

Supporting Information
for
**Does Neighboring Group Participation by Non-Vicinal Esters Play a
Role in Glycosylation Reactions? Effective Probes for the Detection
of Bridging Intermediates**

*David Crich, * Tianshun Hu and Feng Cai*

Chemistry Department, Wayne State University, 5101 Cass Avenue, Detroit, MI,
48202, and Department of Chemistry, University of Illinois at Chicago, 845 West
Taylor Street, Chicago, IL, 60607

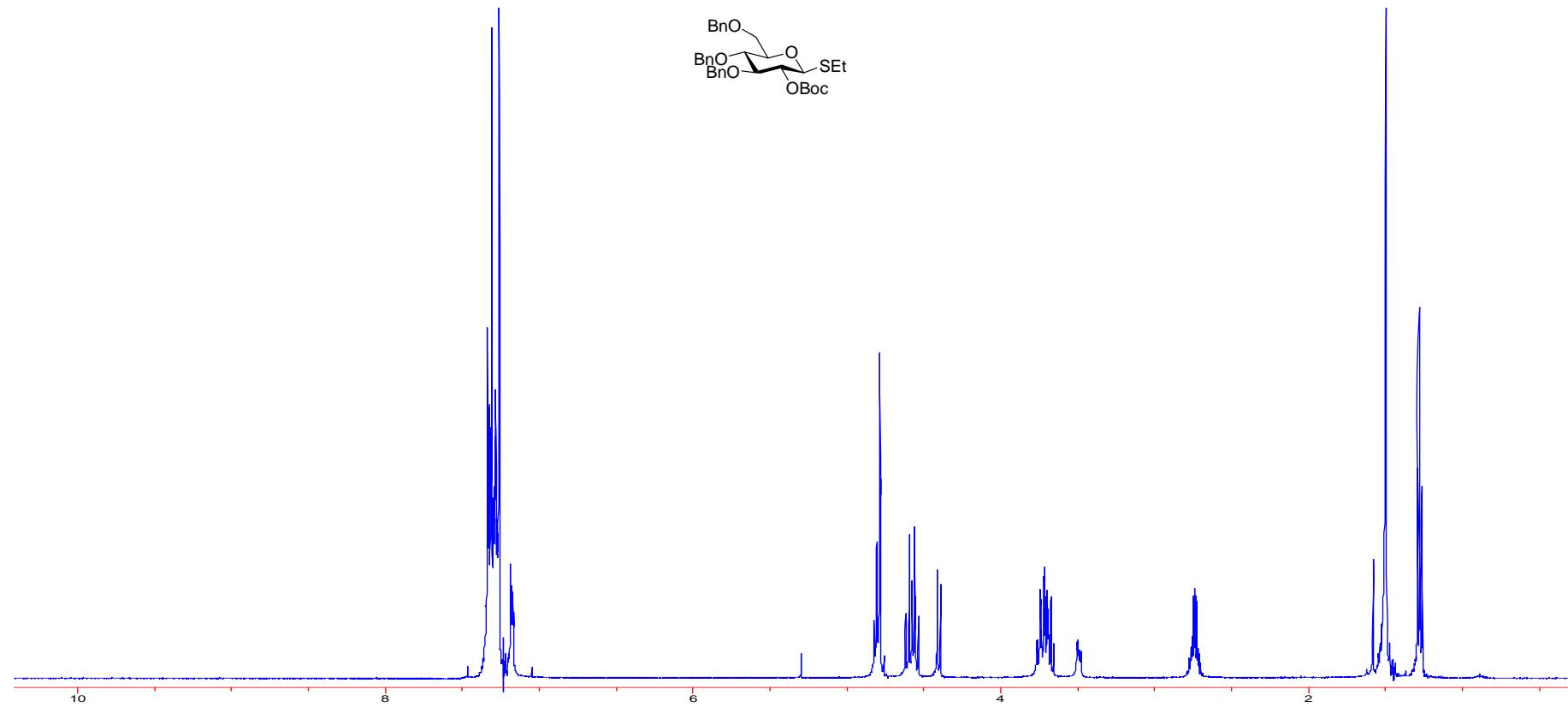
Entry	¹H NMR	¹³C NMR
General Experimental	S-3	
Ethyl 3,4,6-tri- <i>O</i> -benzyl-2- <i>O</i> - <i>tert</i> -butyloxycarbonyl-1-thio- β -D-glucopyranoside 9	S-4	S-5
3,4,6-Tri- <i>O</i> -benzyl-1,2- <i>O</i> -carbonyl- α -D-glucopyranoside 10	S-6	S-7
Phenyl 2- <i>O</i> - <i>tert</i> -butoxycarbonyl-3,4,6-tri- <i>O</i> -benzyl-1-thio- α -D-mannoxyranoside 11	S-8	S-9
3,4,6-Tri- <i>O</i> -benzyl-1,2- <i>O</i> -carbonyl- α -D-mannoxyranoside 12	S-10	S-11
Phenyl 2,4,6-tri- <i>O</i> -benzyl-1-thio- β -D-allopyranoside 14	S-12	S-13
Phenyl 3- <i>O</i> - <i>tert</i> -butoxycarbonyl-2,4,6-tri- <i>O</i> -benzyl-1-thio- β -D-allopyranoside 15	S-14	S-15
2,4,6-Tri- <i>O</i> -benzyl-1,3- <i>O</i> -carbonyl- α -D-allose 16	S-16	S-17
Cyclohexyl 3- <i>O</i> - <i>tert</i> -butoxycarbonyl-2,4,6- <i>O</i> -benzyl- α -D-allopyranoside 17α and Cyclohexyl 3- <i>O</i> - <i>tert</i> -butoxycarbonyl-2,4,6- <i>O</i> -benzyl- β -D-allopyranoside 17β	S-18 S-20	S-19 S-21
3- <i>O</i> - <i>tert</i> -Butoxycarbonyl-2,4,6-tri- <i>O</i> -benzyl-D-allose 18	S-22	S-23
Phenyl 3- <i>O</i> - <i>tert</i> -butoxycarbonyl-2- <i>O</i> -benzyl-4,6- <i>O</i> -benzylidene-1-thio- α -D-manno- pyranoside 21	S-24	S-25

Phenyl	<i>3-O-tert-butoxycarbonyl-2-O-benzyl-4,6-O-benzylidene-1-thio-α-D-manno-pyranoside S-Oxide 22</i>	S-26	S-27
Cyclohexyl	<i>3-O-tert-butoxycarbonyl-2-O-benzyl-4,6-O-benzylidene-α-D-manno-pyranoside 23</i>	S-28	S-29
Ethyl	<i>4-O-tert-butoxycarbonyl-2,3,6-tri-O-benzyl-1-thio-β-D-galactopyranoside 24</i>	S-30	S-31
	<i>4-O-tert-Butoxycarbonyl-2,3,6-O-tribenzyl-α-D-galactopyranosyl acetate 25α</i> and <i>4-O-tert-Butoxycarbonyl-2,3,6-O-benzyl-β-D-galactopyranosyl acetate 25β</i>	S-32 S-34	S-33 S-35
Cyclohexyl	<i>4-O-tert-butoxycarbonyl-2,3,6-O-benzyl-β-D-galactopyranoside 26α</i> and <i>Cyclohexyl 4-O-tert-butoxycarbonyl-2,3,6-O-benzyl-β-D-galactopyranoside 26β</i>	S-36 S-38	S-37 S-39
Phenyl	<i>2,3,6-tri-O-benzyl-4-O-tert-butyloxycarbonyl-1-thio-α-D-mannopyranoside 27</i>	S-40	S-41
	<i>Isopropyl 2,3,6-tri-O-benzyl-4-O-tert-butyloxycarbonyl-α-D-mannopyranoside 28α</i> and <i>isopropyl 2,3,6-tri-O-benzyl-4-O-tert-butyloxycarbonyl-β-D-mannopyranoside 28β</i>	S-42 S-44	S-43 S-45
29	<i>N-(2',3',6'-Tri-O-benzyl-4'-O-tert-butyloxycarbonyl-α-D-mannopyranosyl)-succinimide 29</i>	S-46	S-47
<i>p</i> -Tolyl	<i>4-O-tert-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-thio-α-L-lyxo-hexo-pyranoside 30</i>	S-48	S-49
	<i>4-O-tert-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-α-L-lyxopyranose</i>	S-50	S-51
	<i>4-O-tert-Butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-lyxo-hexopyranosyl acetate 31</i>	S-52	S-53
Cyclohexyl	<i>4-O-tert-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-lyxo-hexopyranoside 32</i>	S-54	S-55
Phenyl	<i>2,3,4-tri-O-benzyl-6-O-tert-butyloxycarbonyl-1-thio-β-D-glucopyranoside 33</i>	S-56	S-57
	<i>Isopropyl 2,3,4-tri-O-benzyl-6-O-tert-butyloxycarbonyl-α-D-glucopyranoside 34α</i> and <i>isopropyl 2,3,4-tri-O-benzyl-6-O-tert-butyloxycarbonyl-β-D-glucopyranoside 34β</i>	S-58	S-59
	<i>Di-(2,3,4-tri-O-benzyl-D-glucopyranoside)-(1,6), (6,1)-dicarbonate 35</i>	S-60	S-61
Ethyl	<i>3,4,6-tri-O-benzyl-2-O-(2-carboxybenzoyl)-1-thio-β-D-glucopyranoside 36</i>	S-62	S-63
	<i>3,4,6-Tri-O-benzyl-1,2-O-phthalidylidene-α-D-glucopyranose 37</i>	S-64	S-65
Phenyl	<i>2,3,6-tri-O-benzyl-4-O-(2-carboxybenzoyl)-1-thio-β-D-galactopyranoside 38</i>	S-66	S-67
	<i>3,4,6-Tri-O-benzyl-1,2-O-phthalate-β-D-galactopyranoside 40</i>	S-68	S-69
Phenyl	<i>2,3,6-tri-O-benzyl-4-O-(4-methoxybenzoyl)-1-thio-β-D-galactopyranoside 41</i>	S-70	S-71
	<i>2,3,6-Tri-O-benzyl-4-O-(4-methoxybenzoyl)-α-D-[1-^{16/18}O]-galactopyranoside 43</i>	S-72	S-73 S-74

		S-75
2,3,6-Tri- <i>O</i> -benzyl-4- <i>O</i> -(4-methoxybenzoyl)-D-[1- ^{16/18} <i>O</i>]-galactopyranosyl acetate 47	S-76	S-77 S-78 S-79 S-80
Phenyl 2,3,6-tri- <i>O</i> -benzyl-4- <i>O</i> -(4-methoxybenzoyl)-1-thio- $\alpha\beta$ -D-galactopyranoside 41α and 41β	S-81	S-82

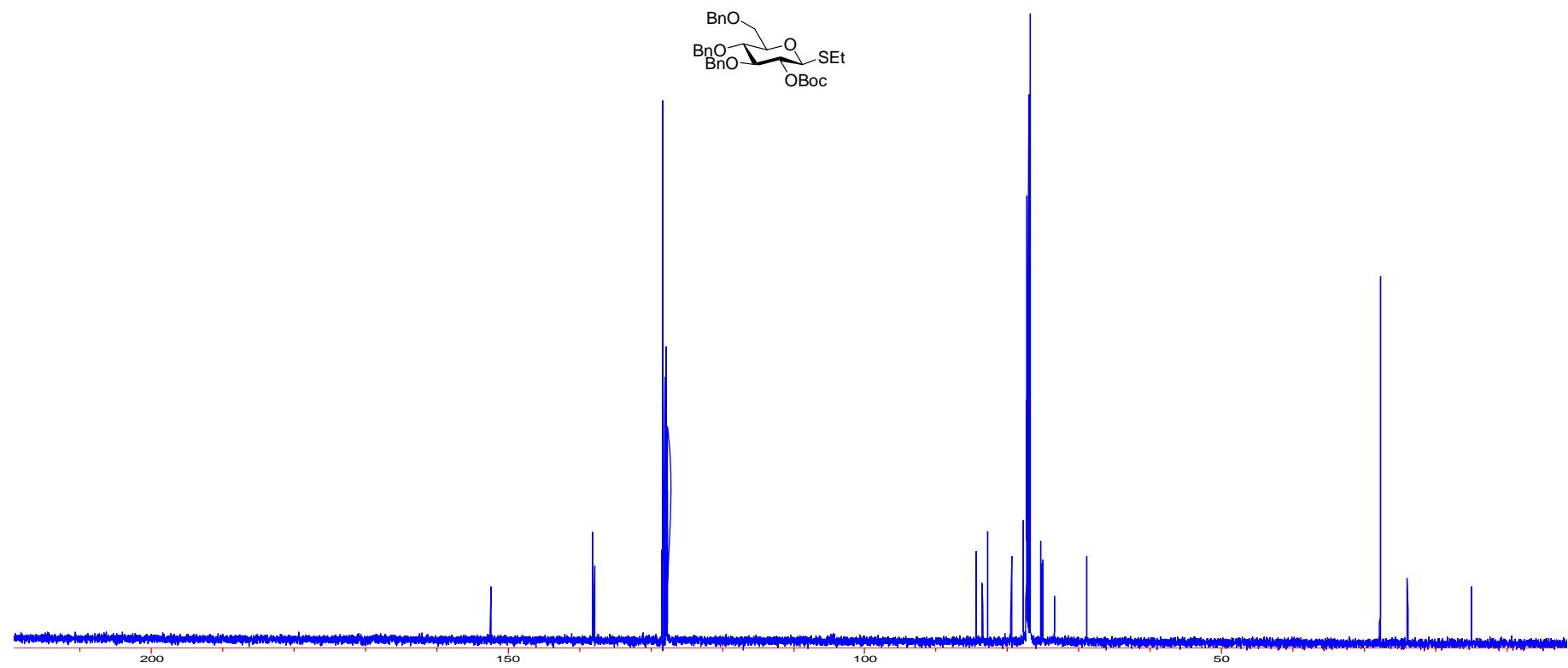
General Experimental. Unless otherwise stated ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution at 500 and 125 MHz, respectively. Specific rotations were recorded in CHCl₃ solution, unless otherwise stated. All solvents were dried and distilled by standard protocols. All reactions were conducted under a blanket of dry nitrogen. All organic extracts were dried over sodium sulfate and concentrated under aspirator vacuum. Chromatographic purifications were carried out over silica gel.

Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyloxycarbonyl-1-thio- β -D-glucopyranoside (**9**)

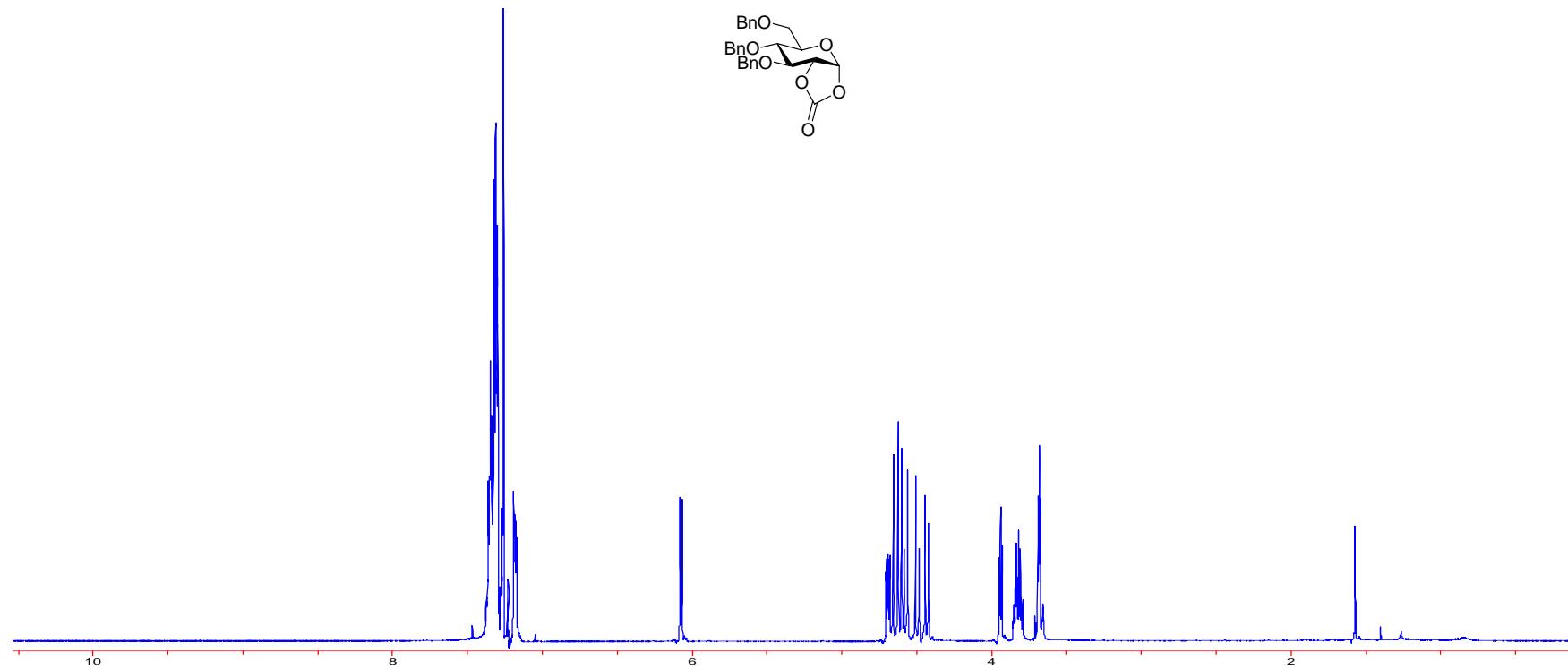


S-4

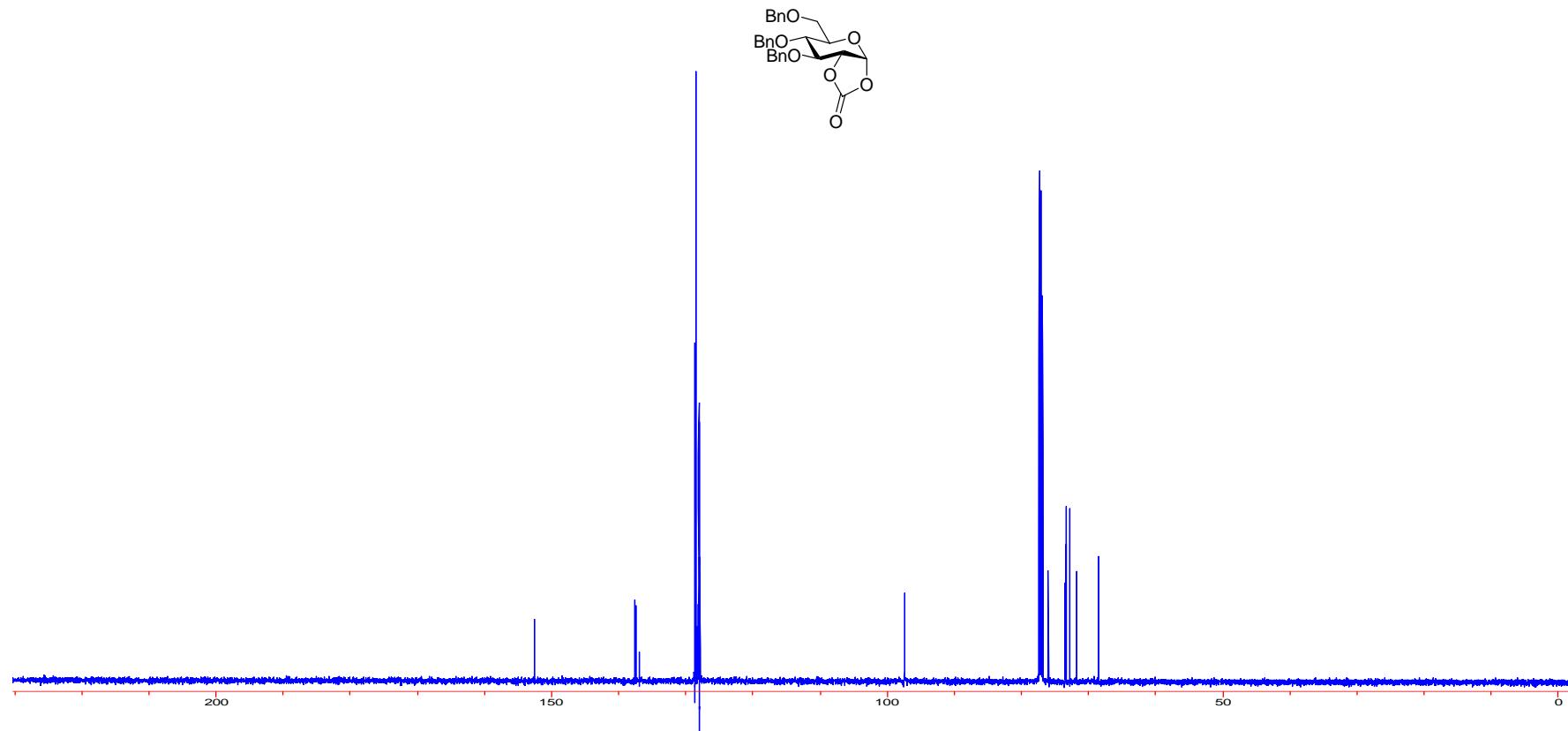
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyloxycarbonyl-1-thio- β -D-glucopyranoside (**9**)



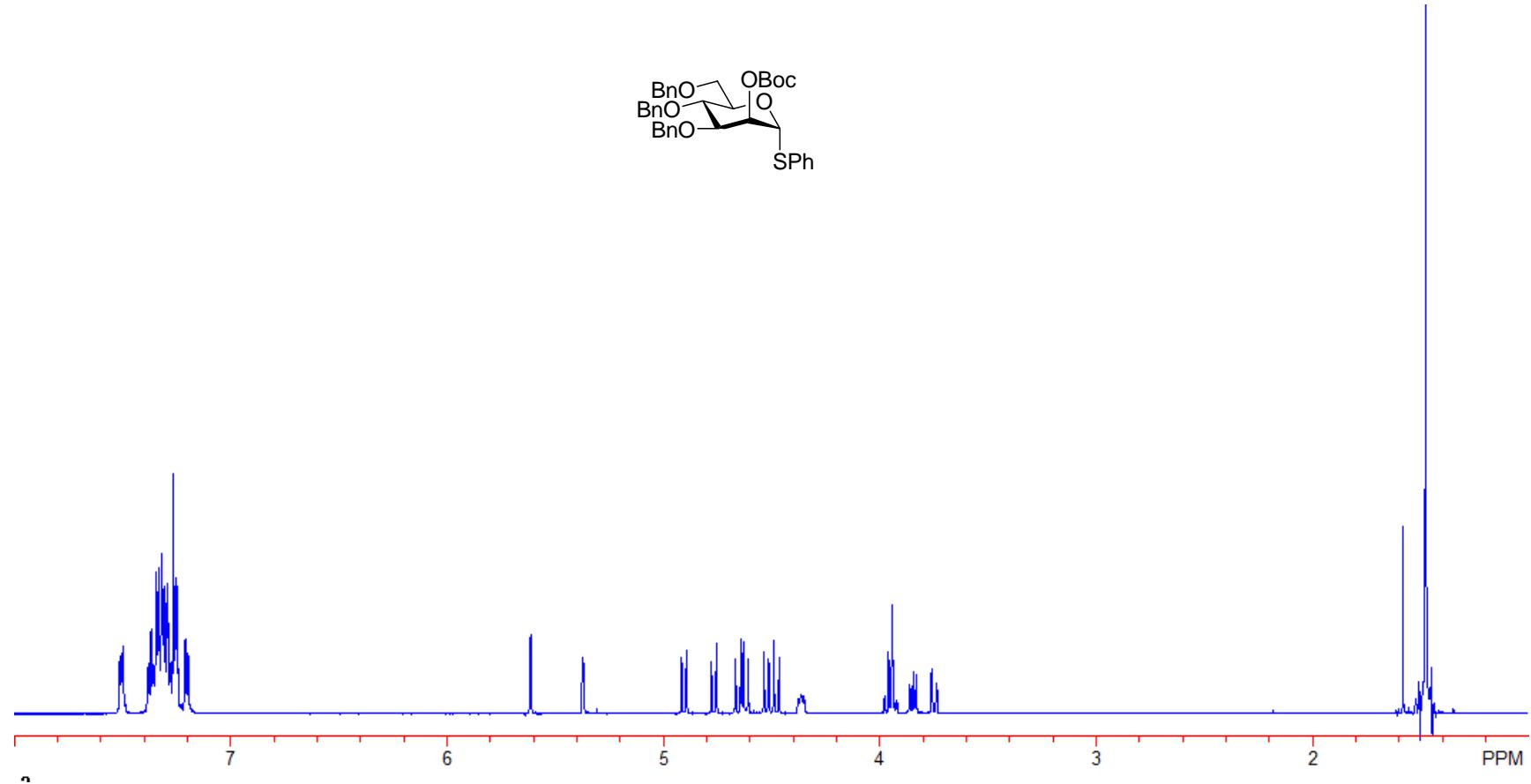
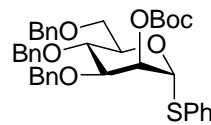
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl- α -D-glucopyranoside (**10**)



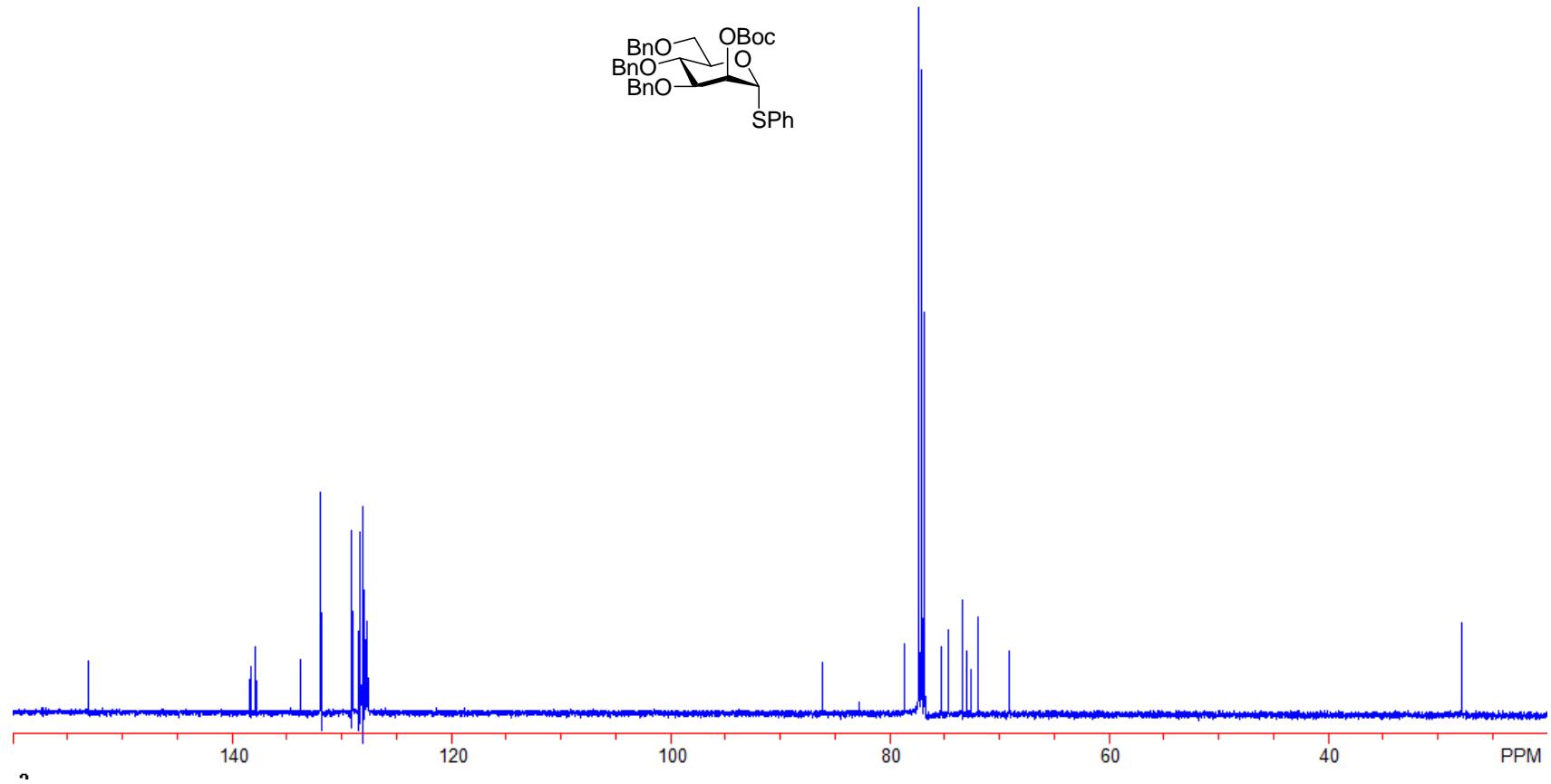
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl- α -D-glucopyranoside (**10**)



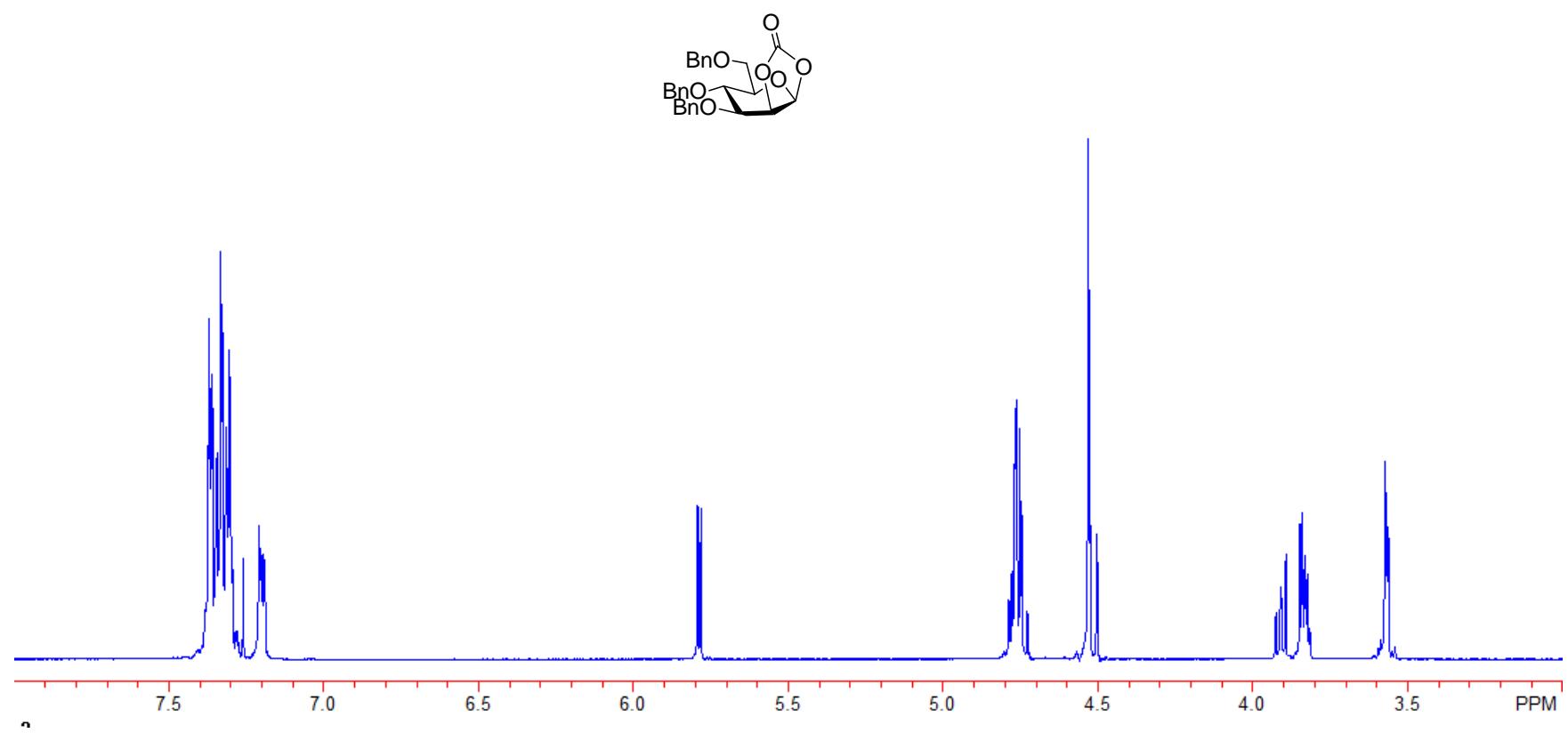
Phenyl 2-*O*-*tert*-butoxycarbonyl-3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (**11**).



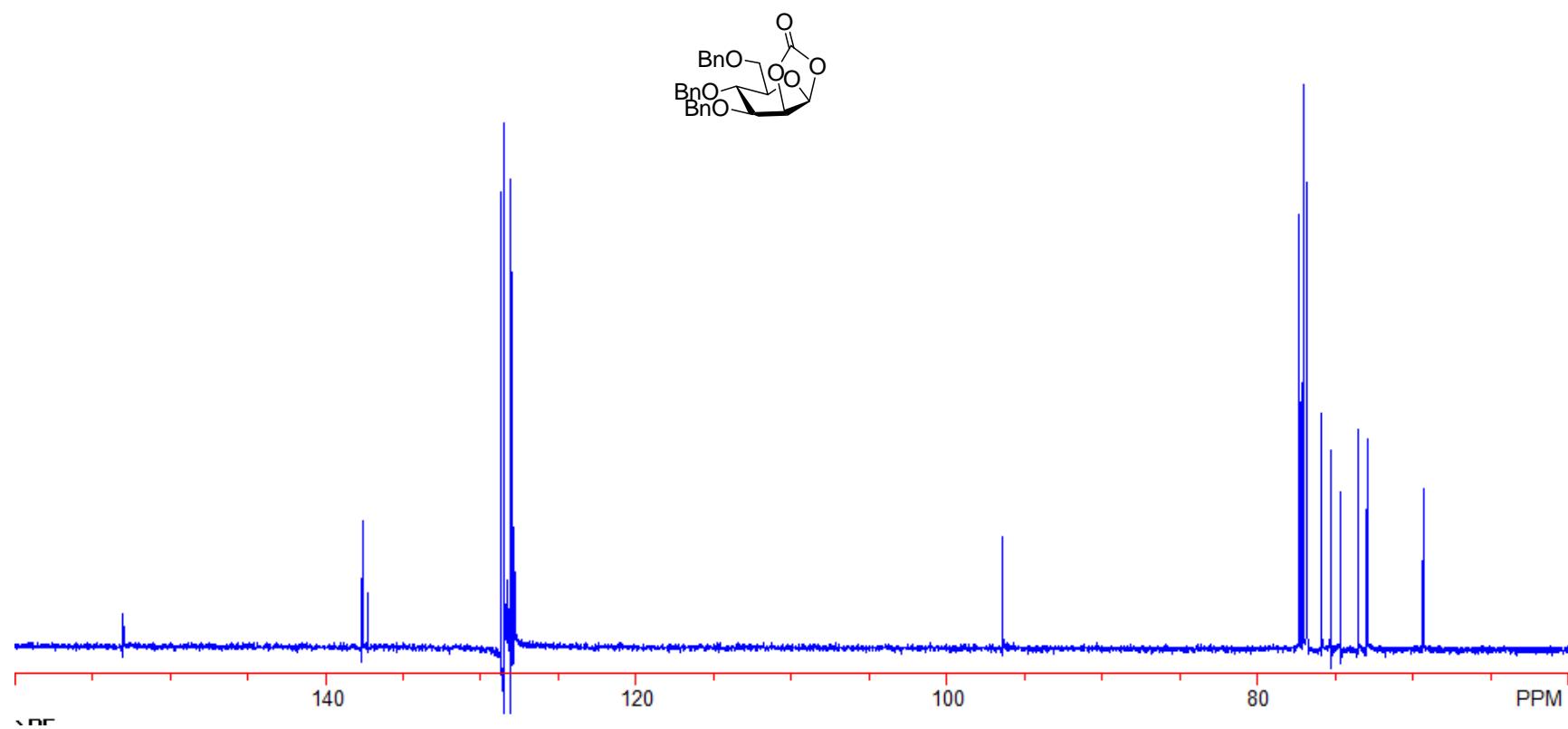
Phenyl 2-*O*-*tert*-butoxycarbonyl-3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside (**11**).



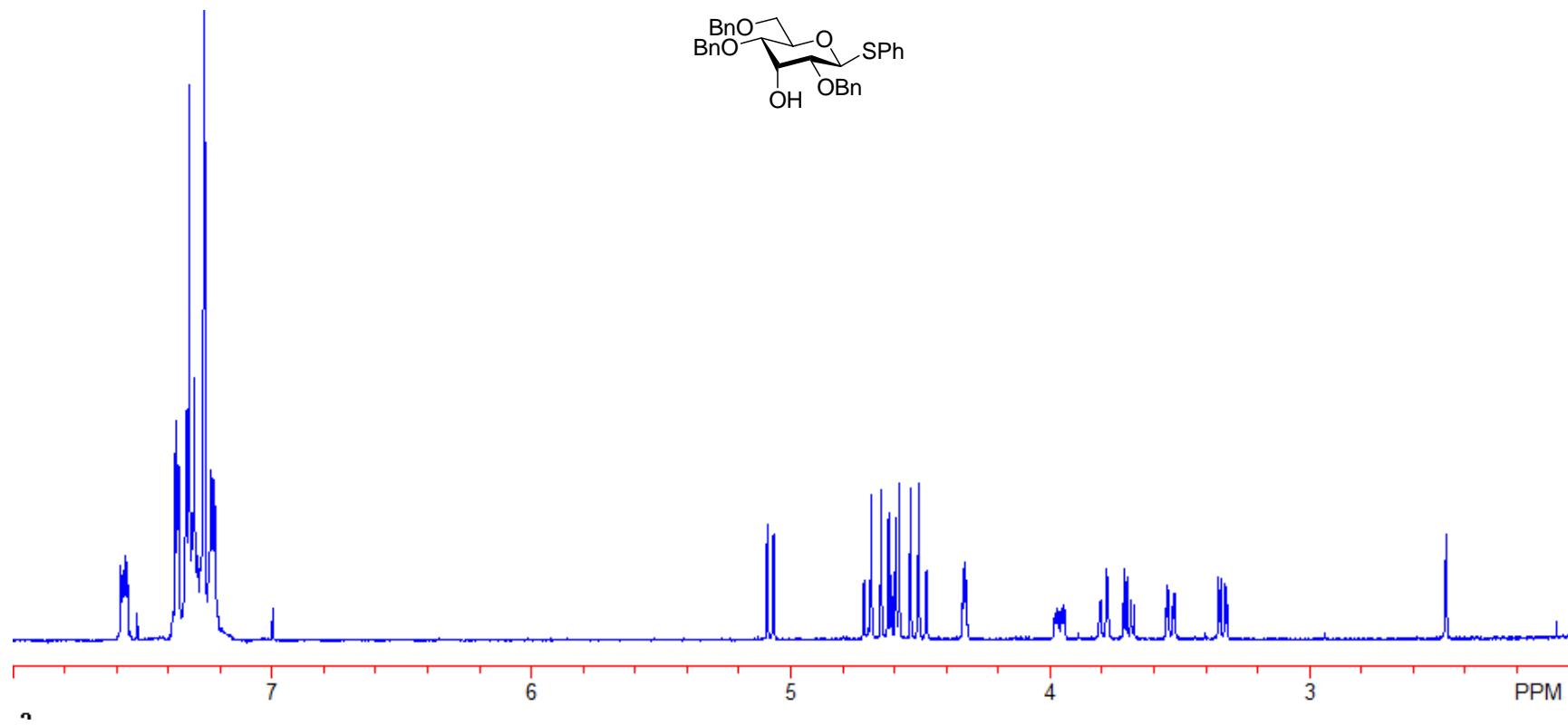
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl- α -D-mannopyranoside (**12**).



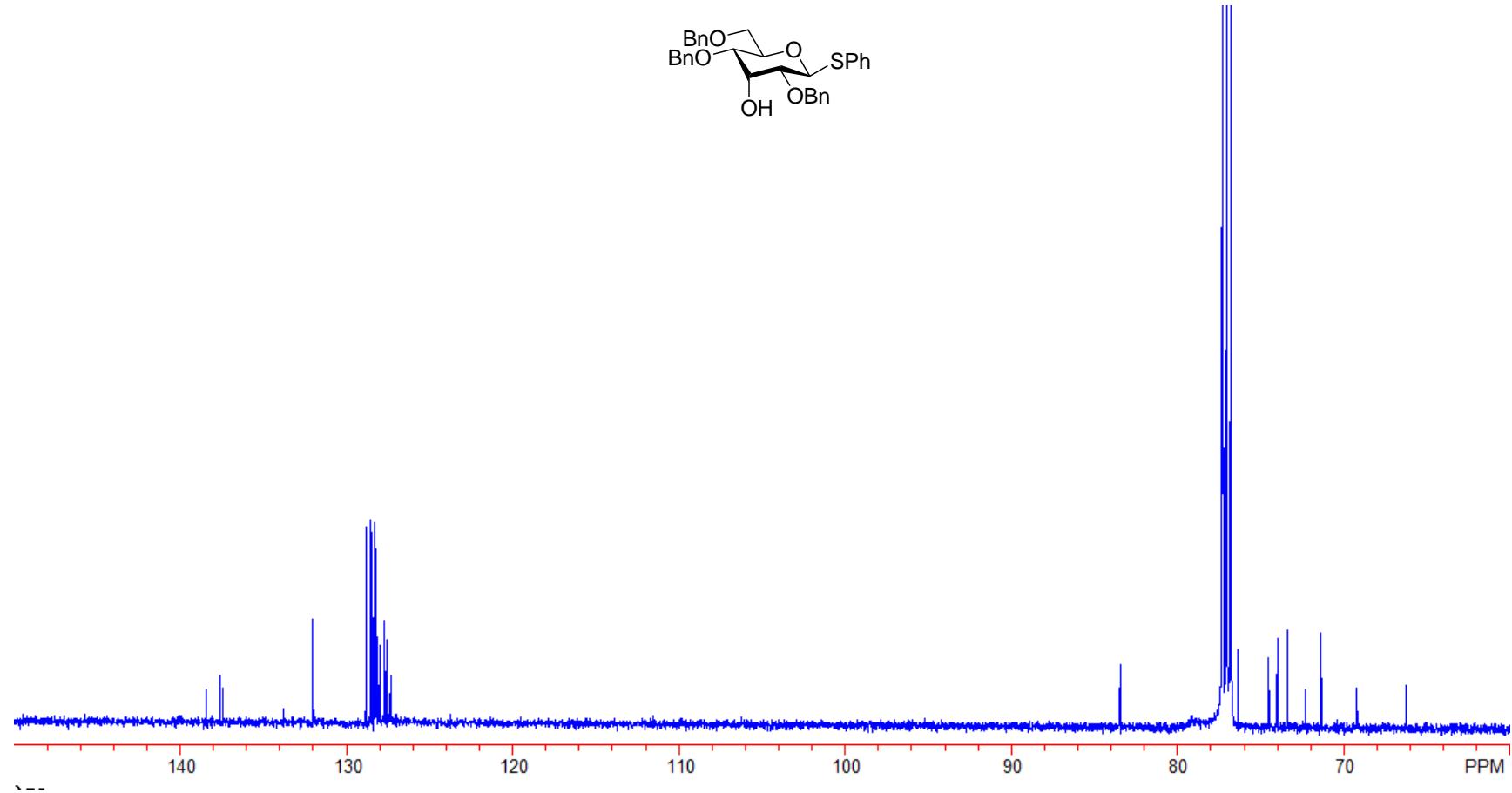
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl- α -D-mannopyranoside (**12**).



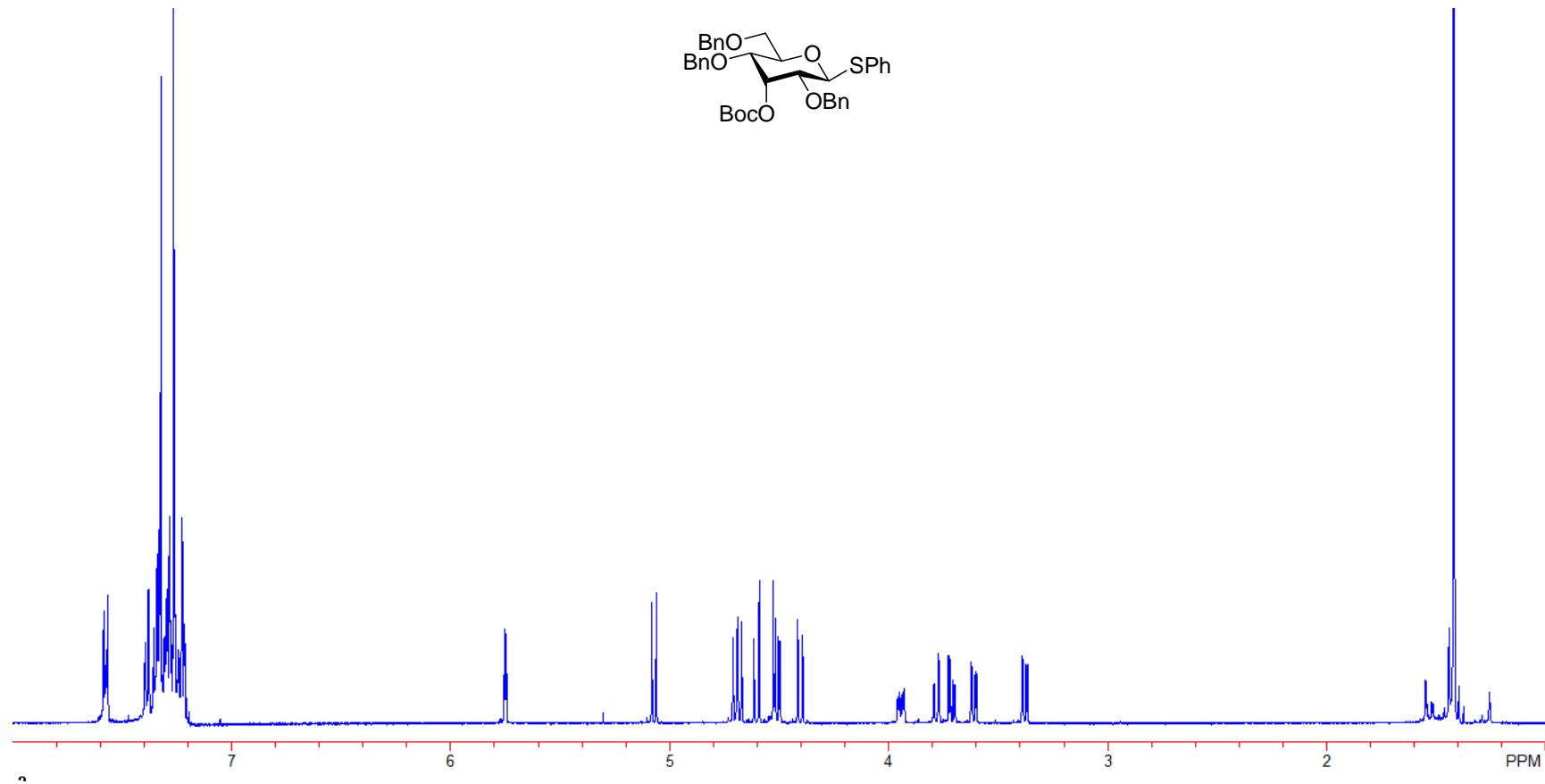
Phenyl 2,4,6-Tri-*O*-benzyl-1-thio- β -D-allopyranoside (**14**).



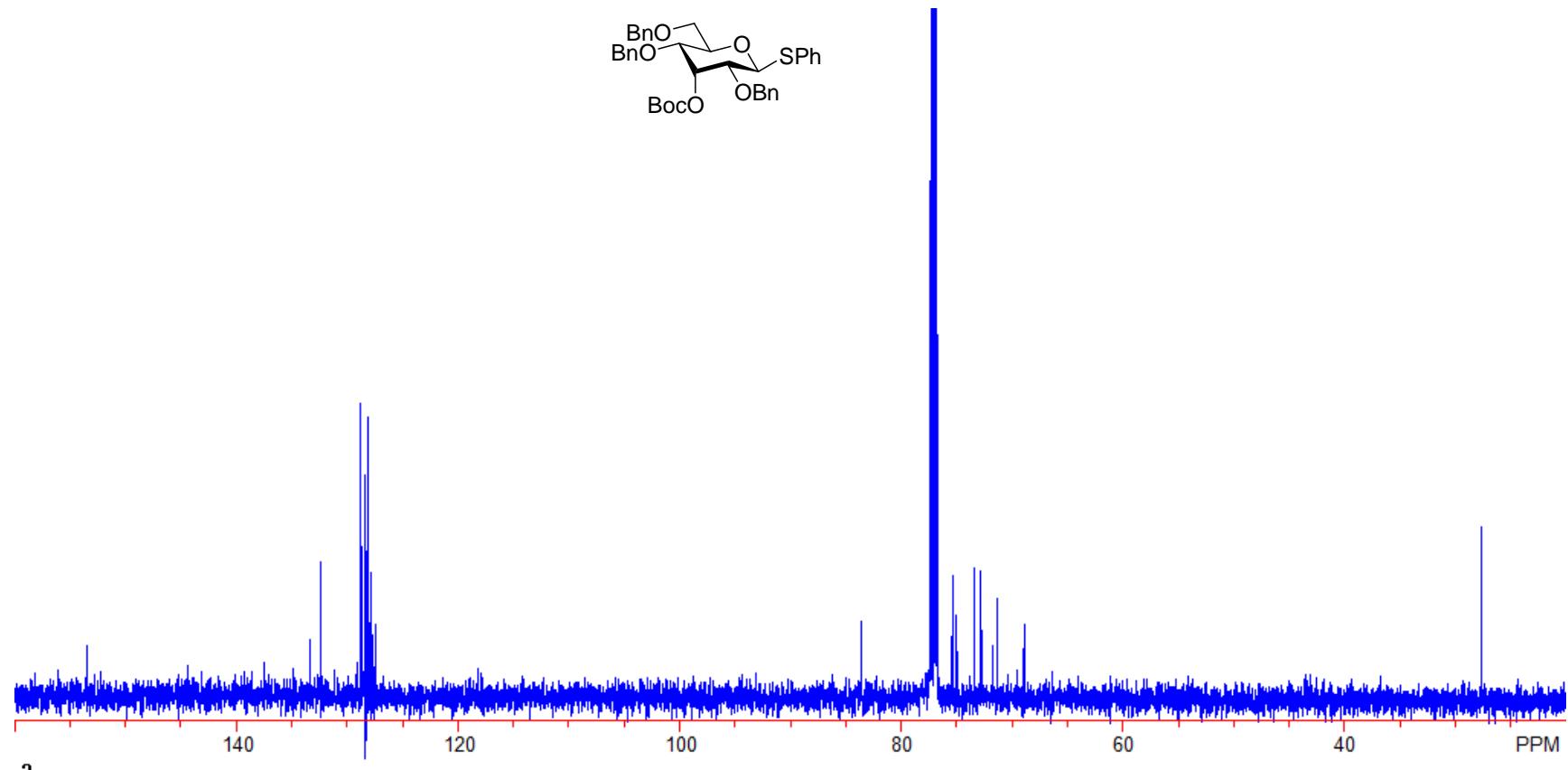
Phenyl 2,4,6-Tri-*O*-benzyl-1-thio- β -D-allopyranoside (**14**).



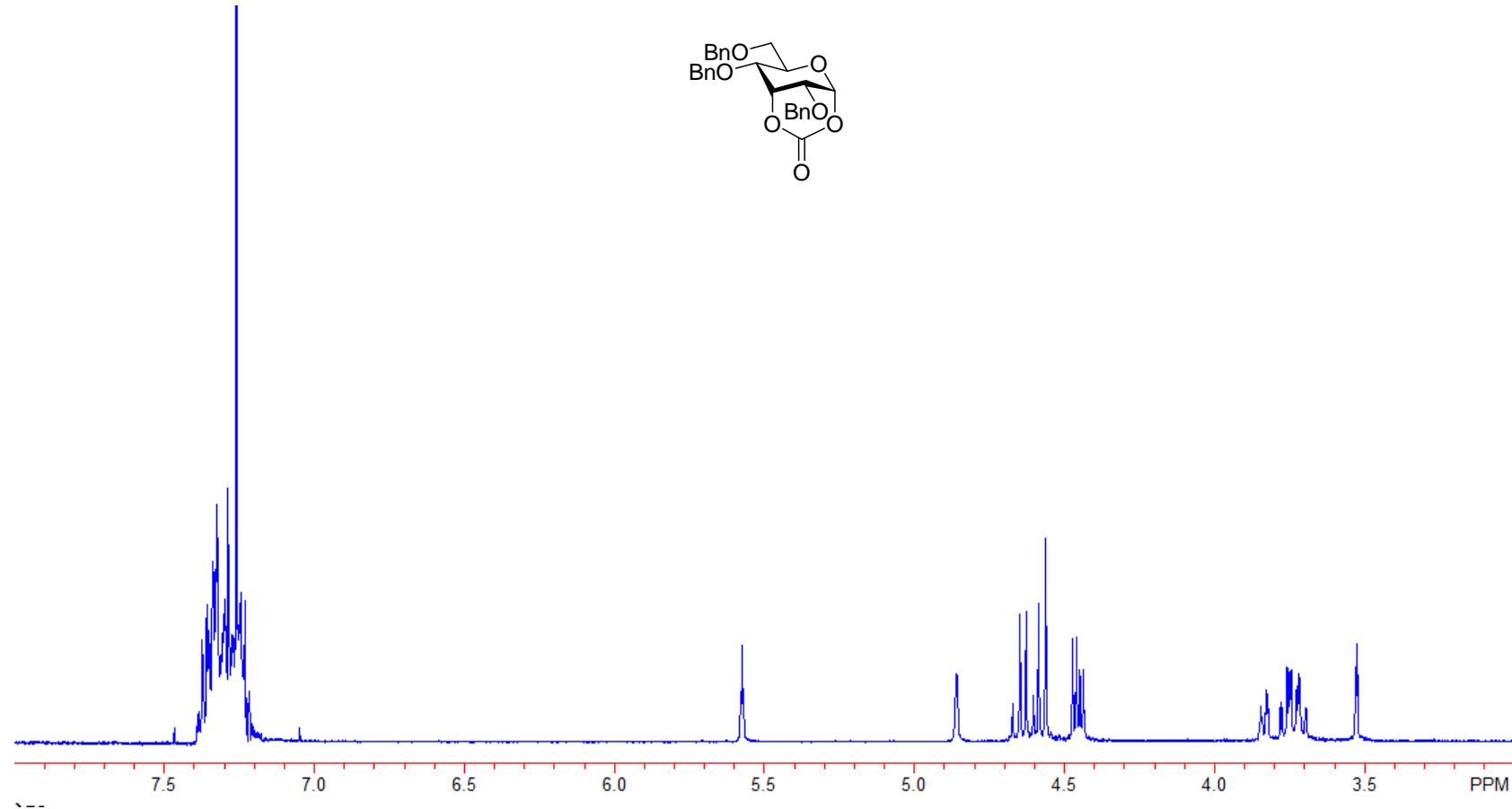
Phenyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-1-thio- β -D-allopyranoside (**15**).



Phenyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-1-thio- β -D-allopyranoside (**15**).

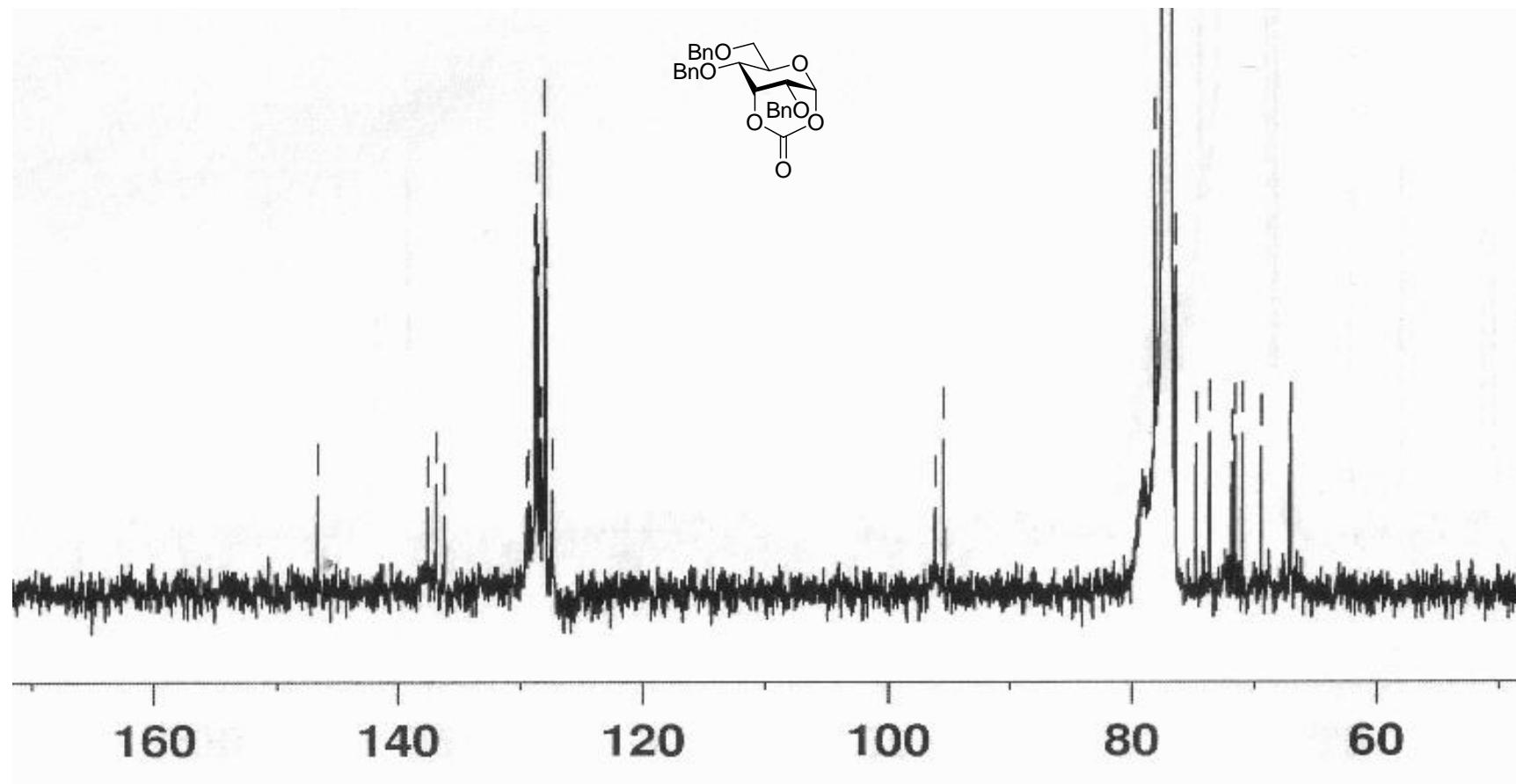


2,4,6-Tri-*O*-benzyl-1,3-*O*-carbonyl- α -D-allose (**16**).

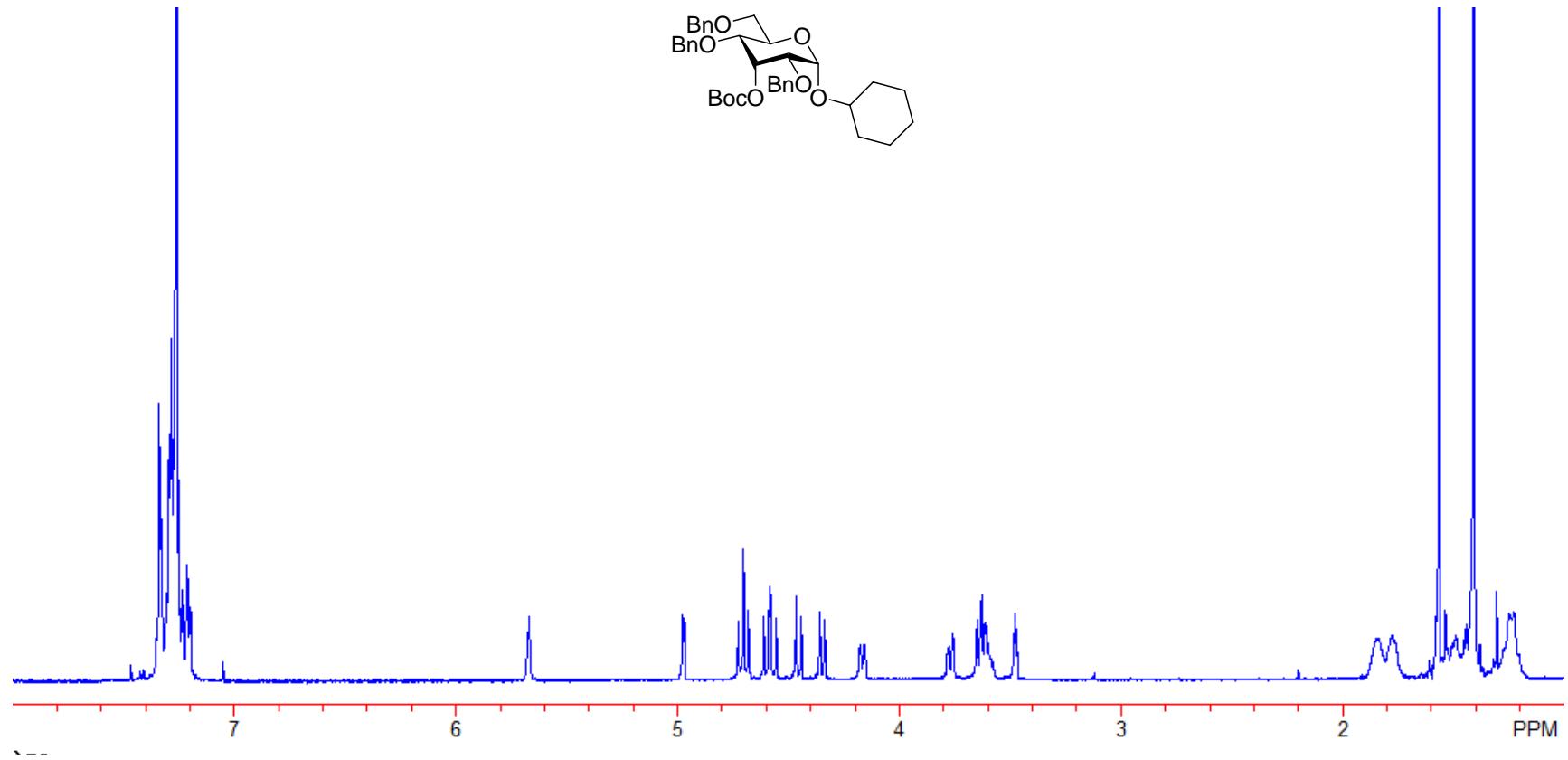


S-16

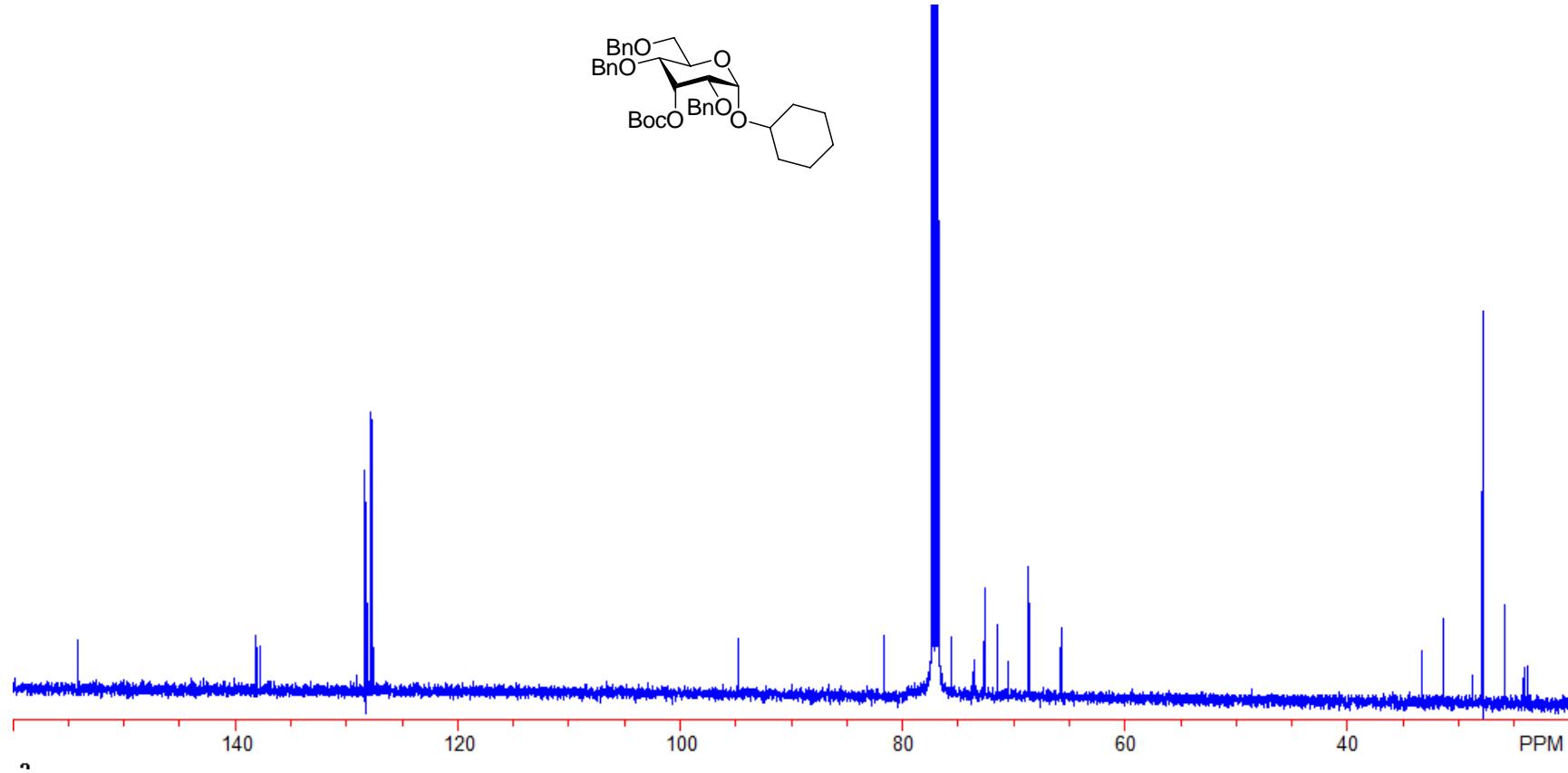
2,4,6-Tri-*O*-benzyl-1,3-*O*-carbonyl- α -D-allose (**16**).



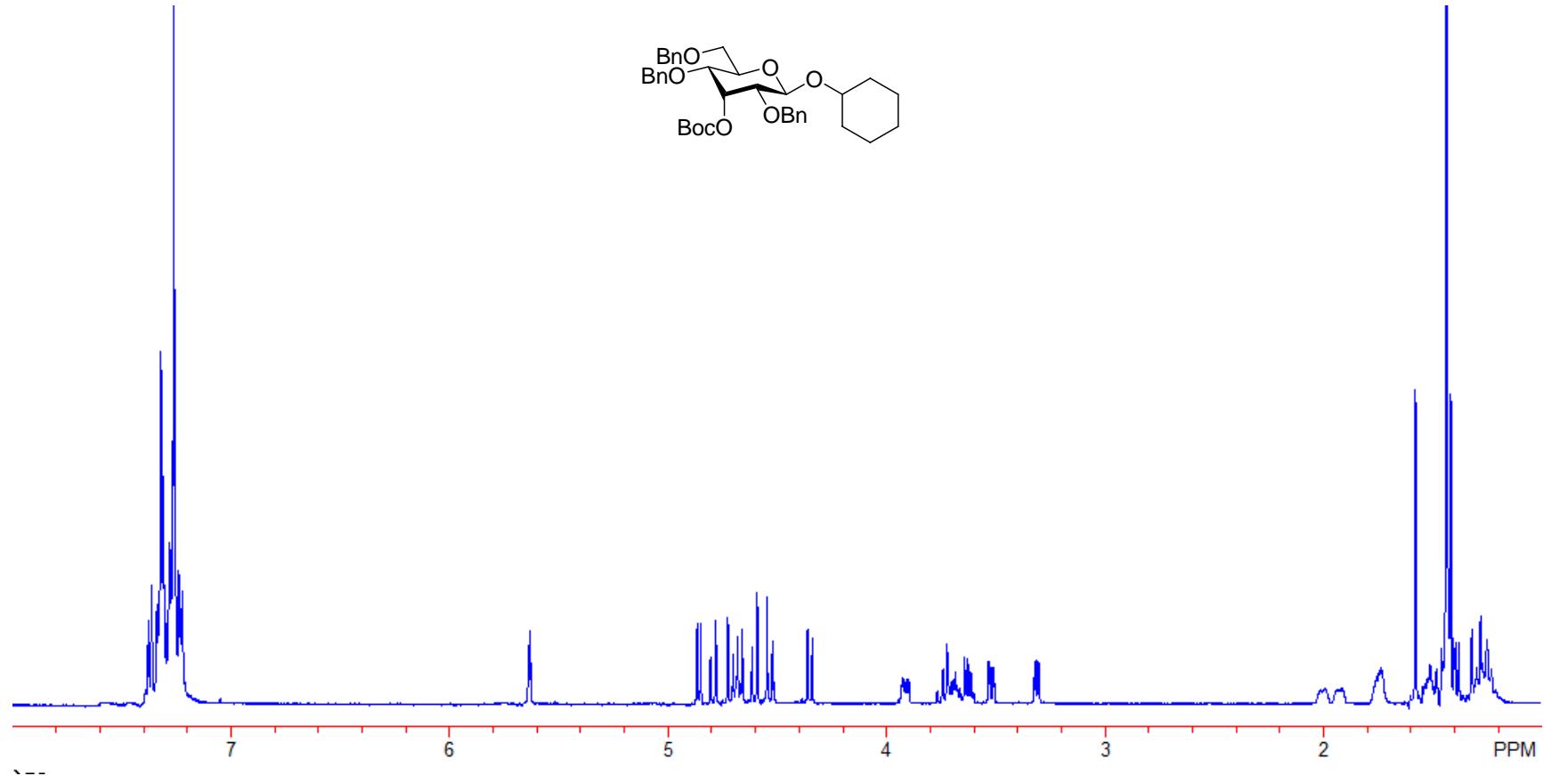
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl- α -D-allopyranoside (**17 α**)



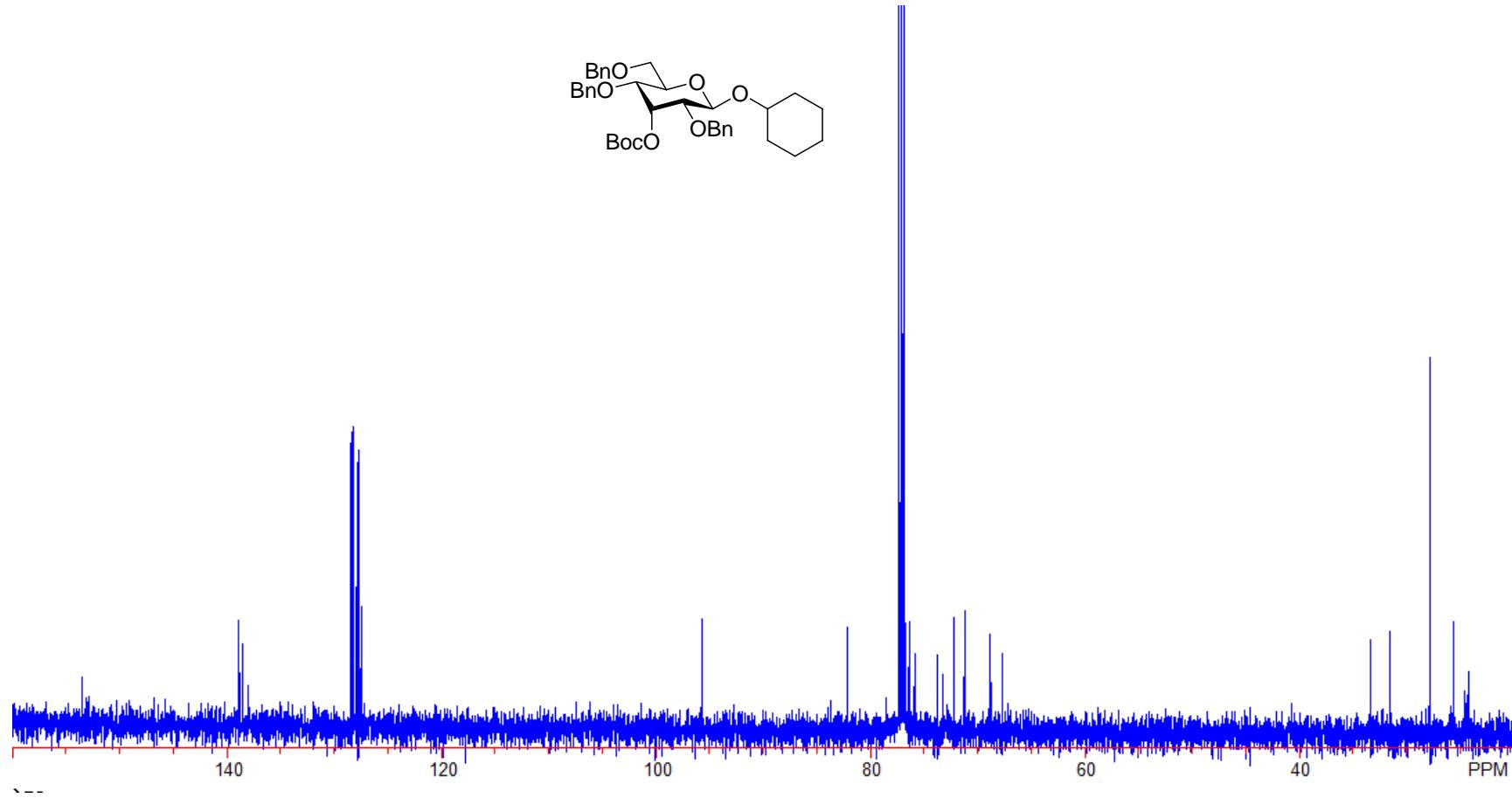
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl- α -D-allopyranoside (**17 α**)



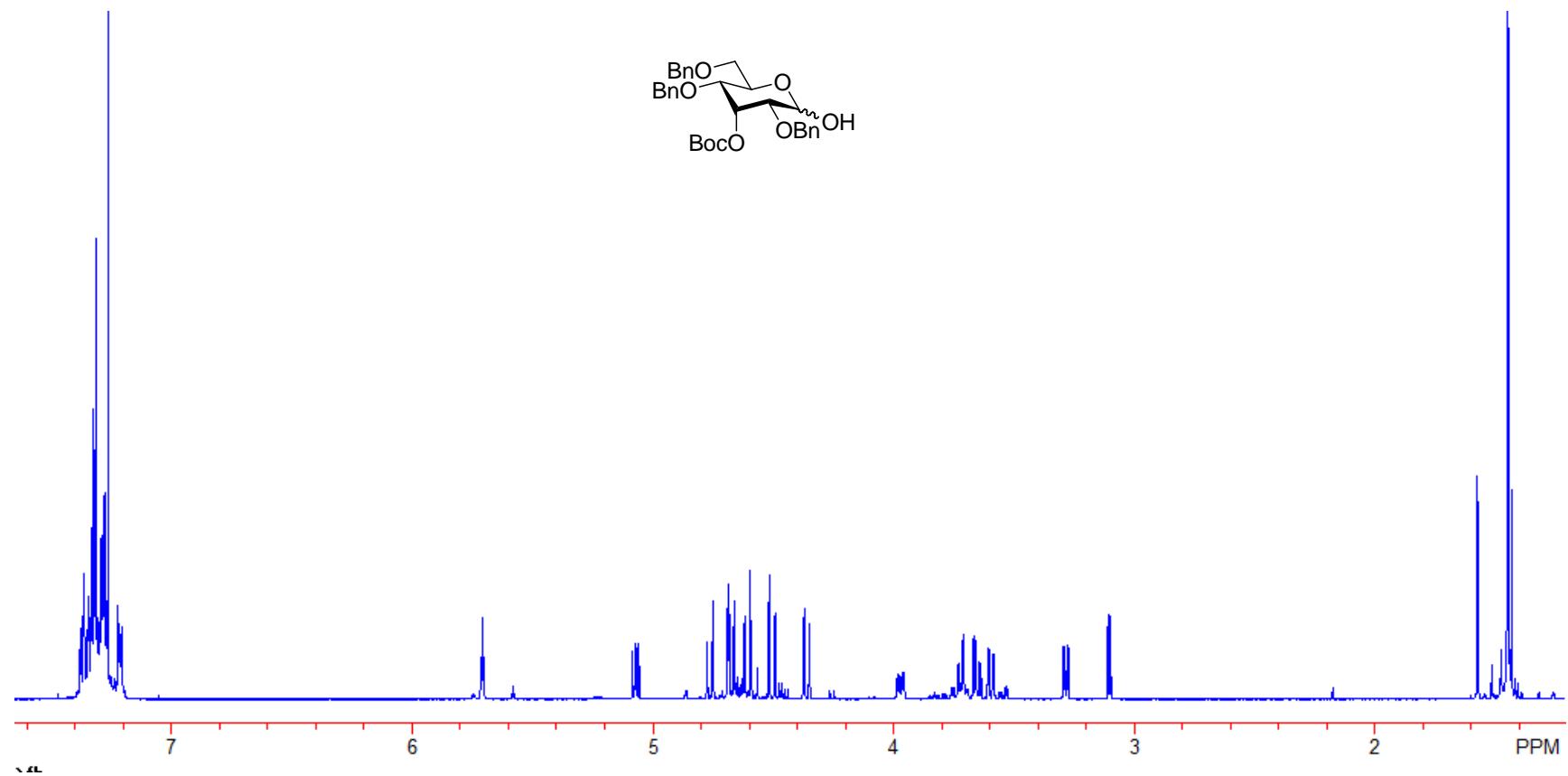
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl- β -D-allopyranoside (**17 β**).



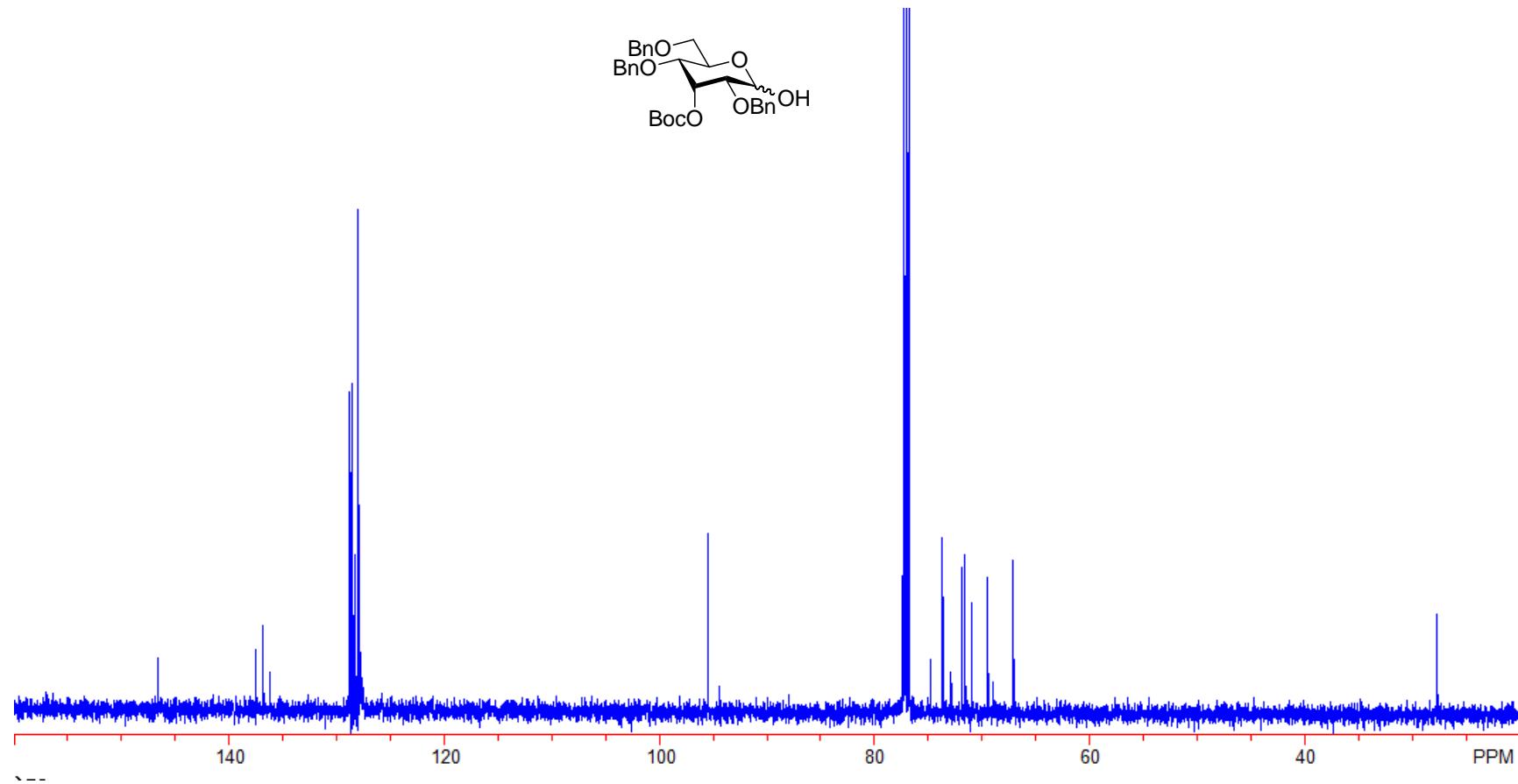
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl- β -D-allopyranoside (**17 β**).



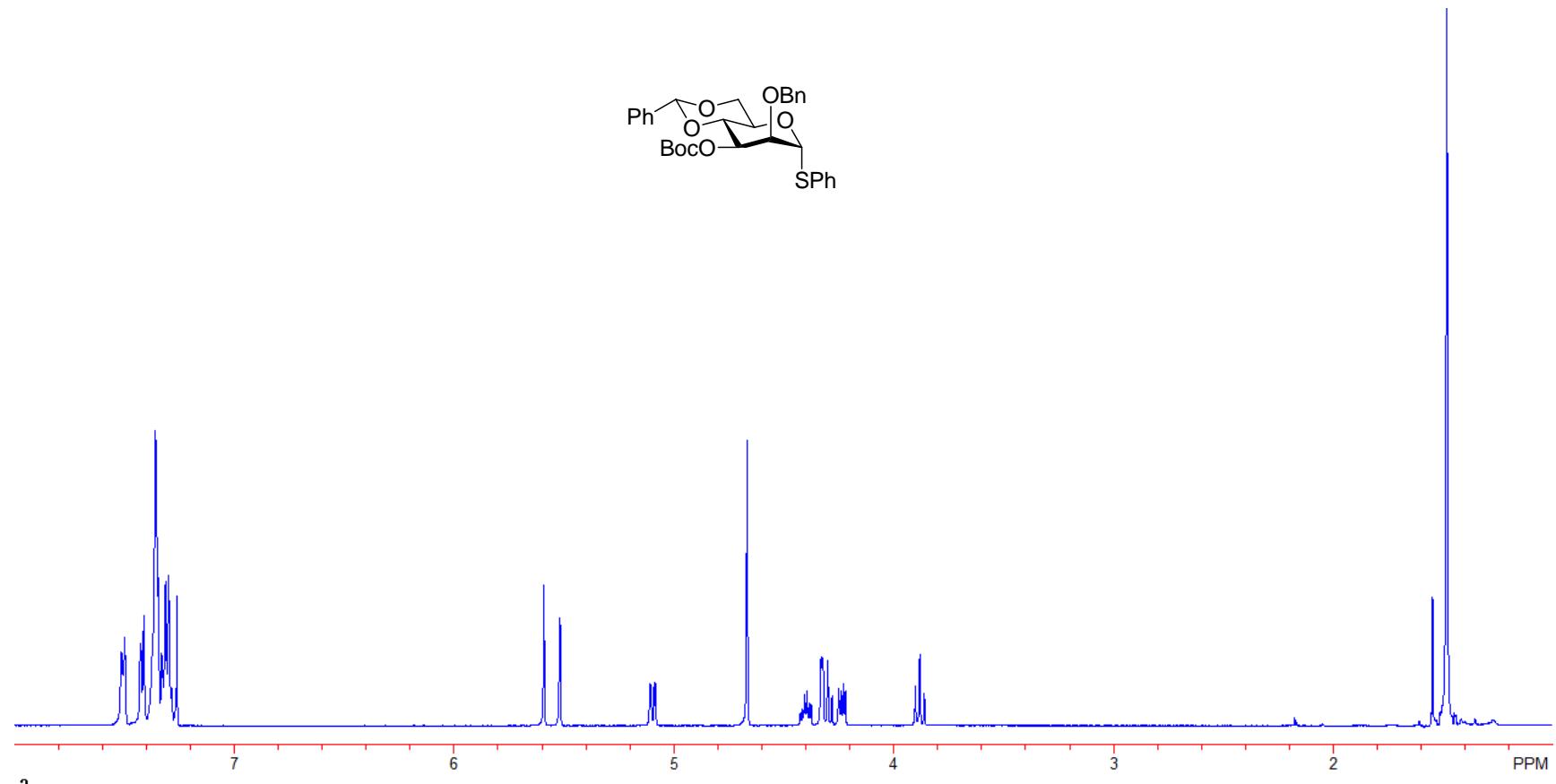
3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-D-allose (**18**).



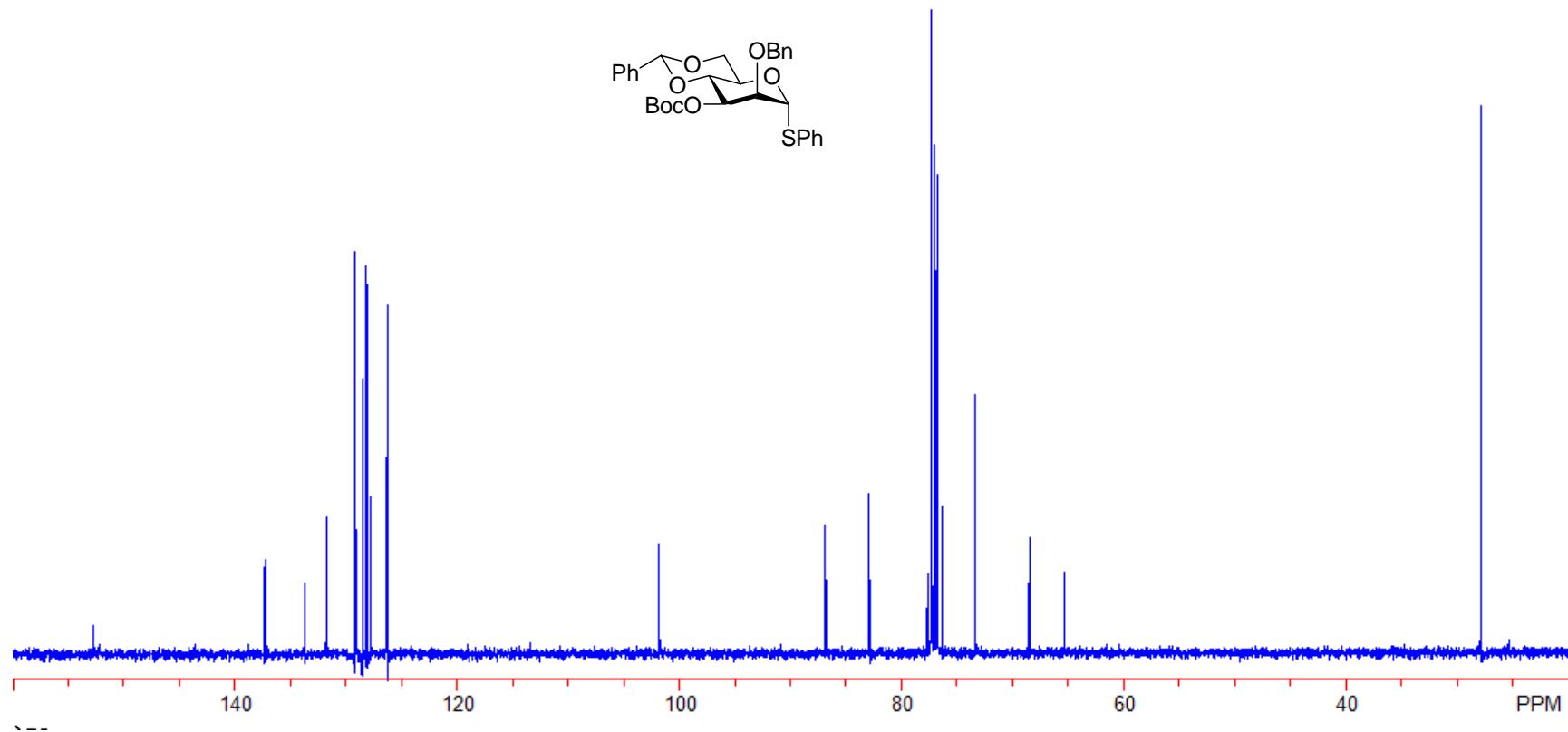
3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-D-allose (**18**).



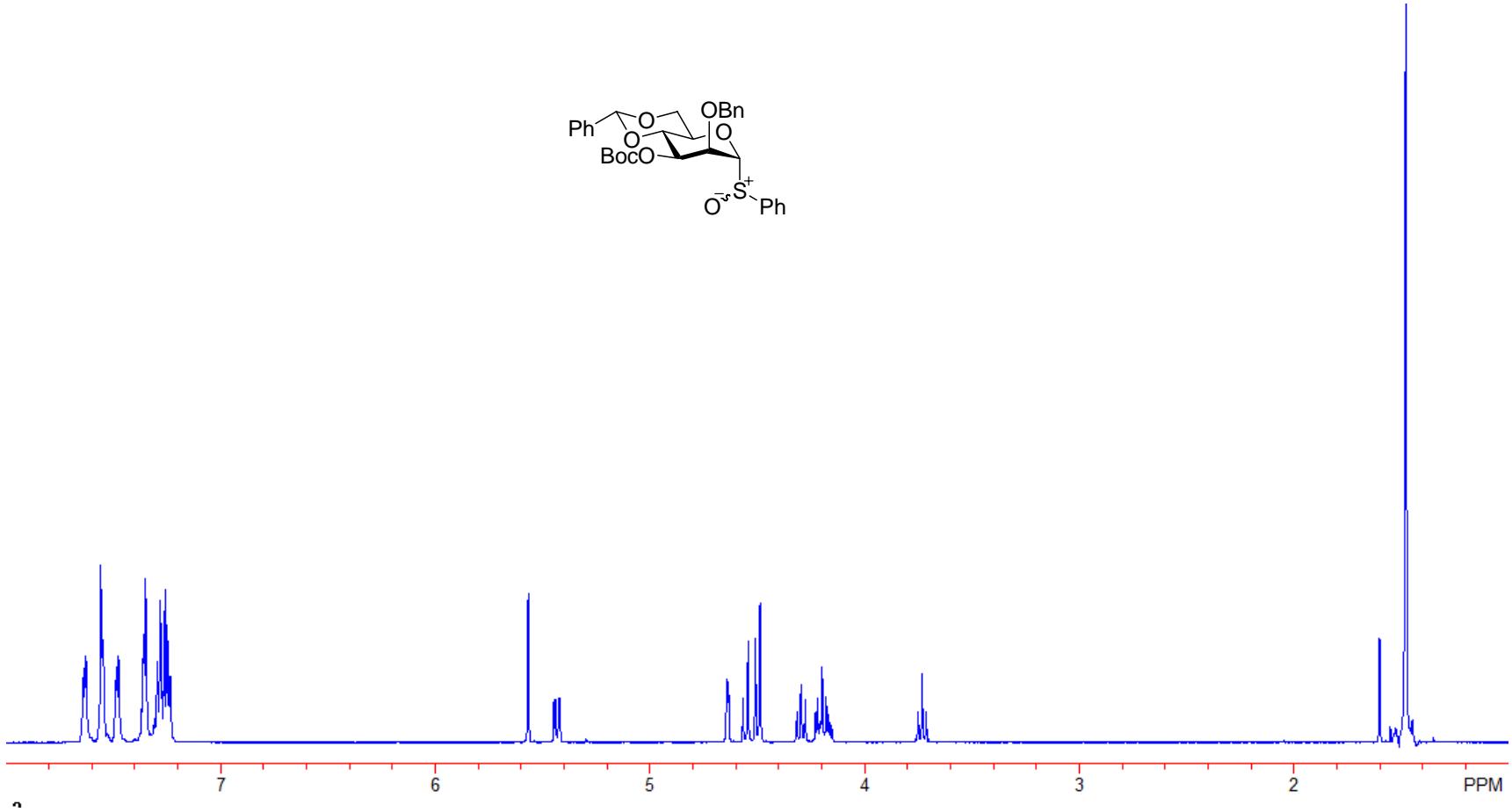
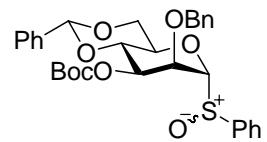
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio- α -D-mannopyranoside (**21**).



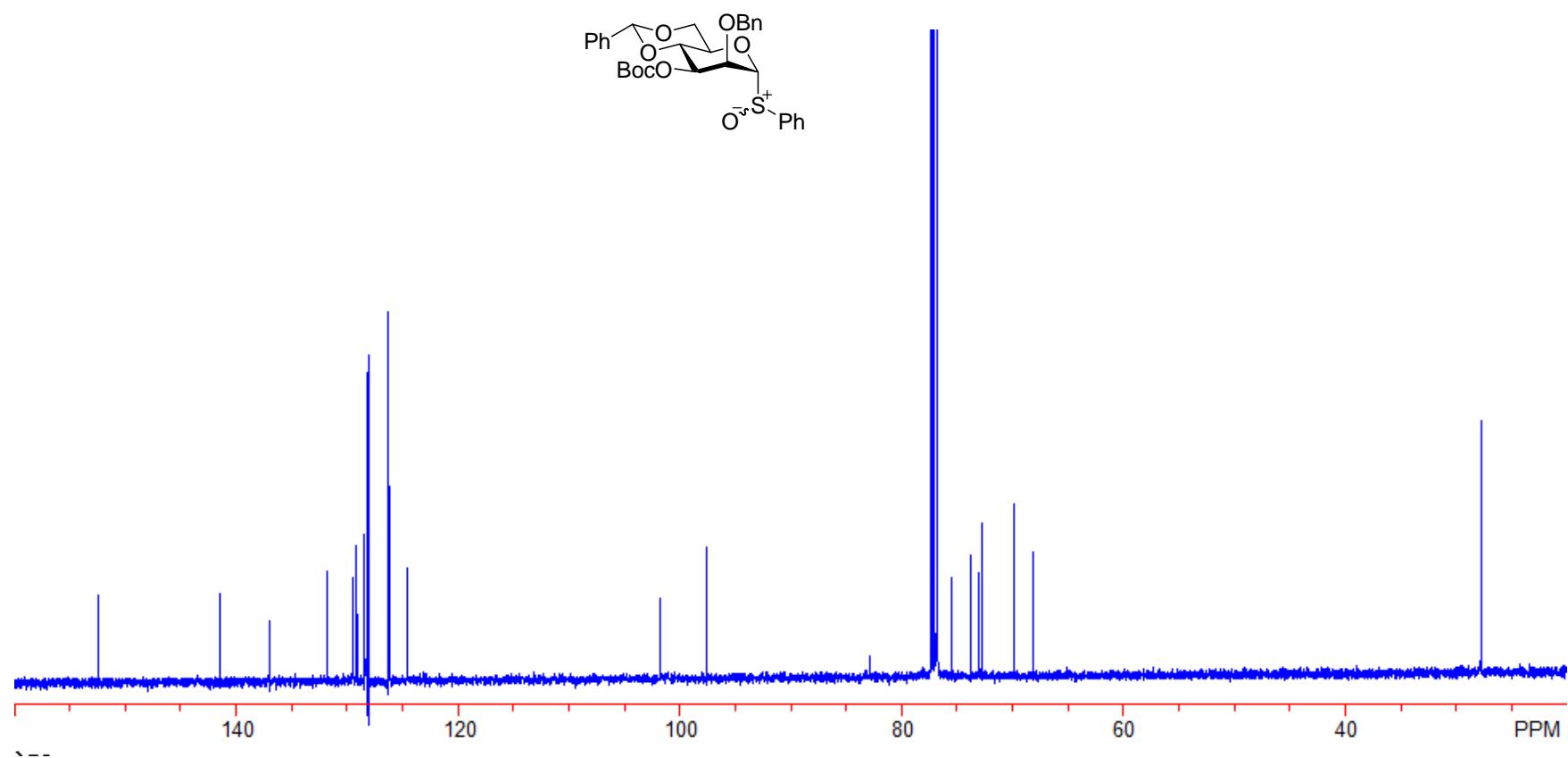
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio- α -D-mannopyranoside (**21**).



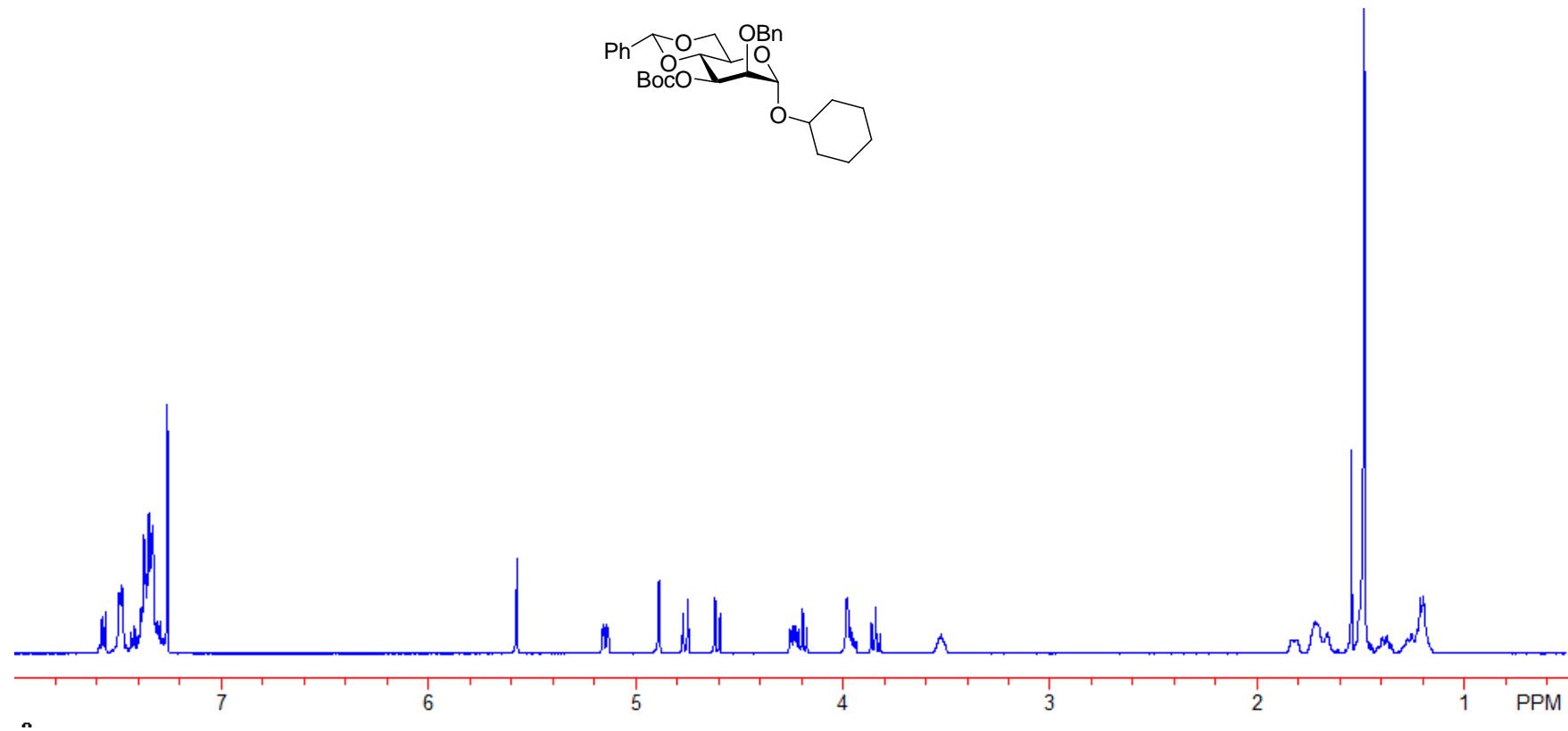
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio- α -D-mannopyranoside *S*-Oxide (**22**).



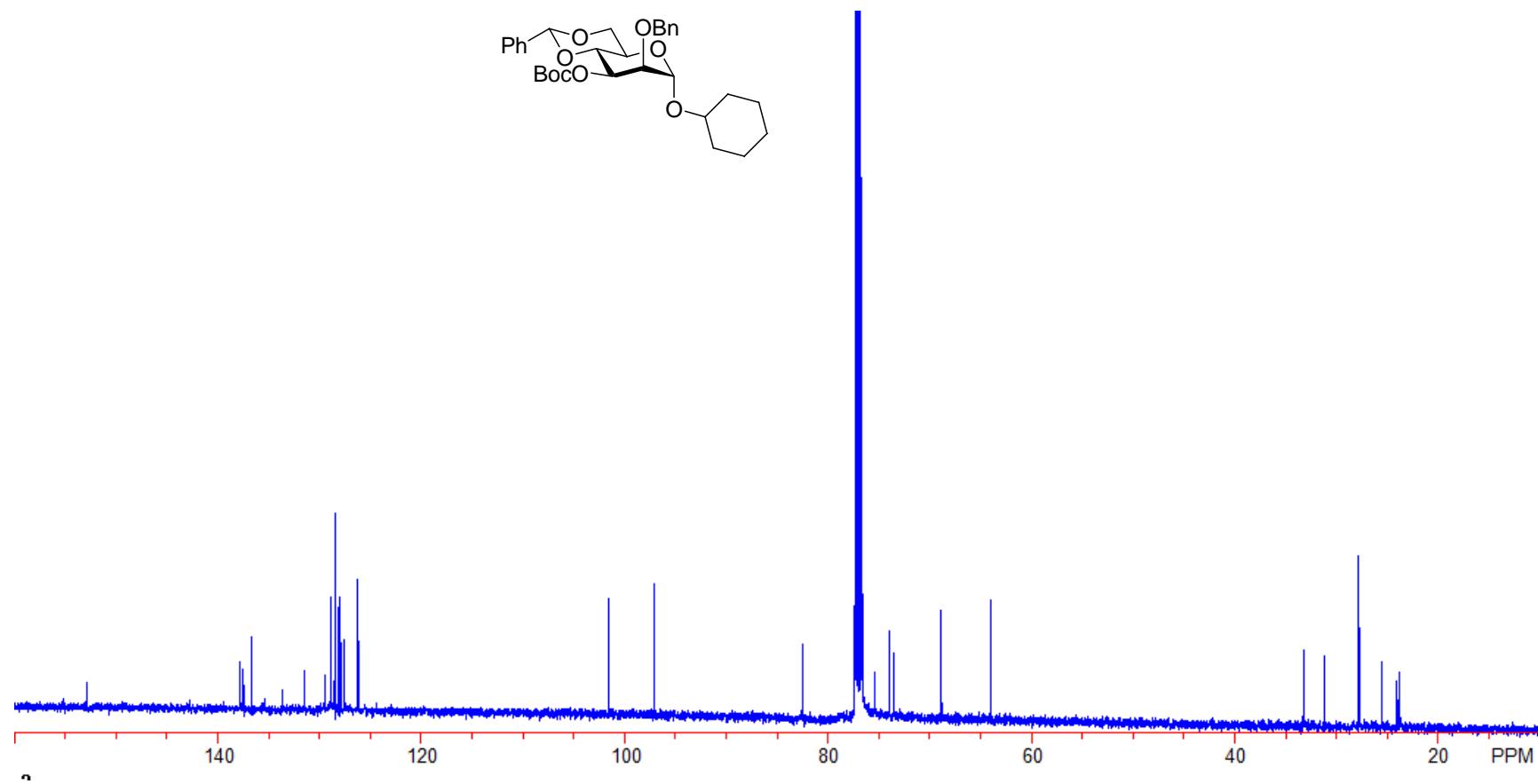
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio- α -D-mannopyranoside *S*-Oxide (**22**).



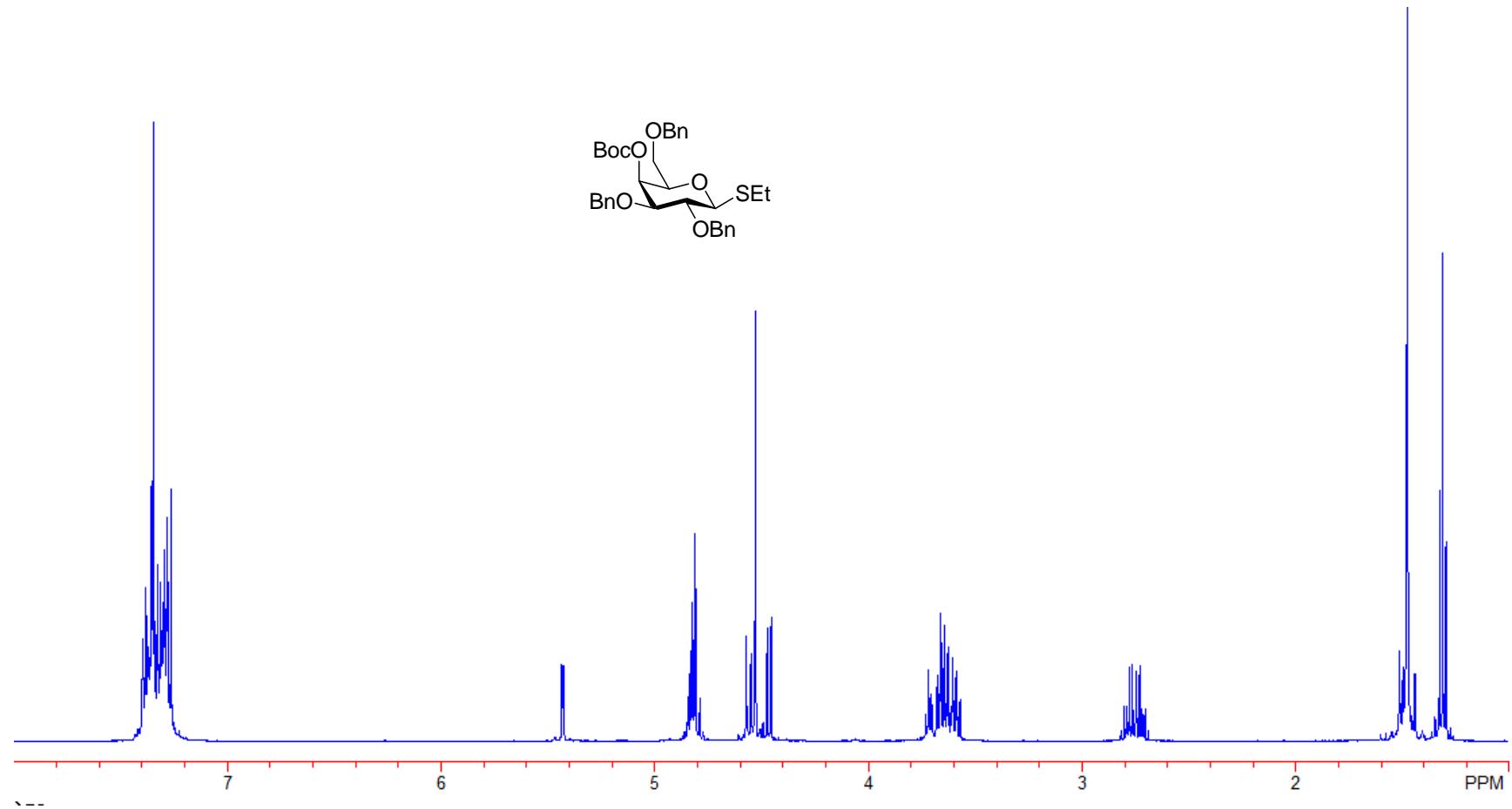
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (**23**).



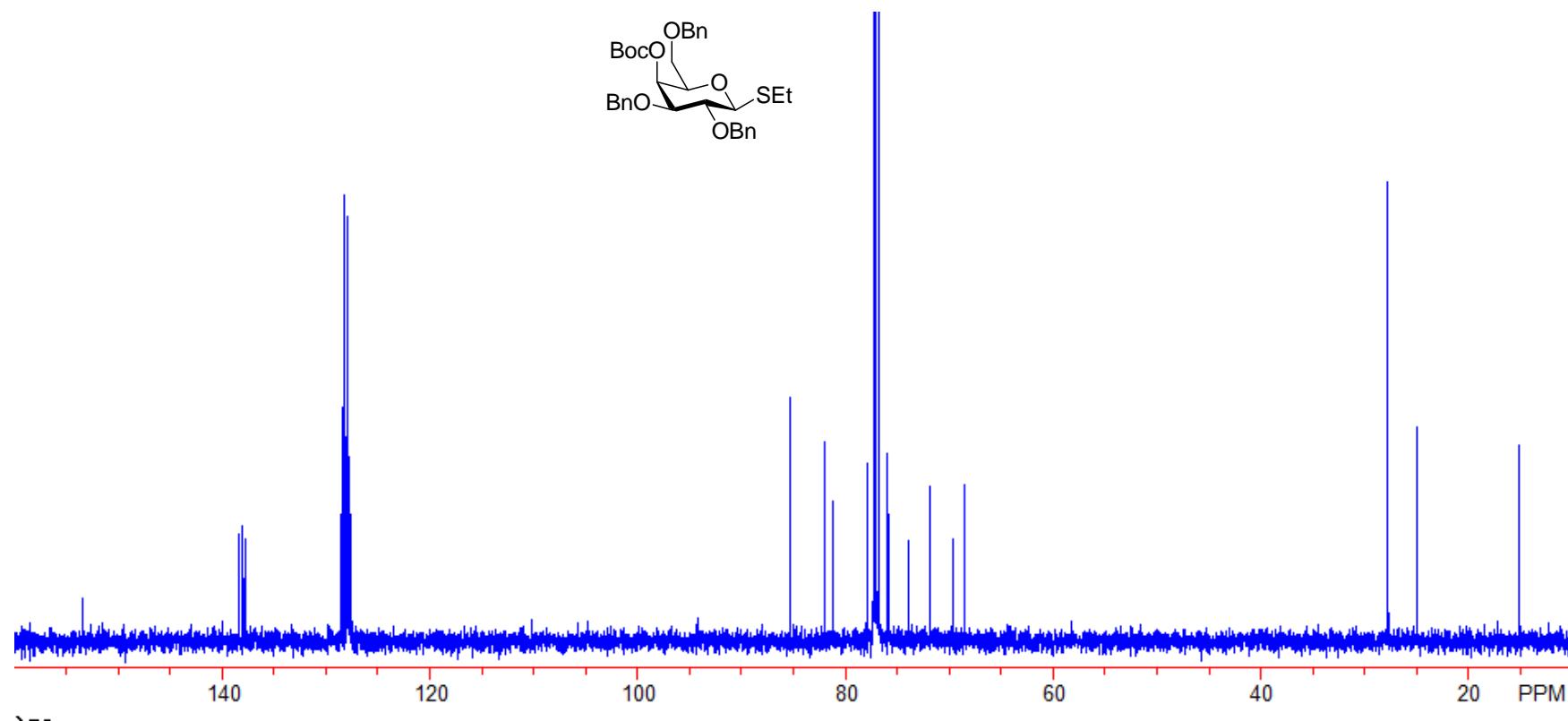
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside (**23**).



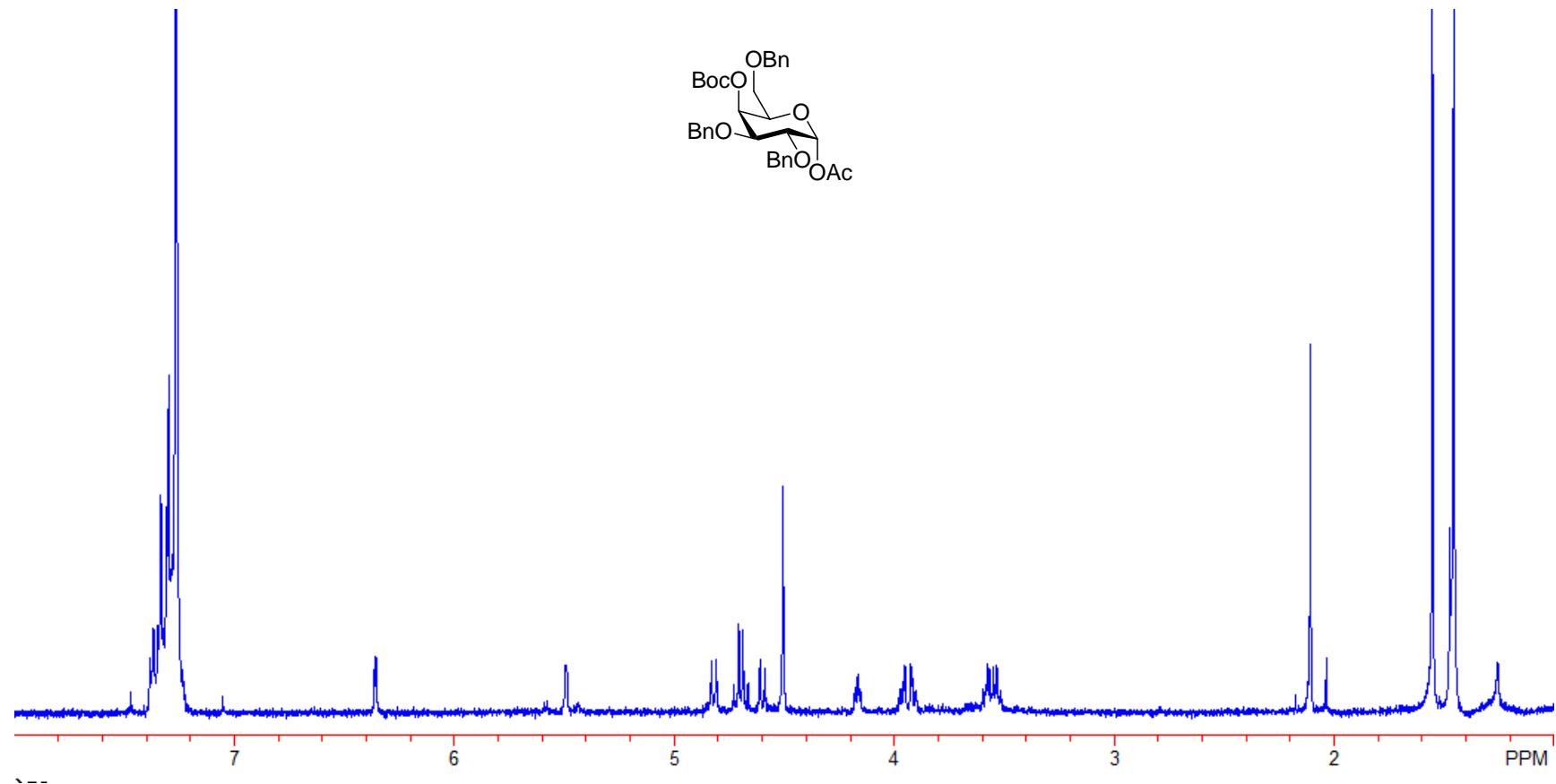
Ethyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-tri-*O*-benzyl-1-thio- β -D-galactopyranoside (**24**).



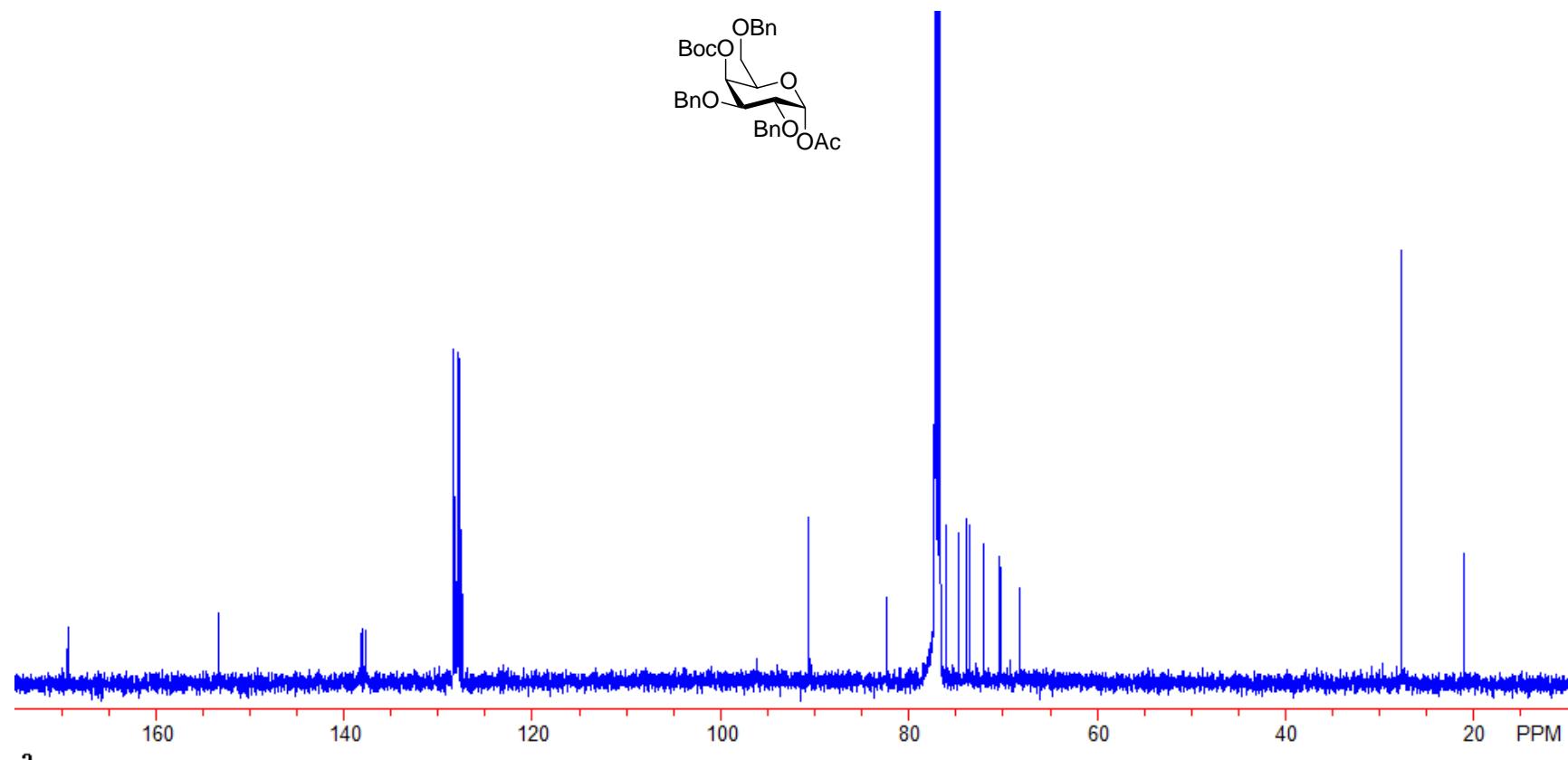
Ethyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-tri-*O*-benzyl-1-thio- β -D-galactopyranoside (**24**).



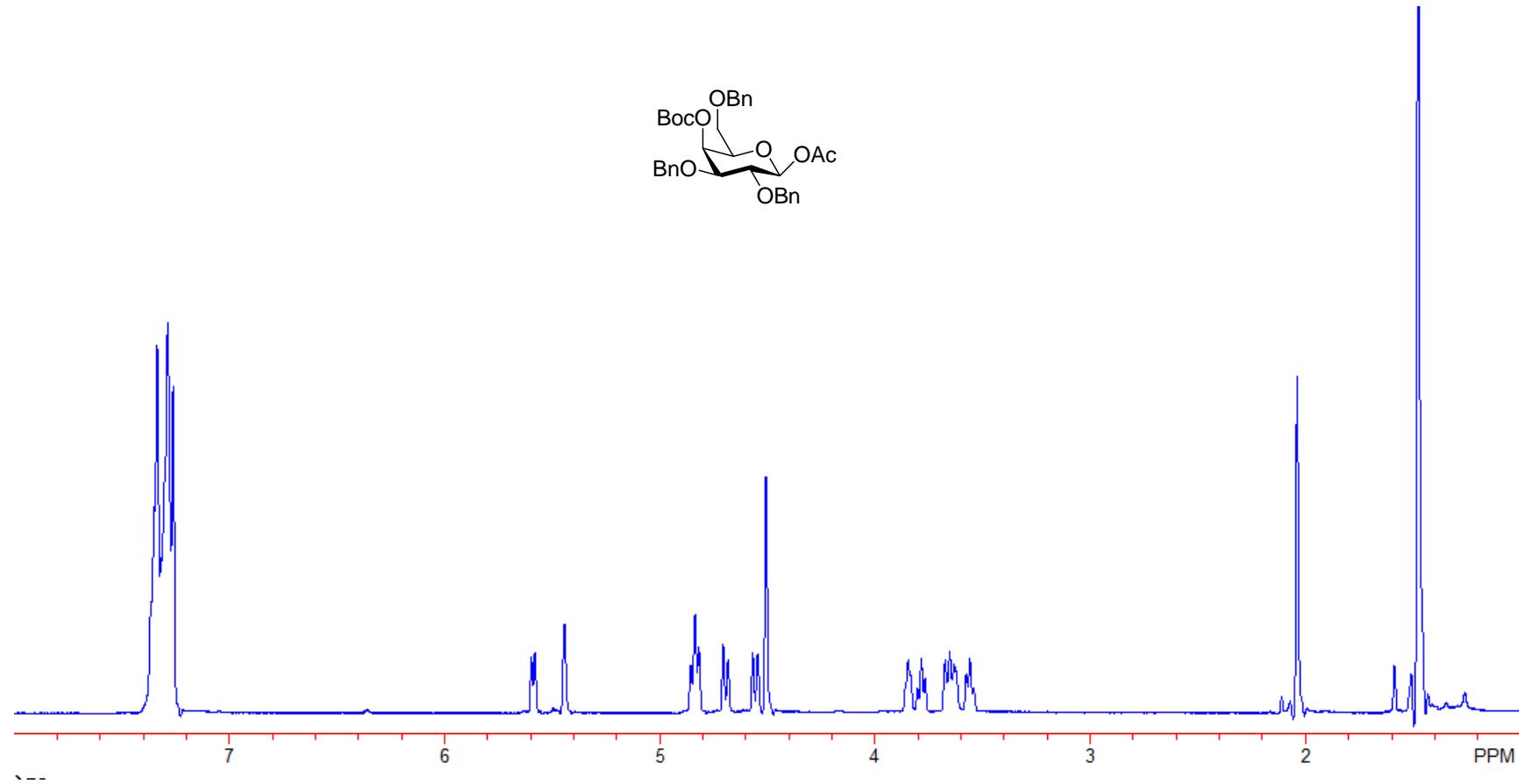
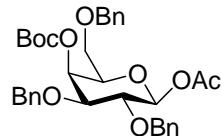
4-*O*-*tert*-Butoxycarbonyl-2,3,6-*O*-tribenzyl- α -D-galactopyranosyl acetate (**25a**).



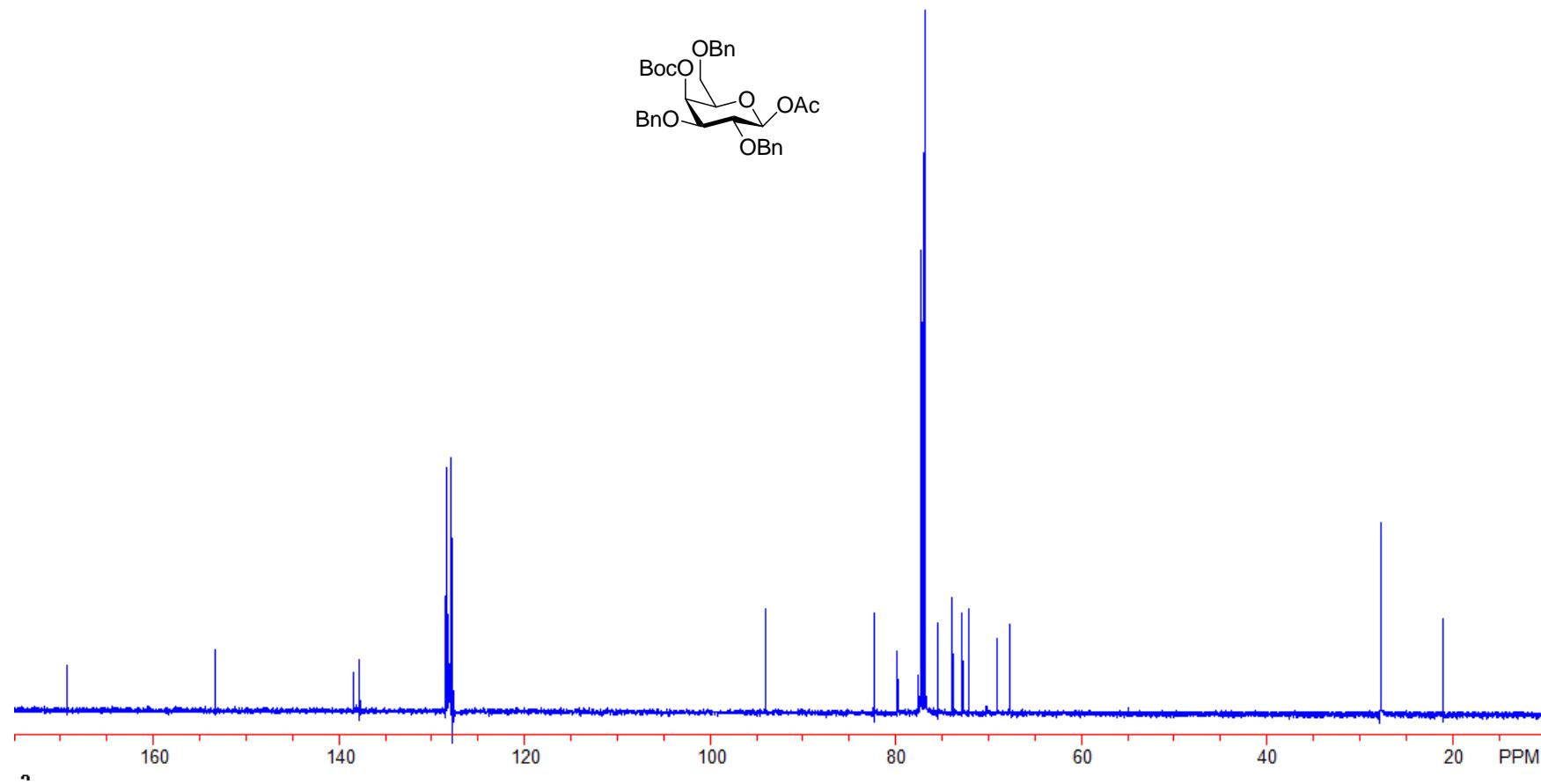
4-*O*-*tert*-Butoxycarbonyl-2,3,6-*O*-tribenzyl- α -D-galactopyranosyl acetate (**25a**).



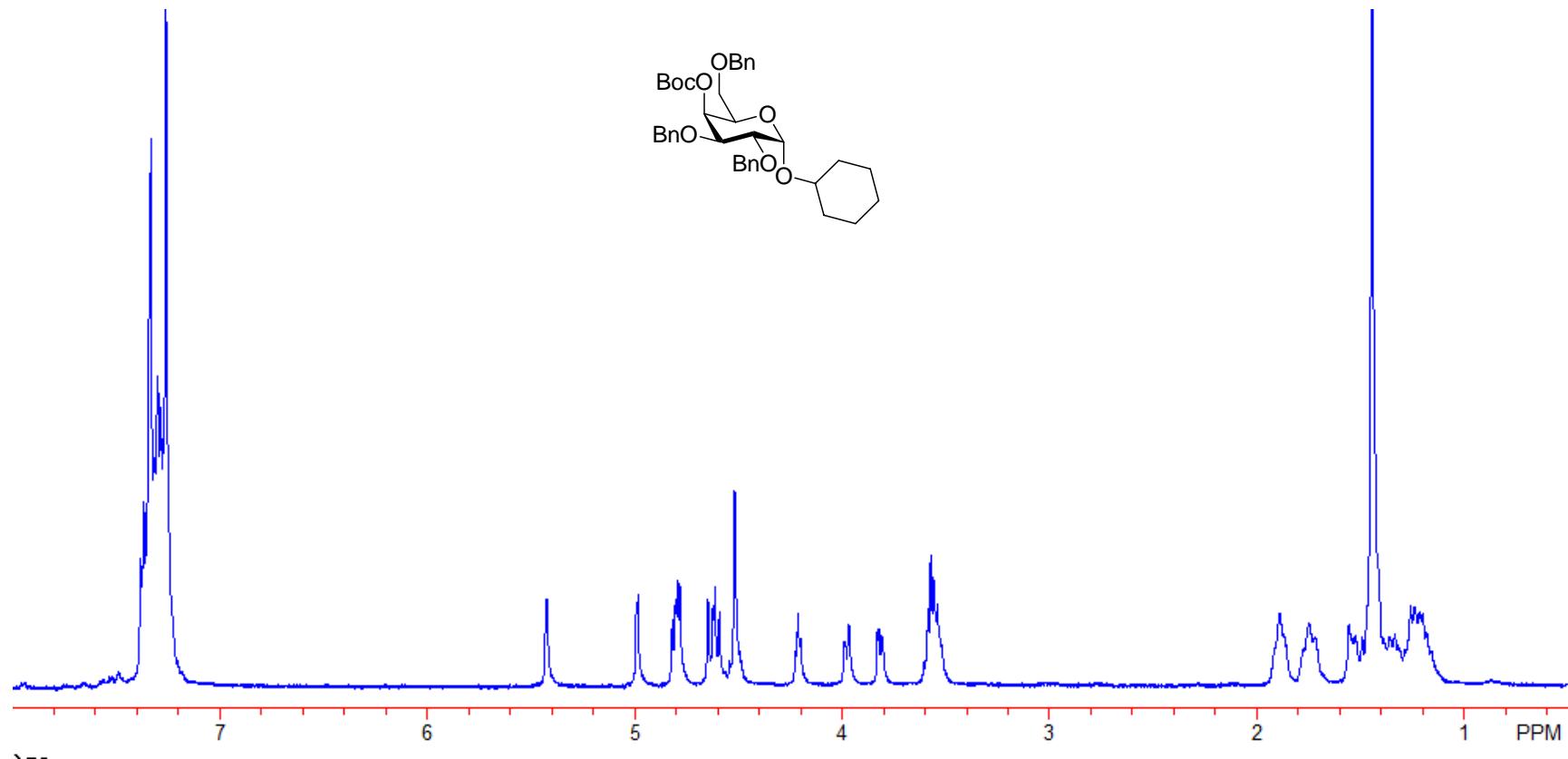
4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl- β -D-galactopyranosyl acetate (**25 β**).



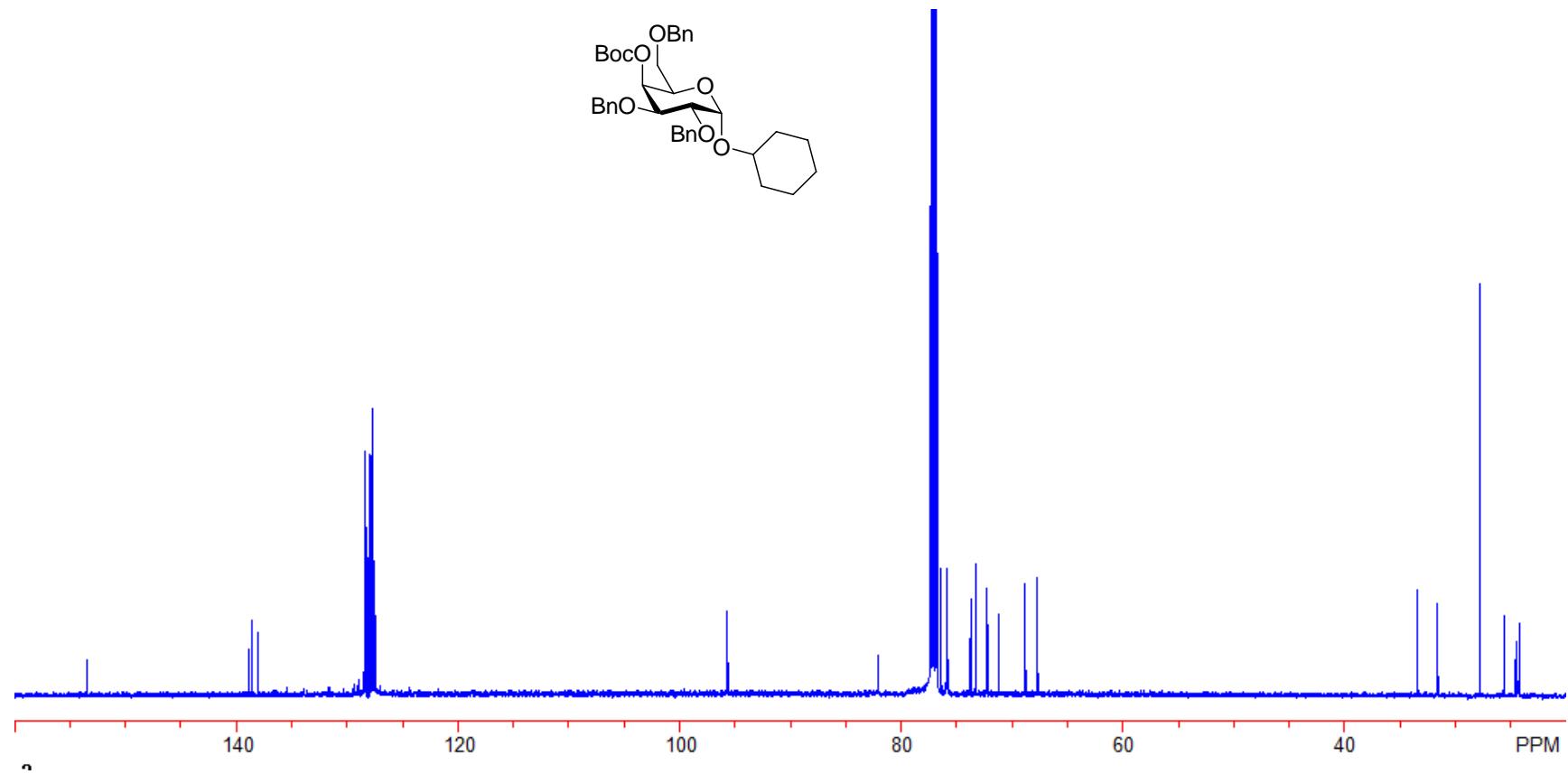
4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl- β -D-galactopyranosyl acetate (**25 β**).



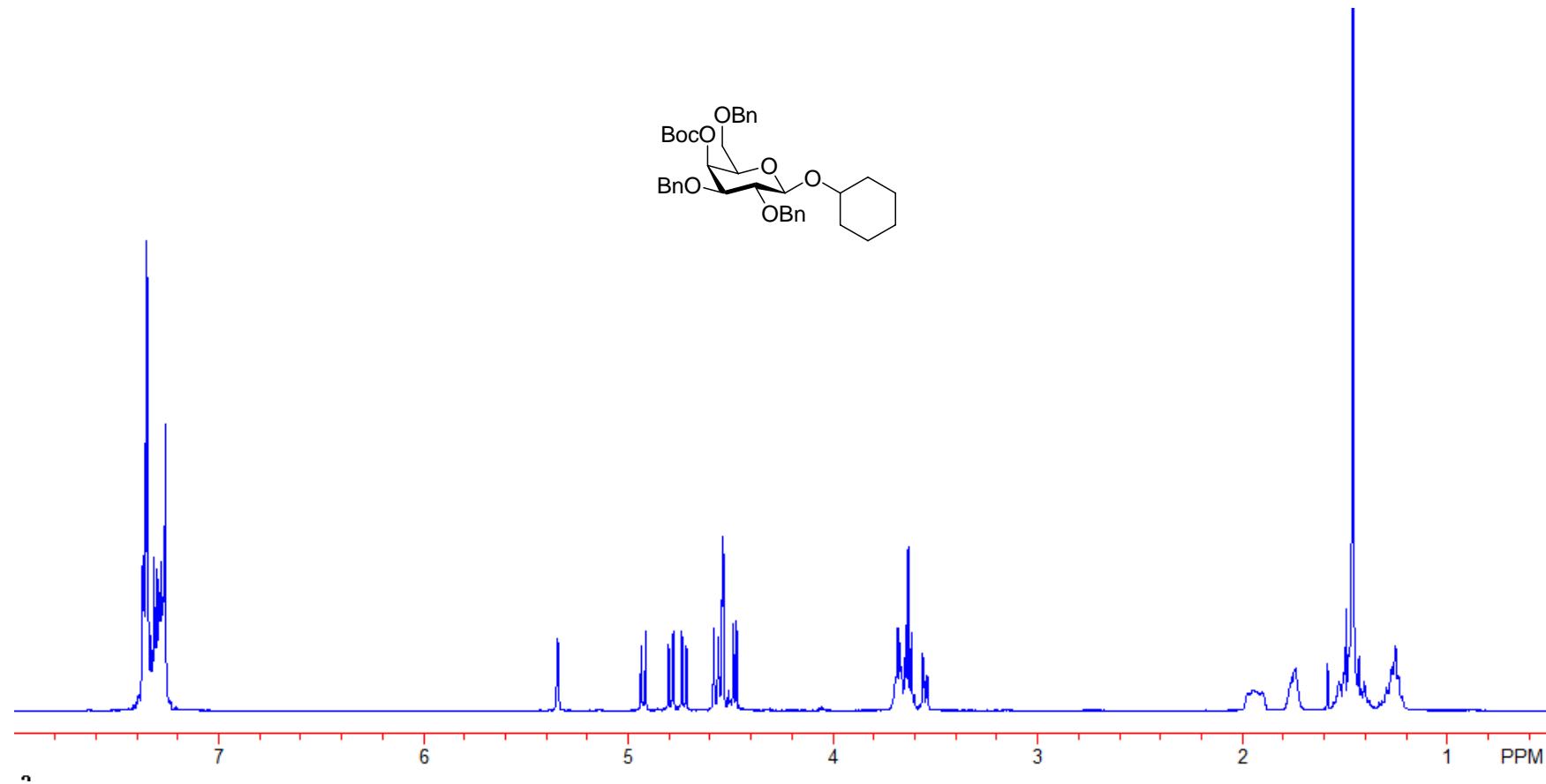
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-D-galactopyranoside (**26a**).



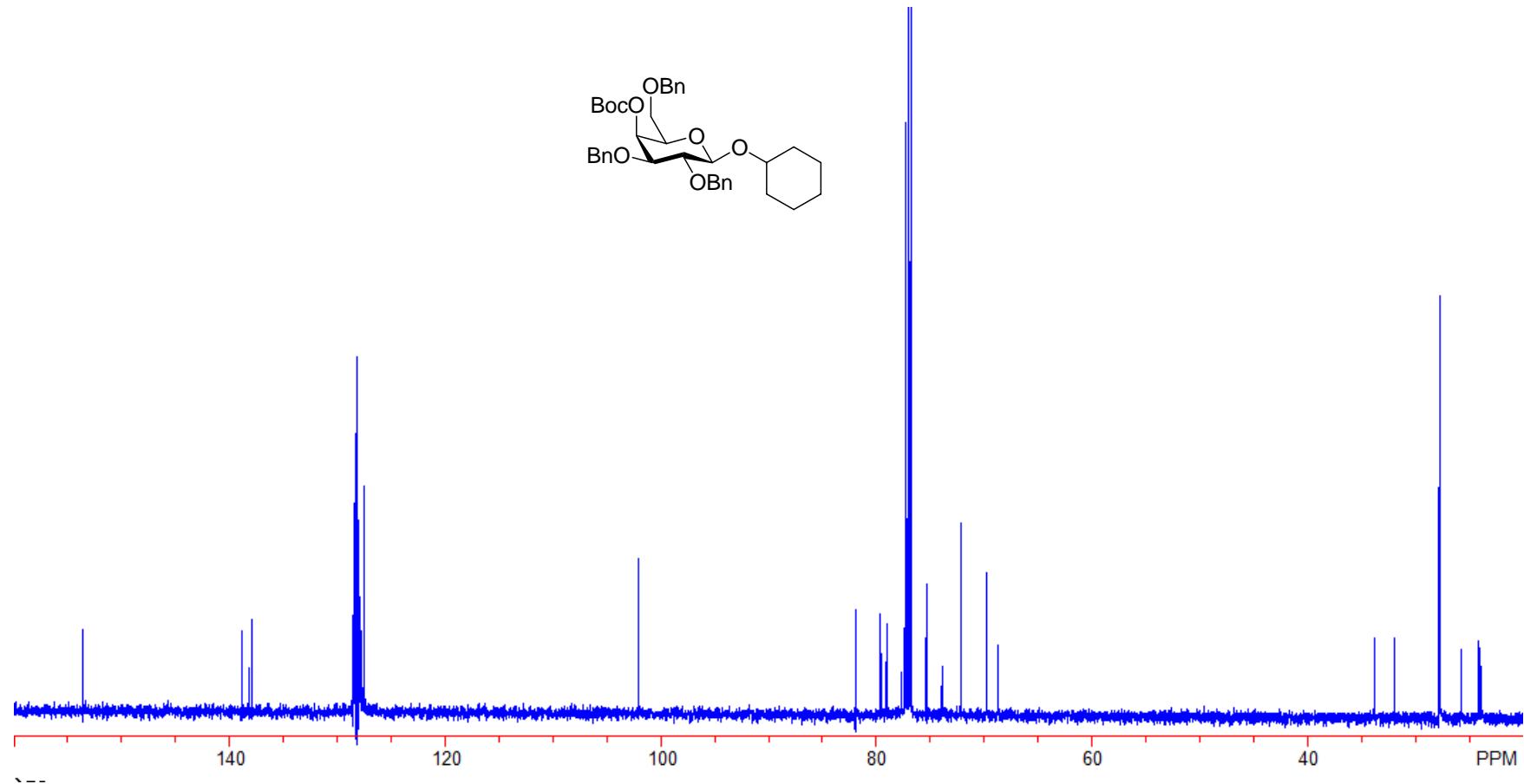
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-D-galactopyranoside (**26α**).



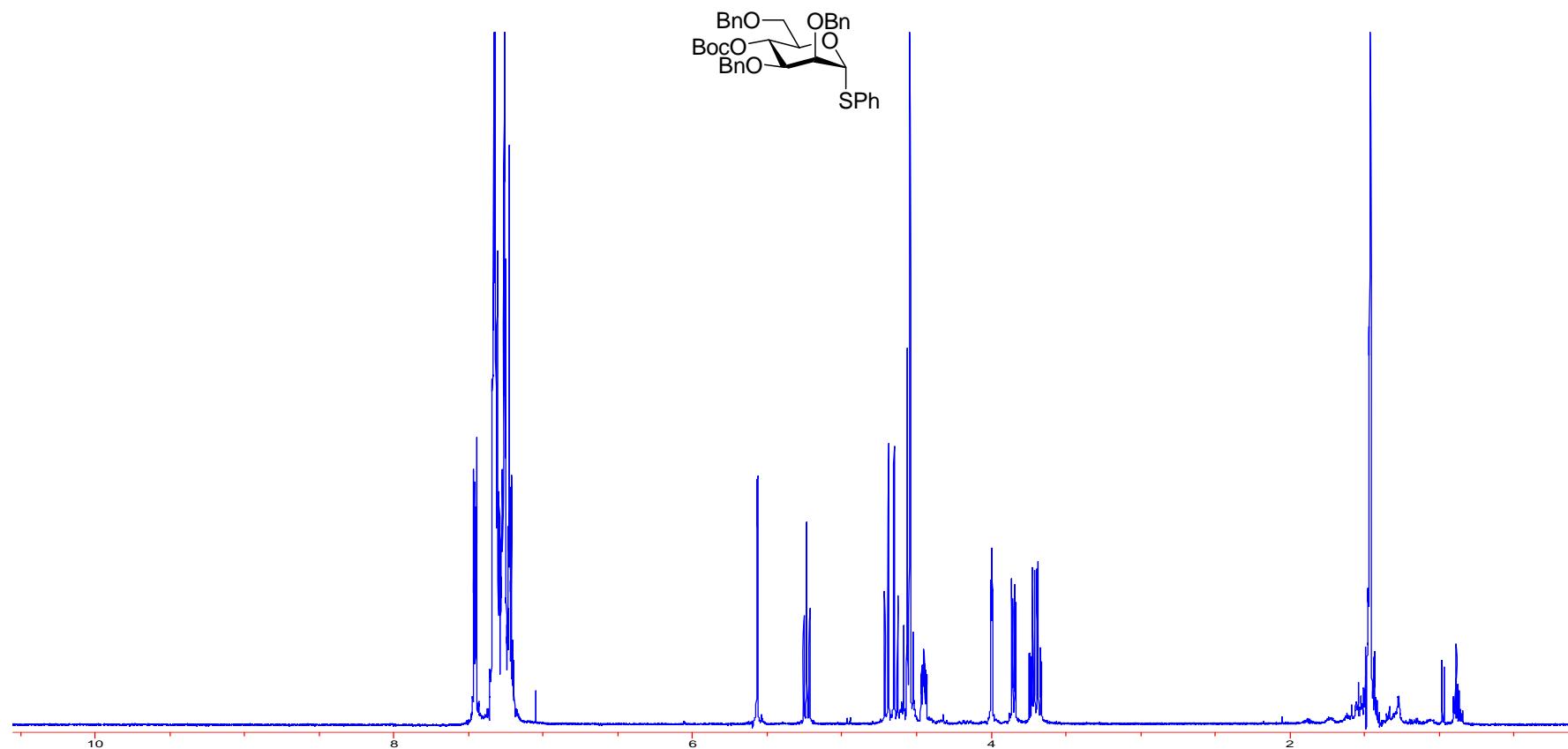
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl- β -D-galactopyranoside (**26 β**).



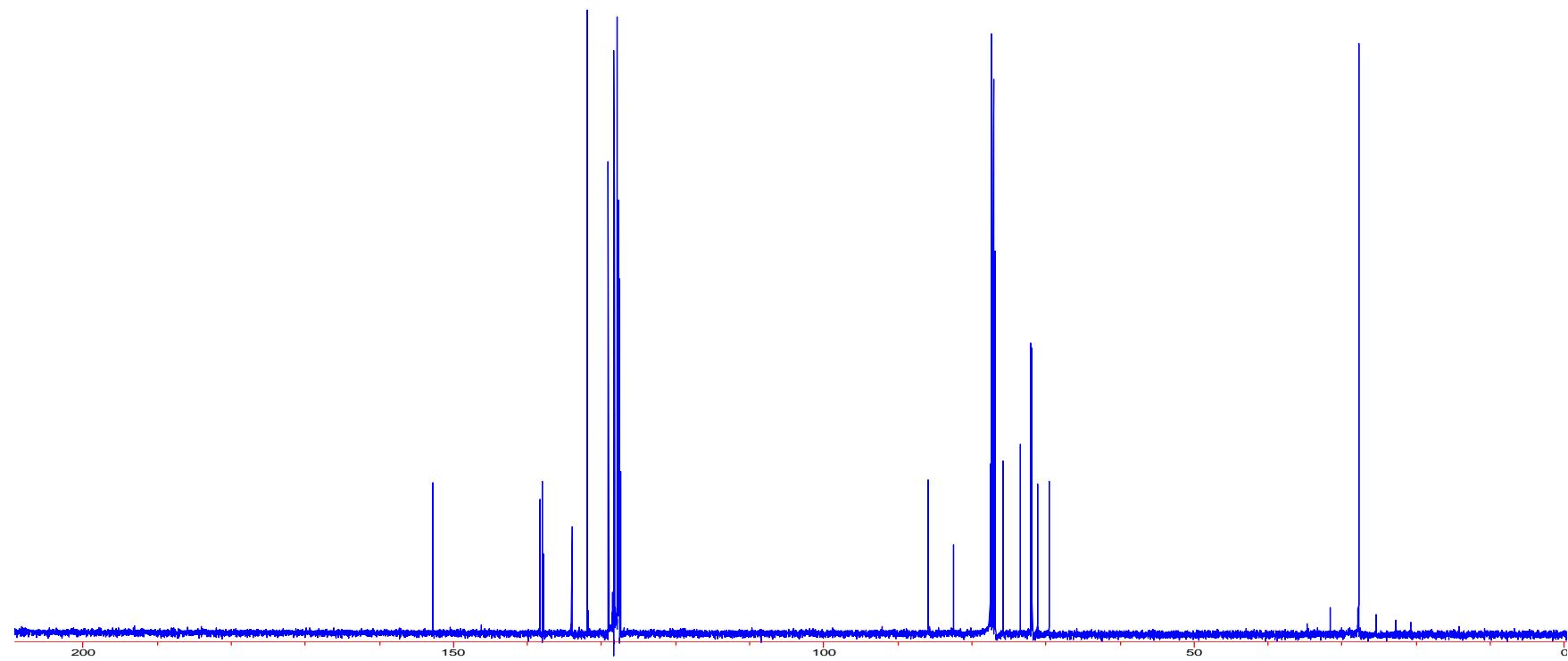
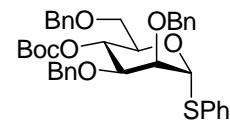
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl- β -D-galactopyranoside (**26 β**).



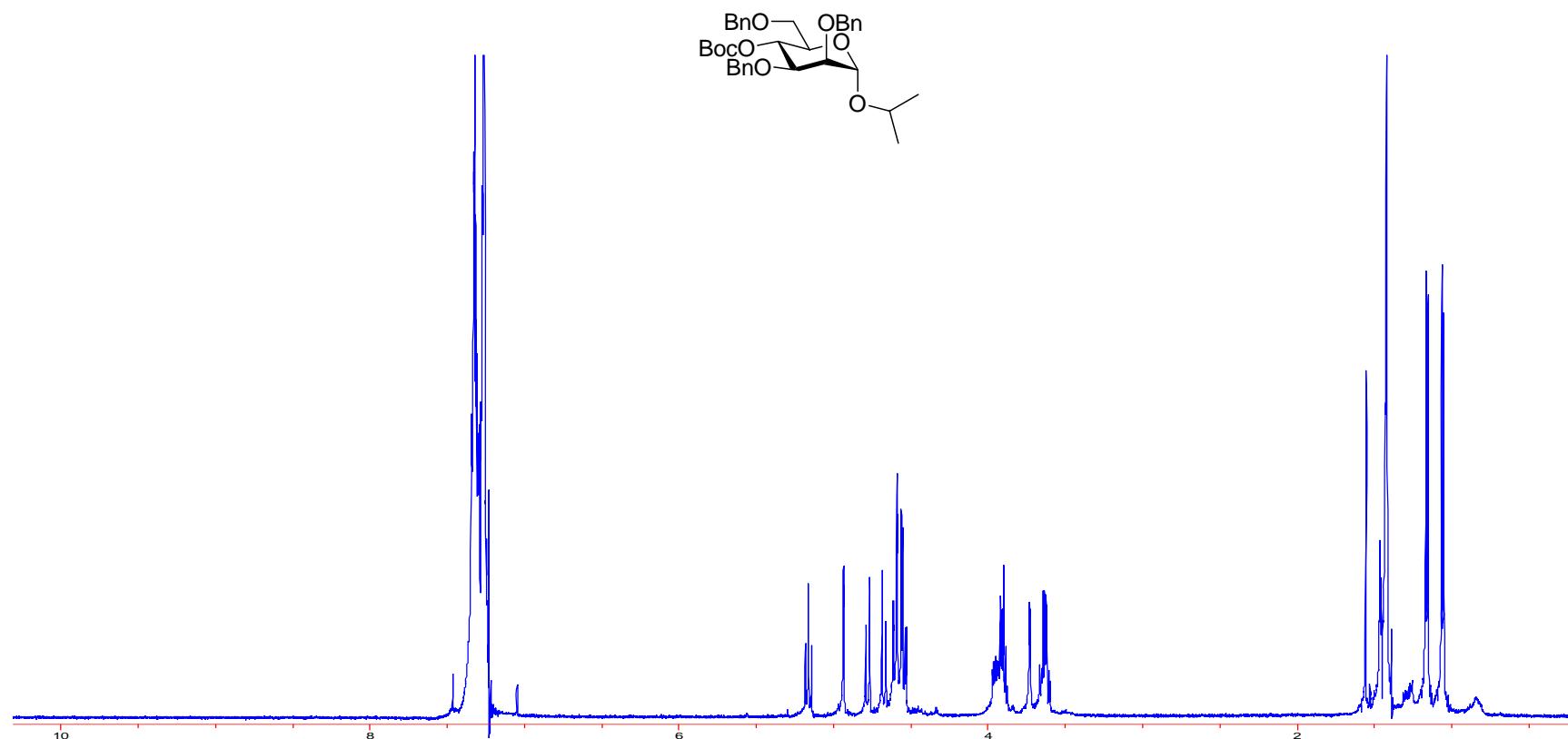
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl-1-thio- α -D-mannopyranoside (**27**)



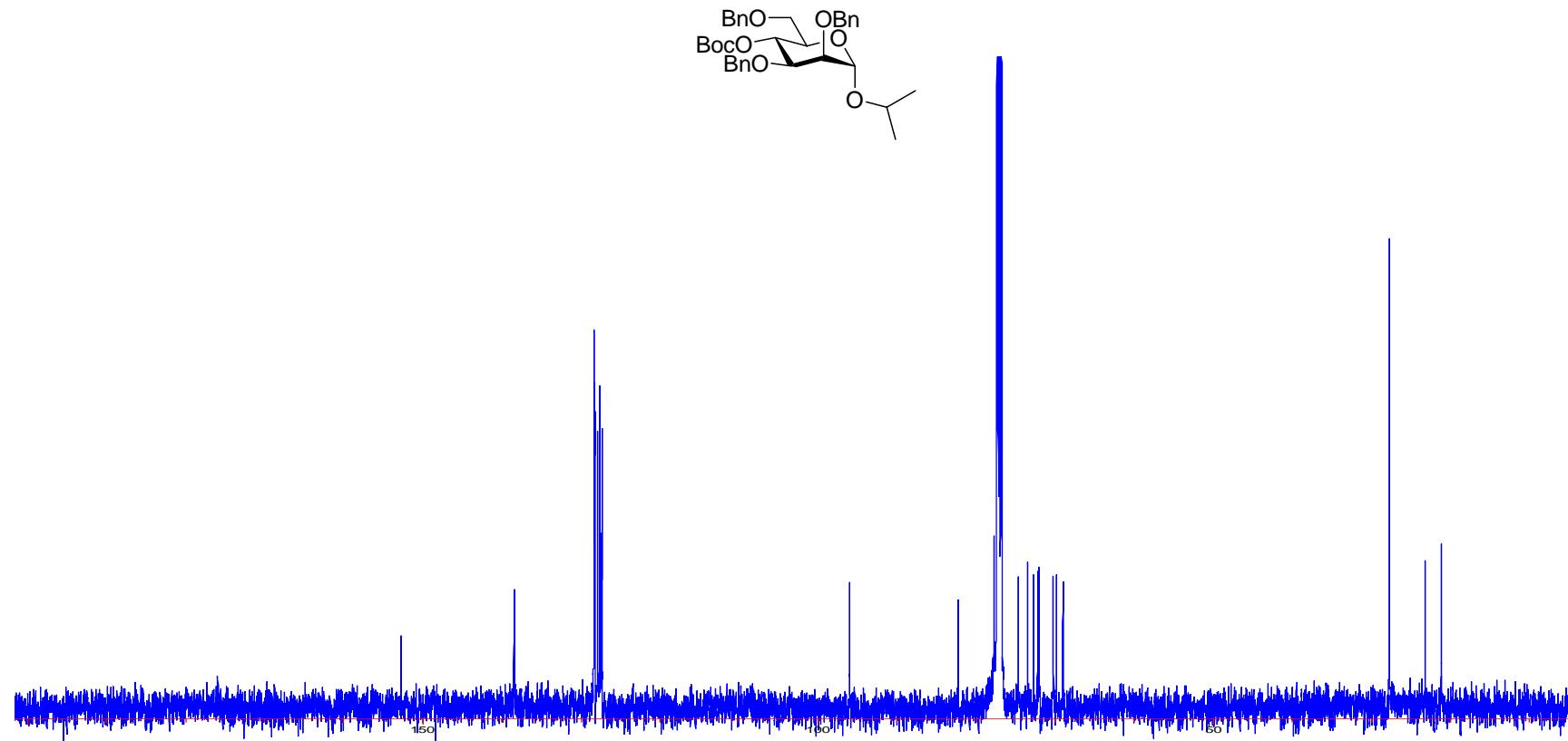
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl-1-thio- α -D-mannopyranoside (**27**)



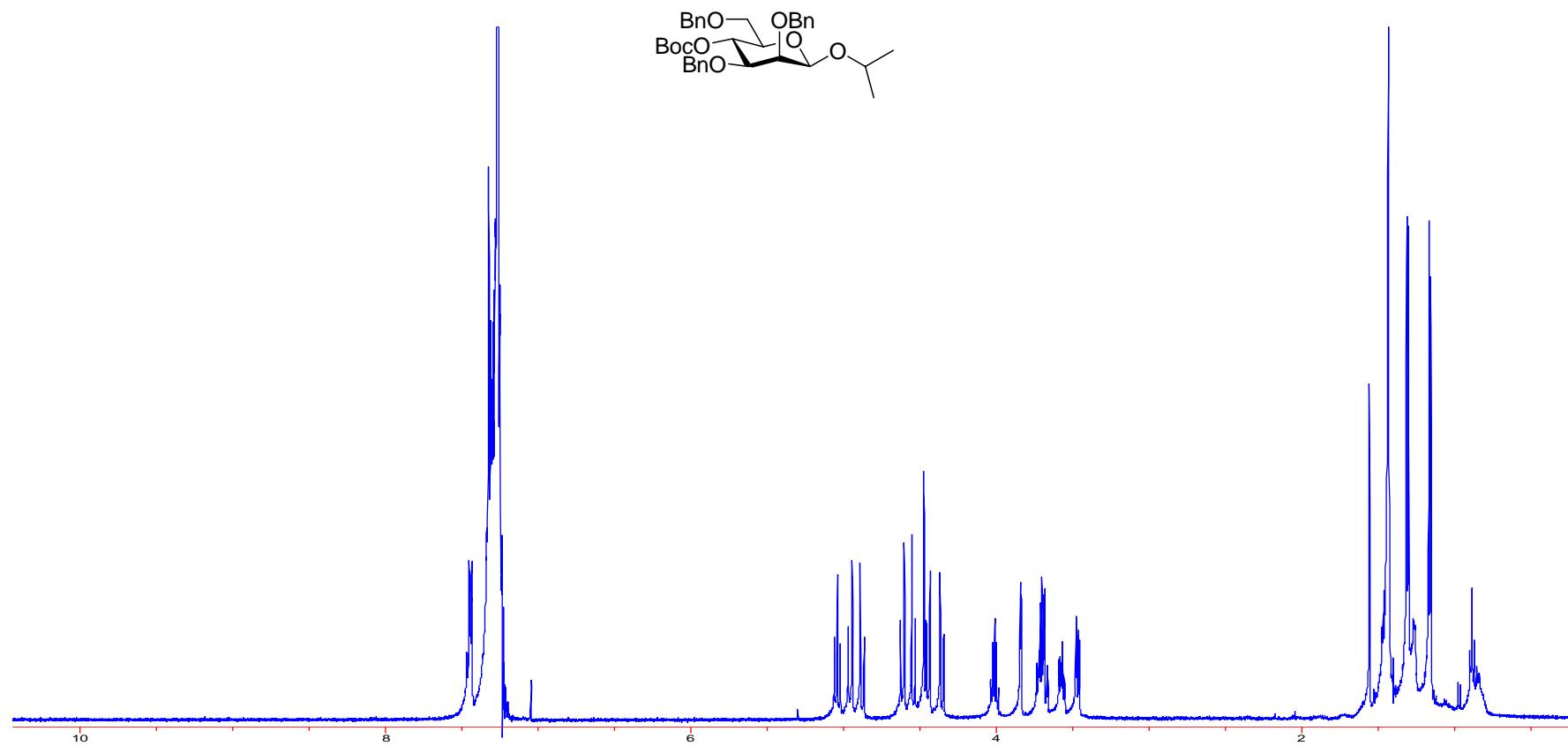
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl- α -D-mannopyranoside (**28a**)



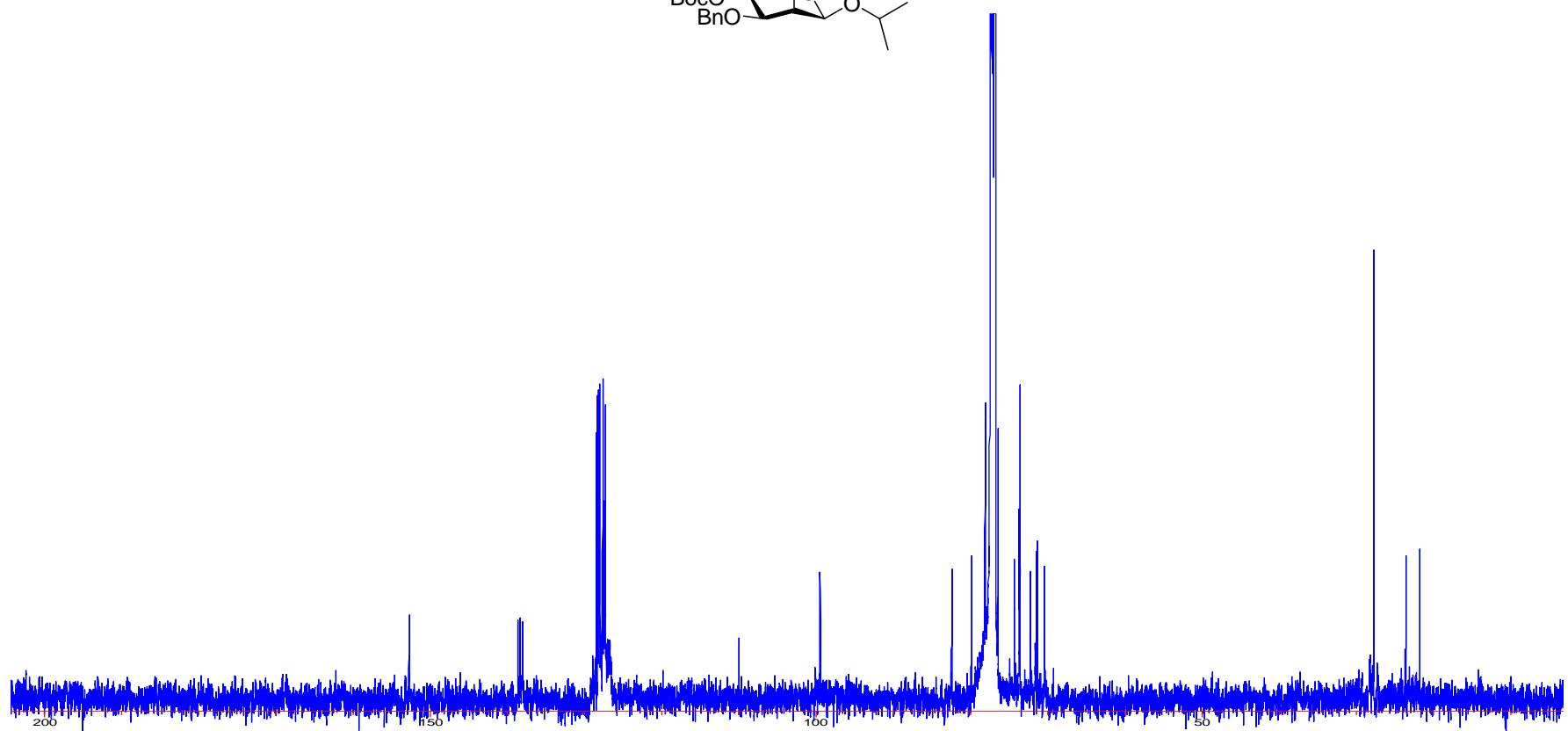
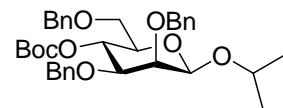
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl- α -D-mannopyranoside (**28a**)



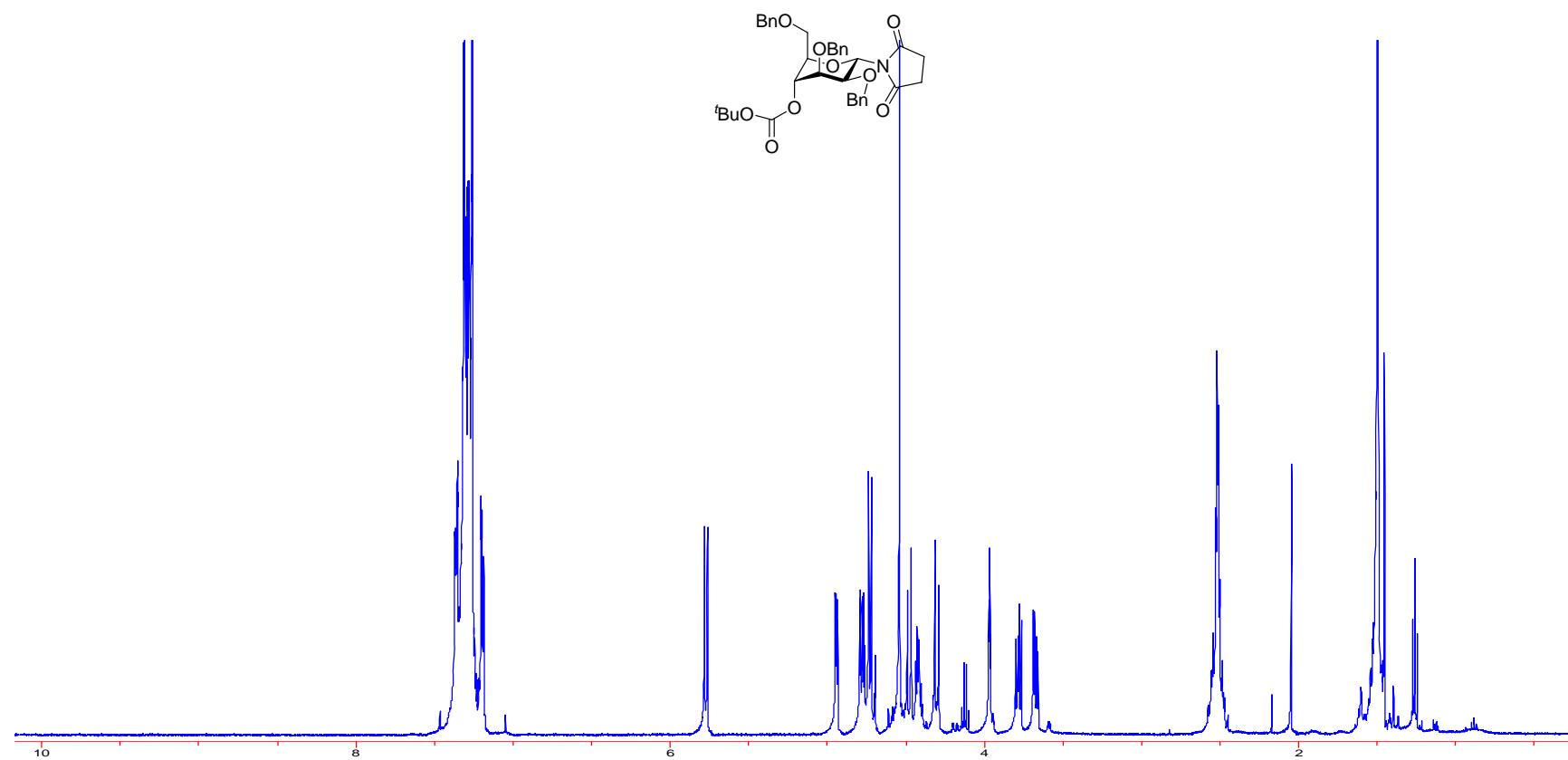
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl- β -D-mannopyranoside (**28 β**)



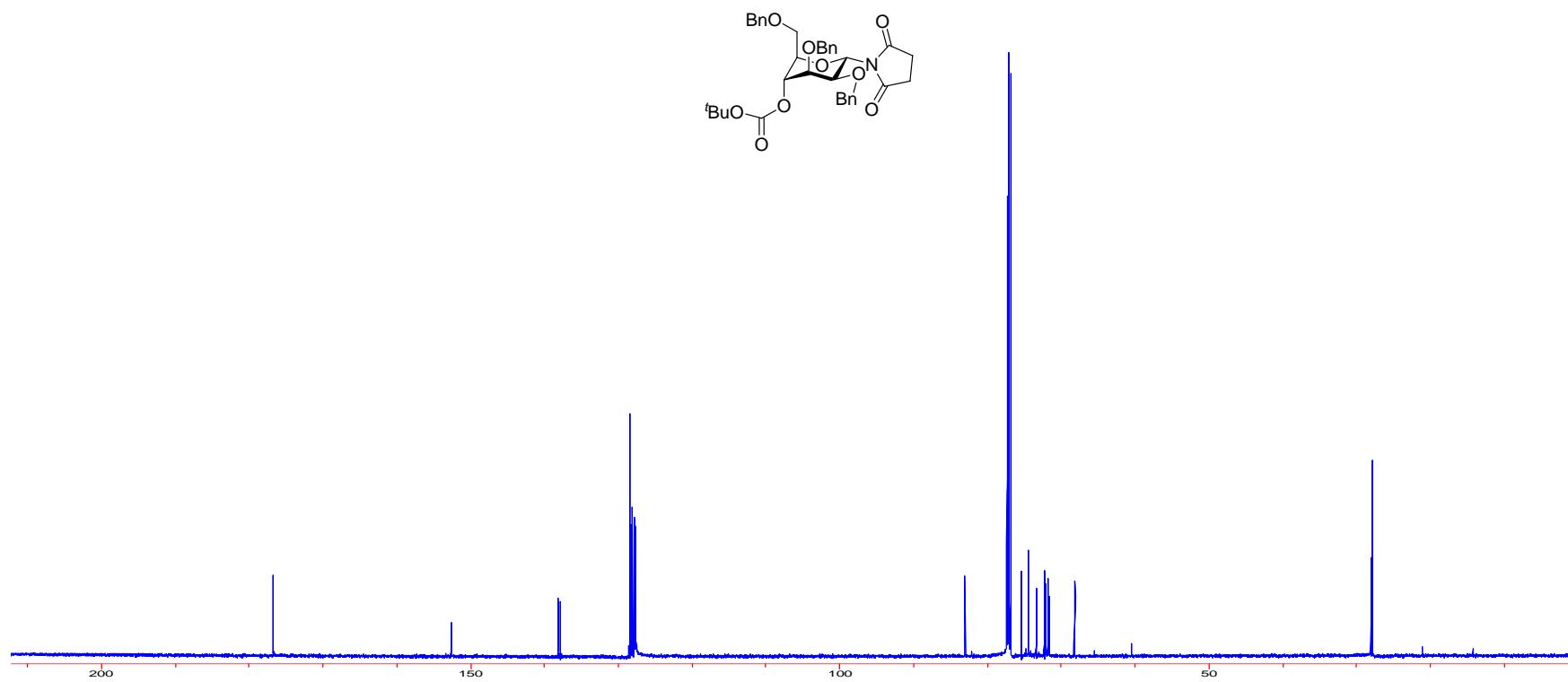
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl- β -D-mannopyranoside (**28 β**)



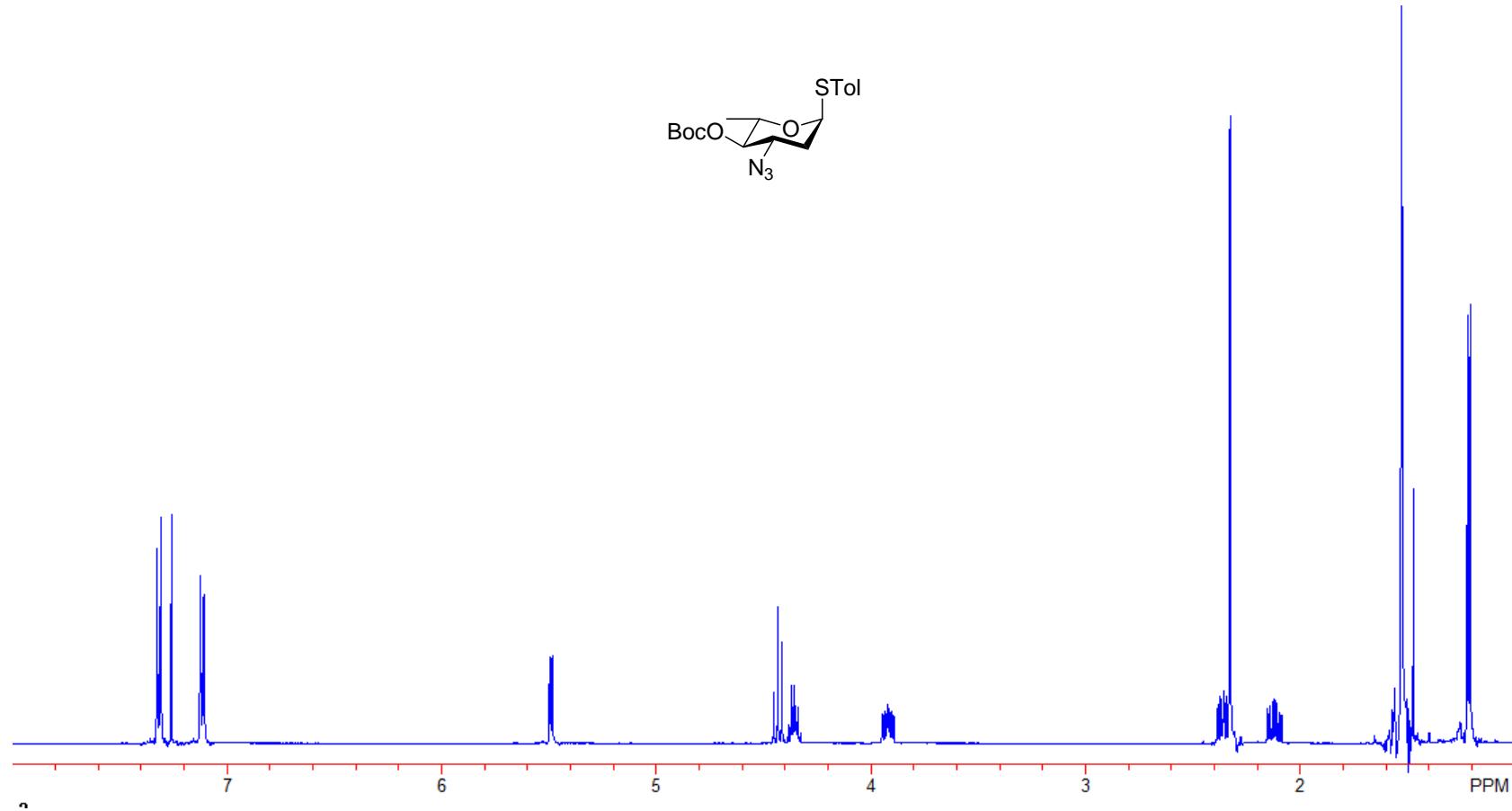
N-(2',3',6'-tri-*O*-benzyl-4'-*O*-*tert*-butyloxycarbonyl- α -D-mannopyranosyl)- succinimide (**29**).



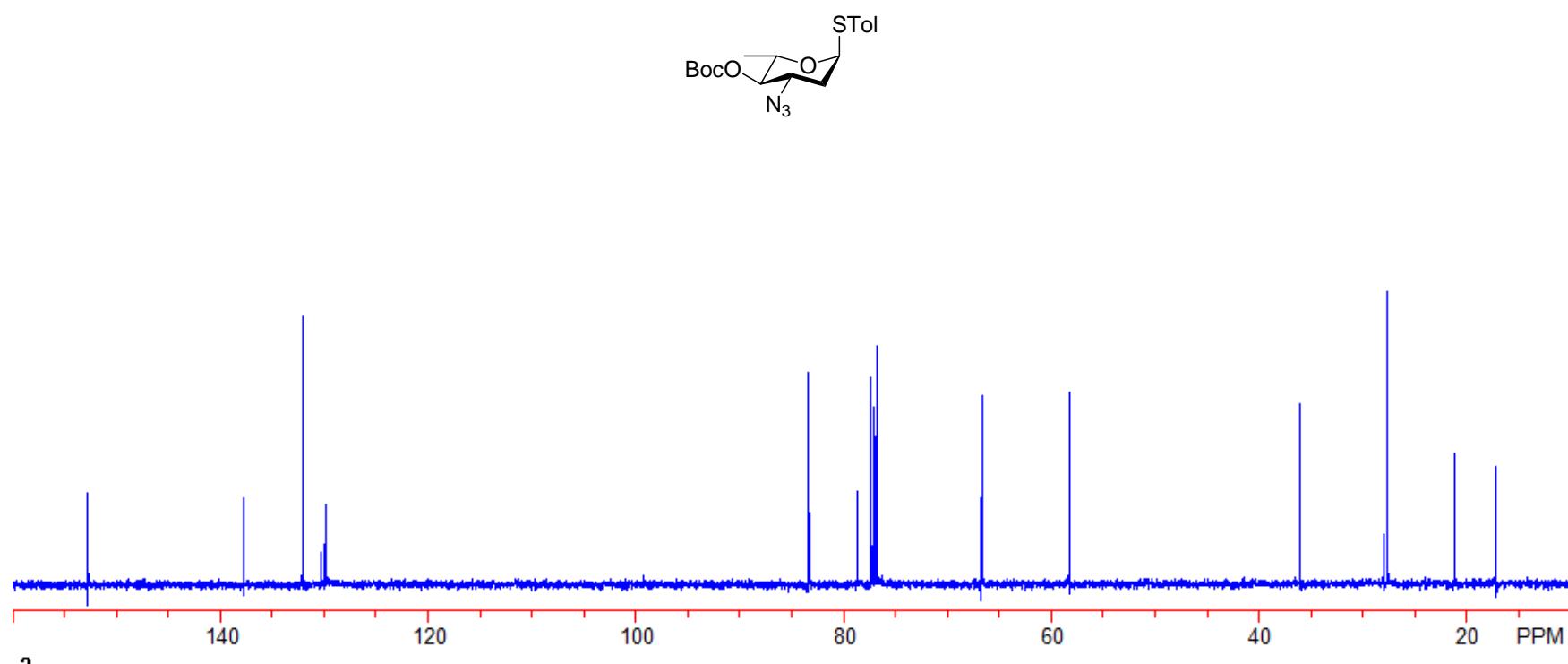
N-(2',3',6'-tri-*O*-benzyl-4'-*O*-*tert*-butyloxycarbonyl- α -D-mannopyranosyl)- succinimide (**29**).



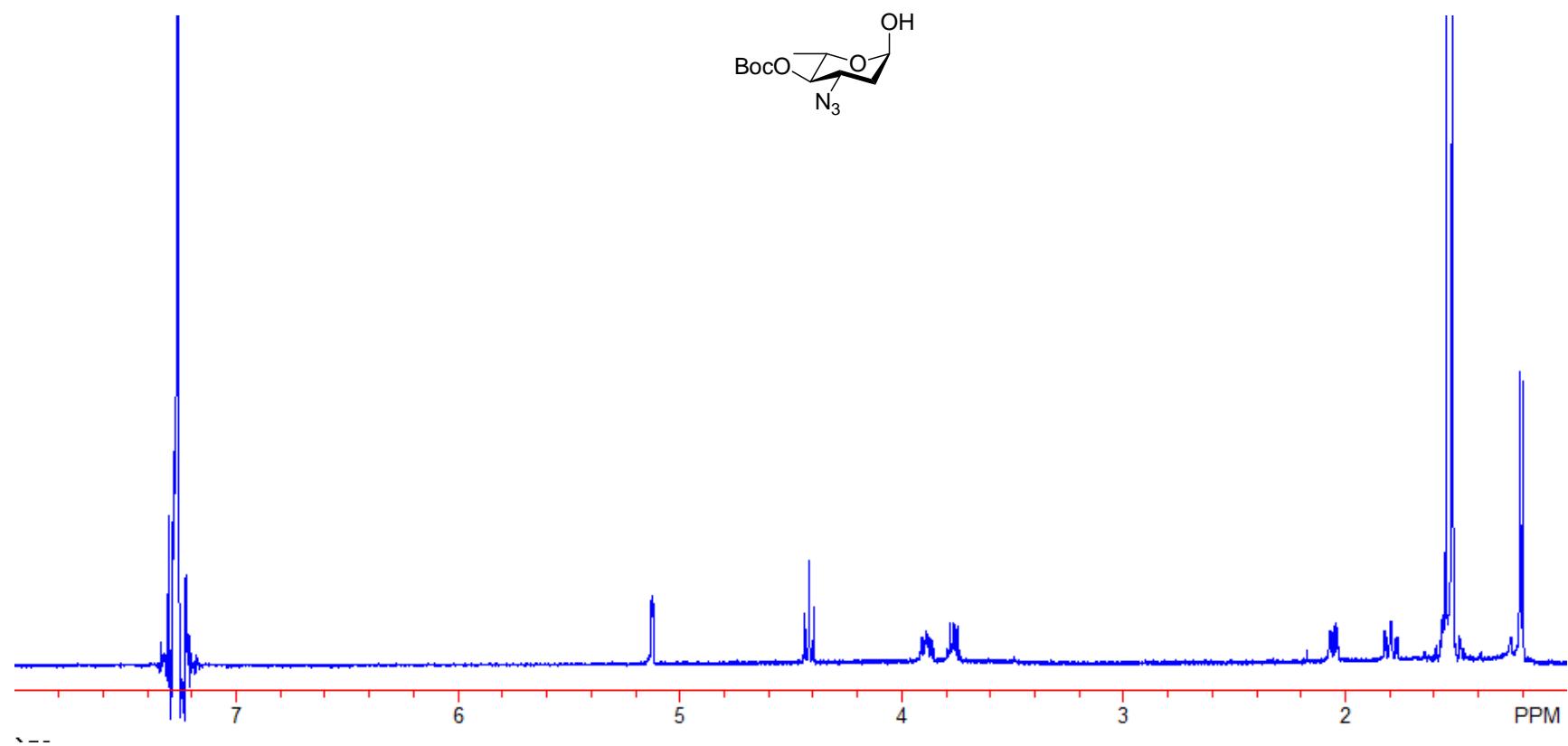
p-Tolyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-thio- α -L-lyxo-hexopyranoside (**30**).



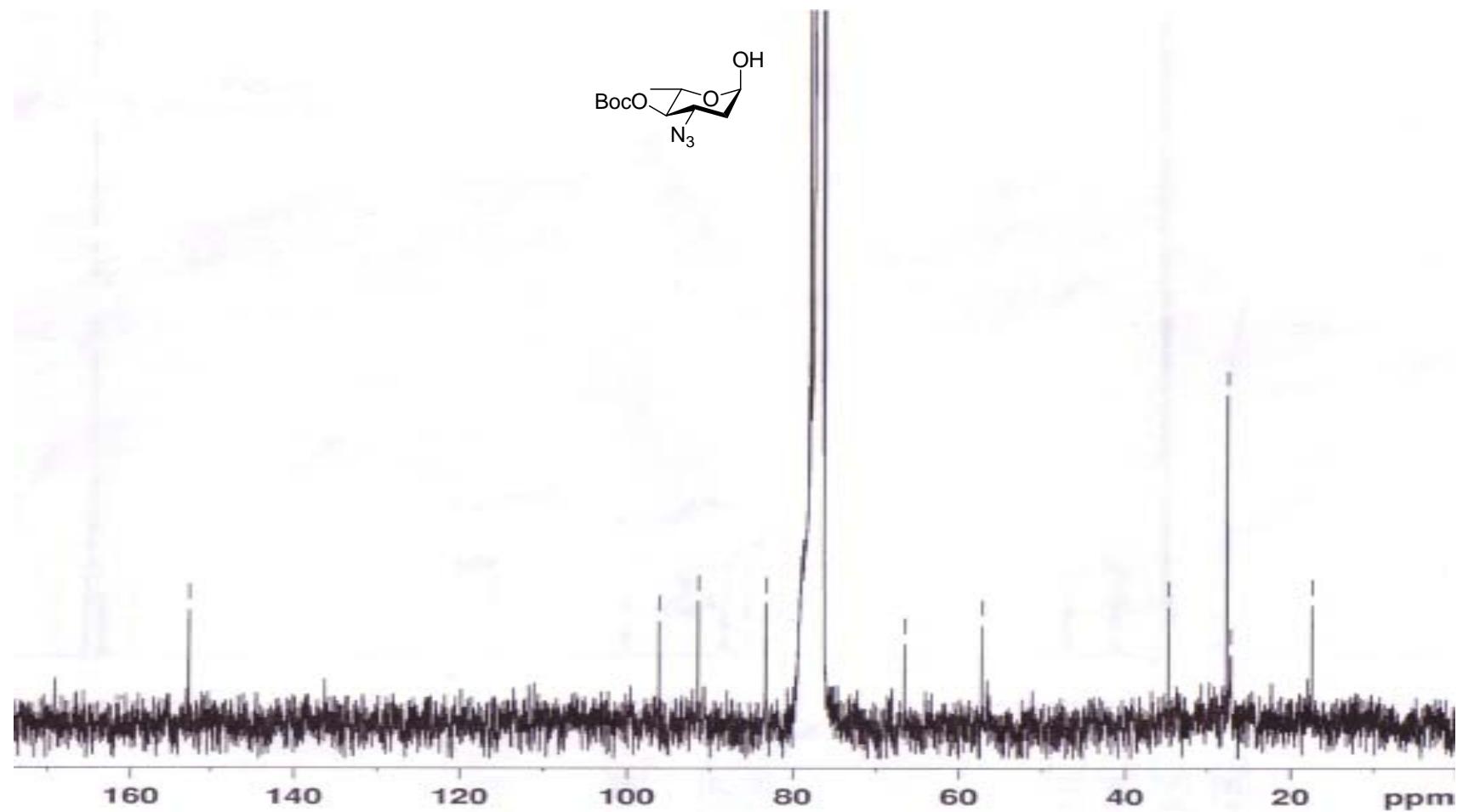
p-Tolyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-thio- α -L-lyxo-hexopyranoside (**30**).



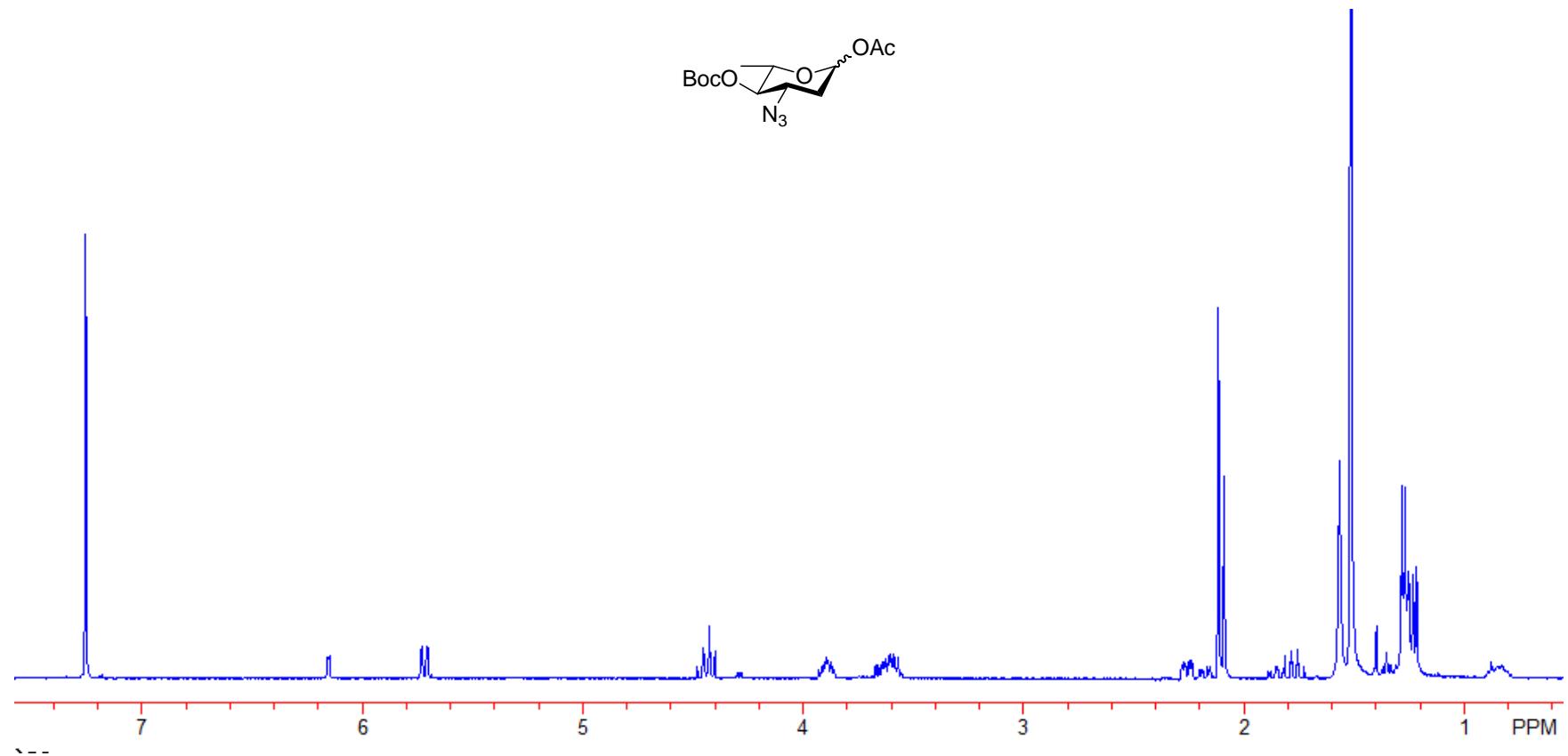
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1- α -L-lyxo-hexopyranoside.



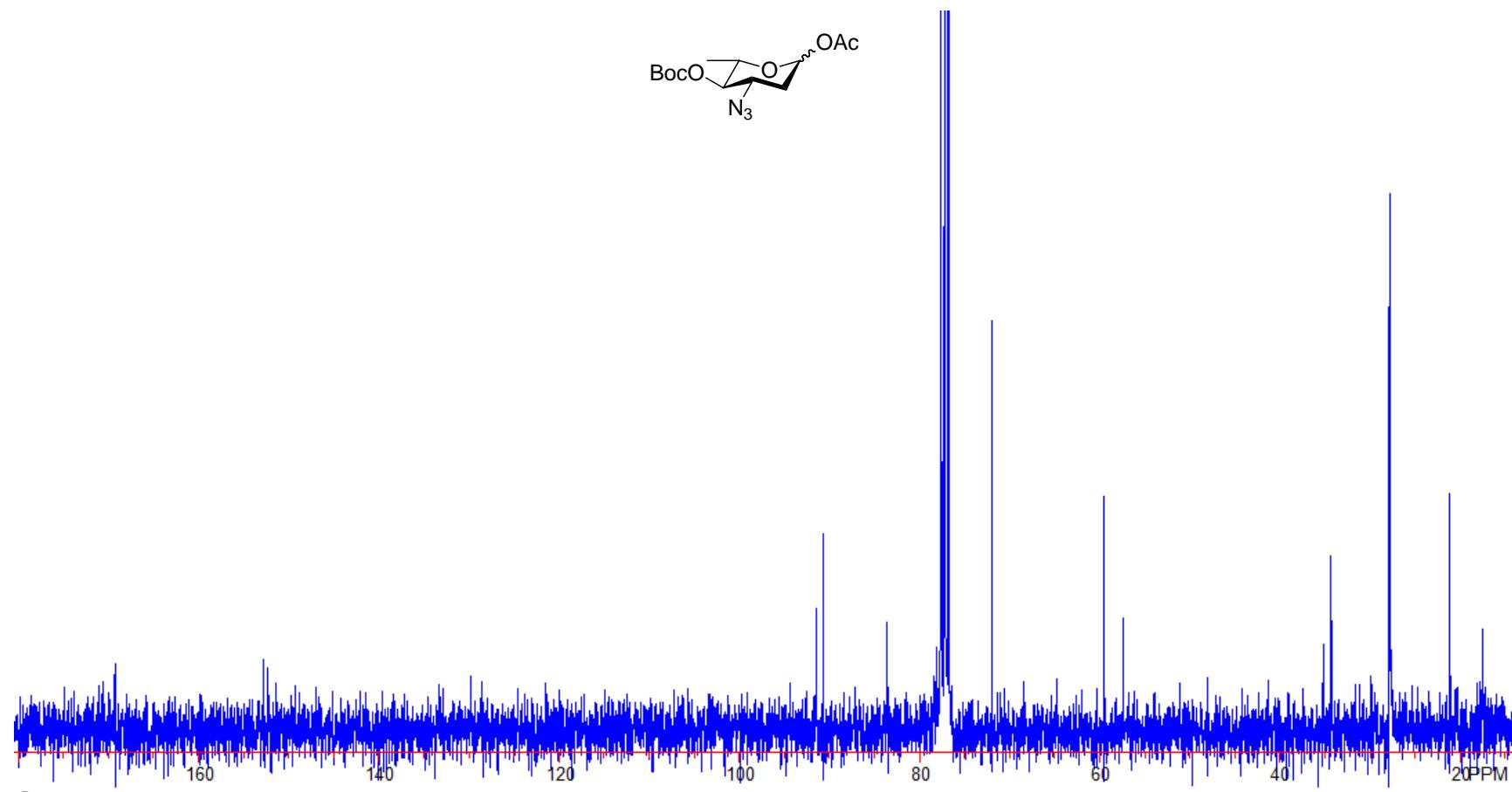
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1- α -L-lyxo-hexopyranoside.



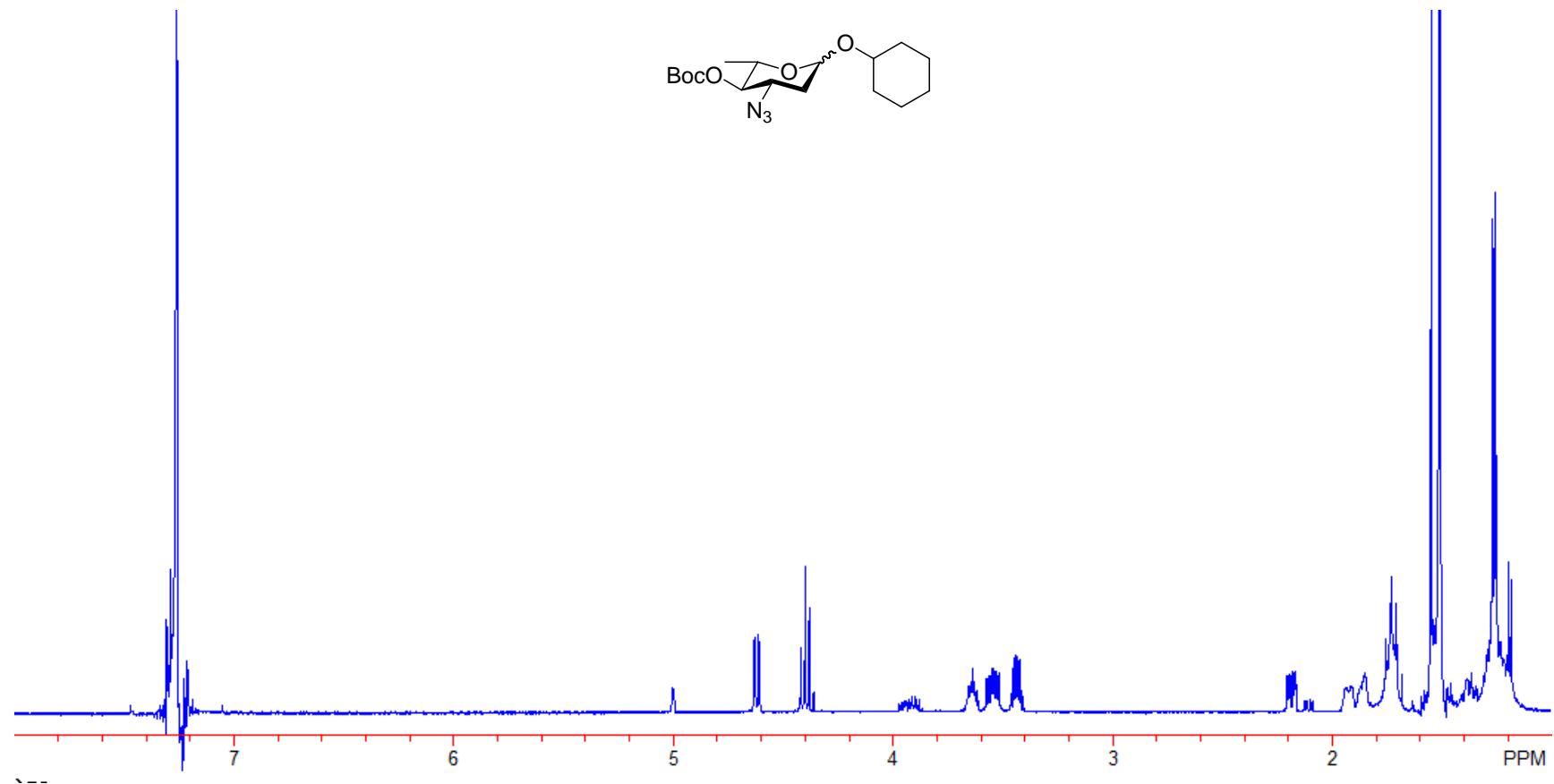
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranosyl acetate (**31**).



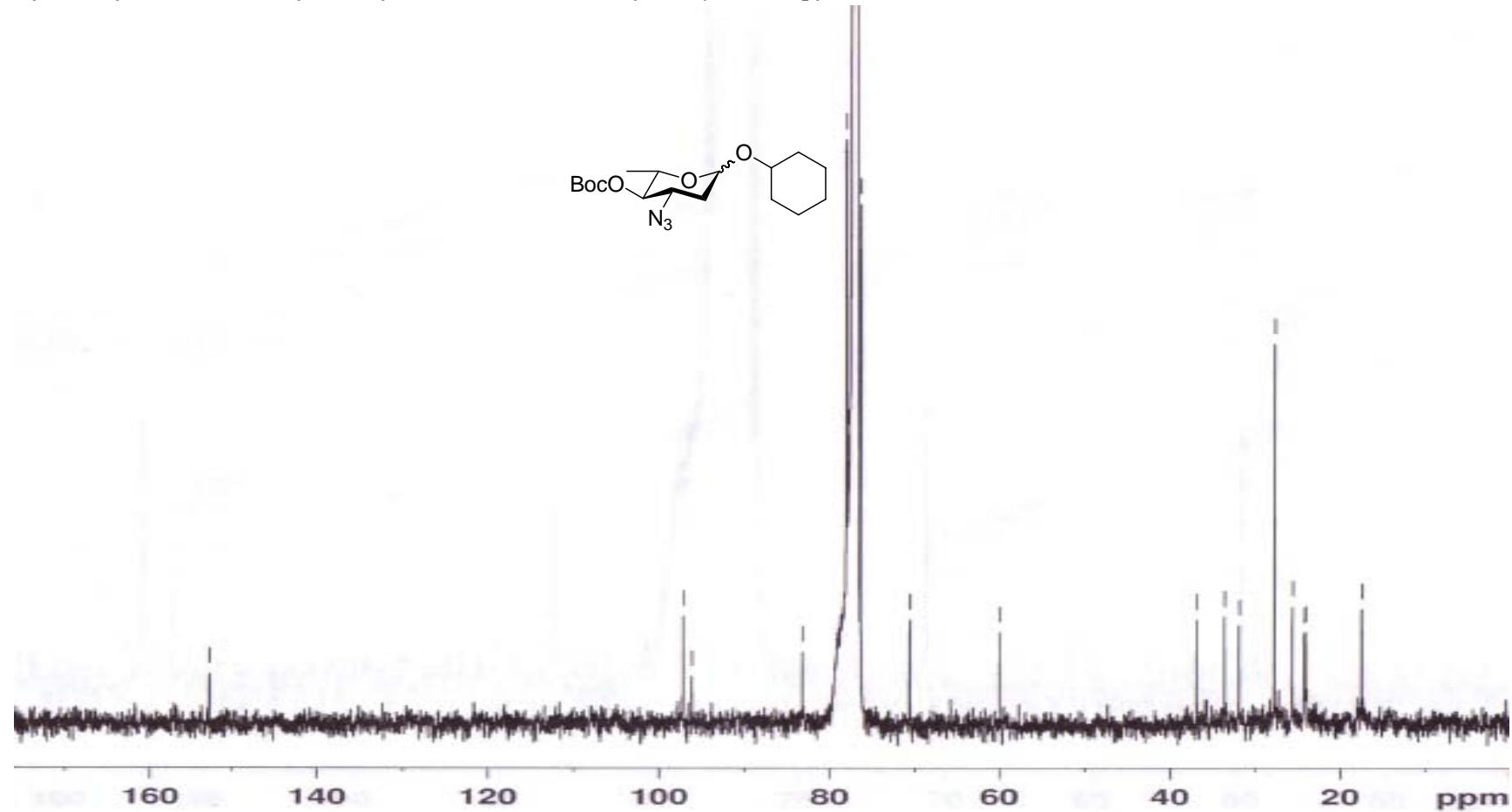
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranosyl acetate (**31**).



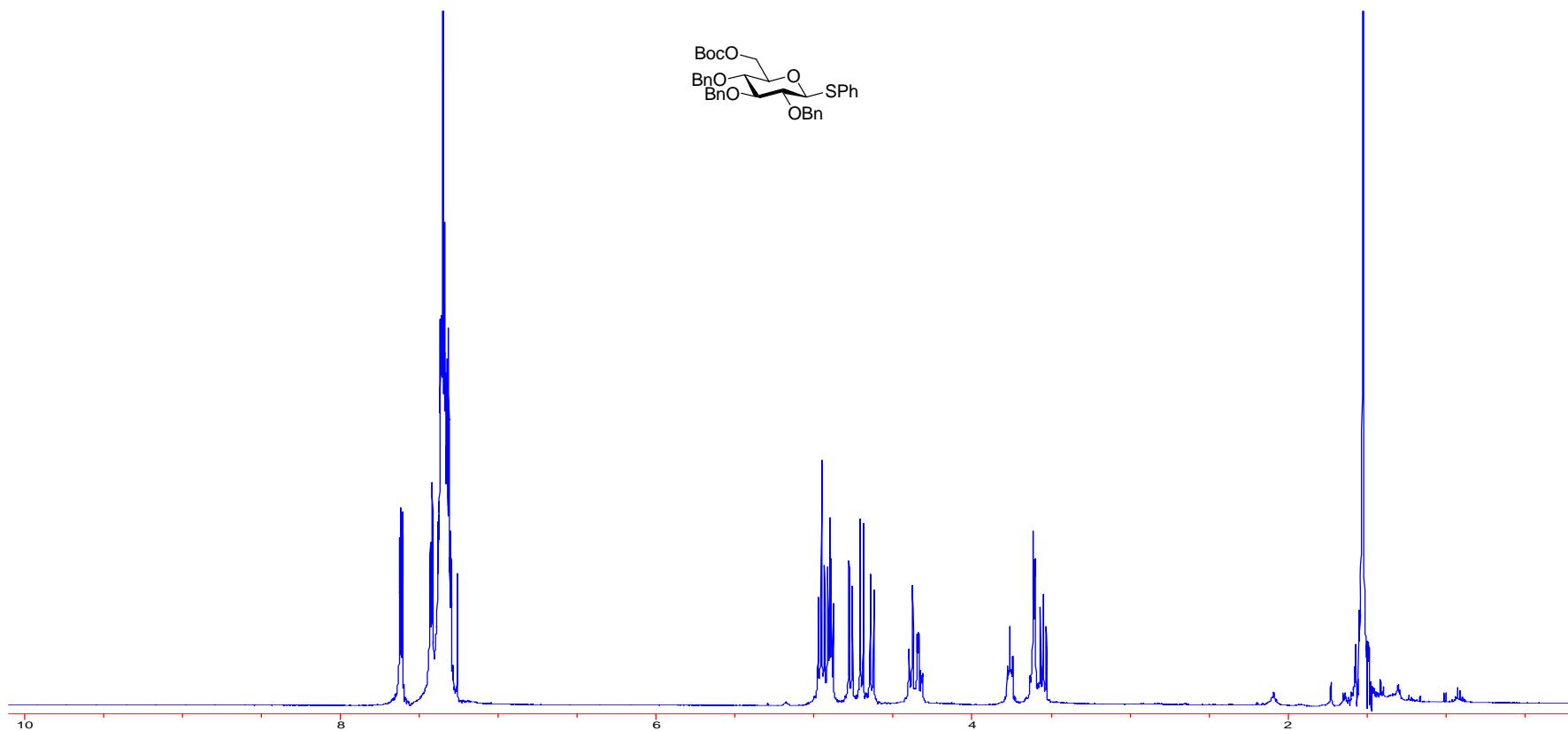
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranoside (**32**).



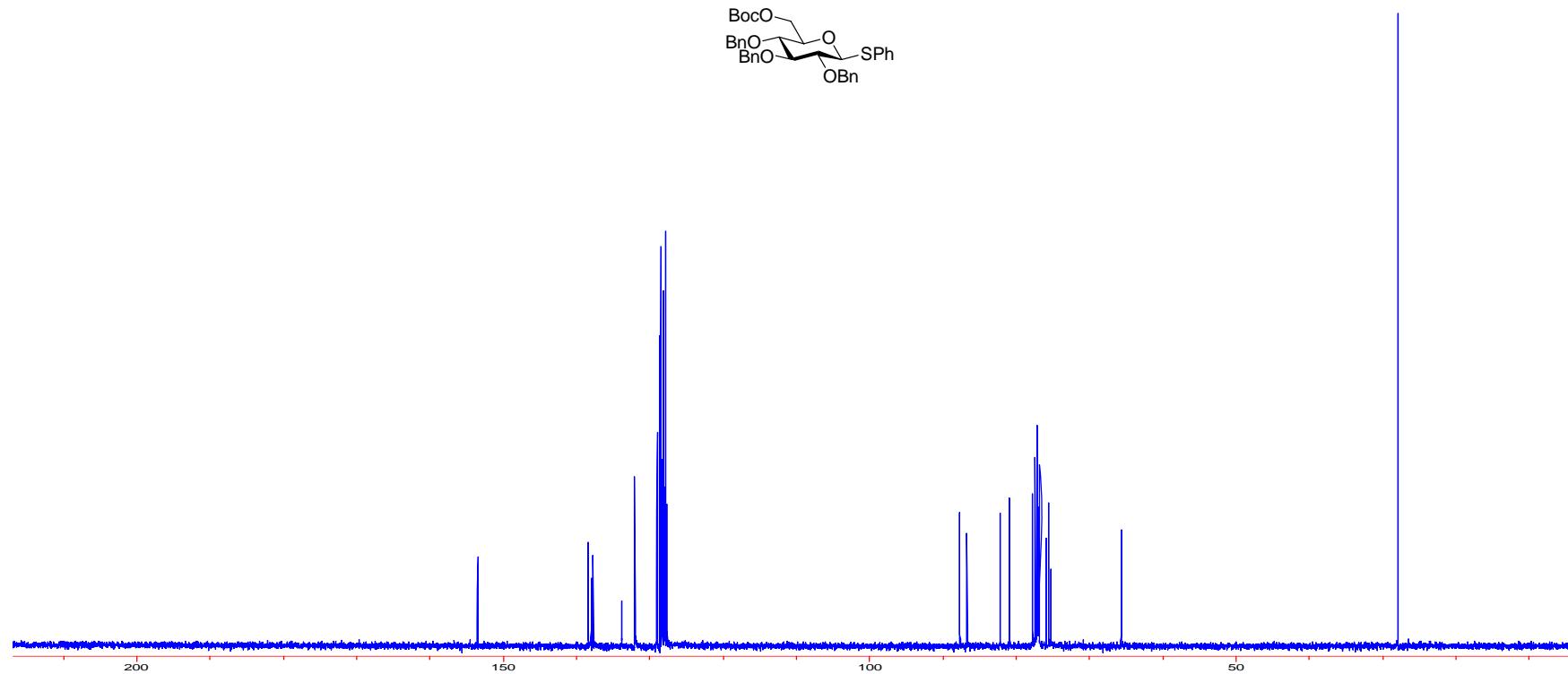
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranoside (**32**).



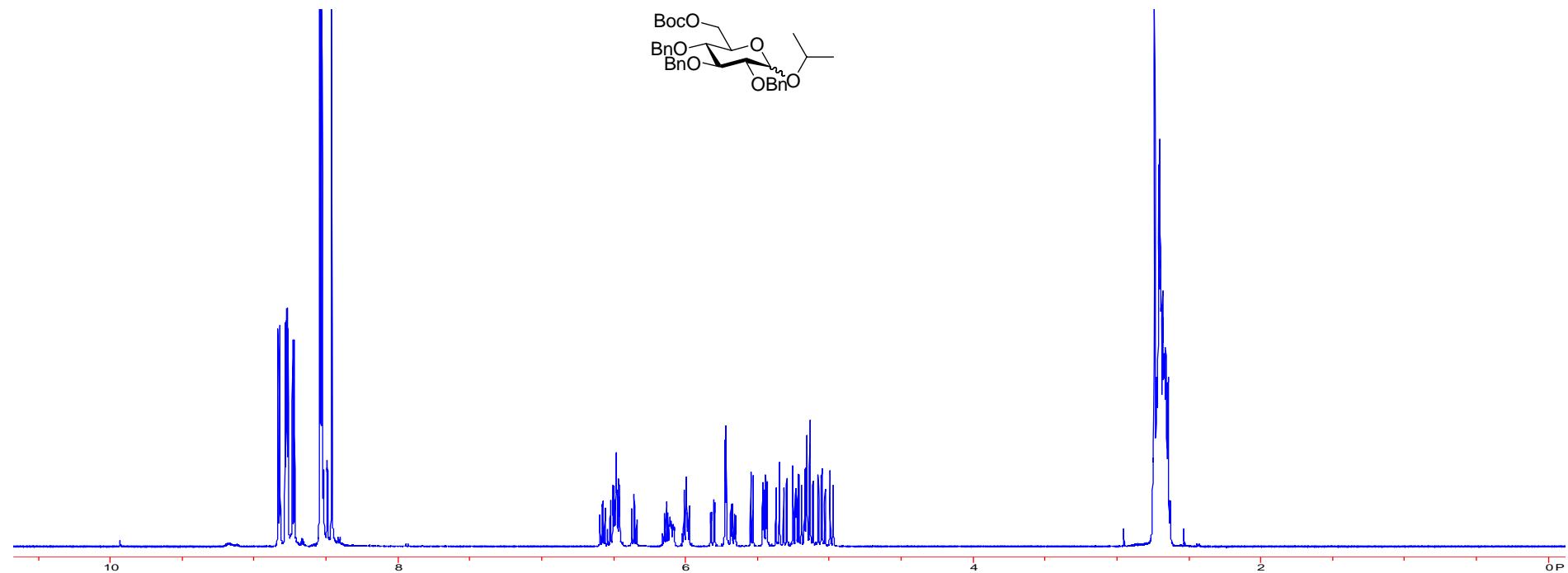
Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-1-thio- β -D-glucopyranoside (**33**)



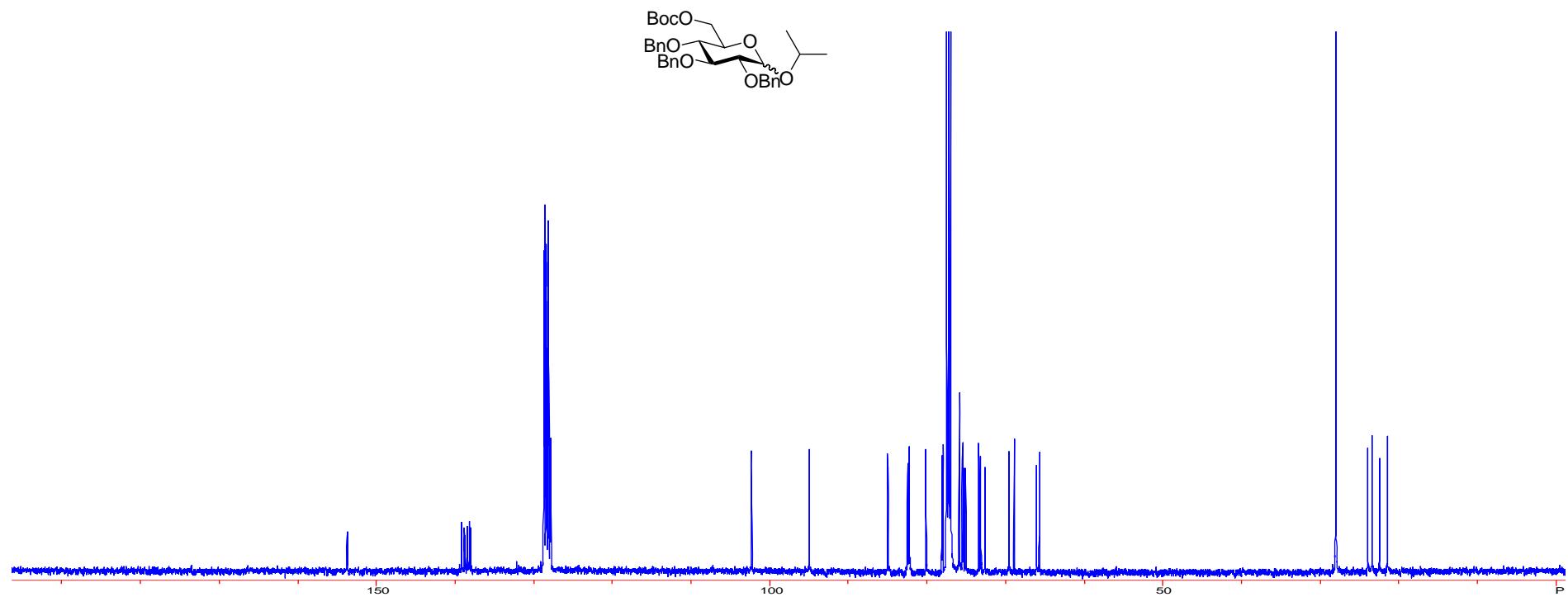
Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-1-thio- β -D-glucopyranoside (**33**)



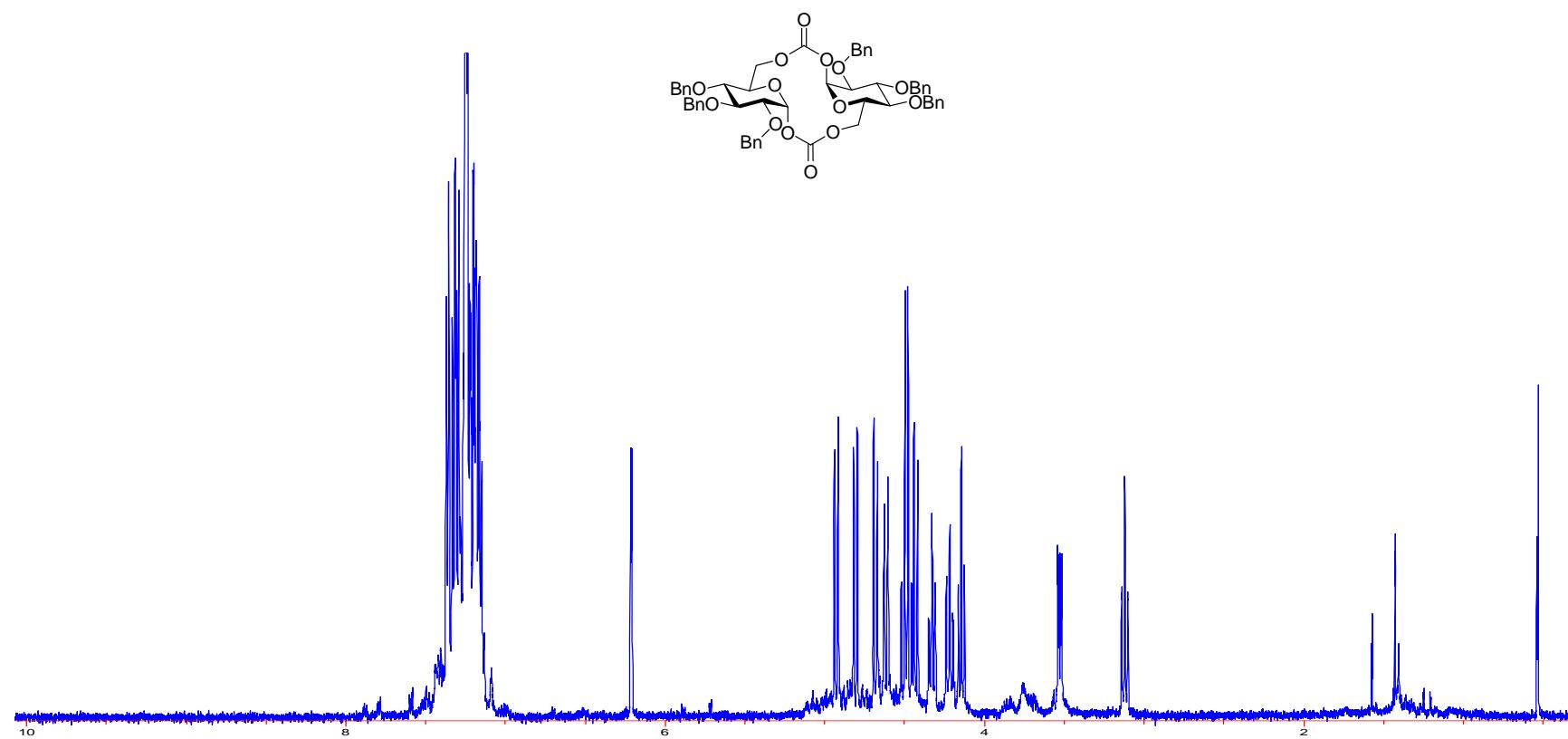
Isopropyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-D-glucopyranoside (**34a** and **34b**).



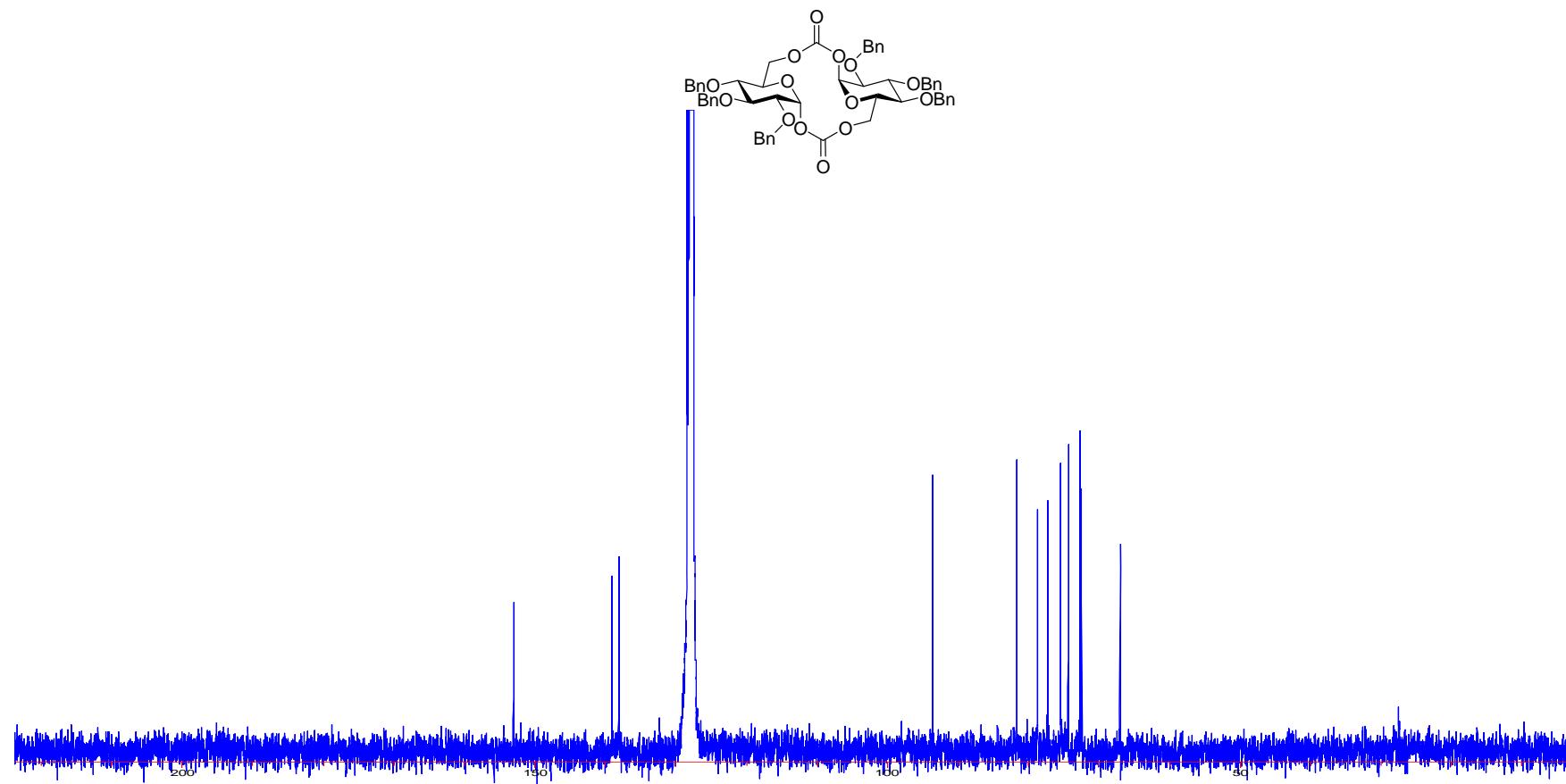
Isopropyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-D-glucopyranoside (**34a** and **34b**).



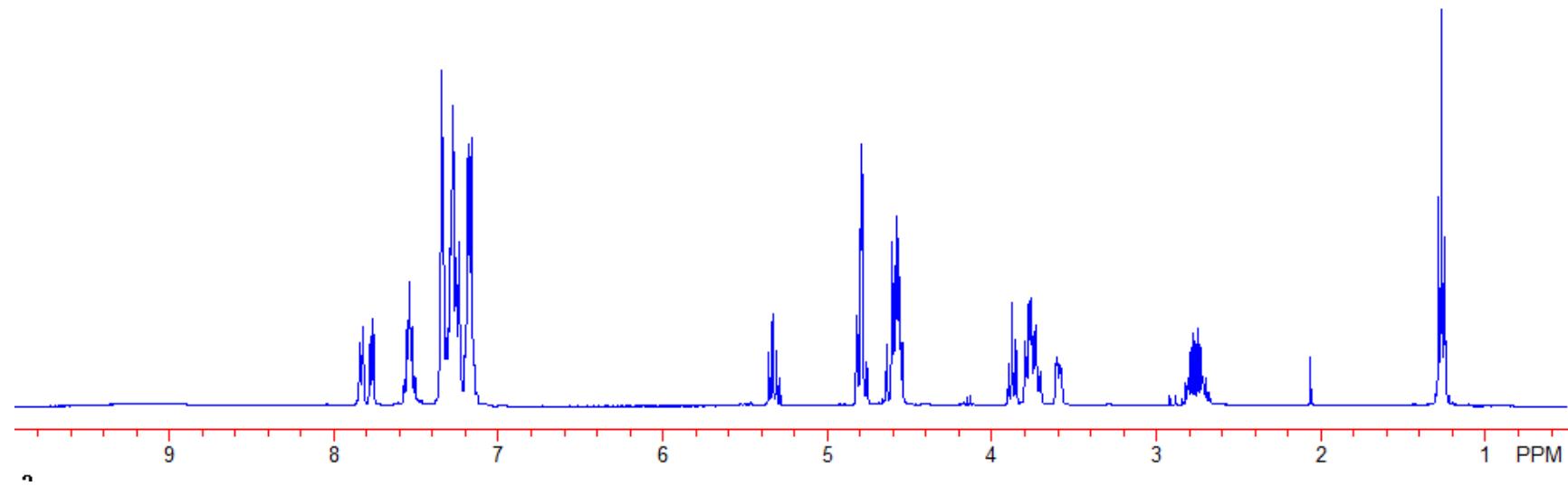
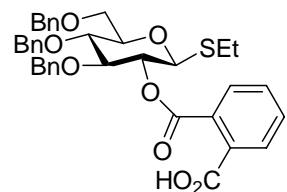
Di-(2,3,4-tri-*O*-benzyl-D-glucopyranoside)-(1,6), (6,1)-dicarbonate (**35**).



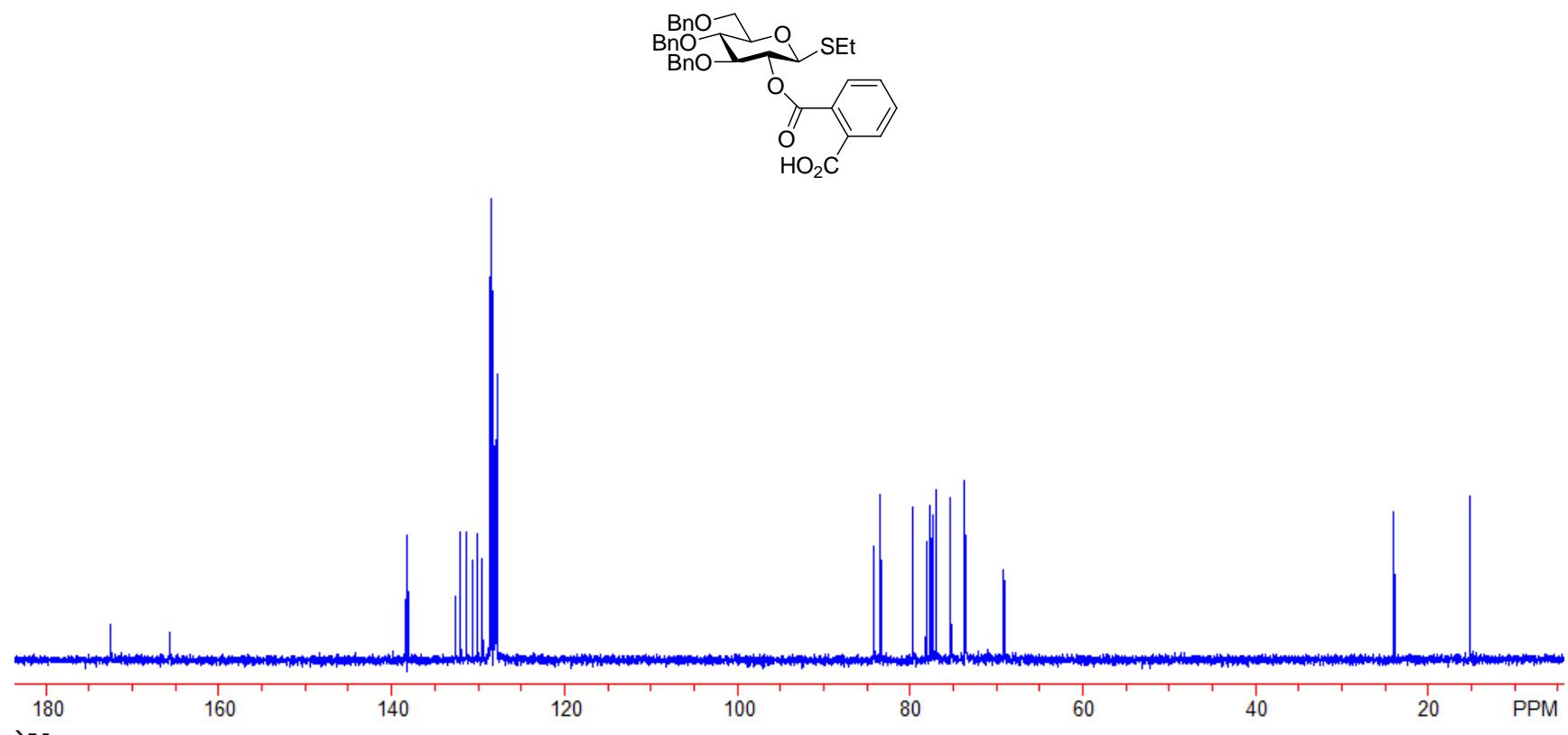
Di-(2,3,4-tri-O-benzyl-D-glucopyranoside)-(1,6), (6,1)-dicarbonate (**35**).



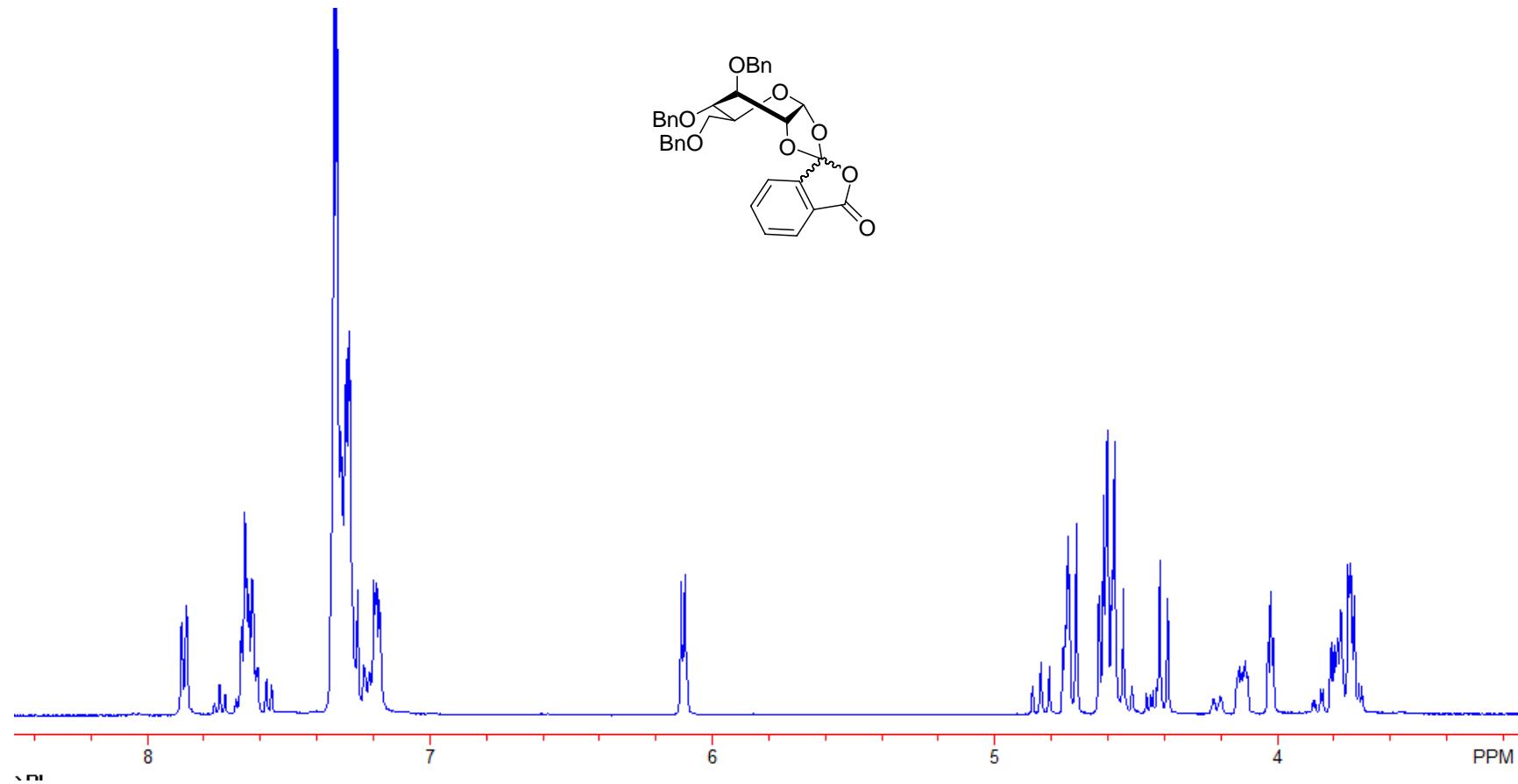
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-carboxybenzoyl)-1-thio- β -D-glucopyranoside (**36**).



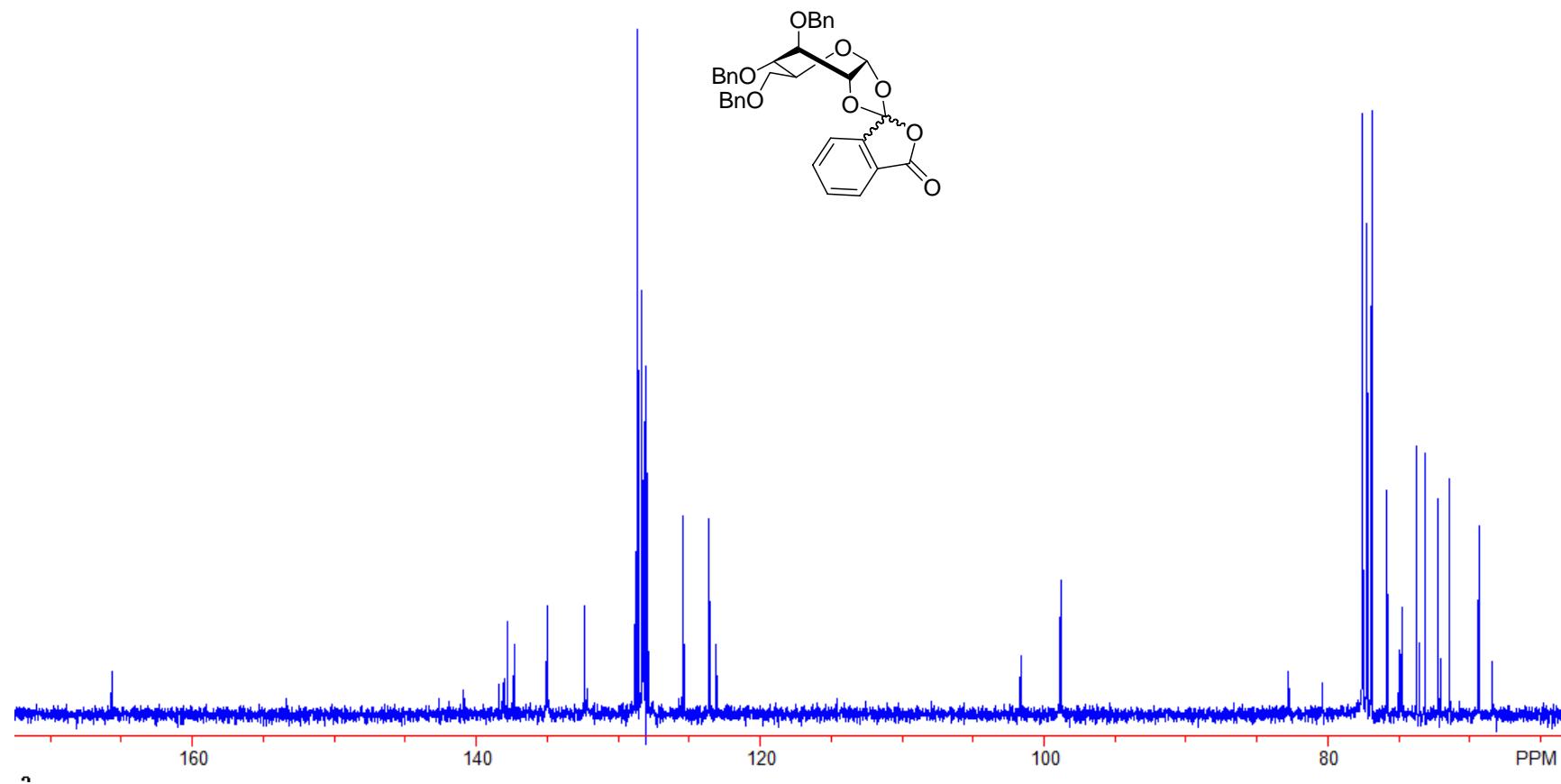
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-carboxybenzoyl)-1-thio- β -D-glucopyranoside (**36**).



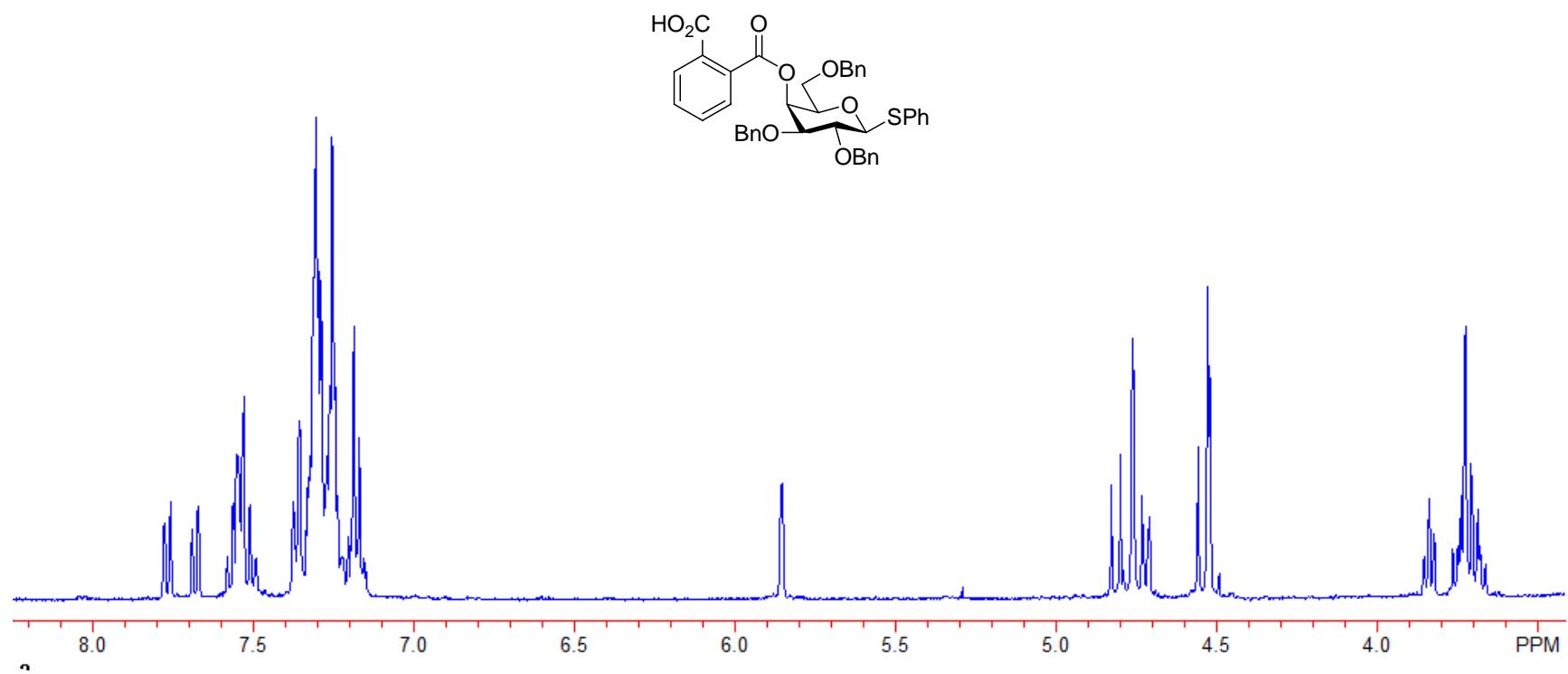
3,4,6-Tri-O-benzyl-1,2-O-phthalidylidene- α -D-glucopyranose (**37**).



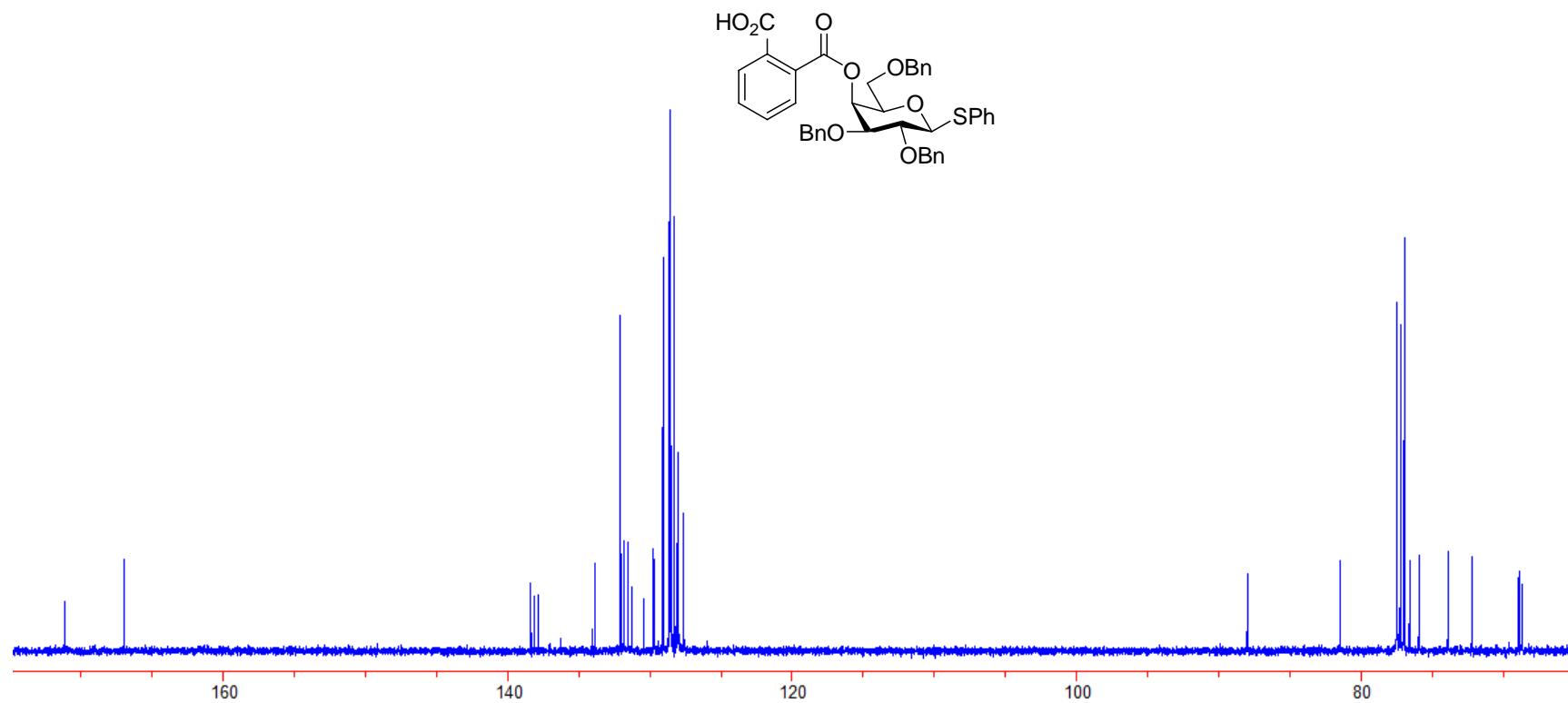
3,4,6-Tri-O-benzyl-1,2-O-phthalidylidene- α -D-glucopyranose (**37**).



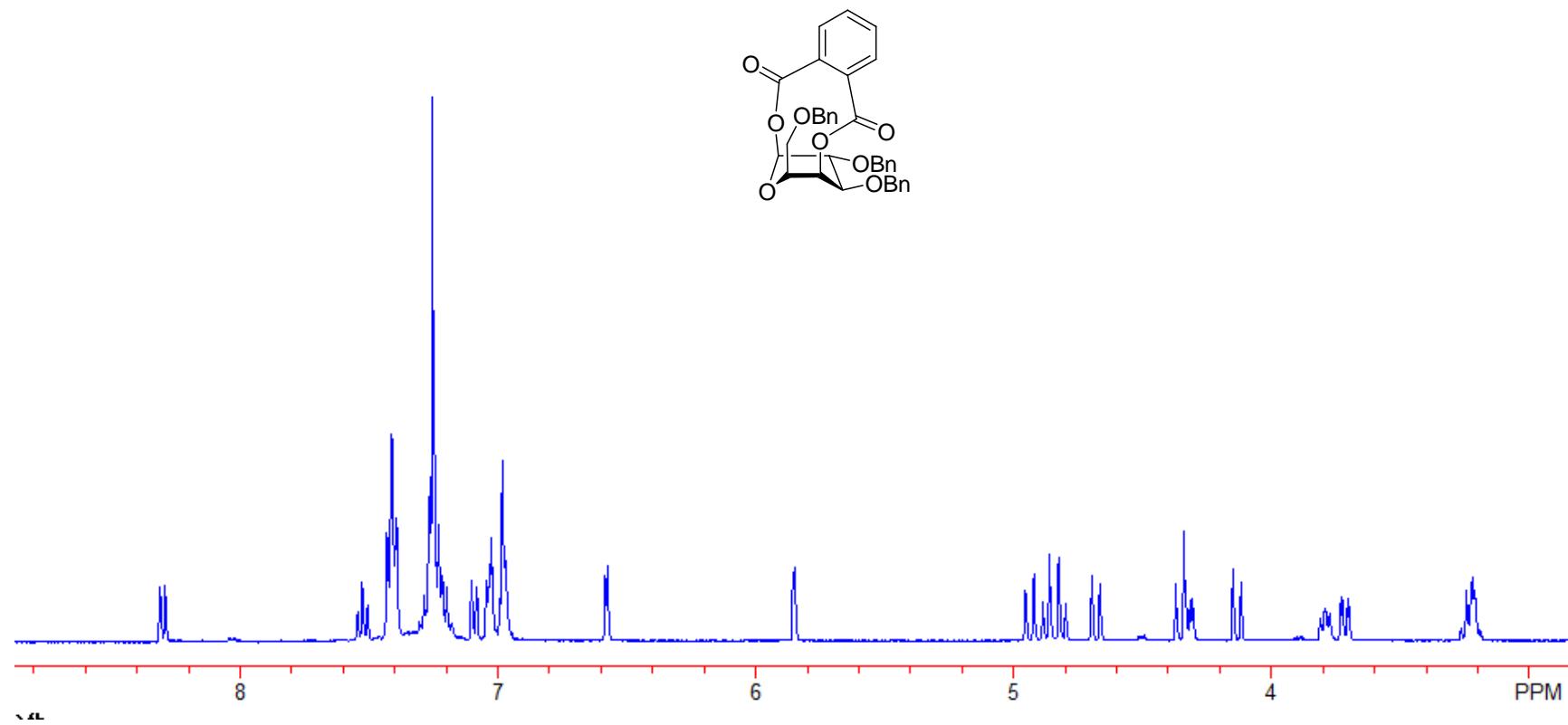
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-carboxybenzoyl)-1-thio- β -D-galactopyranoside (**38**).



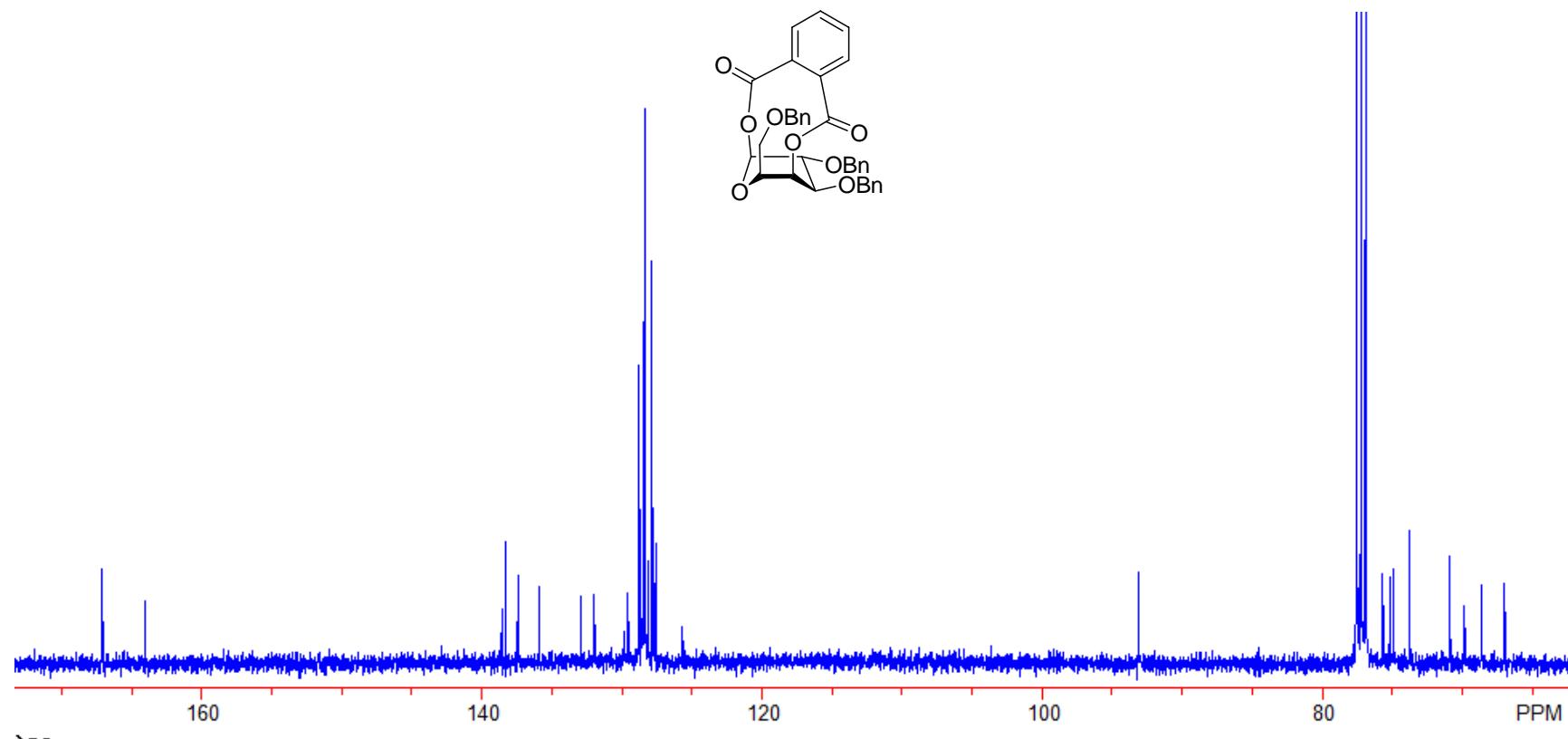
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-carboxybenzoyl)-1-thio- β -D-galactopyranoside (**38**).



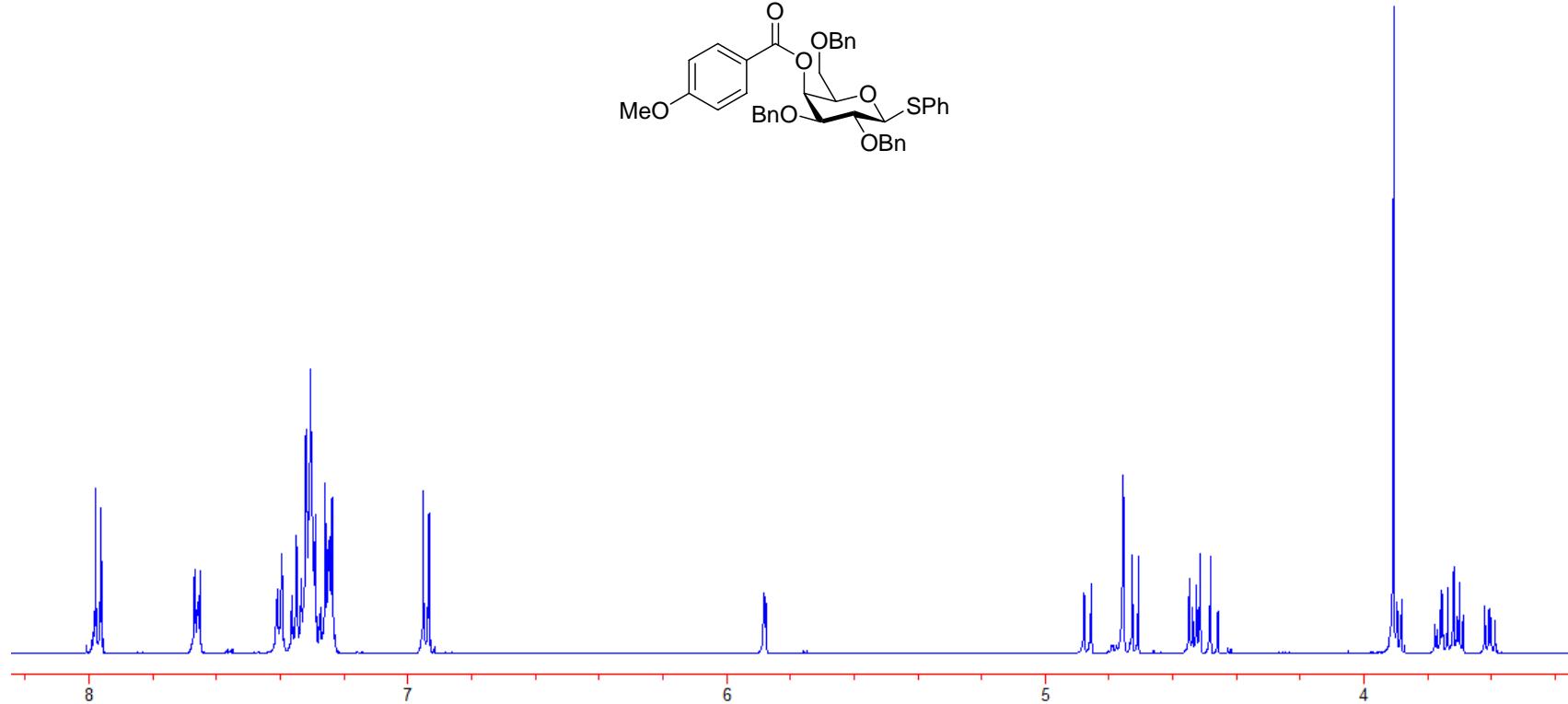
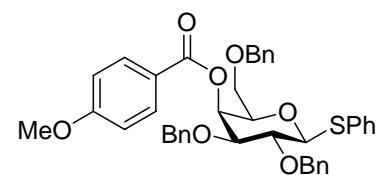
3,4,6-Tri-*O*-benzyl-1,2-*O*-phthaloyl- β -D-galactopyranoside (**40**).



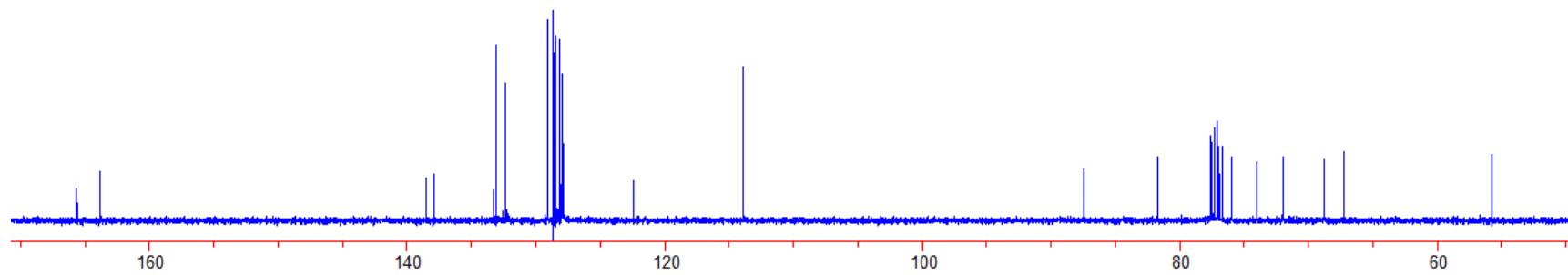
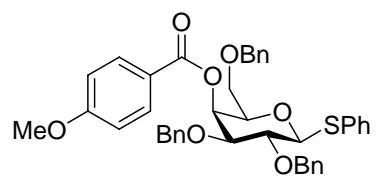
3,4,6-Tri-*O*-benzyl-1,2-*O*-phthaloyl- β -D-galactopyranoside (**40**).



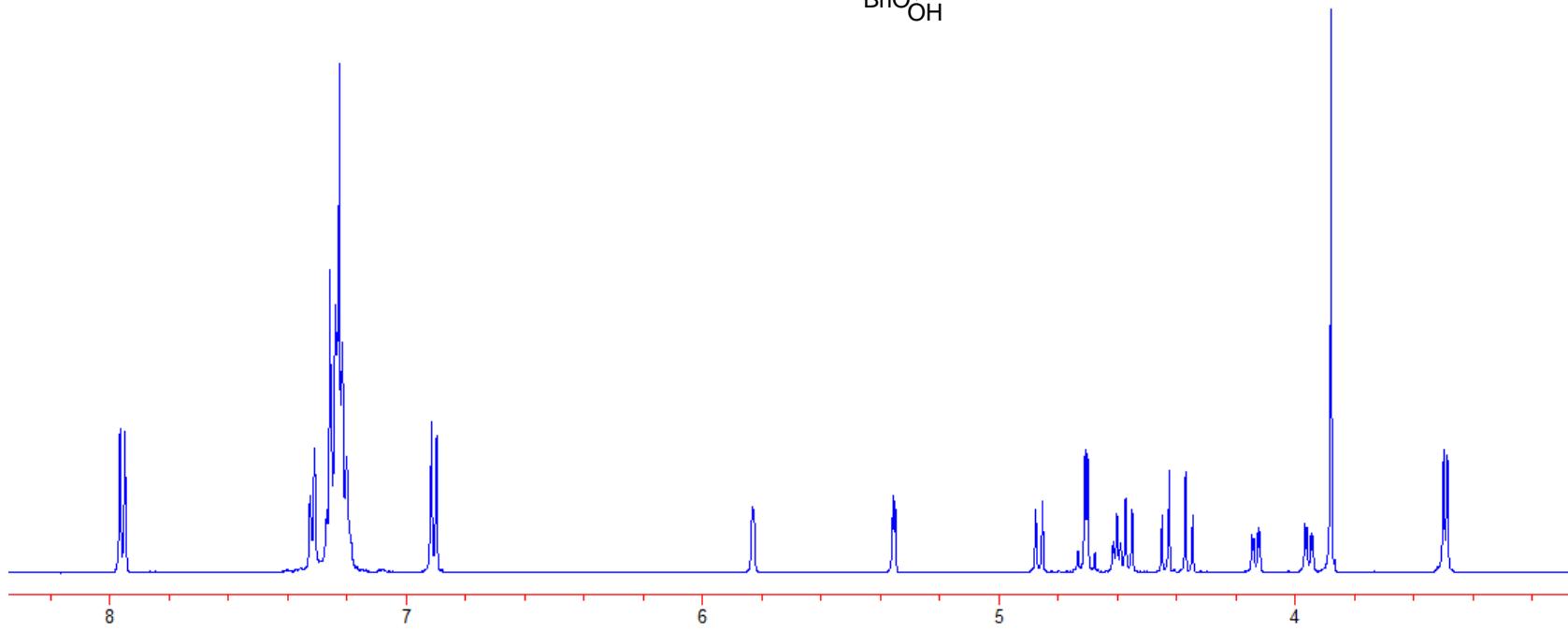
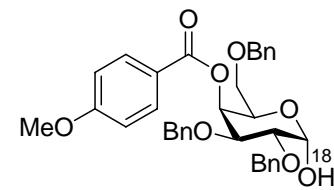
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-1-thio- β -D-galactopyranoside (**41**).



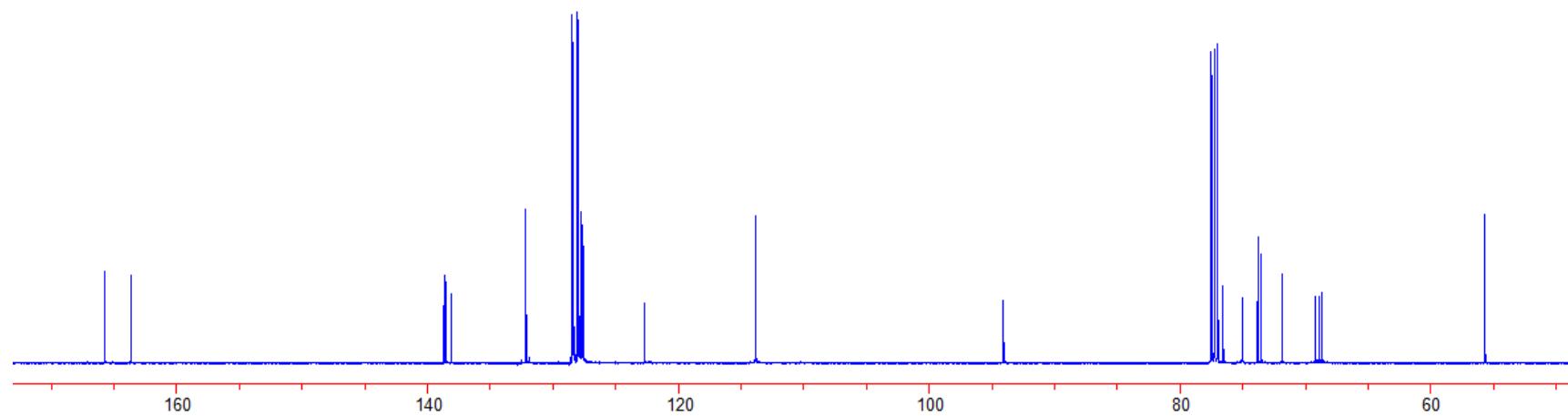
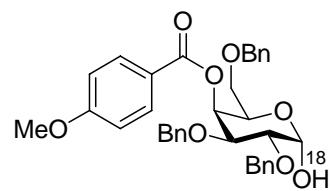
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-1-thio- β -D-galactopyranoside (**41**).



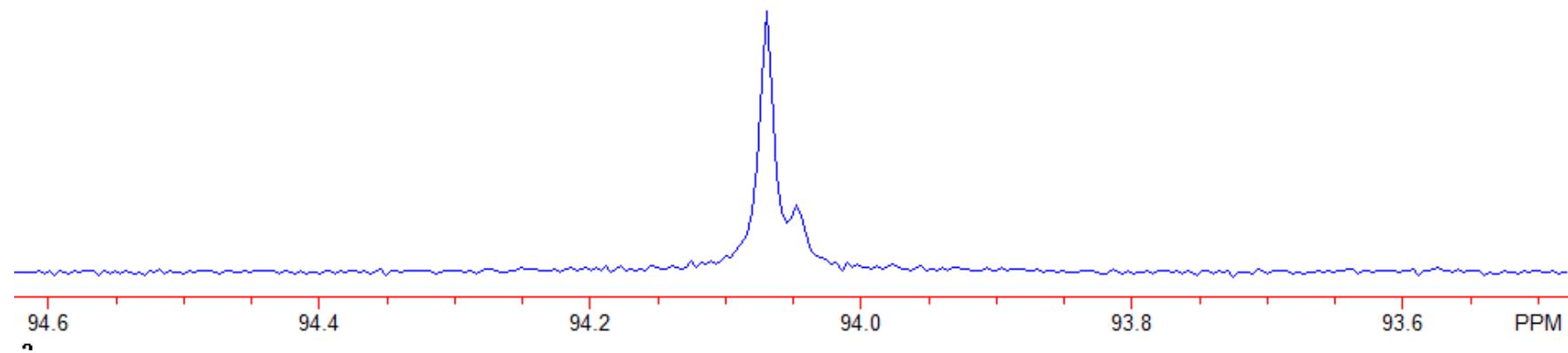
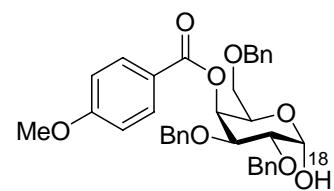
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)- α -D-[1- $^{16/18}O$]-galactopyranoside (**43**).



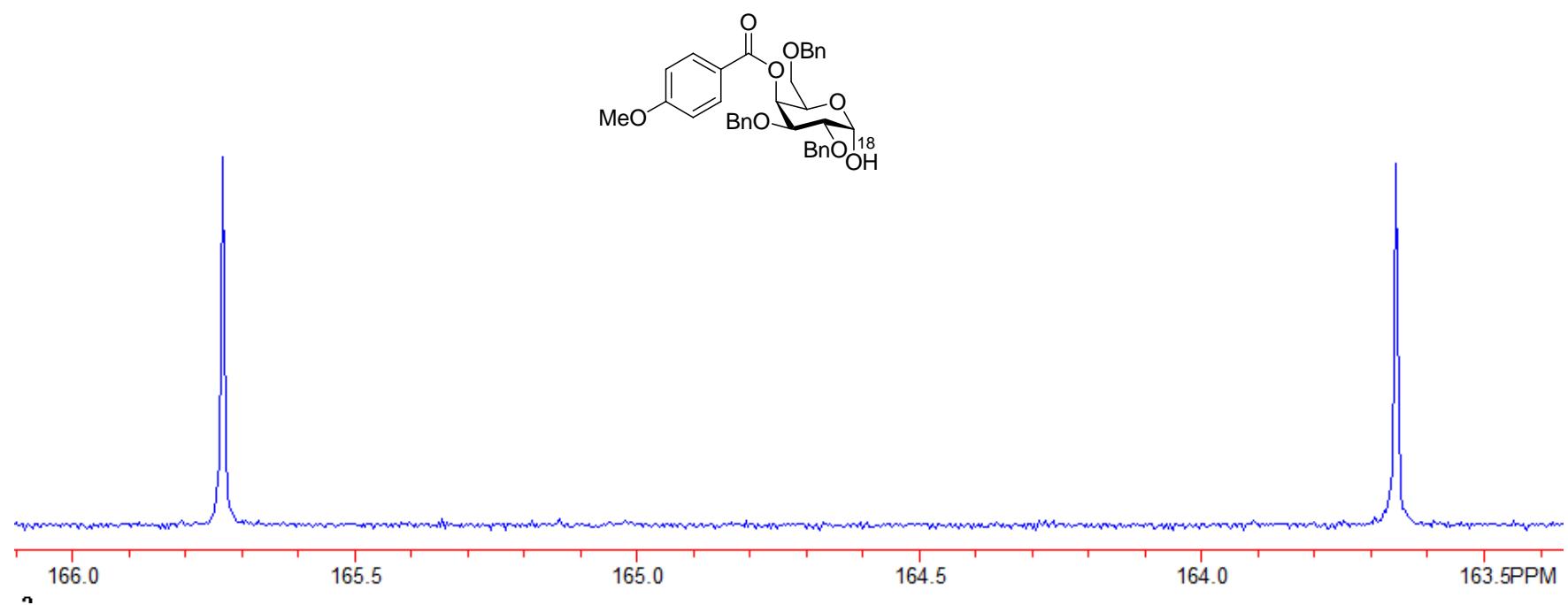
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)- α -D-[1- $^{16/18}O$]-galactopyranoside (**43**).



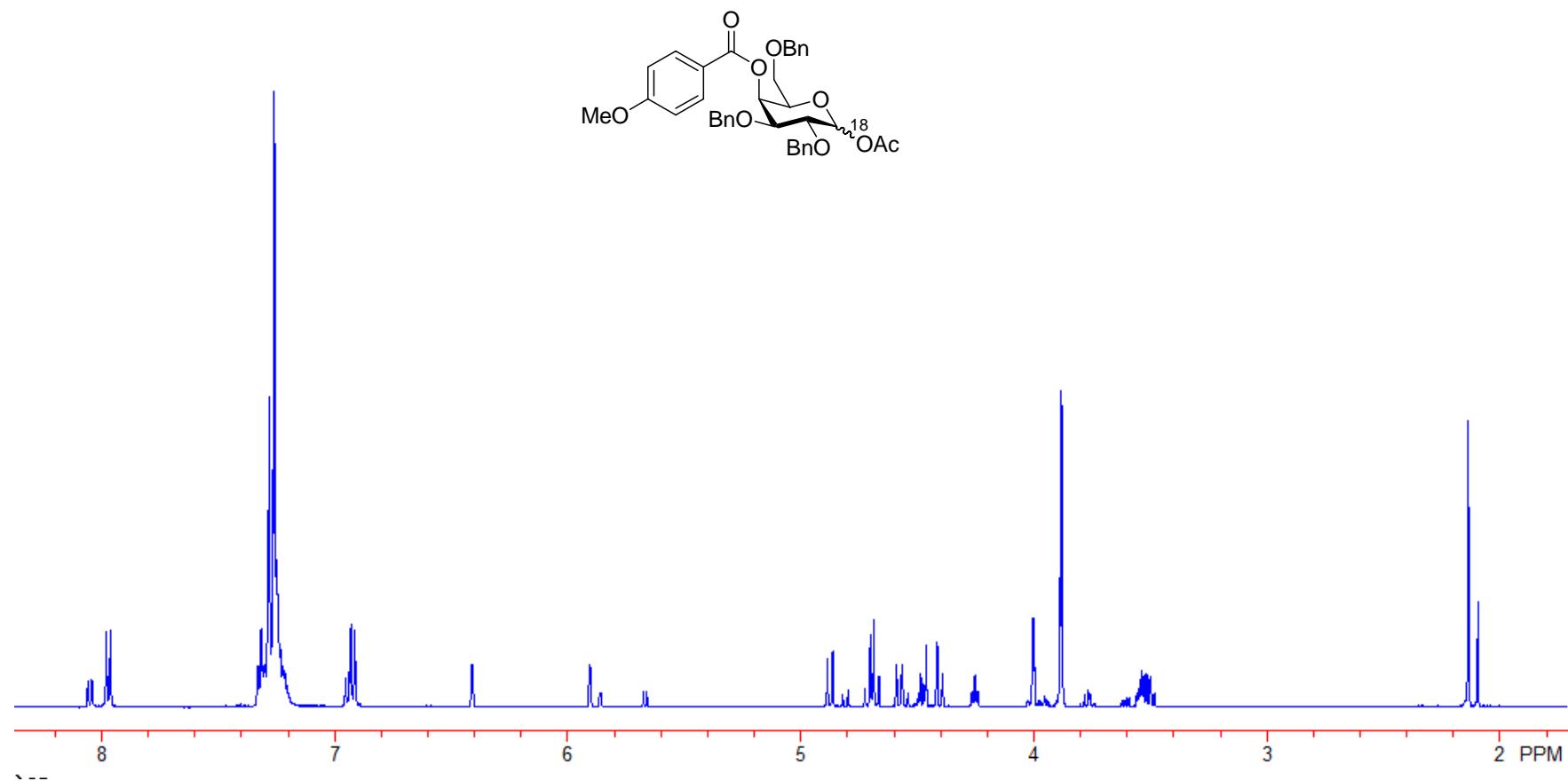
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)- α -D-[1- $^{16/18}O$]-galactopyranoside (**43**, expansion).



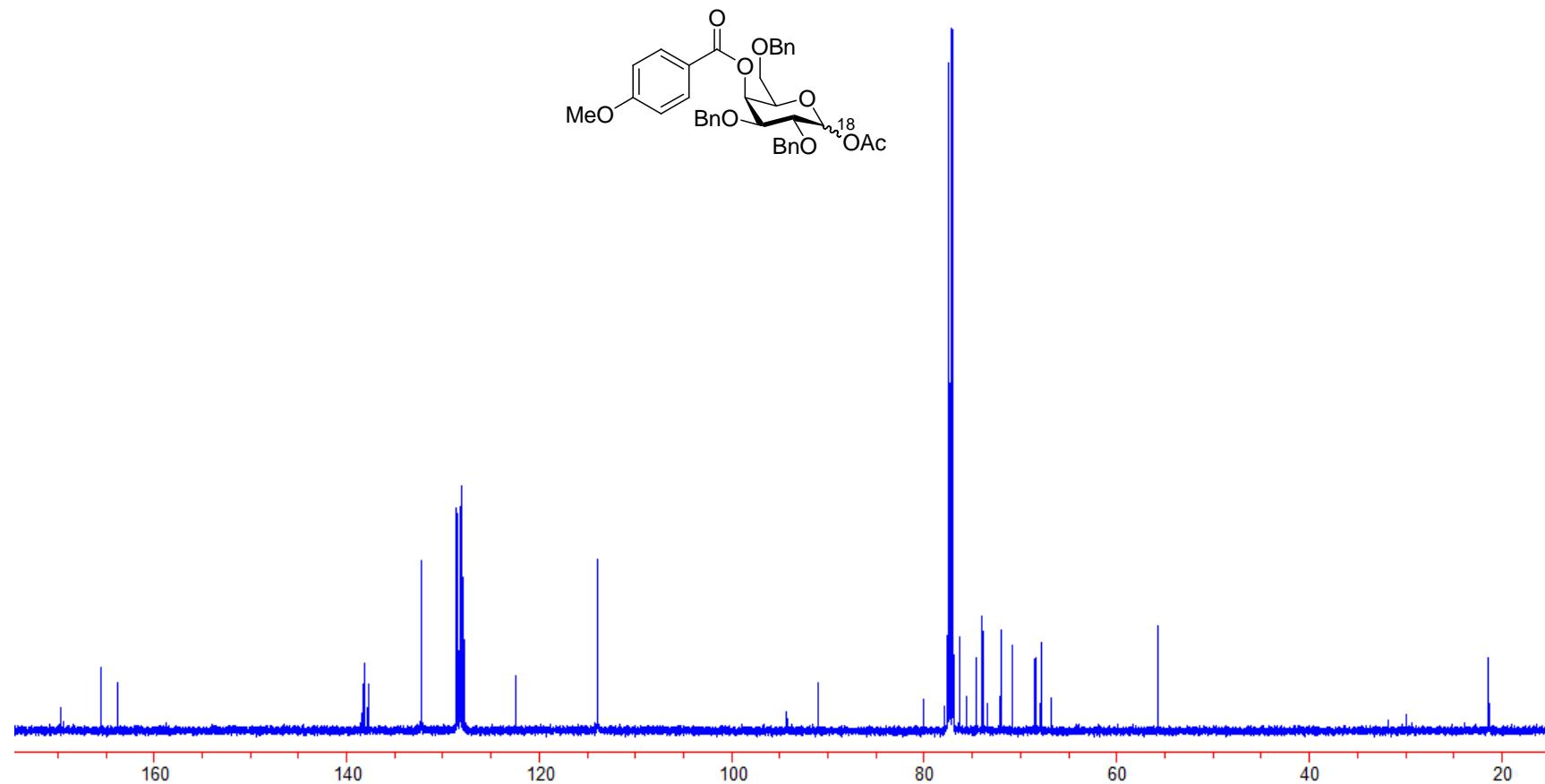
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)- α -D-[1- $^{16/18}O$]-galactopyranoside (**43**, expansion).



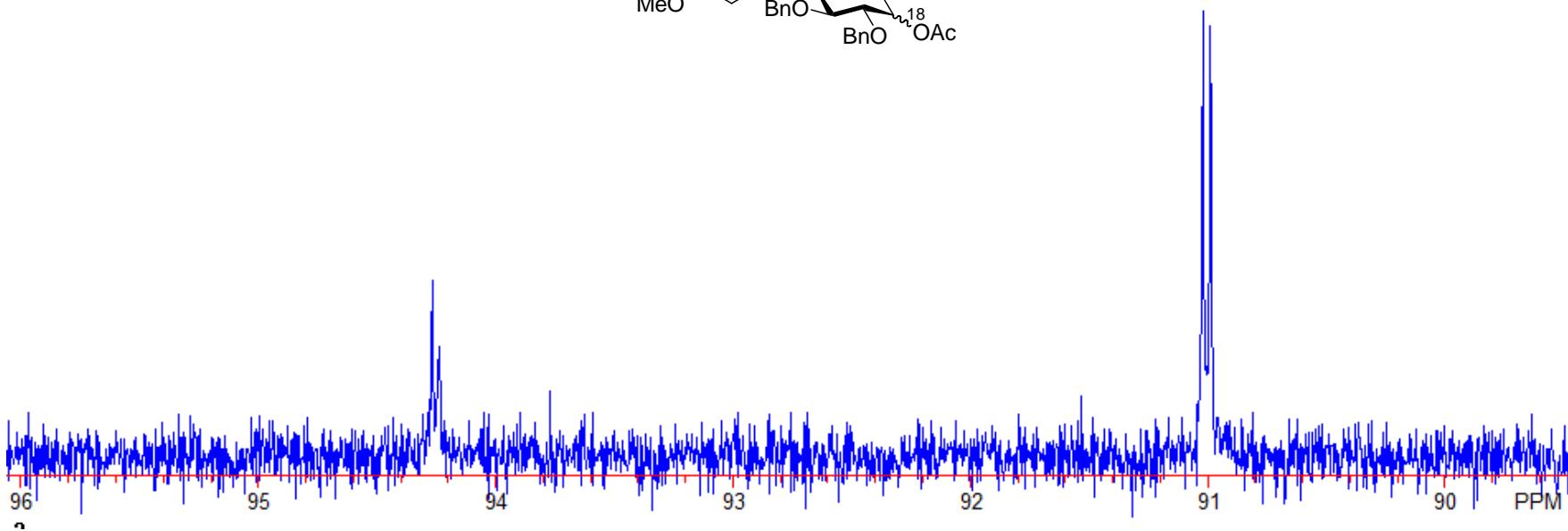
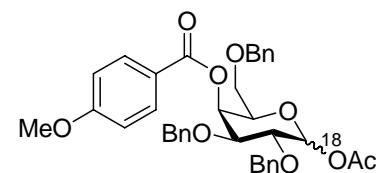
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-^{16/18}*O*]-galactopyranosyl acetate (**47**).



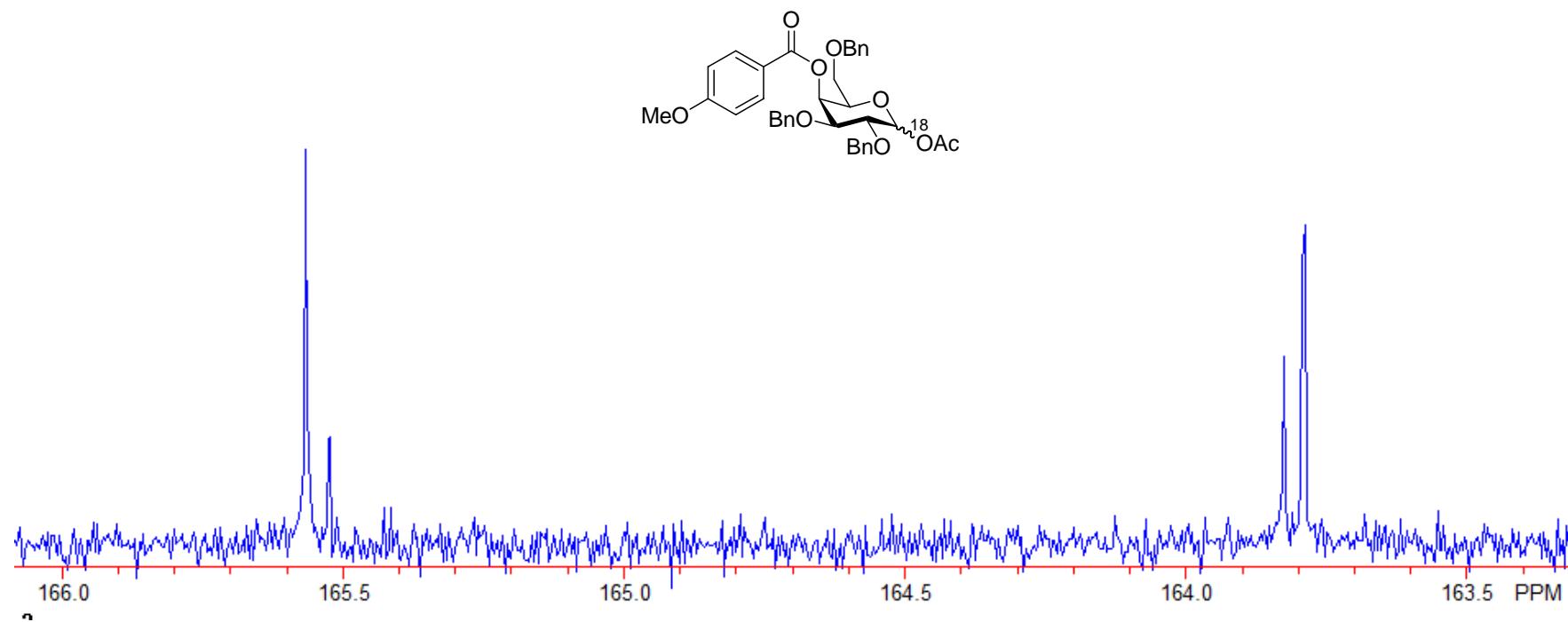
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-^{16/18}*O*]-galactopyranosyl acetate (**47**).



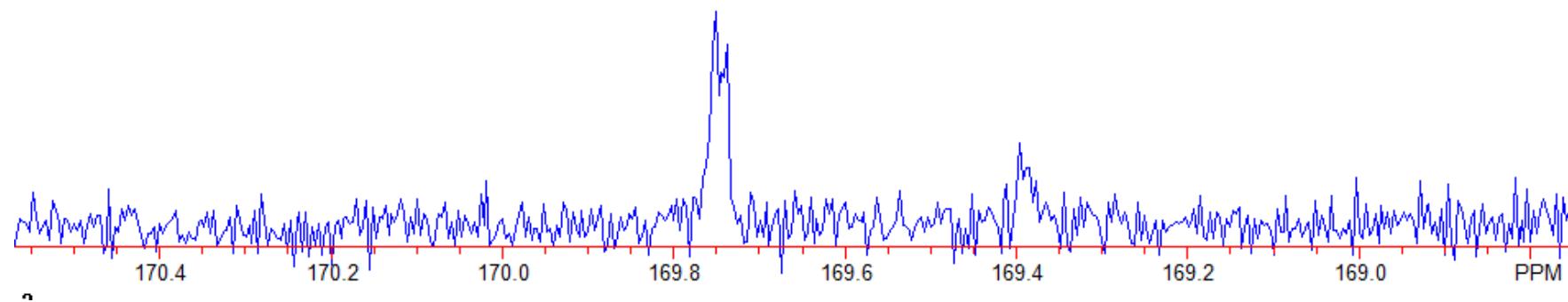
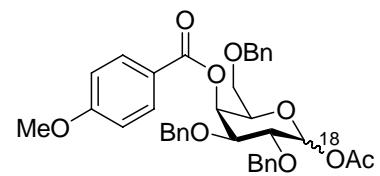
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-^{16/18}*O*]-galactopyranosyl acetate (**47**, expansion).



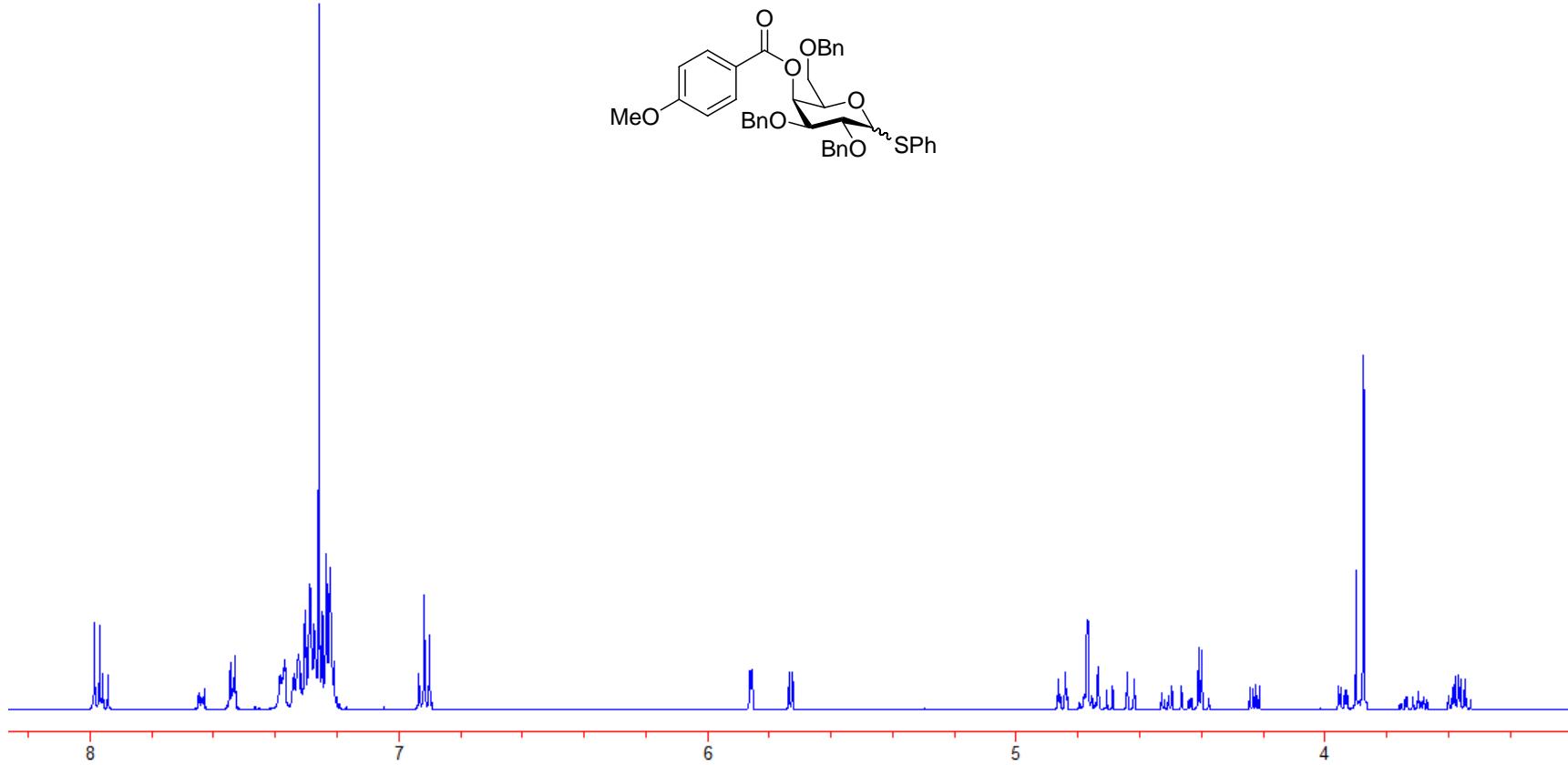
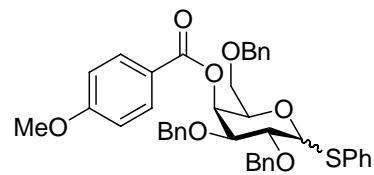
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-^{16/18}*O*]-galactopyranosyl acetate (**47**, expansion).



2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-^{16/18}*O*]-galactopyranosyl acetate (**47**, expansion).



Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-galactopyranoside (**41α** and **41β**).



Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-galactopyranoside (**41α** and **41β**).

