

CHEMISTRY

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Supporting Information

Synthesis and Applications of Silyl 2-Methylprop-2-ene-1-sulfonates in Preparative Silylation and GC-Derivatization Reactions of Polyols and Carbohydrates

Dean Marković,^{*,[a, b, c]} Wandji Augustin Tchawou,^[a] Irina Novosjolova,^[d] Sylvain Laclef,^[a] Dmitrijs Stepanovs,^[d, e] Māris Turks,^{*,[d]} and Pierre Vogel^{*,[a]}

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tert-Butyldimethyl(2-methylallyl)silane (**3a**)¹

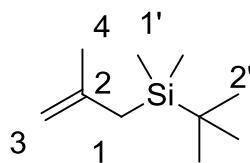
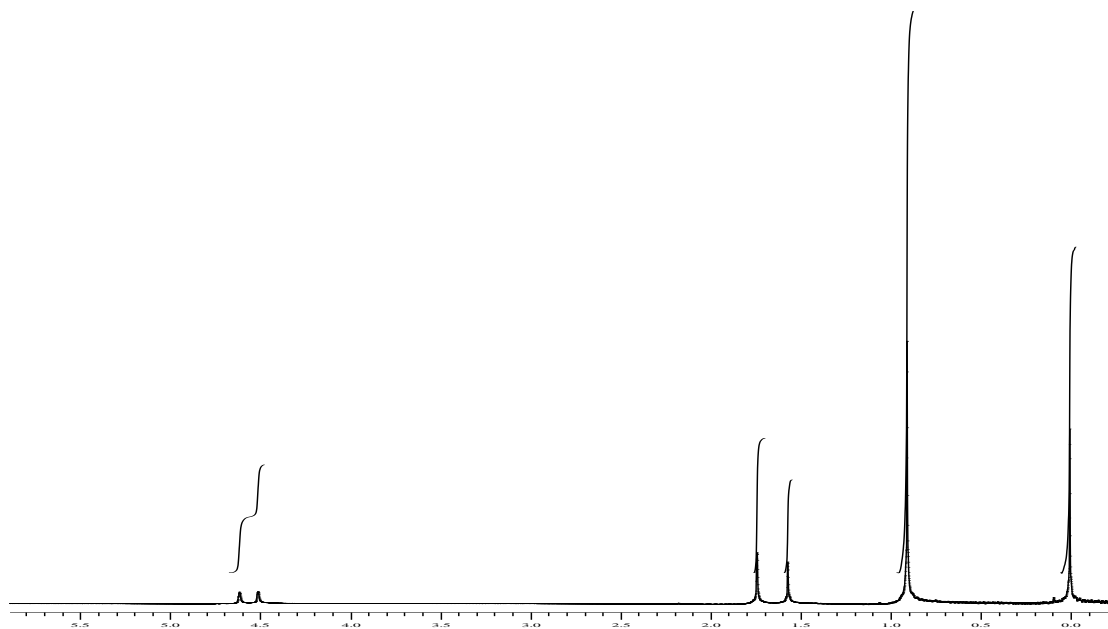


Figure 1. ¹H NMR of *tert*-butyldimethyl(2-methylallyl)silane (**3a**).



¹ Huang, X.; Craita, C.; Awad, L.; Vogel, P. *Chem. Commun.* **2005**, 1297.

Trimethyl(2-methylallyl)silane (**3b**)¹

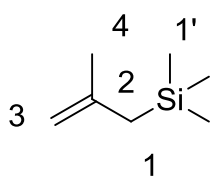
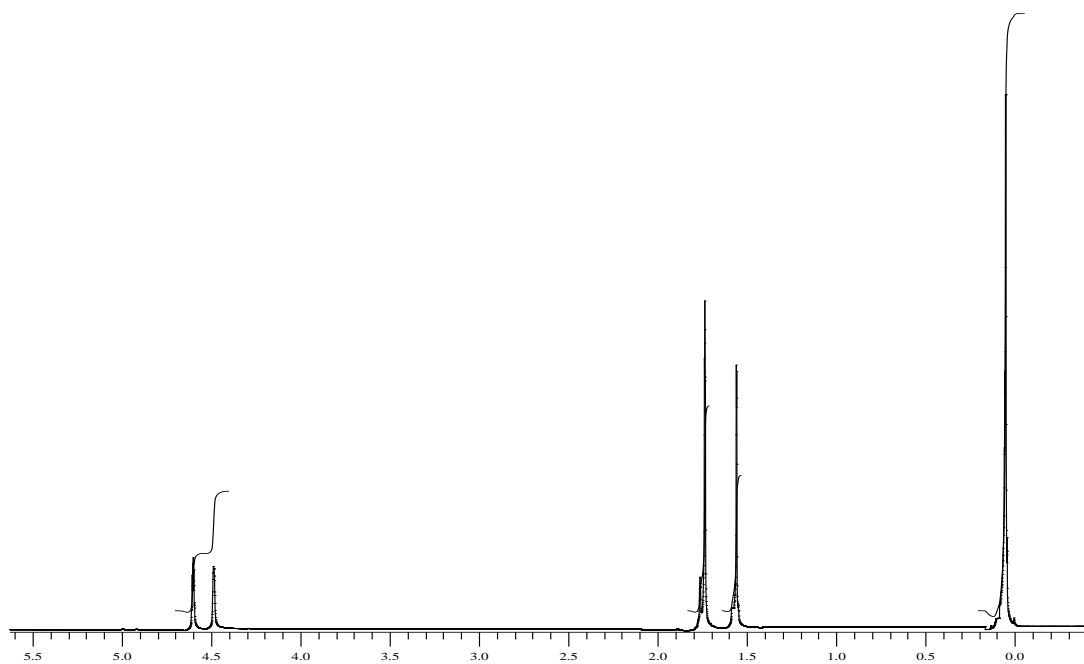


Figure 2. ¹H NMR of trimethyl(2-methylallyl)silane (**3b**).



Triethyl(2-methylallyl)silane (3c)¹

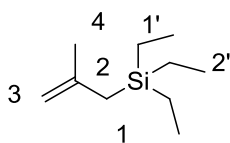
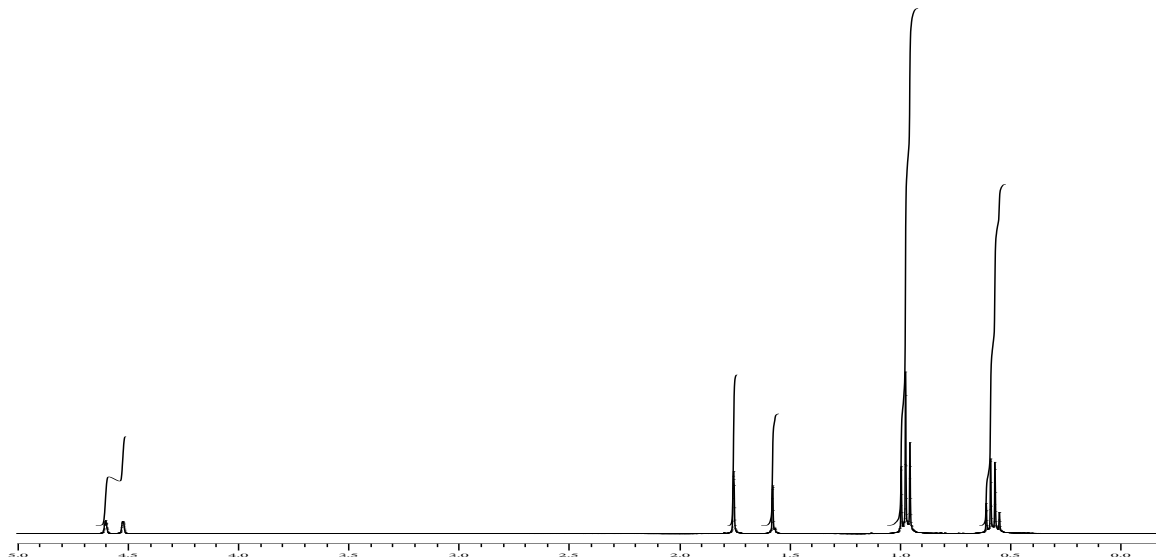
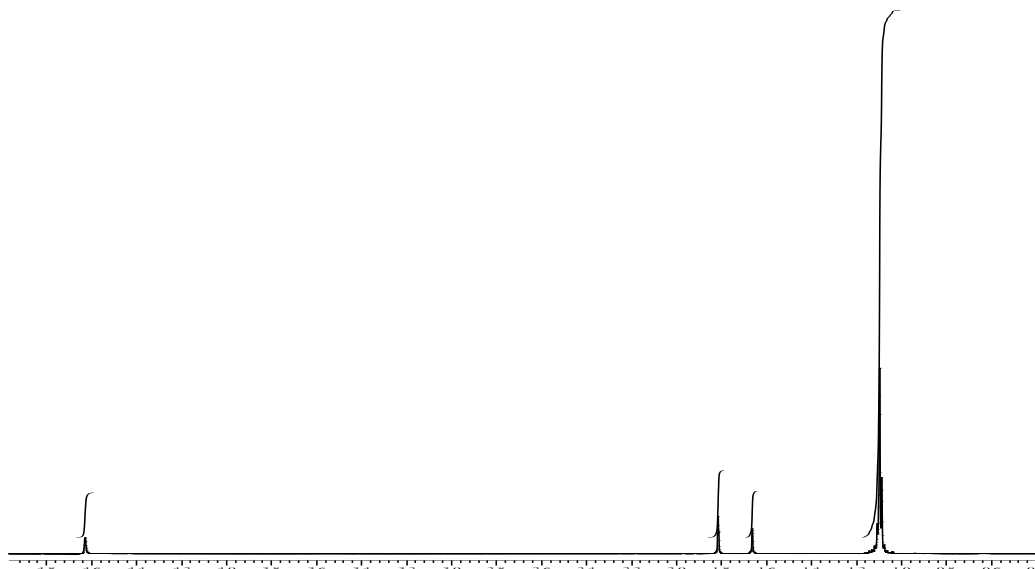


Figure 3. ¹H NMR of triethyl(2-methylallyl)silane (**3c**).



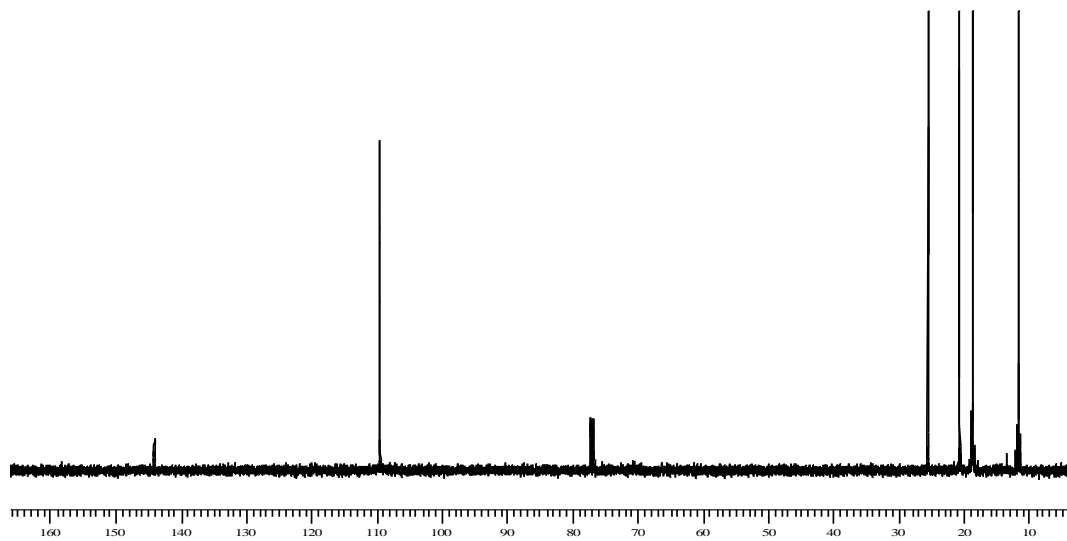
Triisopropyl(2-methylallyl)silane (3d)²

Figure 4. ¹H NMR of triisopropyl(2-methylallyl)silane (**3d**).



¹ Maruoka, K.; Ohmatsu, K.; Ooi, T.; Uraguchi, D. *Tetrahedron Lett.*, **2004**, 45, 4481.

Figure 5. ^{13}C NMR of triisopropyl(2-methylallyl)silane (**3d**).



tert-Butyldimethylsilyl- 2-methylprop-2-ene-1-sulfinate (**1a**)¹

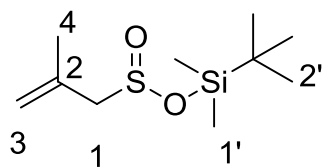
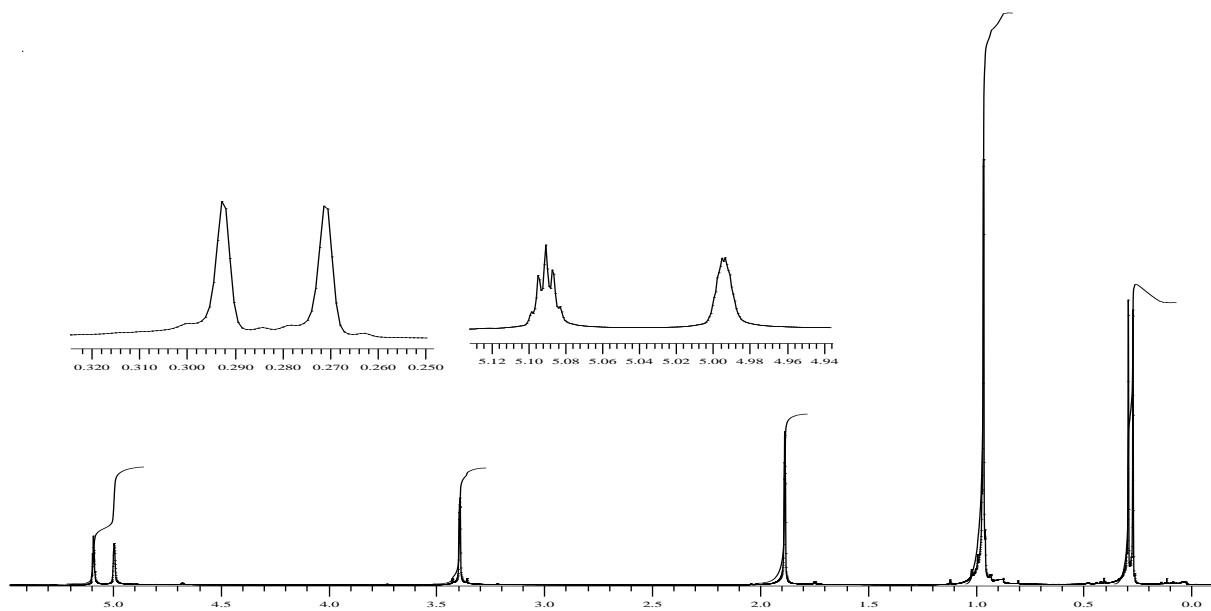


Figure 6. ^1H NMR of *tert*-butyldimethylsilyl- 2-methylprop-2-ene-1-sulfinate (**1a**).



Trimethylsilyl 2-methylprop-2-ene-1-sulfinate (**1b**)¹

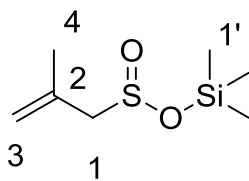
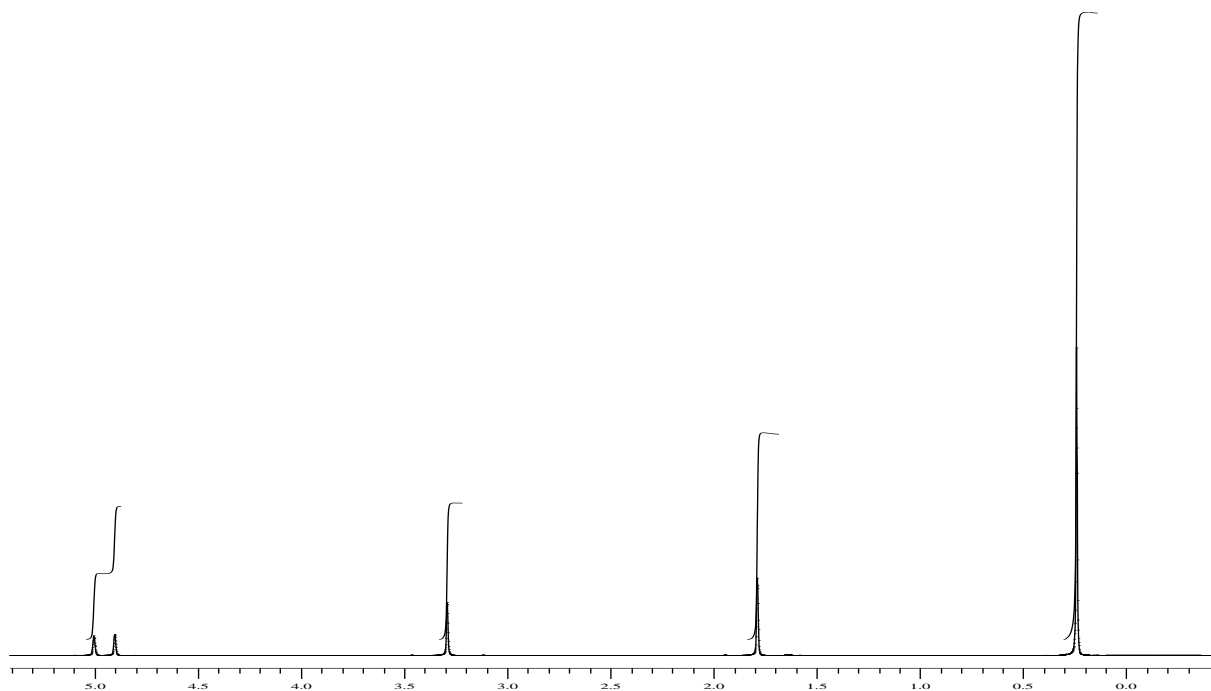


Figure 7. ¹H NMR of trimethylsilyl 2-methylprop-2-ene-1-sulfinate (**1b**).



Triethylsilyl- 2-methylprop-2-ene-1-sulfinate (1c)¹

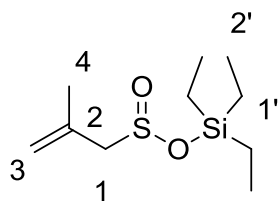
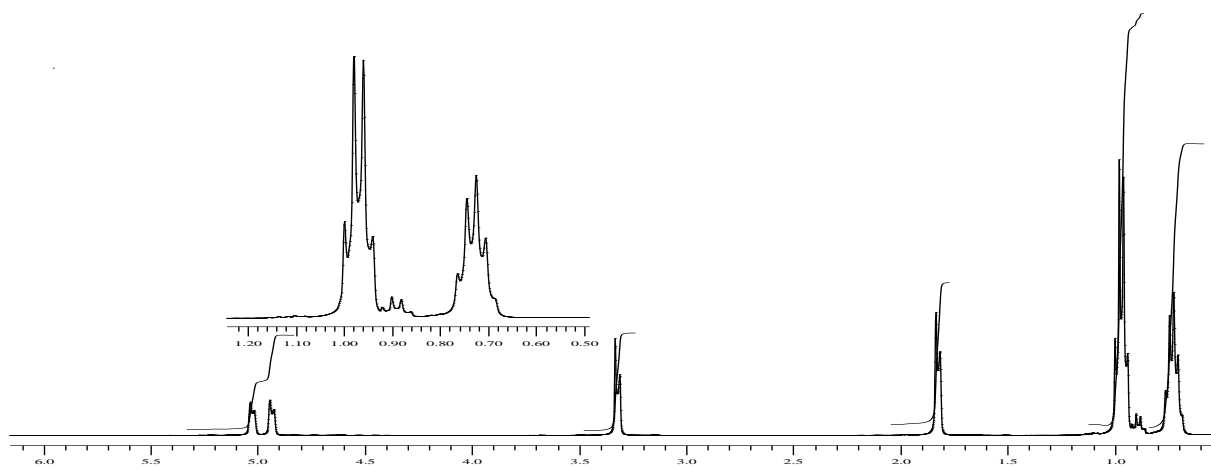


Figure 8. ¹H NMR of triethylsilyl- 2-methylprop-2-ene-1-sulfinate (1c).



Triisopropylsilyl-2-methylprop-2-ene-1-sulfinate (1d)

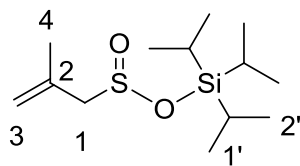
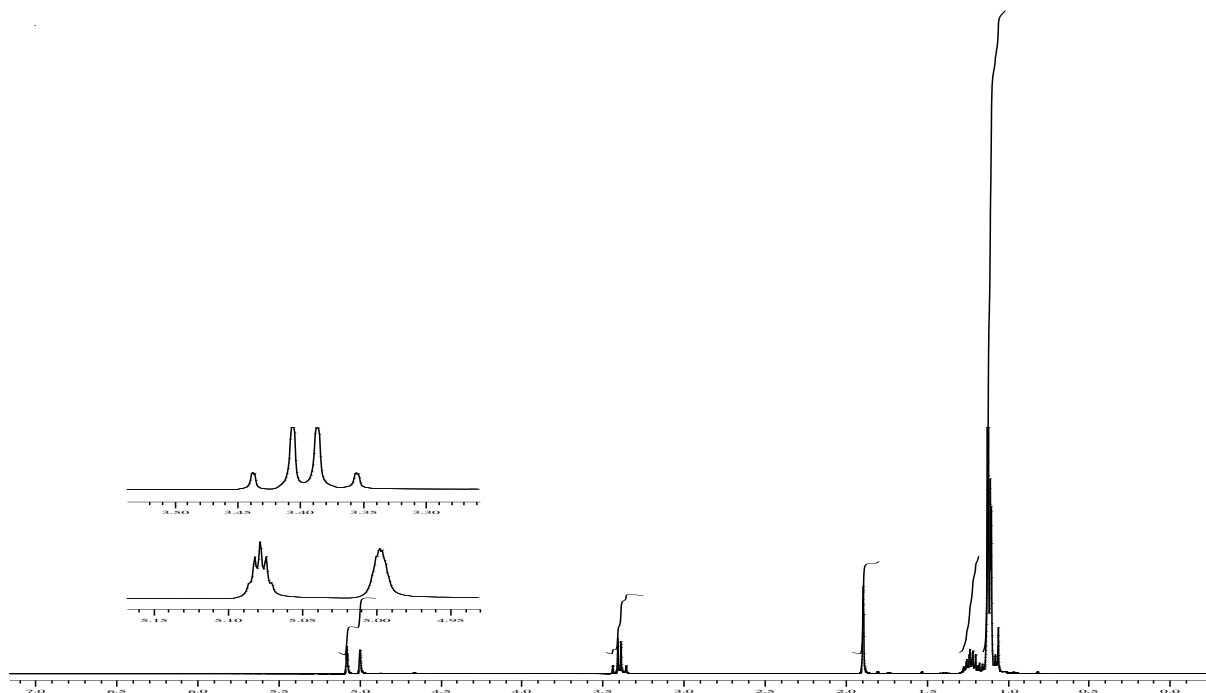


Figure 9. ^1H NMR of triisopropylsilyl-2-methylprop-2-ene-1-sulfinate (**1d**).



3-*O*-(triethylsilyl)cholesterol (**6a**)³

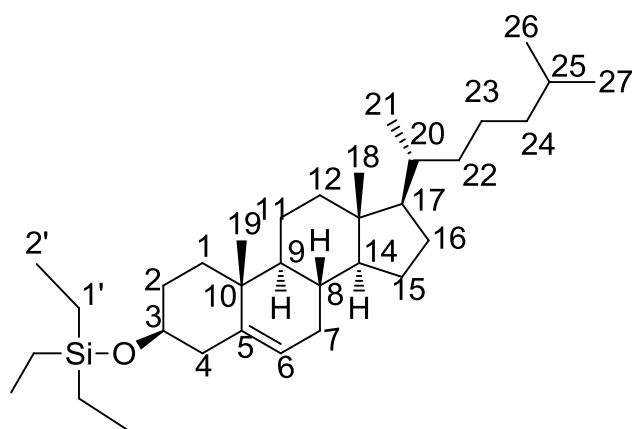
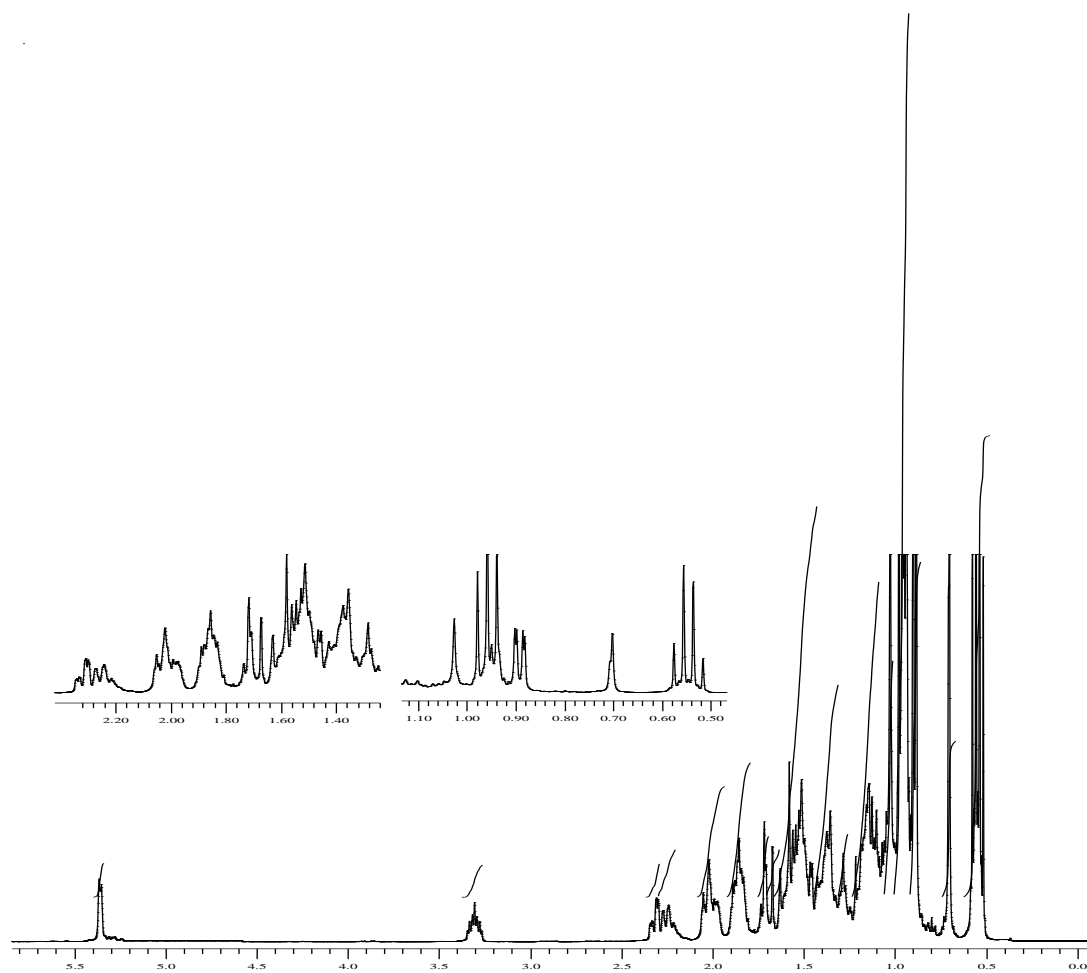


Figure 10. ¹H NMR of 3-*O*-(triethylsilyl)cholesterol (**6a**).



³ Diekman, J.; Djerassi, C. *J. Org. Chem.*, **1967**, *32*, 1005.

1,2:5,6-di-*O*-isopropylidene-3-*O*-triethylsilyl-D-glucofuranose (**6b**)⁴

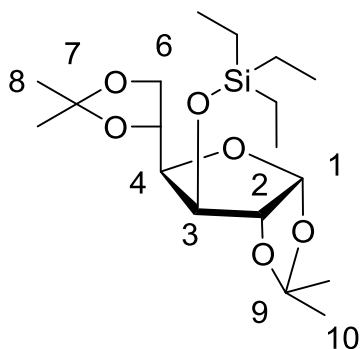
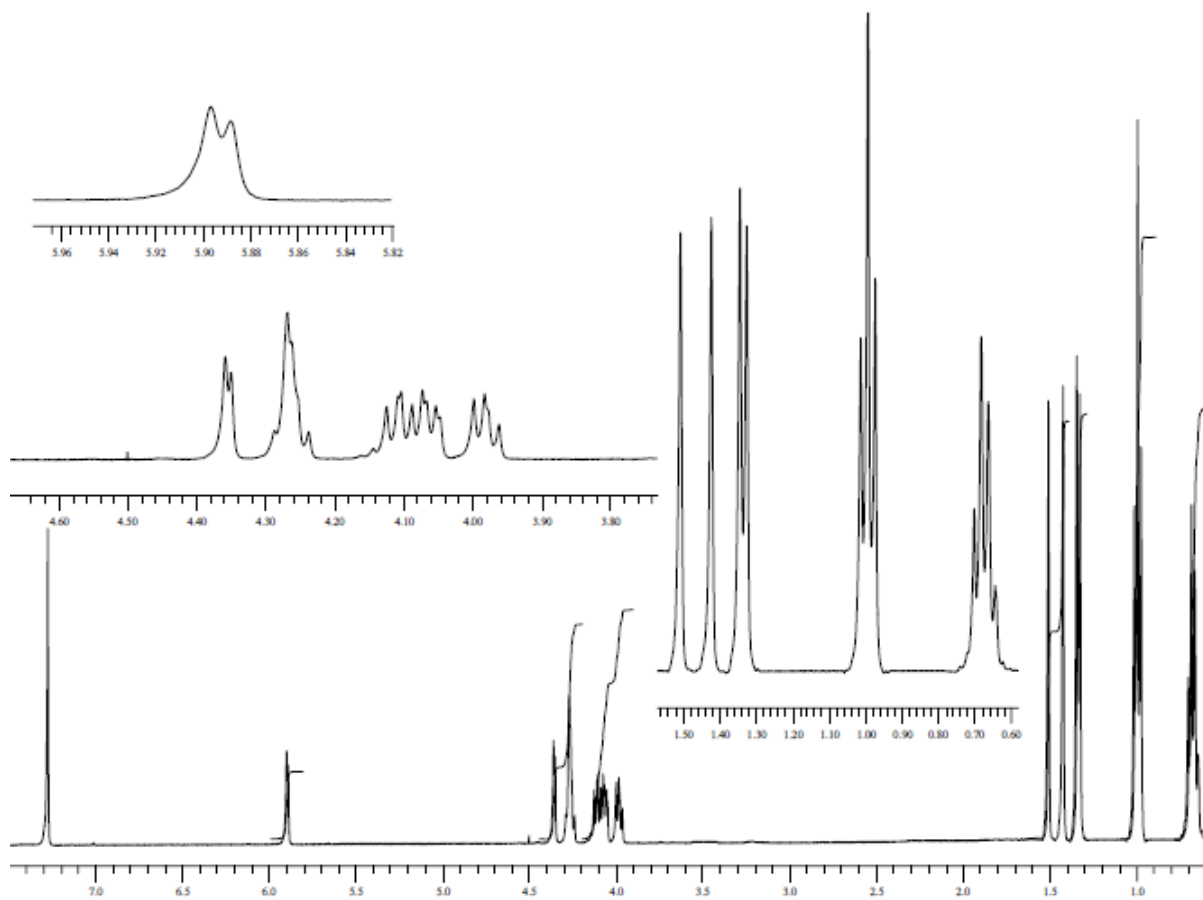


Figure 11. ¹H NMR of 1,2:5,6-di-*O*-isopropylidene-3-*O*-triethylsilyl-D-glucofuranose (**6b**).



⁴ Grayson, E. J.; Ward, S. J.; Hall, A. L.; Rendle, P. M.; Gamblin, D. P.; Batsanov, A. S.; Davis, B. G. *J. Org. Chem.* **2005**, *70*, 9740.

{{(2E)-3,7-dimethyl-2,6-octadien-1-yl}oxy}(triethyl)silane (**6c**)⁵

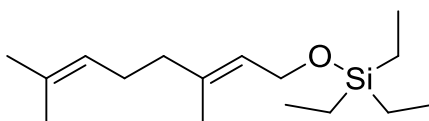
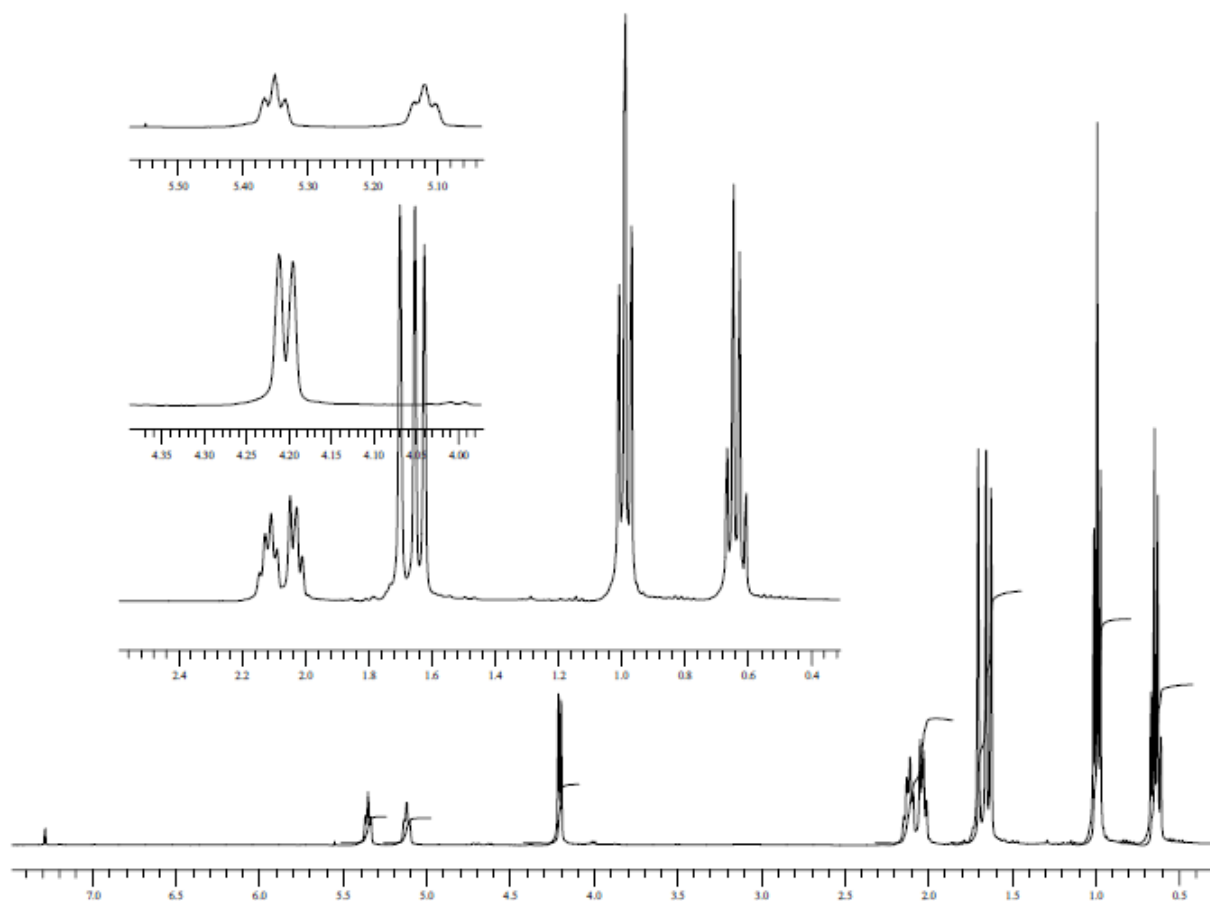


Figure 12. ¹H NMR of {{(2E)-3,7-dimethyl-2,6-octadien-1-yl}oxy}(triethyl)silane (**6c**).



⁵ Bourhis, R.; Frainnet, E.; Moulines, F. *J. Organomet. Chem.* **1977**, *141*, 157.

[(3Z)-3-Hepten-1-yloxy](triethyl)silane (6d)

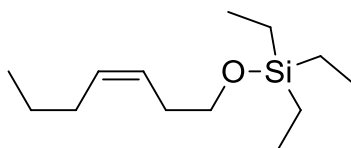
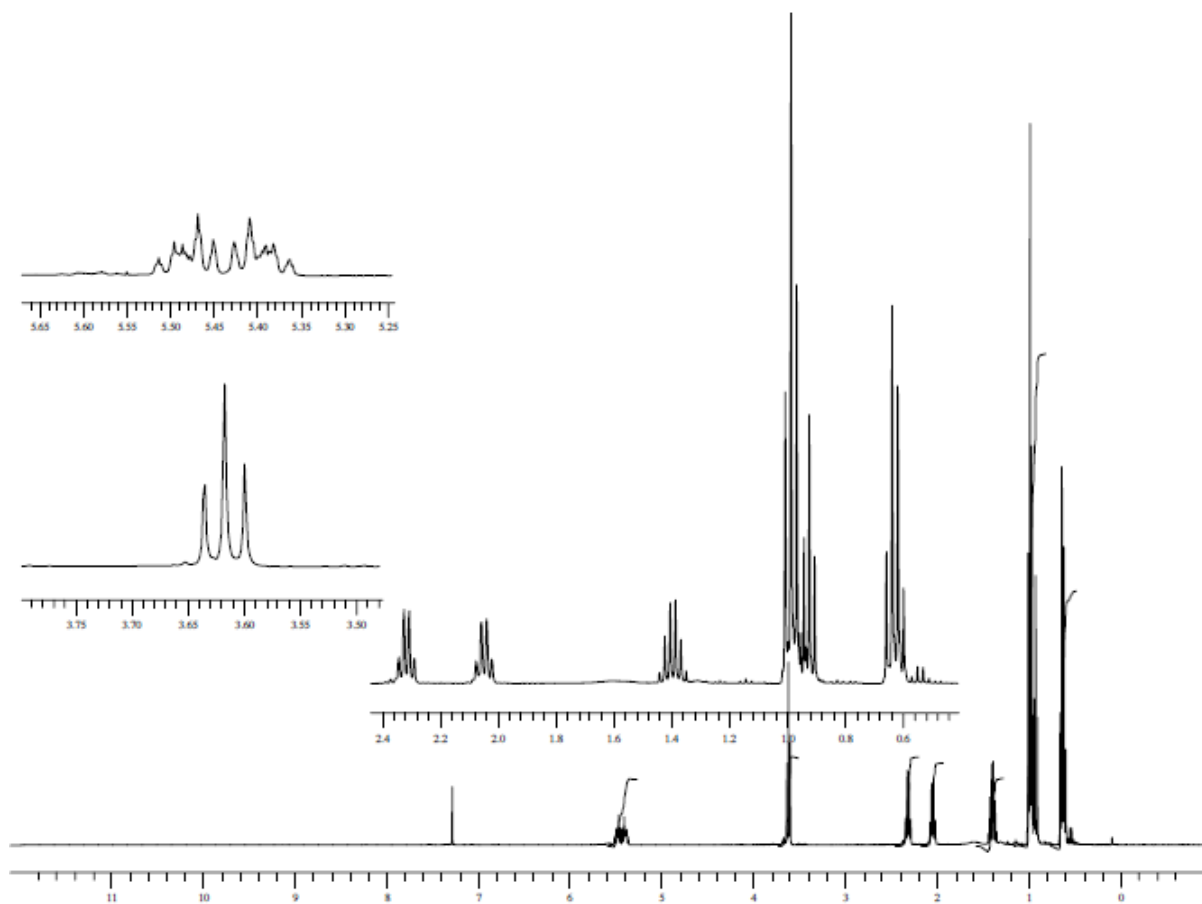


Figure 13. ^1H NMR of [(3Z)-3-Hepten-1-yloxy](triethyl)silane (**6d**).



(-)-2-Methyl-3-[(triethylsilyl)oxy]propionate methyl ester (**6e**).⁶

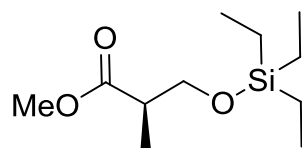
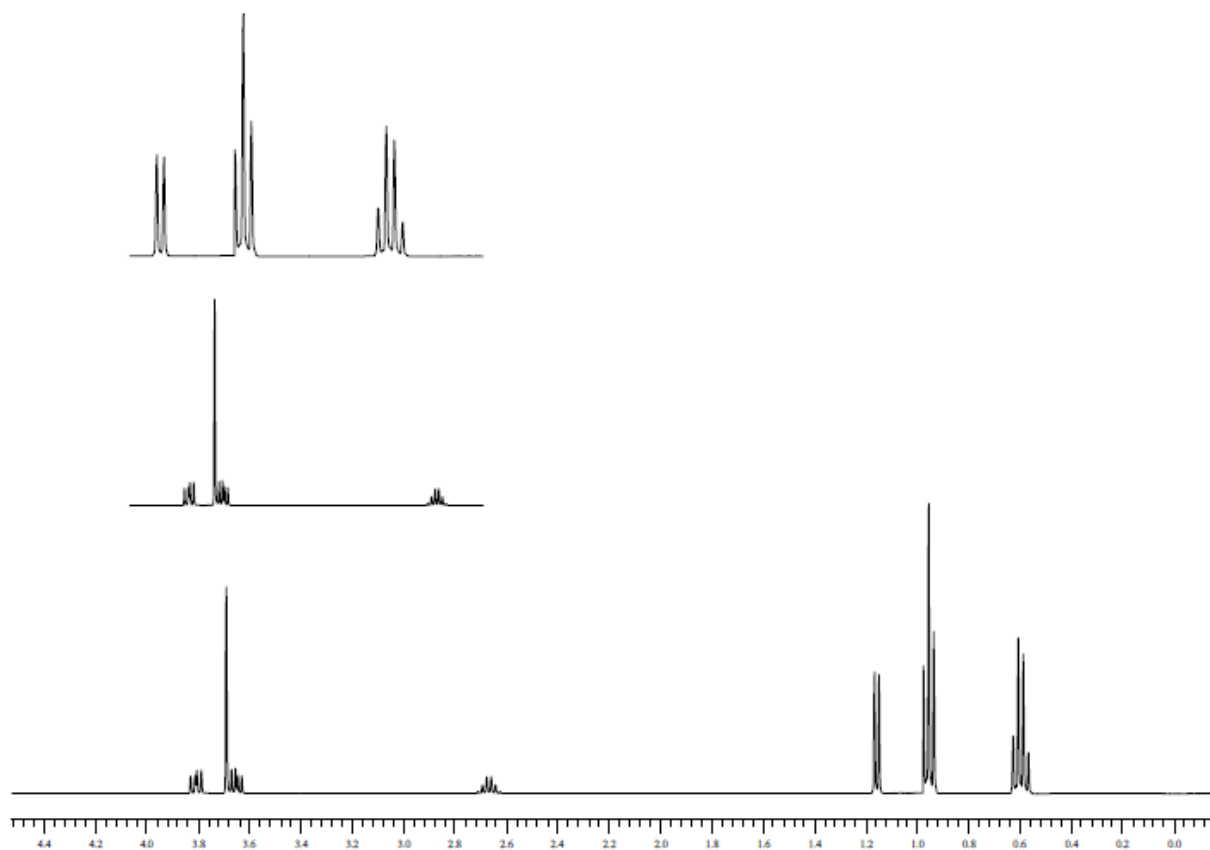


Figure 14. ¹H NMR of (+)-2-Methyl-3-[(triethylsilyl)oxy]propionate methyl ester (**6e**).



⁶ Anderson, O. P.; Barrett, A. G. M.; Edmunds, J. J.; Hachiya, S.-I.; Hendrix, J. A.; Horita, K.; Malecha, J. W.; Parkinson, C. J.; VanSickle, A. *Can. J. Chem.* **2001**, *79*, 1562.

[(1-Methyl-3-buten-1-yl)oxy](triethyl)silane (**6f**)⁷

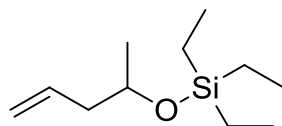
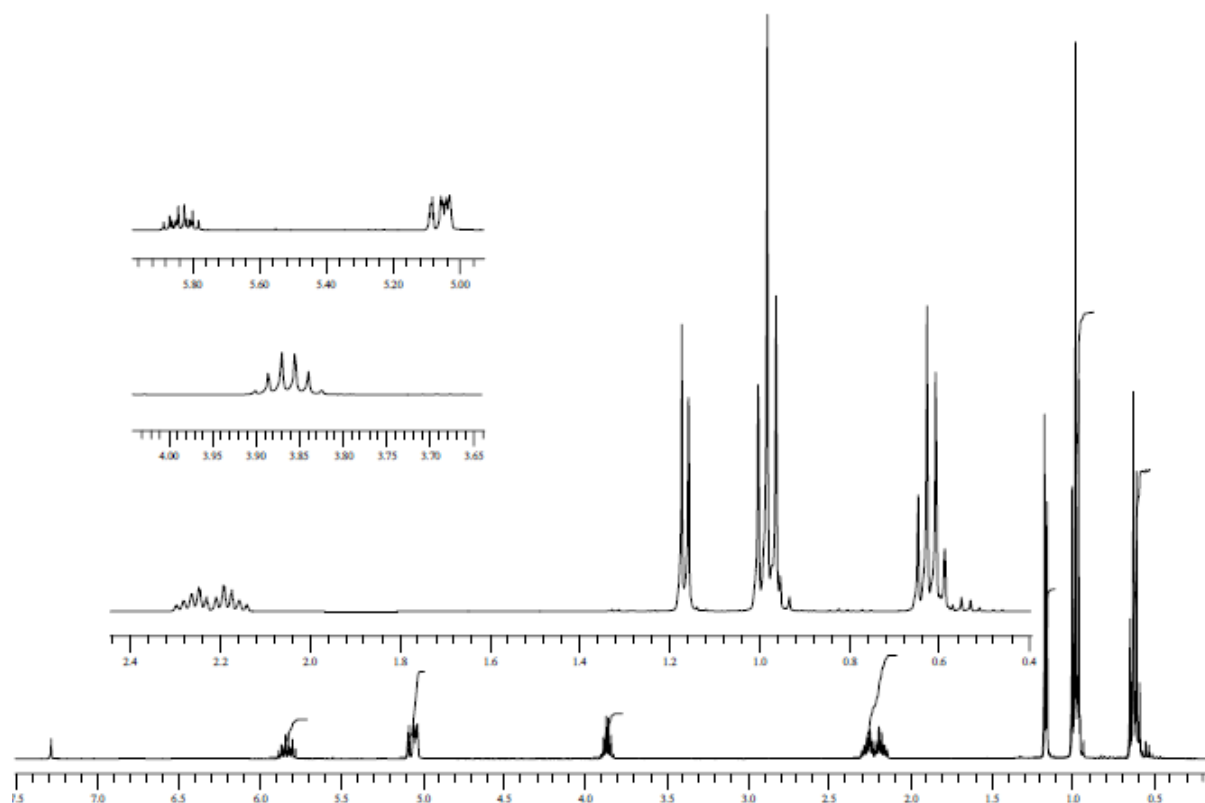


Figure 13. ¹H NMR of [(1-Methyl-3-buten-1-yl)oxy](triethyl)silane (**6f**).



⁷ Lukevits, E. A.; Voronkov, M. G. *Chem. Heterocycl. Compd. (N. Y., NY, U. S.)* **1965**, *1*, 116.

(1,1-Diethylpropoxy)(triethyl)silane (6g)

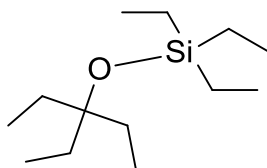
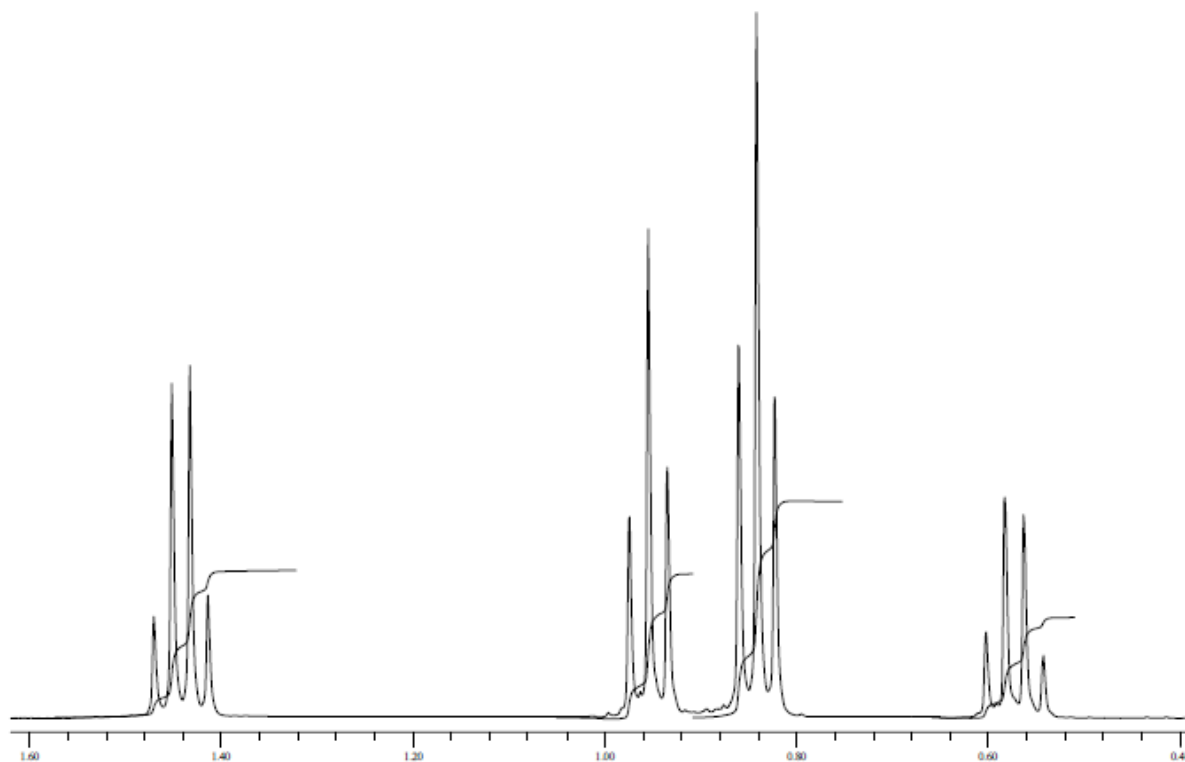


Figure 15. ^1H NMR of (1,1-Diethylpropoxy)(triethyl)silane (**6g**).



2-Furaldehyde *O*-(triethylsilyl)oxime (**6h**)

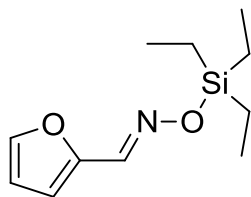
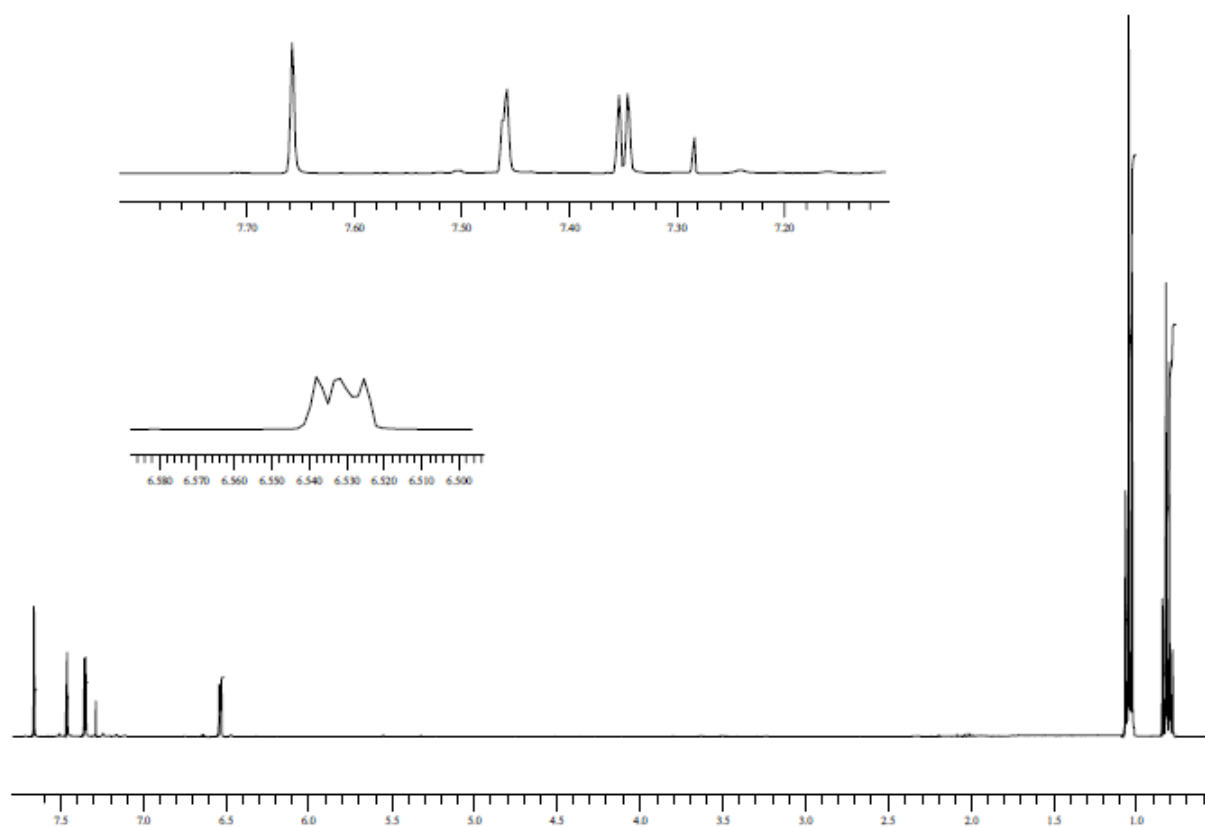


Figure 16. ¹H NMR of [(1-methyl-3-buten-1-yl)oxy](triethyl)silane (**6h**).



1-phenyl-2-[(triethylsilyl)oxy]ethanol (13a)

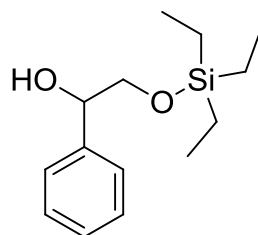
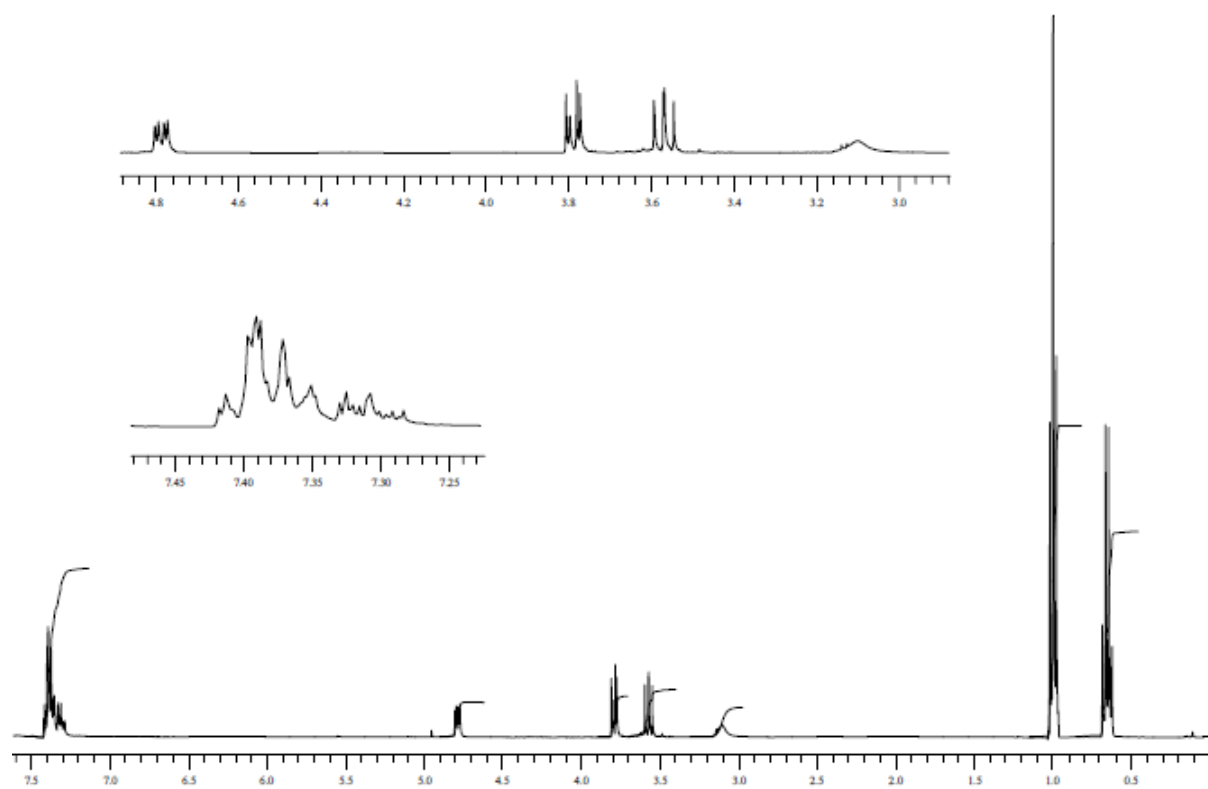


Figure 17. 1-Phenyl-2-[(triethylsilyl)oxy]ethanol (13a).



2-(tert-butyldimethylsilyloxy)-1-phenylethanol (**13b**)

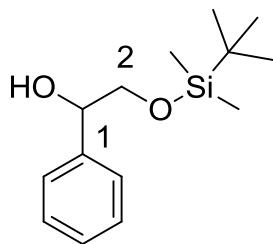
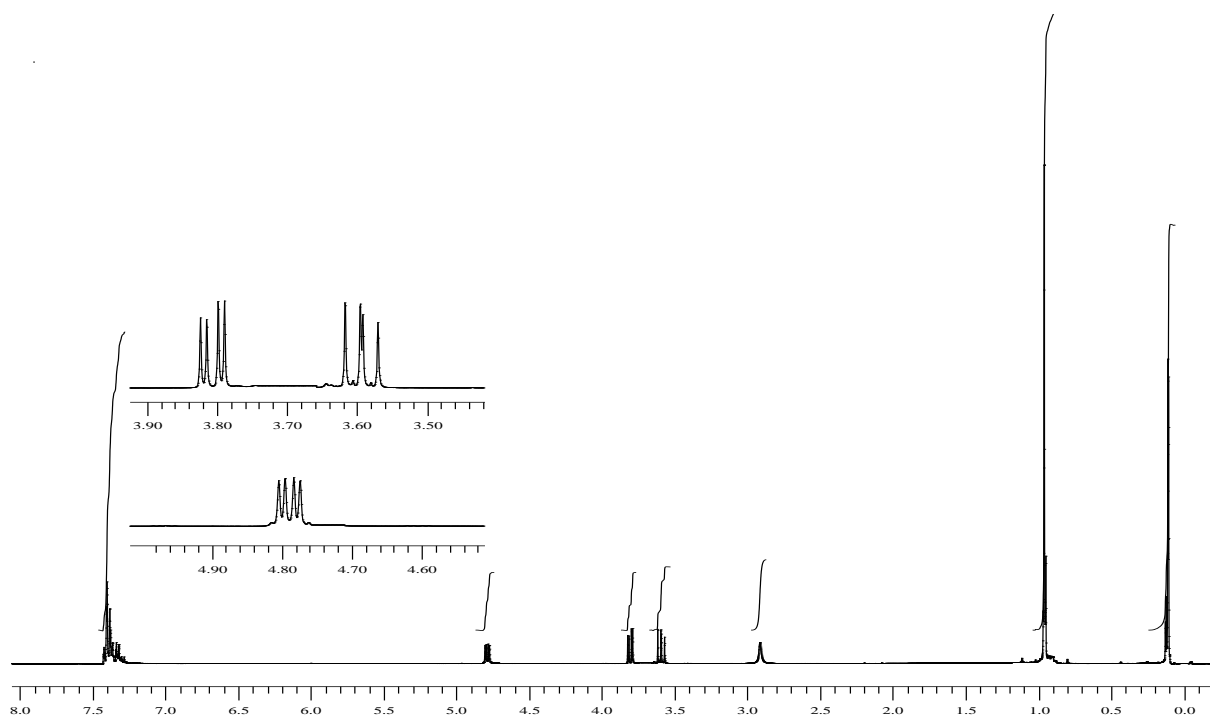


Figure 18. ^1H NMR of 2-(tert-butyldimethylsilyloxy)-1-phenylethanol (**13b**).



1-phenyl-2-(triisopropylsilyloxy)ethanol (**13c**)

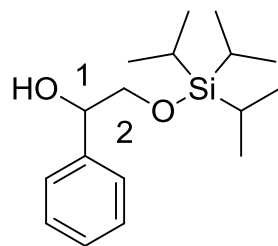


Figure 19. ^1H NMR of 1-phenyl-2-(triisopropylsilyloxy)ethanol (**13c**).

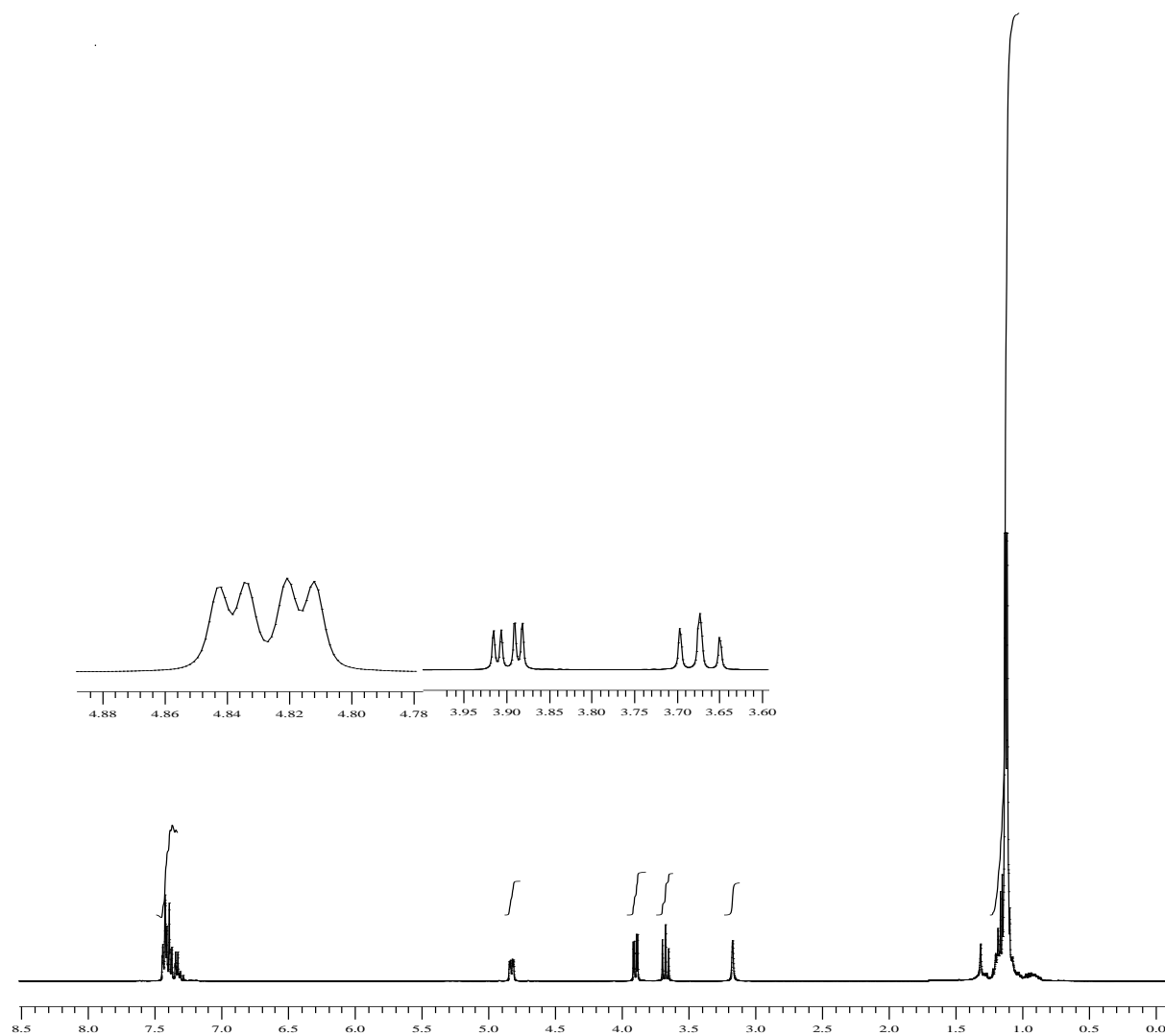
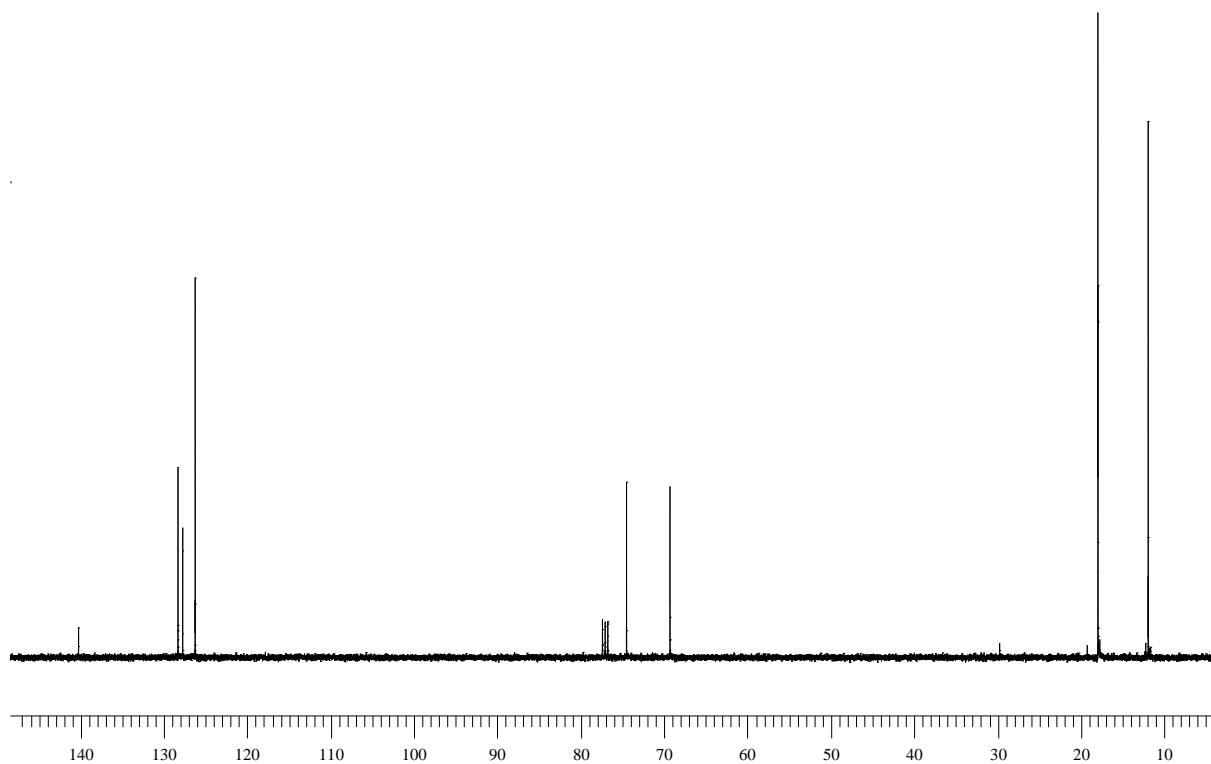


Figure 20. ^{13}C NMR of 1-phenyl-2-(triisopropylsilyloxy)ethanol (**13c**).



Methyl-6-O-(*tert*-butyldimethylsilyl)- α -D-glucopyranoside (**14a**)

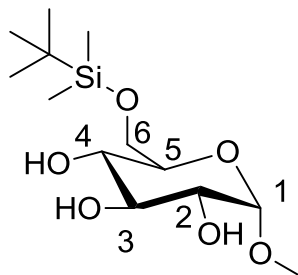


Figure 21. ^1H NMR of Methyl-6-O-(*tert*-butyldimethylsilyl)- α -D-glucopyranoside (**14a**).

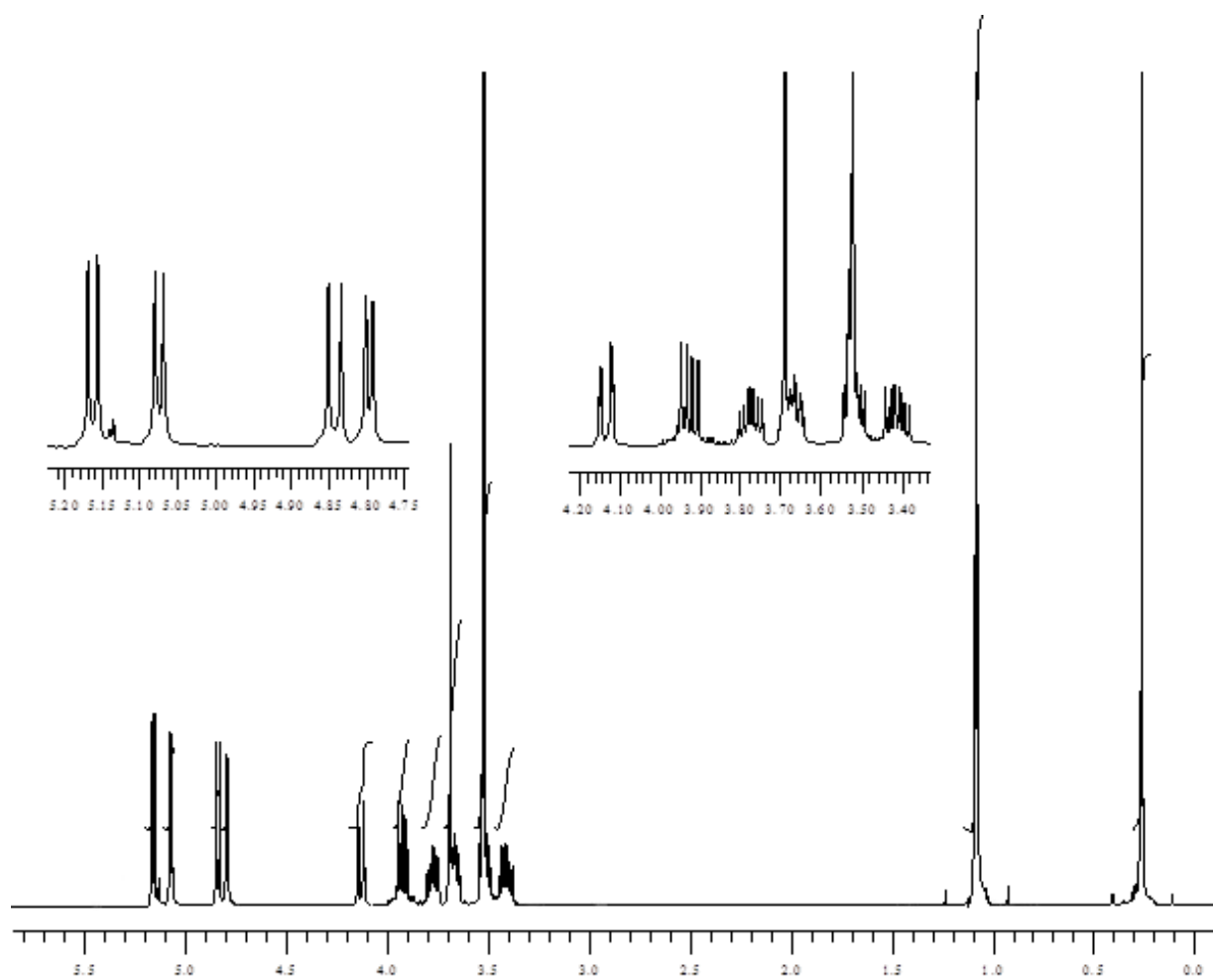


Figure 22. ^{13}C NMR of Methyl-6-O-(*tert*-butyldimethylsilyl)- α -D-glucopyranoside (**14a**)

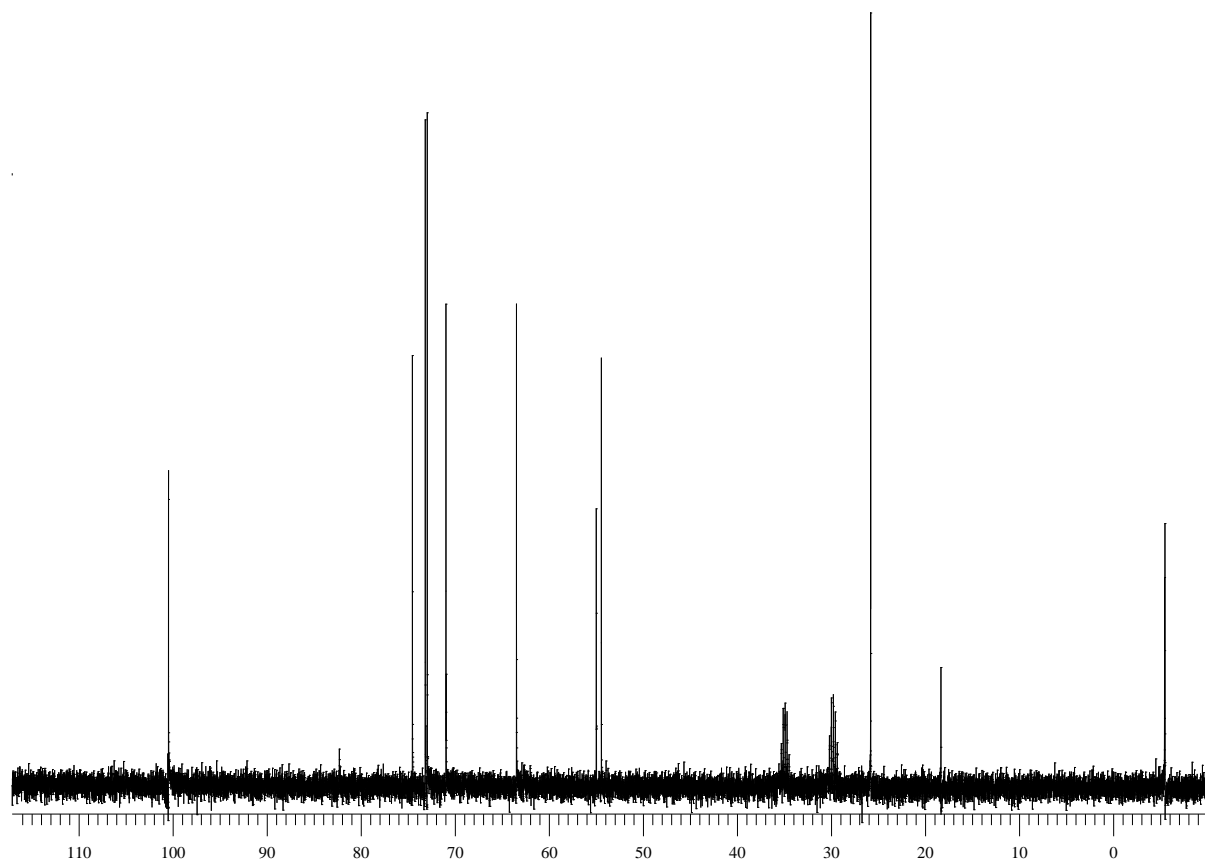
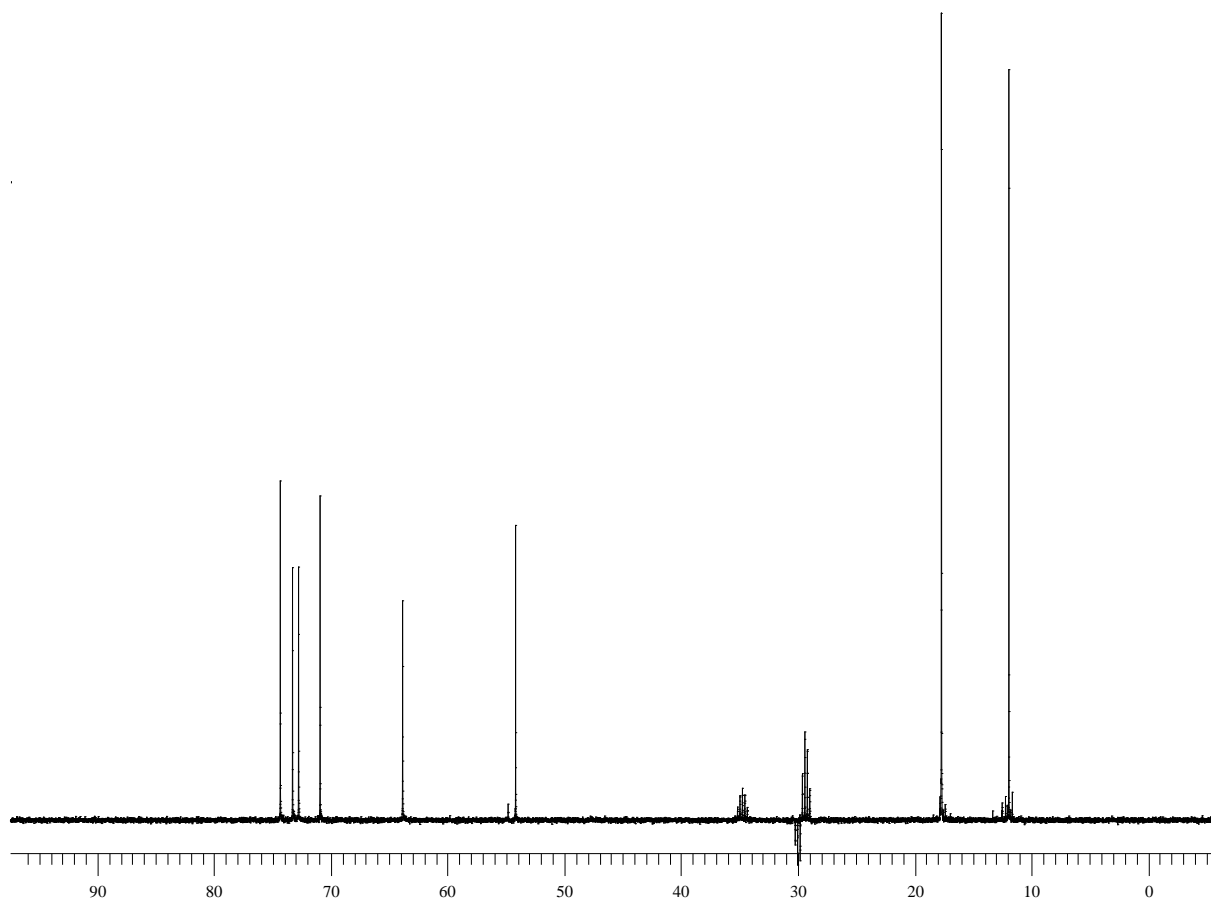


Figure 24. ^{13}C NMR of Methyl-6-O-(triisopropylsilyl)- α -D-glucopyranoside (**14b**).



Methyl-6-O-(triisopropylsilyl)- α -D-mannopyranoside (15)

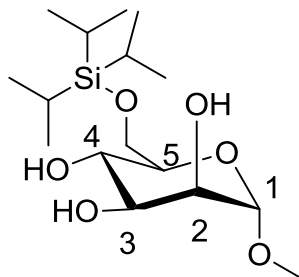


Figure 25. ^1H NMR of Methyl-6-O-(triisopropylsilyl)- α -D-mannopyranoside (15).

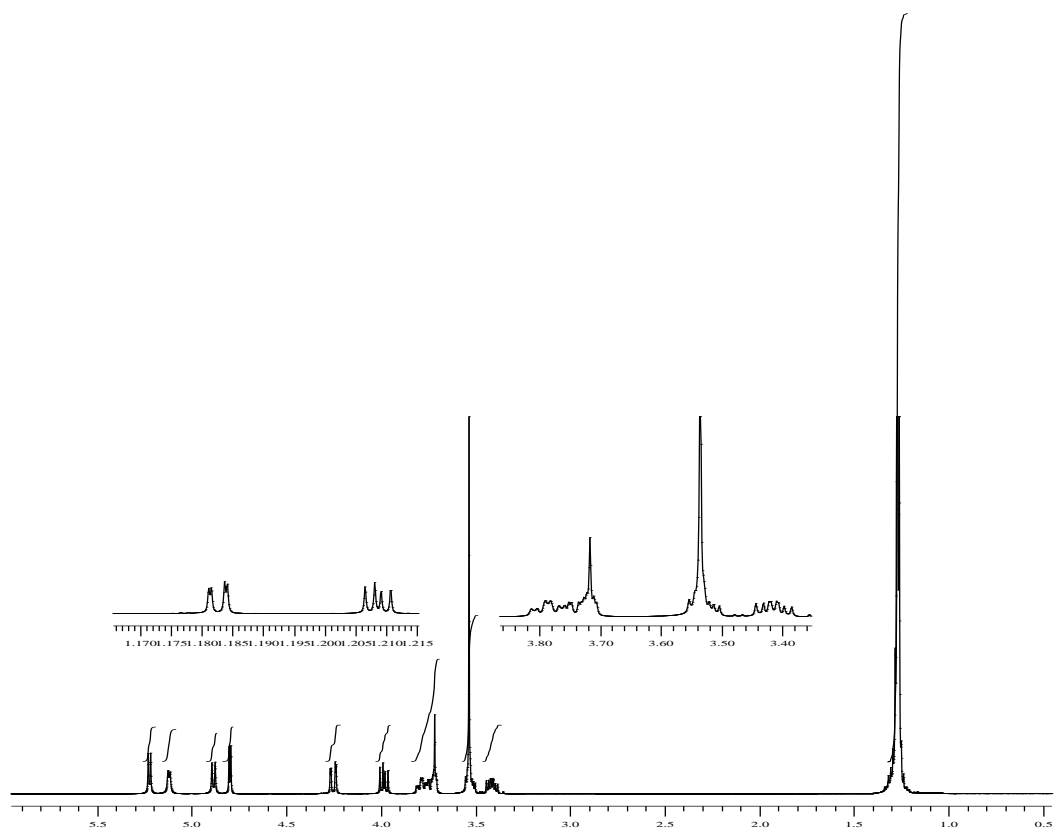
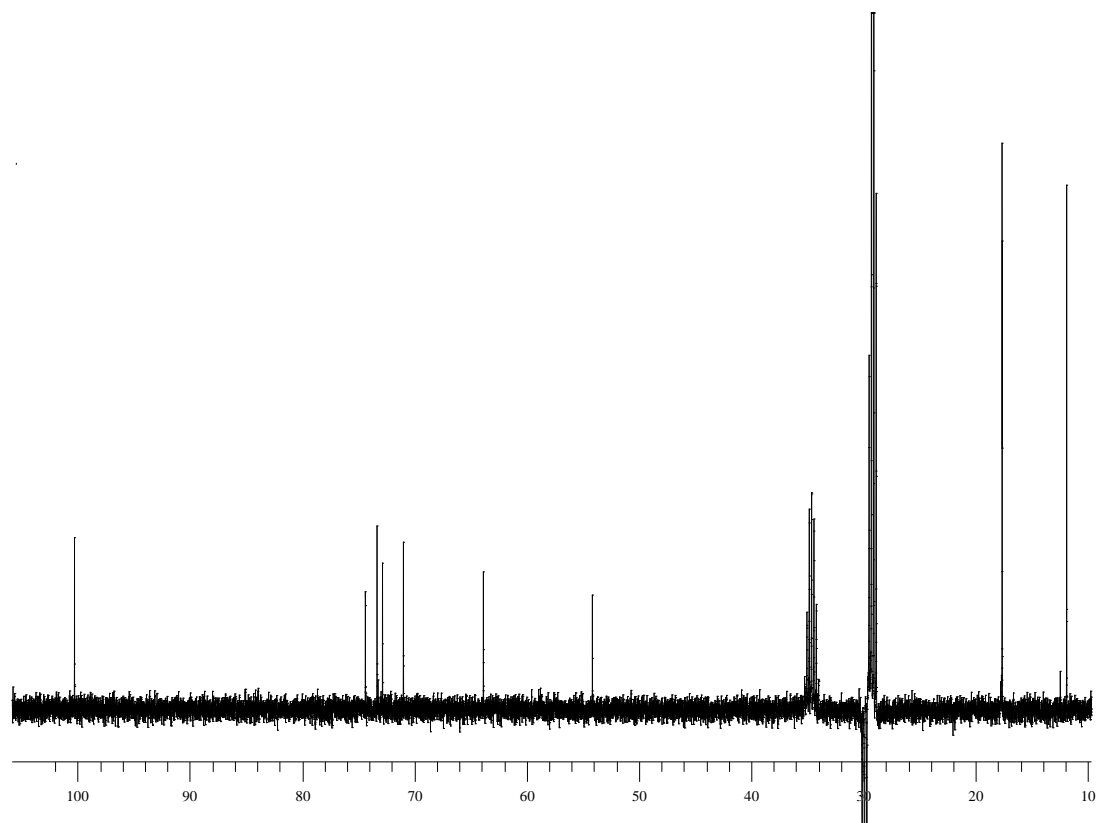


Figure 26. ^{13}C NMR of Methyl-6-O-(triisopropylsilyl)- α -D-mannopyranoside (**15**).



Methyl-6-O-(triisopropylsilyl)- α -D-galactopyranoside (16)

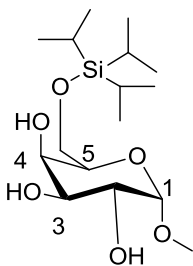


Figure 27. ^1H NMR of Methyl-6-O-(triisopropylsilyl)- α -D-galactopyranoside (16).

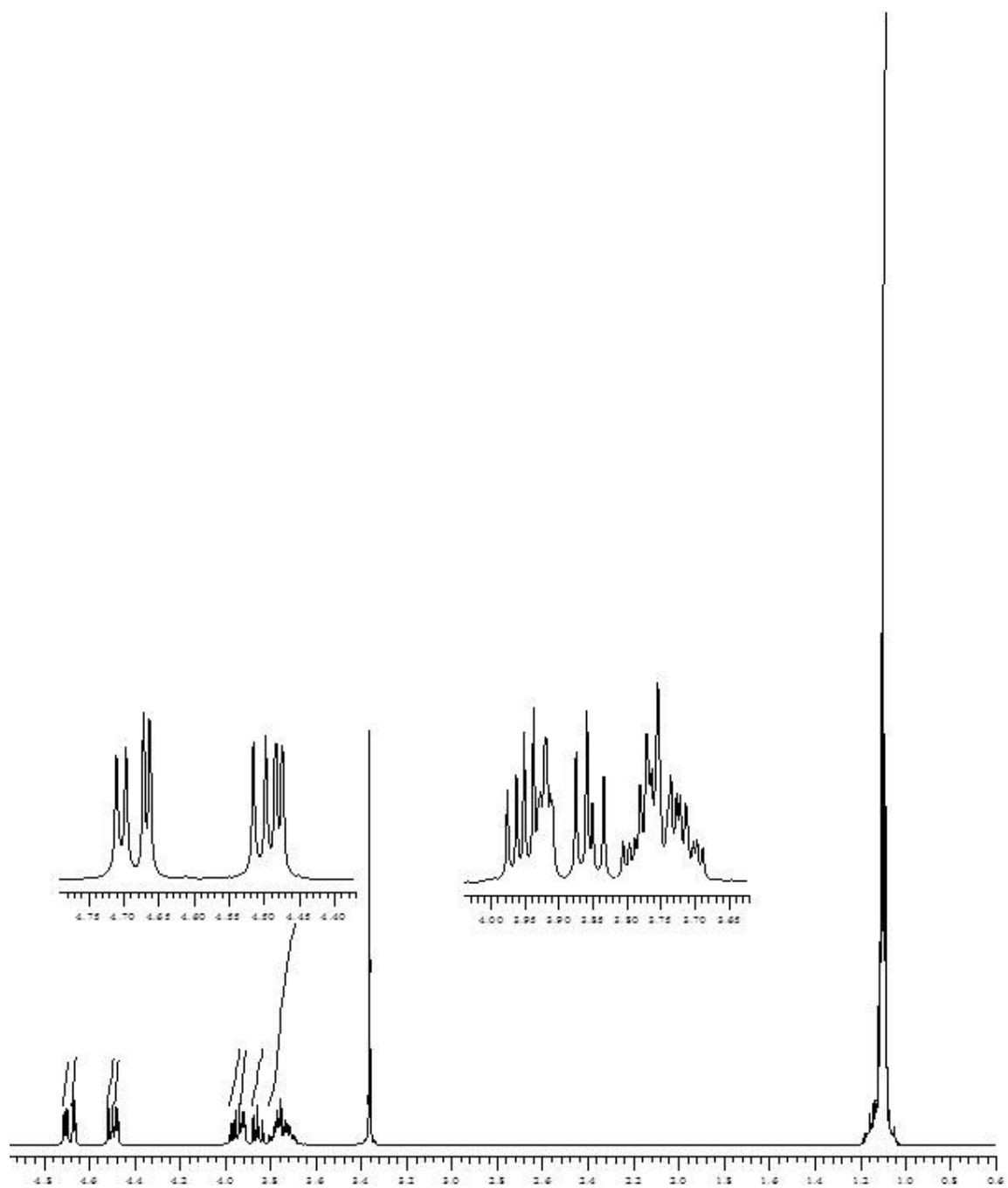
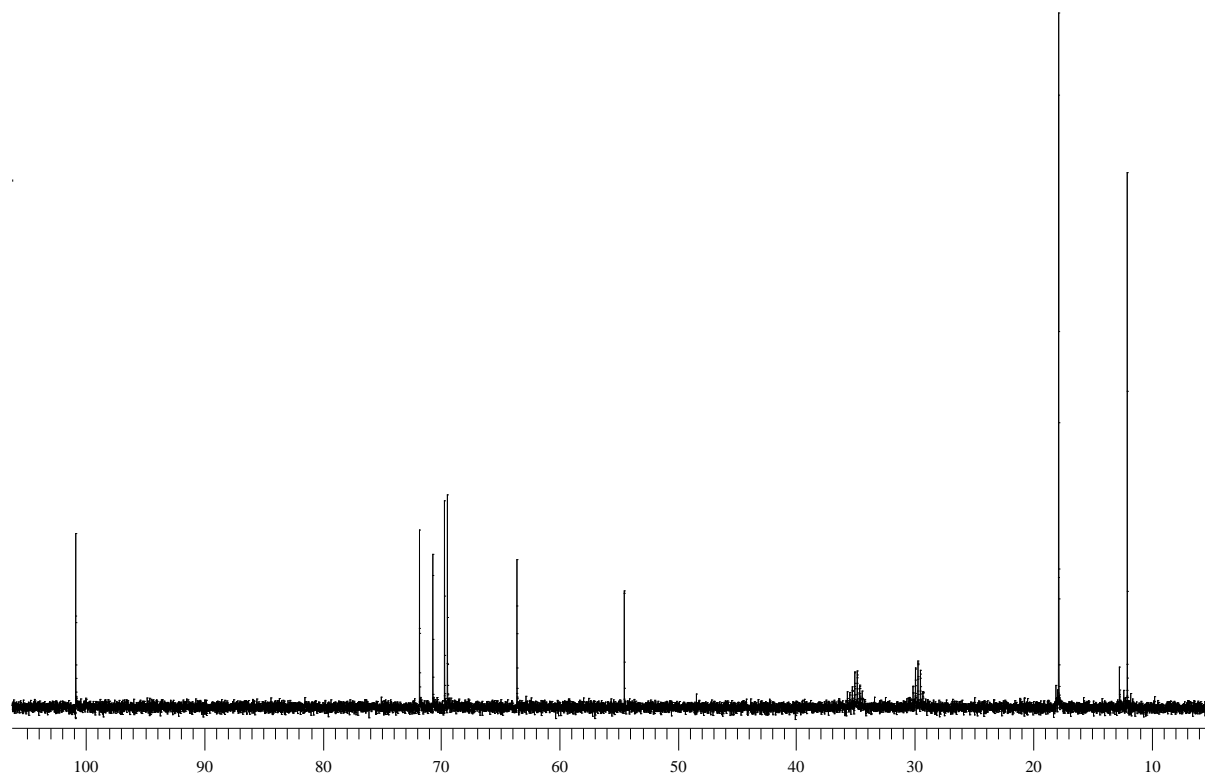


Figure 28. ^{13}C NMR of Methyl-6-O-(triisopropylsilyl)- α -D-galactopyranoside (**16**).



3-O-(*tert*-butyldimethylsilyl)-6-O-(*tert*-butyldimethylsilyl)-D-Glucal (**17a**)

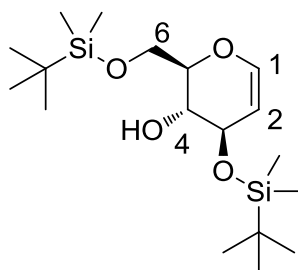


Figure 29. ^1H NMR of 3-O-(*tert*-butyldimethylsilyl)-6-O-(*tert*-butyldimethylsilyl)-D-Glucal (**17a**).

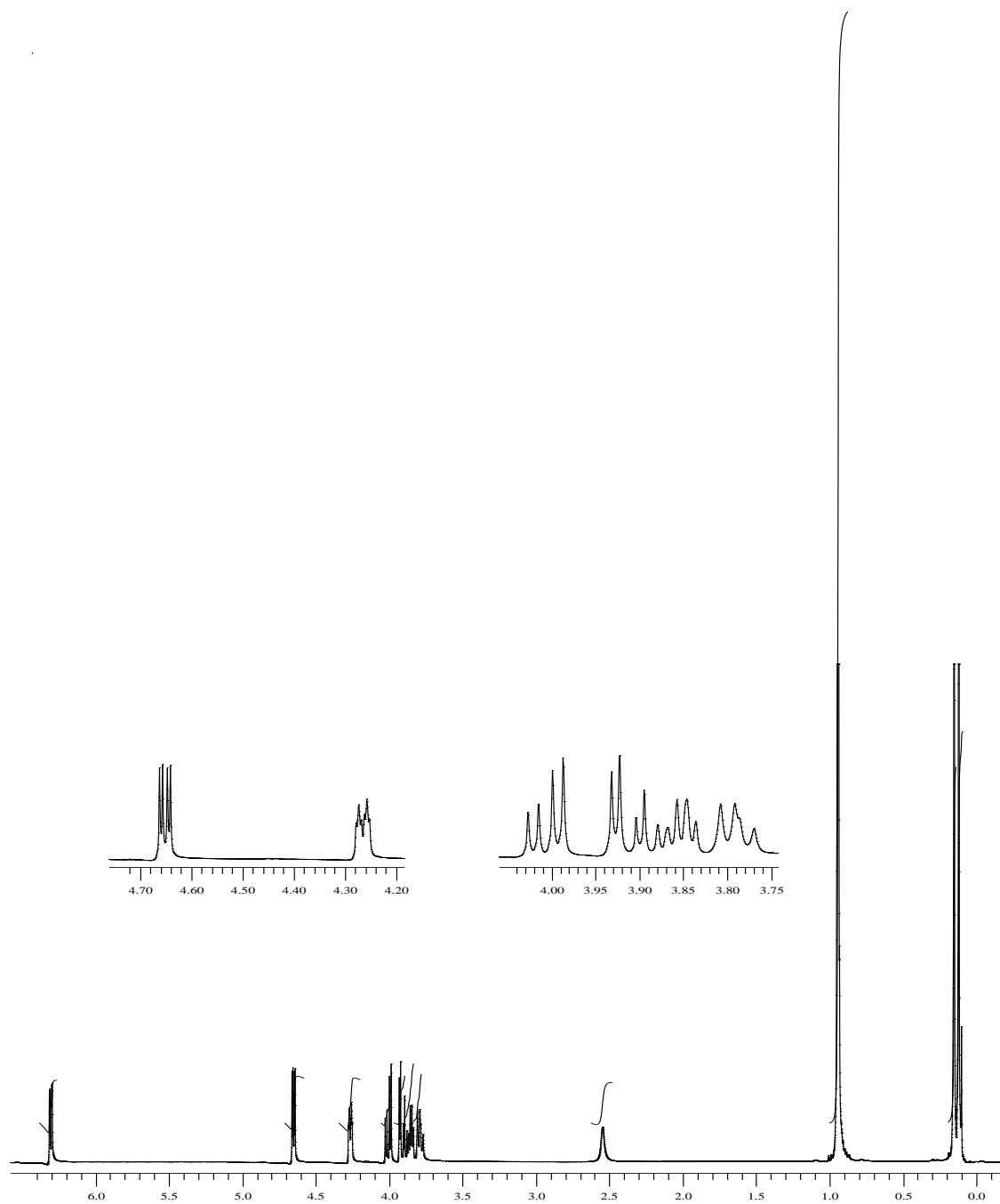
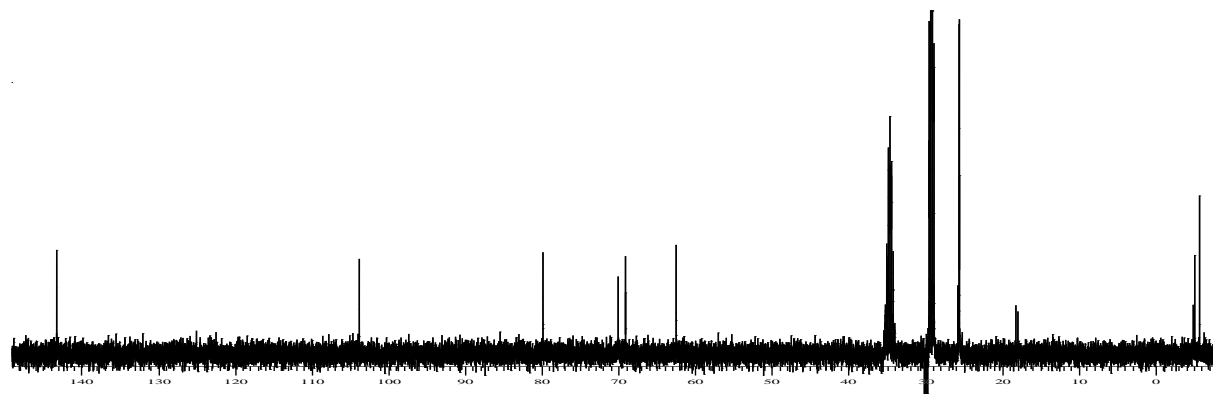


Figure 30. ^{13}C NMR of 3-O-(*tert*-butyldimethylsilyl)-6-O-(*tert*-butyldimethylsilyl)-D-Glucal (**17a**).



6-O-(triisopropylsilyl)-D-Glucal (17b)

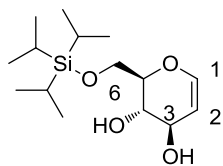


Figure 31. ^1H NMR of 6-O-(*tert*-butyldimethylsilyl)-D-Glucal (**17b**).

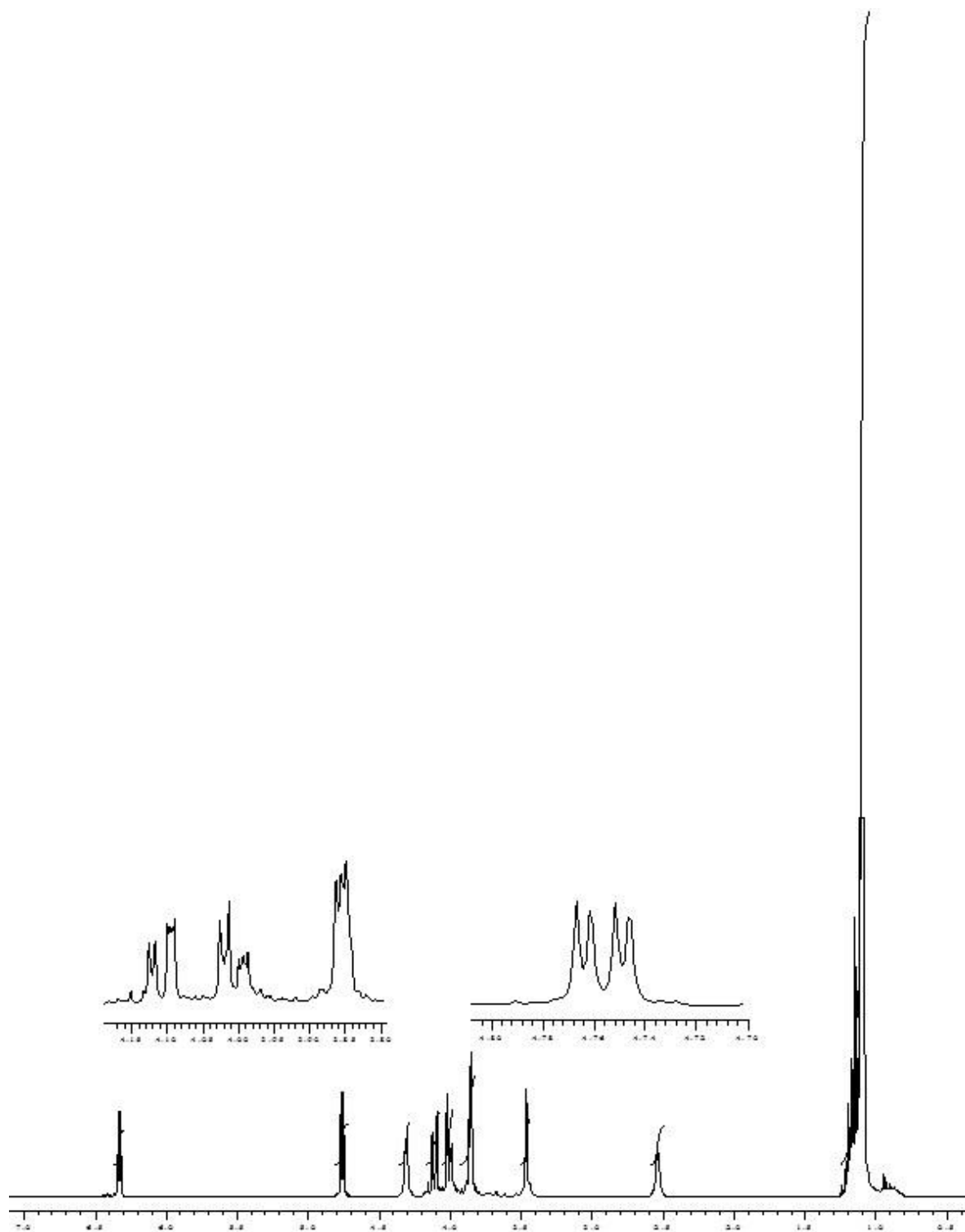
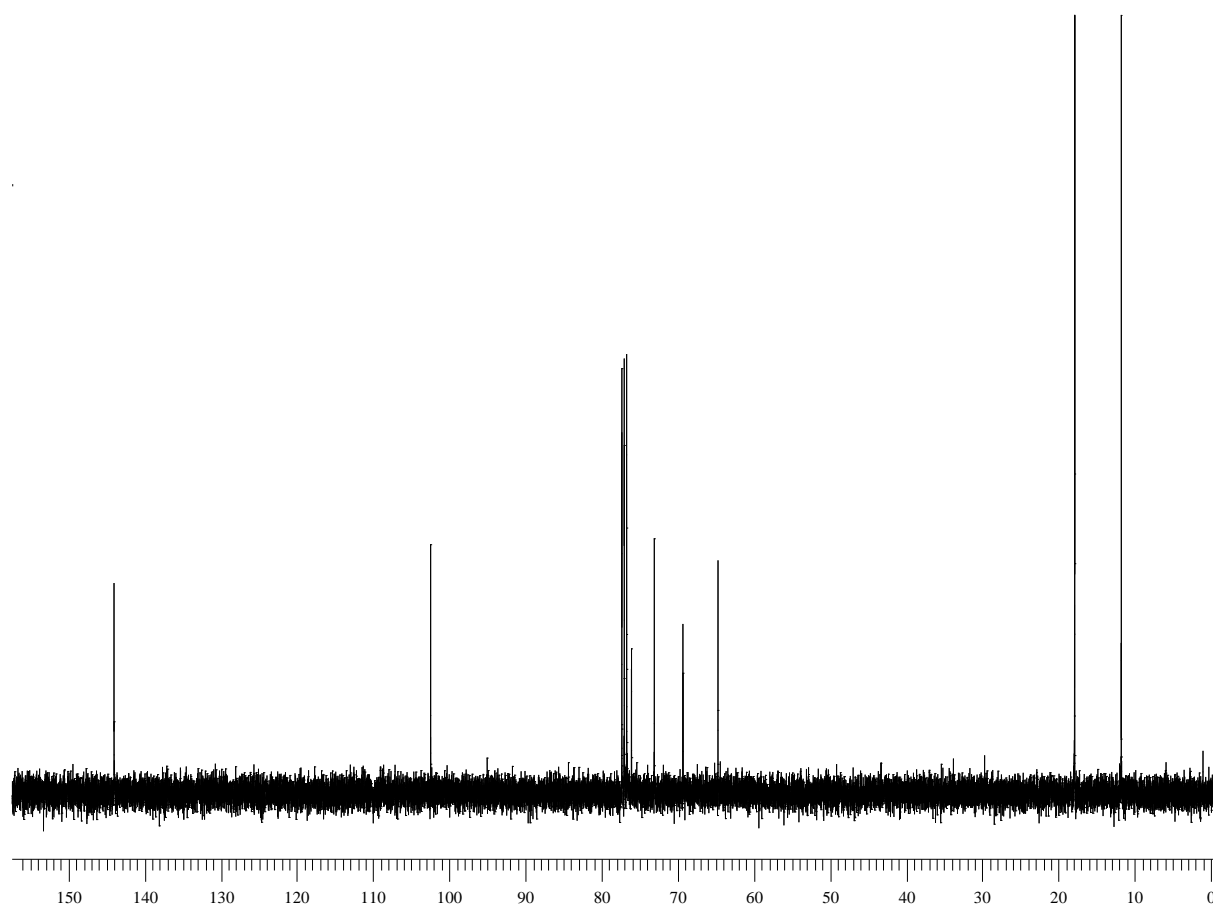


Figure 32. ^{13}C NMR of 6-O-(*tert*-butyldimethylsilyl)-D-Glucal (**17b**).



(+)-Methyl 4,6-O-Benzylidene-2-O-(*tert*-butyldimethylsilyl)- α -D-glucopyranoside (**18a**)

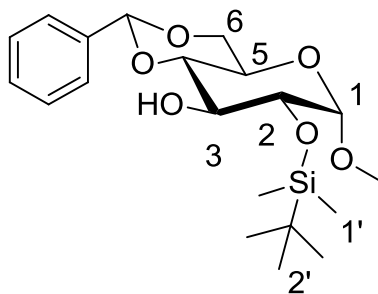


Figure 33. ^1H NMR of (+)-methyl 4,6-O-benzylidene-2-O-(*tert*-butyldimethylsilyl)- α -D-glucopyranoside (**18a**).

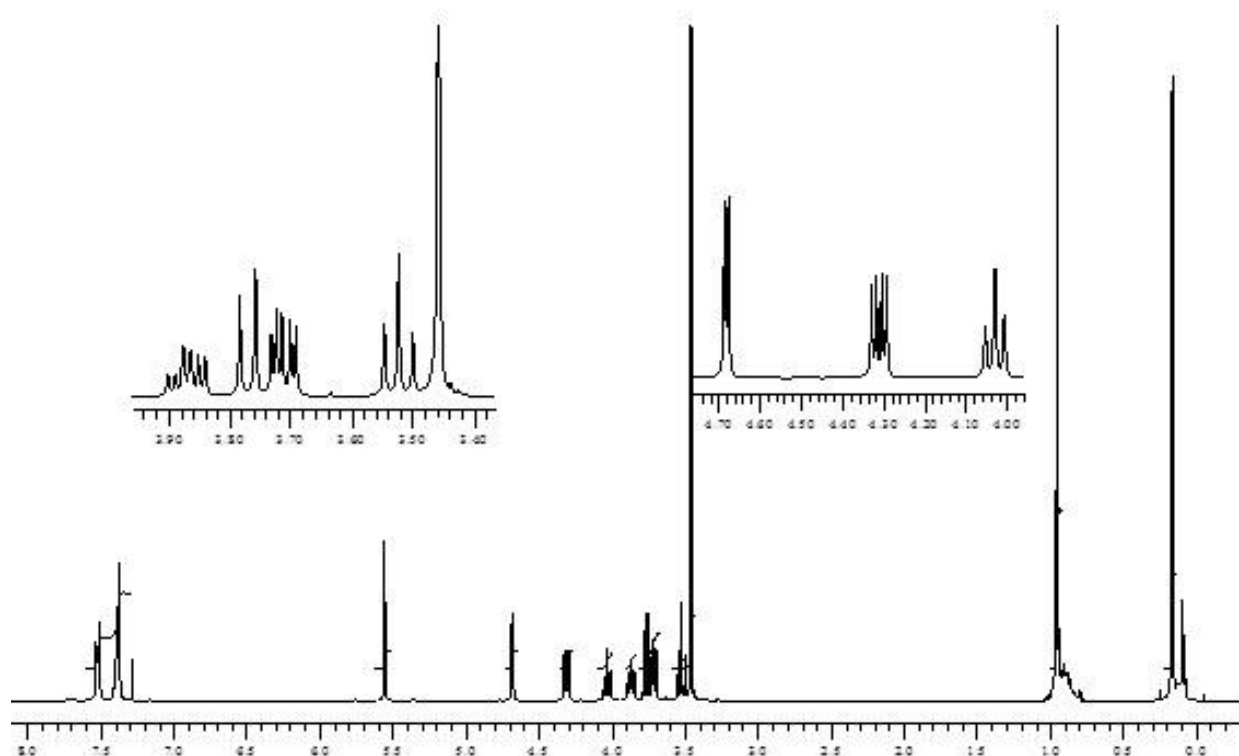
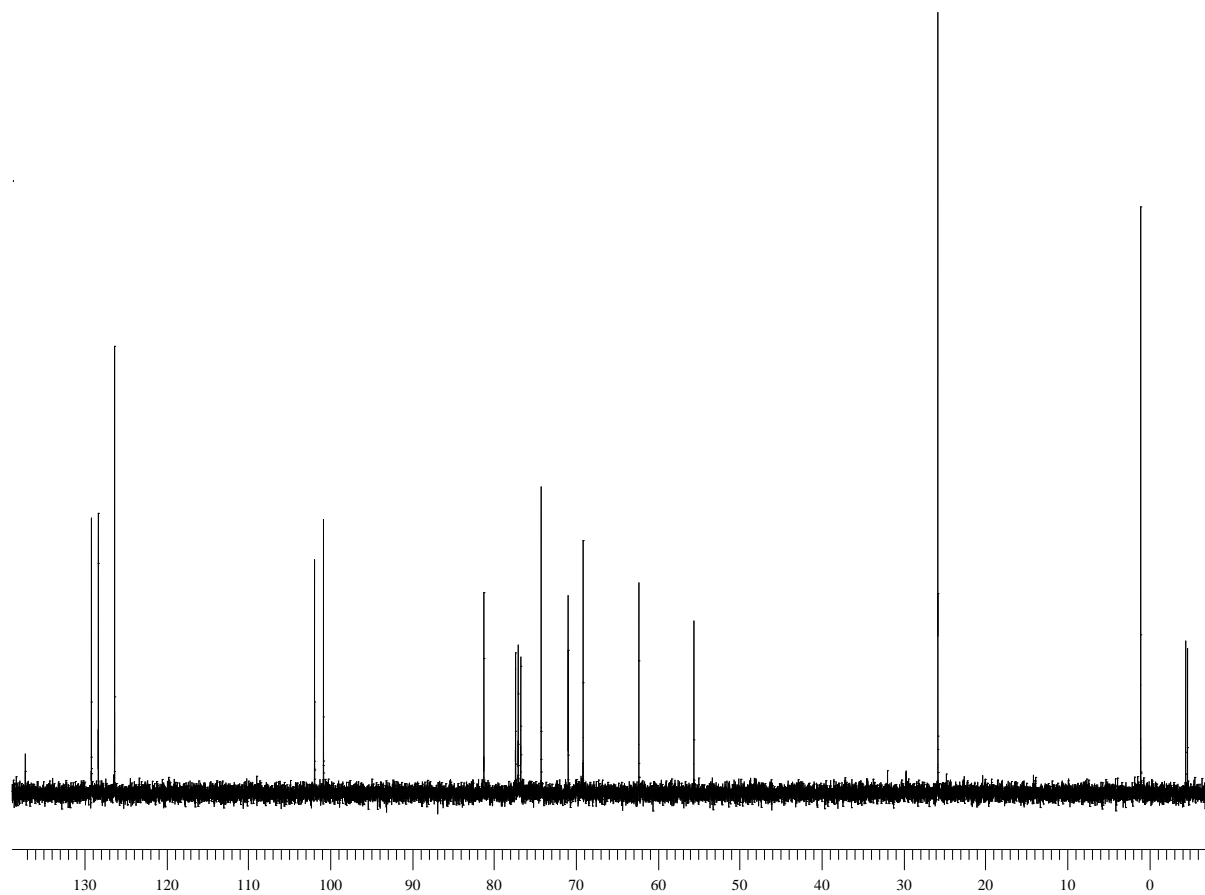


Figure 34. ^{13}C NMR of (+)-methyl 4,6-O-benzylidene-2-O-(*tert*-butyldimethylsilyl)- α -D-glucopyranoside (**18a**).



Methyl 4,6-O-Benzylidene-2-O-(trimethylsilyl)- α -D-glucopyranoside (18b)

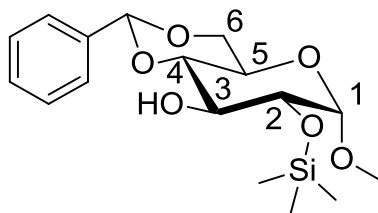


Figure 35. ^1H NMR of methyl 4,6-O-benzylidene-2-O-(trimethylsilyl)- α -D-glucopyranoside (**18b**).

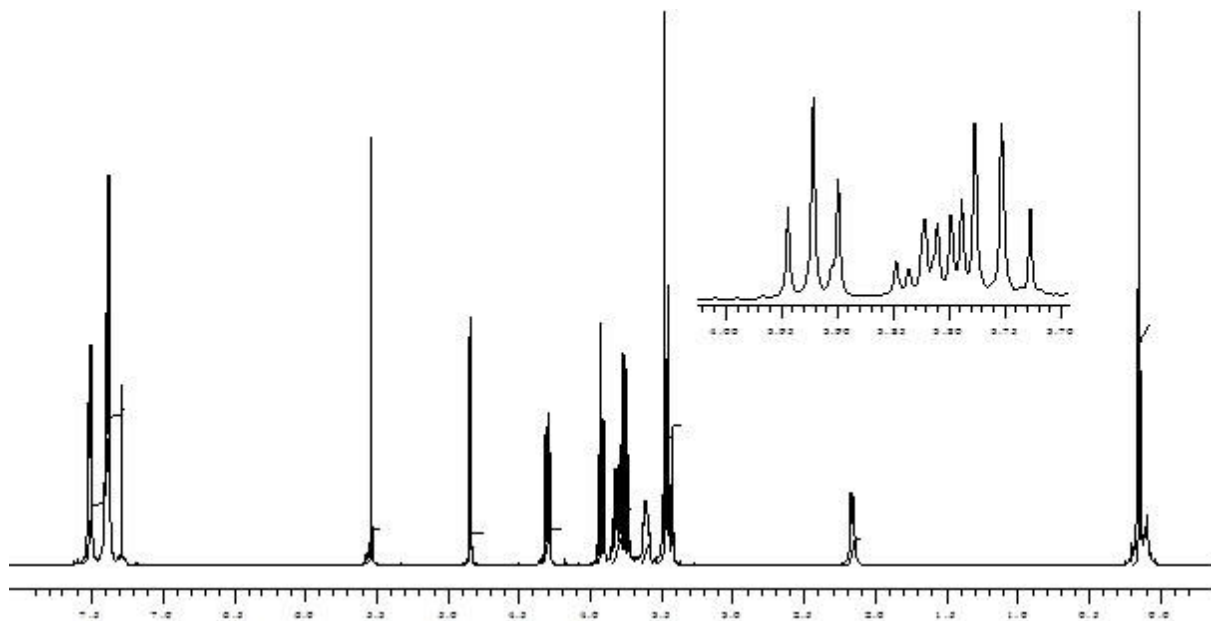


Figure 36. ^{13}C NMR of methyl 4,6-O-benzylidene-2-O-(trimethylsilyl)- α -D-glucopyranoside (**18b**).

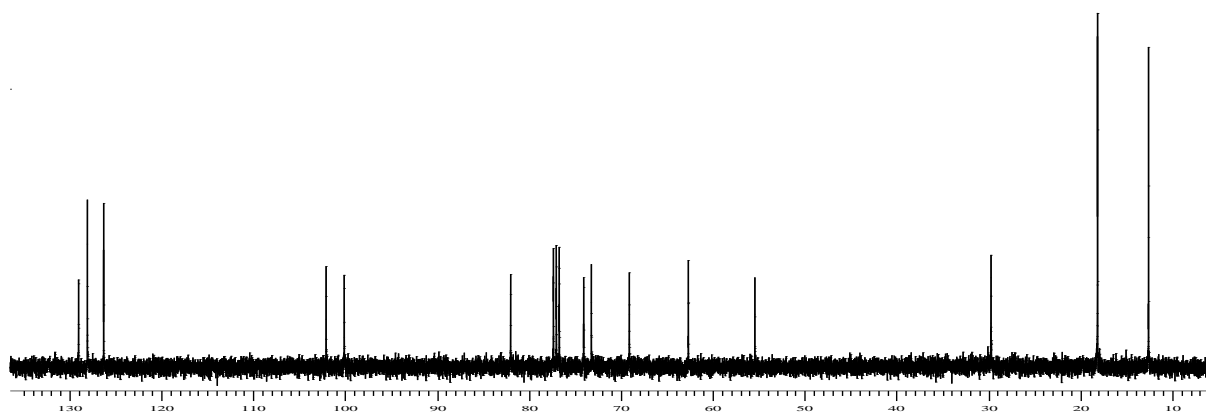
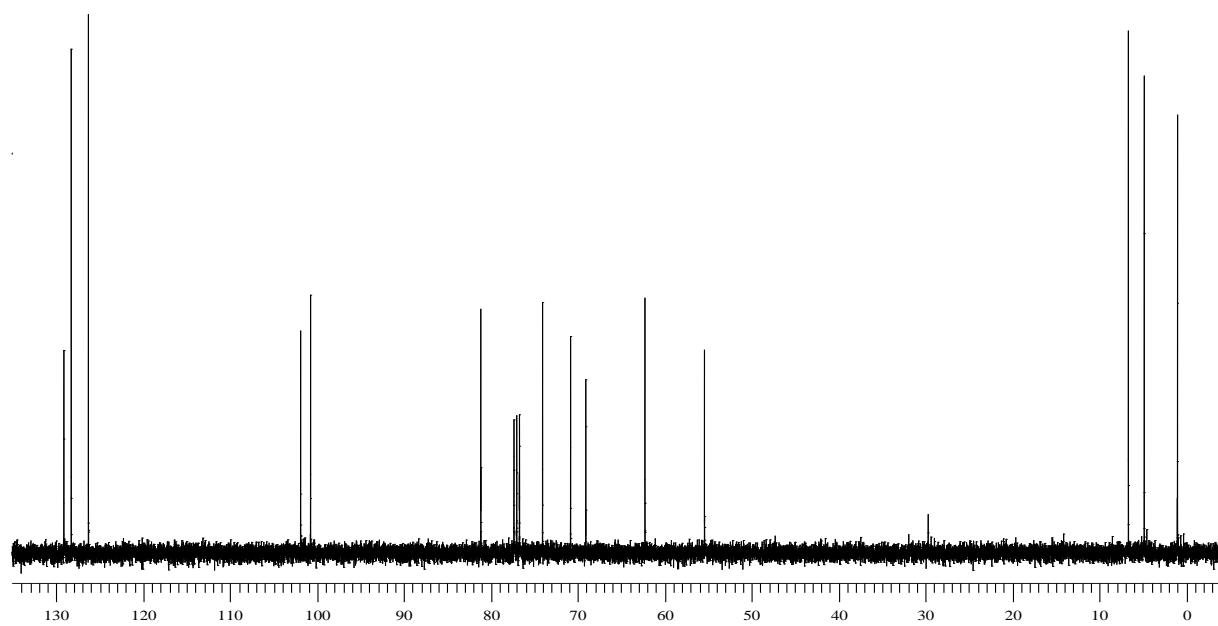


Figure 38. ^{13}C NMR of methyl 4,6-O-benzylidene-2-O-(triethylsilyl)- α -D-glucopyranoside (**18c**).



Methyl 4,6-O-benzylidene-2-O-(triisopropylsilyl)- α -D-glucopyranoside (18d)

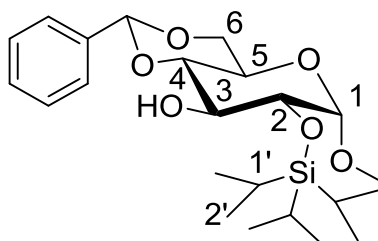


Figure 39. ^1H NMR of Methyl 4,6-O-Benzylidene-2-O-(triisopropylsilyl)- α -D-glucopyranoside (**18d**).

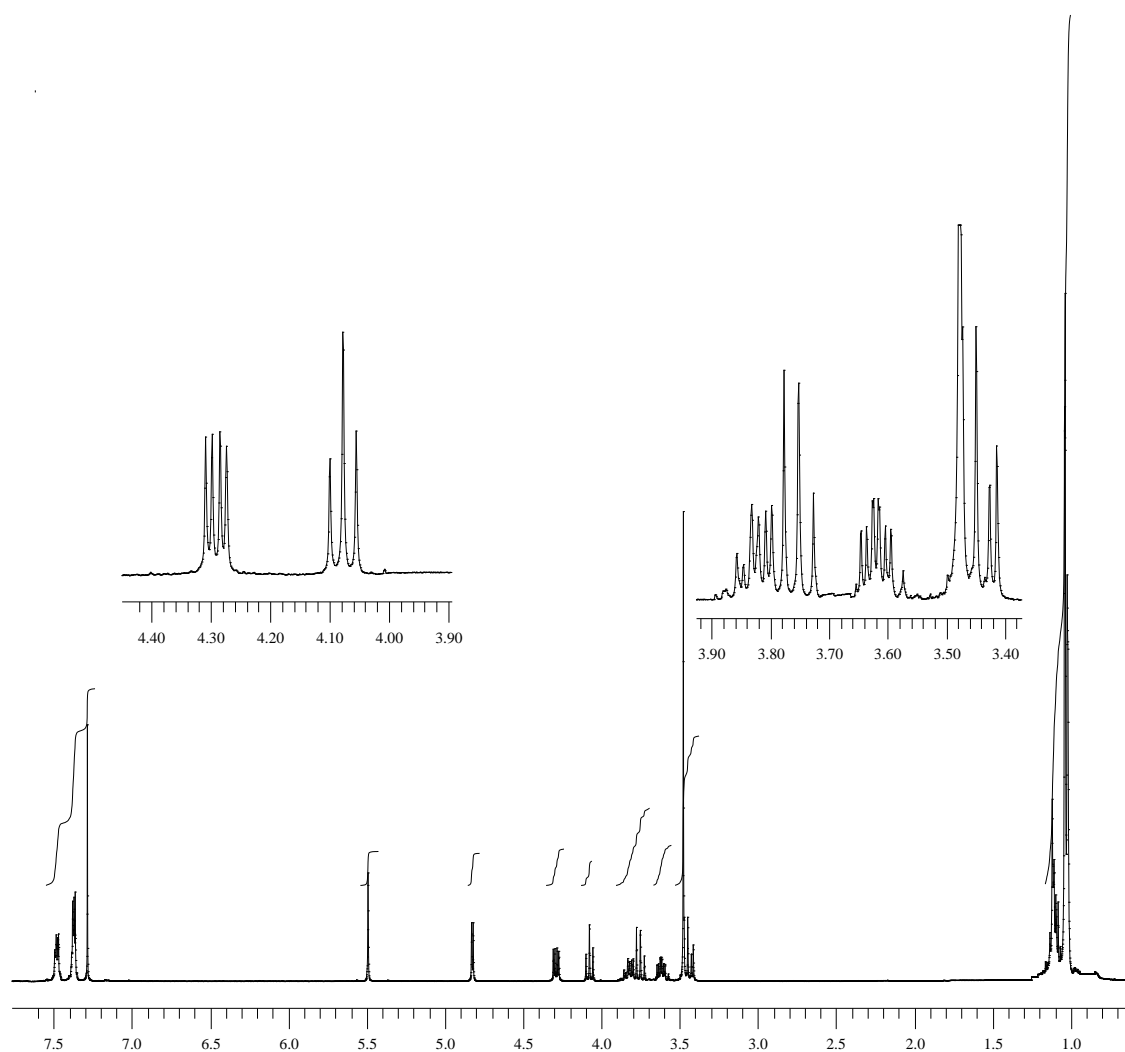
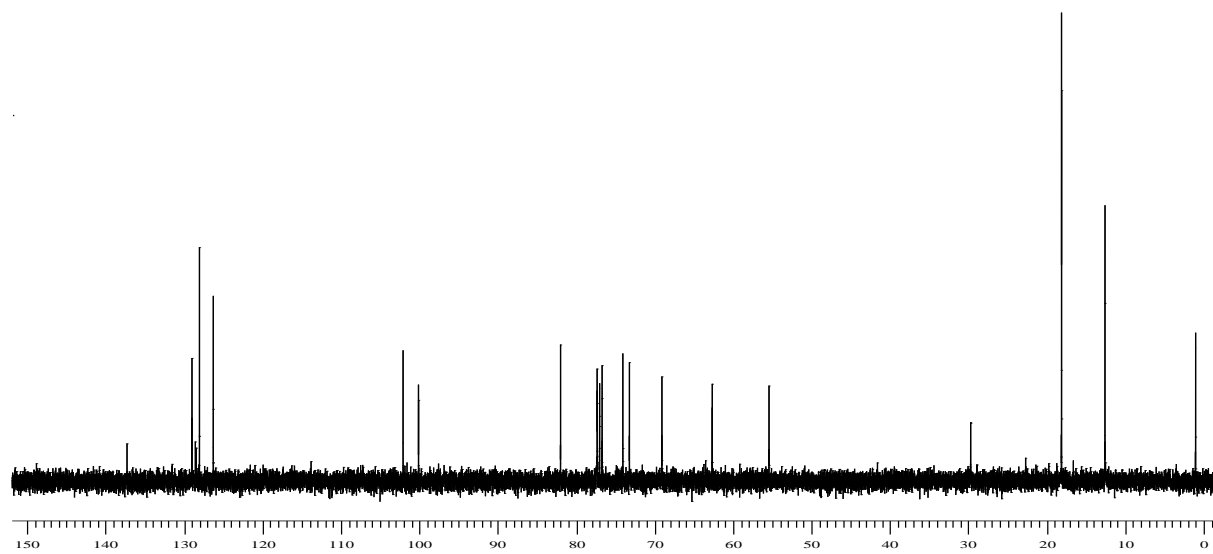


Figure 40. ^{13}C NMR of Methyl 4,6-O-Benzylidene-2-O-(triisopropylsilyl)- α -D-glucopyranoside (**18d**).



(-)-(1Z,2S,3S,4R,5E)-1-ethylidene-2,4,6-trimethyl-7-oxo-3-((1S)-1-phenylethoxy)hept-5-en-1-yl 2-methylpropanoate (20)

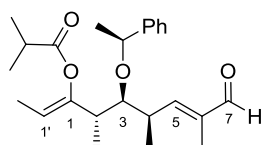


Figure 41. $^1\text{H-NMR}$ of (-)-20 (400 MHz, CDCl_3):

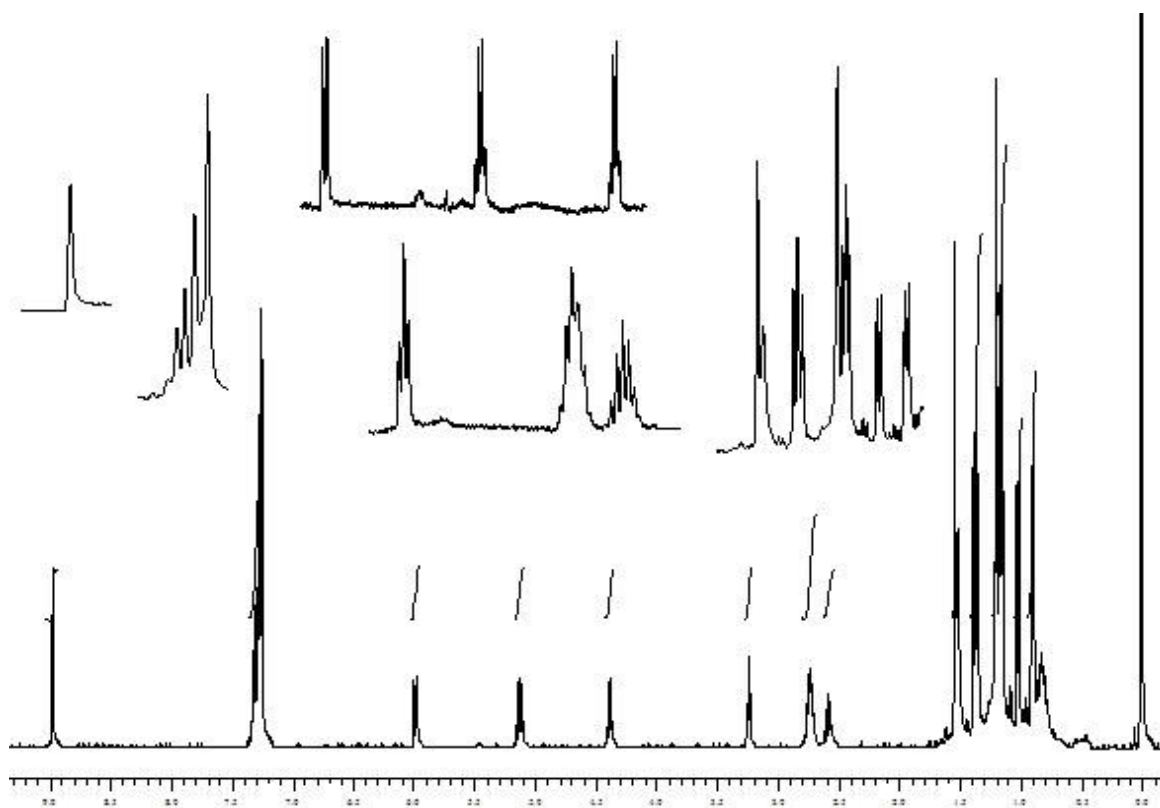
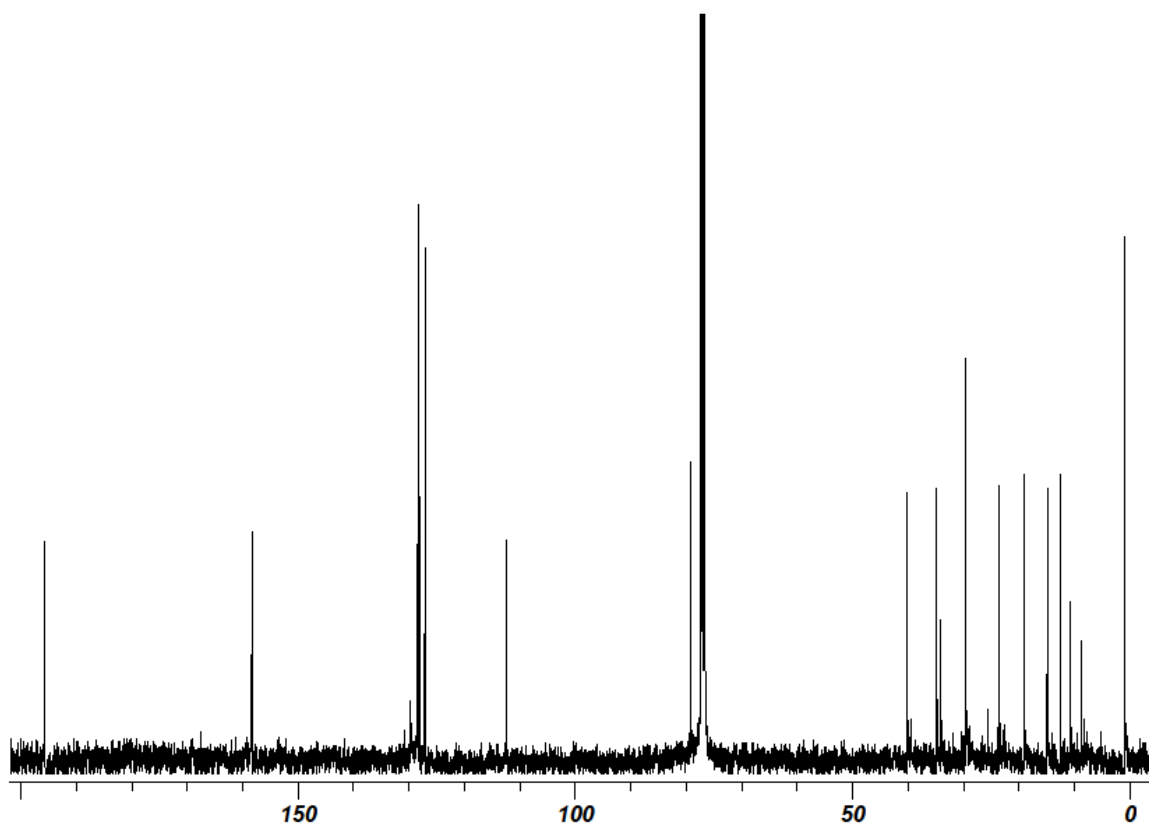


Figure 42 ^{13}C -NMR of 20 (CDCl_3 , 100.6 MHz):



(+)-(1Z,2S,3S,4S,5S,6S)-5-((tert-butyl(dimethyl)silyl)oxy)-1-ethylidene-2,4,6-trimethyl-7-oxo-3-((1S)-1-phenylethoxy)heptyl 2-methylpropanoate (21)

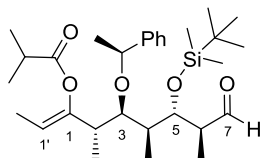


Figure 43. ¹H-NMR of 21 (400 MHz, CDCl₃):

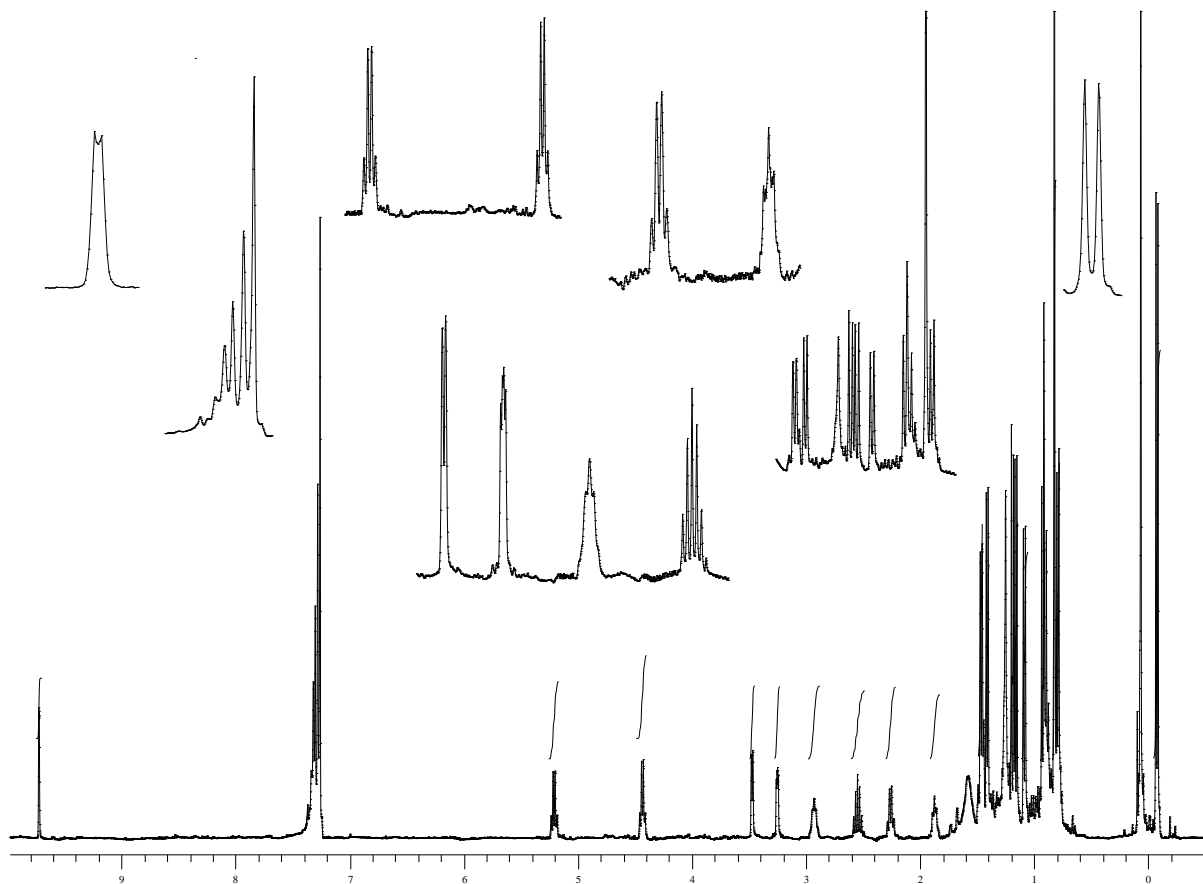
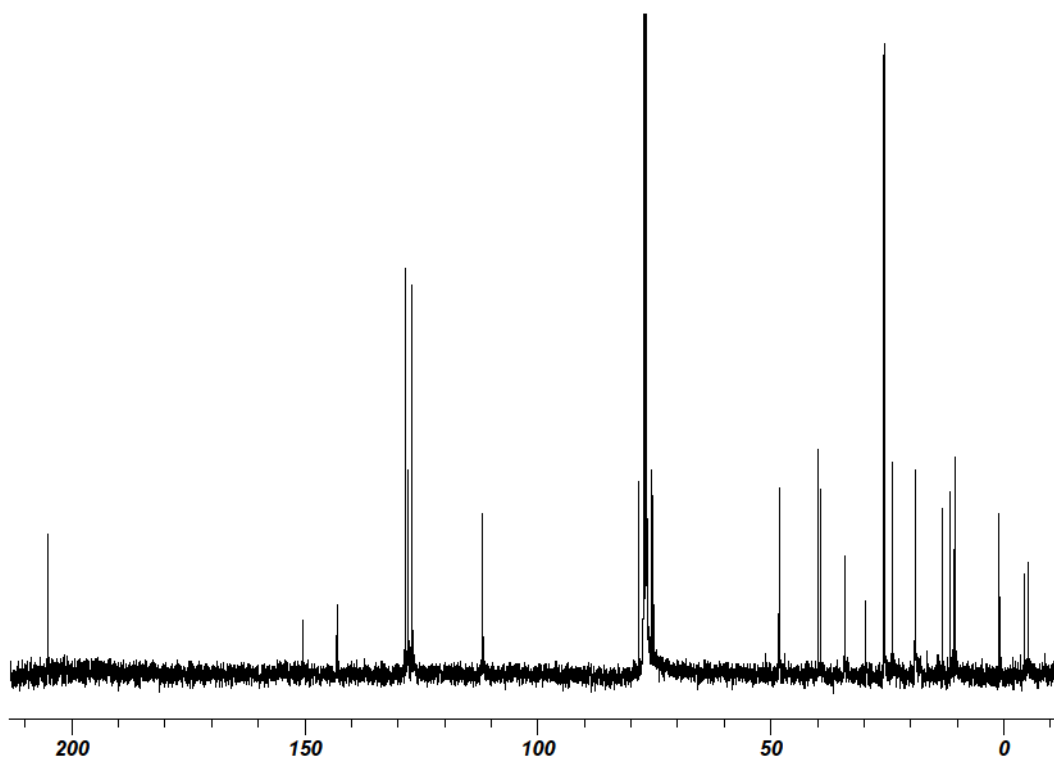


Figure 44. ^{13}C -NMR of 21 (CDCl_3 , 100.6 MHz):



1,2,3,4,6-Penta-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranose (23a)

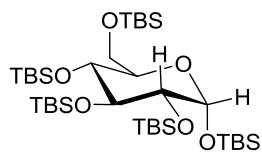


Figure 45. $^1\text{H-NMR}$ (300 MHz, $\text{CD}_3\text{CN}+\text{CDCl}_3$) spectrum of **23a**.

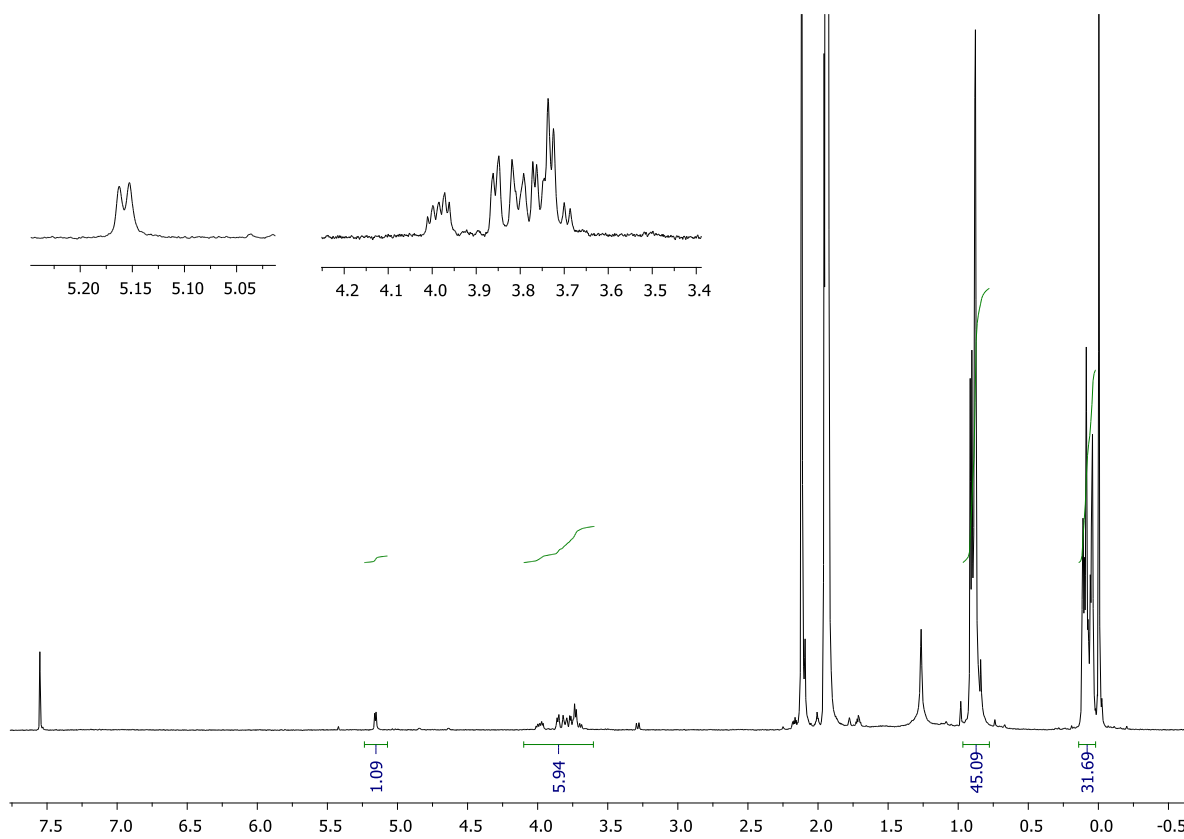
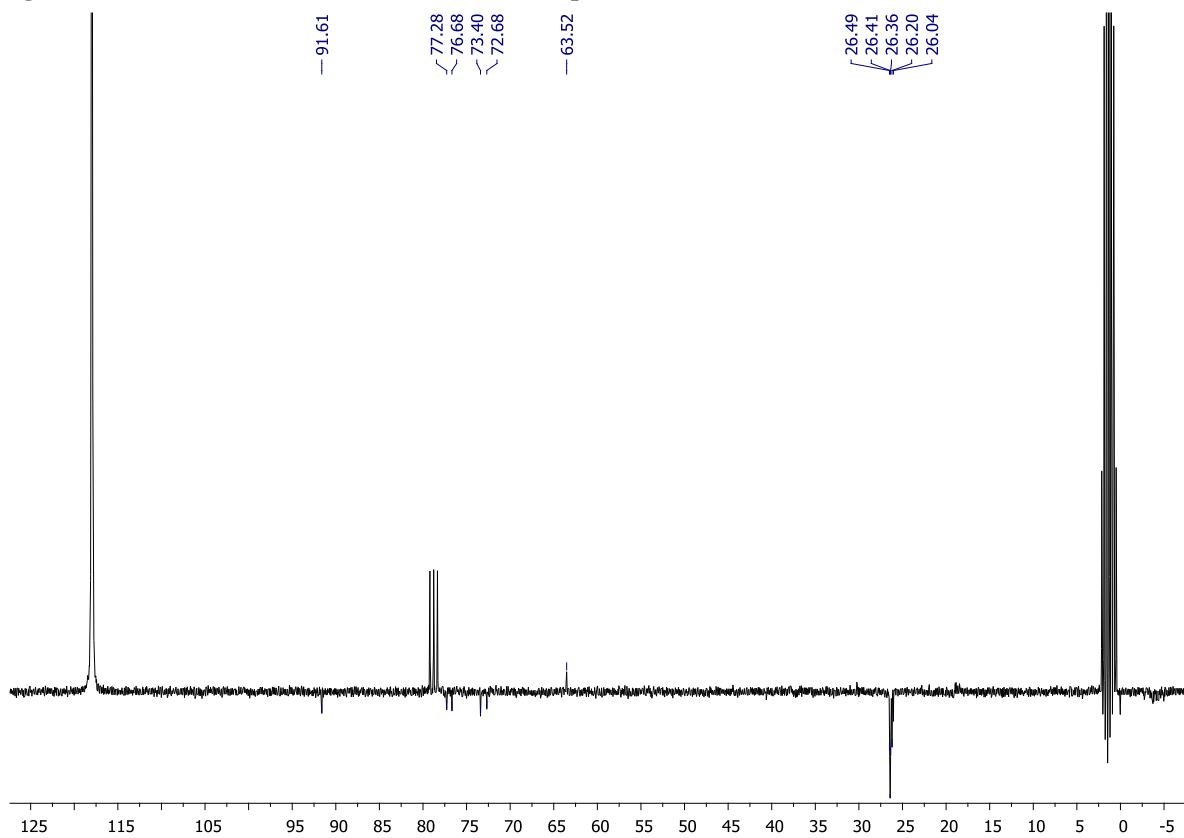


Figure 46. ^{13}C -NMR (75.5 MHz, $\text{CD}_3\text{CN}+\text{CDCl}_3$) spectrum of 23a:



Crystal data for 23a

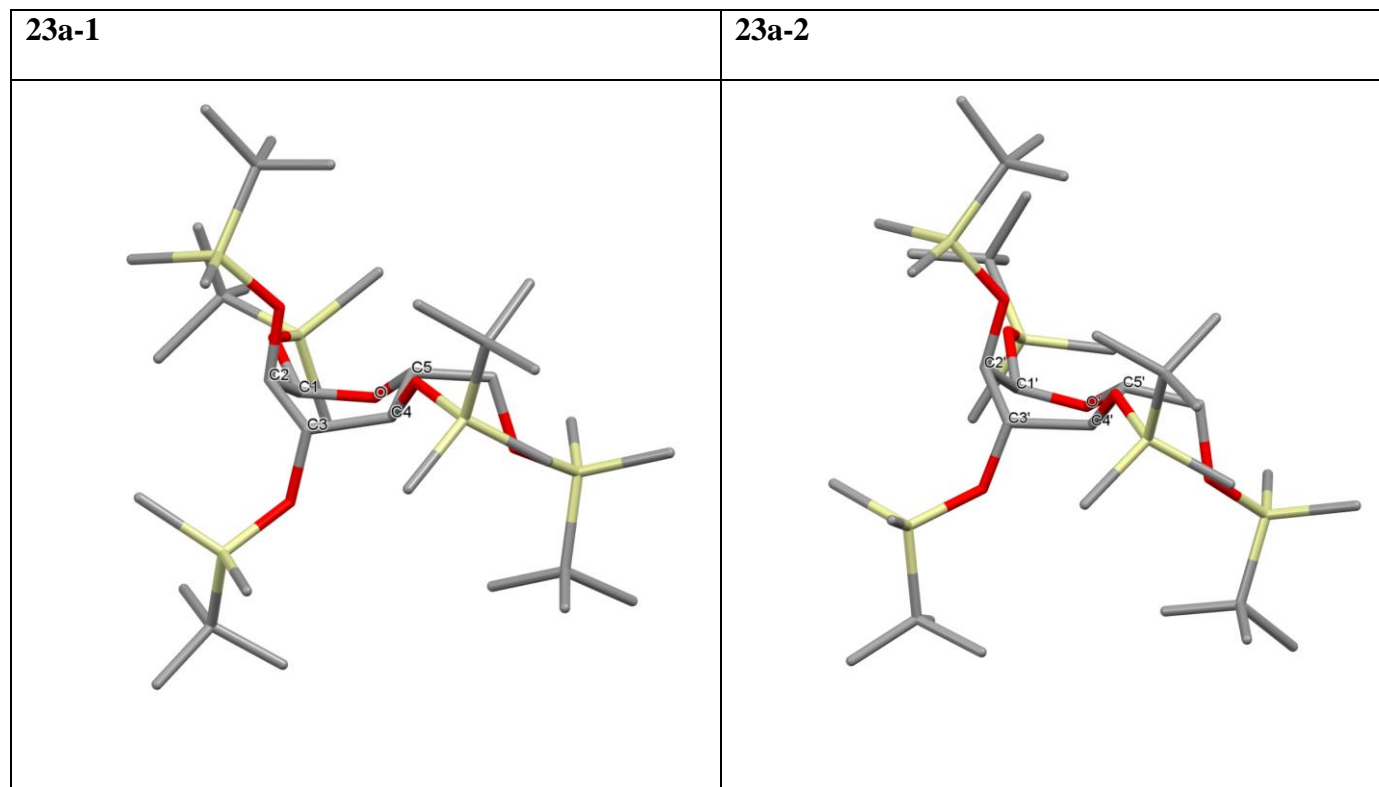
Crystal data for (**23a**) (C₃₆H₈₂O₆Si₅) (*M* = 751.47), monoclinic, *P*2₁, *a* = 12.1077(1), *b* = 36.4878(5), *c* = 12.1834(3) Å, *β* = 112.7115(8)°, *V* = 4965.07(15) Å³, *T* = 173(2) K, *Z* = 4, *μ*(MoKα) = 0.178 mm⁻¹, 21172 reflections measured, 21172 independent reflections, *R*_{1(obs)} = 0.093, *wR*_{1(obs)} = 0.191, *R*_{1(all)} = 0.233, *wR*_{1(all)} = 0.244, *S* = 1.01

CCDC-1421584 (**23a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected bond distances and angles for conformers **23a-1** and **23a-2**.

| 23a-1 (Å / °) | | 23a-2 (Å / °) | |
|----------------------|----------|----------------------|----------|
| C1–O1 | 1.39(1) | C1'–O6 | 1.41(1) |
| C2–O2 | 1.41(1) | C2'–O7 | 1.40(1) |
| C3–O3 | 1.42(1) | C3'–O8 | 1.39(1) |
| C4–O4 | 1.42(1) | C4'–O9 | 1.43(1) |
| C6–O5 | 1.39(1) | C6'–O10 | 1.43(1) |
| Si–O | | | |
| C1–O1–Si1 | 120.3(6) | C1'–O6–Si6 | 122.1(6) |
| C2–O2–Si2 | 125.7(6) | C2'–O7–Si10 | 124.6(6) |
| C3–O3–Si3 | 127.4(6) | C3'–O8–Si9 | 129.6(6) |
| C4–O4–Si4 | 126.5(5) | C4'–O9–Si8 | 124.0(5) |
| C6–O5–Si5 | 125.3(6) | C6'–O10–Si7 | 125.2(6) |
| Si1–O1 | 1.705(7) | Si6–O6 | 1.670(8) |
| Si2–O2 | 1.639(7) | Si10–O7 | 1.622(6) |
| Si3–O3 | 1.658(6) | Si9–O8 | 1.646(5) |
| Si4–O4 | 1.645(7) | Si8–O9 | 1.646(8) |
| Si5–O5 | 1.632(6) | Si7–O10 | 1.627(7) |

Figure 47. X-ray crystal structure of 23a:



1,2,3,4,6-Penta-O-trimethylsilyl- α -D-glucopyranose (23b)

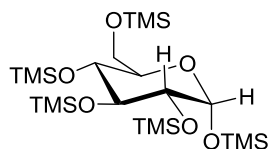
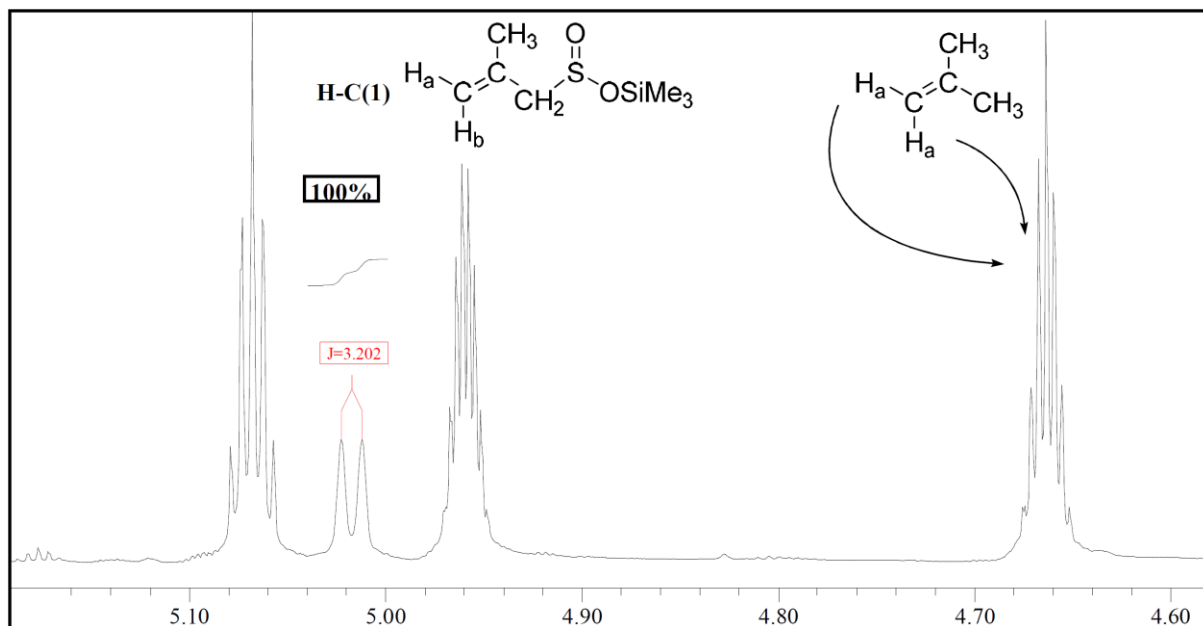


Figure 47⁸

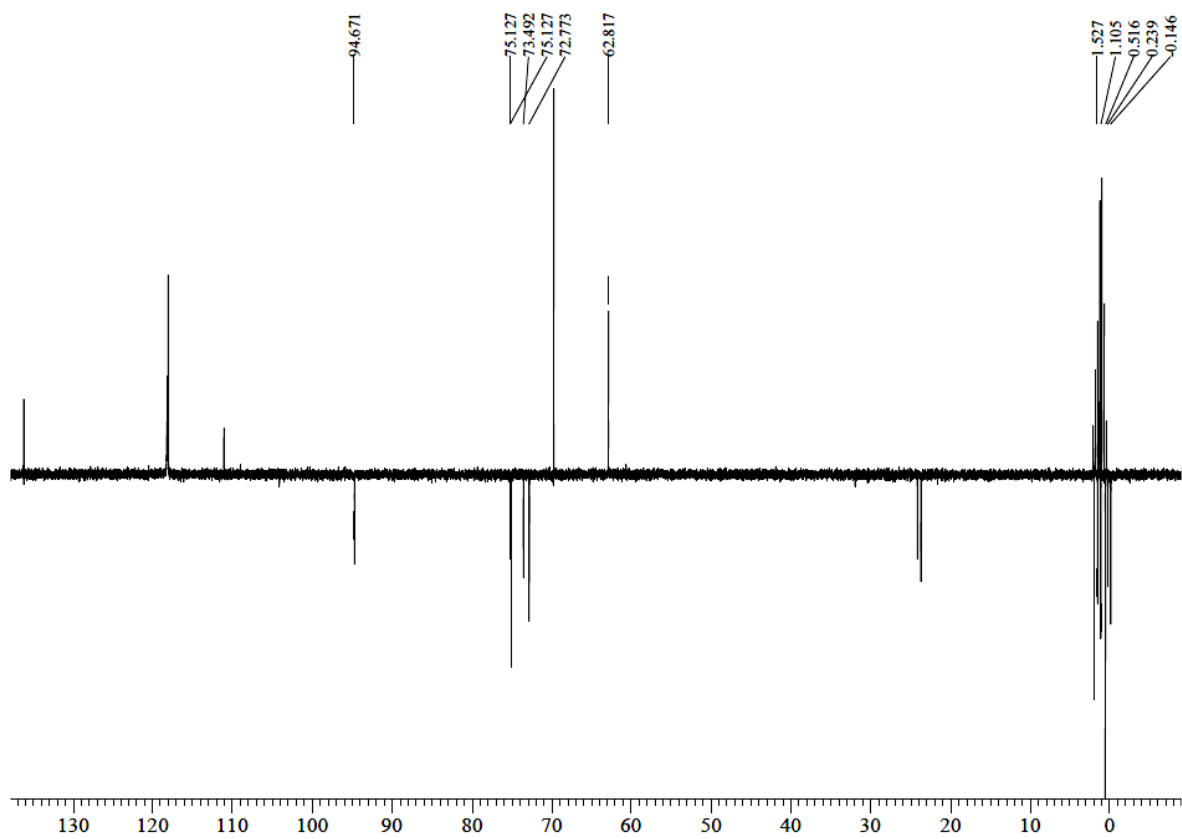
¹H-NMR analysis of *in situ* generated compound **23b** (CD₃CN, 300 MHz): A fragment of ¹H-NMR spectrum of a reaction featuring the H-C(1) of **23b** and H₂C=Q signals of silylating reagent **1b** and isobutylene.



⁸ In a parallel experiment silylation of D(+)-glucose is made in MeCN/CD₃CN and analyzed by GC-MS. The GC-MS traces show clean conversion to one single per-O-silylated product.

Figure 48

^{13}C -NMR analysis of *in situ* generated compound **23b** (CD_3CN , 75.5 MHz)



1,2,3,4,6-Penta-*O*-triethylsilyl- α -D-glucopyranose (23c)

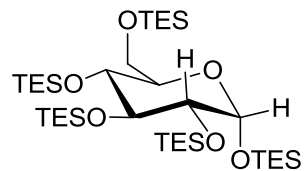


Figure 49

^1H NMR of ((2*S*,3*R*,4*S*,5*S*,6*S*)-6-((triethylsilyloxy)methyl)tetrahydro-2*H*-pyran-2,3,4,5-tetraol)tetrakis(oxy)tetrakis(triethylsilane)

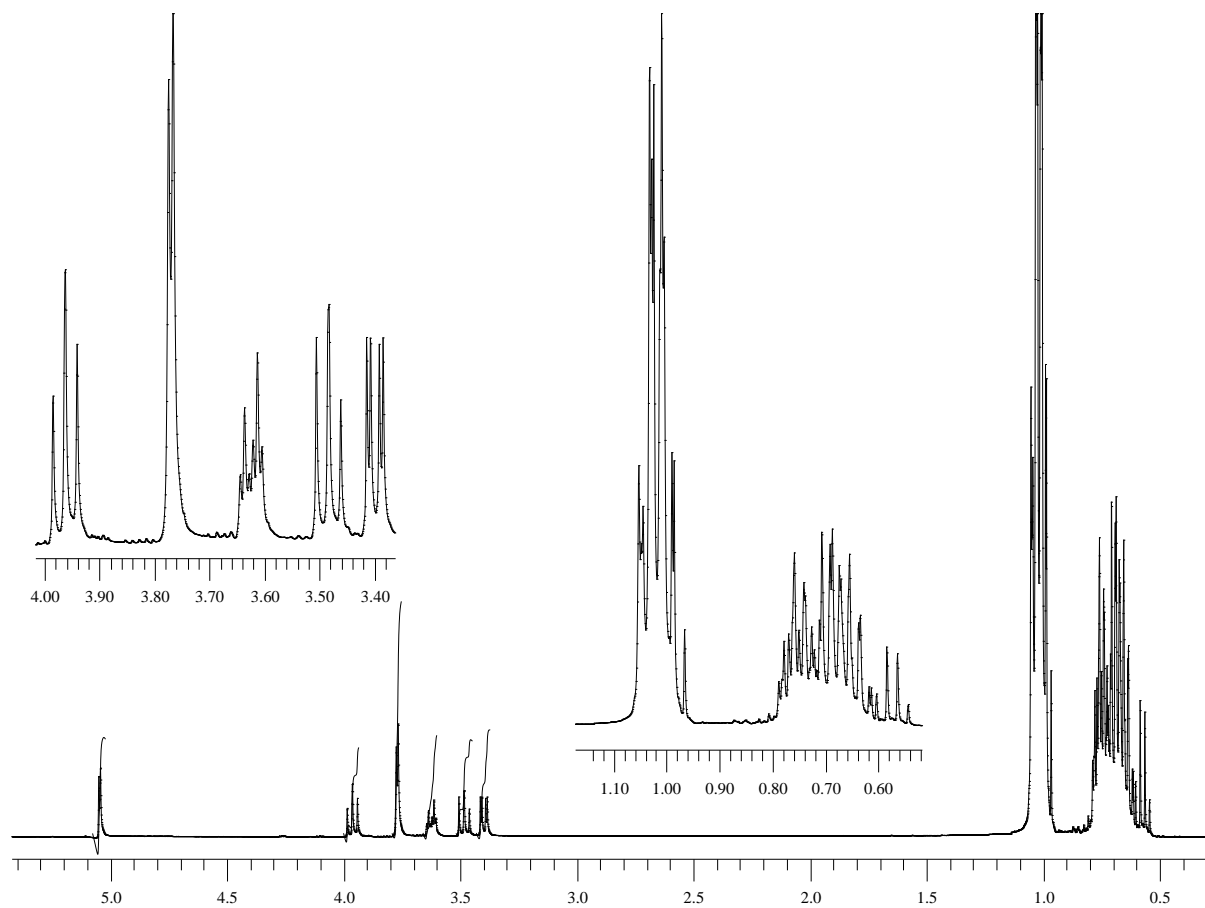
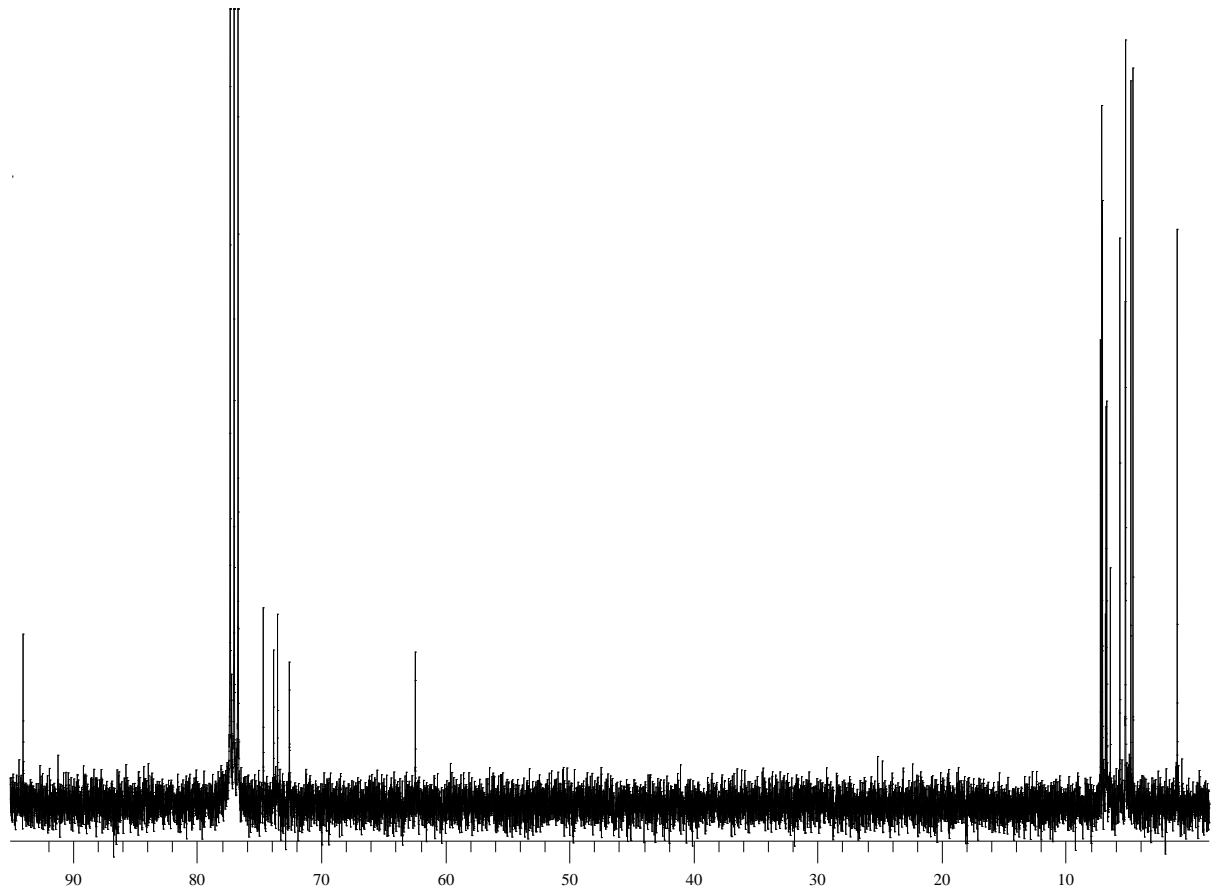


Figure 50

^{13}C NMR of ((2S,3R,4S,5S,6S)-6-((triethylsilyloxy)methyl)tetrahydro-2H-pyran-2,3,4,5-tetraol)tetrakis(oxy)tetrakis(triethylsilane).



1,2,3,4,6-Penta-*O*-trimethylsilyl- α -D-galactopyranose (**25**)

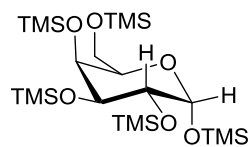
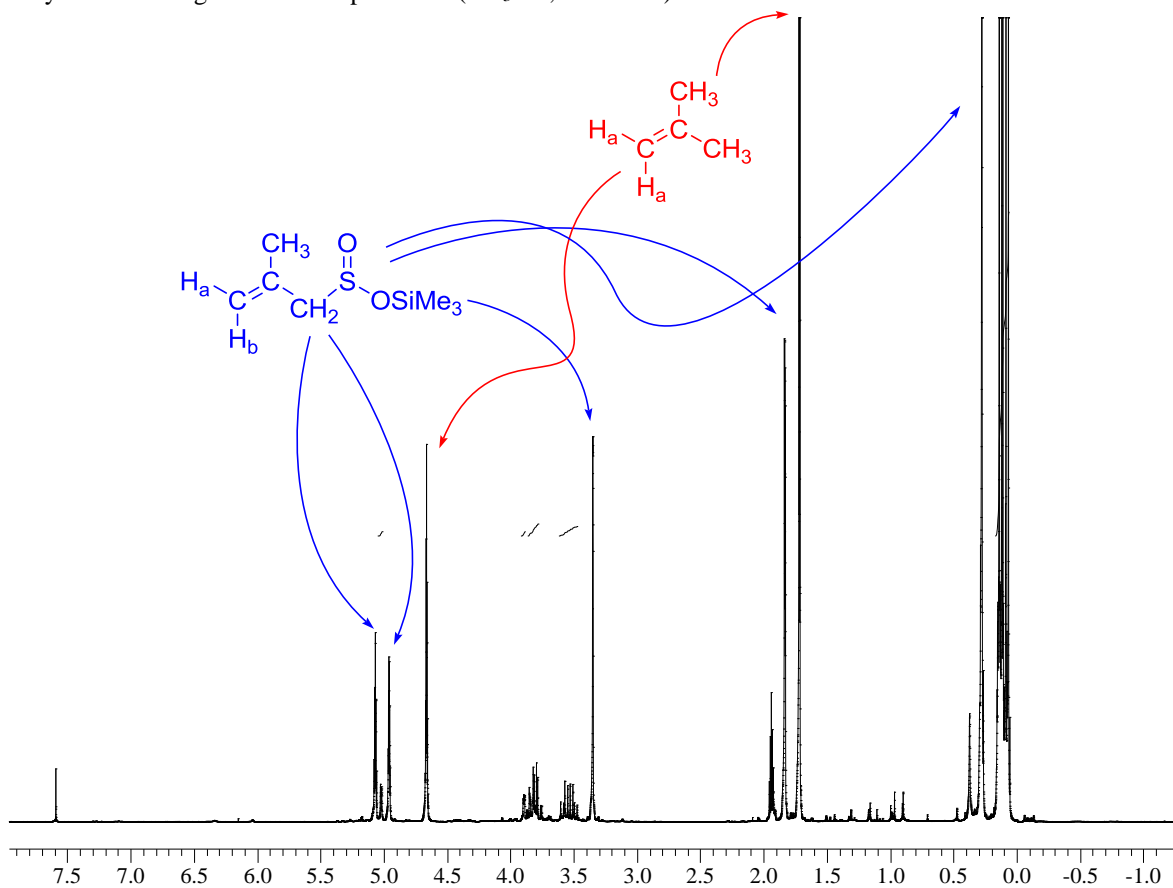


Figure 51

$^1\text{H-NMR}$ analysis of *in situ* generated compound **25** (CD_3CN , 300 MHz): ⁹



⁹ In a parallel experiment silylation of D(+)-galactose is made in MeCN/ CD_3CN and analyzed by GC-MS. The GC-MS traces show clean conversion to one single per-*O*-silylated product.

Figure 52

¹H-NMR analysis of *in situ* generated compound **25** (CD₃CN, 300 MHz): A fragment of ¹H-NMR spectrum of a reaction featuring the H-C(1) of **25** and H₂C=Q signals of silylating reagent **1b** and isobutylene.

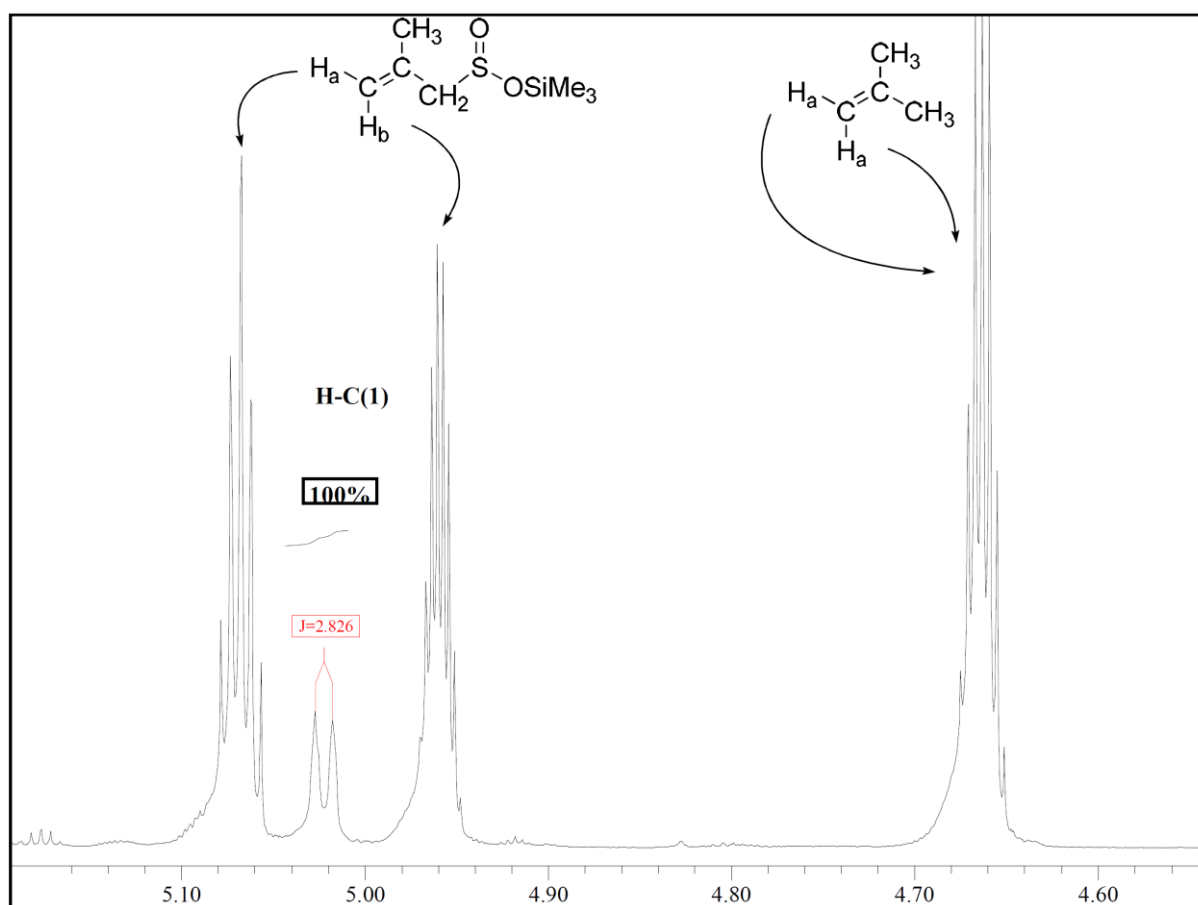
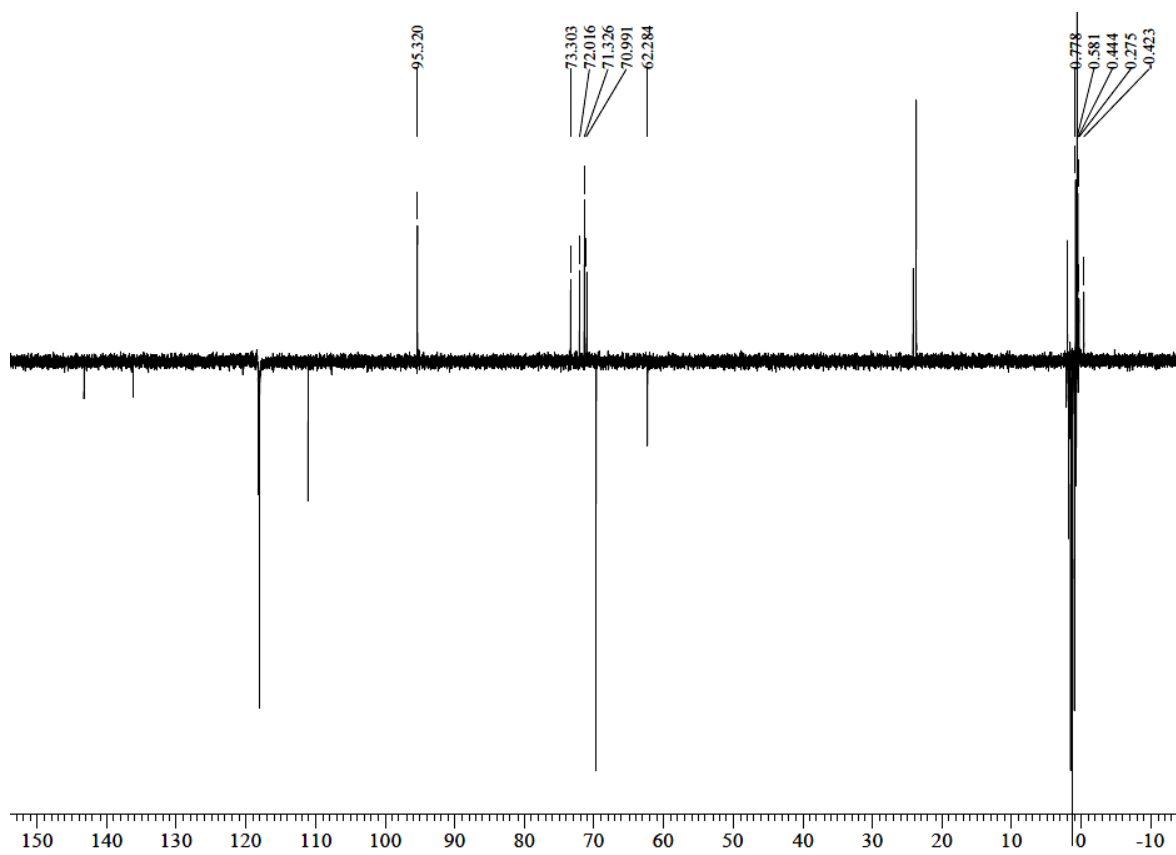


Figure 53
 ^{13}C -NMR analysis of *in situ* generated compound **25** (CD_3CN , 75.5 MHz)



A 2:1 mixture of 1,2,3,4,6-Penta-*O*-trimethylsilyl- α -D-mannopyranose (**α -27**) and 1,2,3,4,6-Penta-*O*-trimethylsilyl- β -D-mannopyranose (**β -27**)

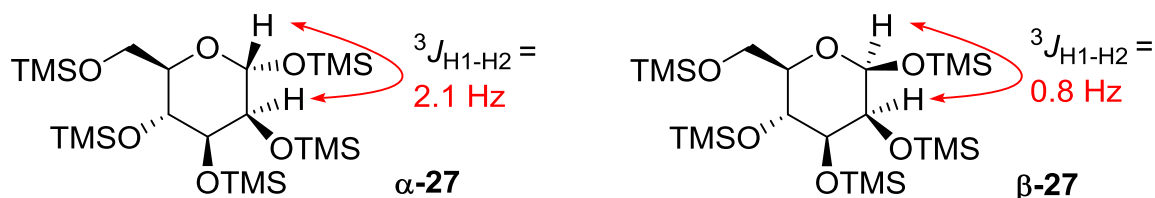
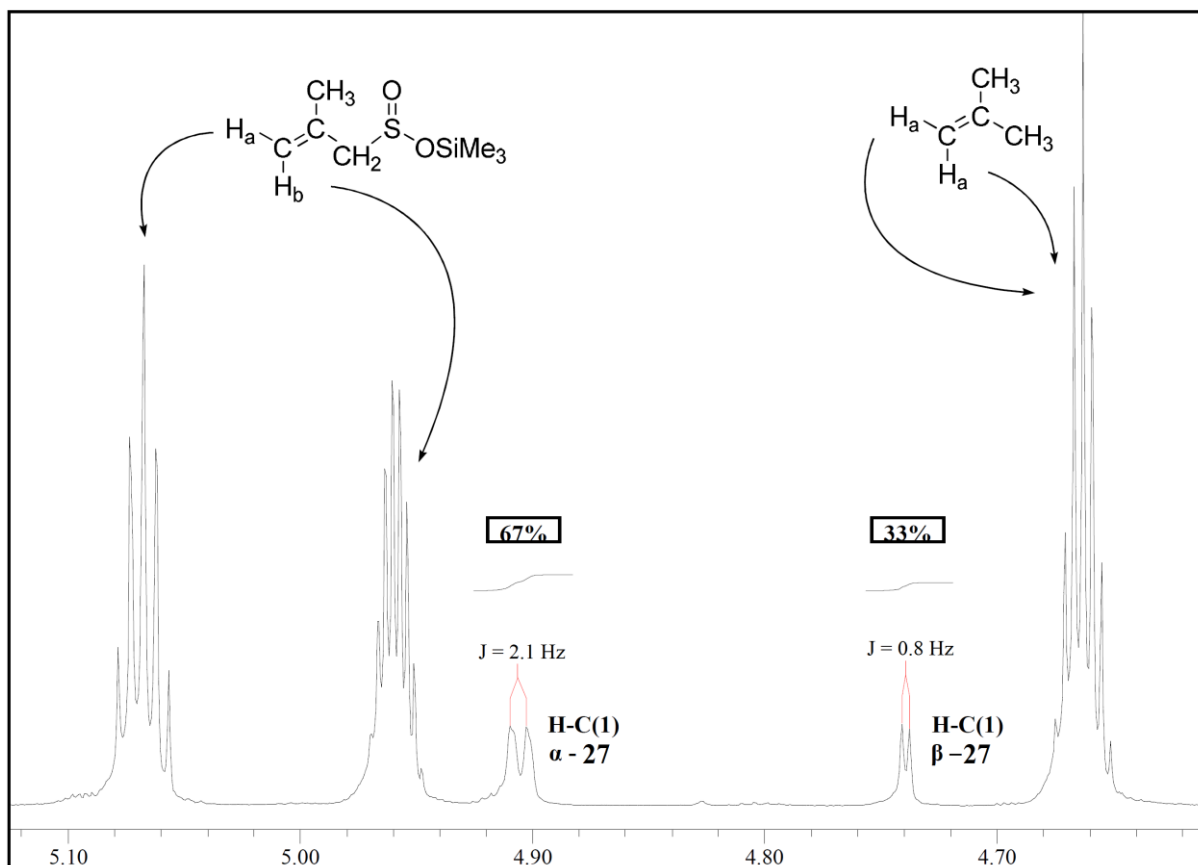


Figure 54¹⁰

¹H-NMR analysis of *in situ* generated compounds **α -27** and **β -27** (CD₃CN, 300 MHz): A fragment of ¹H-NMR spectrum of a reaction featuring the H-C(1) of **α -27** and **β -27** and H₂C=Q signals of silylating reagent **1b** and isobutylene.



¹⁰ In a parallel experiment silylation of D(+)-mannose is made in MeCN/CD₃CN and analyzed by GC-MS. The GC-MS traces show clean conversion to two per-*O*-silylated products in a ratio 2:1.

Figure 55.
GC-MS analysis of *in situ* generated compounds α -27 and β -27.

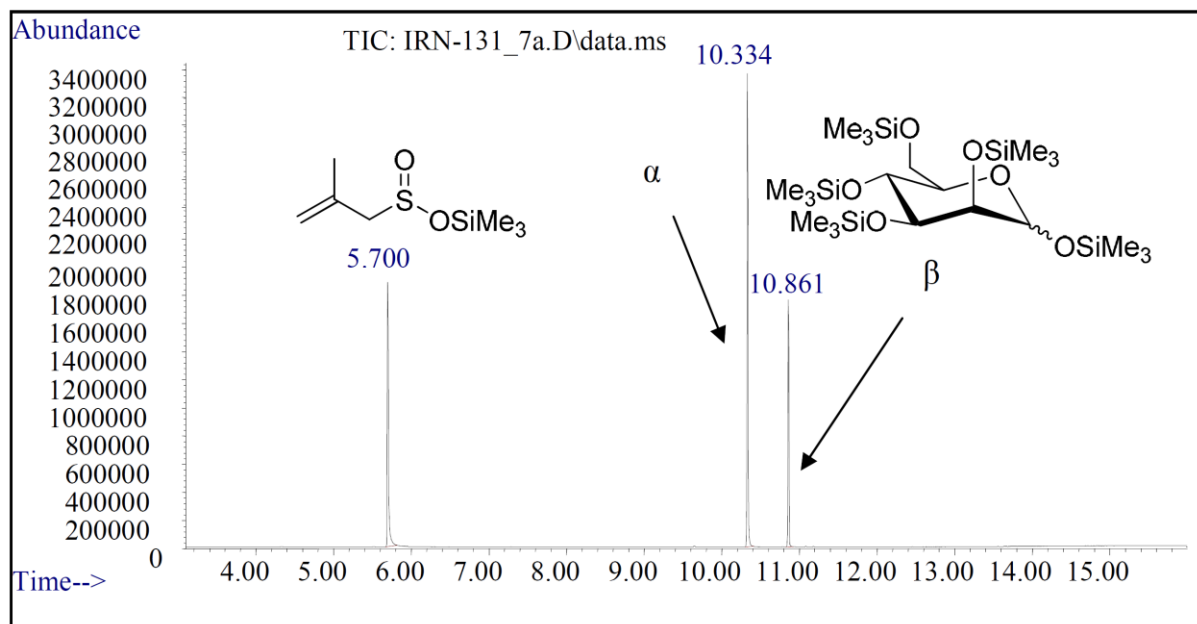


Figure 56
 ^{13}C -NMR (75.5 MHz, CDCl_3) spectrum of α -27 and β -27 (the solvent and the excess of reagent 1b were removed under reduced pressure and the sample was re-dissolved in CDCl_3):

