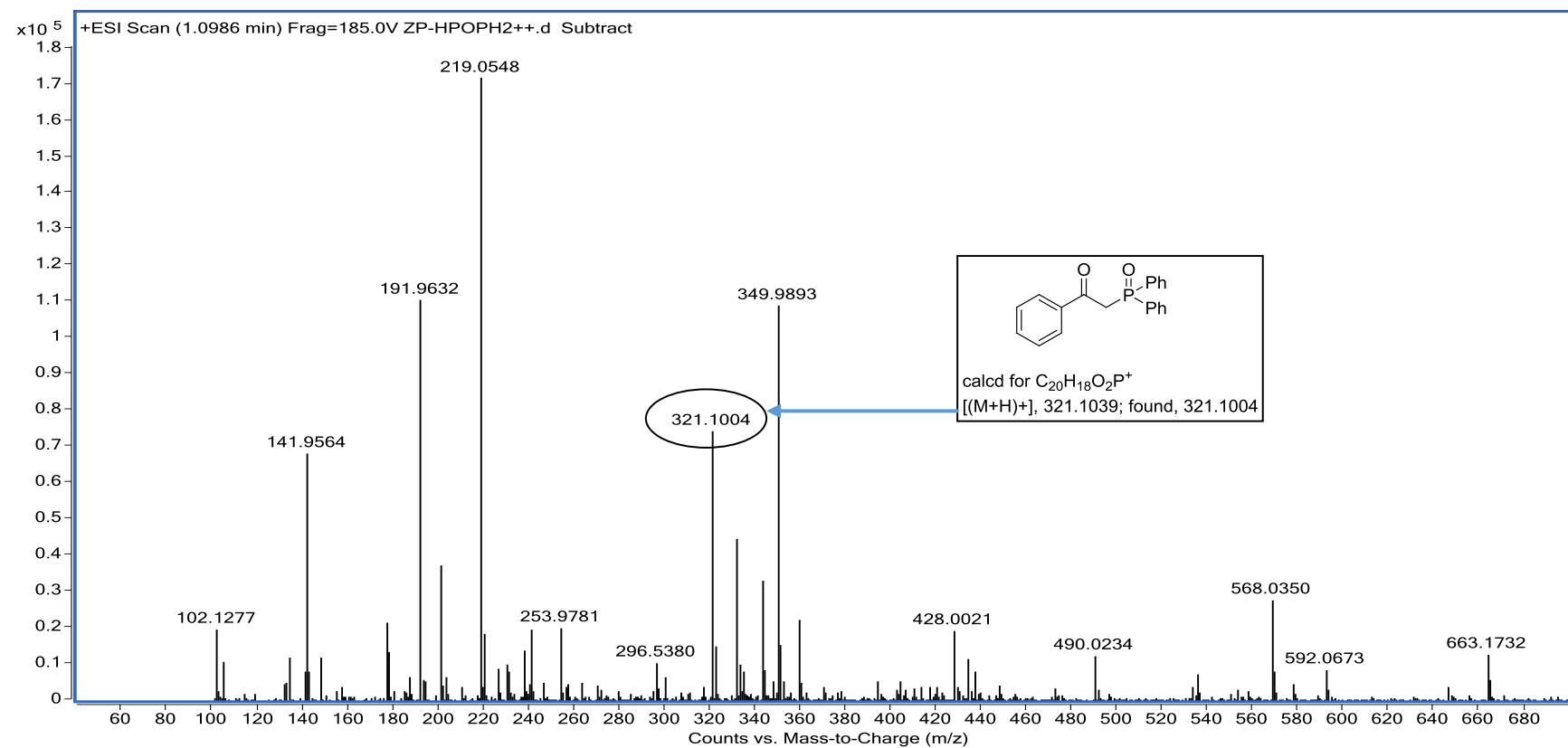


Figure S45. HRMS spectra of compound **3x**

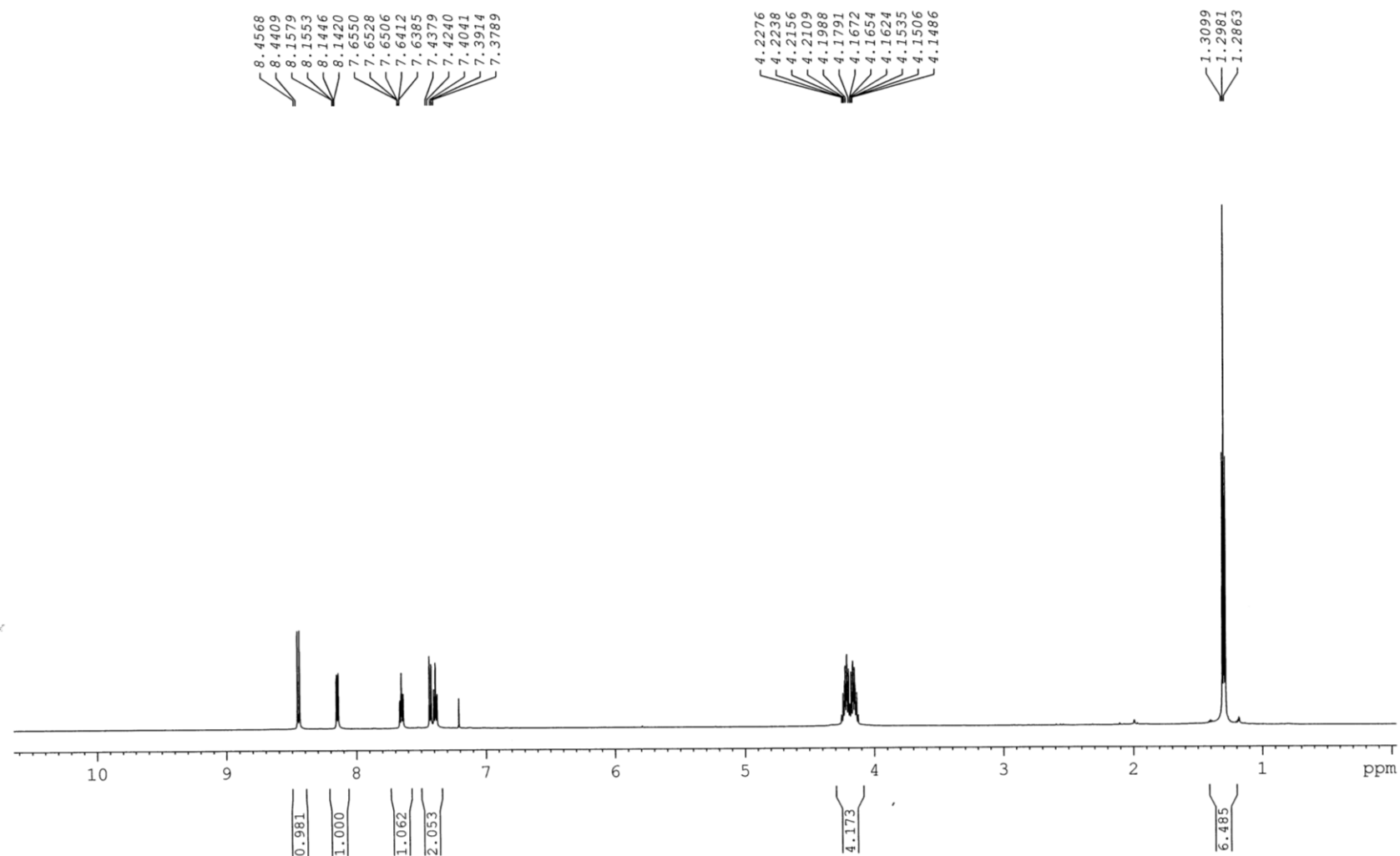


Figure S46. ^1H NMR (600 MHz, CDCl_3) spectra of compound **4a**

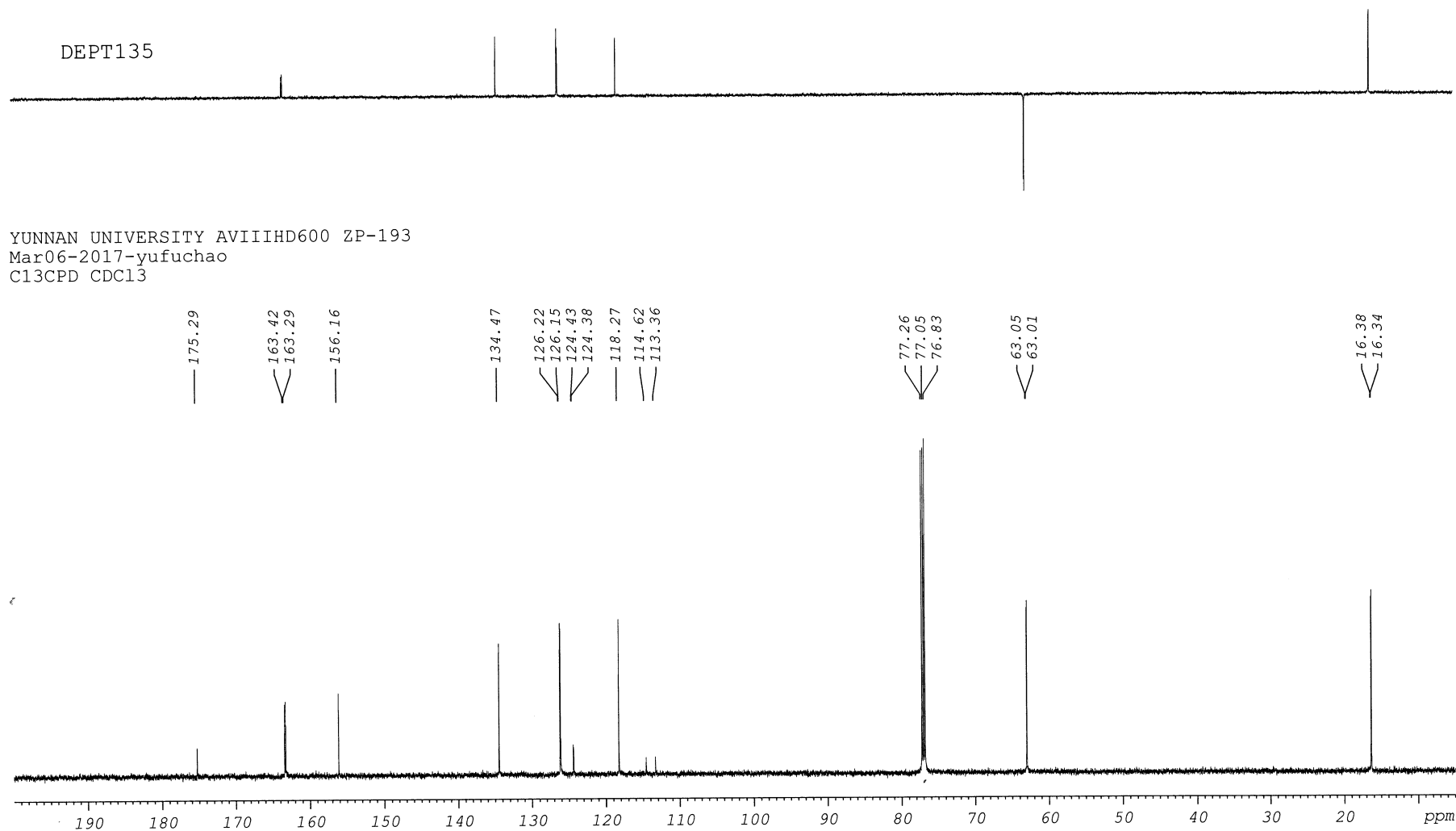


Figure S47. ^{13}C NMR (150 MHz, CDCl_3) spectra of compound **4a**

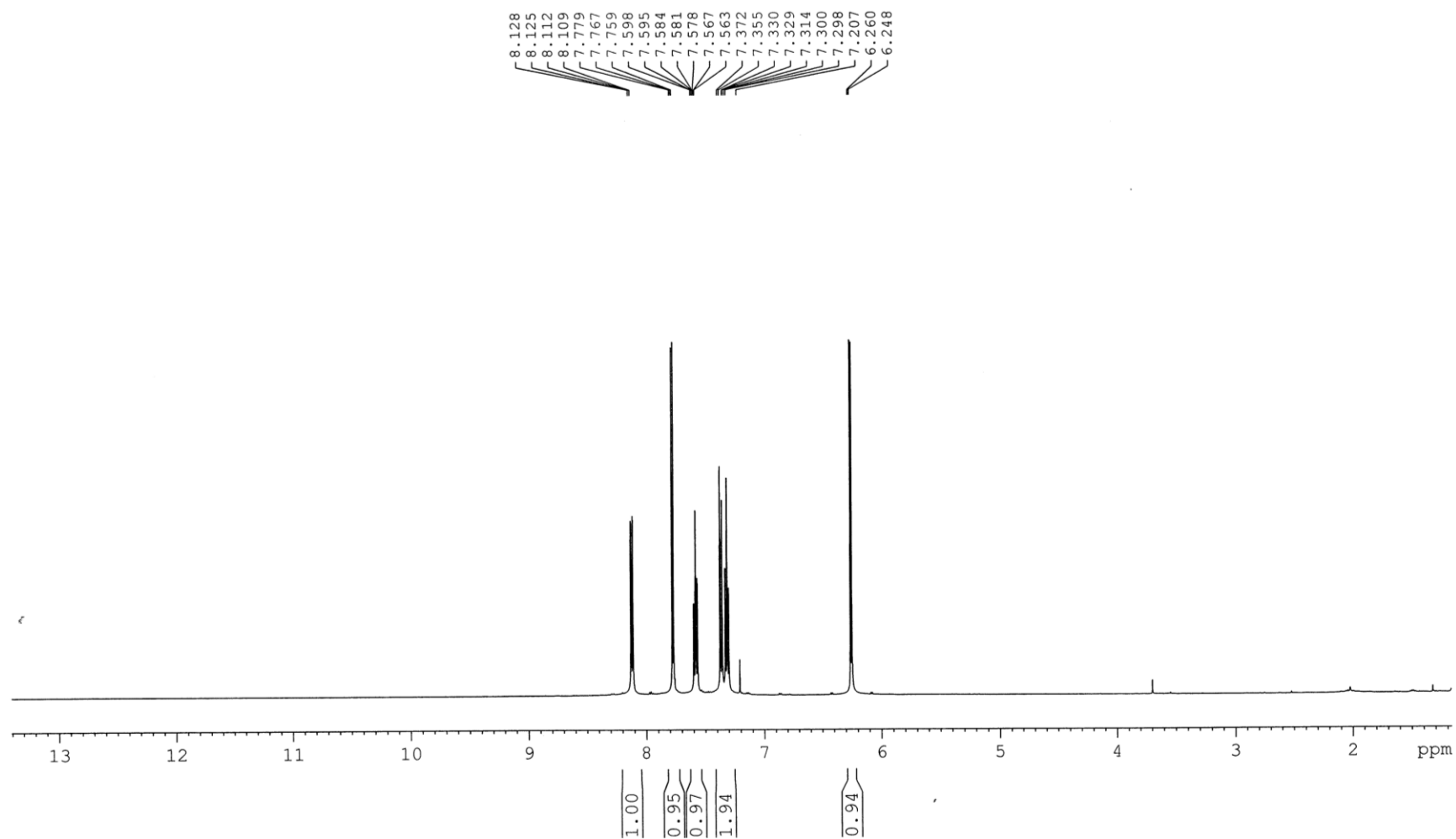
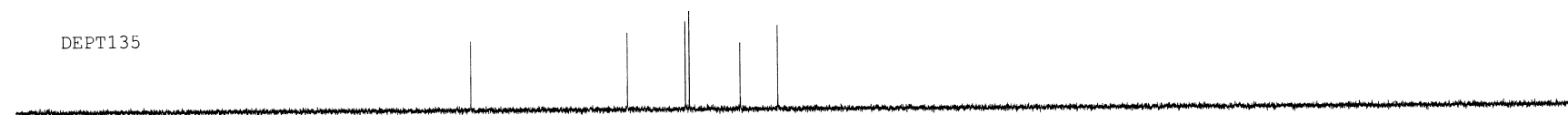


Figure S48. ¹H NMR (500 MHz, CDCl₃) spectra of compound **5**

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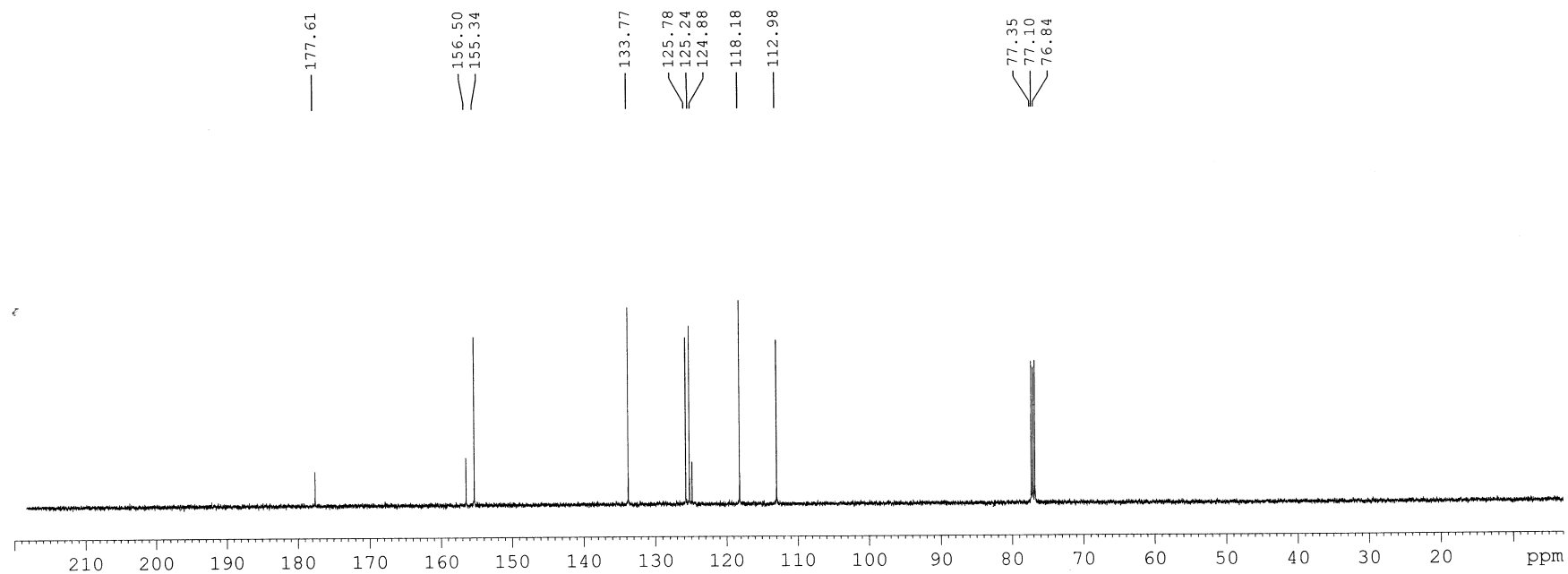


Figure S49. ¹³C NMR (125 MHz, CDCl₃) spectra of compound **5**

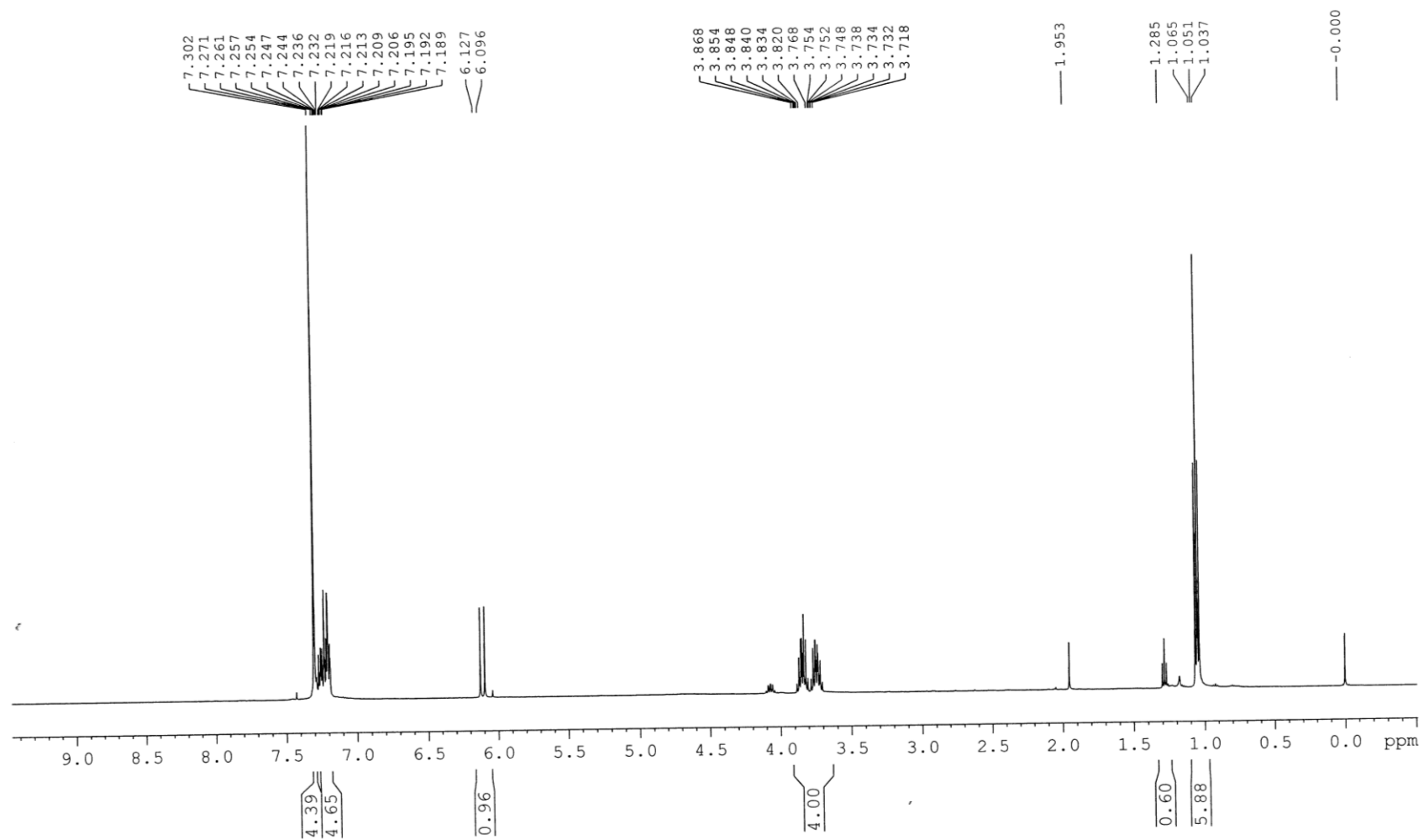


Figure S50. ^1H NMR (500 MHz, CDCl_3) spectra of compound **9**

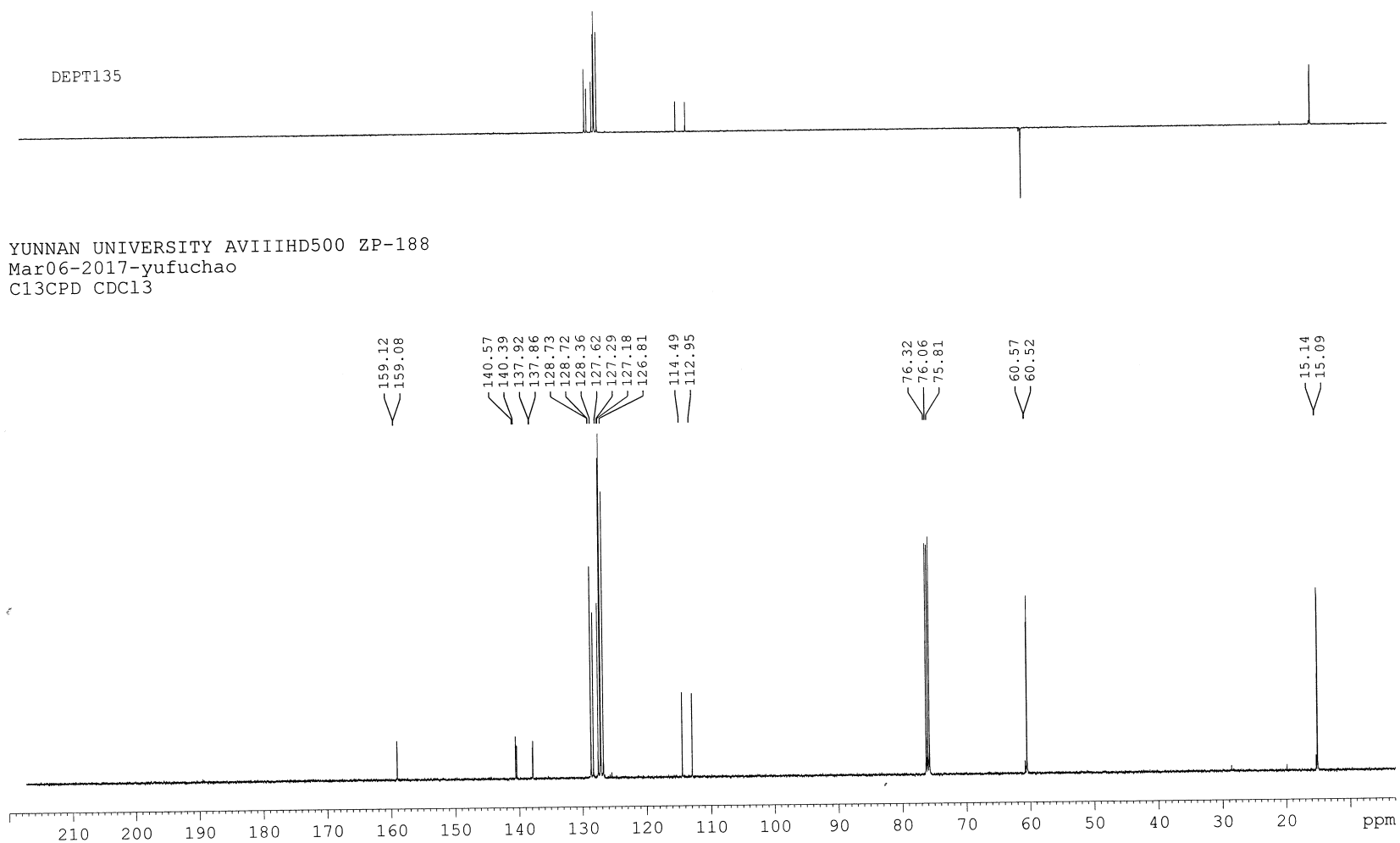


Figure S51. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **9**

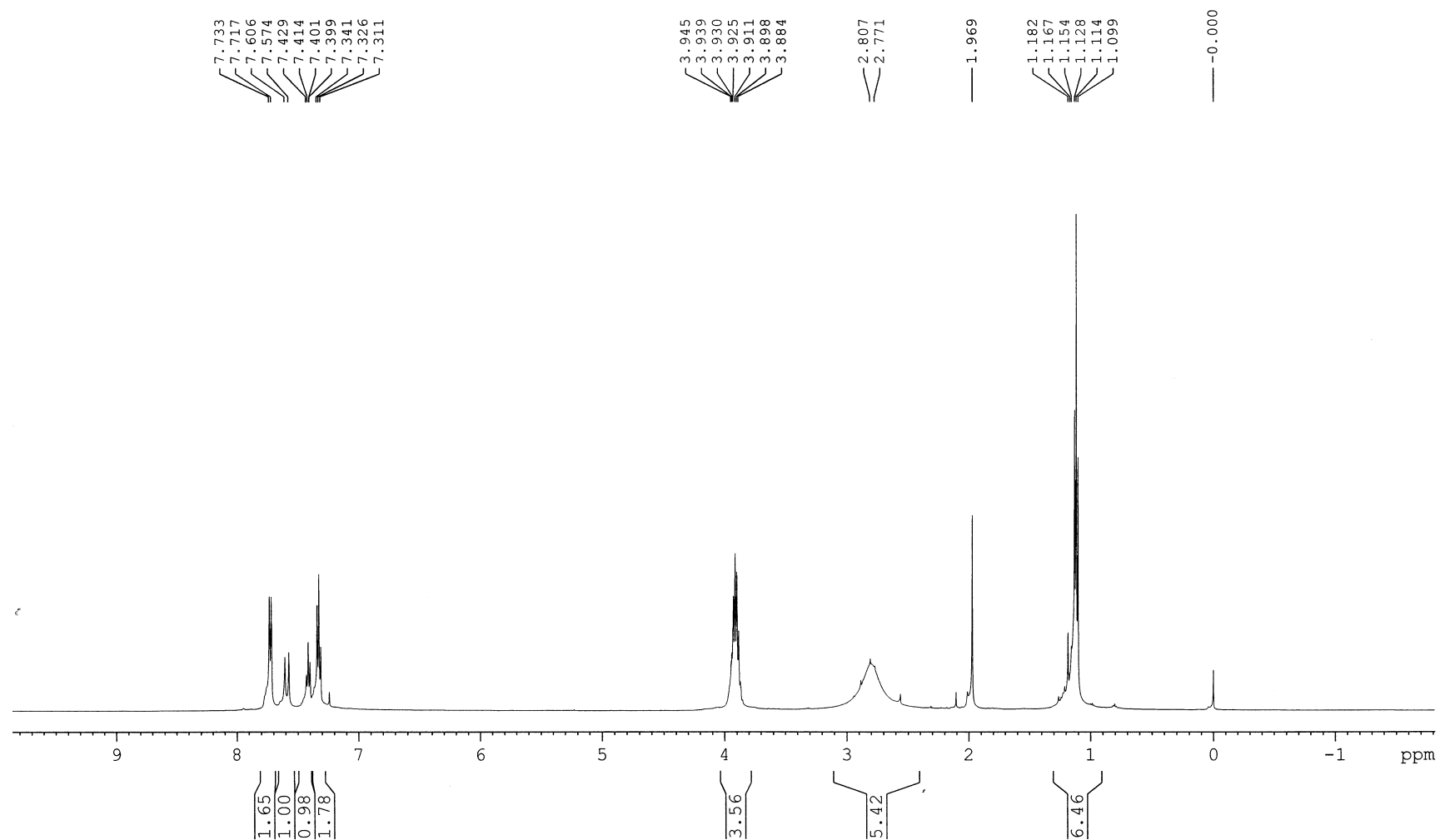


Figure S52. ¹H NMR (500 MHz, CDCl₃) spectra of compound **10a**

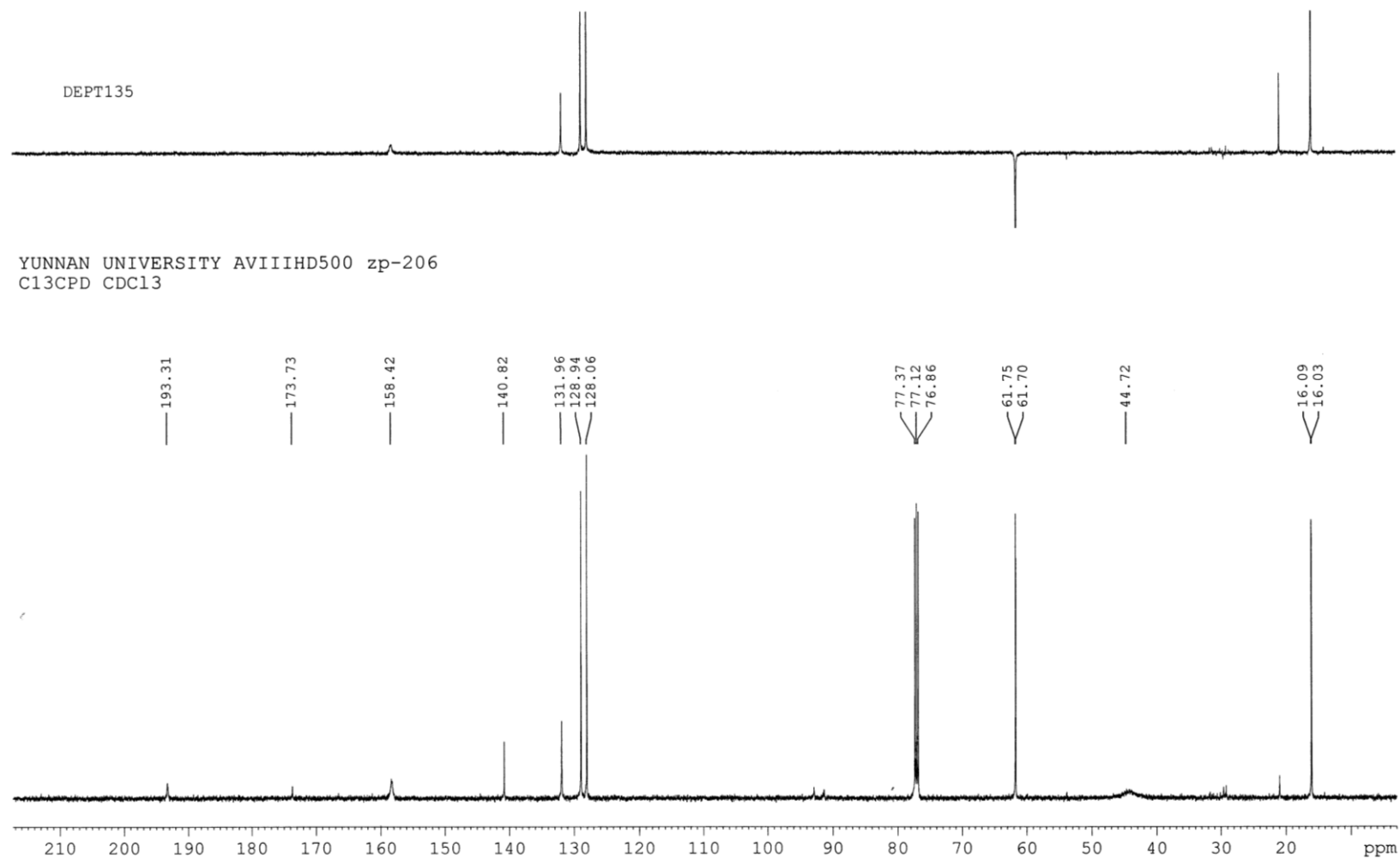


Figure S53. ^{13}C NMR (125 MHz, CDCl_3) spectra of compound **10a**