

Electronic Supplementary Information (ESI)

Enantioselective Total Synthesis and Structural Assignment of Callyspongiolide

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^1H and ^{13}C NMR Spectra of Reported Compounds:

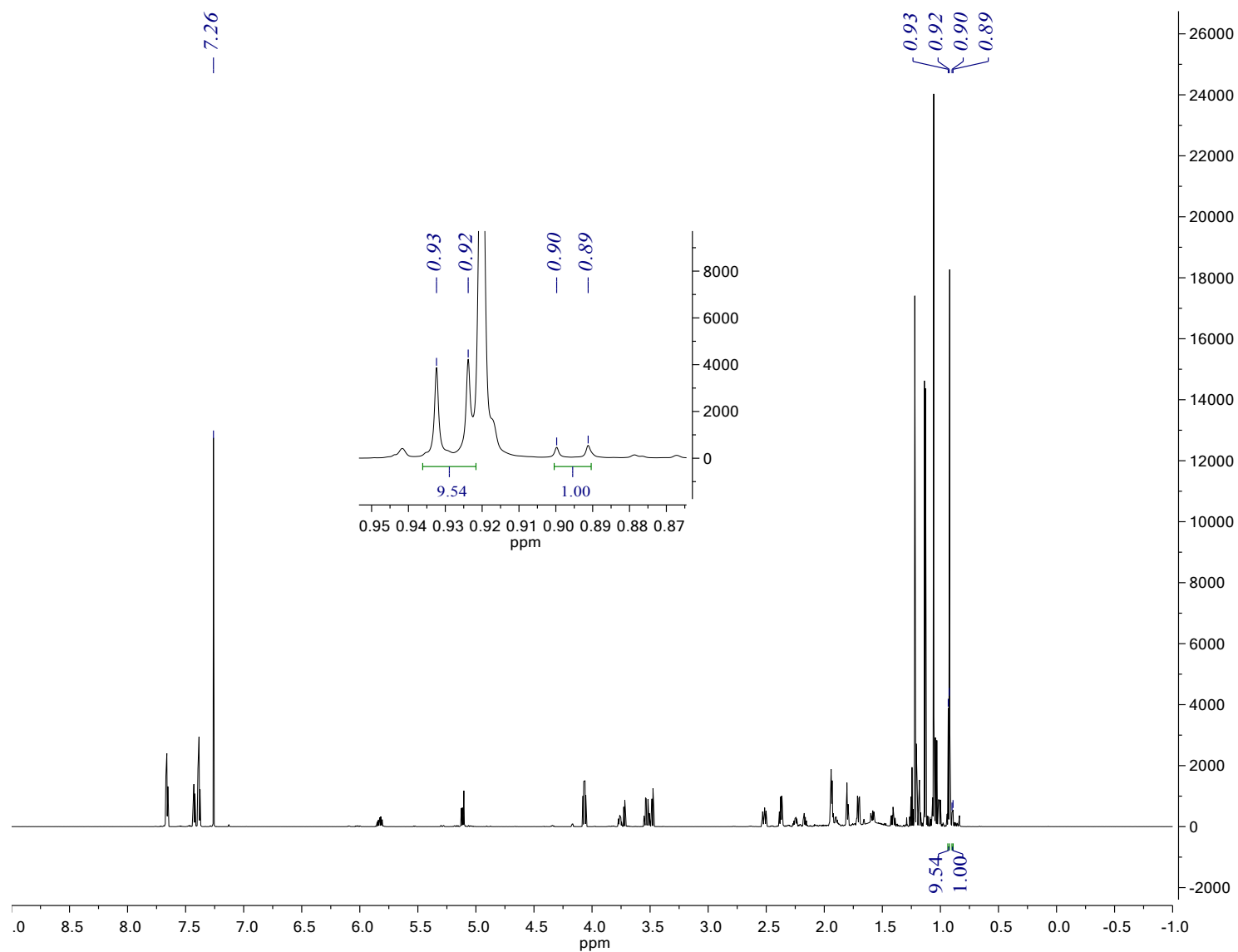


Figure S1. ^1H NMR (500 MHz, CDCl_3) of crude homoallylic alcohol **7**.

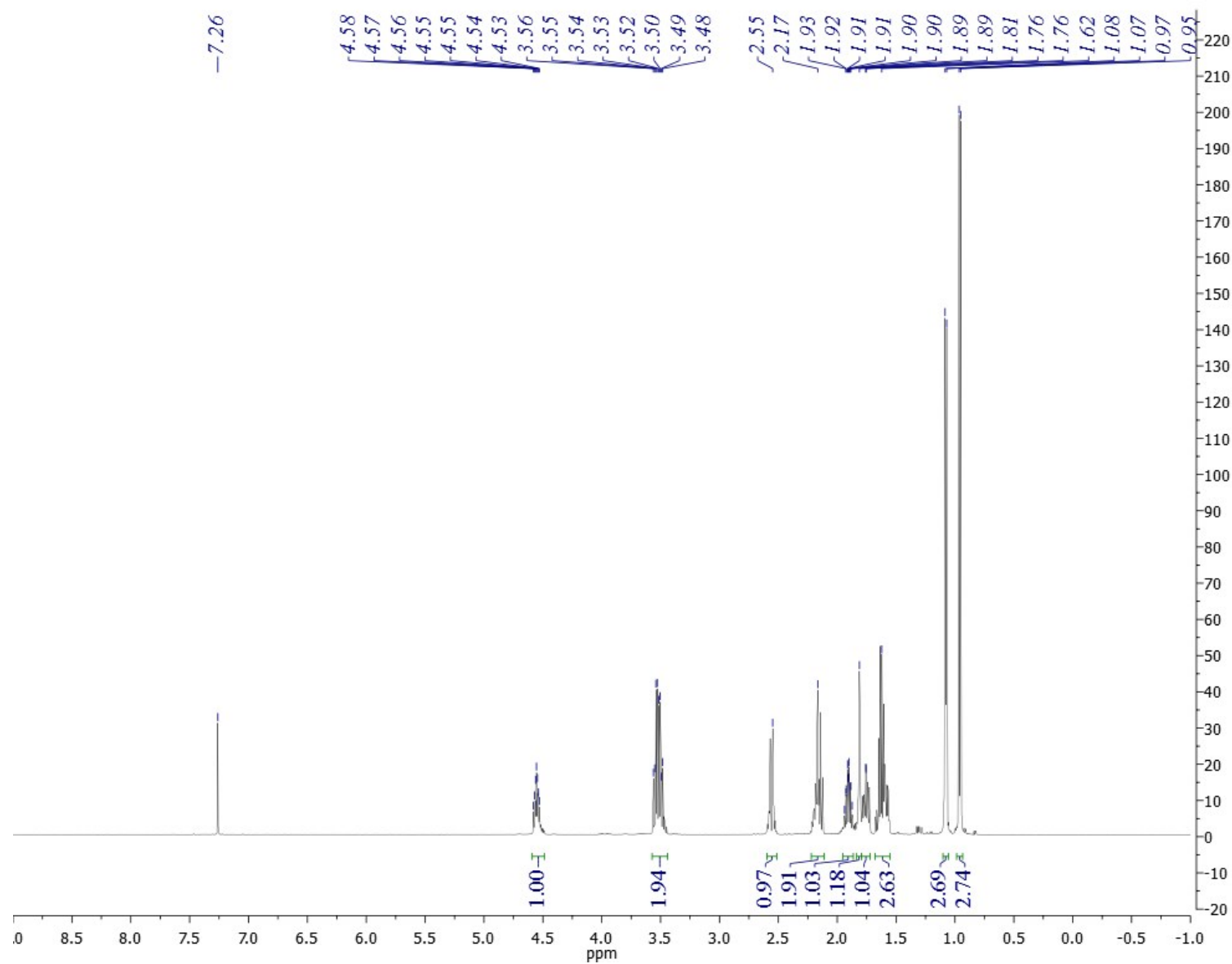


Figure S2. ^1H NMR (500 MHz, CDCl_3) of homoallylic alcohol **7**.

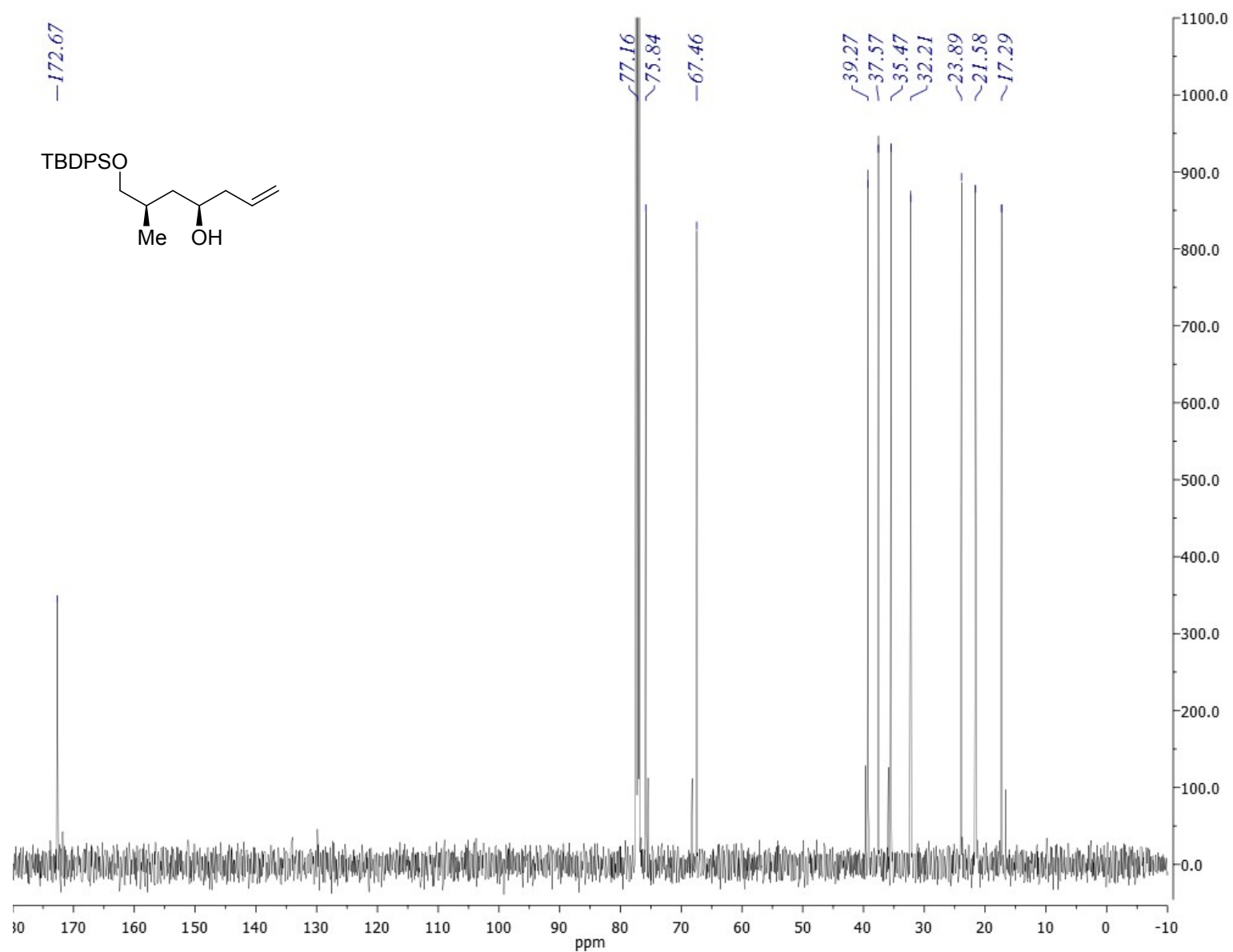


Figure S3. ¹³C NMR (125 MHz, CDCl₃) of homoallylic alcohol **7**.

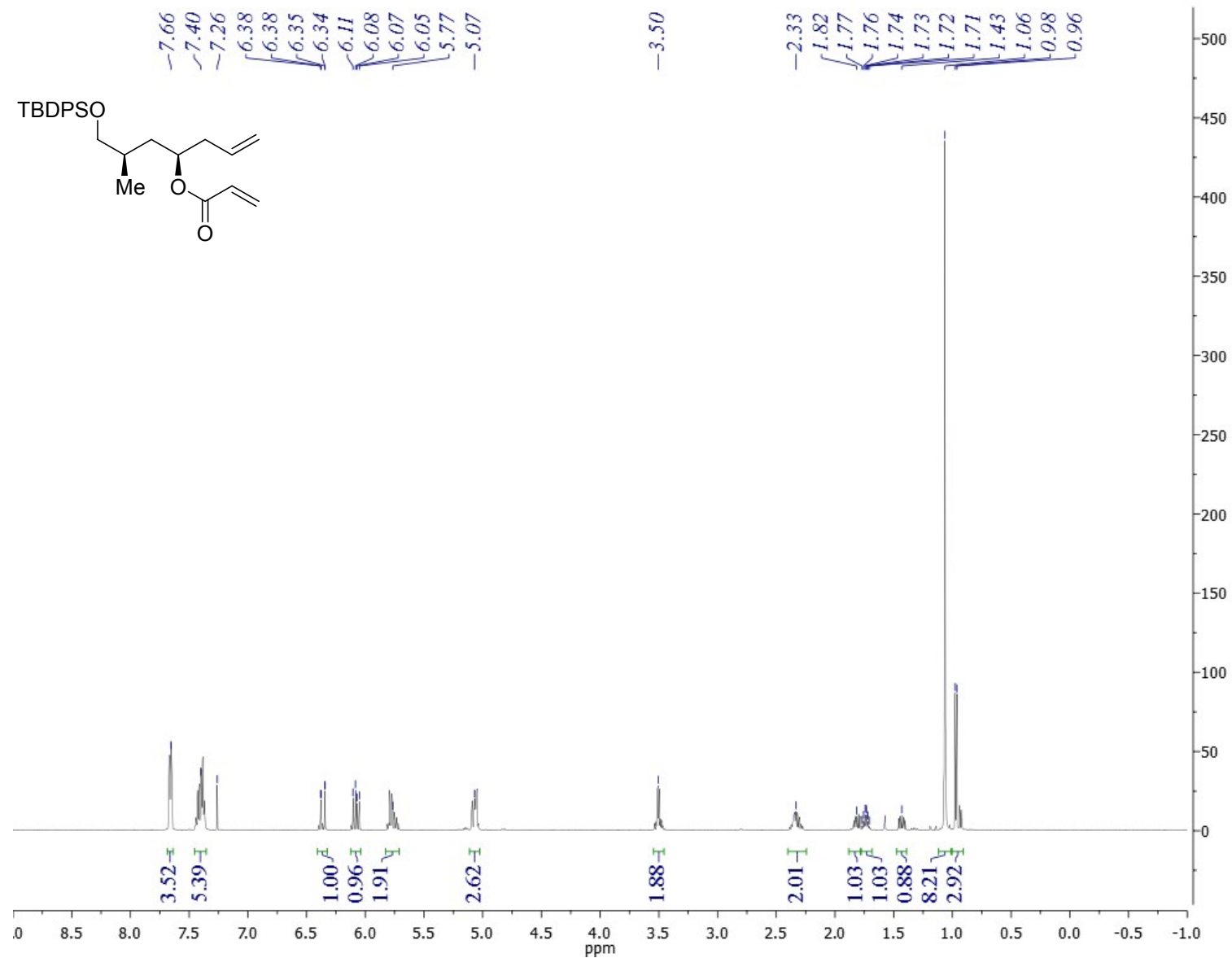


Figure S4. ¹H NMR (500 MHz, CDCl₃) of diene **12**.

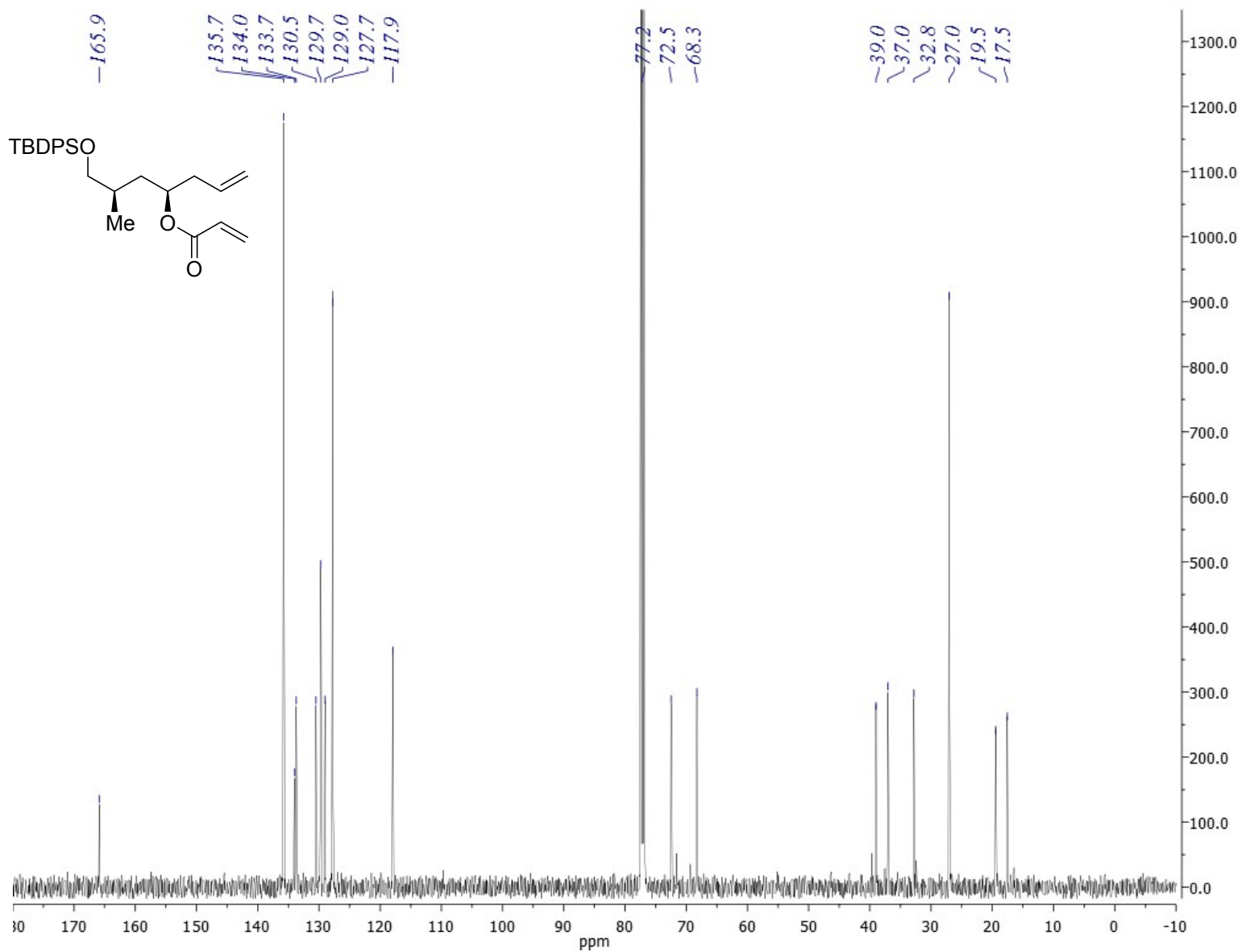


Figure S5. ^{13}C NMR (125 MHz, CDCl_3) of diene **12**.

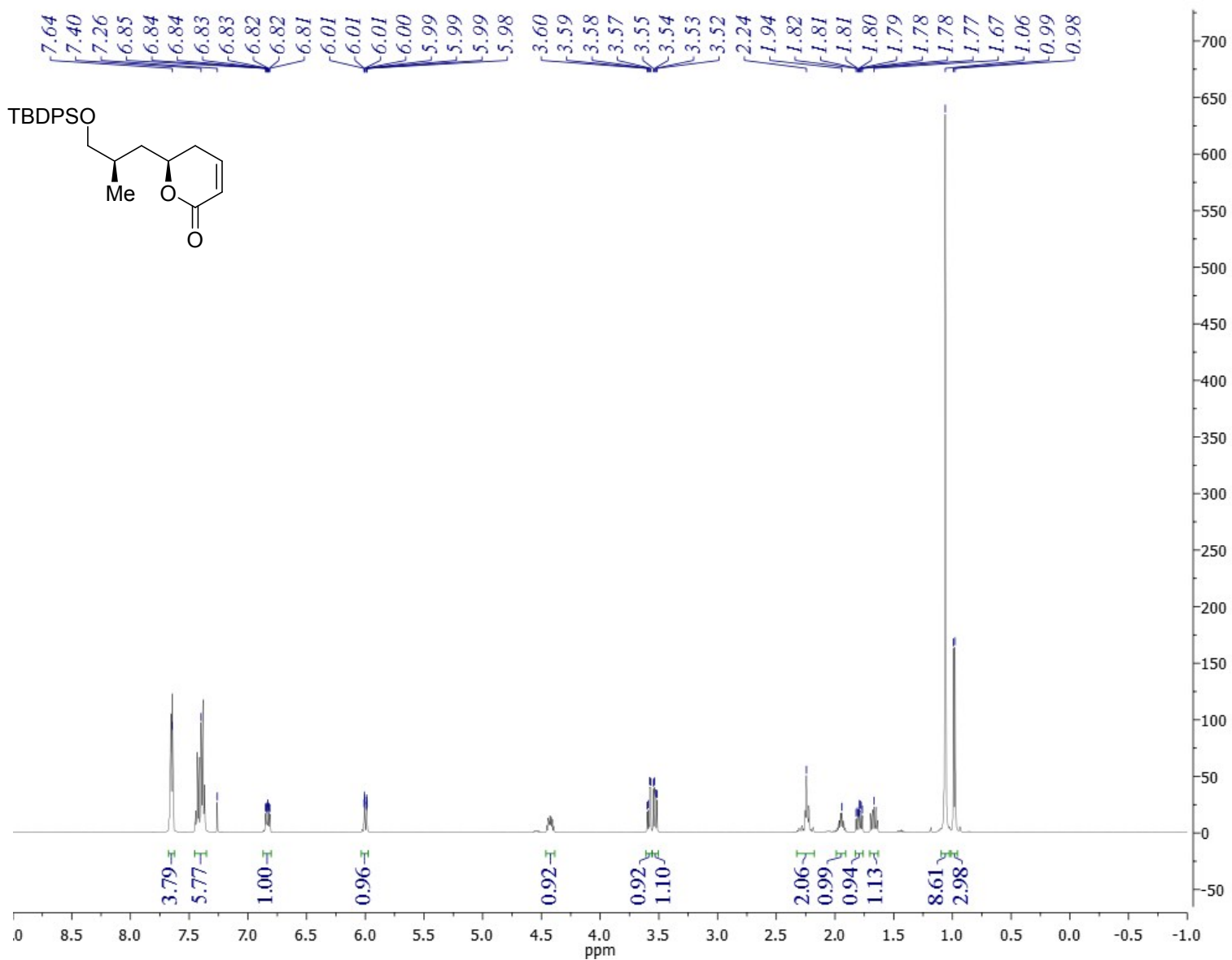


Figure S6. ^1H NMR (500 MHz, CDCl_3) of pyranone **13**.

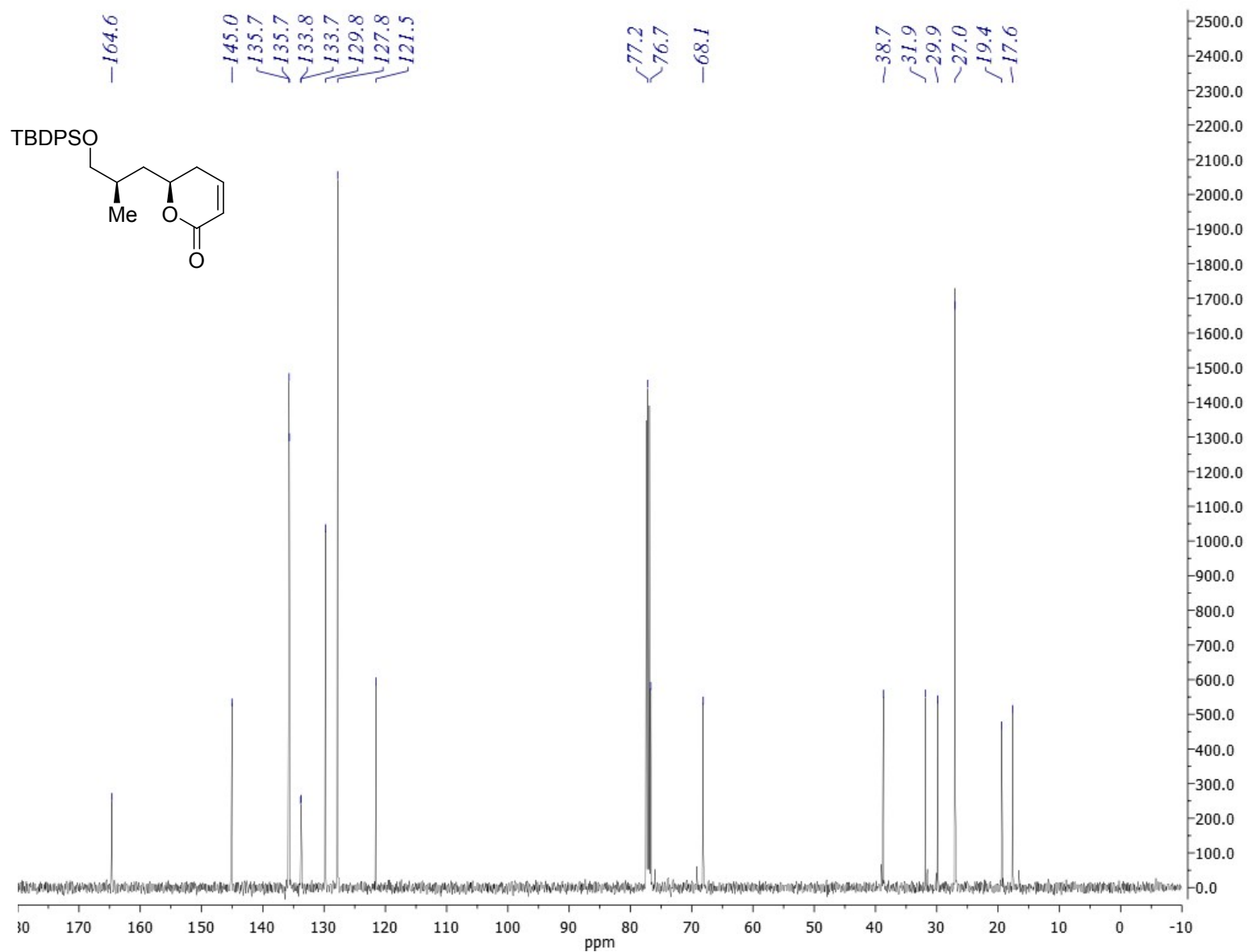


Figure S7. ^{13}C NMR (125 MHz, CDCl_3) of pyranone **13**.

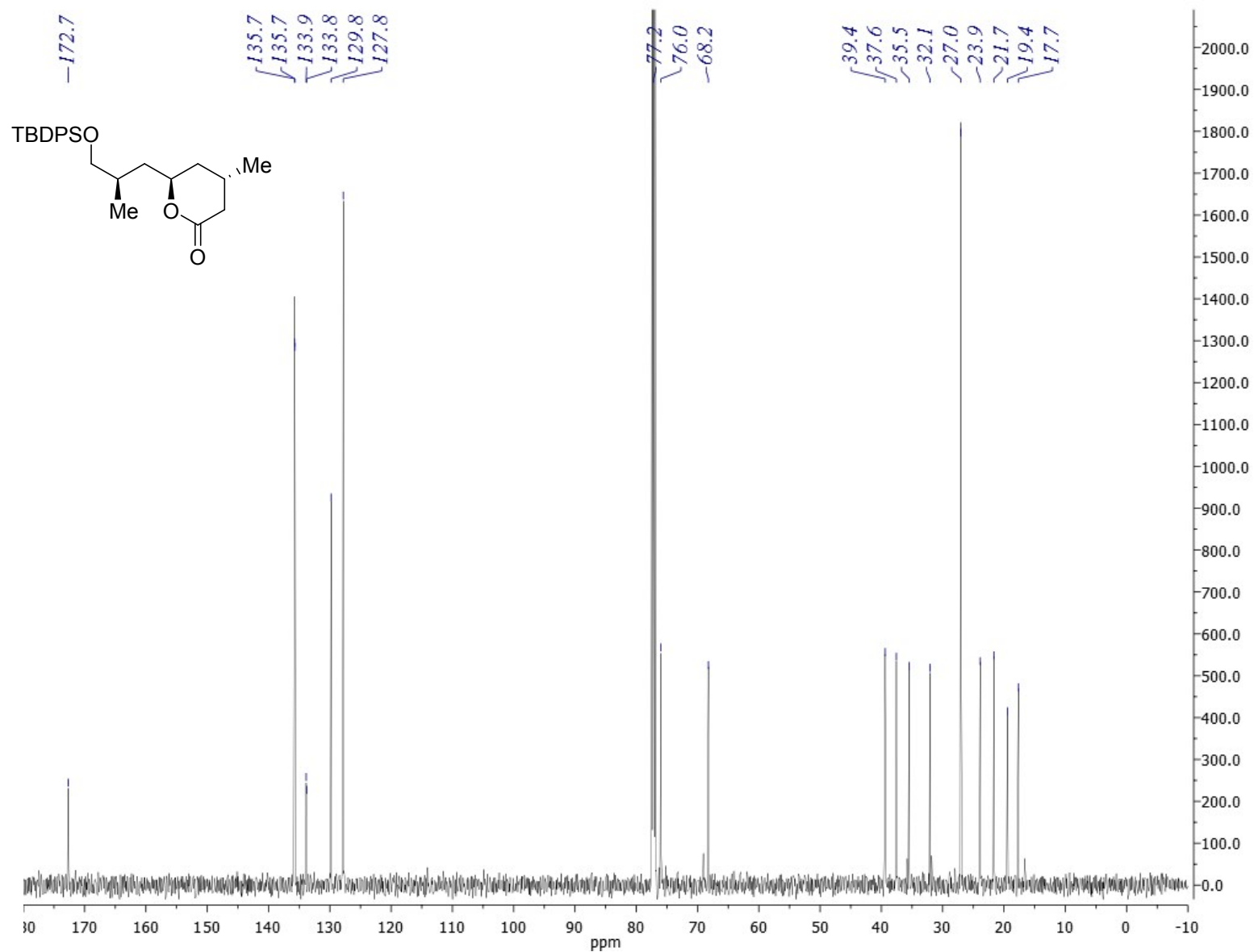


Figure S9. ^{13}C NMR (125 MHz, CDCl_3) of lactone **14**.

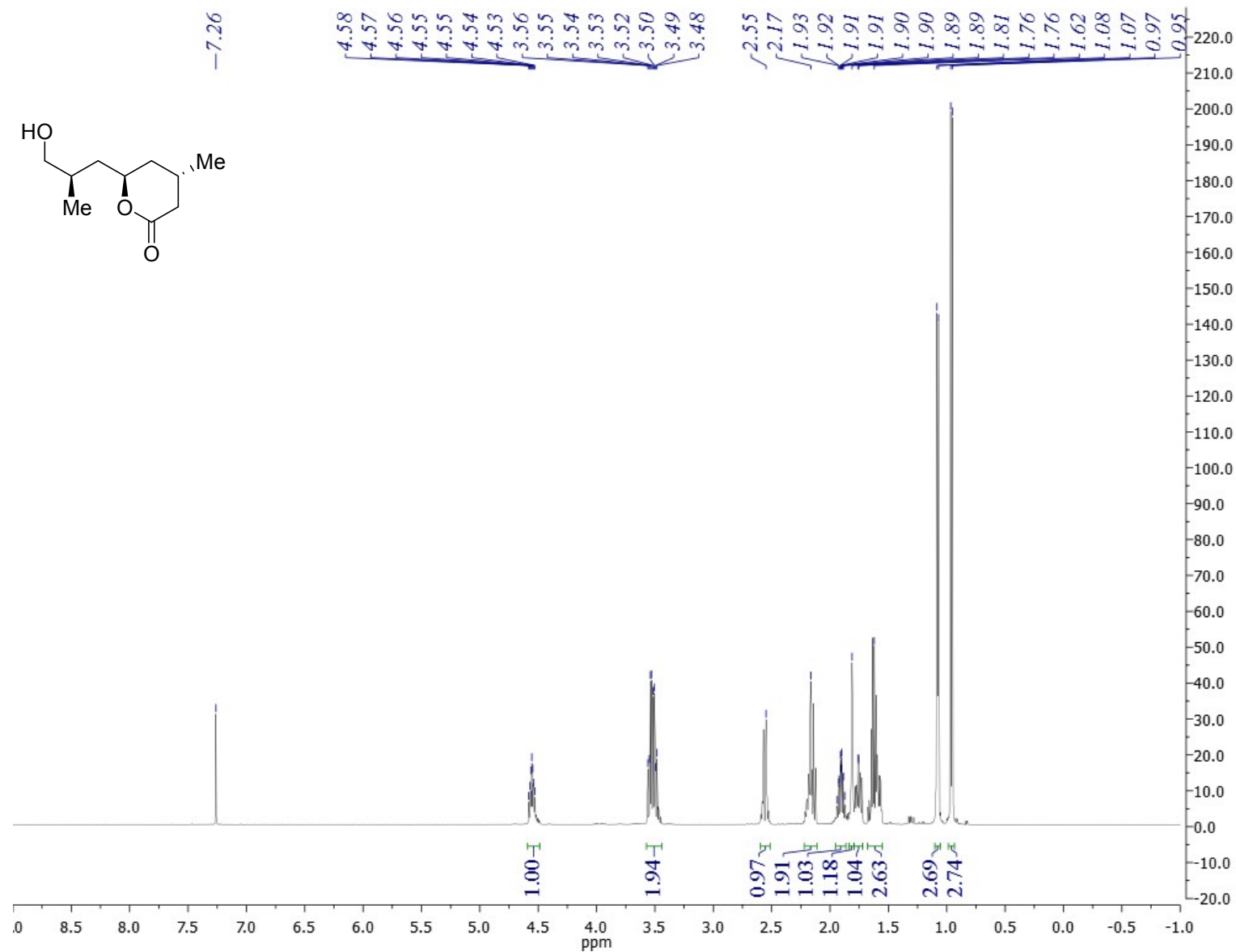


Figure S10. ¹H NMR (500 MHz, CDCl₃) of alcohol 6.

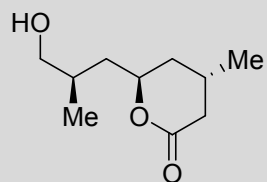


Figure S11. ^{13}C NMR (125 MHz, CDCl_3) of alcohol **6**.

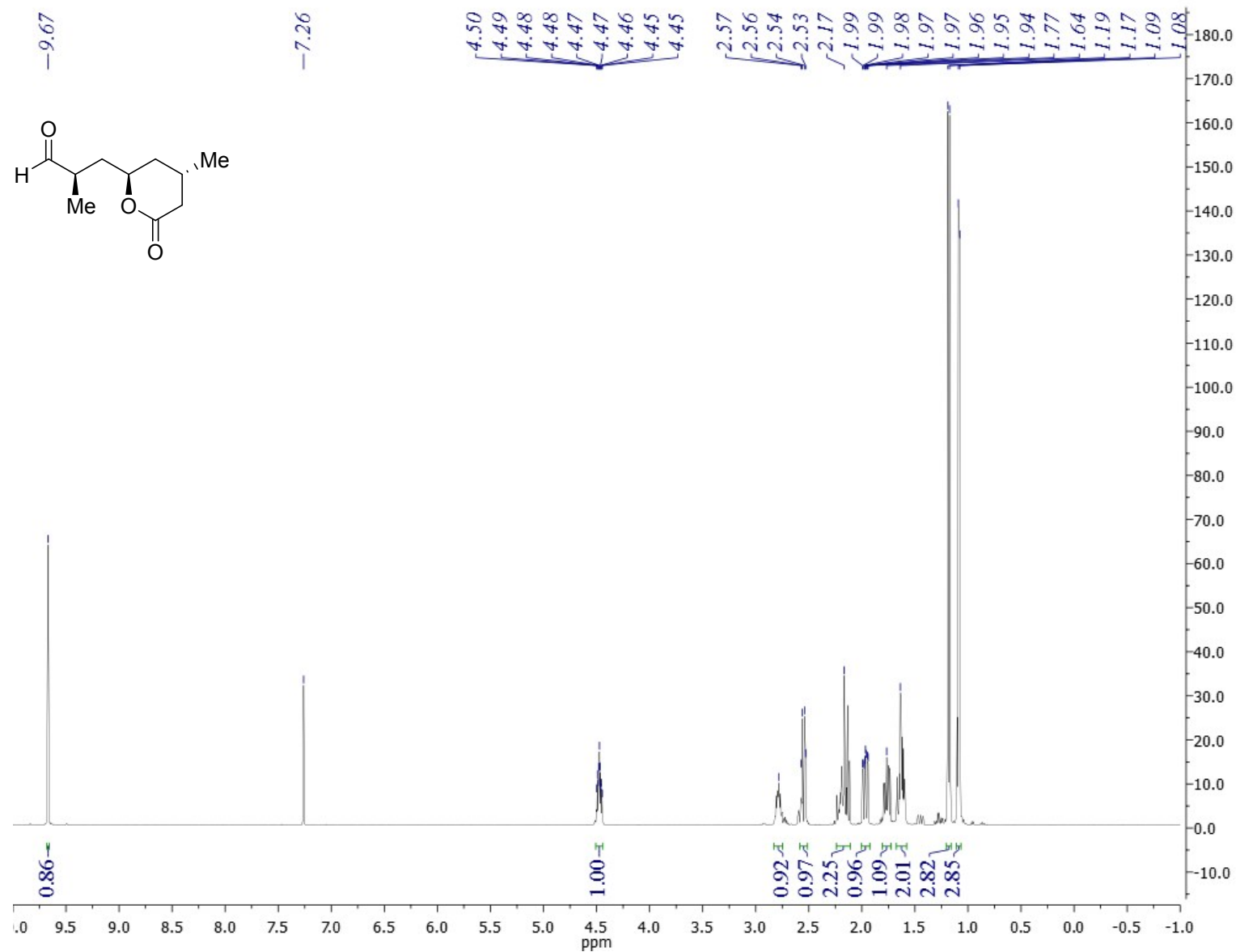


Figure S12. ¹H NMR (500 MHz, CDCl₃) of aldehyde **15**.

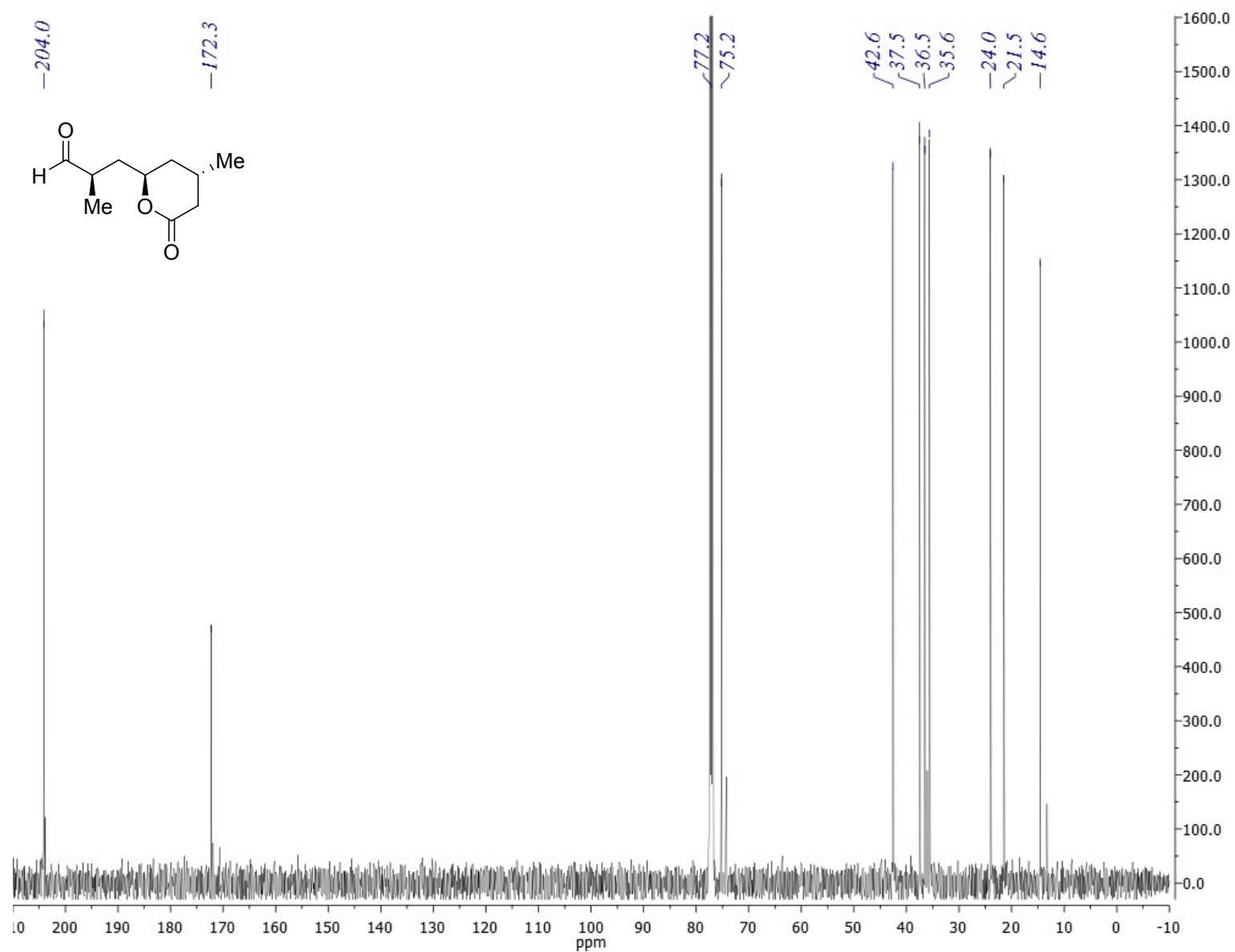


Figure S13. ¹³C NMR (125 MHz, CDCl₃) of aldehyde **15**.

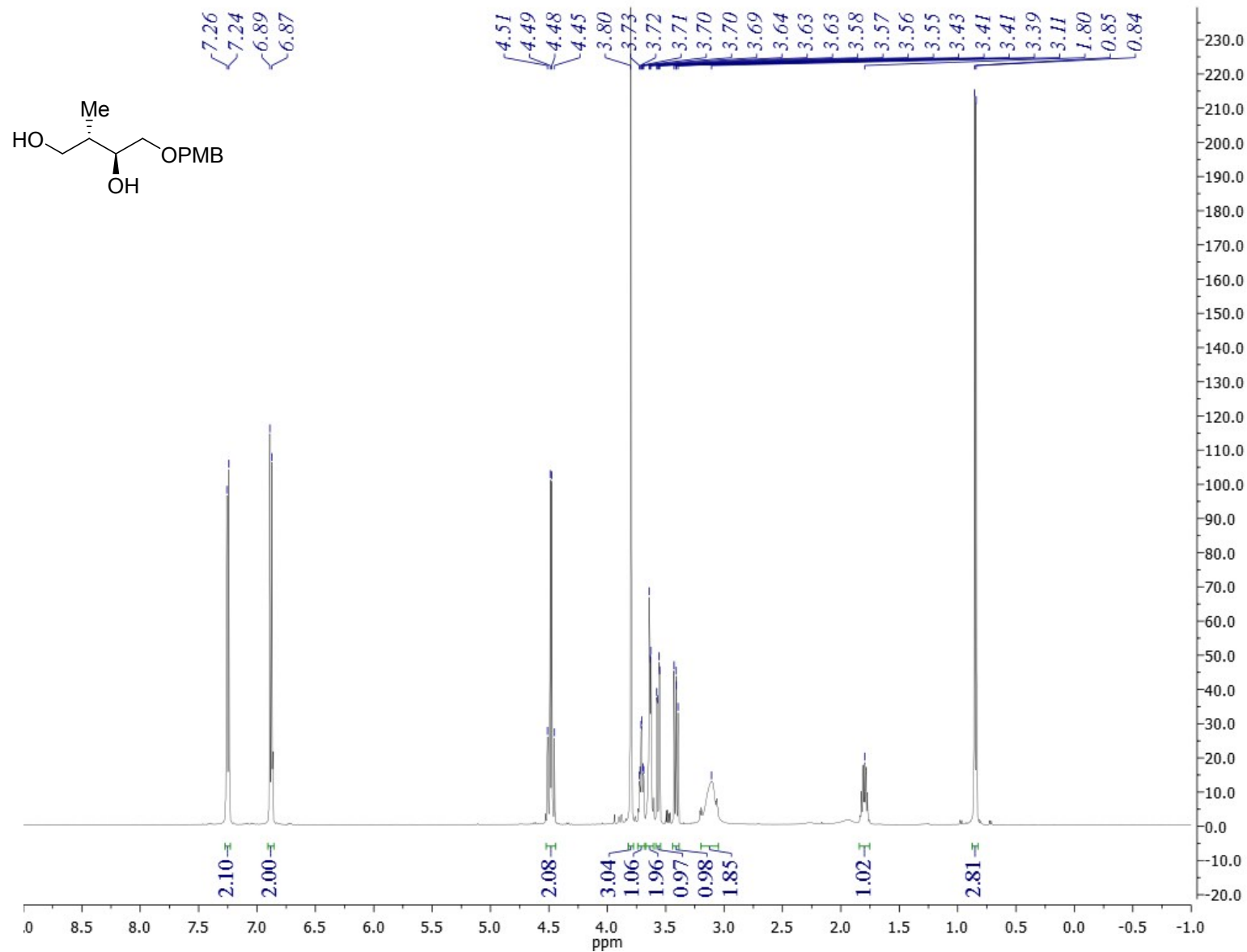


Figure S14. ¹H NMR (500 MHz, CDCl₃) of diol 18.

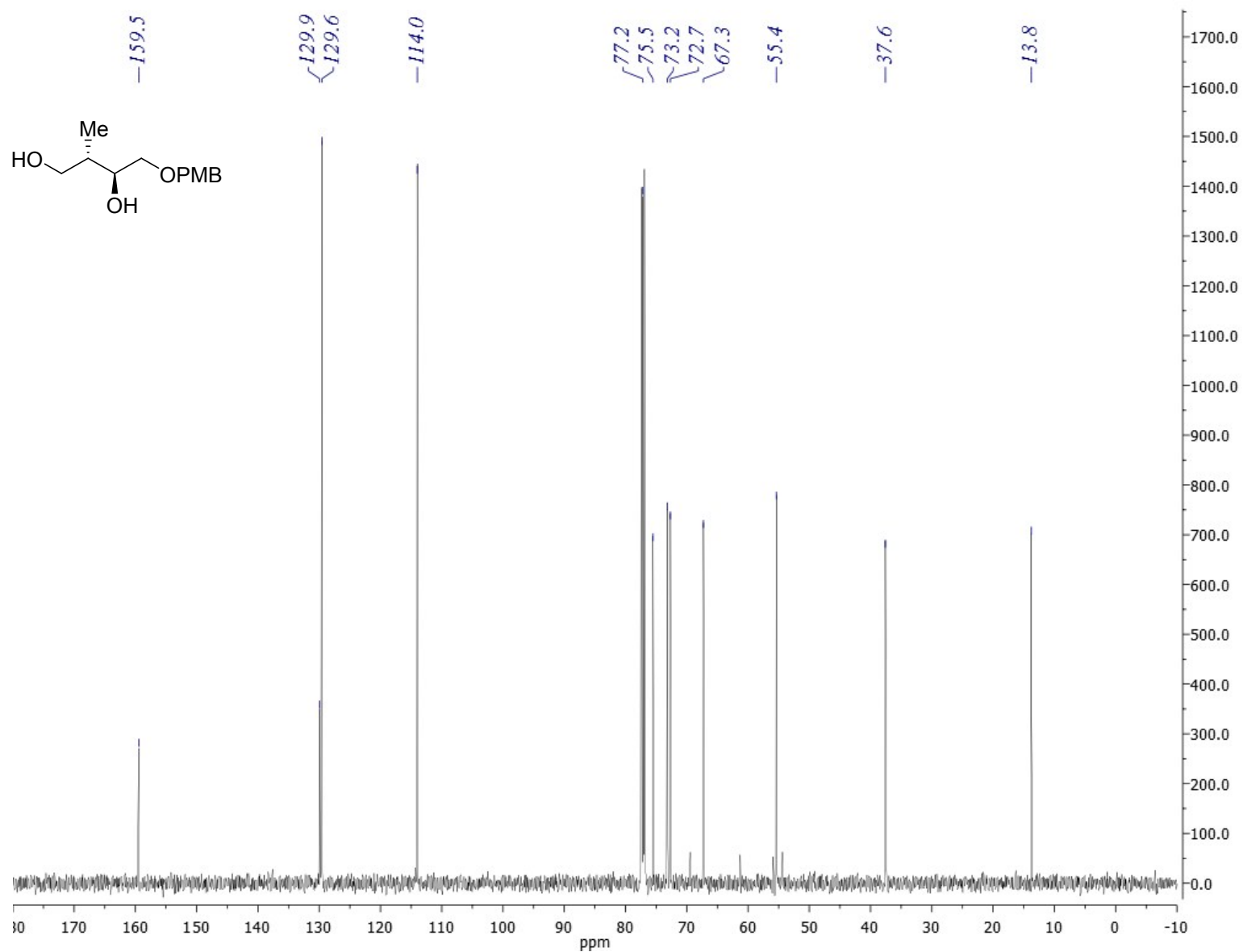


Figure S15. ^{13}C NMR (125 MHz, CDCl_3) of diol **18**.

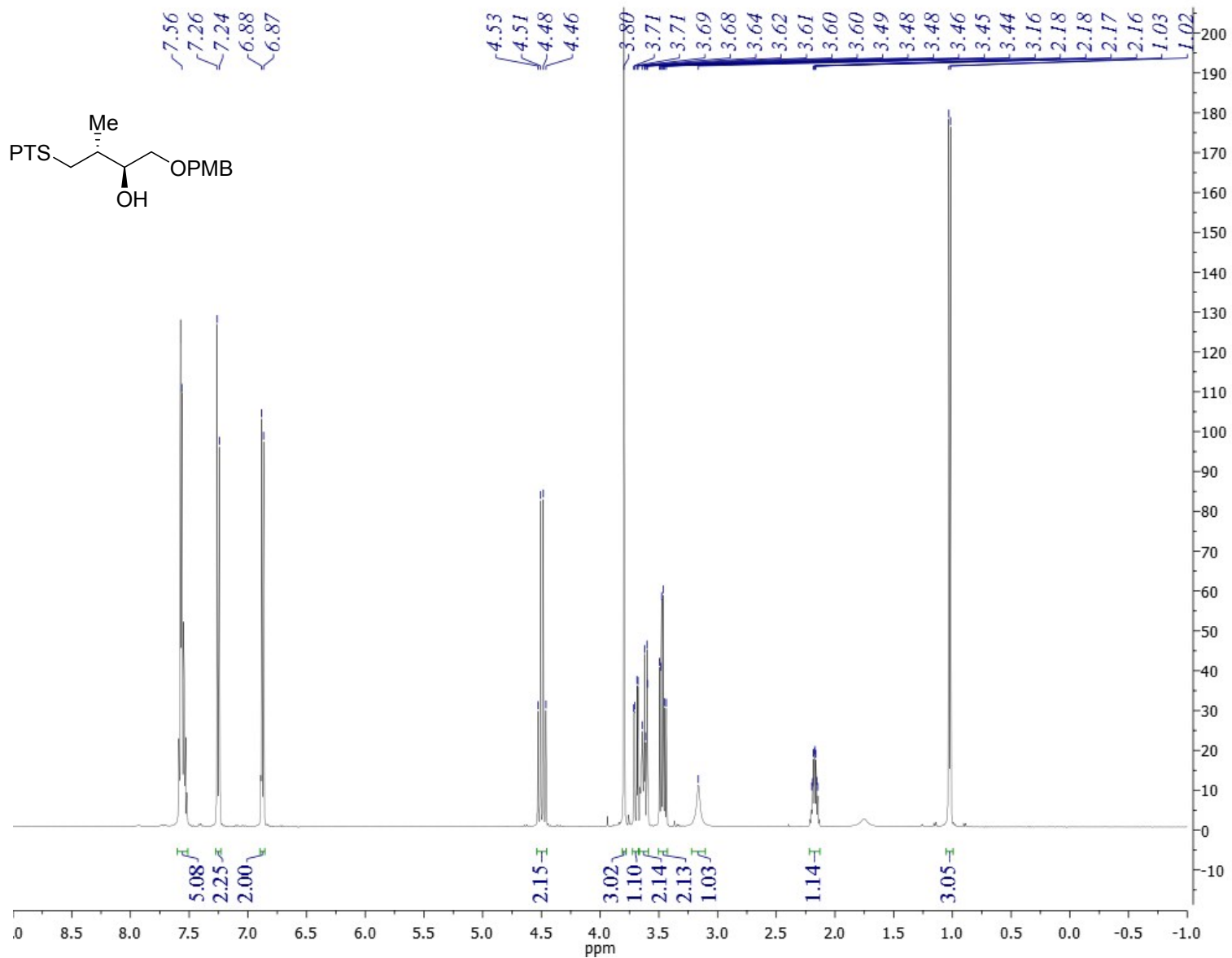


Figure S16. ¹H NMR (500 MHz, CDCl₃) of sulfide **19**.

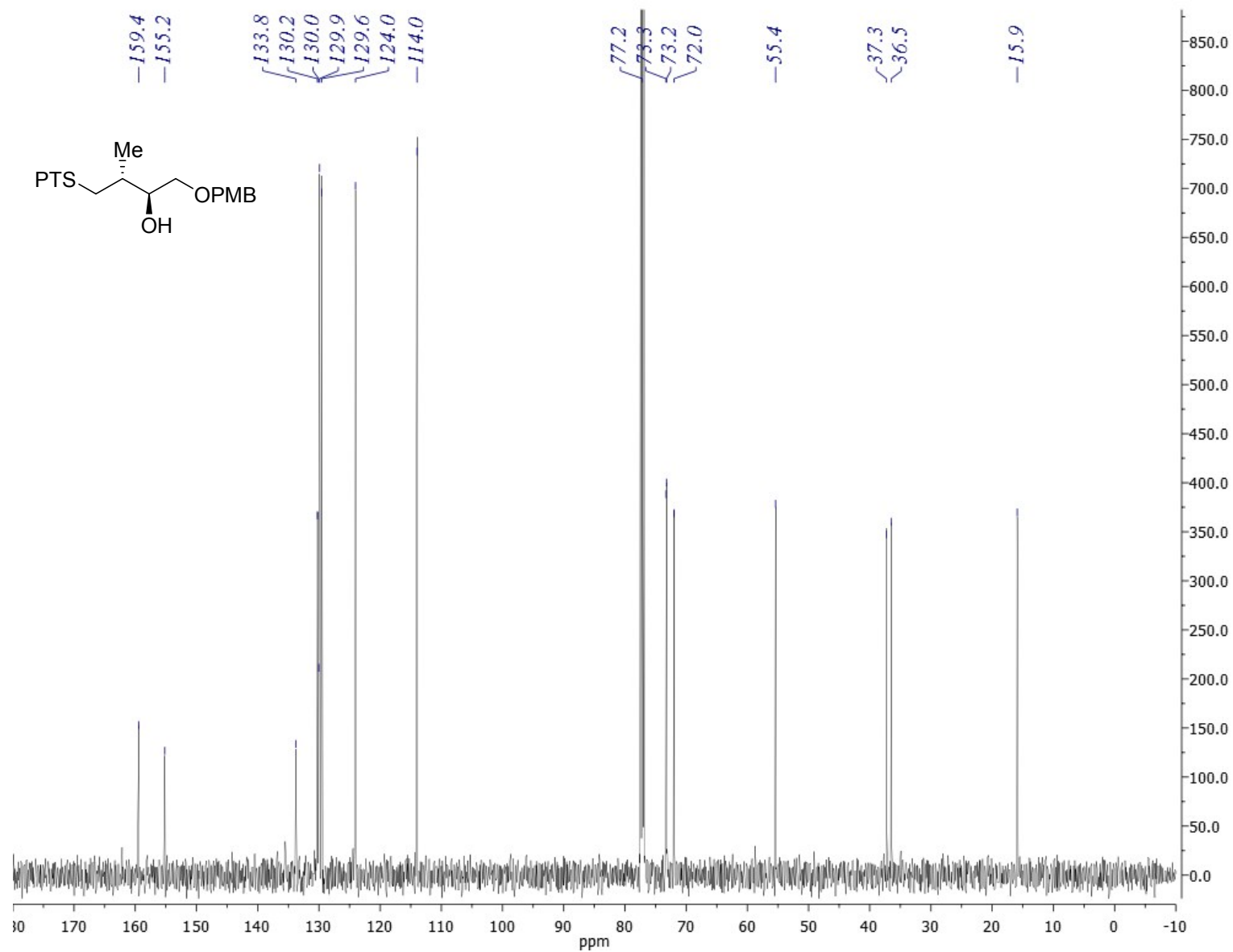


Figure S17. ^{13}C NMR (125 MHz, CDCl_3) of sulfide **19**.

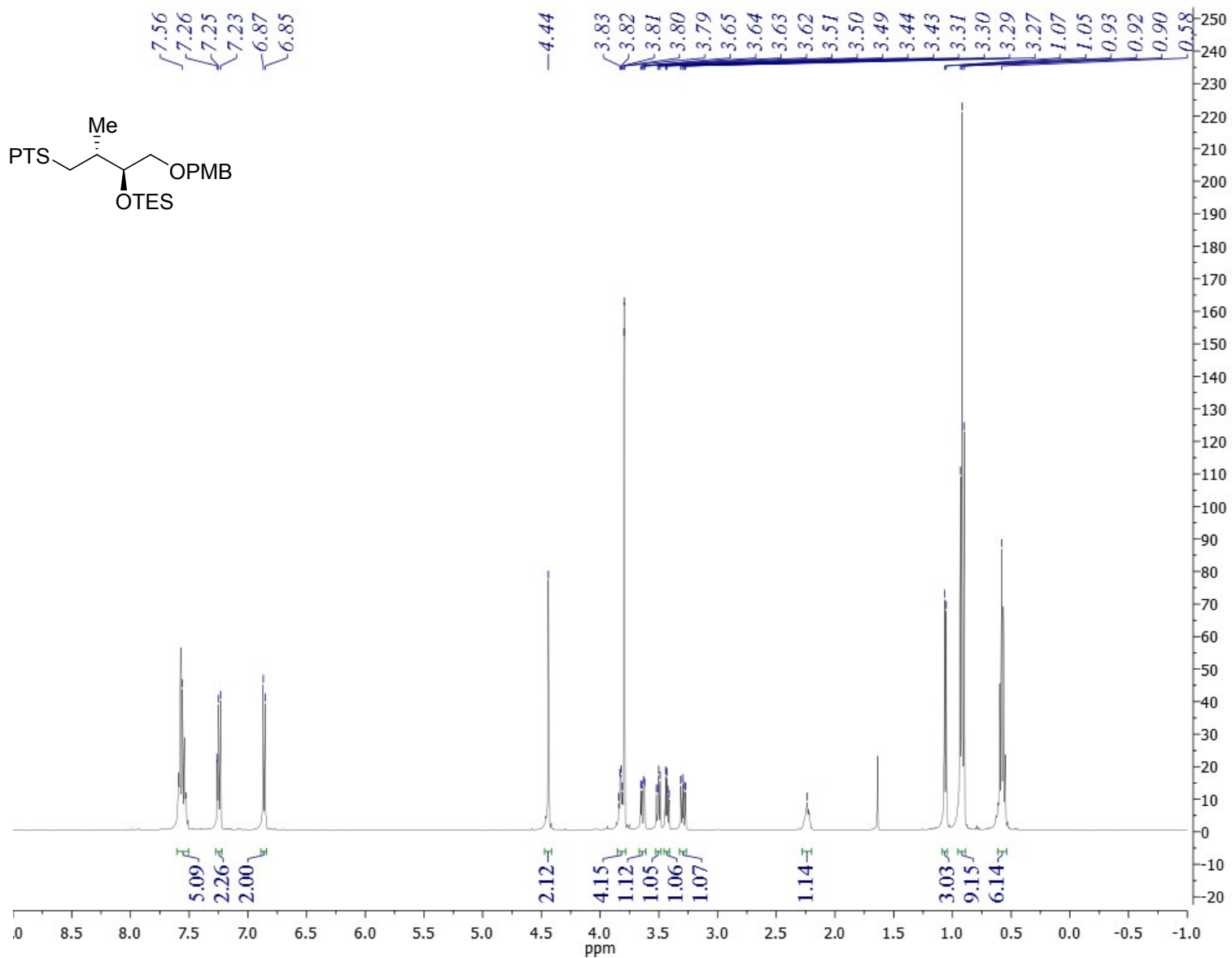


Figure S18. ¹H NMR (500 MHz, CDCl₃) of TES ether **20**.

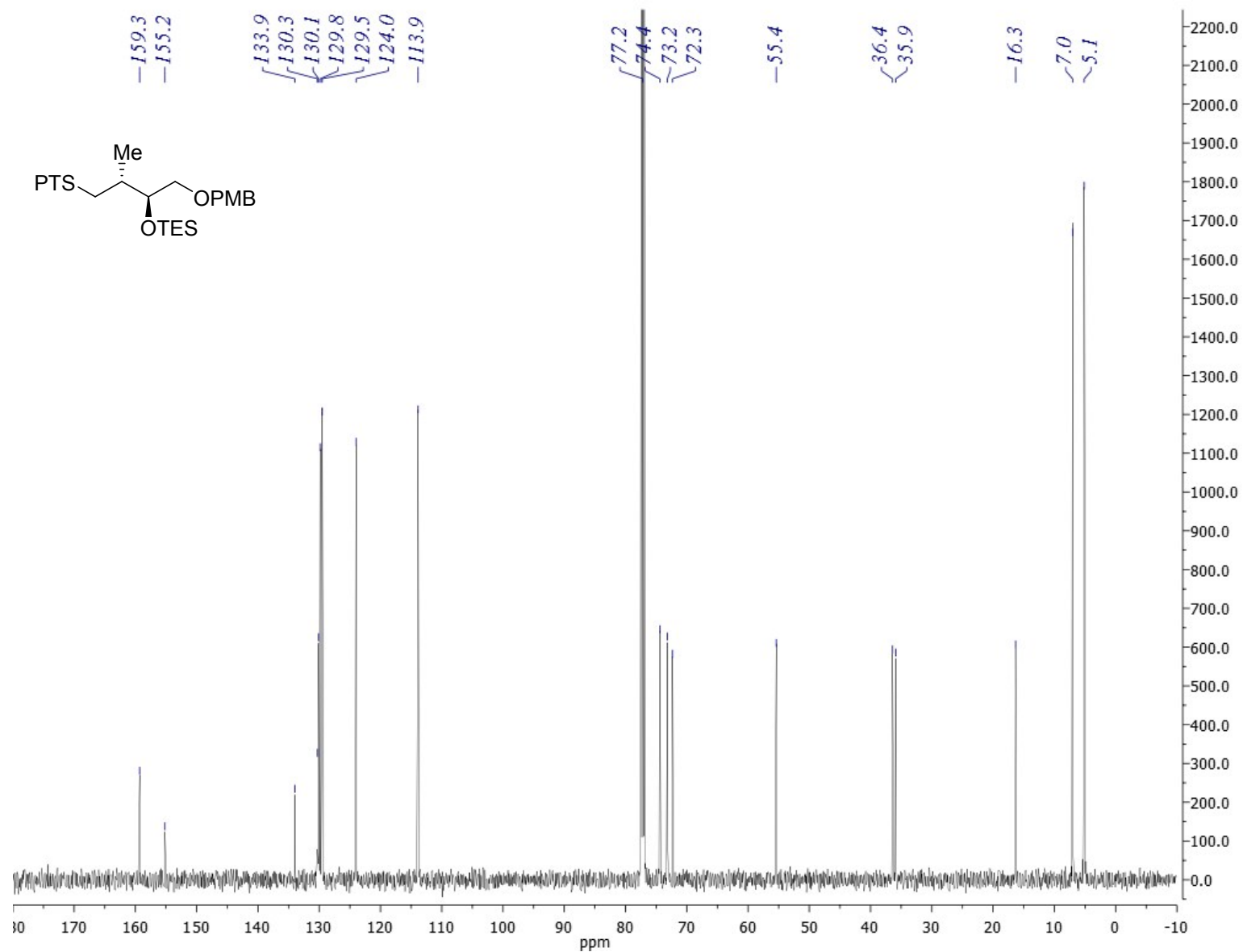


Figure S19. ^{13}C NMR (125 MHz, CDCl_3) of TES ether **20**.

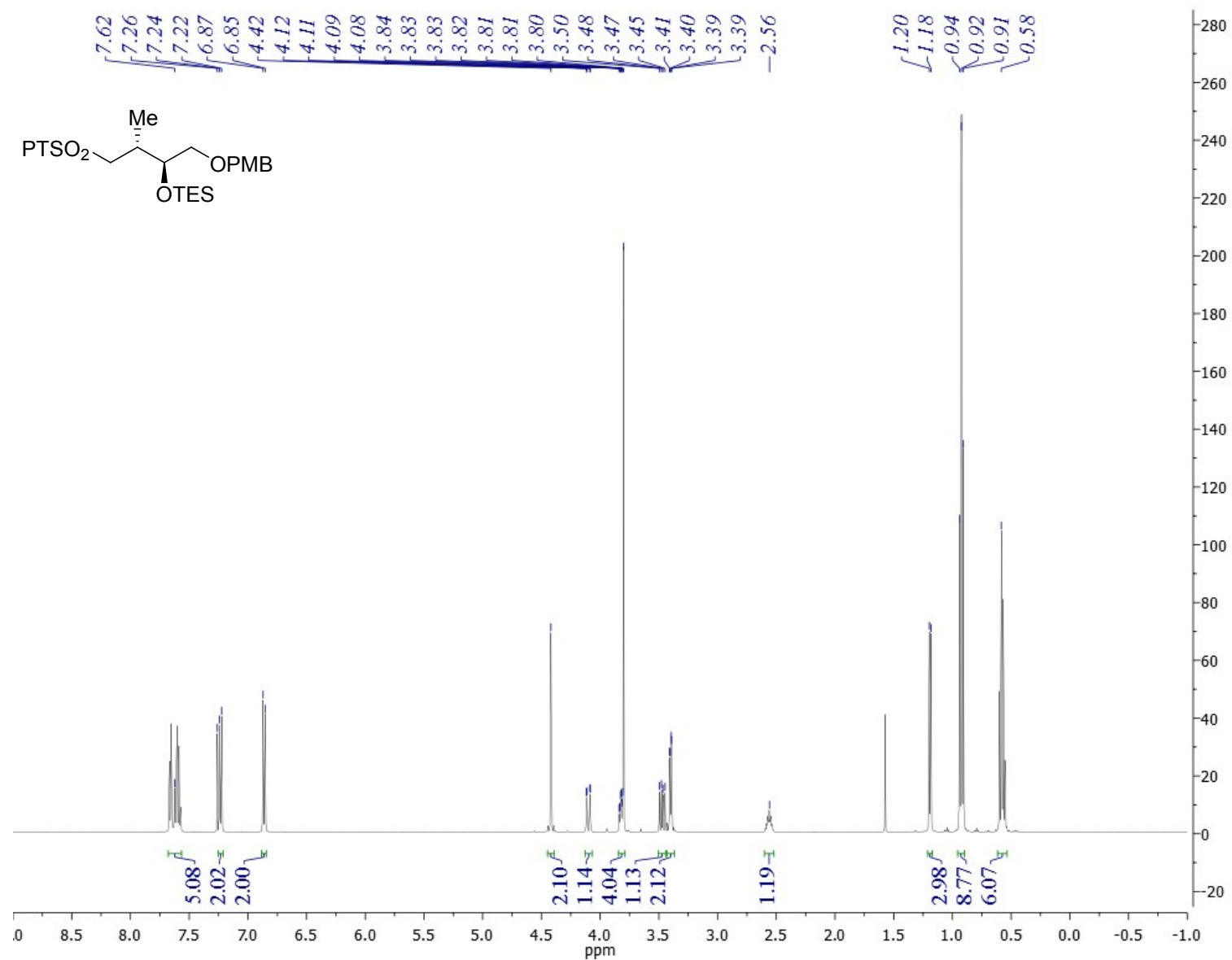


Figure S20. ¹H NMR (500 MHz, CDCl₃) of sulfone **21**.

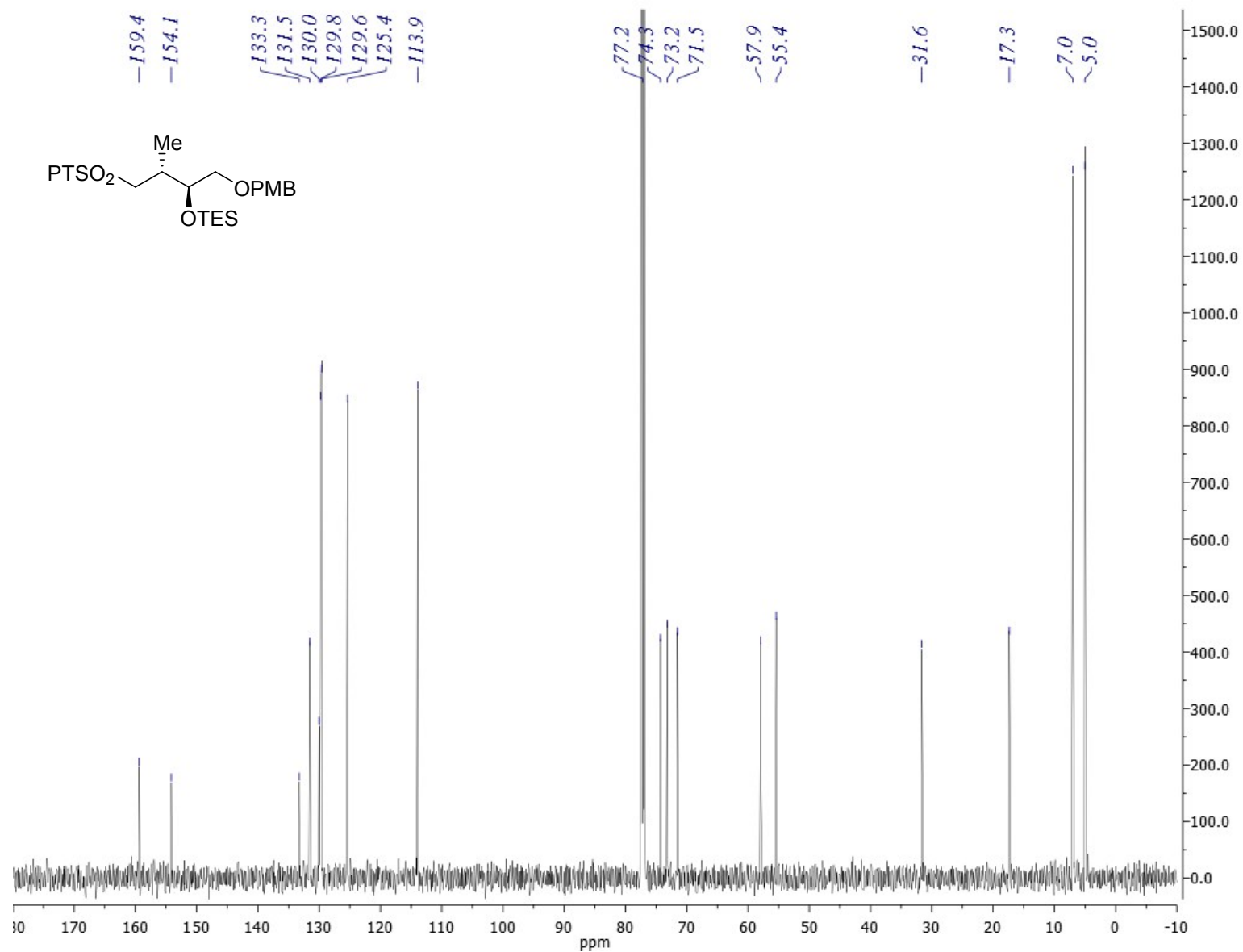


Figure S21. ¹³C NMR (125 MHz, CDCl₃) of sulfone **21**.

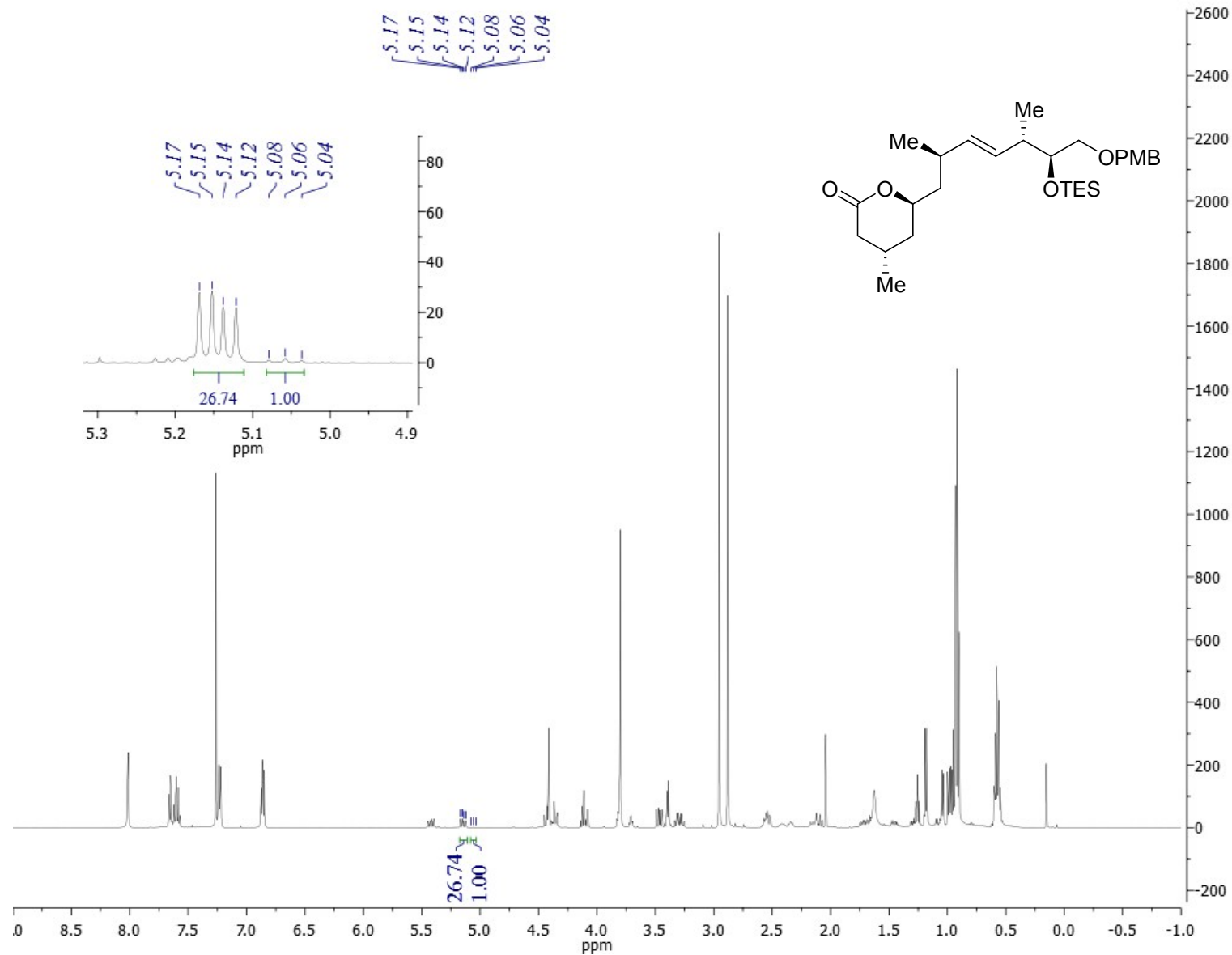


Figure S22. ^1H NMR (500 MHz, CDCl_3) of crude lactone **22**.

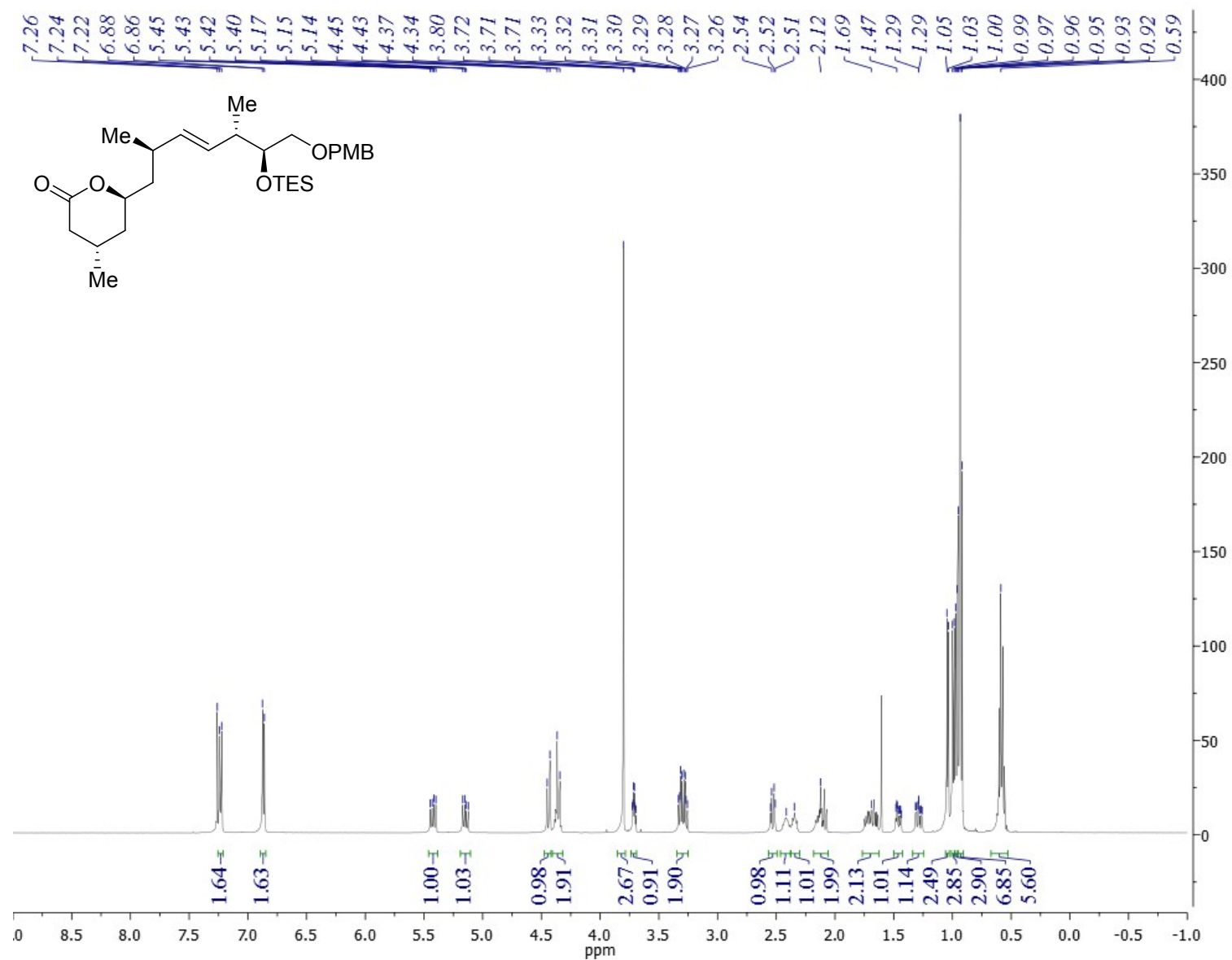


Figure S23. ¹H NMR (500 MHz, CDCl₃) of lactone **22**.

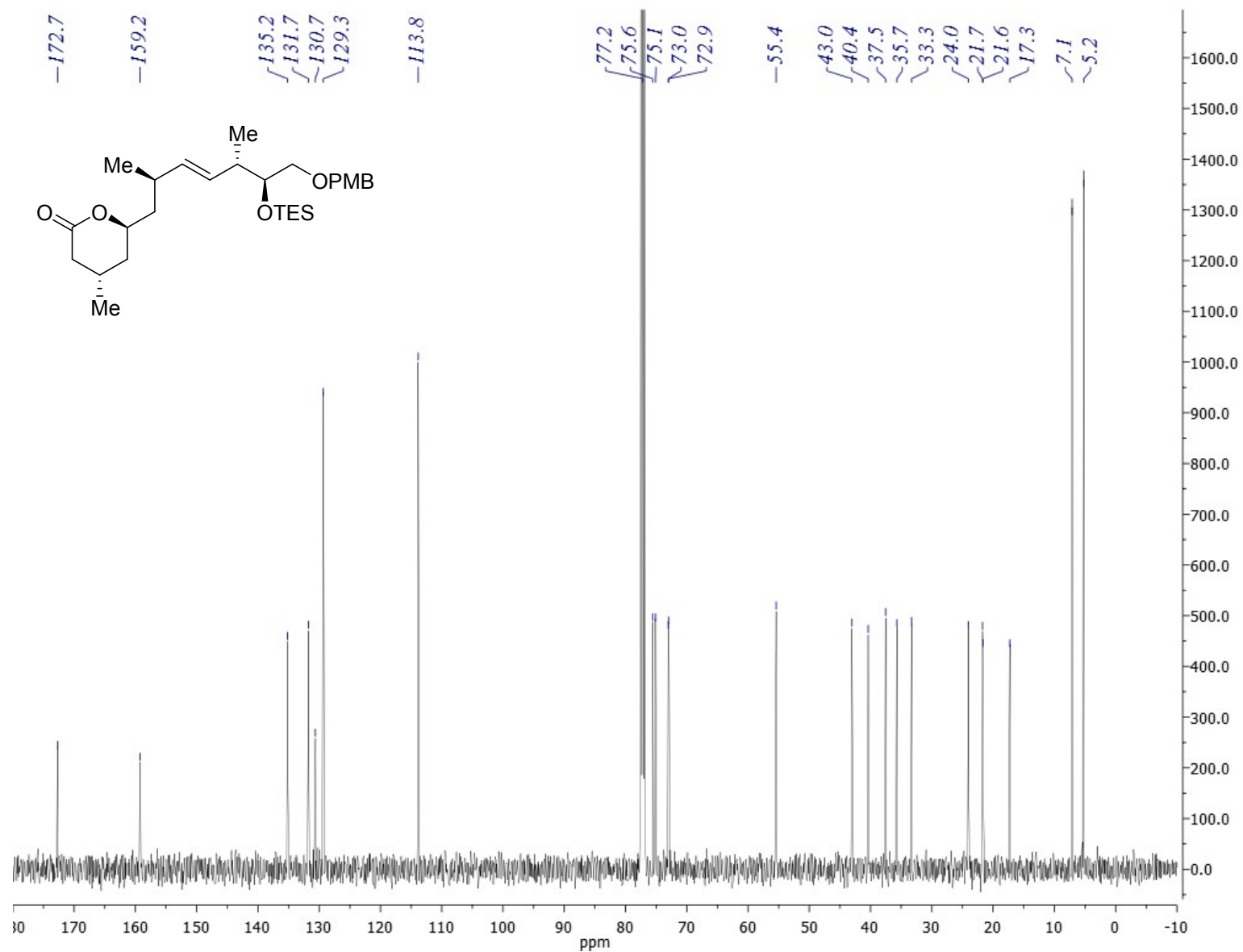


Figure S24. ¹³C NMR (125 MHz, CDCl₃) of lactone **22**.

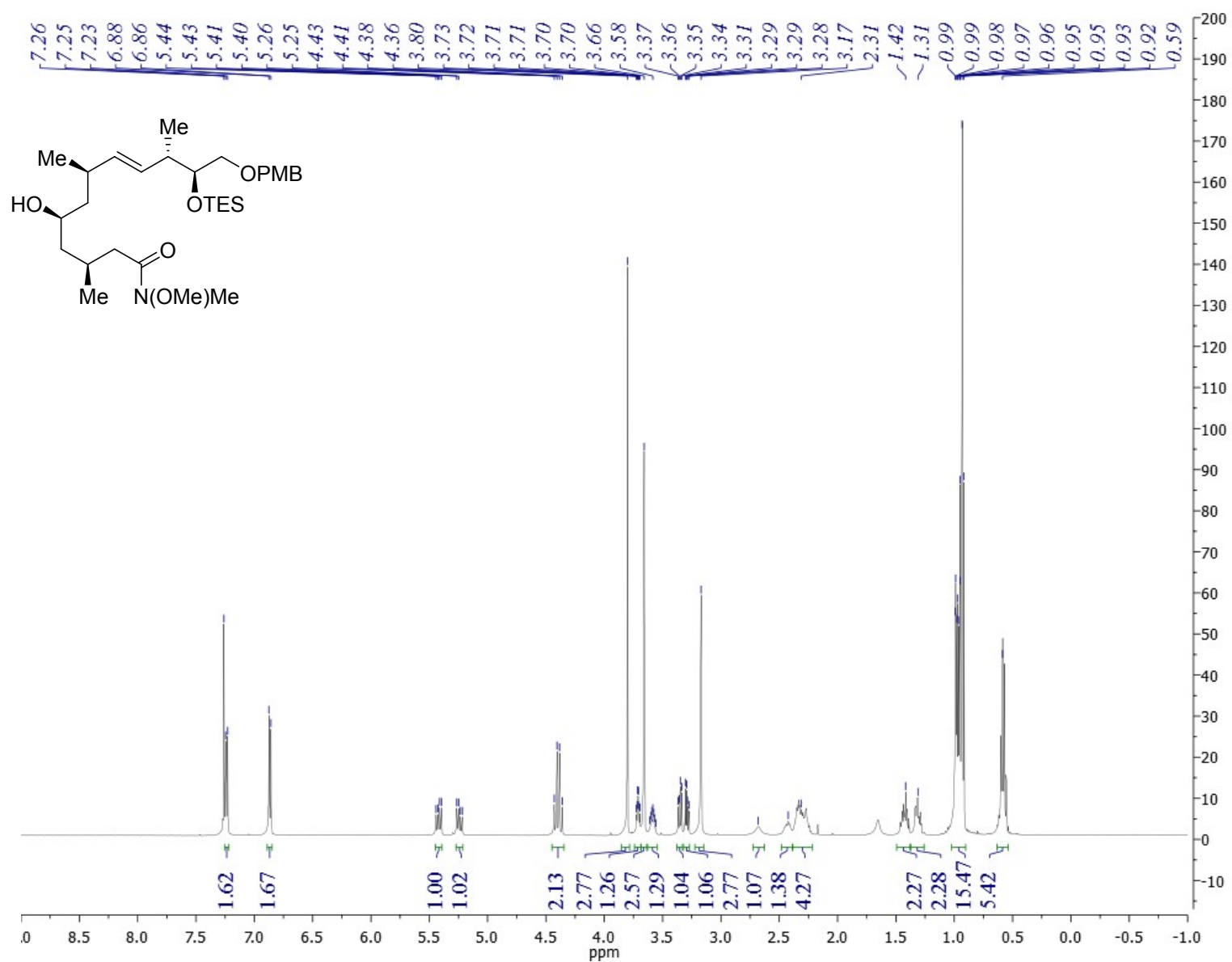


Figure S25. ¹H NMR (500 MHz, CDCl₃) of Weinreb amide **23**.

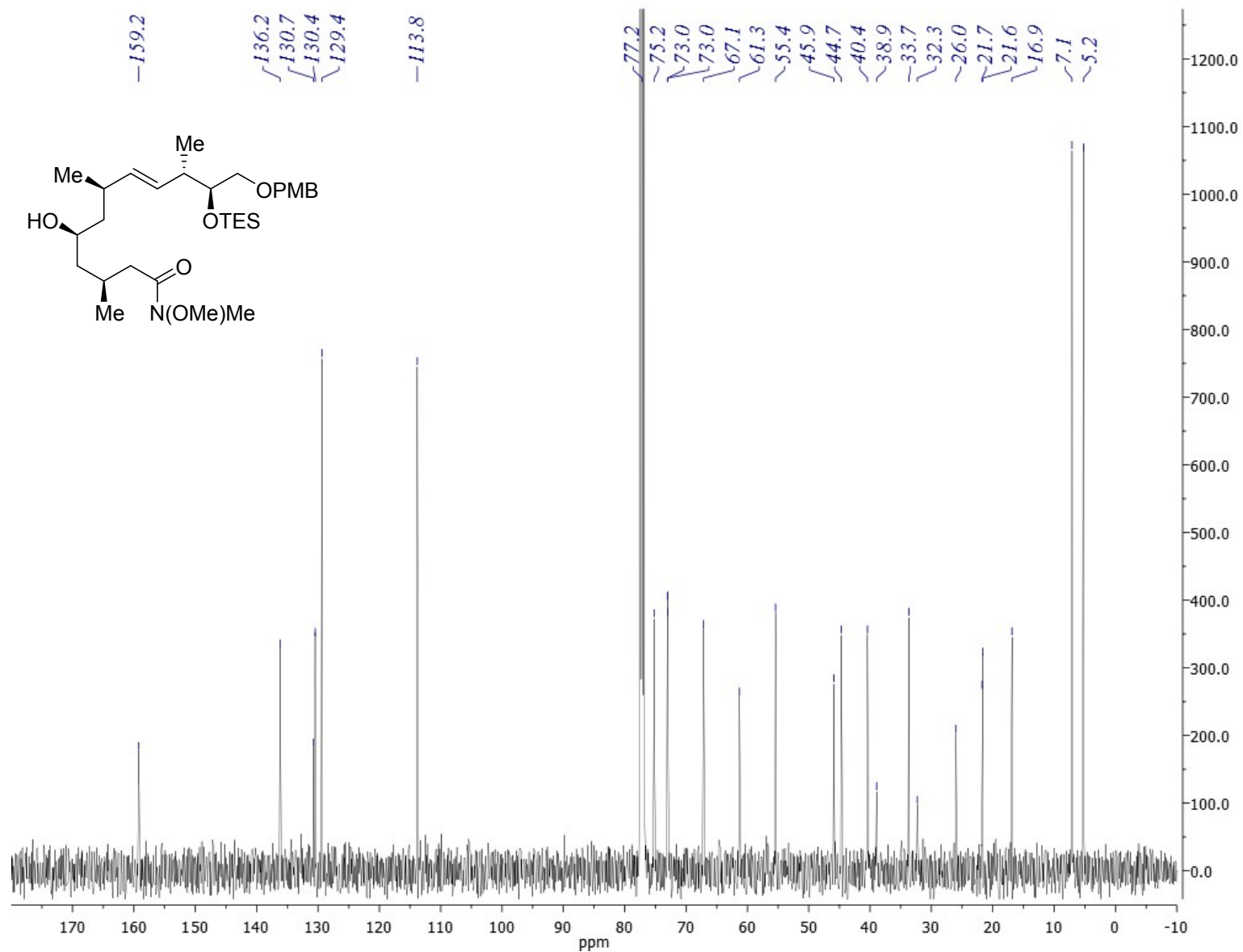


Figure S26. ¹³C NMR (125 MHz, CDCl₃) of Weinreb amide **23**.

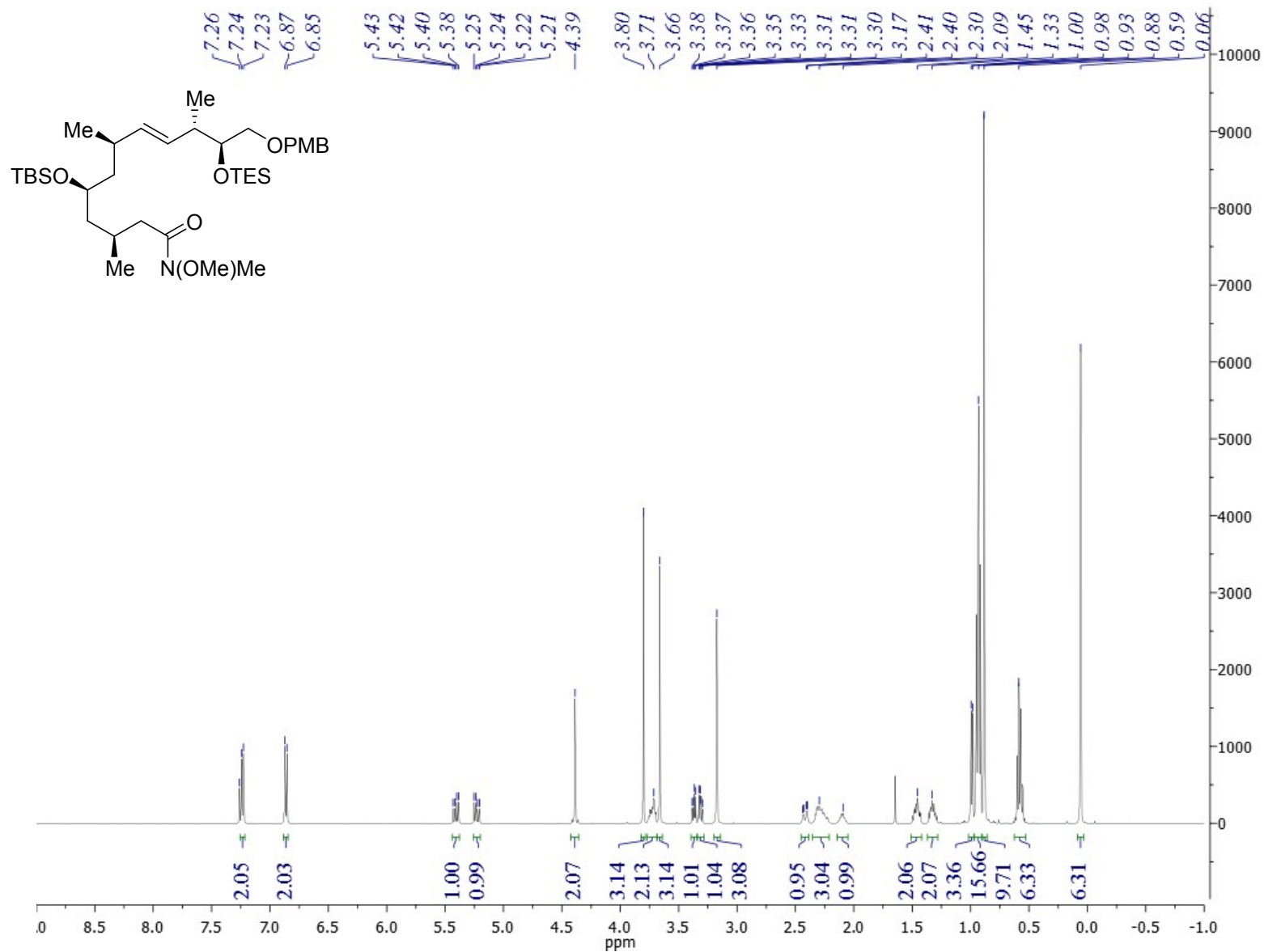


Figure S27. ¹H NMR (500 MHz, CDCl₃) of TBS ether **24**.

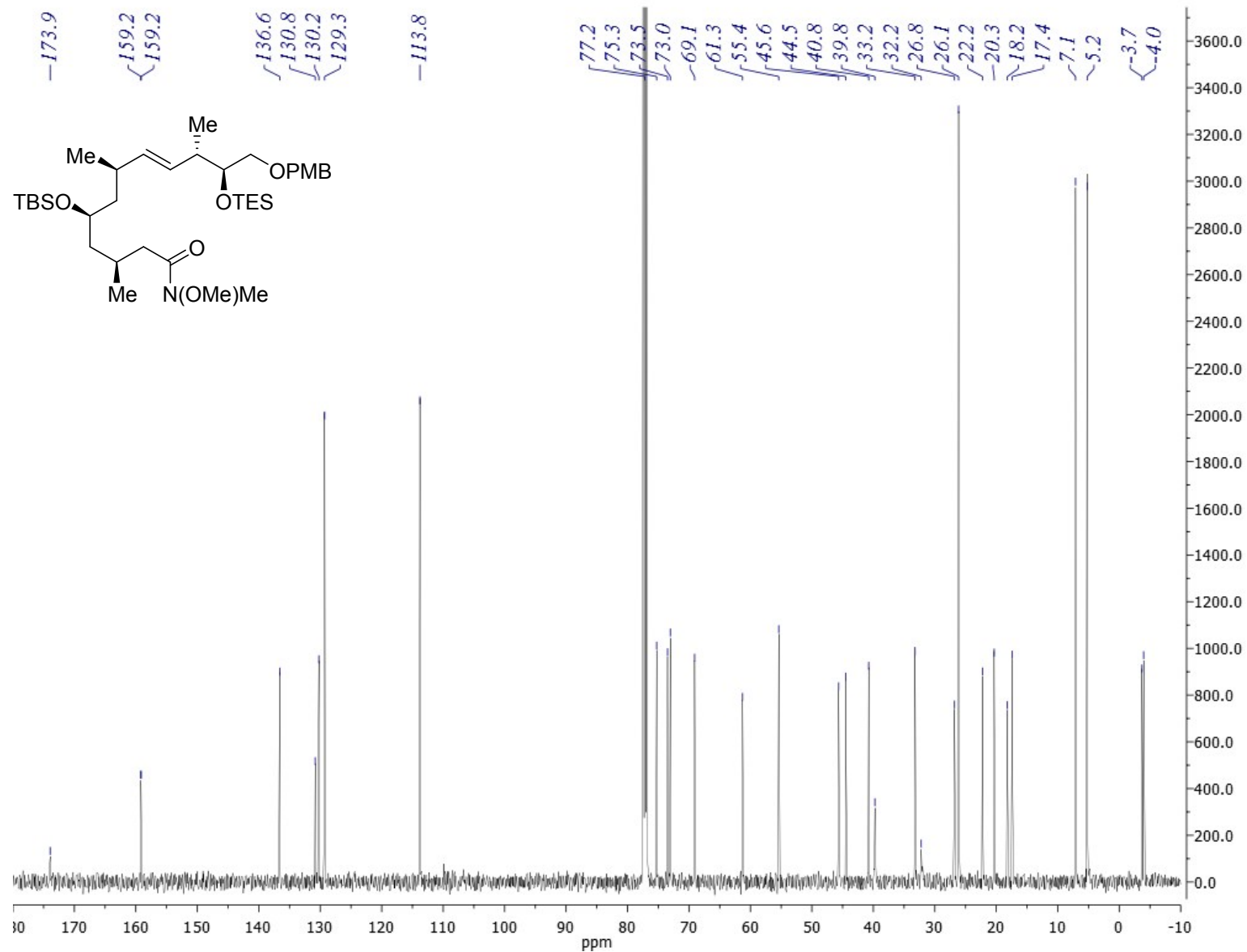


Figure S28. ^{13}C NMR (125 MHz, CDCl_3) of TBS ether **24**.

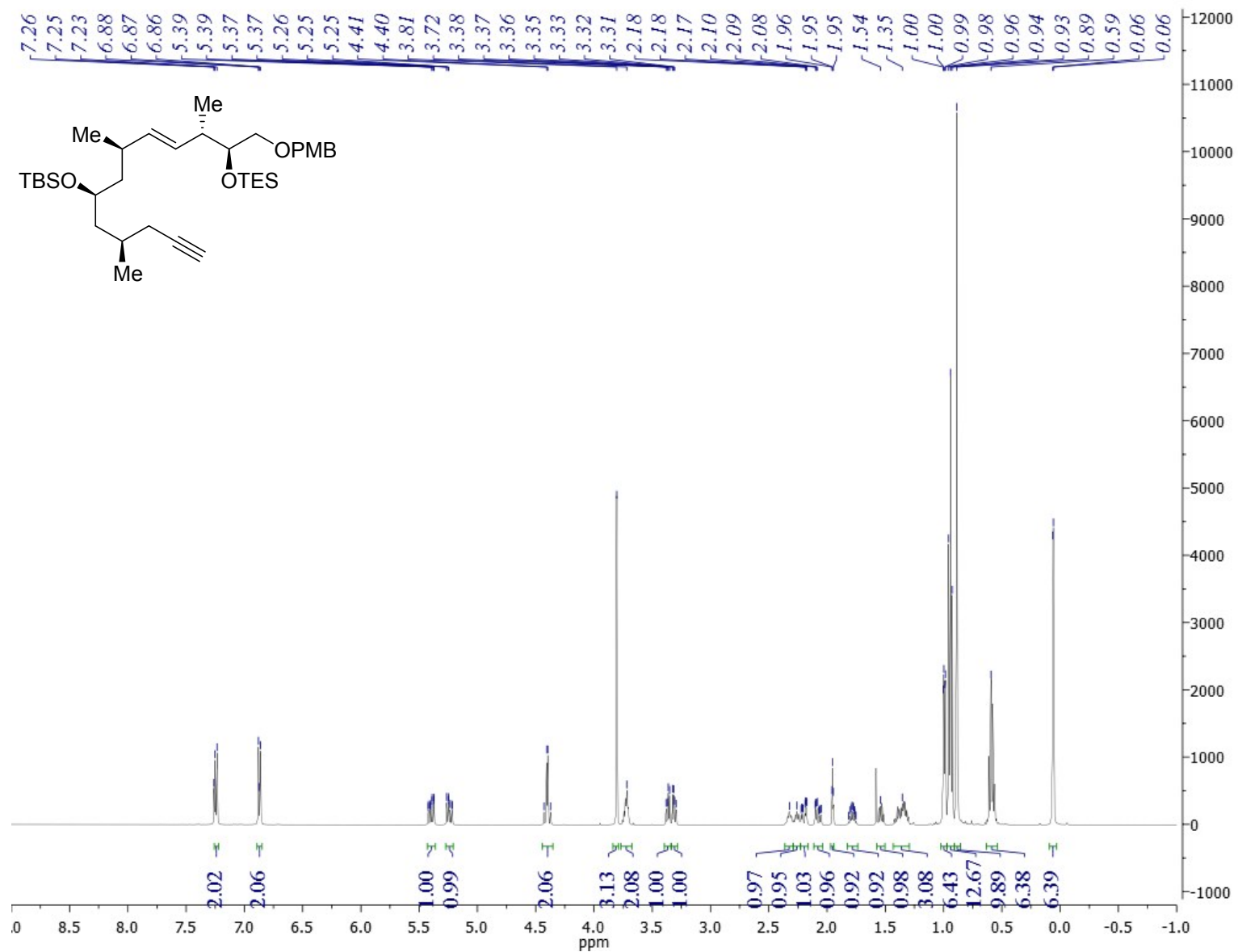


Figure S29. ^1H NMR (500 MHz, CDCl_3) of alkyne **25**.

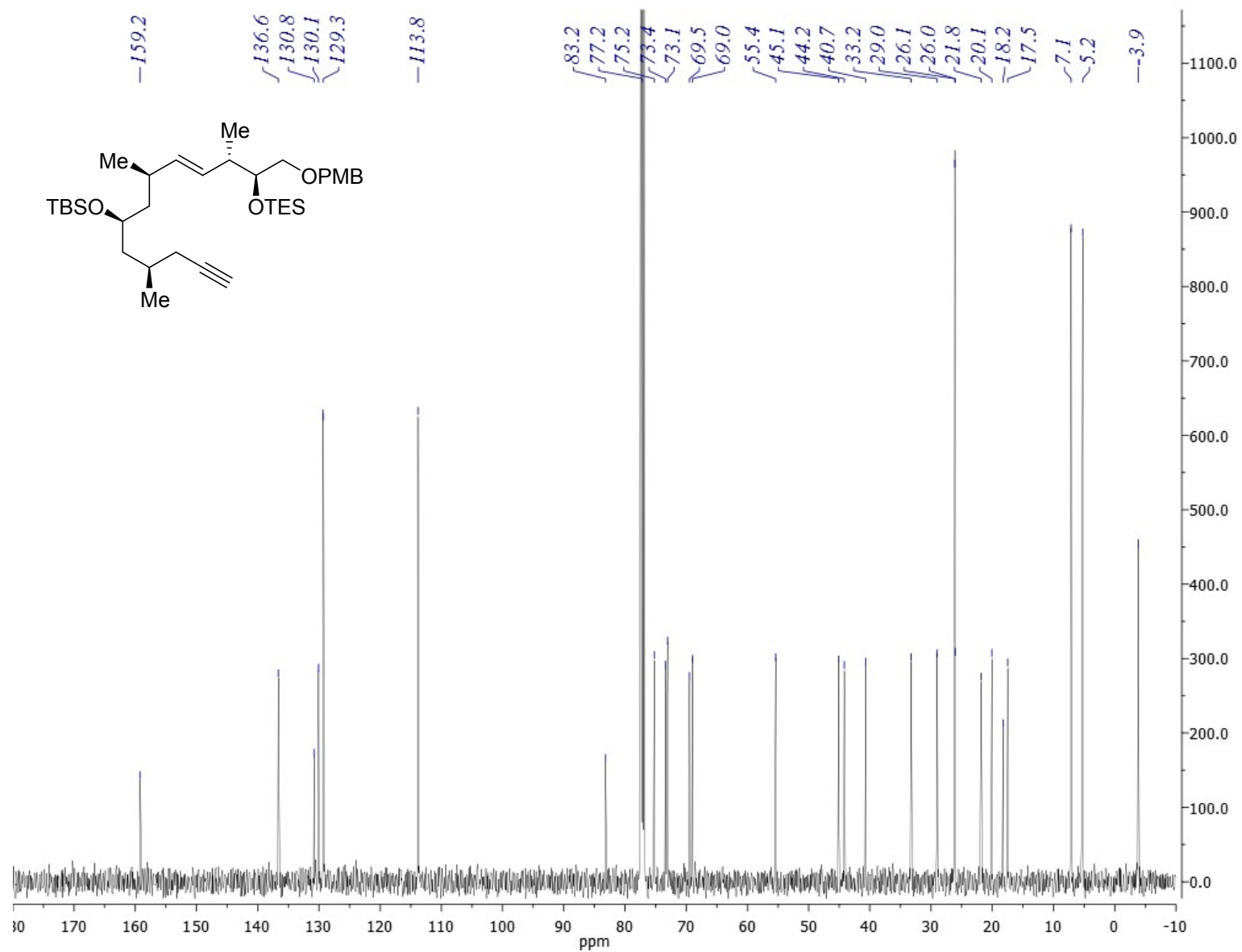


Figure S30. ¹³C NMR (125 MHz, CDCl₃) of alkyne **25**.

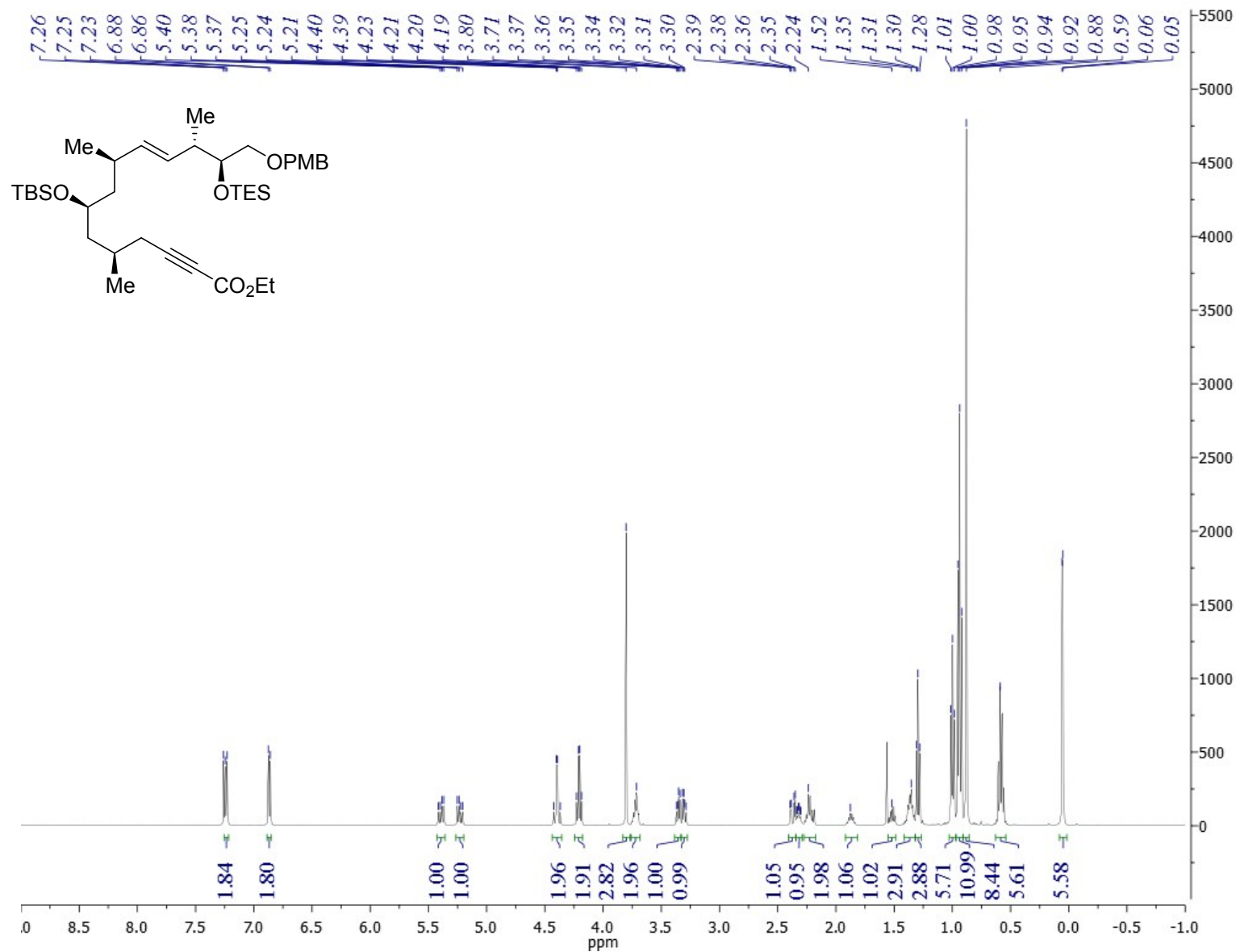


Figure S31. ^1H NMR (500 MHz, CDCl_3) of alkynyl ester **26**.

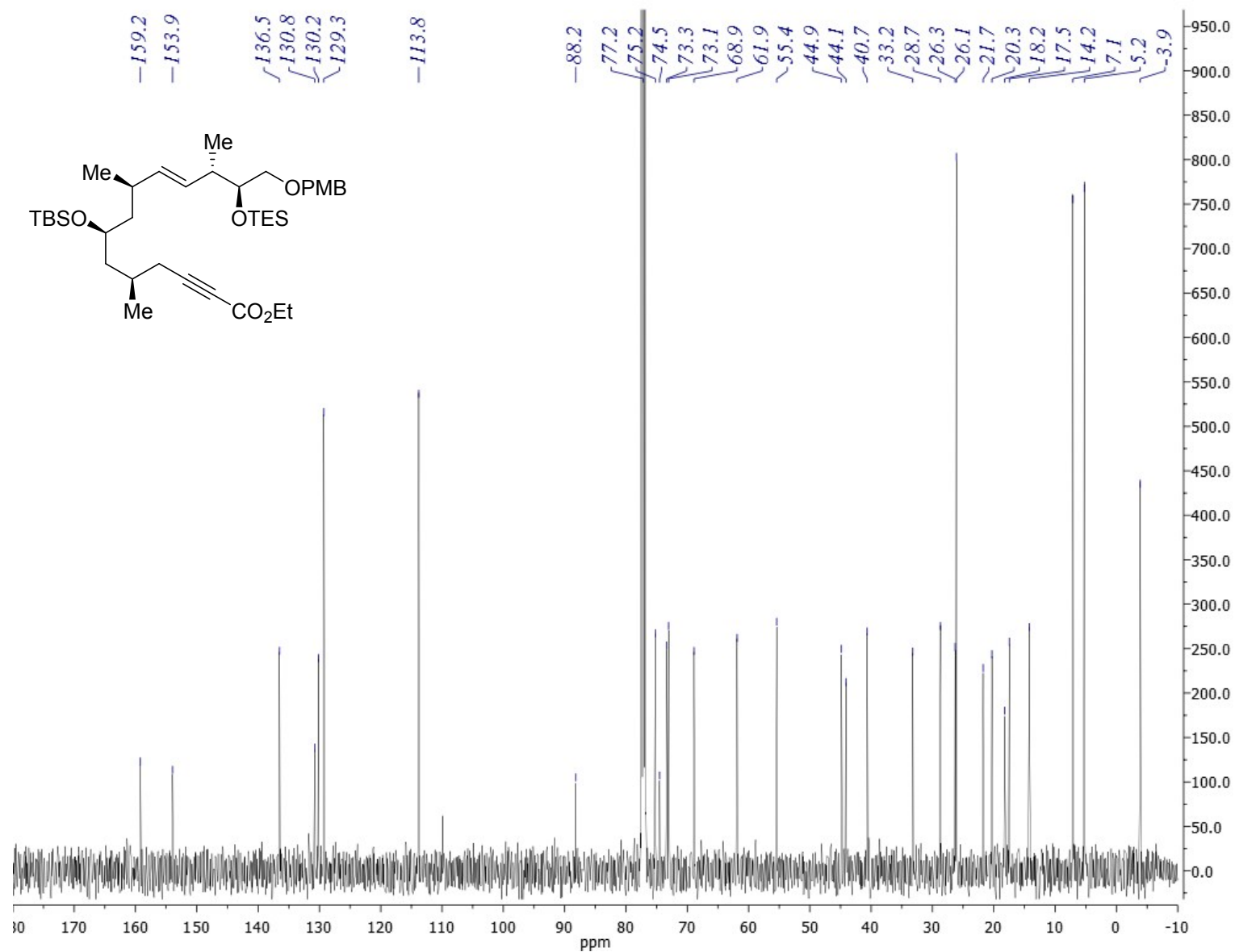


Figure S32. ^{13}C NMR (125 MHz, CDCl_3) of alkynyl ester **26**.

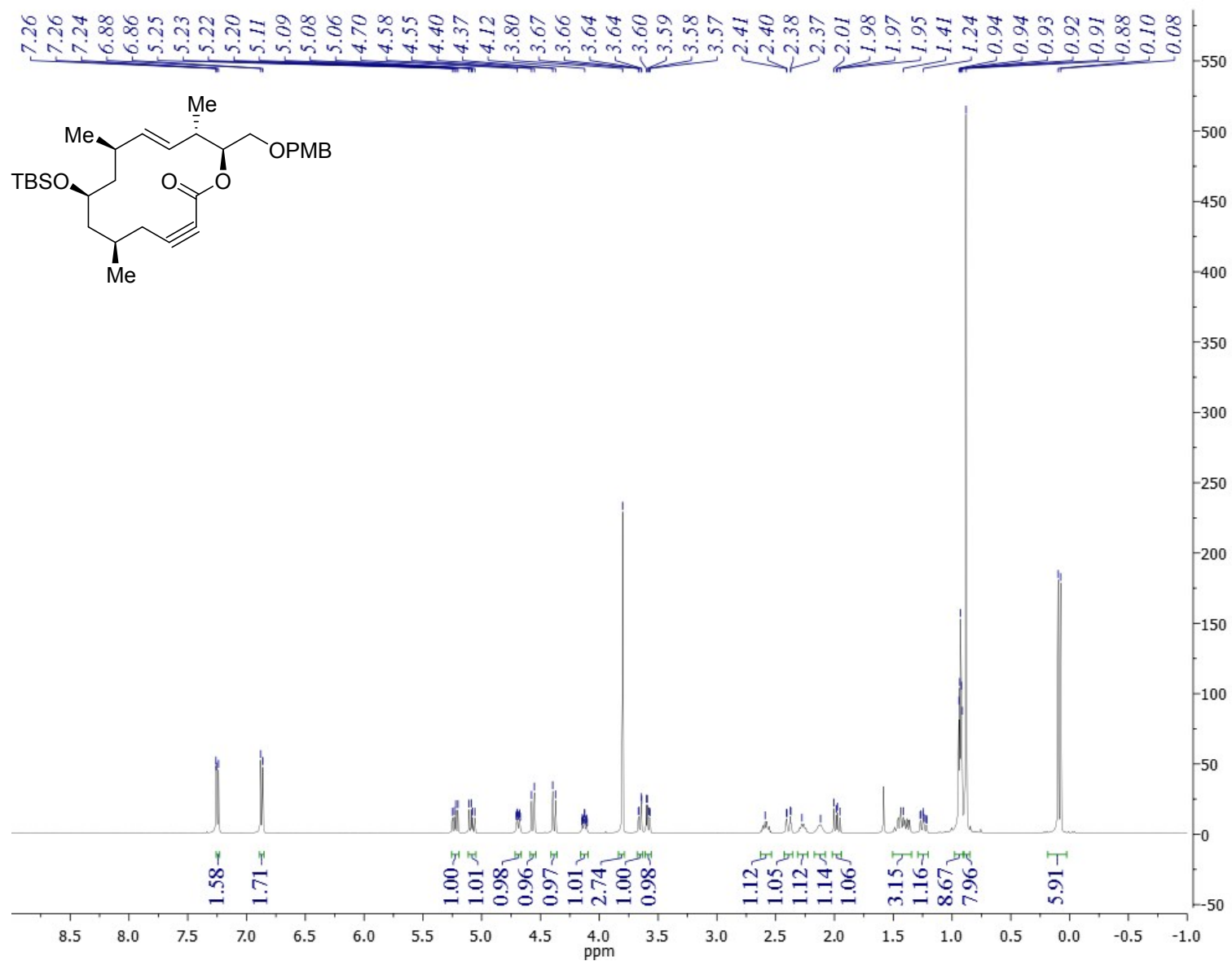


Figure S33. ^1H NMR (500 MHz, CDCl_3) of alkynyl lactone **27**.

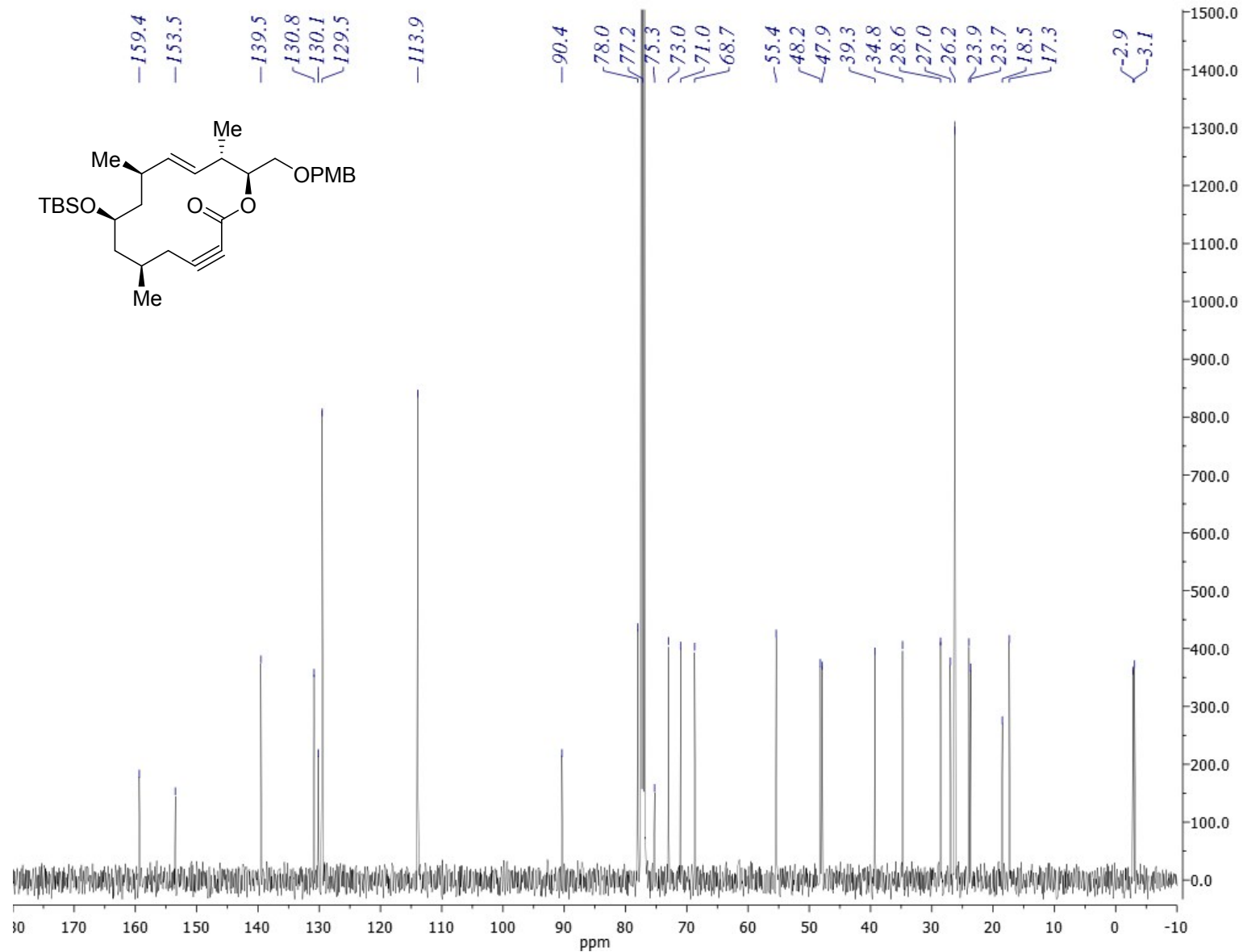


Figure S34. ^{13}C NMR (125 MHz, CDCl_3) of alkynyl lactone **27**.

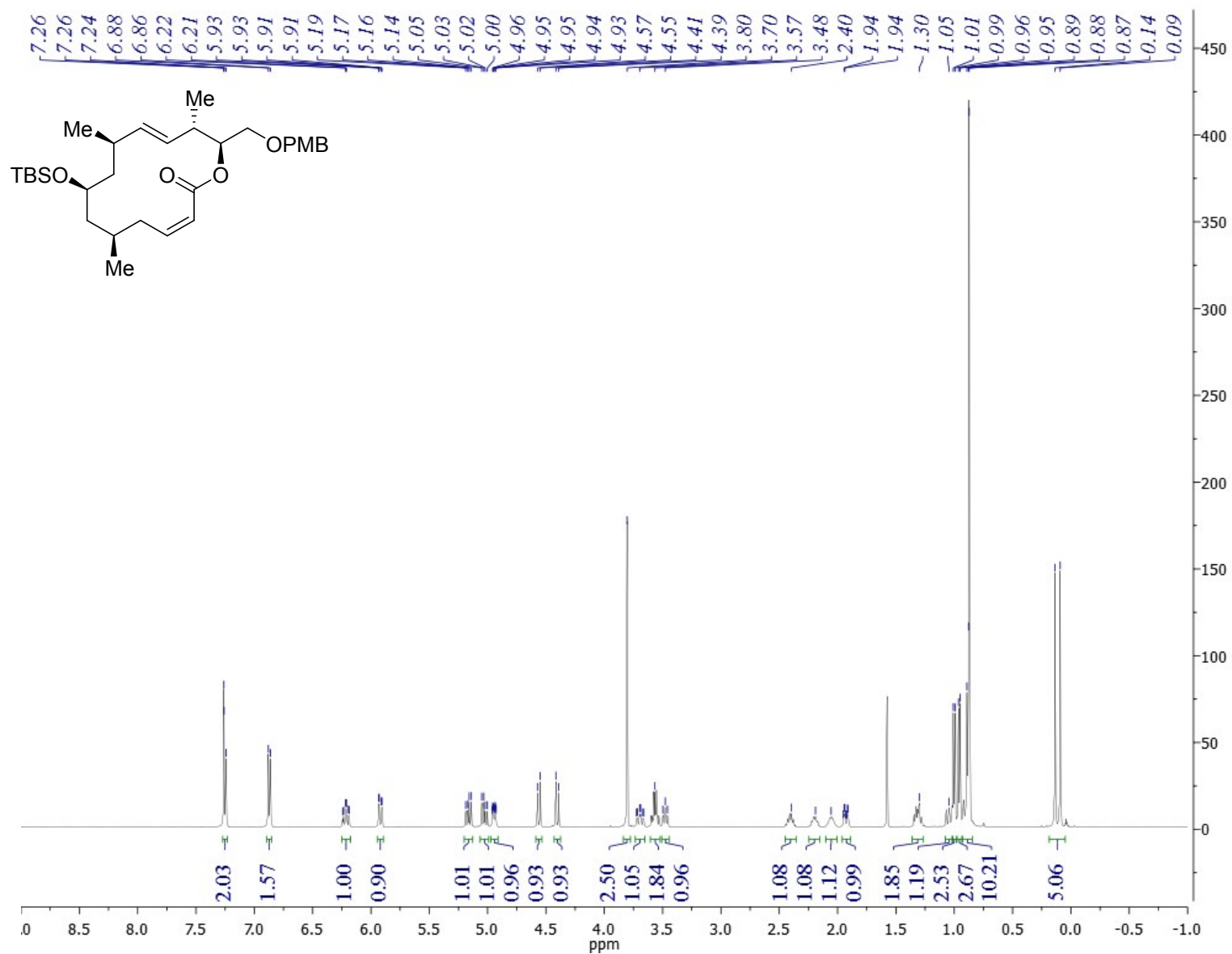


Figure S35. ^1H NMR (500 MHz, CDCl_3) of *cis*-lactone **28**.

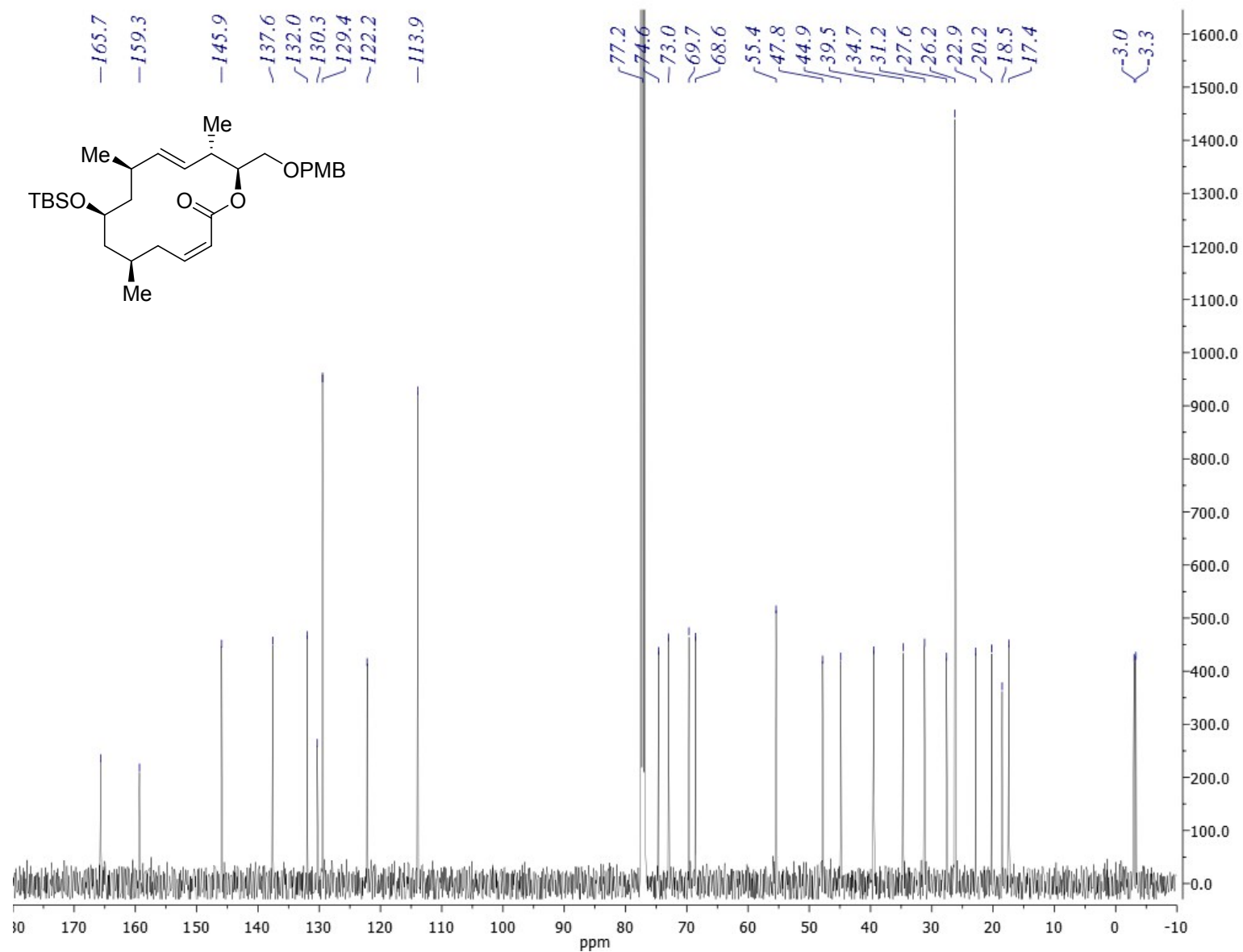


Figure S36. ^{13}C NMR (125 MHz, CDCl_3) of *cis*-lactone **28**.



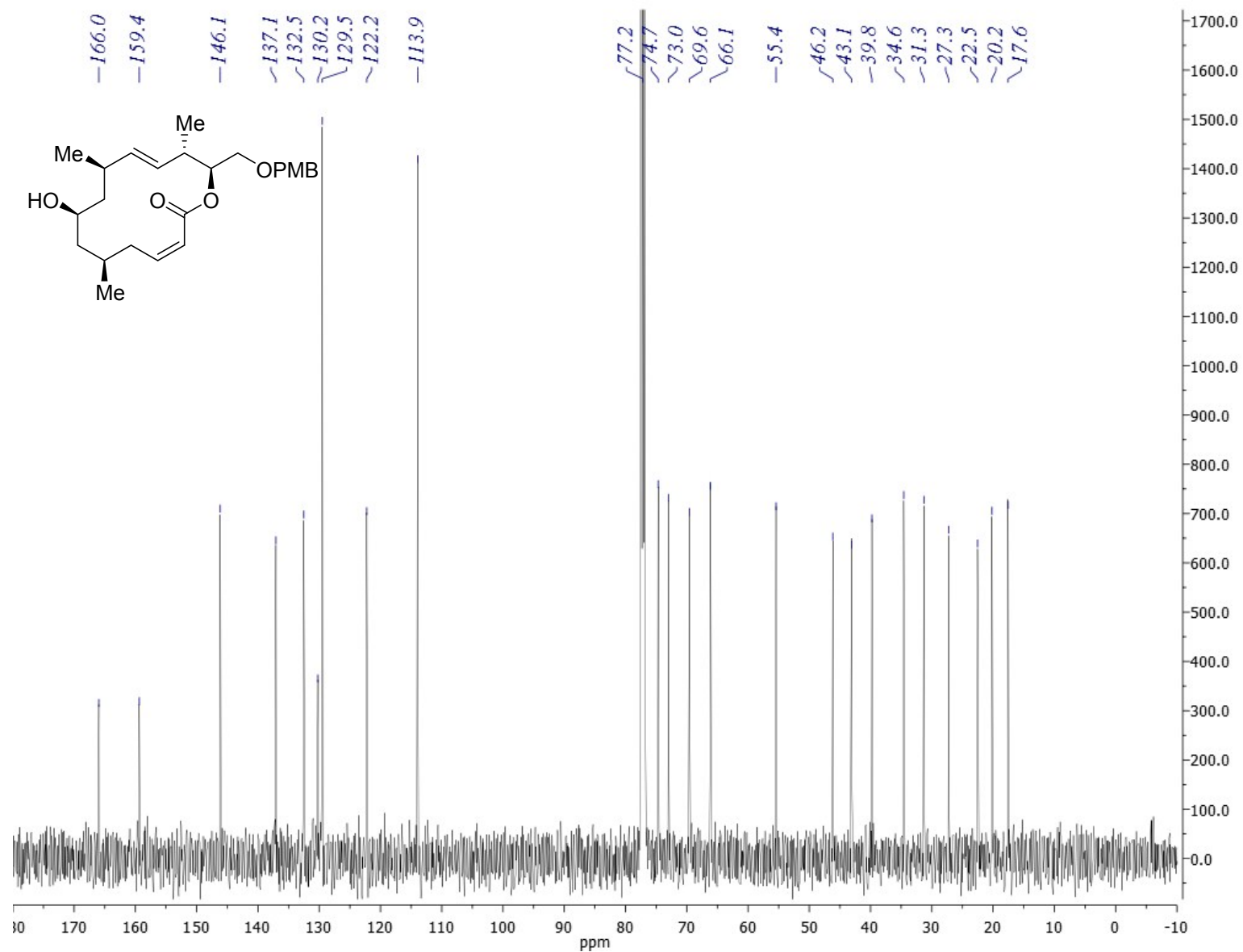


Figure S38. ¹³C NMR (125 MHz, CDCl₃) of alcohol 29.

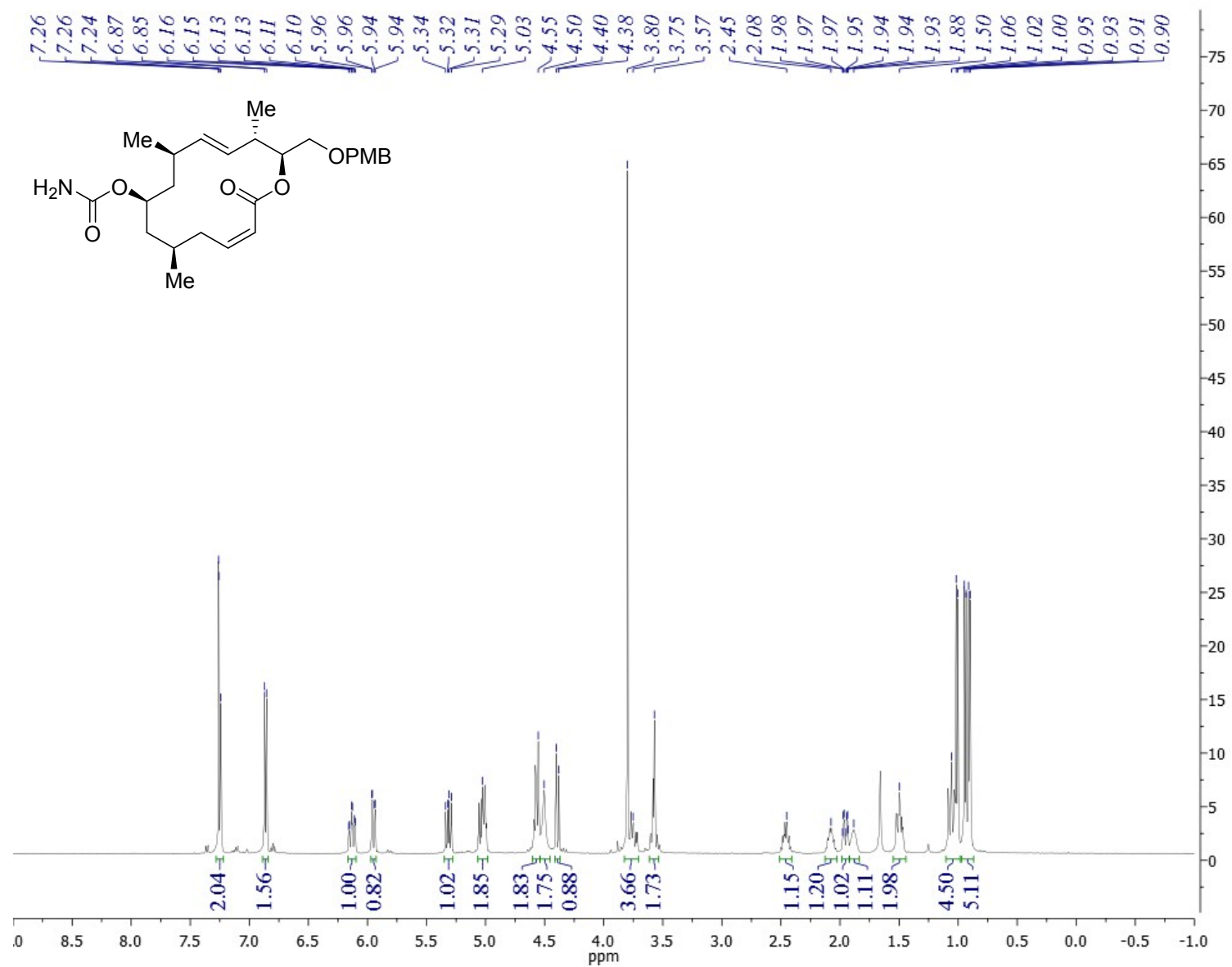


Figure S39. ^1H NMR (500 MHz, CDCl_3) of carbamate **30**.

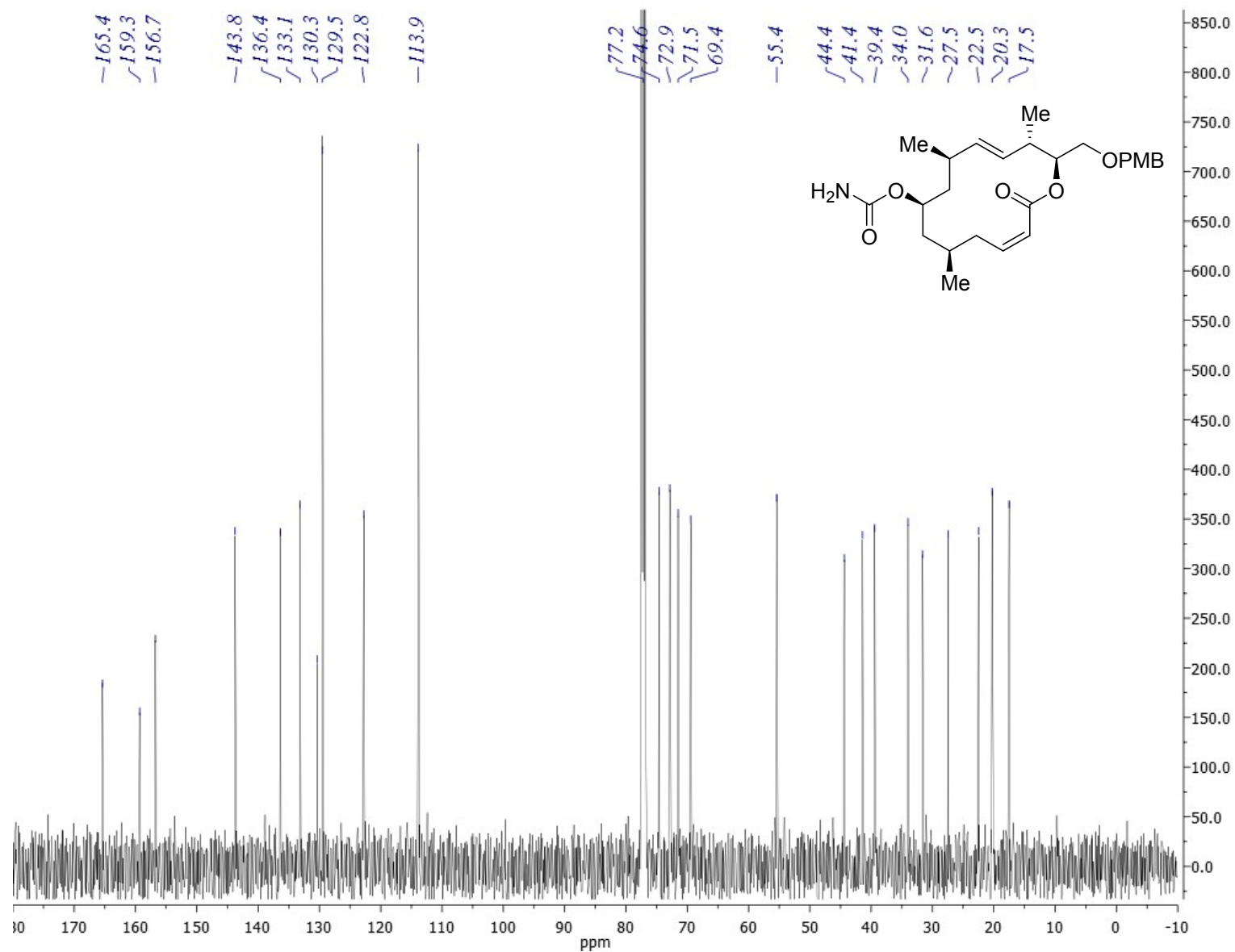


Figure S40. ^{13}C NMR (125 MHz, CDCl_3) of carbamate **30**.

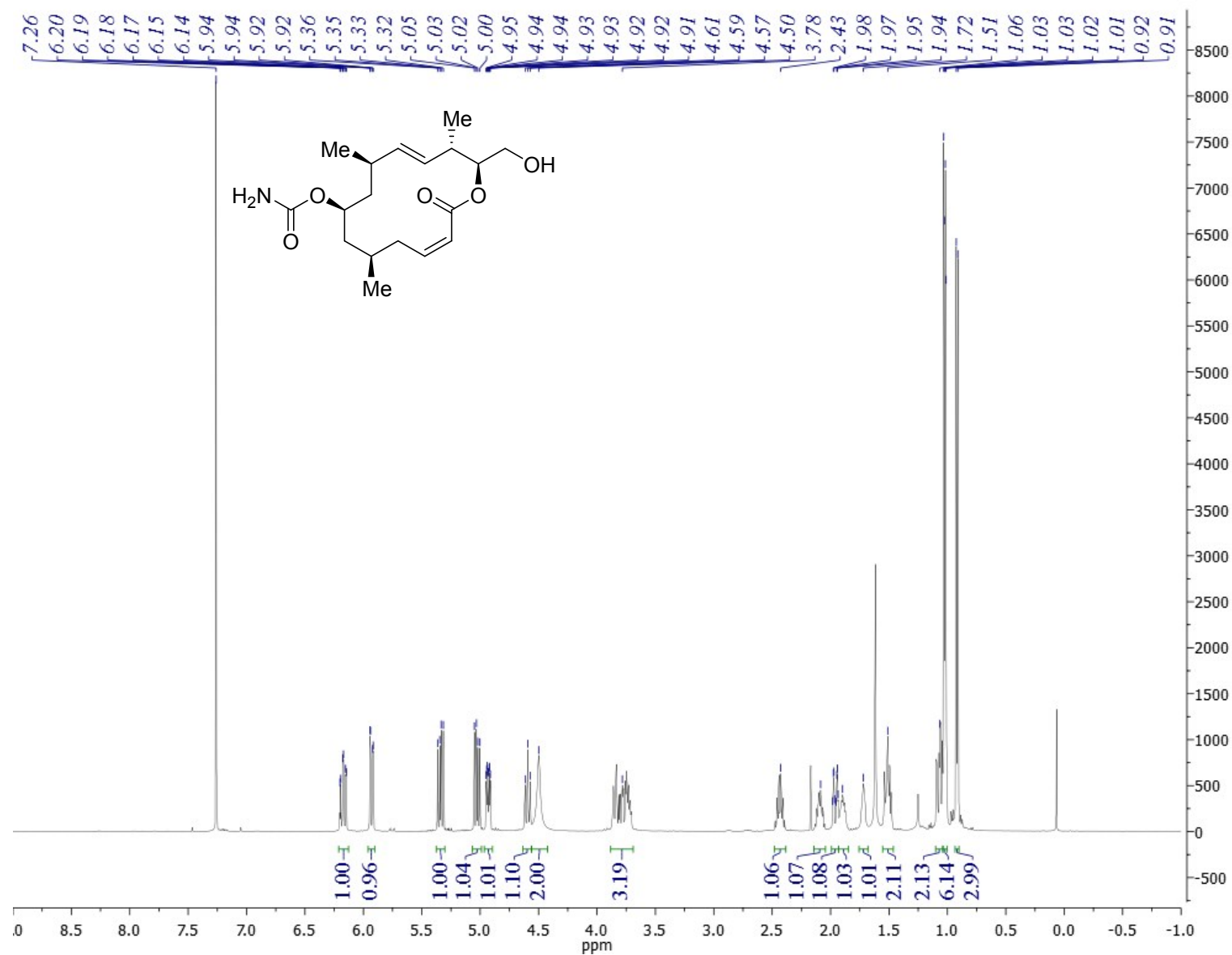


Figure S41. ¹H NMR (500 MHz, CDCl₃) of alcohol **31**.

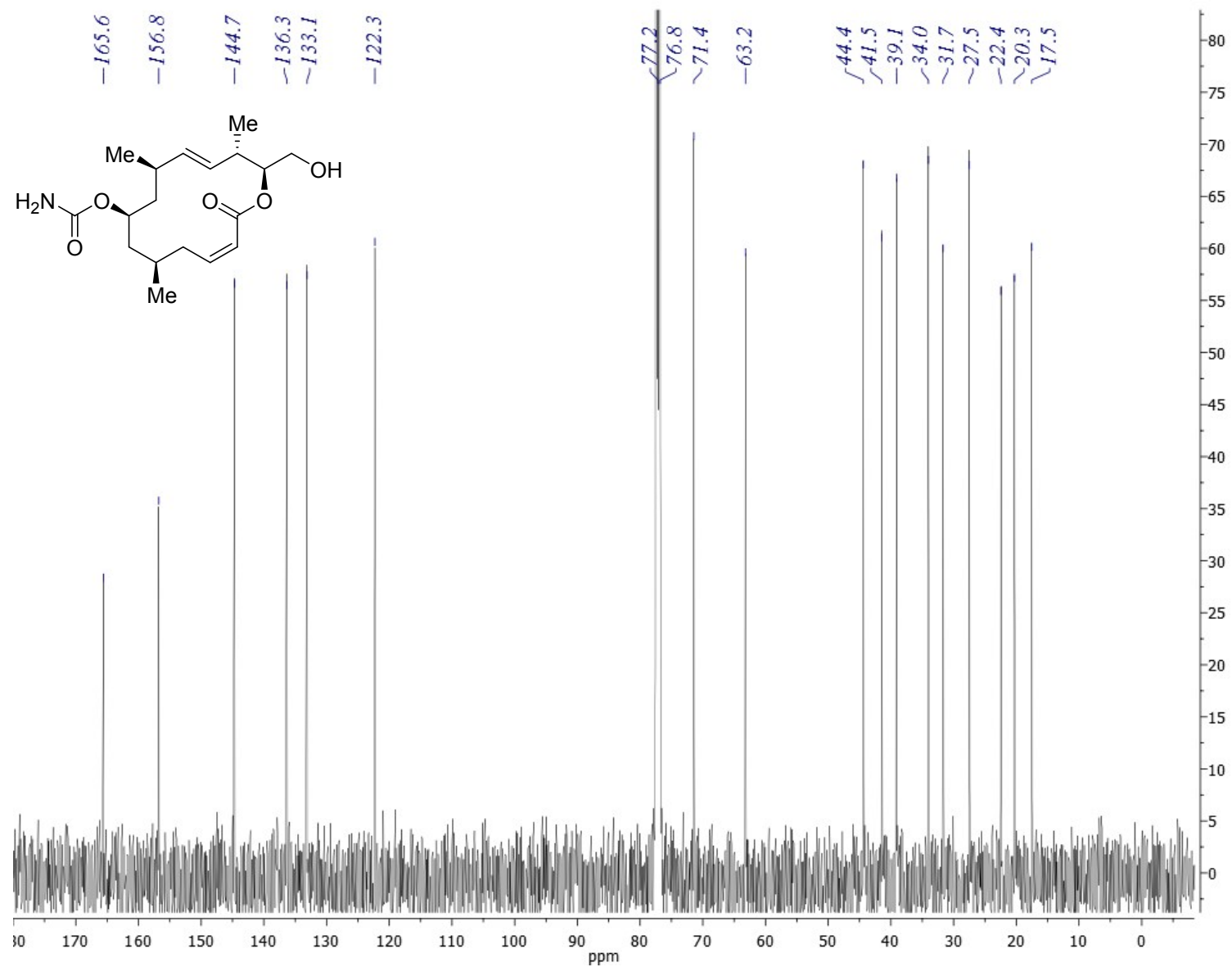


Figure S42. ¹³C NMR (125 MHz, CDCl₃) of alcohol **31**.

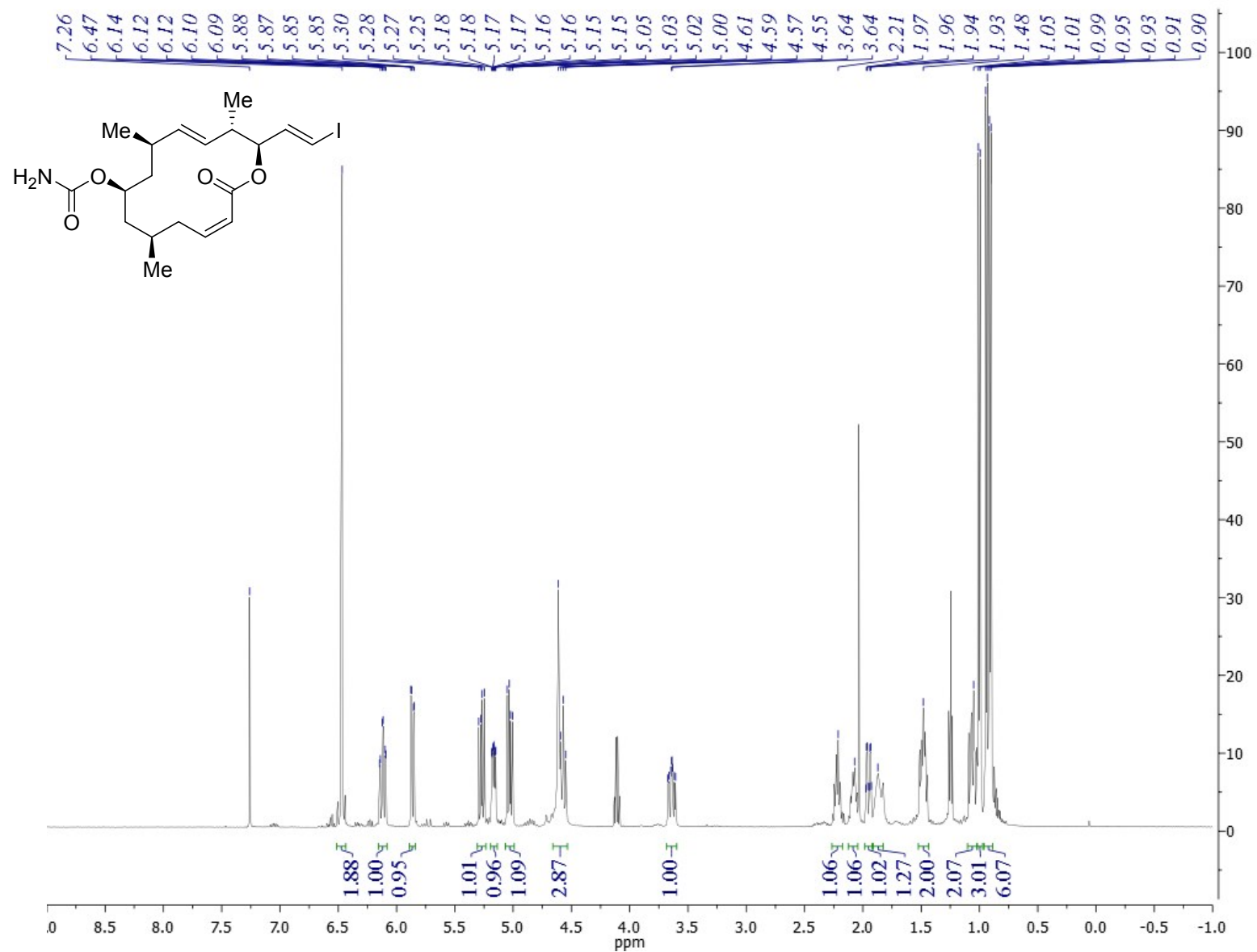


Figure S43. ^1H NMR (500 MHz, CDCl_3) of vinyl iodide **32**.

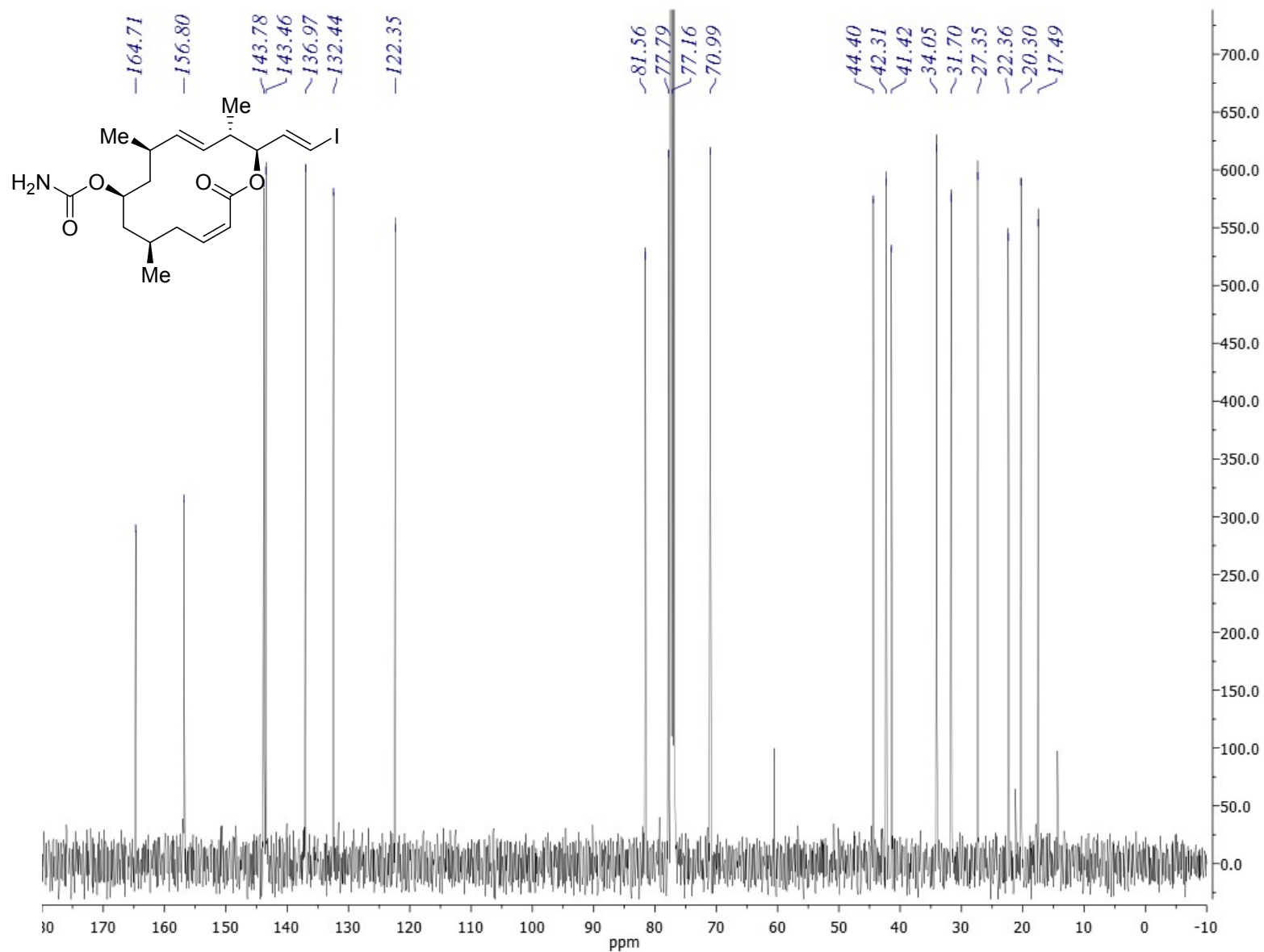


Figure S44. ^{13}C NMR (125 MHz, CDCl_3) of vinyl iodide **32**.

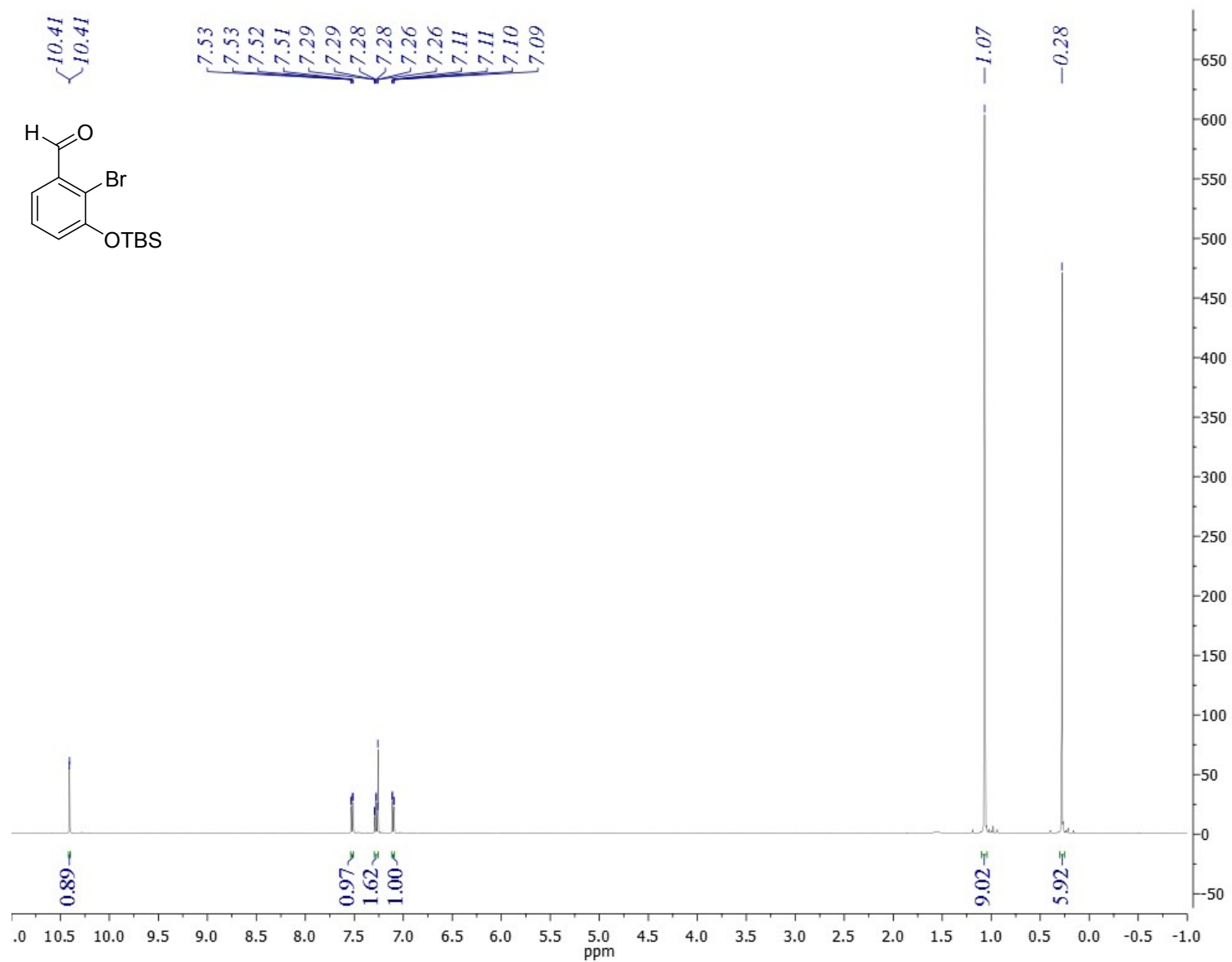


Figure S45. ¹H NMR (500 MHz, CDCl₃) of TBS phenol **33**.

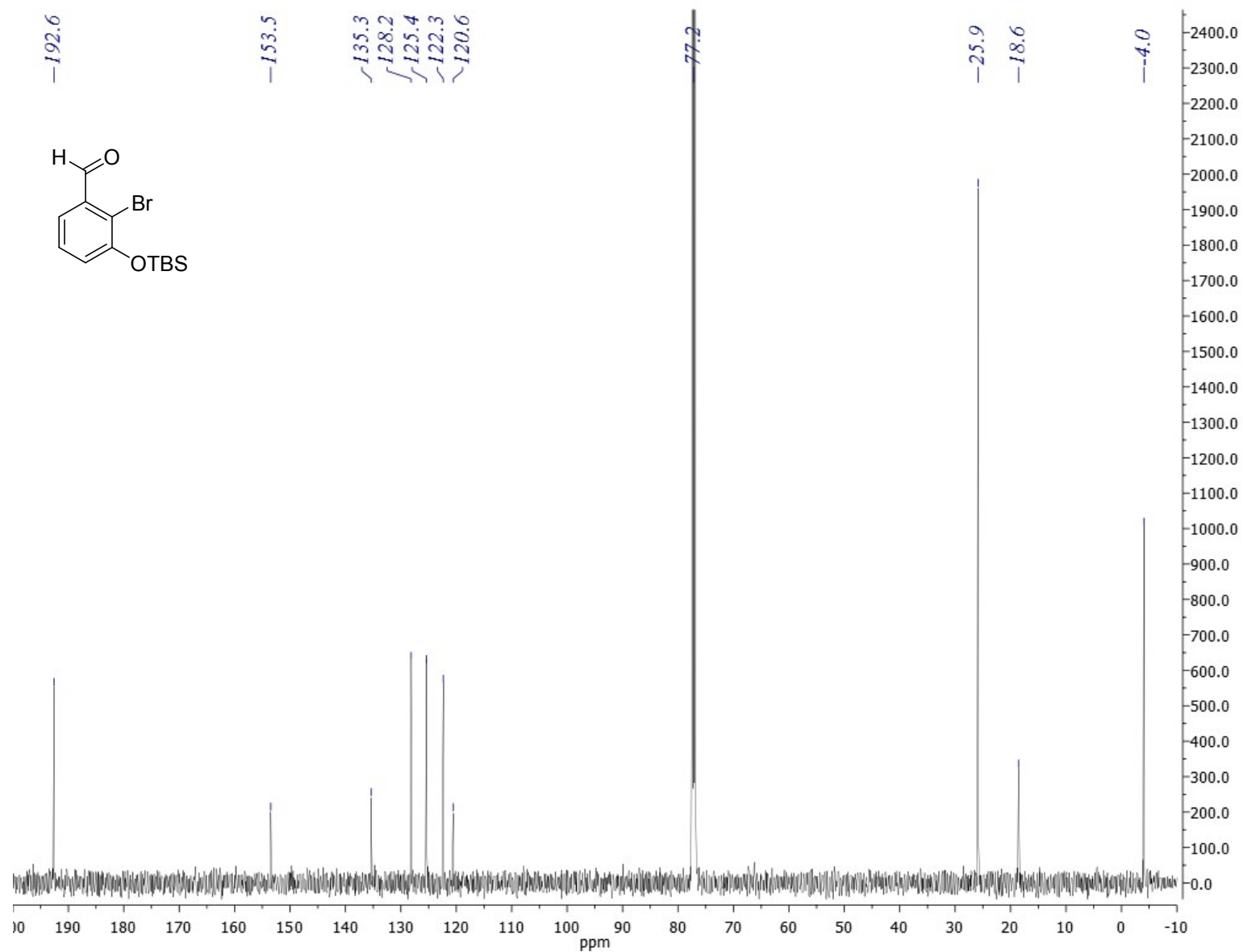


Figure S46. ¹³C NMR (125 MHz, CDCl₃) of TBS phenol **33**.

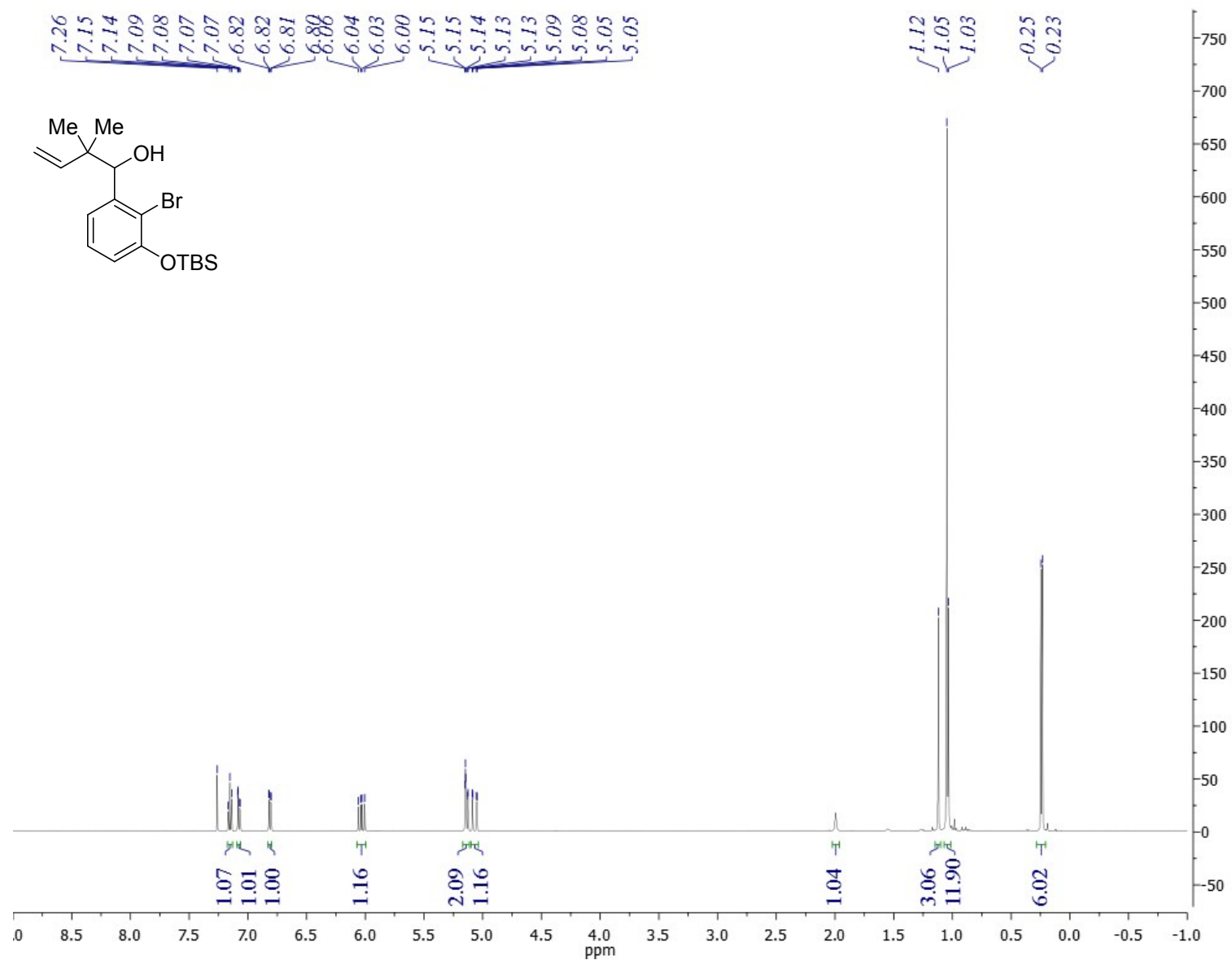


Figure S47. ¹H NMR (500 MHz, CDCl₃) of alcohol **34**.

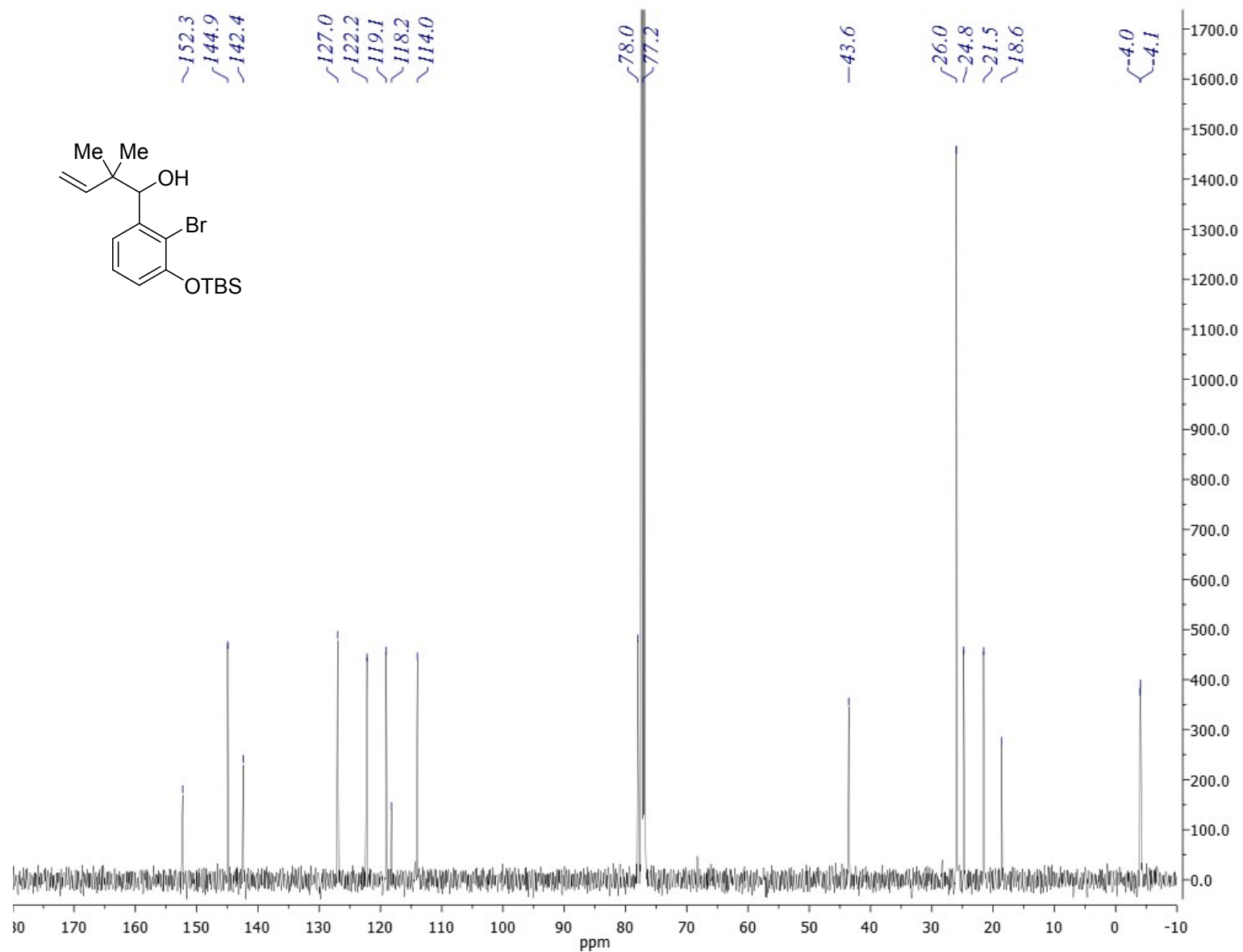


Figure S48. ^{13}C NMR (125 MHz, CDCl_3) of alcohol **34**.

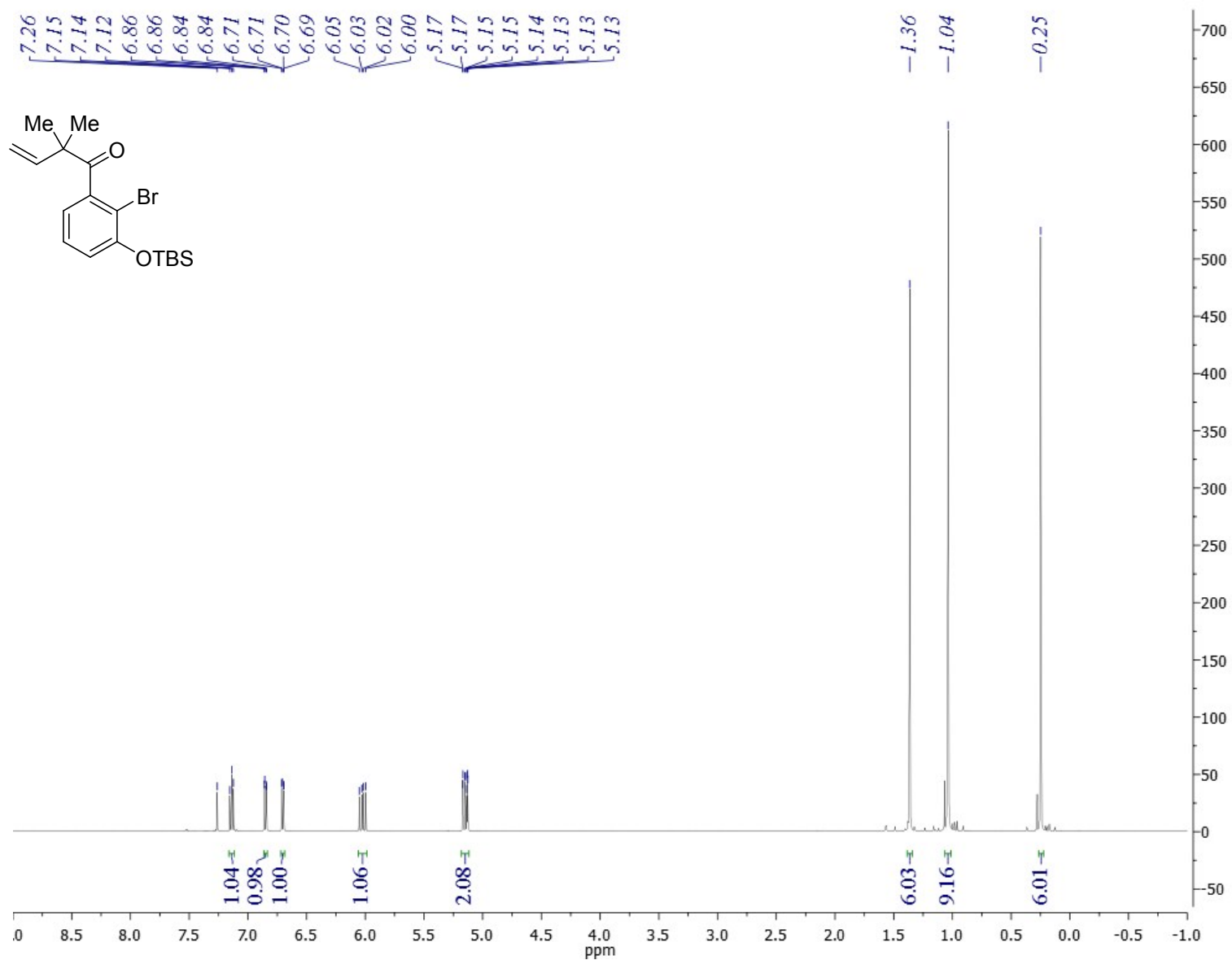


Figure S49. ¹H NMR (500 MHz, CDCl₃) of ketone **35**.

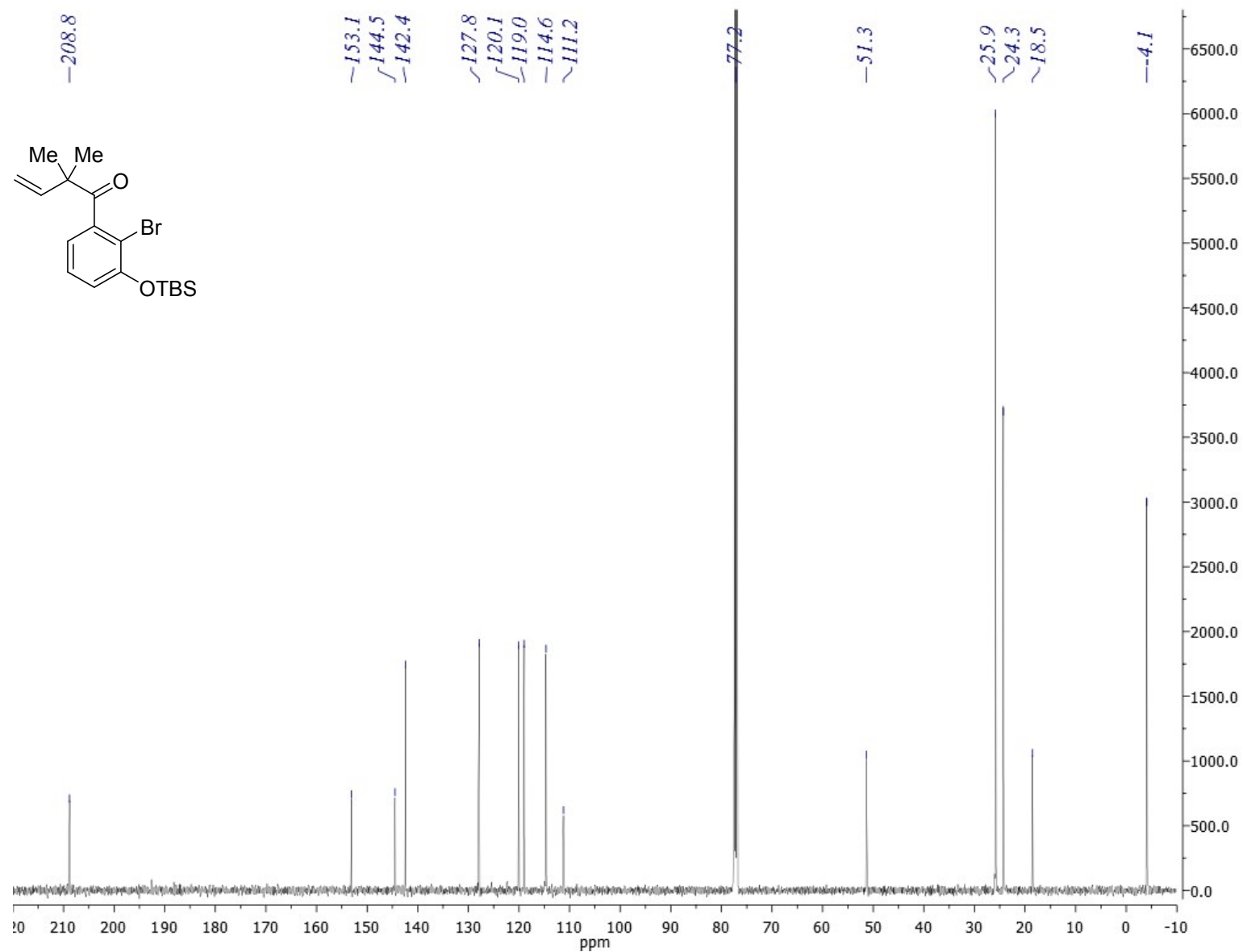


Figure S50. ¹³C NMR (125 MHz, CDCl₃) of ketone **35**.

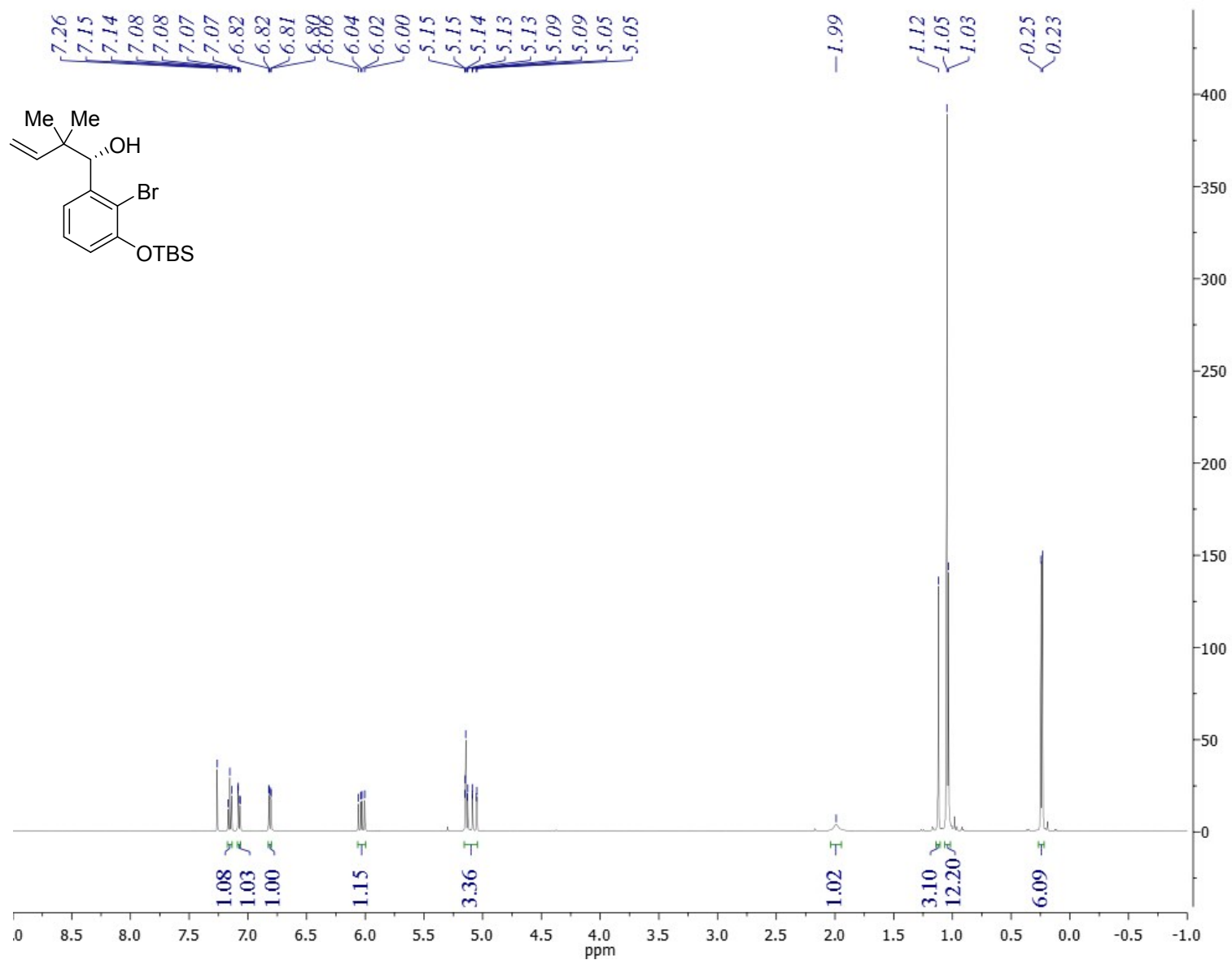


Figure S51. ¹H NMR (500 MHz, CDCl₃) of alcohol (S)-34.

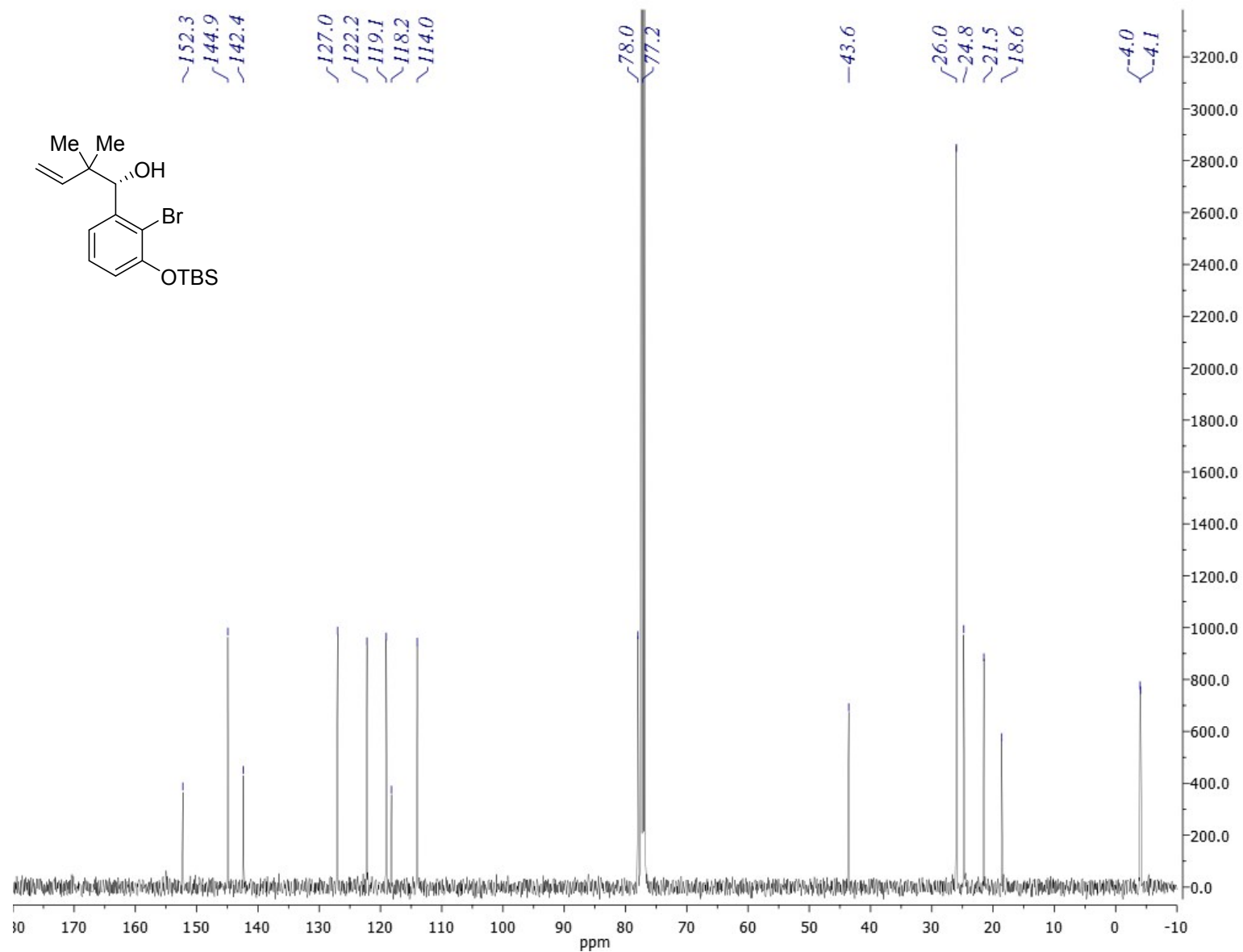


Figure S52. ^{13}C NMR (125 MHz, CDCl_3) of alcohol (S)-34.

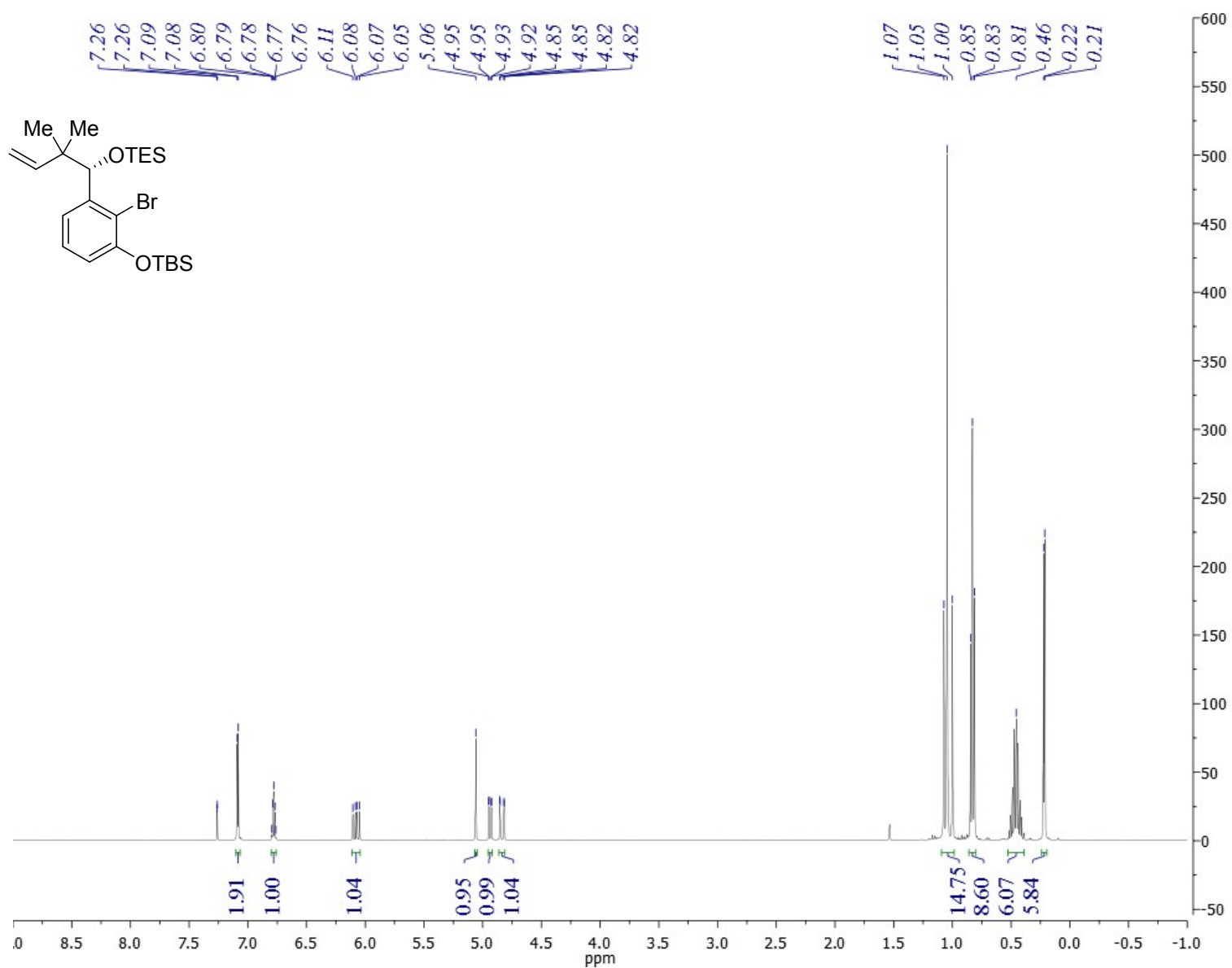


Figure S53. ¹H NMR (500 MHz, CDCl₃) of TES ether (*S*)-8.

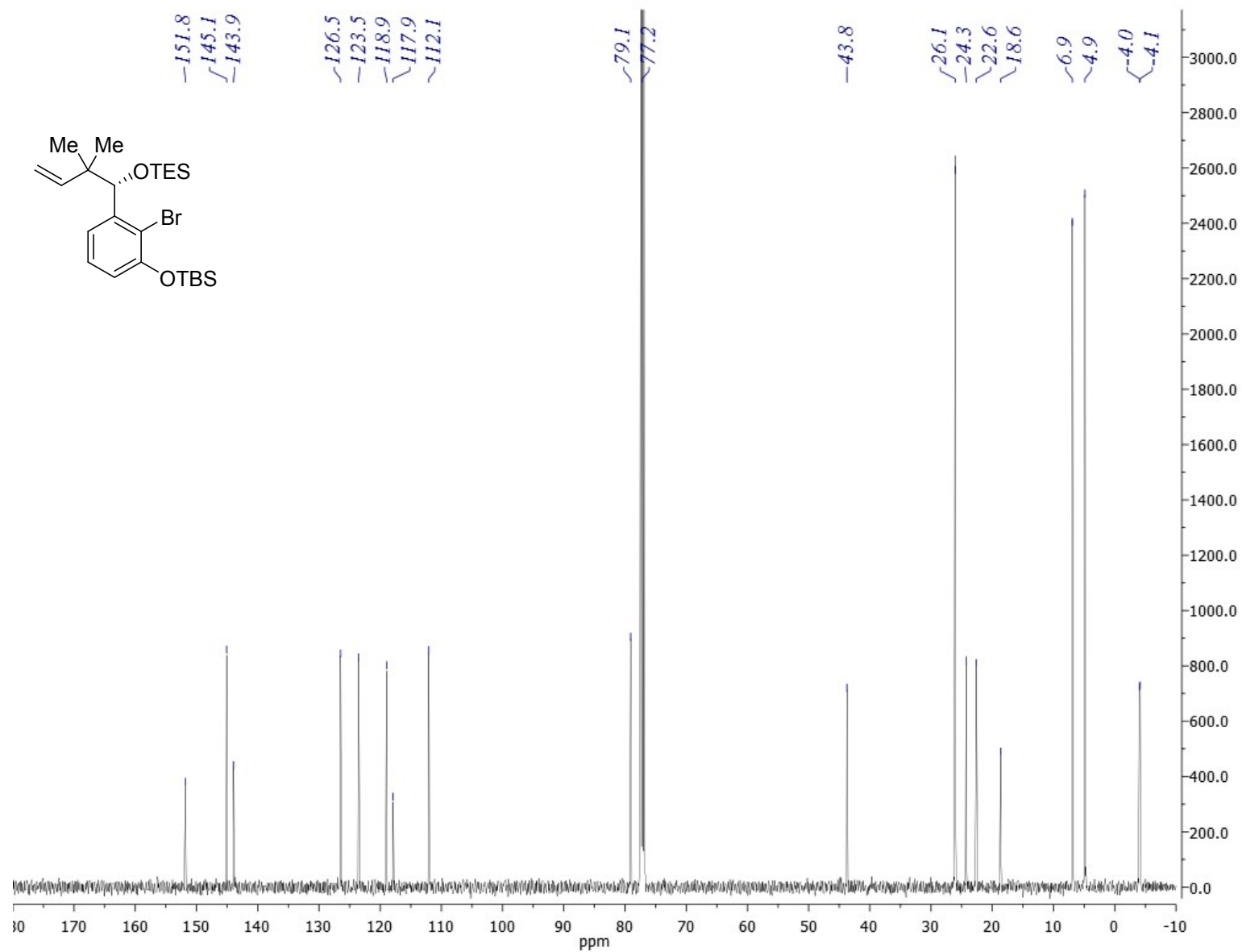


Figure S54. ¹³C NMR (125 MHz, CDCl₃) of TES ether (S)-8.

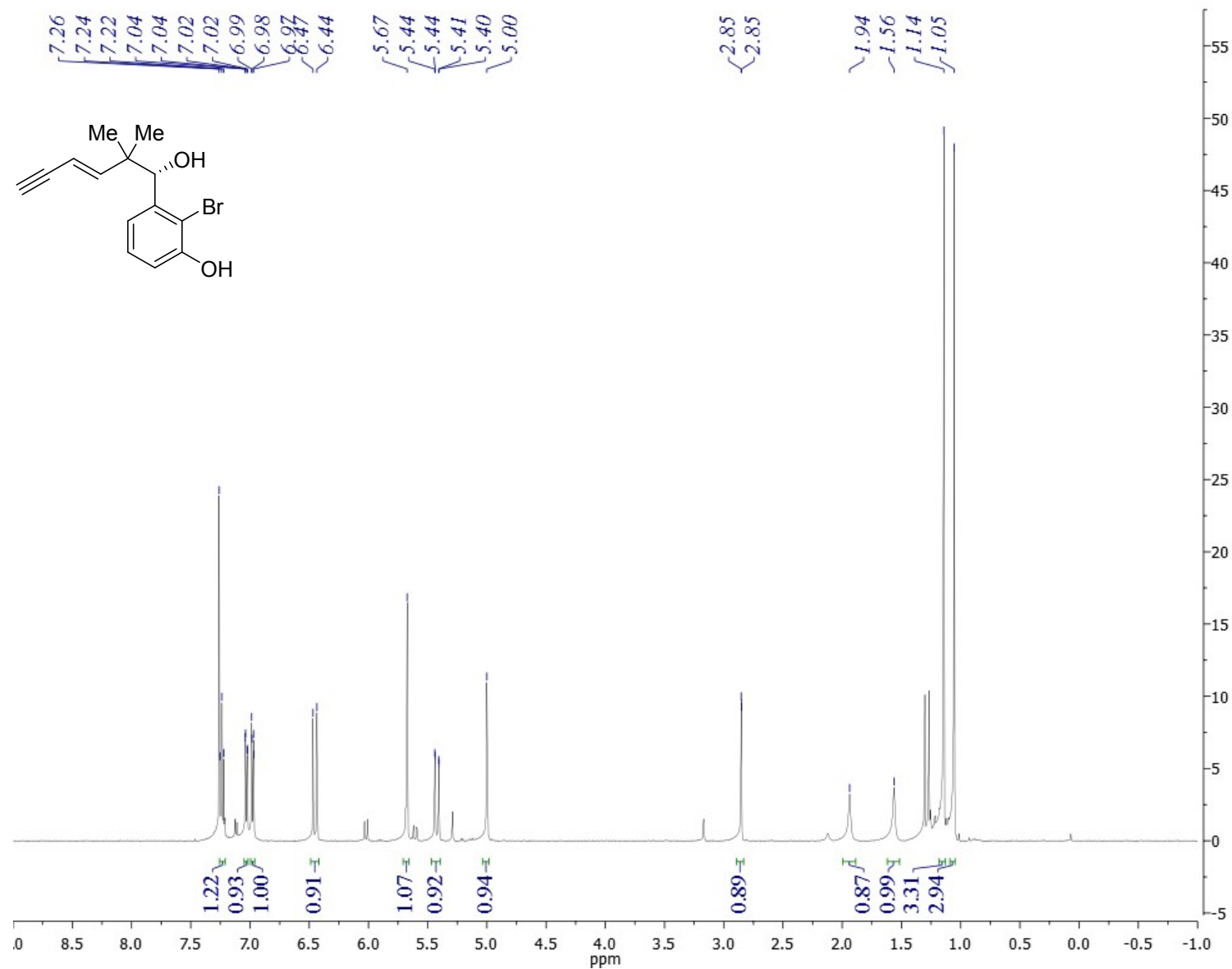


Figure S55. ¹H NMR (500 MHz, CDCl₃) of enyne (S)-4.

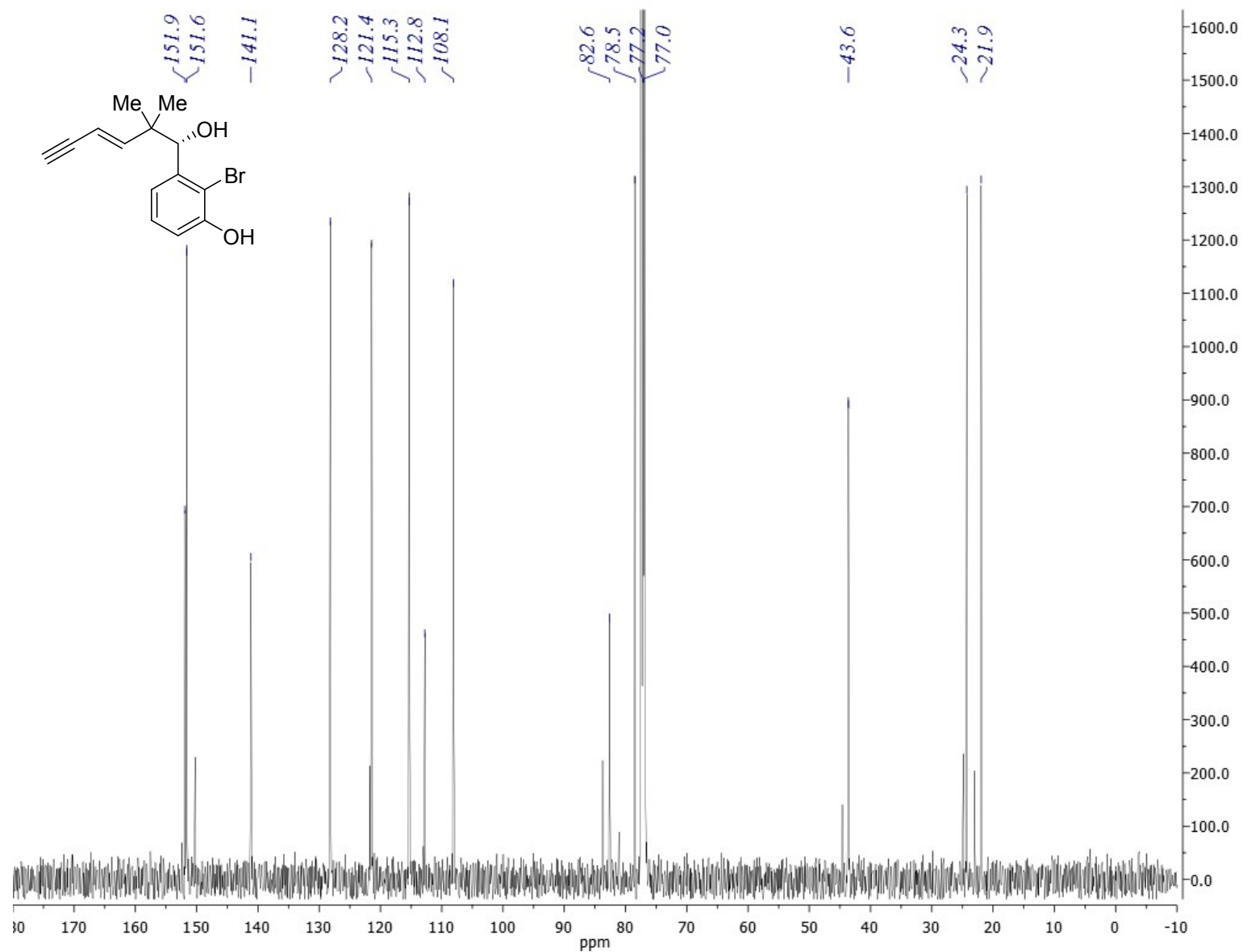


Figure S56. ^{13}C NMR (125 MHz, CDCl_3) of enyne (S)-4.



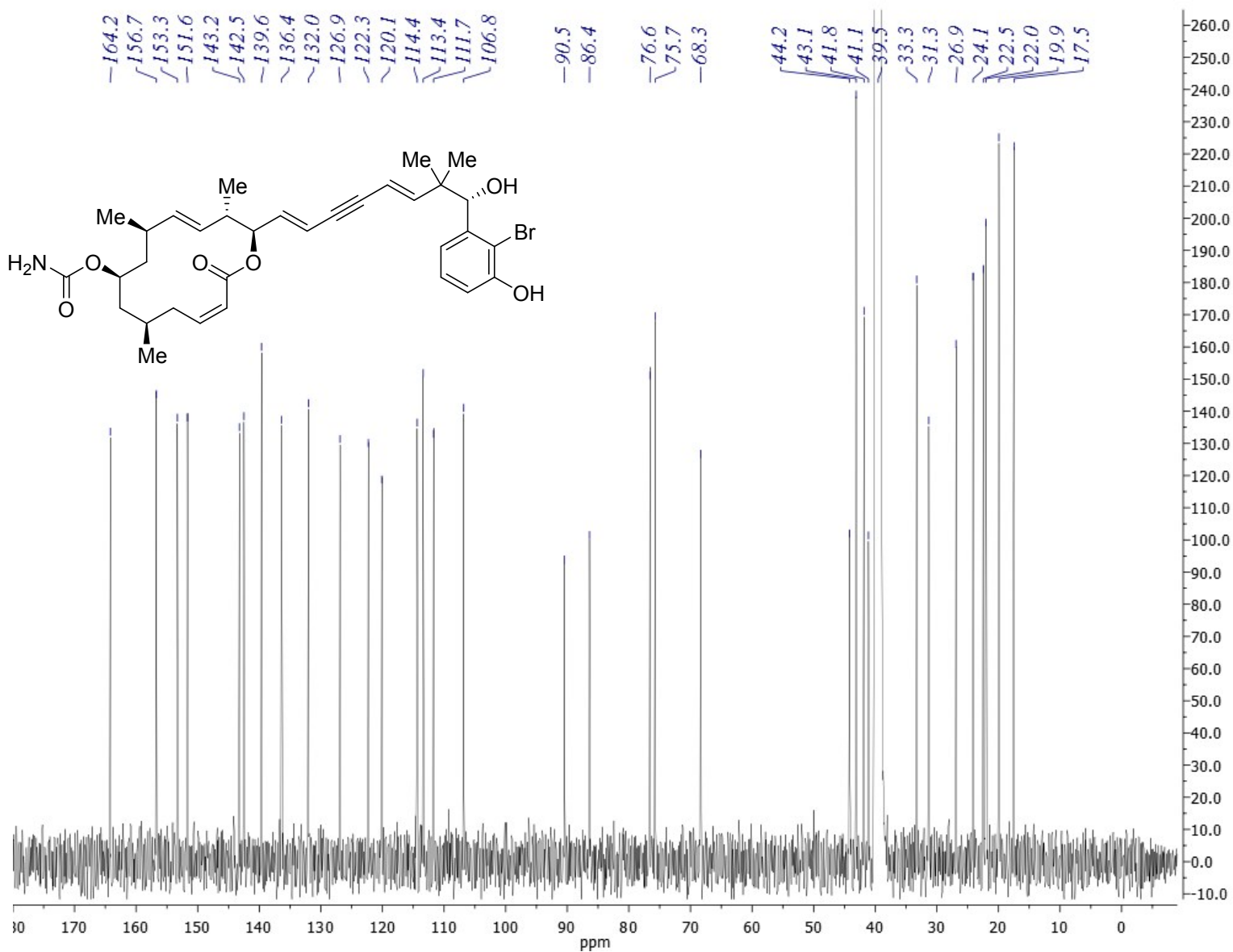


Figure S58. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) of callyspongiolide (*S*)-2.

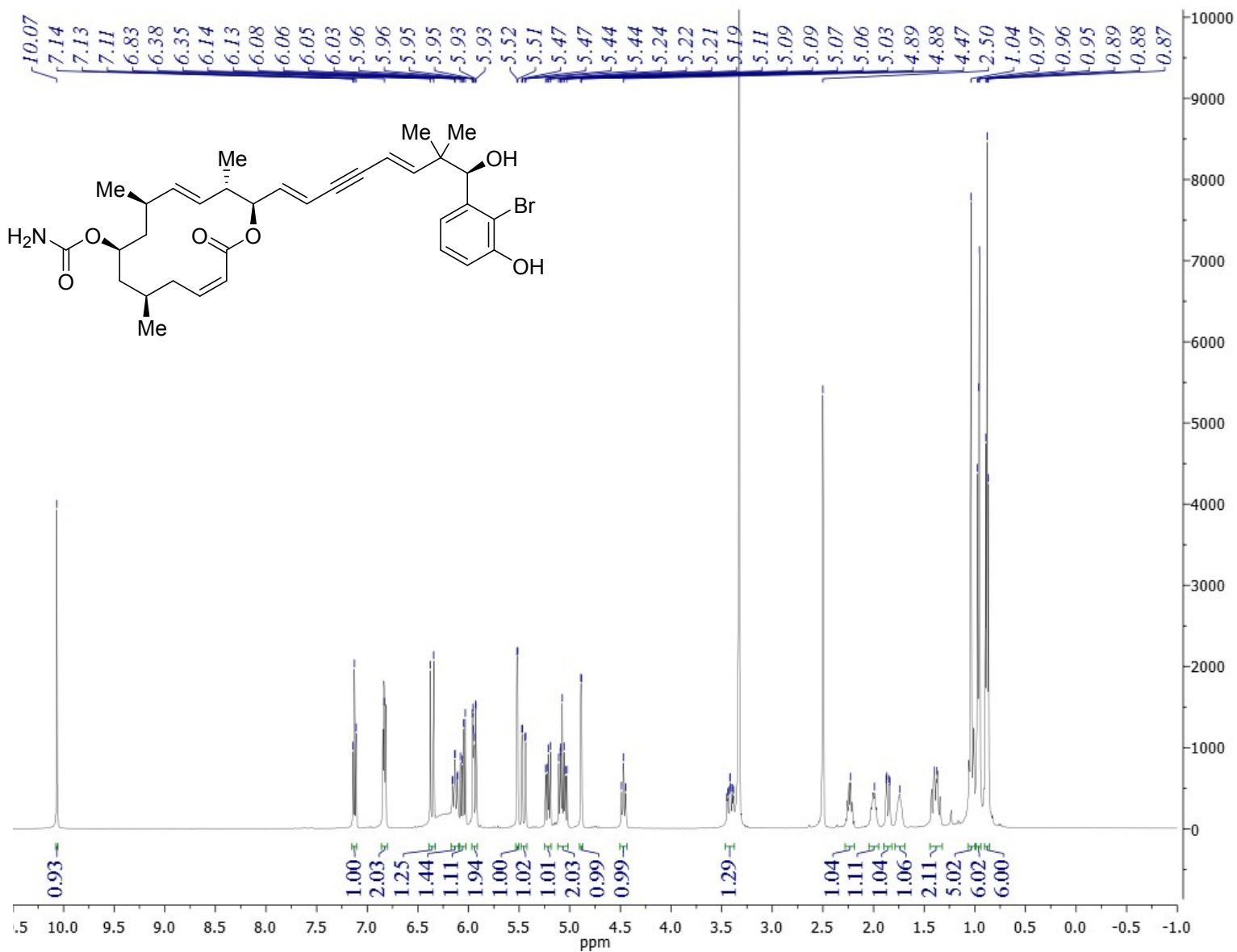


Figure S59. ¹H NMR (500 MHz, DMSO-*d*₆) of callyspongiolide (*R*)-2.

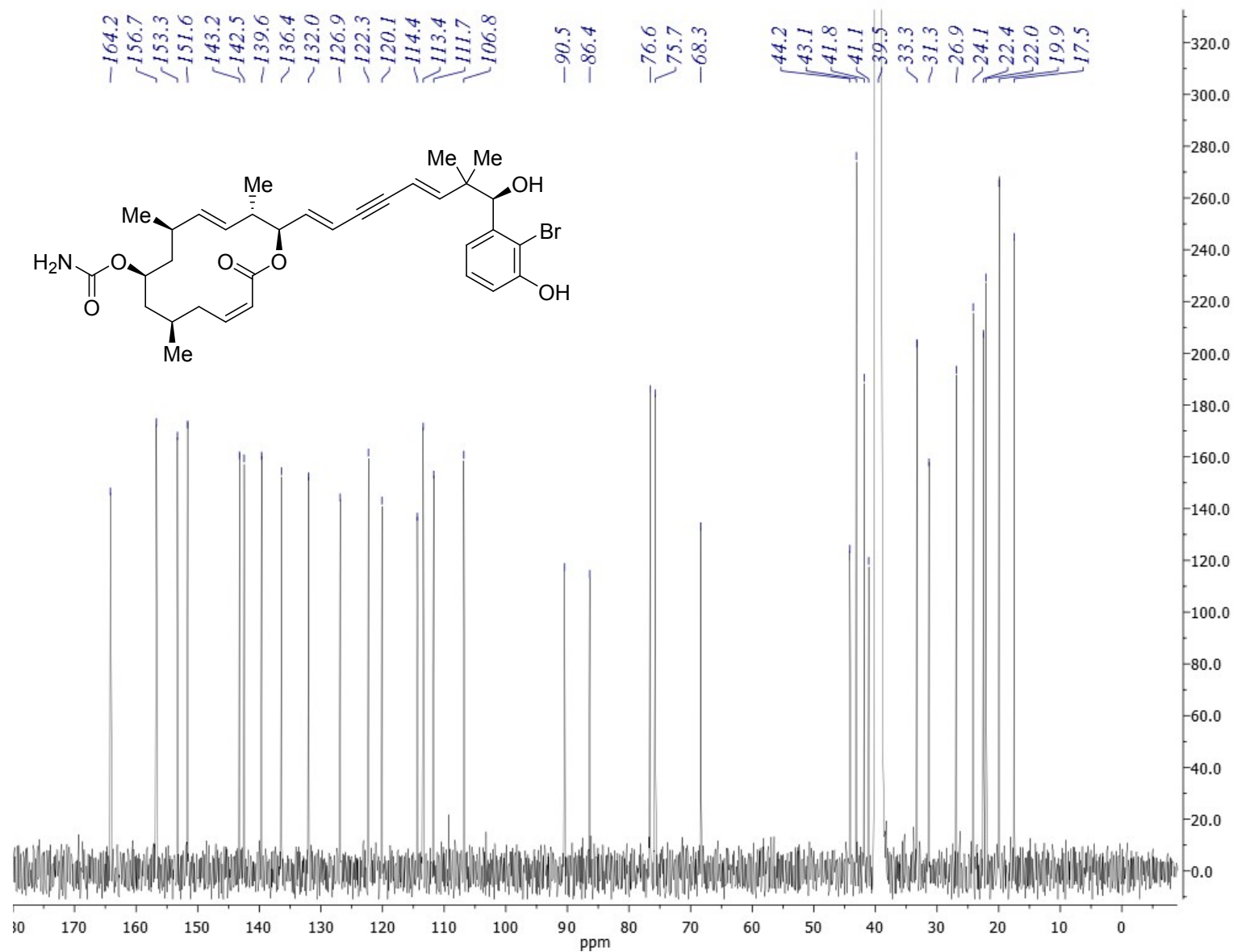


Figure S60. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) of callyspongiolide (*R*)-2.

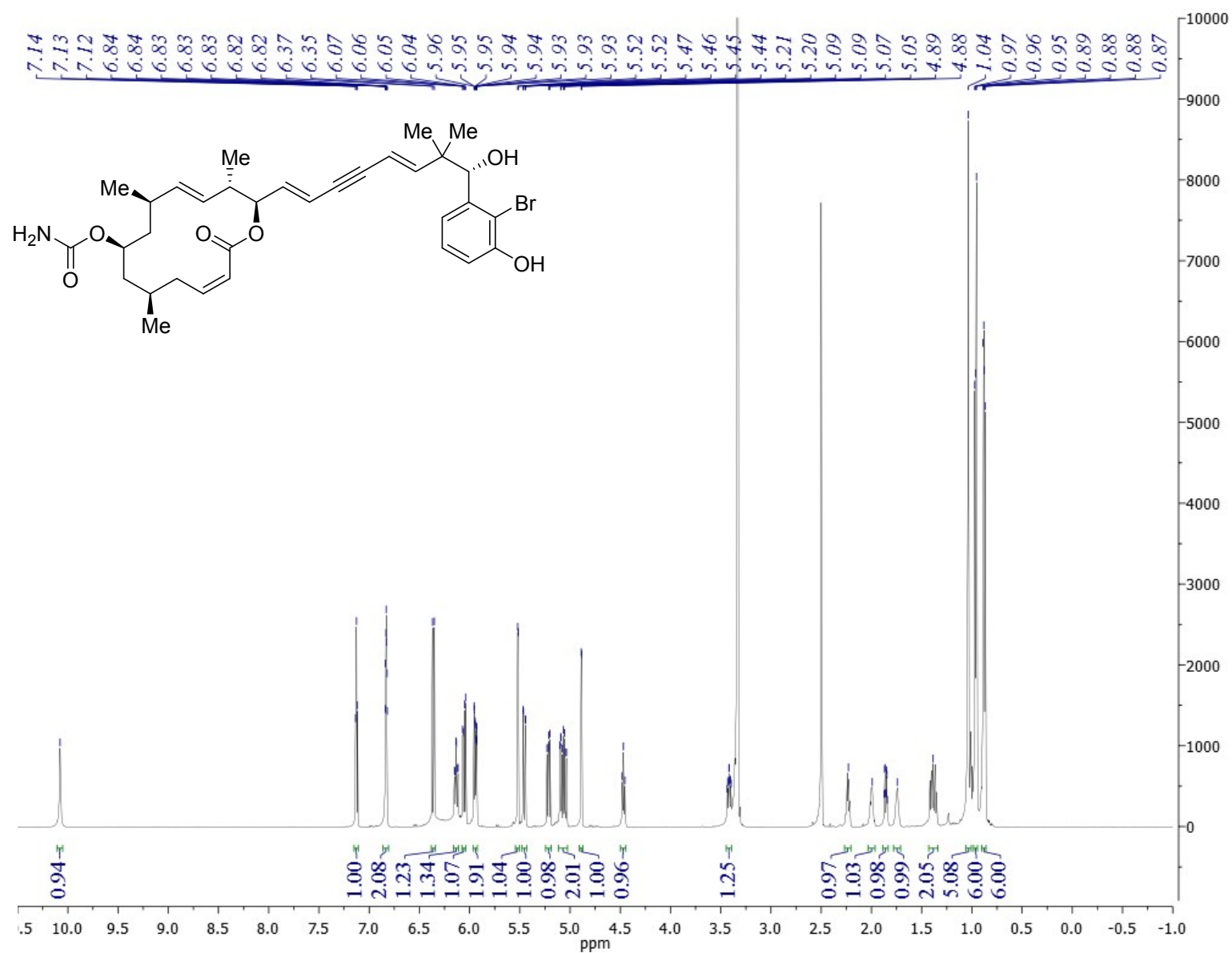


Figure S61. ^1H NMR (800 MHz, $\text{DMSO}-d_6$) of callyspongiolide (S)-2.

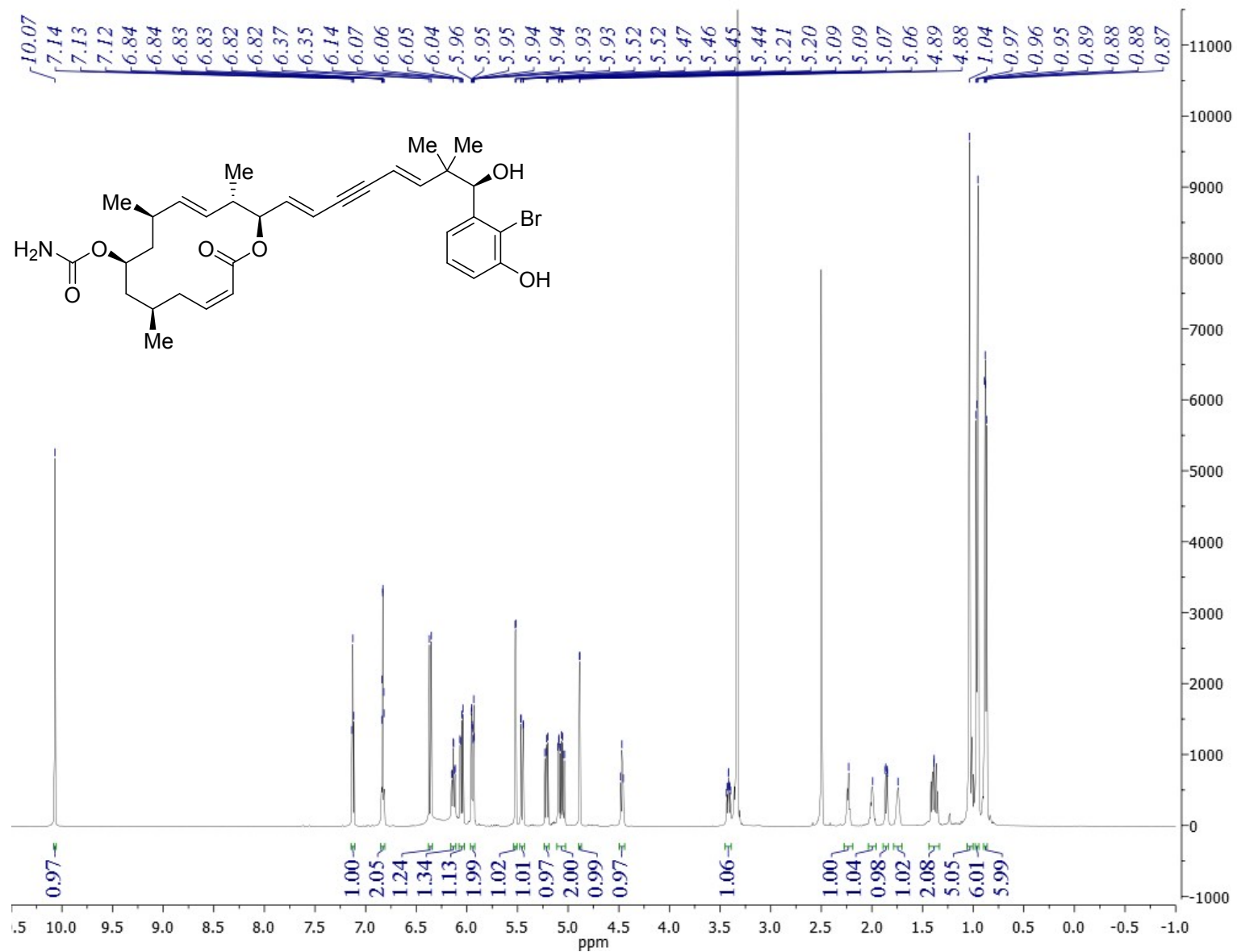


Figure S62. ¹H NMR (800 MHz, DMSO-*d*₆) of callyspongiolide (*R*)-2.

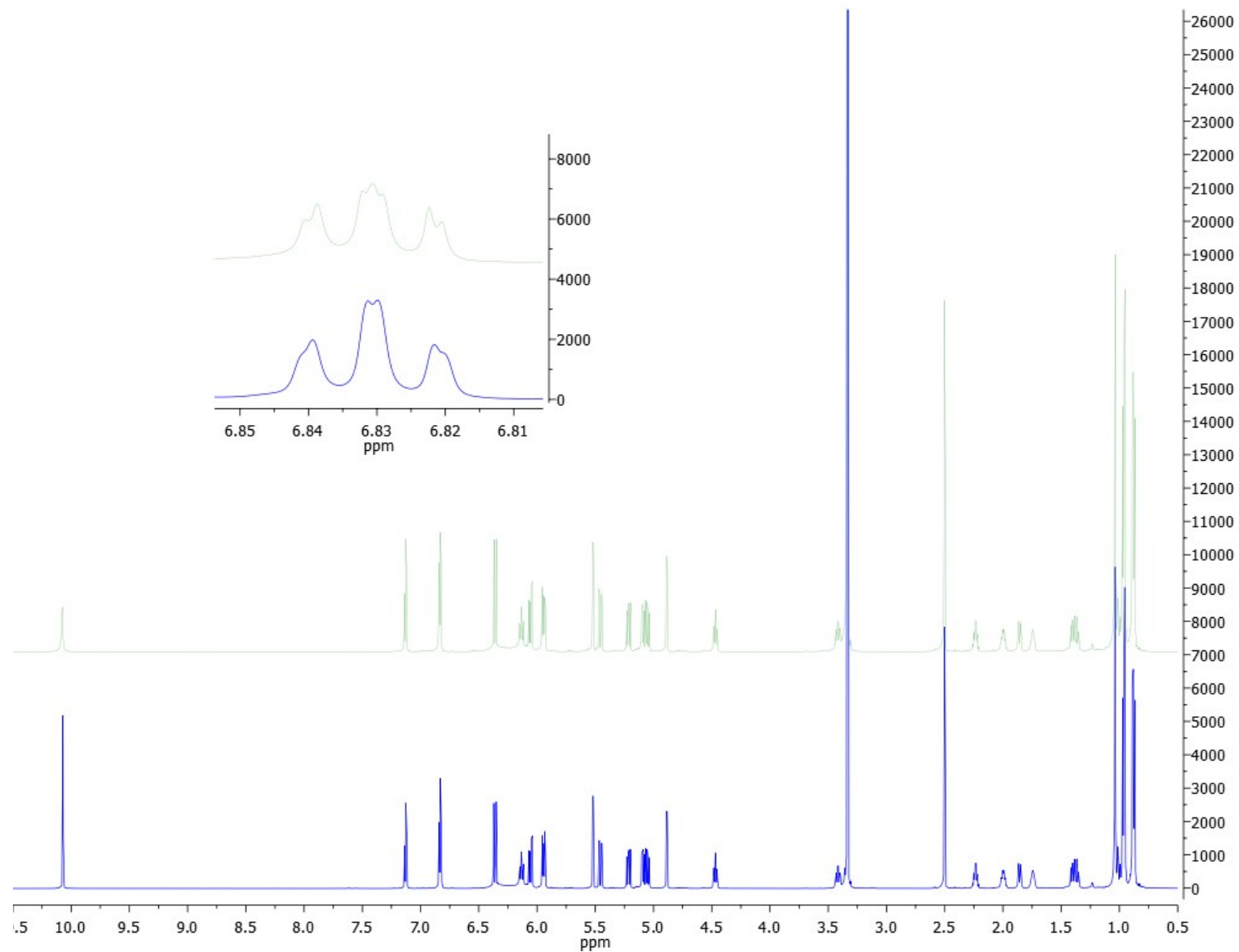


Figure S63. ^1H NMR overlay (800 MHz, DMSO- d_6) of callyspongiolide (*S*)-**2** (top) and (*R*)-**2** (bottom).

Chiral HPLC Chromatograms:

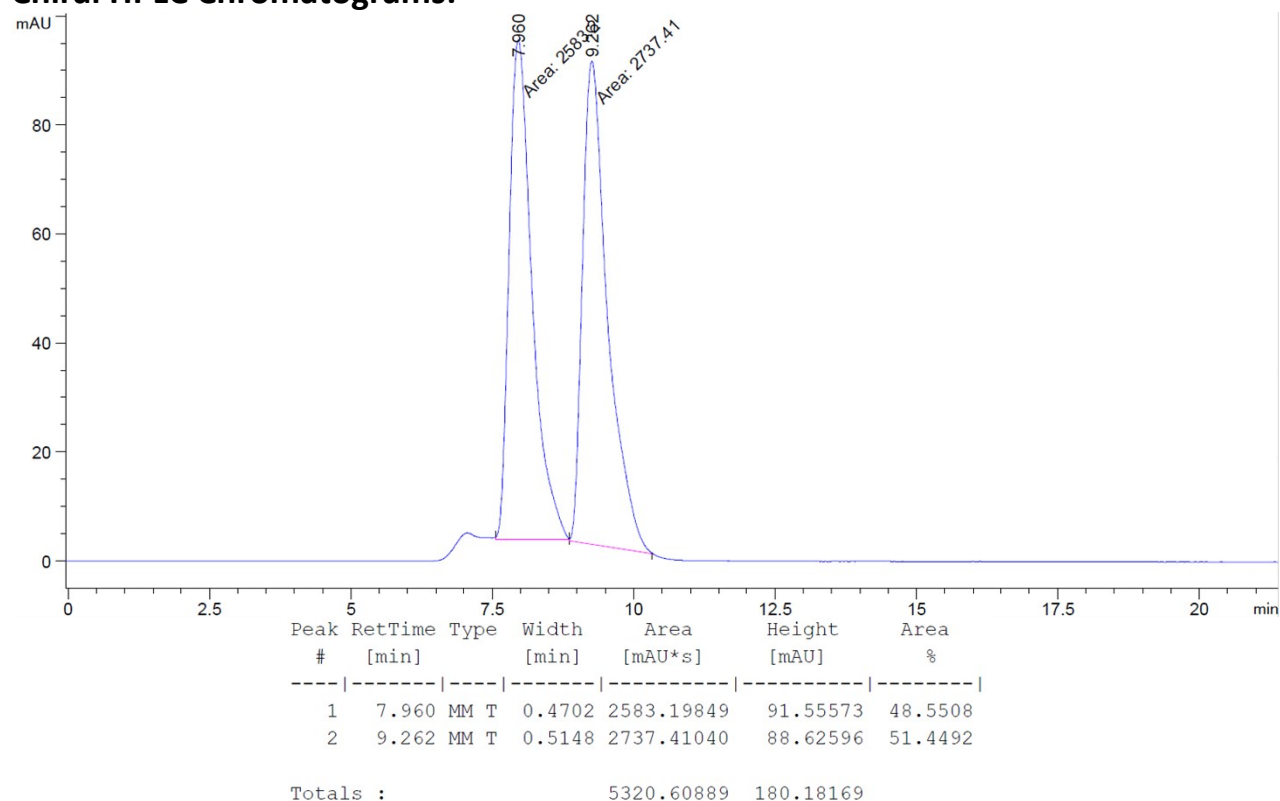


Figure S64. Racemic alcohol 34.

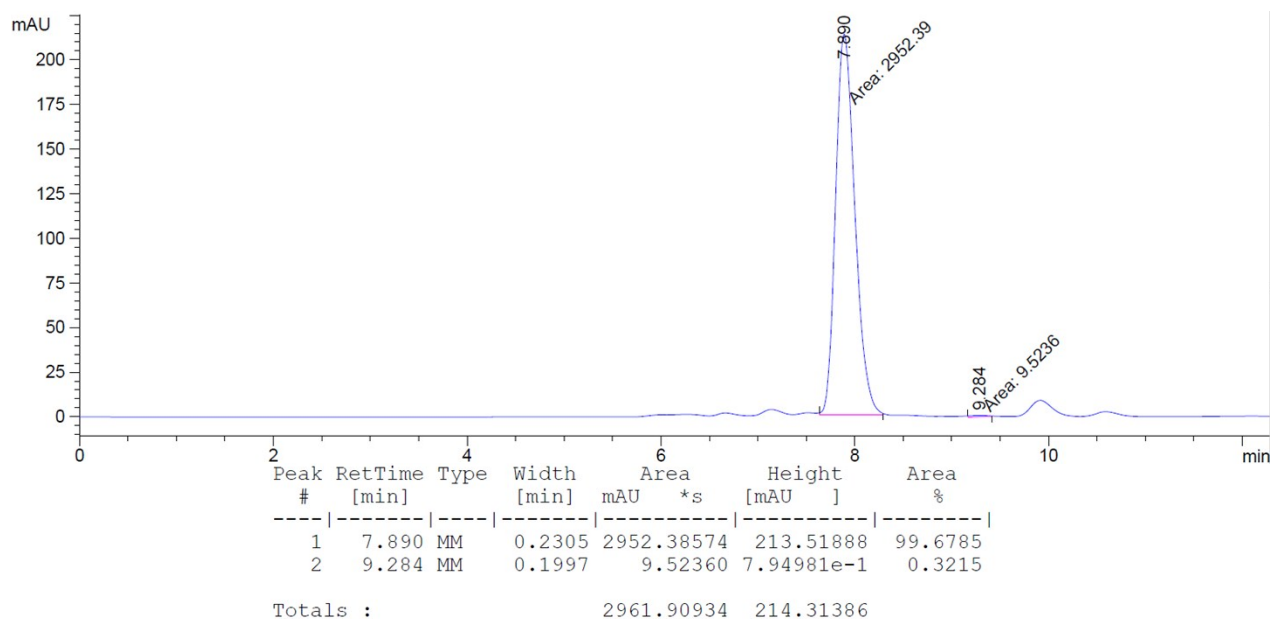


Figure S65. Chiral alcohol (S)-34.