

Supplementary Information

Exploitation of Sugar Ring Flipping for a Hinge-Type Tether Assisting a [2+2] Cycloaddition

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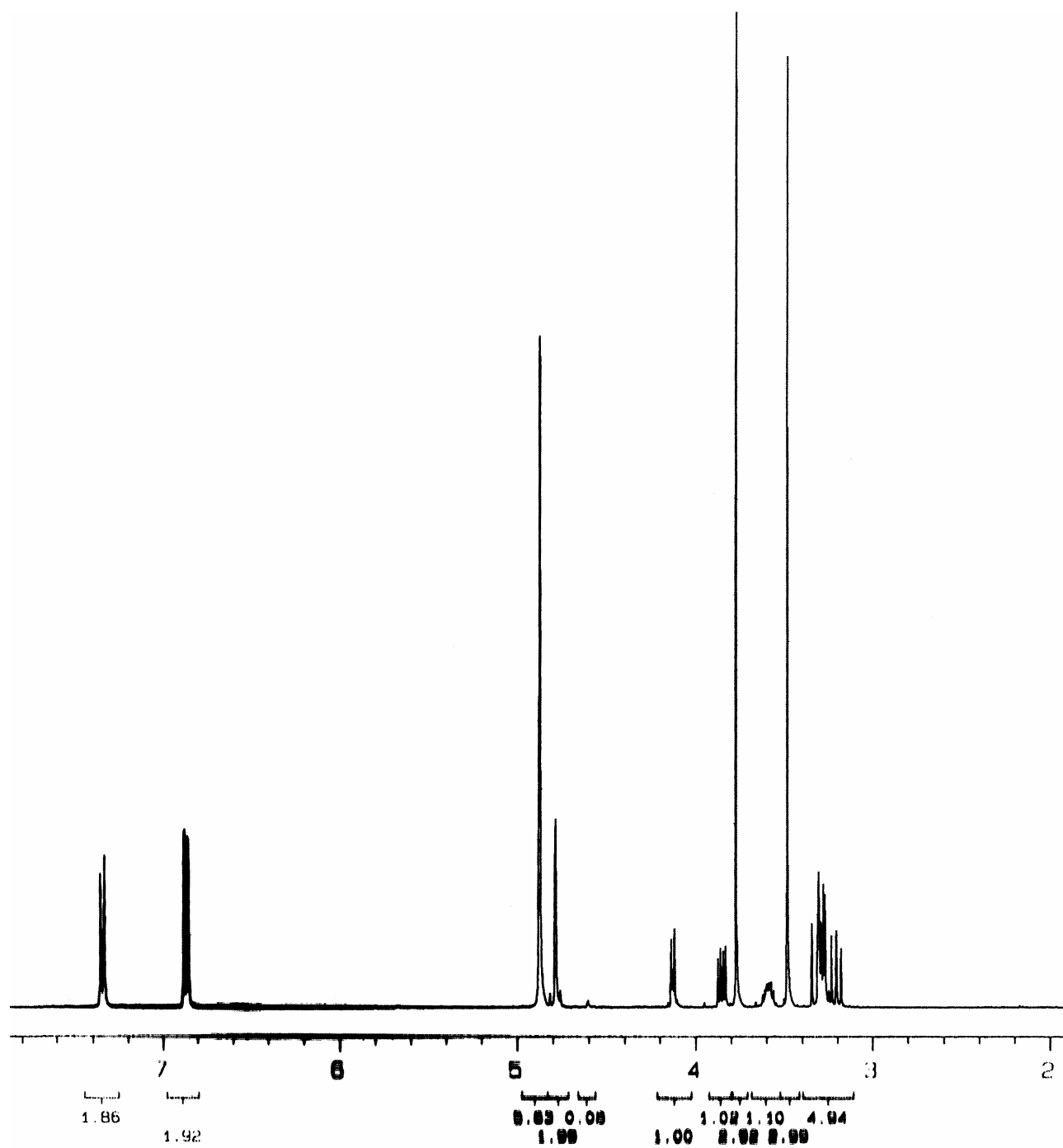


Figure S1. ¹H NMR of methyl 3-*O*-*p*-methoxybenzyl-β-*D*-xylopyranoside (**2**).

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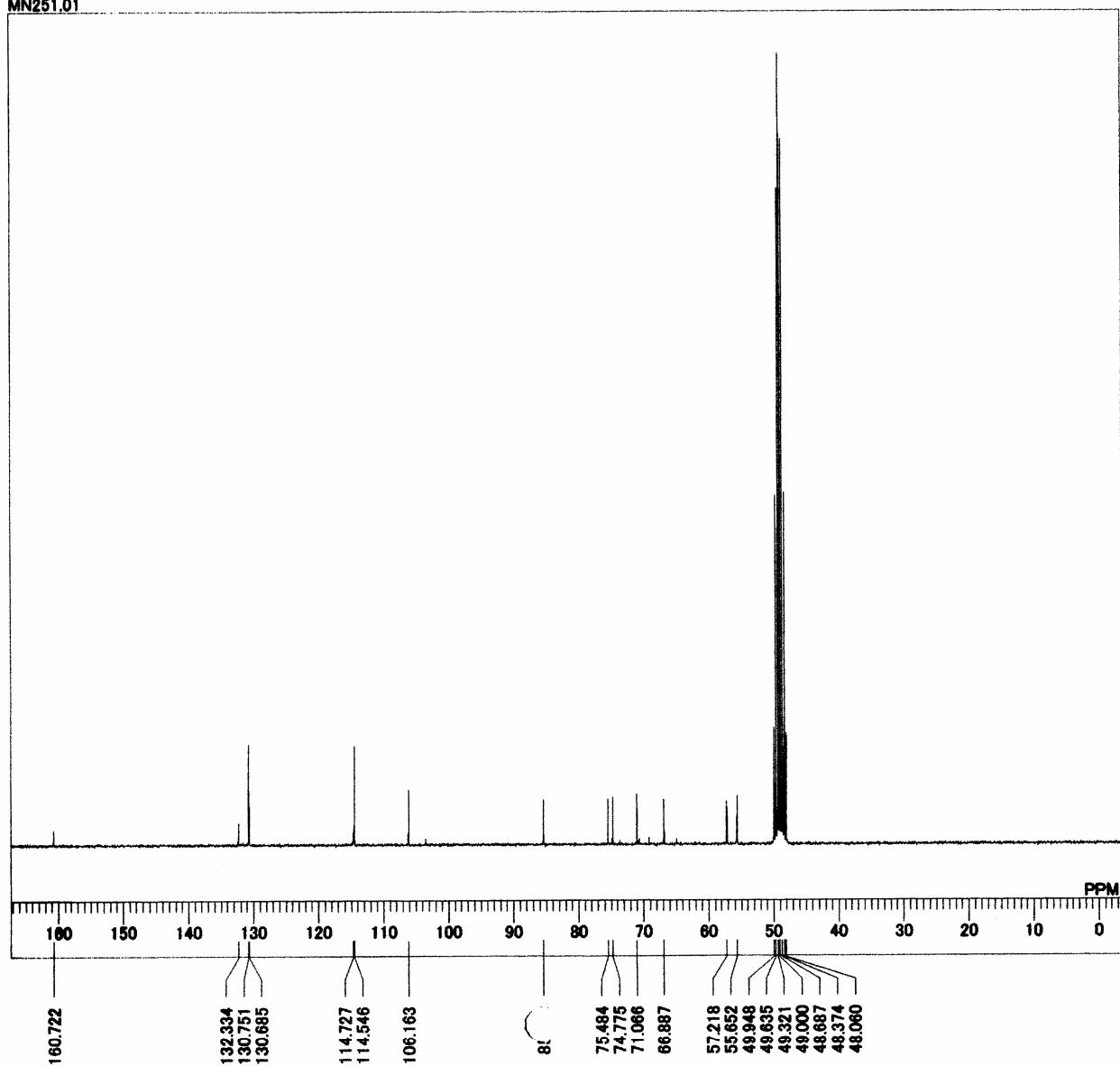


Figure S2. ^{13}C NMR of methyl 3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**2**).

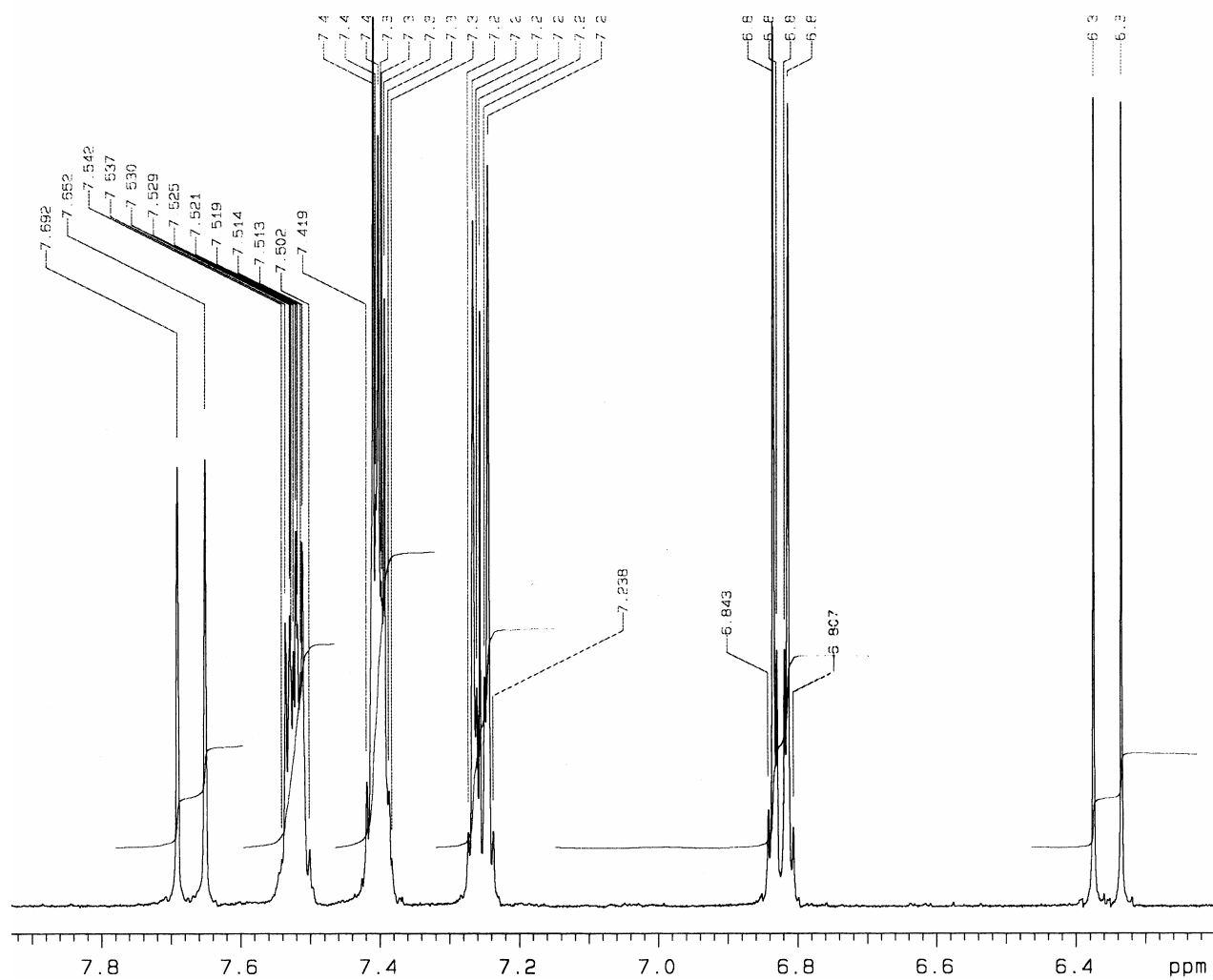


Figure S3. ${}^1\text{H}$ NMR of methyl 4-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**3**)-1.

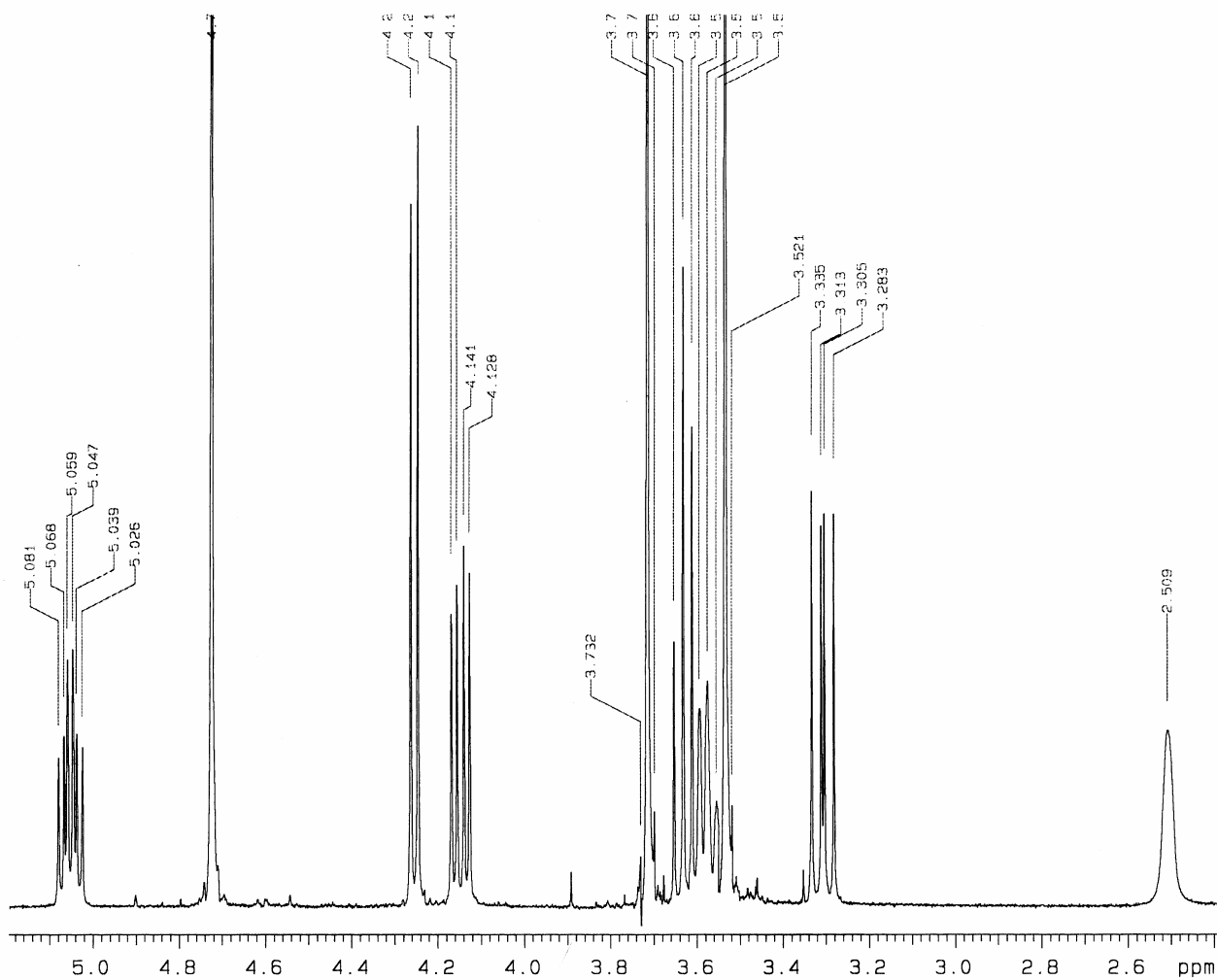


Figure S4. ¹H NMR of methyl 4-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl-β-*D*-xylopyranoside (**3**)-2.

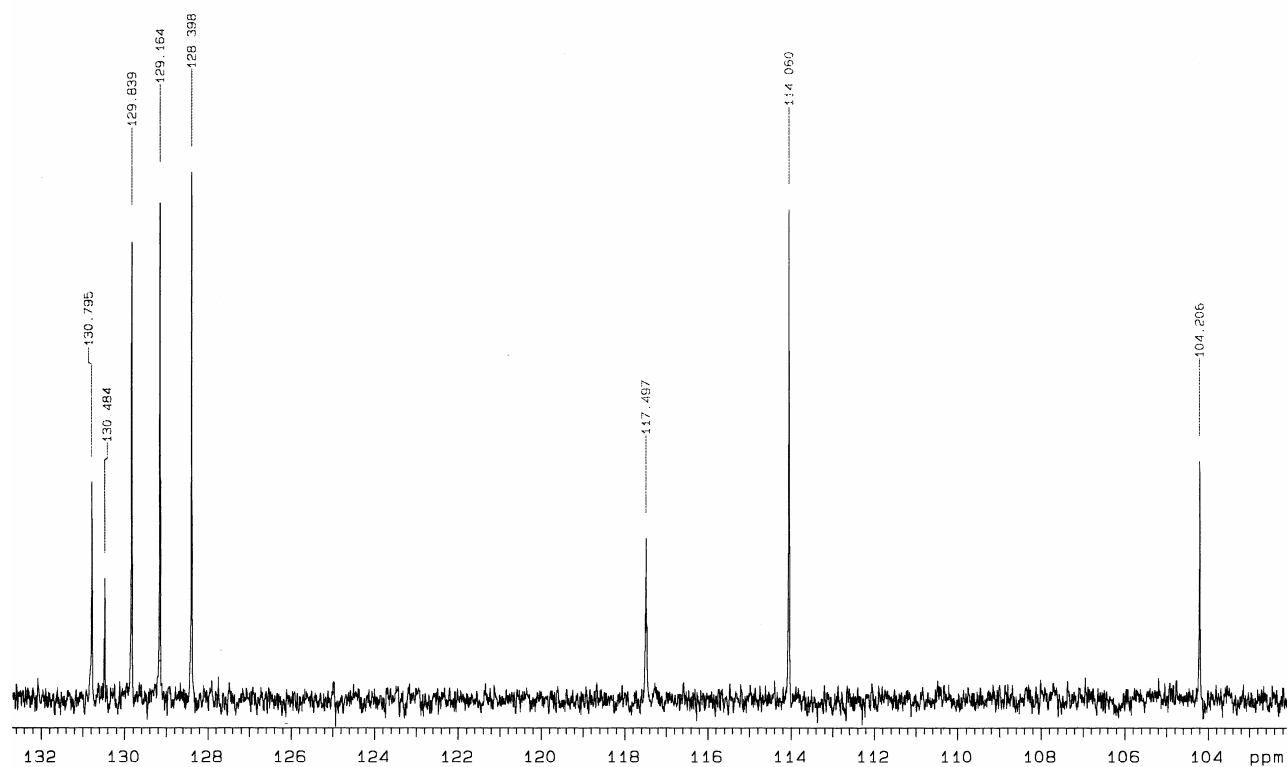


Figure S5. ^{13}C NMR of methyl 4-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**3**)-1.

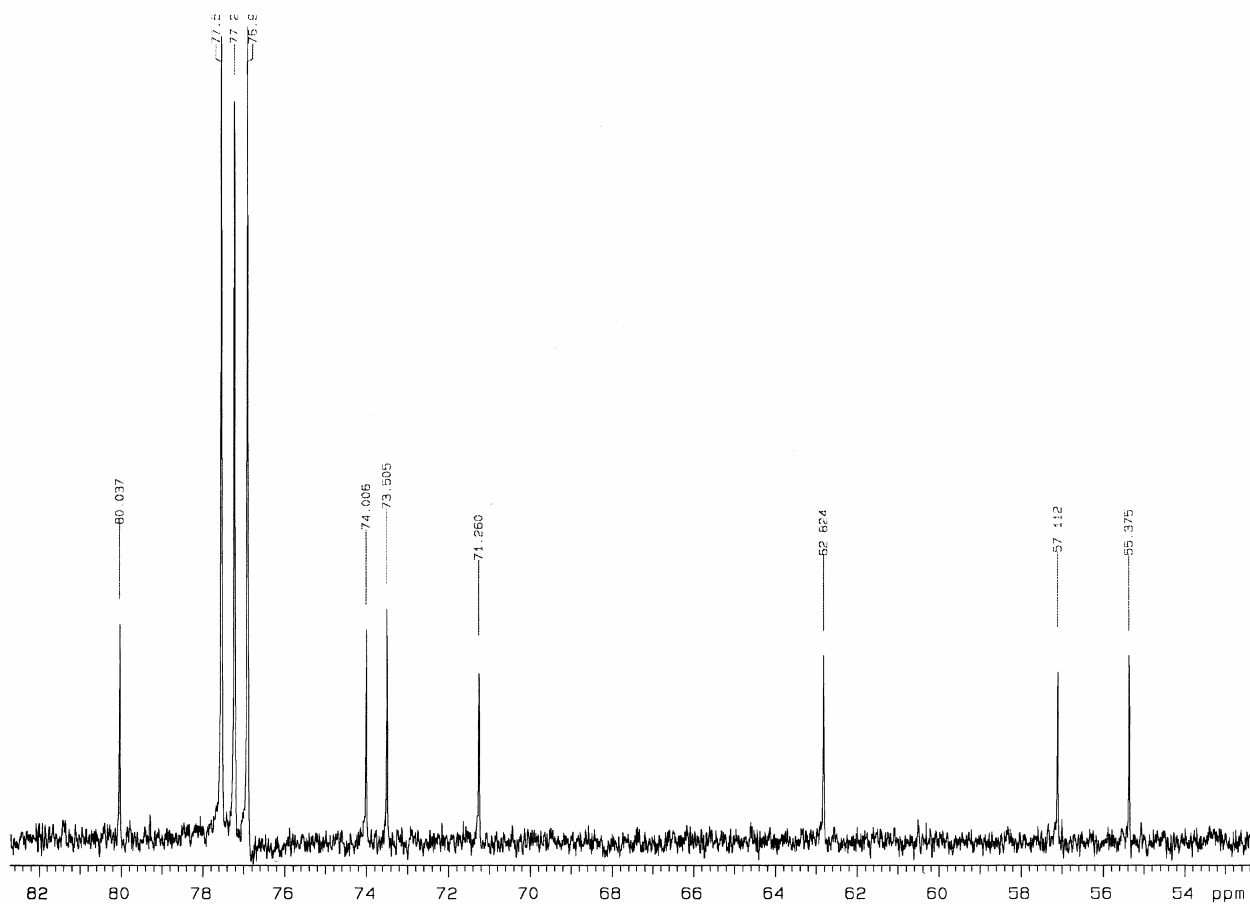


Figure S6. ^{13}C NMR of methyl 4-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**3**)-2.

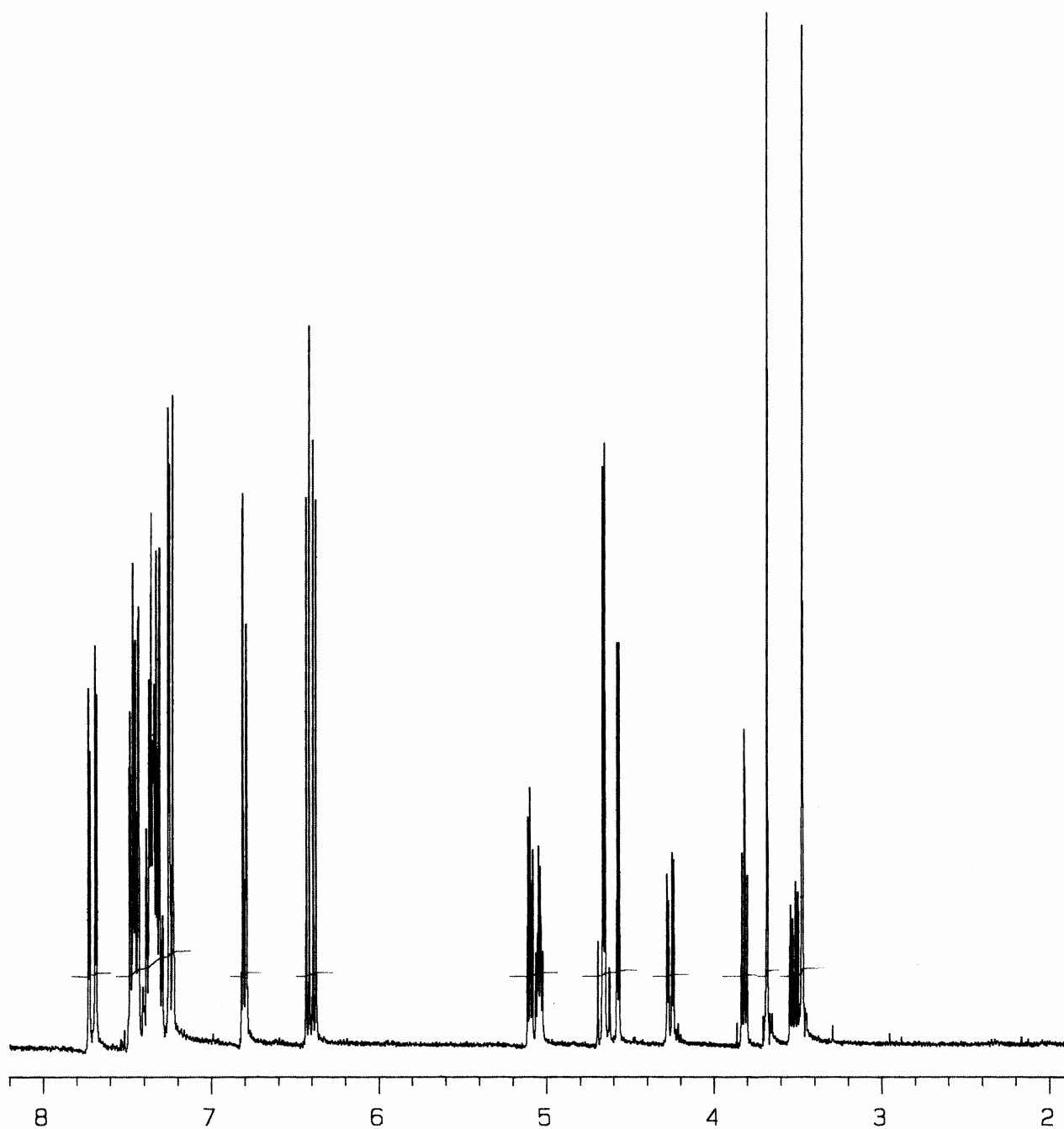


Figure S7. ^1H NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**4**).

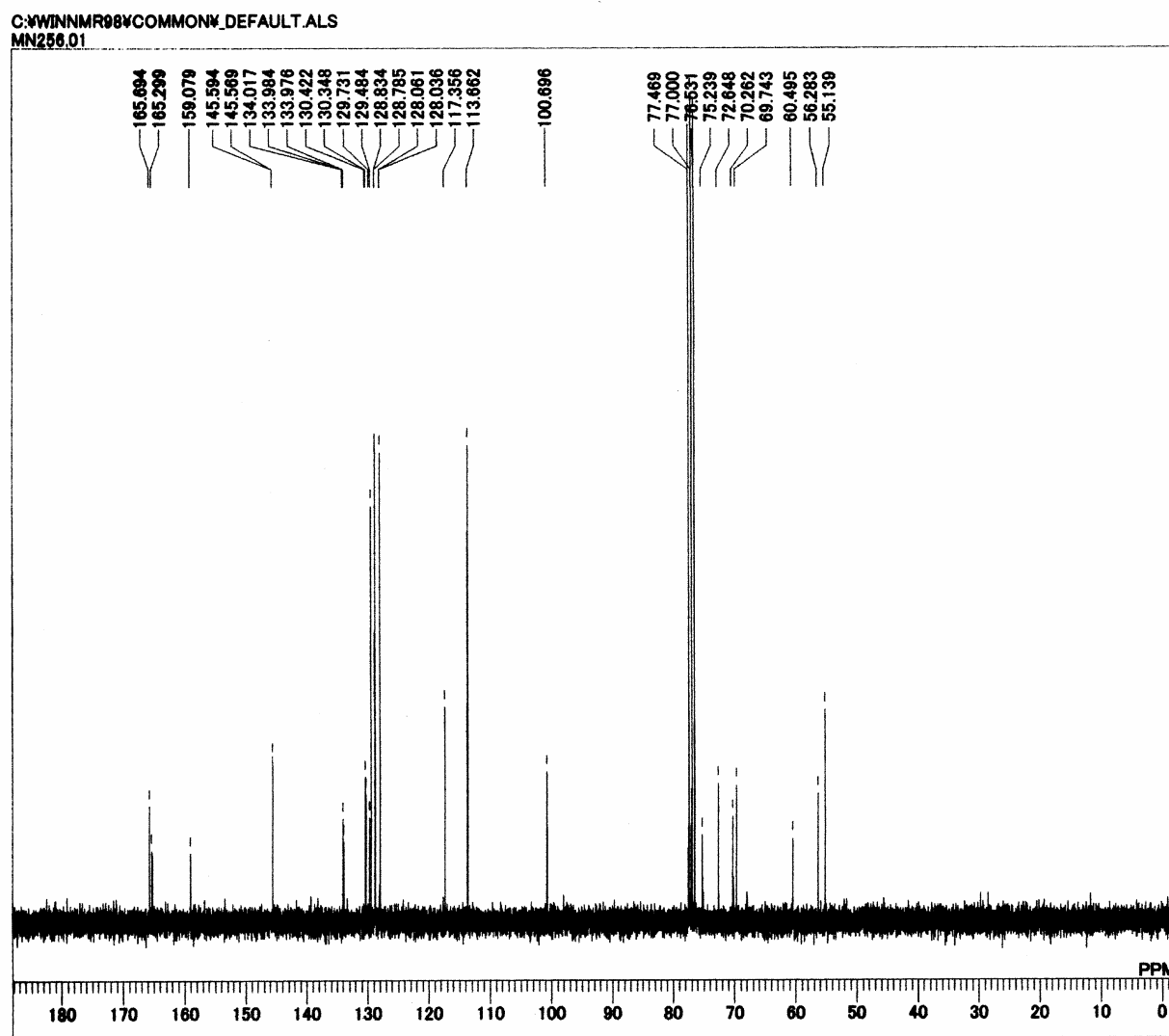


Figure S8. ^{13}C NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**4**).

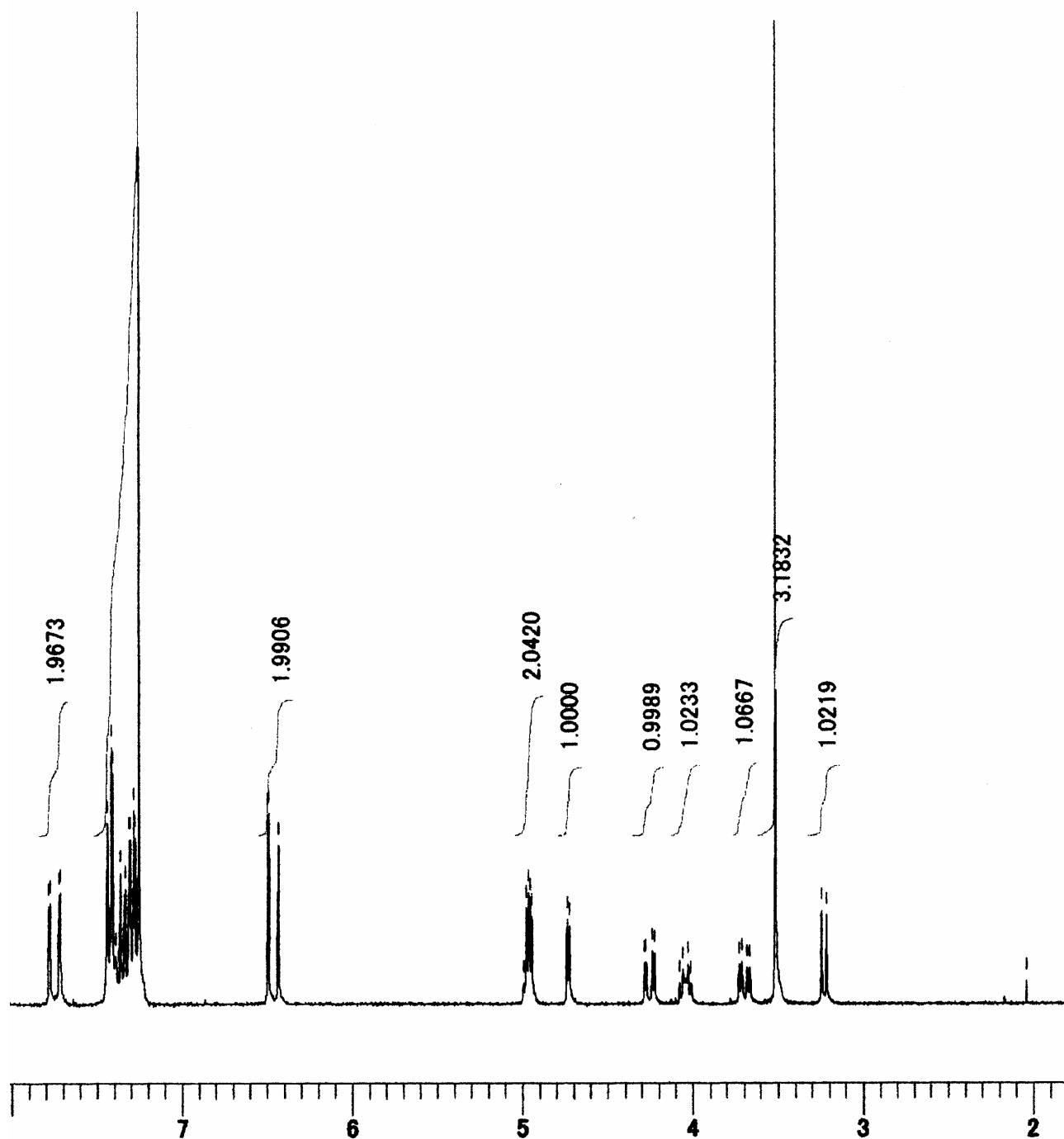


Figure S9. ¹H NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl-β-D-xylopyranoside (**5**).

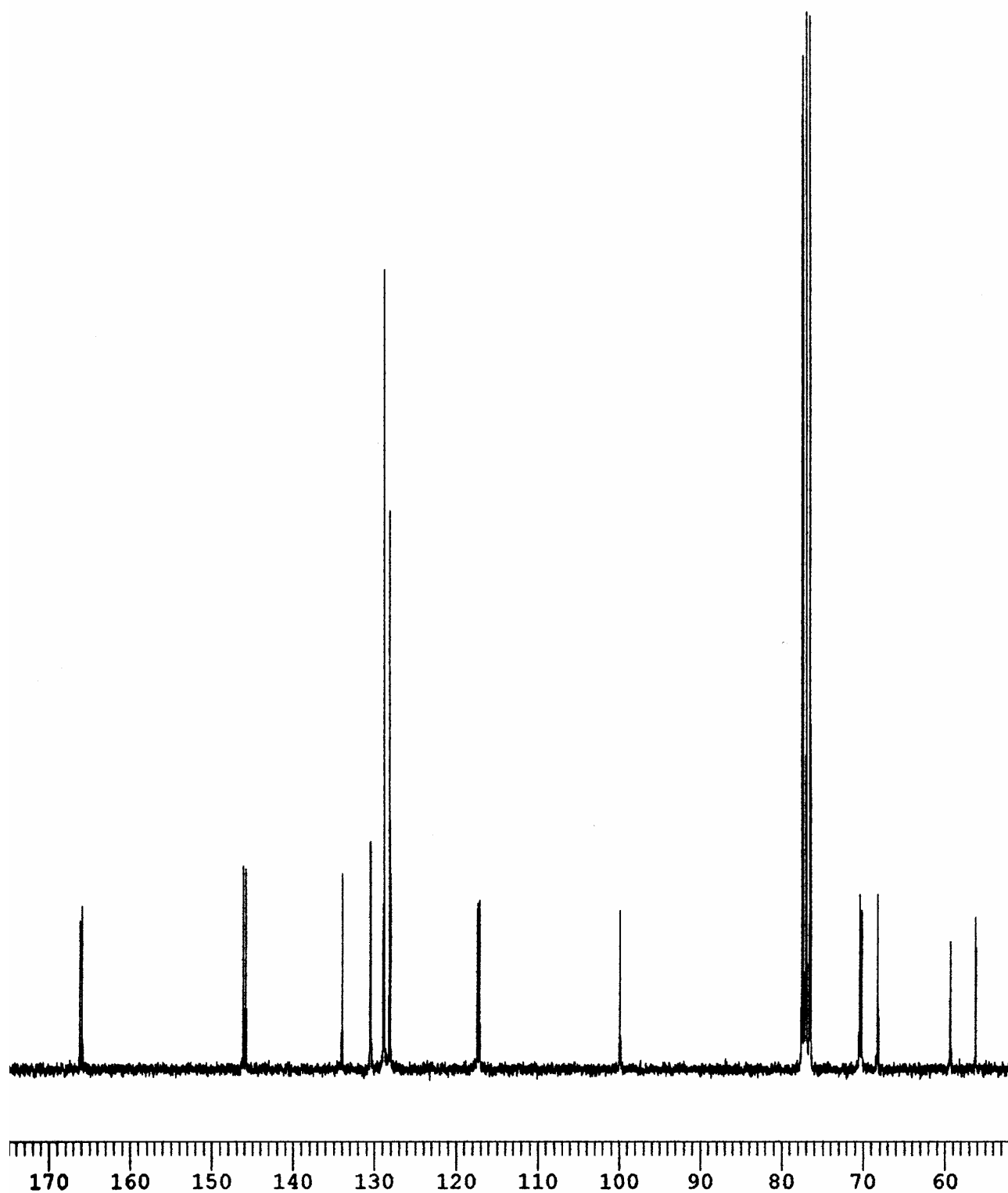


Figure S10. ^{13}C NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl- β -D-xylopyranoside (**5**).

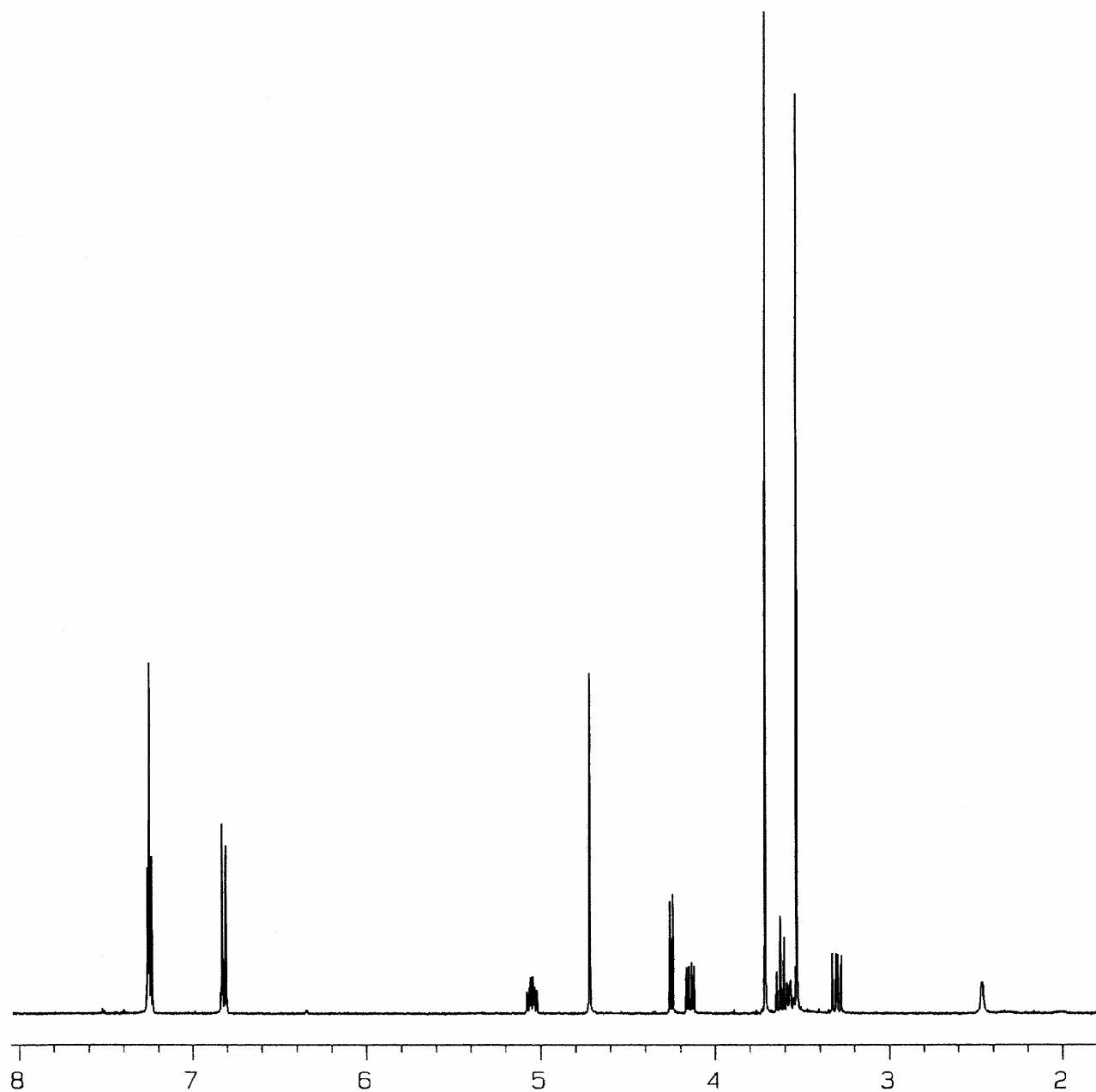


Figure S11. ^1H NMR of methyl 4-*O*-(*E*)-cinnamoyl-*d*₇-3-*O*-*p*-methoxybenzyl- β -*D*-xylopyranoside (**3d₇**).

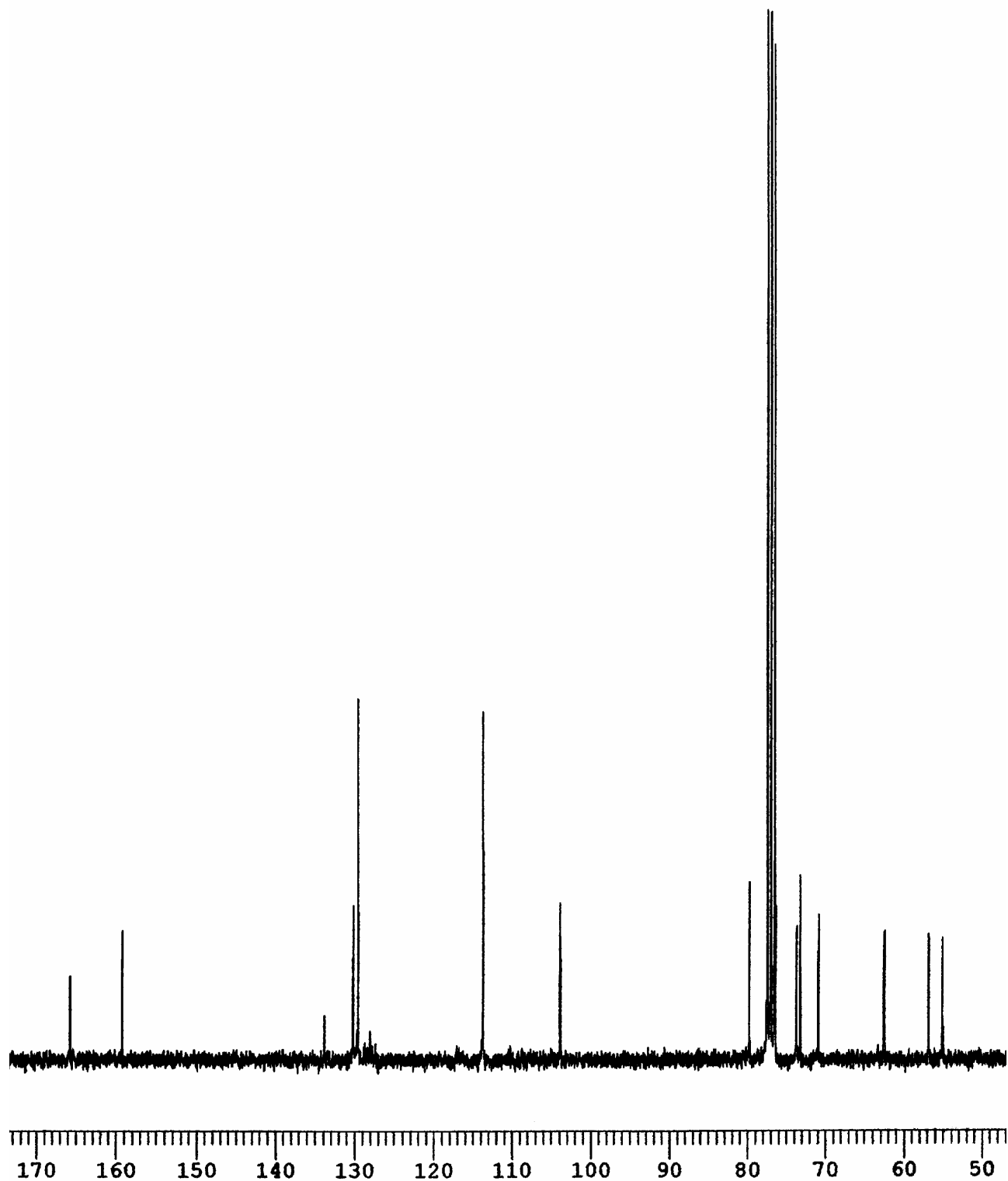


Figure S12. ^{13}C NMR of methyl 4-*O*-(*E*)-cinnamoyl-*d*₇-3-*O*-*p*-methoxybenzyl- β -*D*-xylopyranoside (**3d₇**).

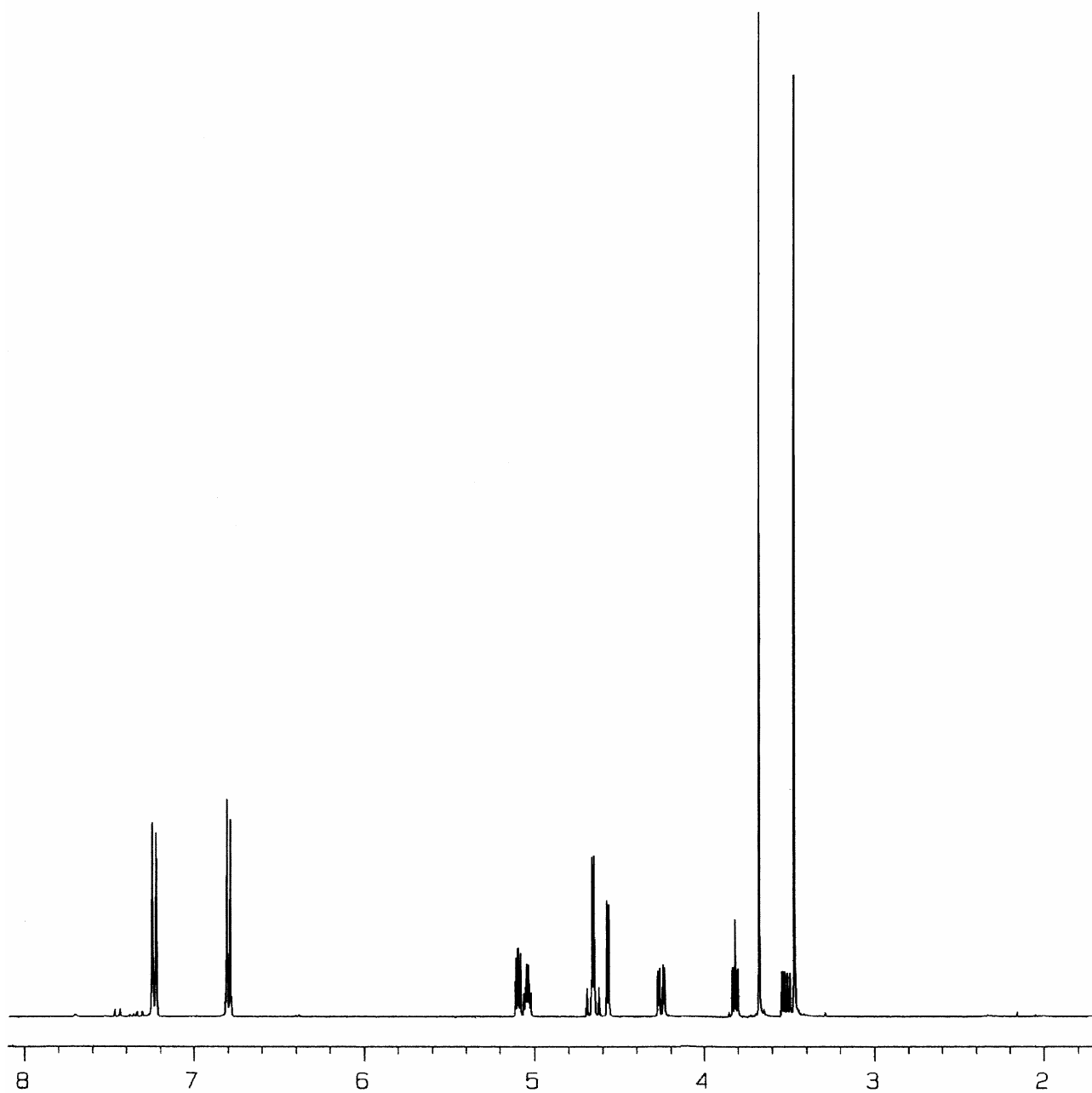


Figure S13. ^1H NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl-*d*₇-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**4d₁₄**).

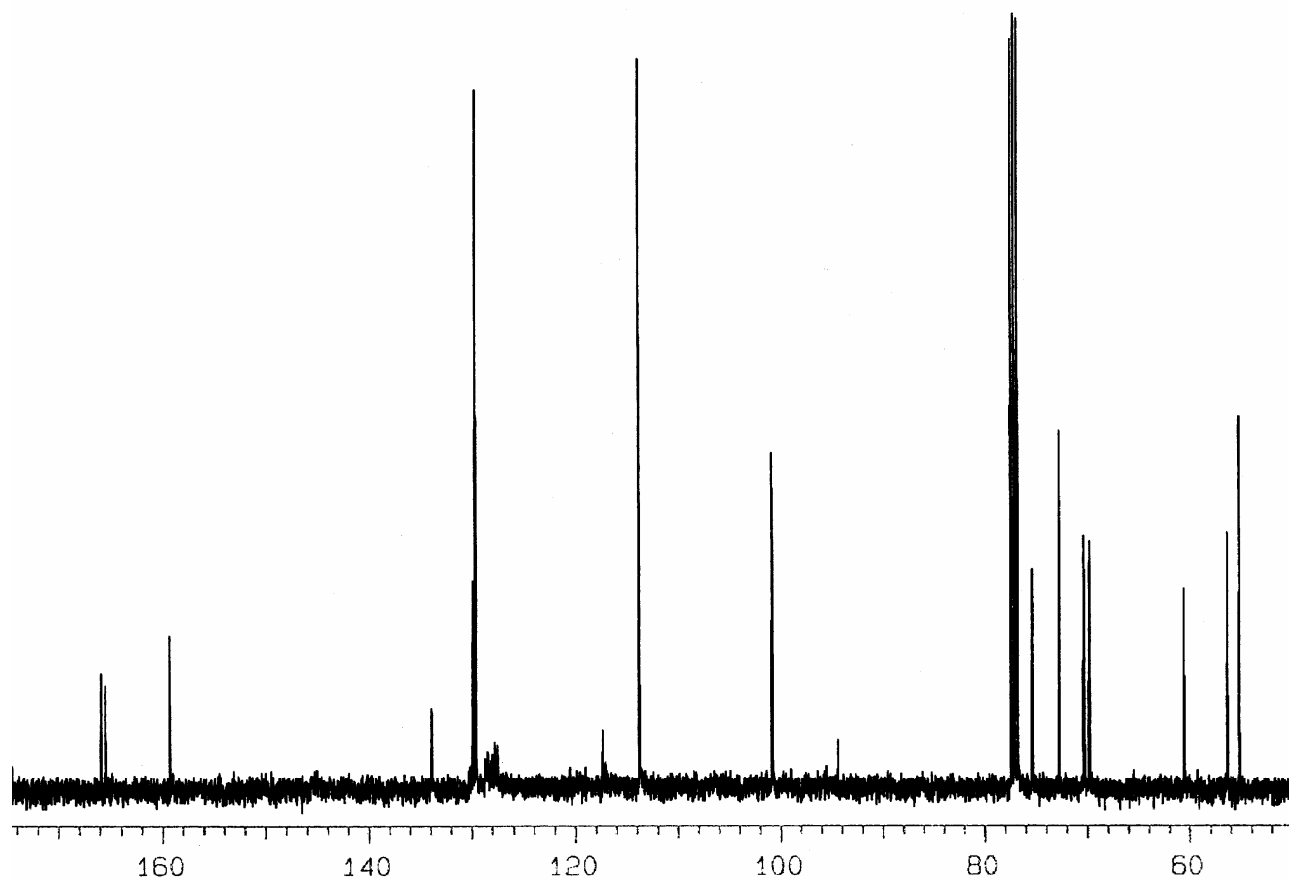


Figure S14. ^{13}C NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl-*d*₇-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**4d₁₄**).

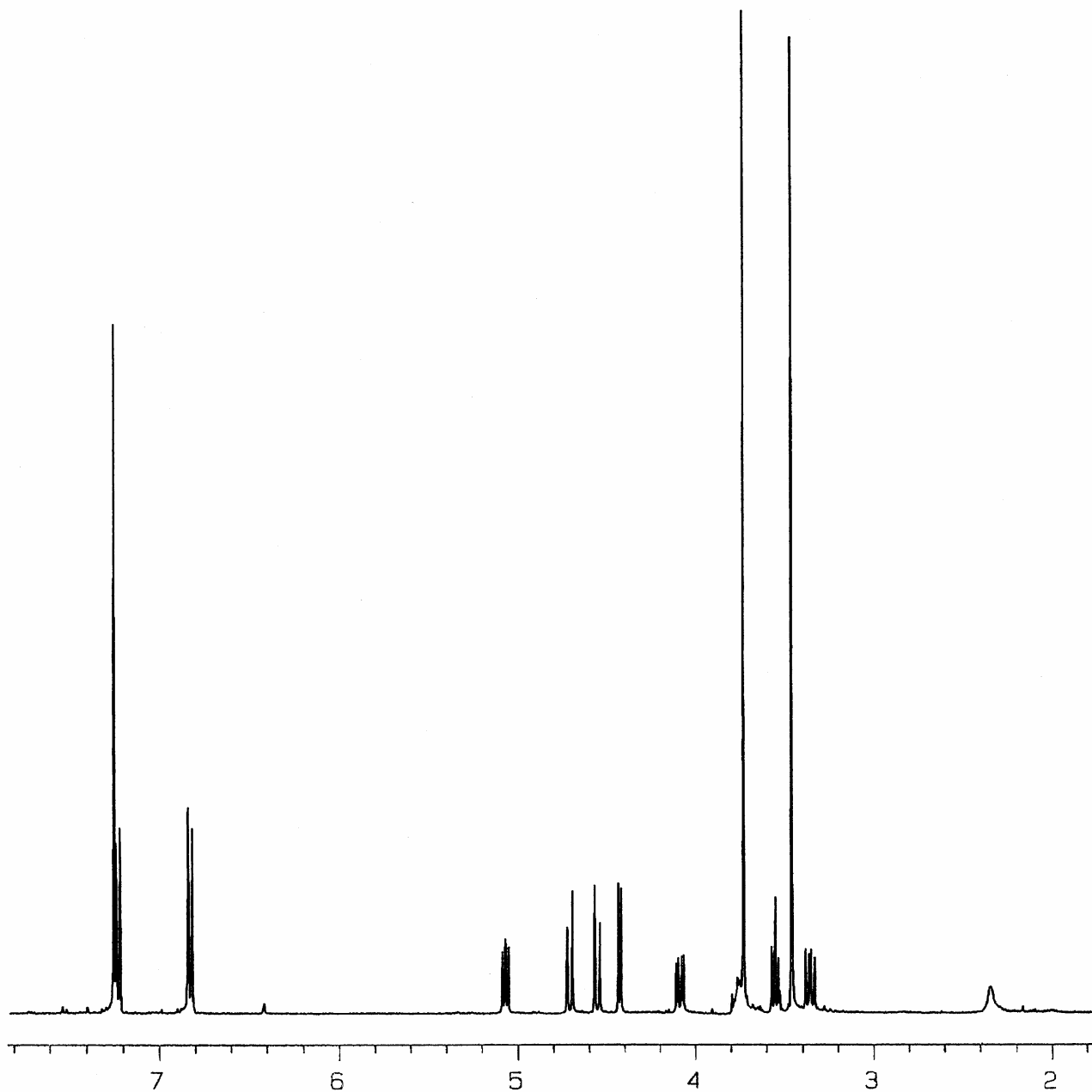


Figure S15. ^1H NMR of methyl 2-*O*-(*E*)-cinnamoyl-*d*₇-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**6**).

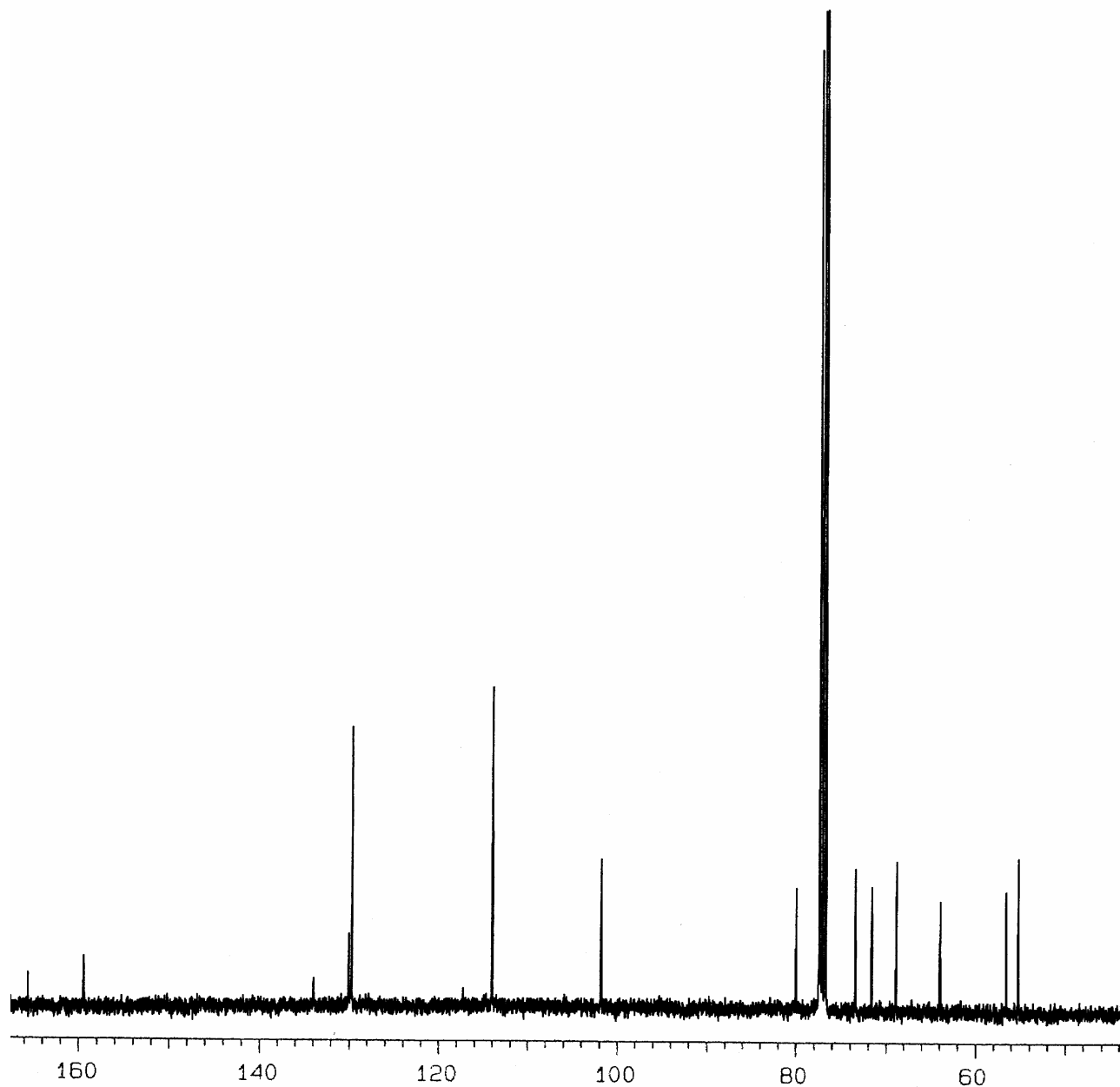


Figure S16. ^{13}C NMR of methyl 2-*O*-(*E*)-cinnamoyl-*d*-7-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**6**).

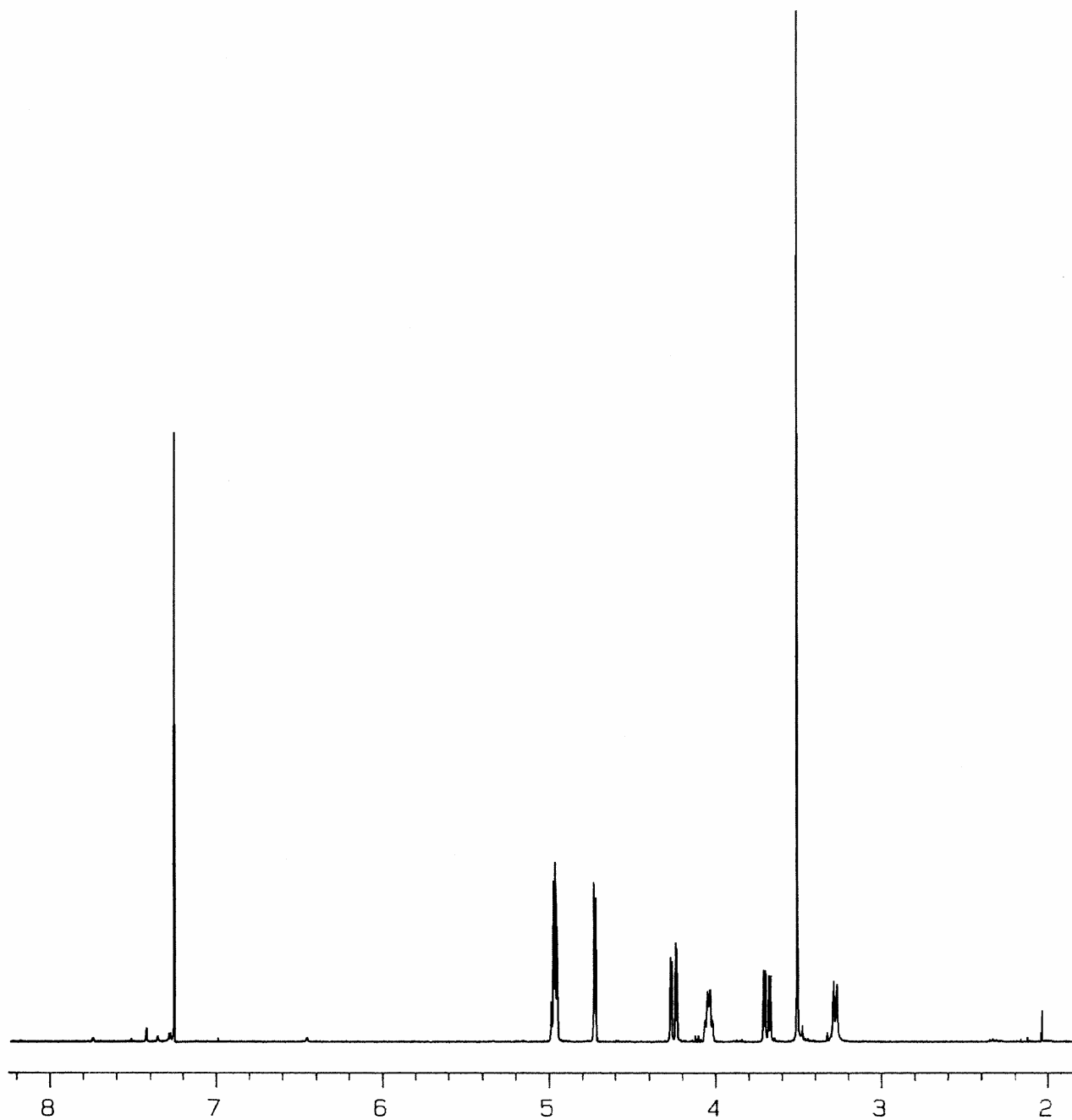


Figure S17. ¹H NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl-*d*₇-β-D-xylopyranoside (**5d₁₄**).

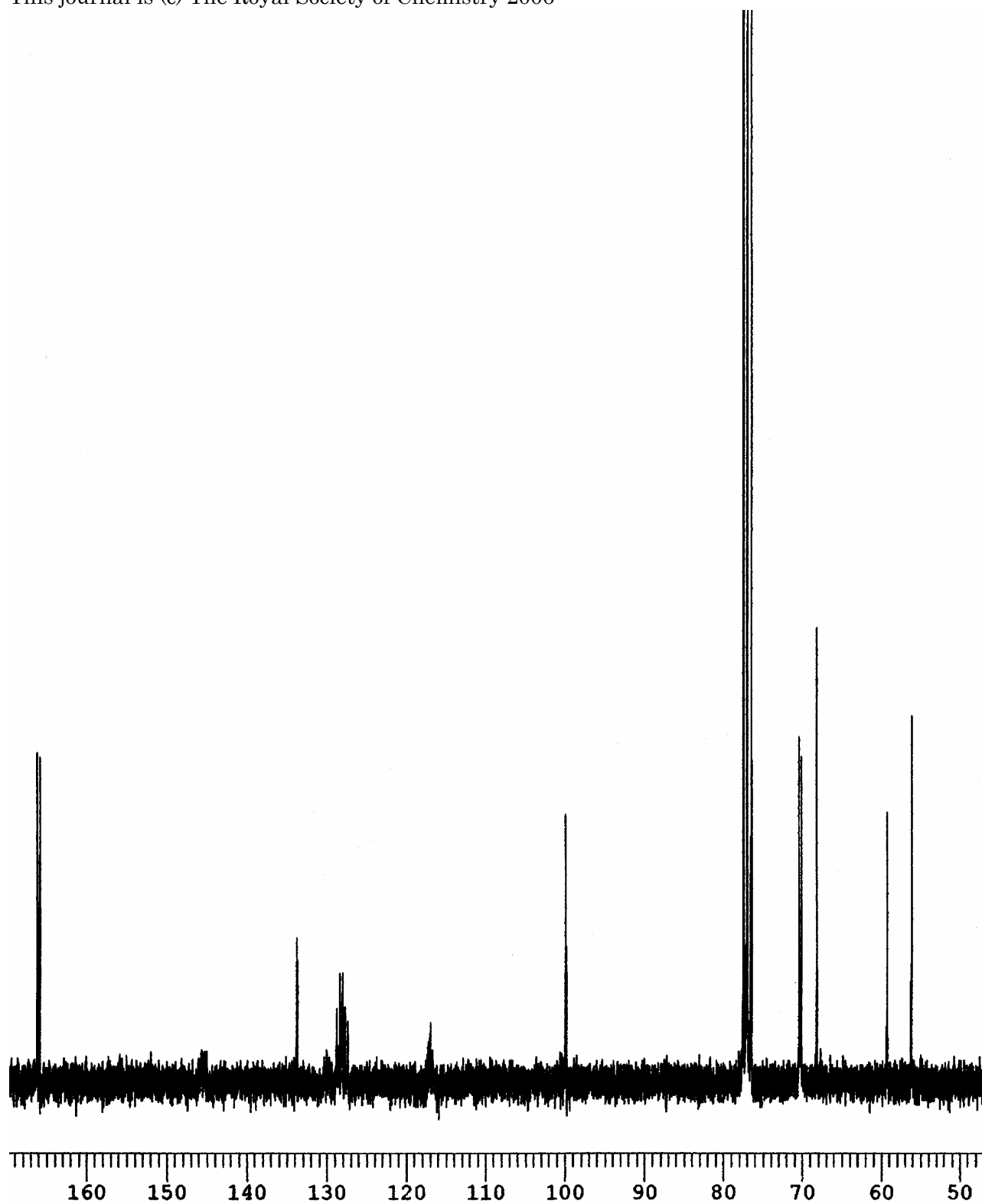


Figure S18. ^{13}C NMR of methyl 2,4-di-*O*-(*E*)-cinnamoyl- d_7 - β -D-xylopyranoside (**5d₁₄**).

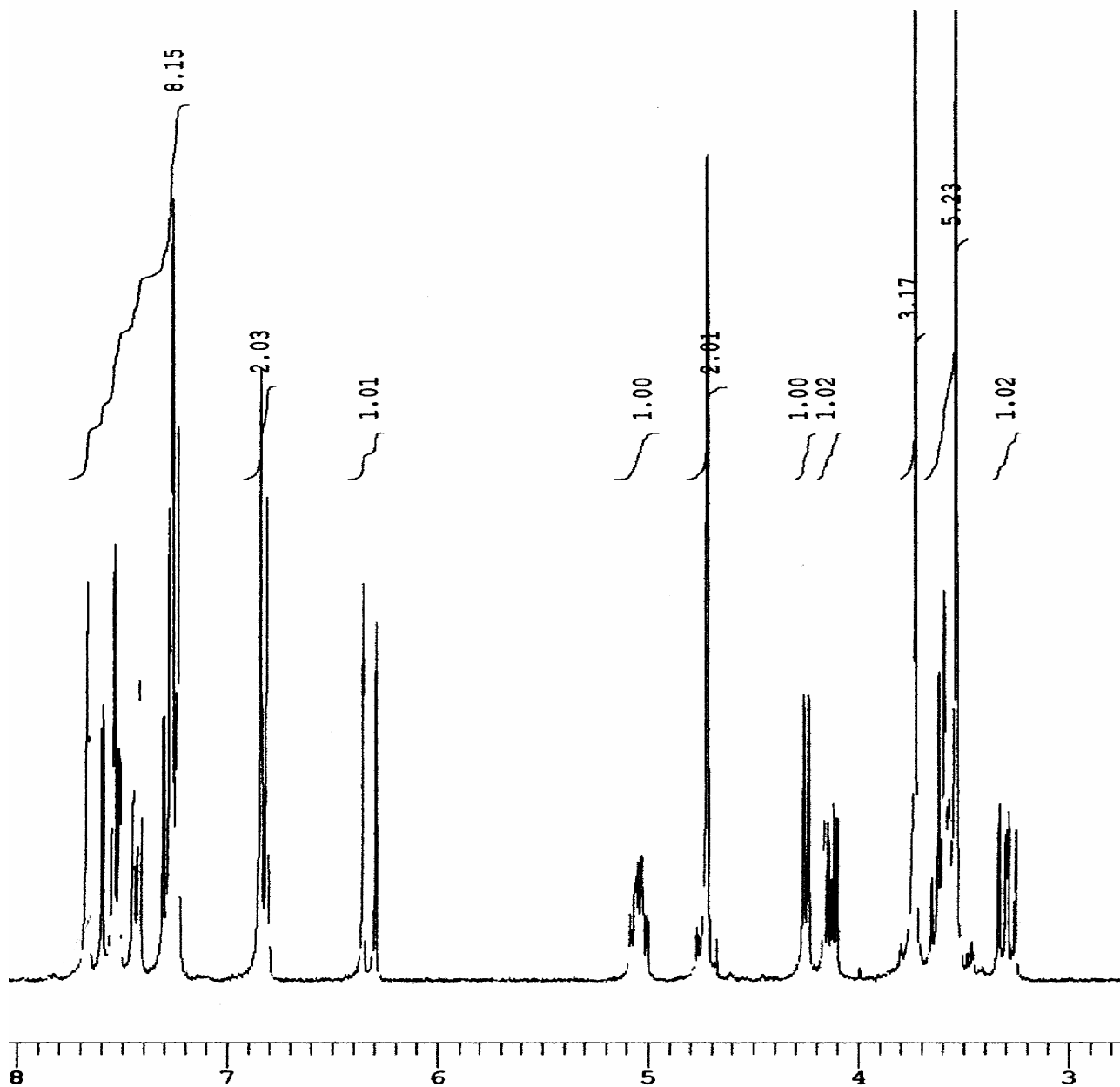


Figure S19. ¹H NMR of methyl 4-*O*-(*E*)-3-bromocinnamoyl-3-*O*-*p*-methoxybenzyl-β-D-xylopyranoside (**3Br**).

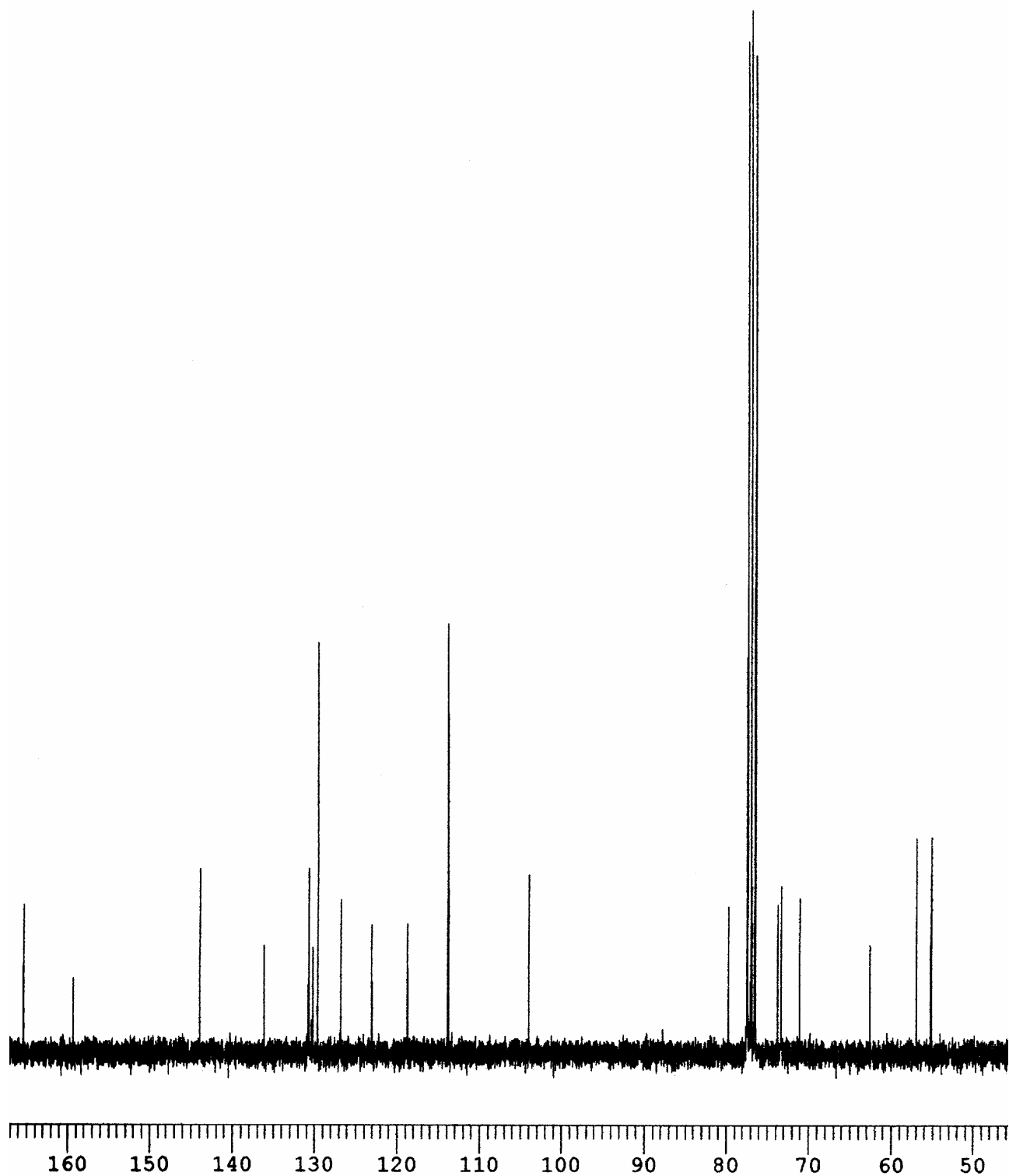


Figure S20. ^{13}C NMR of methyl 4-*O*-(*E*)-3-bromocinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (**3Br**).

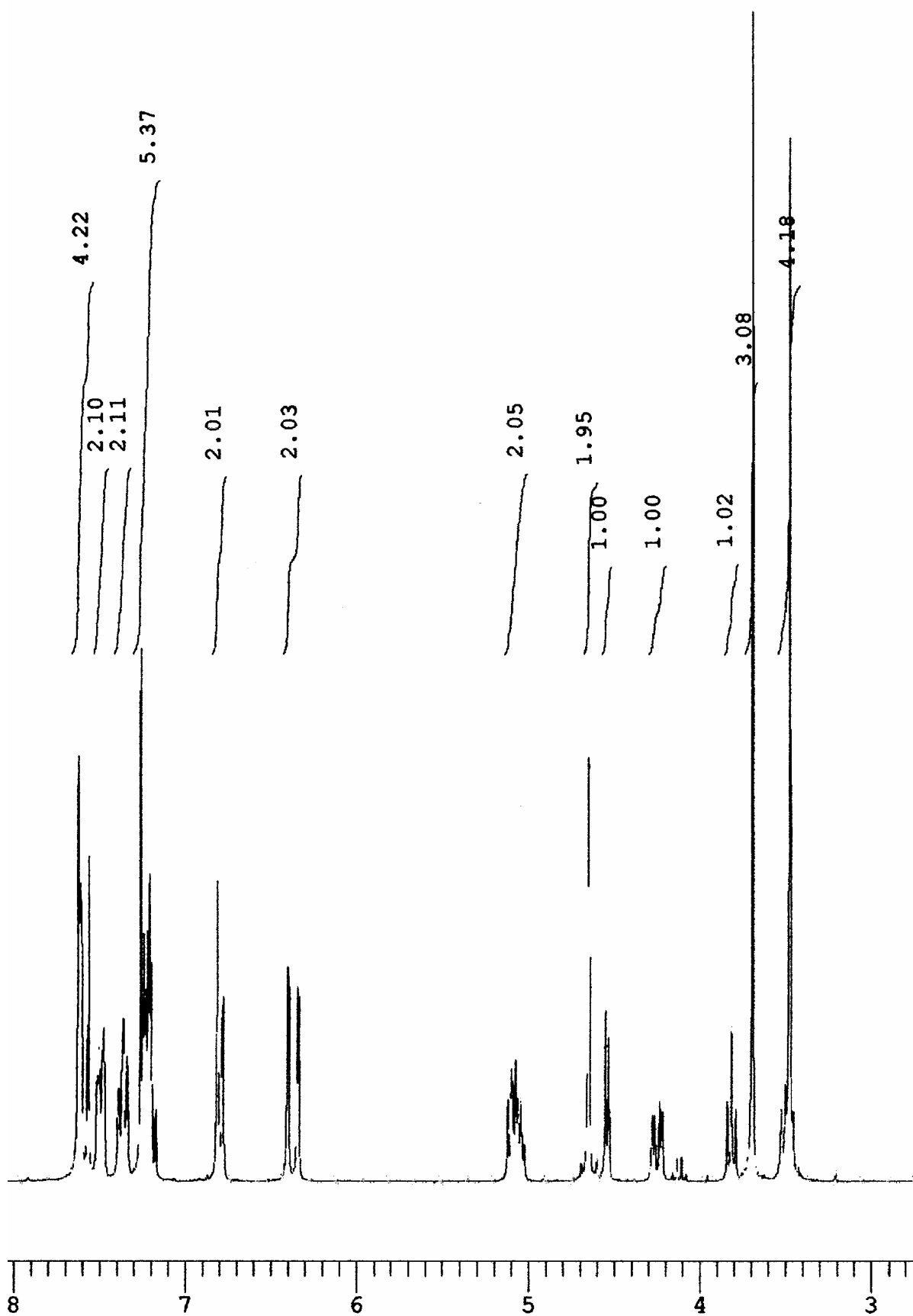


Figure S21. ¹H NMR of methyl 2,4-di-*O*-(*E*)-3-bromocinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside

(4Br).

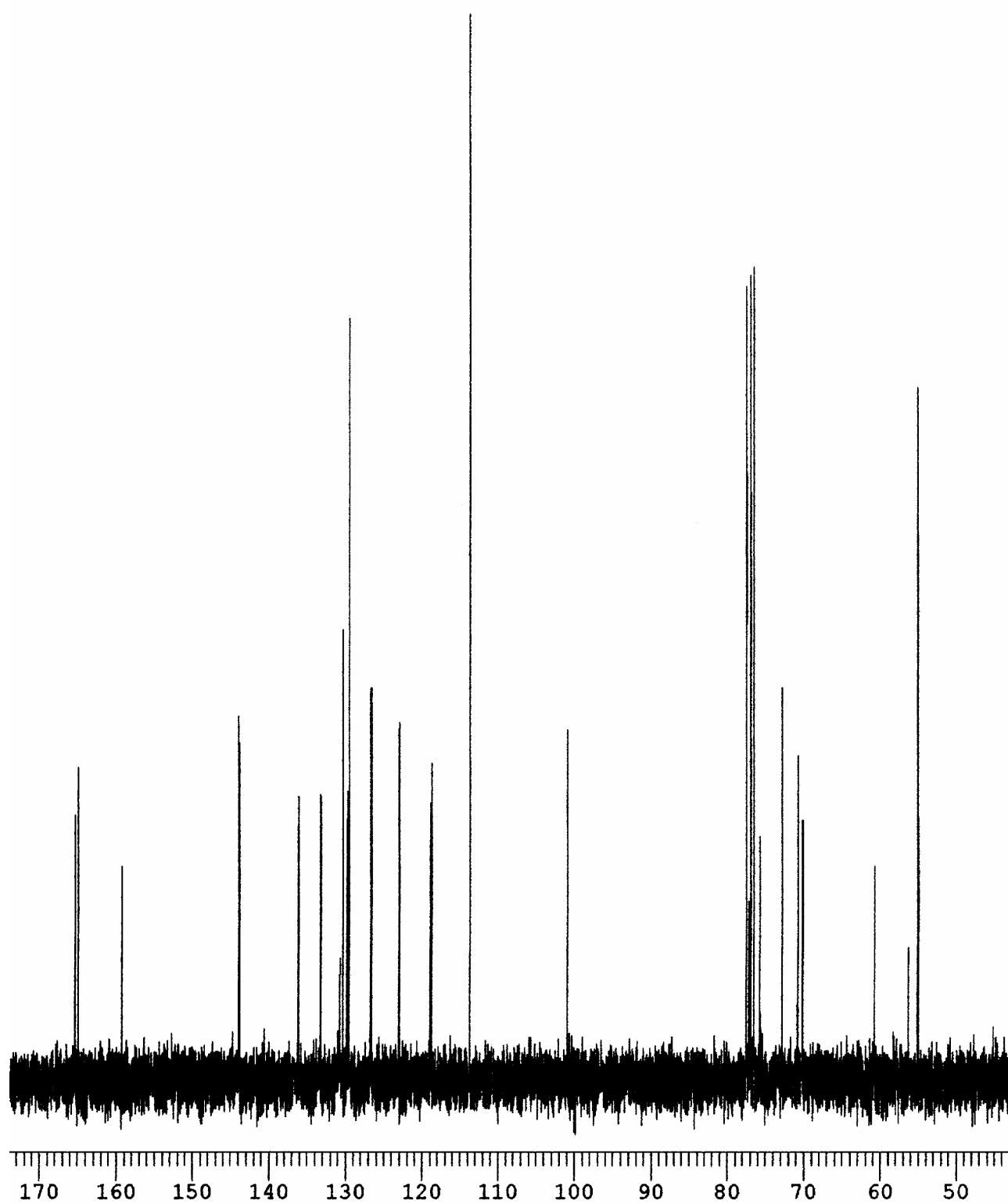


Figure S22. ^{13}C NMR of methyl 2,4-di-*O*-(*E*)-3-bromocinnamoyl-3-*O*-*p*-methoxybenzyl- β -D-xylopyranoside (4Br).

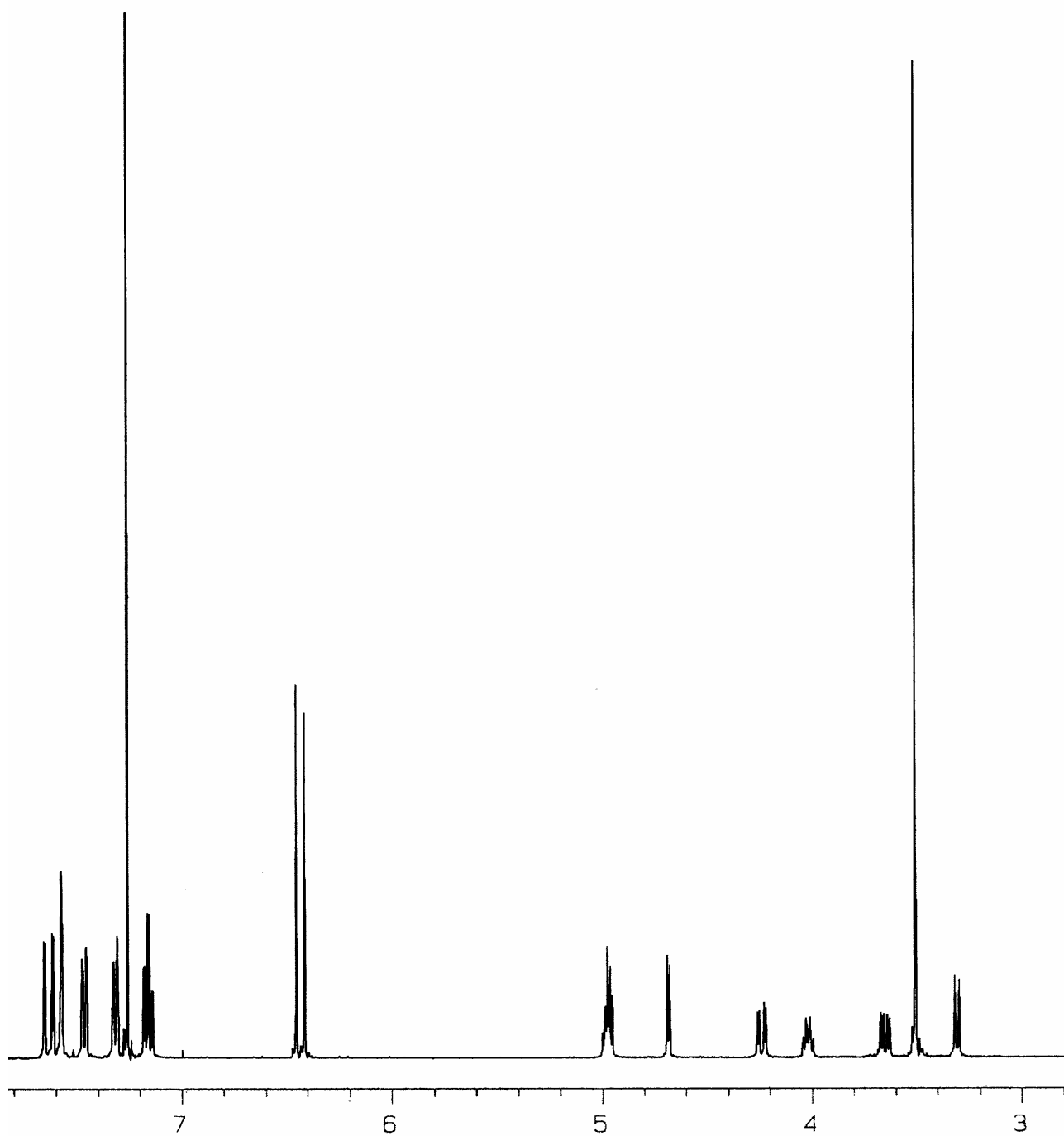


Figure S23. ^1H NMR of methyl 2,4-di-*O*-(*E*)-3-bromocinnamoyl- β -D-xylopyranoside (**5Br**).

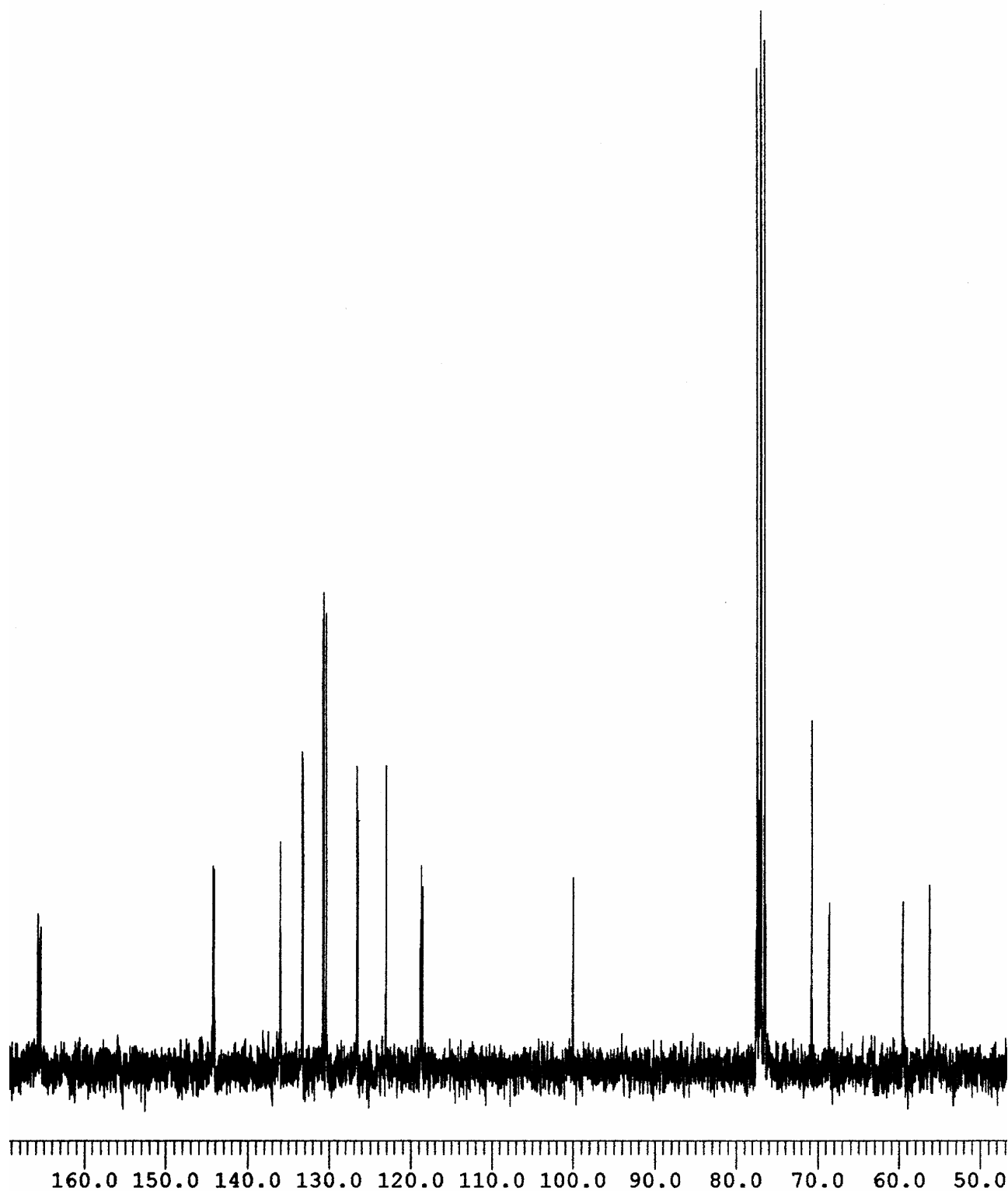


Figure S24. ^{13}C NMR of methyl 2,4-di-*O*-(*E*)-3-bromocinnamoyl- β -D-xylopyranoside (**5Br**).

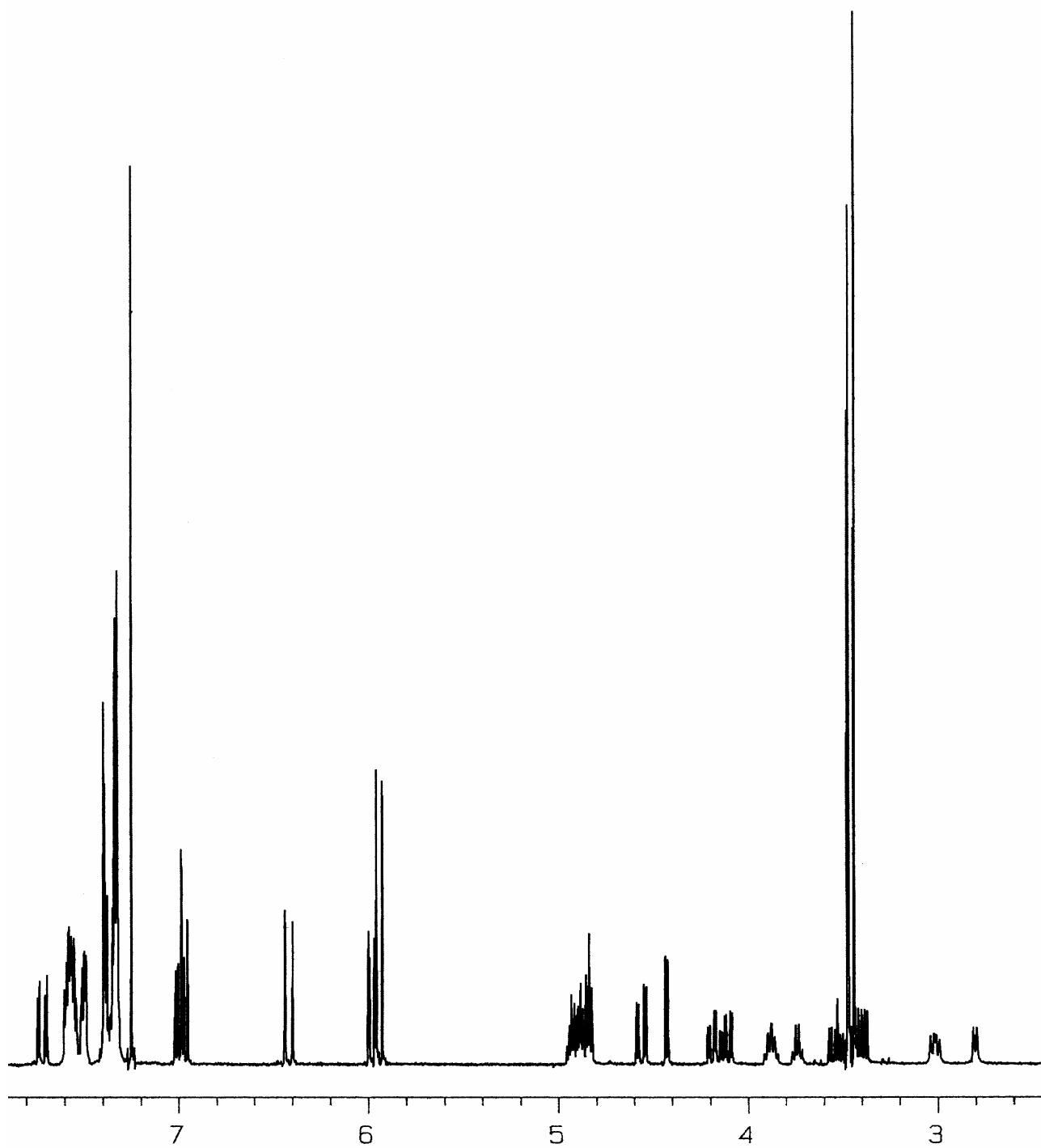


Figure S25. ^1H NMR for the mixture of **5**_{trans-cis}, **5**_{trans-cis}, and **5**_{trans-cis} (**Fr2**).

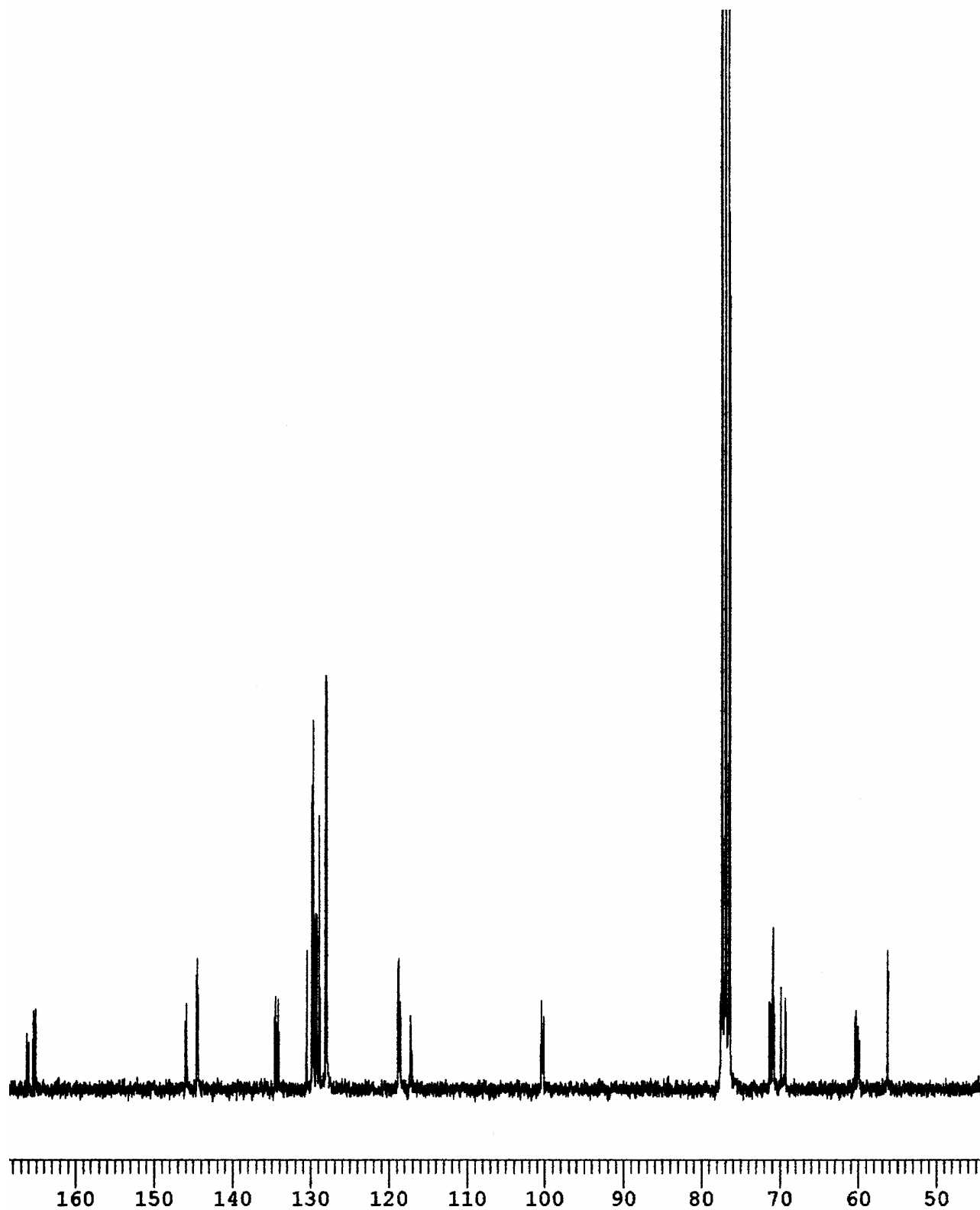


Figure S26. ^{13}C NMR for the mixture of **5**_{trans-cis}, **5**_{trans-cis}, and **5**_{trans-cis} (**Fr2**).

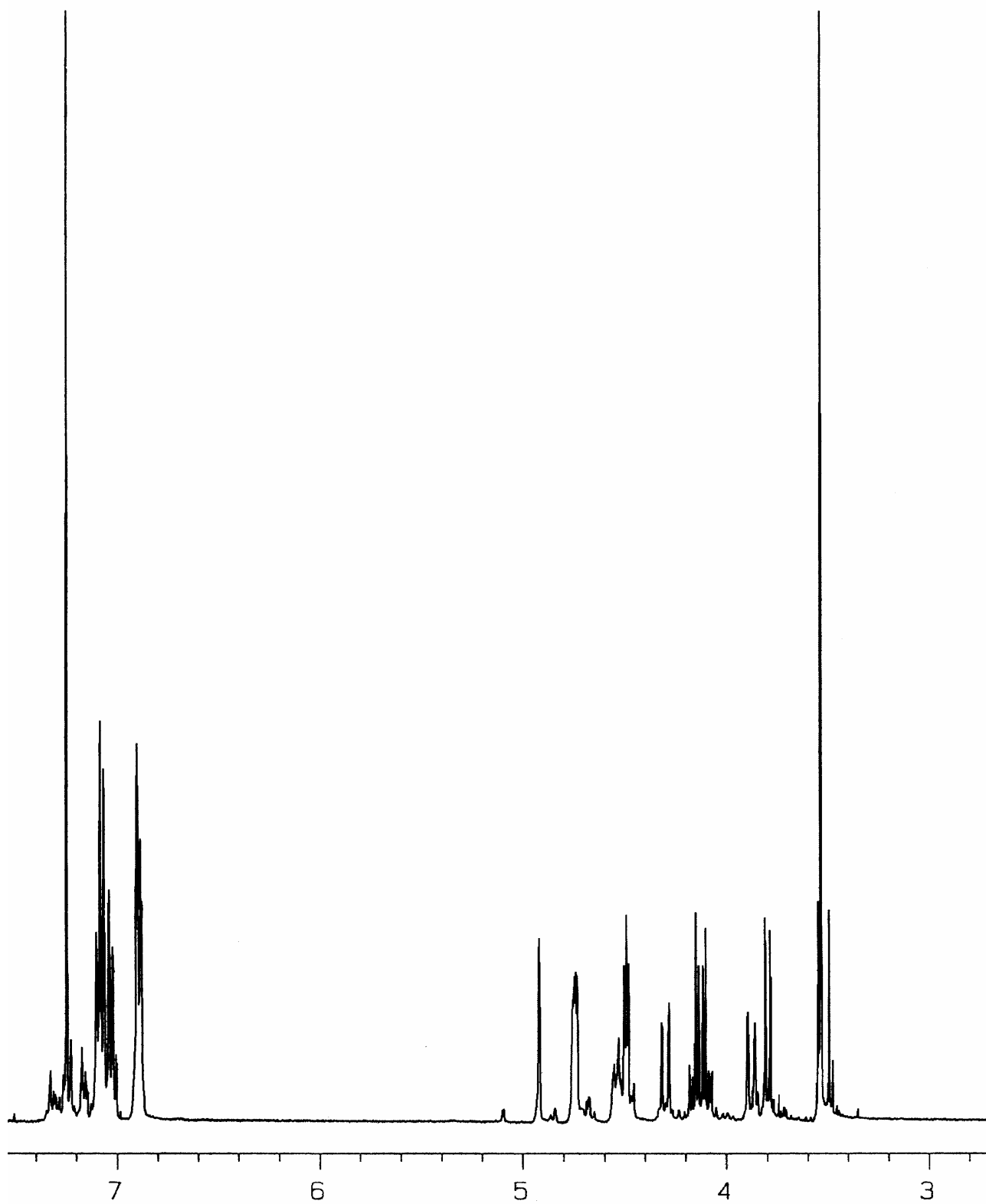


Figure S27. ^1H NMR of methyl β -D-xylopyranoside-2,4- β -truxinate (**7A**).

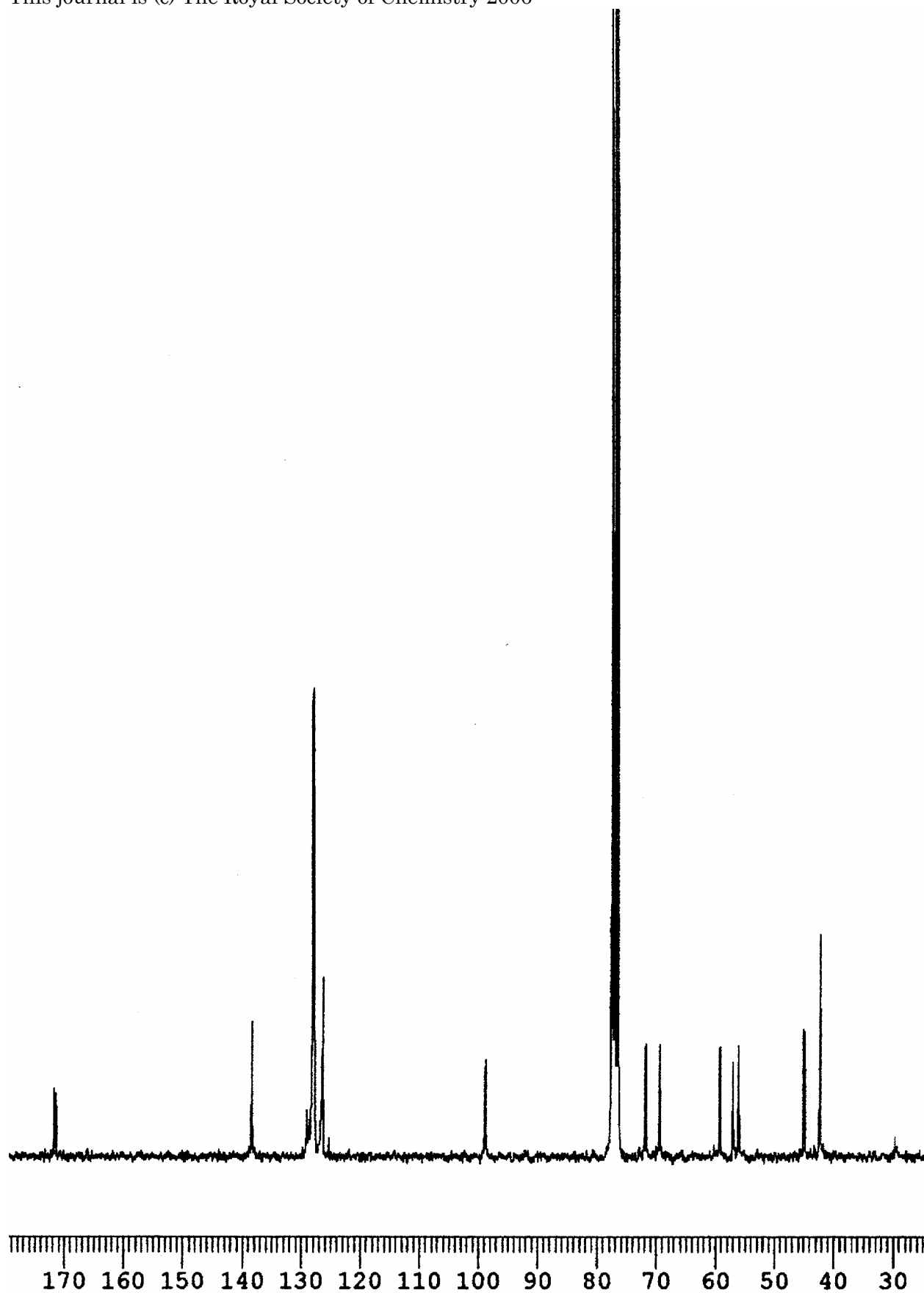


Figure S28. ^{13}C NMR of methyl β -D-xylopyranoside-2,4- β -truxinate (**7A**).

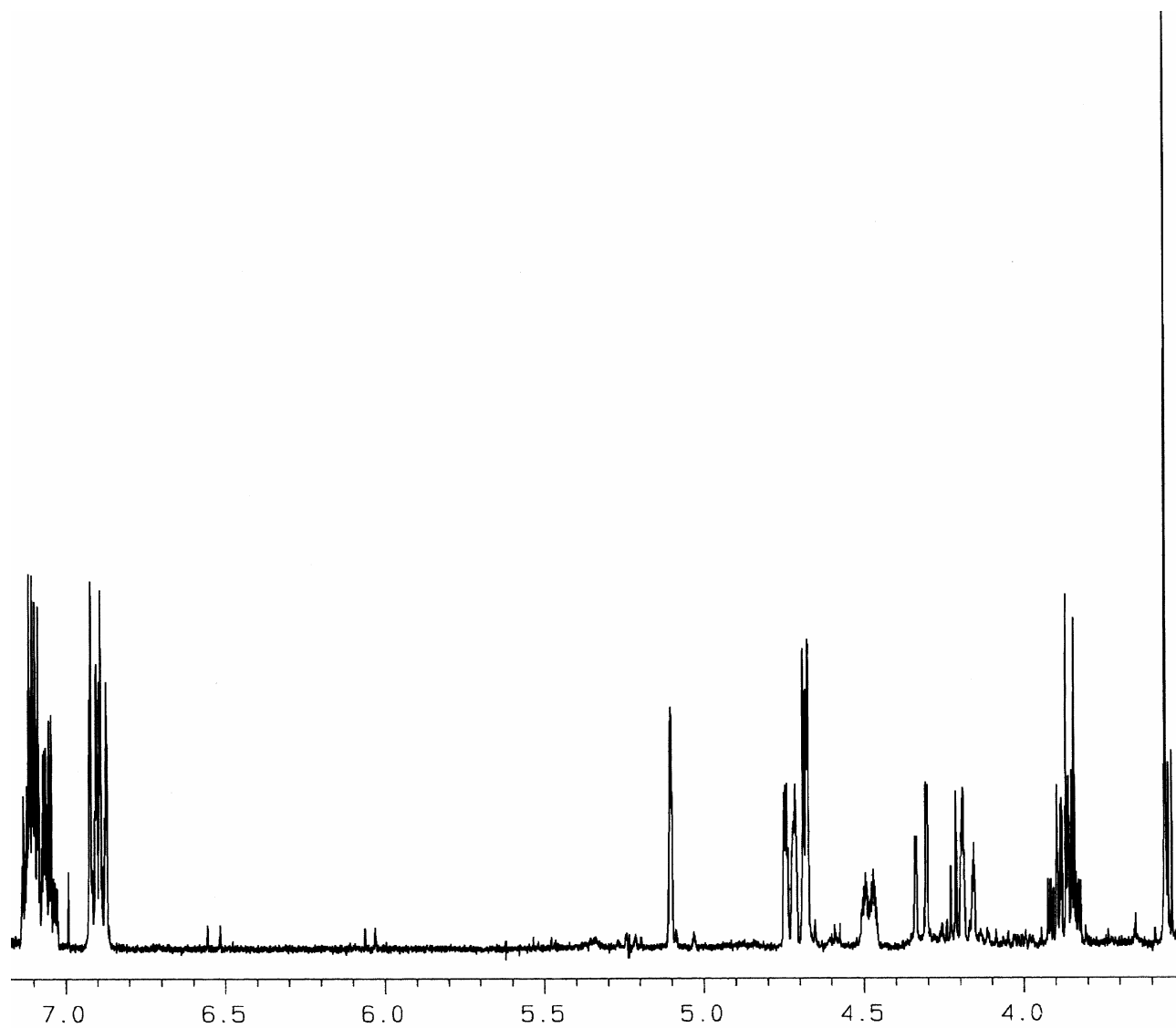


Figure S29. ^1H NMR of methyl β -D-xylopyranoside-2,4- β -truxinate (**7B**).

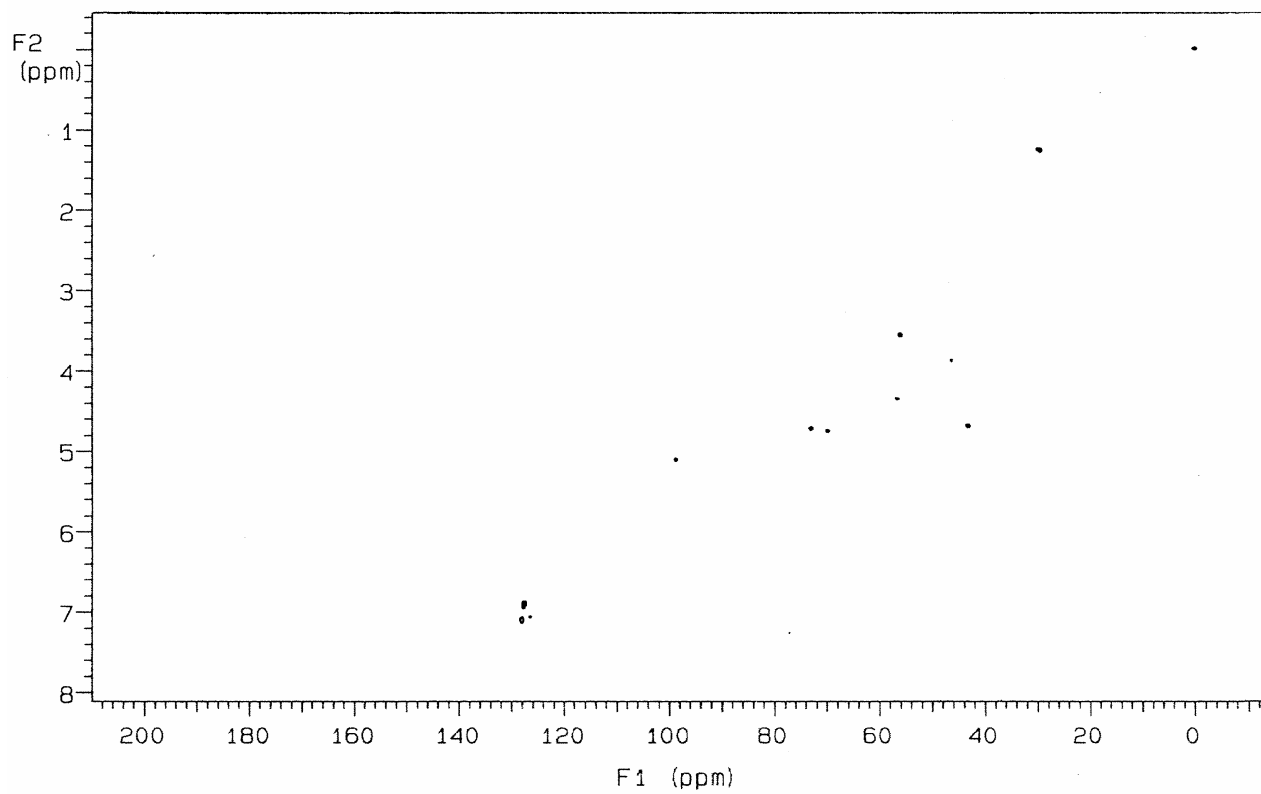


Figure S30. HMQC of methyl β -D-xylopyranoside-2,4- β -truxinate (**7B**).

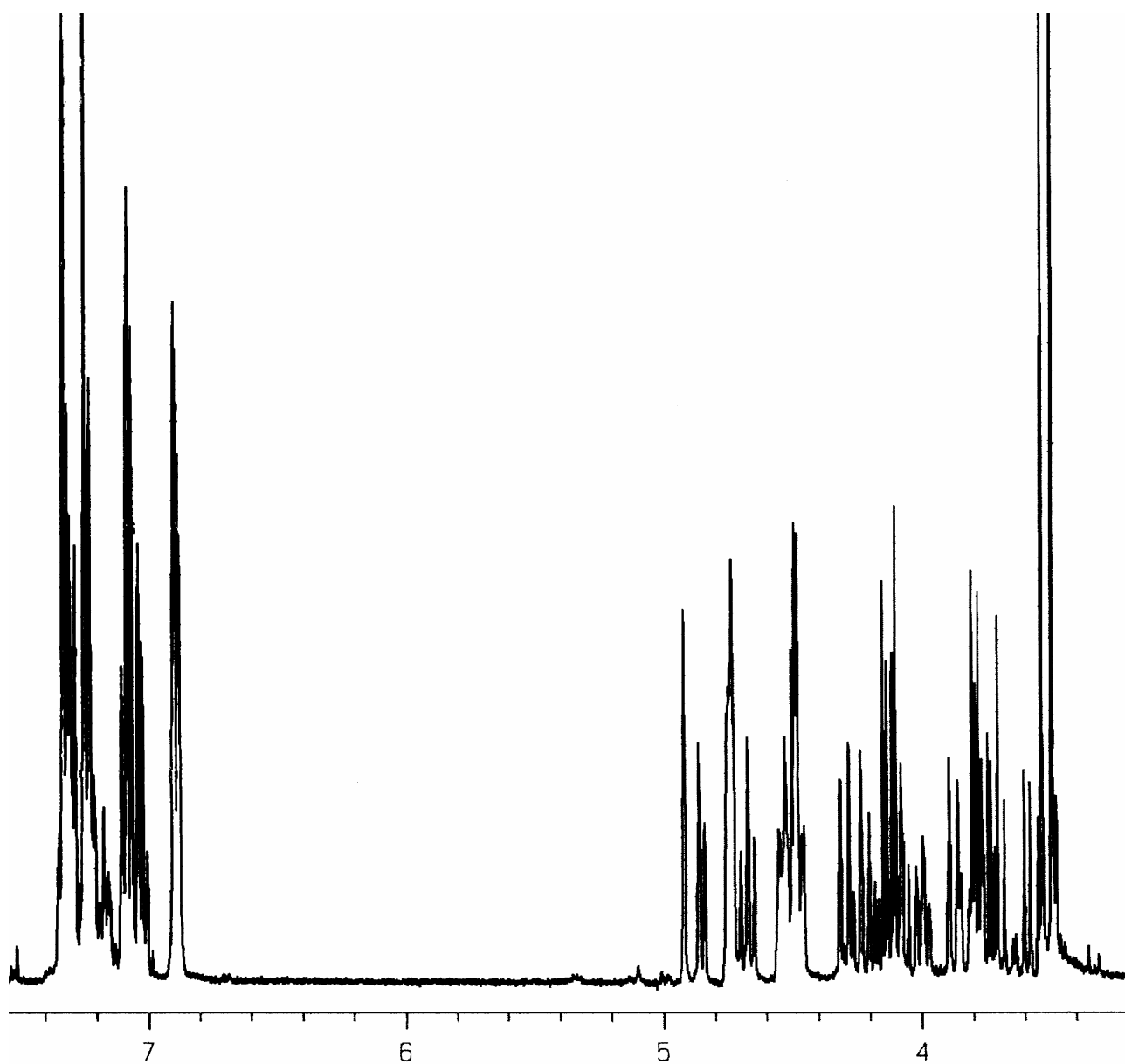


Figure S31. ^1H NMR for the mixture of **7A**, **7C**, and **7D** (**Fr4**).

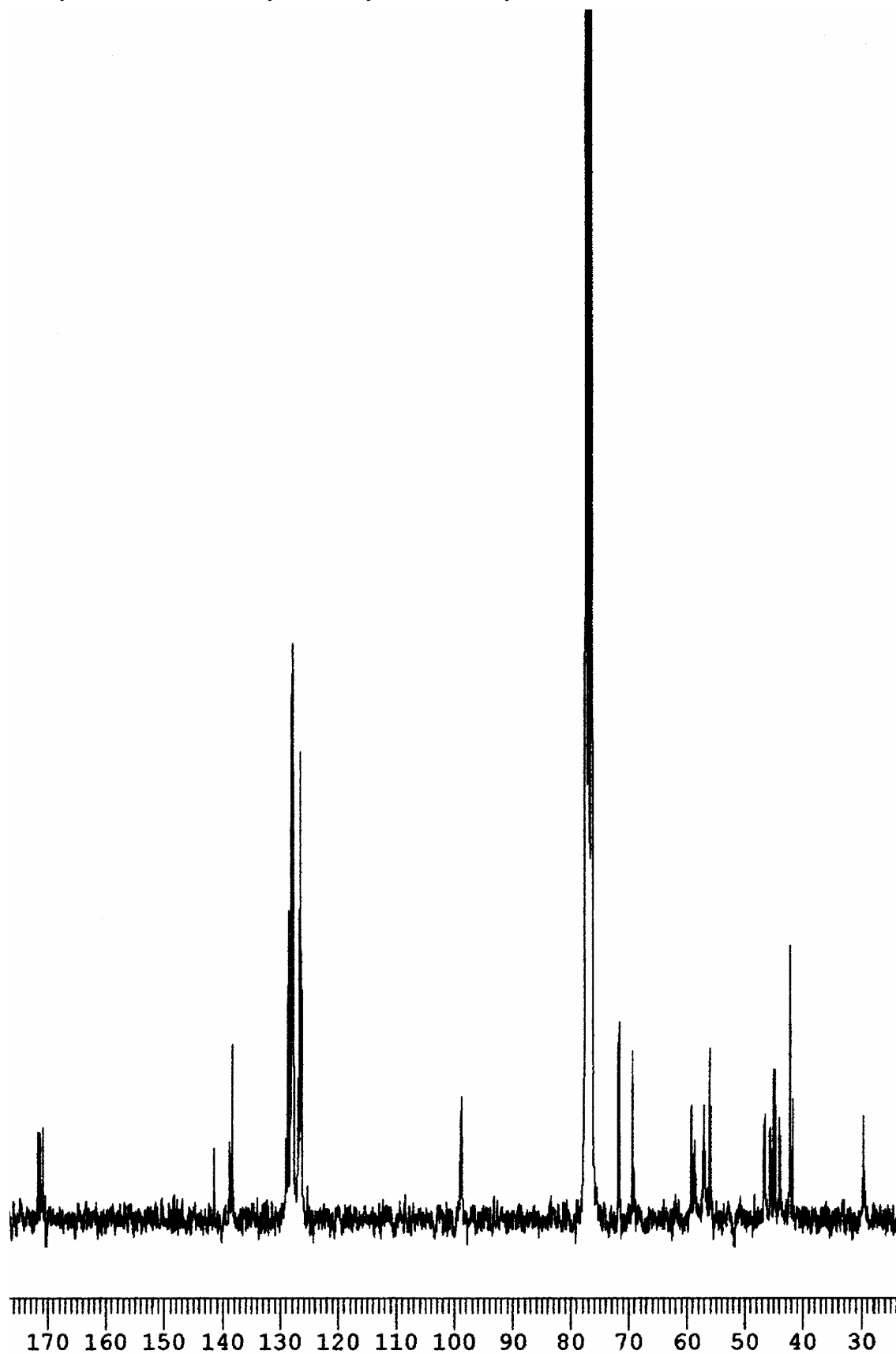


Figure S32. ^{13}C NMR for the mixture of **7A**, **7C**, and **7D** (**Fr4**).

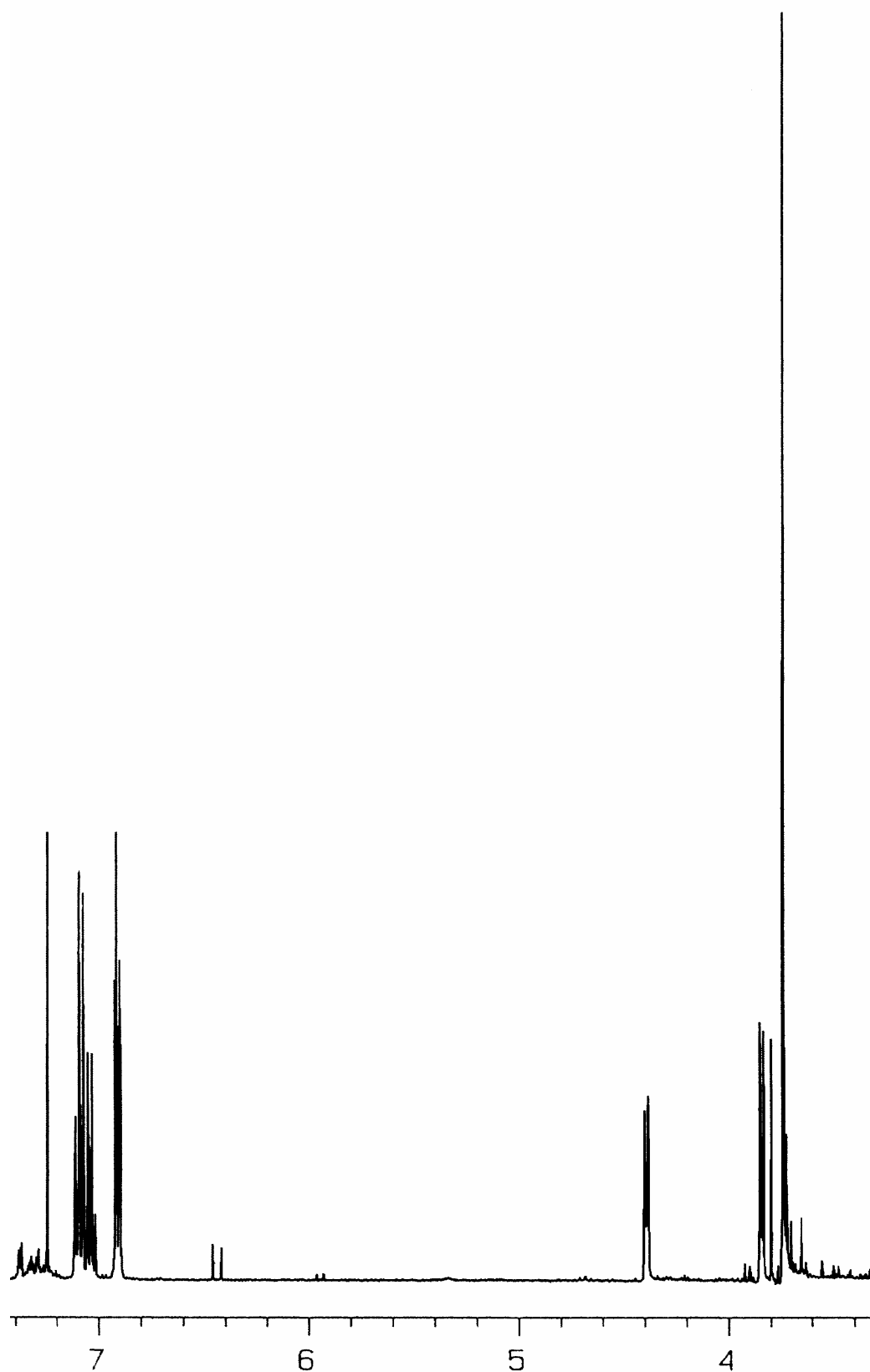


Figure S33. ¹H NMR of β-truxinate (**8β**).

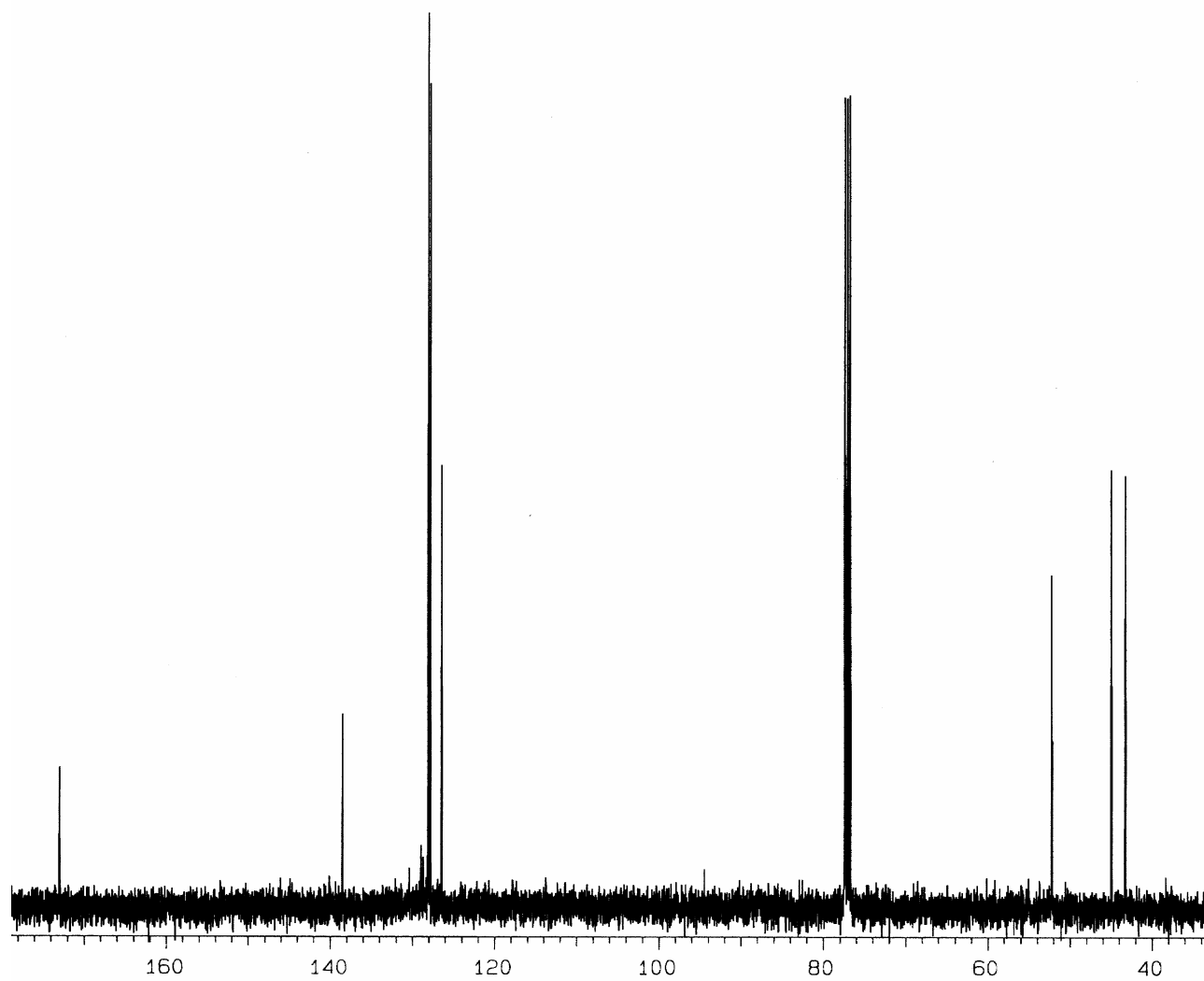


Figure S34. ^{13}C NMR of β -truxinate (**8 β**).

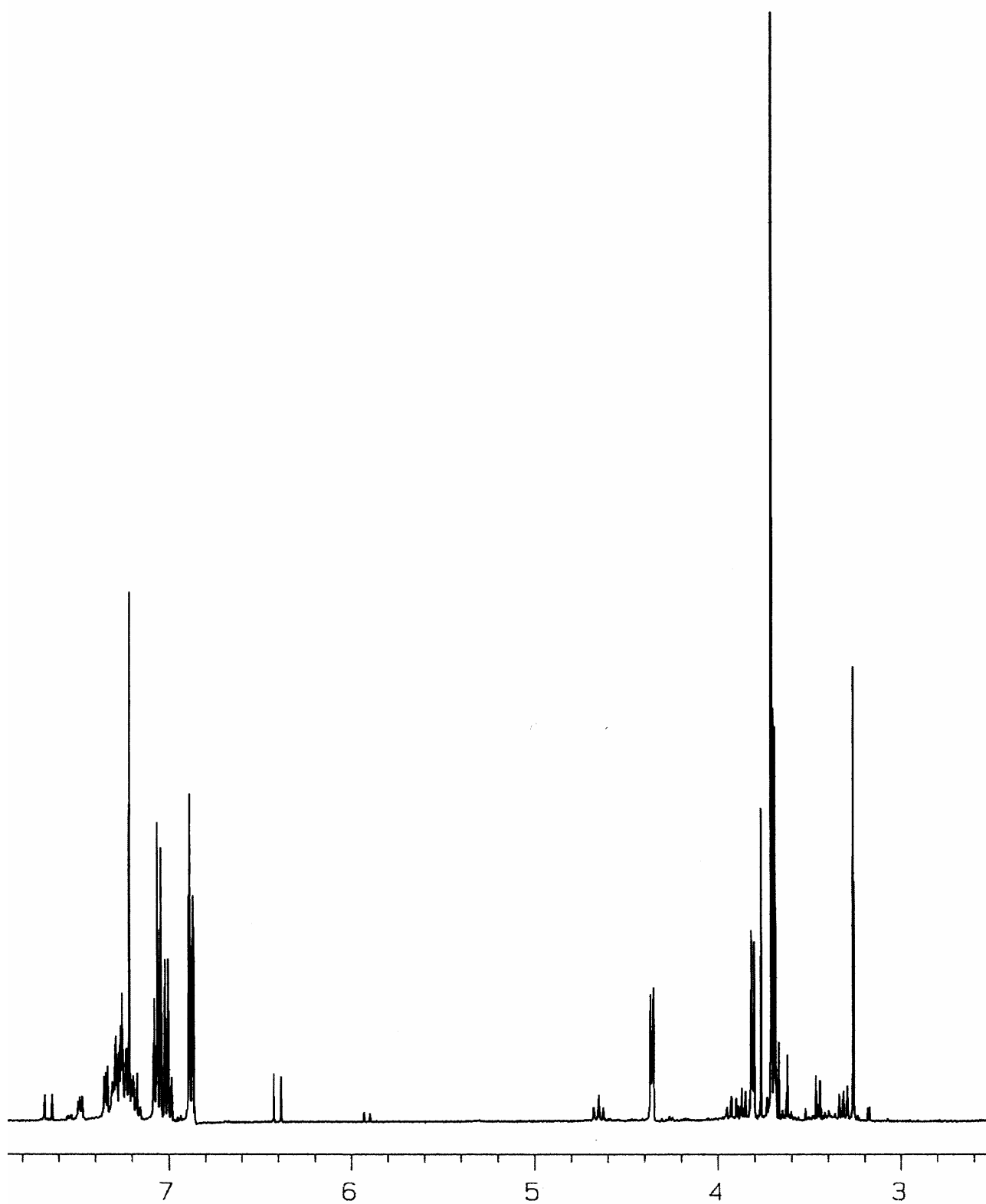


Figure S35. ^1H NMR for the mixture of **8 β** , **8 δ** , and **8 ξ** (**Fr4**).

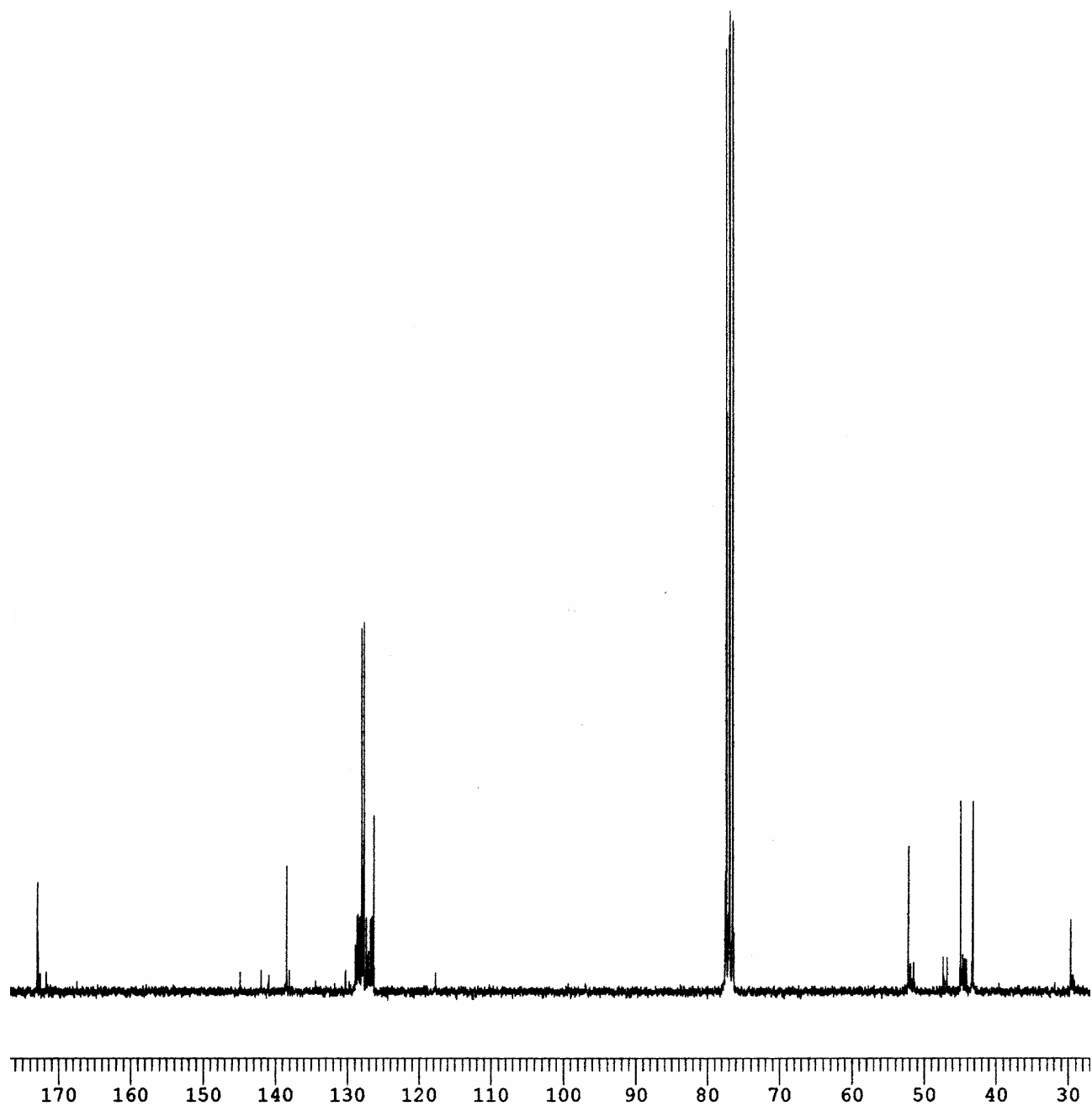


Figure S36. ^{13}C NMR for the mixture of **8 β** , **8 δ** , and **8 ξ** (**Fr4**).

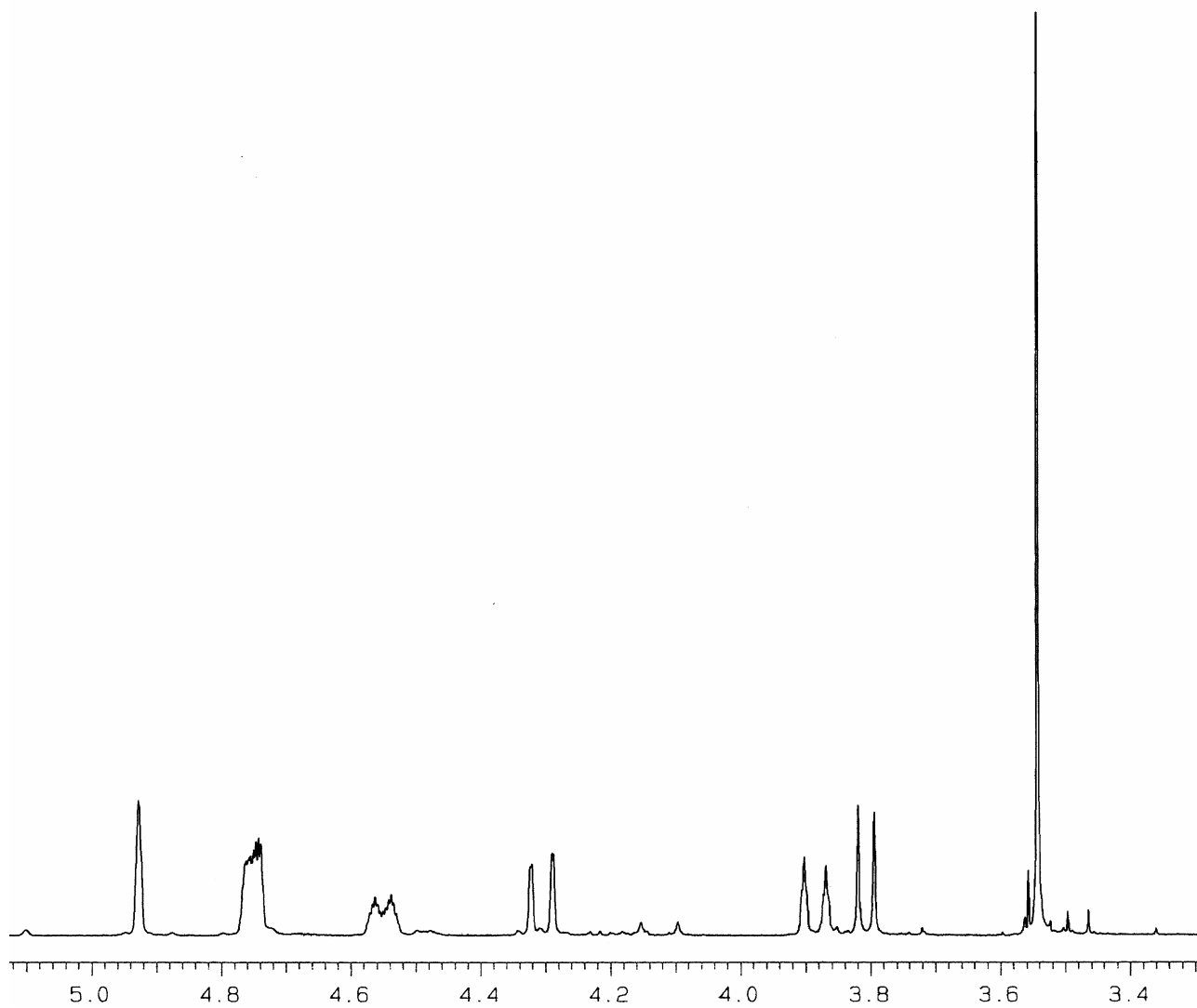


Figure S37. ^1H NMR of methyl β -D-xylopyranoside-2,4- β -truxinate- d_{14} (**7d₁₄A**).

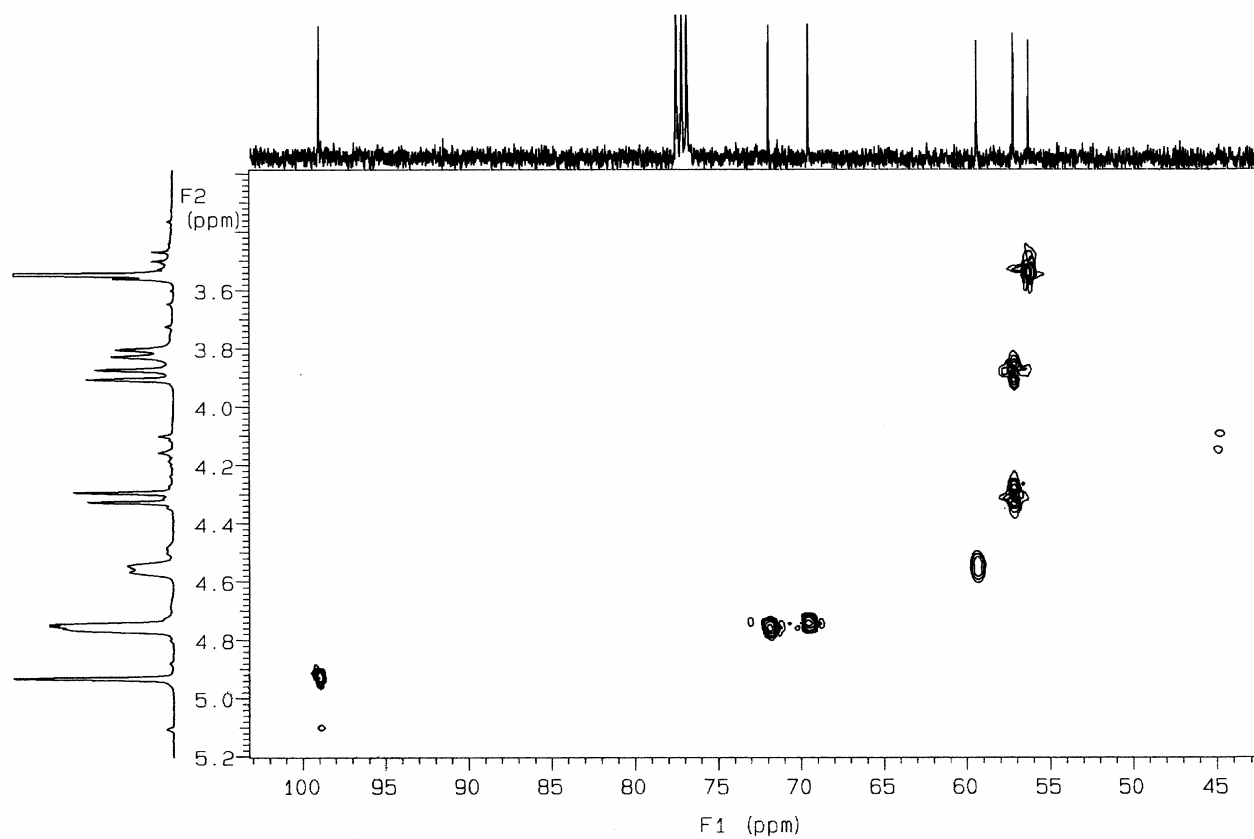


Figure S38. HMQC of methyl β -D-xylopyranoside-2,4- β -truxinate- d_{14} (**7d₁₄A**).

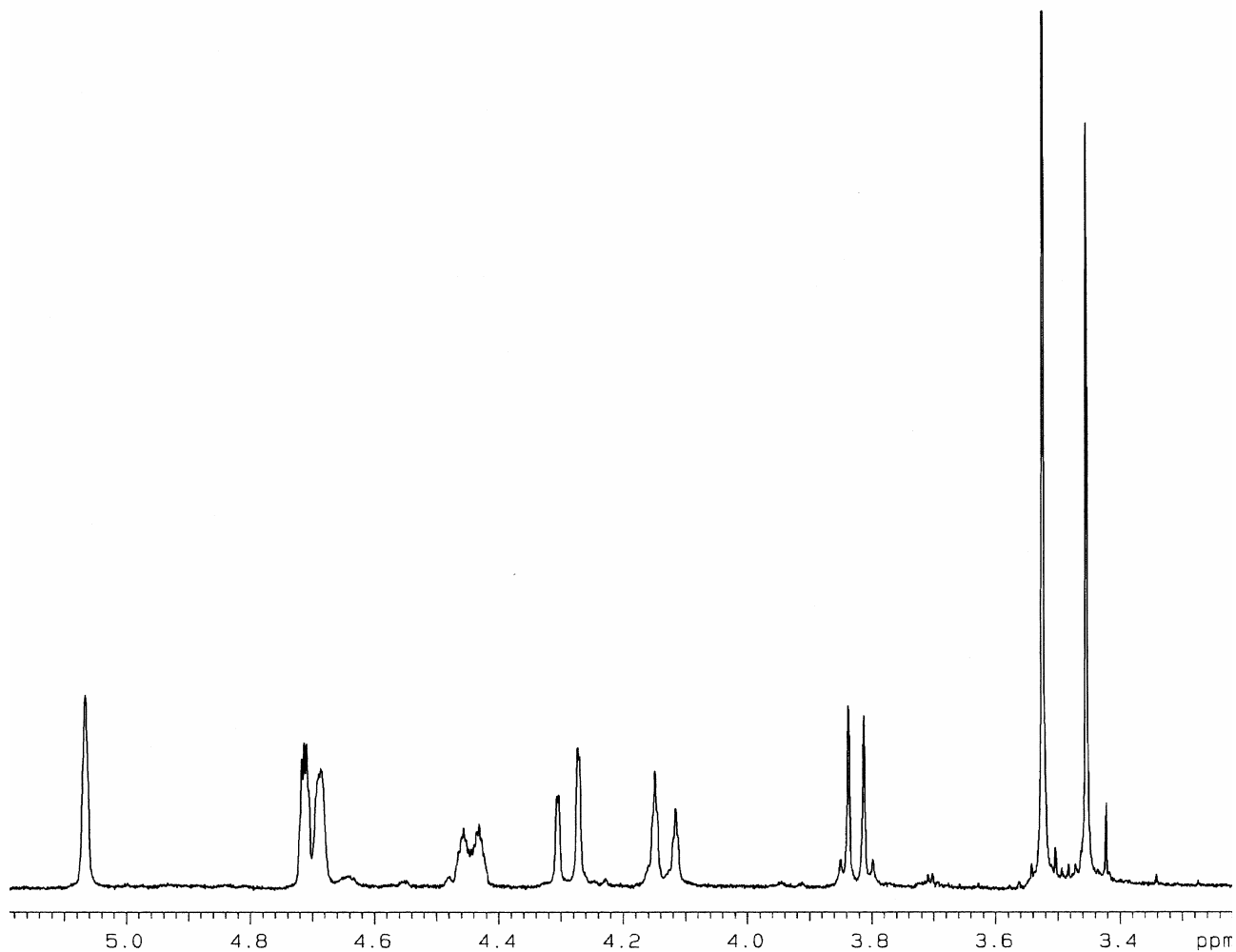


Figure S39. ^1H NMR of methyl β -D-xylopyranoside-2,4- β -truxinate- d_{14} (**7d₁₄B**).

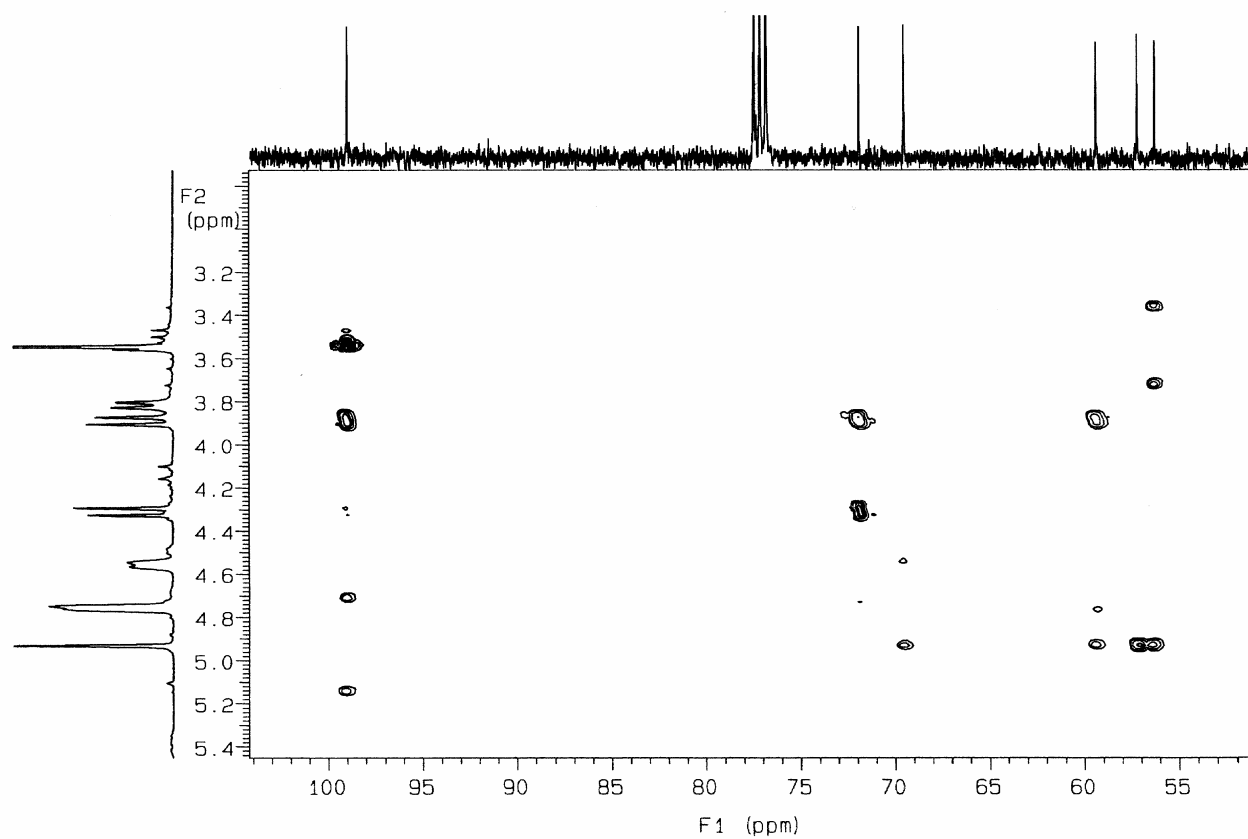


Figure S40. HMBC of methyl β -D-xylopyranoside-2,4- β -truxinate- d_{14} (**7d₁₄A**).

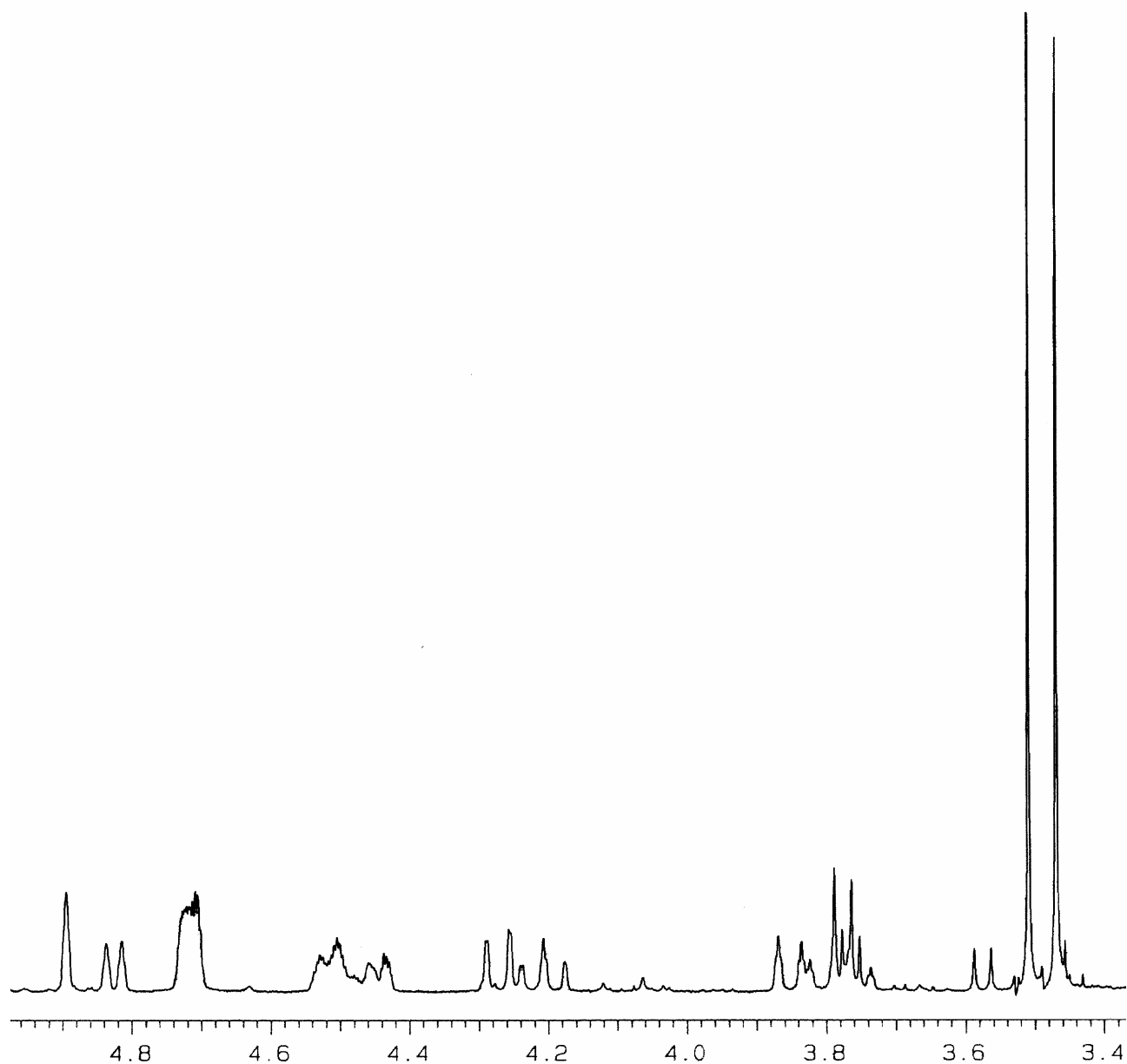


Figure S41. ¹H NMR for the mixture of **7d₁₄A**, **7d₁₄C**, and **7d₁₄D (Fr3)**.

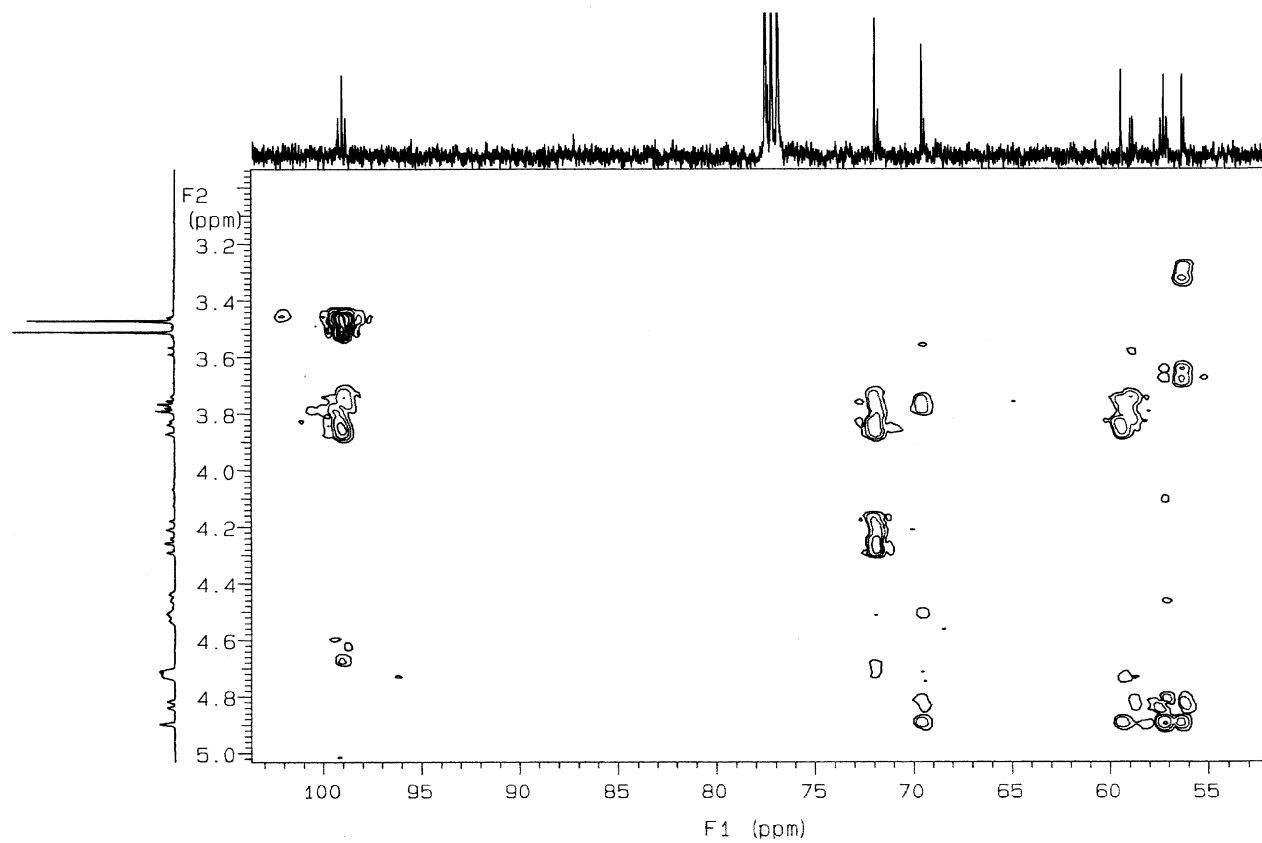


Figure S42. HMBC for the mixture of **7d₁₄A**, **7d₁₄C**, and **7d₁₄D (Fr3)**.

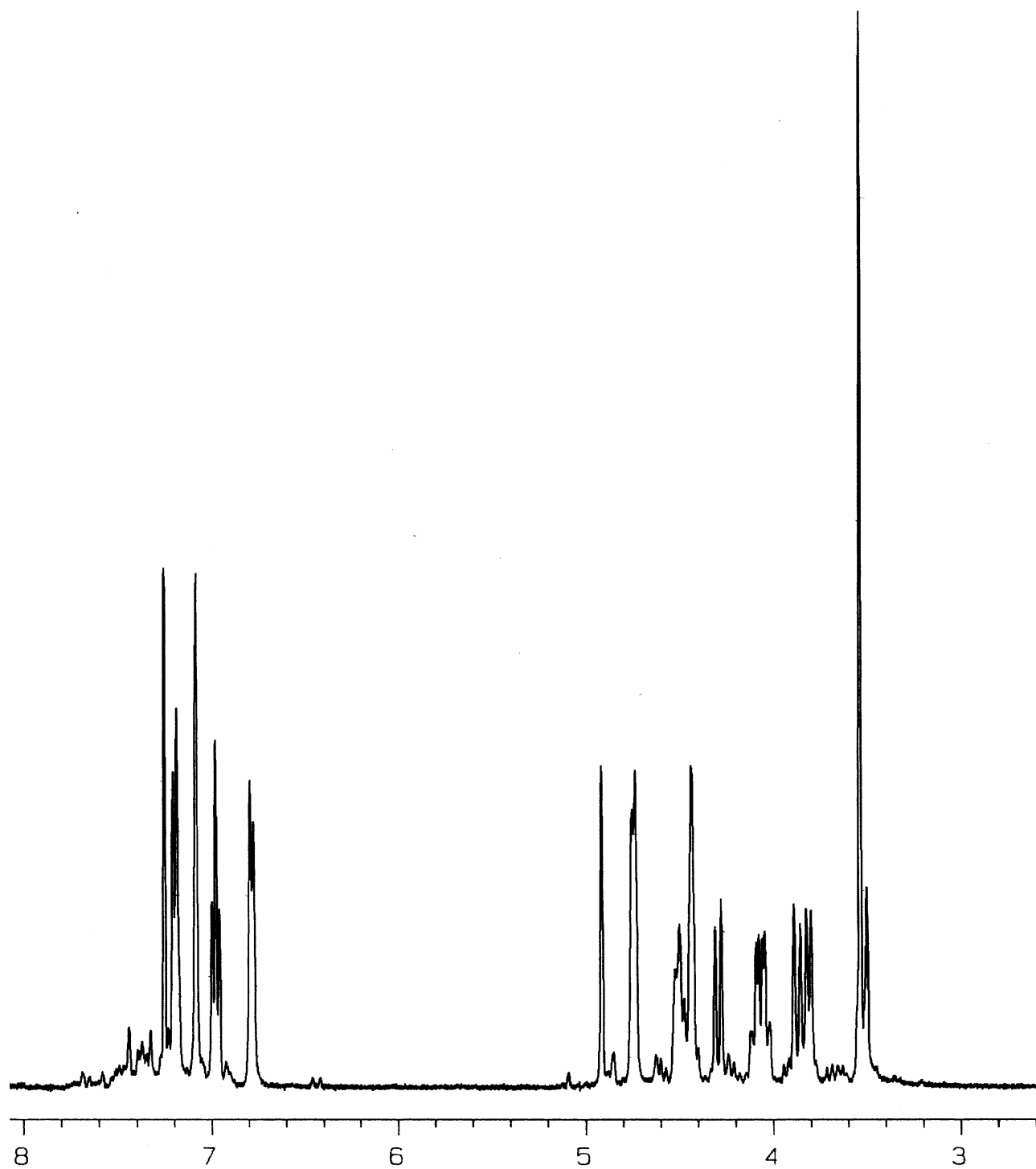
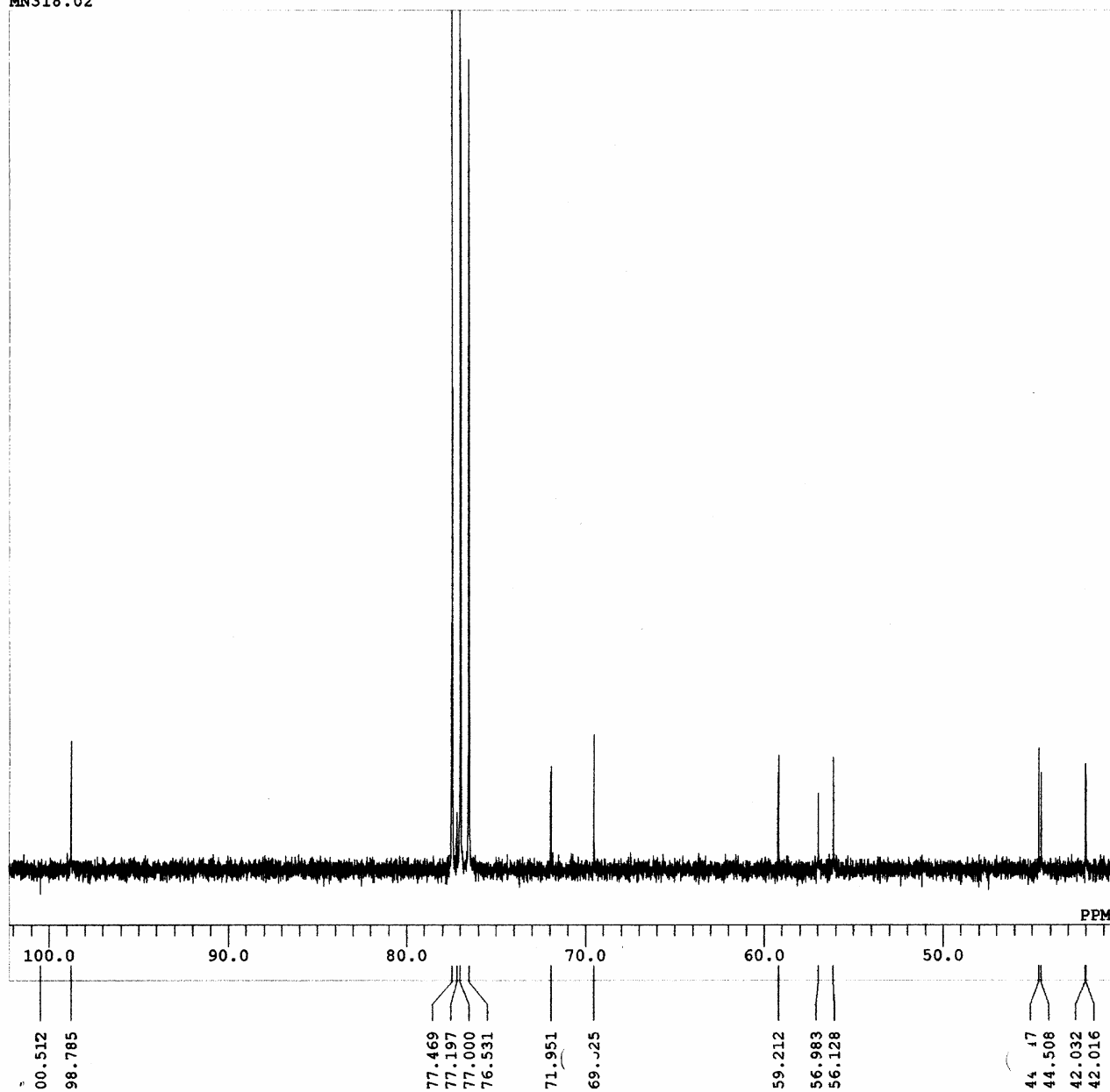


Figure S43. ¹H NMR of methyl β -D-xylopyranoside-2,4- β -3,3'-dibromotruxinate (**7BrA**).

Figure S44. ¹³C NMR of methyl β-D-xylopyranoside-2,4-β-3,3'-dibromotruvinate (**7BrA**).

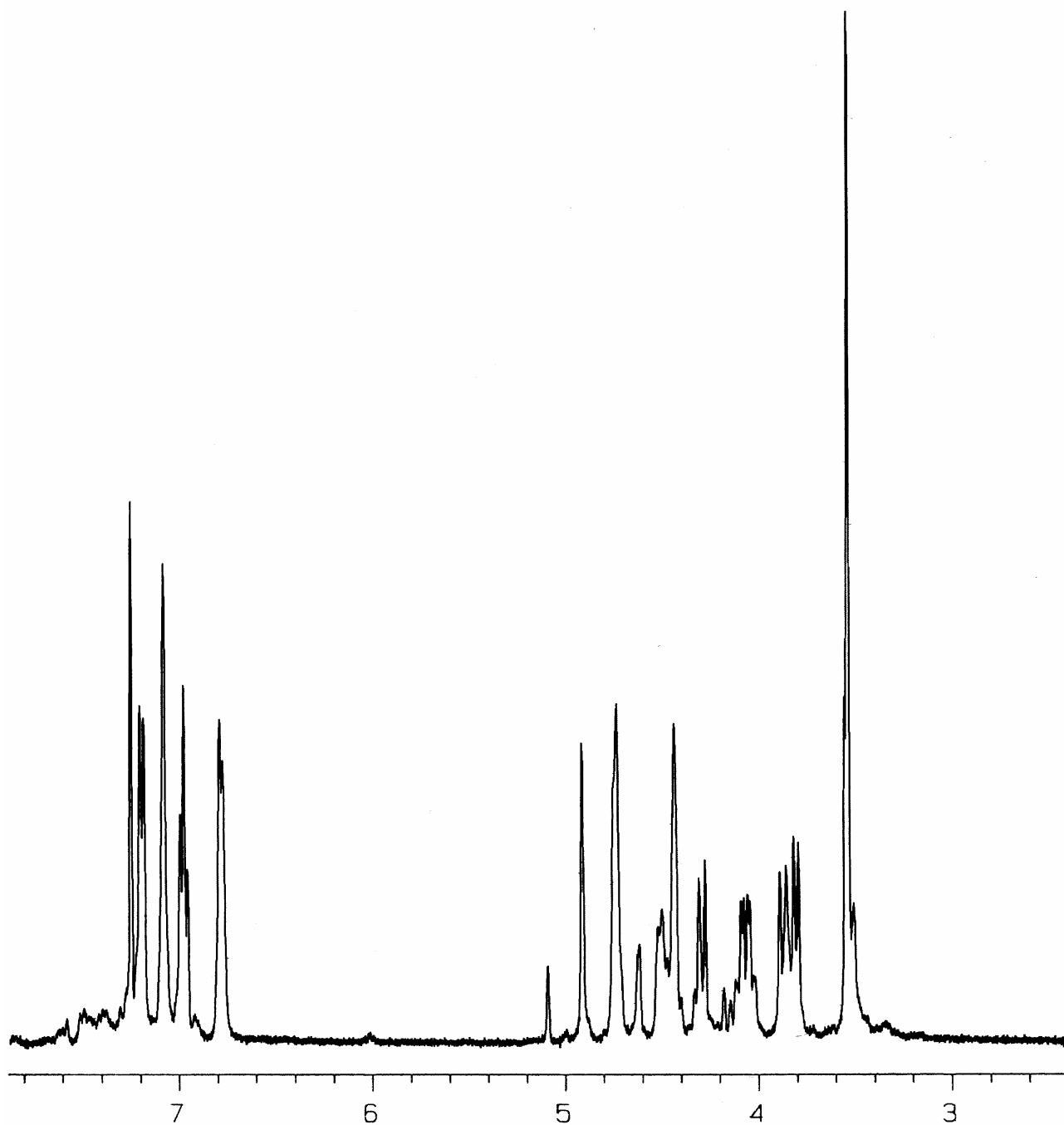


Figure S45. ^1H NMR for the mixture of **7BrA** and **7BrB** (**Fr1**).

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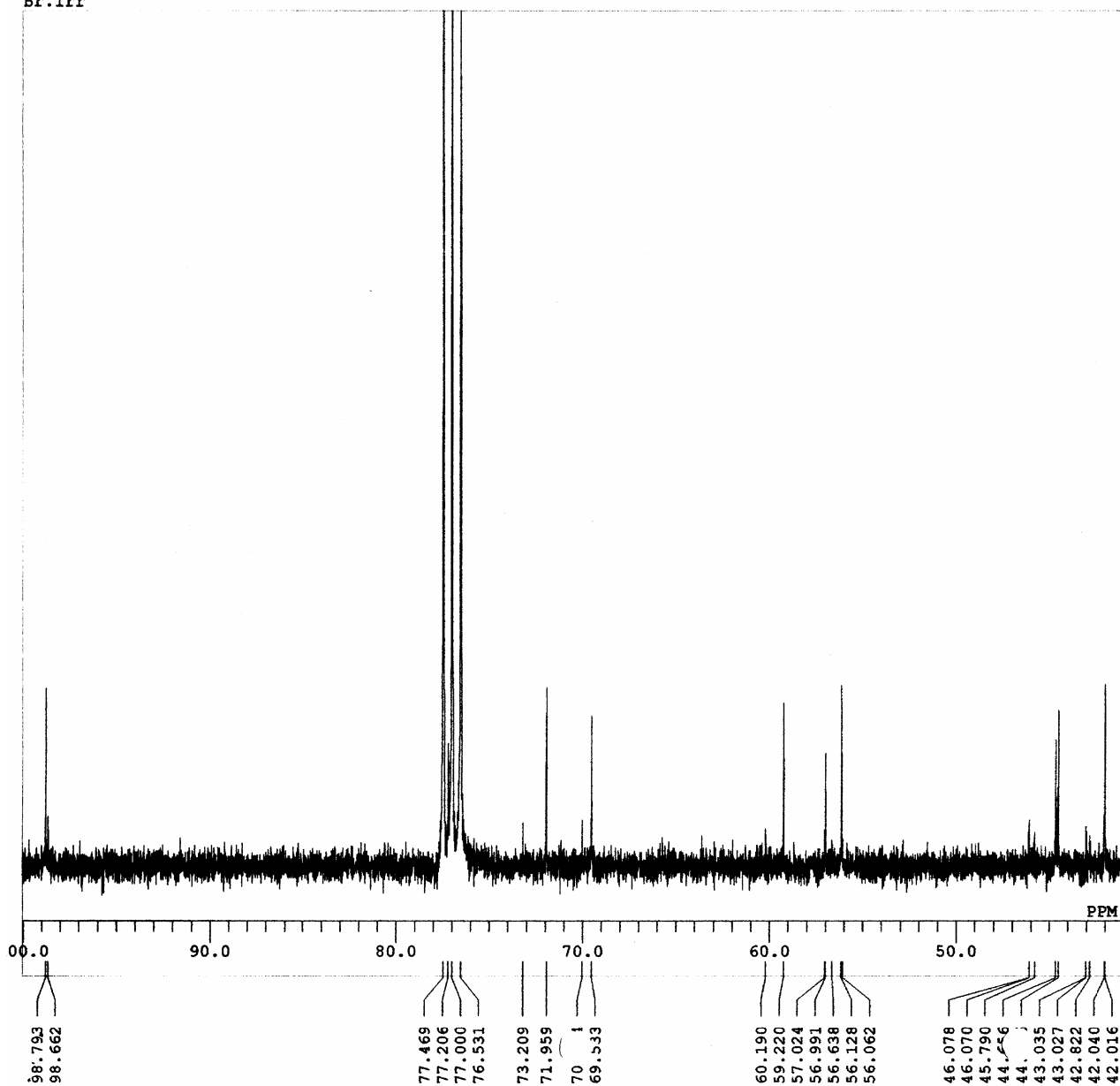


Figure S46. ^{13}C NMR for the mixture of **7BrA** and **7BrB (Fr1)**.

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ester1

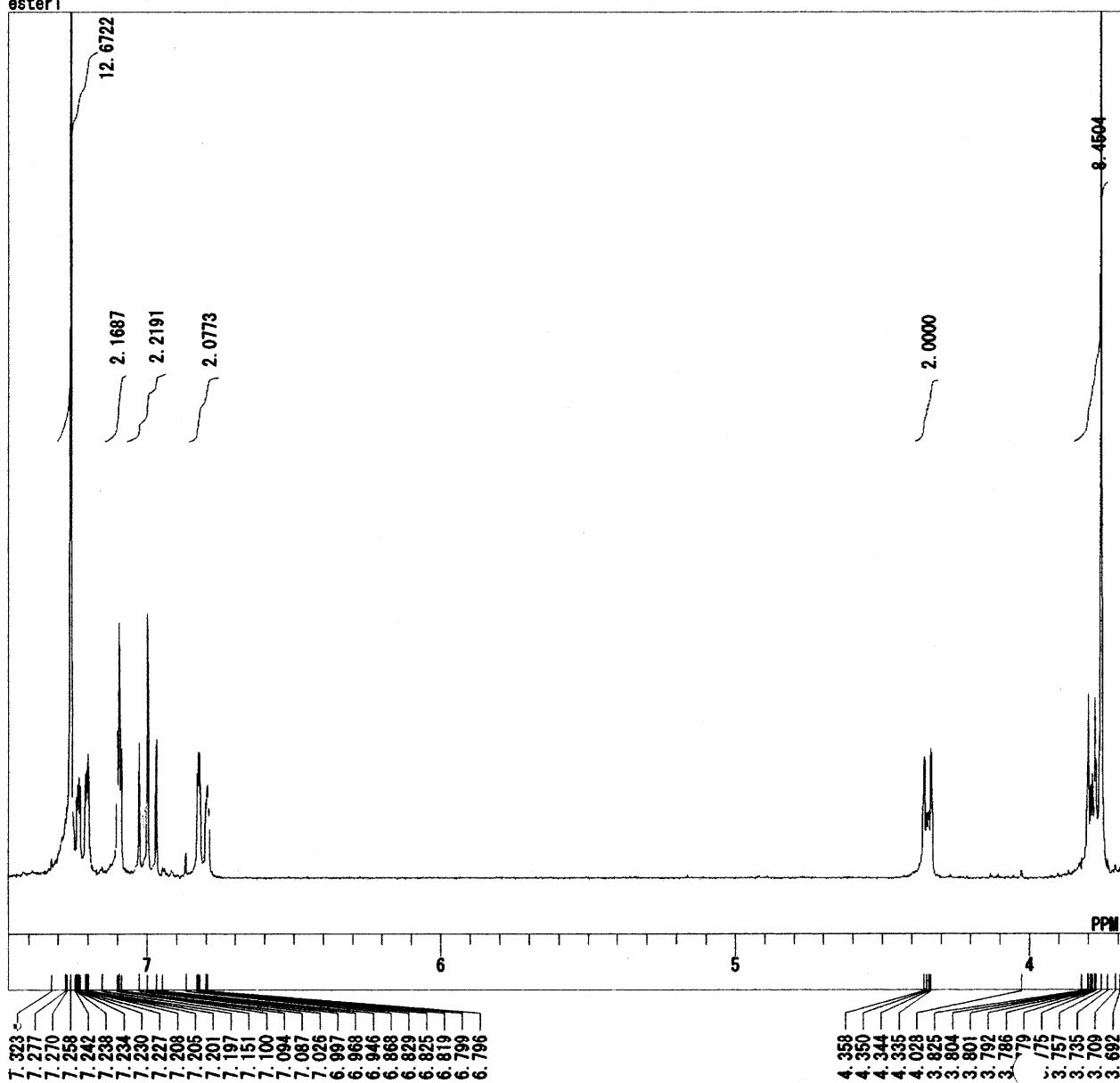


Figure S47. ^1H NMR of β -3,3'-dibromotruvinate (**8Br β**).

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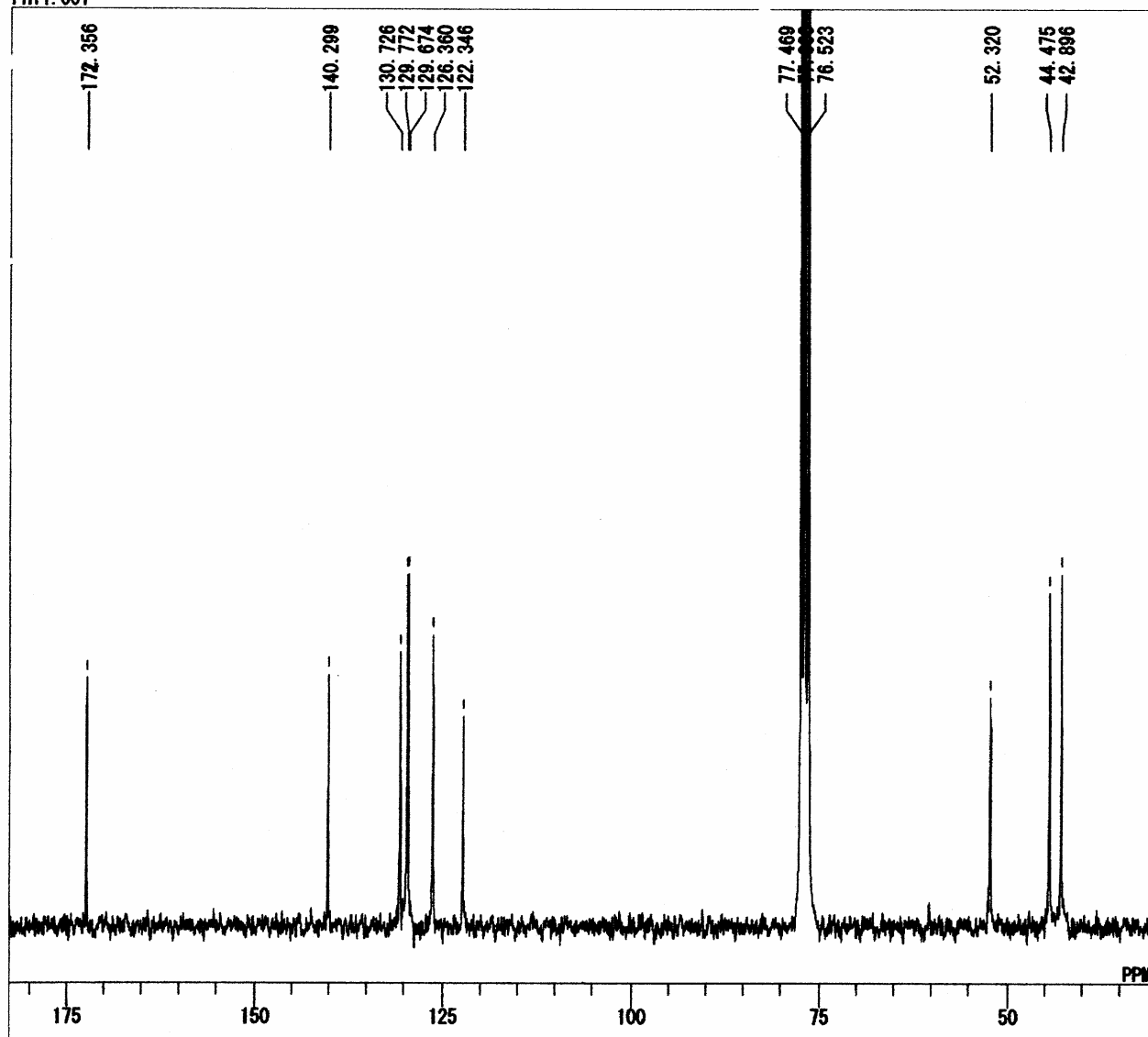


Figure S48. ^{13}C NMR of β -3,3'-dibromotruvinate (**8Br β**).