

Supporting Information

An Optimized Preparation of 1,1-Dimethylallyl Esters and Their Application to Solid-Phase Peptide Synthesis

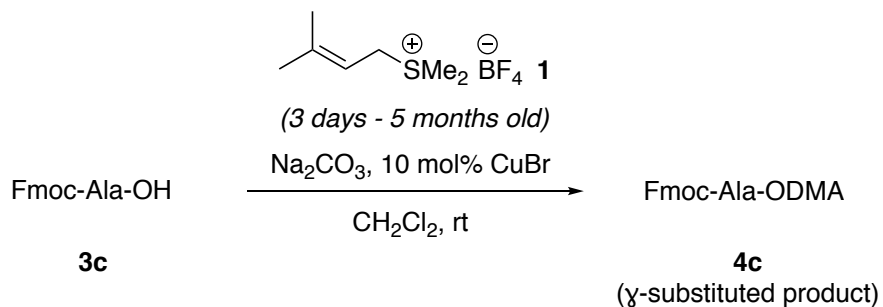
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I. Table S1. The effect of sulfonium salt (1) age on the yield of DMA esterification of 3c^{a,b}



Sulfonium salt (1) age	Yield, %	γ / α ^c	mp (°C) ^d
3 days	88	97 / 3	64-66
2.5 months	89	96 / 4	62-64
5 months	84	97 / 3	61-63

^a Sulfonium salt **1** stored at -20 °C throughout period explored. ^b Reactions performed on 0.25 mmol scale using optimized conditions. ^c γ / α product ratio was determined by ¹H NMR integration. ^d Melting point of **1** recorded during same period that stability was explored.

II. Prenyldimethylsulfonium tetrafluoroborate (1) ^1H NMR stability studies

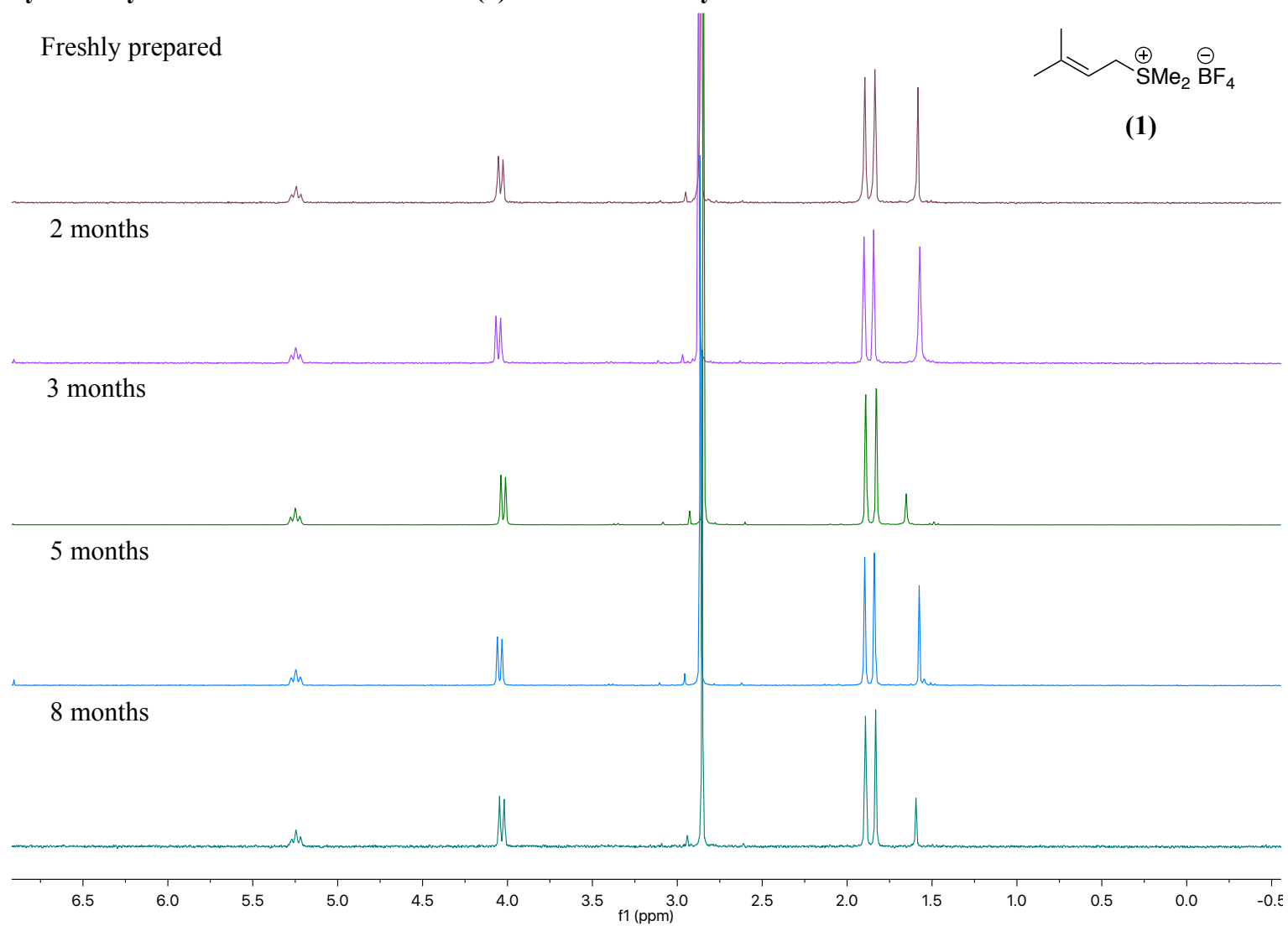


Figure S1. ^1H NMR (300 MHz, CDCl_3)

III. ^1H and ^{13}C NMR Spectra

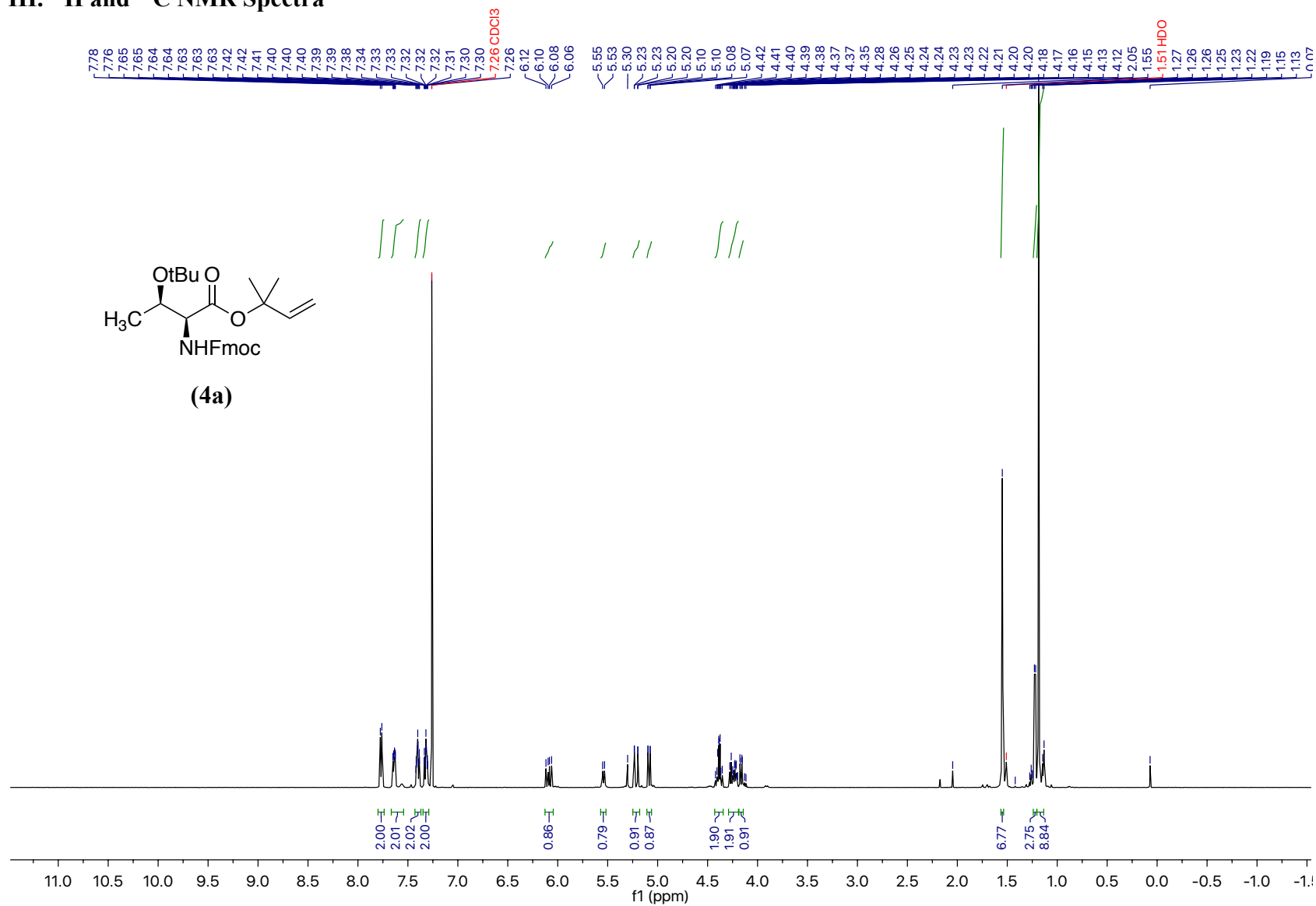


Figure S2. ^1H NMR (500 MHz, CDCl_3)

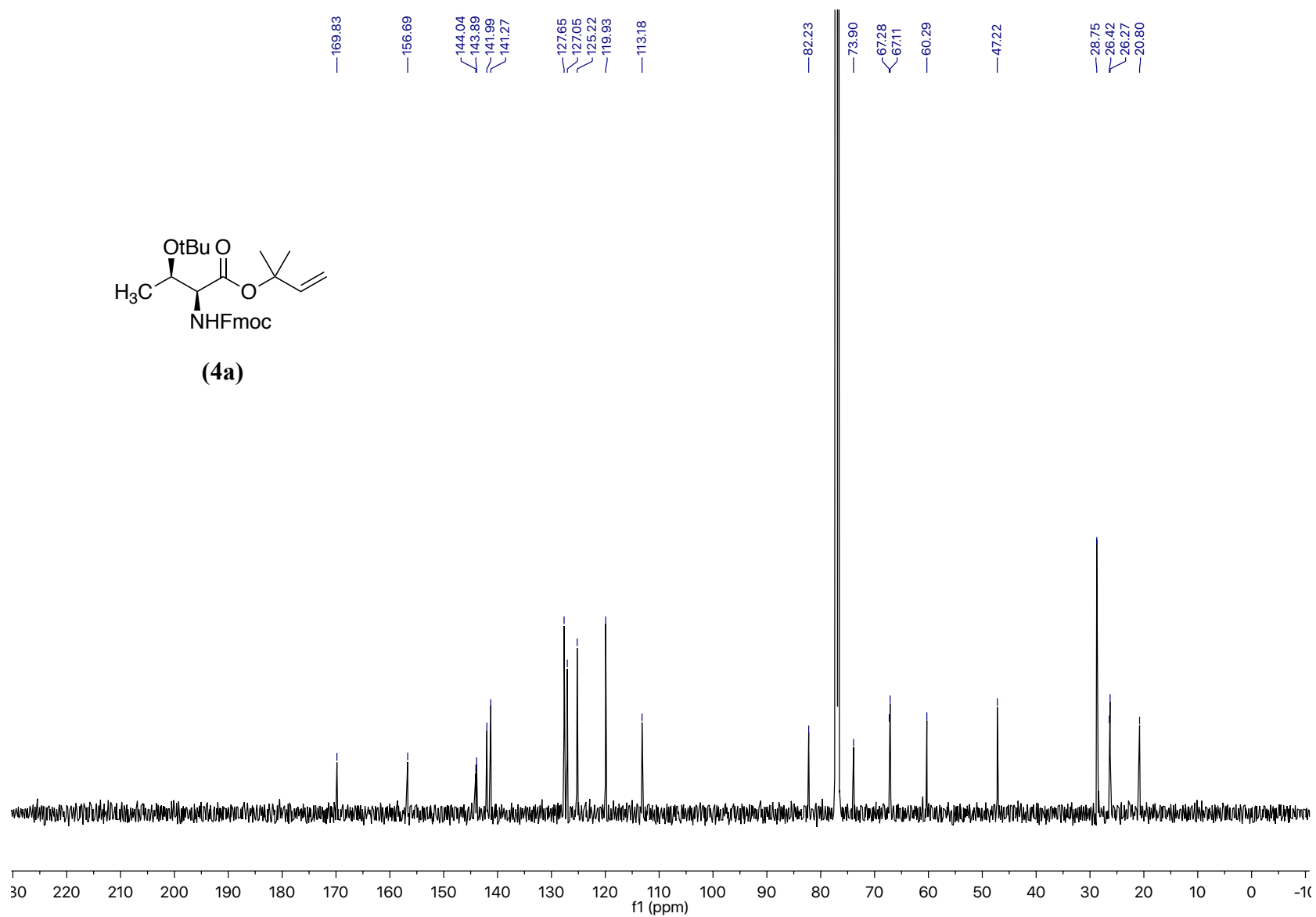


Figure S3. ^{13}C NMR (125 MHz, CDCl_3)

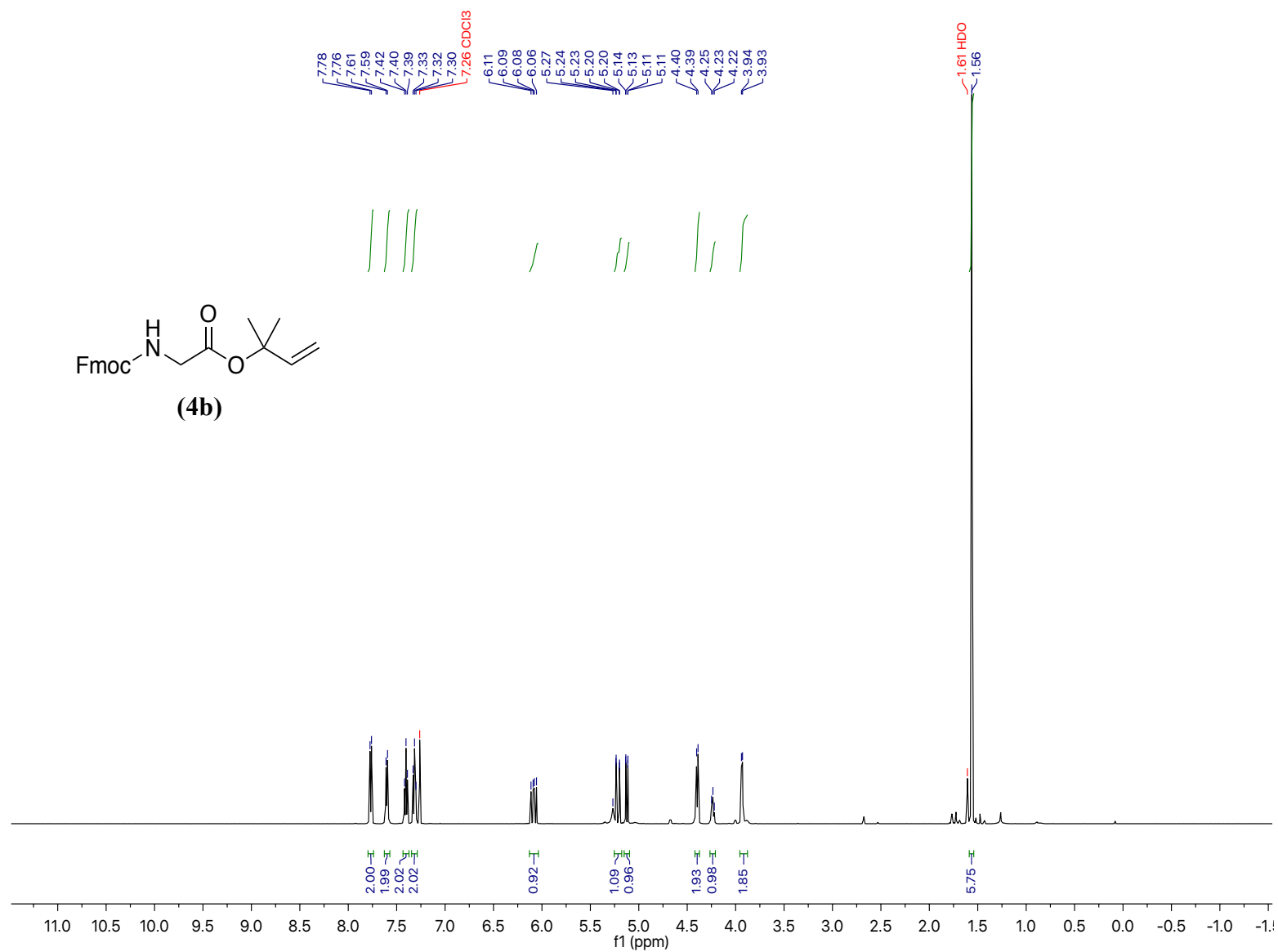


Figure S4. ¹H NMR (500 MHz, CDCl₃)

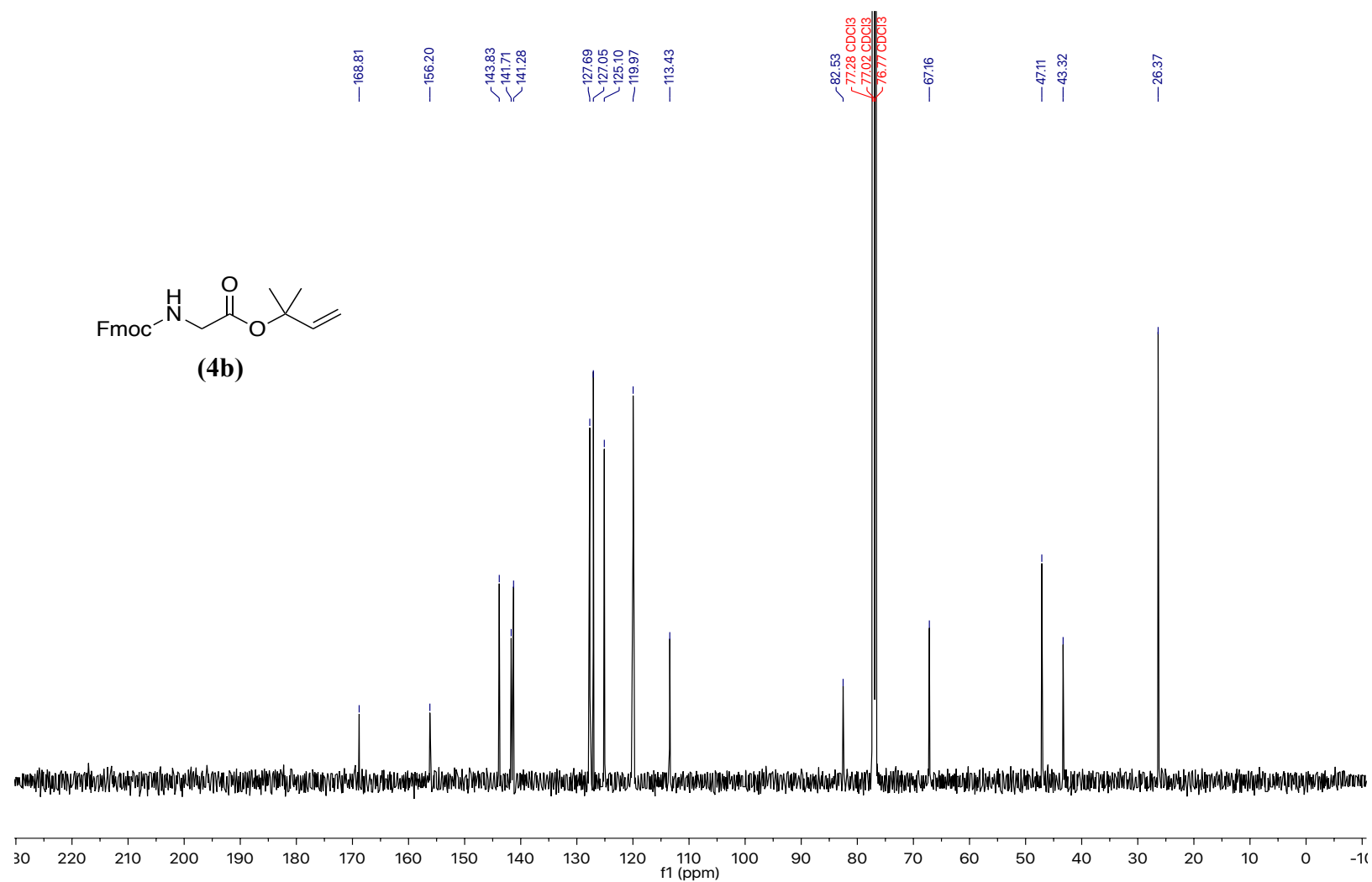


Figure S5. ¹³C NMR (125 MHz, CDCl₃)

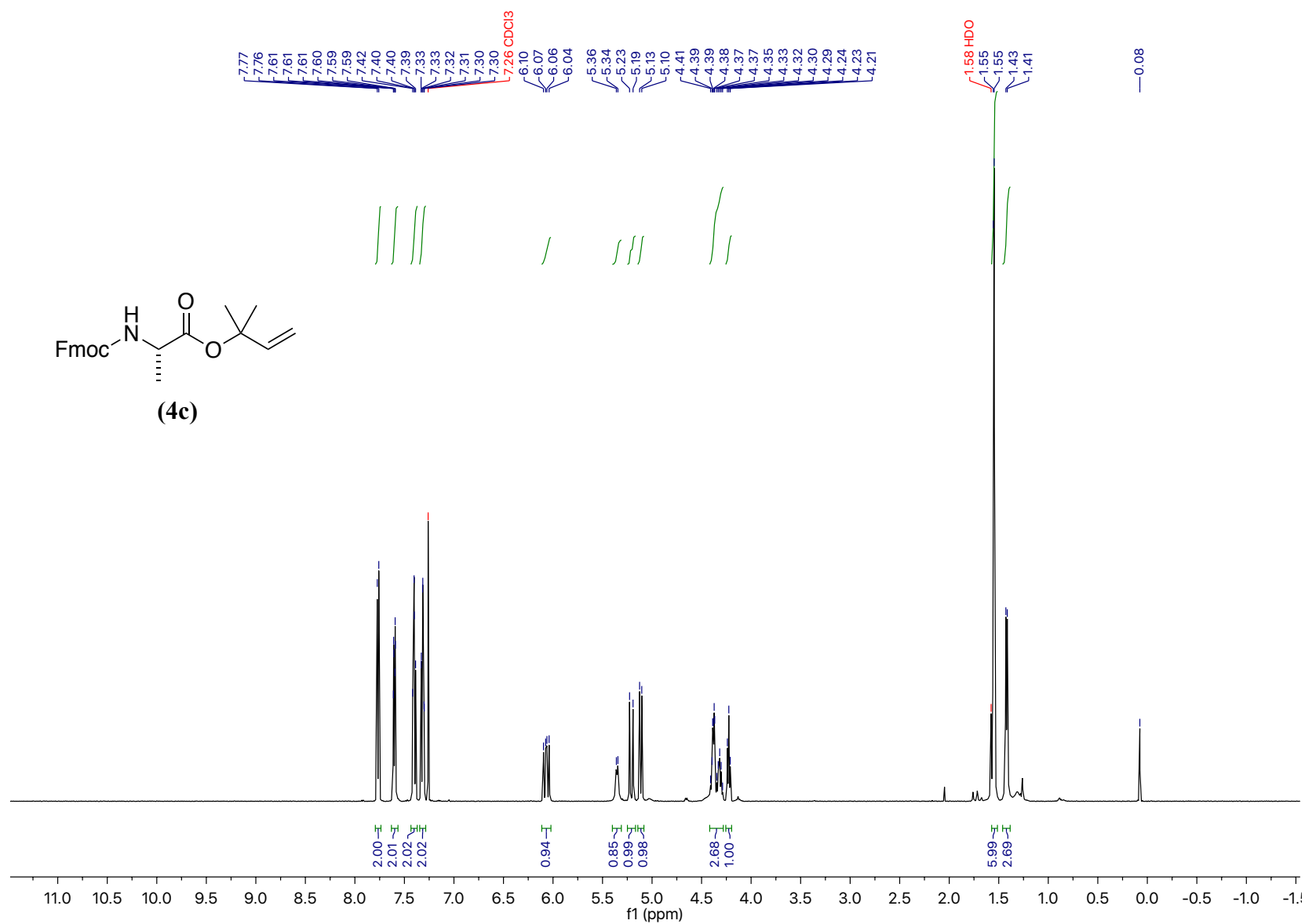


Figure S6. ¹H NMR (500 MHz, CDCl₃)

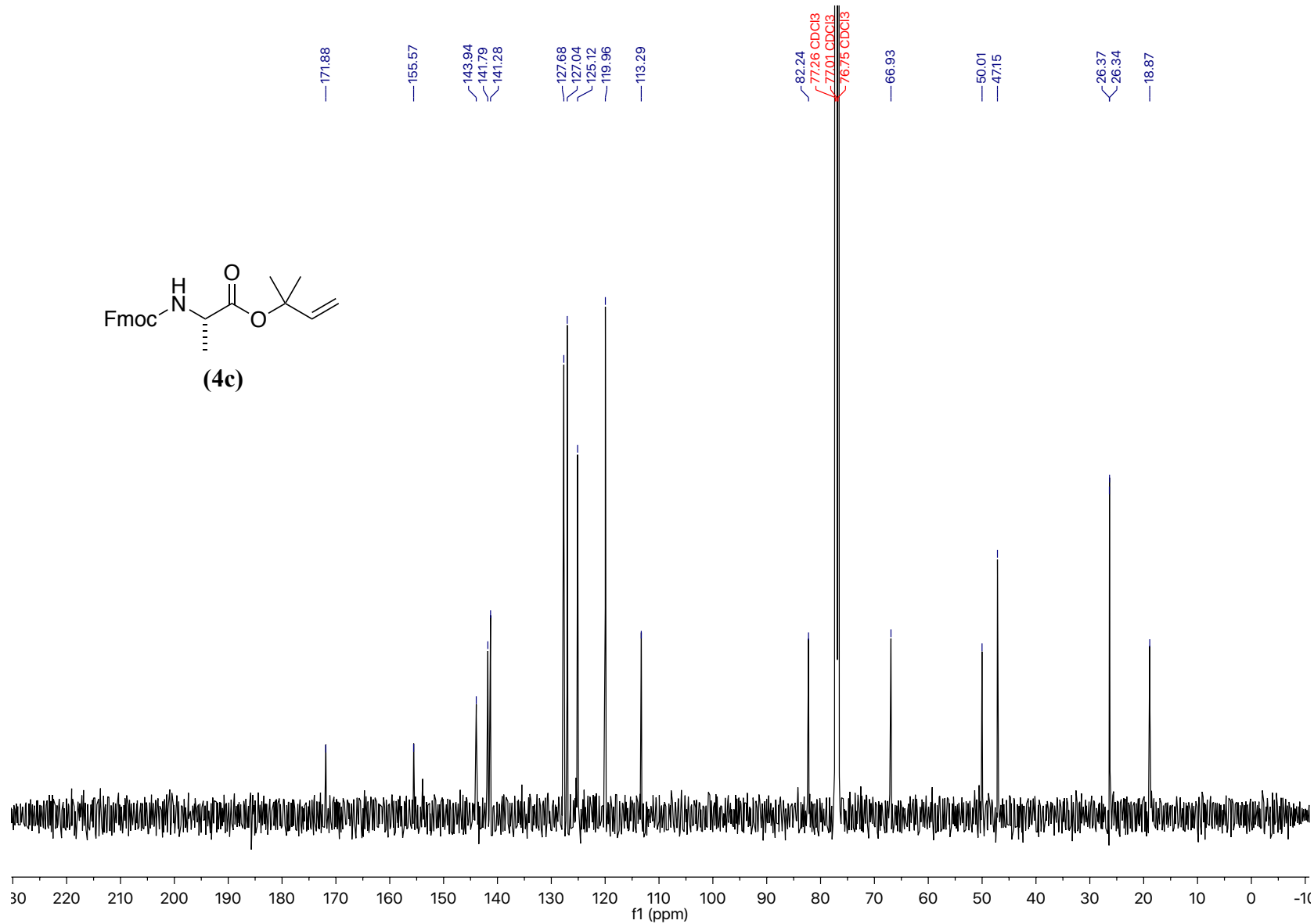


Figure S7. ^{13}C NMR (125 MHz, CDCl_3)

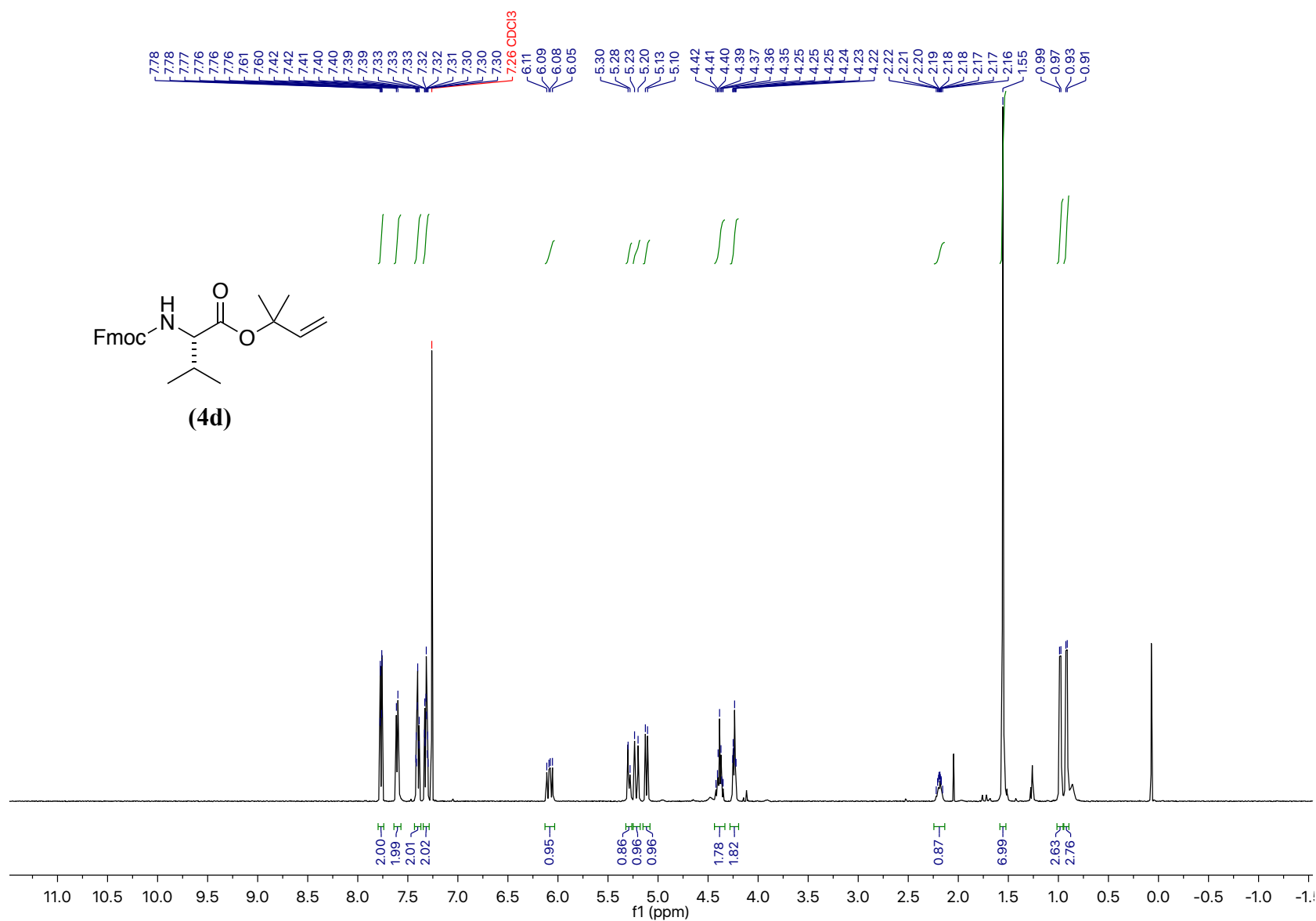


Figure S8. ¹H NMR (500 MHz, CDCl₃)

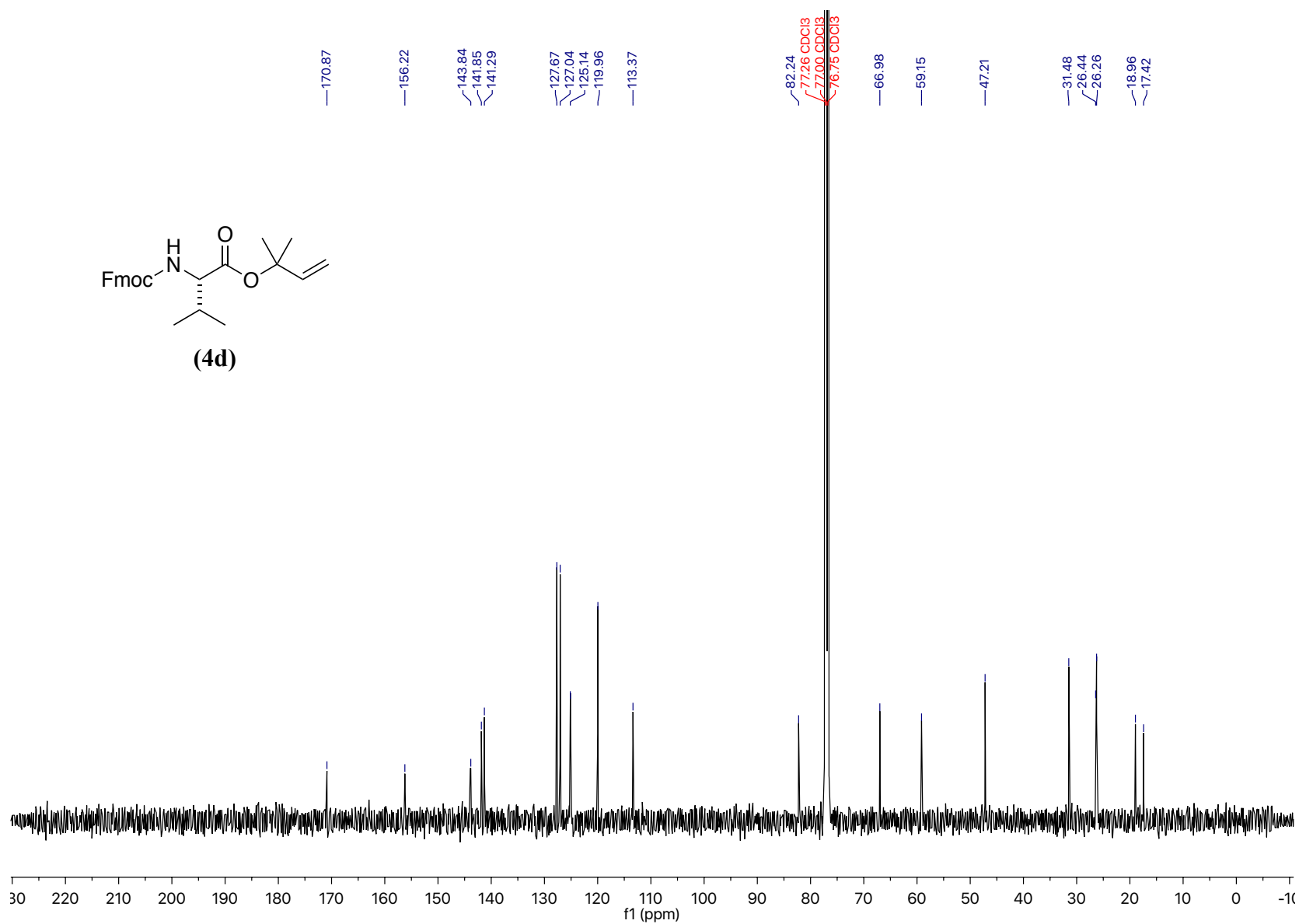


Figure S9. ^{13}C NMR (125 MHz, CDCl_3)

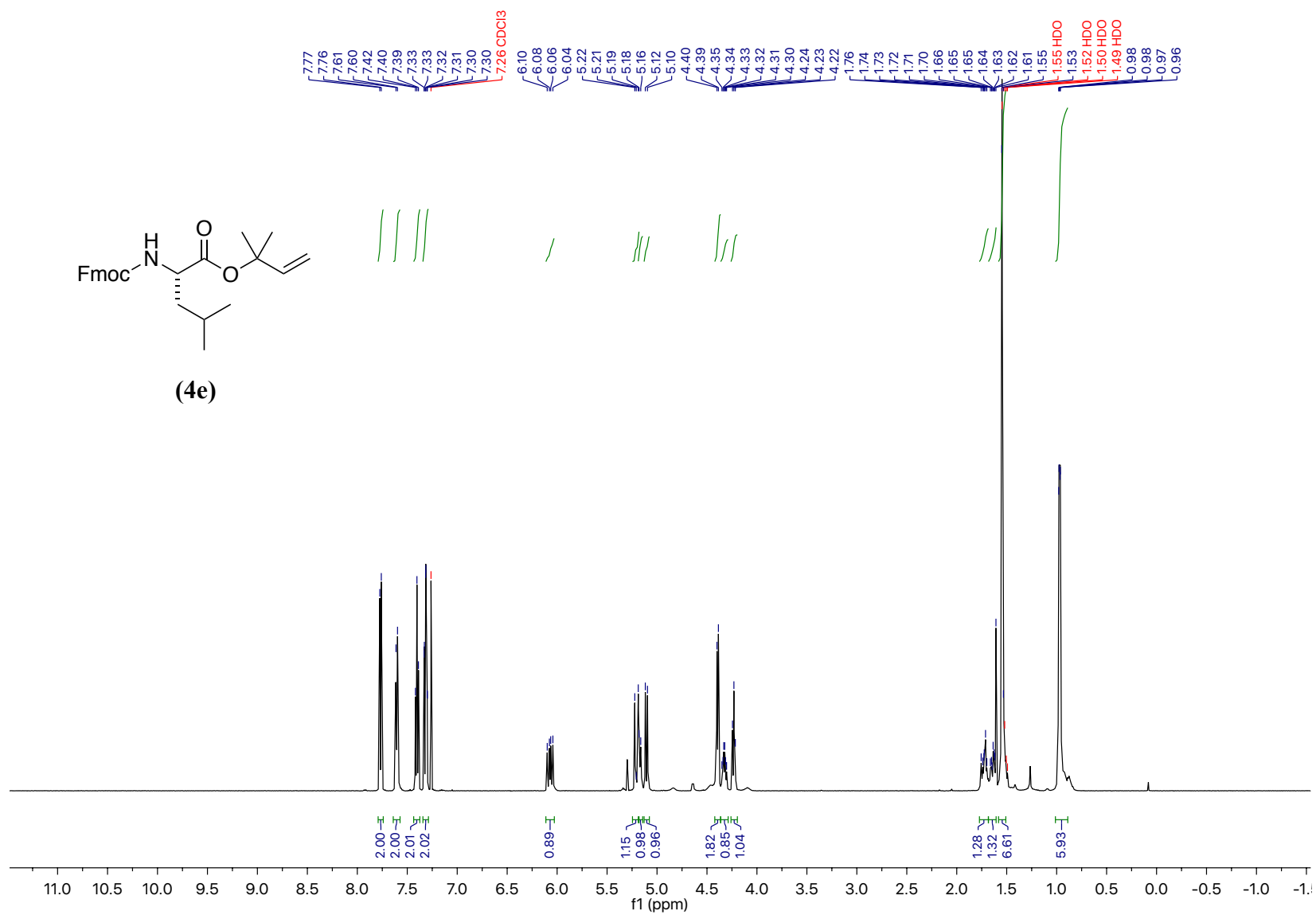


Figure S10. ^1H NMR (500 MHz, CDCl_3)

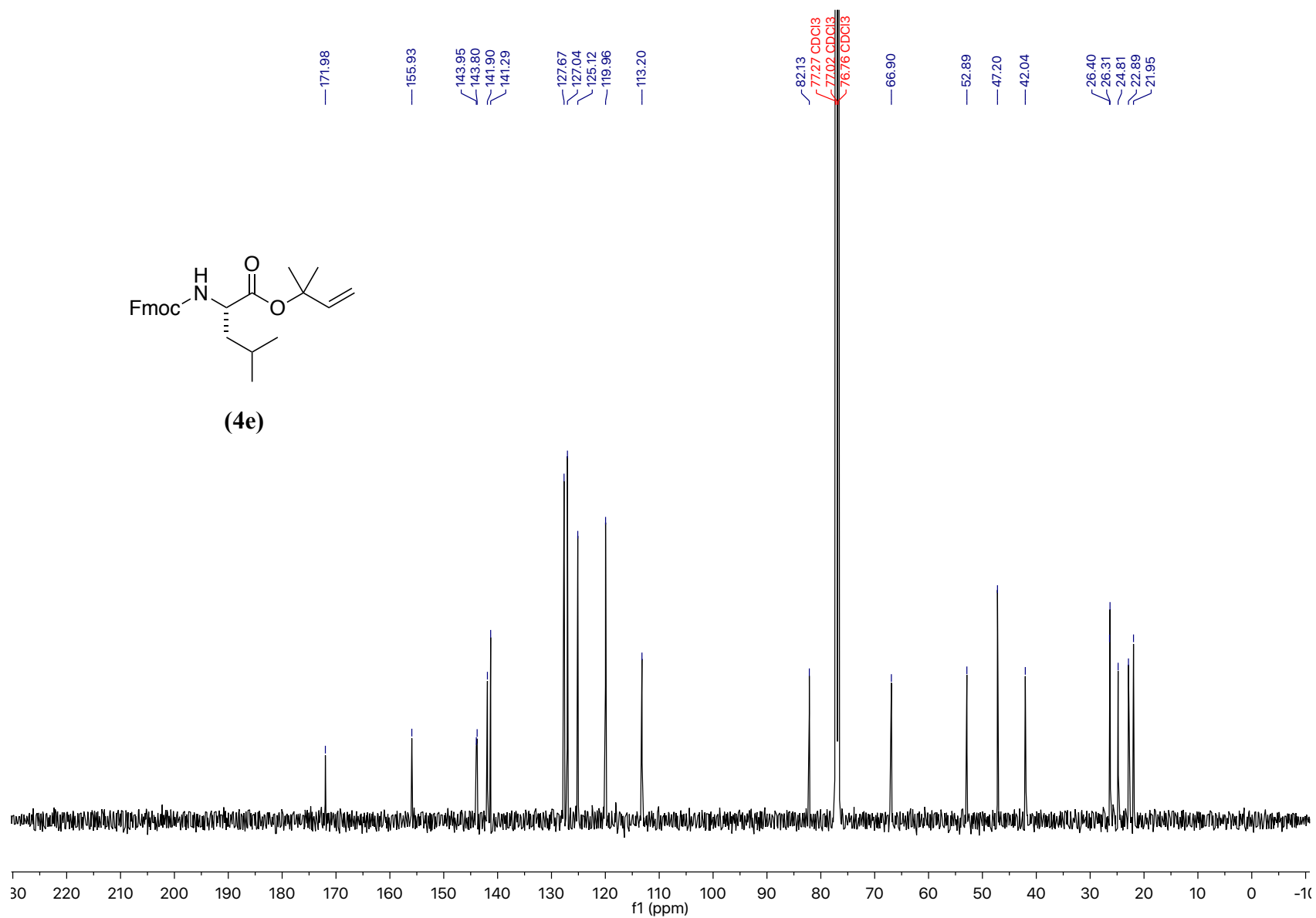


Figure S11. ^{13}C NMR (125 MHz, CDCl_3)

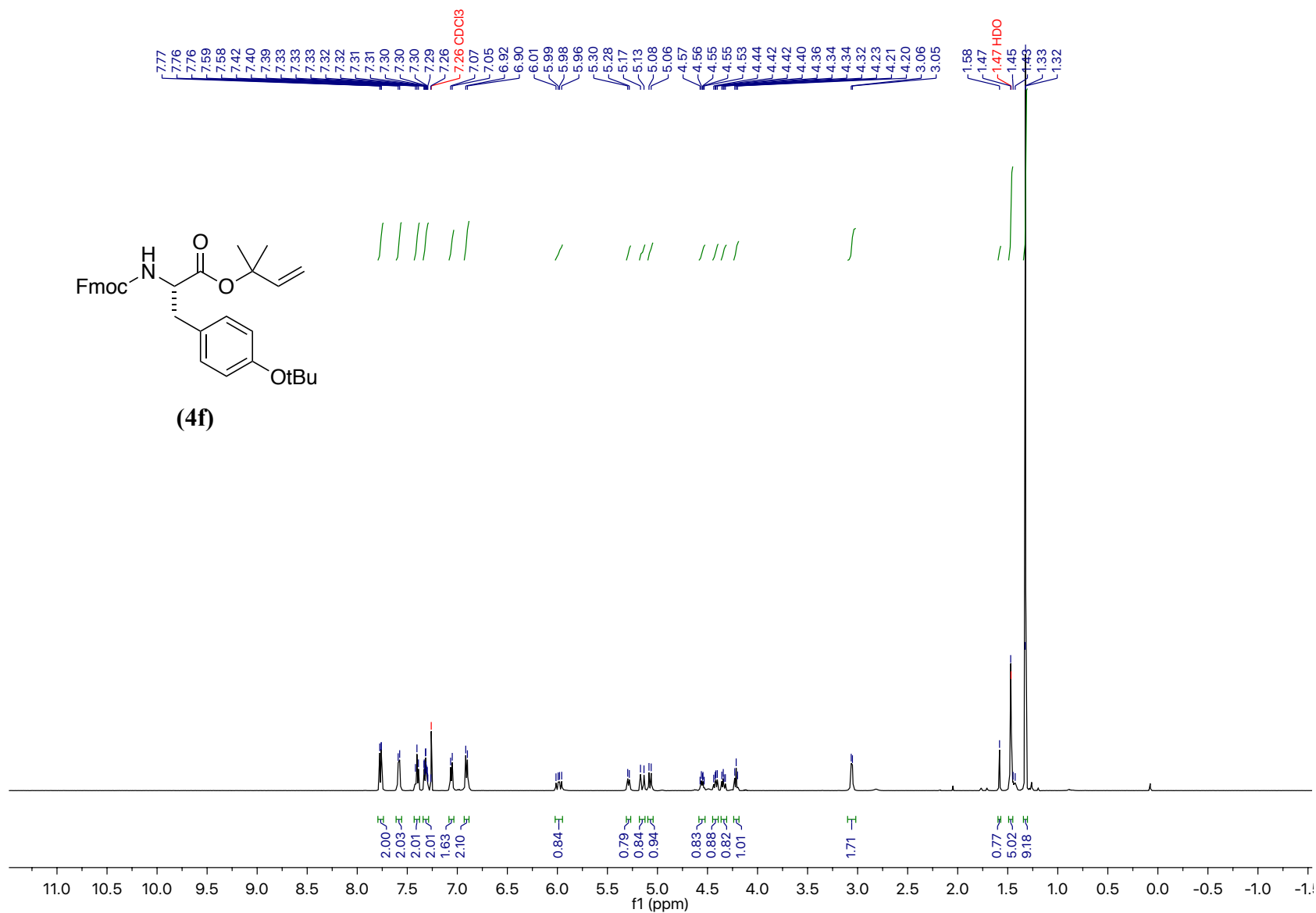


Figure S12. ¹H NMR (500 MHz, CDCl₃)

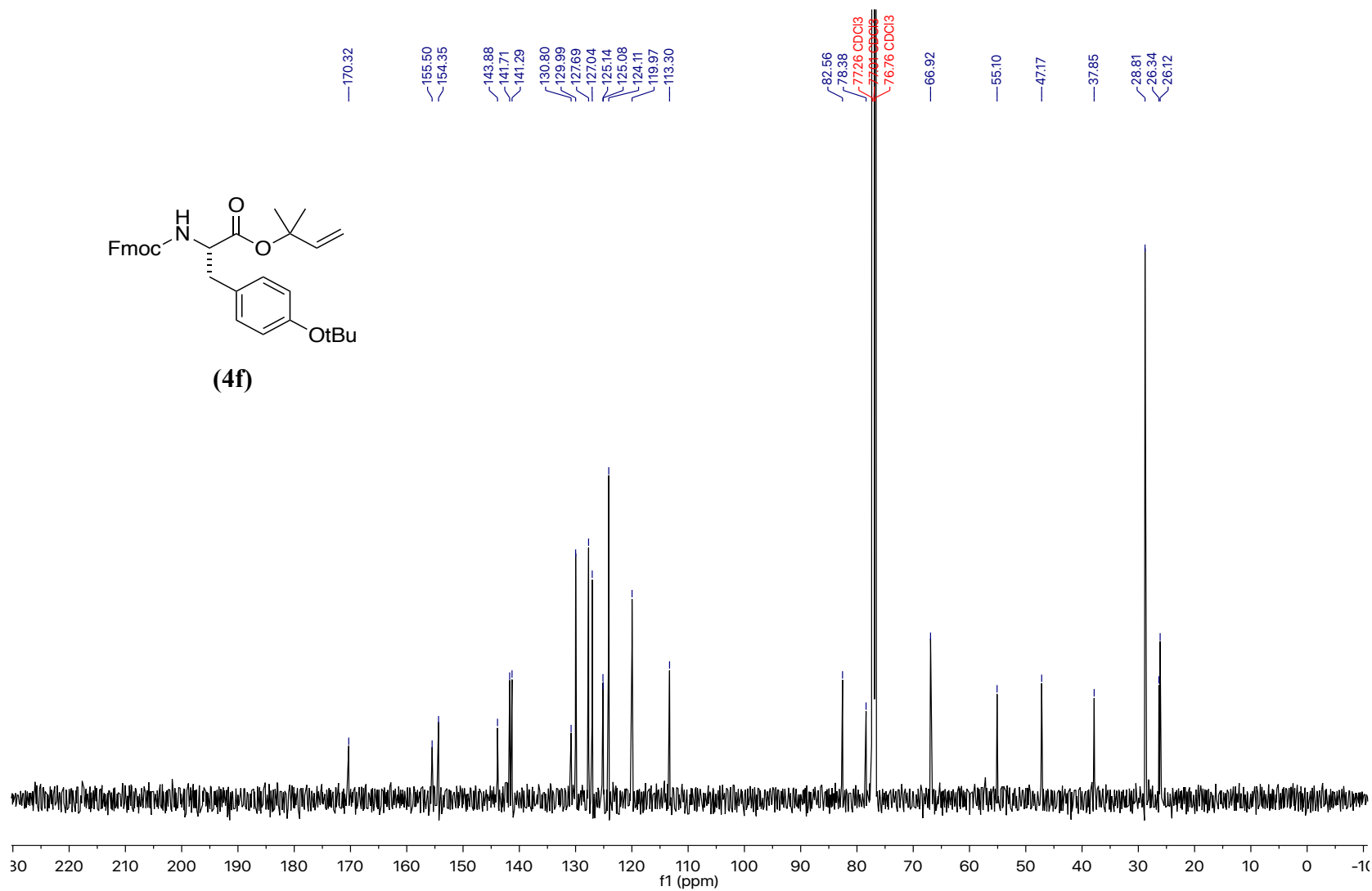


Figure S13. ^{13}C NMR (125 MHz, CDCl_3)

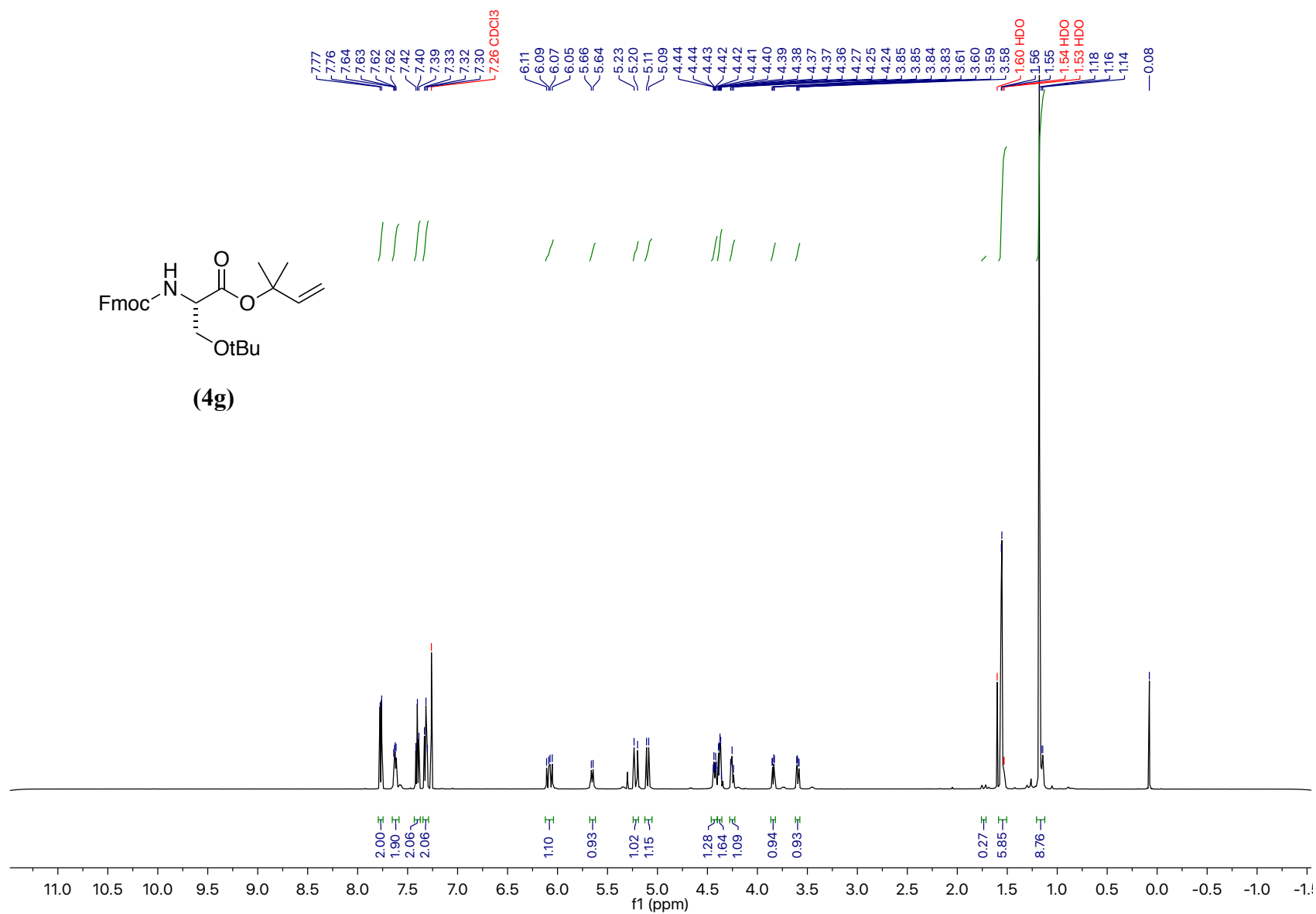


Figure S14. ¹H NMR (500 MHz, CDCl₃)

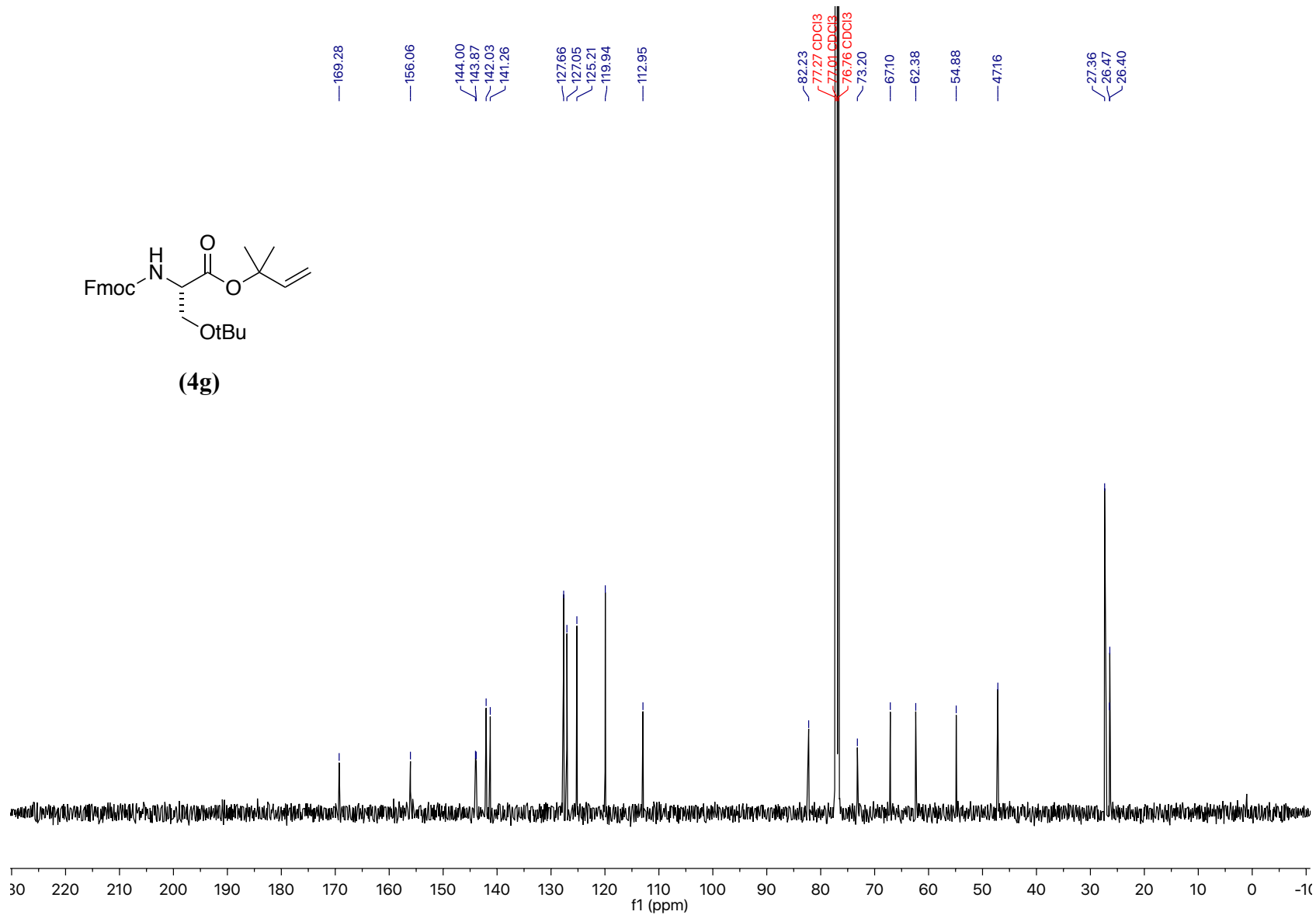
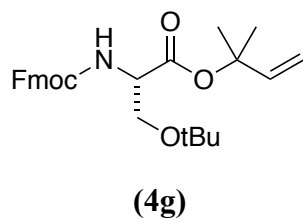
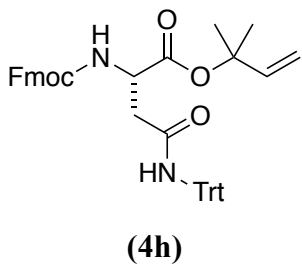


Figure S15. ¹³C NMR (125 MHz, CDCl₃)



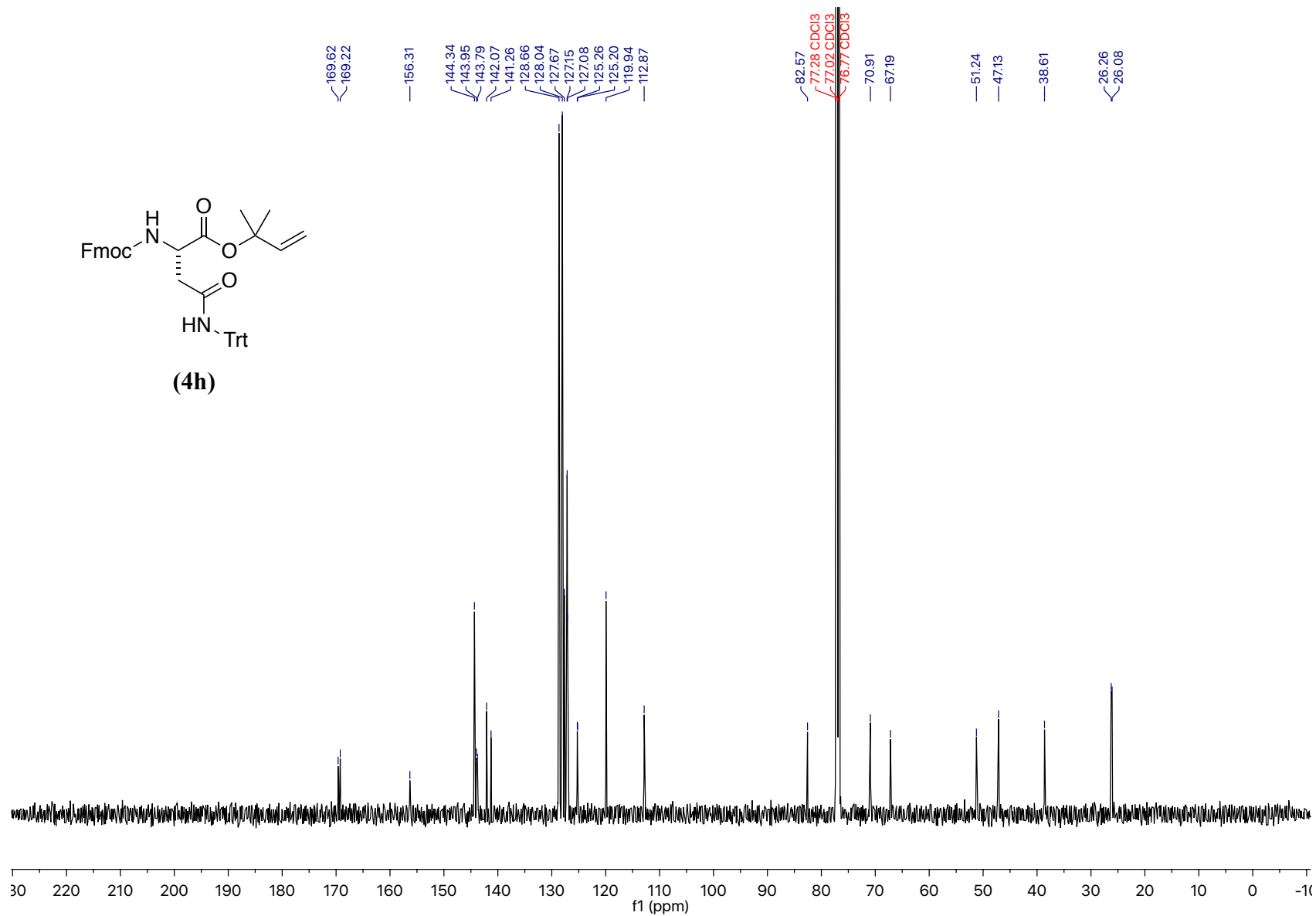


Figure S17. ^{13}C NMR (125 MHz, CDCl_3)

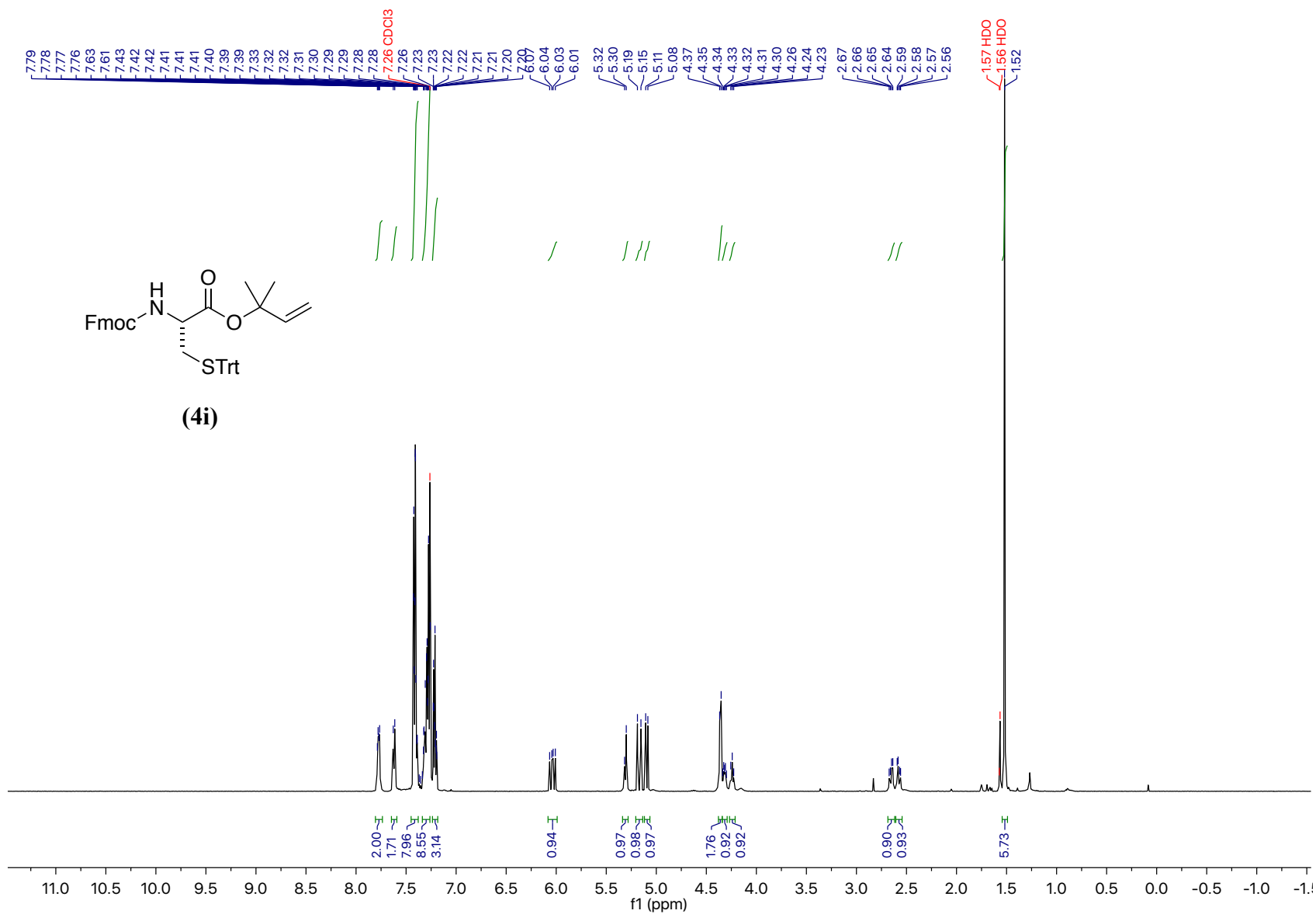


Figure S18. ¹H NMR (500 MHz, CDCl₃)

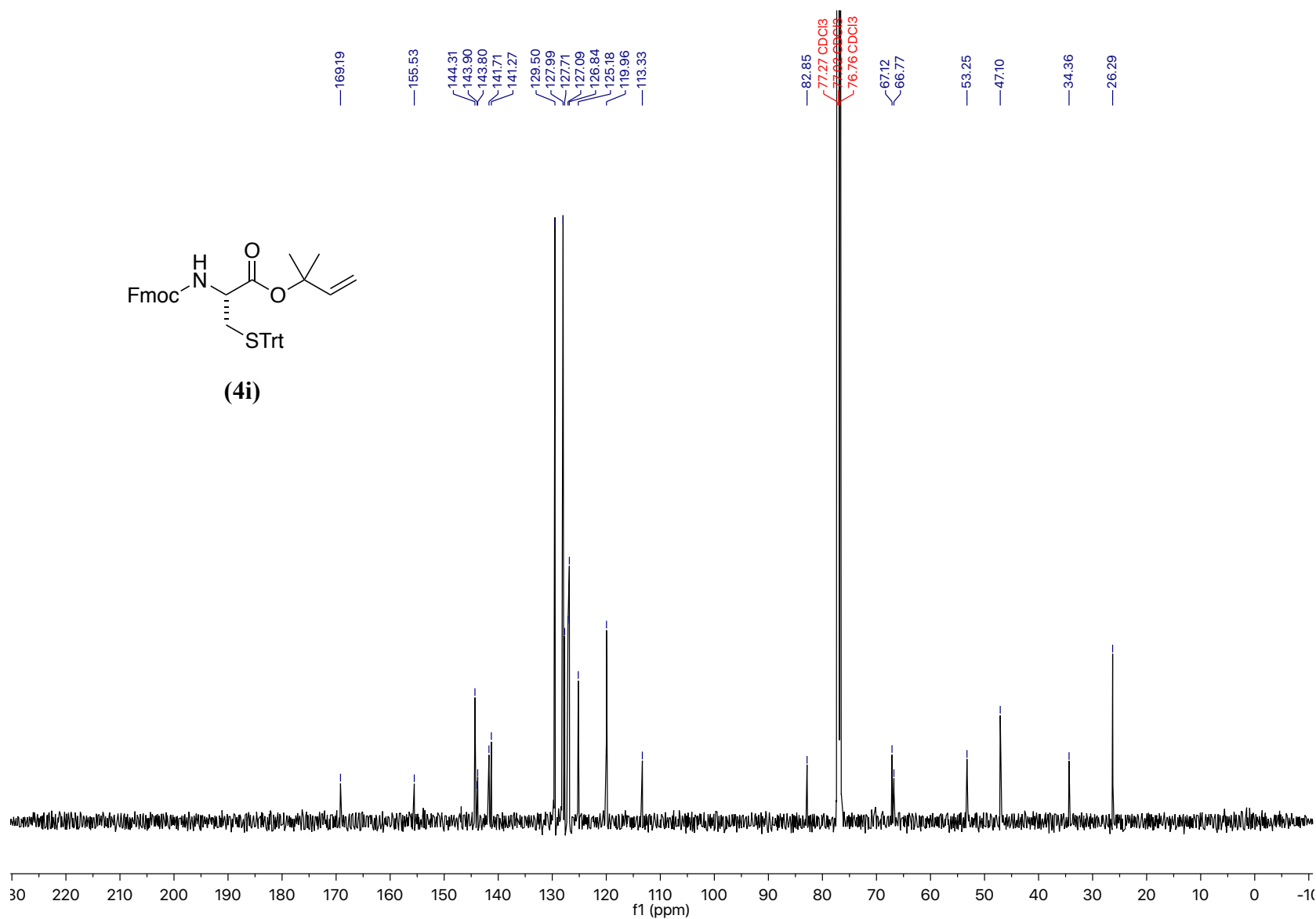


Figure S19. ^{13}C NMR (125 MHz, CDCl_3)

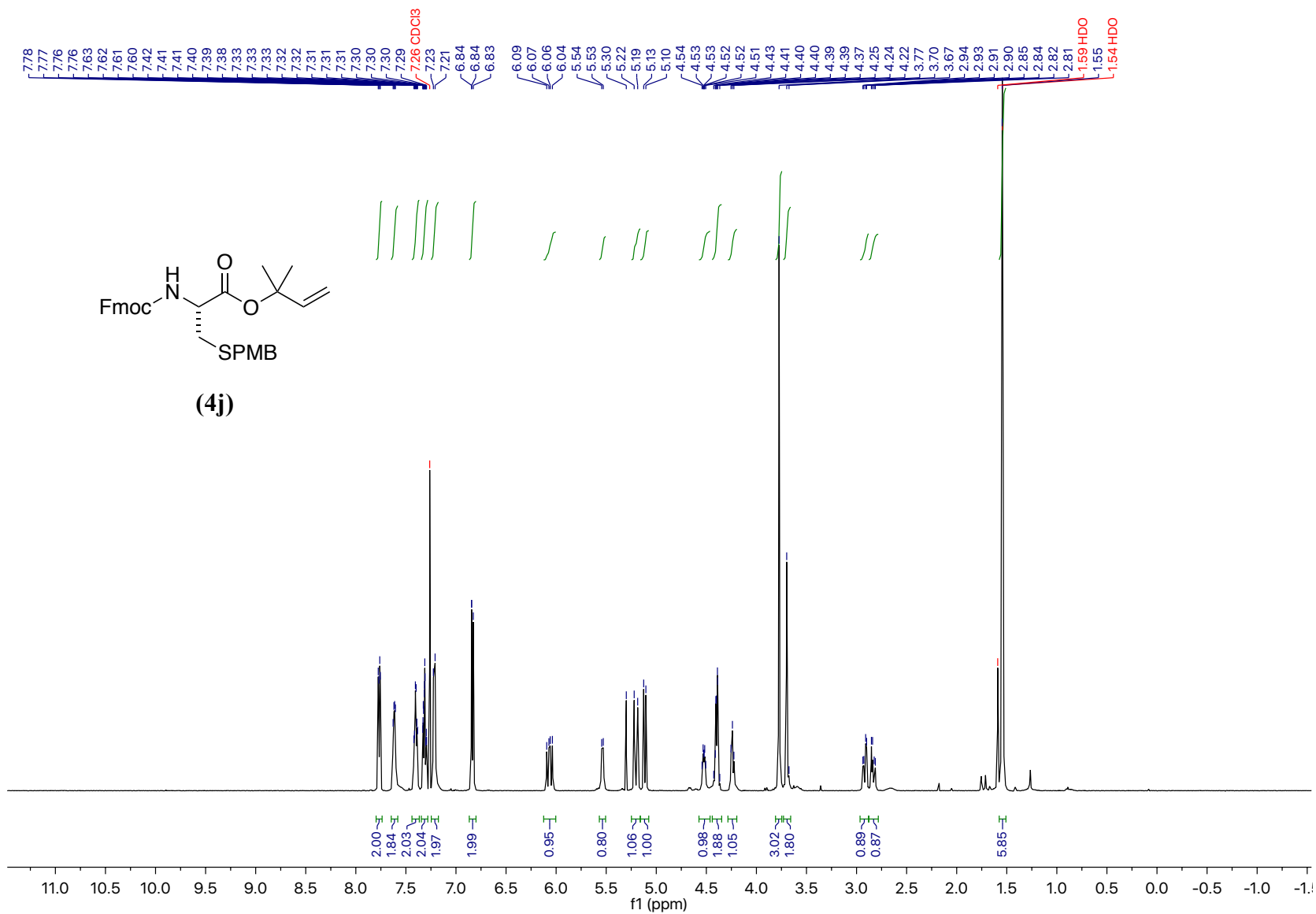


Figure S20. ¹H NMR (500 MHz, CDCl₃)

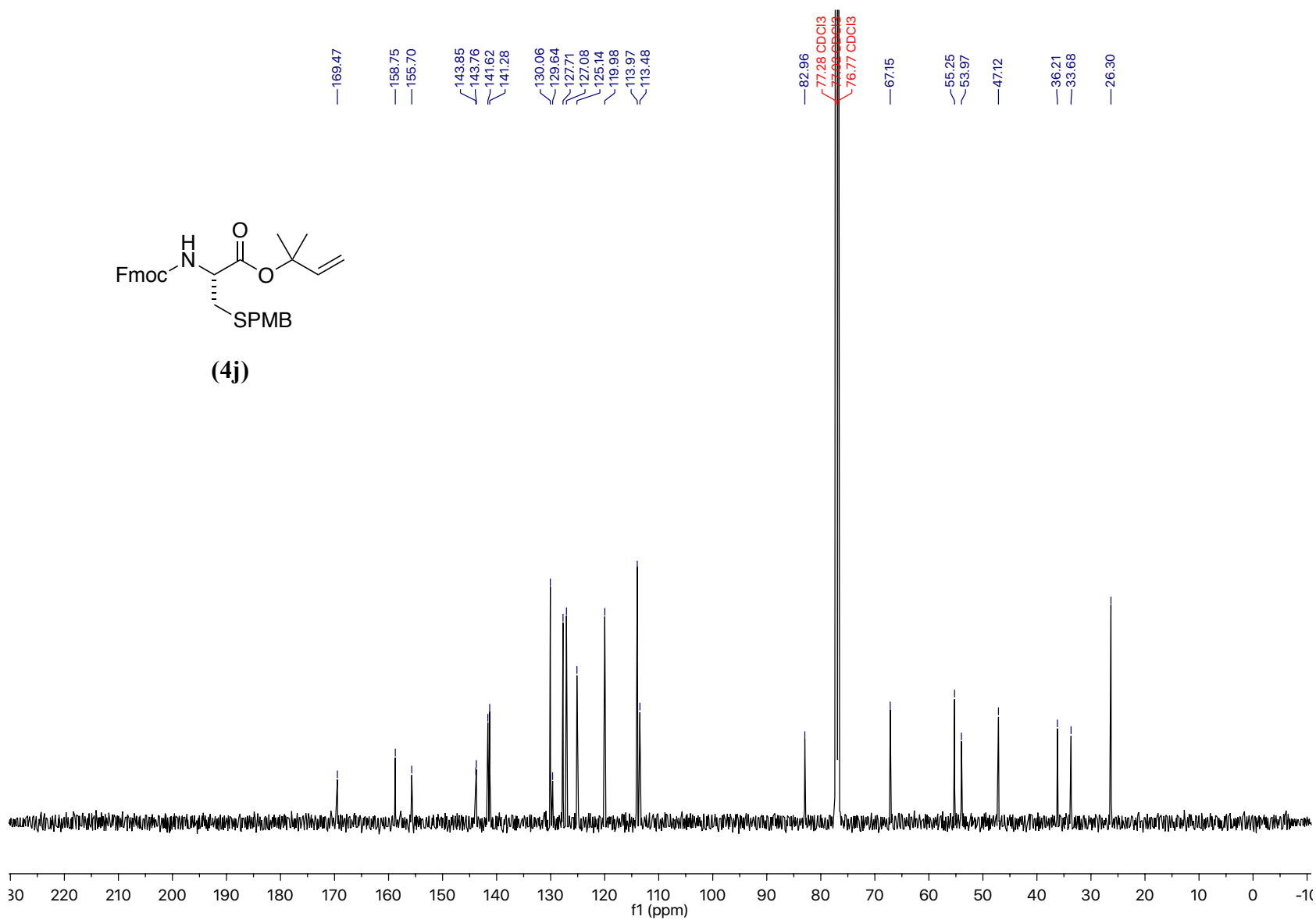


Figure S21. ^{13}C NMR (125 MHz, CDCl_3)

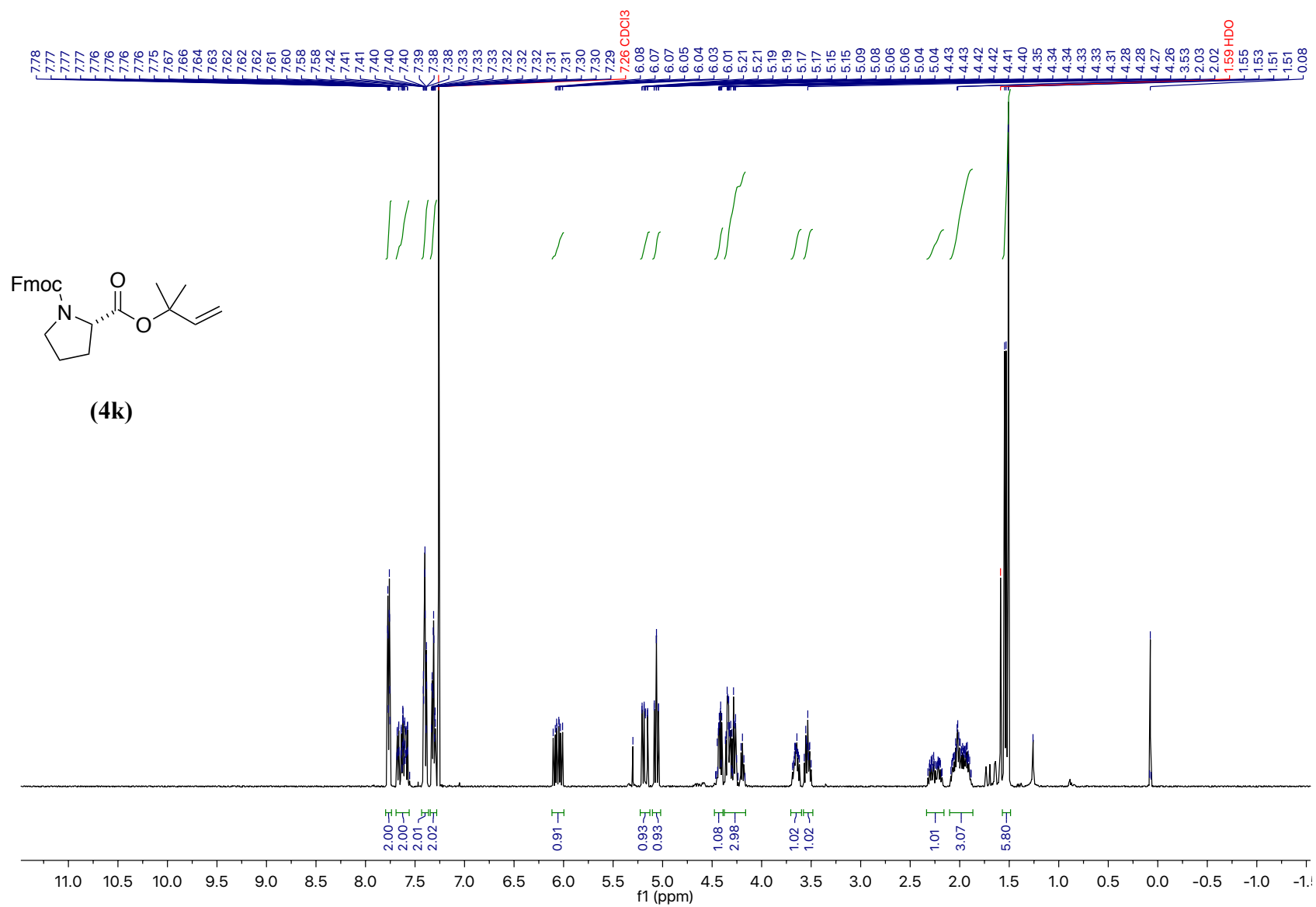


Figure S22. ¹H NMR (500 MHz, CDCl₃)

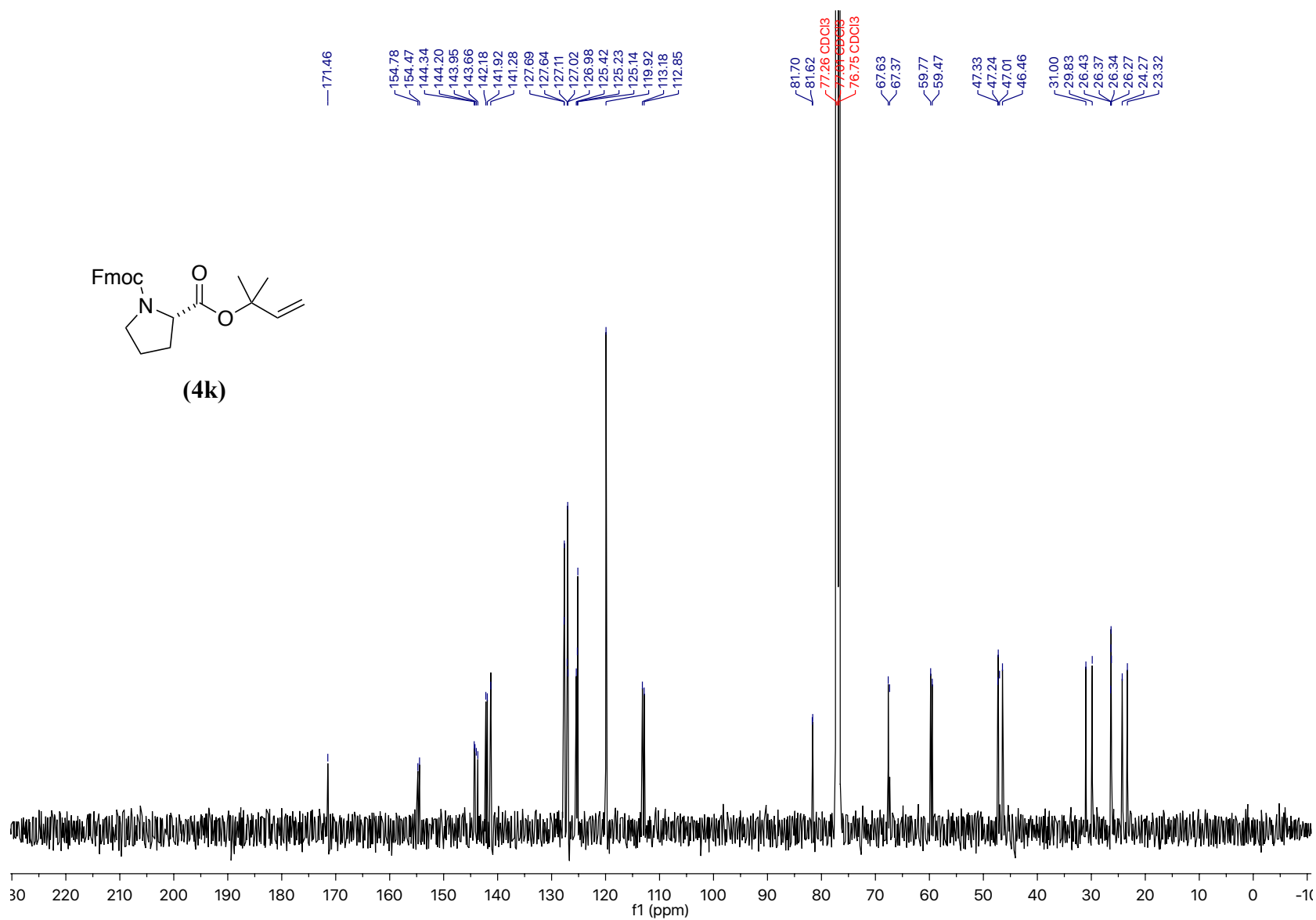


Figure S23. ^{13}C NMR (125 MHz, CDCl_3)

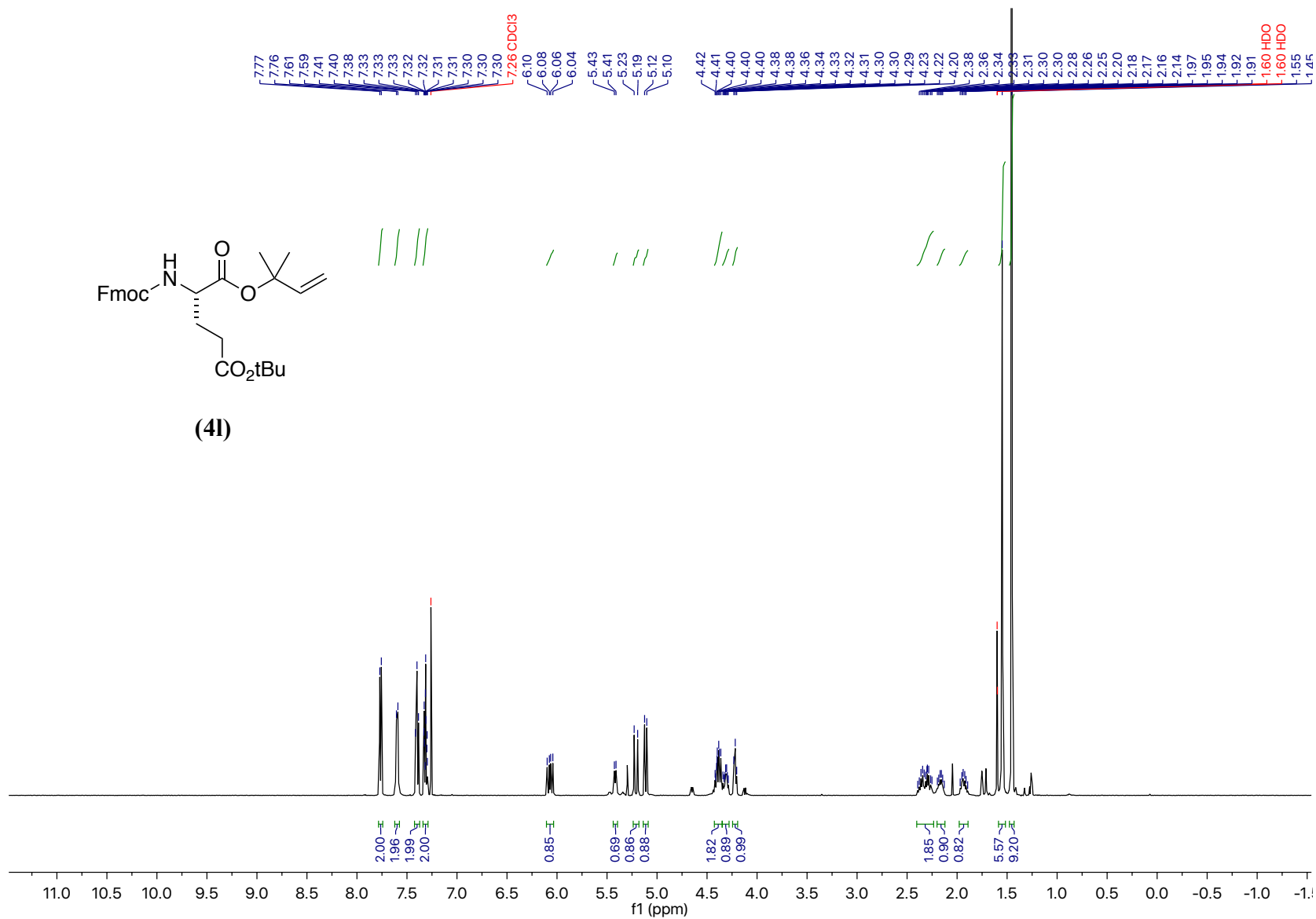


Figure S24. ^1H NMR (500 MHz, CDCl_3)

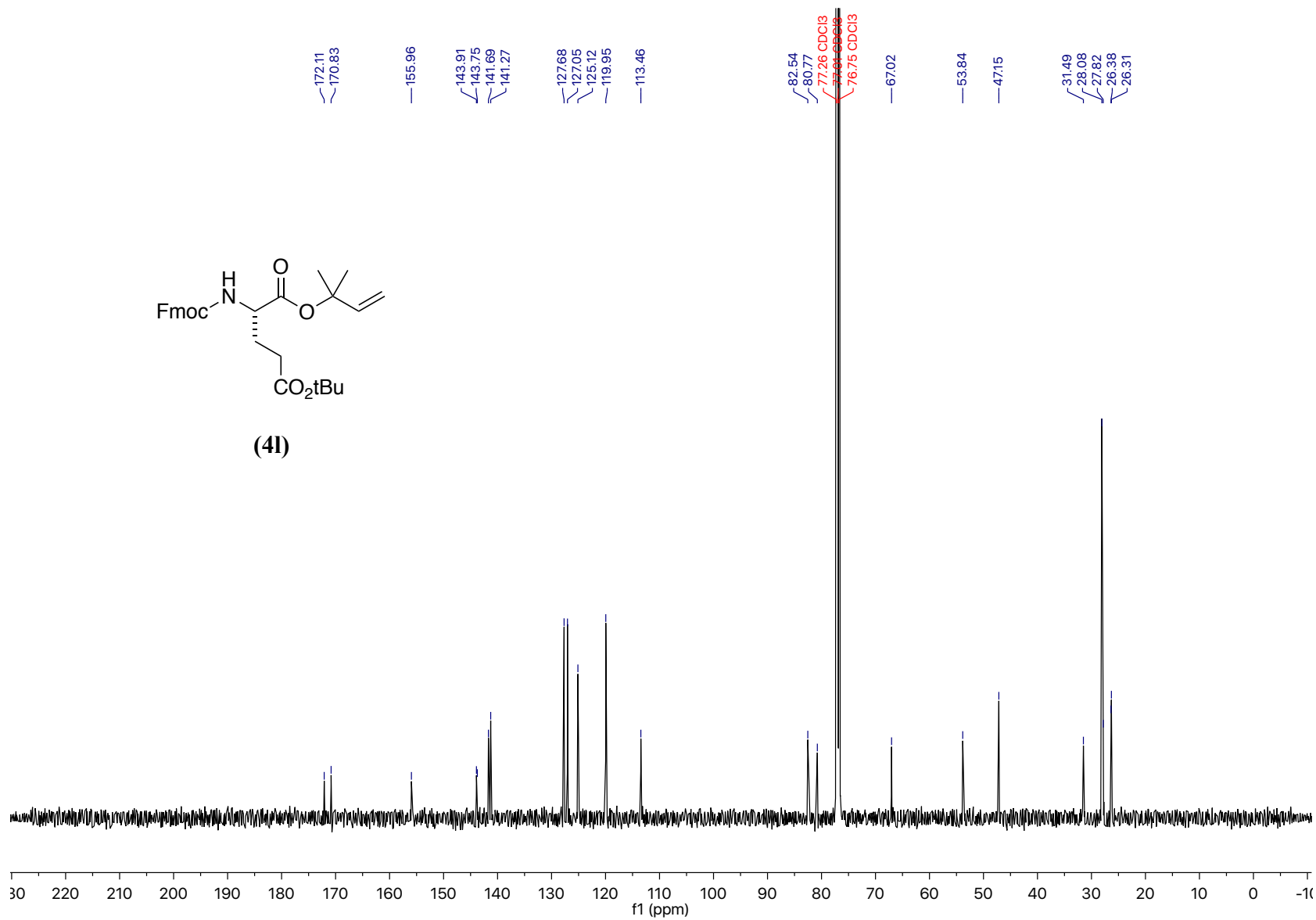


Figure S25. ^{13}C NMR (125 MHz, CDCl_3)

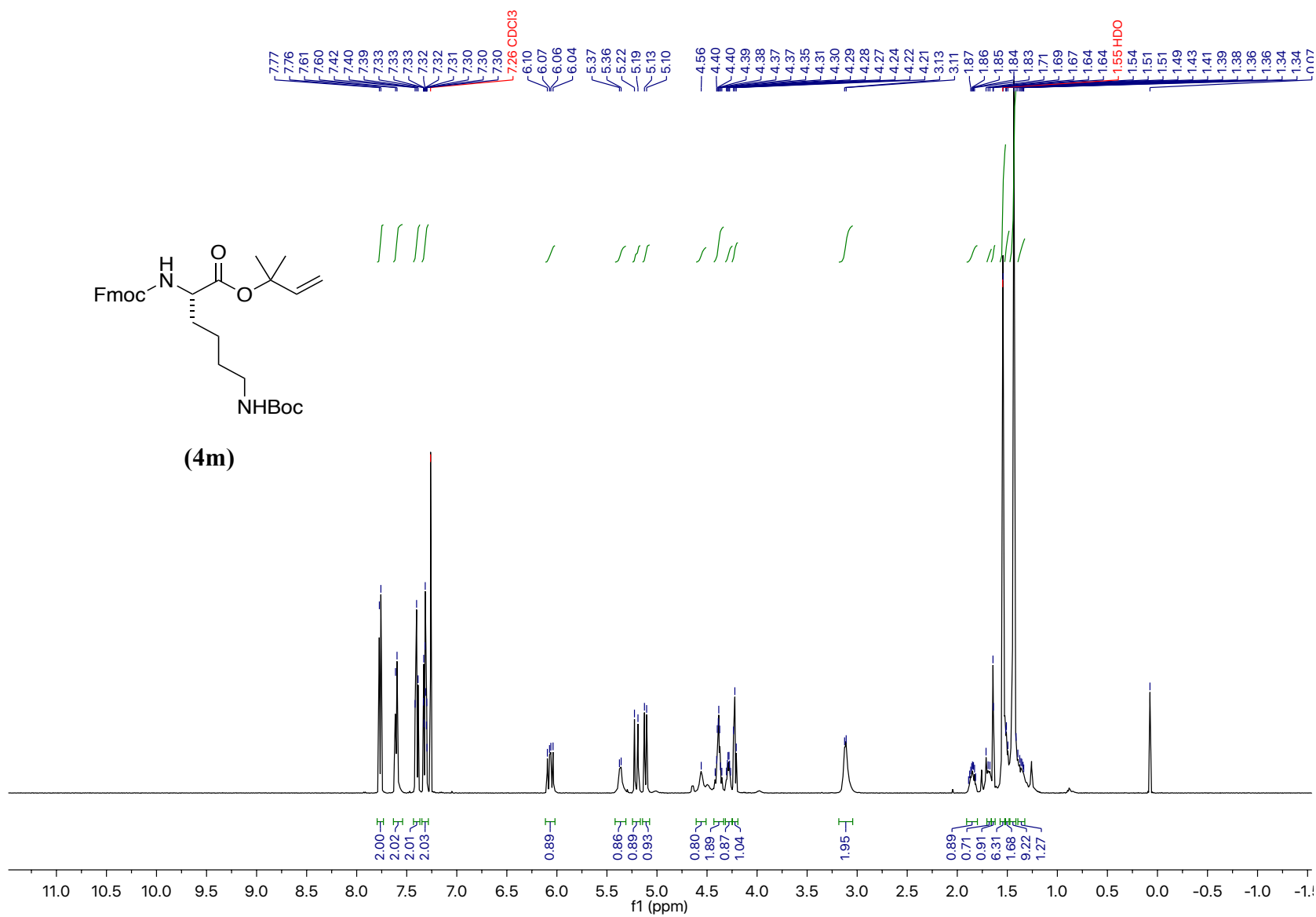


Figure S26. ^1H NMR (500 MHz, CDCl_3)

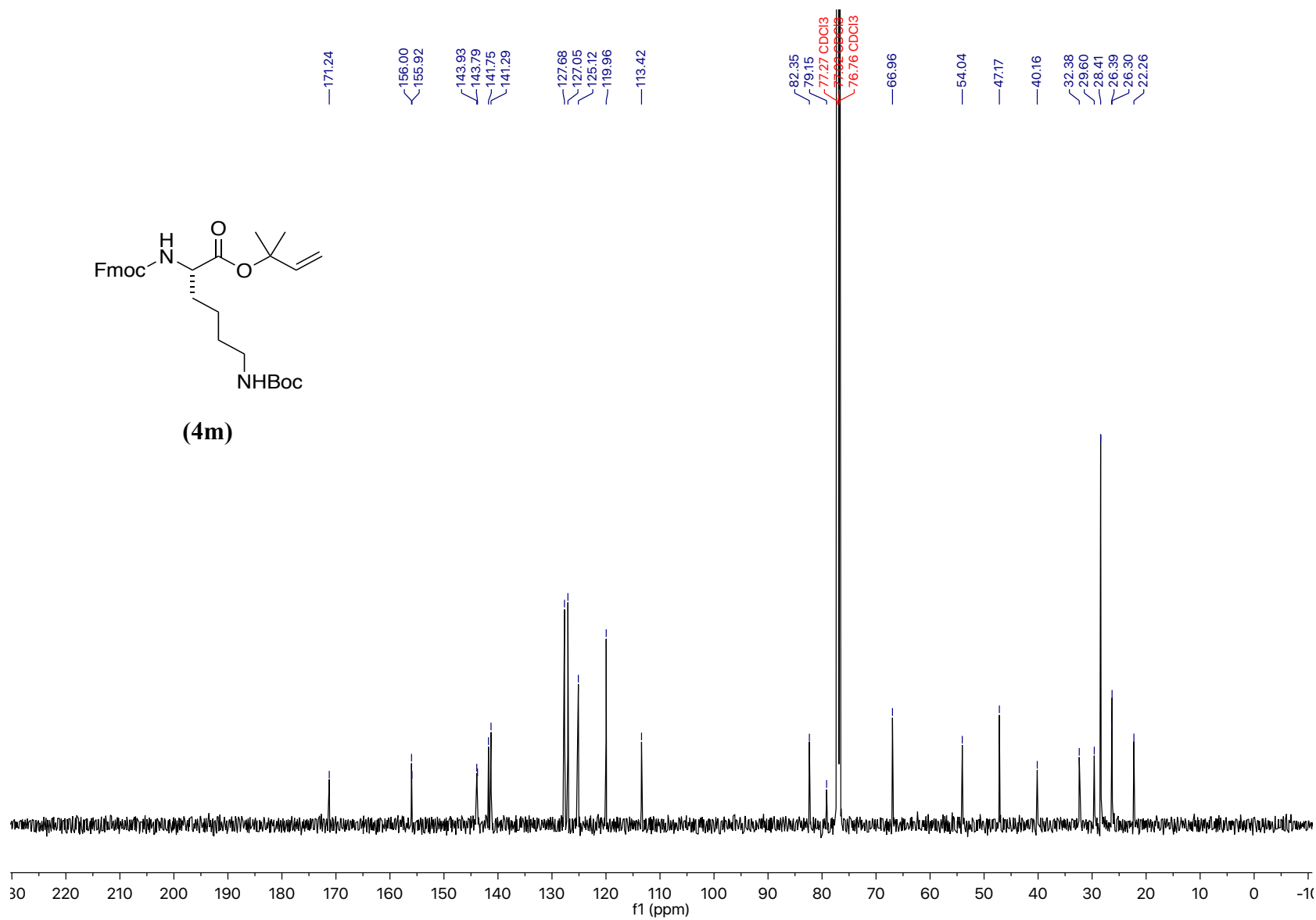


Figure S27. ^{13}C NMR (125 MHz, CDCl_3)

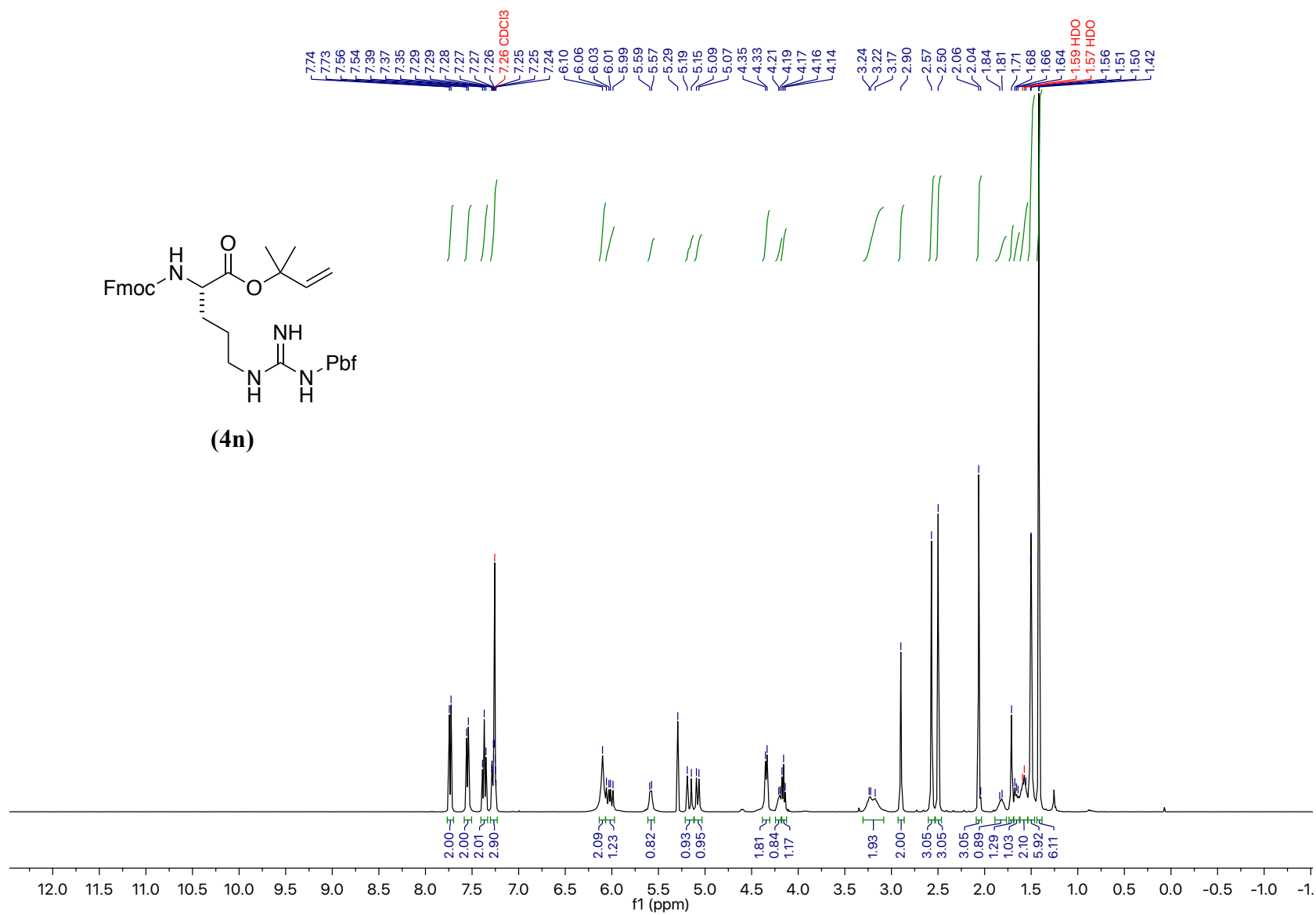


Figure S28. ^1H NMR (400 MHz, CDCl_3)

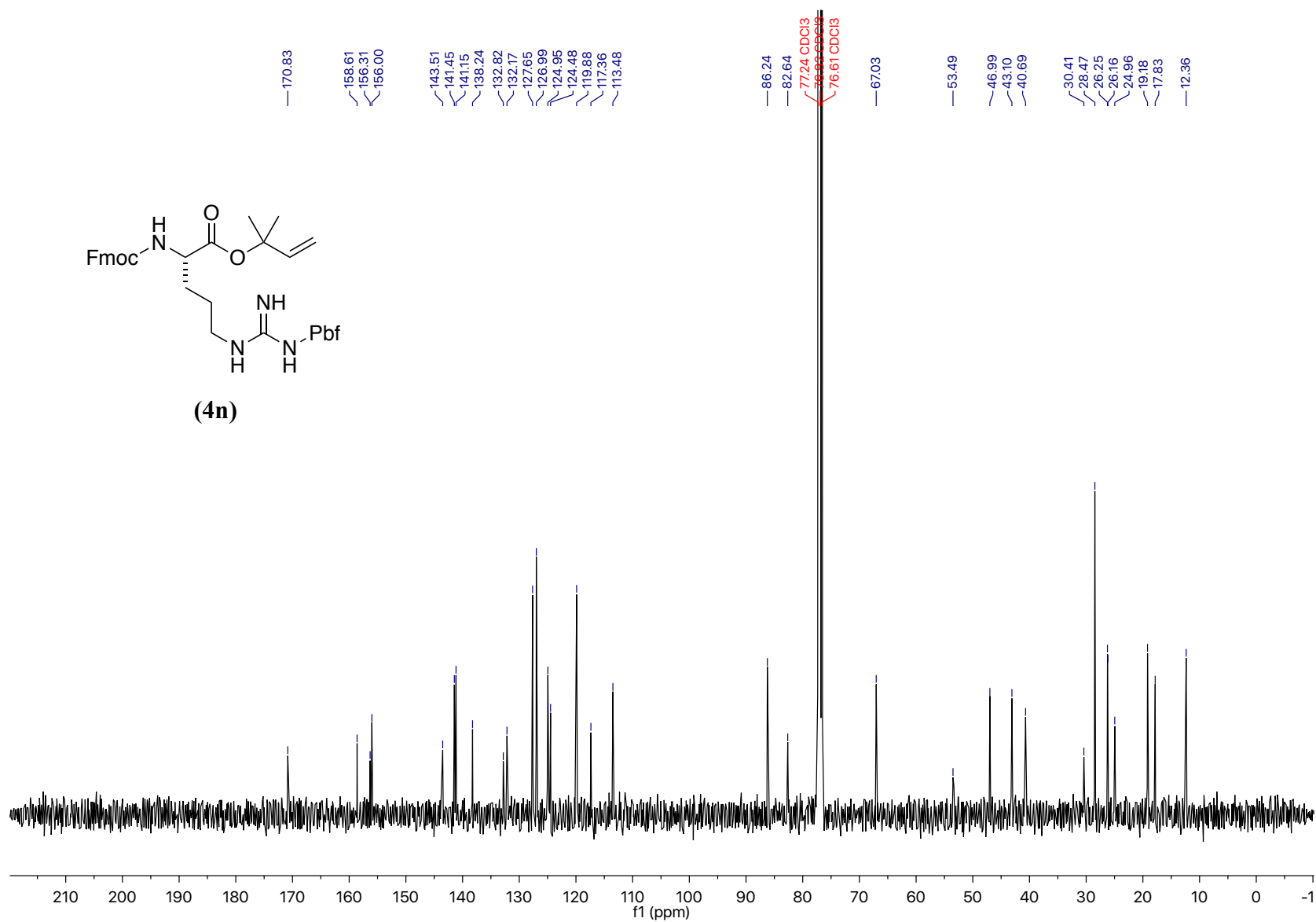


Figure S29. ^{13}C NMR (100 MHz, CDCl_3)

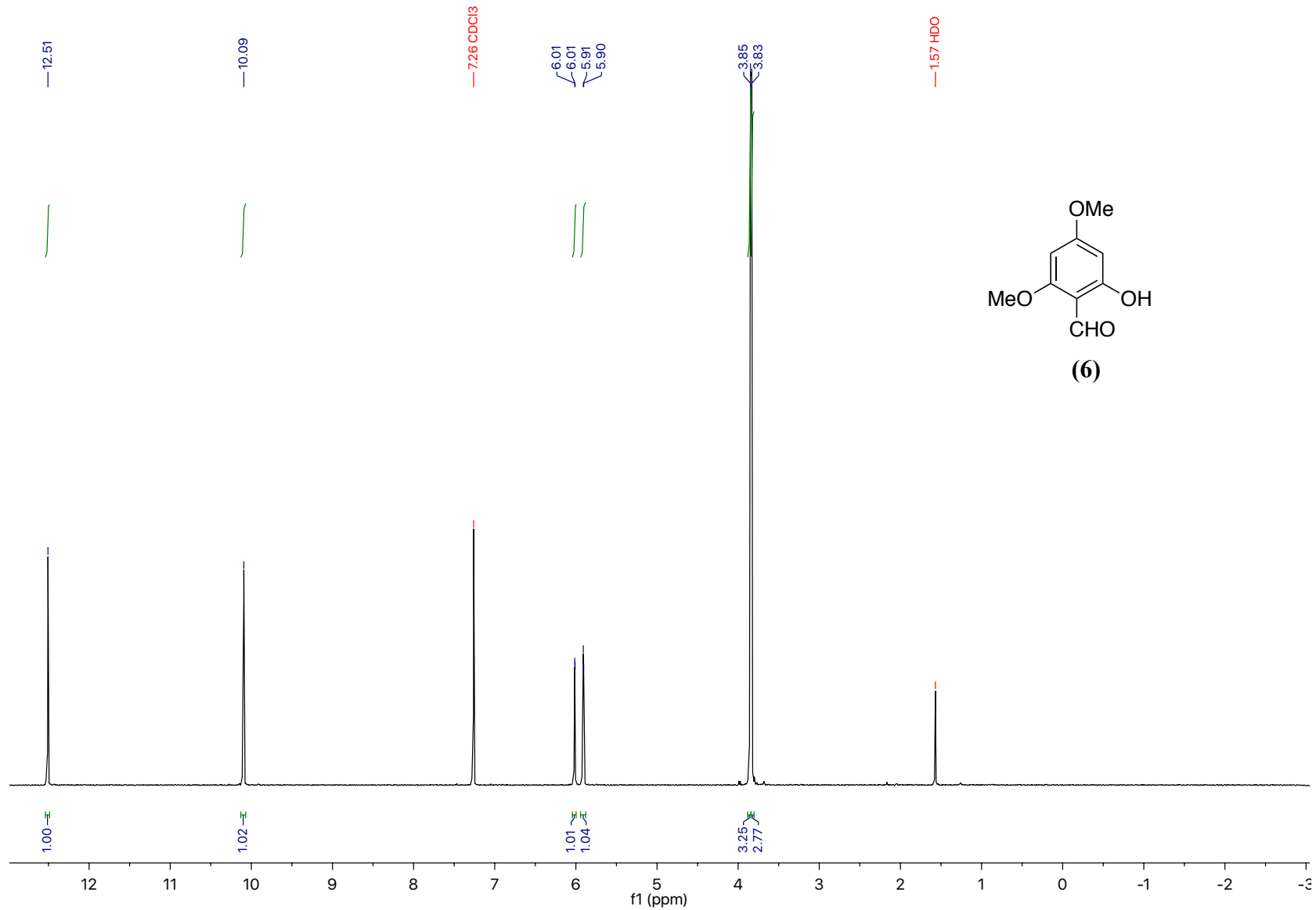


Figure S30. ¹H NMR (500 MHz, CDCl₃)

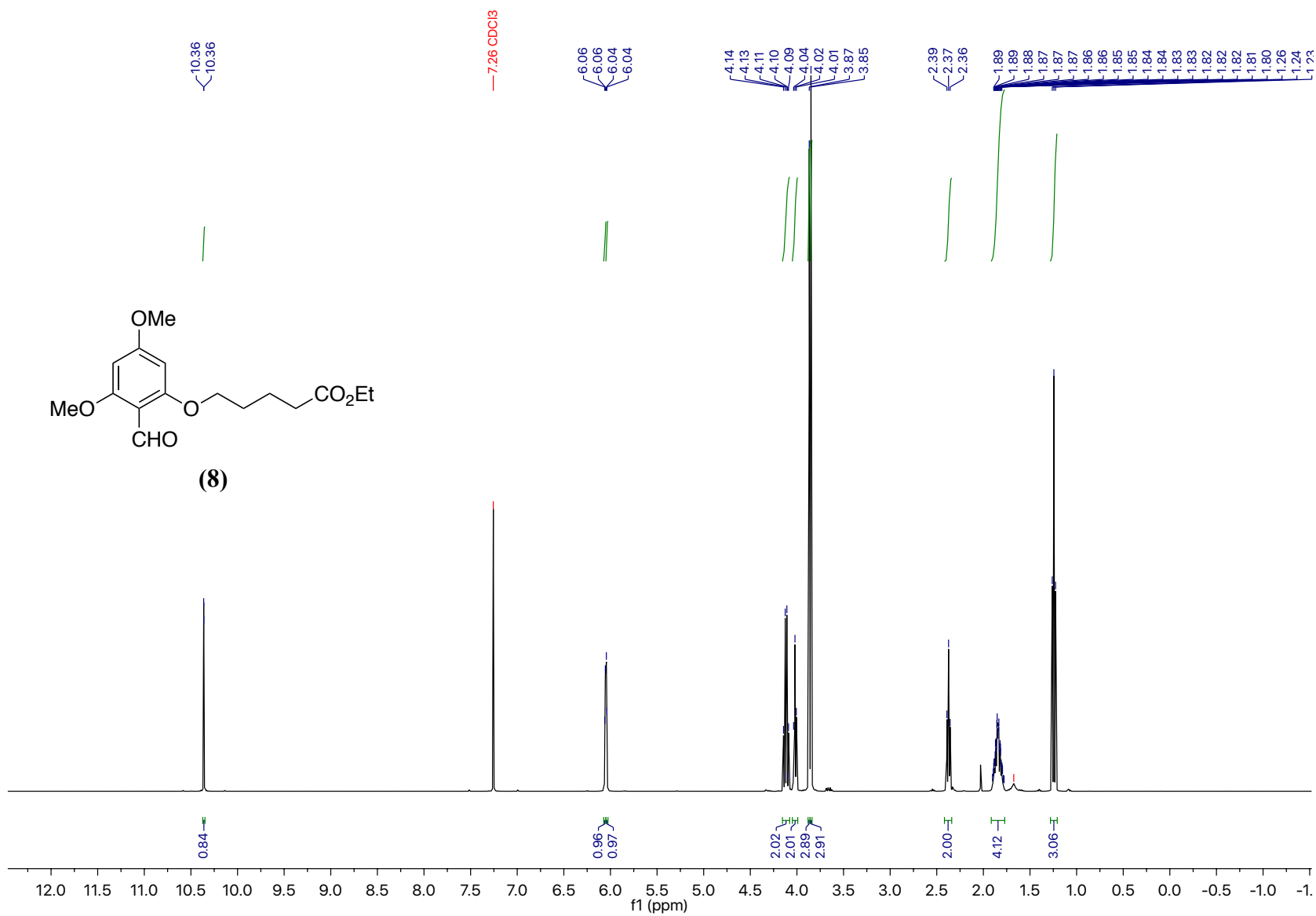


Figure S31. ¹H NMR (400 MHz, CDCl₃)

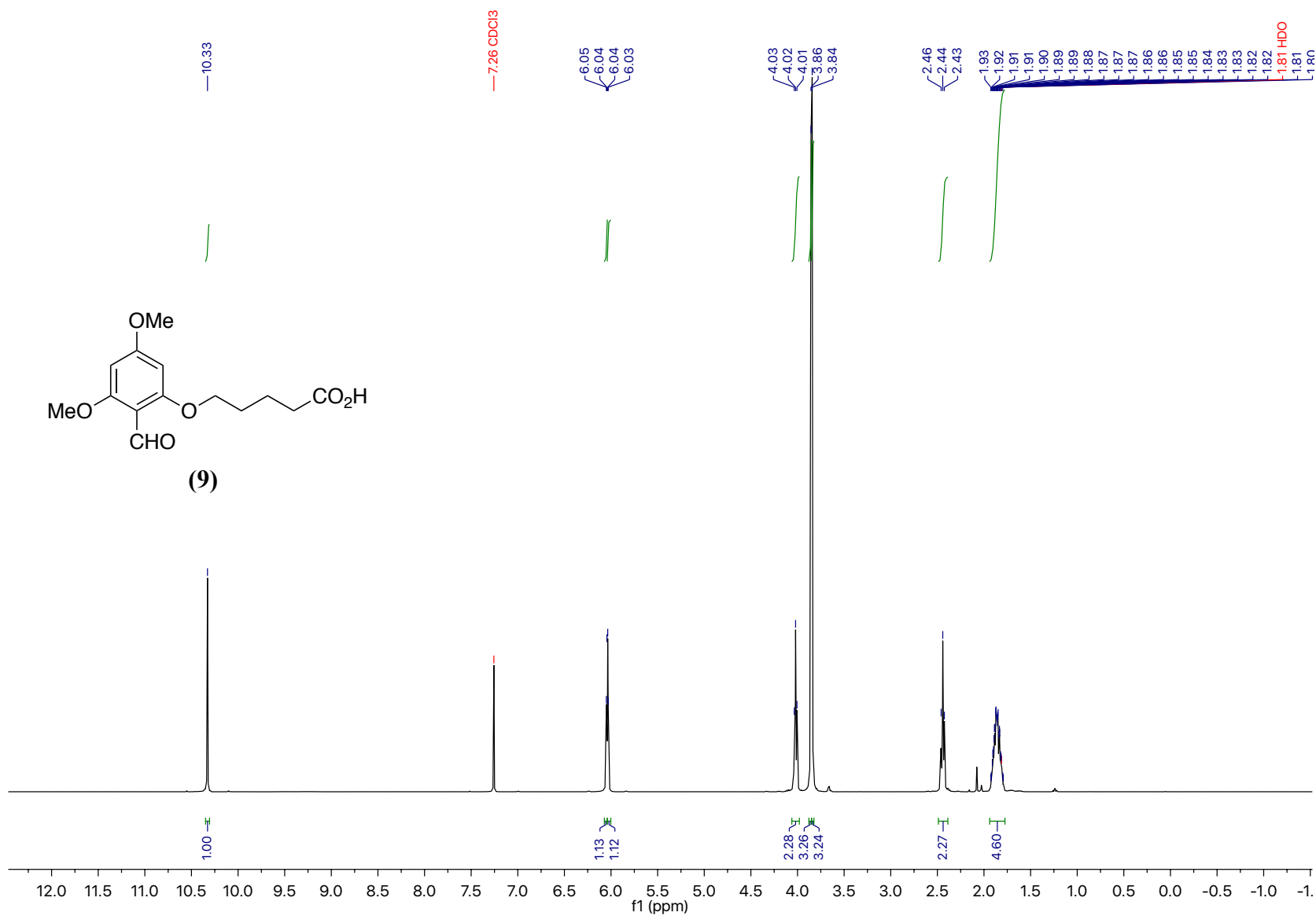


Figure S32. ¹H NMR (400 MHz, CDCl₃)

IV. UPLC-MS Chromatograms

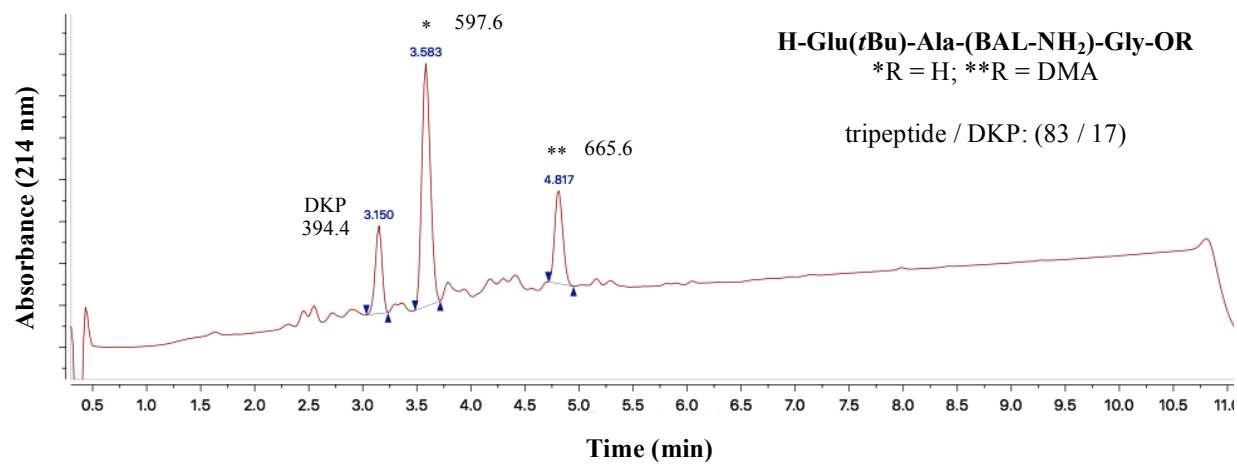


Figure S33. UPLC-MS chromatogram of **13a**

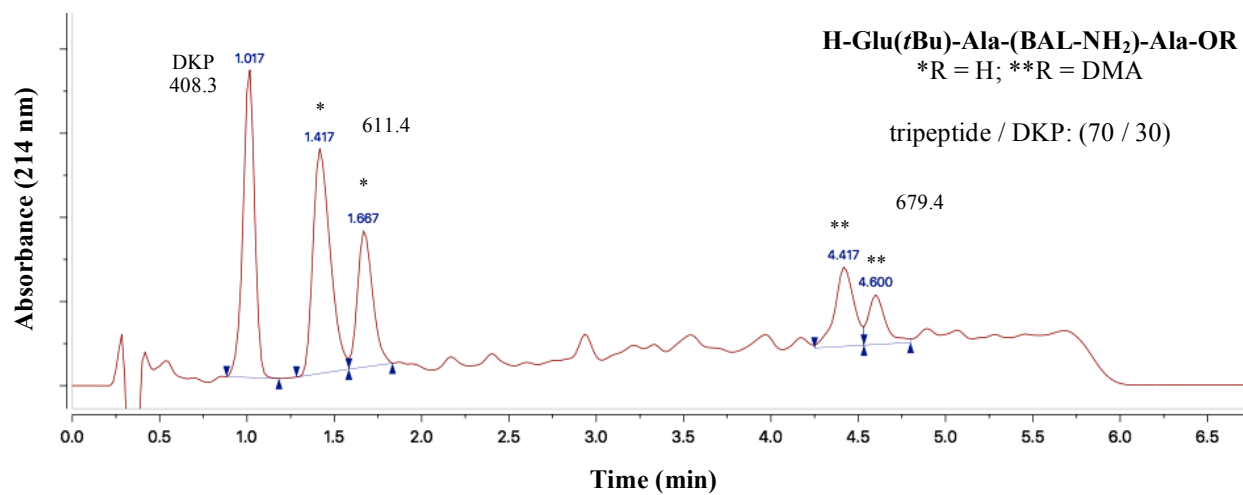


Figure S34. UPLC-MS chromatogram of **13b**

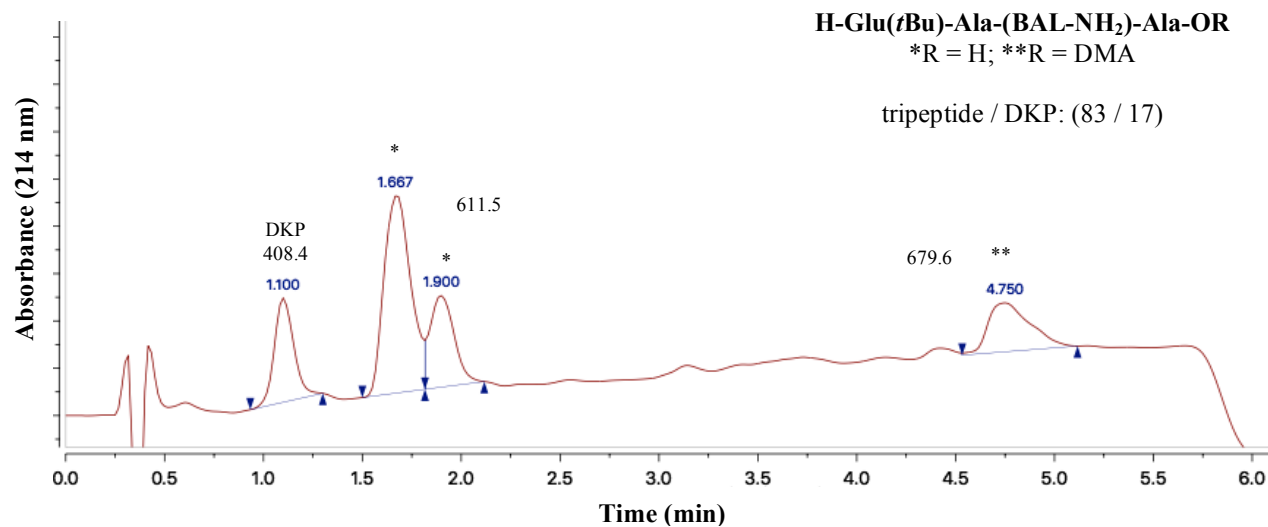


Figure S35. UPLC-MS chromatogram of **13b** using short (3 min) piperidine-promoted Fmoc deprotection at dipeptide stage

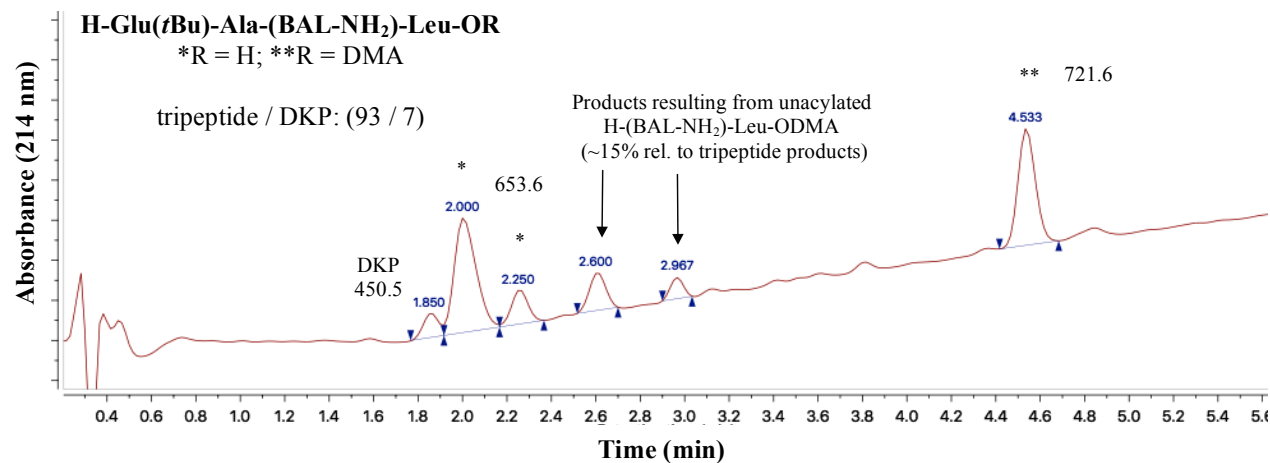


Figure S36. UPLC-MS chromatogram of **13c**

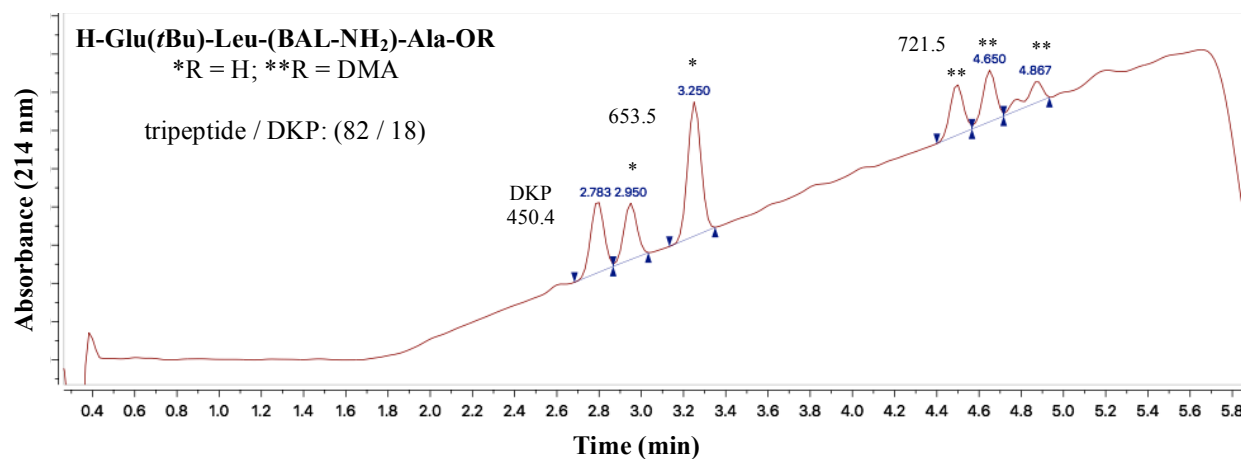


Figure S37. UPLC-MS chromatogram of **13d**

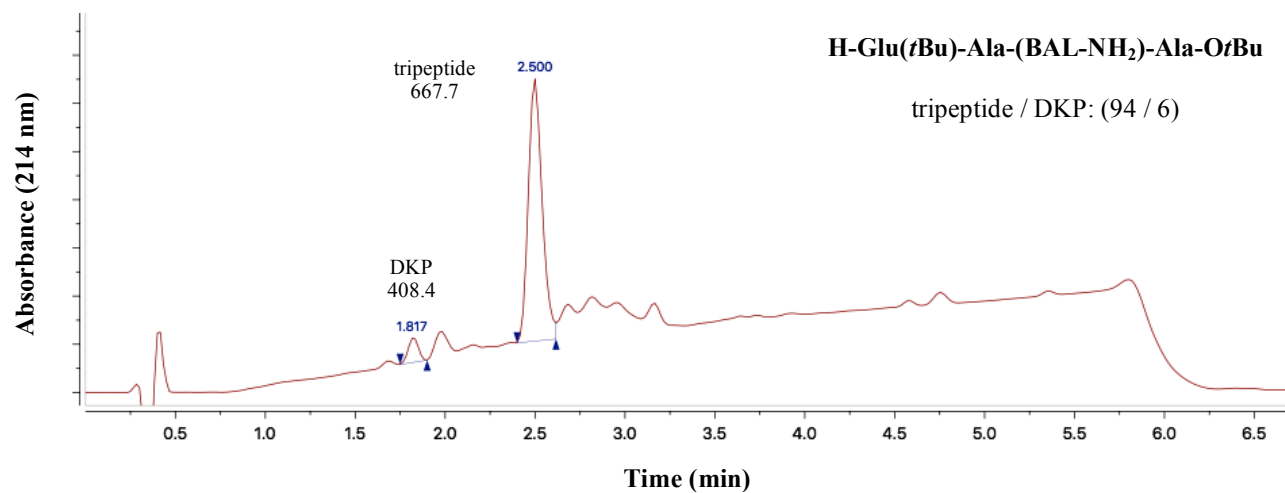


Figure S38. UPLC-MS chromatogram of **13e**