

Supporting information for

Multi-gram scale synthesis of a bleomycin (BLM) carbohydrate moiety: exploring the antitumor beneficial effect of BLM disaccharide attached to 10-hydroxycamptothecine (10-HCPT)

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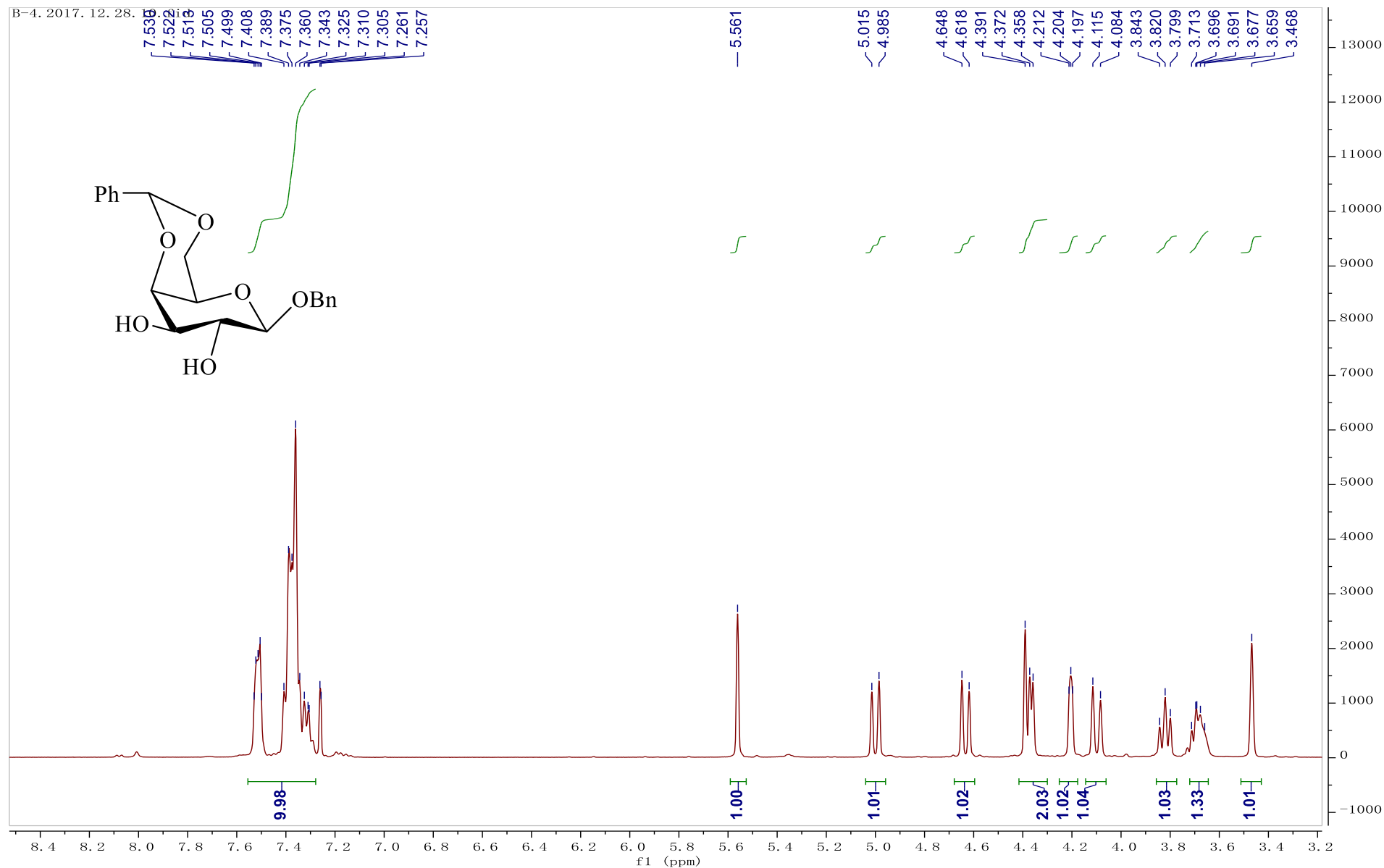


Fig. S1 ^1H NMR of benzyl 4,6-O-benzylidene- β -D-galactopyranoside (7) (CDCl₃, 400 MHz)

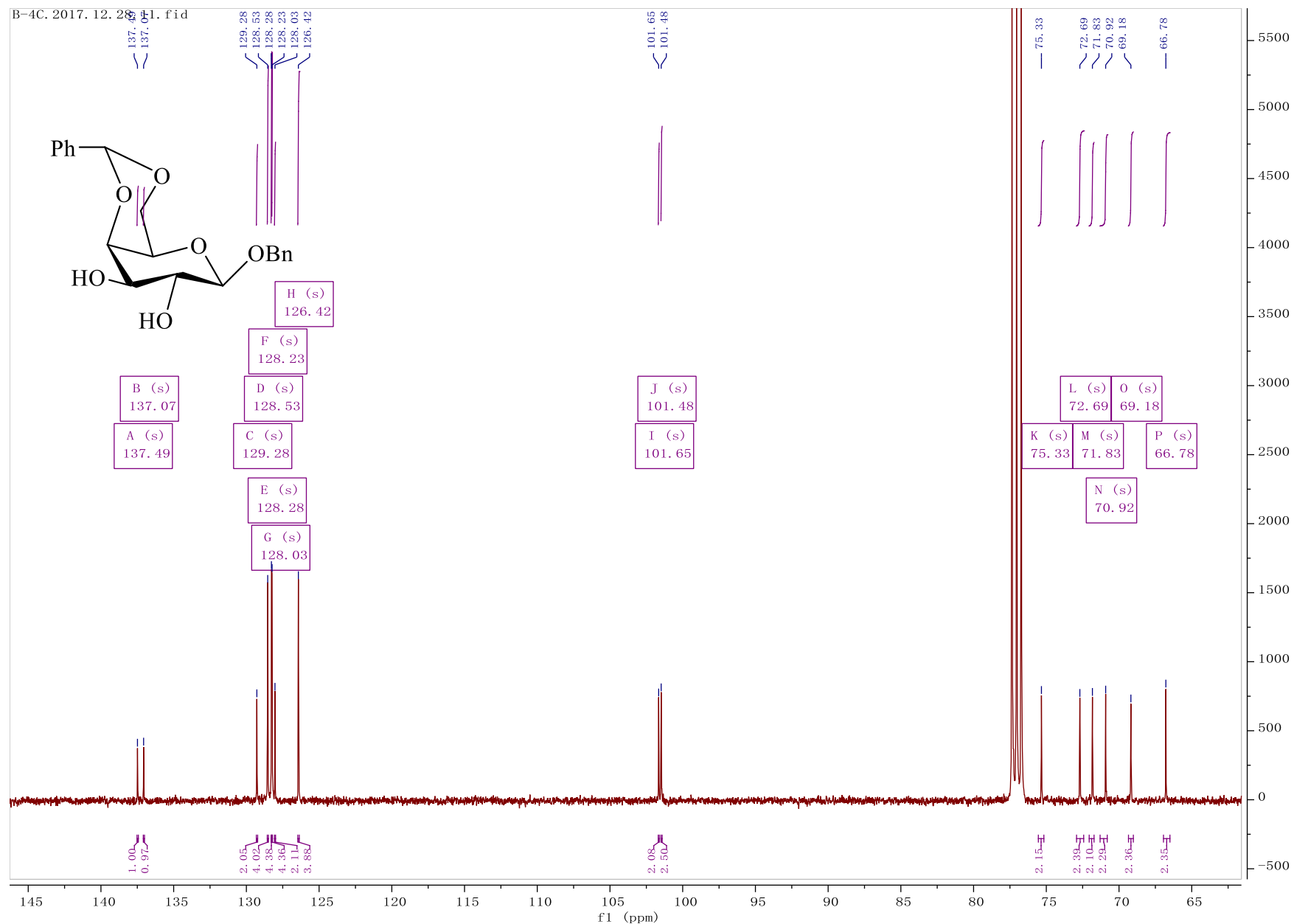


Fig. S2 ^{13}C NMR of benzyl 4,6-O-benzylidene- β -D-galactopyranoside (7) (CDCl_3 , 100 MHz)

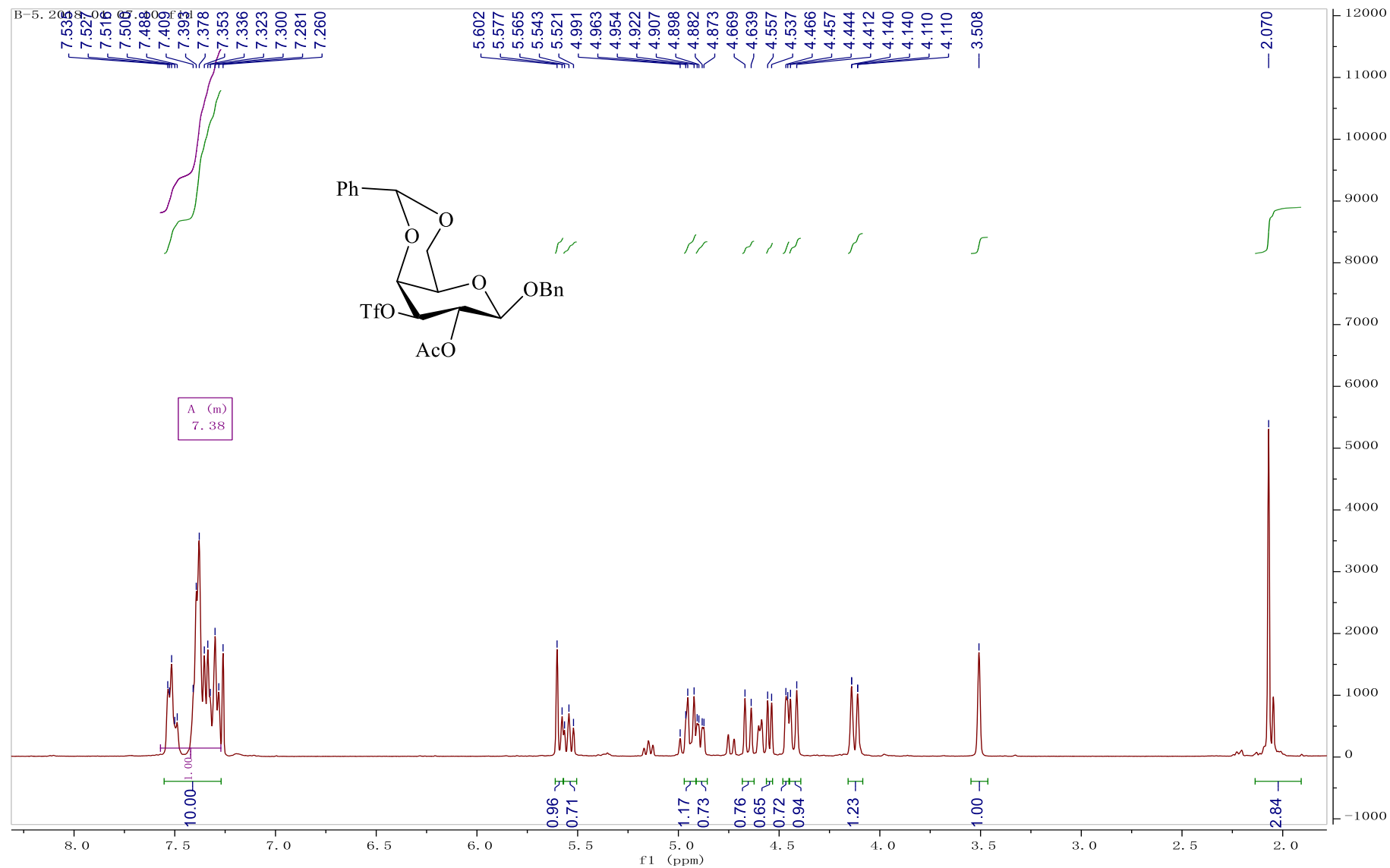


Fig. S3. ^1H NMR of benzyl 2-O-acetyl-3-O-tfyl-4, 6-O-benzylidene - β -D-galactopyranoside (**8**) (CDCl_3 , 400 MHz)

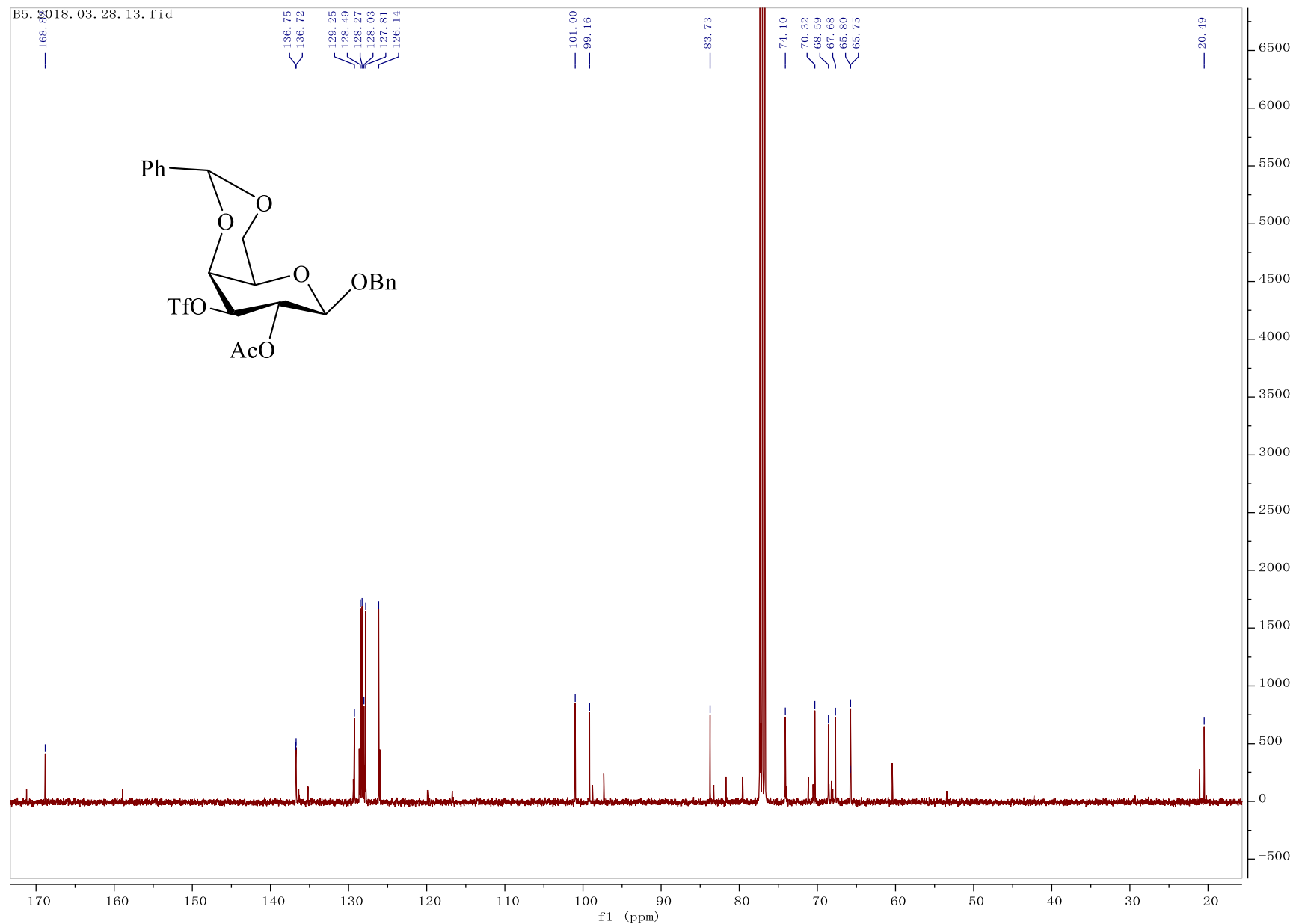


Fig.S4 ^{13}C NMR of benzyl 2-O-acetyl-3-O-tfyl-4, 6-O-benzylidene - β -D-galactopyranoside (**8**) (CDCl_3 , 100 MHz)

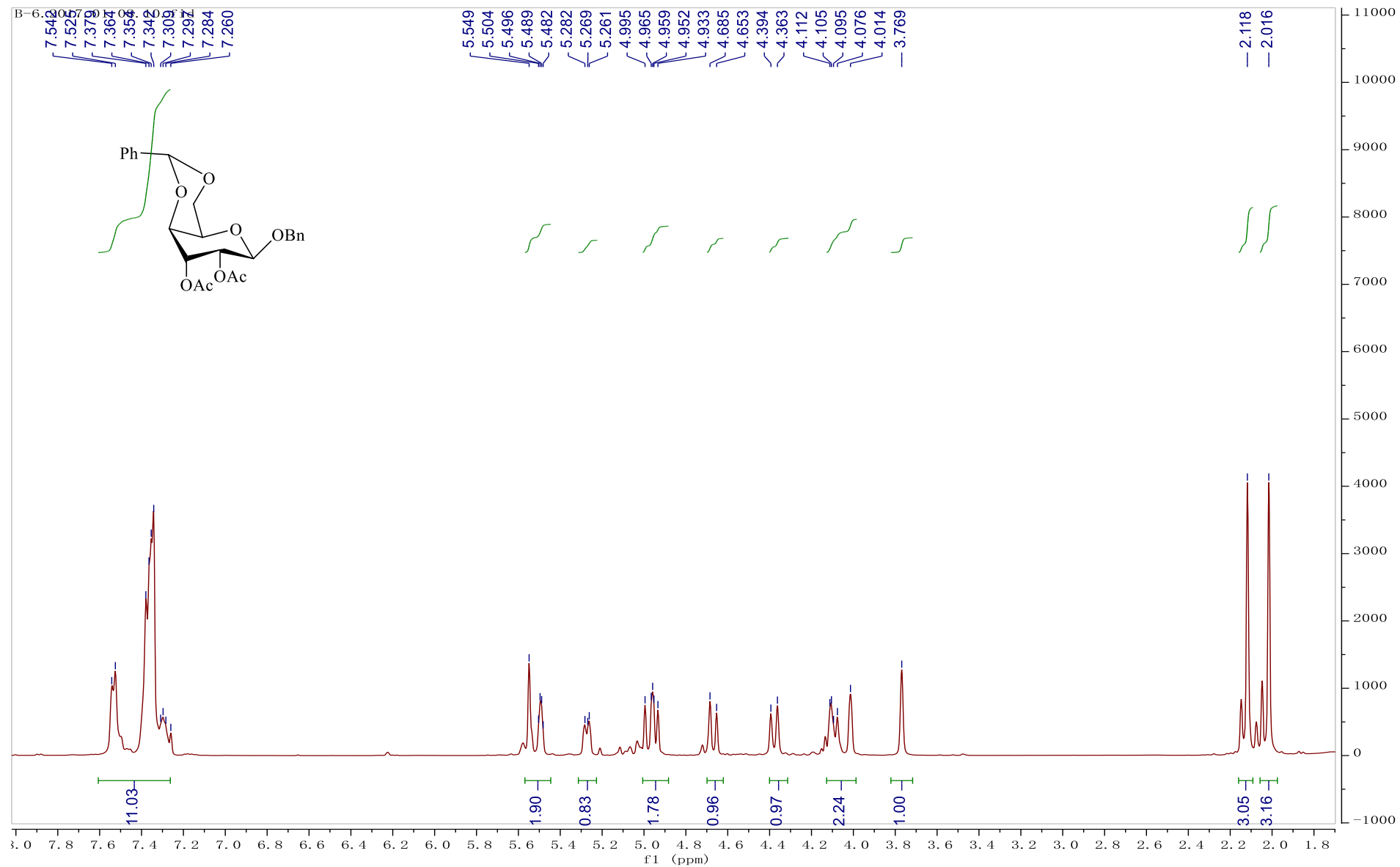


Fig. S5. ¹H NMR of benzyl 2,3-O-diacetyl-4,6-O-benzylidene- β -L-gulopyranoside (**9**) (CDCl₃, 400 MHz)

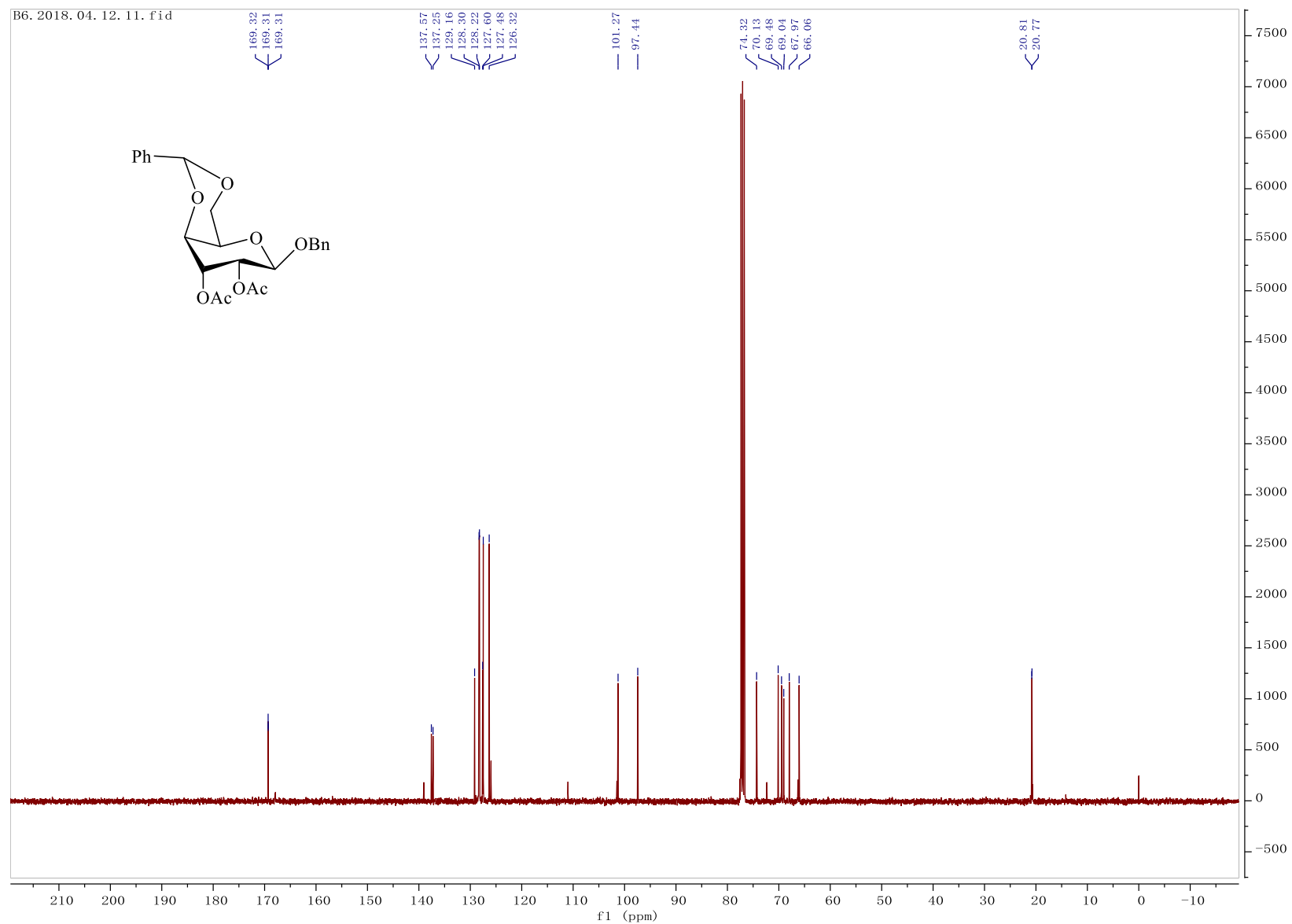


Fig. S6. ¹³CNMR of benzyl 2,3-O-diacetyl-4,6-O-benzylidene- β -L-gulopyranoside (**9**) (CDCl₃, 100 MHz)

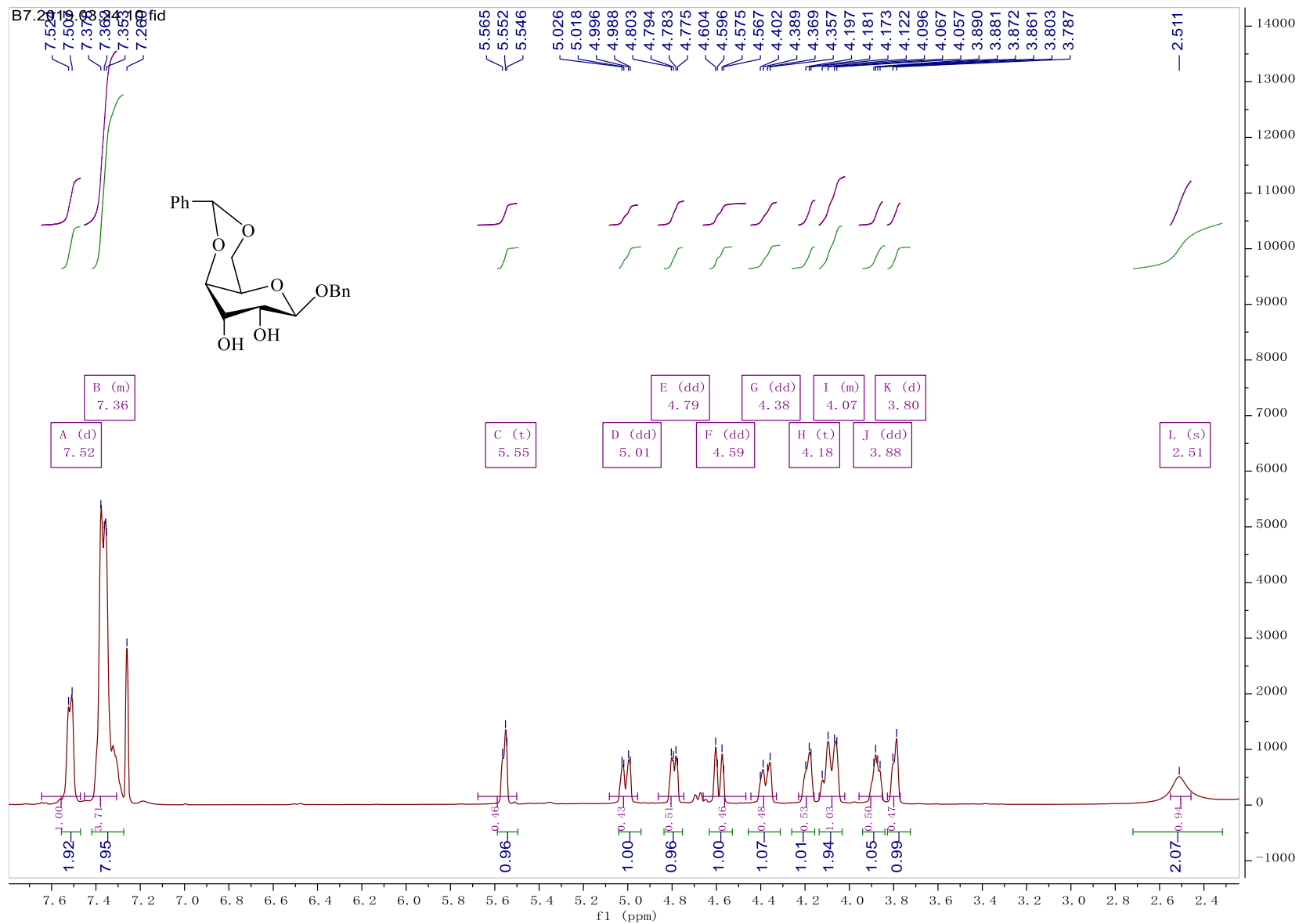


Fig. S7. ^1H NMR of benzyl 4, 6-O-benzylidene - β -L-gulopyranoside (**10**) (CDCl_3 , 400 MHz)

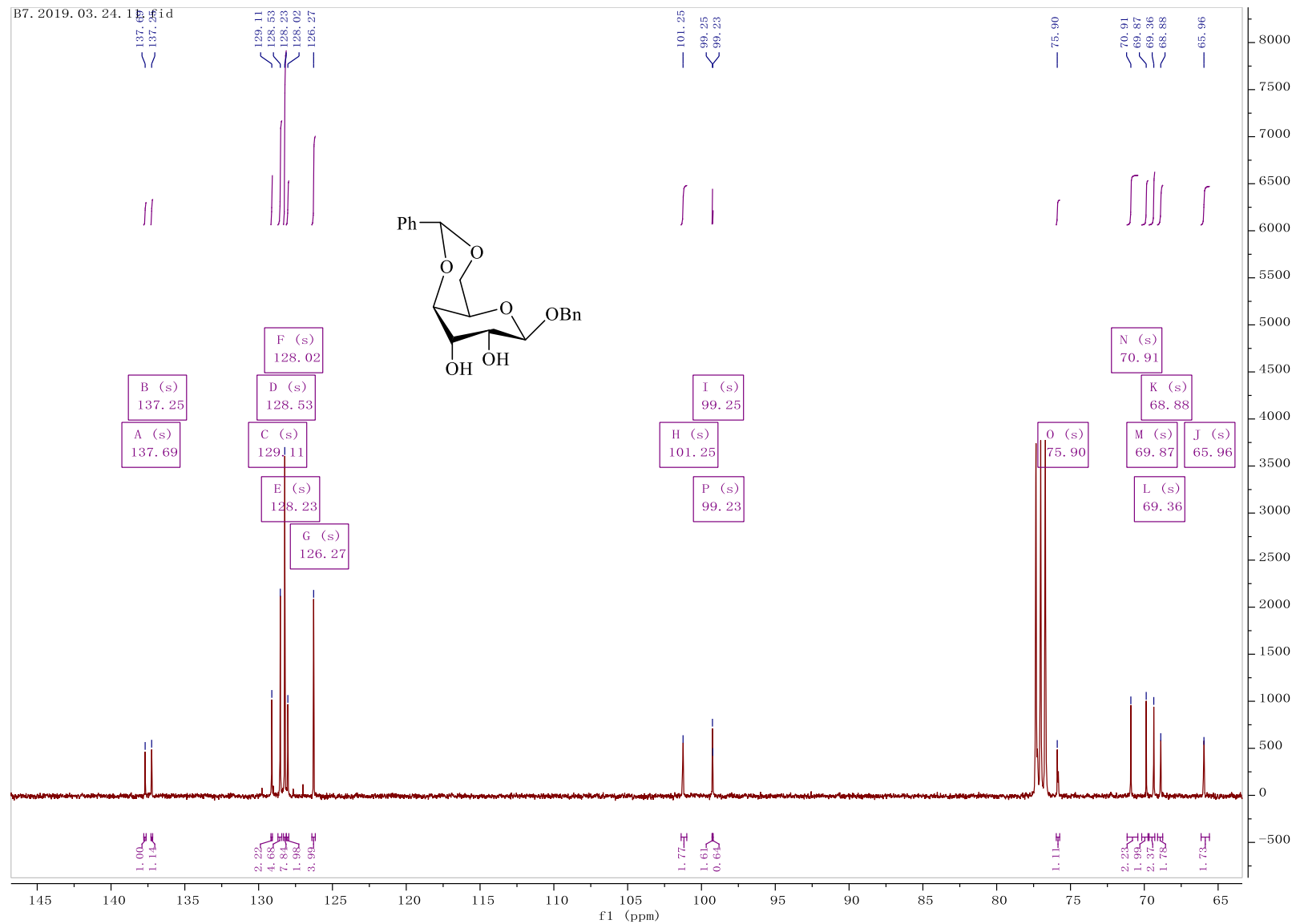


Fig. S8. ^{13}C NMR of benzyl 4,6-O-benzylidene- β -L-gulopyranoside (**10**) (CDCl_3 , 100 MHz)

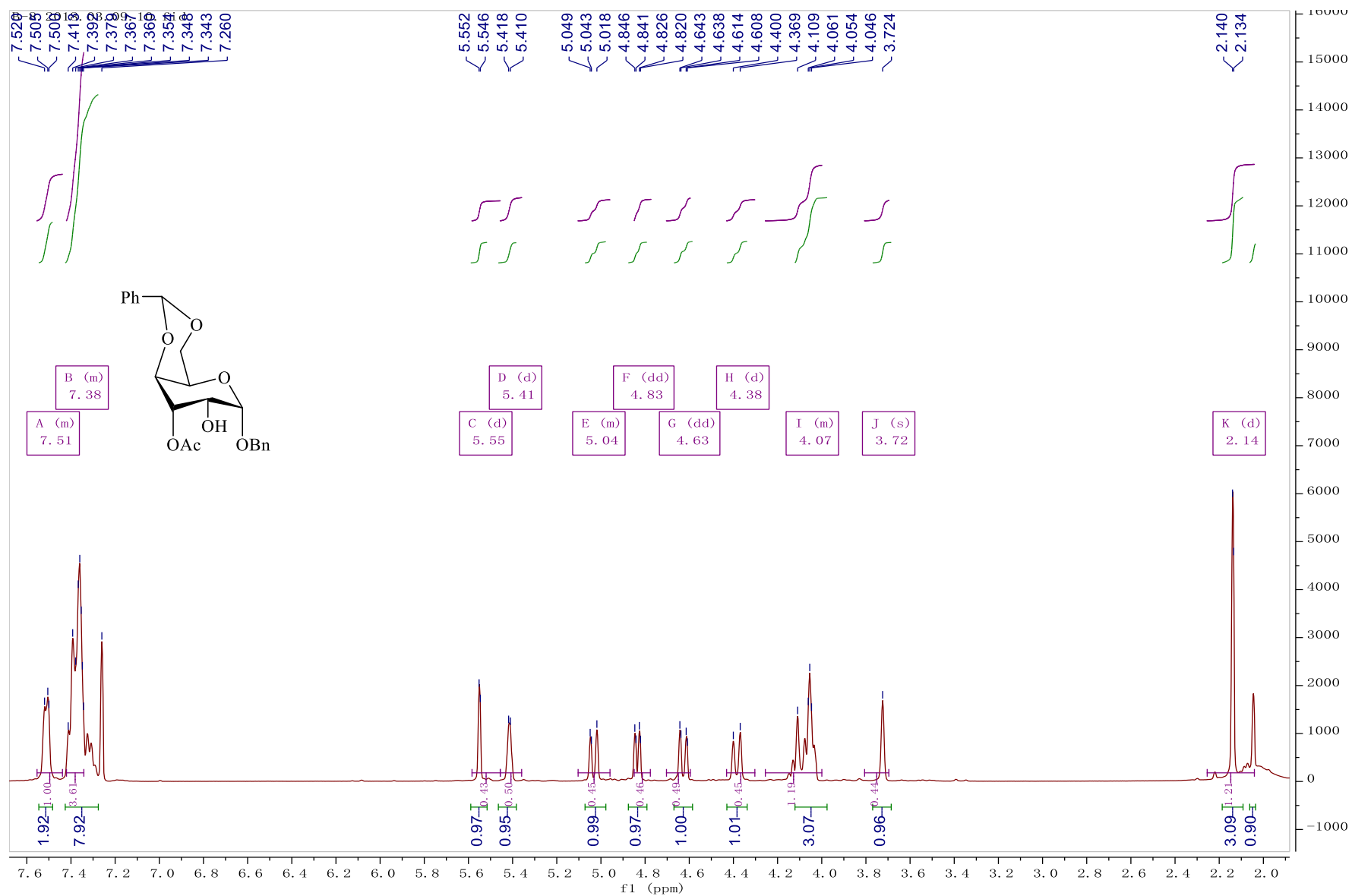


Fig. S9. ^1H NMR of benzyl 3-O-acetyl-4,6-O-benzylidene- β -L-gulopyranoside (**3**) (CDCl_3 , 400 MHz)

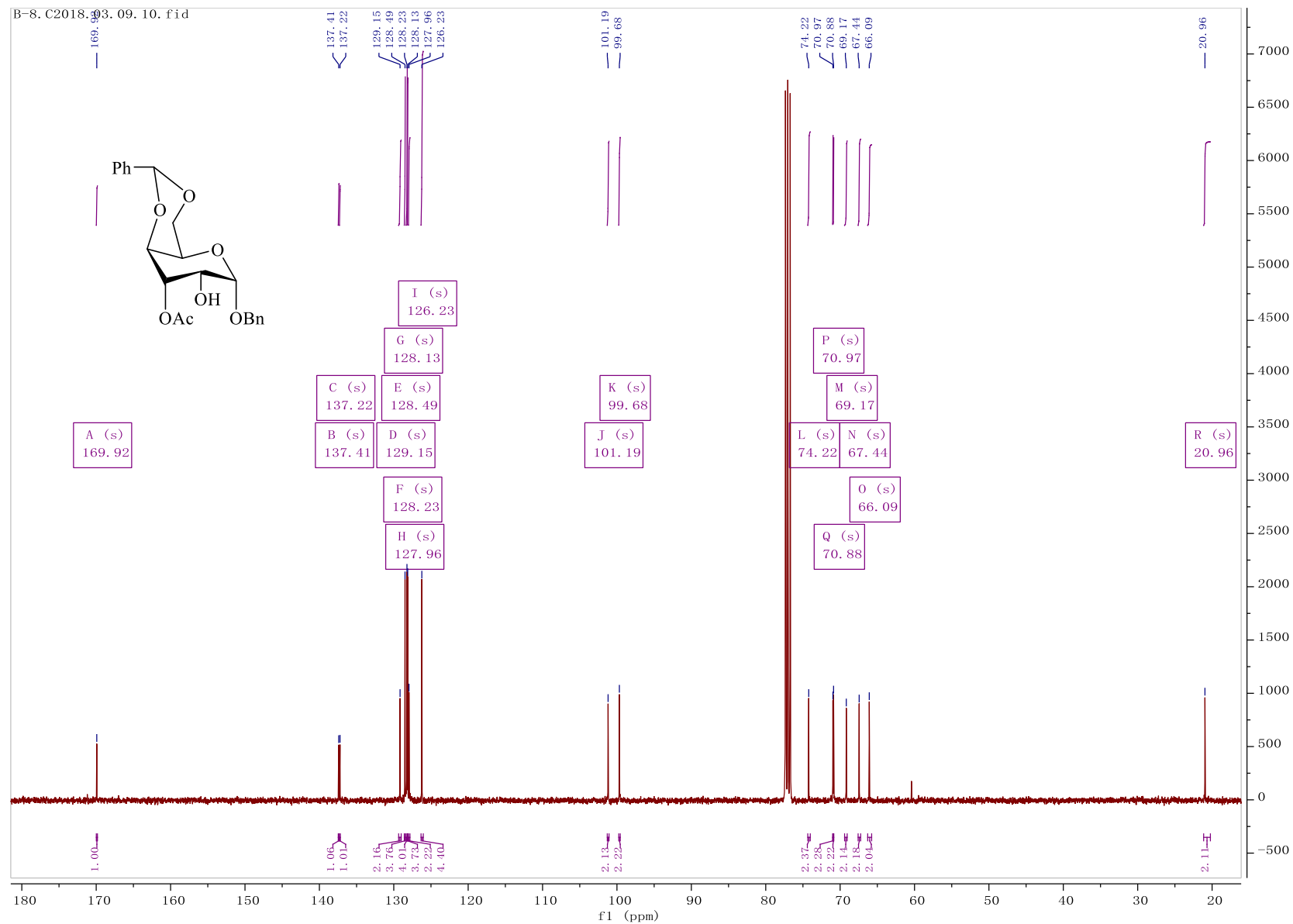


Fig. S10. ^{13}C NMR of benzyl 3-O-acetyl-4,6-O-benzylidene- β -L-gulopyranoside (**3**) (CDCl_3 , 100 MHz)

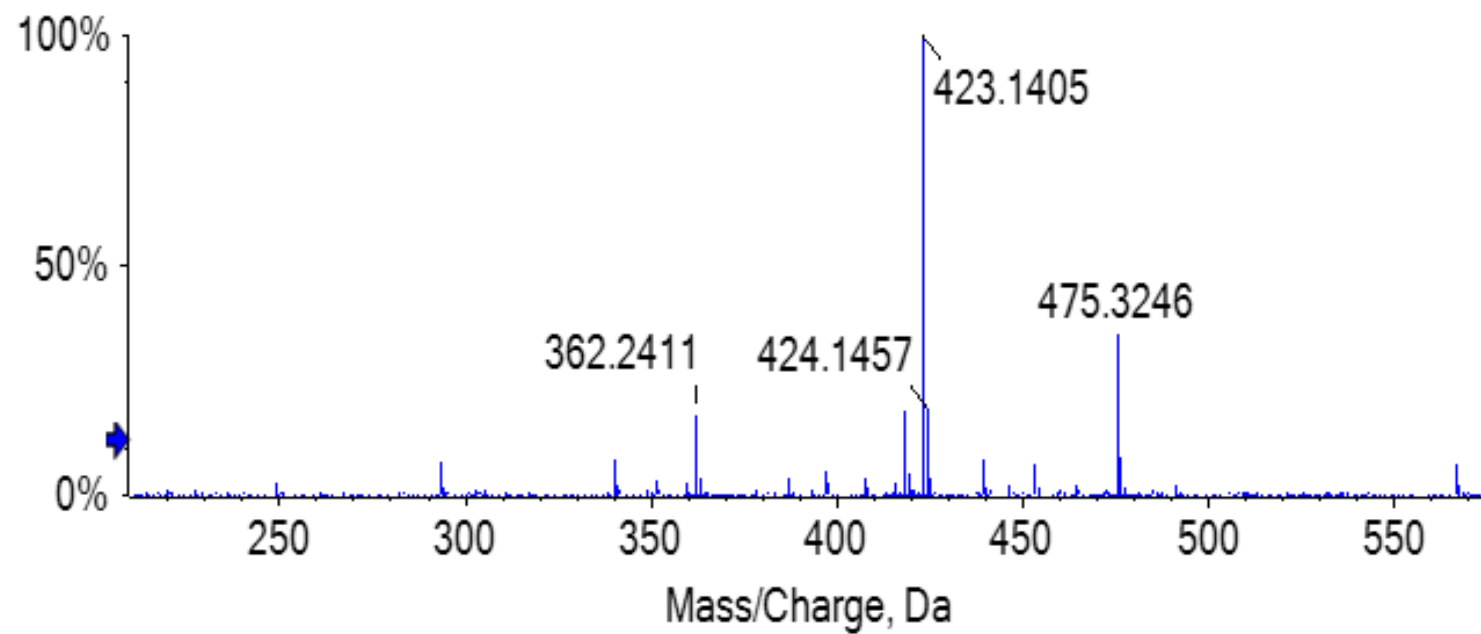


Fig. S11, HRMS of benzyl 3-O-acetyl-4, 6-O-benzylidene - β -L-gulopyranoside (**3**) $[M+Na^+] = 423.1405$

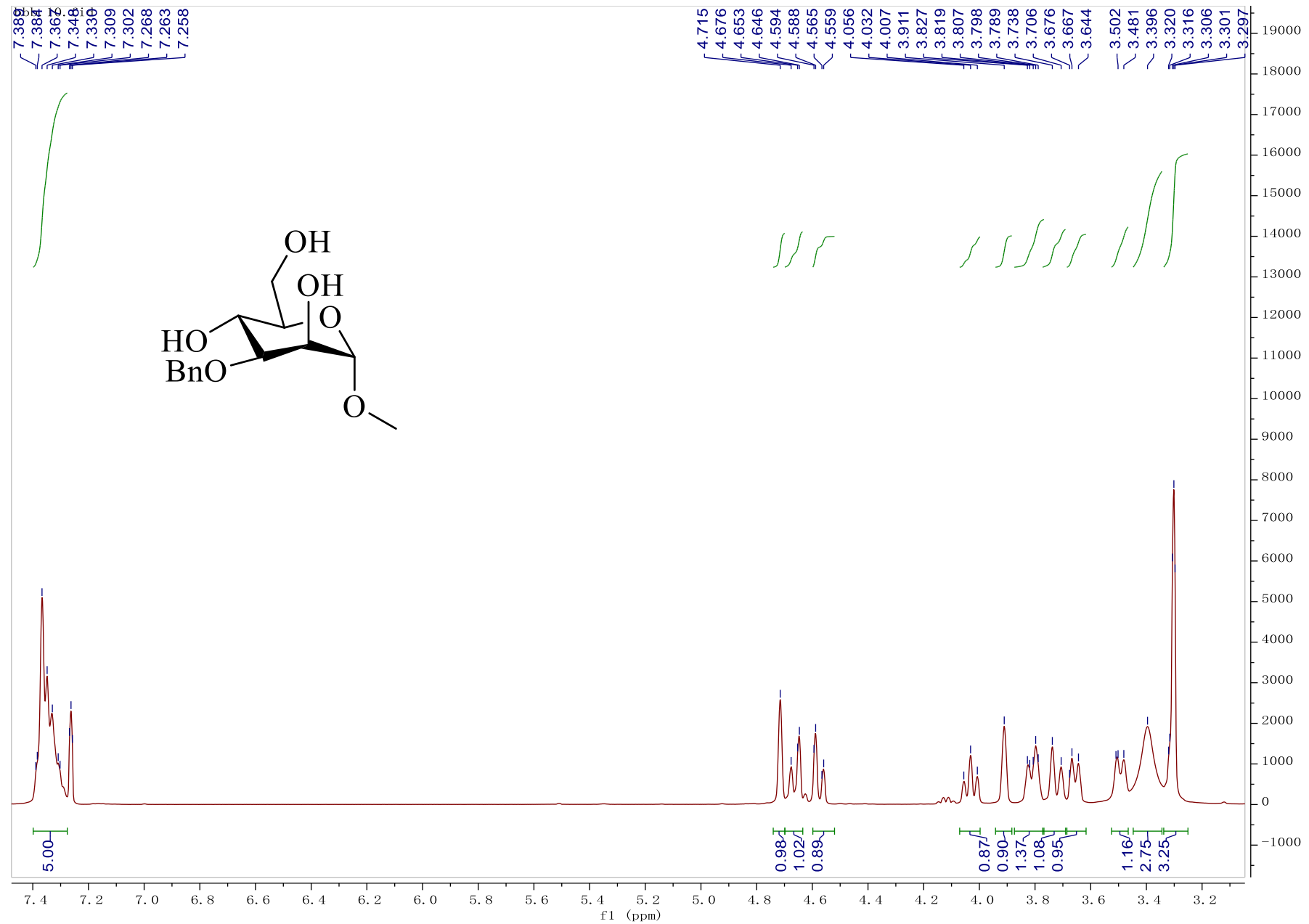


Fig. S12. ^1H NMR of methyl 3-benzyl- α -D-mannopyranoside (**13**) (CDCl_3 , 400 MHz)

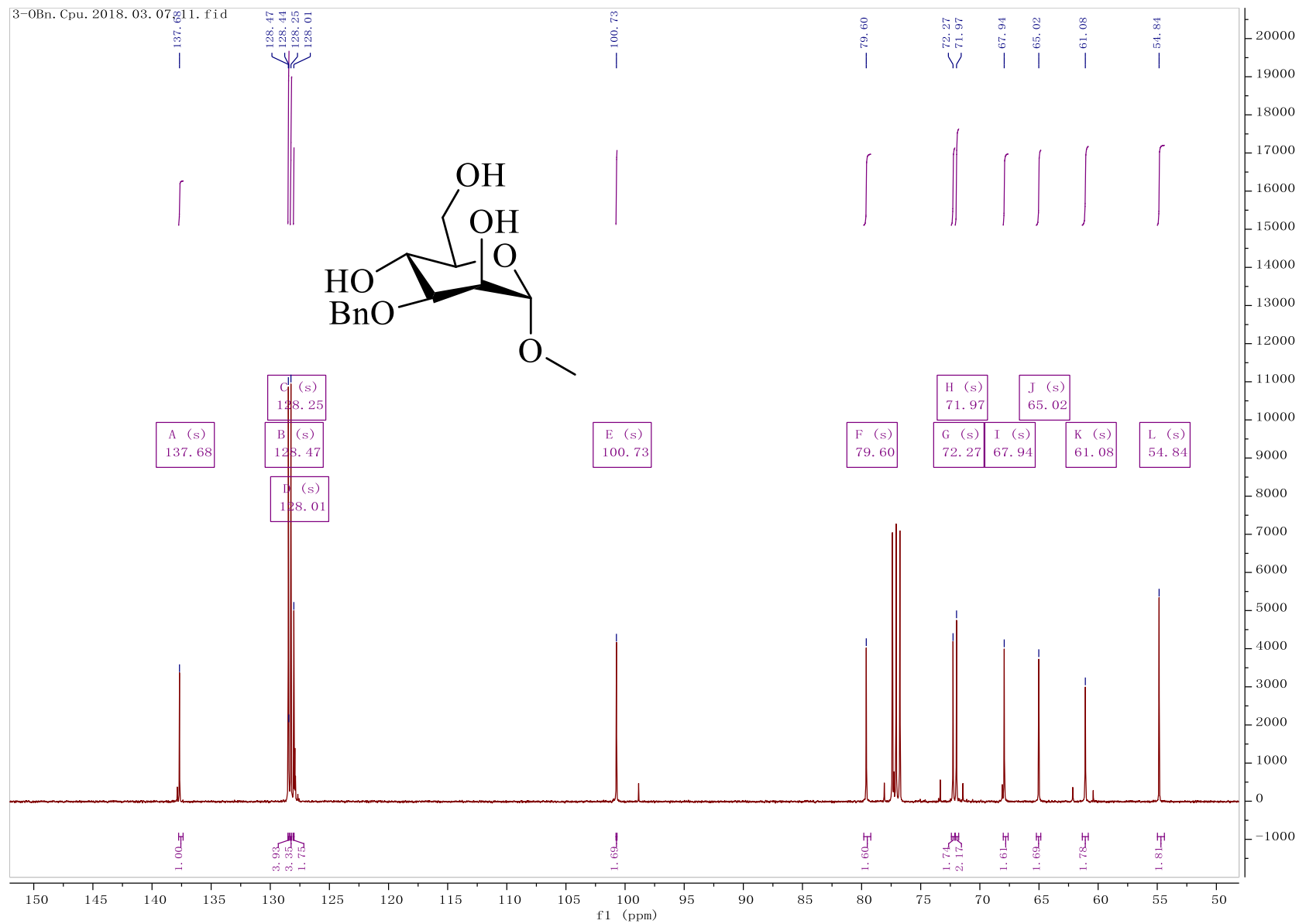


Fig. S13. ^{13}C NMR of methyl 3-benzyl- α -D-mannopyranoside (**13**) (CDCl_3 , 100 MHz)

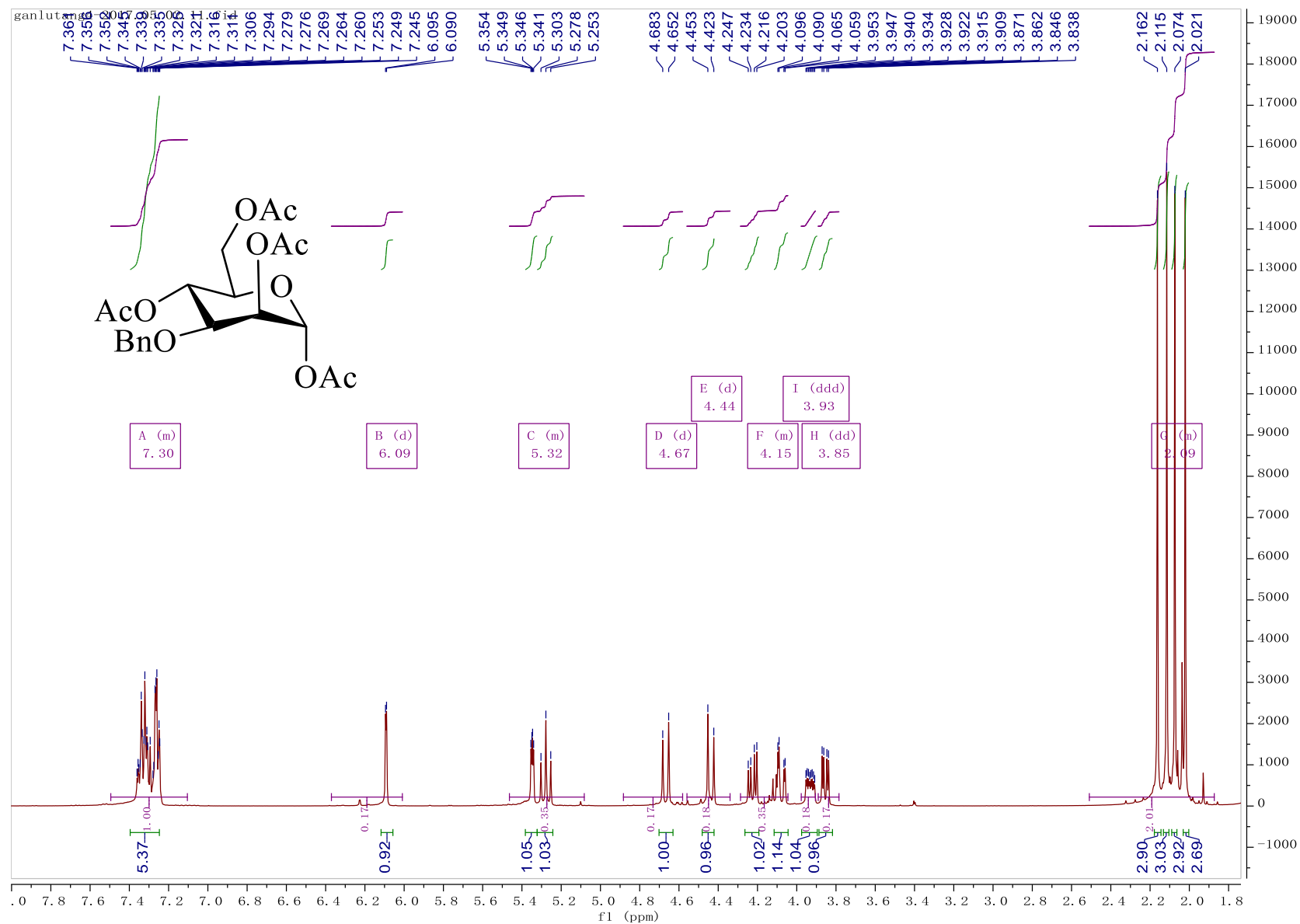


Fig. S14. ¹H NMR of 1, 2, 4, 6-tetra-O-acetyl-3-benzyl- α -D-mannopyranoside (**14**) (CDCl₃, 400 MHz)

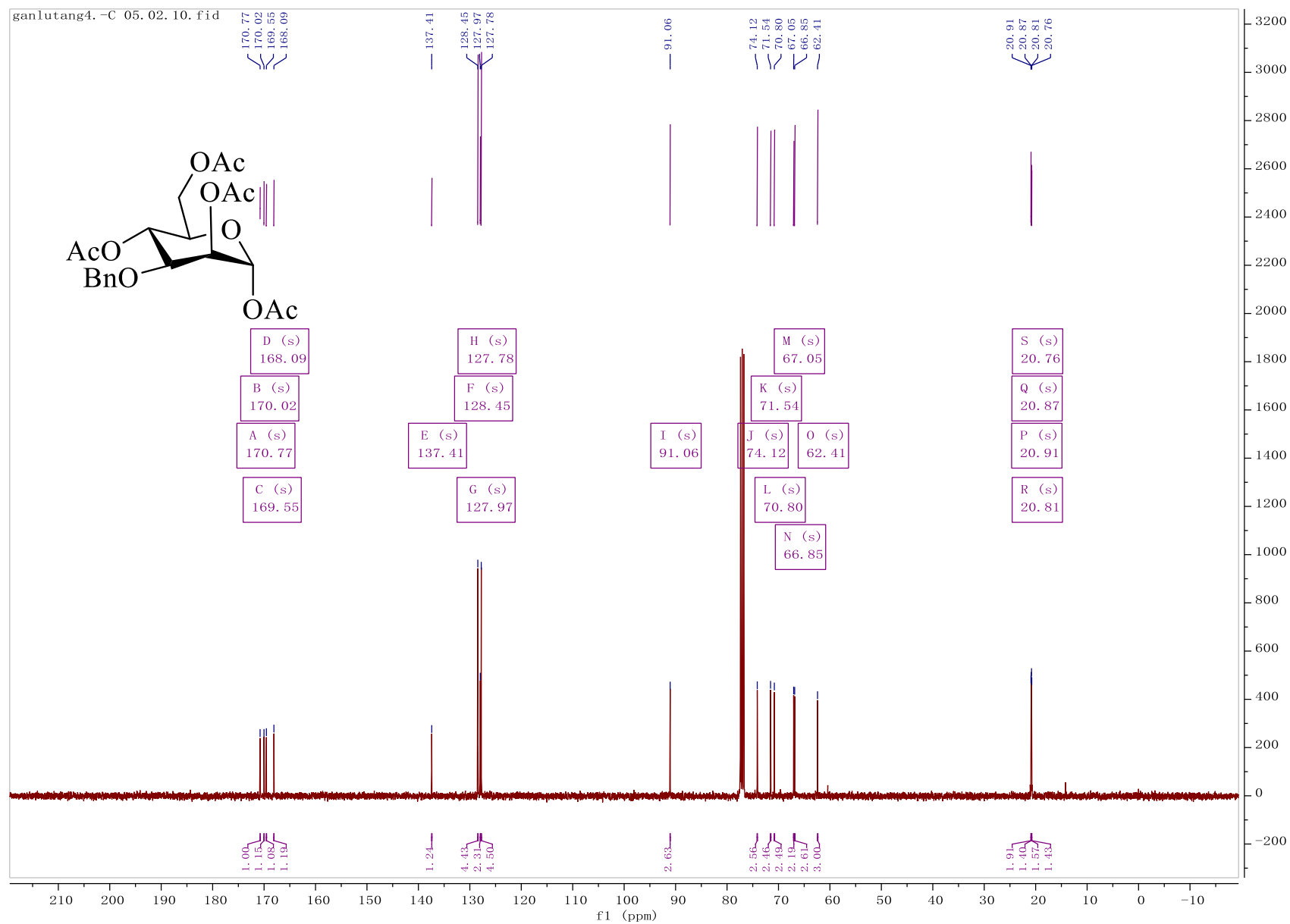


Fig. 15 ^{13}C NMR of 1, 2, 4, 6-tetra-O-acetyl-3-benzyl- α -D-mannopyranoside (**14**) (CDCl_3 , 100 MHz)

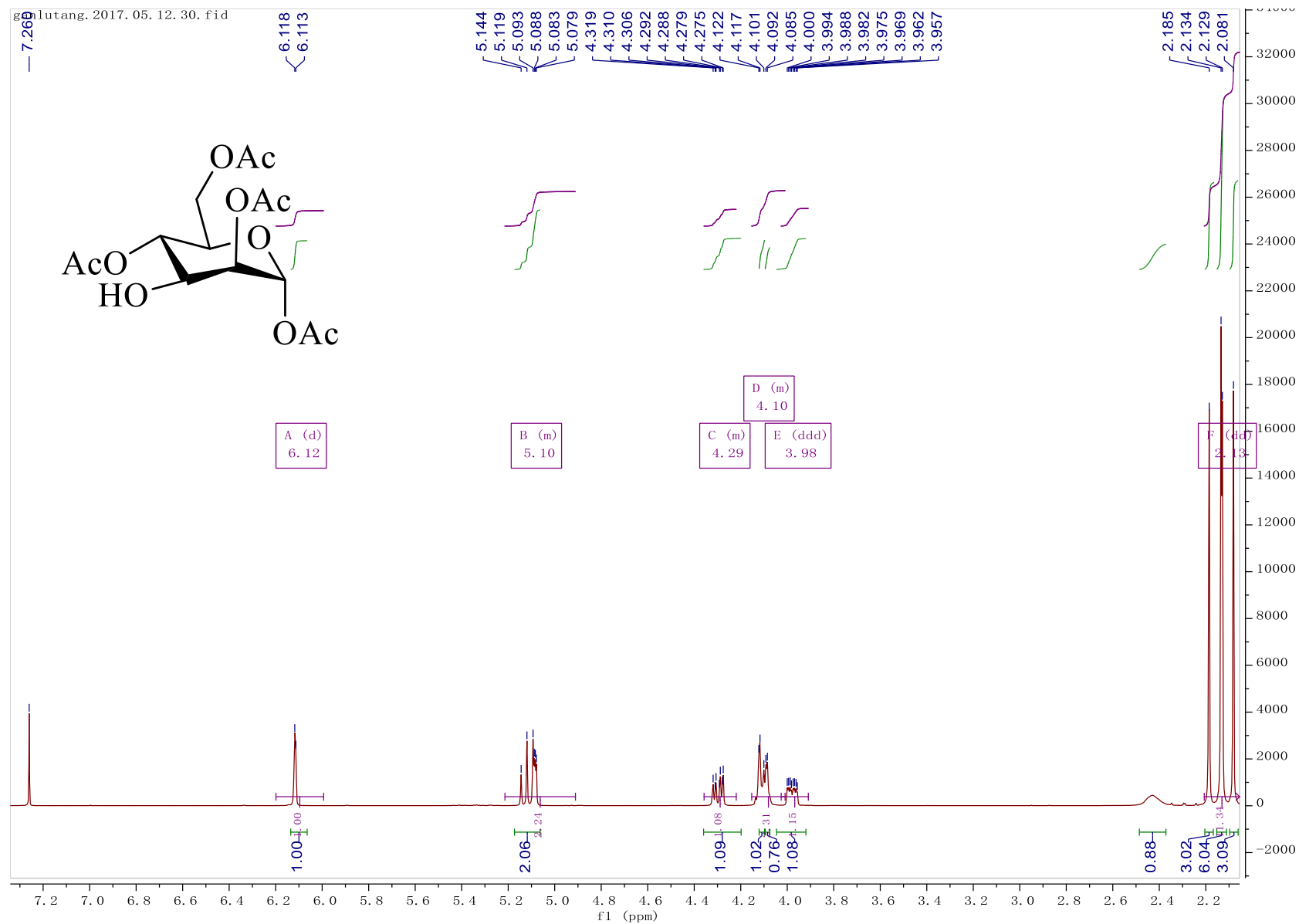


Fig. S16. ^1H NMR of 1, 2, 4, 6-tetra-O-acetyl- α -D-mannopyranose (**15**) (CDCl_3 , 400 MHz)

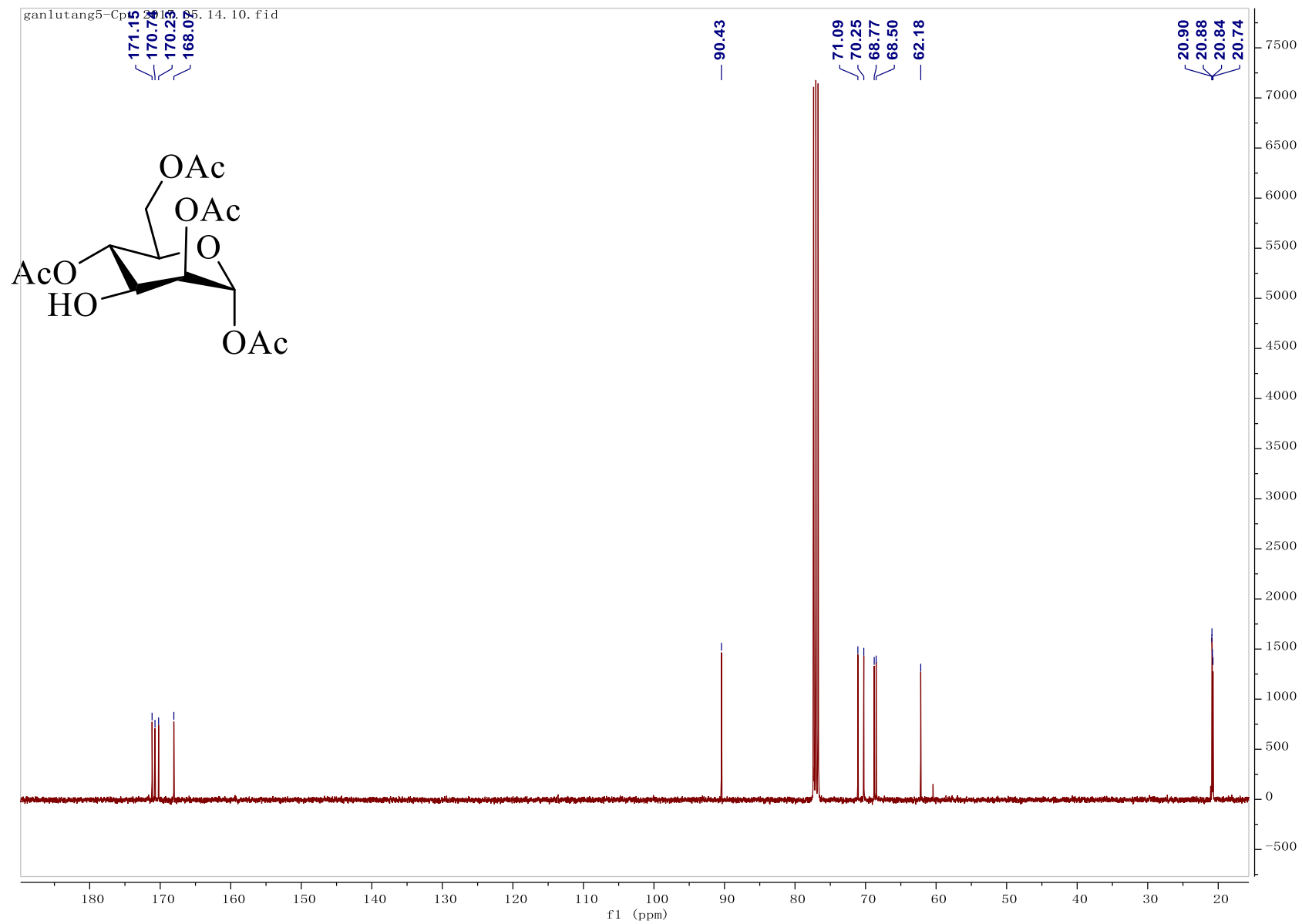


Fig. S17. ^{13}C NMR of 1, 2, 4, 6-tetra-O-acetyl- α -D-mannopyranose (**15**) (CDCl_3 , 100 MHz)

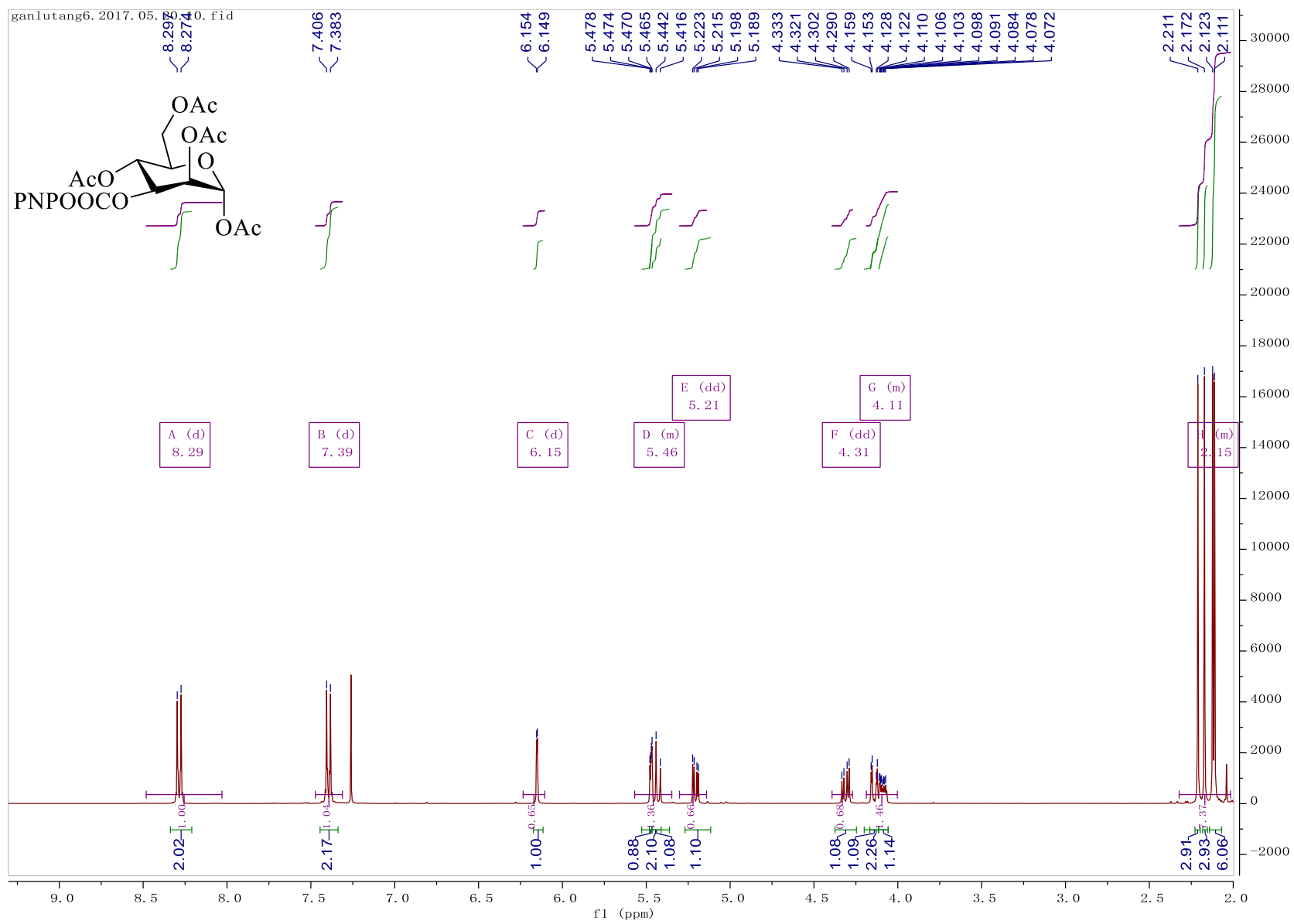


Fig. S18. ^1H NMR of 1,2,4,6-tetra-O-acetyl-3-O-(p-nitrophenylcarbamoyl)- α -D-mannopyranose (**16**) (CDCl_3 , 400 MHz)

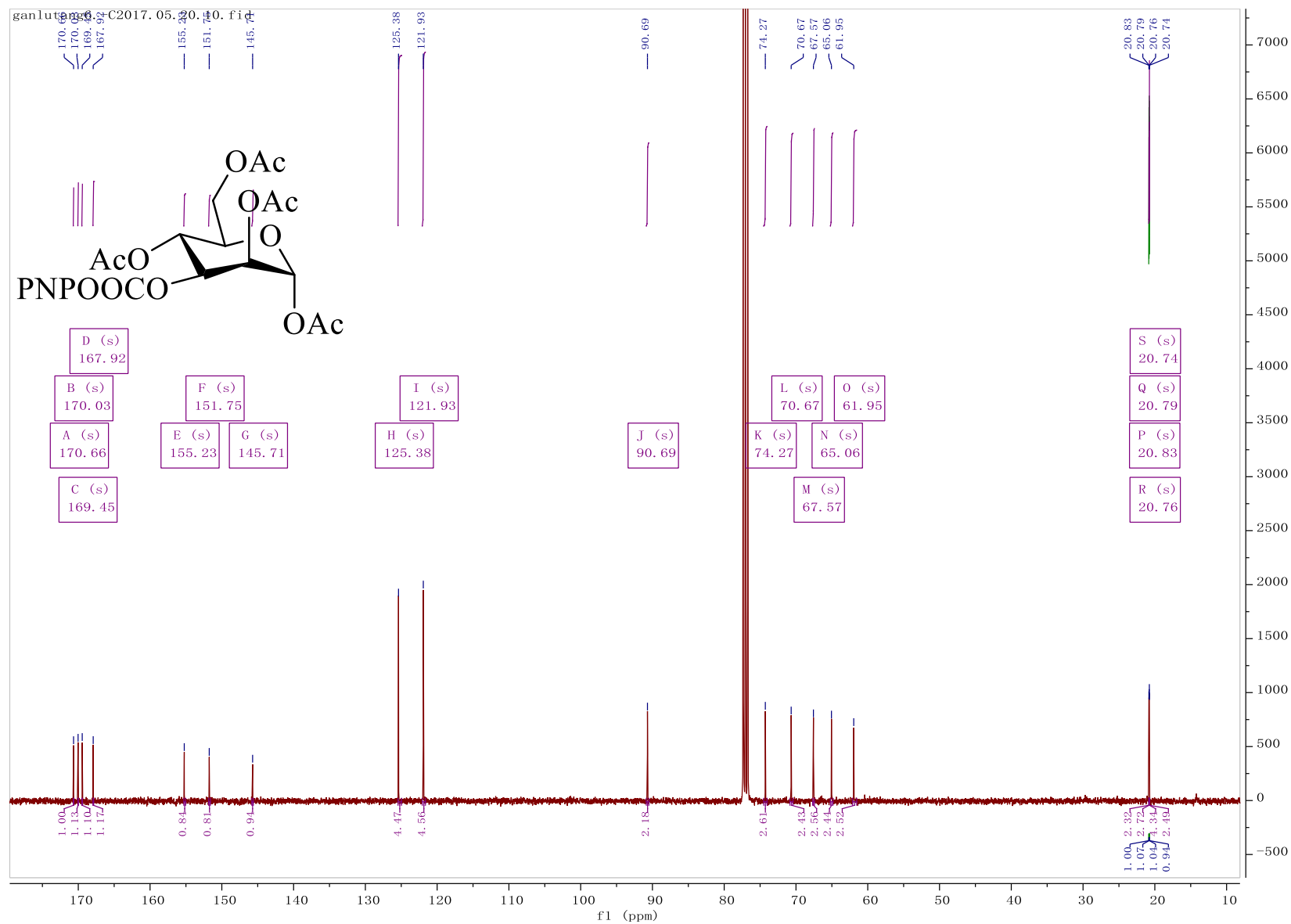


Fig. S19. ^{13}C NMR of 1,2,4,6-tetra-O-acetyl-3-O-(p-nitrophenylcarbamoyl) - α -D-mannopyranose (**16**) (CDCl_3 , 100 MHz)

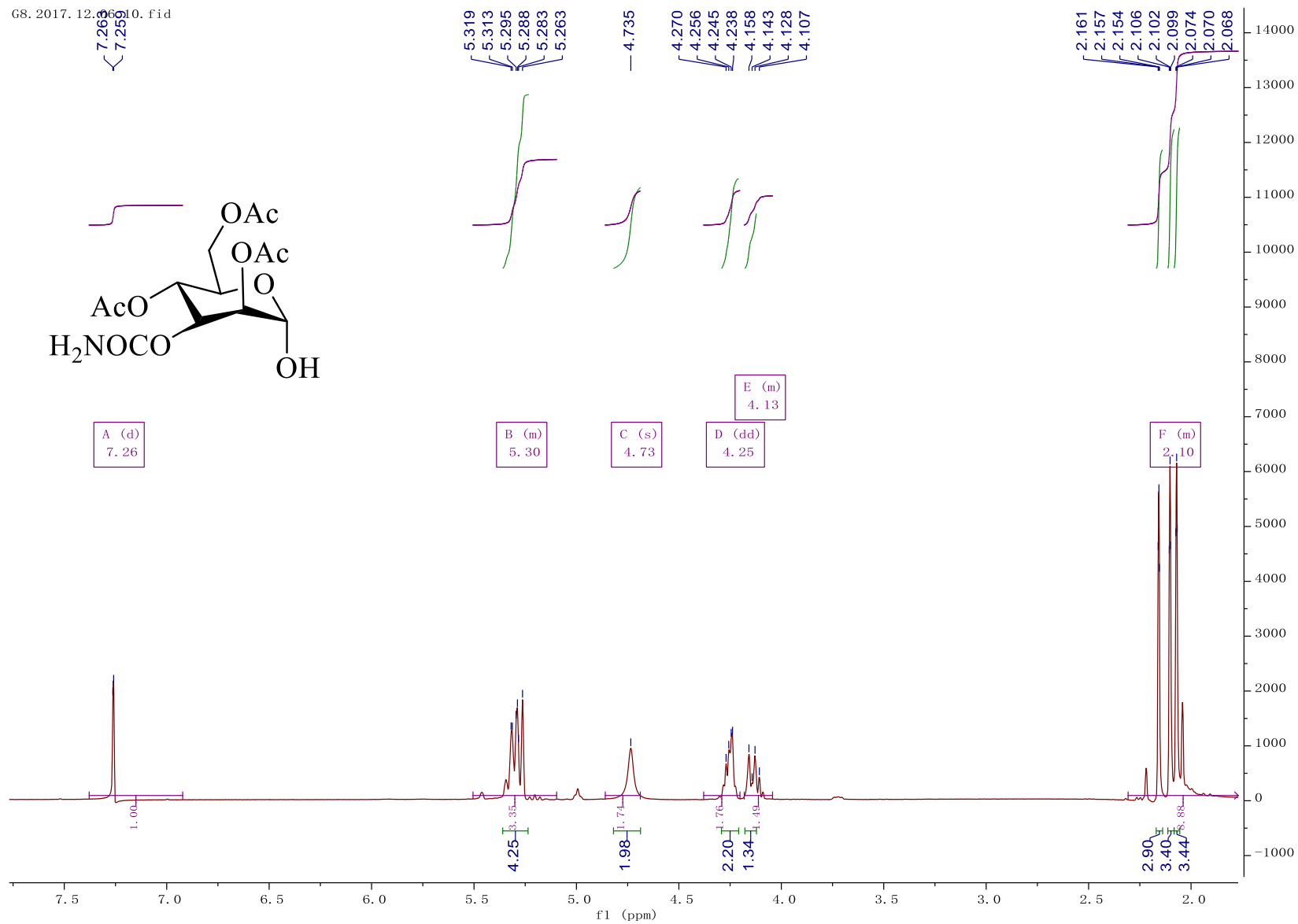


Fig. S20. ^1H NMR of 2,4,6-tri-O-acetyl-3-O-carbamoyl- α -D-mannopyranose (**17**) (CDCl_3 , 400 MHz)

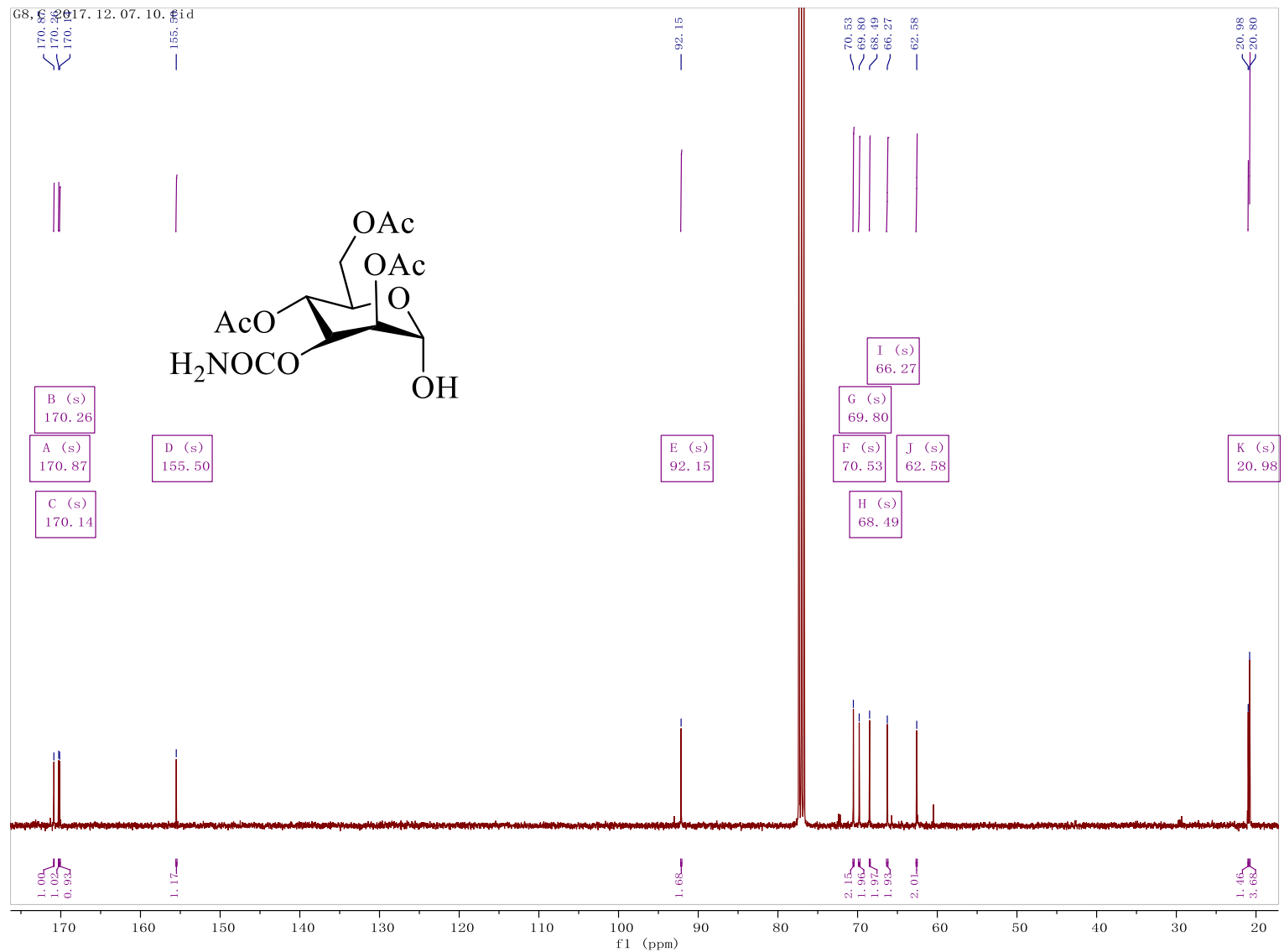


Fig. S21. ^{13}C NMR of 2,4,6-tri-O-acetyl-3-O-carbamoyl - α -D-mannopyranose (**17**) (CDCl_3 , 100 MHz)

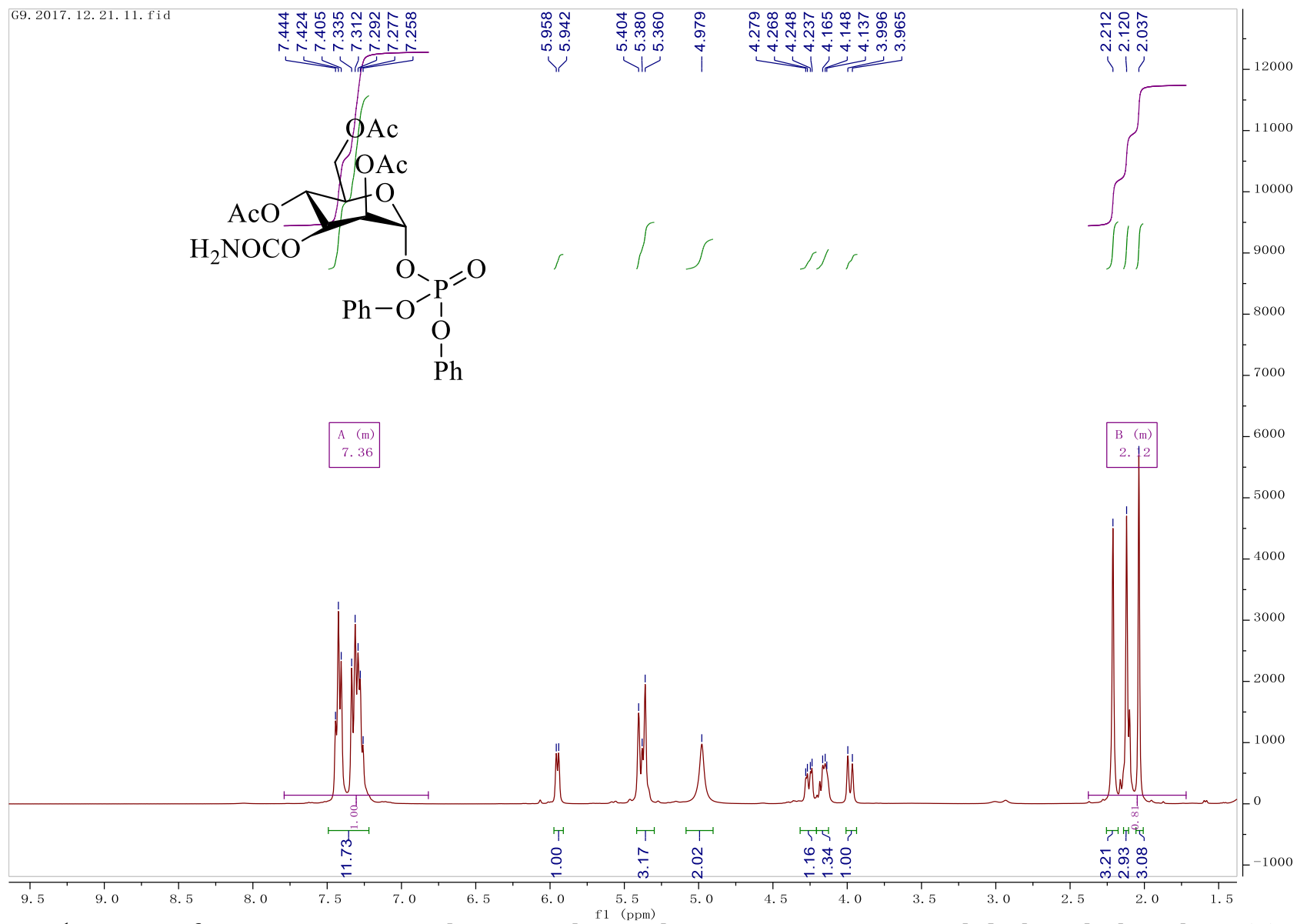


Fig.S22. ¹H NMR of 2, 4, 6-tri-O-acetyl-3-O-carbamoyl- α -D-mannopyranosyl diphenyl phosphate (**4**) (CDCl₃, 400 MHz)

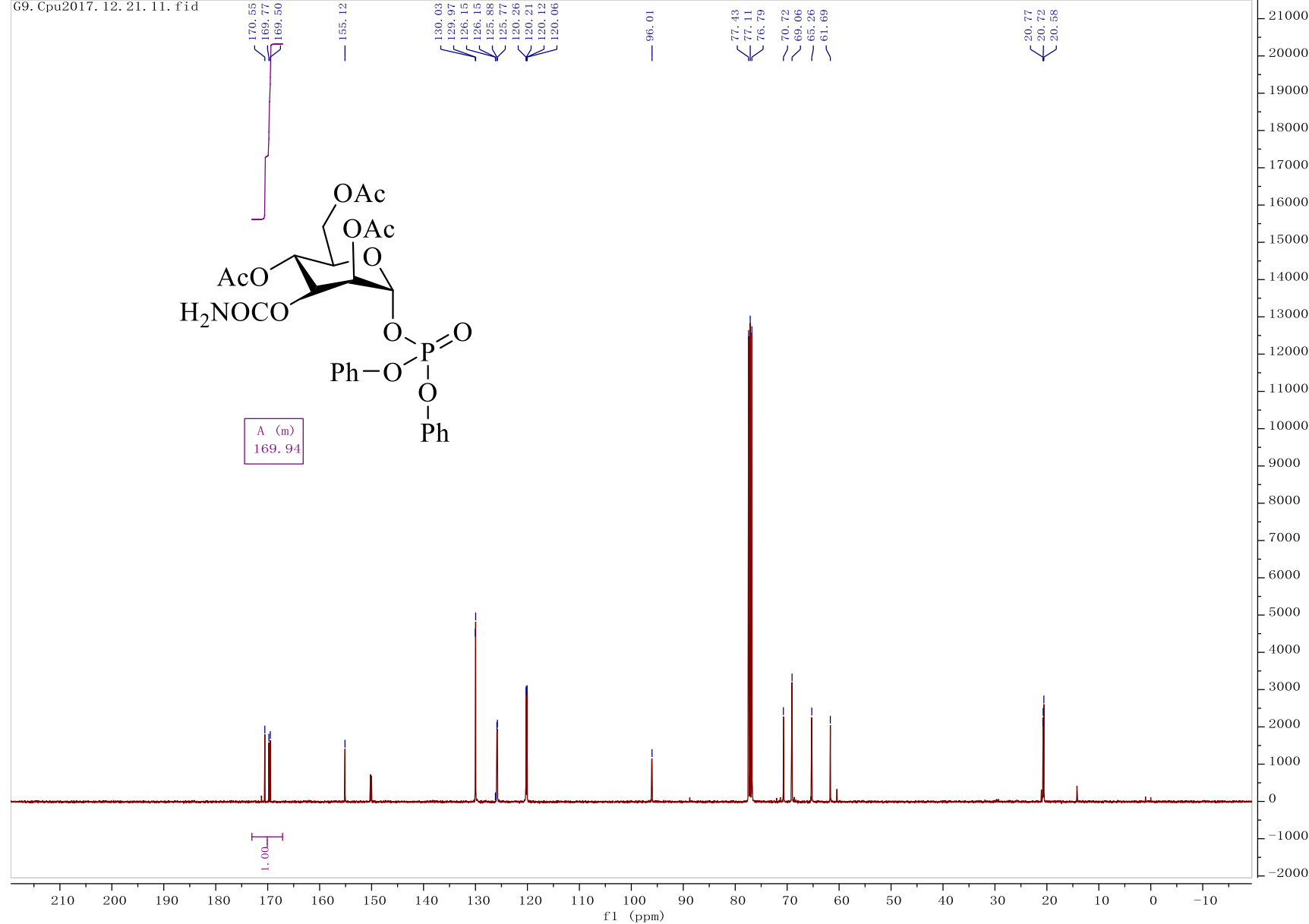


Fig. S23. ^{13}C NMR of 2, 4, 6-tri-O-acetyl-3-O-carbamoyl - α -D-mannopyranosyl diphenyl phosphate (**4**) (CDCl_3 , 100 MHz)

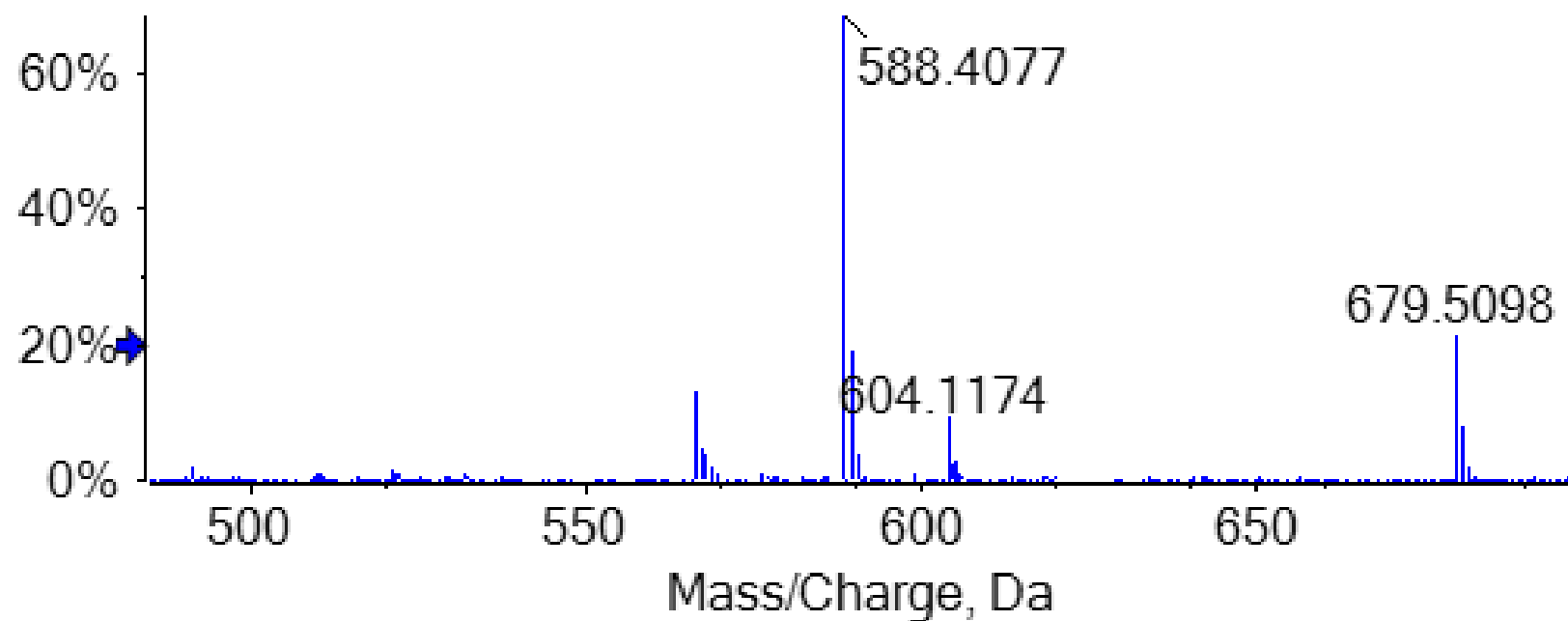


Fig. S 24 *HRMS of 2, 4, 6-tri-O-acetyl-3-O-carbamoyl - α -D-mannopyranosyl diphenyl phosphate (4) $[M+Li]^+ = 588.4077$; $[M+Na]^+ = 604.1174$*

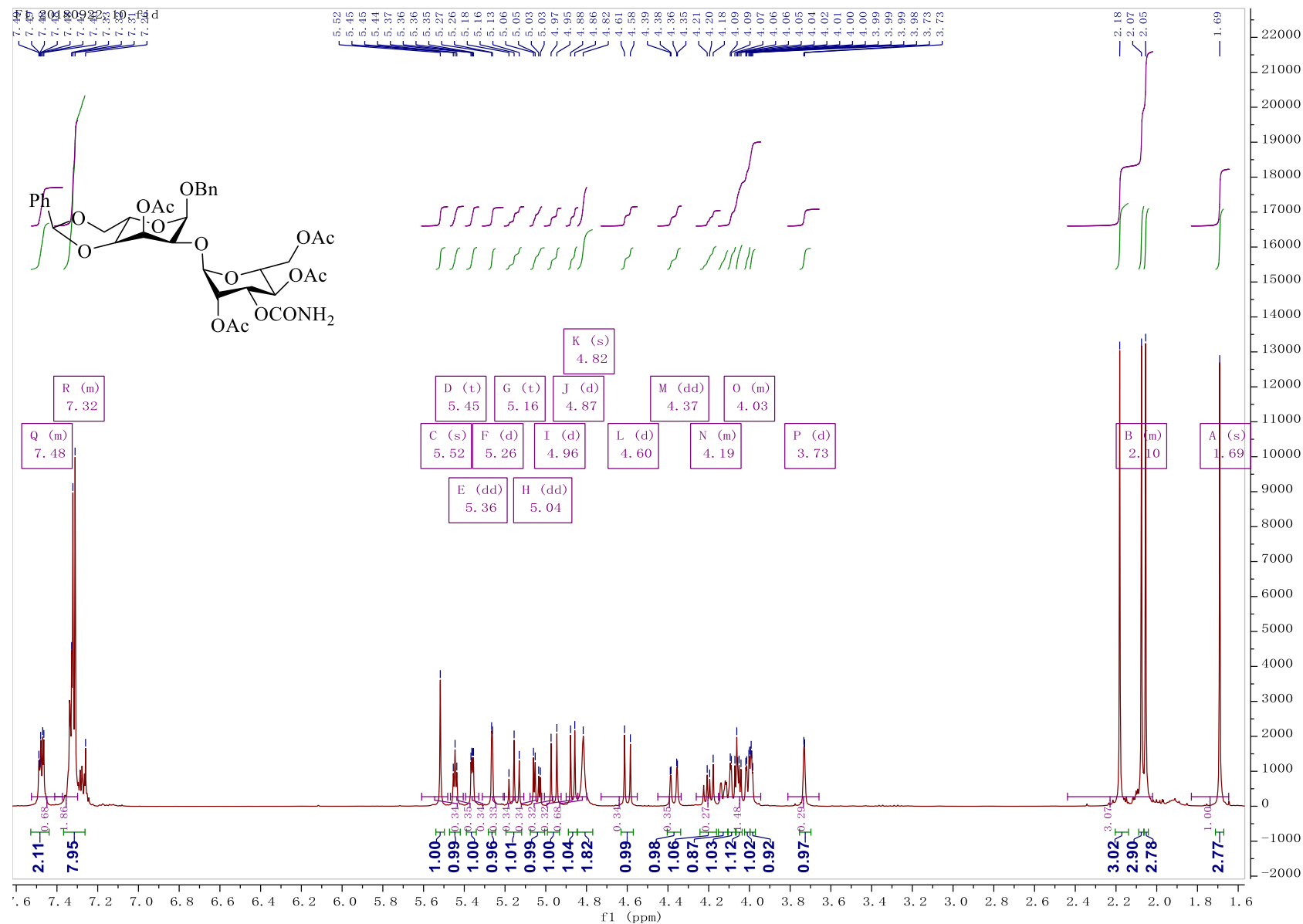


Fig.S25. ^1H NMR of benzyl 3-O-acetyl-4,6-O-benzylidene-2-O-(2,4,6-tri-O-acetyl-3-O-carbamoyl- α -D-manno- pyranosyl)- β -L-gulopyranoside (**18**) (CDCl_3 , 400 MHz)

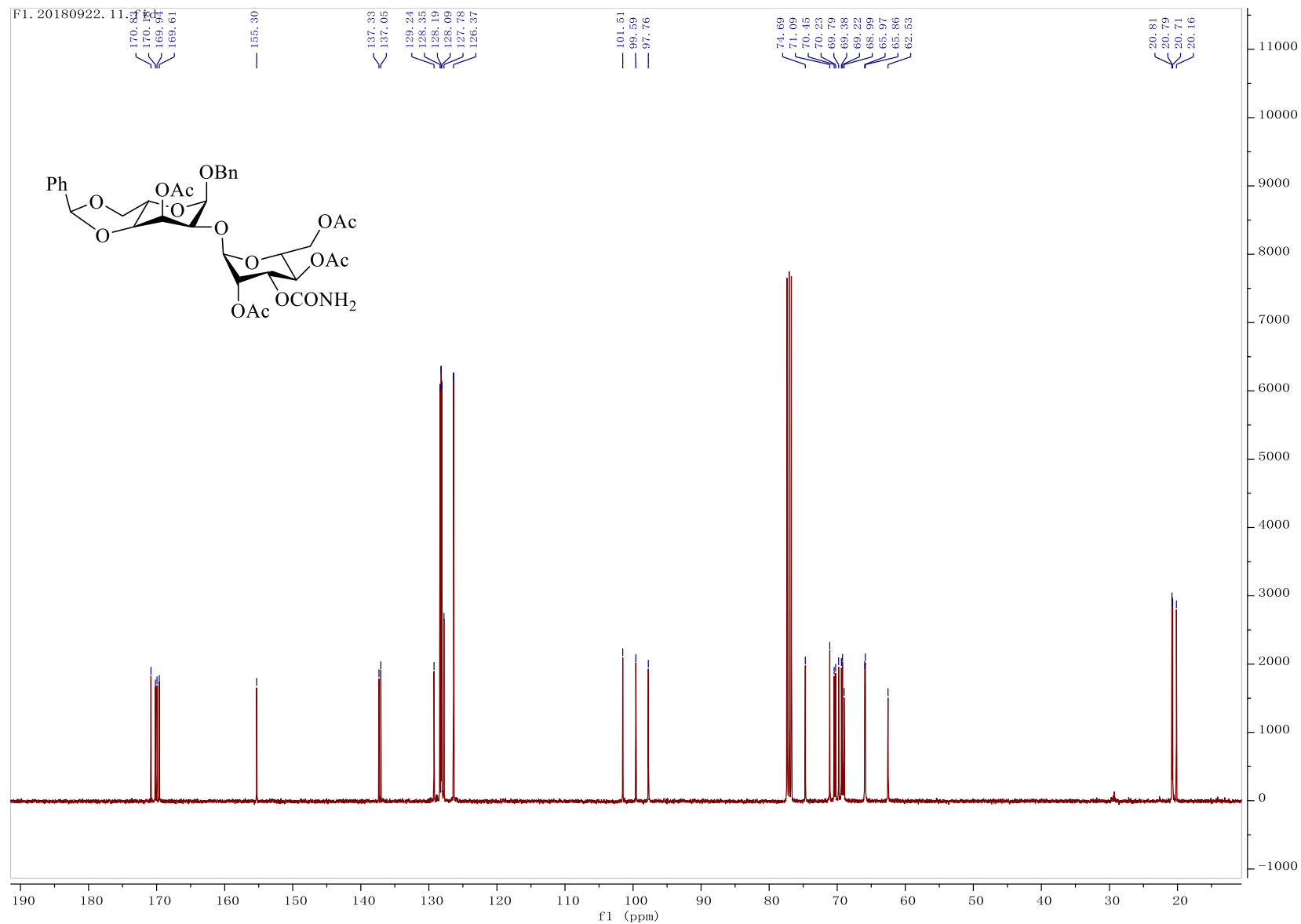


Fig. S26. ^{13}C NMR of benzyl 3-O-acetyl-4,6-O-benzylidene-2-O-(2,4,6-tri-O-acetyl-3-O-carbamoyl- α -D-manno-pyranosyl)- β -L-gulopyranoside (**18**) (CDCl_3 , 100 MHz)

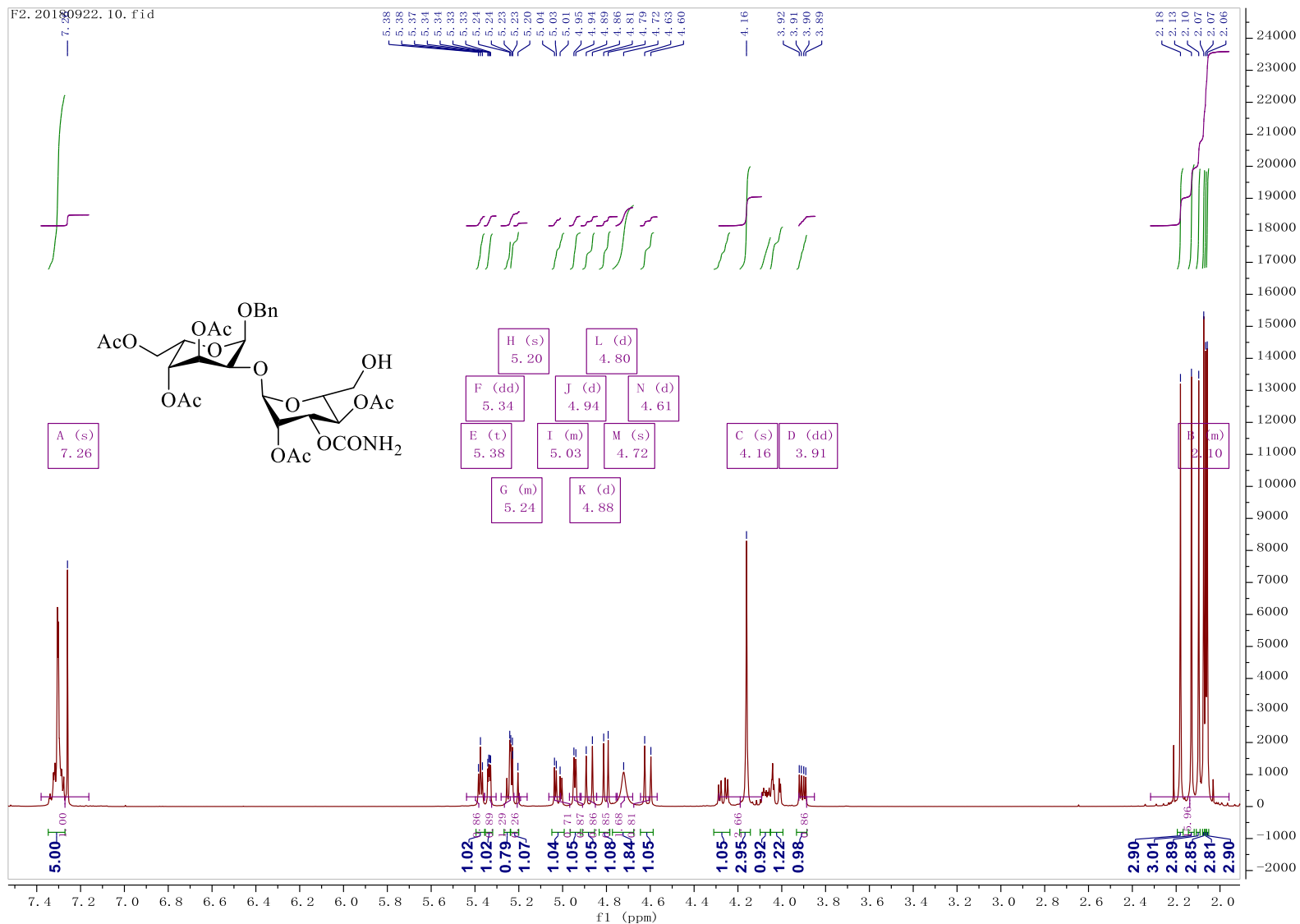


Fig. S27. ^1H NMR of benzyl 3, 4, 6-tri-O-acetyl-2-O-(2, 4, 6-tri-O-acetyl-3-O-carbamoyl- α -D-mannopyranosyl)- β -L-gulopyranosyl diphenyl phosphate (**19**) (CDCl_3 , 400 MHz)

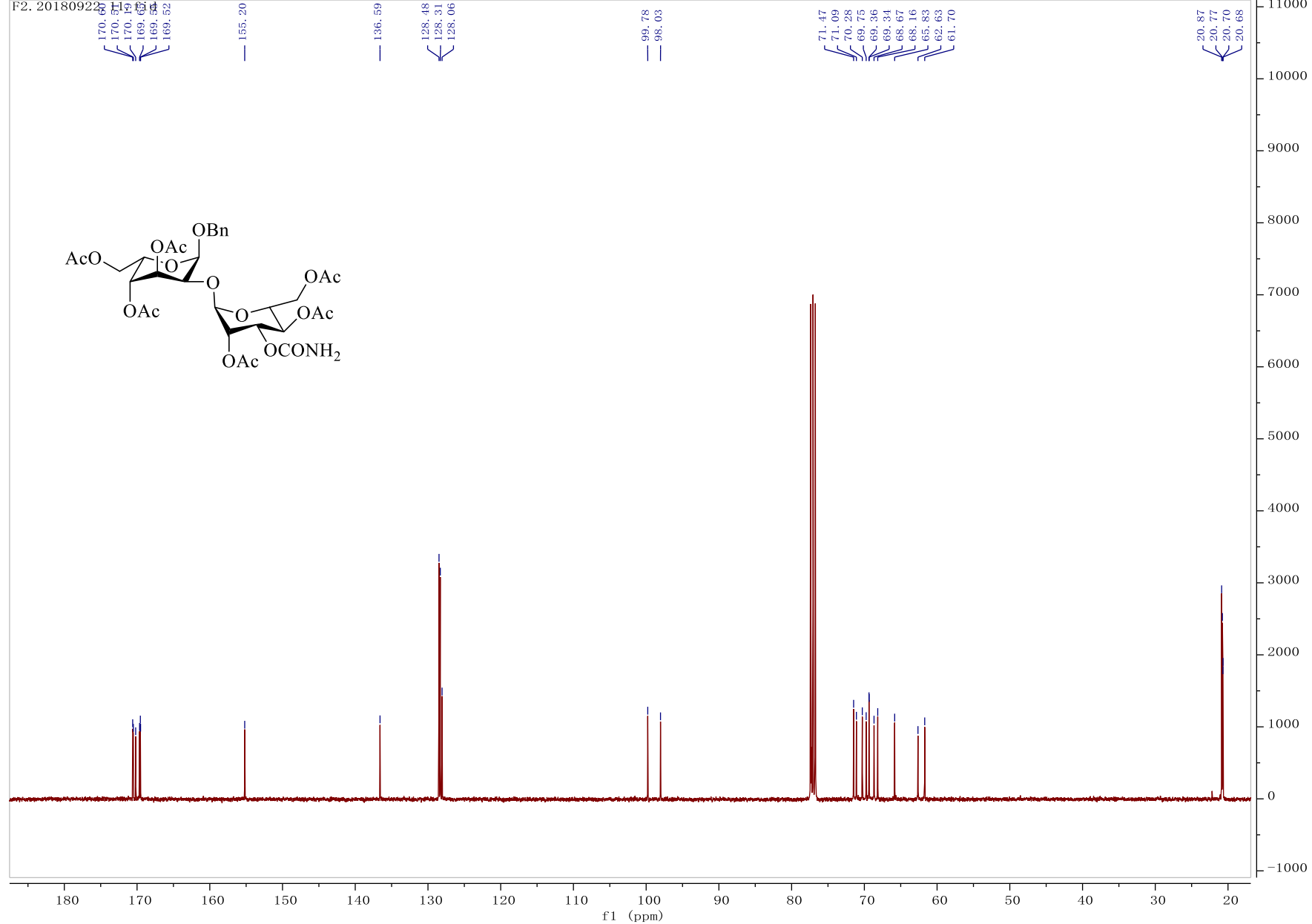


Fig.S28. ¹³C NMR of benzyl 3, 4, 6-tri-O-acetyl-2-O-(2, 4, 6-tri-O-acetyl-3-O-carbamoyl- α -D- mannopyranosyl)- β -L-gulopyranosyl diphenyl phosphate (**19**) (CDCl₃, 100 MHz)

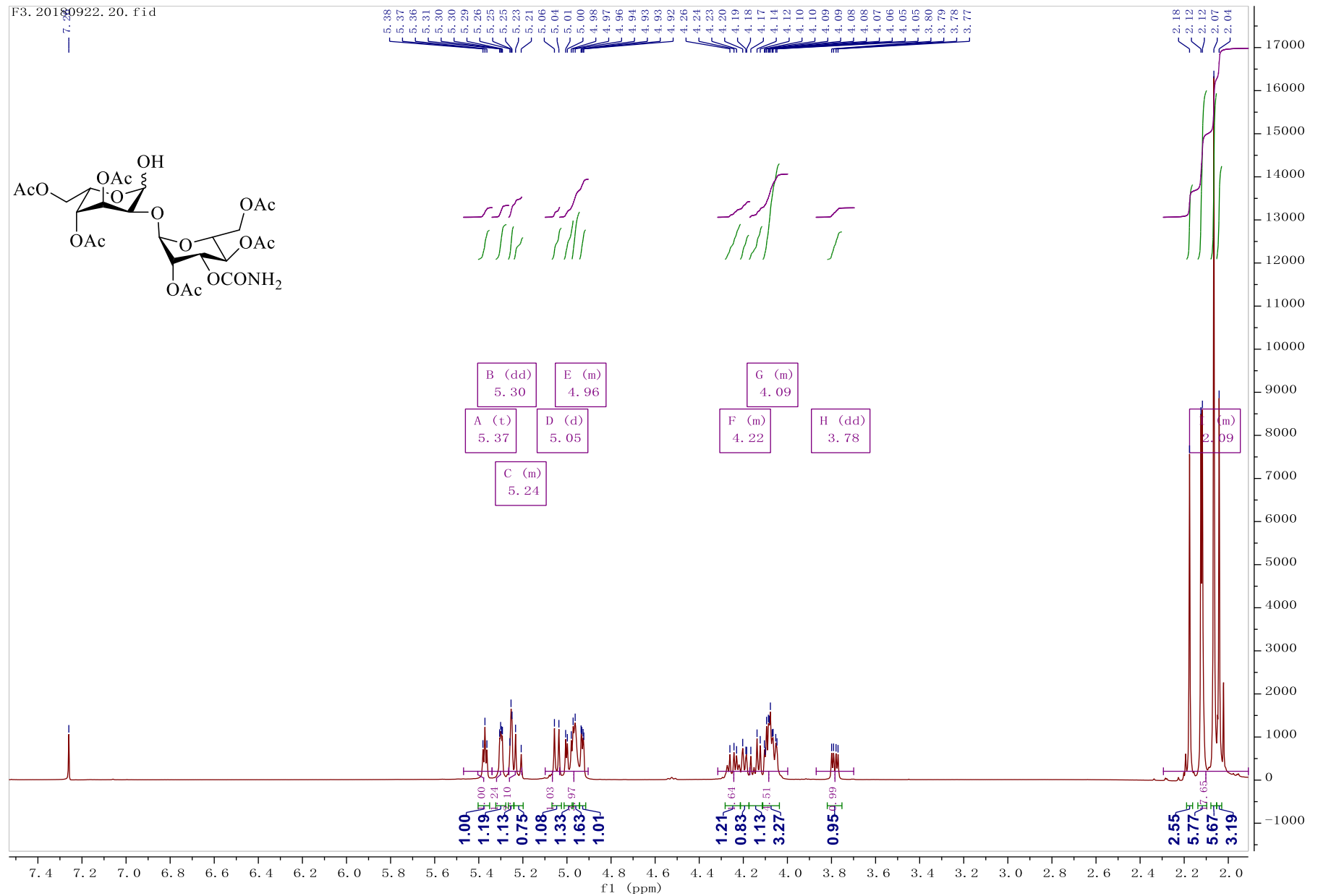


Fig. S29 ^1H NMR of 3,4,6-tri-O-acetyl-2-O-(2,4,6-tri-O-acetyl-3-O-carbamoyl- α -D-mannopyranosyl)- β -L-gulopyranoside (**20**) (CDCl_3 , 400 MHz)

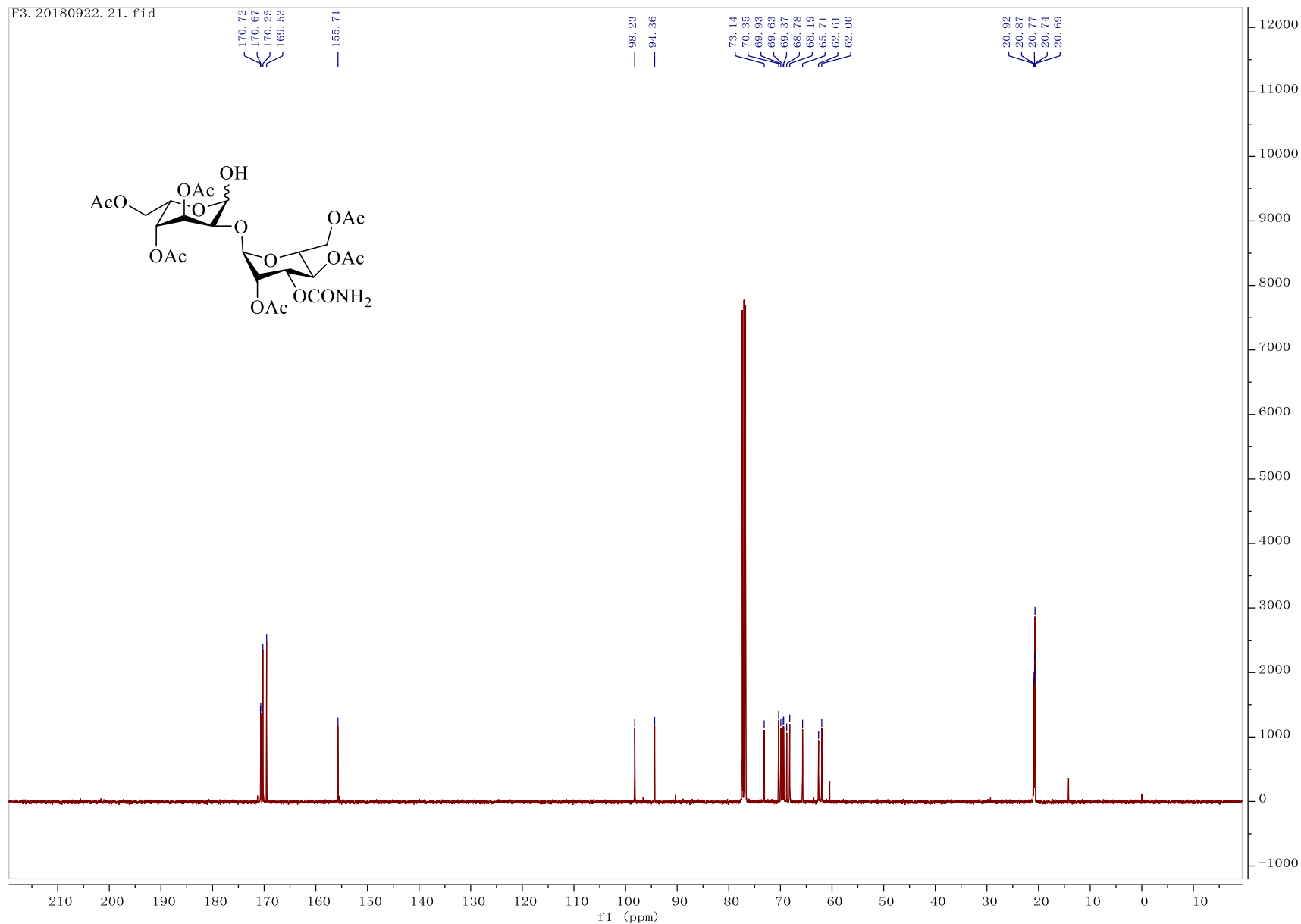


Fig. S30. ^{13}C NMR of 3,4,6-tri-O-acetyl-2-O-(2,4,6-tri-O-acetyl-3-O-carbamoyl- α -D-mannopyranosyl)- β -L-gulopyranoside (**20**) (CDCl_3 , 100 MHz)

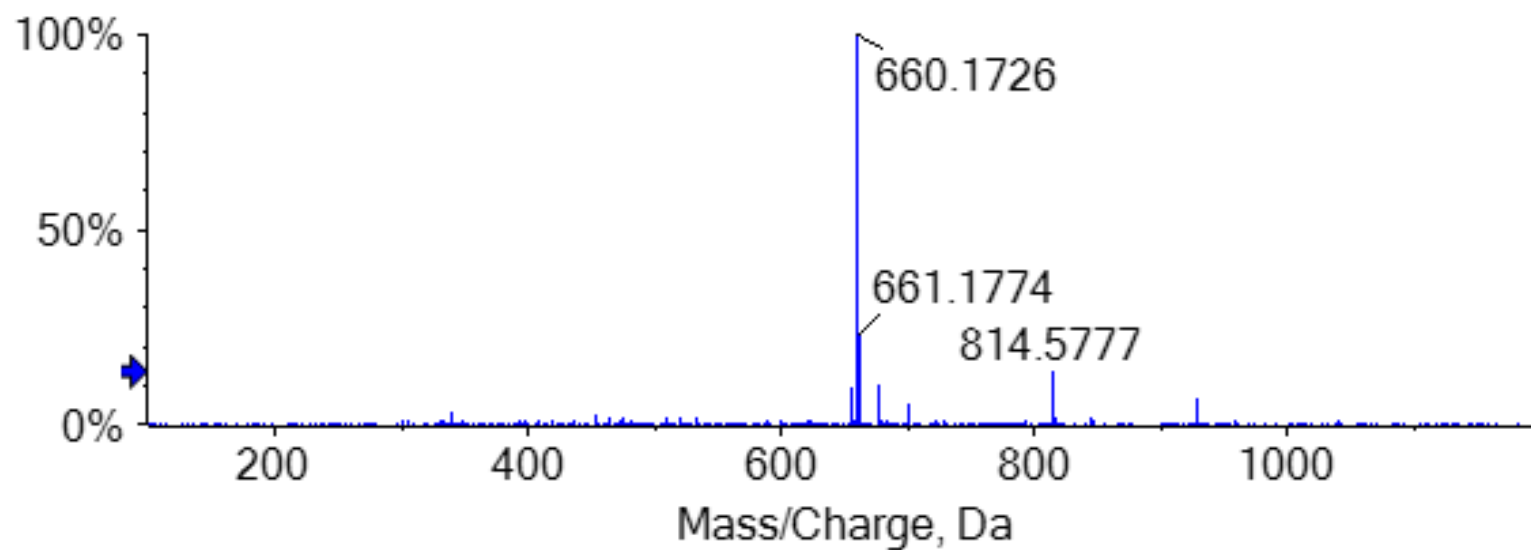


Fig.31 HRMS of 3,4,6-tri-O-acetyl-2-O-(2,4,6-tri-O-acetyl-3-O-carbamoyl- α -D-mannopyranosyl)- β -L-gulopyranoside (**20**) $[M+Na^+]=660.1726$

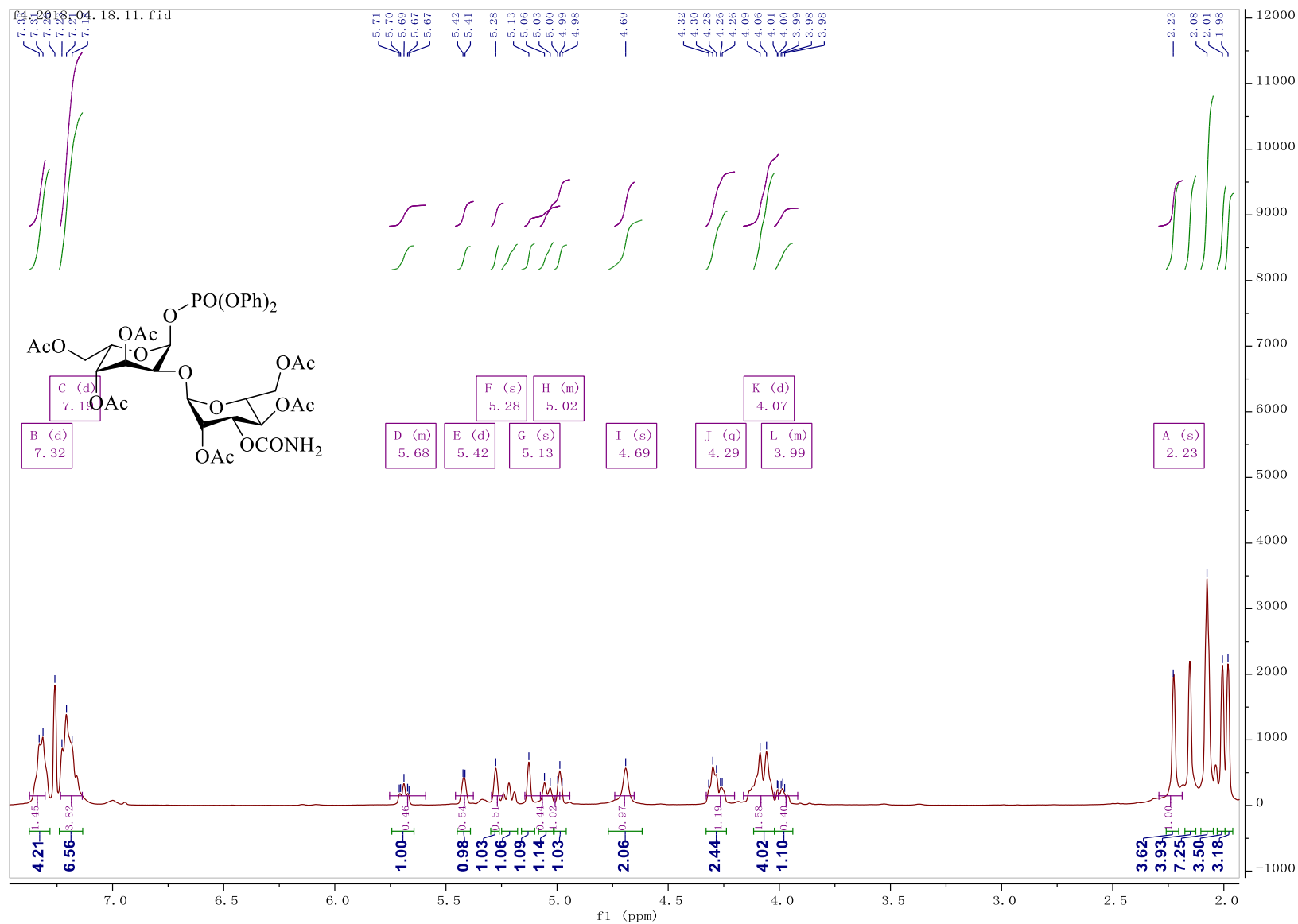


Fig. S32 ^1H NMR of 3,4,6-Tri-O-acetyl-2-O-(3,4,6-tri-O-acetyl-2-O-(carbamoyl)- α -D-mannopyranosyl)- β -L-gulopyranosyl Diphenyl Phosphate (23) (CDCl_3 , 400 MHz)

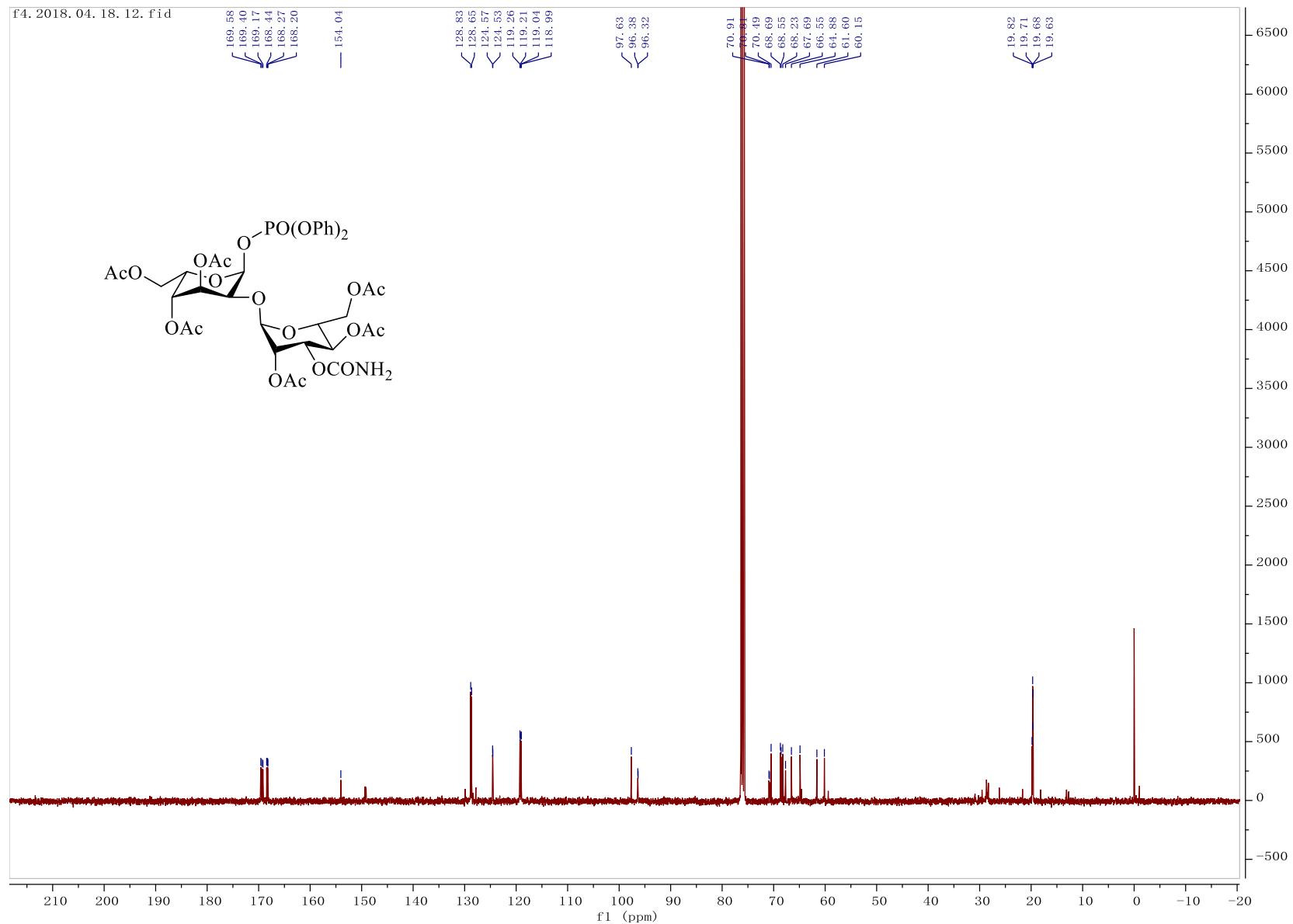


Fig. S33. ^{13}C NMR of 3,4,6-Tri-O-acetyl-2-O-(3,4,6-tri-O-acetyl-2-O-(carbamoyl)- α -D-mannopyranosyl)- β -L-gulopyranosyl Diphenyl Phosphate (**23**) (CDCl_3 , 100 MHz)

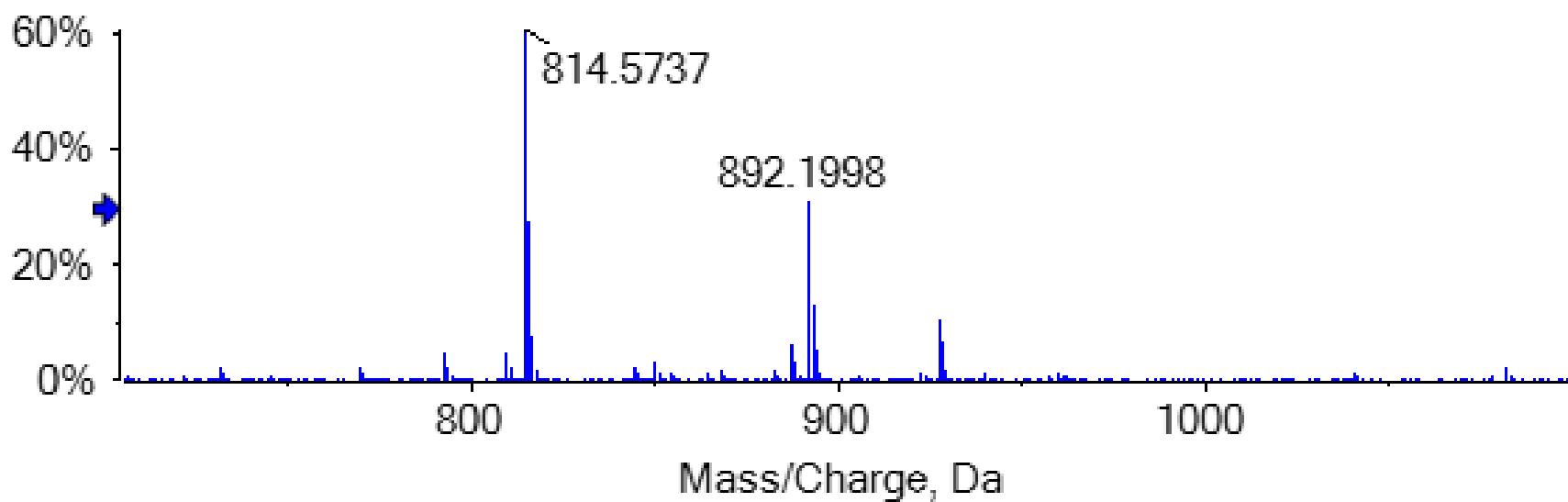


Fig. 34 HRMS of 3,4,6-Tri-O-acetyl-2-O-(3,4,6-tri-O-acetyl-2-O-(carbamoyl)- α -D-mannopyranosyl)- β -L-gulopyranosyl Diphenyl Phosphate (**23**) $[M+Na]^+ = 892.1998$

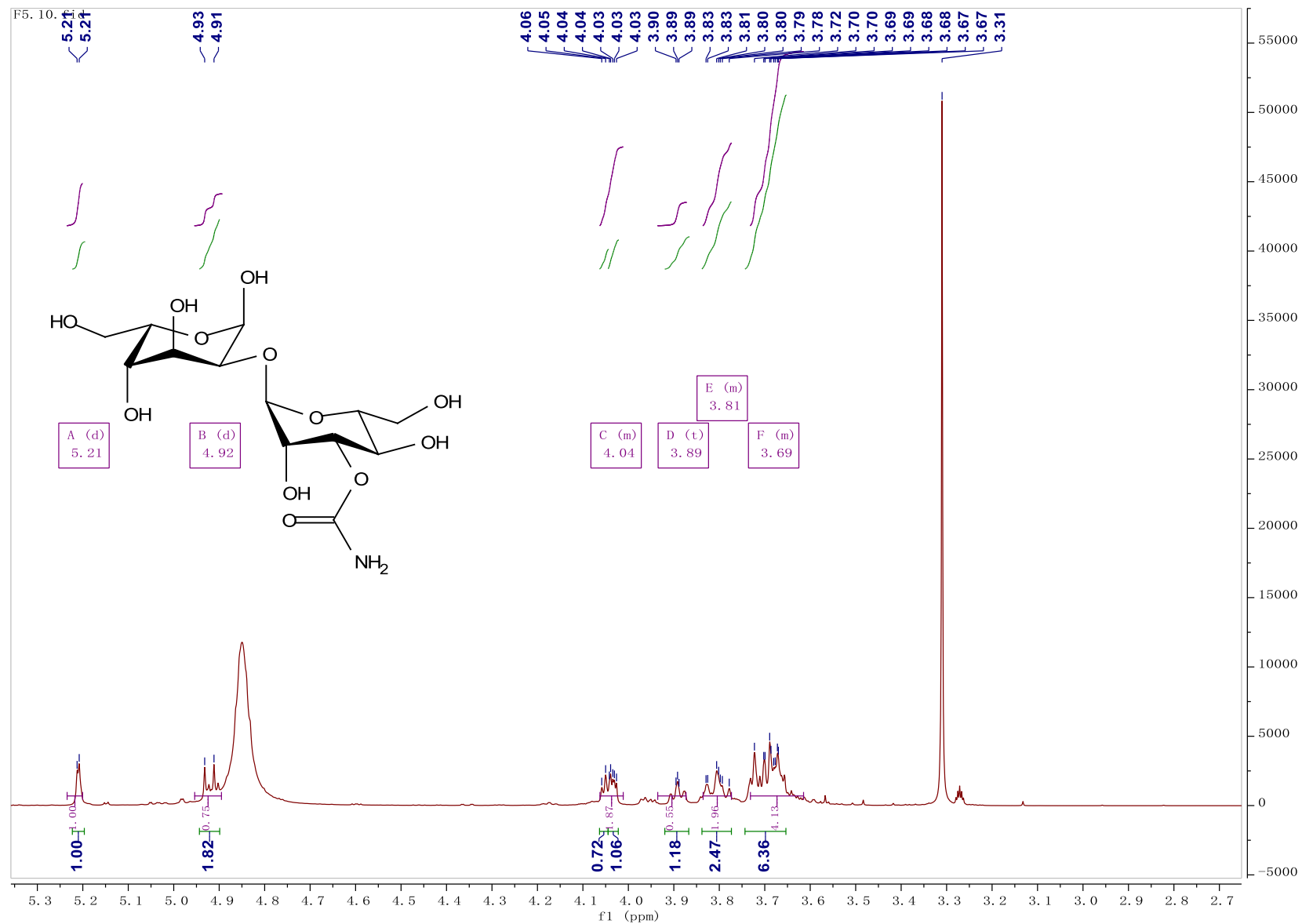


Fig. S35. ^1H NMR of 2-O-(3-O-Carbamoyl- α -D-mannopyranosyl)-L-gulopyranose (2) (CD_3OD , 400 MHz)

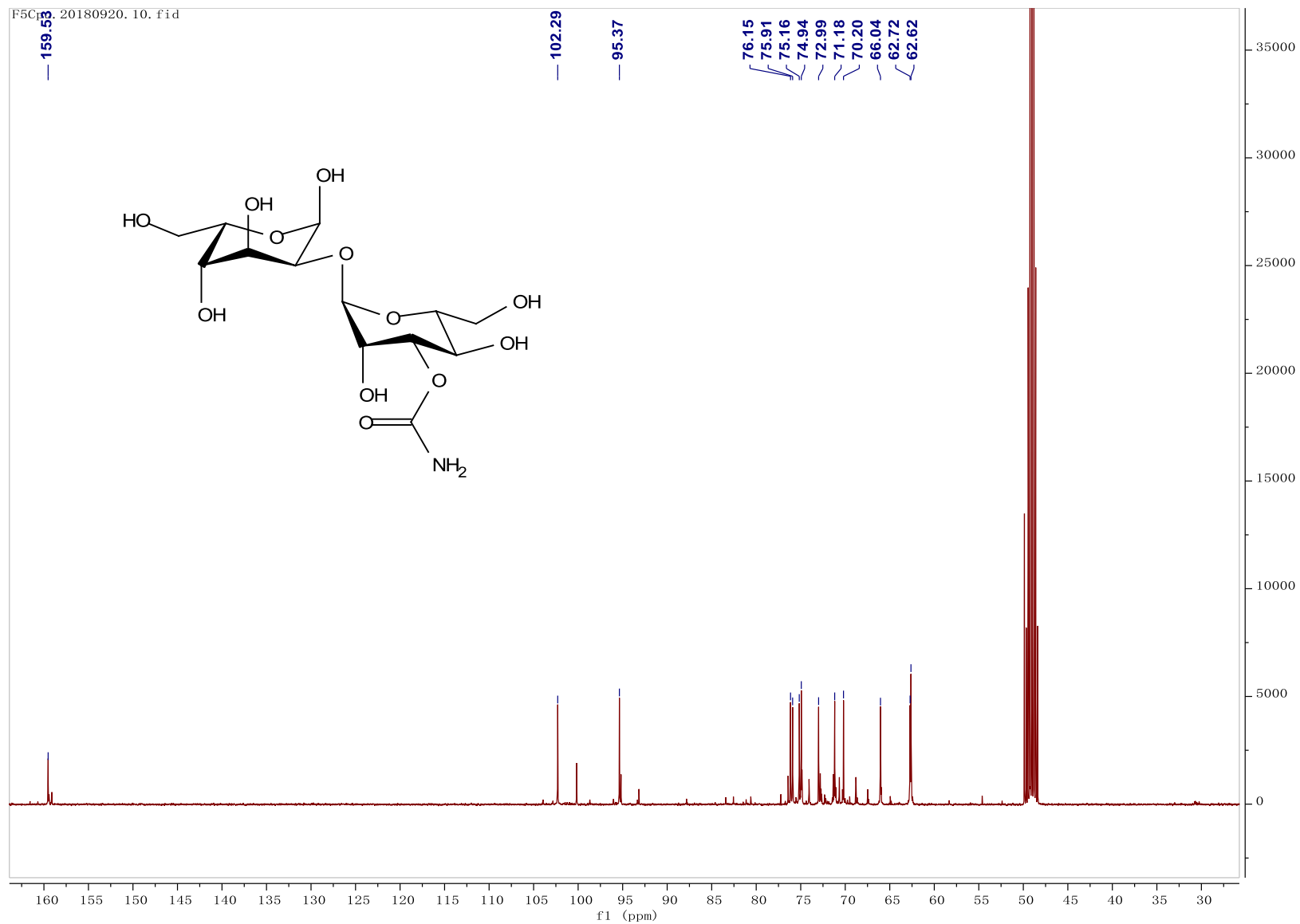


Fig. S36 ^{13}C NMR of 2-O-(3-O-Carbamoyl- α -D-mannopyranosyl)-L-gulopyranose (2) (CD_3OD , 100 MHz)

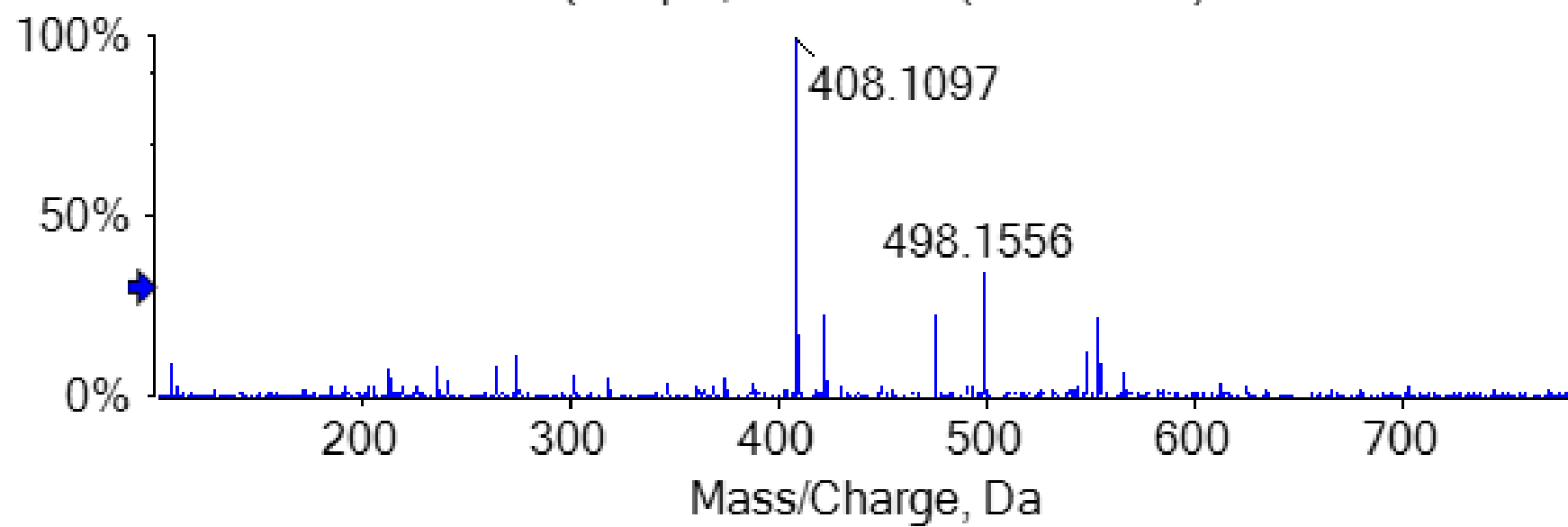


Fig. S37. *HRMS of 2-O-(3-O-Carbamoyl- α -D-mannopyranosyl)-L-gulopyranose (2)*
[M+Na⁺] = 408.1097

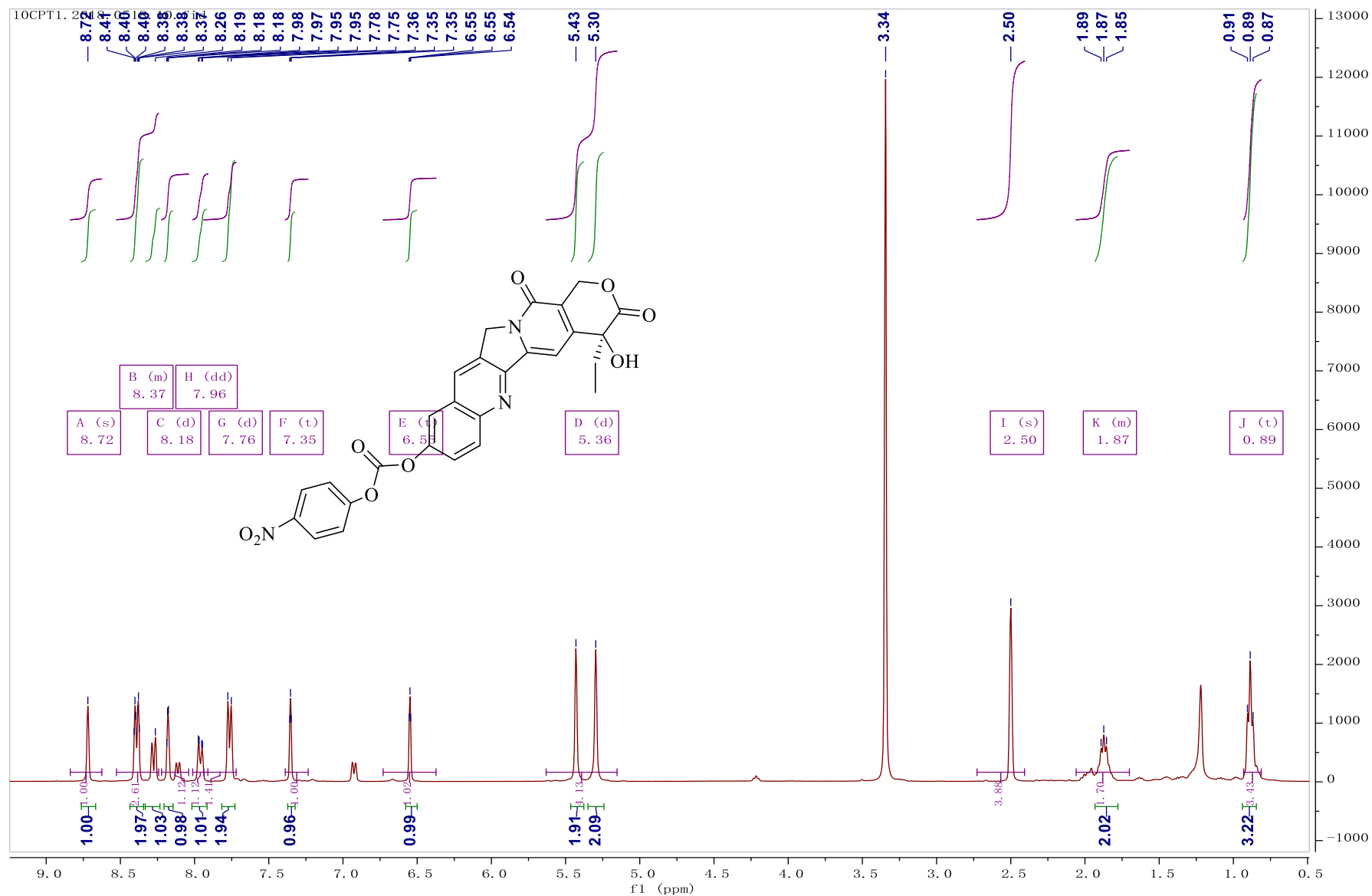


Fig. S38. ¹H NMR of activated 10-hydroxycamptothecin (21) (CD₃SOCD₃, 400 MHz)

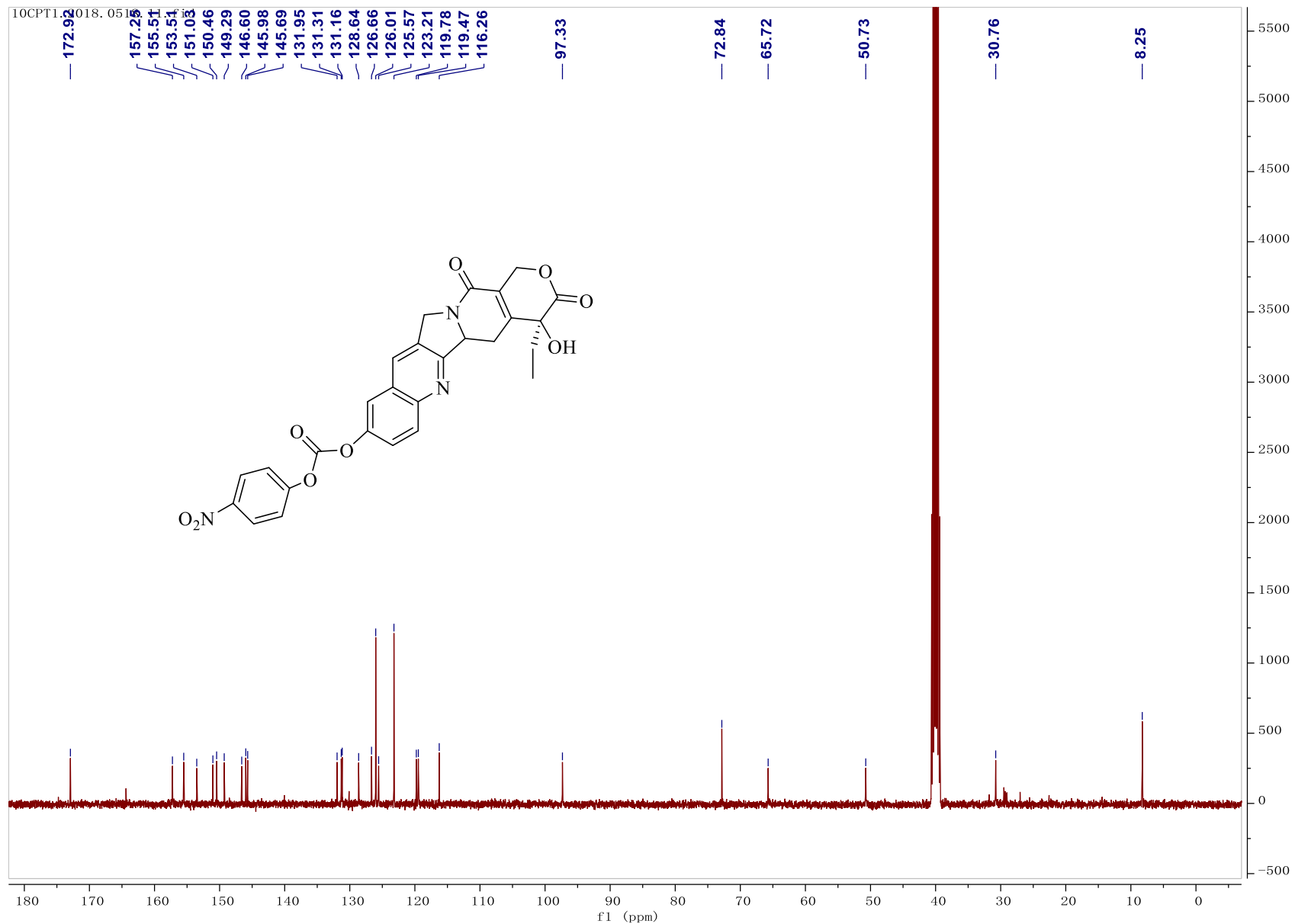


Fig. S39. ¹³C NMR of activated 10-hydroxycamptothecin (**21**) (CD₃SOCD₃, 100 MHz)

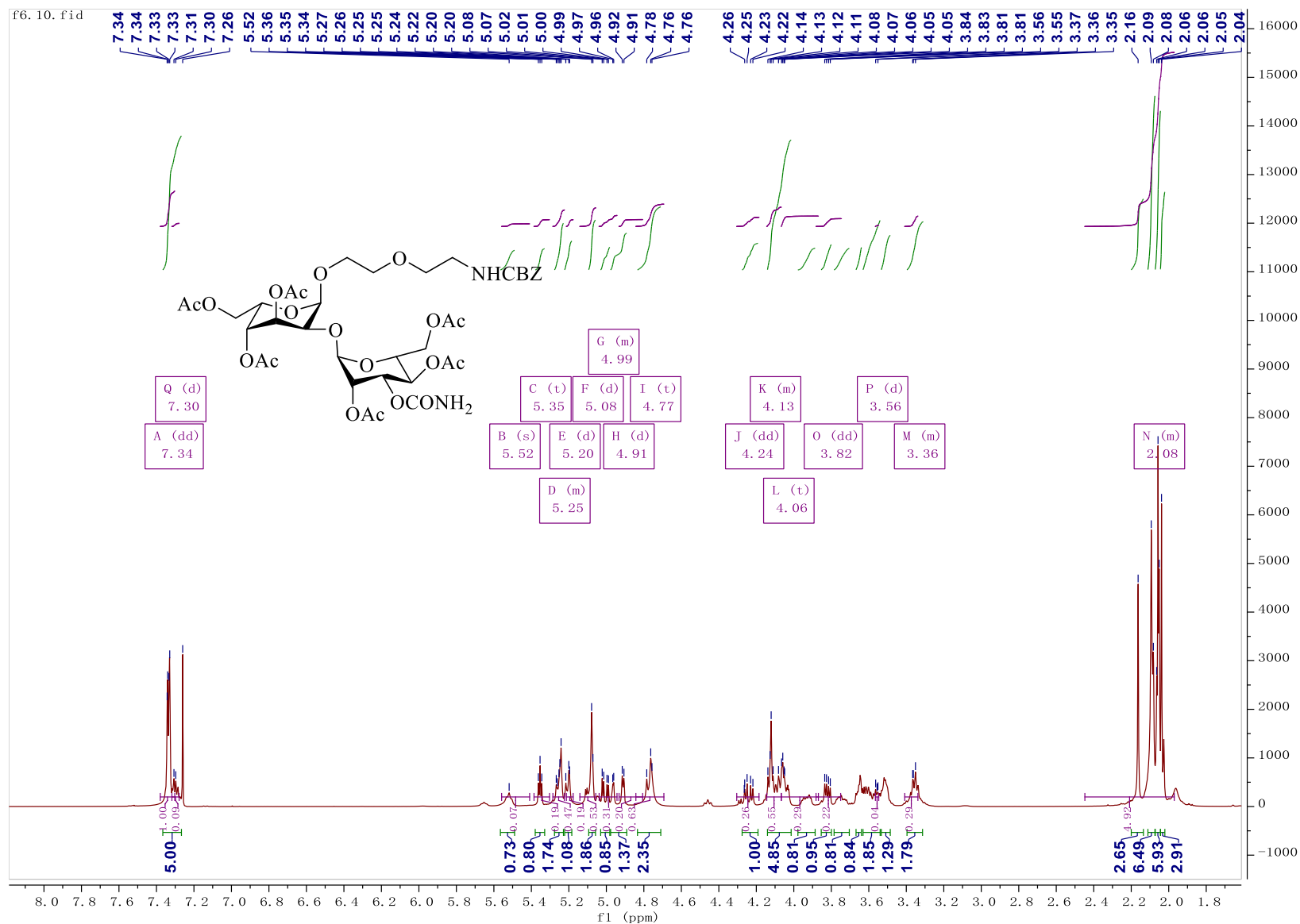


Fig. S 40. ^1H NMR of 2-[2-(Benzyloxycarbonylamino)ethoxy]ethyl 3,4,6-Tri-Oacetyl-2-O-(3,4,6-tri-O-acetyl-2-O-(carbamoyl)- α -D-mannopyranosyl)- α,β -L-gulopyranose (24) (CDCl_3 , 400 MHz)

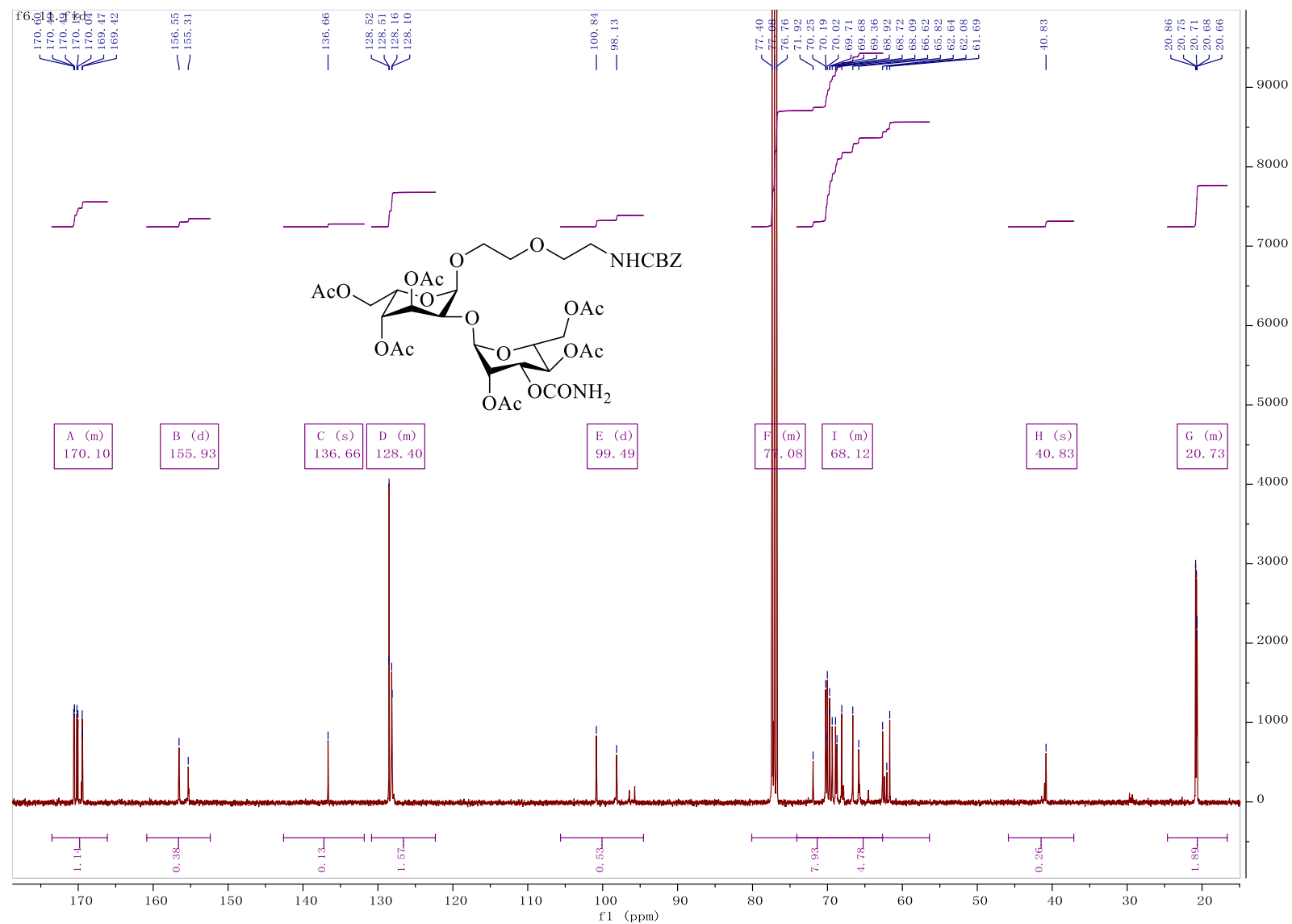


Fig. S 41. ¹H NMR of 2-[2-(Benzyloxycarbonylamino)ethoxy]ethyl 3,4,6-Tri-Oacetyl-2-O-(3,4,6-tri-O-acetyl-2-O-(carbamoyl)- α -D-mannopyranosyl)- α,β -L-gulopyranose (**24**) (CDCl₃, 100 MHz)

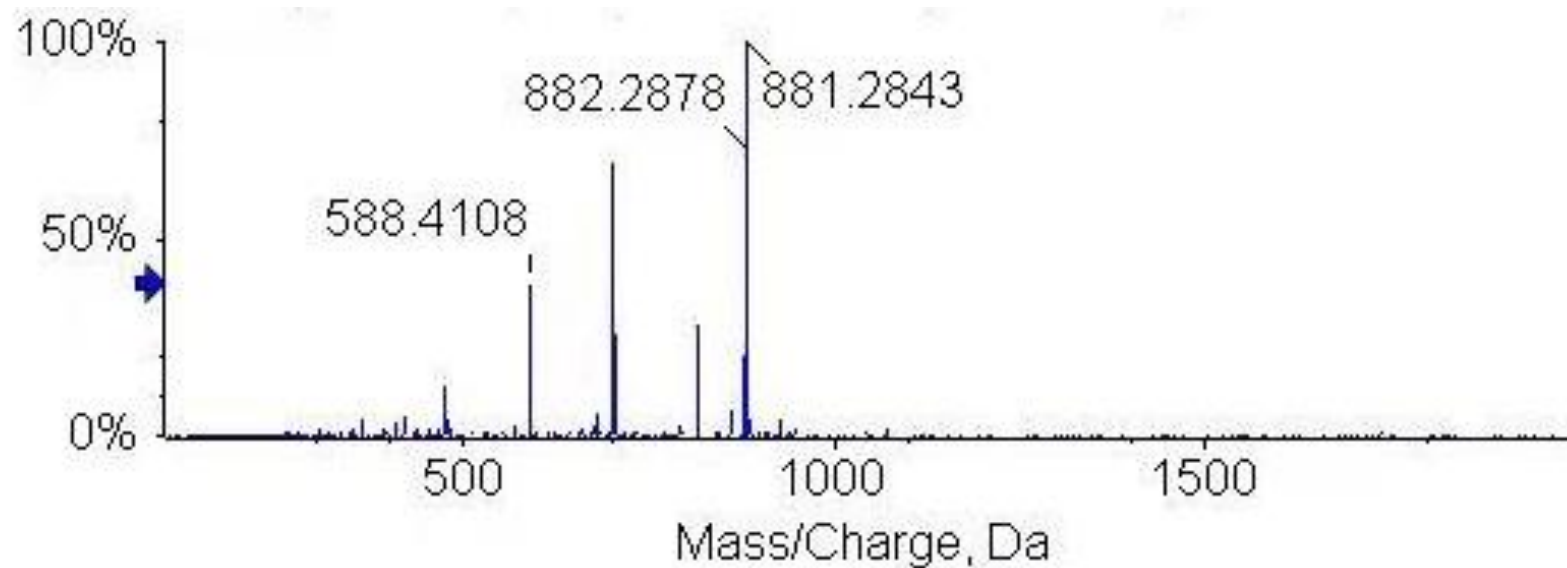


Fig 42. 2-[2-(Benzyloxycarbonylamino)ethyloxy]ethyl 3,4,6-Tri-Oacetyl-2-O-(3,4,6-tri-O-acetyl-2-O-(carbamoyl)- α -D-mannopyranosyl)- α,β -L-gulopyranose (**24**) $[M+Na^+] = 881.2843$

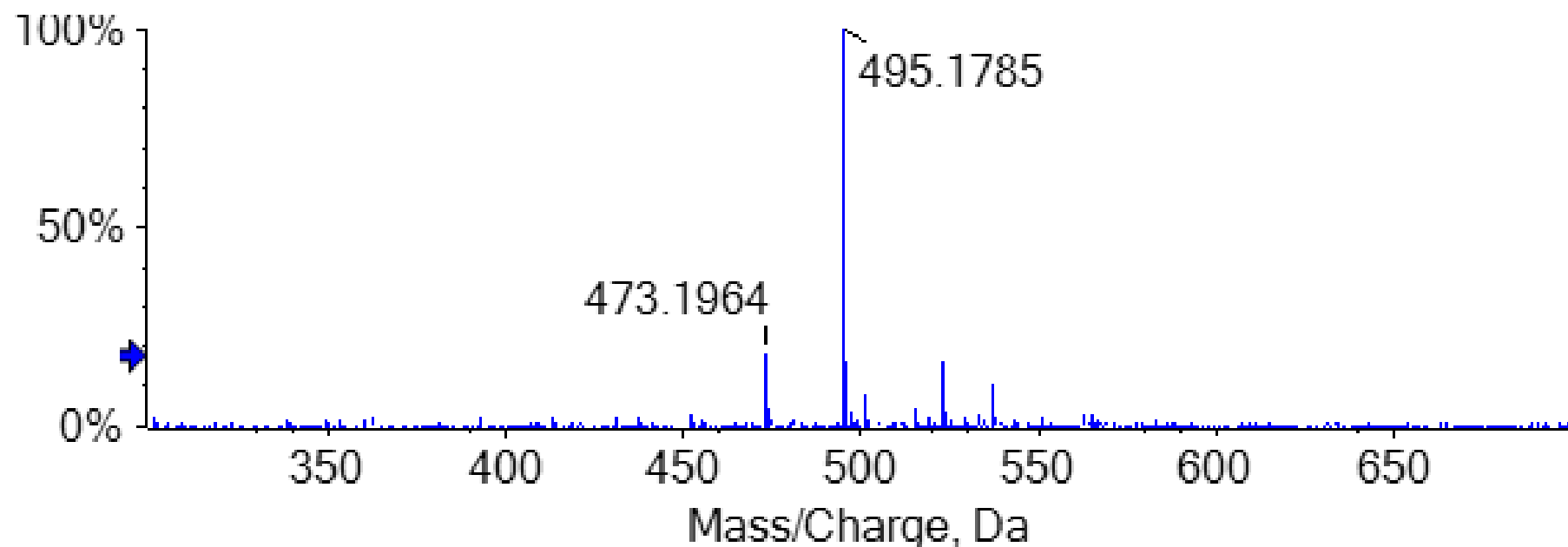


Fig. 43. HRMS of 2-[2-(amino)ethyloxy]ethyl 2-O-(3-O-Carbamoyl- α -D-mannopyranosyl) - α,β -L-gulopyranose $[M+Na^+] = 495.1785$

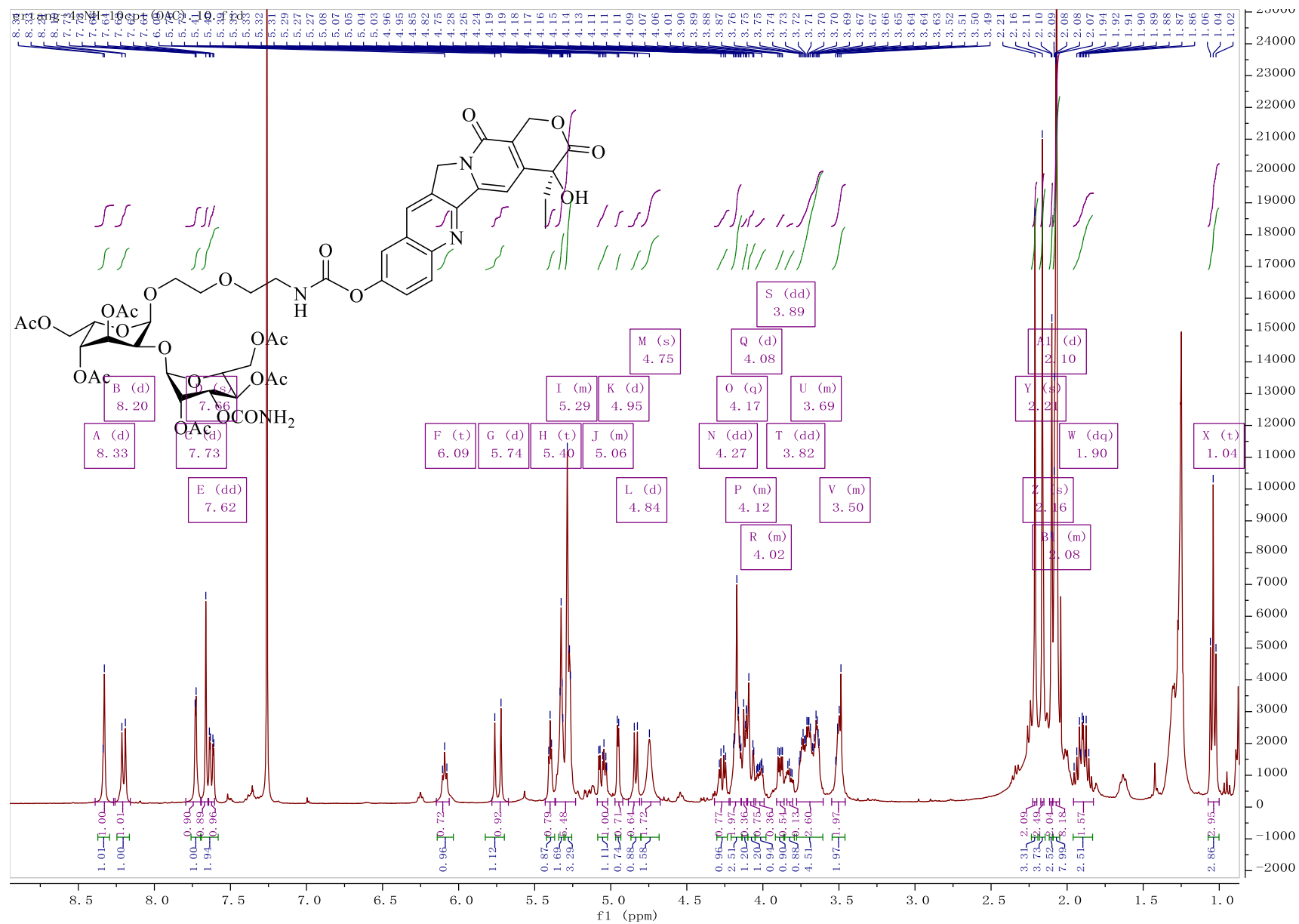


Fig. S 44 ^1H NMR of Conjugate 26 (CCl_3D , 400 MHz)

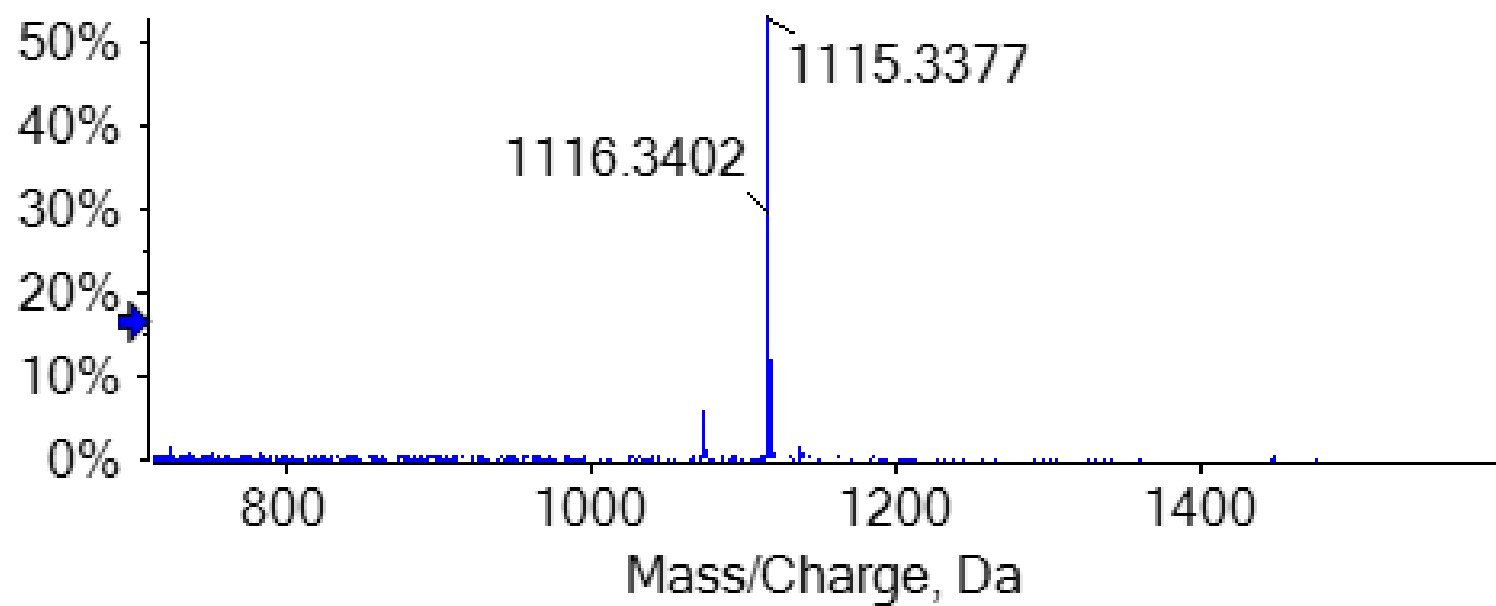


Fig. 45. *HRMS of Conjugate 26* $[M+H^+] = 1115.3377$

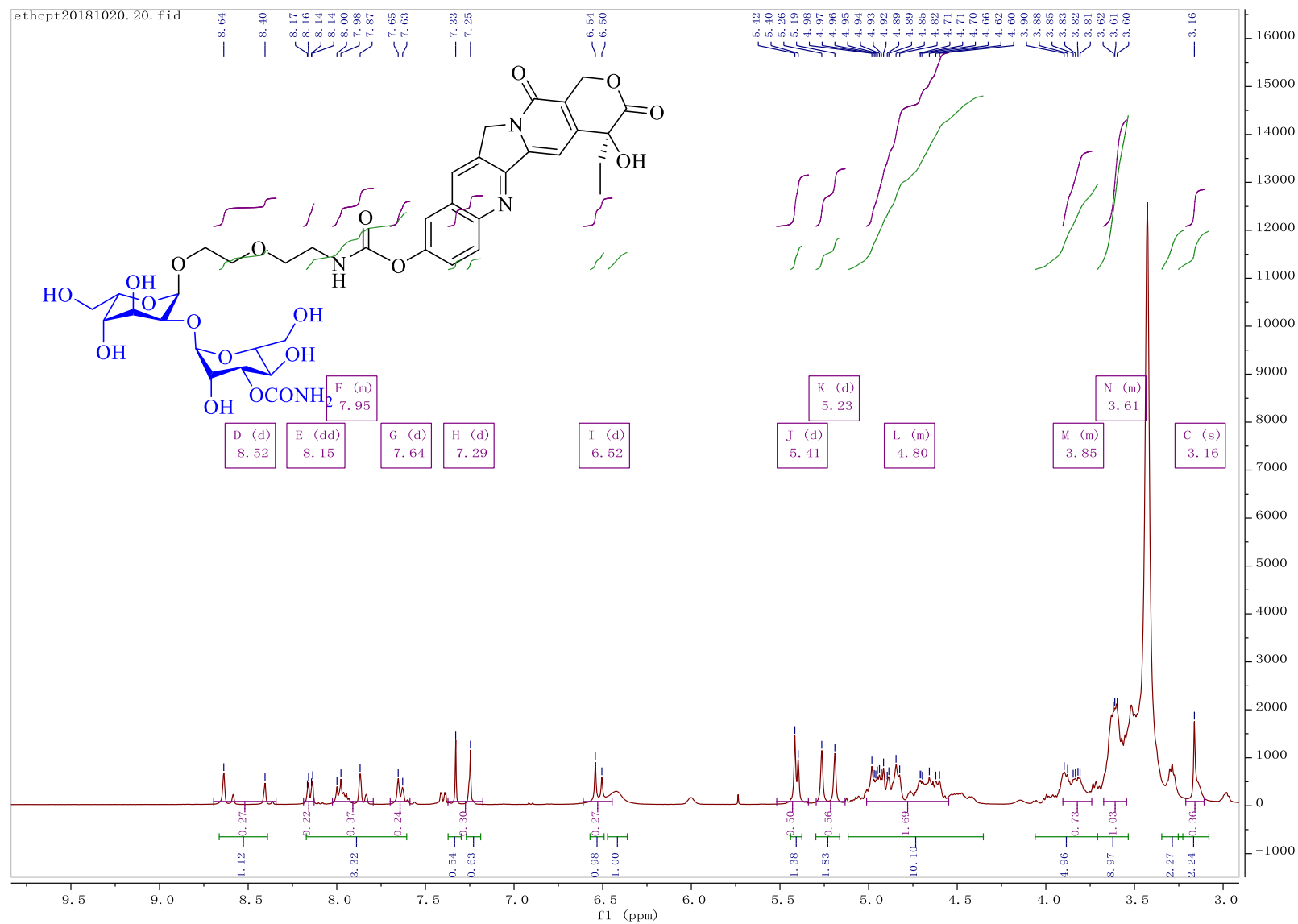


Fig. S46 ^1H NMR of Conjugate 1 (CD_3SOCD_3) 400 MHz)

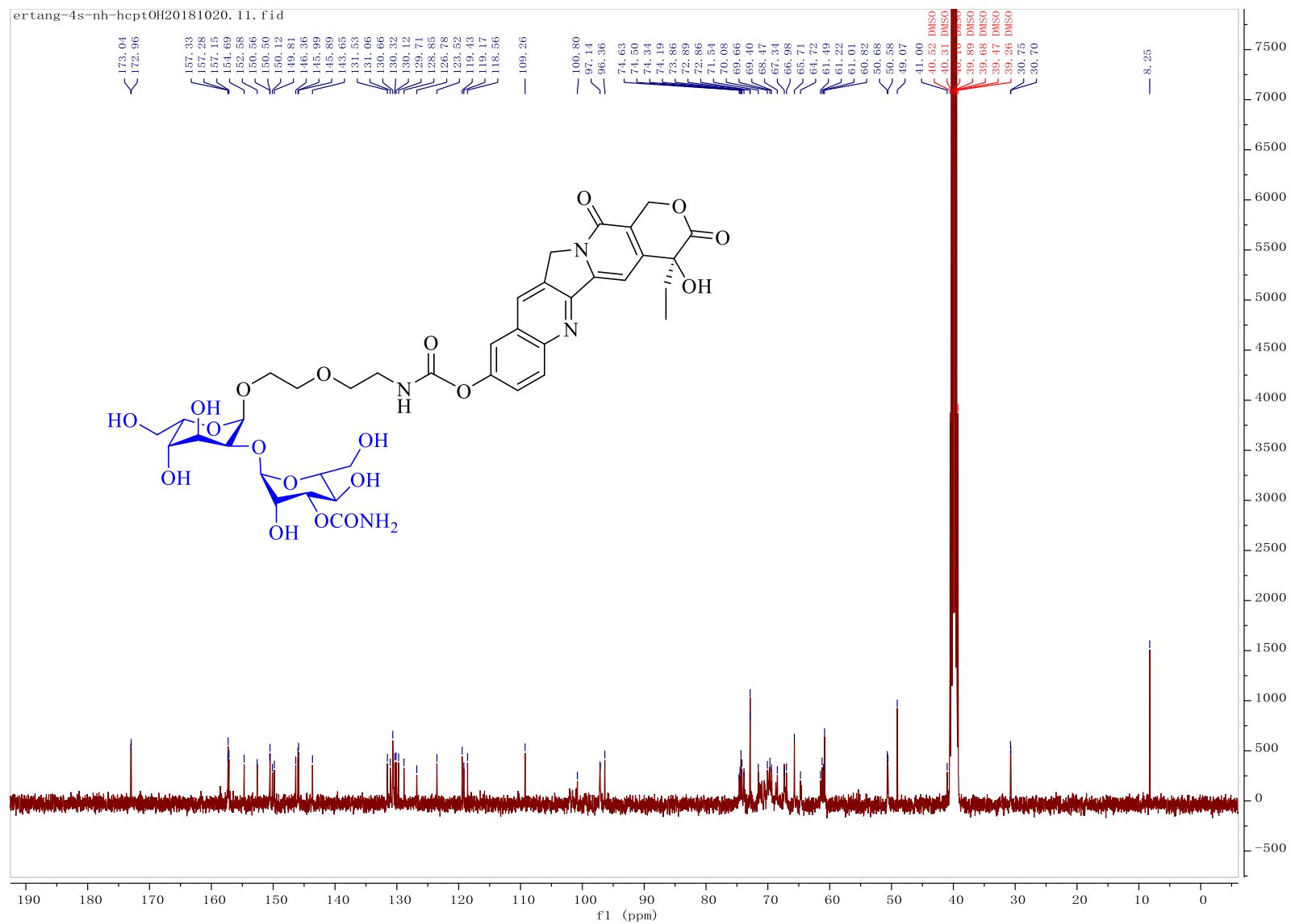


Fig. S47 ^{13}C NMR of Conjugate **1** (CD_3SOCD_3 , 400 MHz)

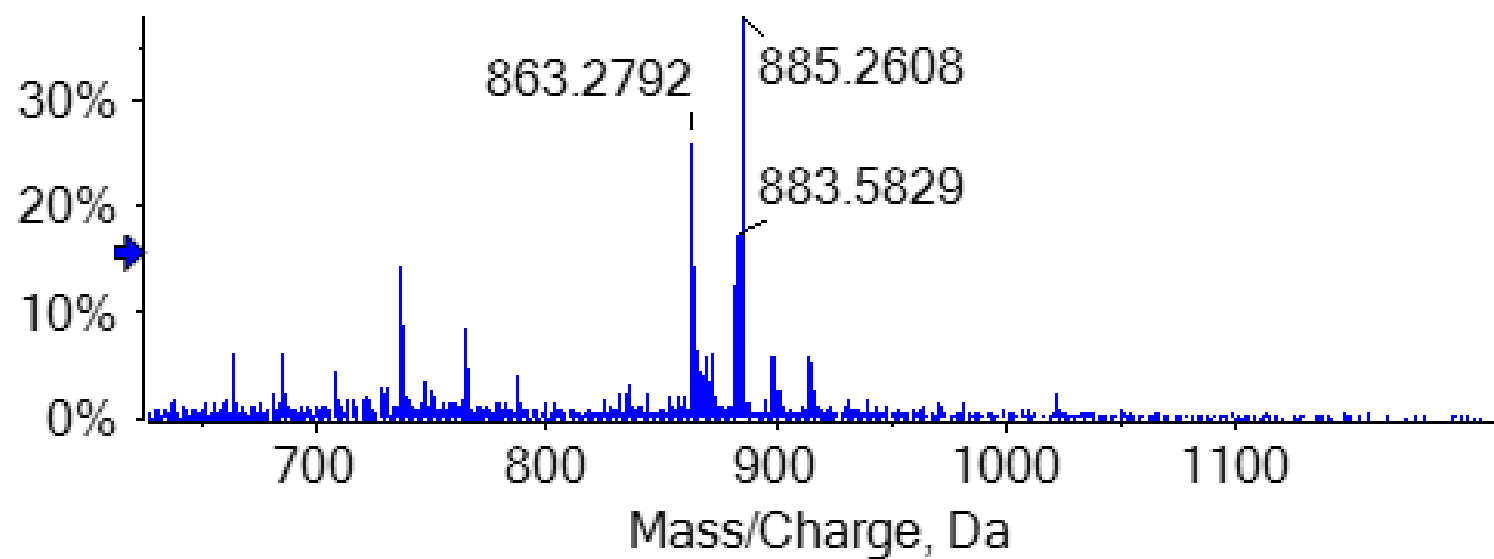


Fig. S48. *HRMS of Conjugate 1* $[M+H^+]=863.2792$, $[M +Na^+]=885.2608$