

A Versatile Set of Aminooxy Amino Acids for the Synthesis of Neoglycopeptides

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General experimental procedures.

Unless otherwise noted, all reactions were run at rt and under ambient atmosphere. Chromatographic separations were performed using silica gel (230-400 mesh). Organic solutions were dried with Na_2SO_4 , and solvents were removed using standard rotary evaporation under reduced pressure. Products were dried under high vacuum. Commercial reagents were used in all cases without further purification. Spectral characterizations of **1b**, **2b**, and **3b** were performed at elevated temperatures because of the presence of distinct rotational isomers under most conditions.

SPPS was performed using commercial MBHA resin using standard Boc-chemistry-based procedures¹⁰ with the following variations. The amino acids were activated with 2-(1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) and $\text{NEt}(i\text{-Pr})_2$ in DMF. All commercial amino acids were used in a 10-fold excess to the resin loading and allowed to react for 10 min. **1b**, **2b**, **3b** and **4b** were used in a 2 to 3-fold excess and allowed to react for 25 min. Boc deprotections were carried out using neat TFA. Resin washings between steps were performed with a continuous flow of DMF for 1 min. Final deprotection and resin cleavage was accomplished by treatment with liquid HF or bromotrimethylsilane:TFA:thioanisole (v:v:v, 0.6:3:0.8).

Figure S1. ^1H NMR spectrum of **1b** (400 MHz, CDCl_3 , 55 $^\circ\text{C}$).



Figure S2. ^{13}C NMR spectrum of **1b** (100 MHz, CDCl_3 , 55 $^\circ\text{C}$).

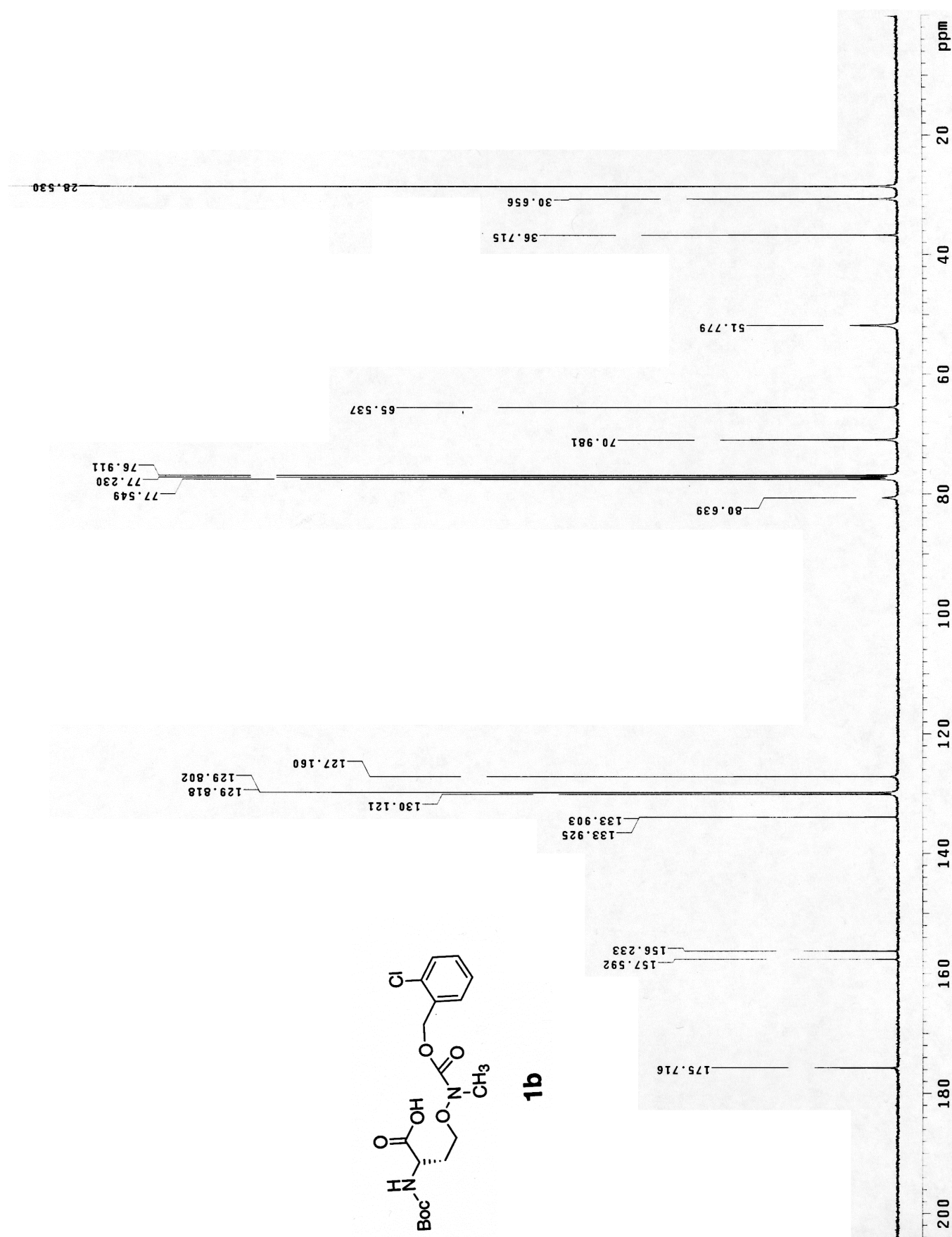


Figure S3. ^1H NMR spectrum of **2b** (400 MHz, CD_3CN , 55 $^\circ\text{C}$).

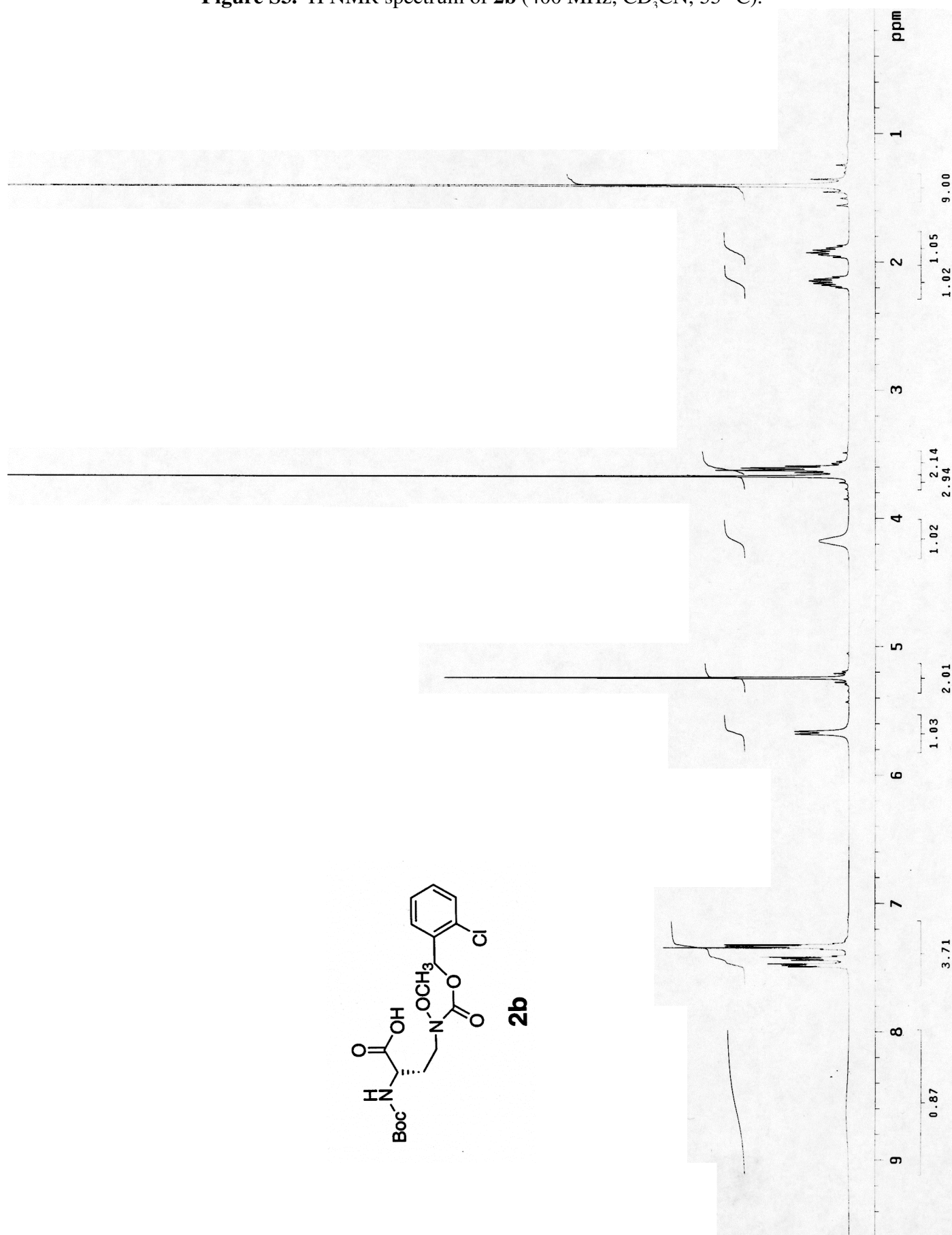


Figure S4. ^{13}C NMR spectrum of **2b** (100 MHz, CD_3CN , 55 $^\circ\text{C}$).

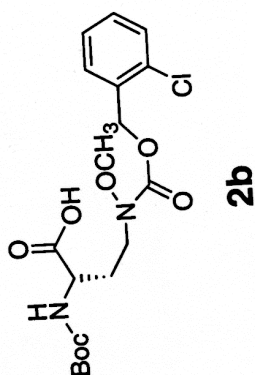
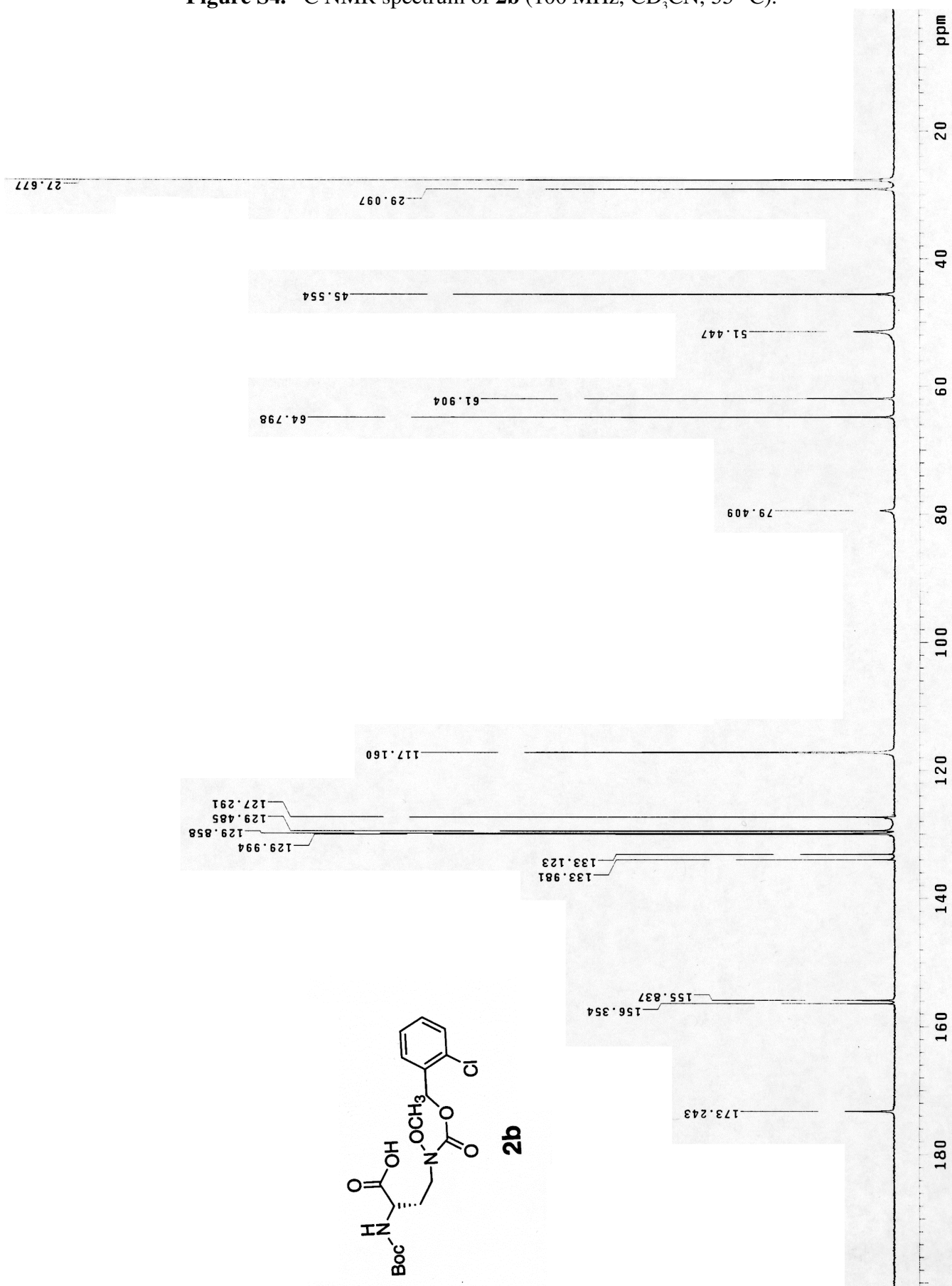


Figure S5. ^1H NMR spectrum of **3b** (400 MHz, CD_3CN , 55 $^\circ\text{C}$).

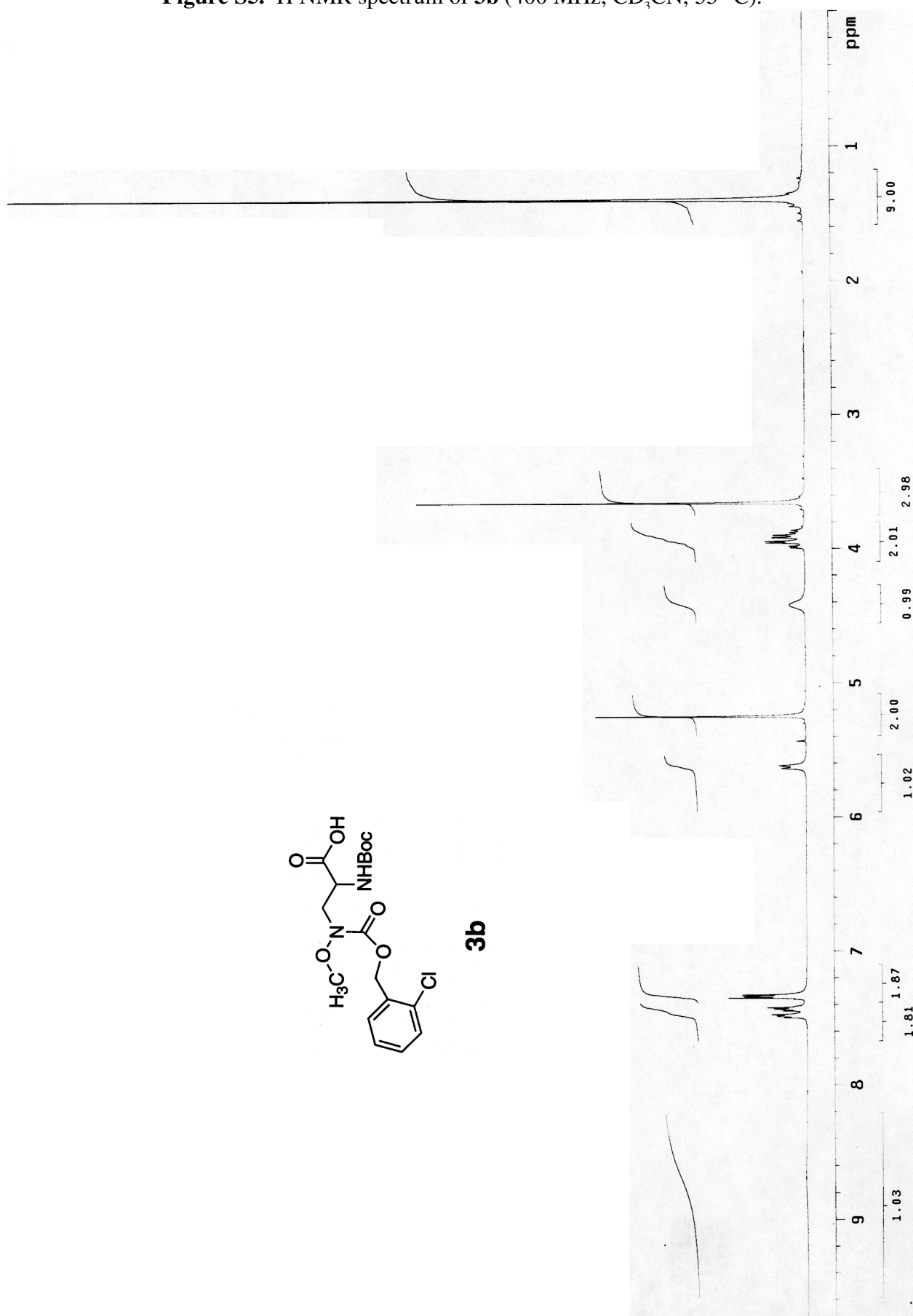


Figure S6. ^{13}C NMR spectrum of **3b** (100 MHz, CD_3CN , 55 $^\circ\text{C}$).

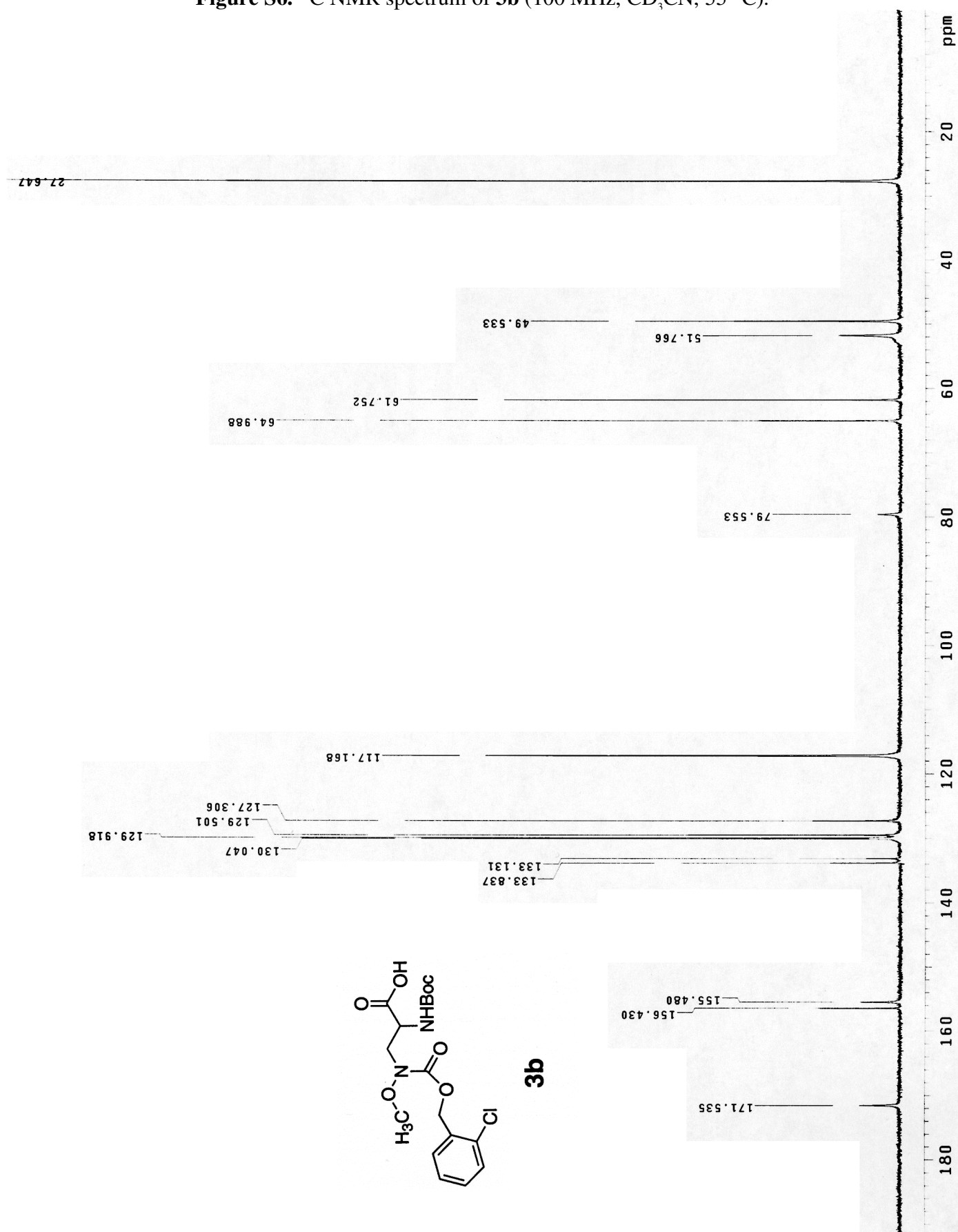


Figure S7. ^1H NMR spectrum of **4b** (400 MHz, CD_3CN , 55 $^\circ\text{C}$).

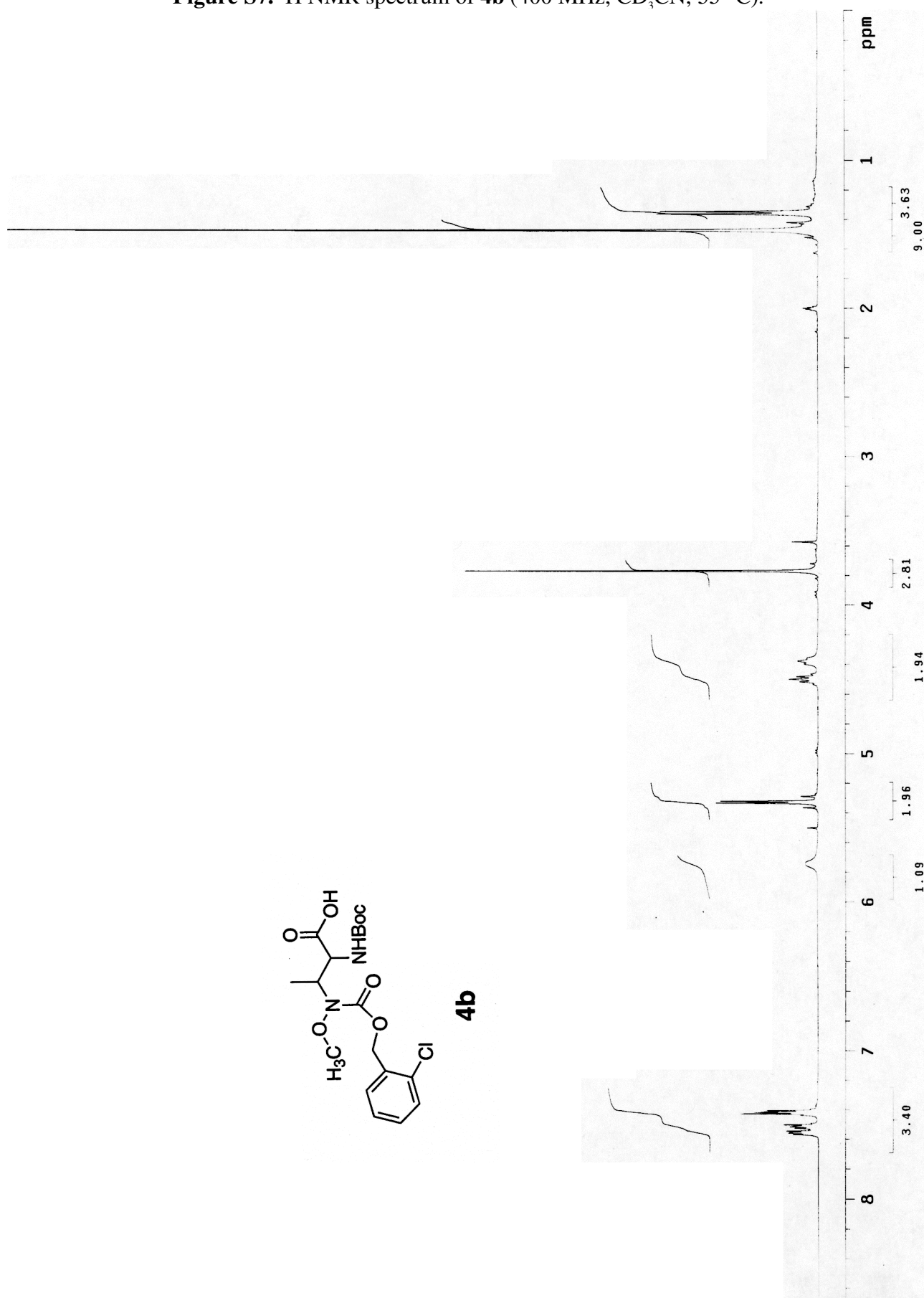


Figure S8. ^{13}C NMR spectrum of **4b** (100 MHz, CD_3CN).

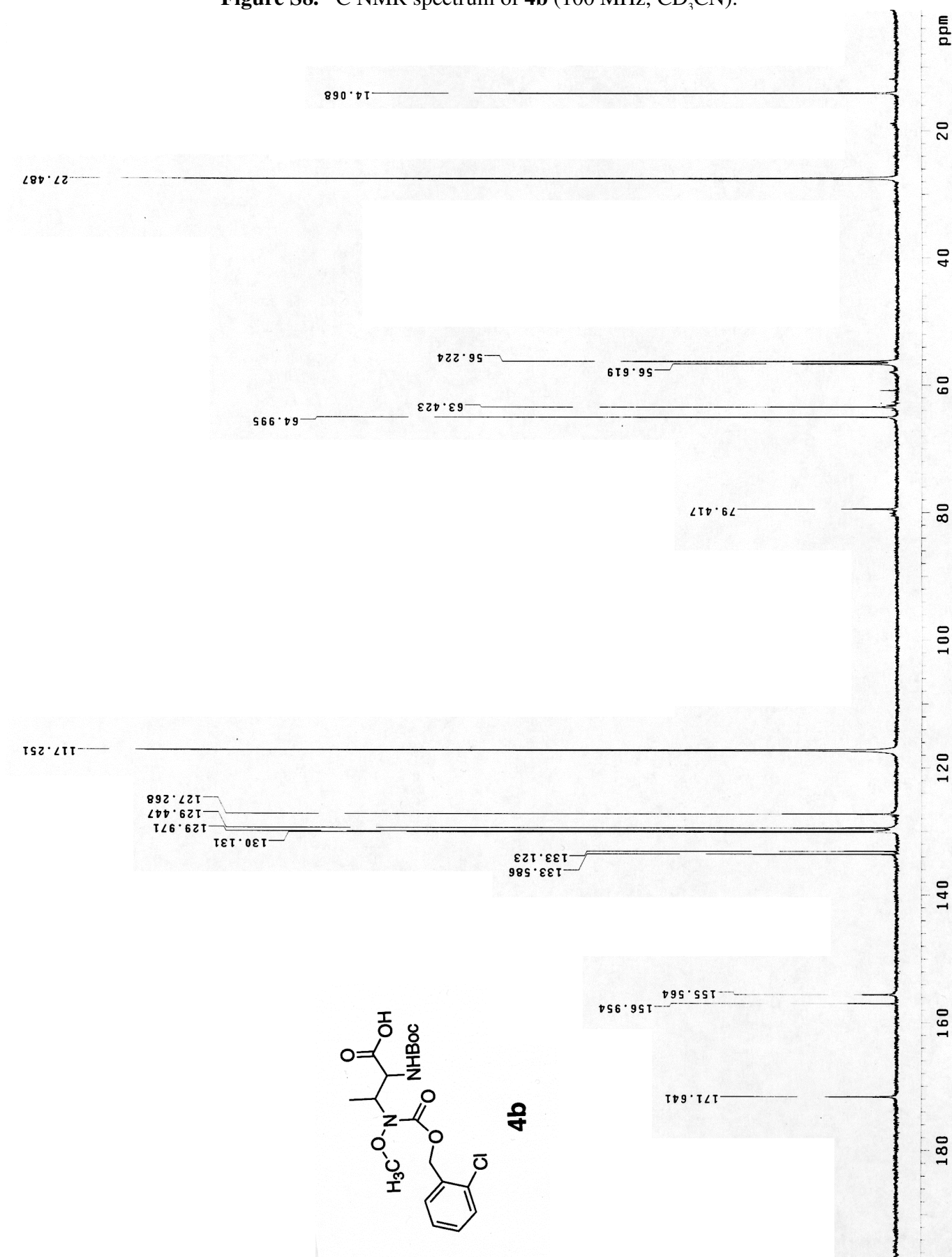


Figure S9. ^1H NMR spectrum of **5** (400 MHz, CDCl_3).

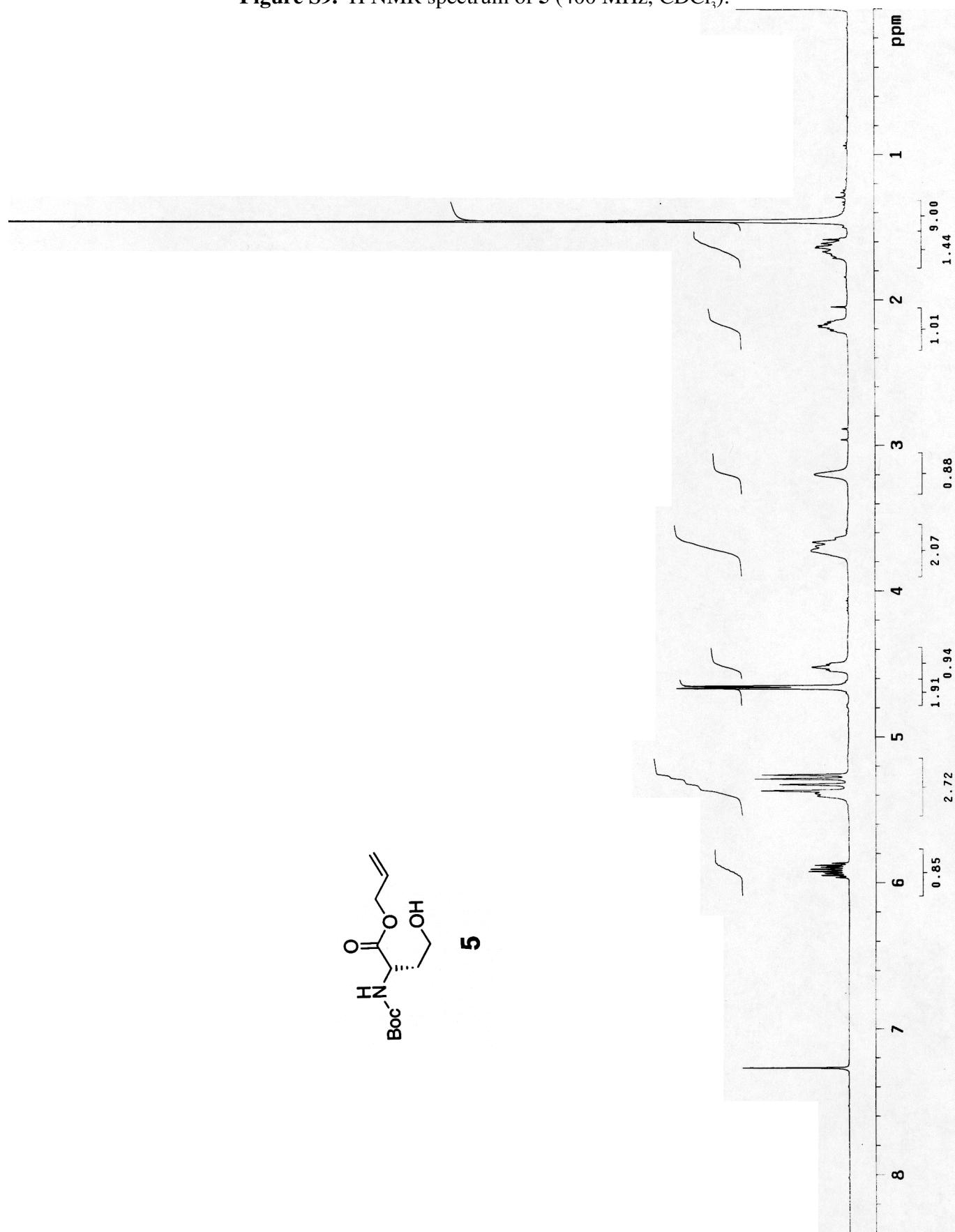


Figure S10. ^{13}C NMR spectrum of **5** (100 MHz, CDCl_3).

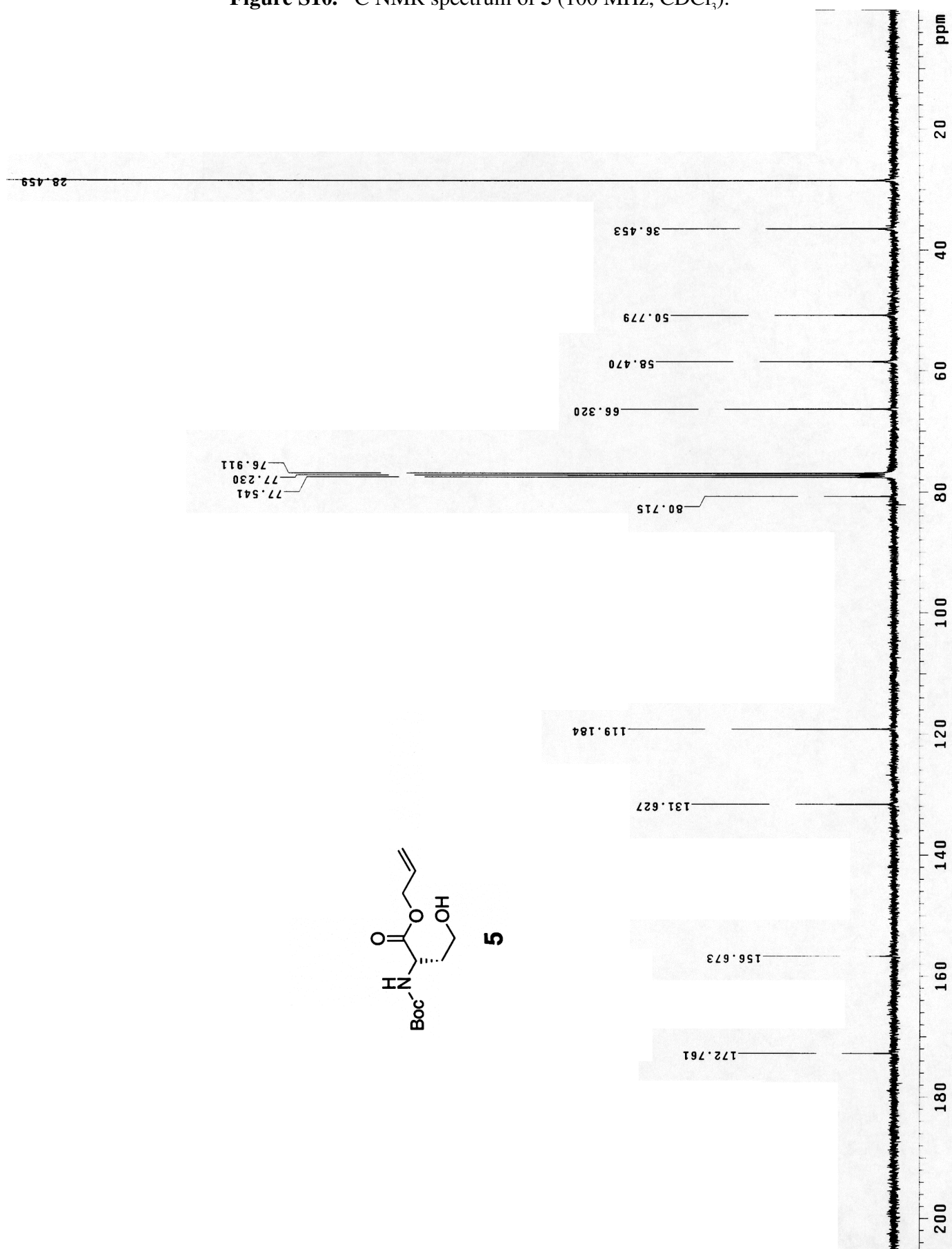


Figure S11. ^1H NMR spectrum of **6** (400 MHz, CDCl_3).

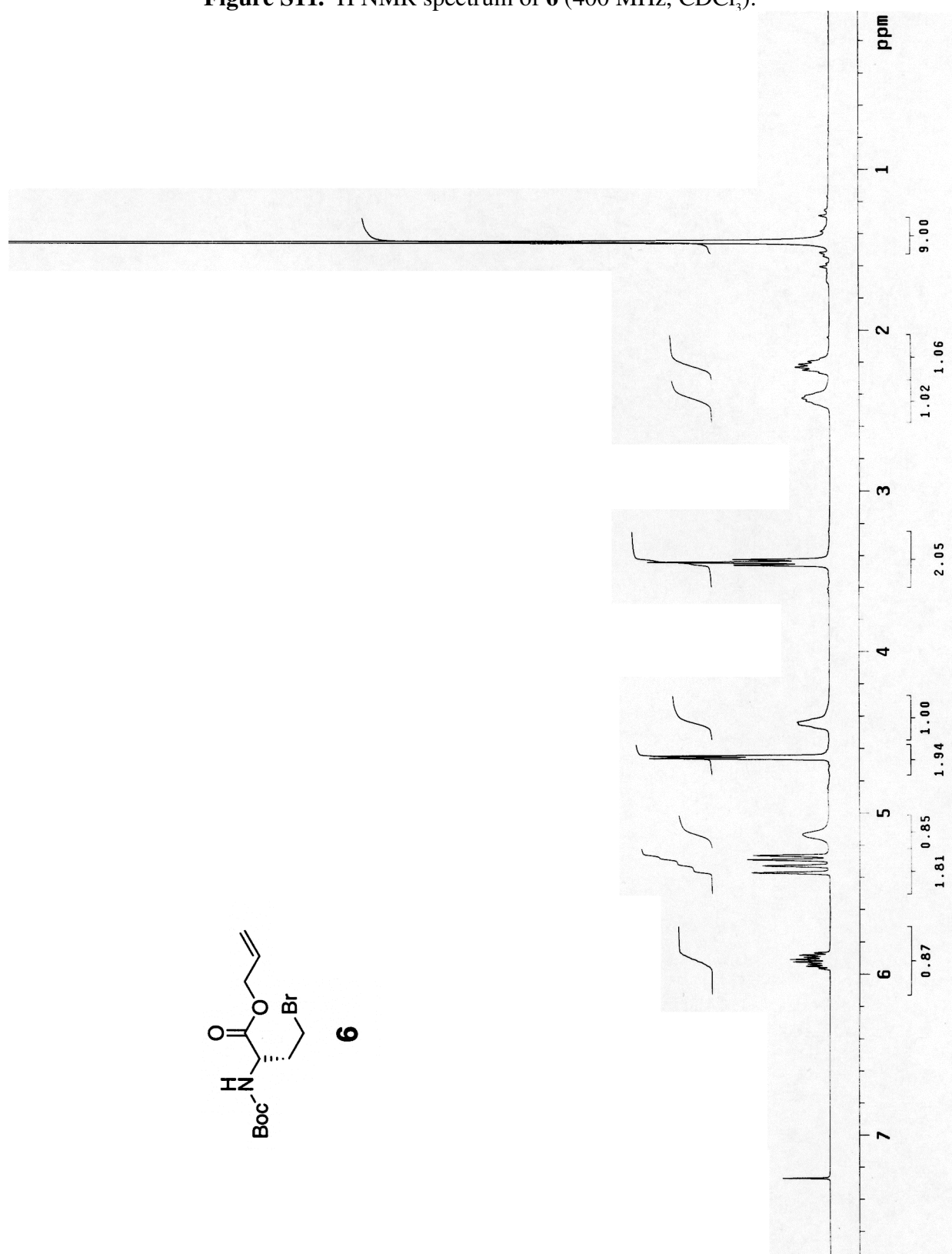


Figure S12. ^{13}C NMR spectrum of **6** (100 MHz, CDCl_3).

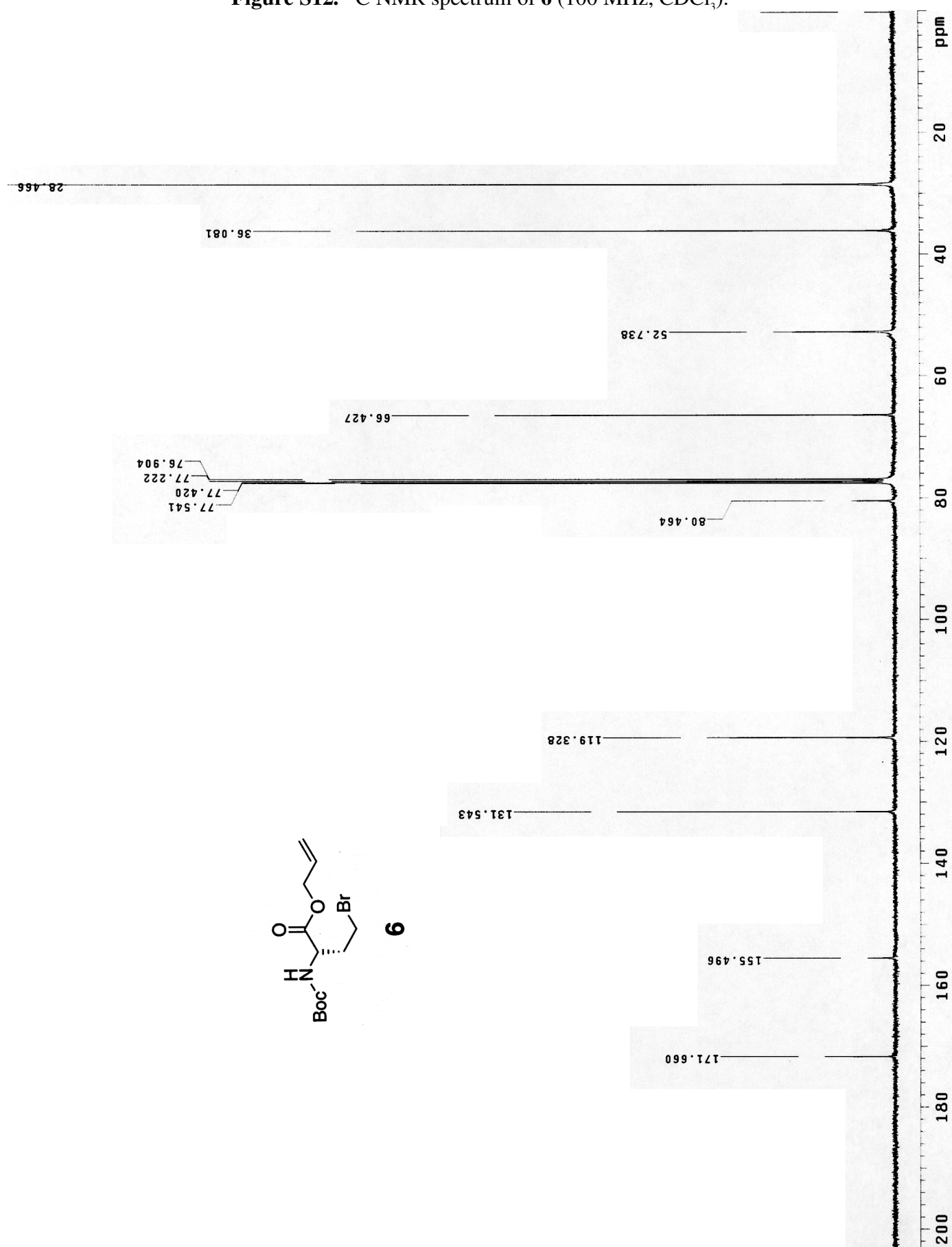


Figure S13. ^1H NMR spectrum of **7** (400 MHz, CDCl_3).

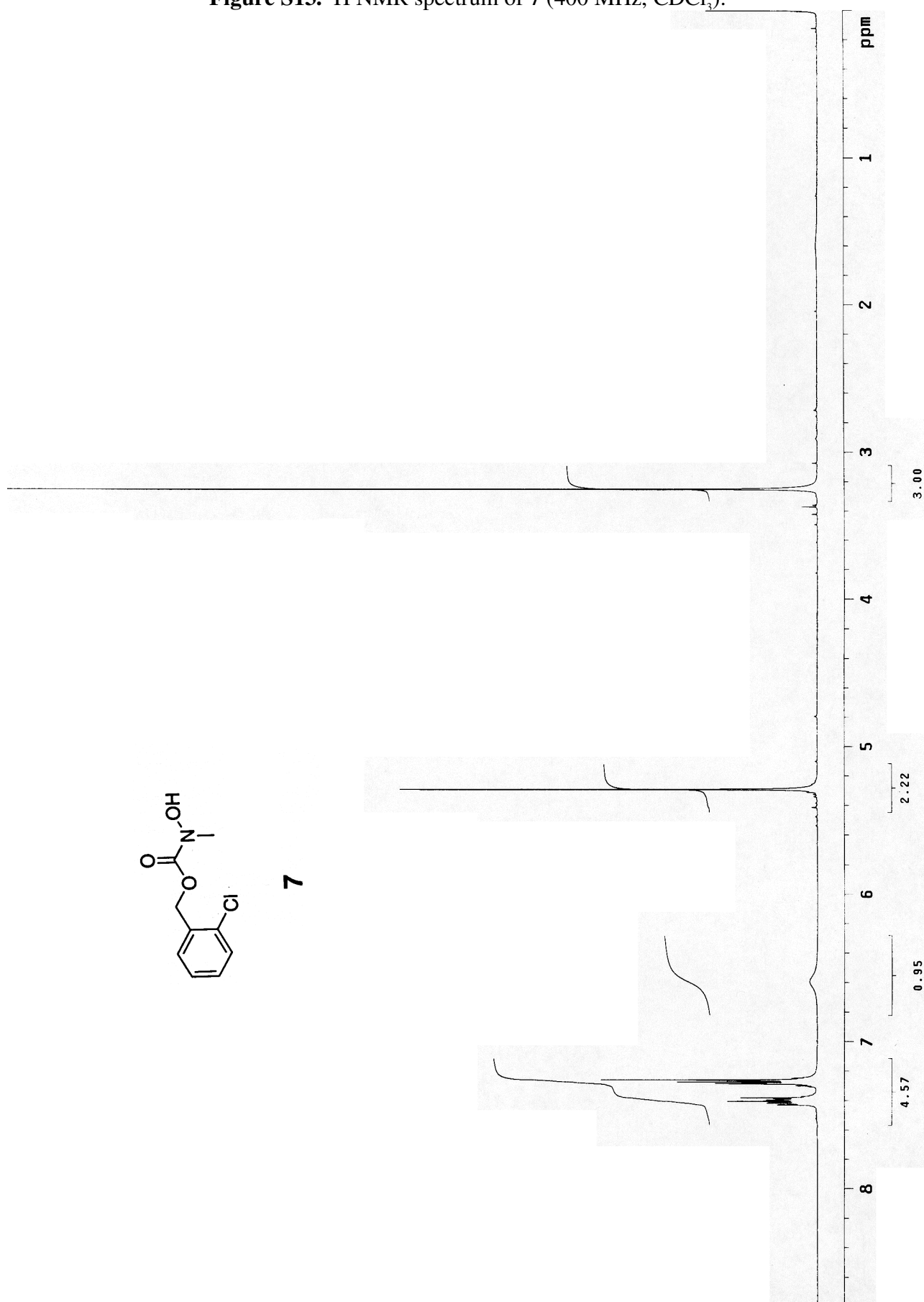


Figure S14. ^{13}C NMR spectrum of **7** (100 MHz, CDCl_3).

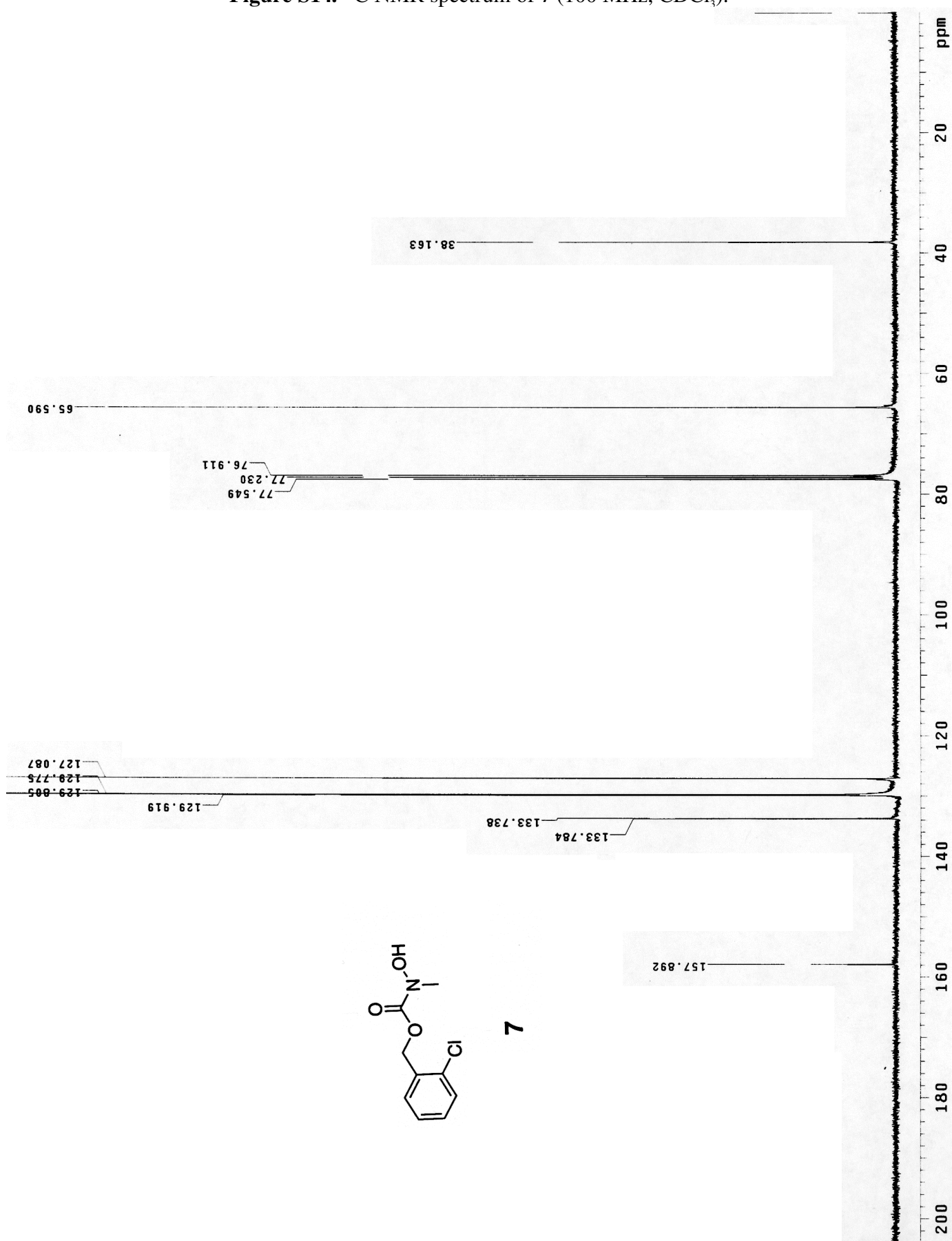


Figure S15. ^1H NMR spectrum of **8** (400 MHz, CDCl_3).

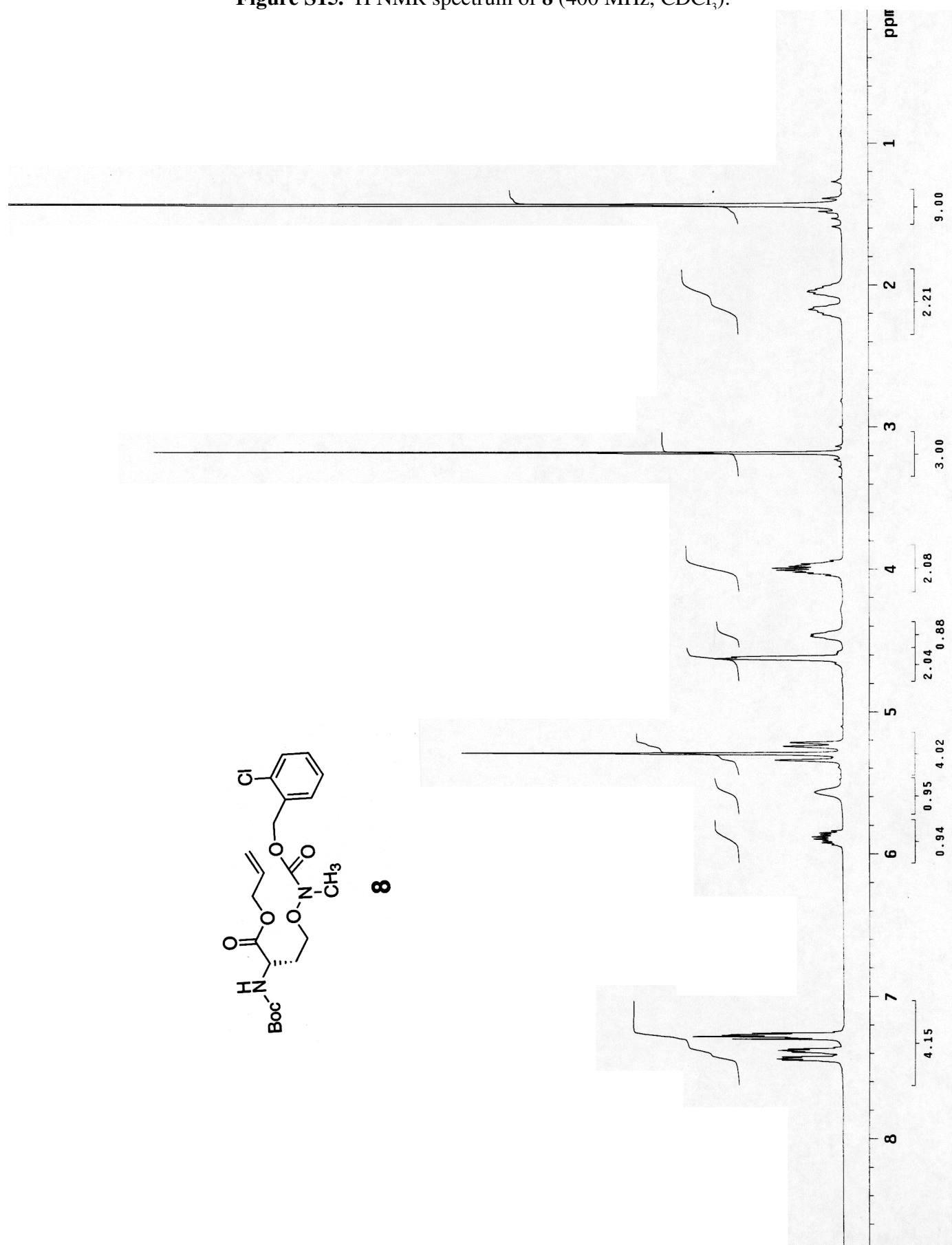


Figure S16. ^{13}C NMR spectrum of **8** (100 MHz, CDCl_3).

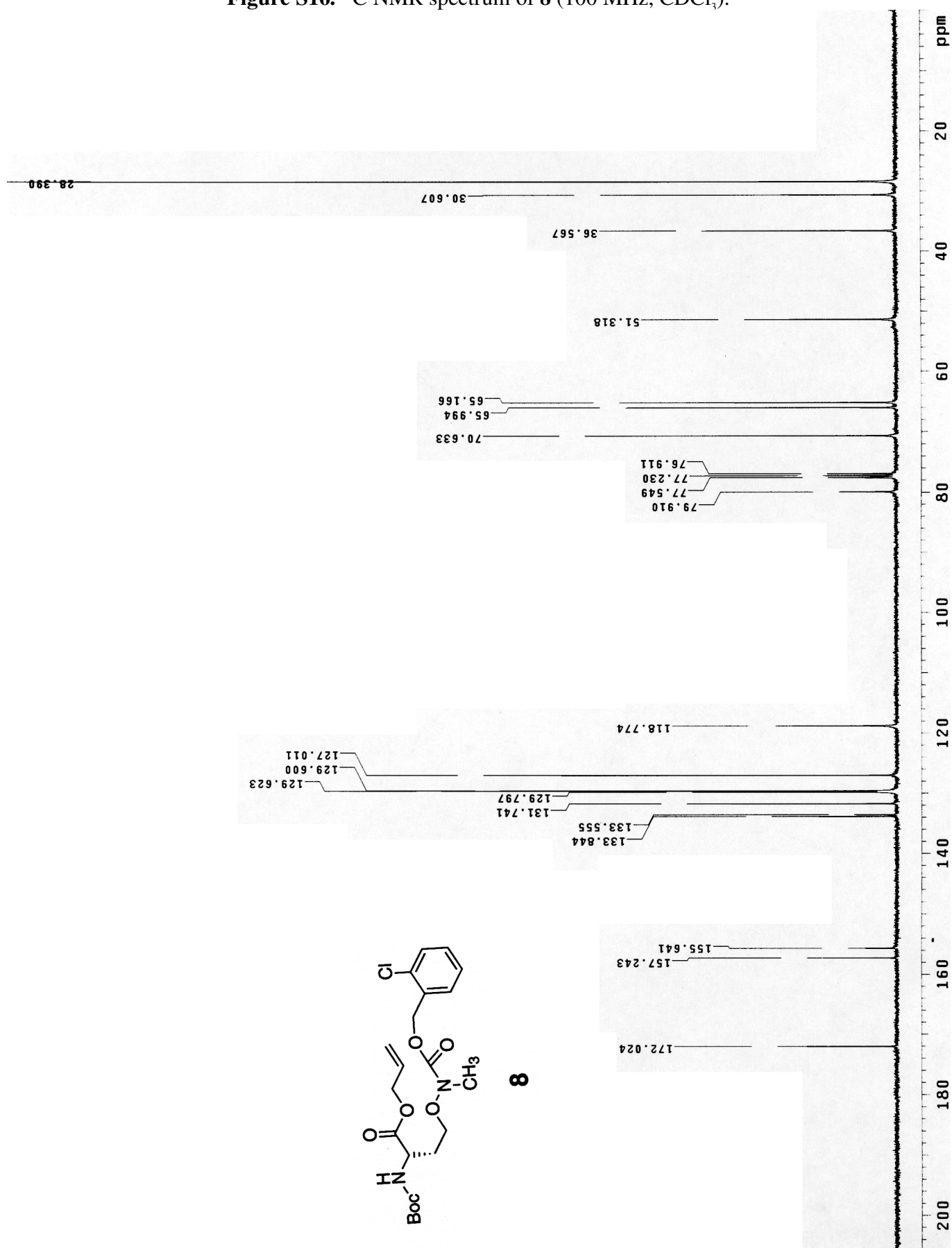


Figure S17. ^1H NMR spectrum of **9** (400 MHz, CDCl_3).

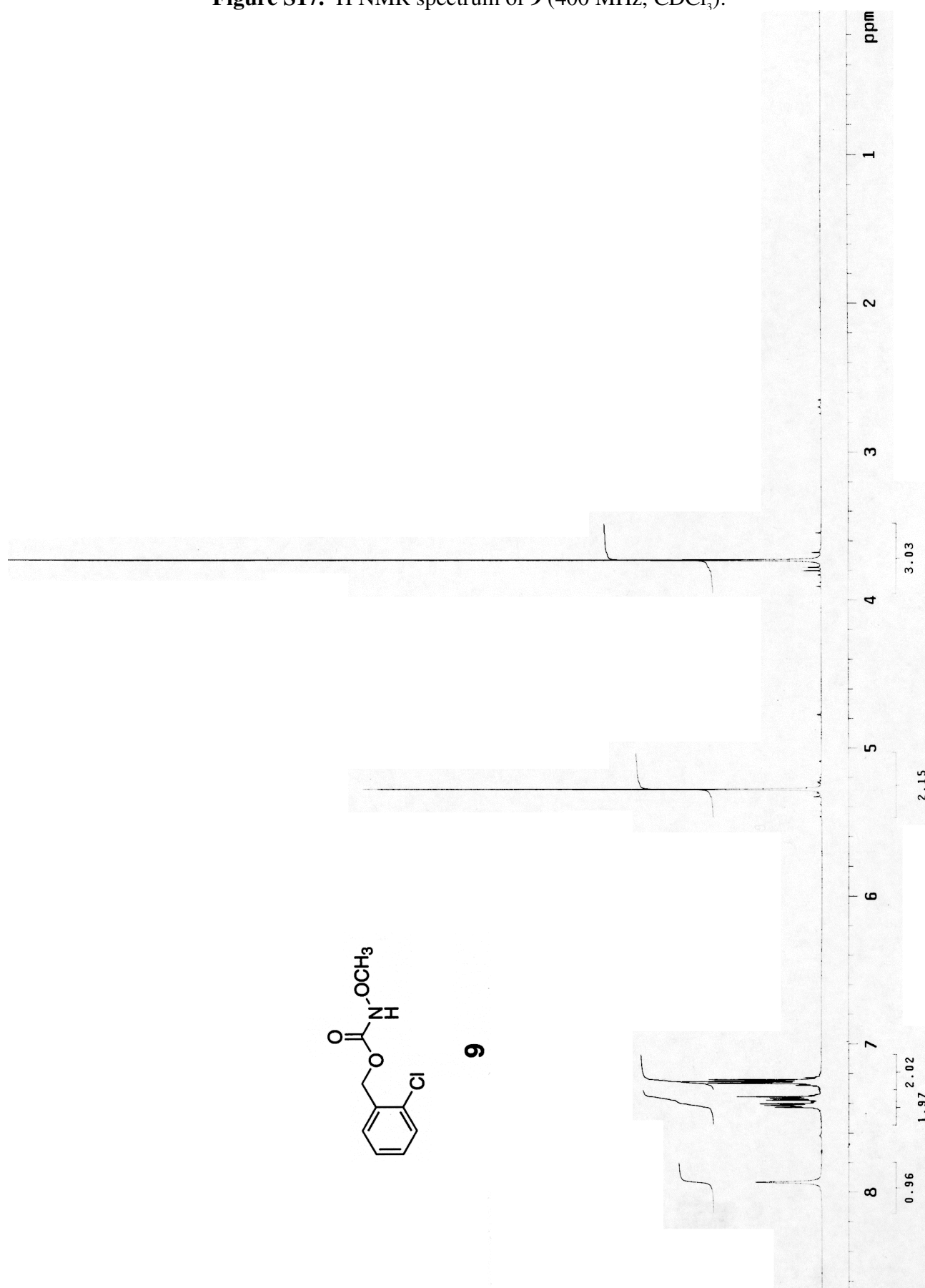


Figure S18. ^{13}C NMR spectrum of **9** (100 MHz, CDCl_3).

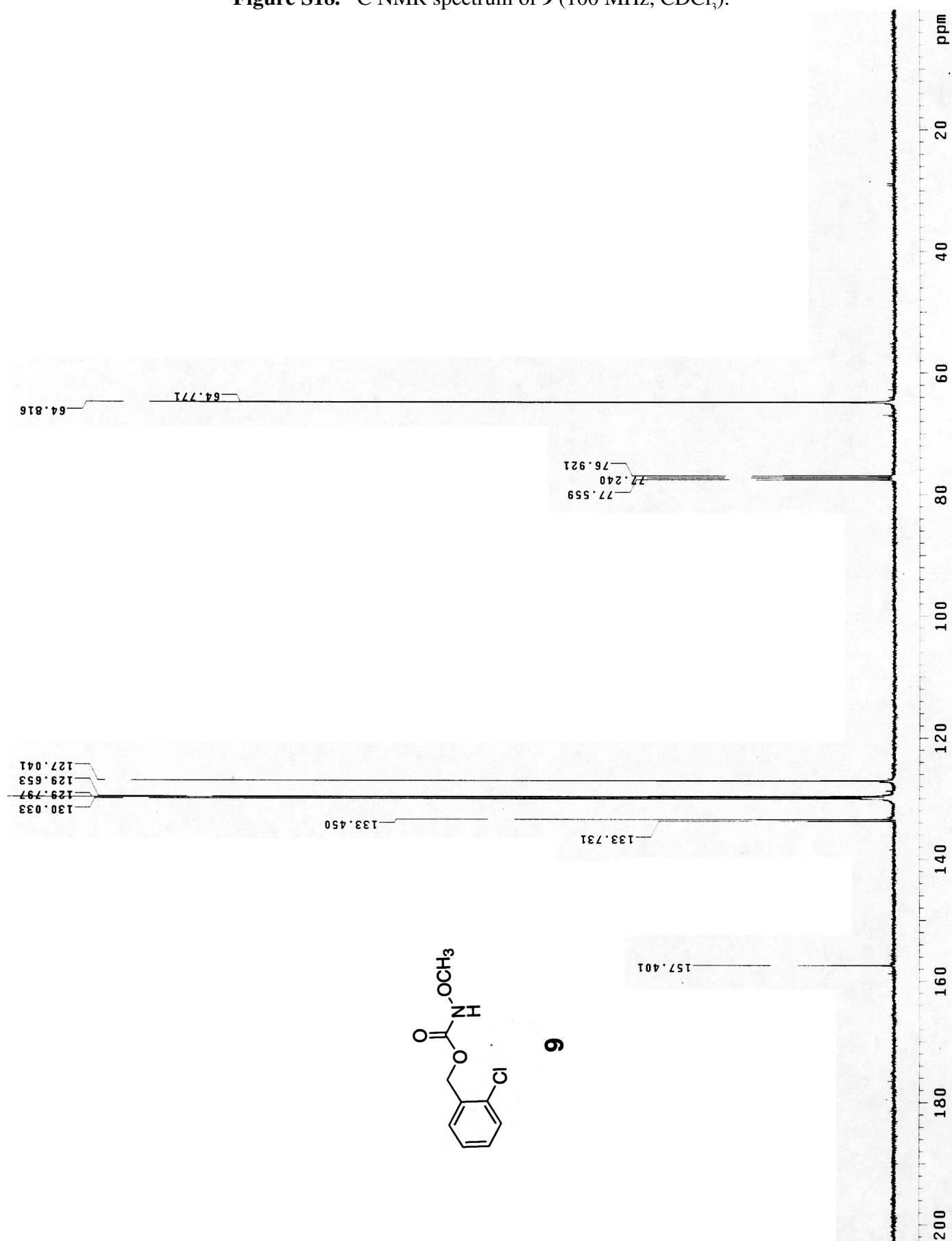
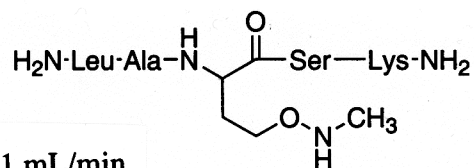
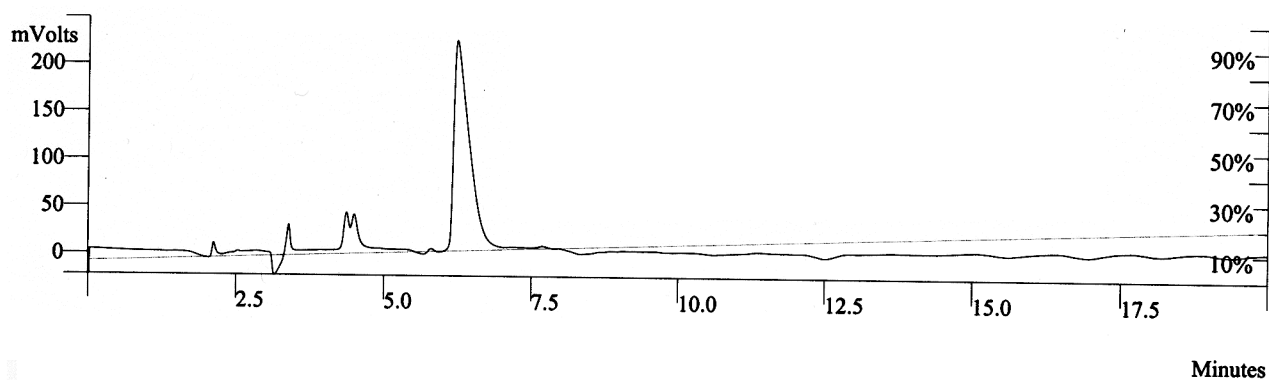


Figure S19. HPLC chromatograms of **14** and **18**

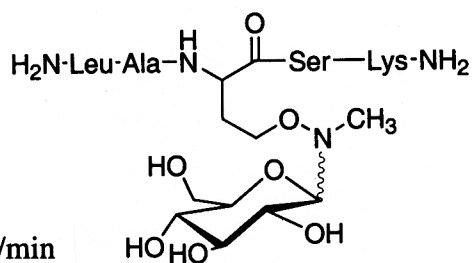
Kromasil C18 5 μ m 100Å, 5-20% B over 20 min, 1 mL/min



14



Kromasil C18 5 μ m 100Å, 5-20% B over 20 min, 1 mL/min



18

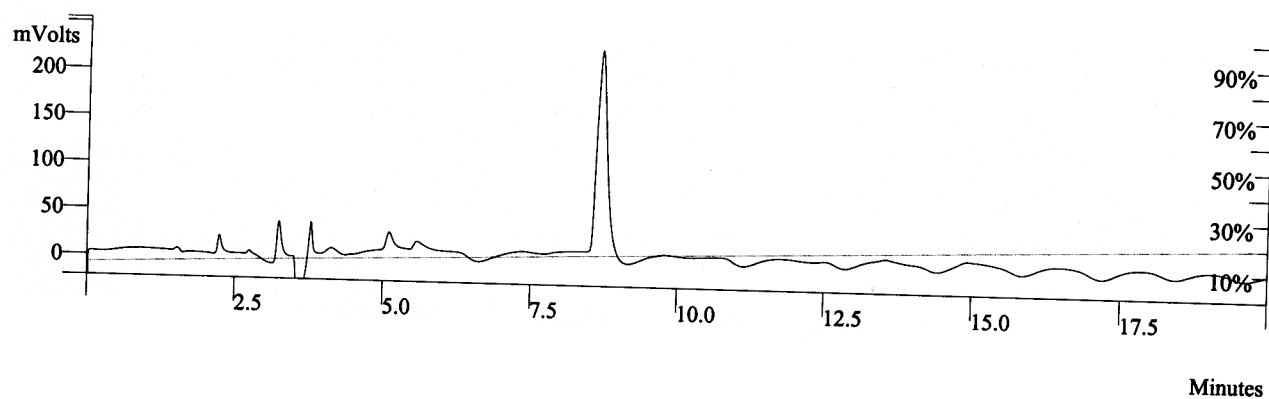
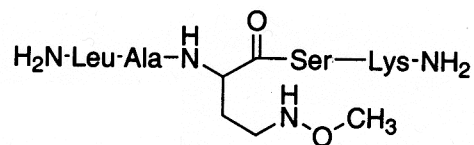
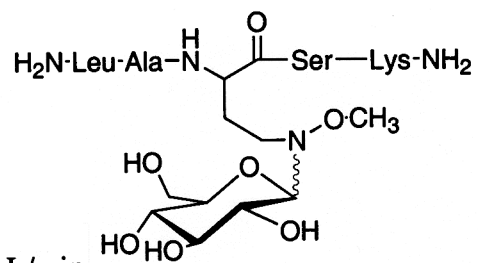
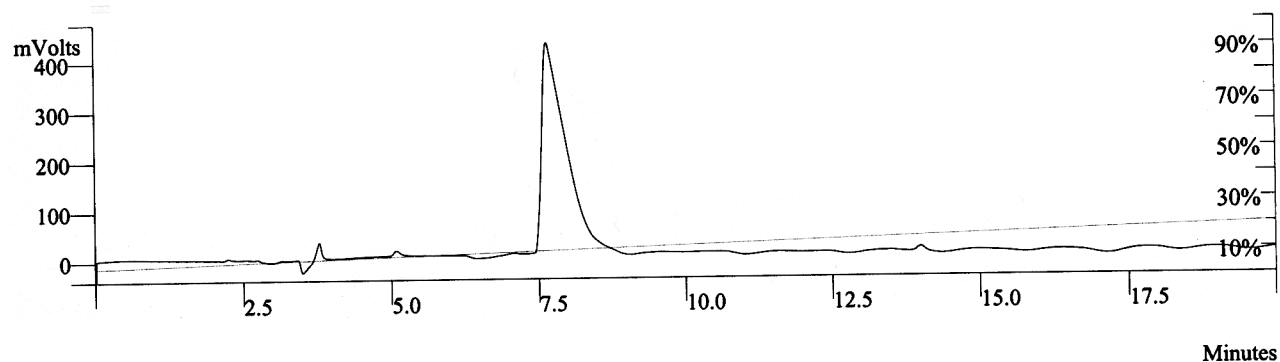


Figure S20. HPLC chromatograms of **15** and **19**



Kromasil C18 5 μ m 100Å, 5-20% B over 20 min, 1 mL/min

15



Kromasil C18 5 μ m 100Å, 5-20% B over 20 min, 1 mL/min

19

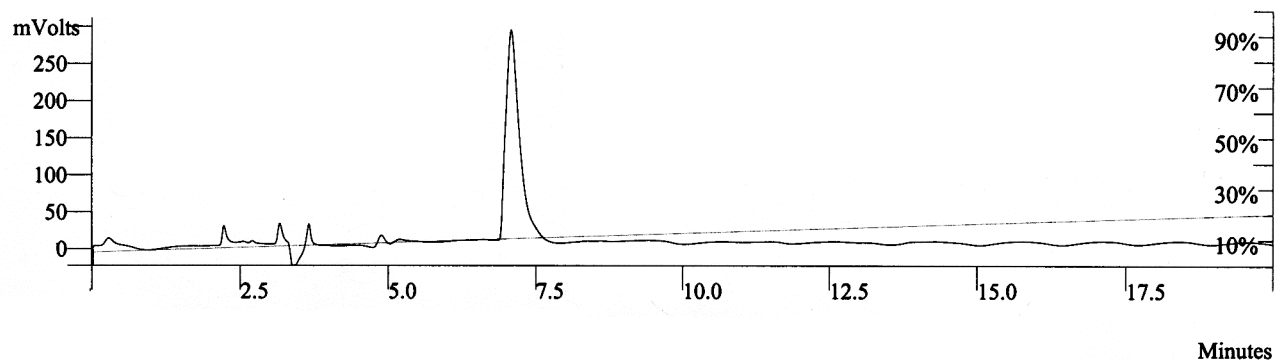
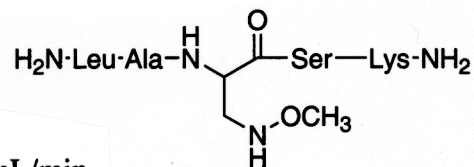
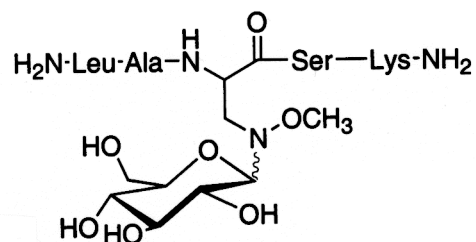
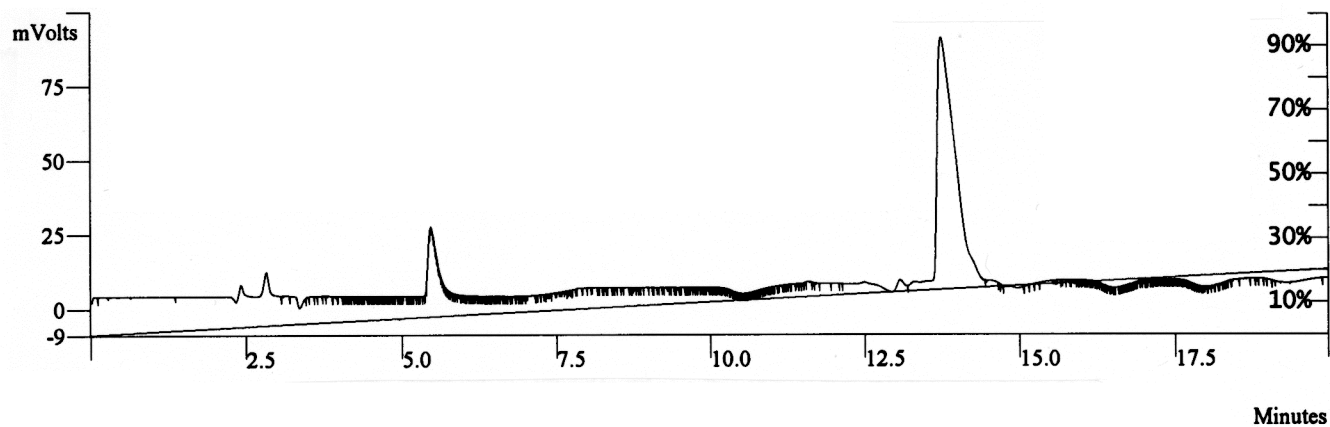


Figure S21. HPLC chromatograms of **16** and **20**



16

Microsorb C18 5 μm 100 \AA , 0-20% B over 20 min, 1 mL/min



20

Kromasil C18 5 μm 100 \AA , 5-20% B over 20 min, 1 mL/min

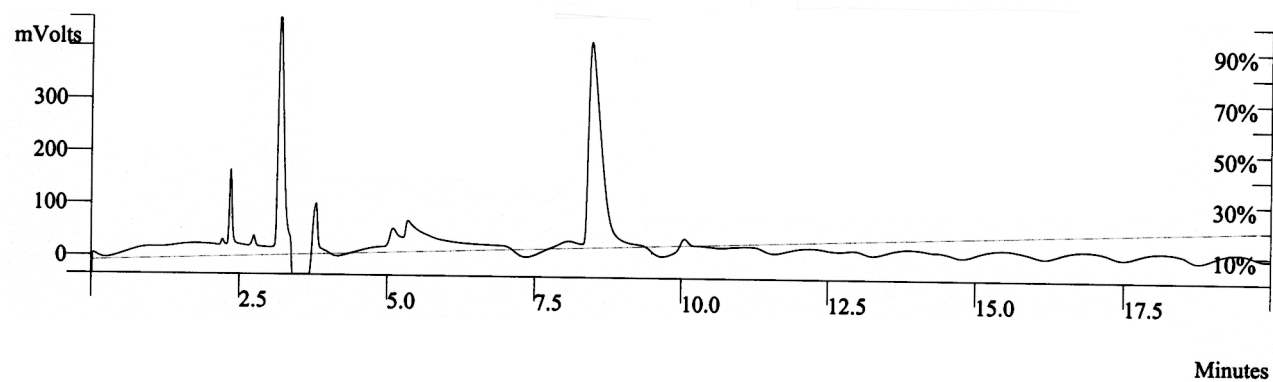


Figure S22. HPLC chromatogram of **17**

