Electronic Supporting Information

Synthesis of 6'-galactosyllactose, a deviant human milk oligosaccharide, with the aid of *Candida antarctica* lipase-B

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Table of Contents

Kinetic study of N435 deacetylation reaction with **1β**.

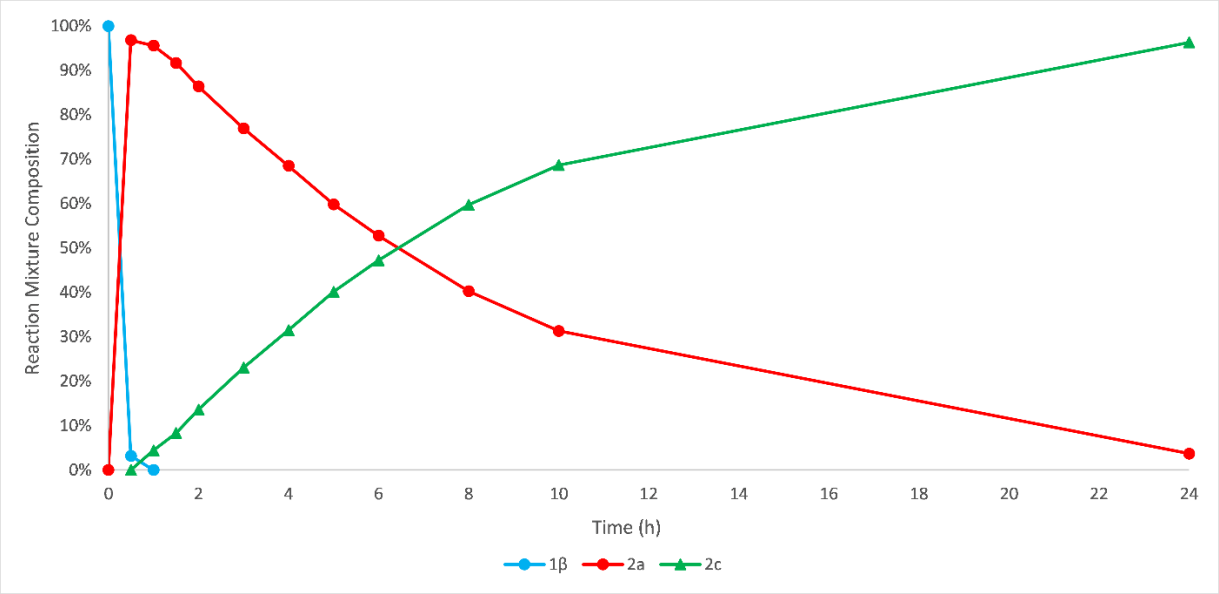
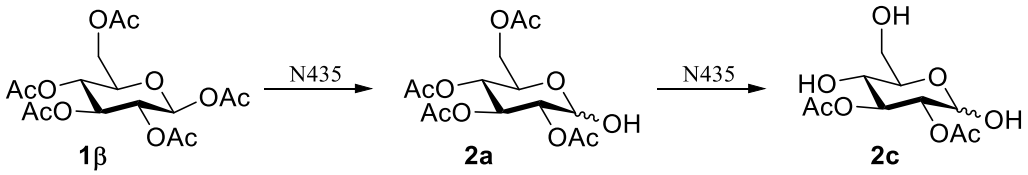
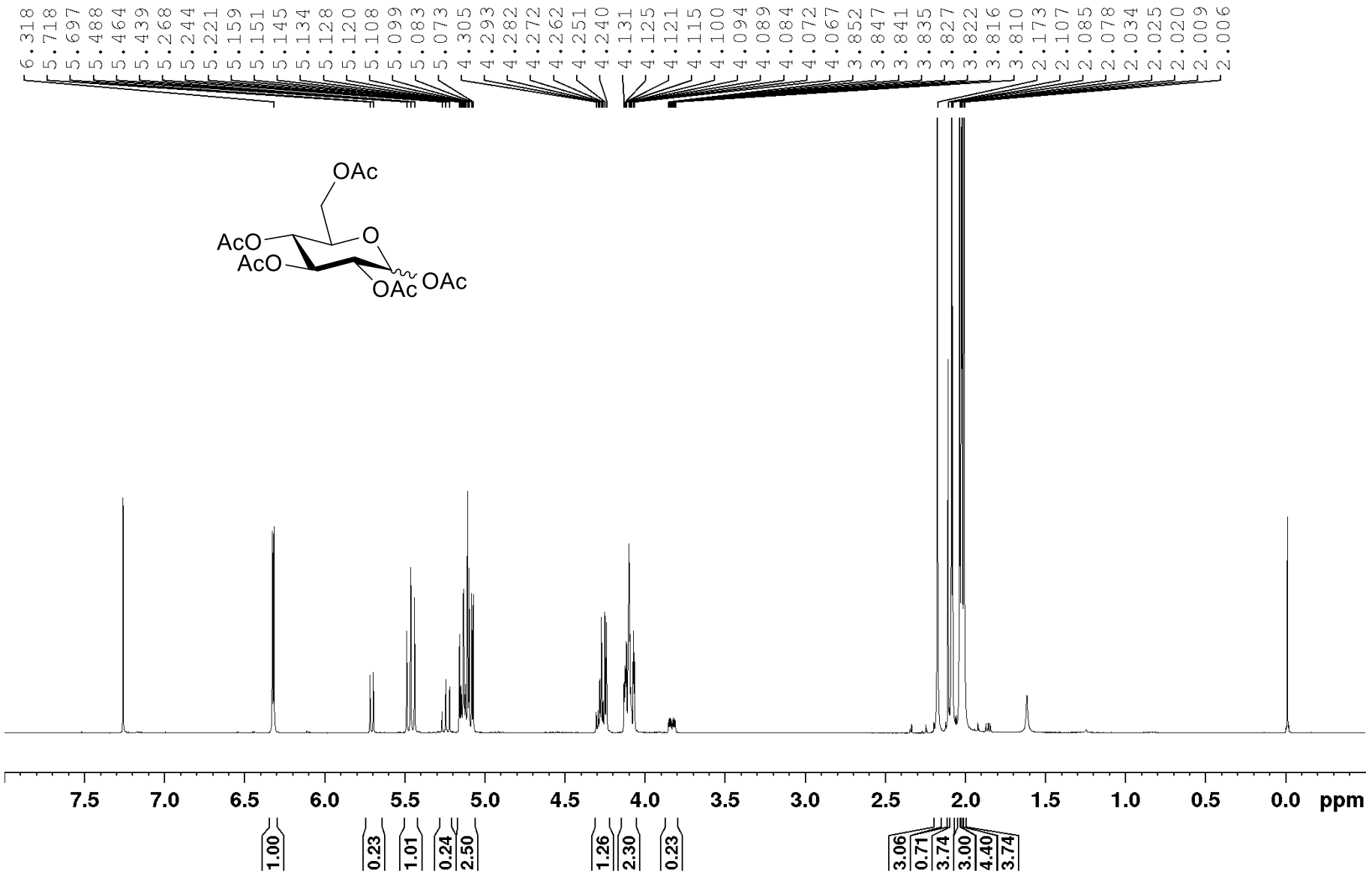


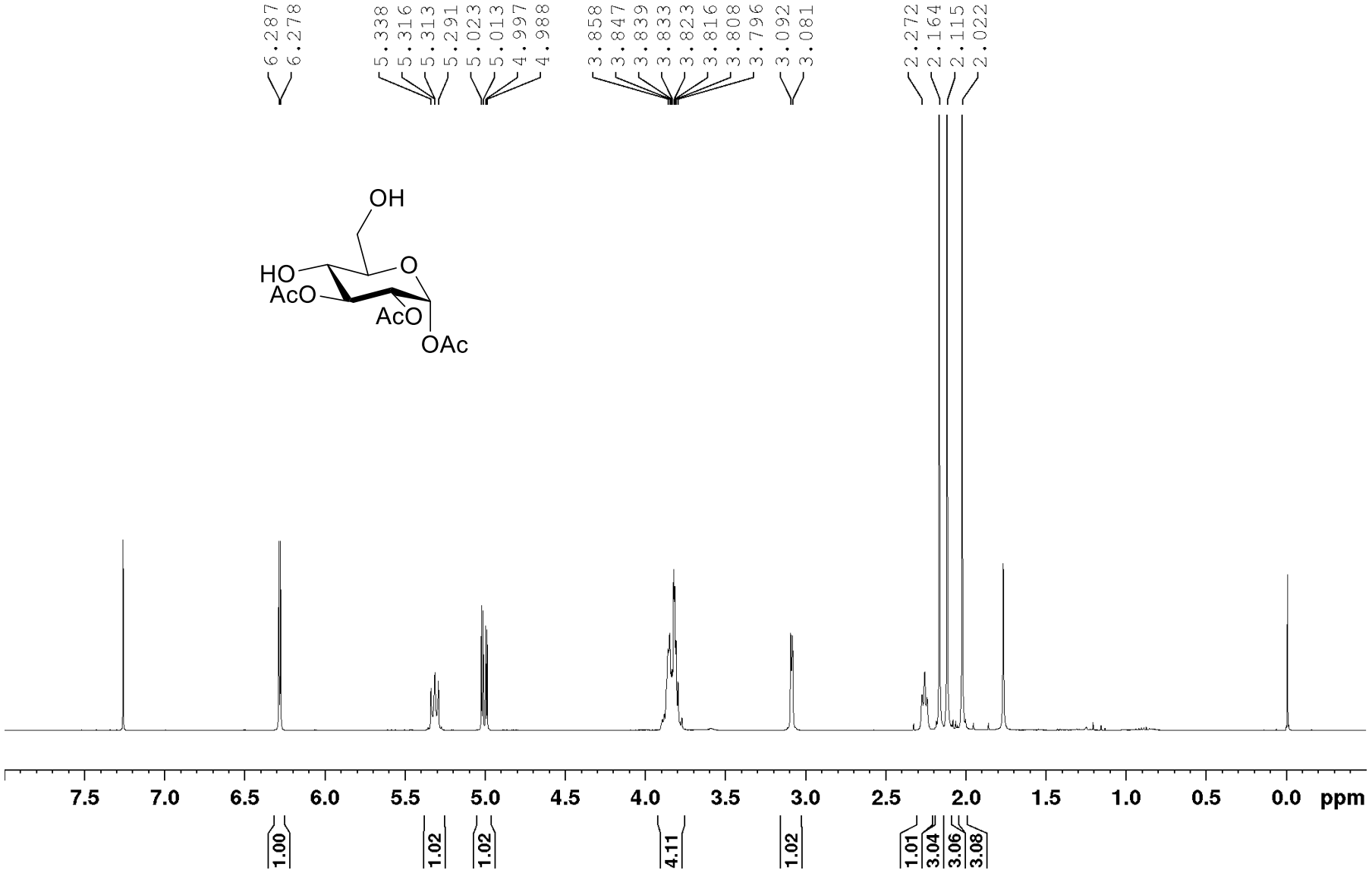
Figure S1 Reaction conditions: ***1β*** *(100 mg), N435 (100 mg), MTBE (10 mL), n-BuOH (3.5 equiv, 82 µL), 45 °C, 24 h*



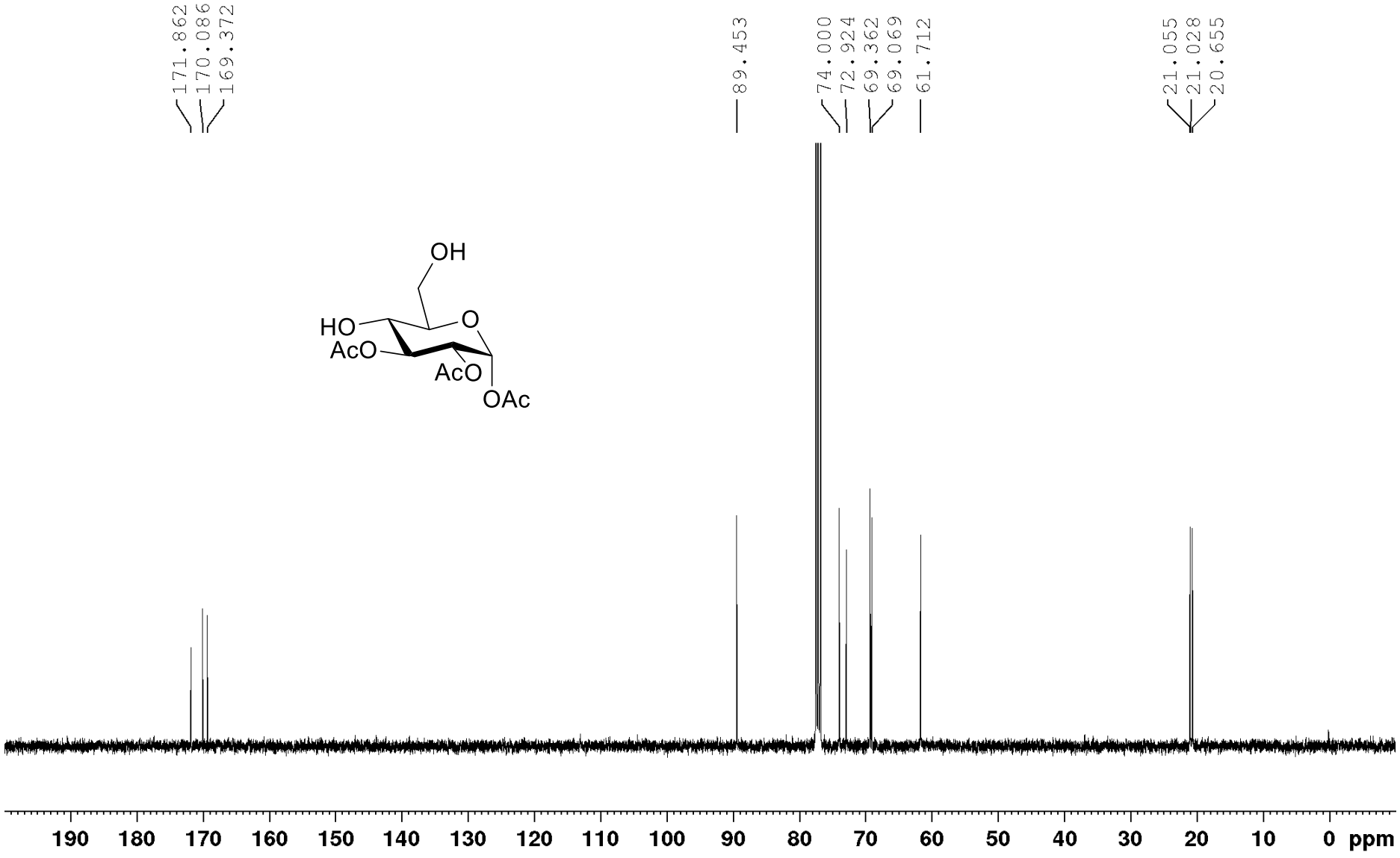
1,2,3,4,6-penta-O-acetyl-D-glucopyranoside **1** (α:β 81:19) ^{1}H NMR ($CDCl_3$)



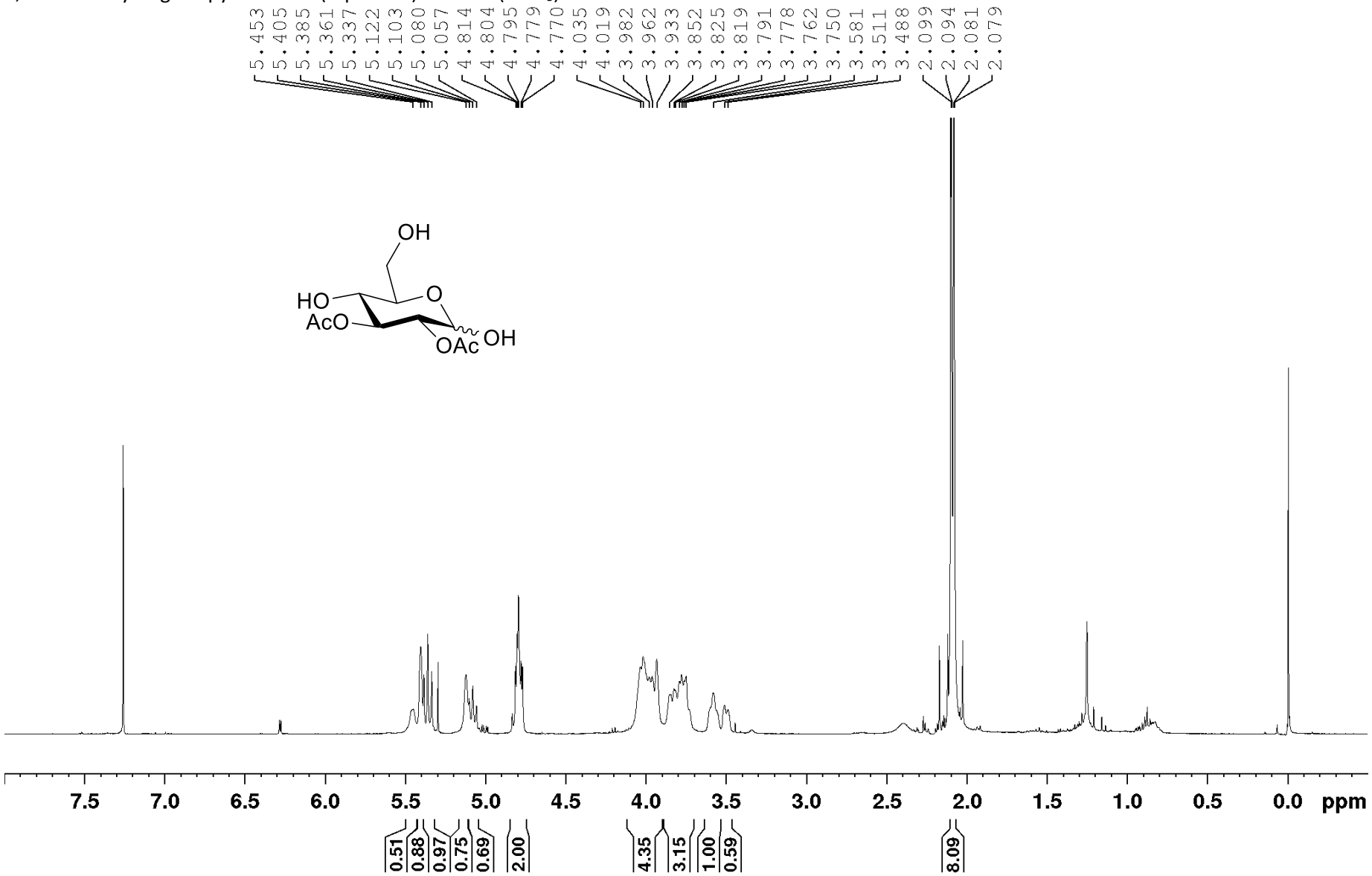
1,2,3-tri-O-acetyl-α-D-glucopyranoside **2** ^{1}H NMR ($CDCl_3$)



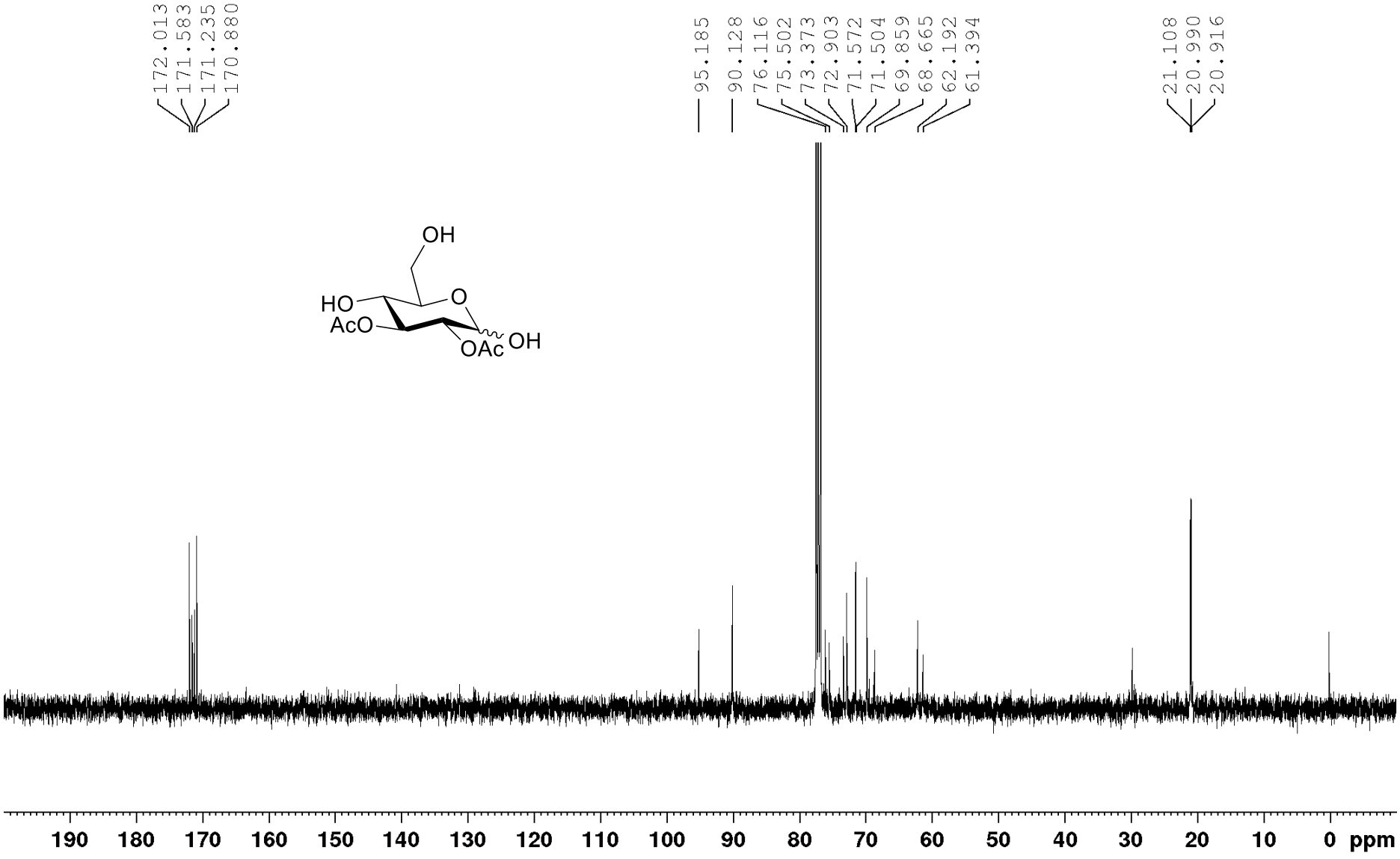
1,2,3-tri-O-acetyl-α-D-glucopyranoside **2** ^{13}C NMR ($CDCl_3$)



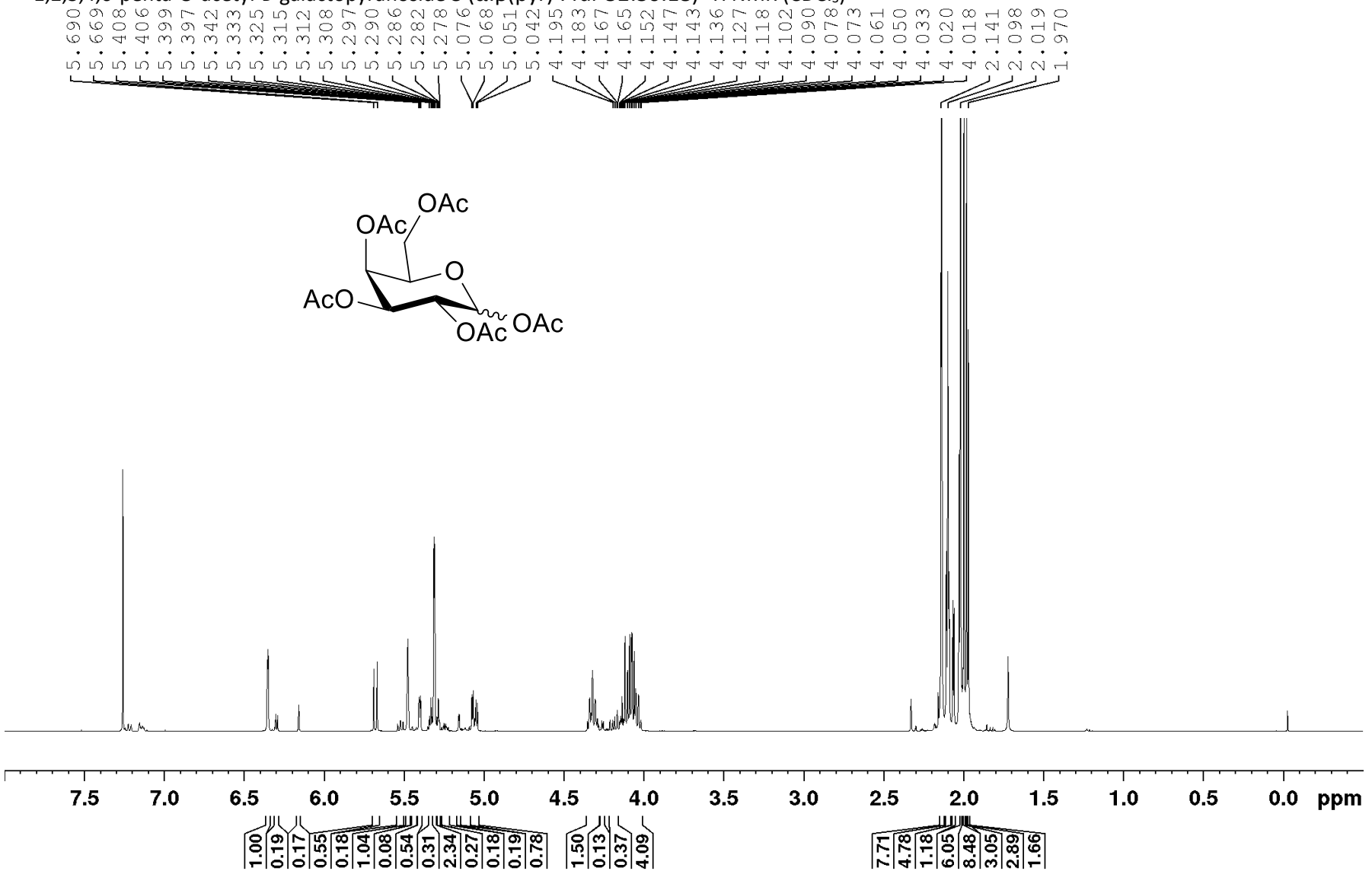
2,3-di-O-acetyl-D-glucopyranose **2c** (α:β 63:37) ^{1}H NMR ($CDCl_3$)



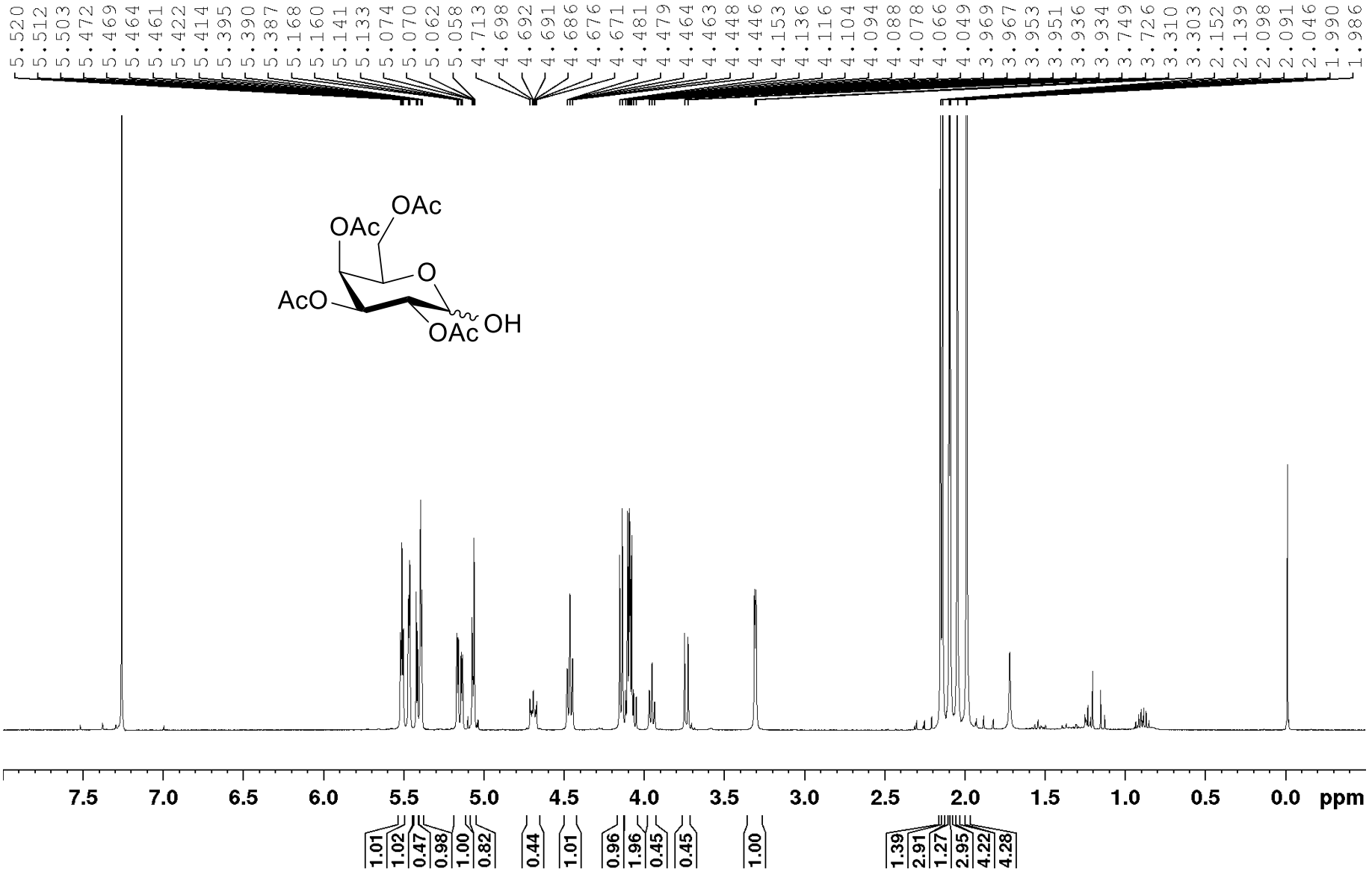
2,3-di-O-acetyl-D-glucopyranose **2c** (α:β 63:37) ^{13}C NMR ($CDCl_3$)



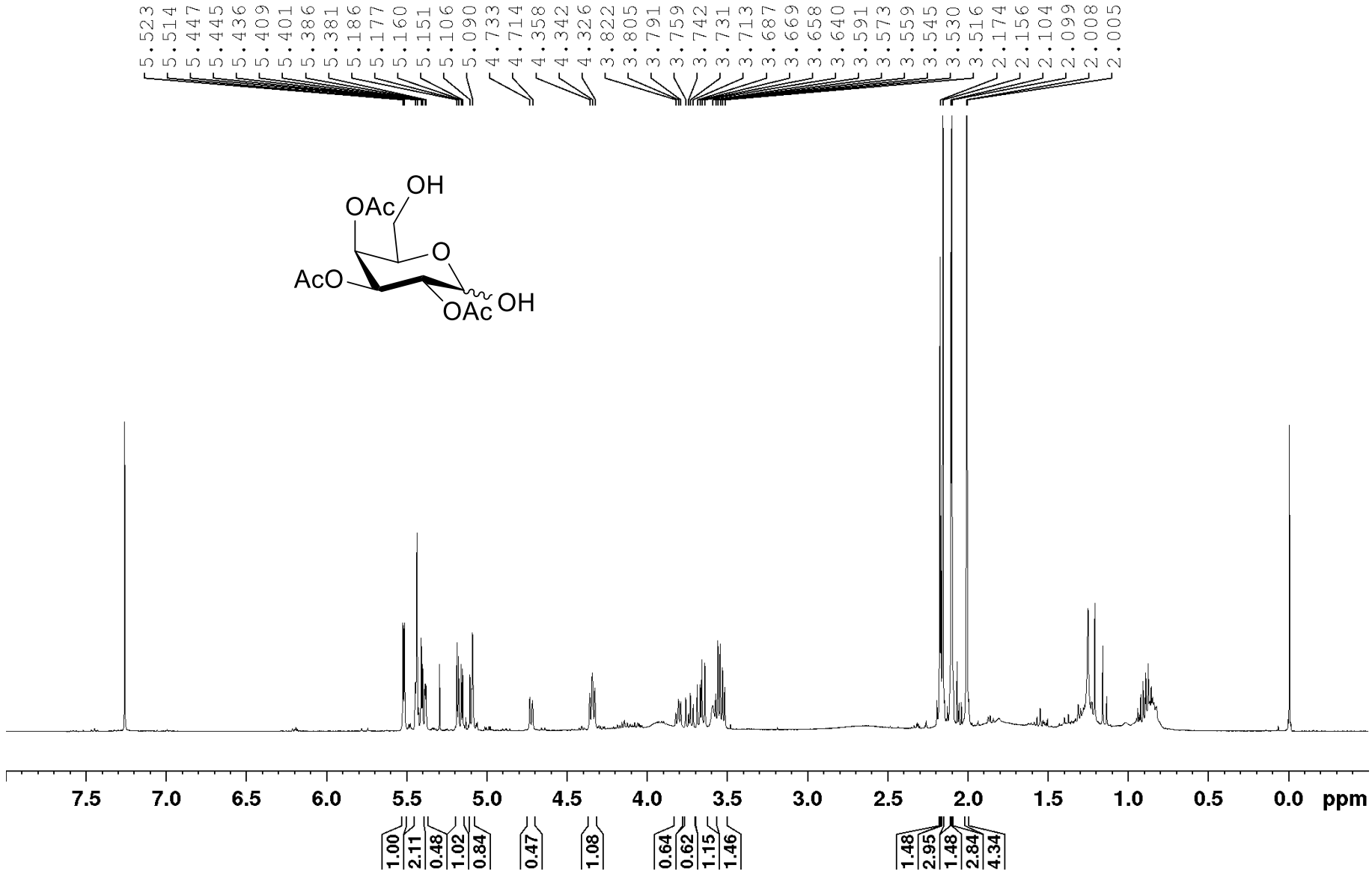
1,2,3,4,6-penta-O-acetyl-D-galactopyranoside **3** (α:β(pyr) : fur 52:30:18) ^{1}H NMR ($CDCl_3$)



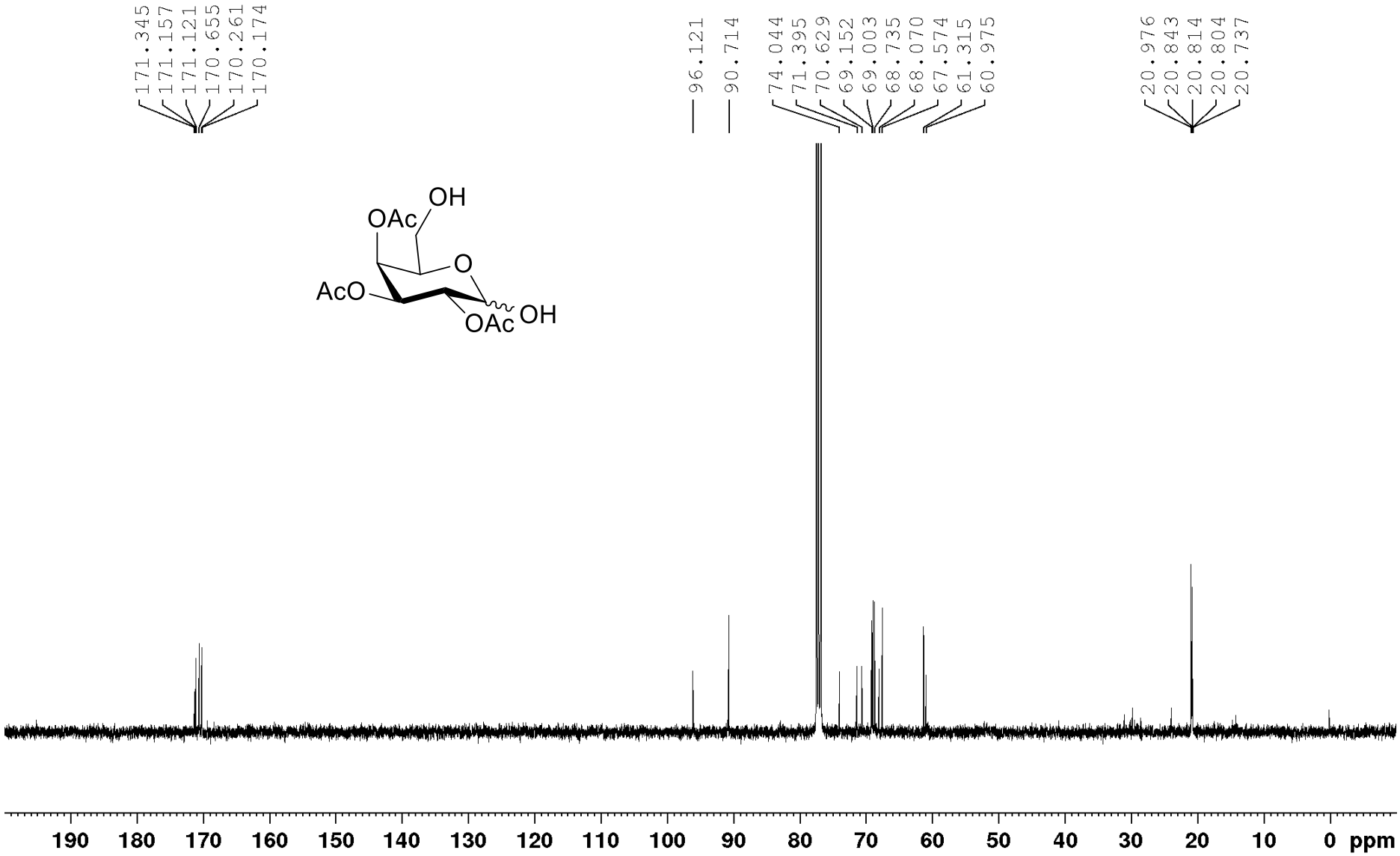
2,3,4,6-tetra-O-acetyl-D-galactopyranose **4** (α:β 69:31) ^{1}H NMR ($CDCl_3$)



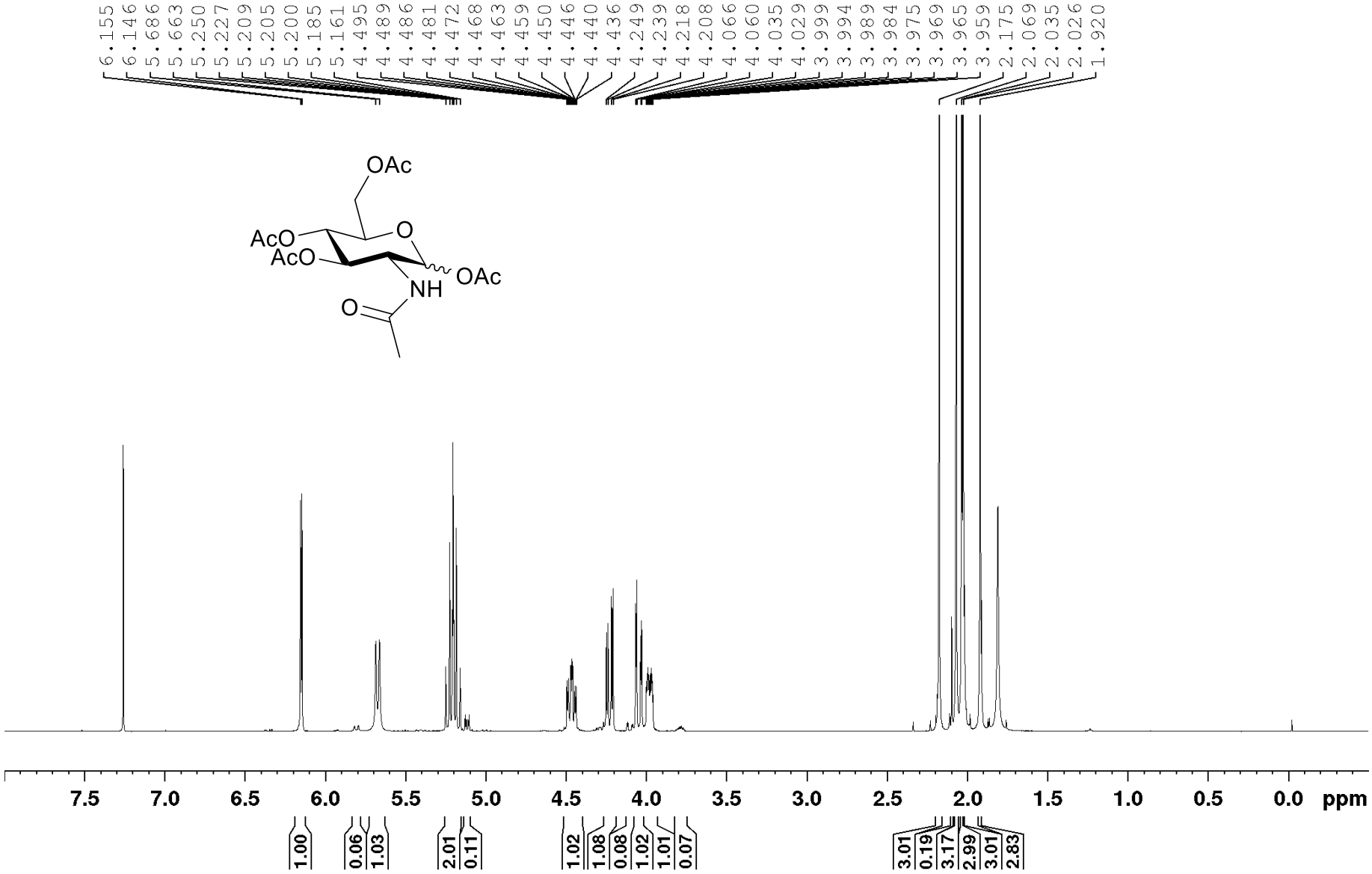
2,3,4-tri-O-acetyl-D-galactopyranoside **5a** (α:β 68:32) ^{1}H NMR ($CDCl_3$)



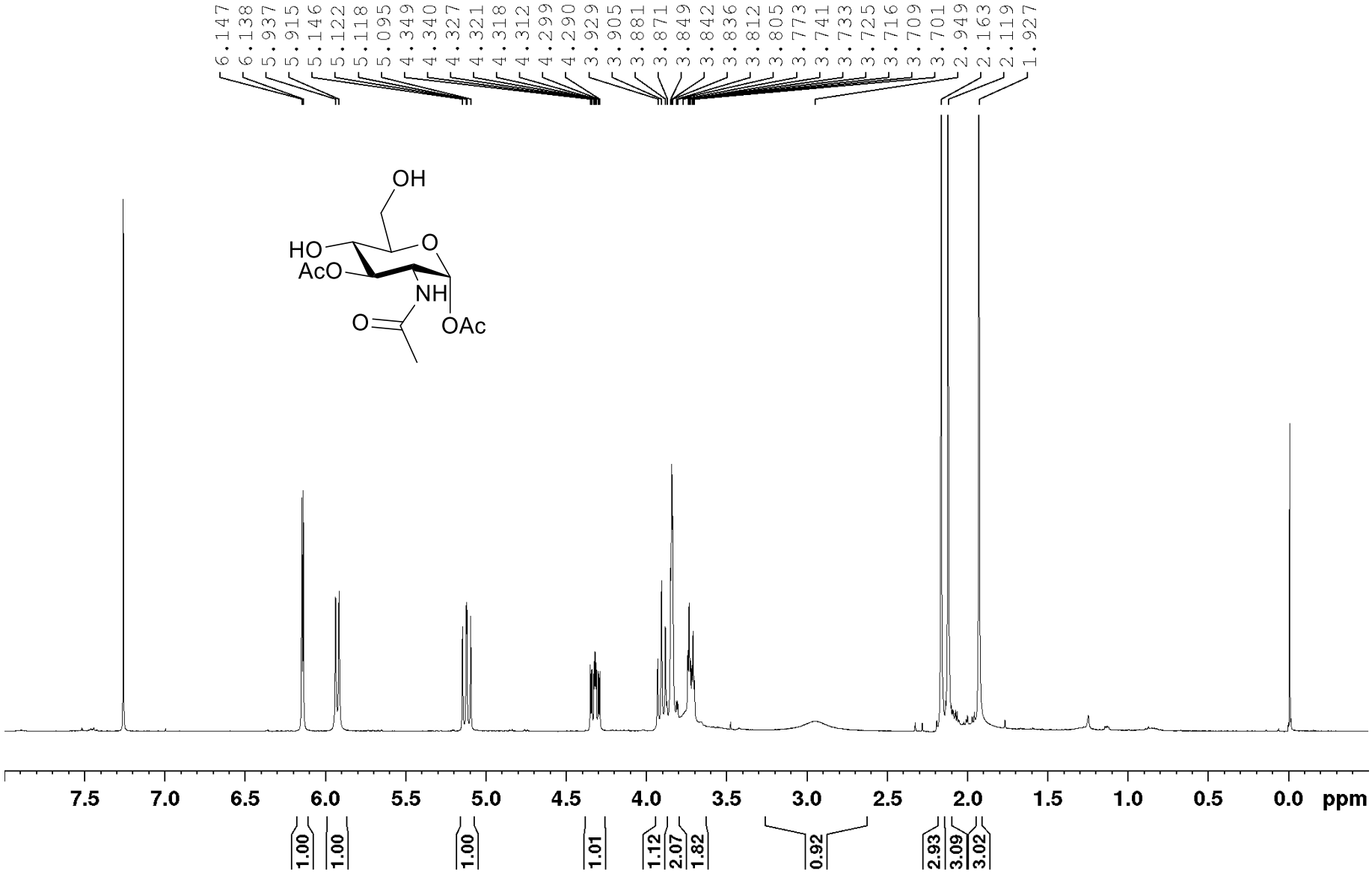
2,3,4-tri-O-acetyl-D-galactopyranoside **5a** (α:β 68:32) ^{13}C NMR ($CDCl_3$)



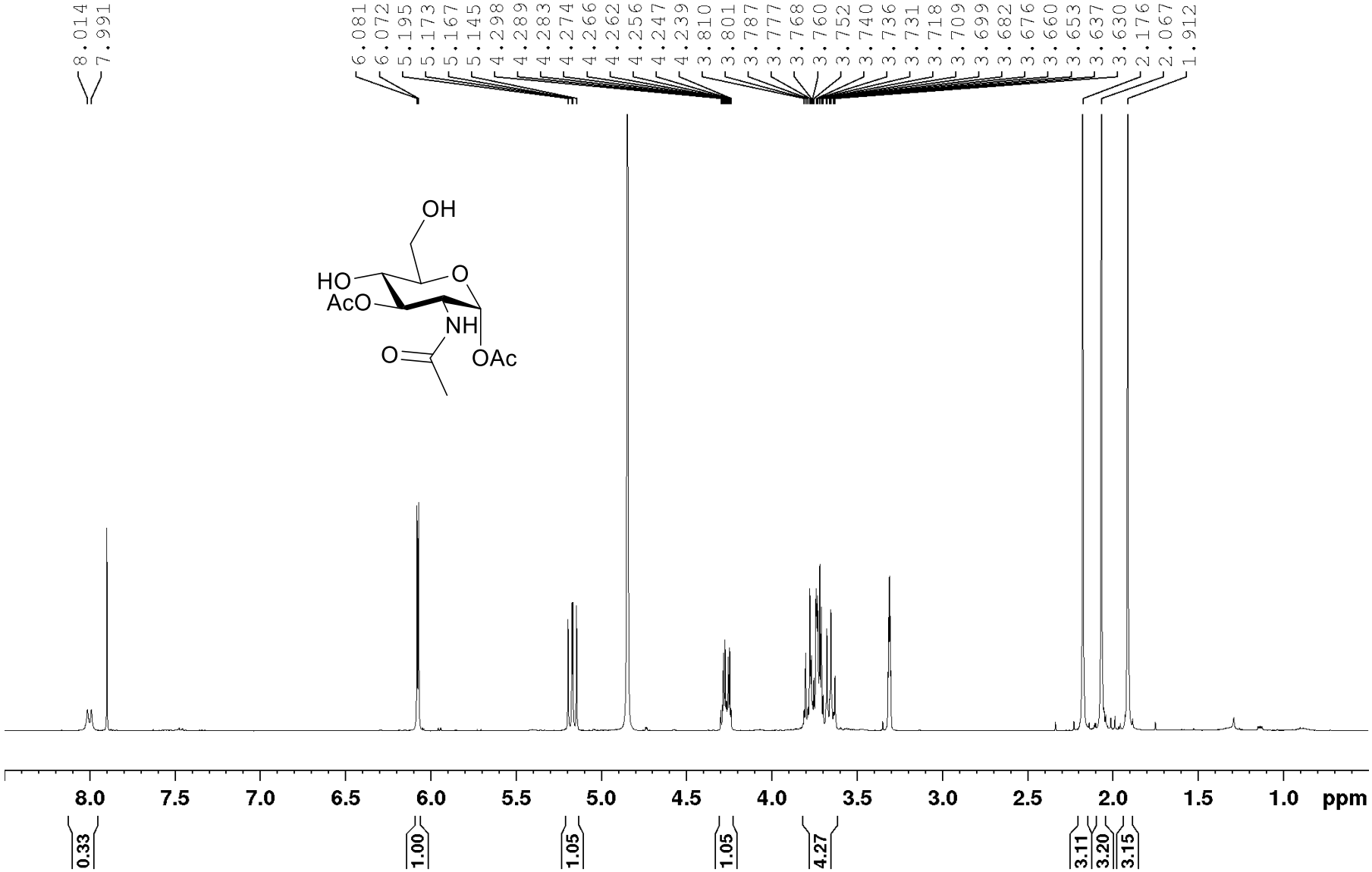
2-acetamido-1,3,4,6-tetra-O-acetyl-2-deoxy-D-glucopyranoside **6** (α:β 95:5) ^{1}H NMR ($CDCl_3$)



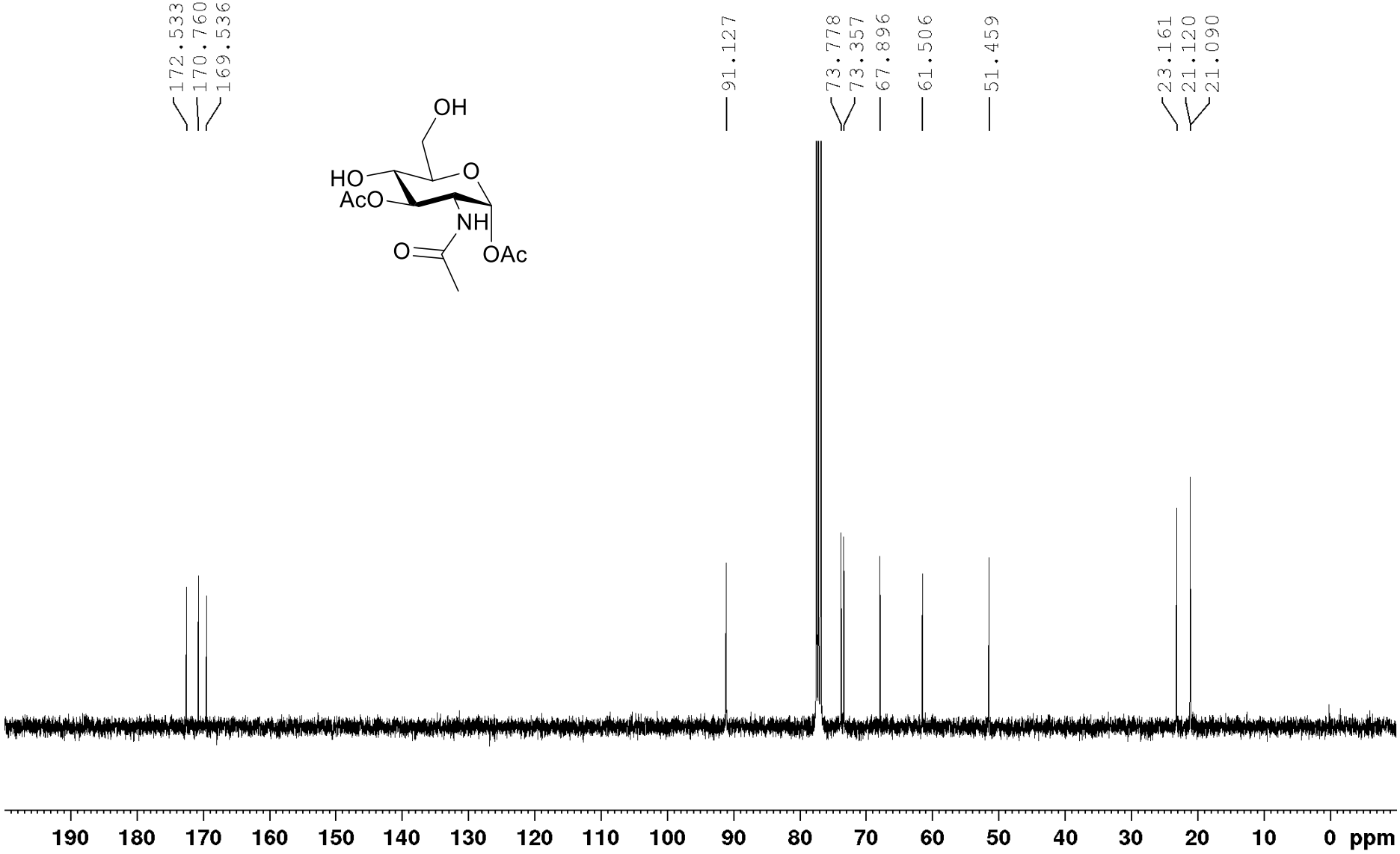
2-acetamido-1,3-di-O-acetyl-2-deoxy-α-D-glucopyranoside **7** ^{1}H NMR ($CDCl_3$)



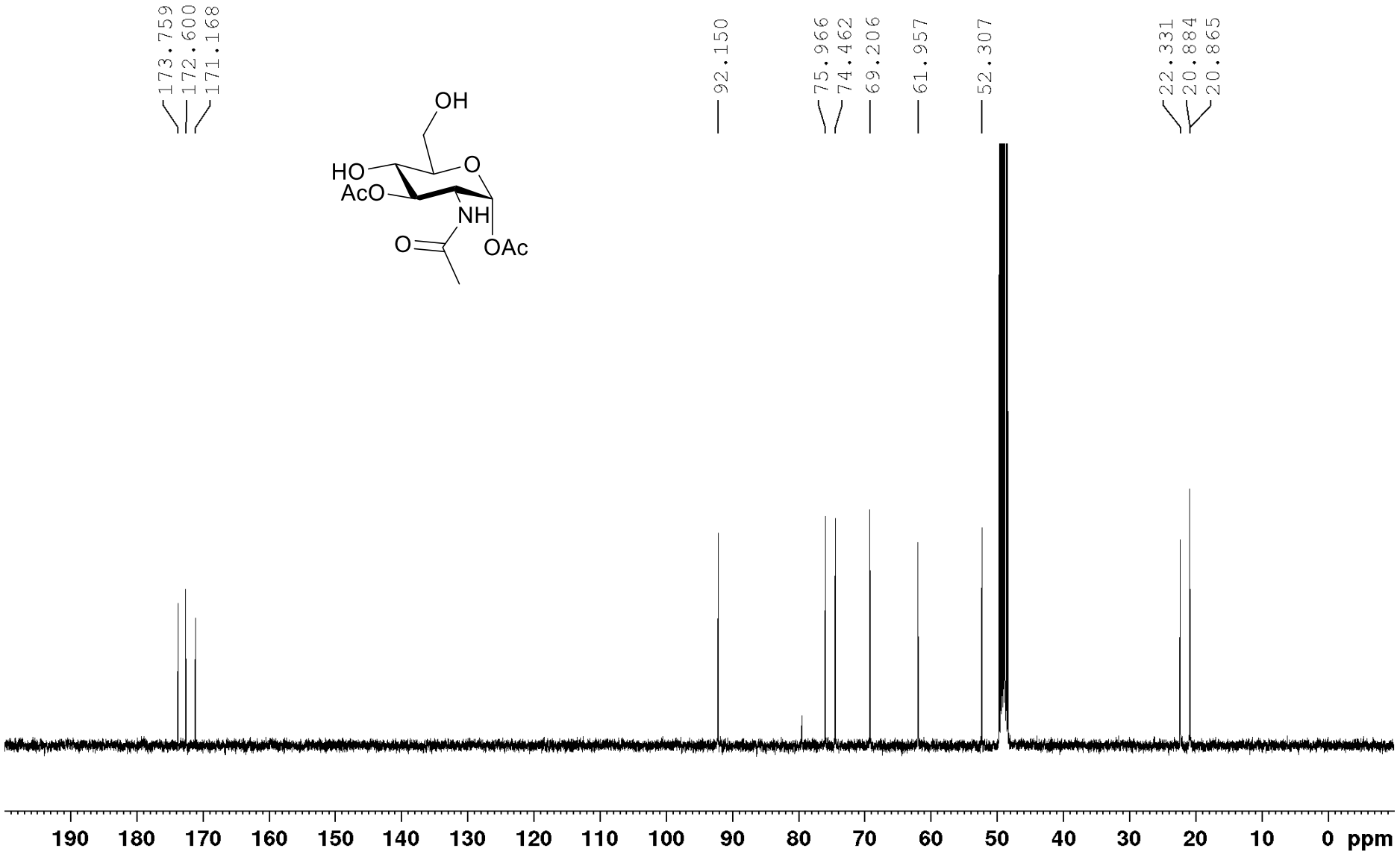
2-acetamido-1,3-di-O-acetyl-2-deoxy-α-D-glucopyranoside **7** ^{1}H NMR (CD_3OD)



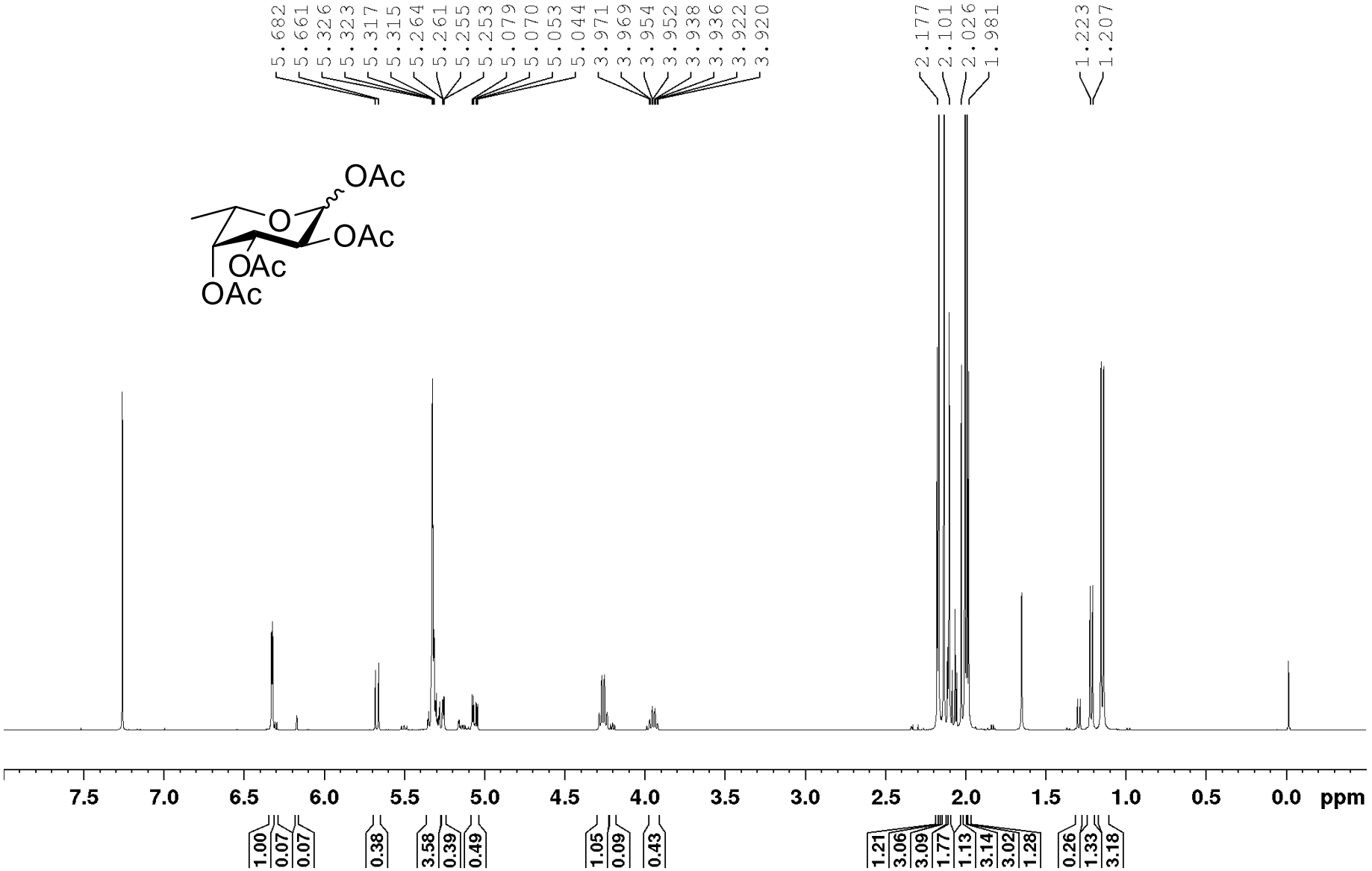
2-acetamido-1,3-di-O-acetyl-2-deoxy-α-D-glucopyranoside **7** ^{13}C NMR ($CDCl_3$)



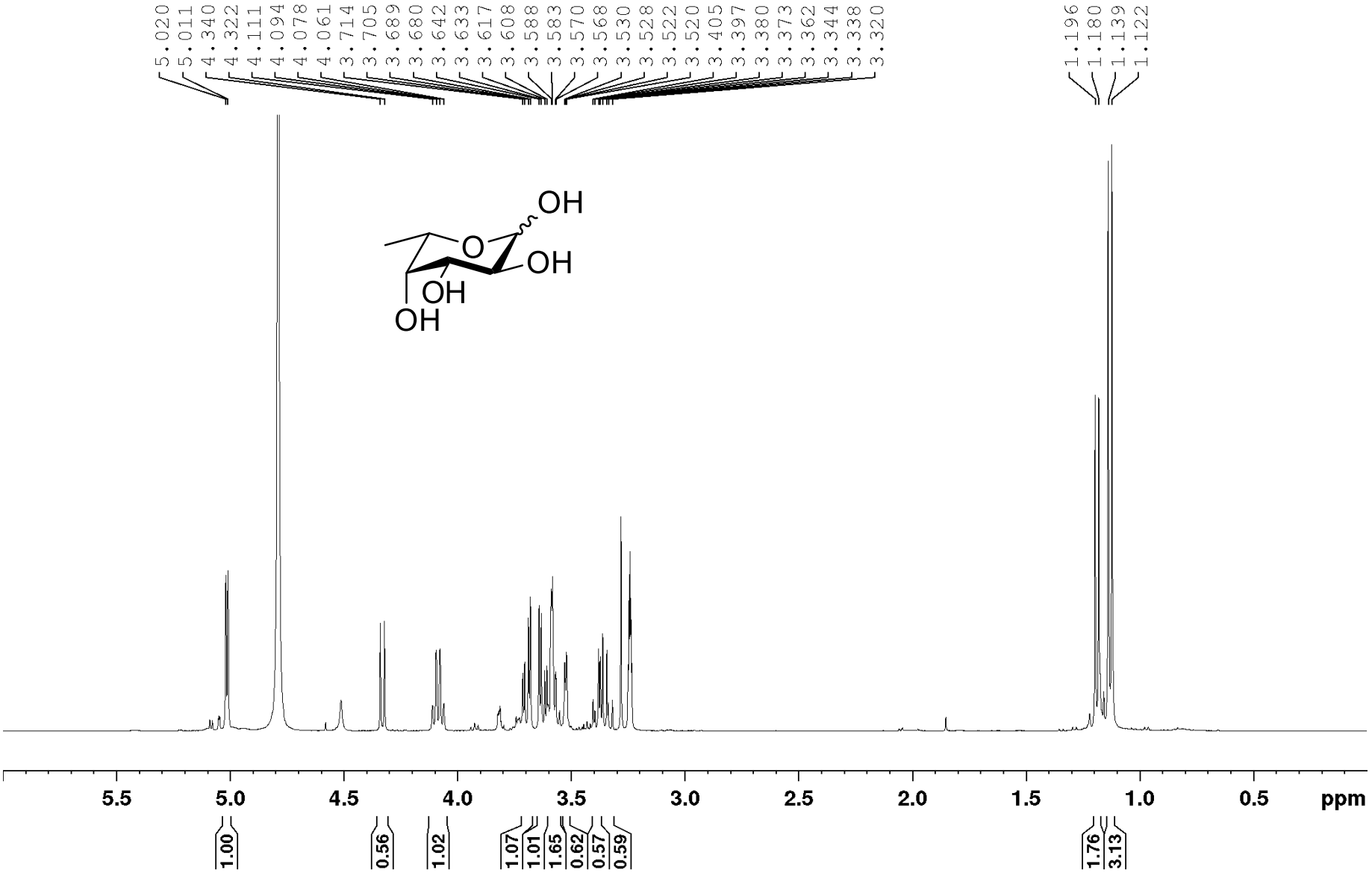
2-acetamido-1,3-di-O-acetyl-2-deoxy-α-D-glucopyranoside **7** ^{13}C NMR (CD_3OD)



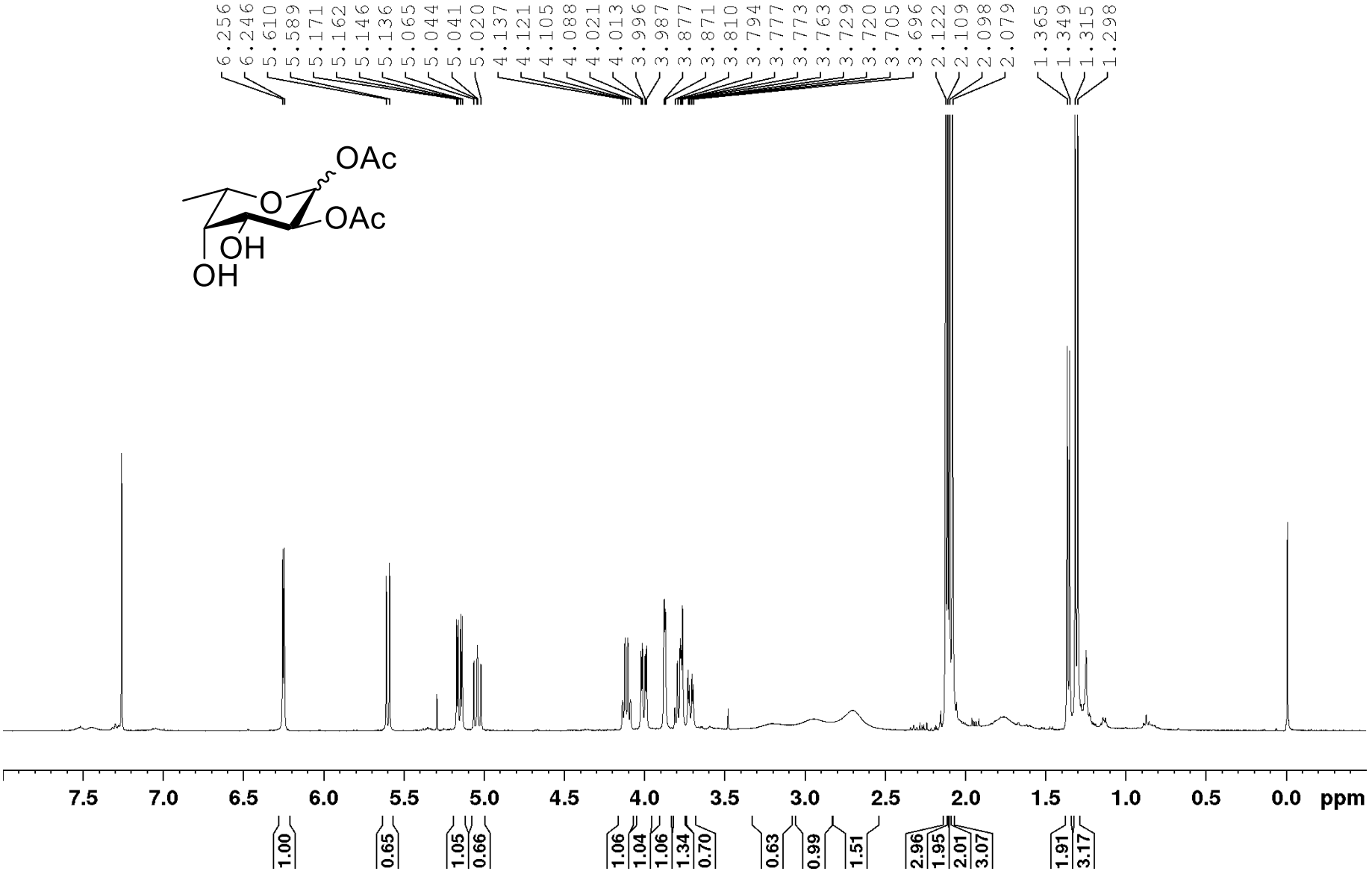
1,2,3,4-tetra-O-acetyl-6-deoxy-L-galactopyranoside **8** (α:β(pyr) : fur 66:25:9) ^{1}H NMR ($CDCl_3$)



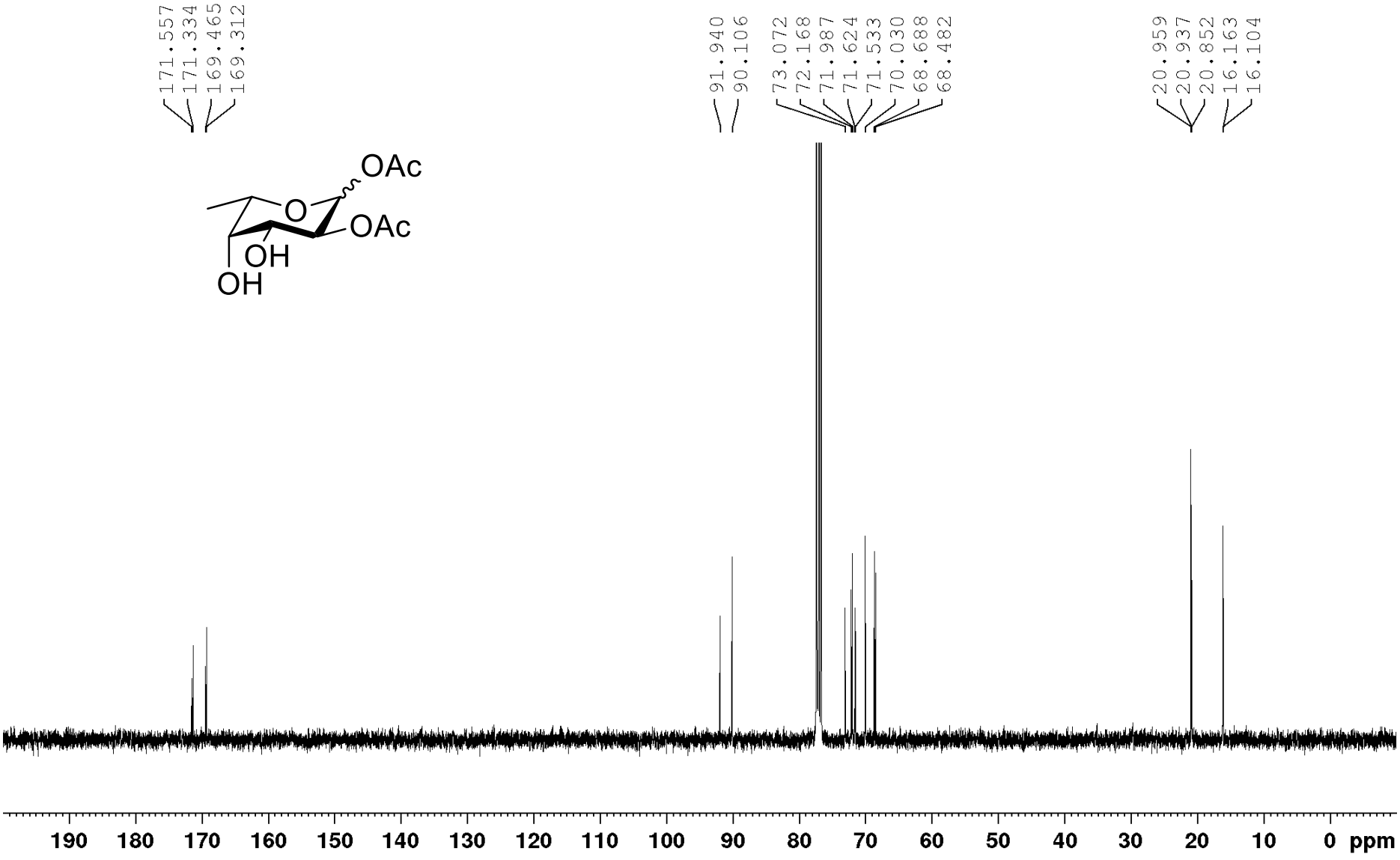
L-fucose **9** (α:β 64:36) ^{1}H NMR (D_2O)



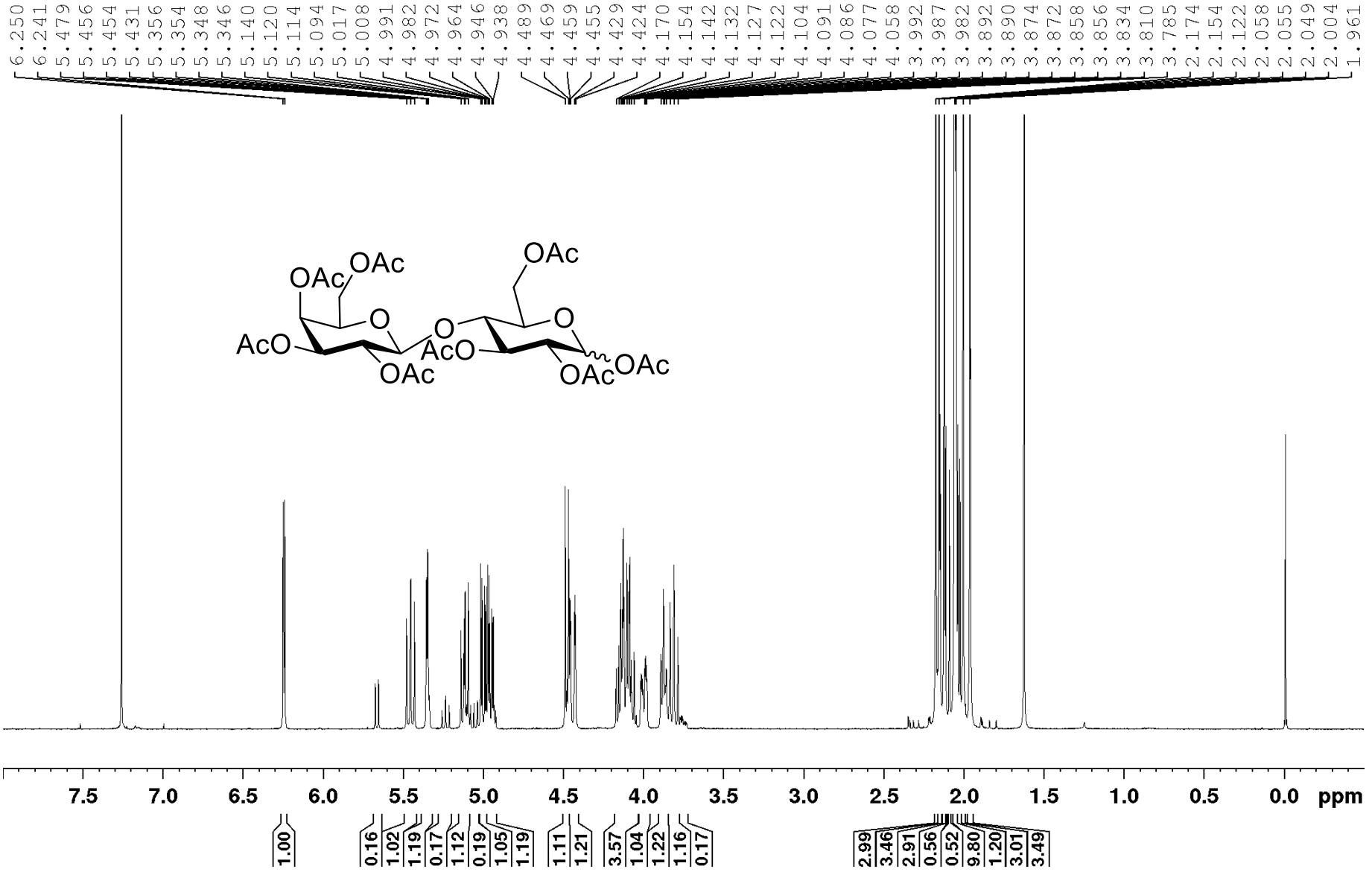
1,2-di-O-acetyl-6-deoxy-L-galactopyranoside **10** (α:β 61:39) ^{1}H NMR ($CDCl_3$)



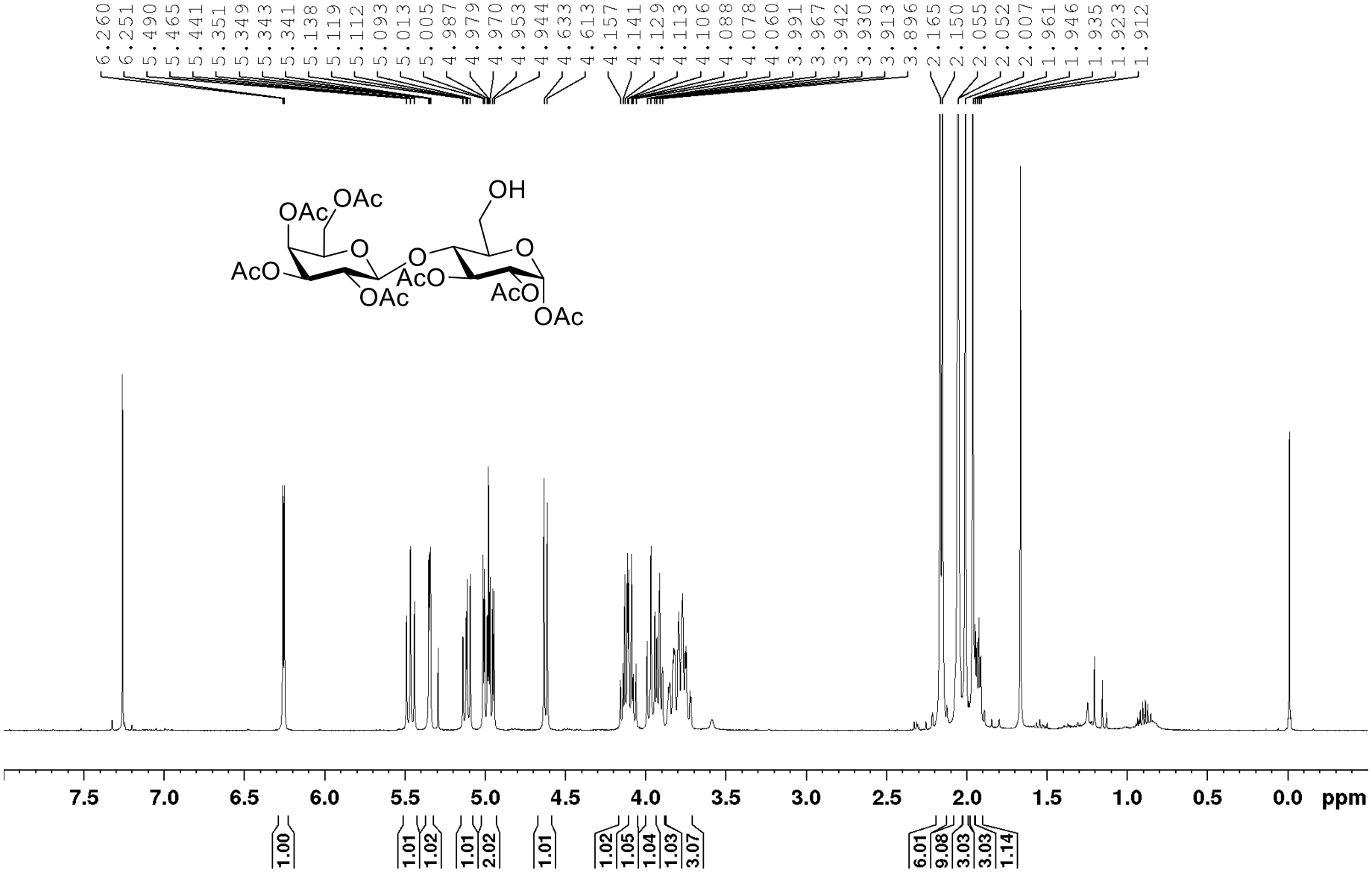
1,2-di-O-acetyl-6-deoxy-L-galactopyranoside **10** (α:β 61:39) ^{13}C NMR ($CDCl_3$)



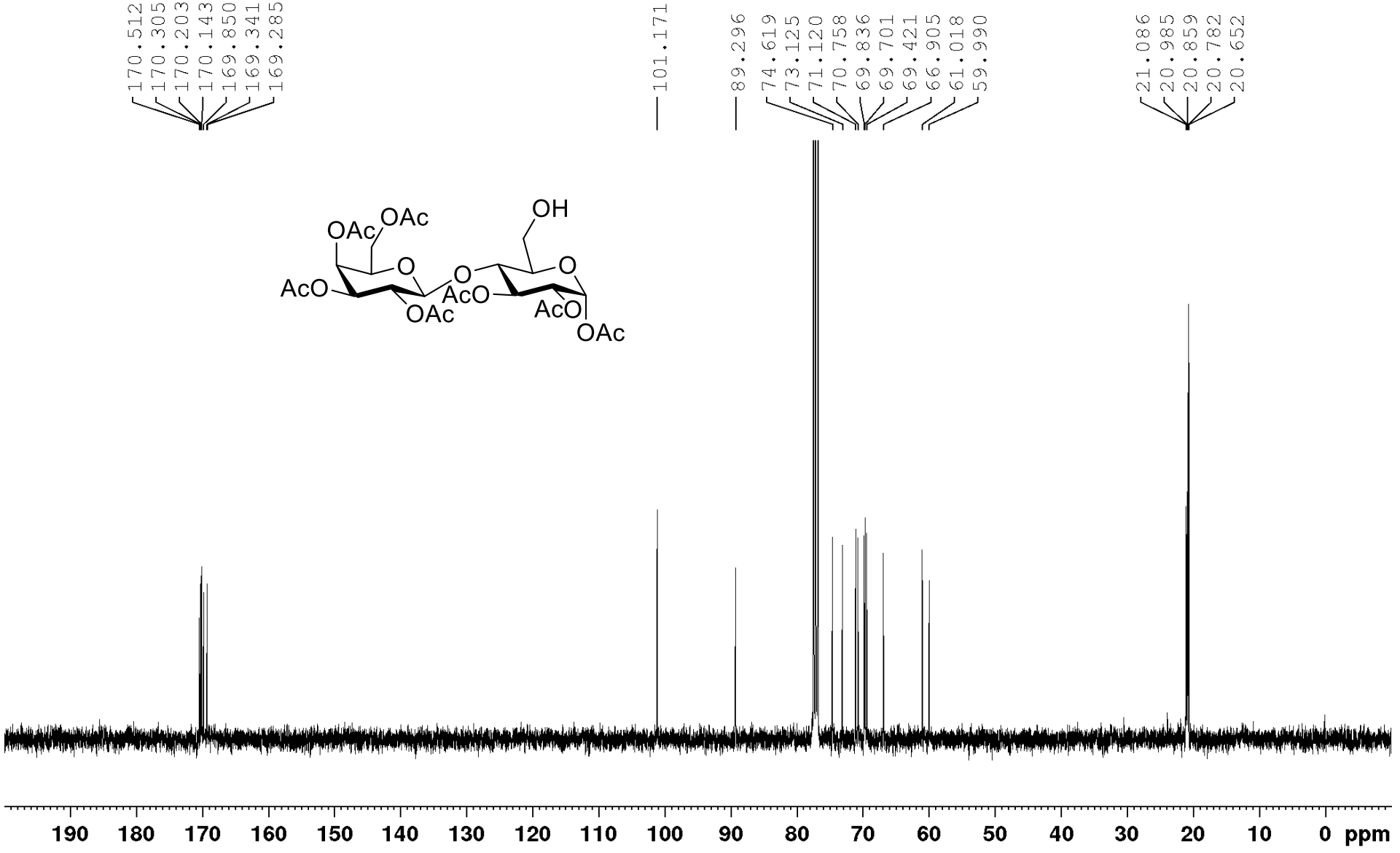
2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-O-acetyl-D-glucopyranoside **11** (α:β 86:14) ^{1}H NMR ($CDCl_3$)



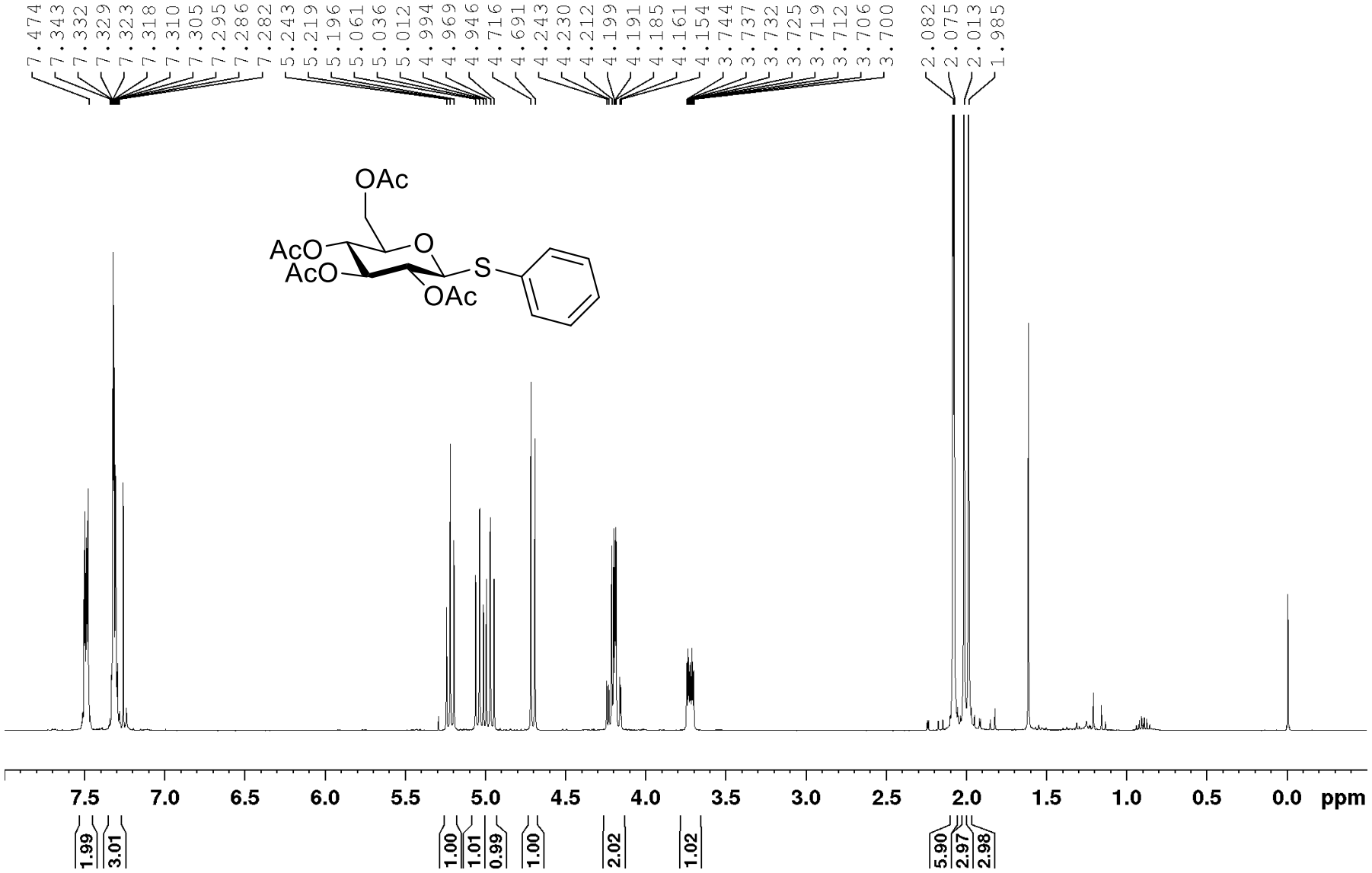
2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-1,2,3-tri-O-acetyl-D-glucopyranoside **12** ^{1}H NMR ($CDCl_3$)



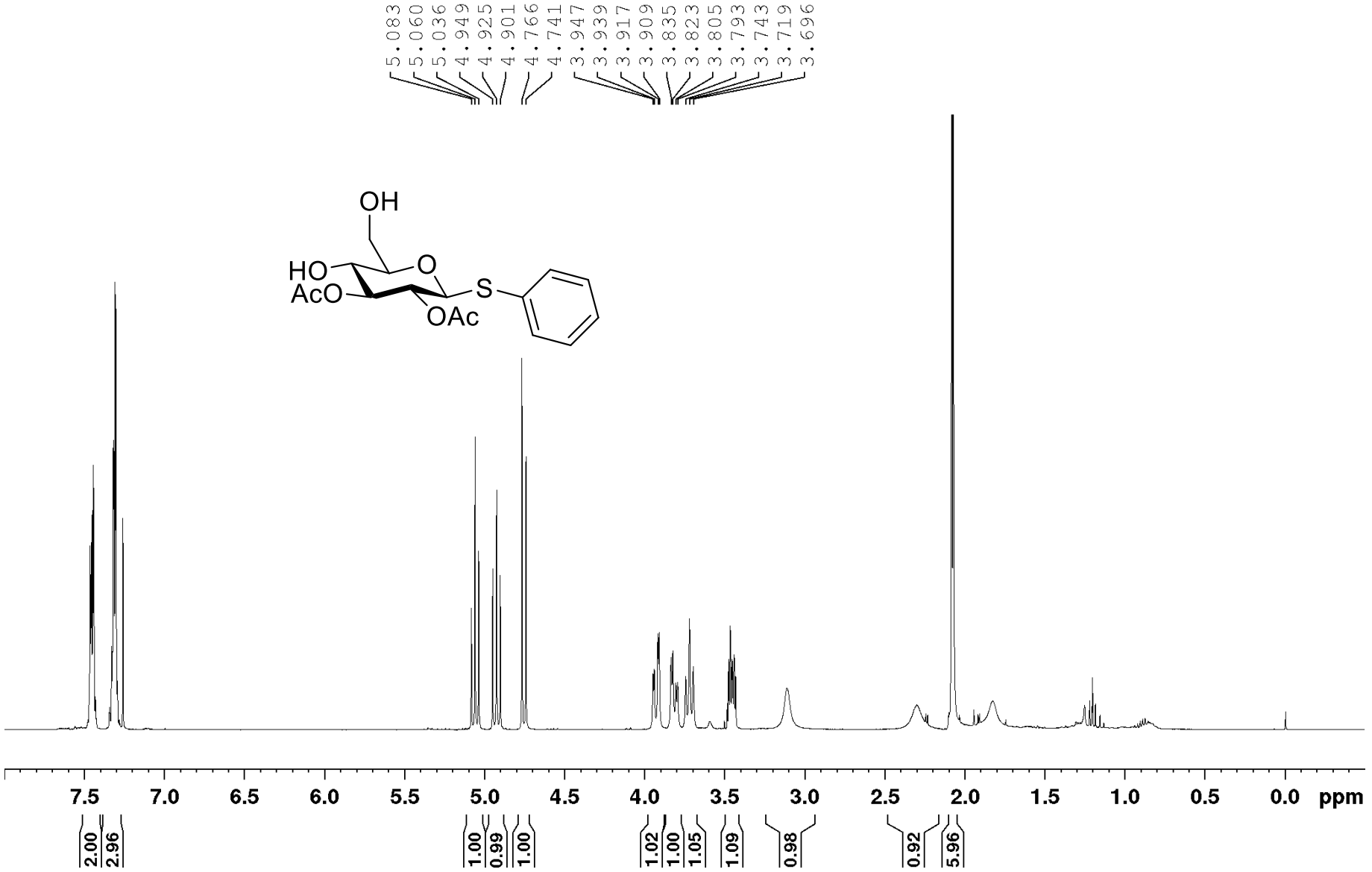
2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-1,2,3-tri-O-acetyl-D-glucopyranoside **12** ^{13}C NMR ($CDCl_3$)



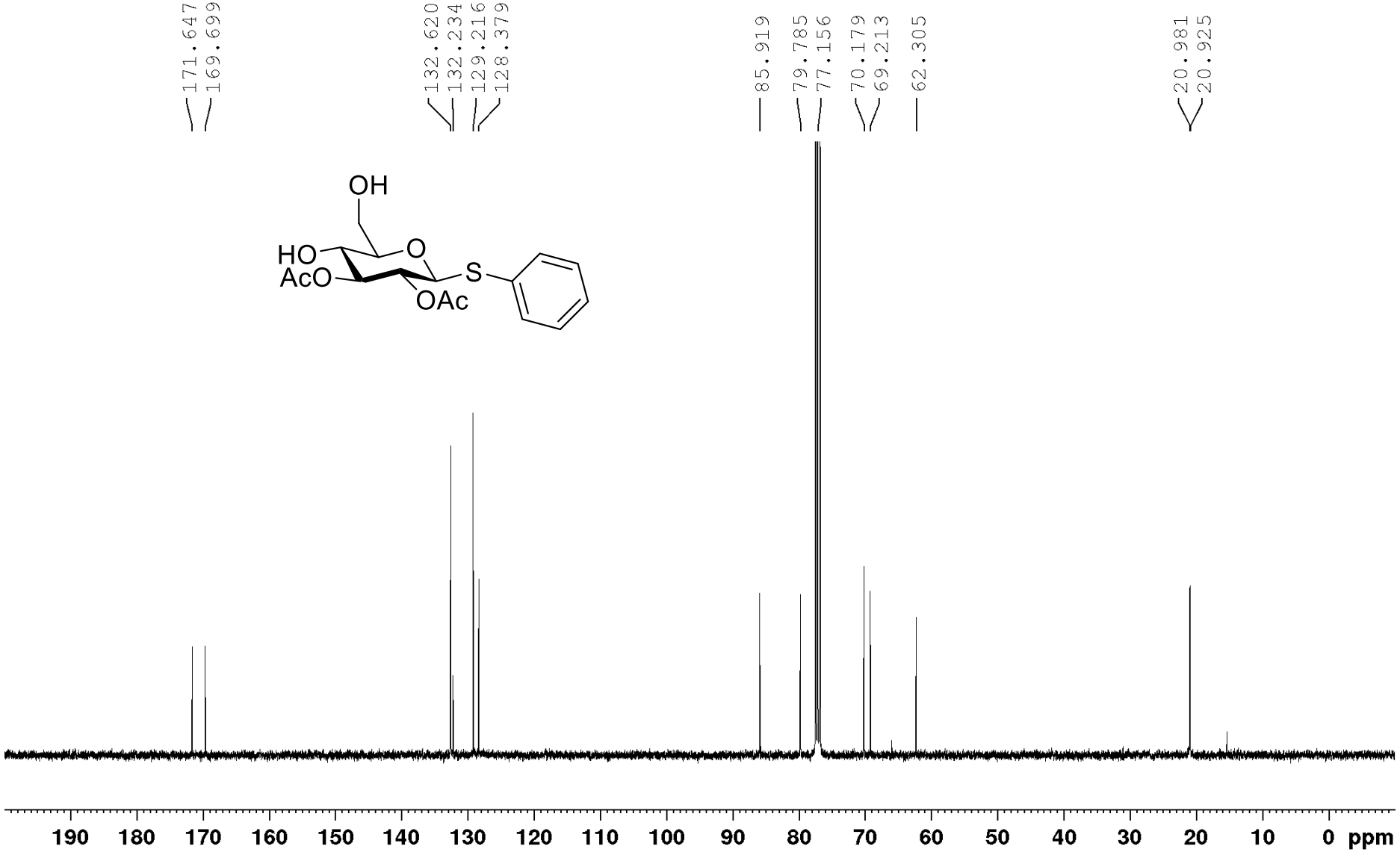
Phenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside **13** ^{1}H NMR ($CDCl_3$)



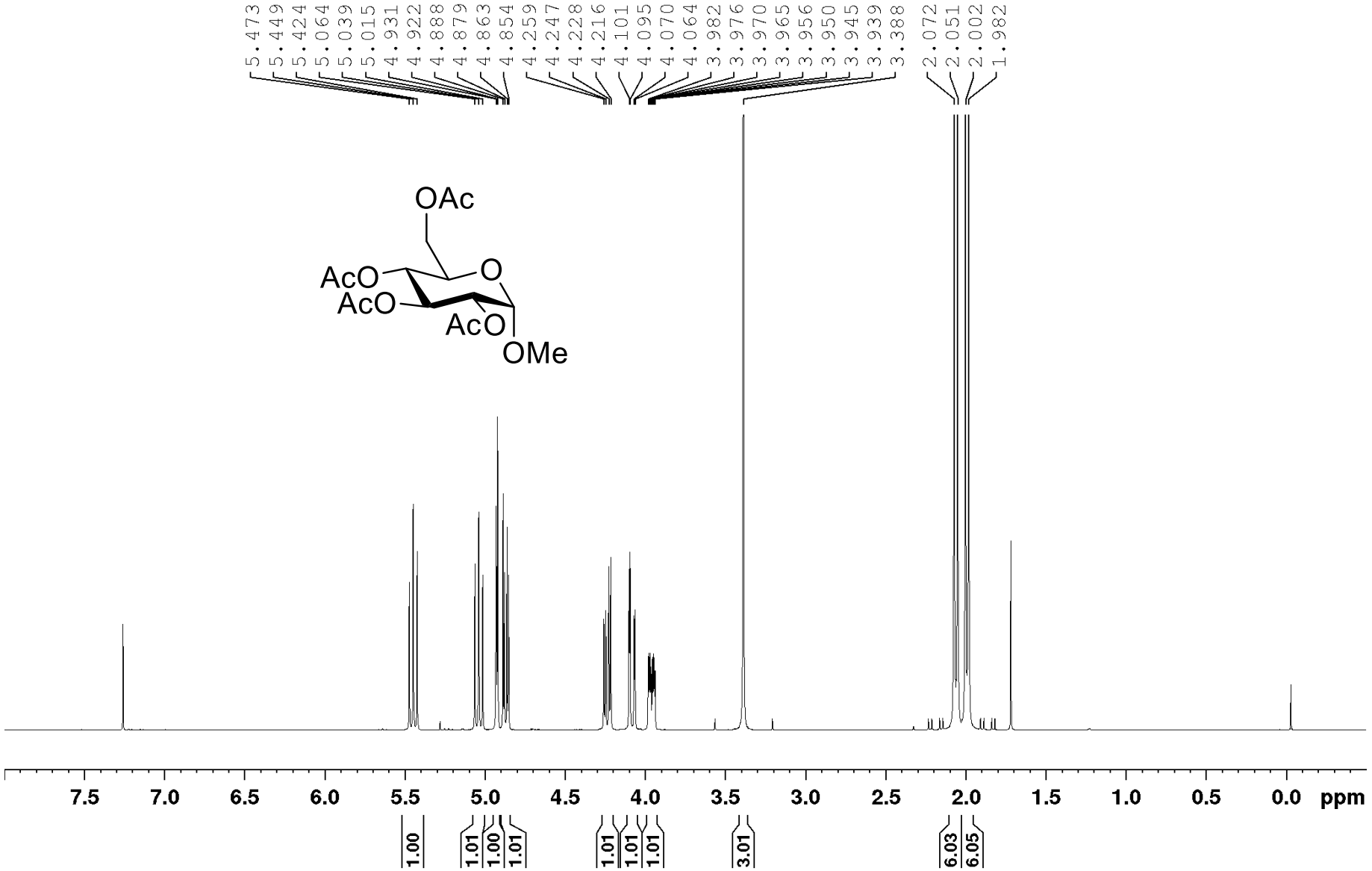
Phenyl 2,3-di-O-acetyl-1-thio-β-D-glucopyranoside **14** ^{1}H NMR ($CDCl_3$)



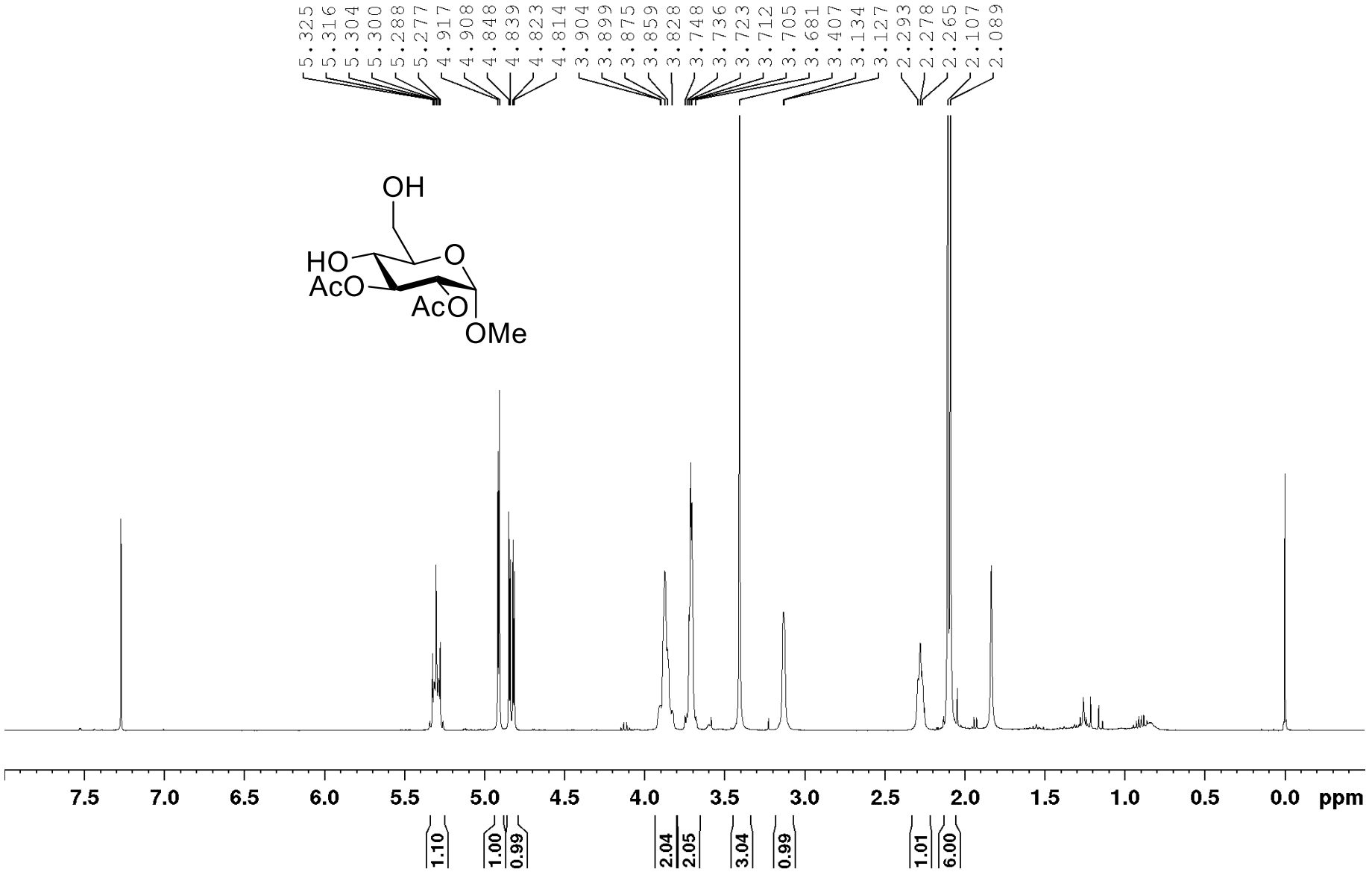
Phenyl 2,3-di-O-acetyl-1-thio-β-D-glucopyranoside **14** ^{13}C NMR ($CDCl_3$)



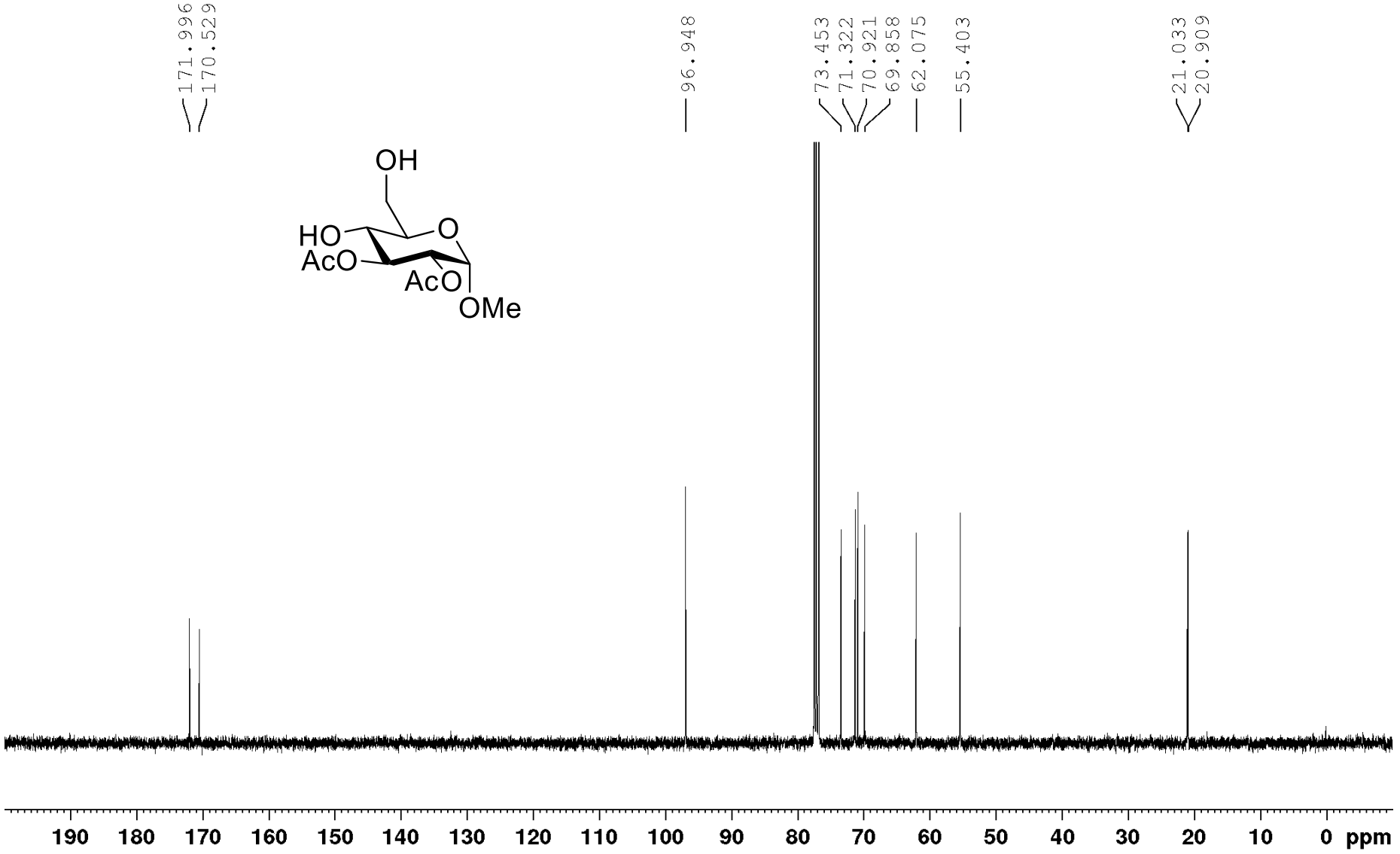
Methyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside **15** ^{1}H NMR ($CDCl_3$)



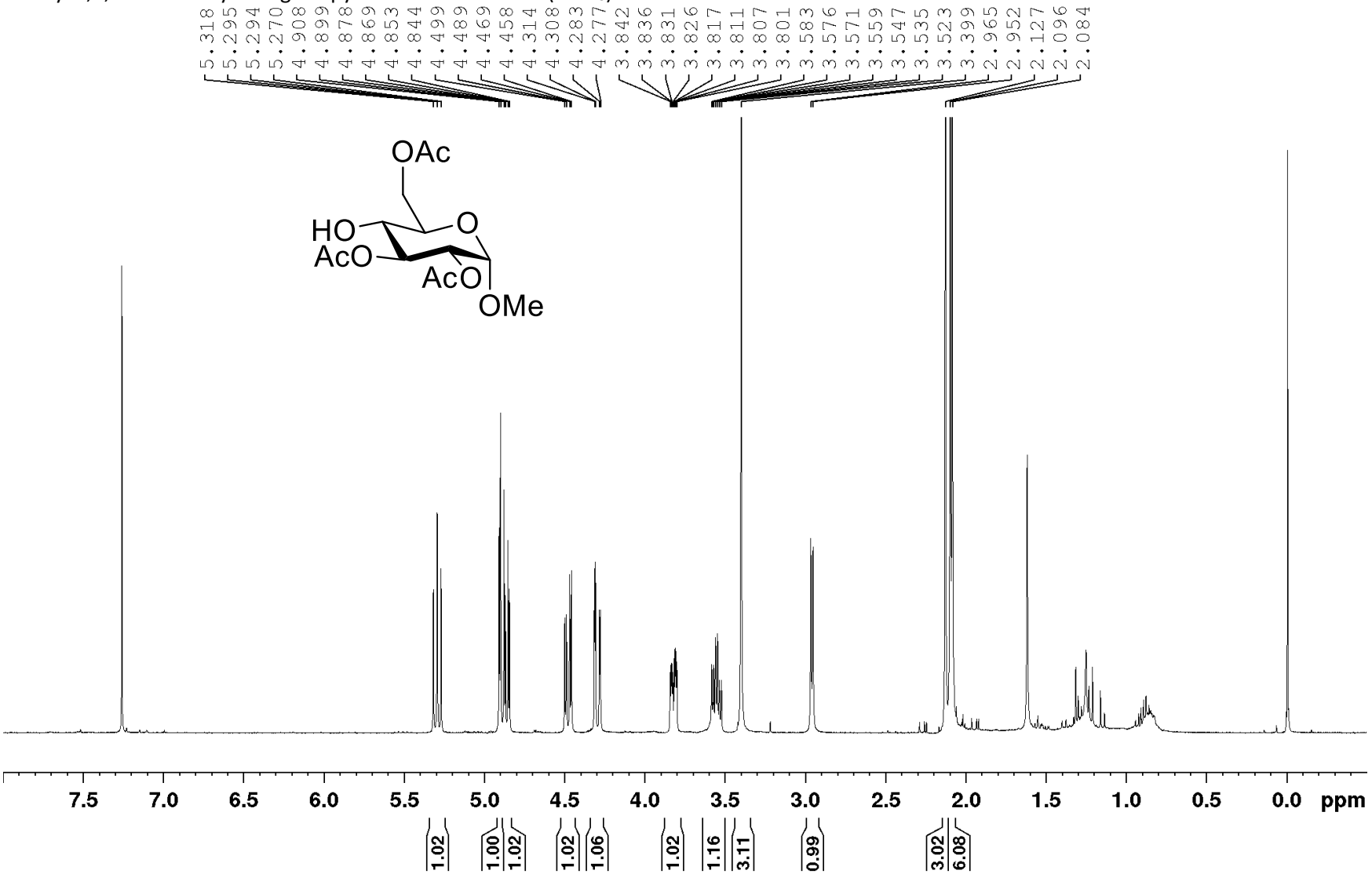
Methyl 2,3-di-O-acetyl-α-D-glucopyranoside **16** ^{1}H NMR ($CDCl_3$)



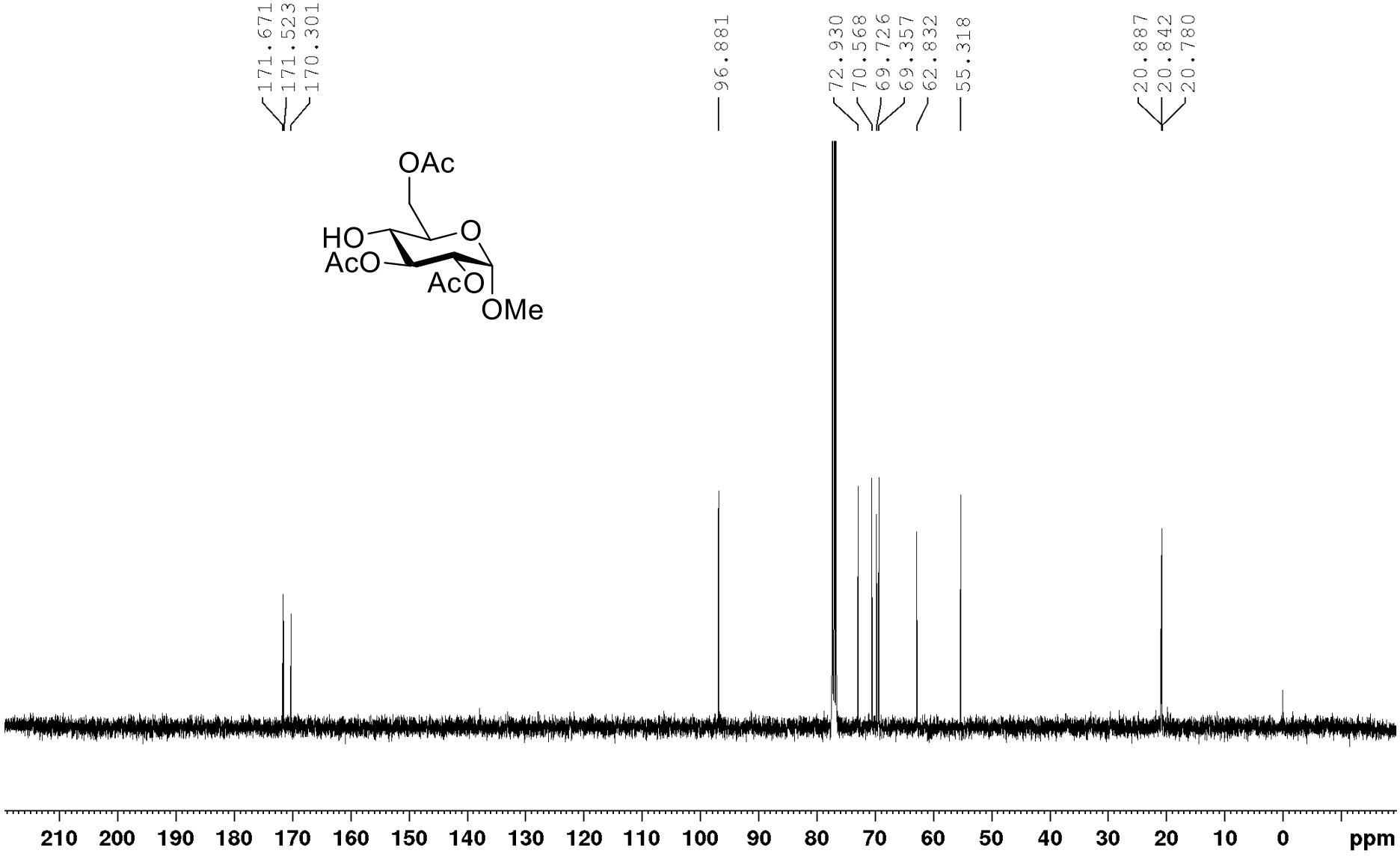
Methyl 2,3-di-O-acetyl-α-D-glucopyranoside **16** ^{13}C NMR ($CDCl_3$)



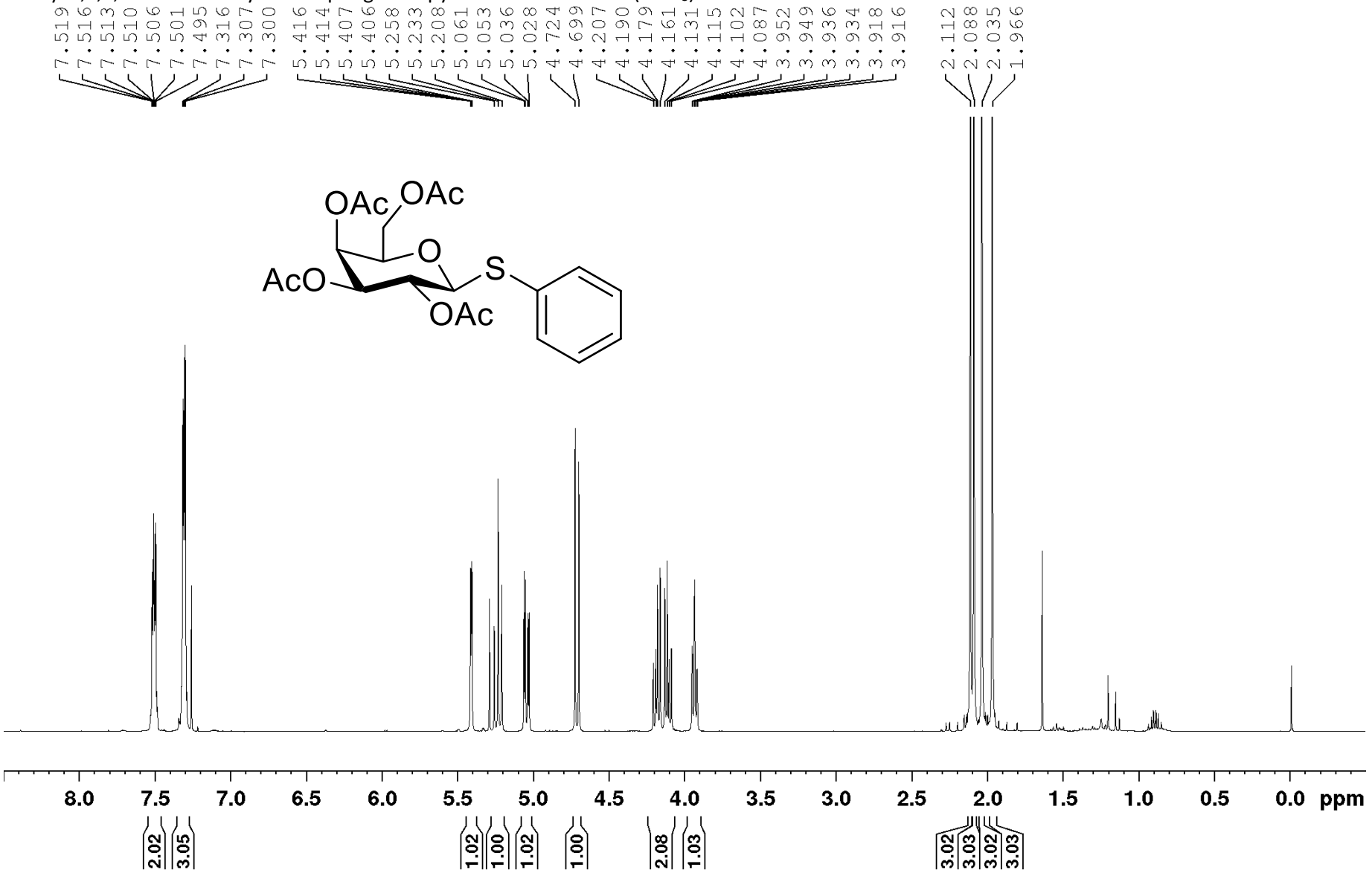
Methyl 2,3,6-tri-O-acetyl-α-D-glucopyranoside **17** ^{1}H NMR ($CDCl_3$)



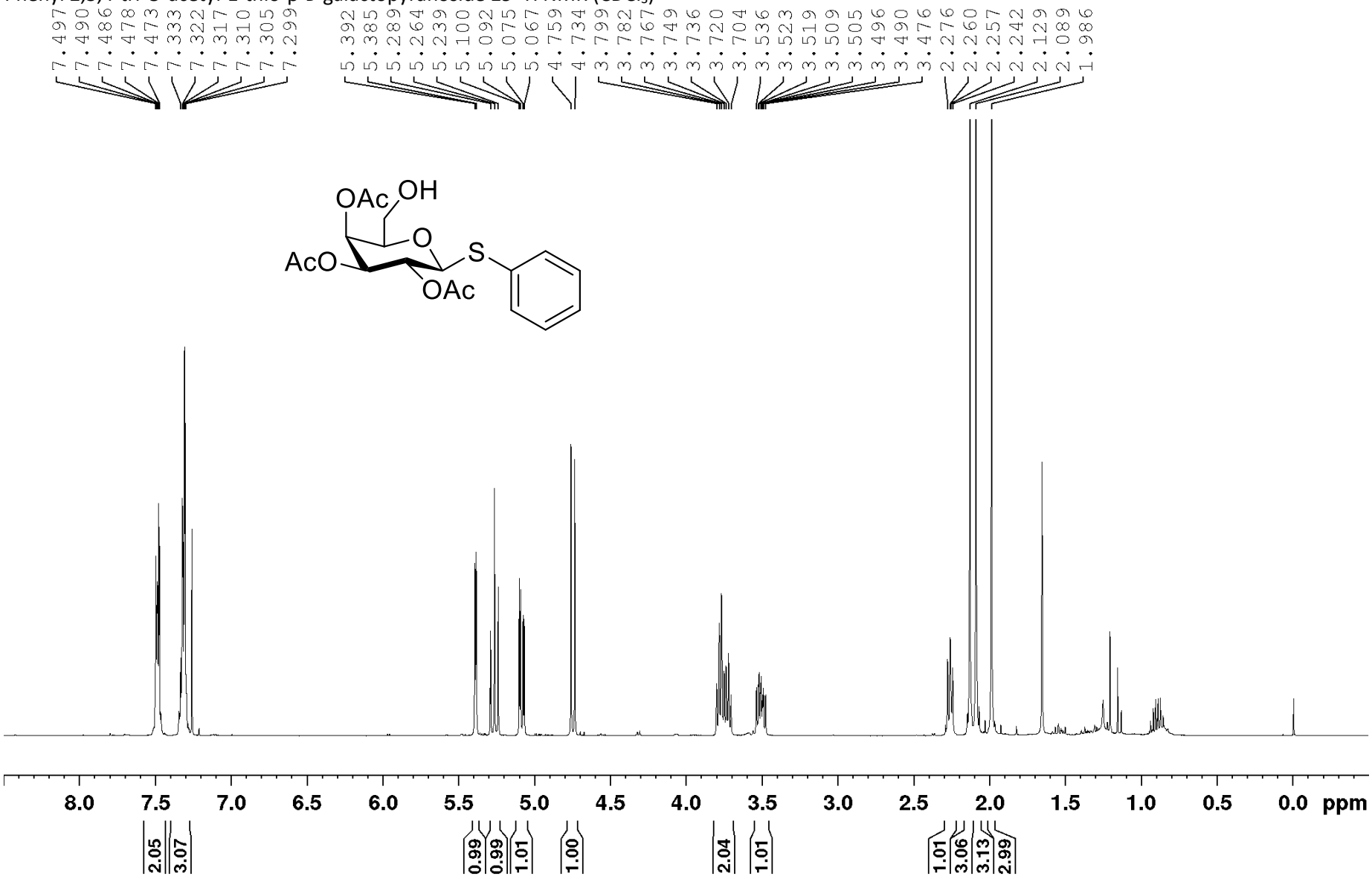
Methyl 2,3,6-tri-O-acetyl-α-D-glucopyranoside **17** ^{13}C NMR ($CDCl_3$)



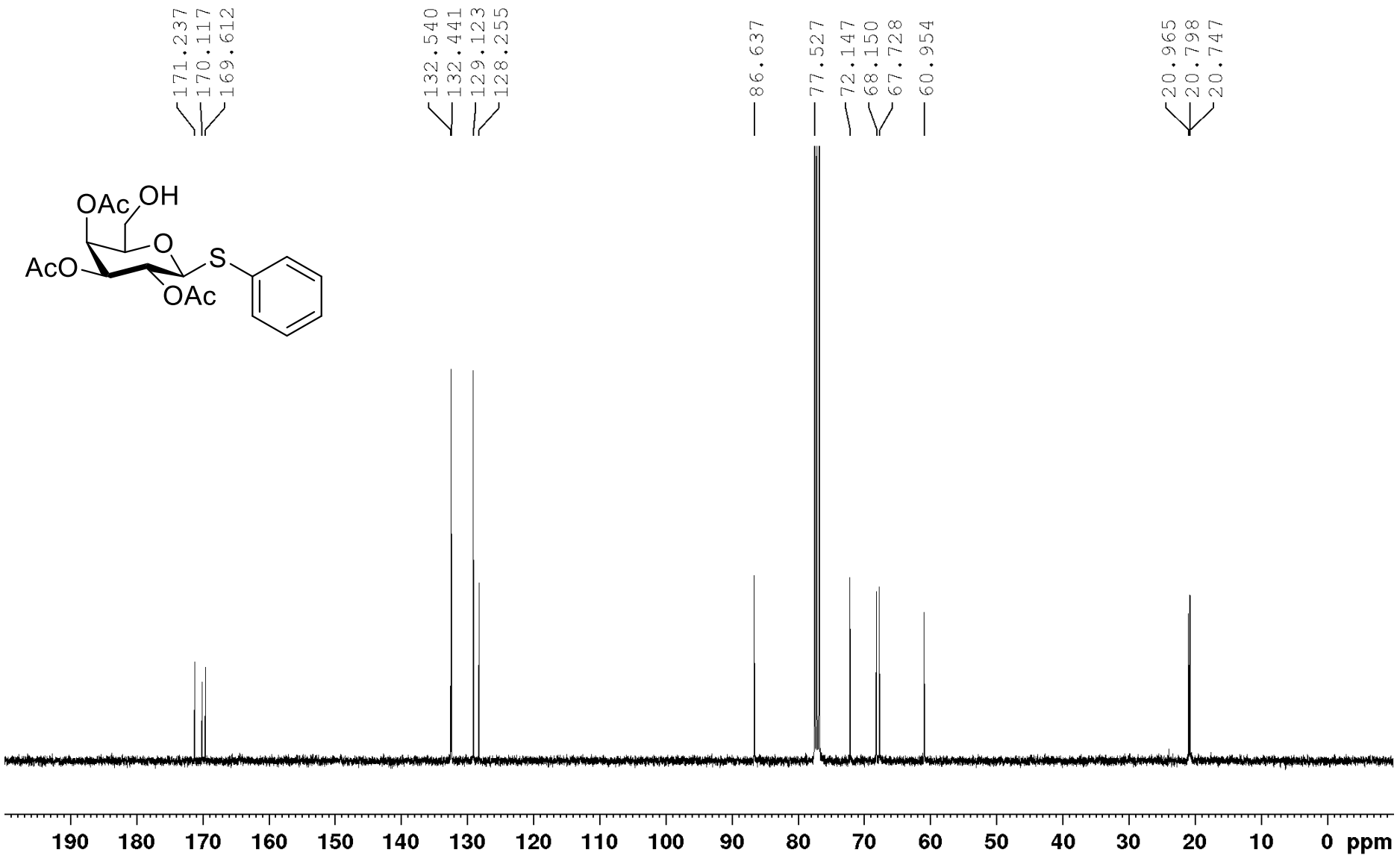
Phenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside **18** ^{1}H NMR ($CDCl_3$)



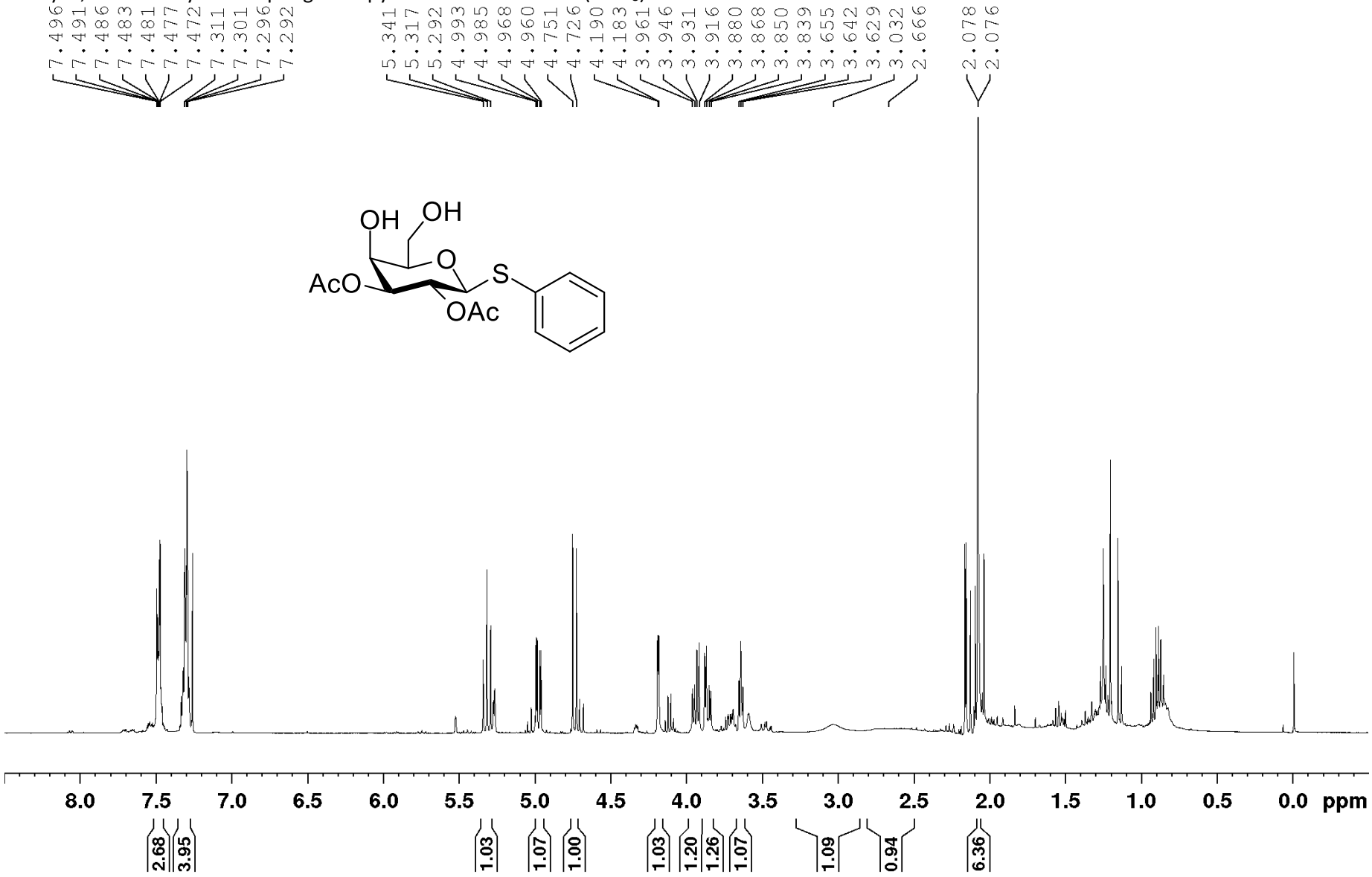
Phenyl 2,3,4-tri-O-acetyl-1-thio-β-D-galactopyranoside **19** ^{1}H NMR ($CDCl_3$)



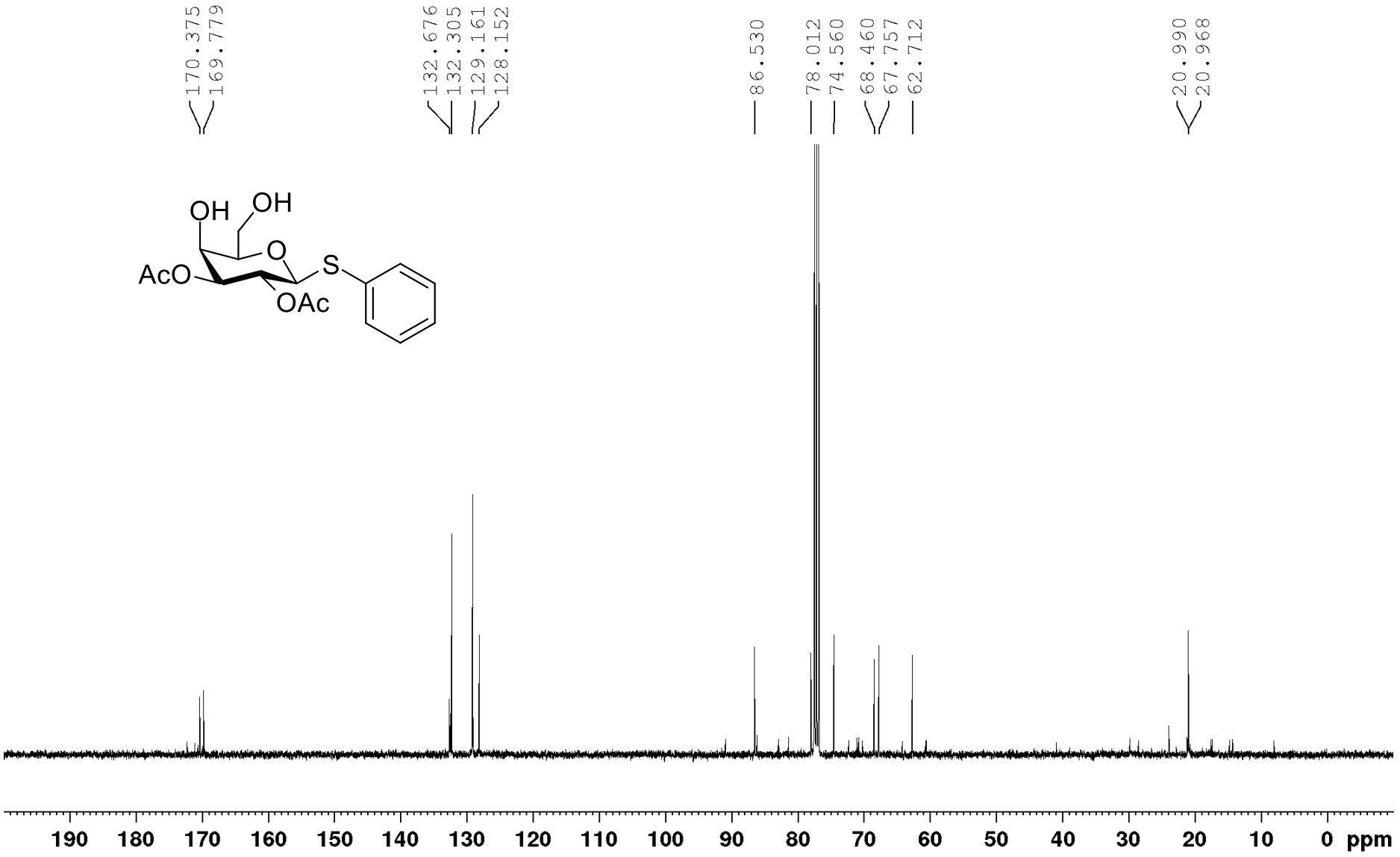
Phenyl 2,3,4-tri-O-acetyl-1-thio-β-D-galactopyranoside **19** ^{13}C NMR ($CDCl_3$)



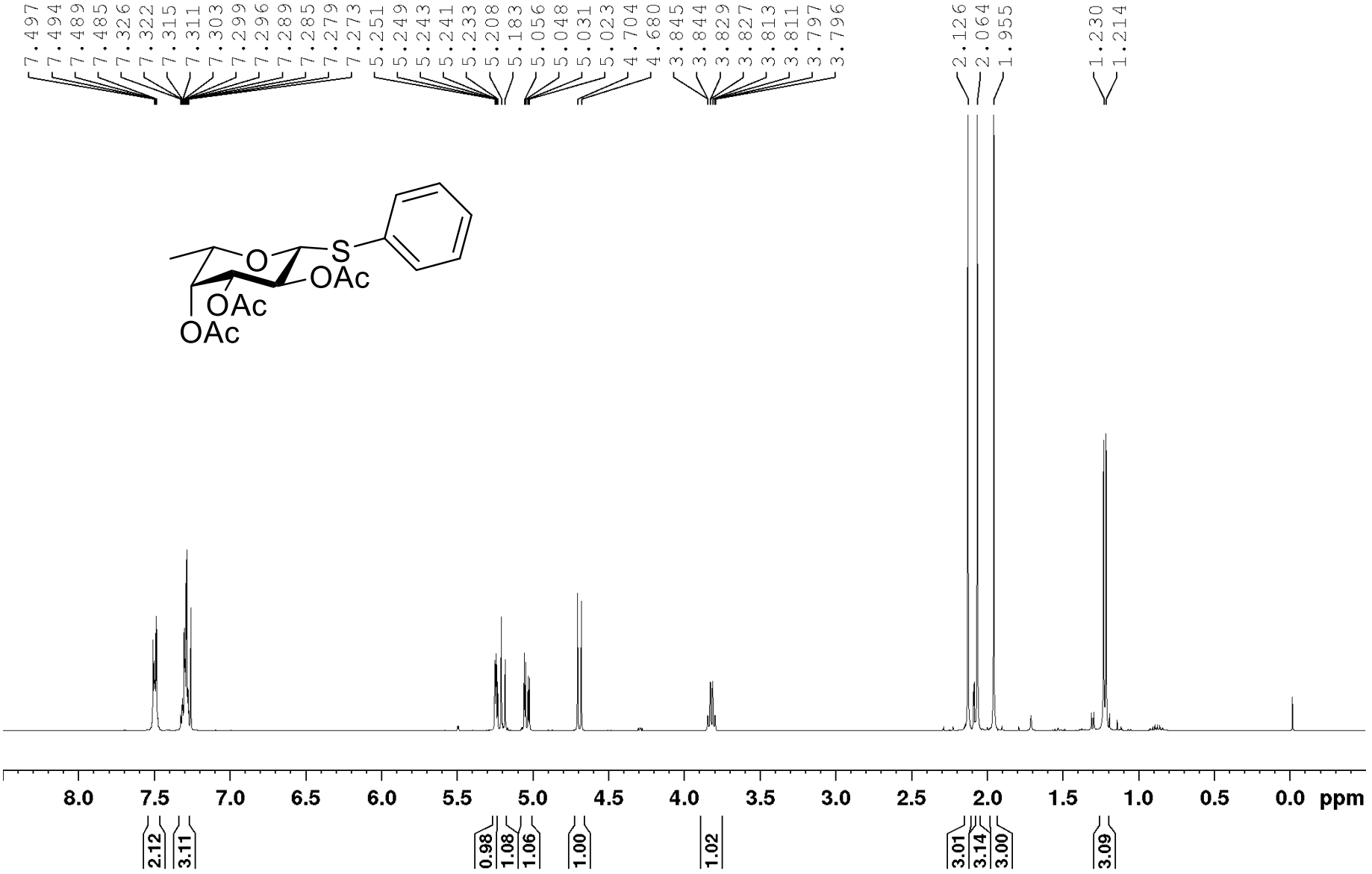
Phenyl 2,3-di-O-acetyl-1-thio-β-D-galactopyranoside **19a** ^{1}H NMR ($CDCl_3$)



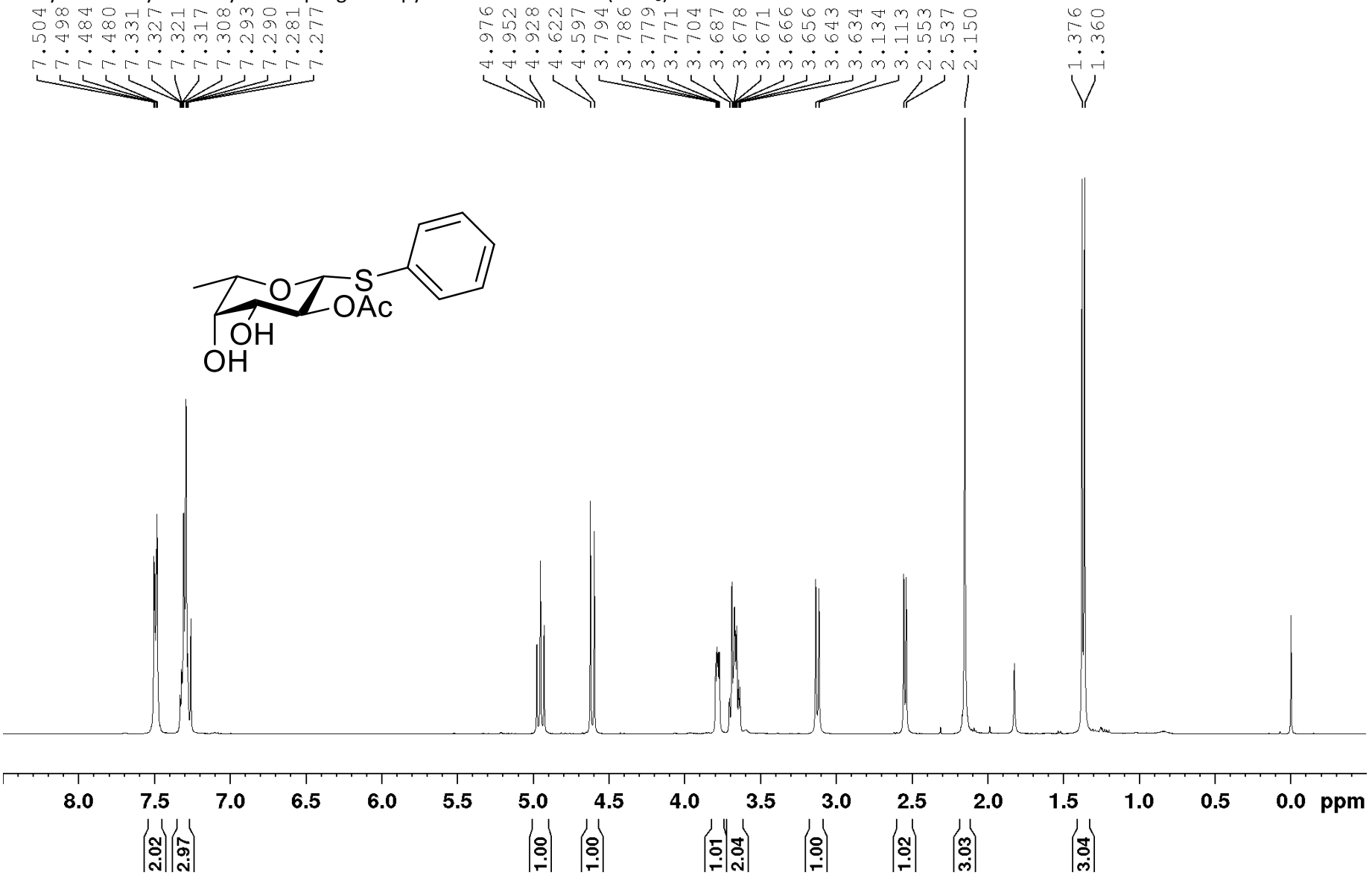
Phenyl 2,3-di-O-acetyl-1-thio-β-D-galactopyranoside **19a** ^{13}C NMR ($CDCl_3$)



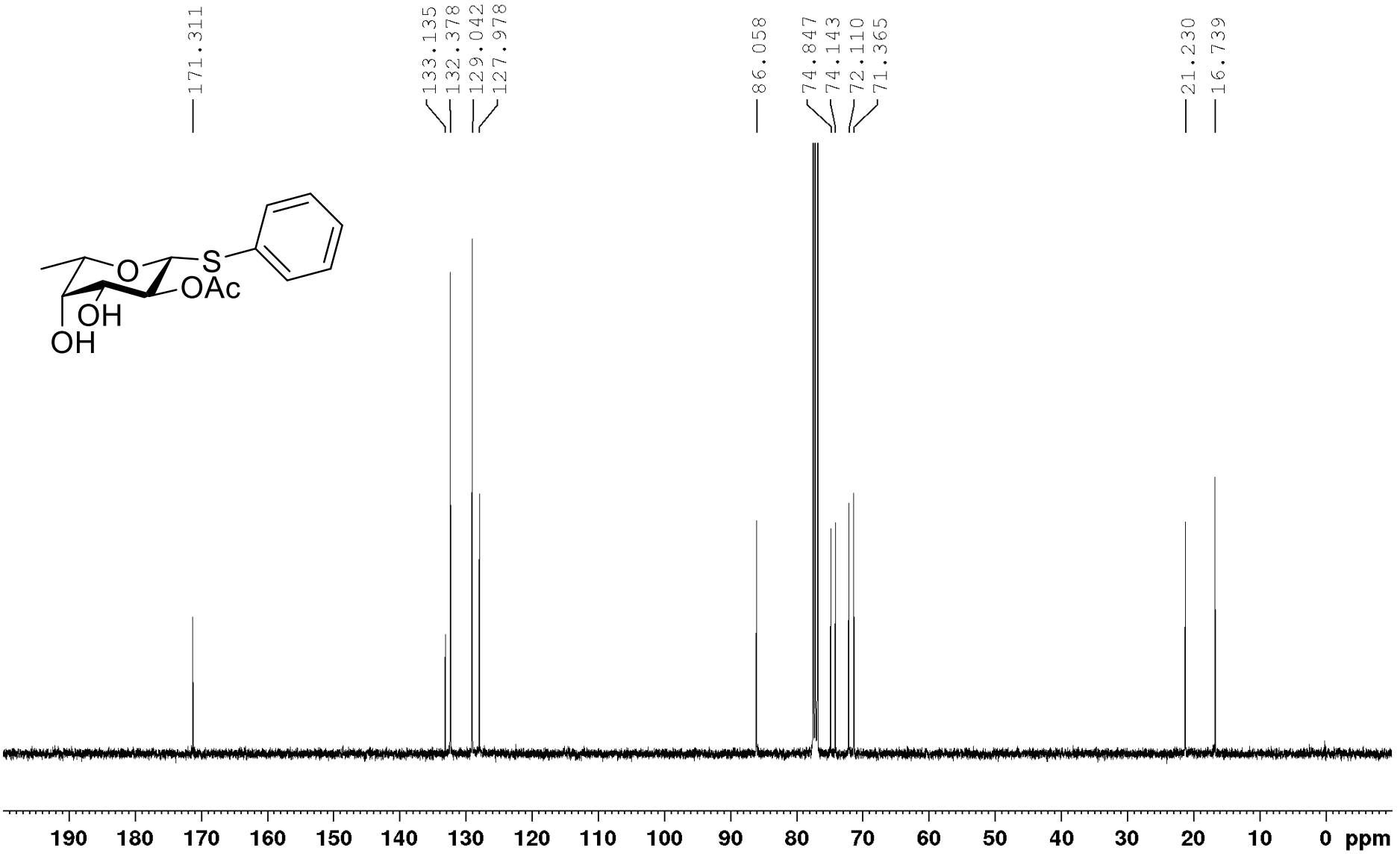
Phenyl 2,3,4-tri-O-acetyl-6-deoxy-1-thio-β-L-galactopyranoside **20** ^{1}H NMR ($CDCl_3$)



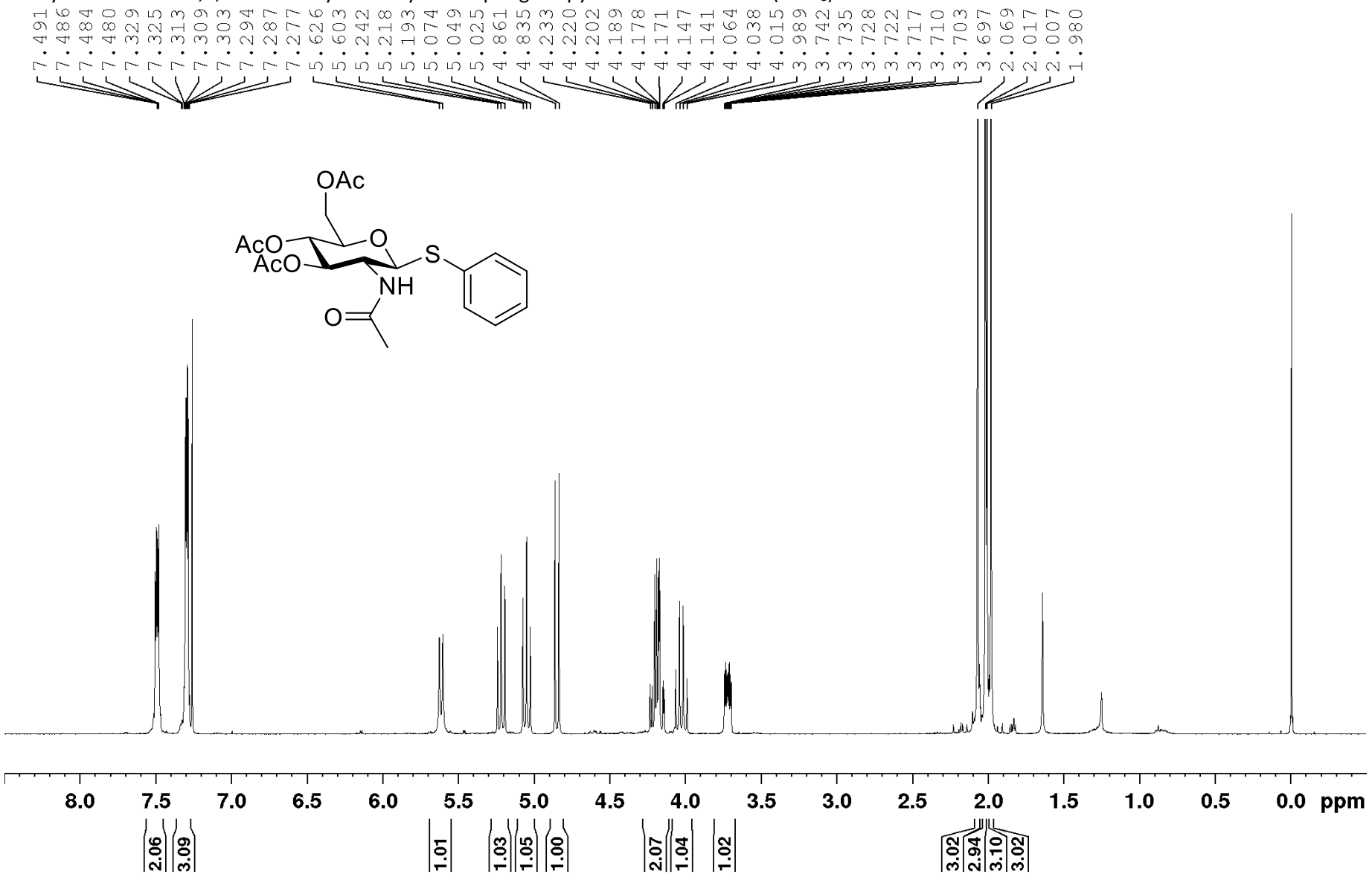
Phenyl 2-O-acetyl-6-deoxy-1-thio-β-L-galactopyranoside **21** ^{1}H NMR ($CDCl_3$)



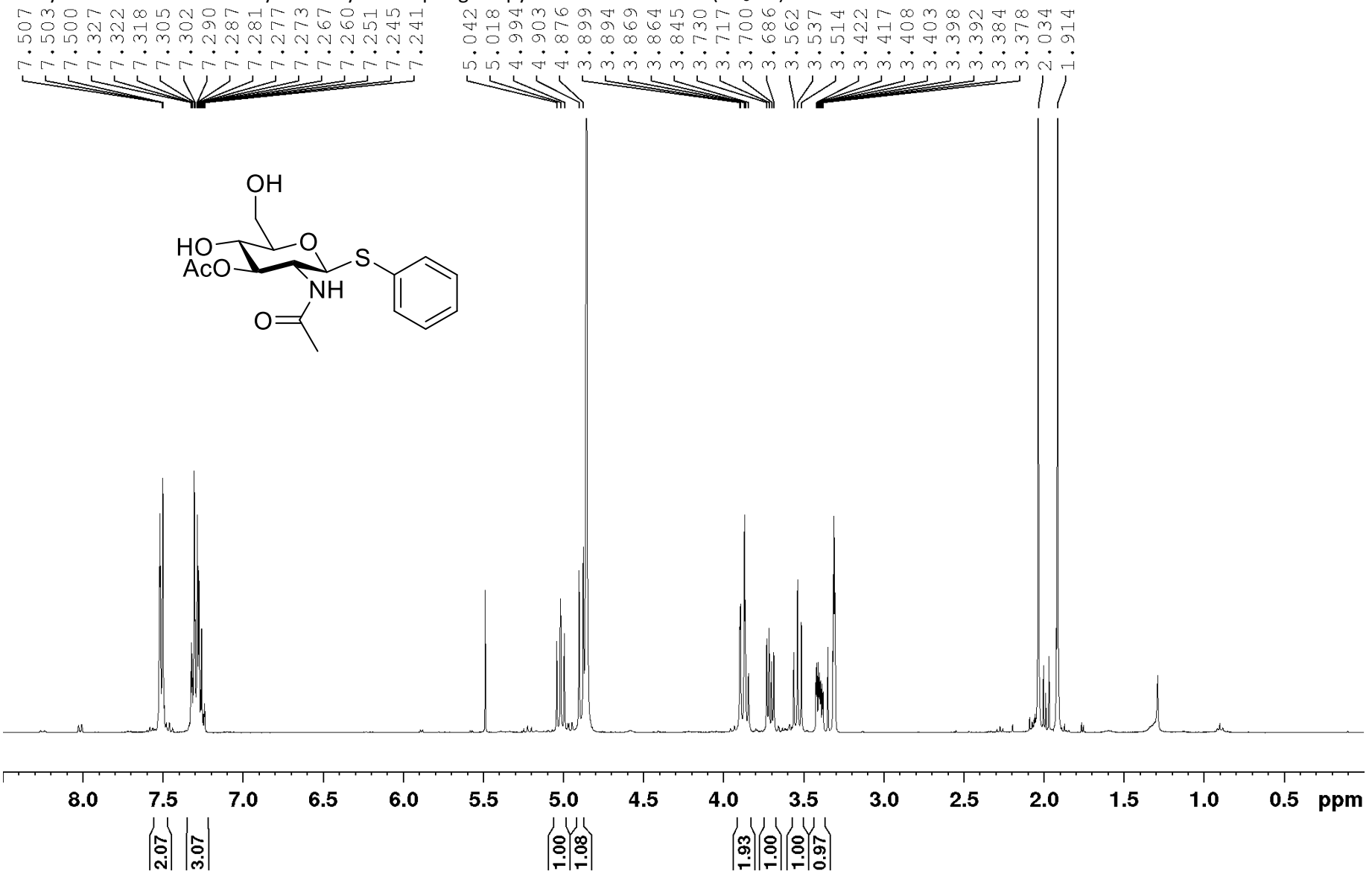
Phenyl 2-O-acetyl-6-deoxy-1-thio-β-L-galactopyranoside **21** ^{13}C NMR ($CDCl_3$)



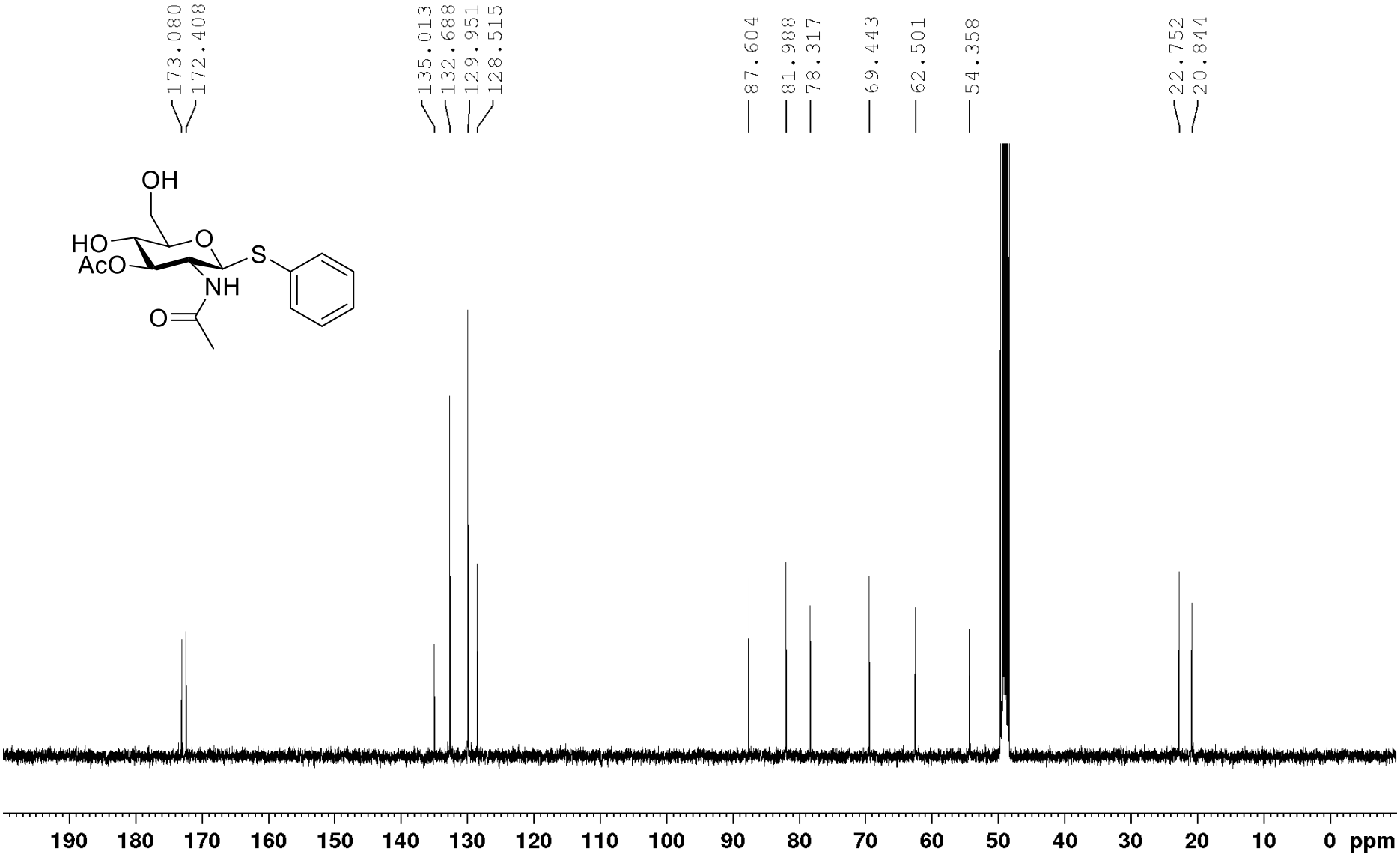
Phenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **22** ^{1}H NMR ($CDCl_3$)



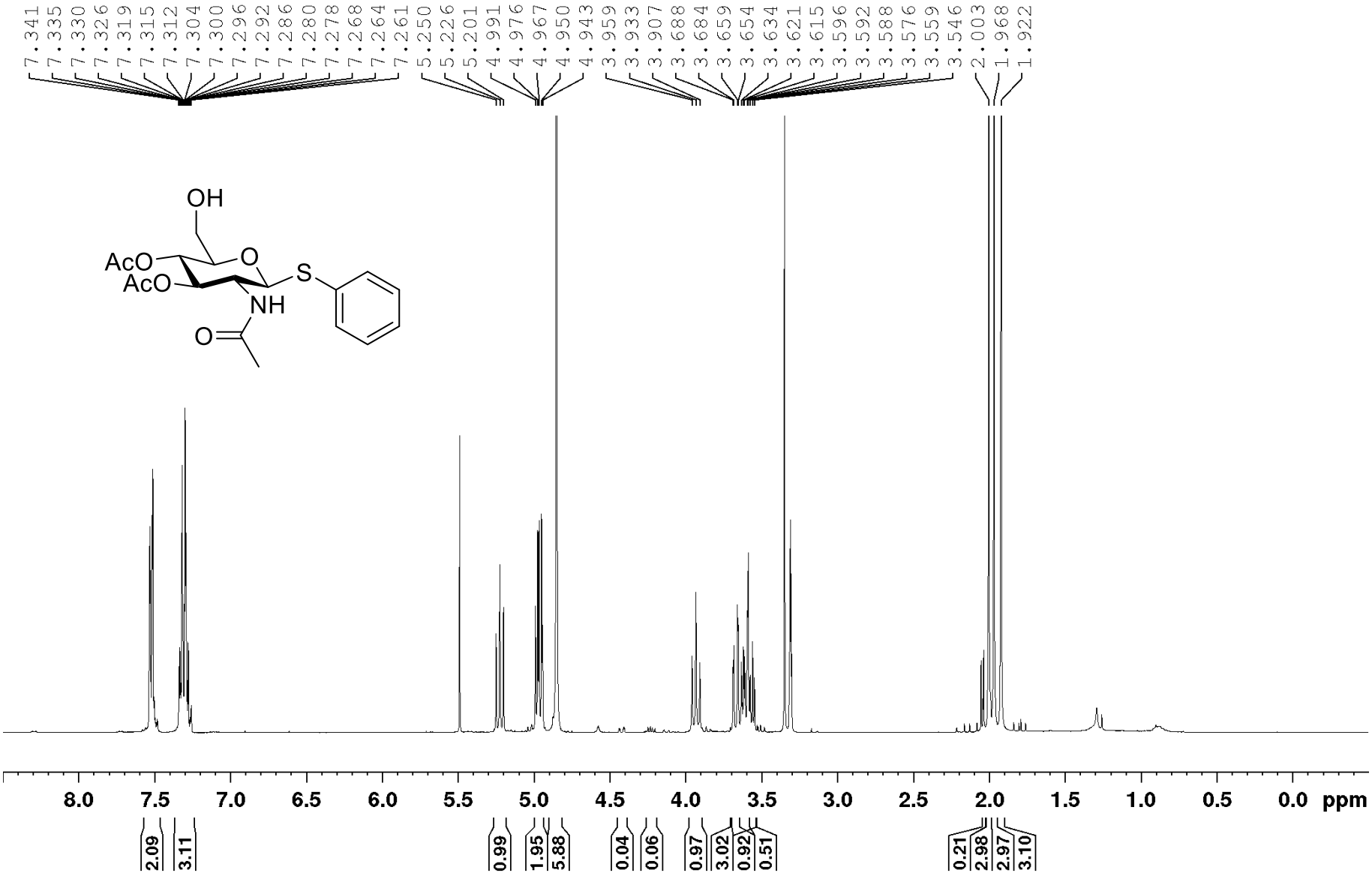
Phenyl 2-acetamido-3-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **23** ^{1}H NMR (CD_3OD)



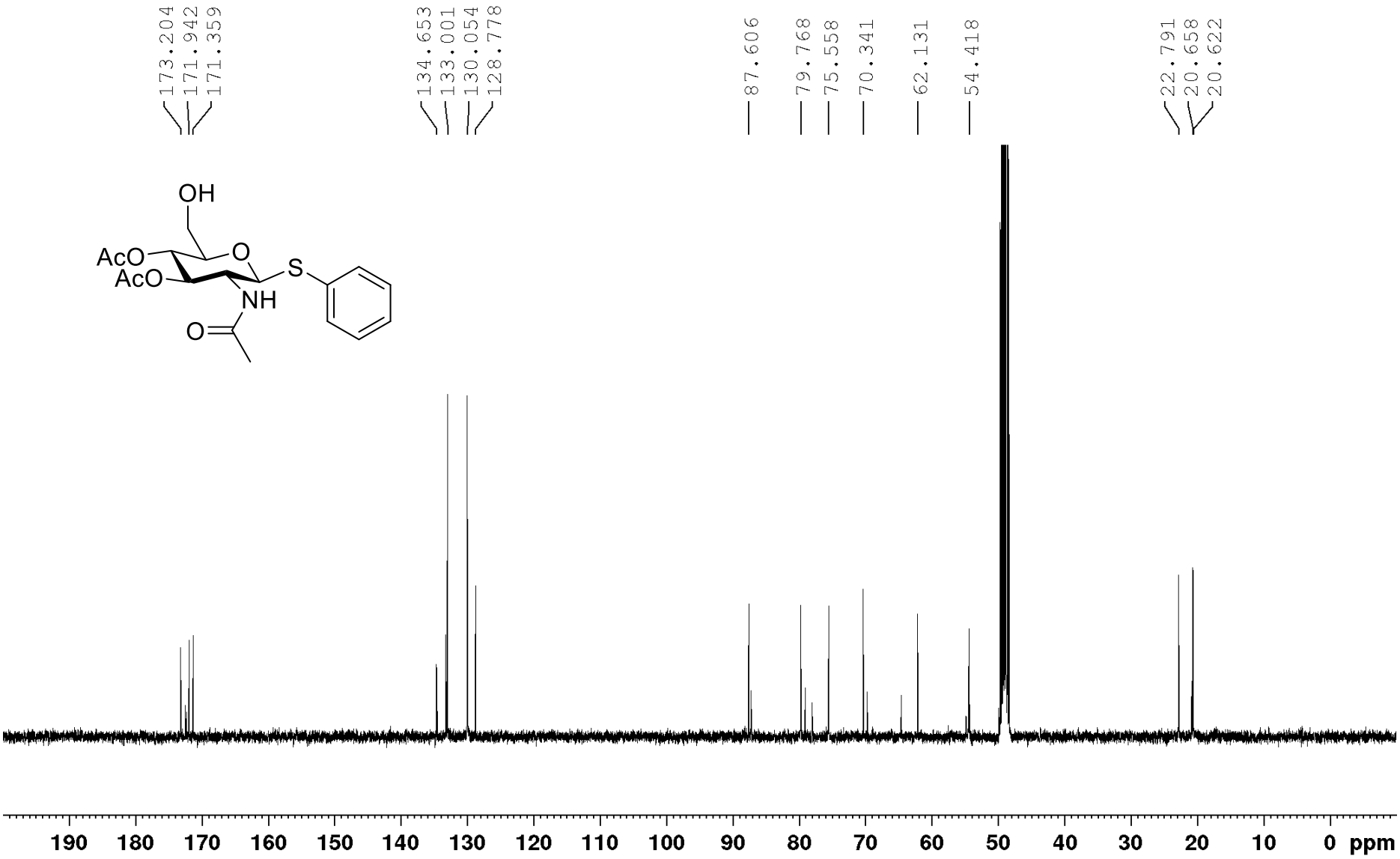
Phenyl 2-acetamido-3-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **23** ^{13}C NMR (CD_3OD)



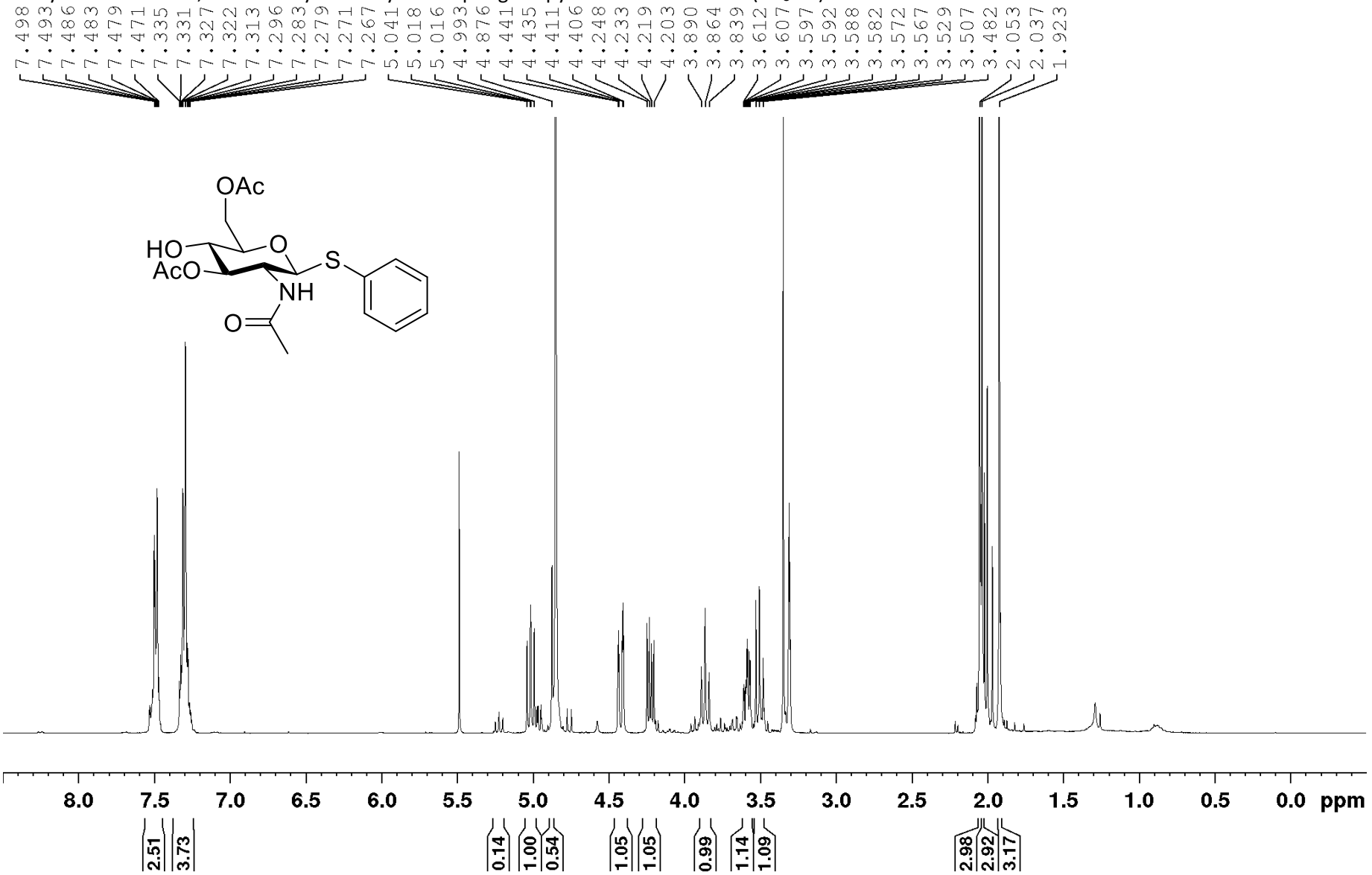
Phenyl 2-acetamido-3,4-di-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **24** ^{1}H NMR (CD_3OD)



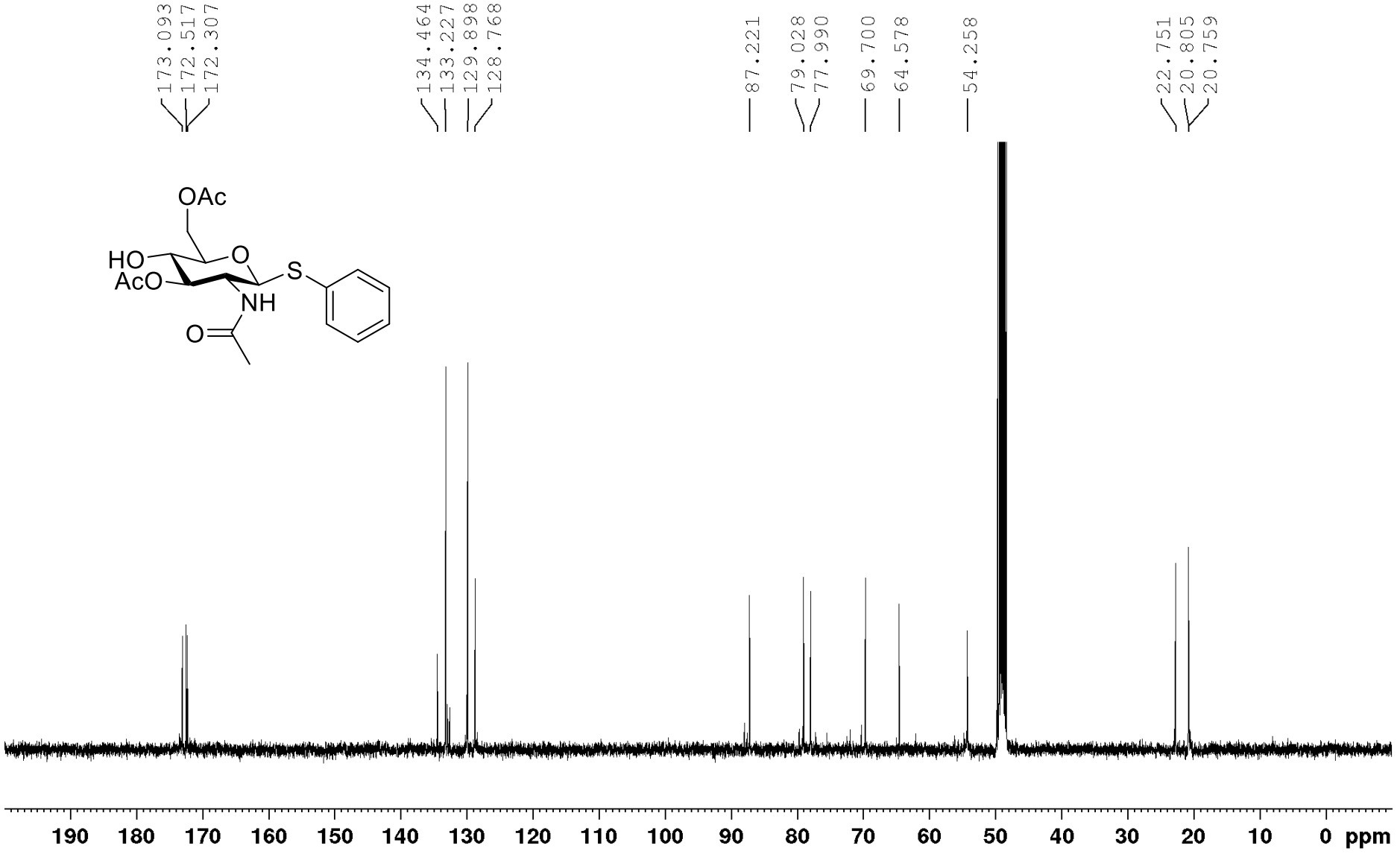
Phenyl-2-acetamido-3,4-di-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **24** ^{13}C NMR (CD_3OD)



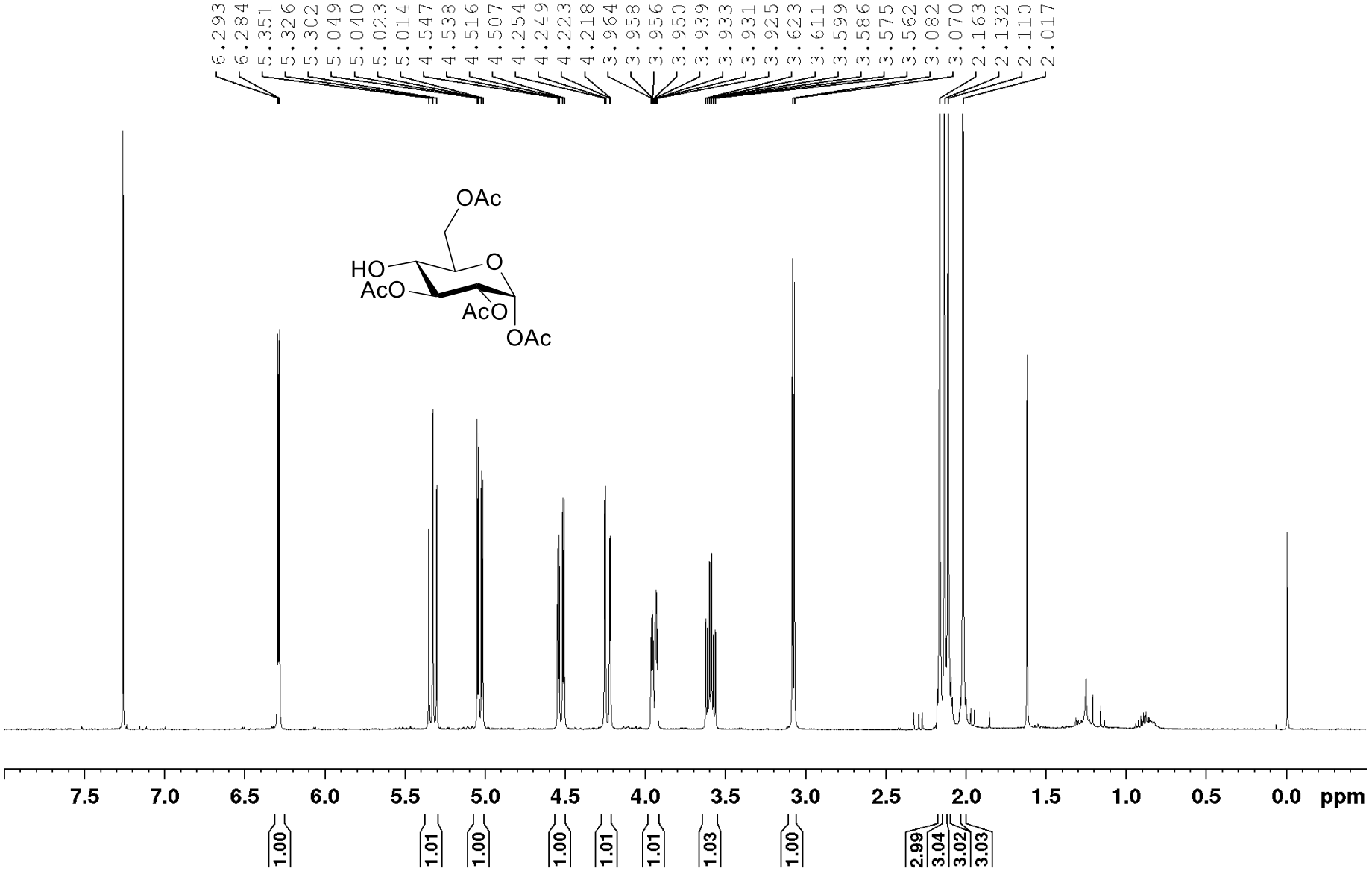
Phenyl 2-acetamido-3,6-di-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **25** ^{1}H NMR (CD_3OD)



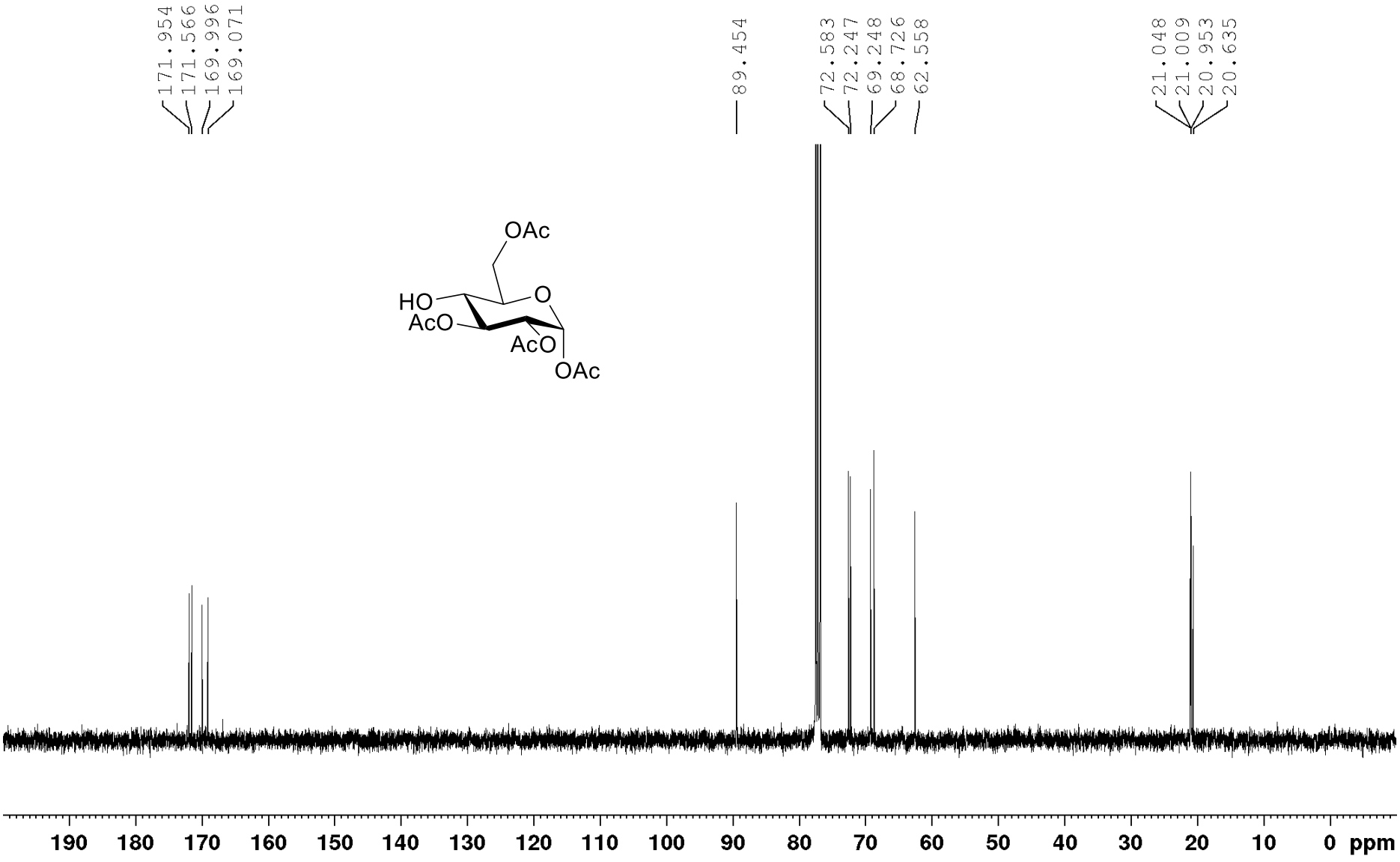
Phenyl-2-acetamido-3,6-di-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside **25** ^{13}C NMR (CD_3OD)



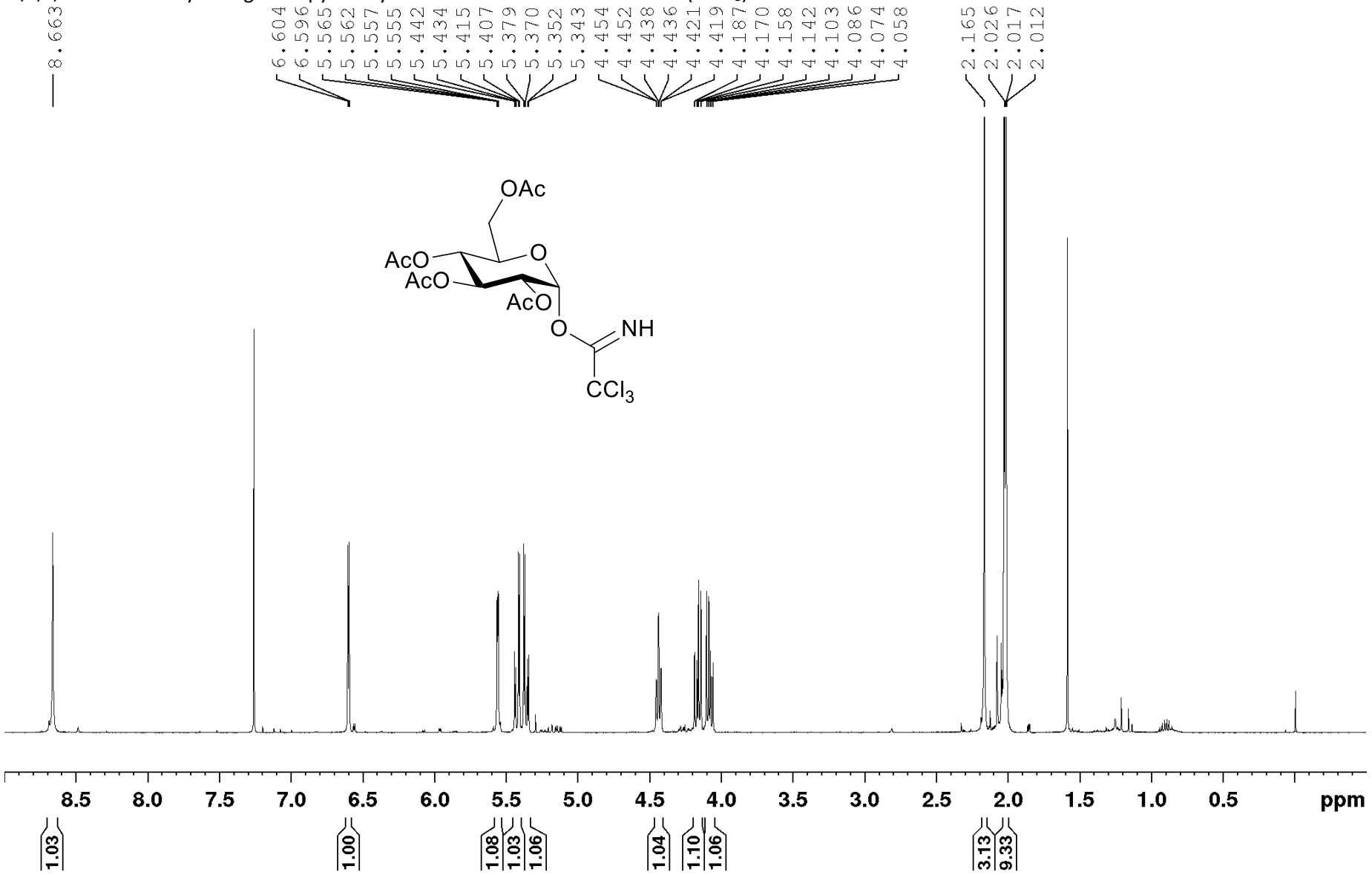
1,2,3,6-tetra-O acetyl-α-D-glucopyranoside **26** ^{1}H NMR ($CDCl_3$)



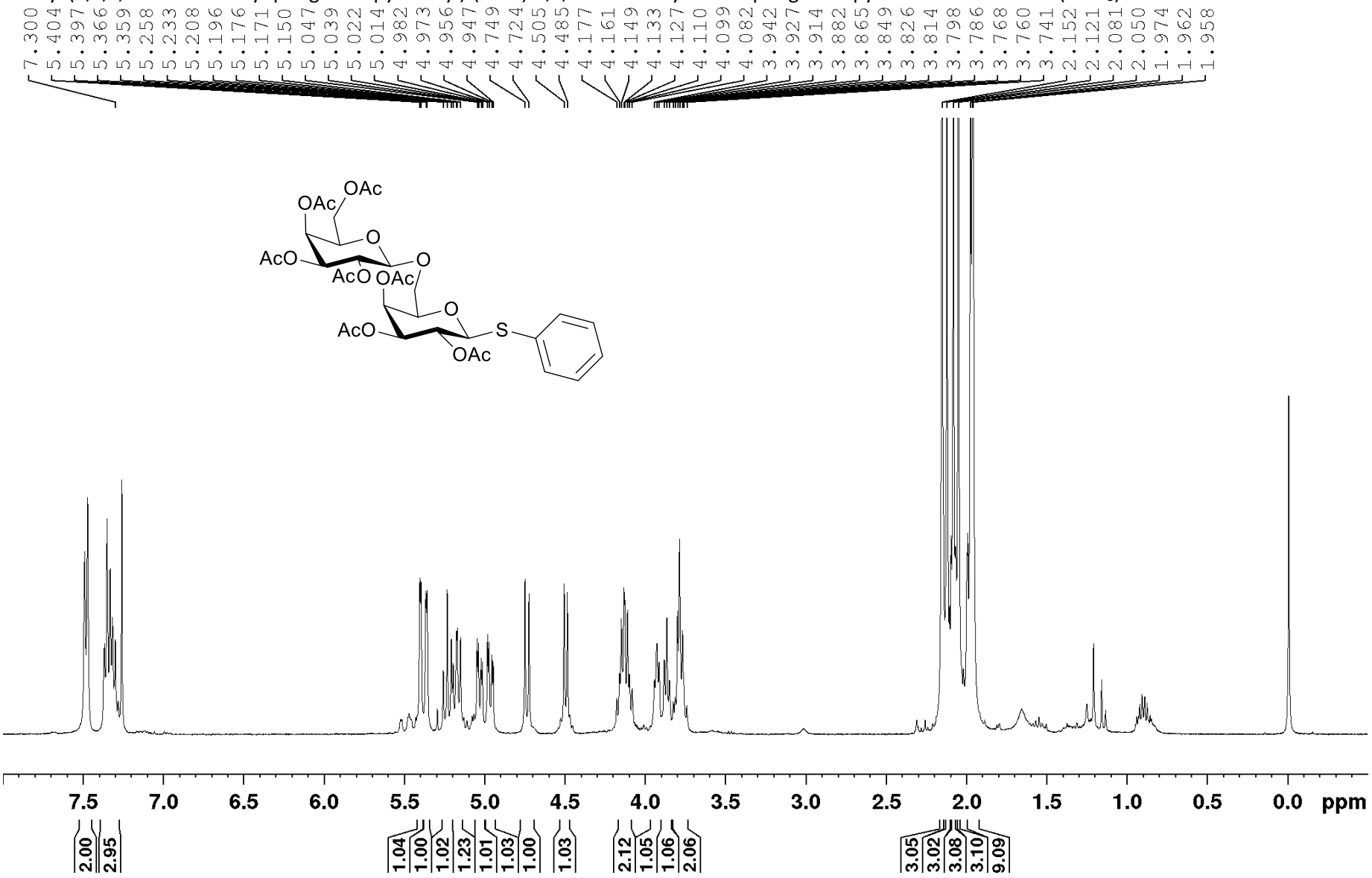
1,2,3,6-tetra-O acetyl-α-D-glucopyranoside **26** ^{1}H NMR ($CDCl_3$)



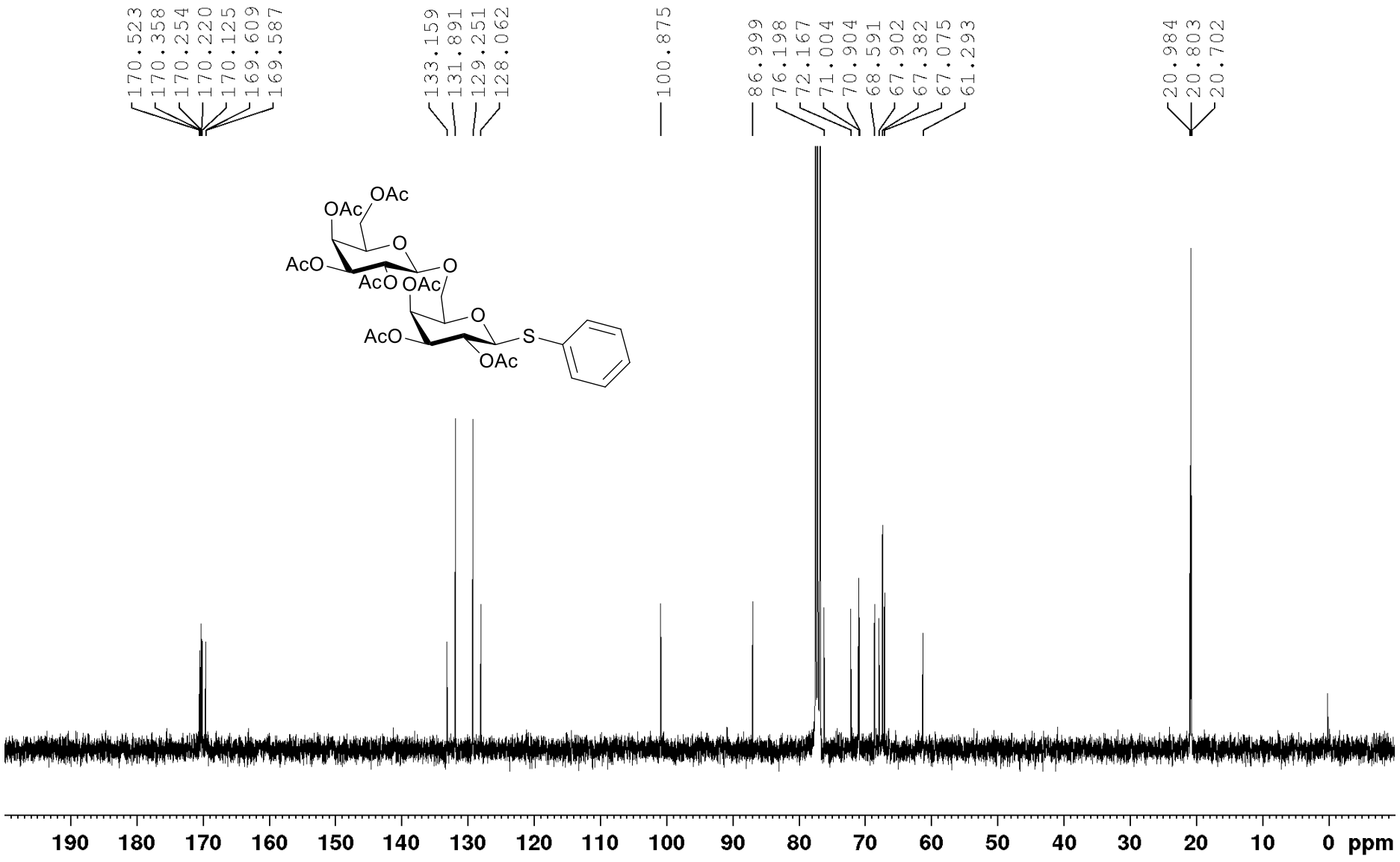
2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl trichloroacetimidate **27** ^{1}H NMR ($CDCl_3$)



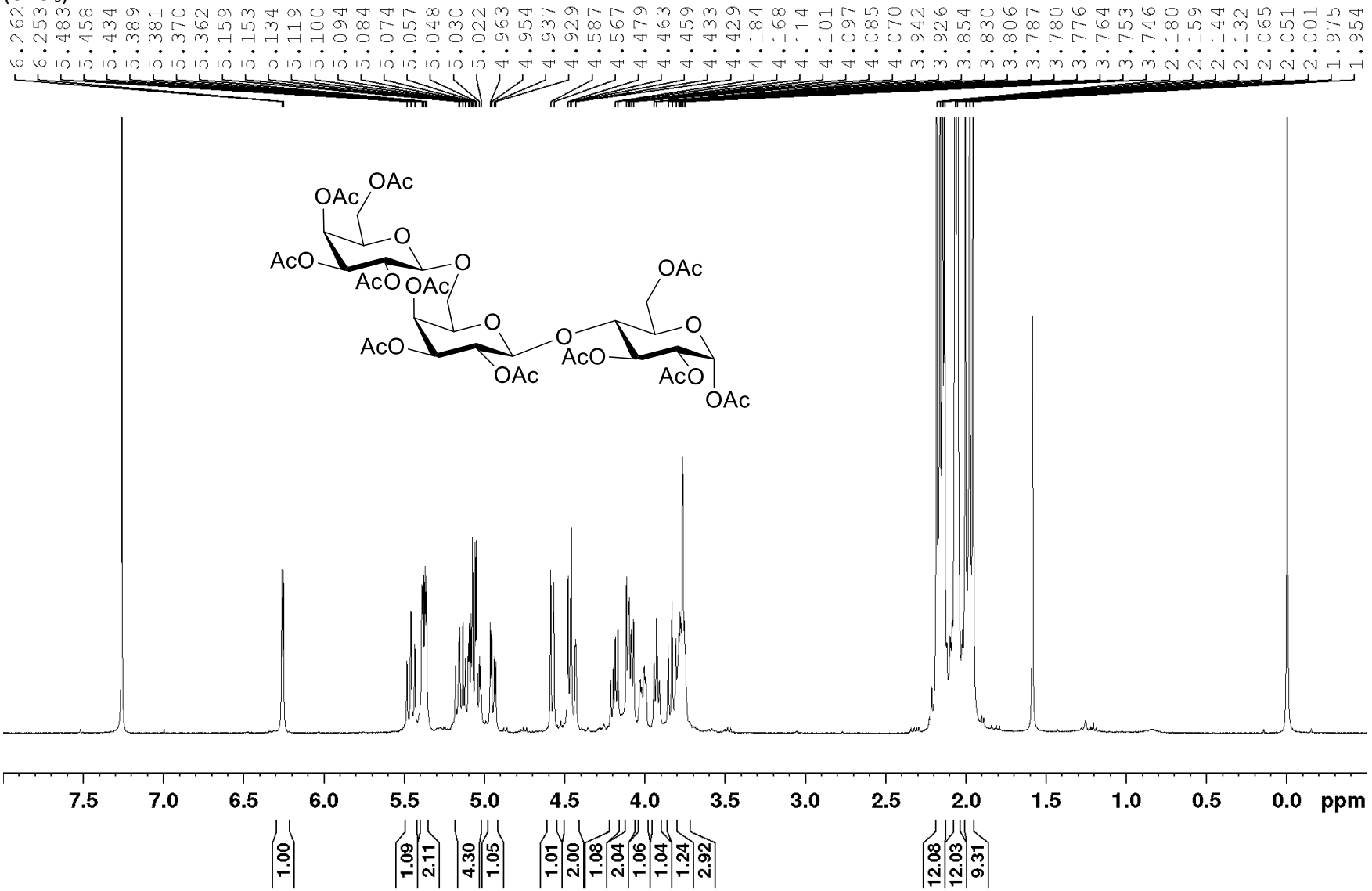
Phenyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-acetyl-1-thio-β-D-galactopyranoside **28** ^{1}H NMR ($CDCl_3$)



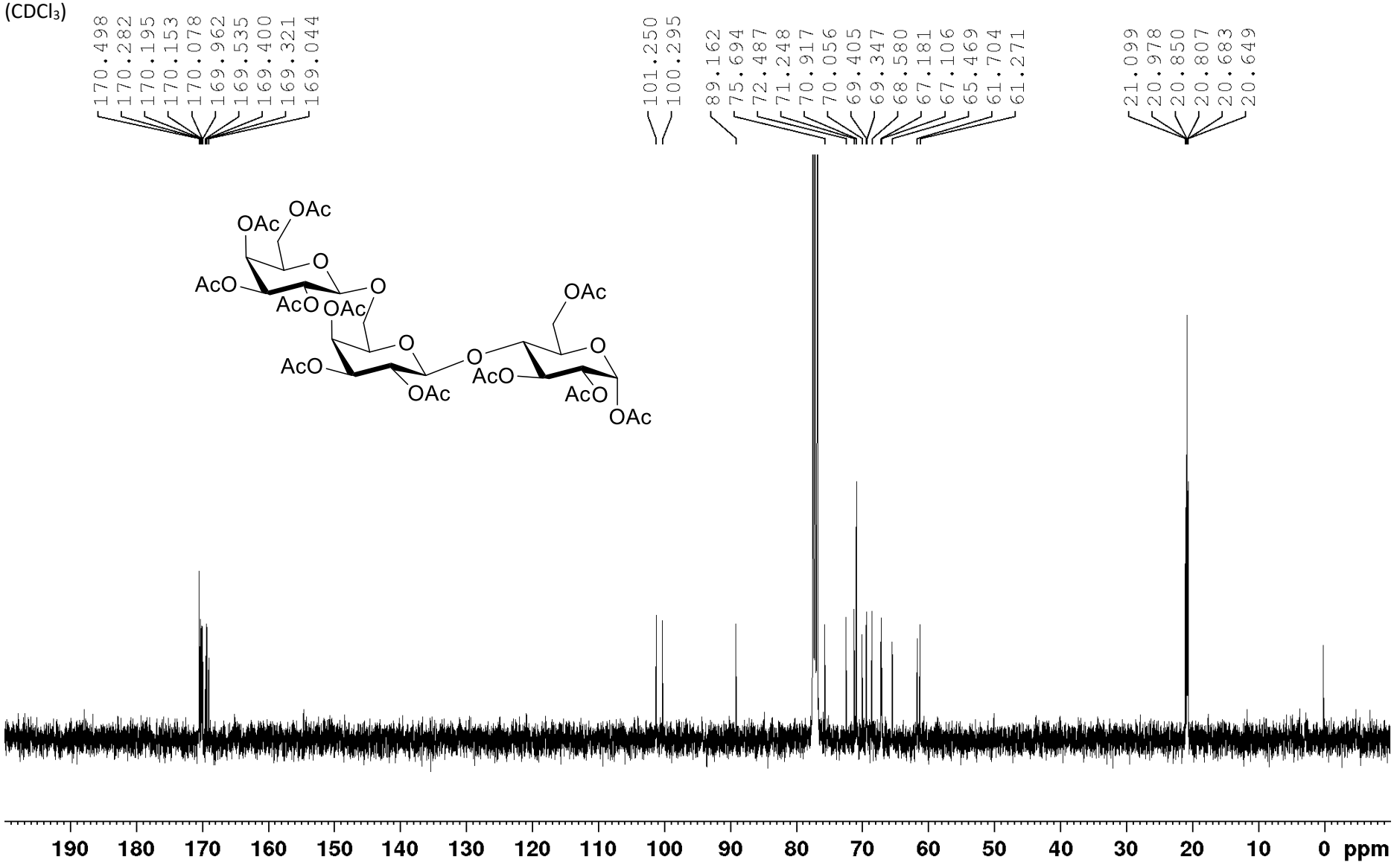
Phenyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-acetyl-1-thio-β-D-galactopyranoside **28** ^{13}C NMR ($CDCl_3$)



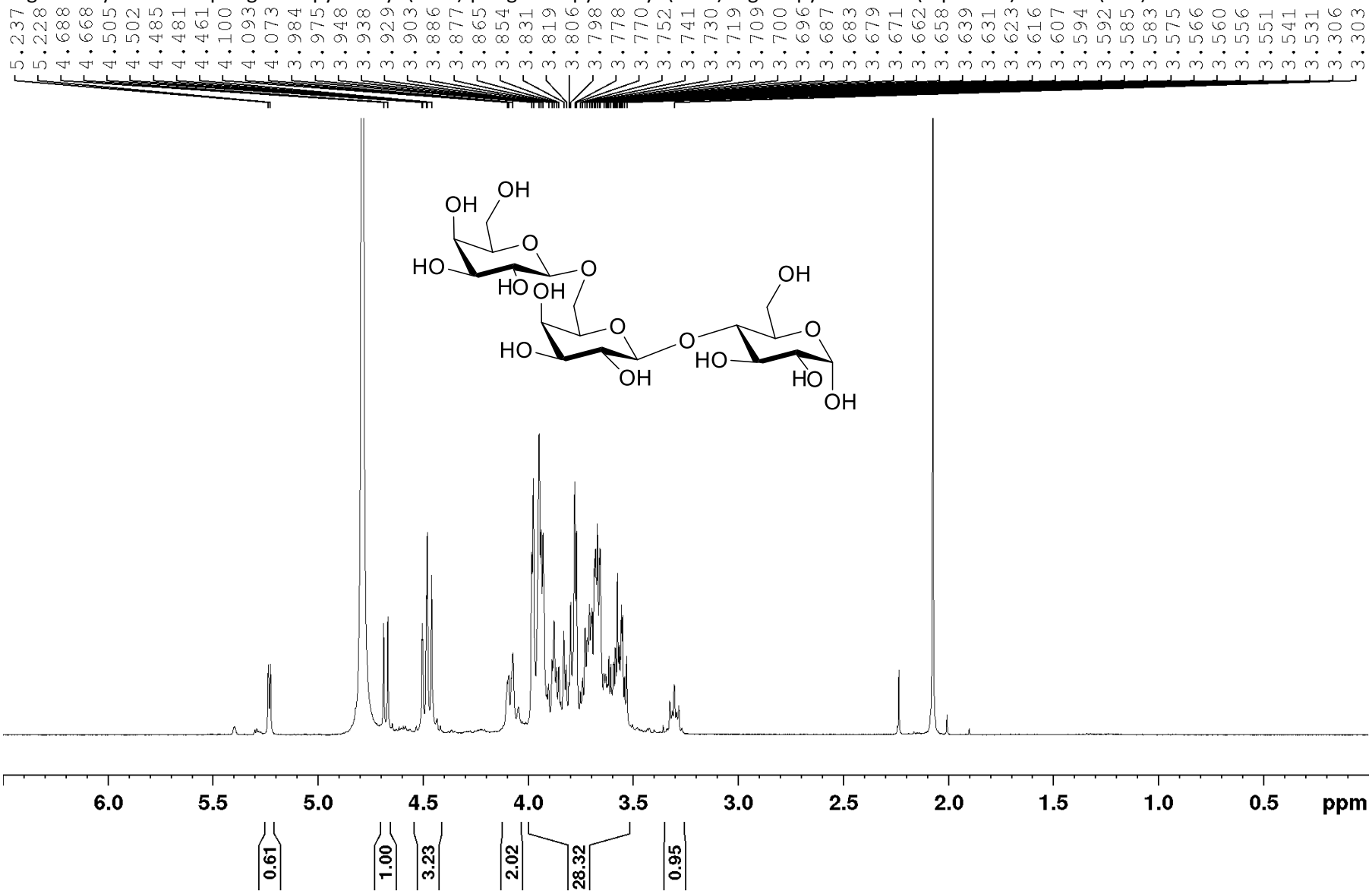
2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-O-acetyl-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-O-acetyl-α-D-glucopyranoside **29** ^{1}H NMR ($CDCl_3$)



2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-O-acetyl-β-D-galactopyranosyl-(1→4)-1,2,3,6-tetra-O-acetyl-α-D-glucopyranoside **29** ^{1}H NMR ($CDCl_3$)



6’-galactosyllactose or β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→4)-D-glucopyranose **30** (α:β 38:62) ^{1}H NMR (D_2O)



6’-galactosyllactose or β-D-galactopyranosyl-(1→6)-β-D-galactopyranosyl-(1→4)-D-glucopyranose **30** (α:β 38:62) ^{13}C NMR (D_2O)