Supporting Information

Diisopropylethylamine-Triggered, Highly Efficient, Self-Catalyzed Regioselective Acylation of Carbohydrates and Diols

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Content

General Information: All commercially available starting materials and solvents were of reagent grade and were used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. High-resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) and Q-TOF detection. Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded with a JNM-ECZ600R/S3 instrument at 298K in $CDCl_3$ using the residual signals from $CHCl_3$ (^{1}H: δ = 7.26 ppm; ^{13}C: δ = 77.2 ppm) as the internal standard. ^{1}H NMR peak assignments were made by first-order analysis of the spectra and were supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

General Method for Testing the H-bonds between the Diols and Catalysts by Variable-Temperature NMR Experiments: The catalyst (0.2 equiv. of TBAOAc, 0.2 equiv. of DIPEA or without catalyst) was added to a solution of 1-phenyl-1,2-ethanediol (10 mg) in dry CD_3CN (0.5 mL), and then a series of variable-temperature ^{1}H NMR tests were performed from 20 °C to 50 °C.

General Method for the Regioselective Acylation of Diols and Polyols: Diol and polyol reactants (50 mg) were allowed to react with anhydride (1.1-2.2 equiv.) in 1 mL of dry acetonitrile or a mixed solvent (MeCN–DMF, 10:1) at 40 °C for 8 h to 12 h in the presence of DIPEA (0.1–0.2 equiv.). After cooling and evaporation of the solvent, the reaction mixture was directly purified by flash column chromatography (hexanes–EtOAc 3:1 to 1:1) and afforded the pure selectively protected derivatives.

Spectroscopic data of all known products were in accordance with those reported in the literature.

Testing the H-bonds between the Diols and Catalysts by variable-temperature NMR experiments (Figure **S1** to Figure **S3**):

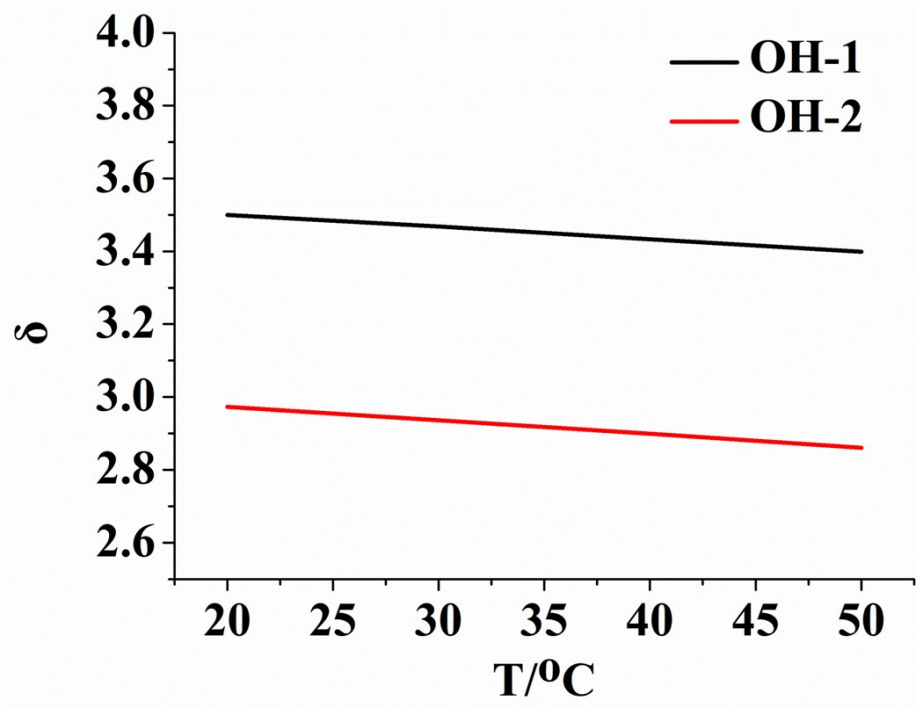


Figure **S1**. The values of OH chemical shifting transformation constant with temperature k were measured for 1-phenyl-1,2-ethanediol in CD_3CN. k_1=3.4*10^{-3} K^{-1}, R^2=0.9997; k_2=3.7*10^{-3} K^{-1}, R^2=1.

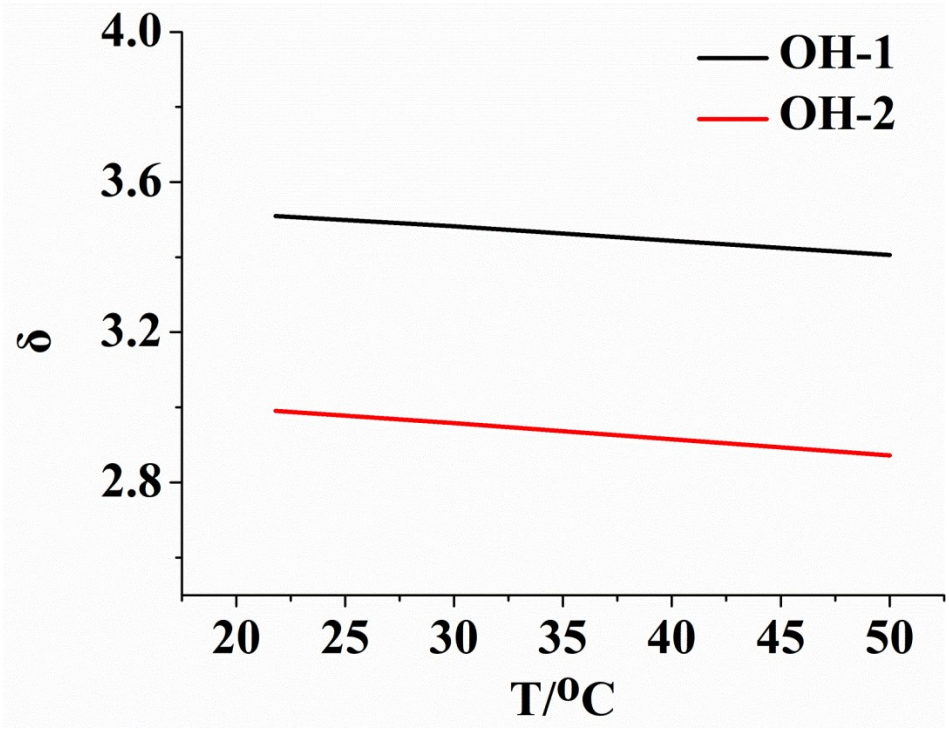


Figure **S2**. The values of OH chemical shifting transformation constant with temperature k were measured for 1-phenyl-1,2-ethanediol and 0.2 equiv. of DIPEA in CD_3CN. k_1=3.7*10^{-3} K^{-1}, R^2=0.999; k_2=4.2*10^{-3} K^{-1}, R^2=0.9998.

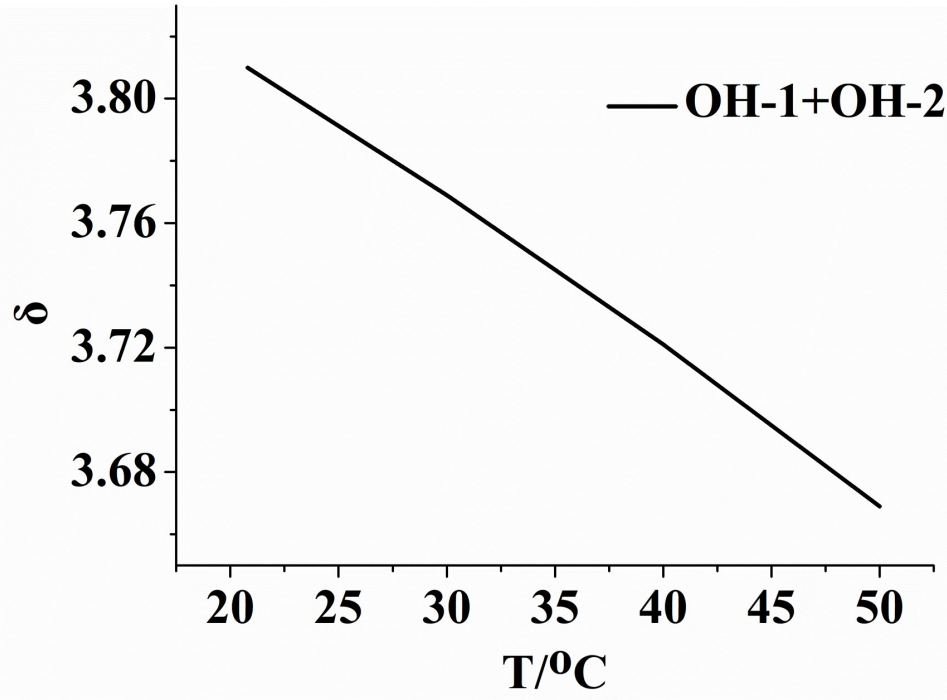


Figure **S3**. The values of OH chemical shifting transformation constant with temperature k were measured for 1-phenyl-1,2-ethanediol and 0.2 equiv. of TBAOAc in CD_3CN. k=4.8*10^{-3} K^{-1}, R^2=0.9989.

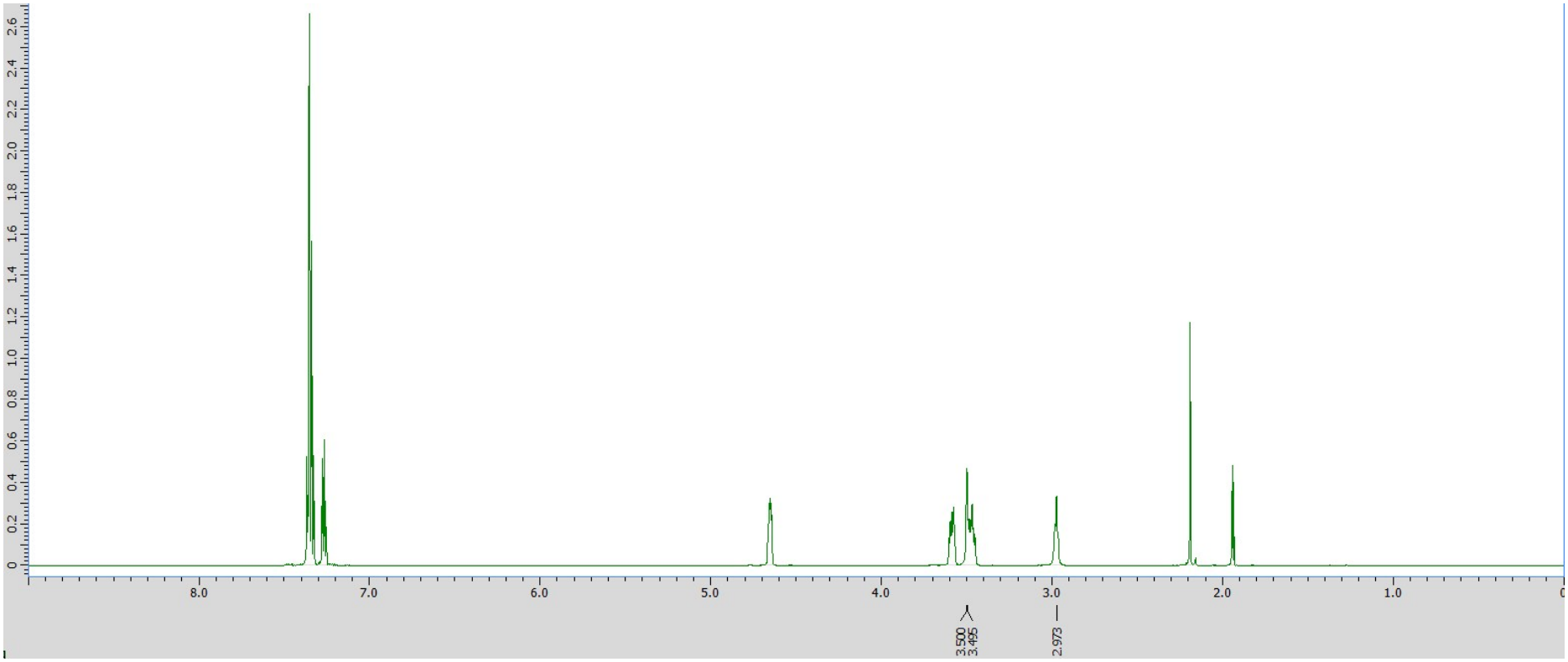


Figure S4. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol in CD_3CN at 20 ℃.

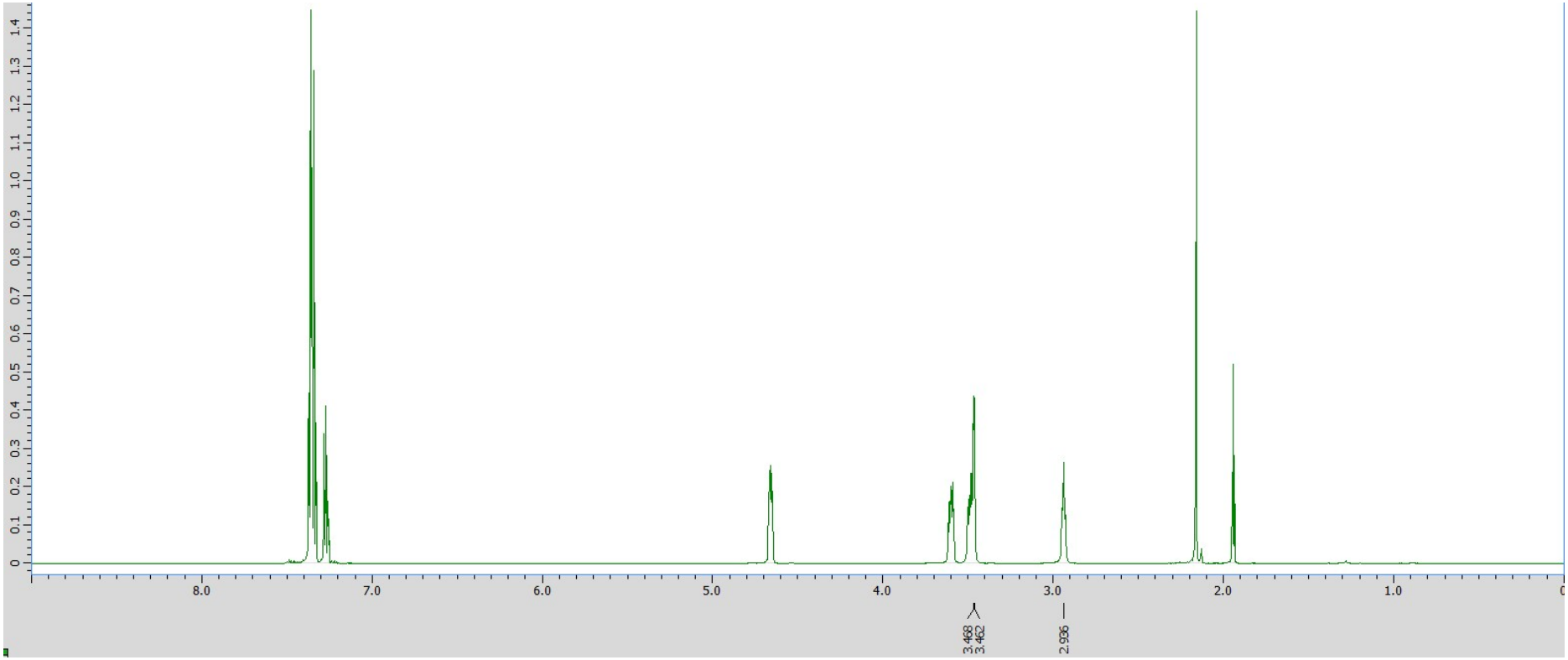


Figure S5. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol in CD_3CN at 30 ℃.

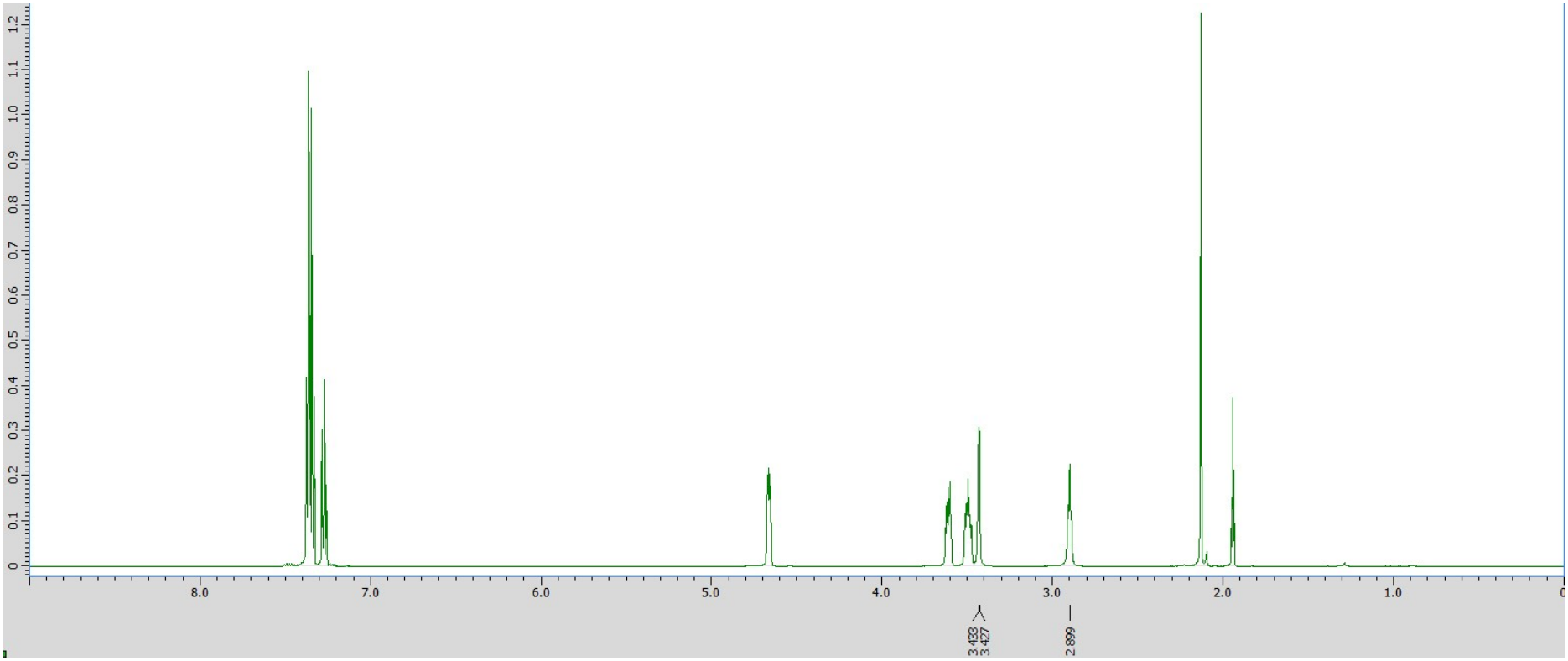


Figure S6. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol in CD_3CN at 40 ℃.

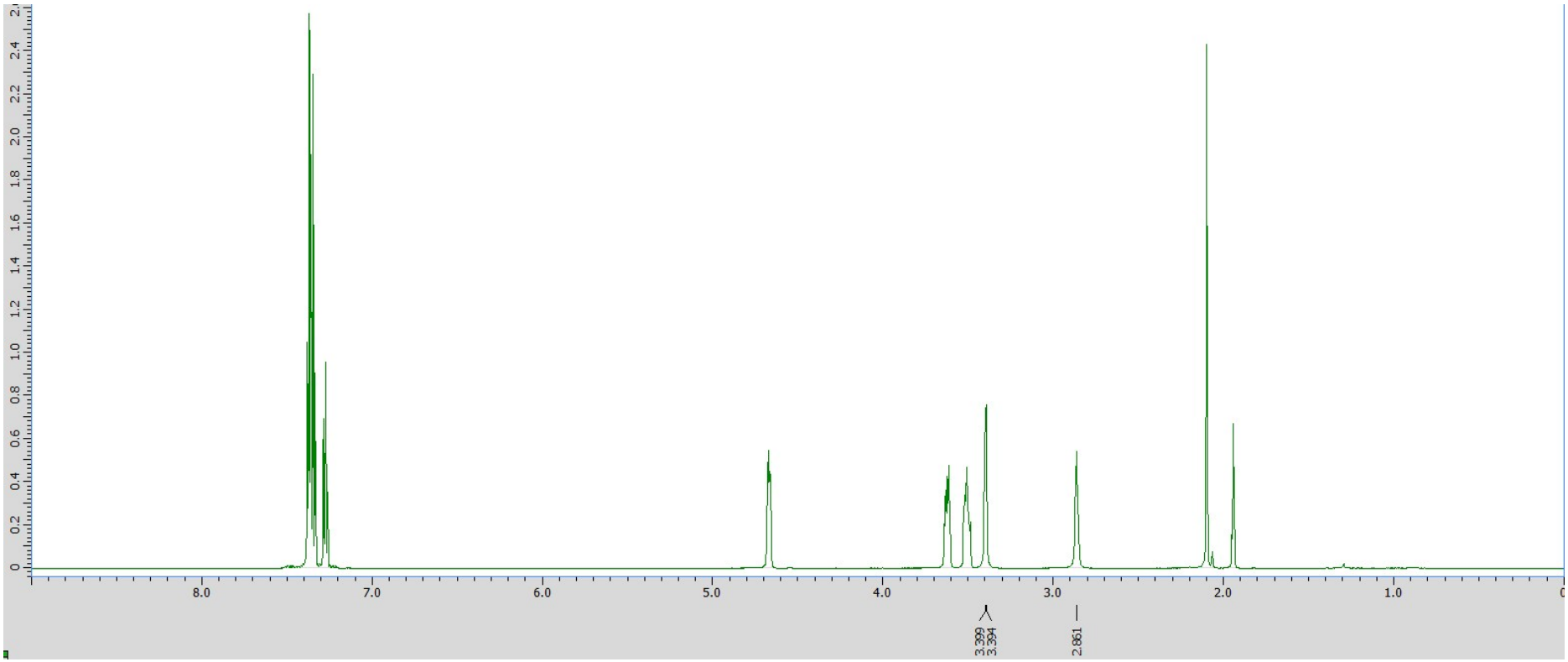


Figure S7. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol in CD_3CN at 50 ℃.

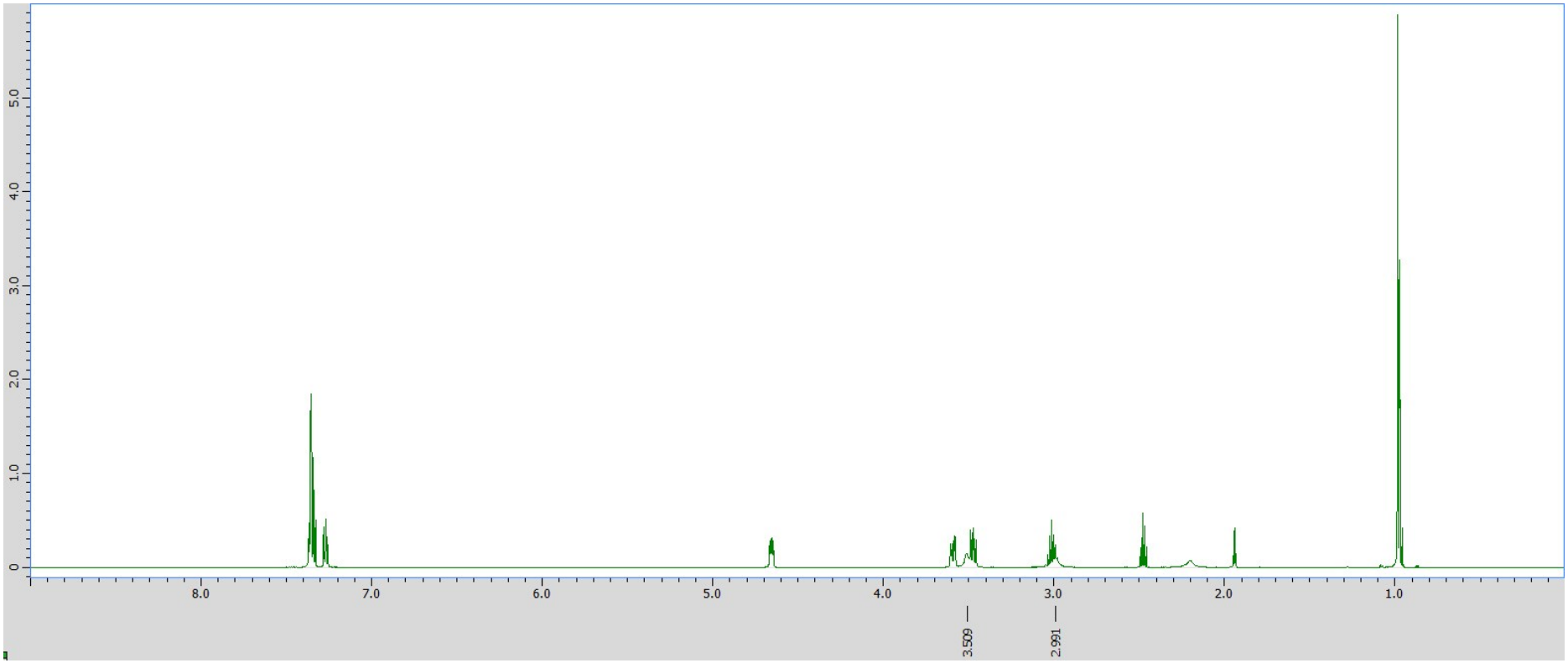


Figure S8. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of DIPEA in CD_3CN at 21.8 ℃.

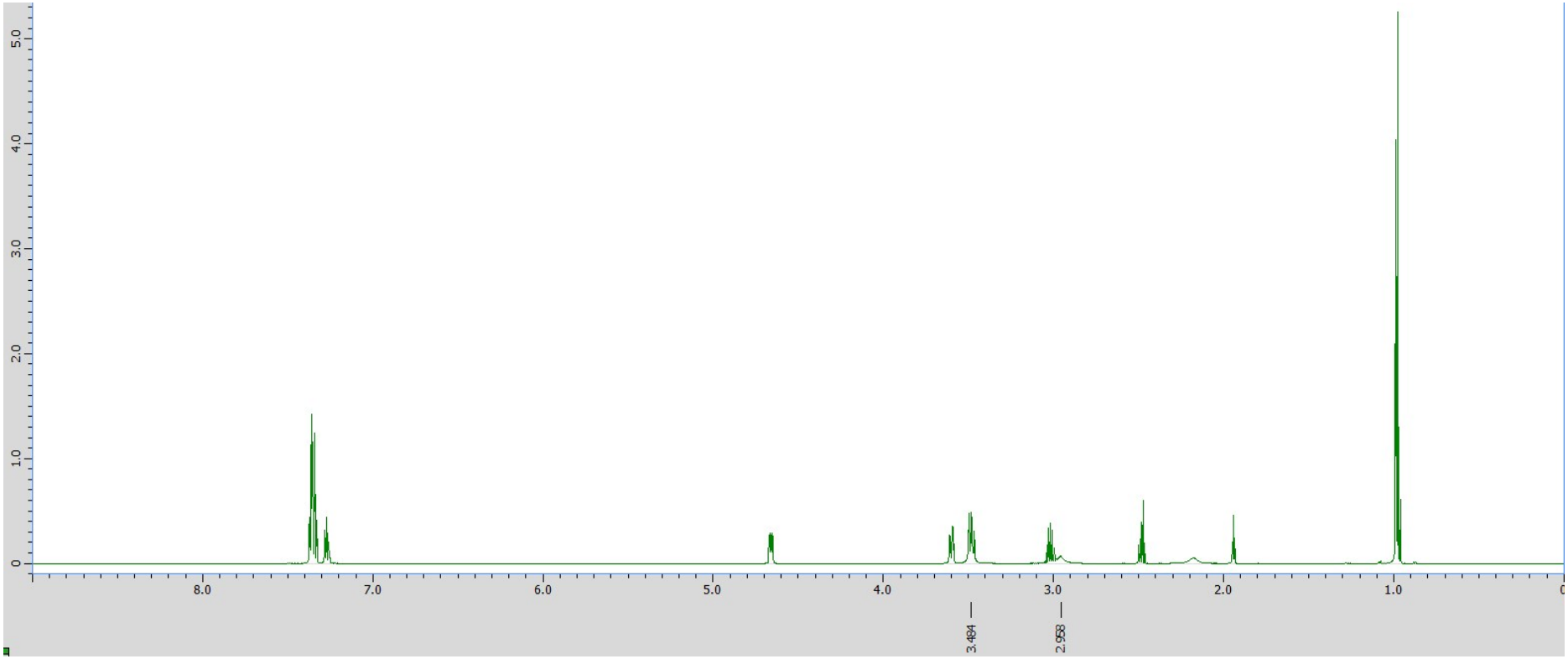


Figure S9. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of DIPEA in CD_3CN at 30 ℃.

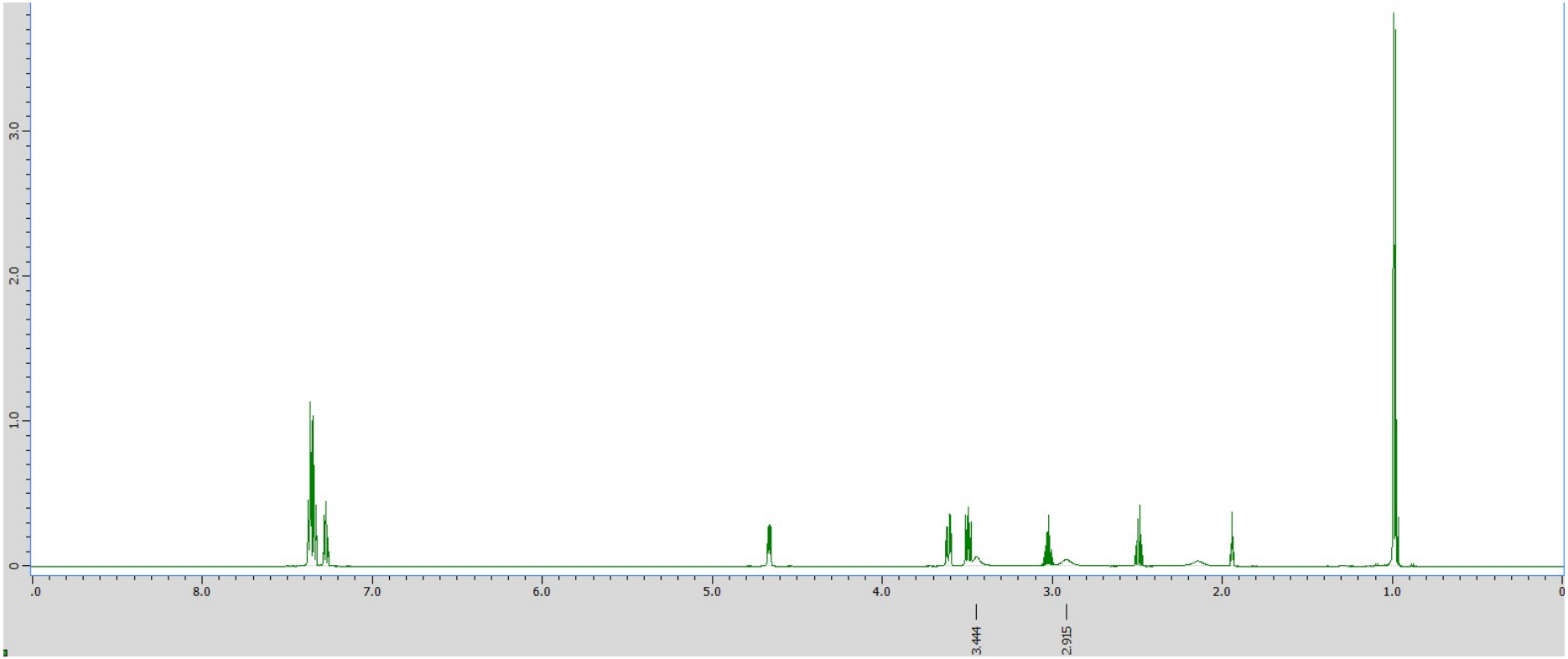


Figure S10. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of DIPEA in CD_3CN at 40 ℃.

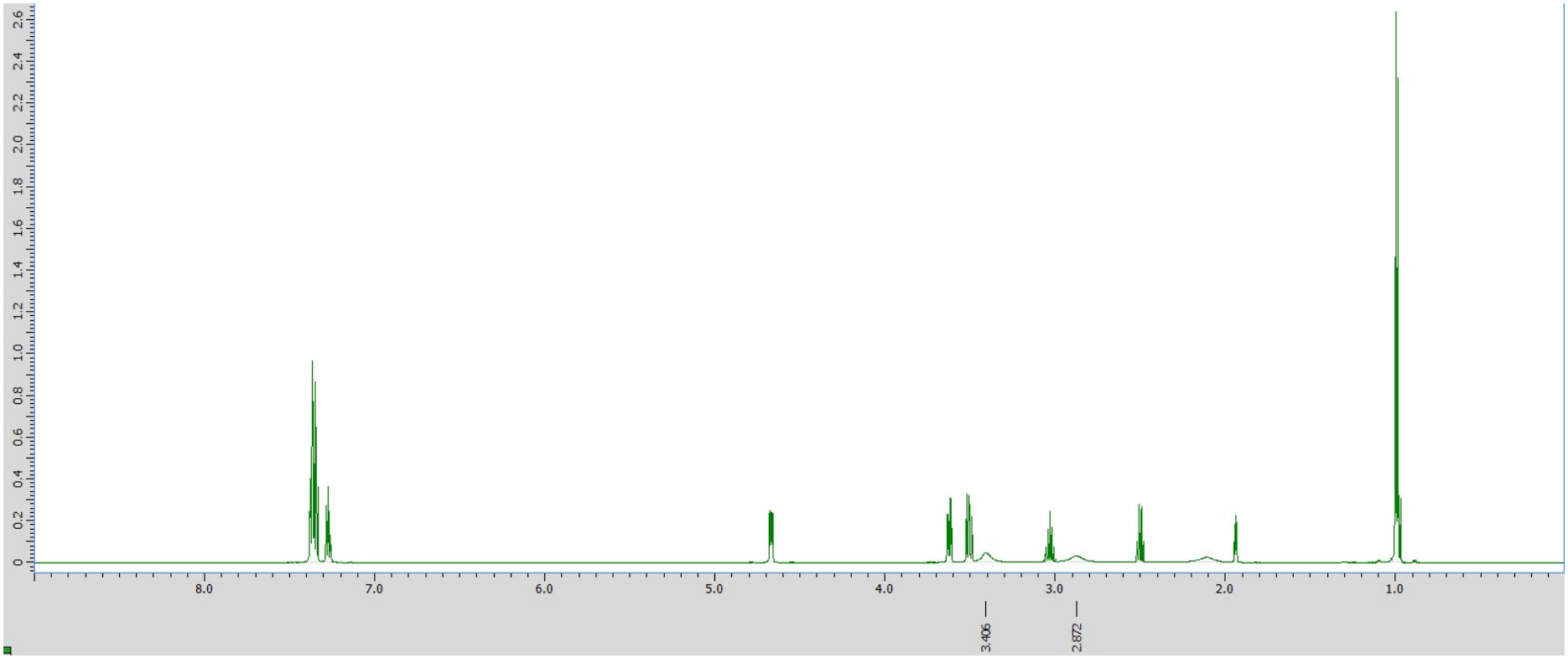


Figure S11. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of DIPEA in CD_3CN at 50 ℃.

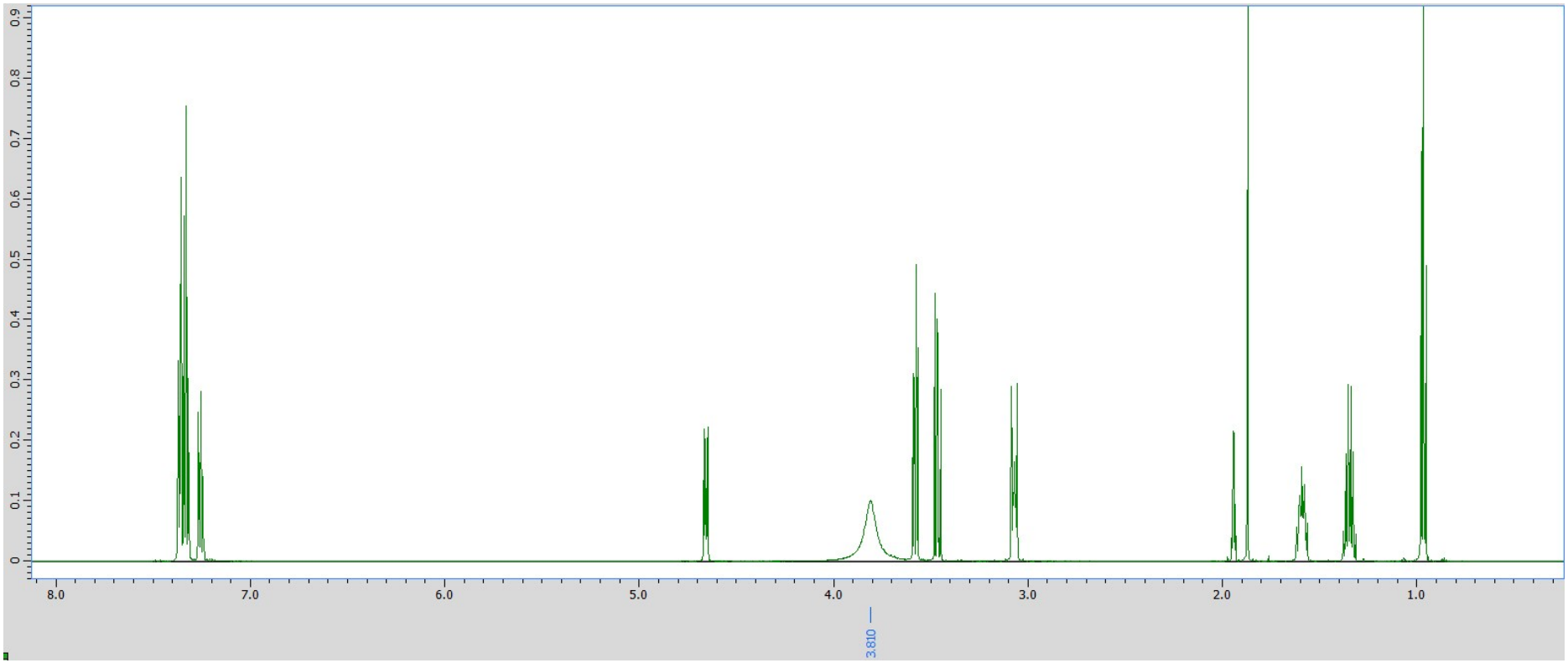


Figure S12. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of TBAOAc in CD_3CN at 20.8 ℃.

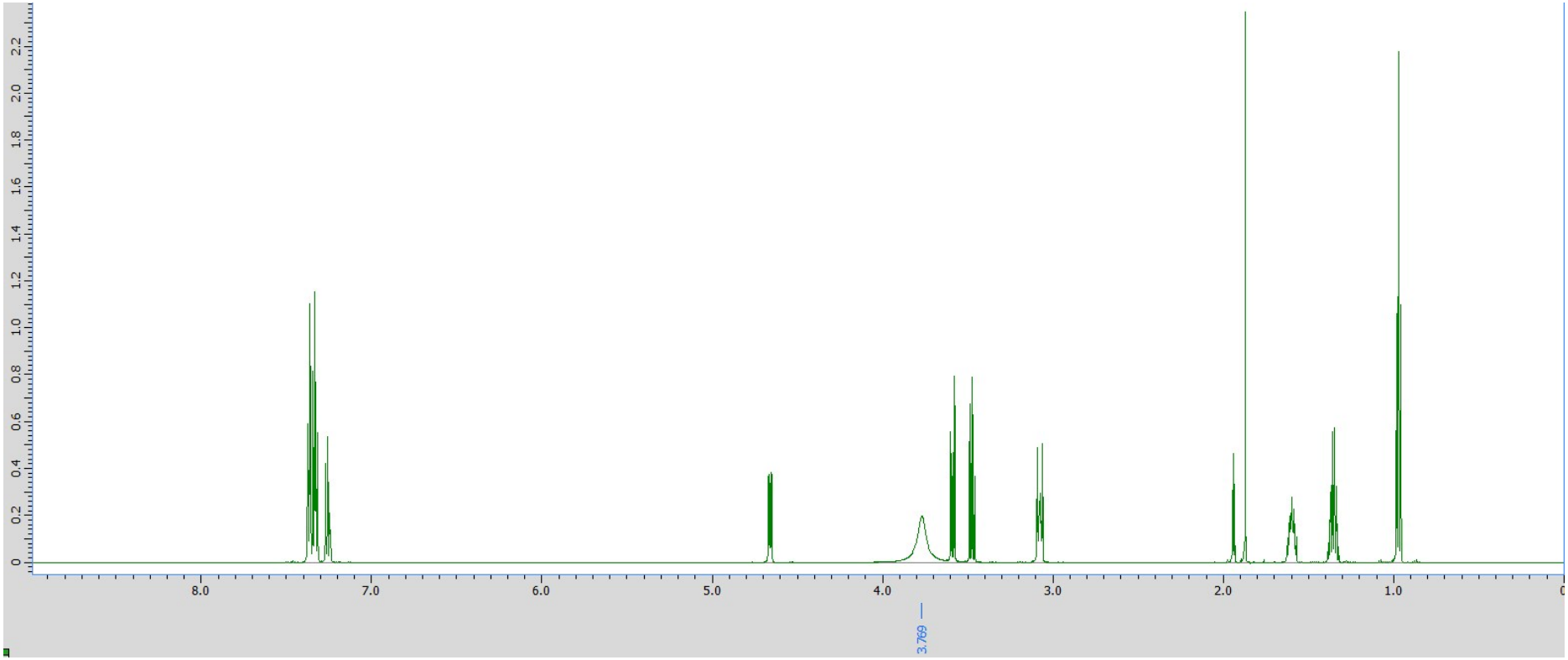


Figure S13. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of TBAOAc in CD_3CN at 30 ℃.

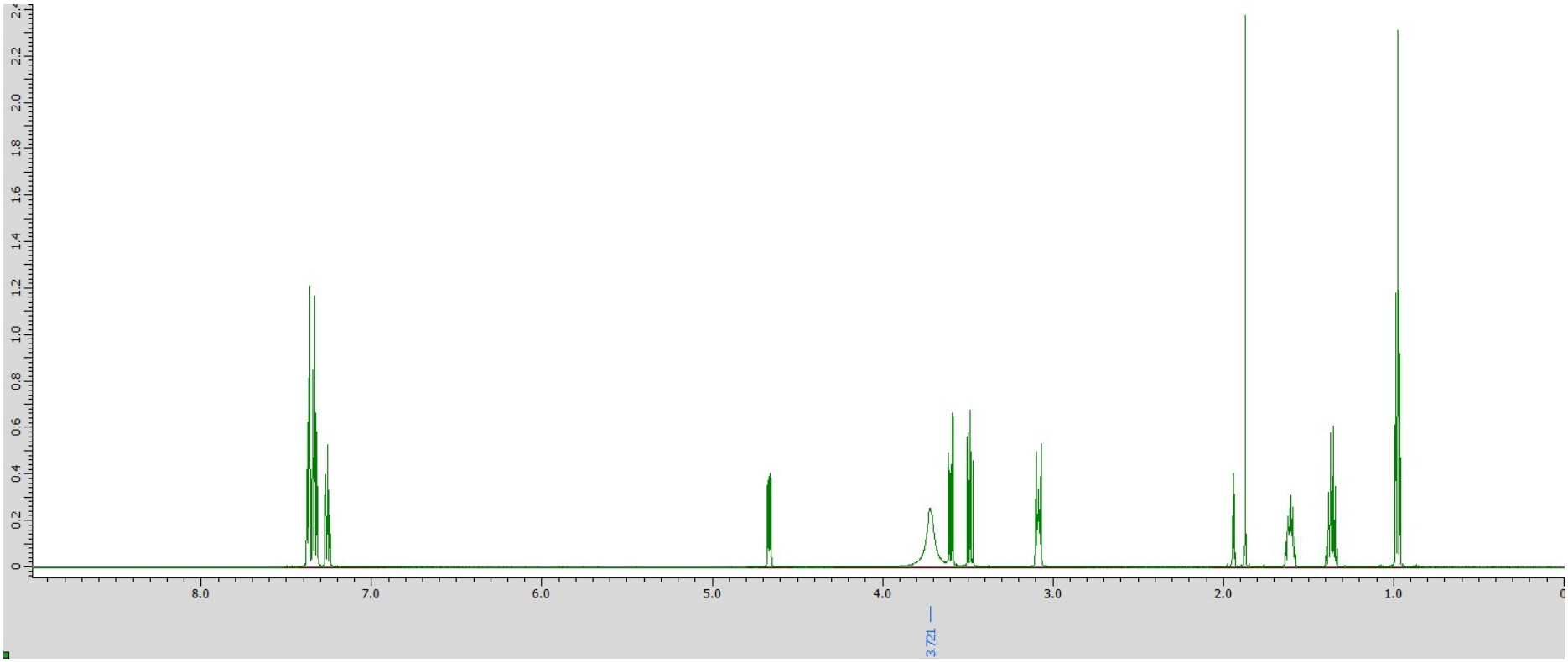


Figure S14. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of TBAOAc in CD_3CN at 40 ℃.

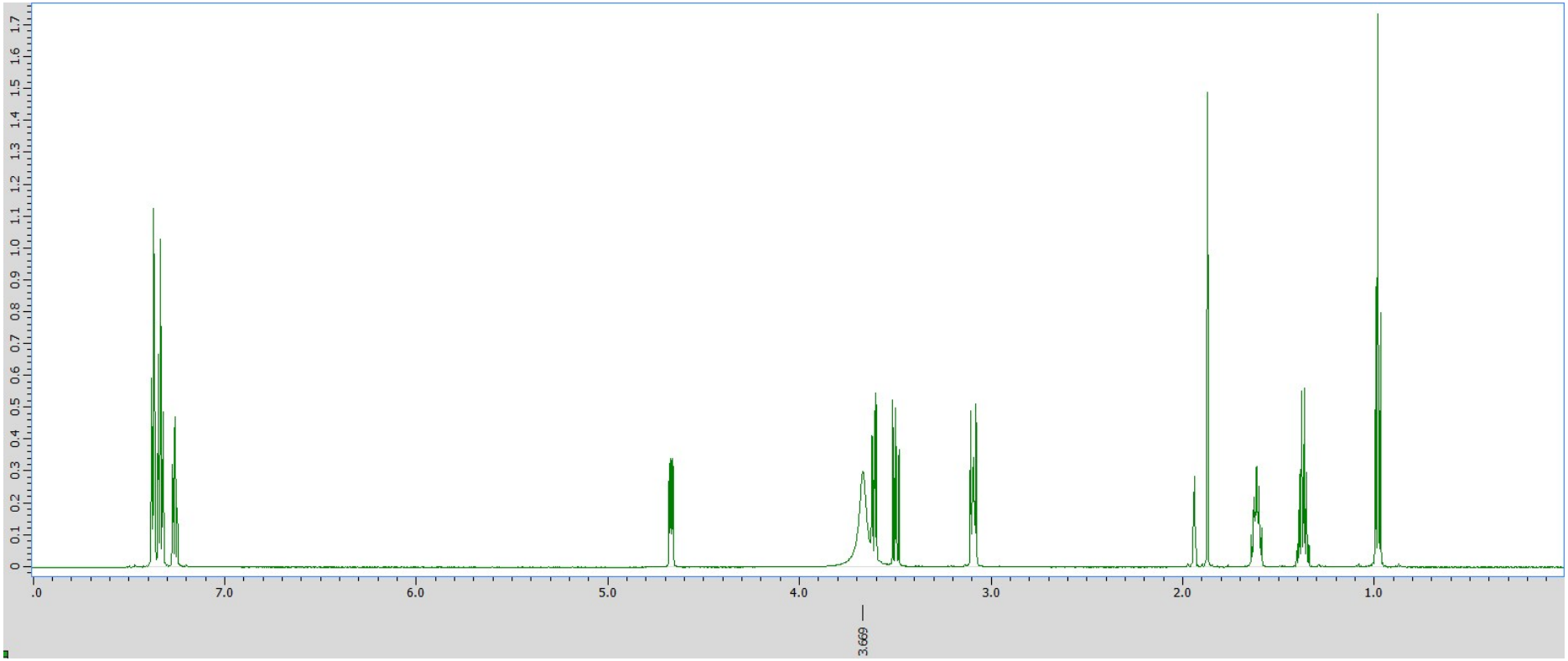


Figure S15. Recorded ^{1}H NMR of 1-phenyl-1,2-ethanediol and 0.2 equiv. of TBAOAc in CD_3CN at 50 ℃.

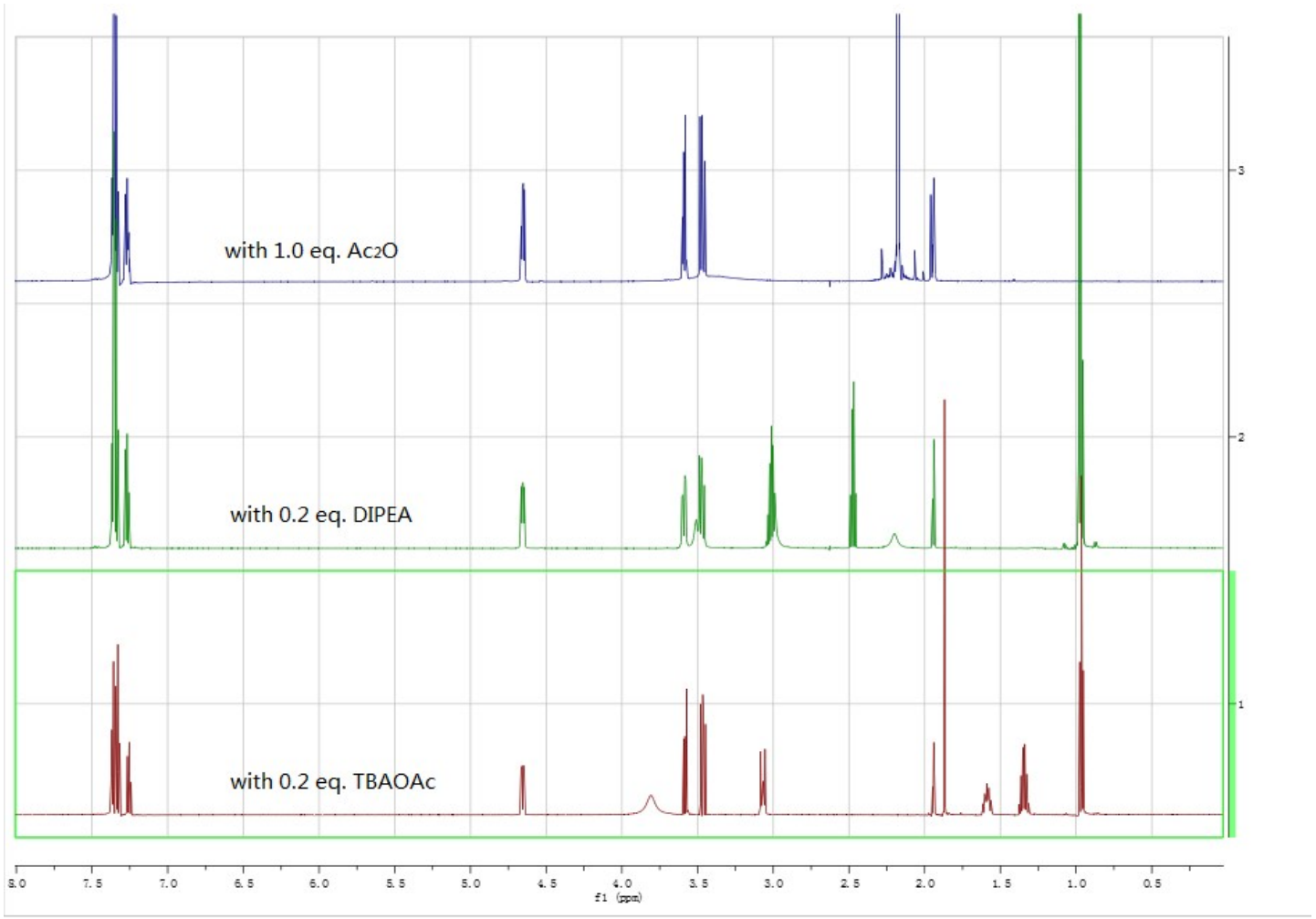


Figure S16. ^{1}H NMR comparison of 1-phenyl-1,2-ethanediol with 0.2 equiv. of TBAOAc/0.2 equiv. of DIPEA/1.0 equiv. of Ac_2O in CD_3CN at 20 ^{o}C.

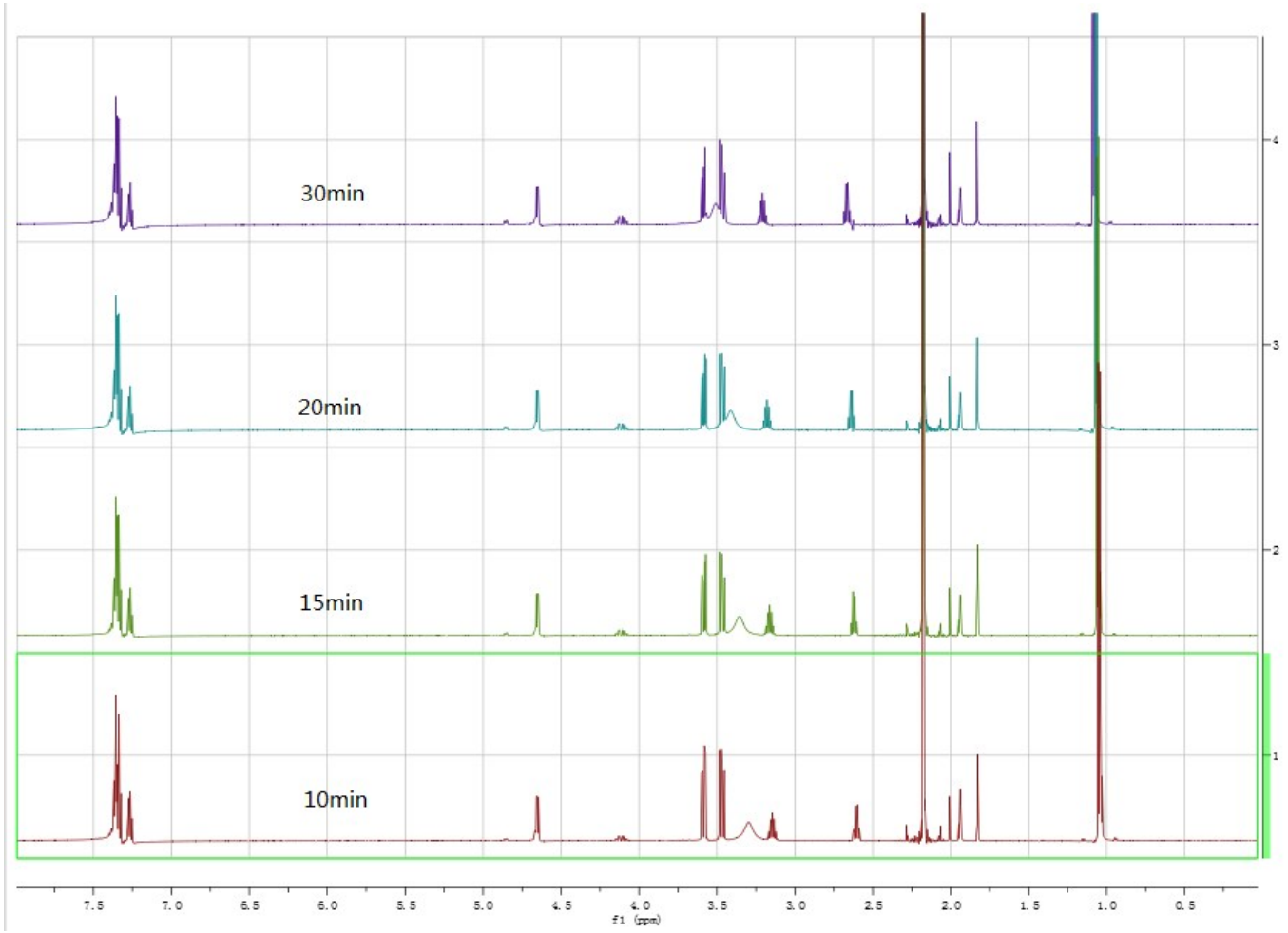


Figure S17. ^{1}H NMR tracking the reaction of 1-phenyl-1,2-ethanediol with 0.2 equiv. of DIPEA and 1.0 equiv. Ac_2O in CD_3CN at 20 ^{o}C.

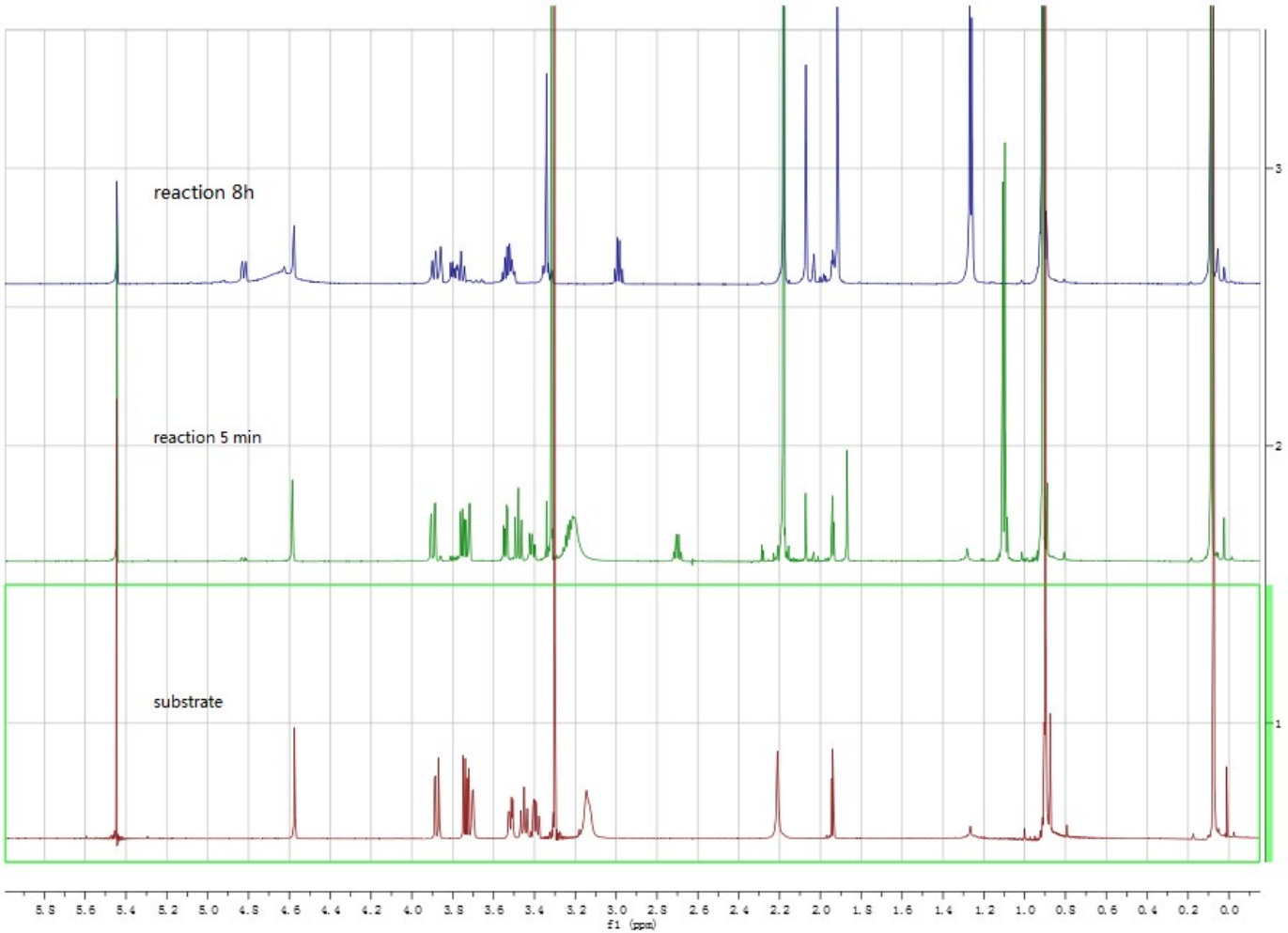
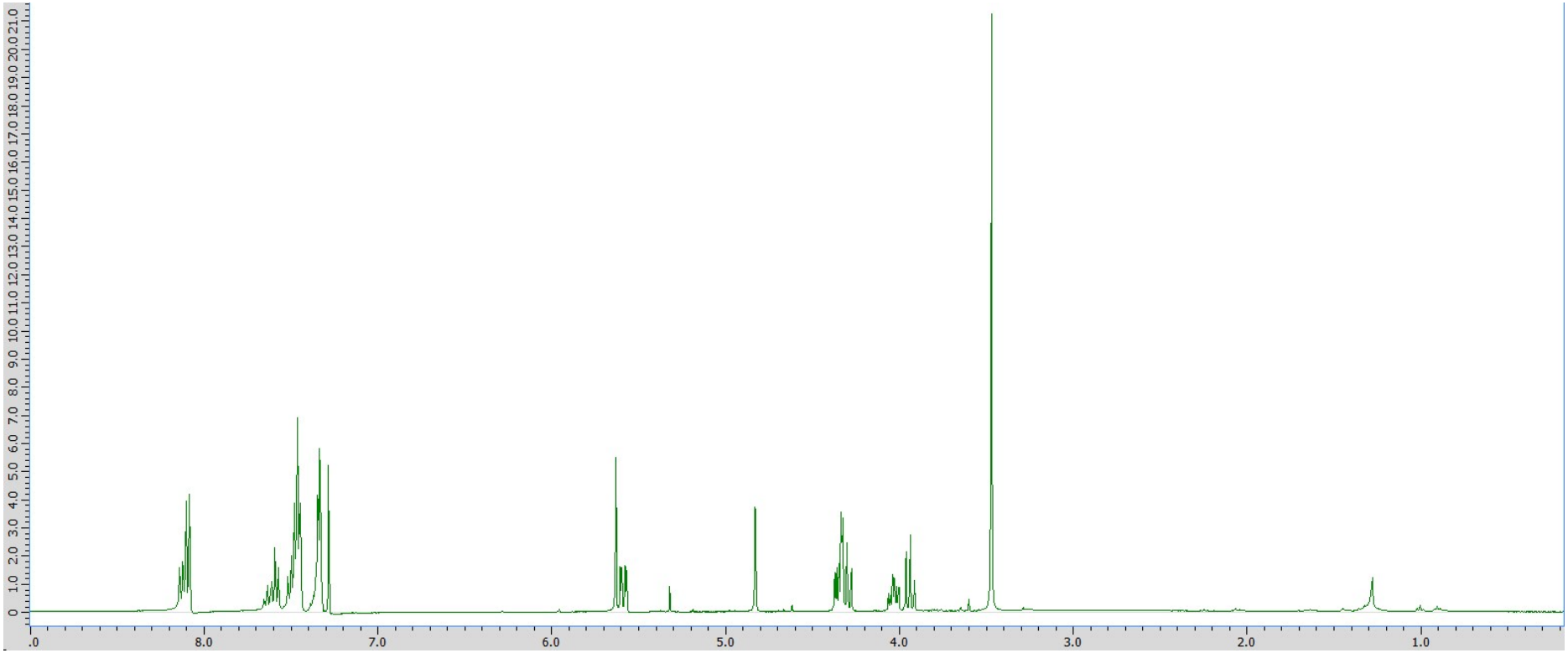


Figure S18. ^{1}H NMR tracking the reaction of Methyl 6-*O*-(tert-butyldimethylsilyloxy)-α-D-mannopyranoside with 0.2 equiv. of DIPEA and 1.1 eqiuv. Ac_2O in CD_3CN at 40 °C.

NMR Spectra of Products:

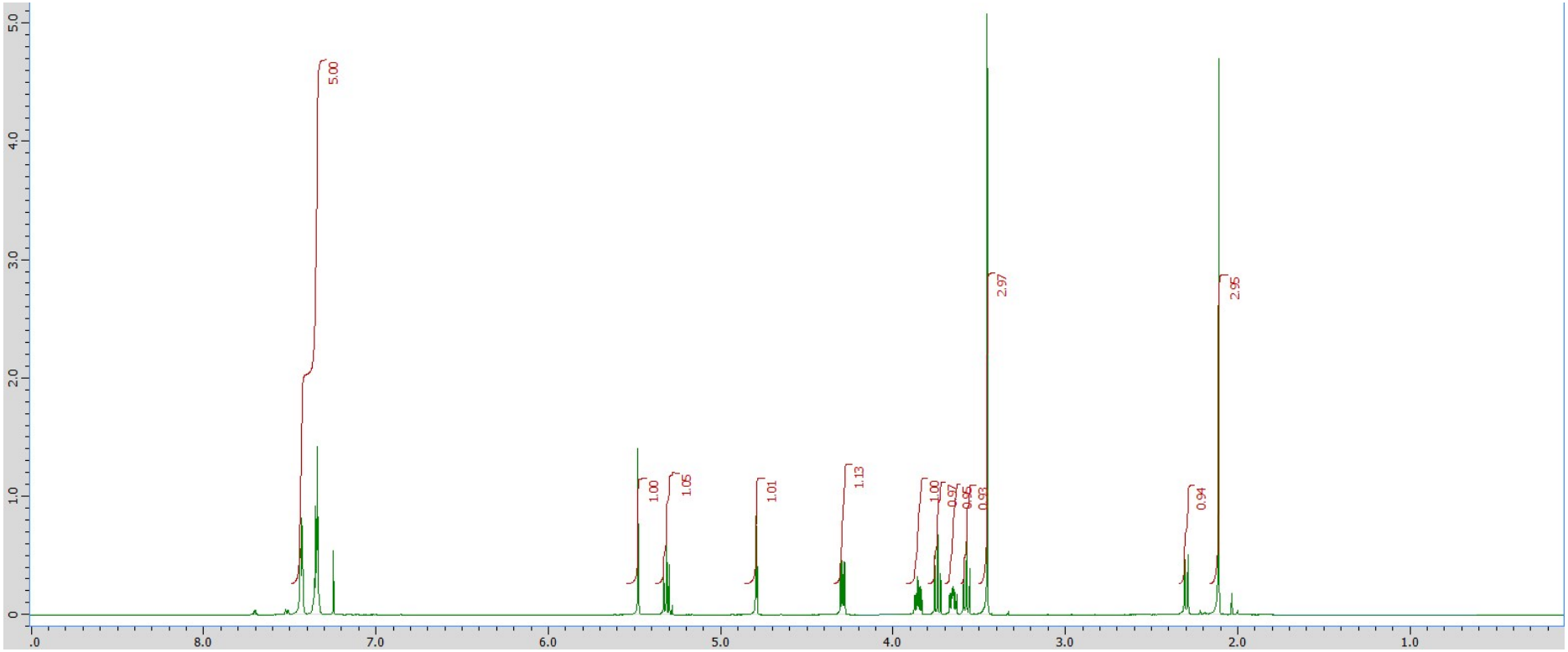
Methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-*α*-D-mannopyranoside (5a)[3]:

^{1}H-NMR of compound **5a** ($CDCl_3$)



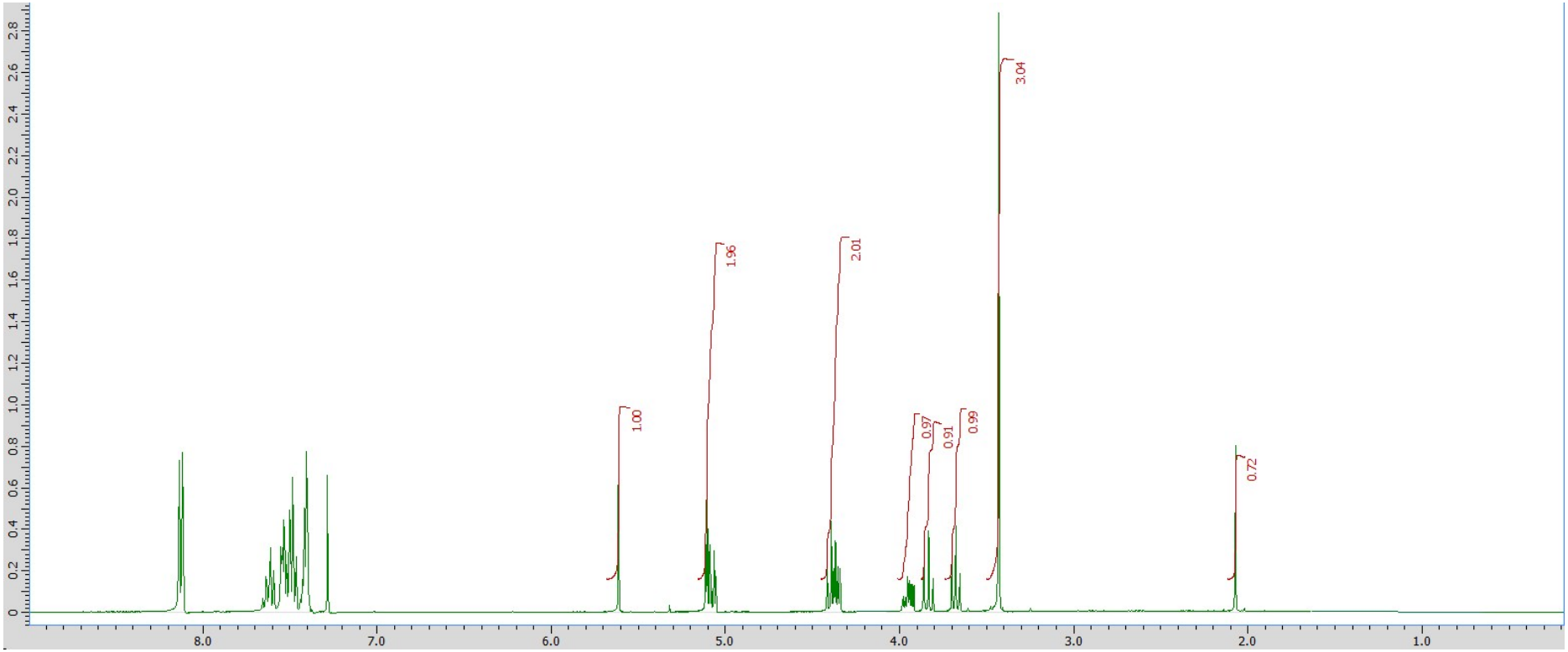
Methyl 2-*O*-acetyl-4, 6-*O*-benzylidene-*α*-D-glucopyranoside (7a)[1]:

^{1}H-NMR of compound **7a** ($CDCl_3$)



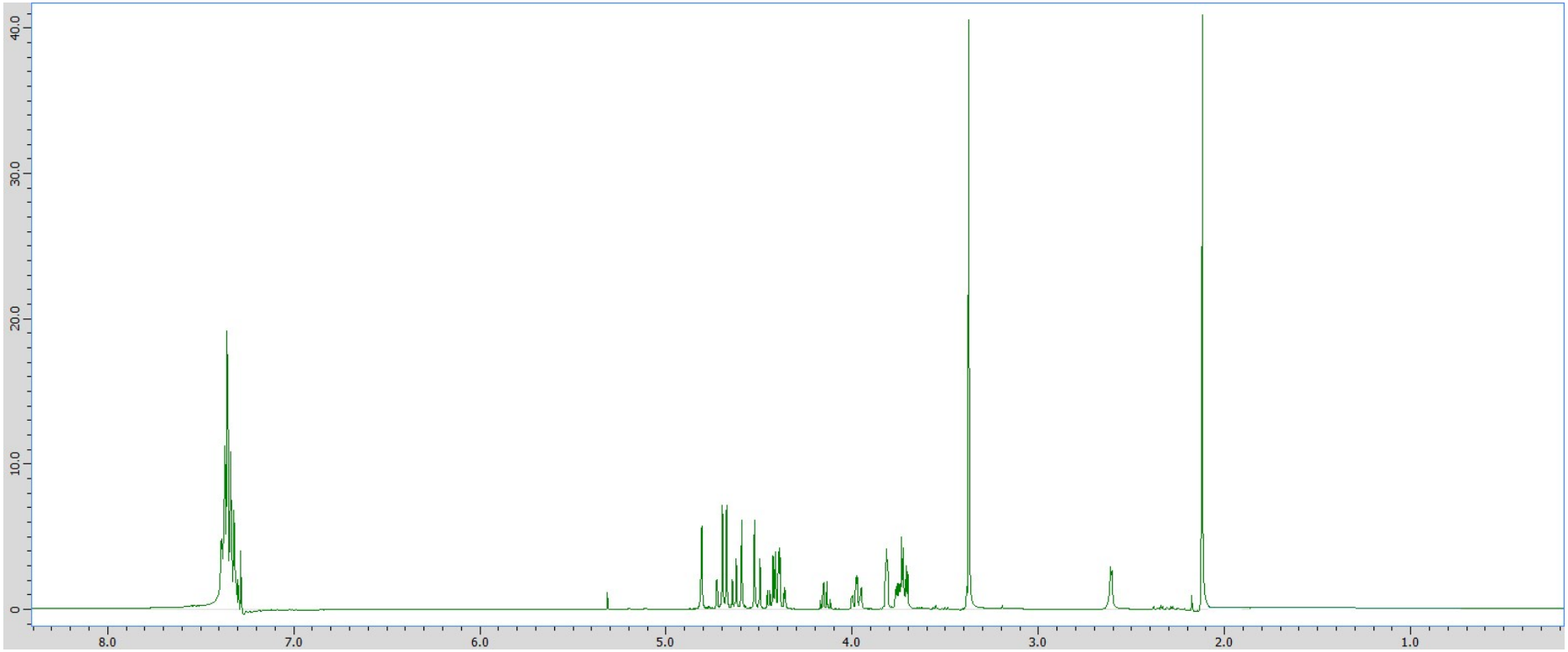
Methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-*α*-D-glucopyranoside (8a)[3]:

^{1}H-NMR of compound **8a** ($CDCl_3$)



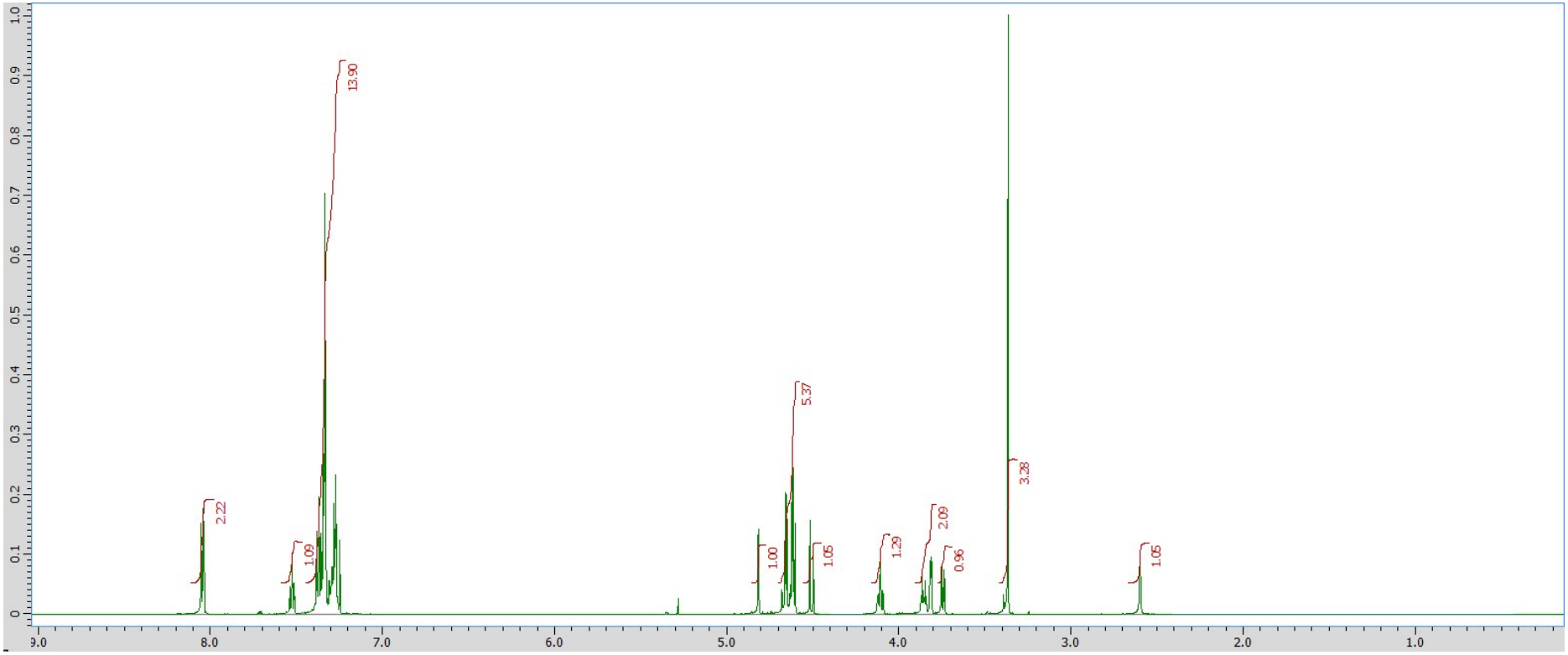
Methyl 2, 3-di-*O*-benzyl-6-*O*-acetyl-*α*-D-mannopyranoside (10)[1]:

^{1}H-NMR of compound **10** ($CDCl_3$)



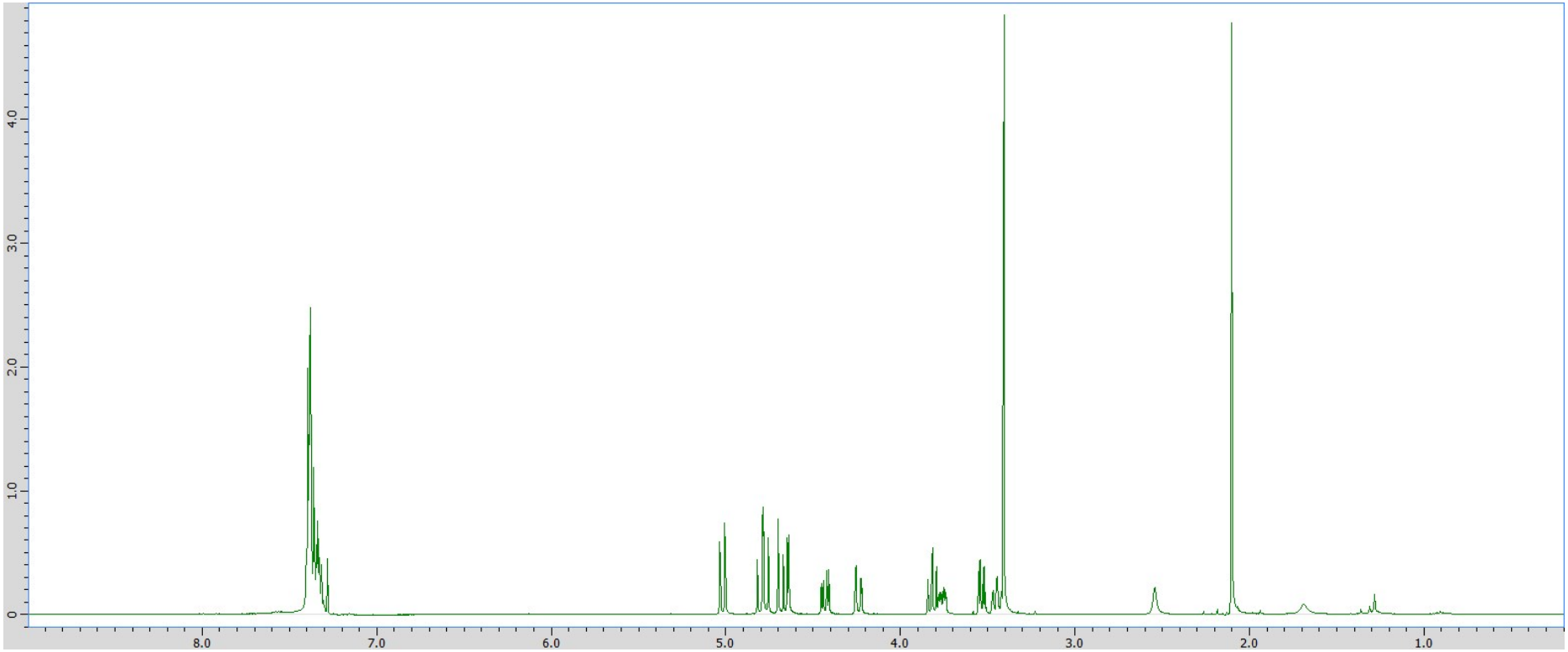
Methyl 2, 3-di-*O*-benzyl-6-*O*-benzoyl-*α*-D-mannopyranoside (11)[3]:

^{1}H-NMR of compound **11** ($CDCl_3$)



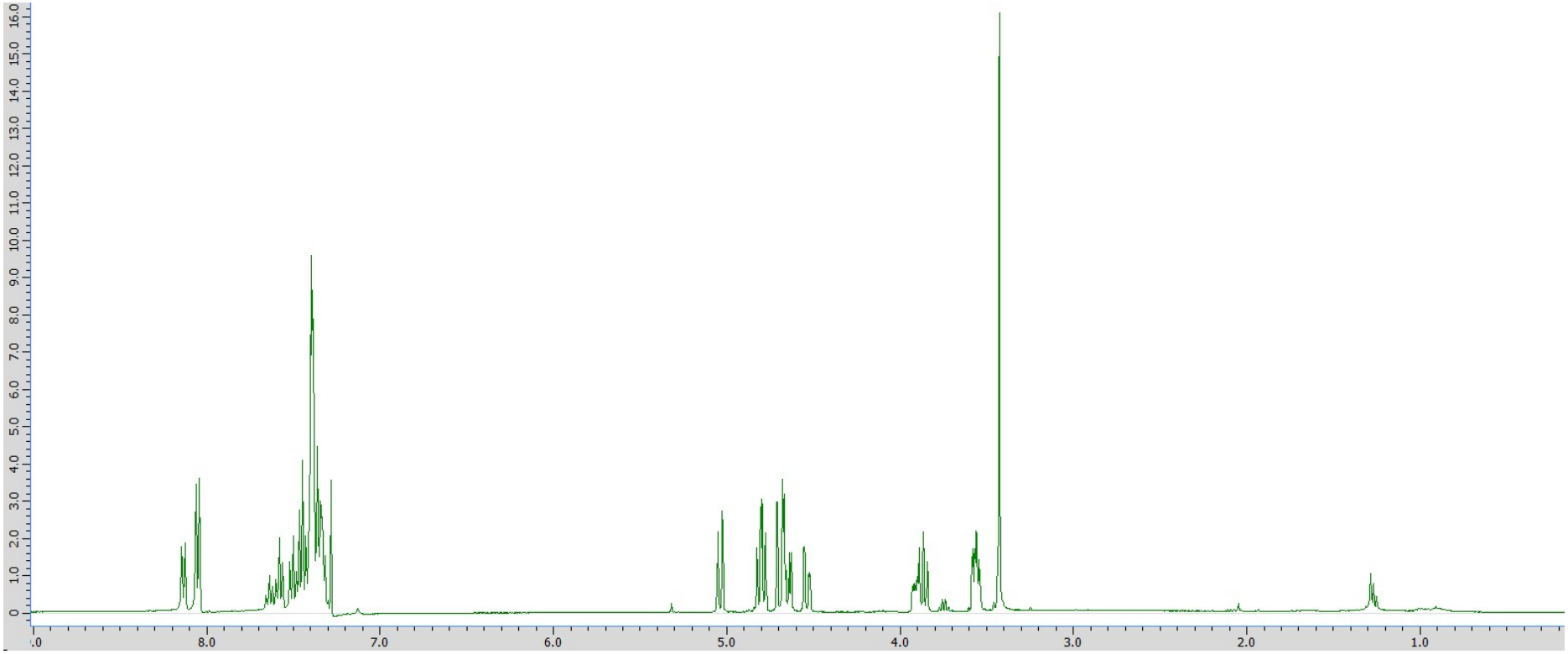
Methyl 2, 3-di-*O*-benzyl-6-*O*-acetyl-*α*-D-glucopyranoside (13)[1]:

^{1}H-NMR of compound **13** ($CDCl_3$)



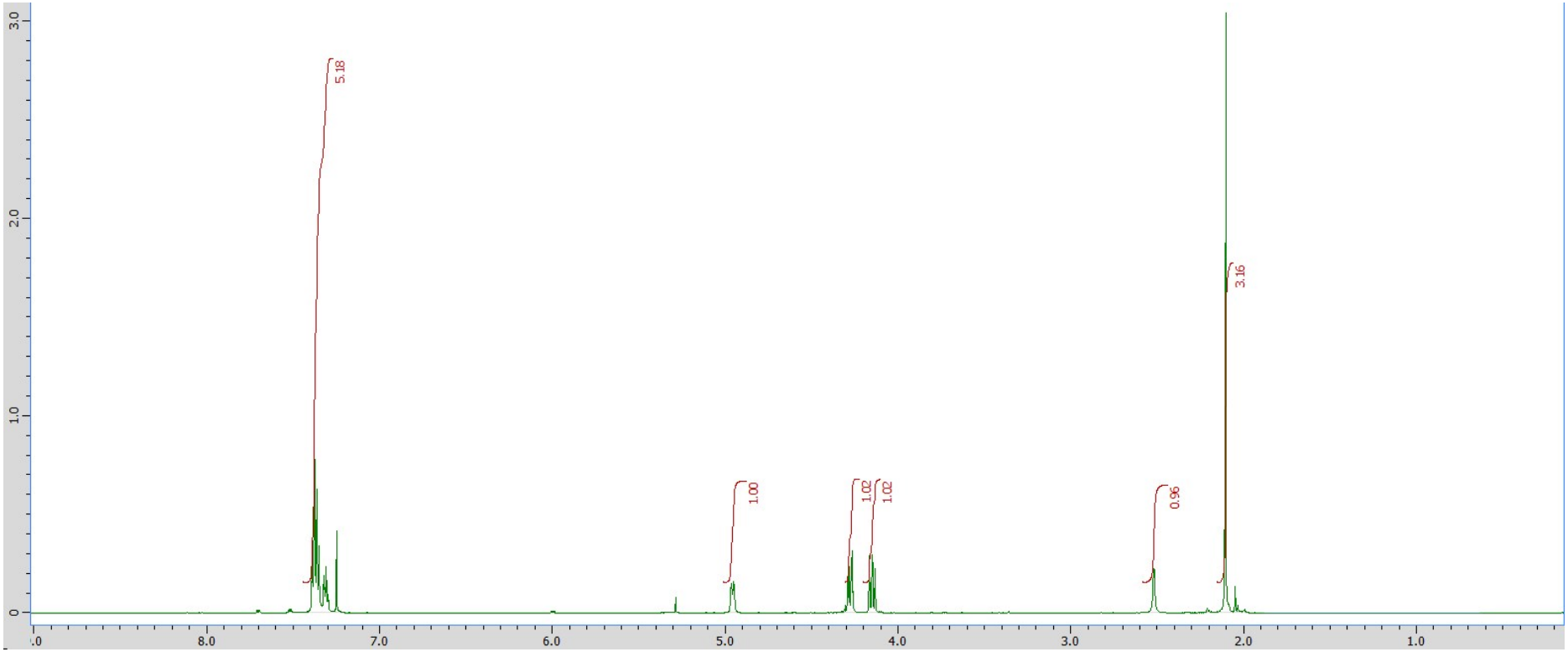
Methyl 2, 3-di-*O*-benzyl-6-*O*-benzoyl-*α*-D-glucopyranoside (14)[3]:

^{1}H-NMR of compound **14** ($CDCl_3$)



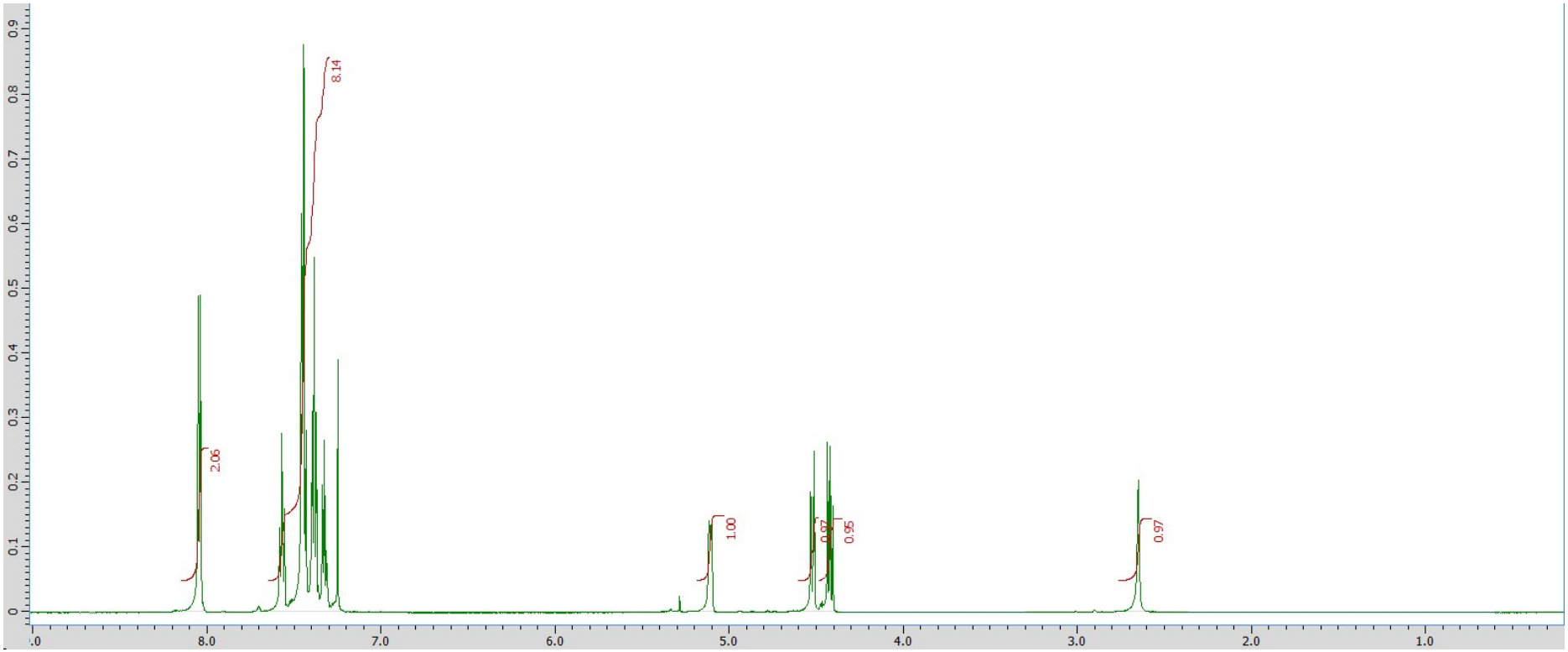
2-*O*-acetyl-1-phenyl-1,2-ethanediol (16)[1]:

^{1}H-NMR of compound **16** ($CDCl_3$)



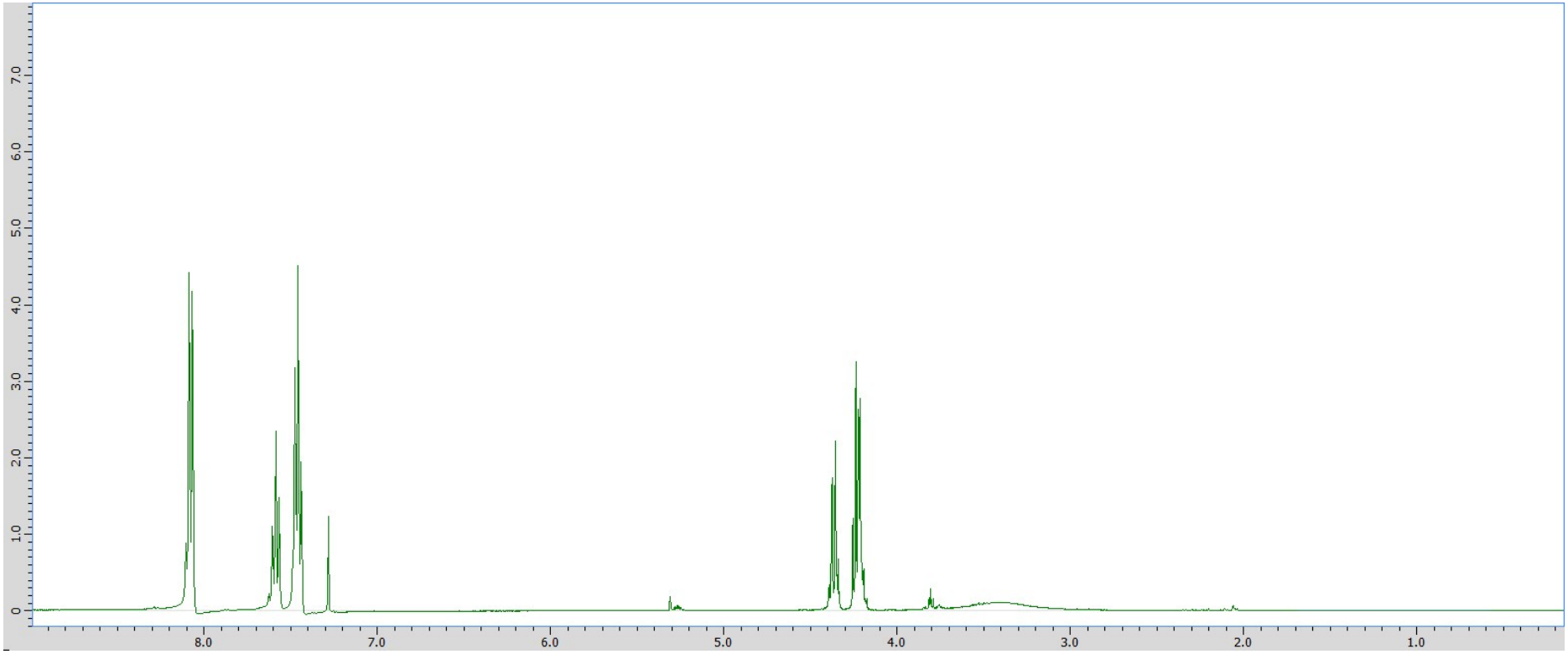
2-*O*-benzoyl-1-phenyl-1,2-ethanediol (17)[3]:

^{1}H-NMR of compound **17** ($CDCl_3$)



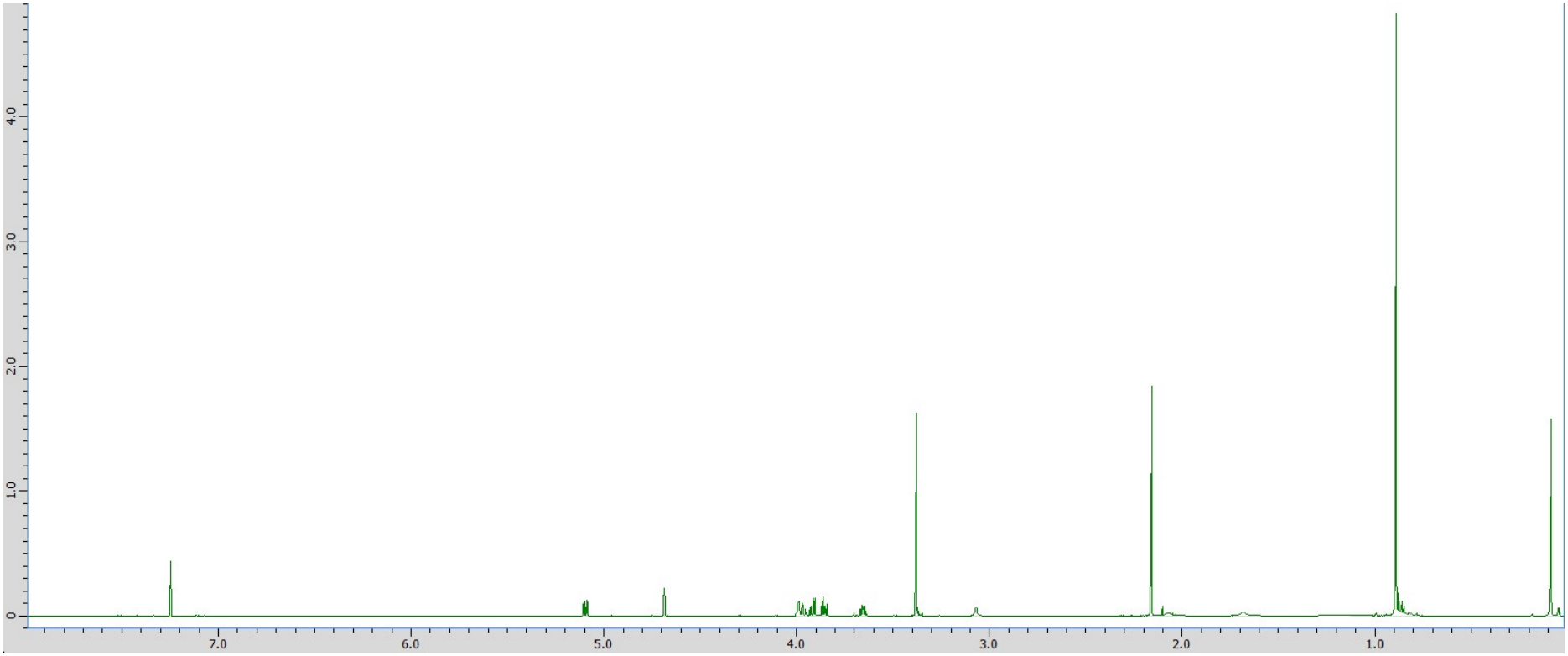
1-*O*-benzoyl-1,2-propanediol (20)[3]:

^{1}H-NMR of compound **20** ($CDCl_3$)



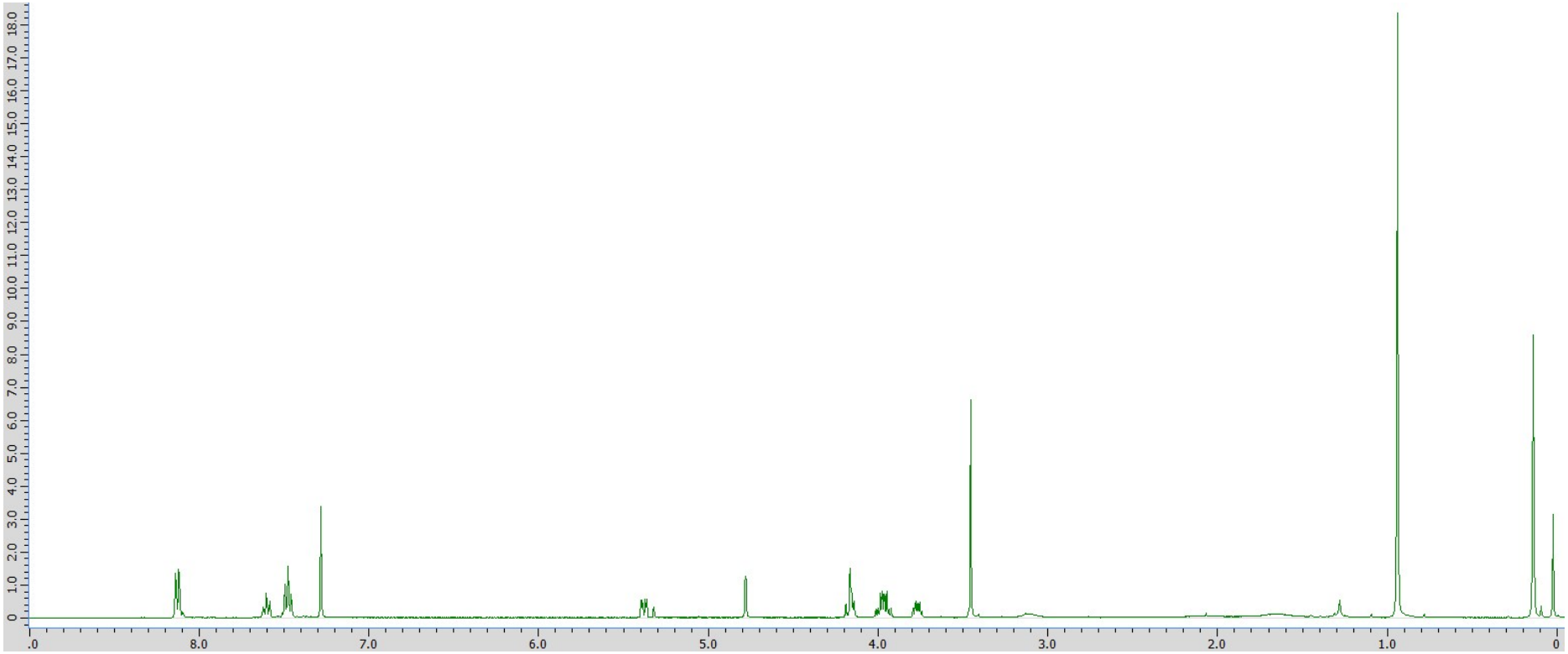
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyloxy)-α-D-mannopyranoside (21)[2]:

^{1}H-NMR of compound **21** ($CDCl_3$)



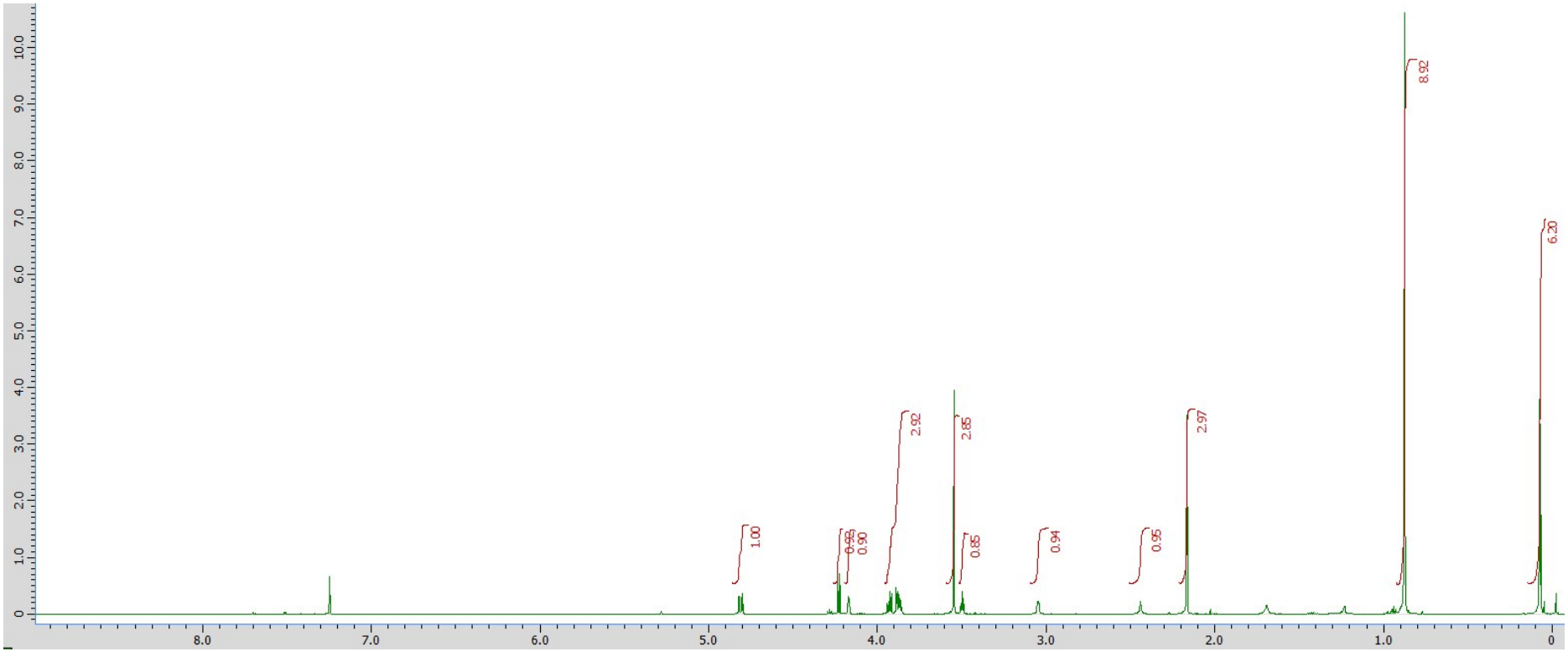
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyloxy)-α-D-mannopyranoside (22)[3]:

^{1}H-NMR of compound **22** ($CDCl_3$)



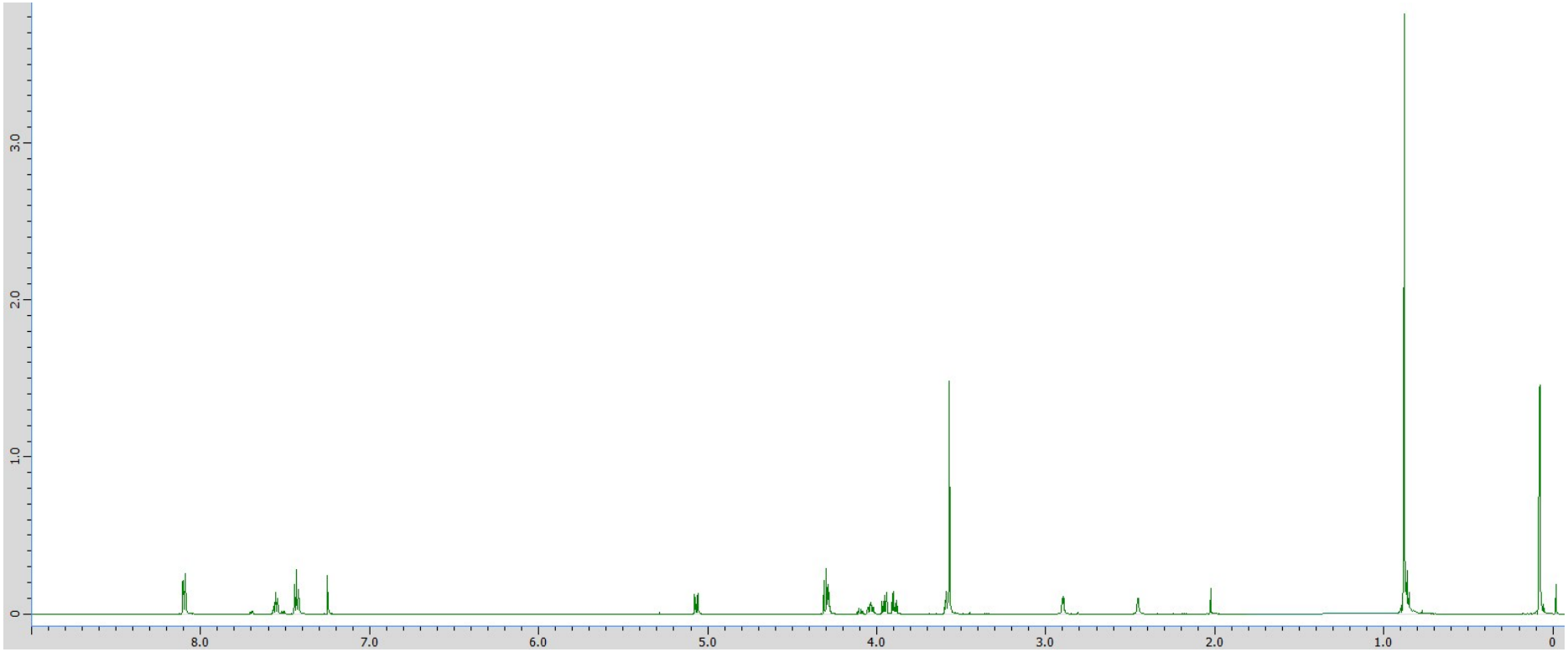
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-galactopyranoside (24)[2]:

^{1}H-NMR of compound **24** ($CDCl_3$)



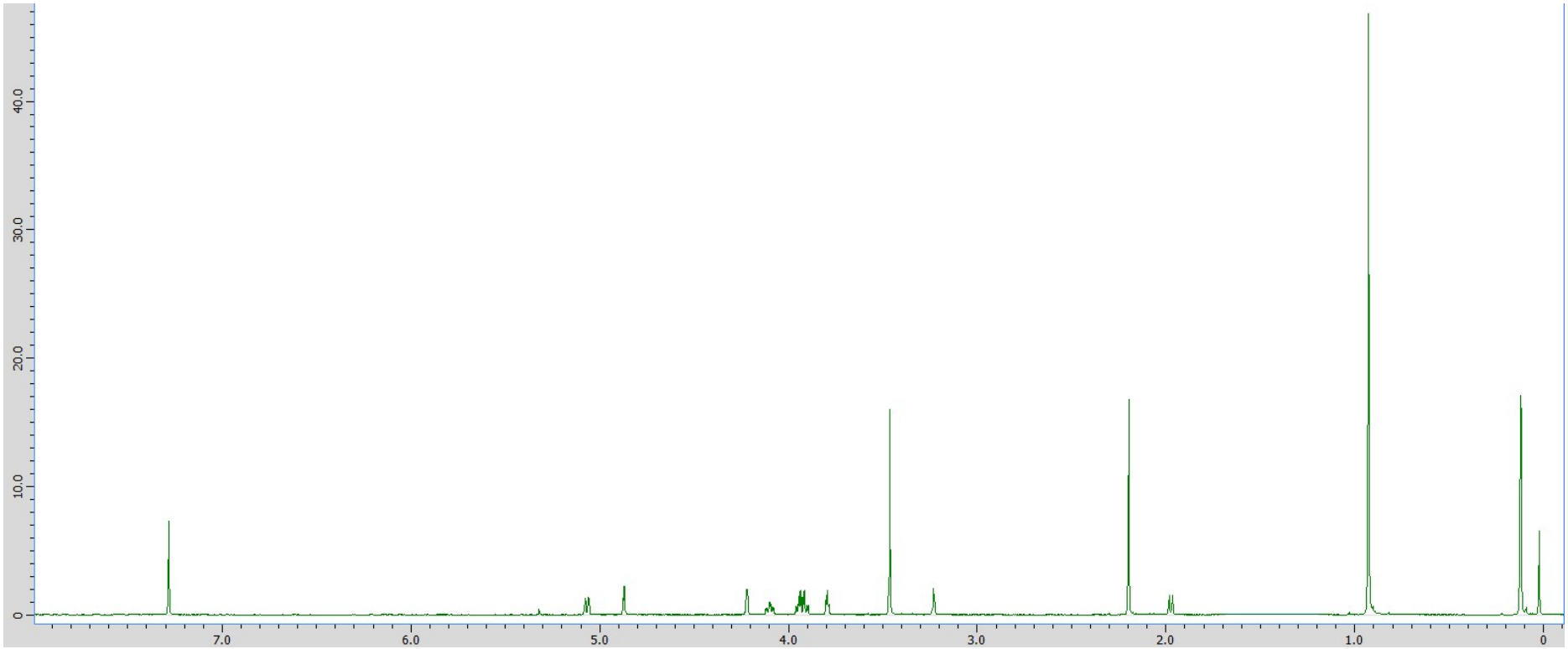
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-galactopyranoside (25)[3]:

^{1}H-NMR of compound **25** ($CDCl_3$)



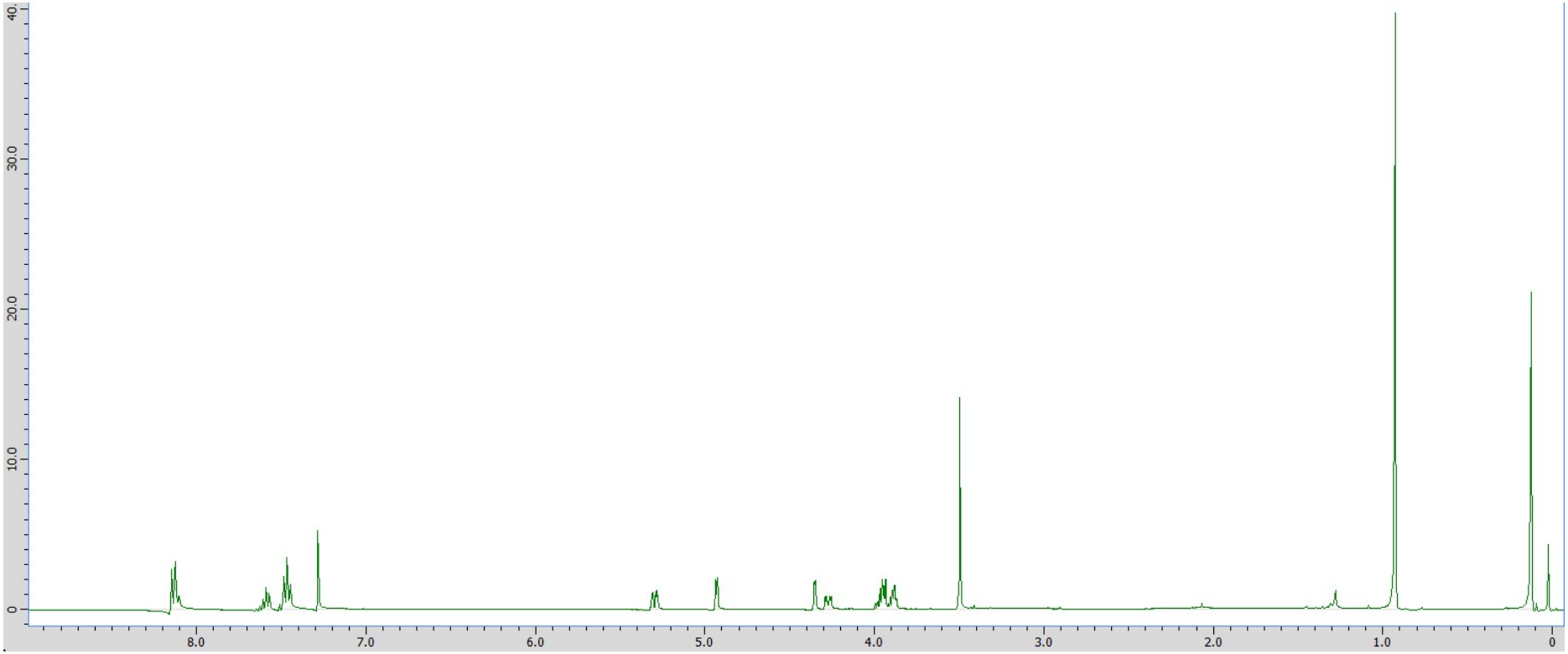
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*α*-D-galactopyranoside (27)[2]:

^{1}H-NMR of compound **27** ($CDCl_3$)



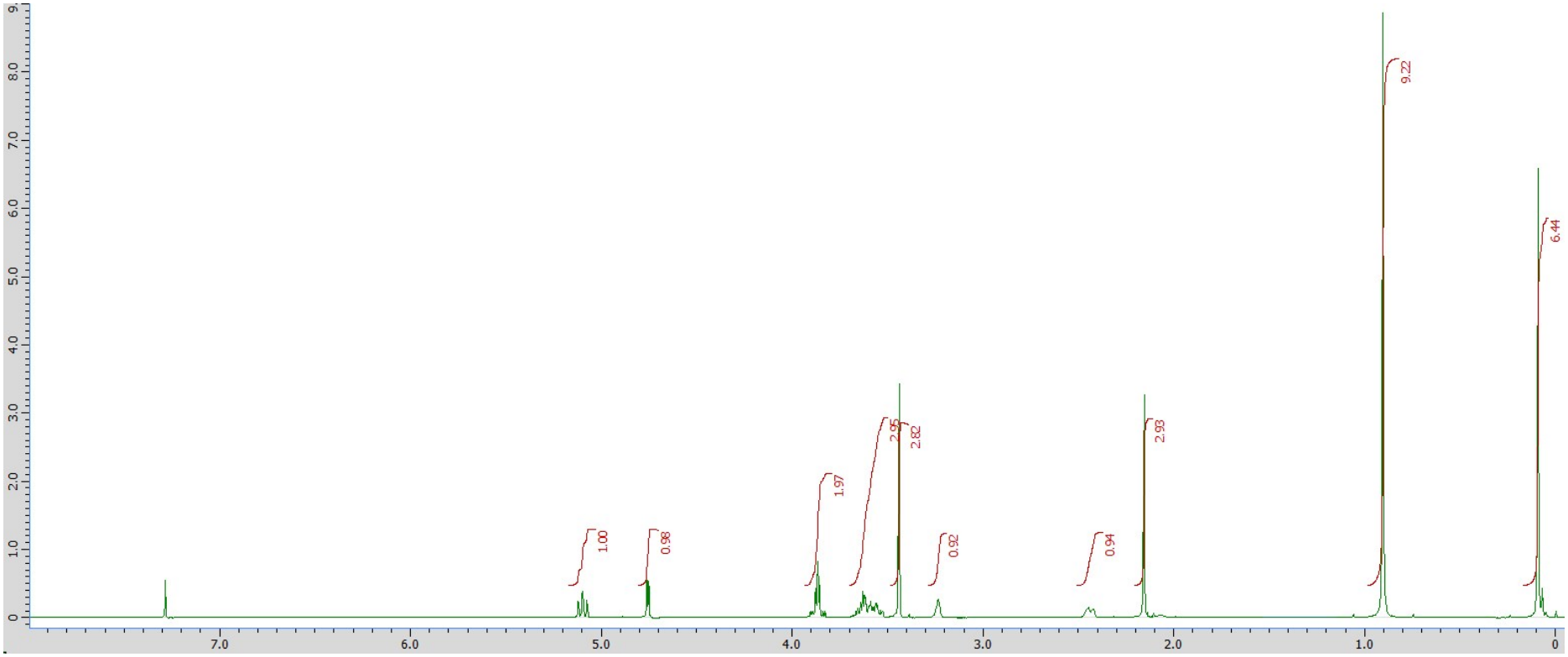
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*α*-D-galactopyranoside (28)[3]:

^{1}H-NMR of compound **28** ($CDCl_3$)



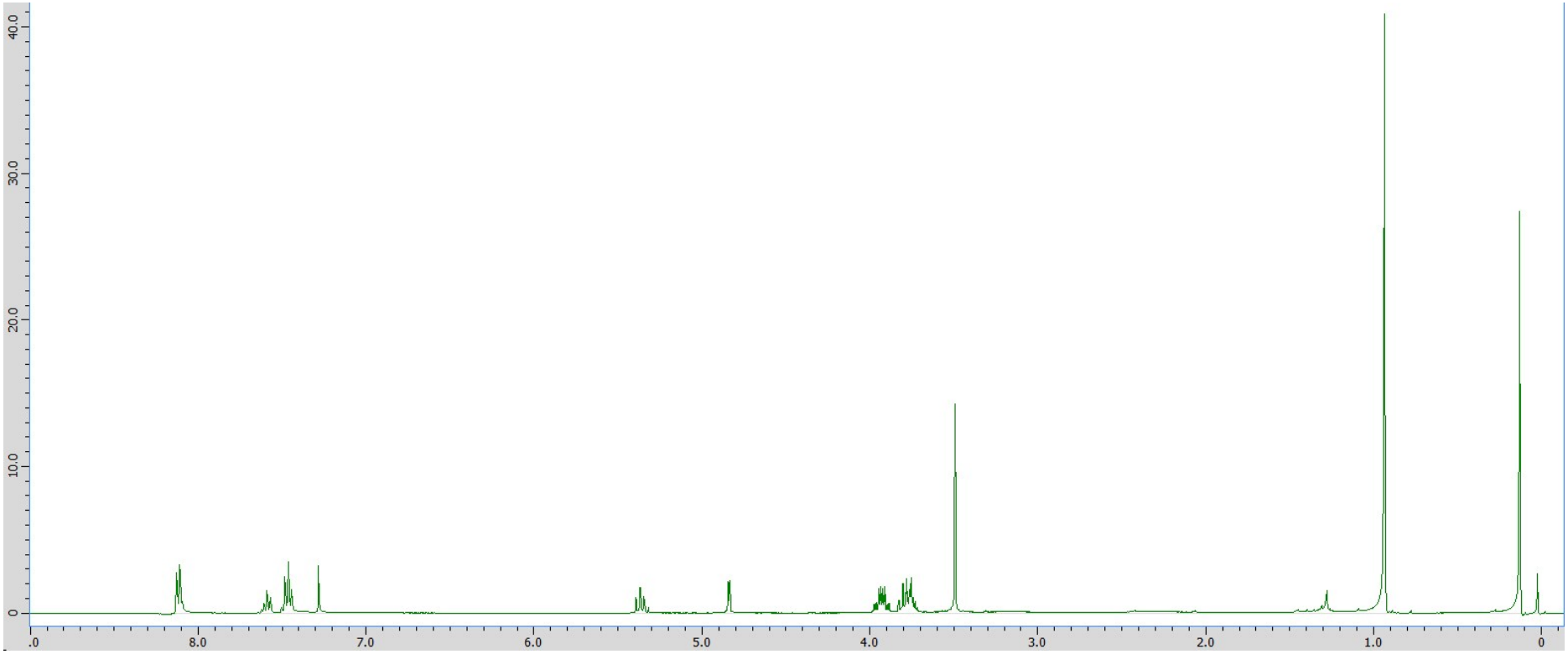
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*α*-D-glucopyranoside (30)[2]:

^{1}H-NMR of compound **30** ($CDCl_3$)



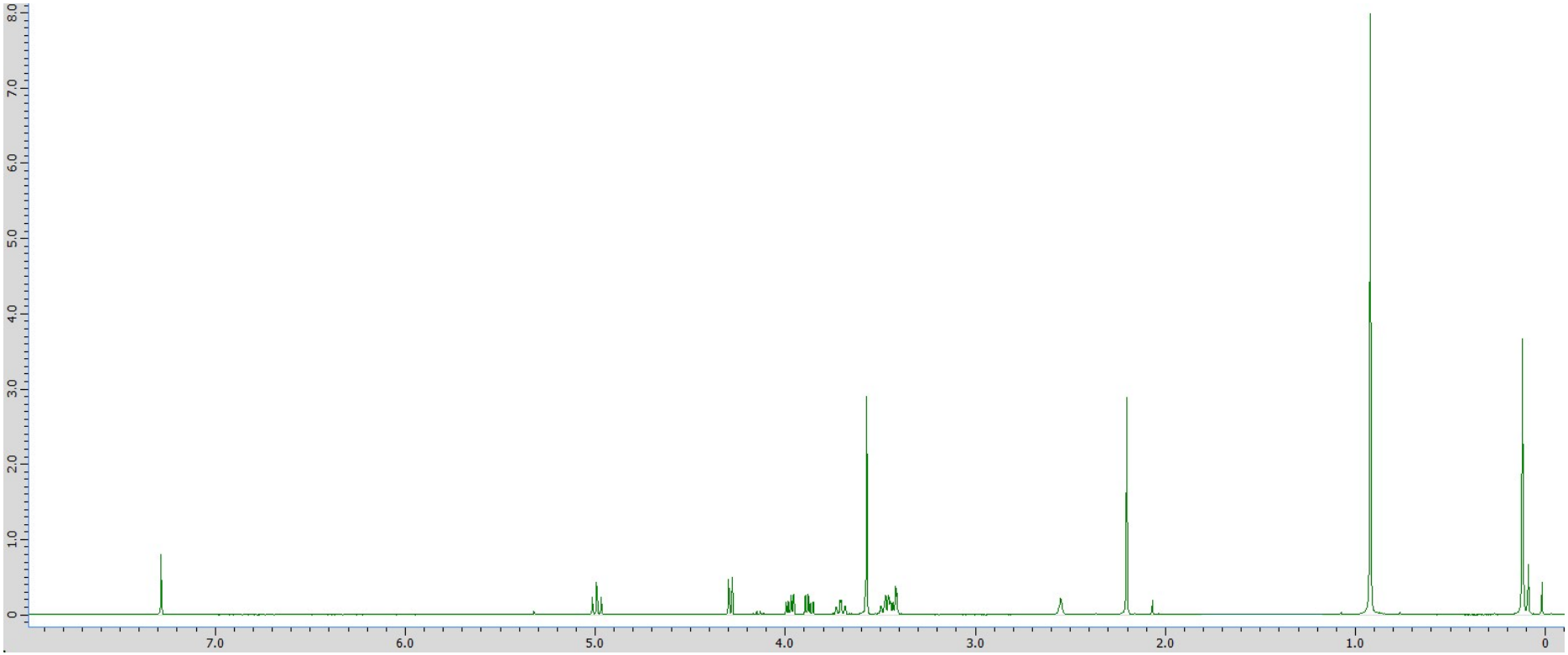
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*α*-D-glucopyranoside (31)[3]:

^{1}H-NMR of compound **31** ($CDCl_3$)



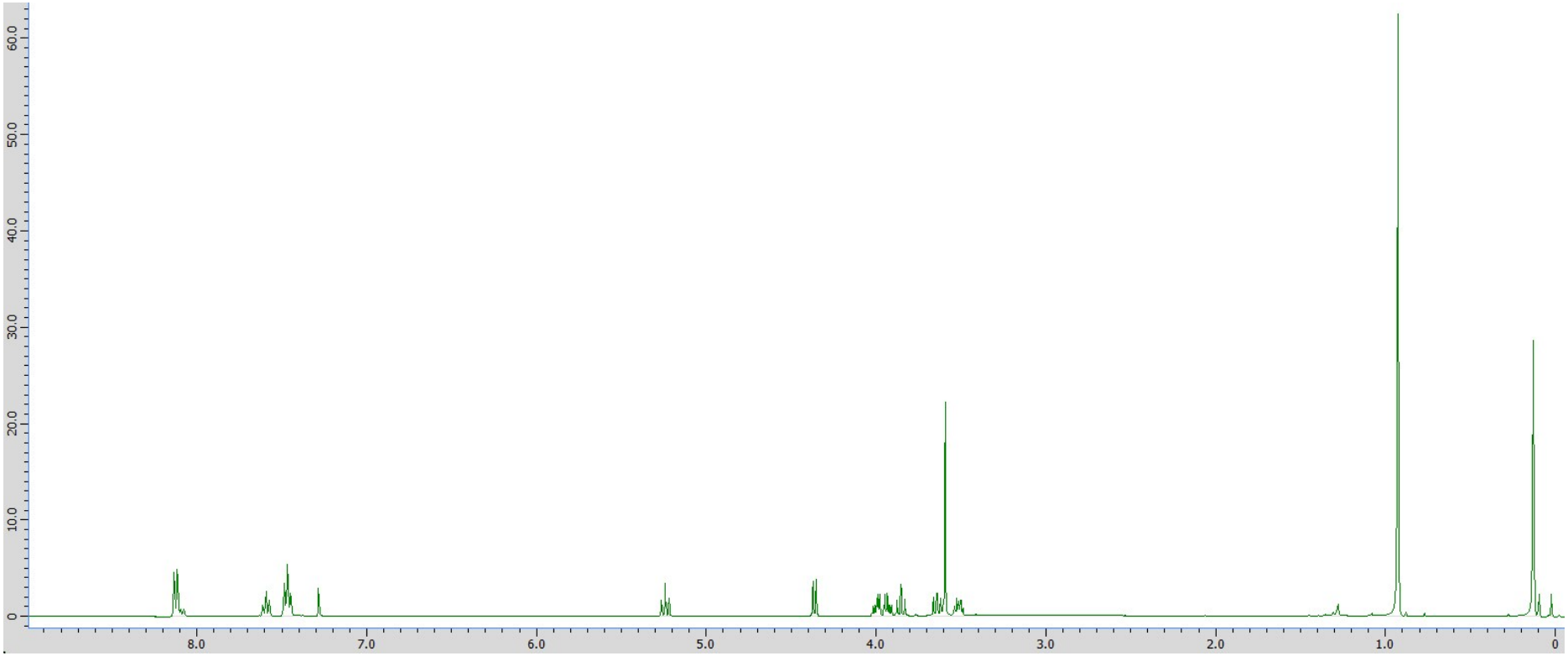
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-glucopyranoside(33)[2].

^{1}H-NMR of compound **33** ($CDCl_3$)



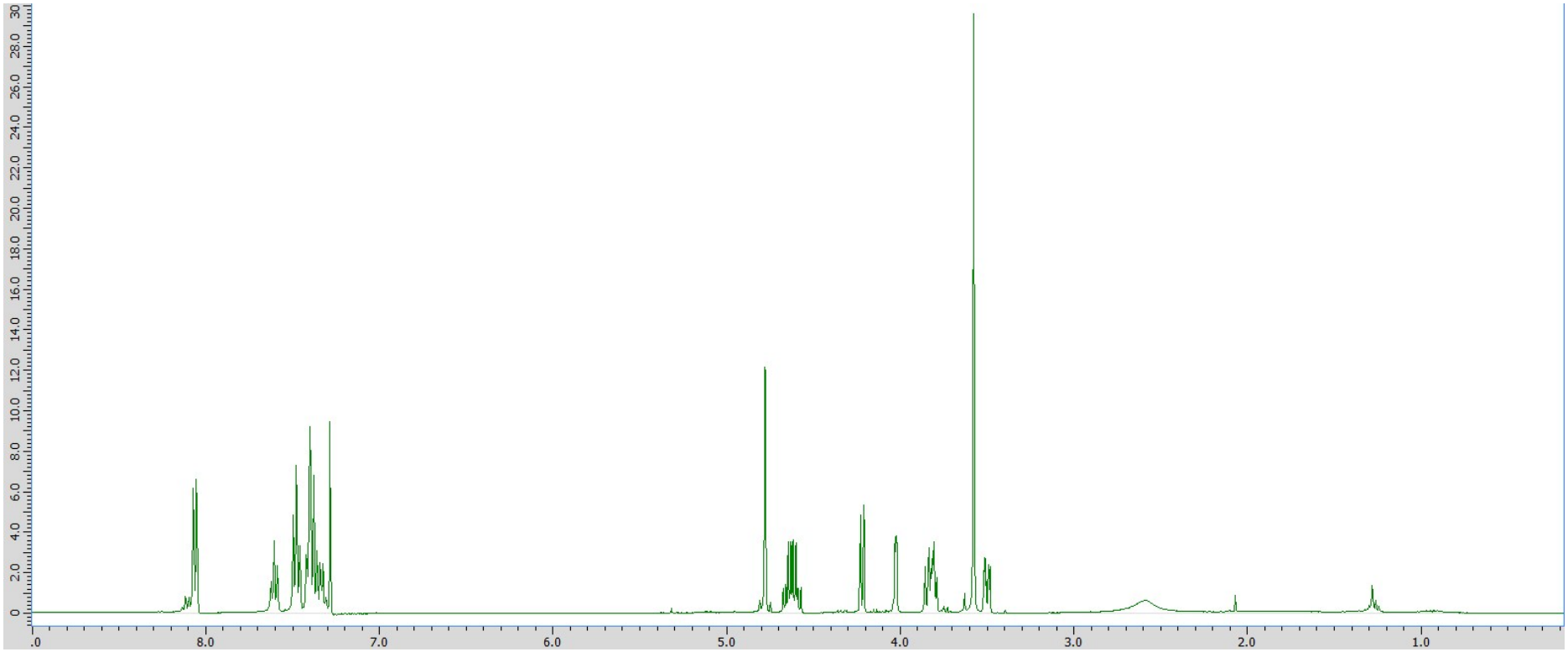
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-glucopyranoside(34)[3].

^{1}H-NMR of compound **34** ($CDCl_3$)



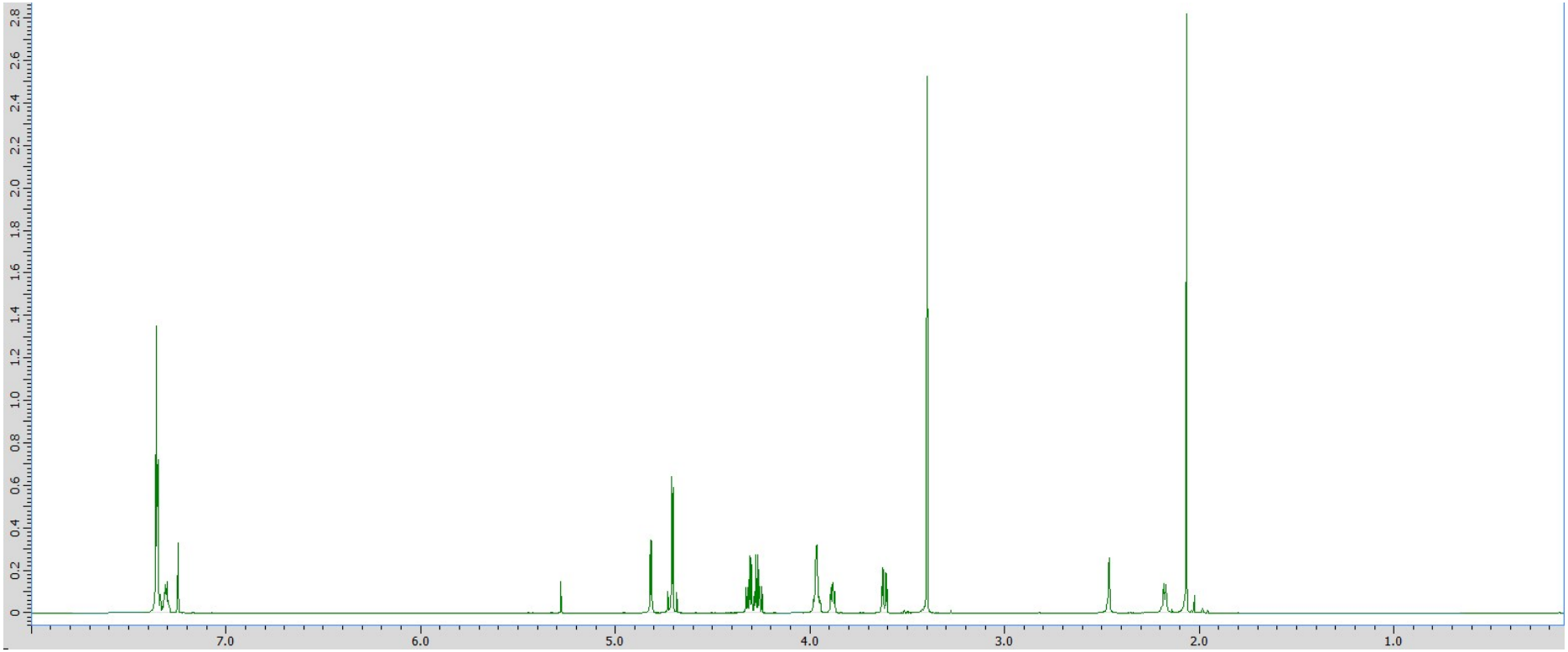
Methyl 3-*O*-benzyl-6-*O*-benzoyl-*β*-D-galactopyranoside (38)[3]:

^{1}H-NMR of compound **38** ($CDCl_3$)



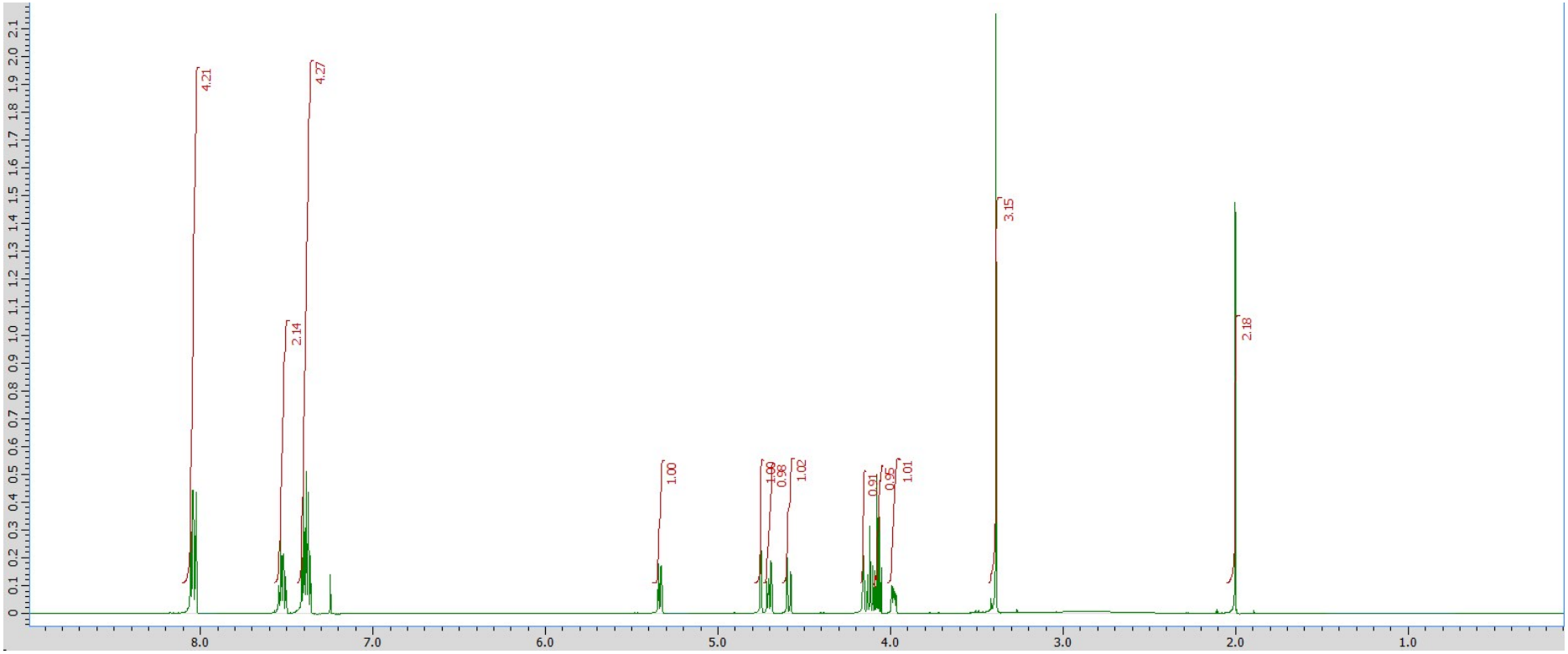
Methyl 3-*O*-benzyl-6-*O*-acetyl-*α*-D-galactopyranoside (40)[2]:

^{1}H-NMR of compound **40** ($CDCl_3$)



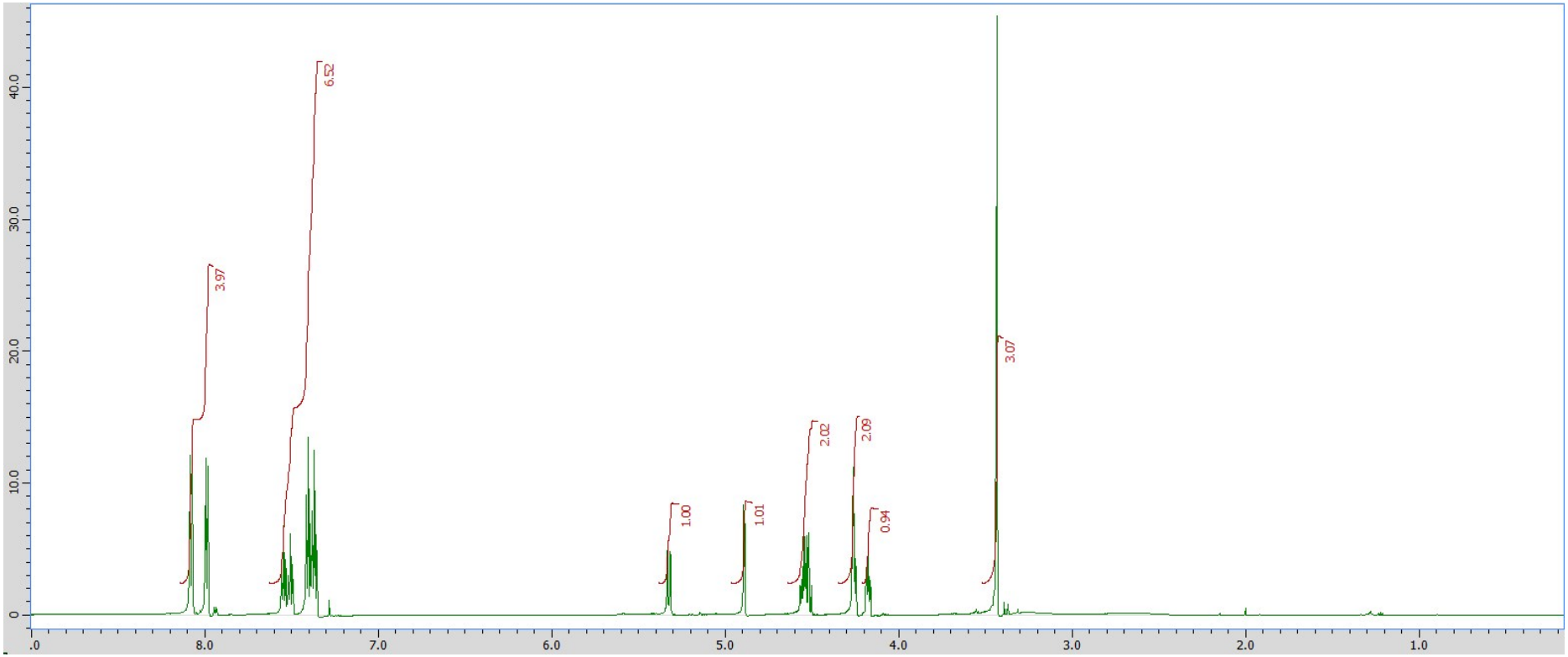
Methyl 3, 6-di-*O*-benzoyl-*α*-D-mannopyranoside (42)[3]:

^{1}H-NMR of compound **42** ($CDCl_3$)



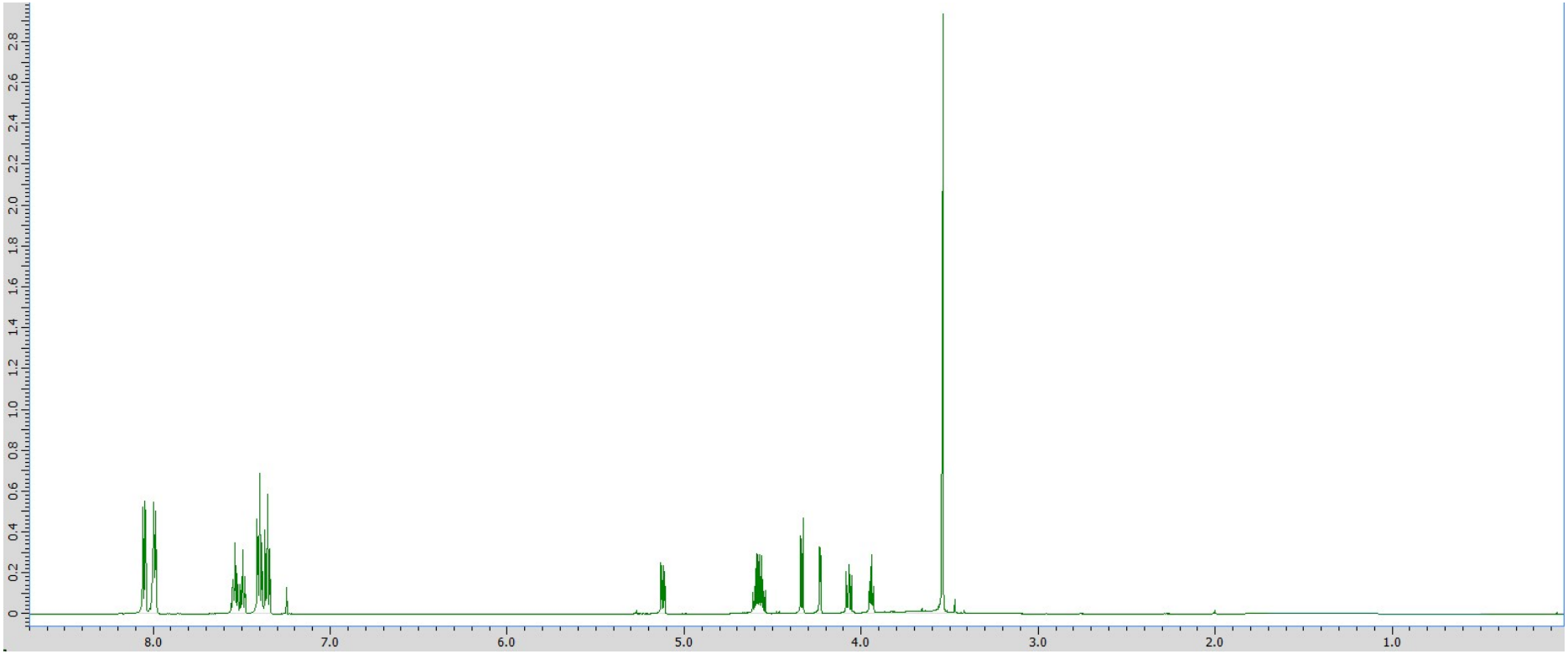
Methyl 3, 6-di-*O*-benzoyl-*α*-D-galactopyranoside (45)[3]:

^{1}H-NMR of compound **45** ($CDCl_3$)



Methyl 3, 6-di-*O*-benzoyl-*β*-D-galactopyranoside (48)[3]:

^{1}H-NMR of compound **48** ($CDCl_3$)



References

1. Y. Zhou, M. Rahm, B. Wu, X. Zhang, B. Ren and H. Dong, *J. Org. Chem.*, 2013, **78**, 11618.
2. B. Ren, M. Rahm, X. Zhang, Y. Zhou and H. Dong, *J. Org. Chem.*, 2014, **79**, 8134.
3. X. Zhang, B. Ren, J. Ge, Z. Pei and H. Dong, *Tetrahedron*, 2016, **72**, 1005.