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

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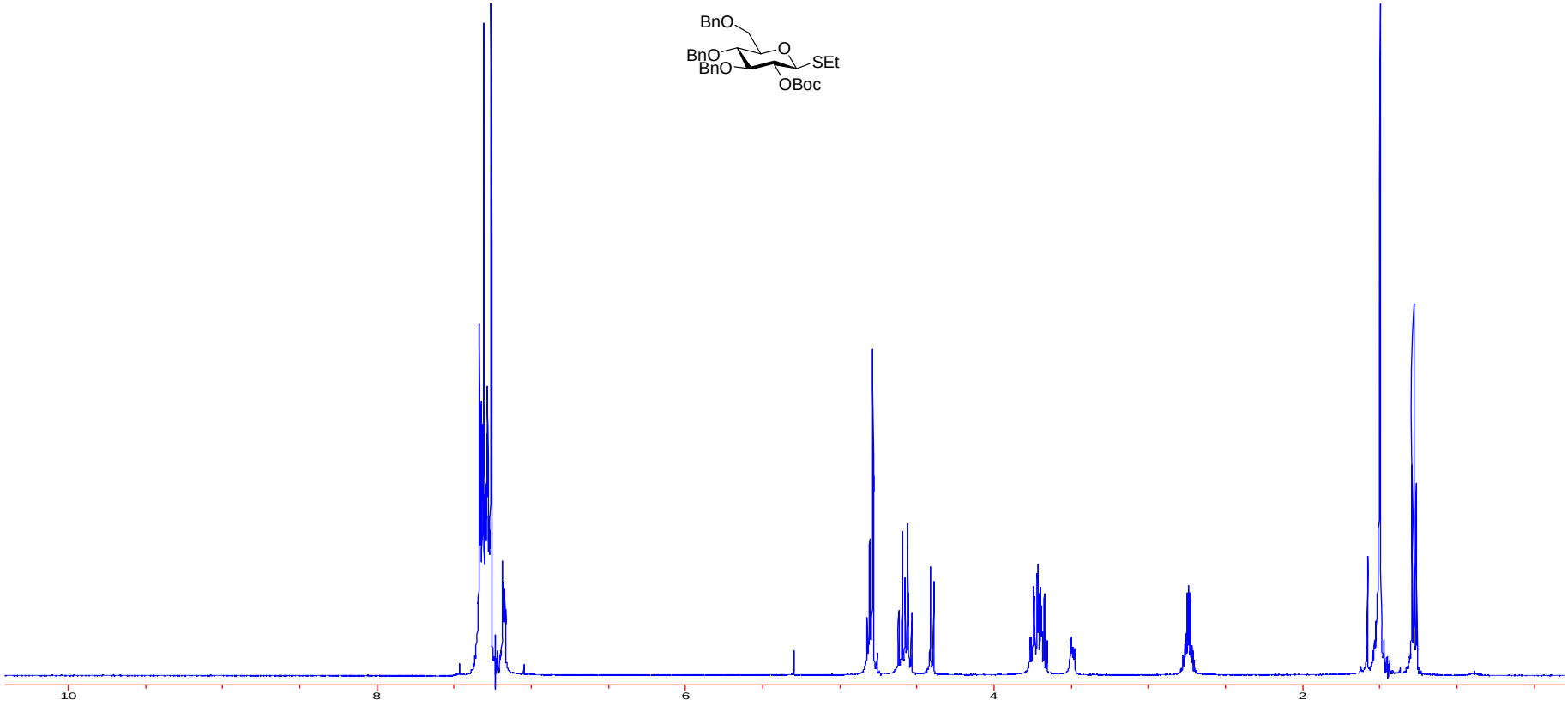
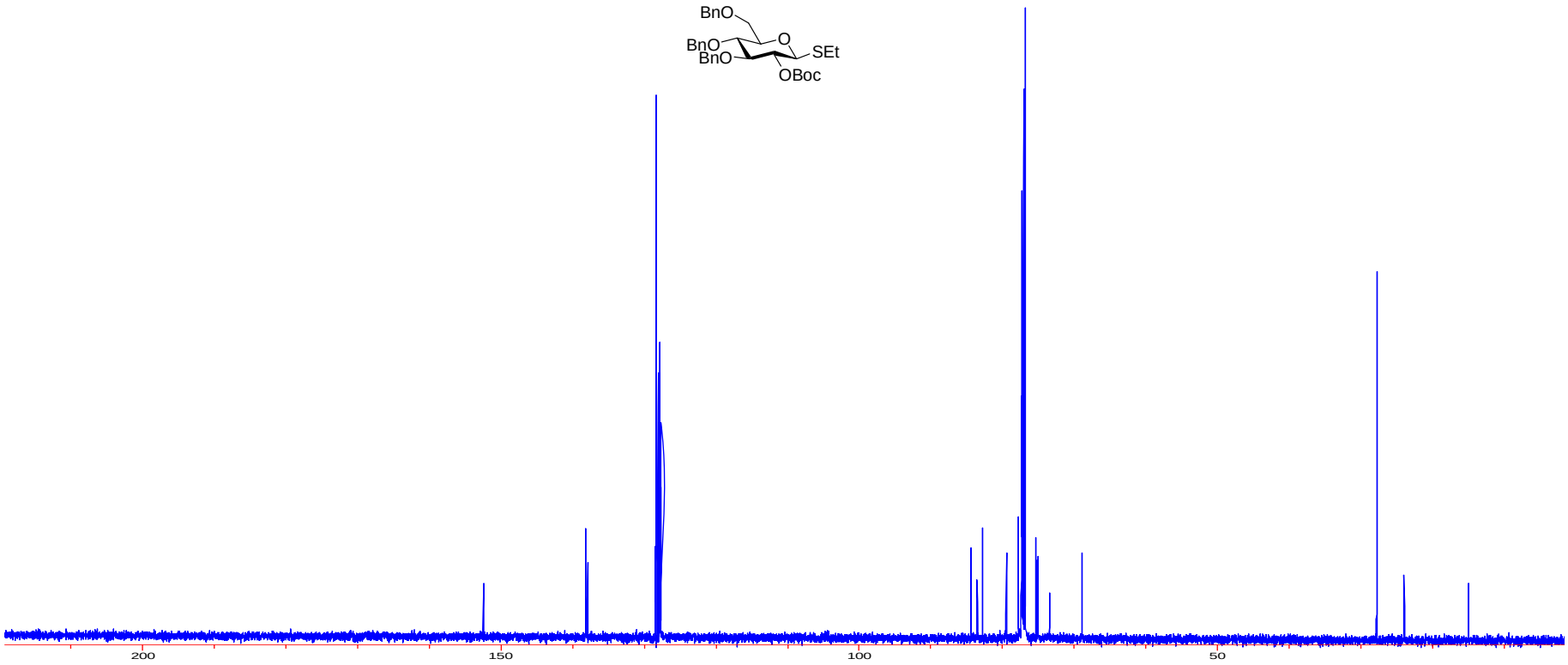
General Experimental. Unless otherwise stated ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 500 and 125 MHz, respectively. Specific rotations were recorded in $CHCl_3$ solution, unless otherwise stated. All solvents were dried and distilled by standard protocols. All reactions were 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.

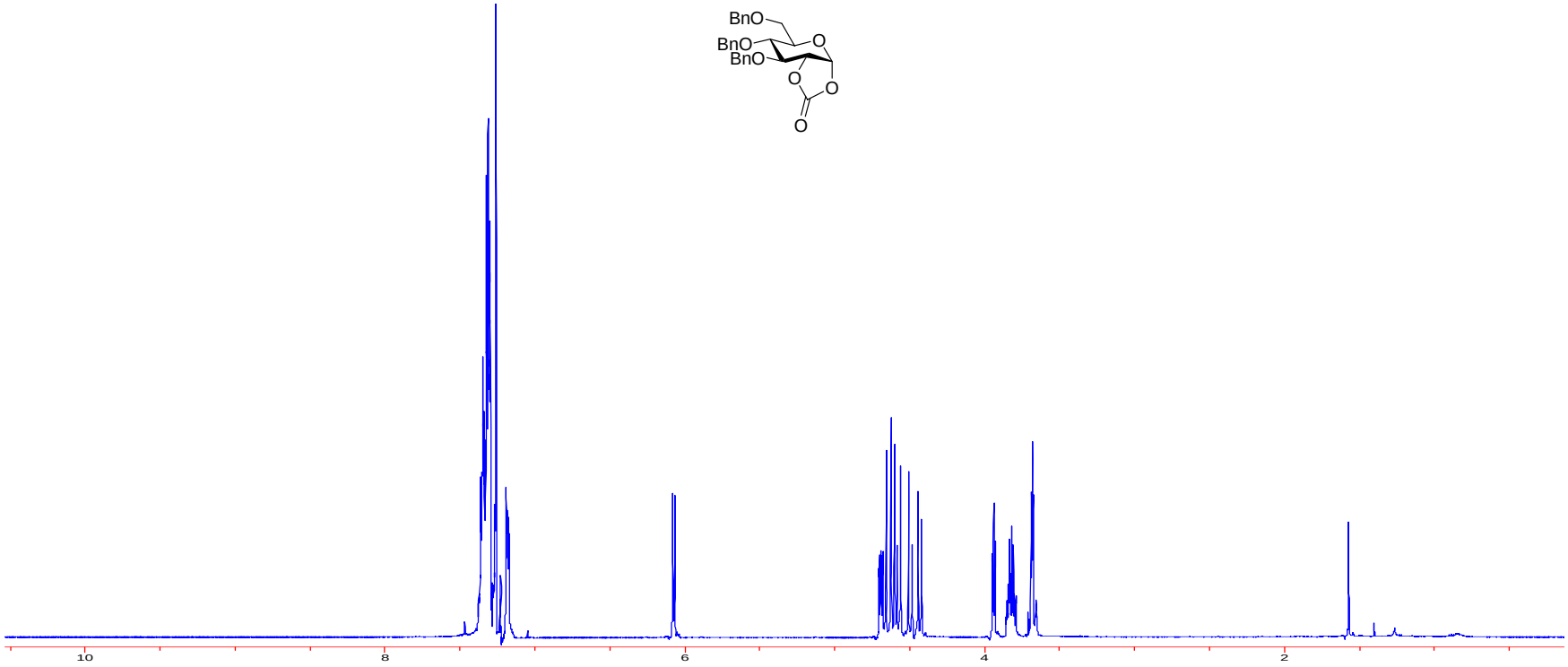
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-glucopyranoside (**9**)



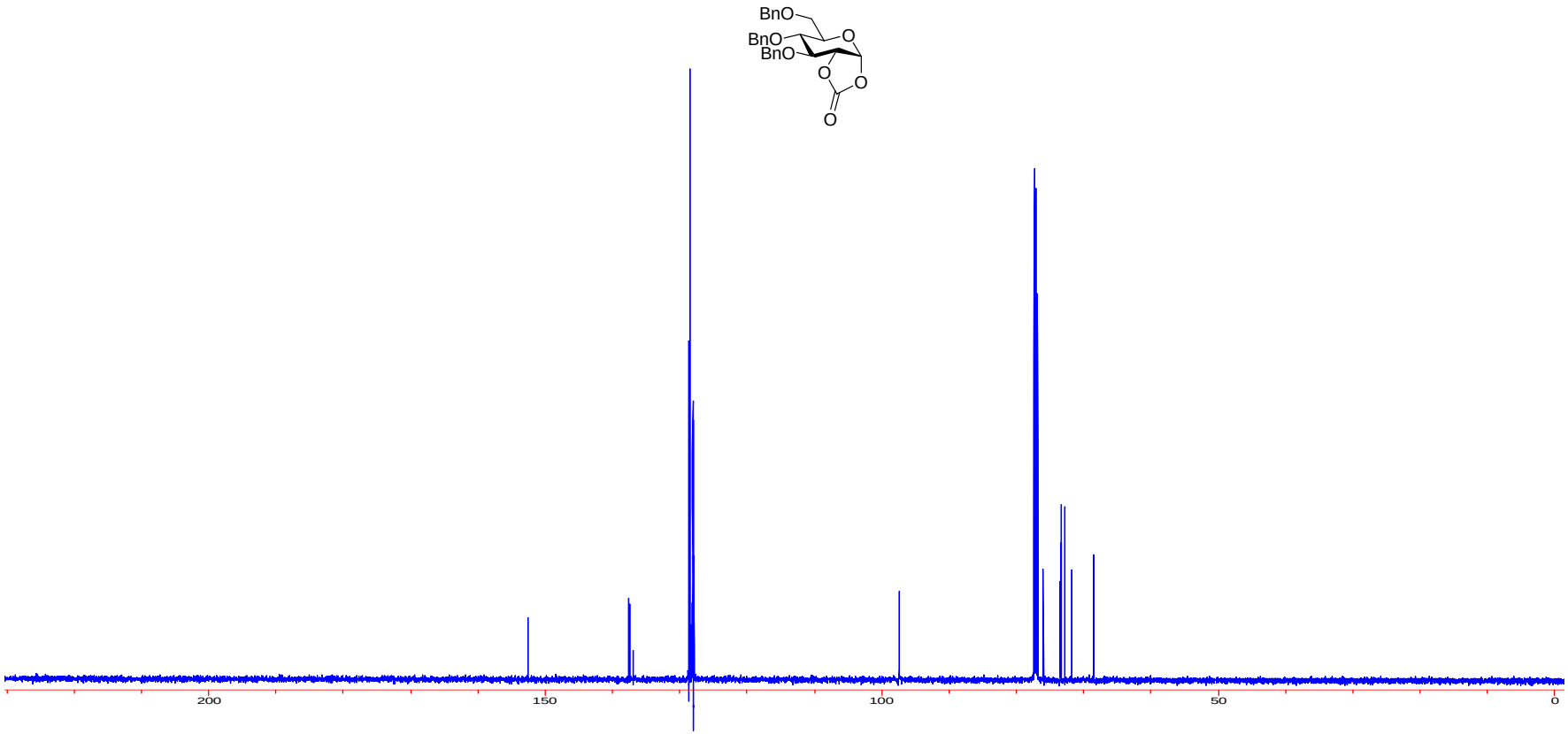
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-glucopyranoside (**9**)



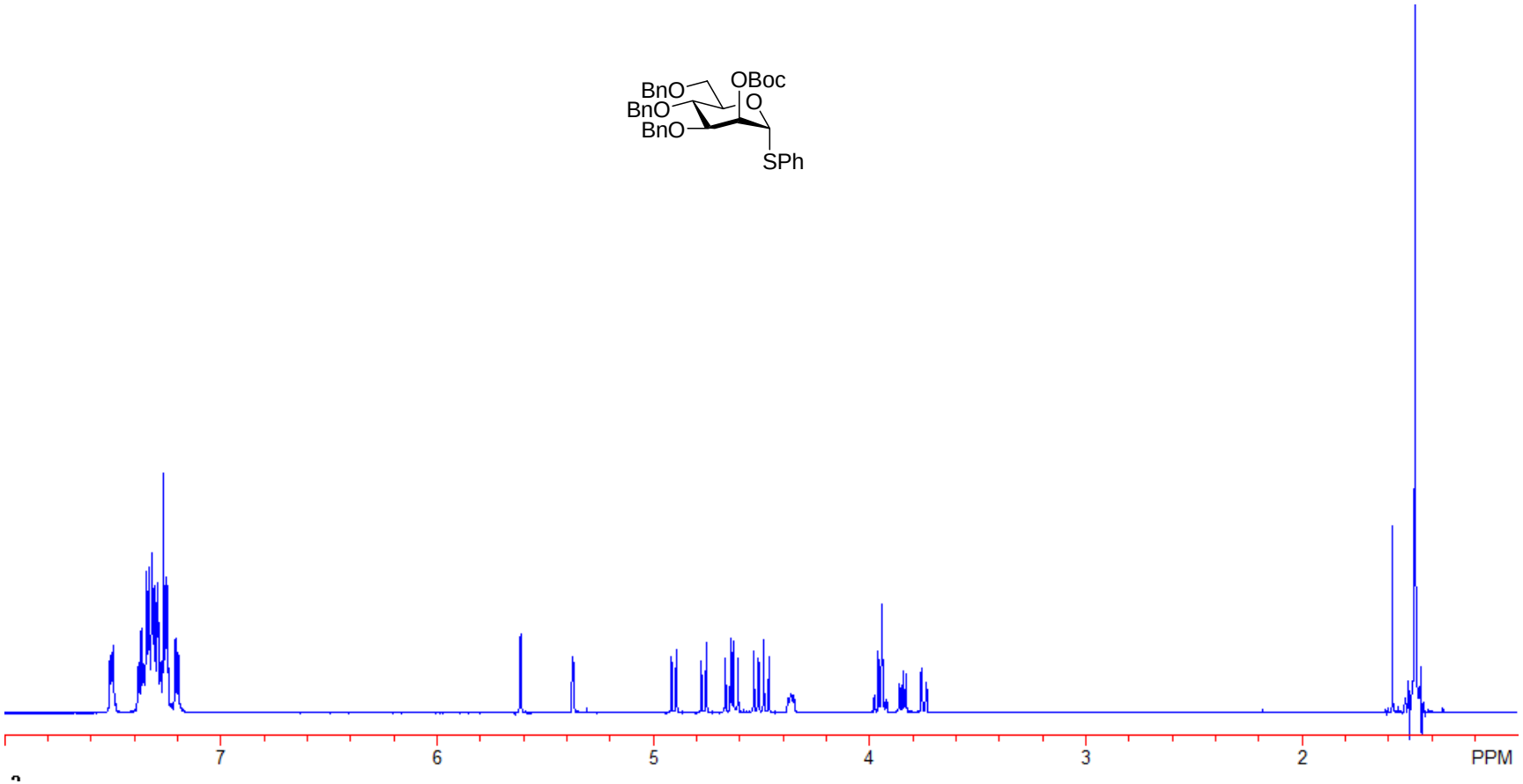
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl-α-D-glucopyranoside (**10**)



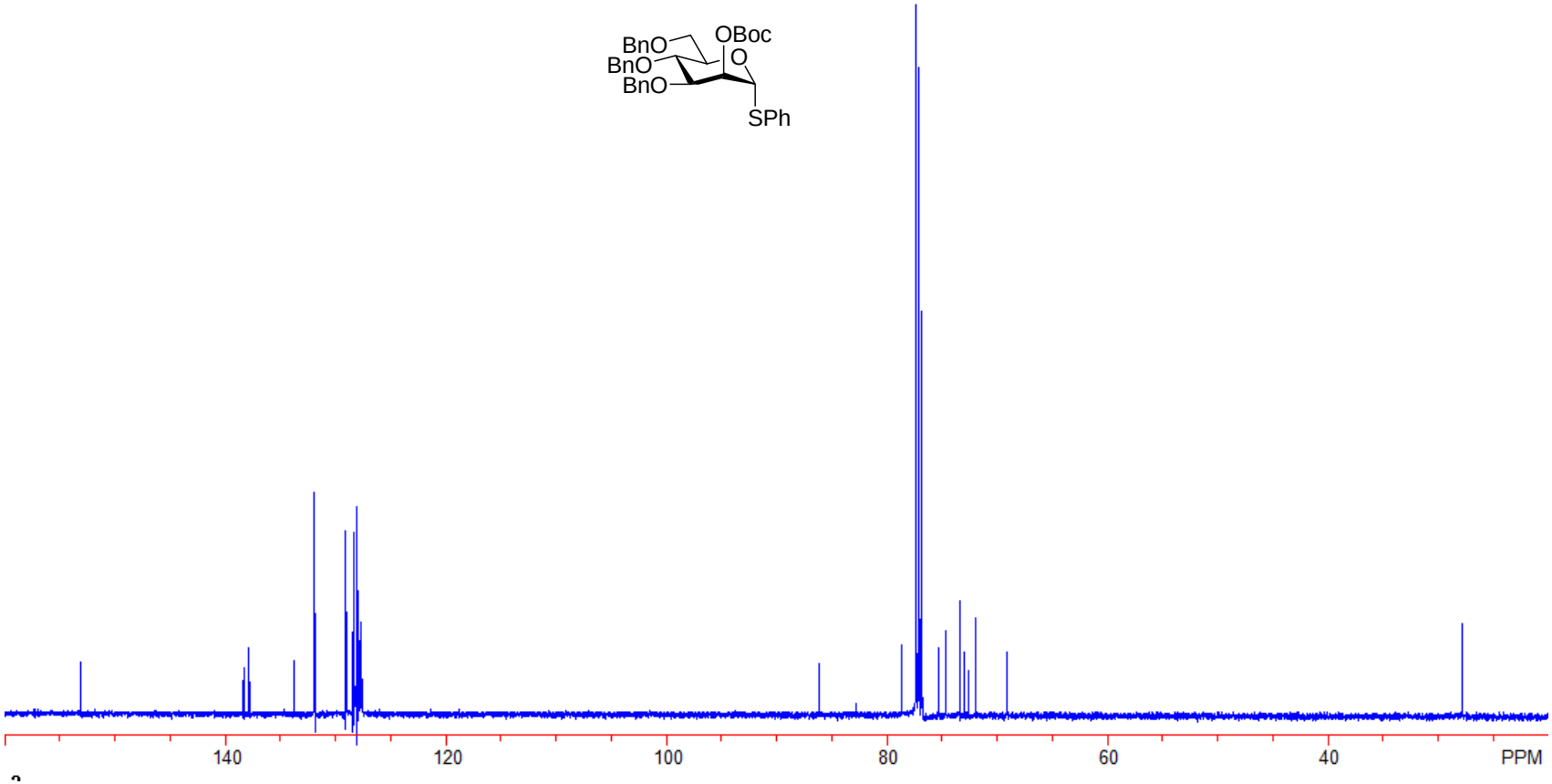
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl-α-D-glucopyranoside (**10**)



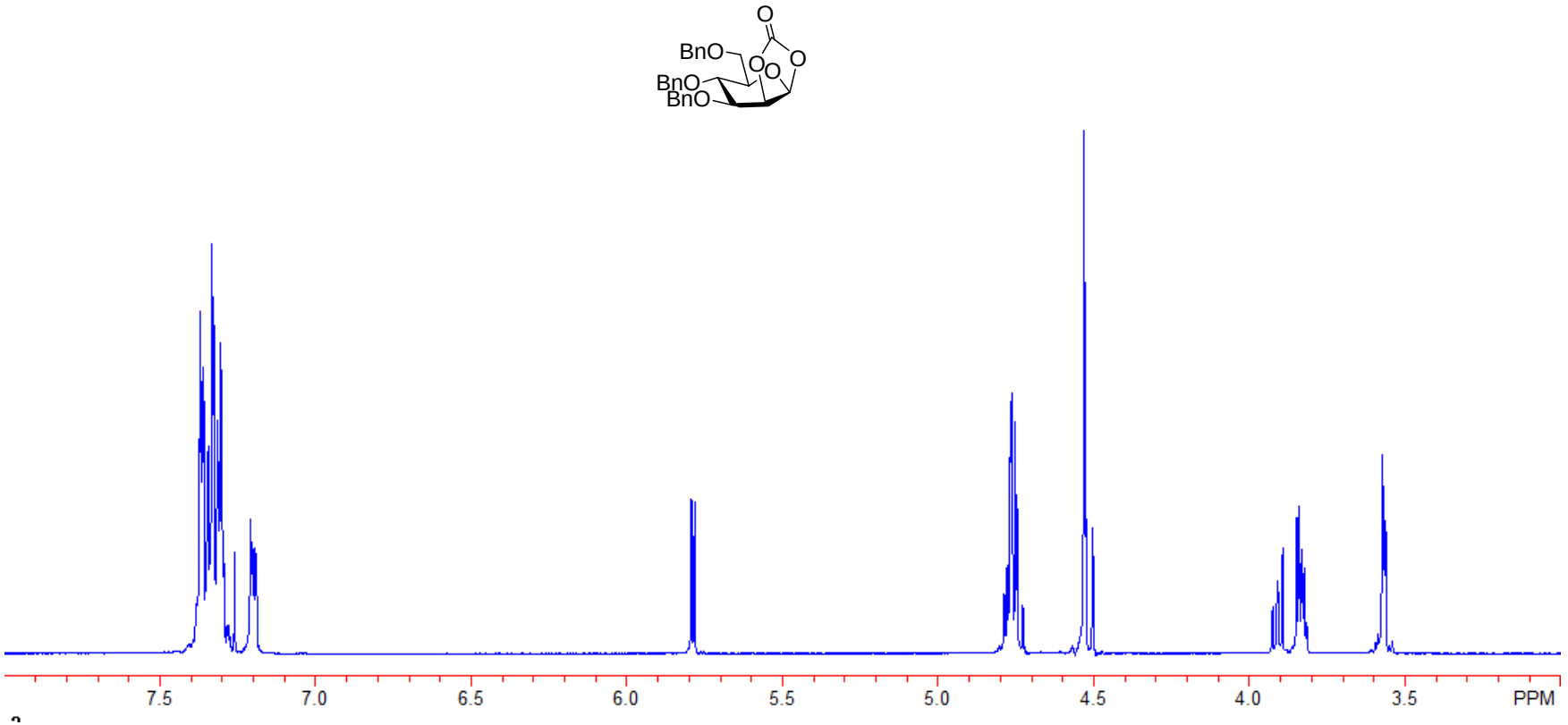
Phenyl 2-*O*-*tert*-butoxycarbonyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**11**).



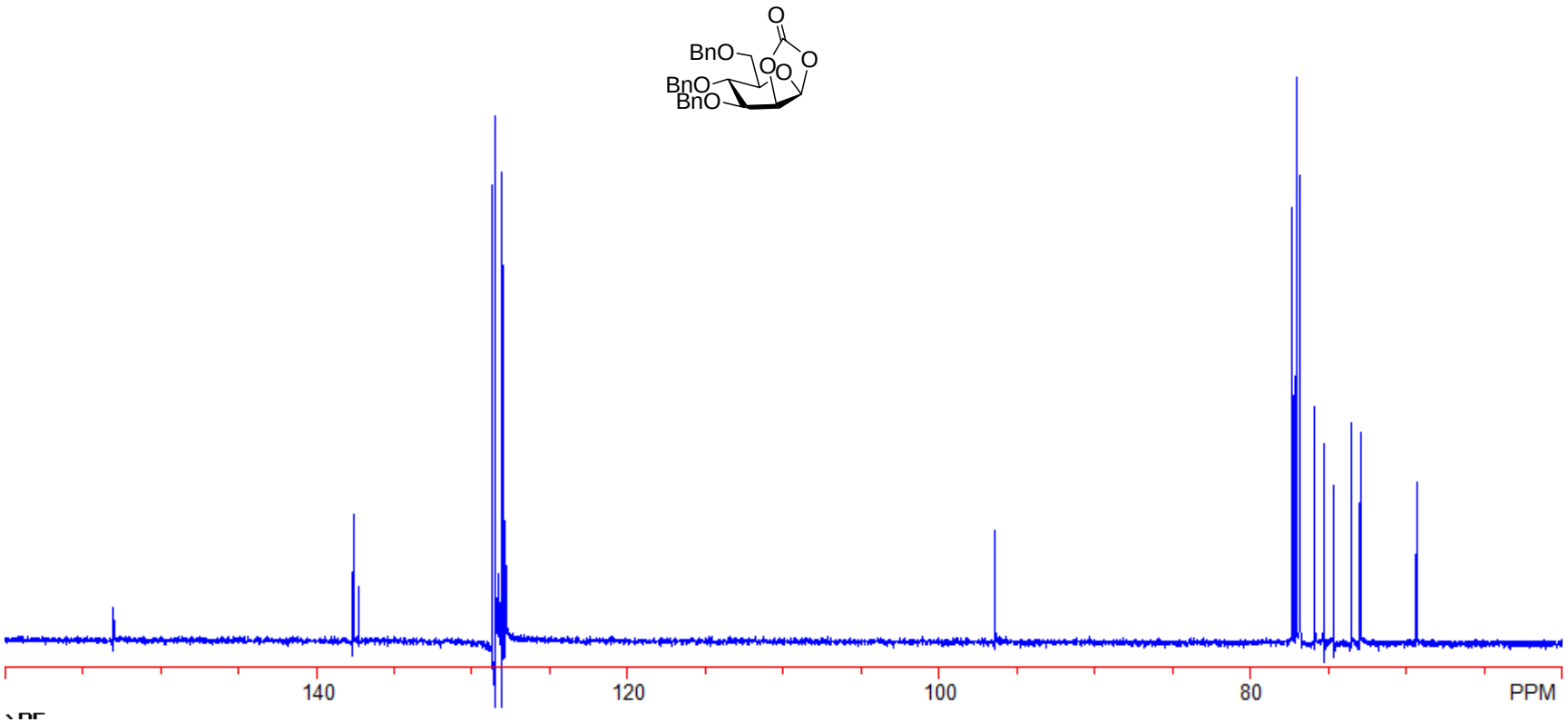
Phenyl 2-*O*-*tert*-butoxycarbonyl-3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**11**).



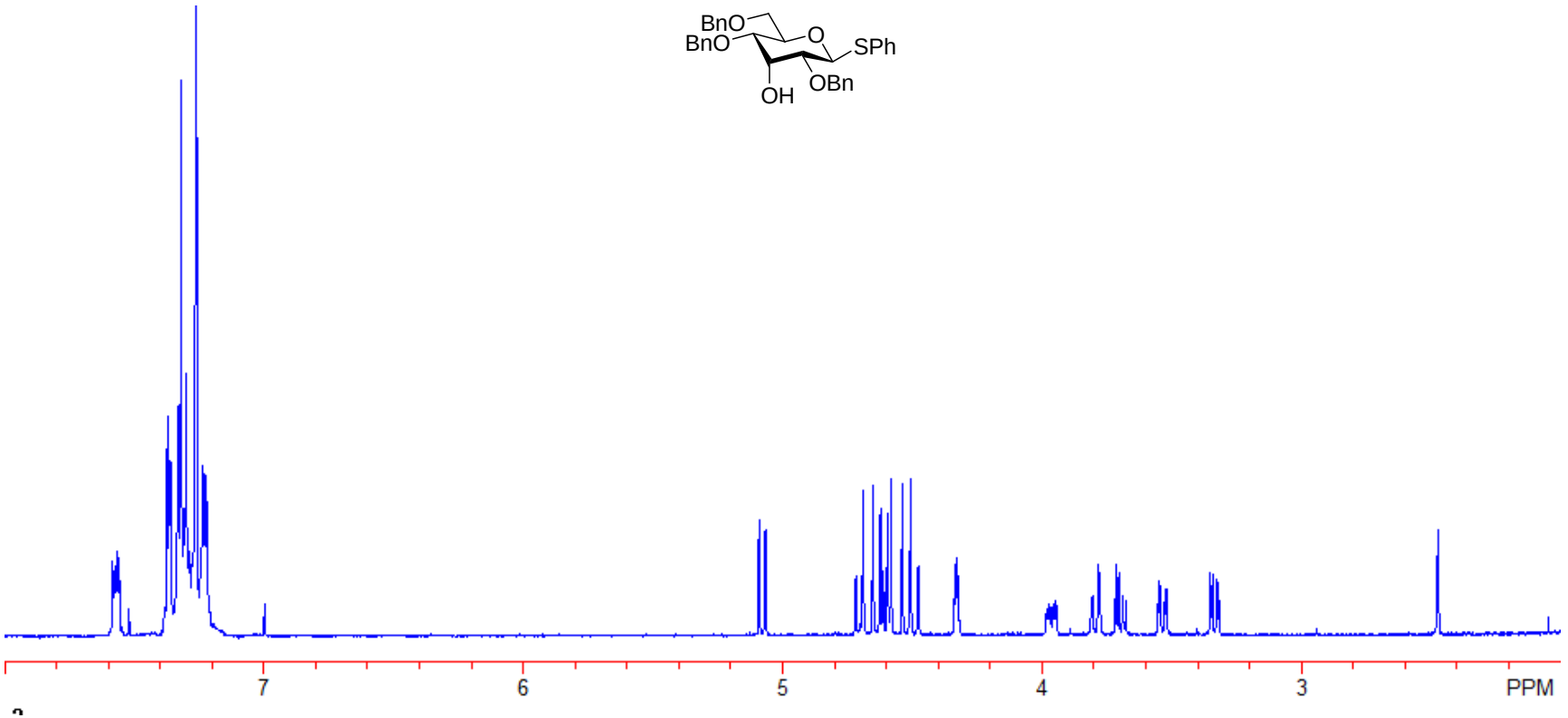
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl-α-D-mannopyranoside (**12**).



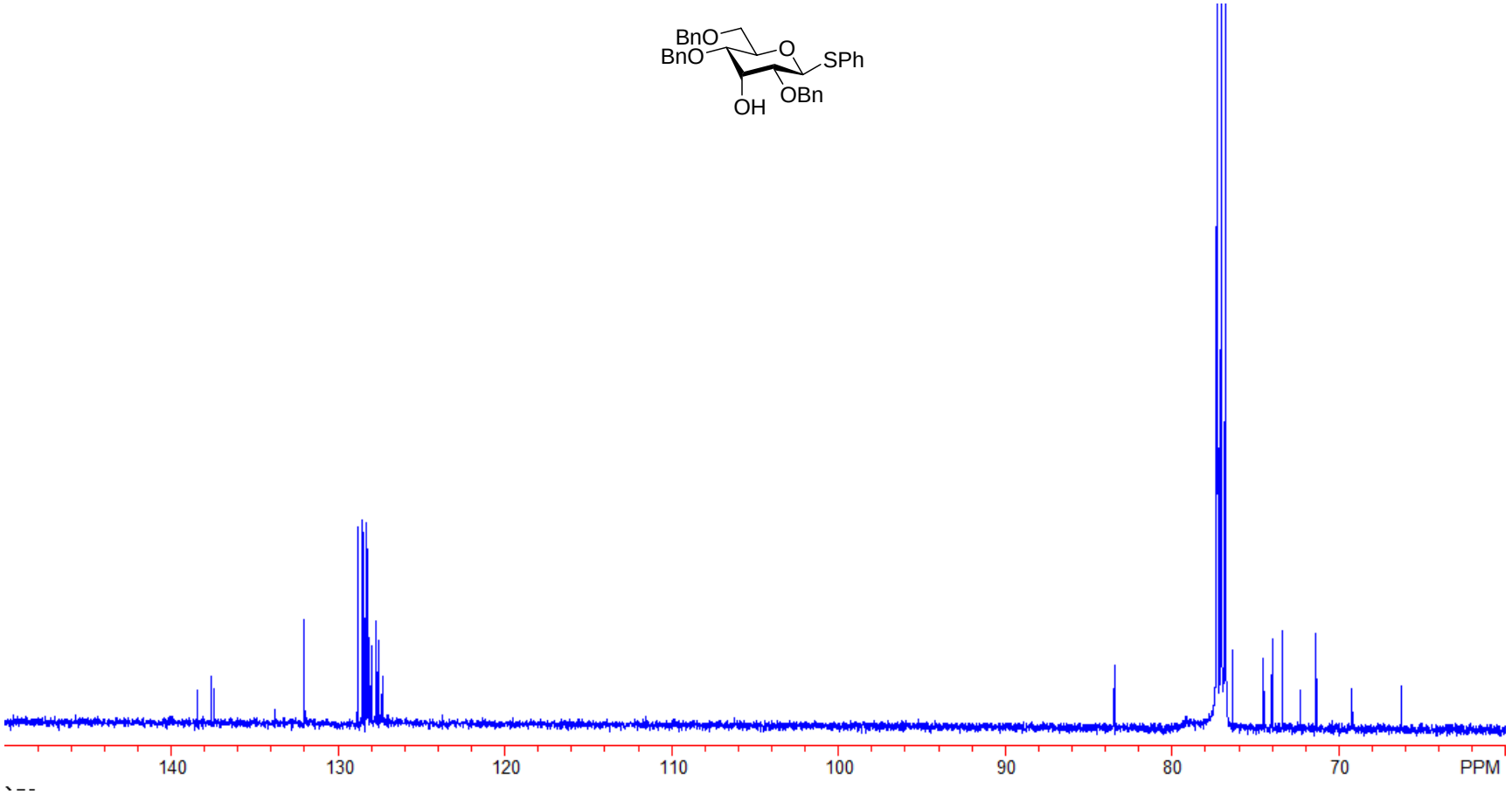
3,4,6-Tri-*O*-benzyl-1,2-*O*-carbonyl-α-D-mannopyranoside (**12**).



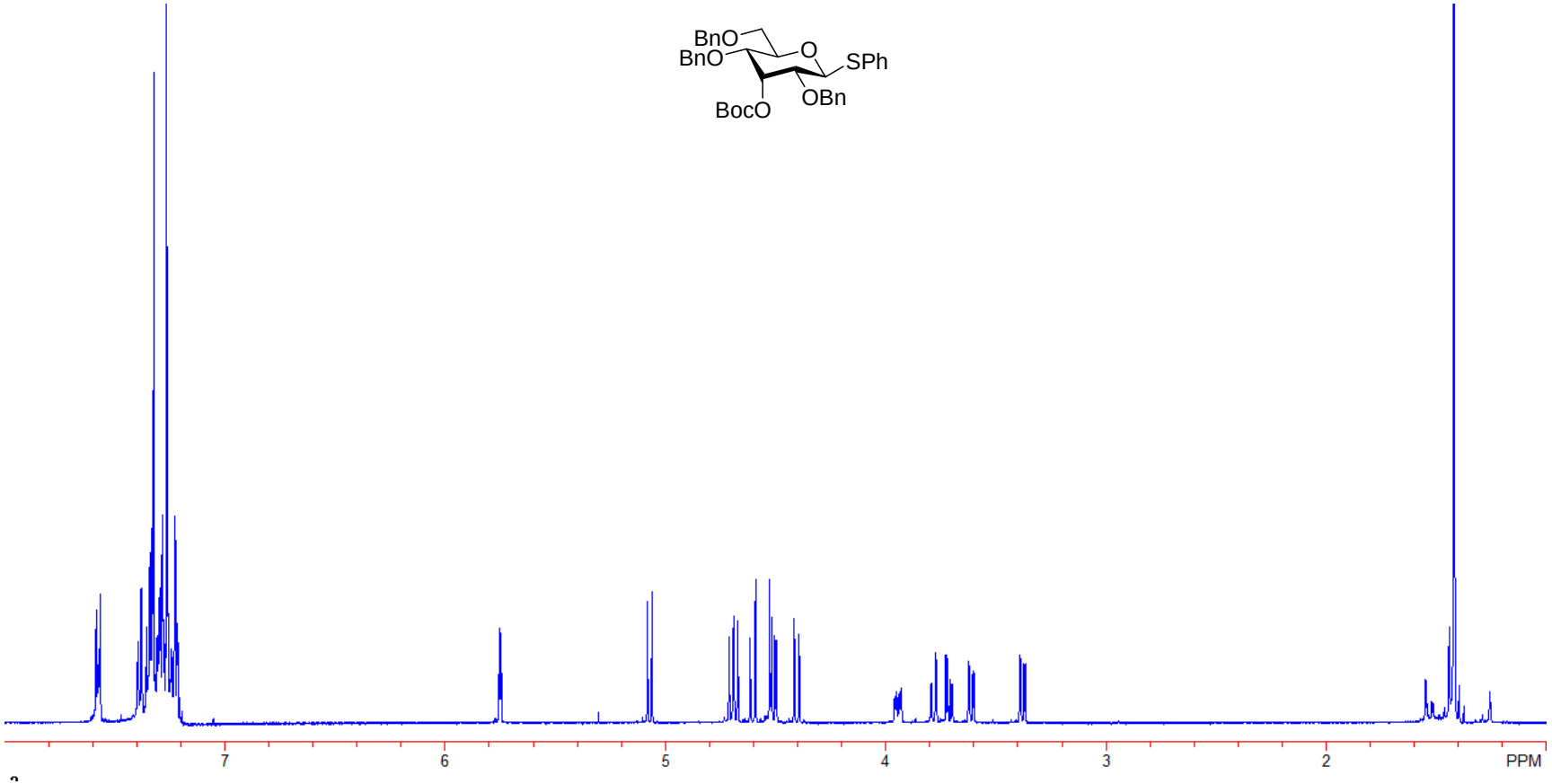
Phenyl 2,4,6-Tri-*O*-benzyl-1-thio-β-D-allopyranoside (**14**).



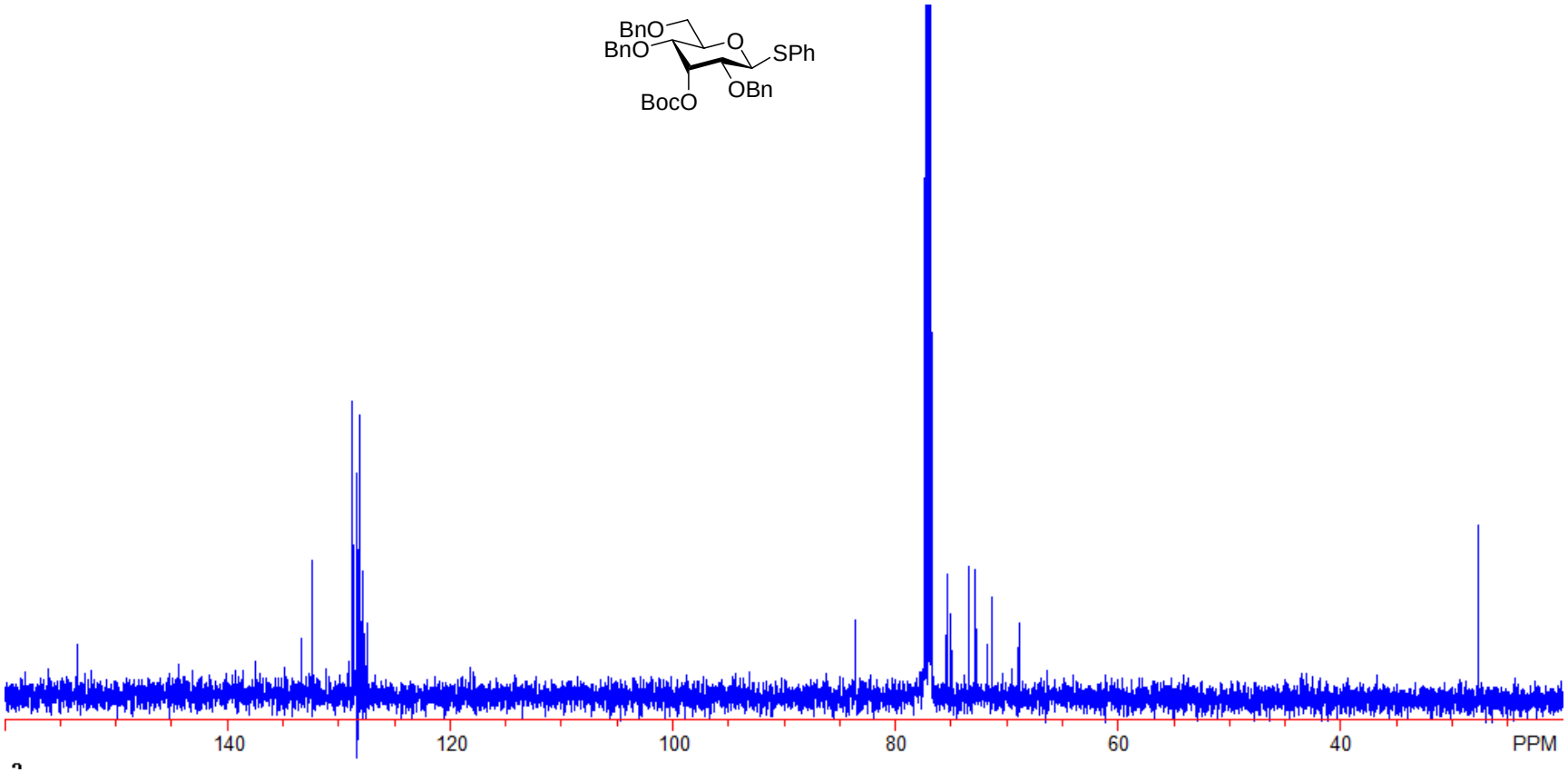
Phenyl 2,4,6-Tri-*O*-benzyl-1-thio-β-D-allopyranoside (**14**).



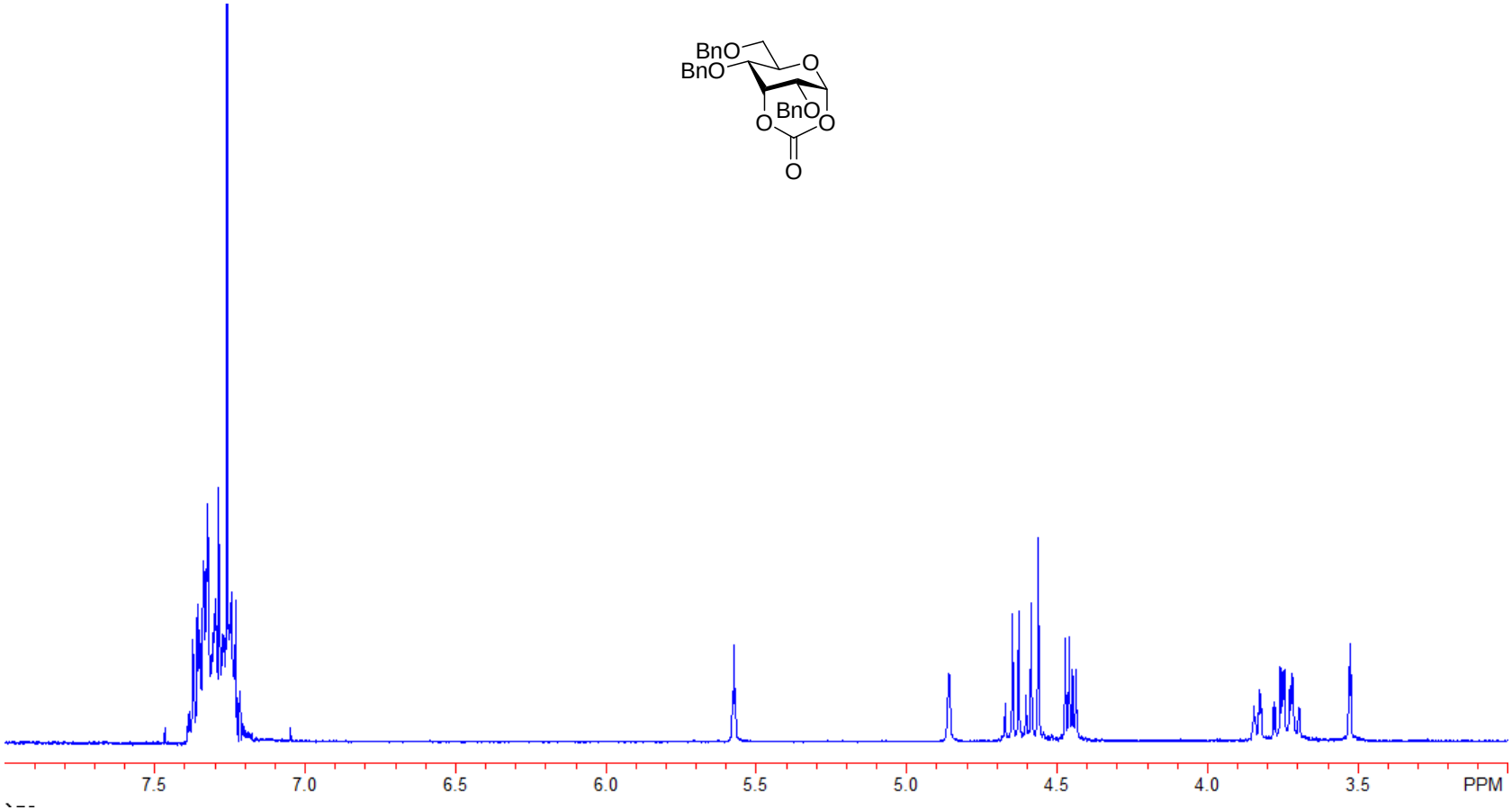
Phenyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-allopyranoside (**15**).



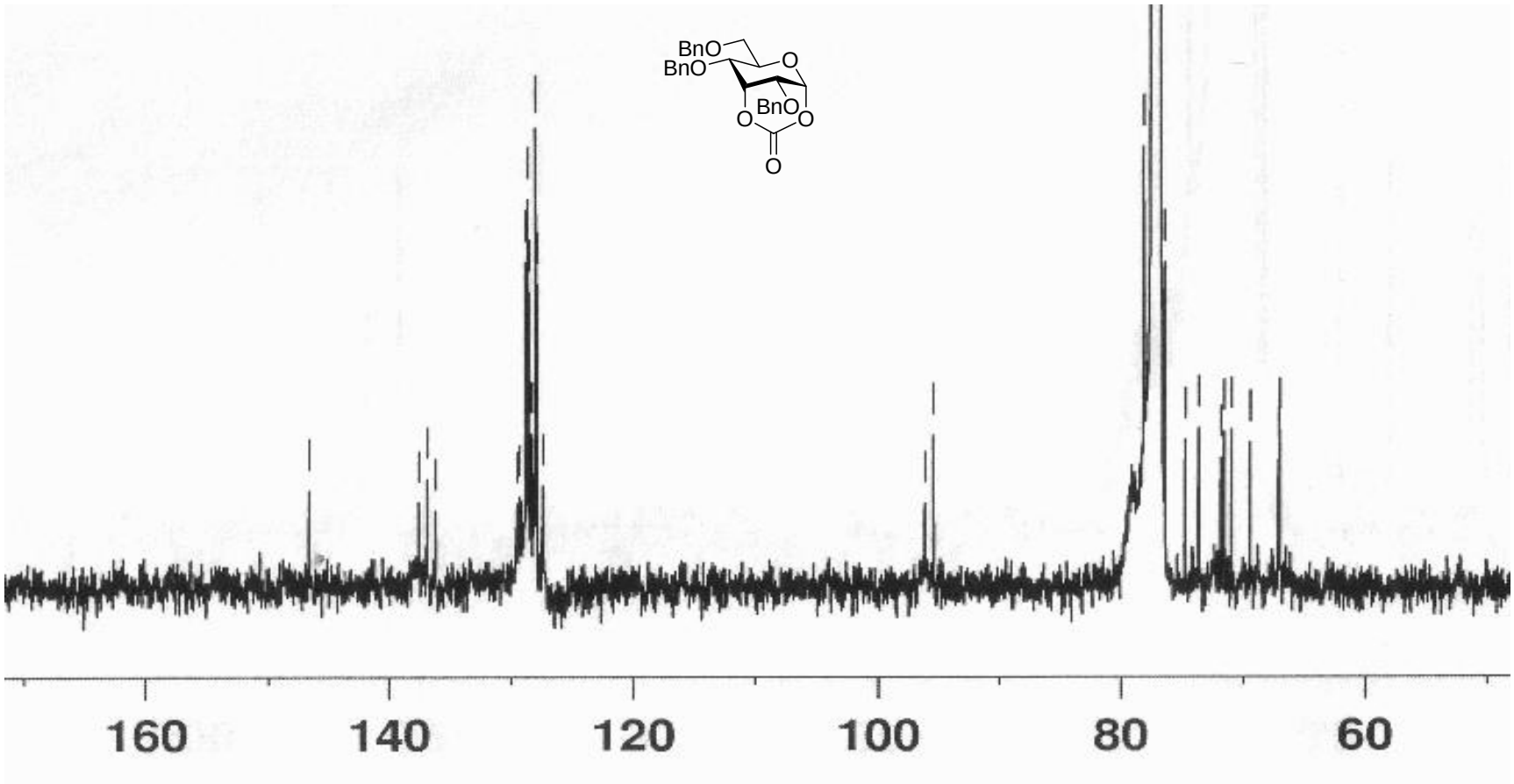
Phenyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-allopyranoside (**15**).



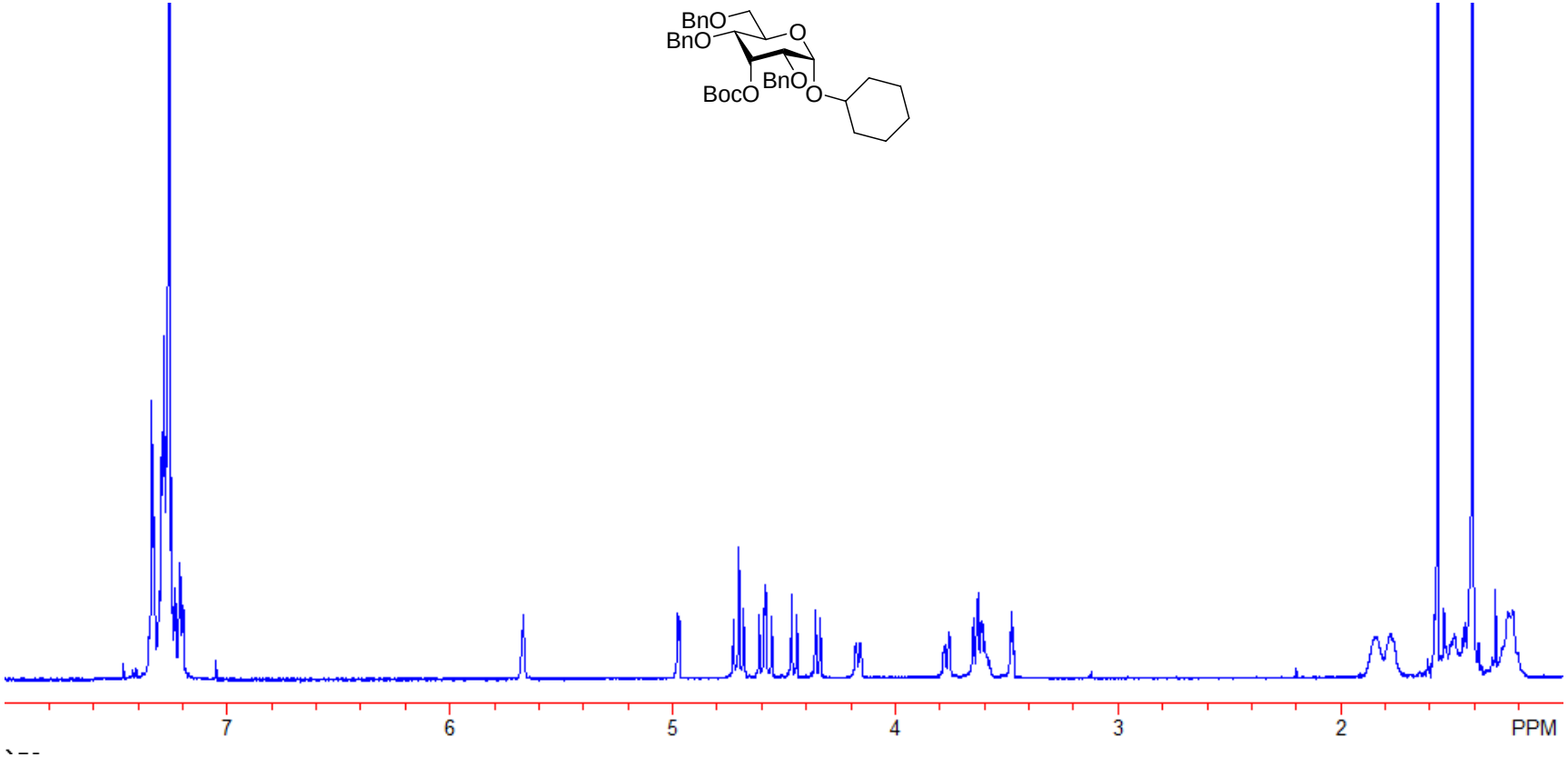
2,4,6-Tri-*O*-benzyl-1,3-*O*-carbonyl-α-D-allose (**16**).



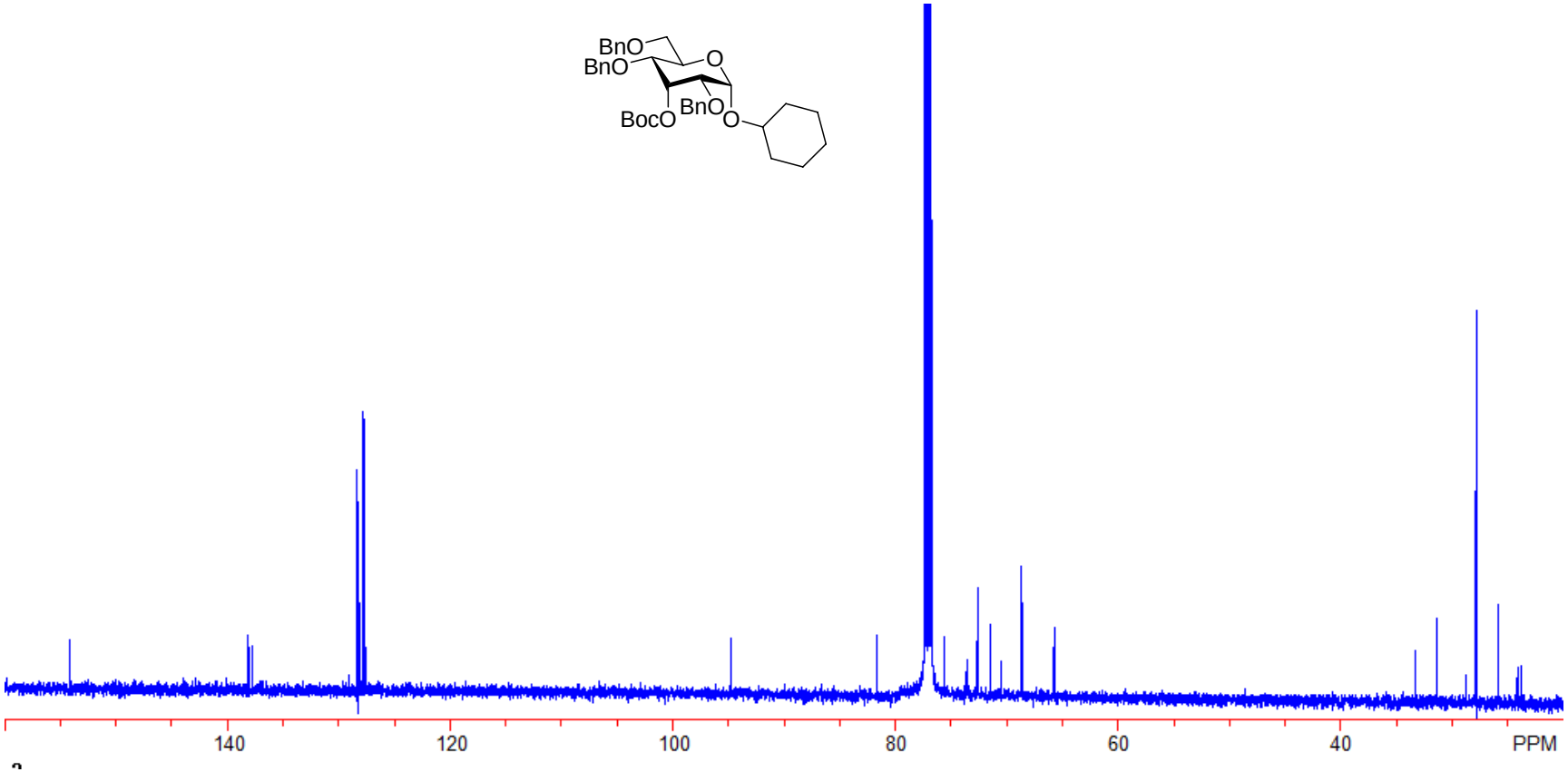
2,4,6-Tri-*O*-benzyl-1,3-*O*-carbonyl-α-D-allose (**16**).



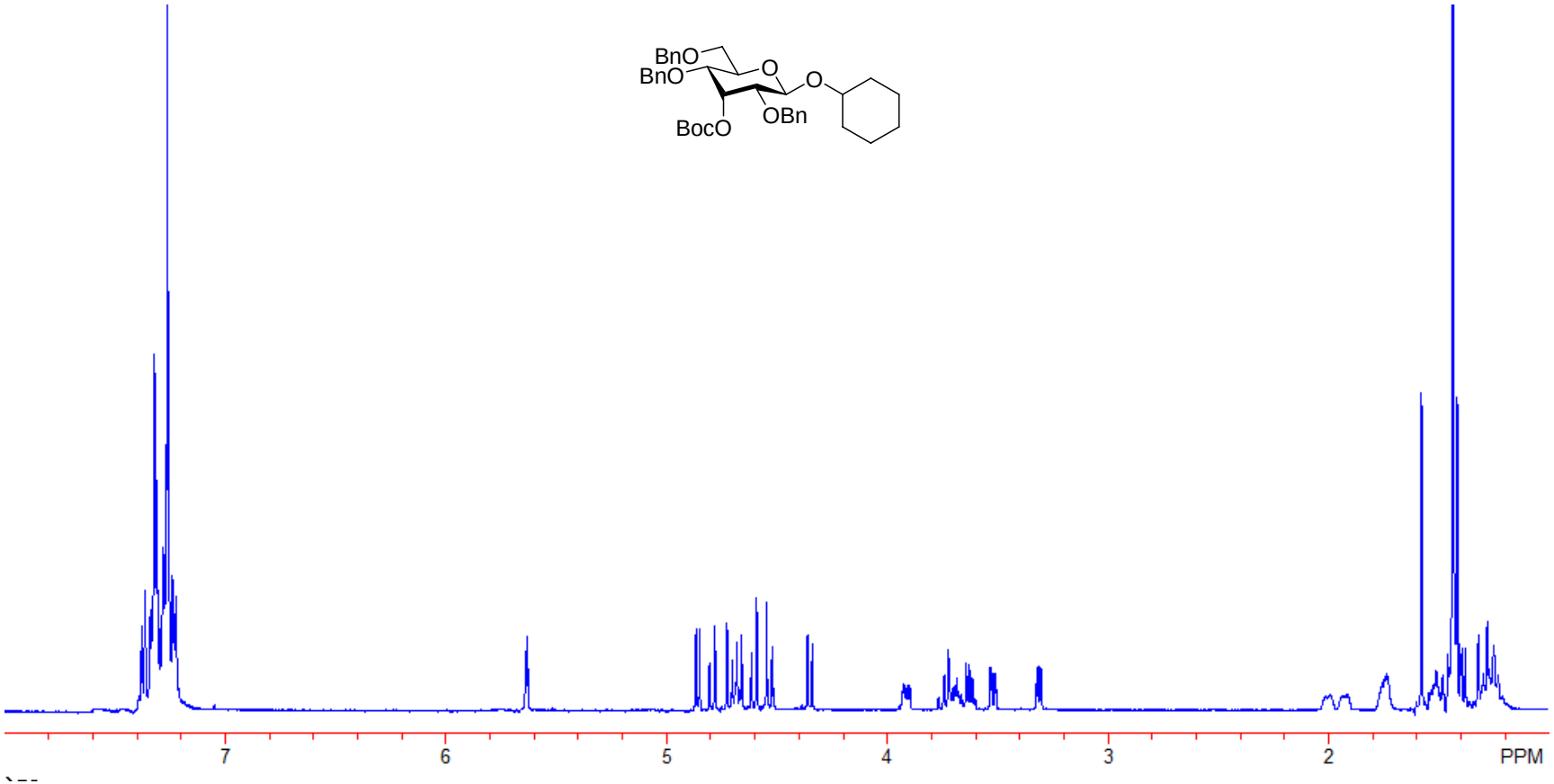
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl-α-D-allopyranoside (**17α**)



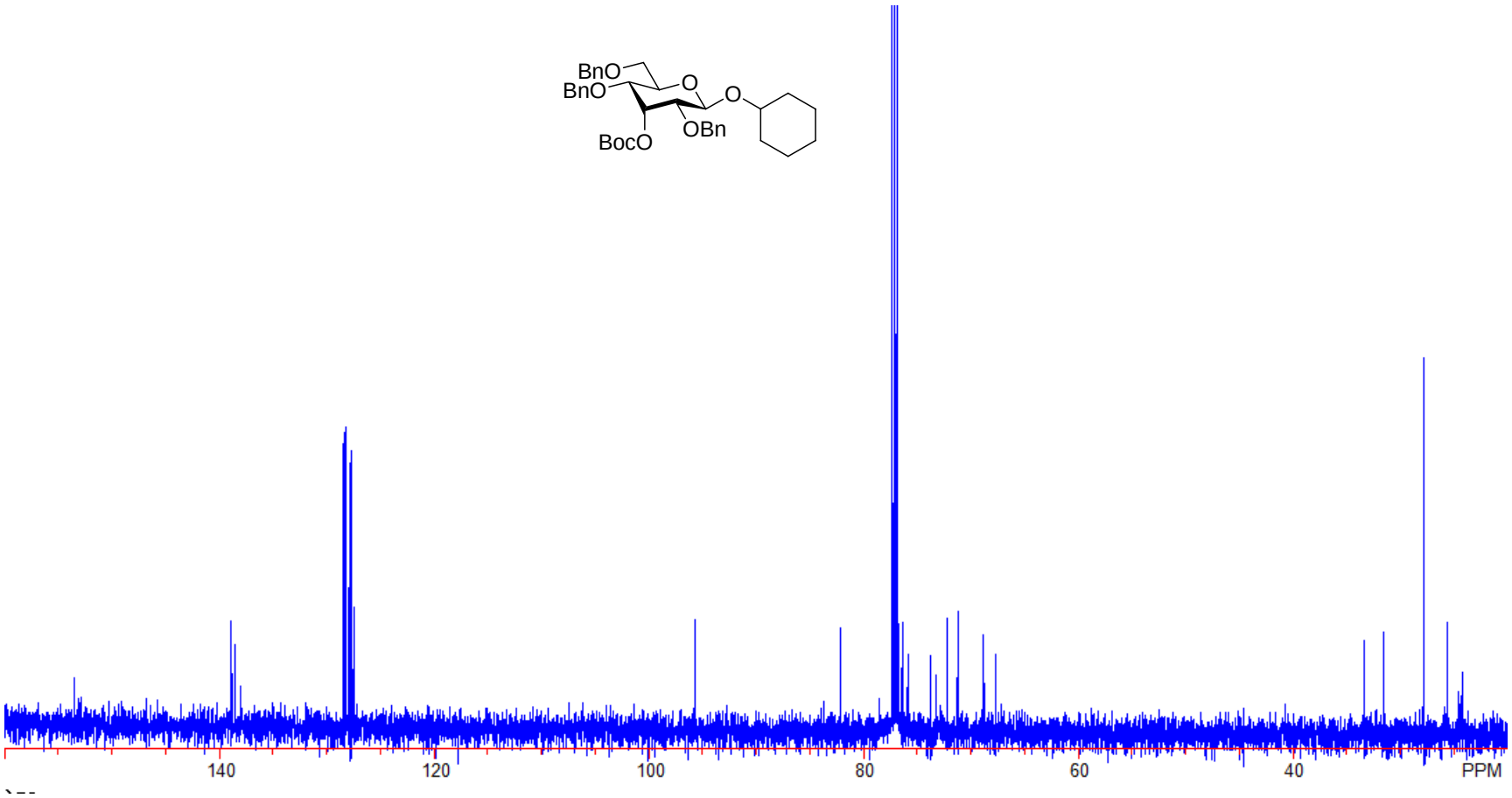
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl-α-D-allopyranoside (**17α**)



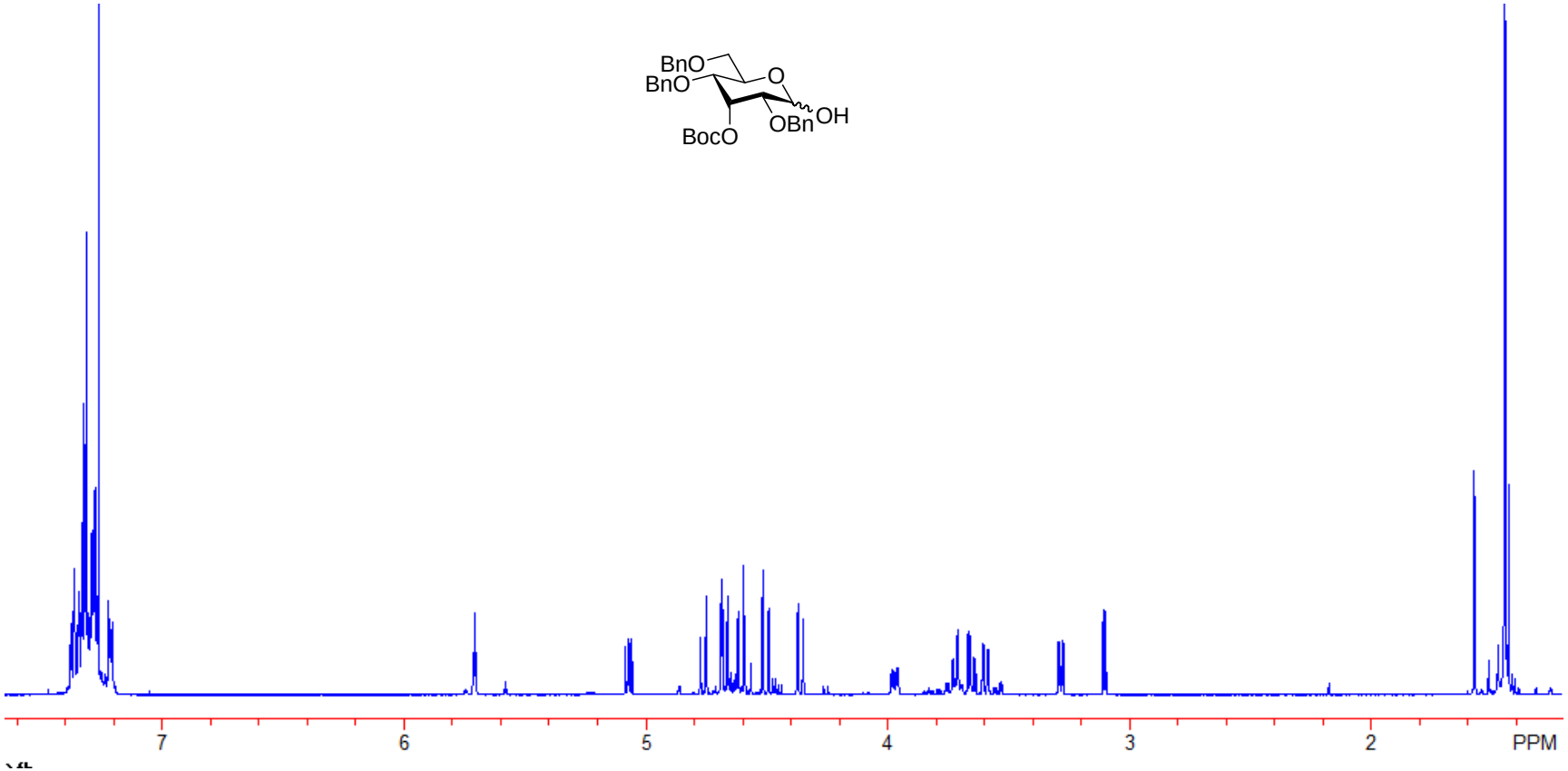
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl-β-D-allopyranoside (**17β**).



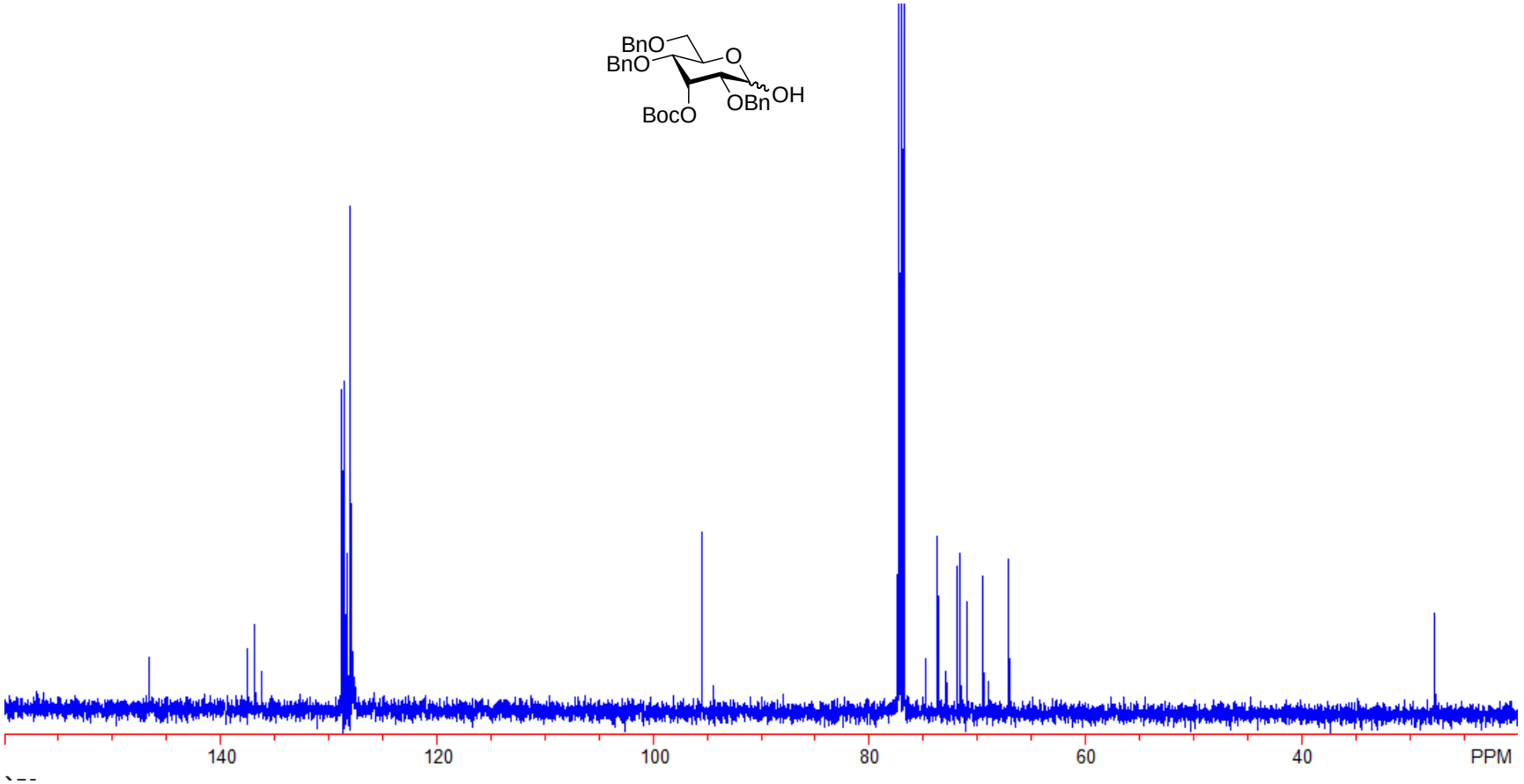
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2,4,6-*O*-benzyl-β-D-allopyranoside (**17β**).



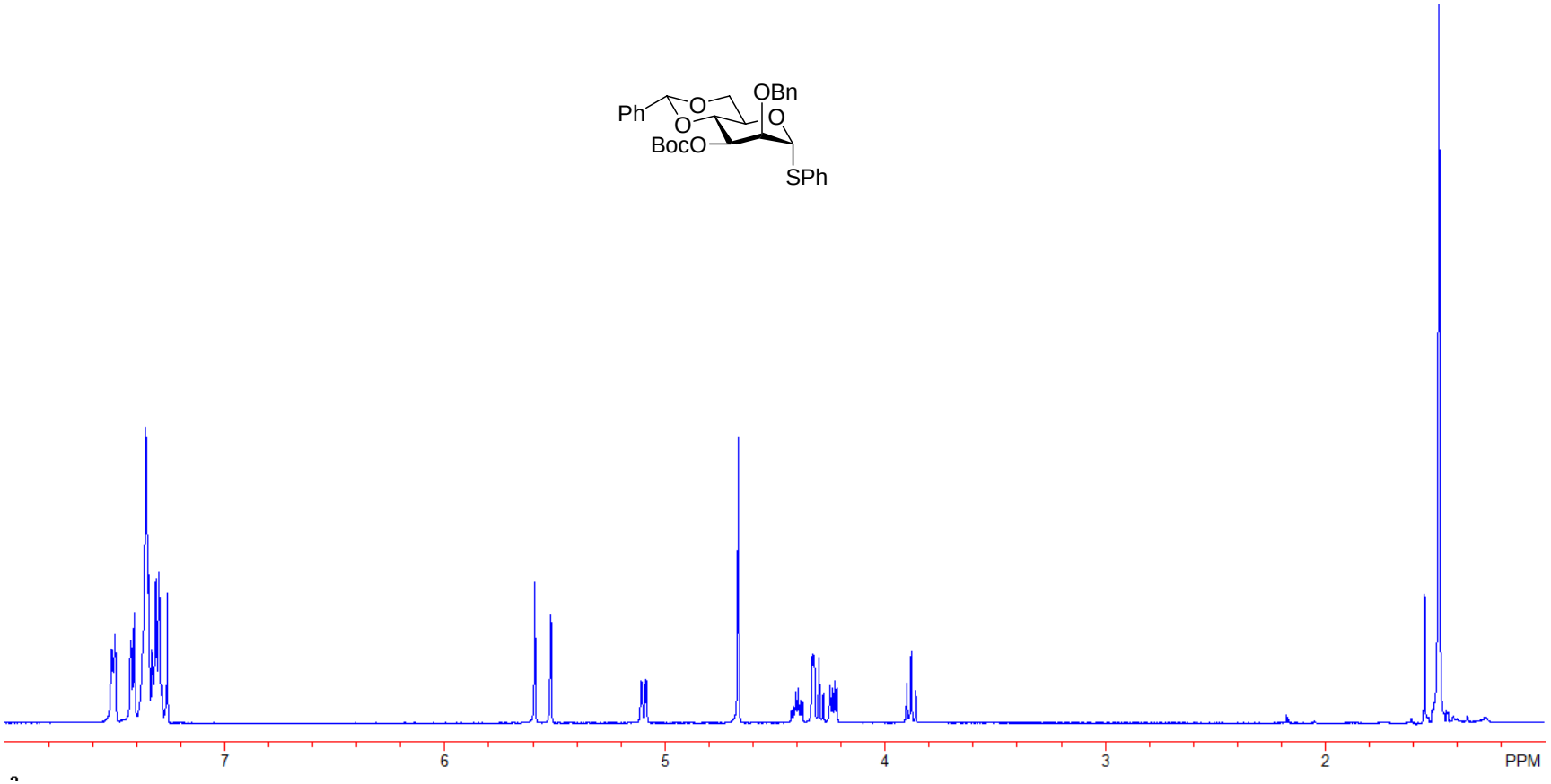
3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-D-allose (**18**).



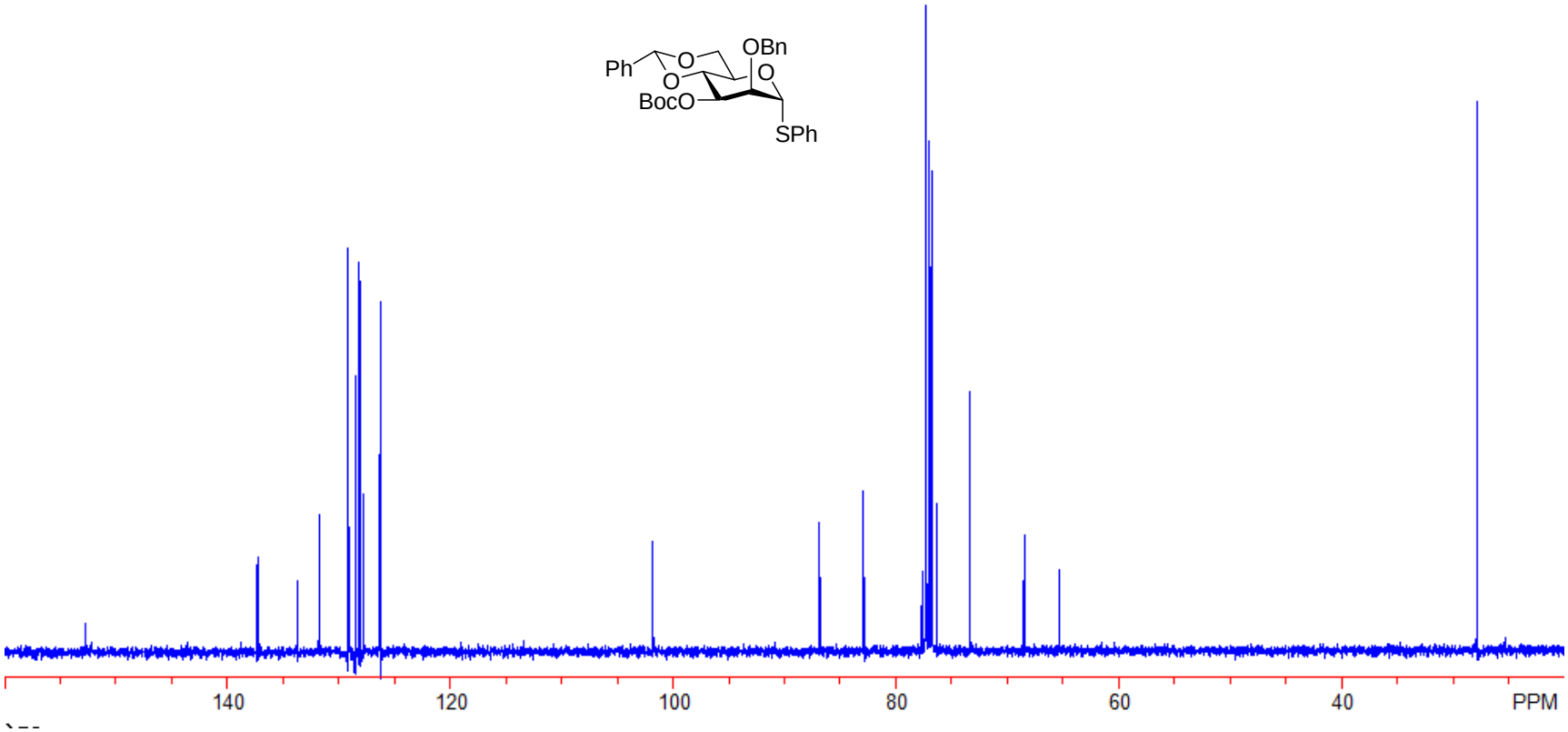
3-*O*-*tert*-butoxycarbonyl-2,4,6-tri-*O*-benzyl-D-allose (**18**).



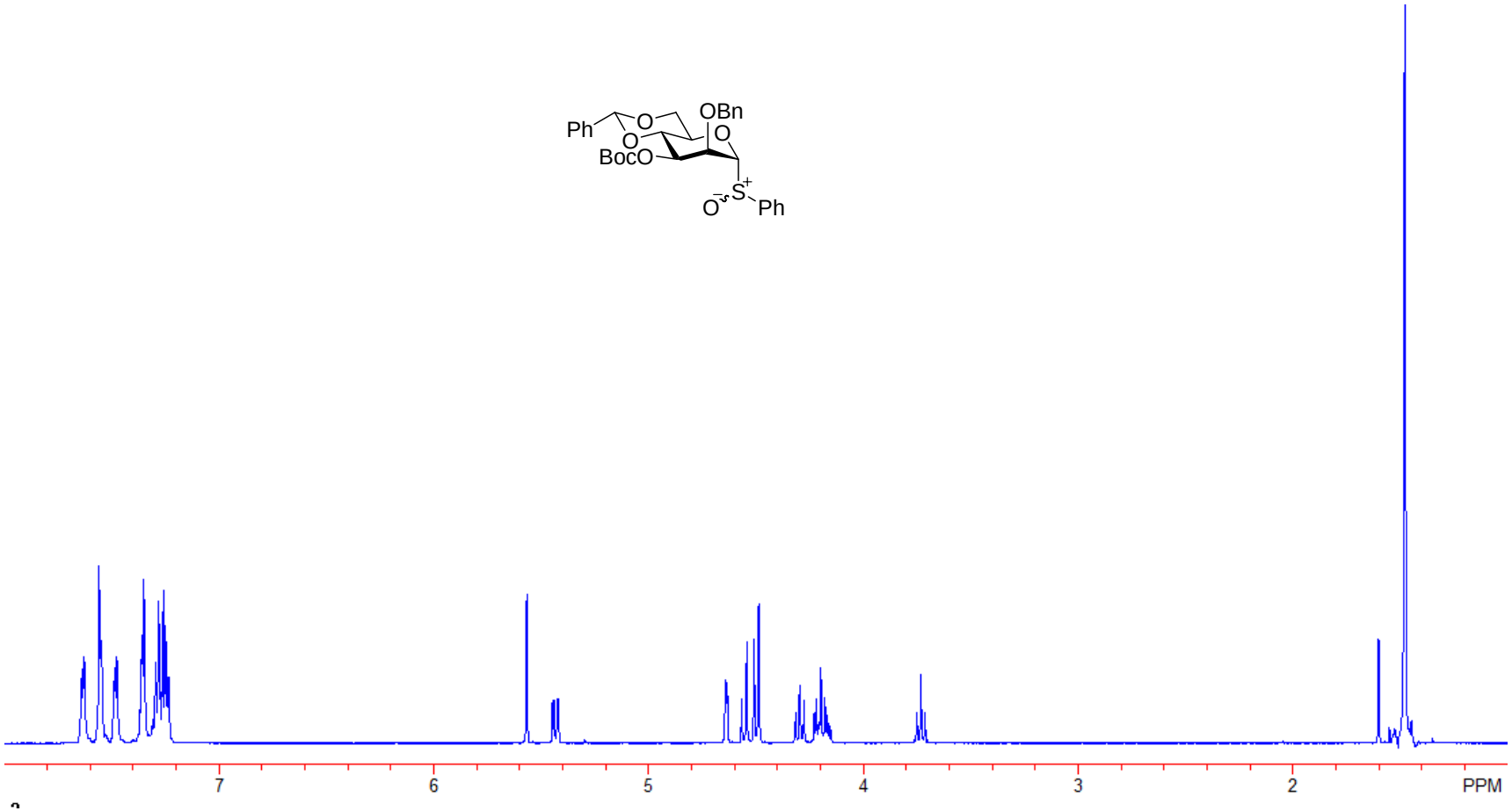
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**21**).



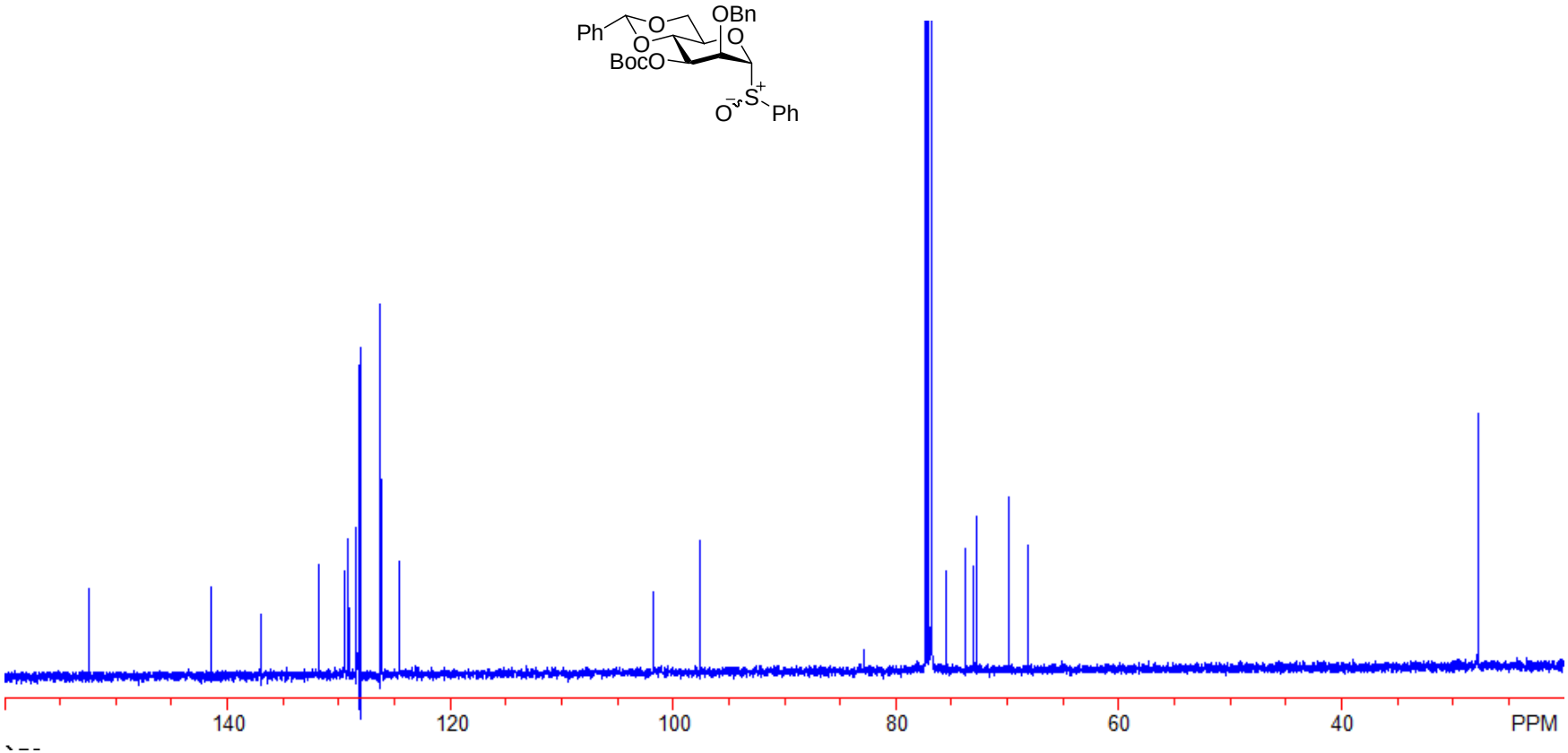
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**21**).



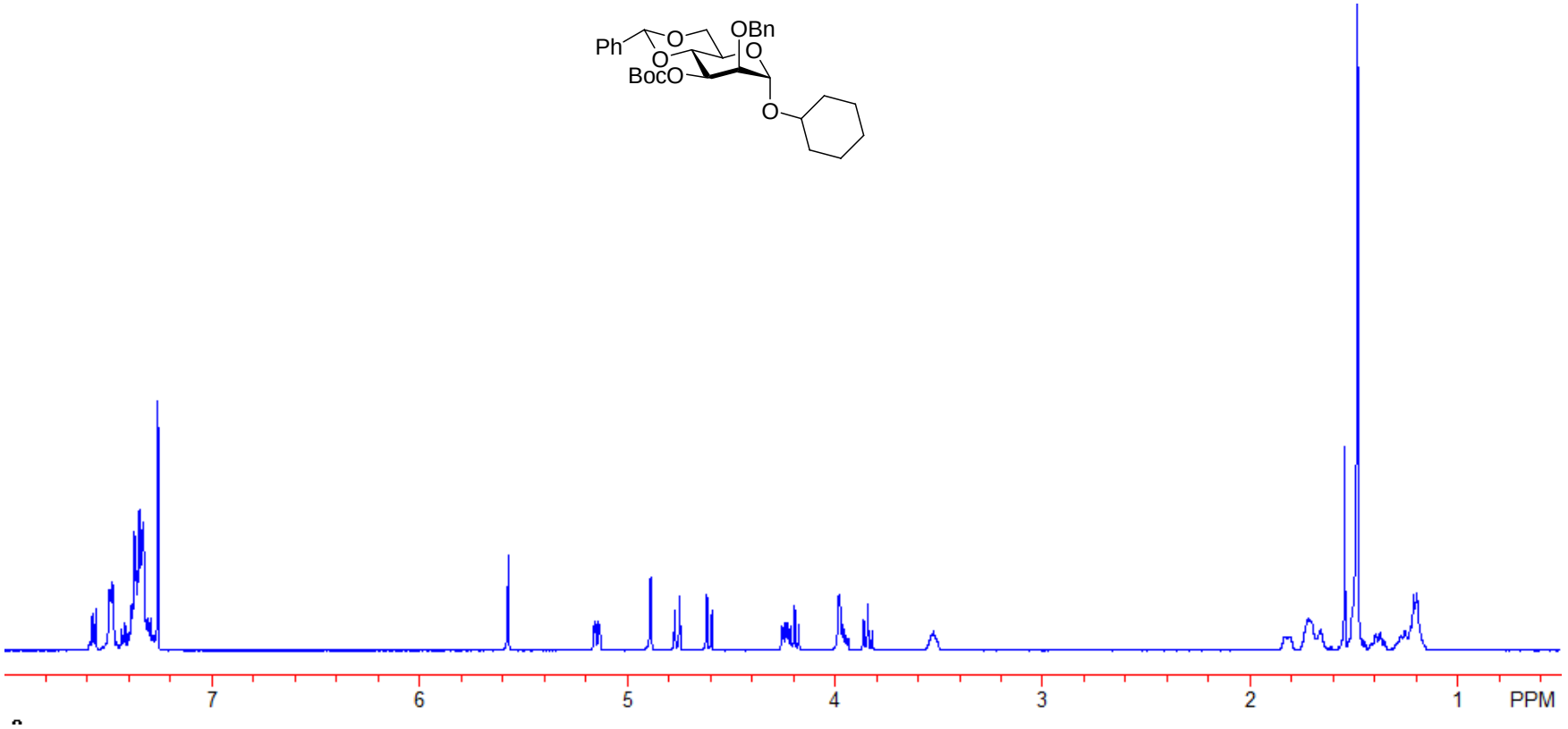
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside *S*-Oxide (**22**).



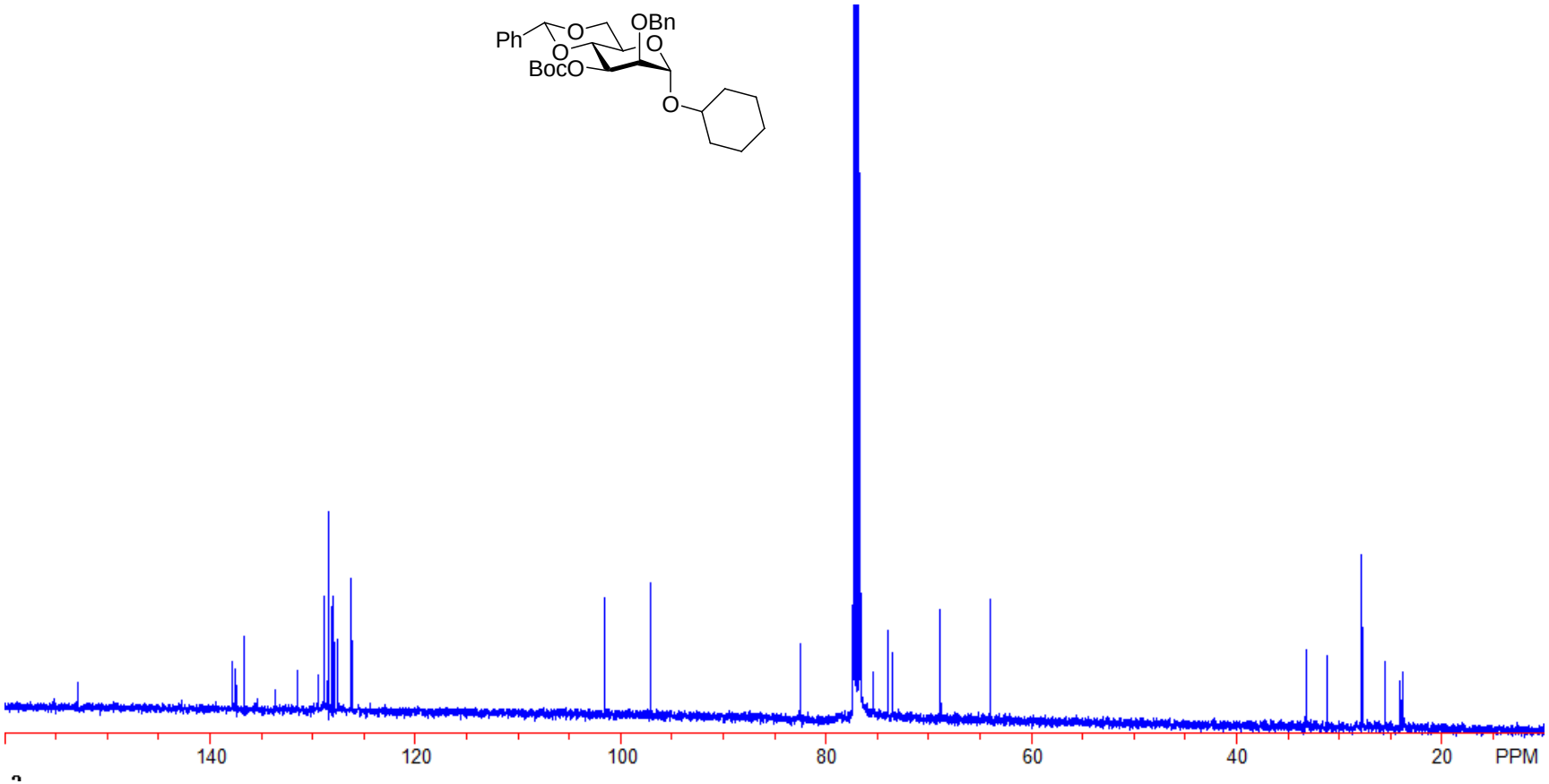
Phenyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside *S*-Oxide (**22**).



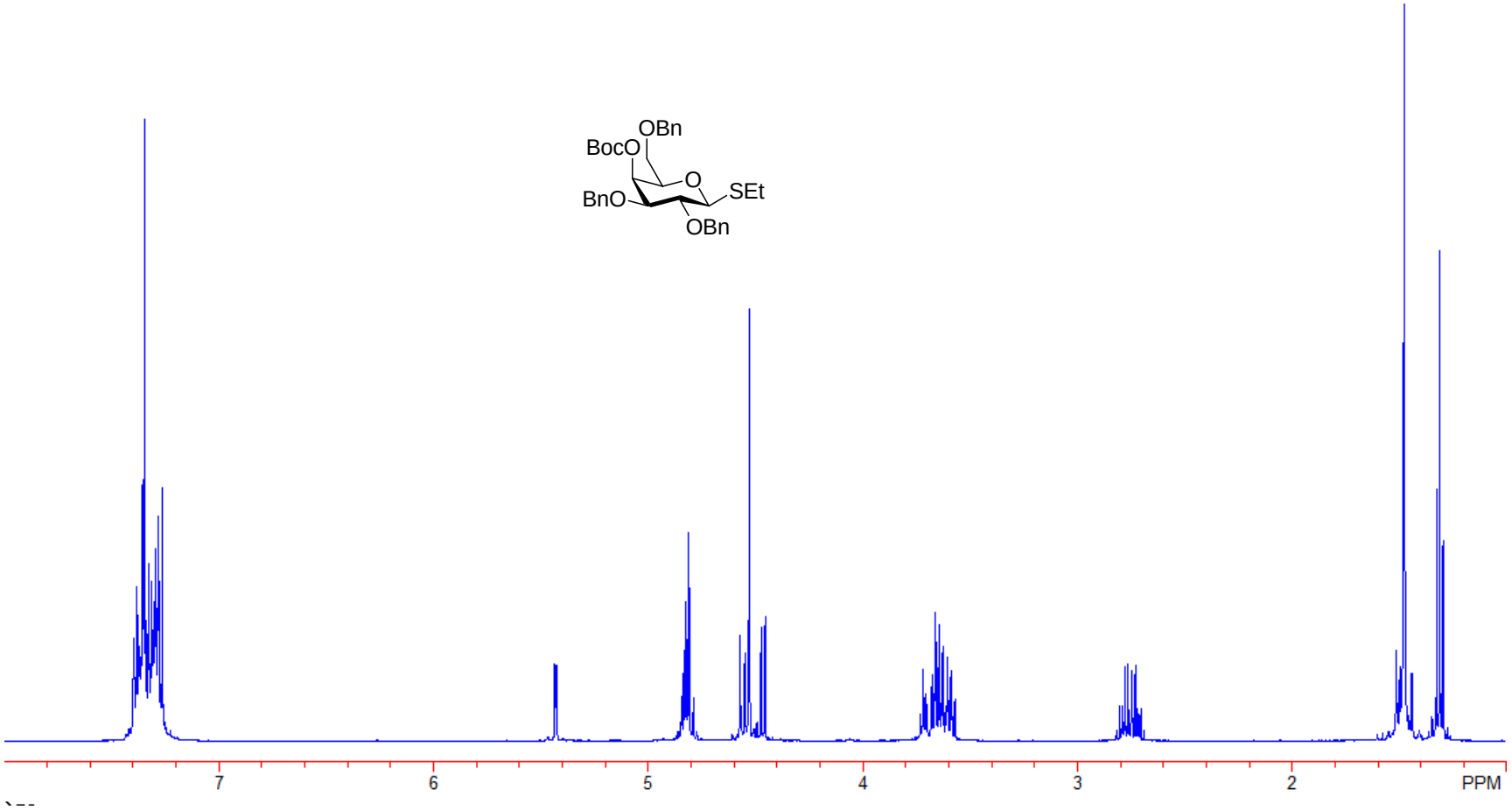
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**23**).



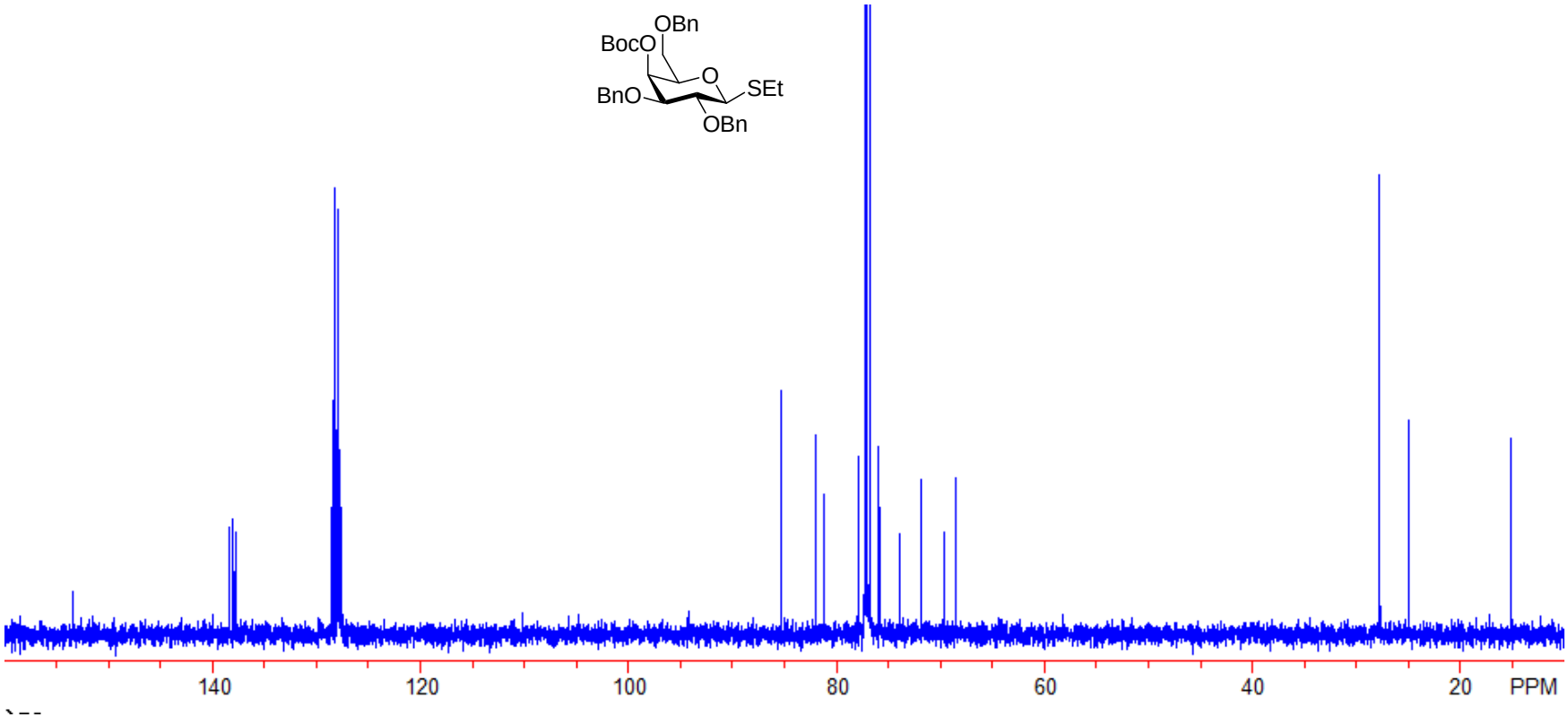
Cyclohexyl 3-*O*-*tert*-butoxycarbonyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**23**).



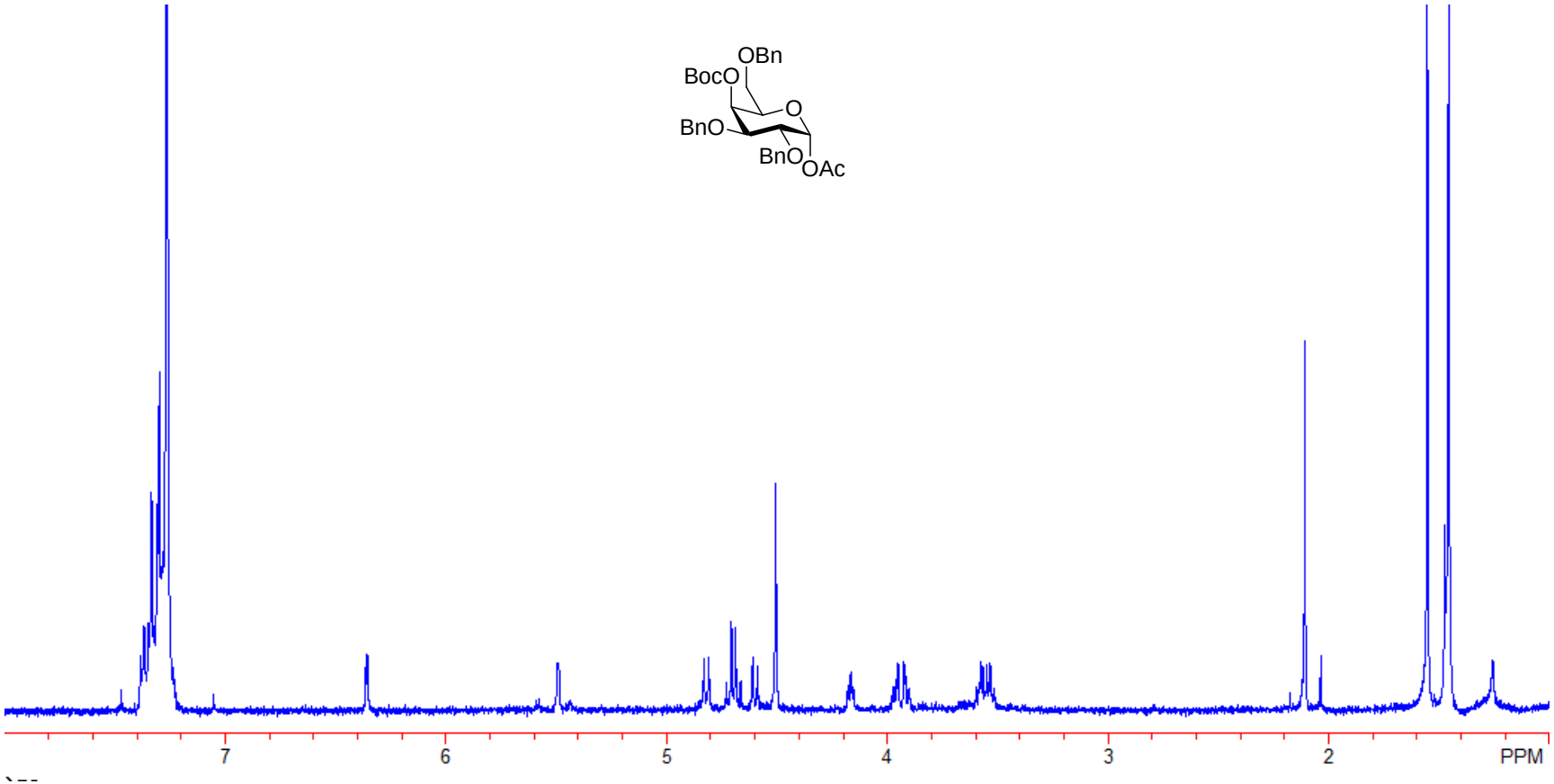
Ethyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (**24**).



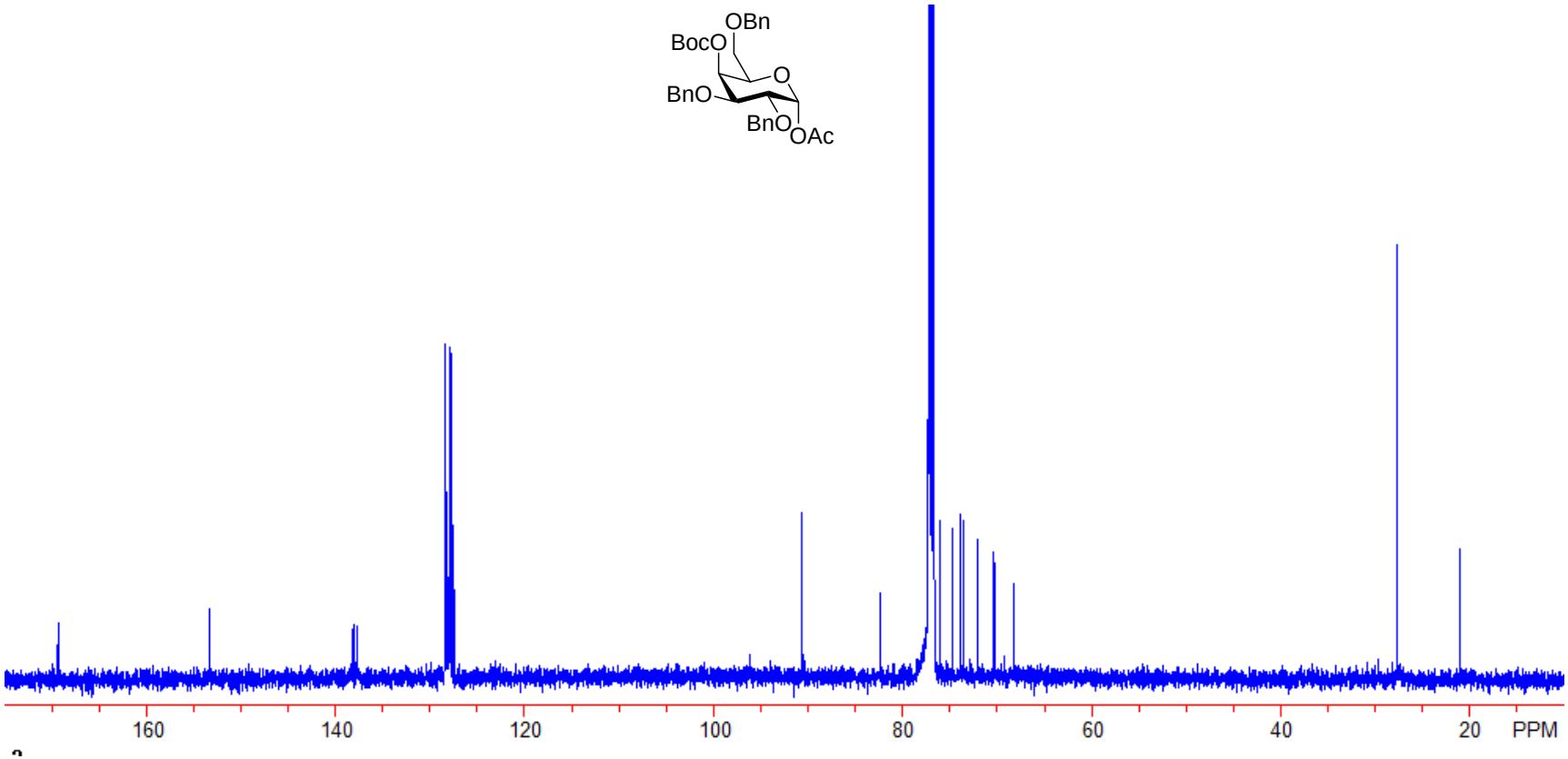
Ethyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (**24**).



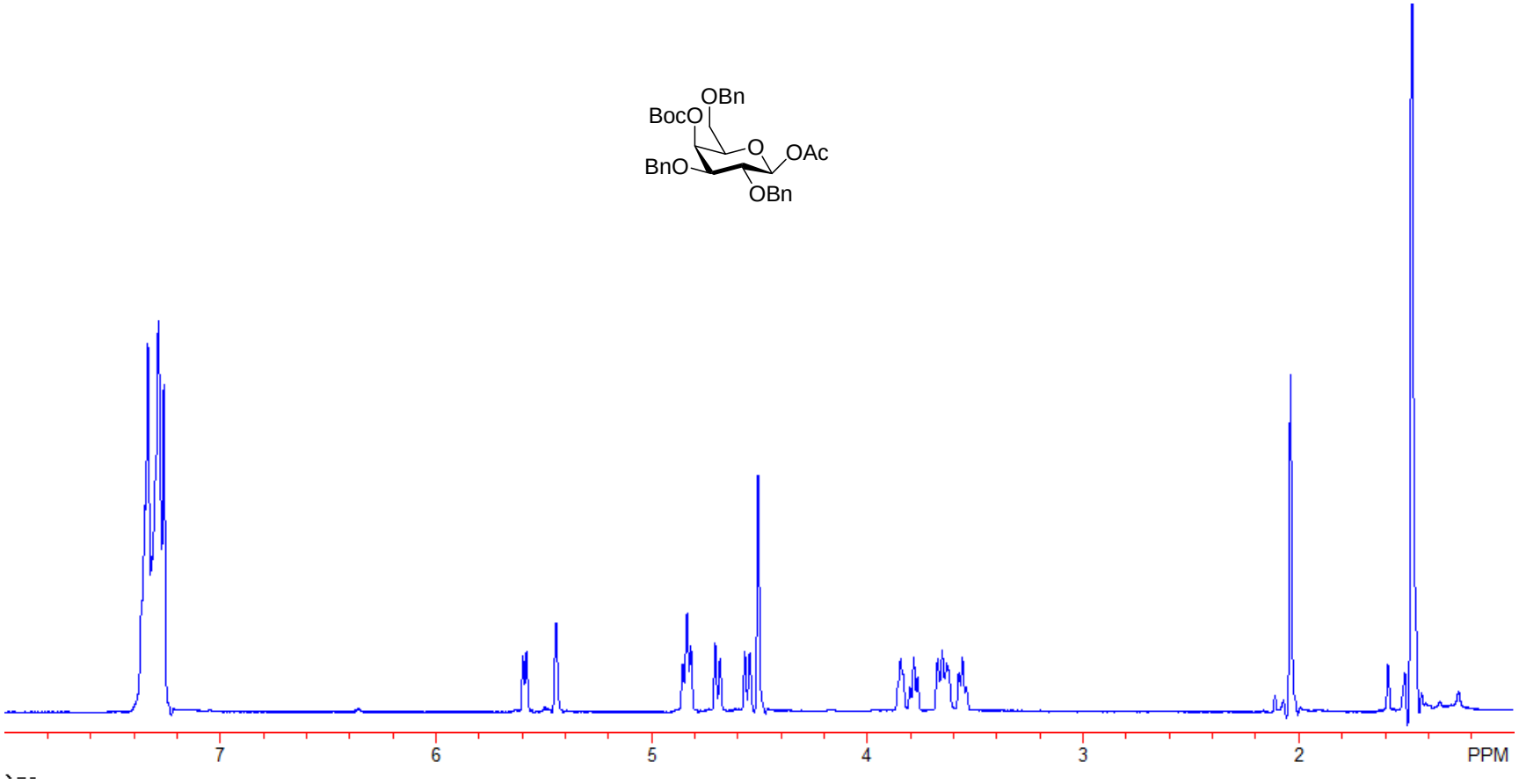
4-*O*-*tert*-Butoxycarbonyl-2,3,6-*O*-tribenzyl-α-D-galactopyranosyl acetate (**25α**).



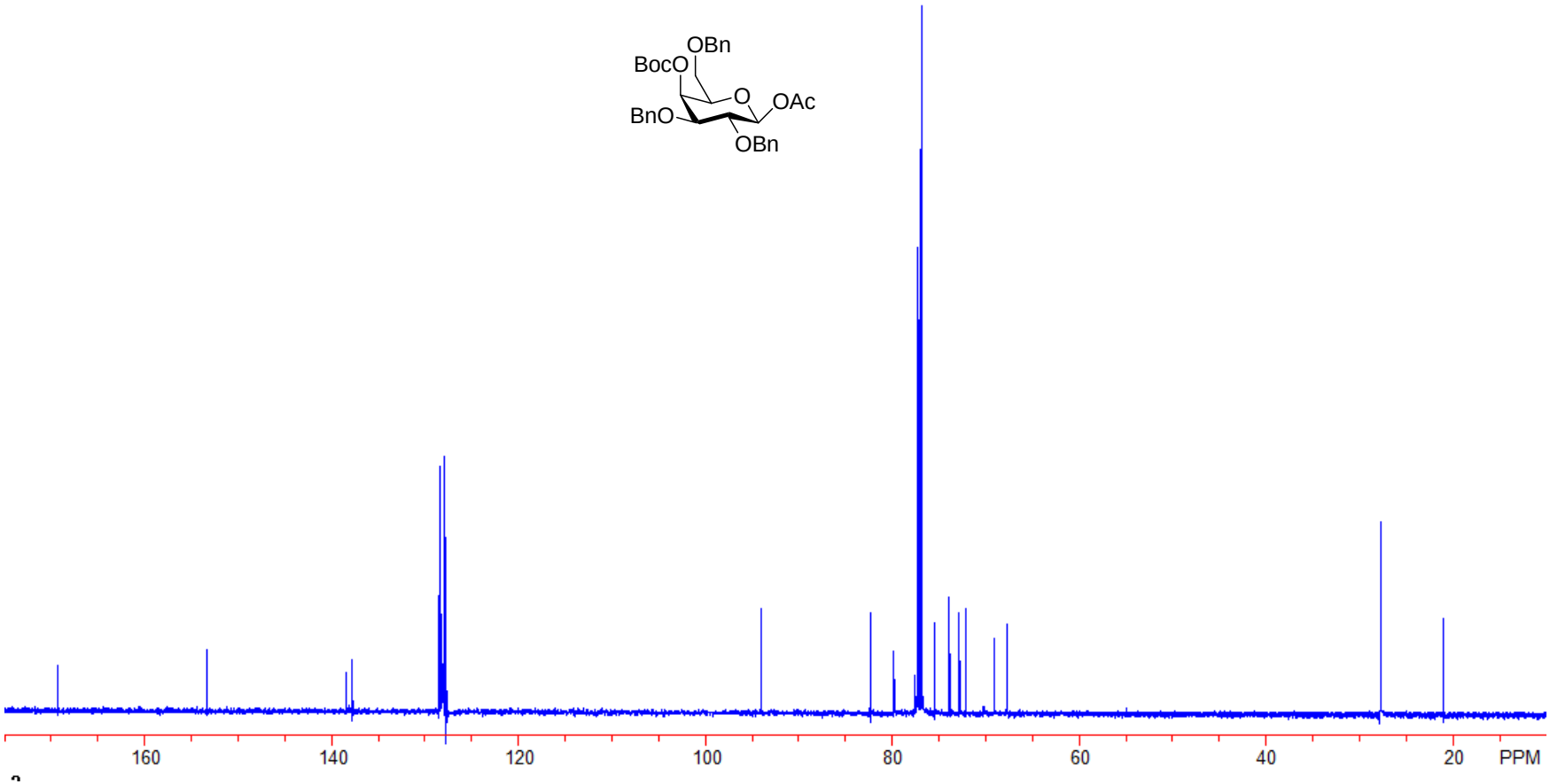
4-*O*-*tert*-Butoxycarbonyl-2,3,6-*O*-tribenzyl-α-D-galactopyranosyl acetate (**25α**).



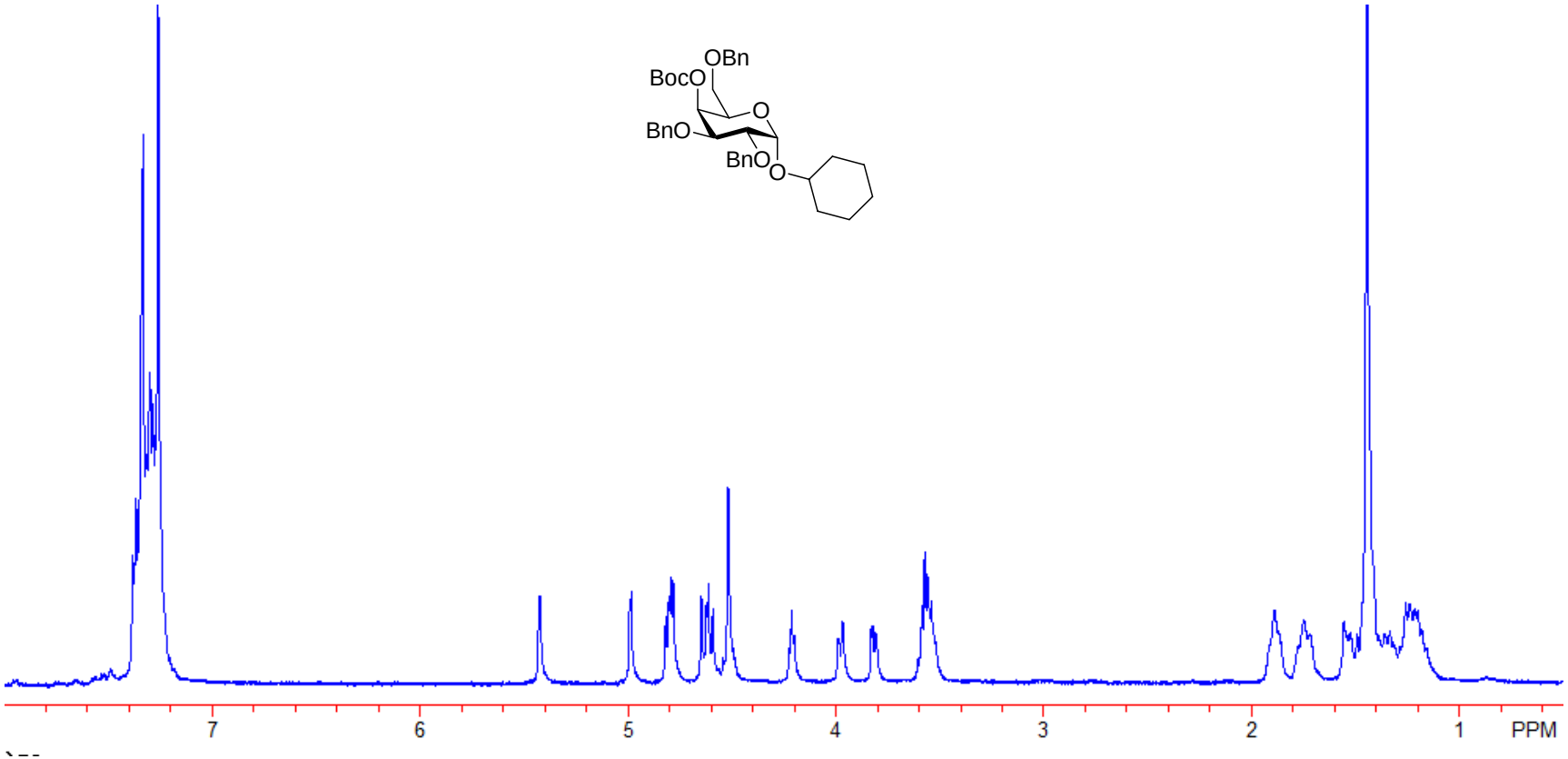
4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-β-D-galactopyranosyl acetate (**25β**).



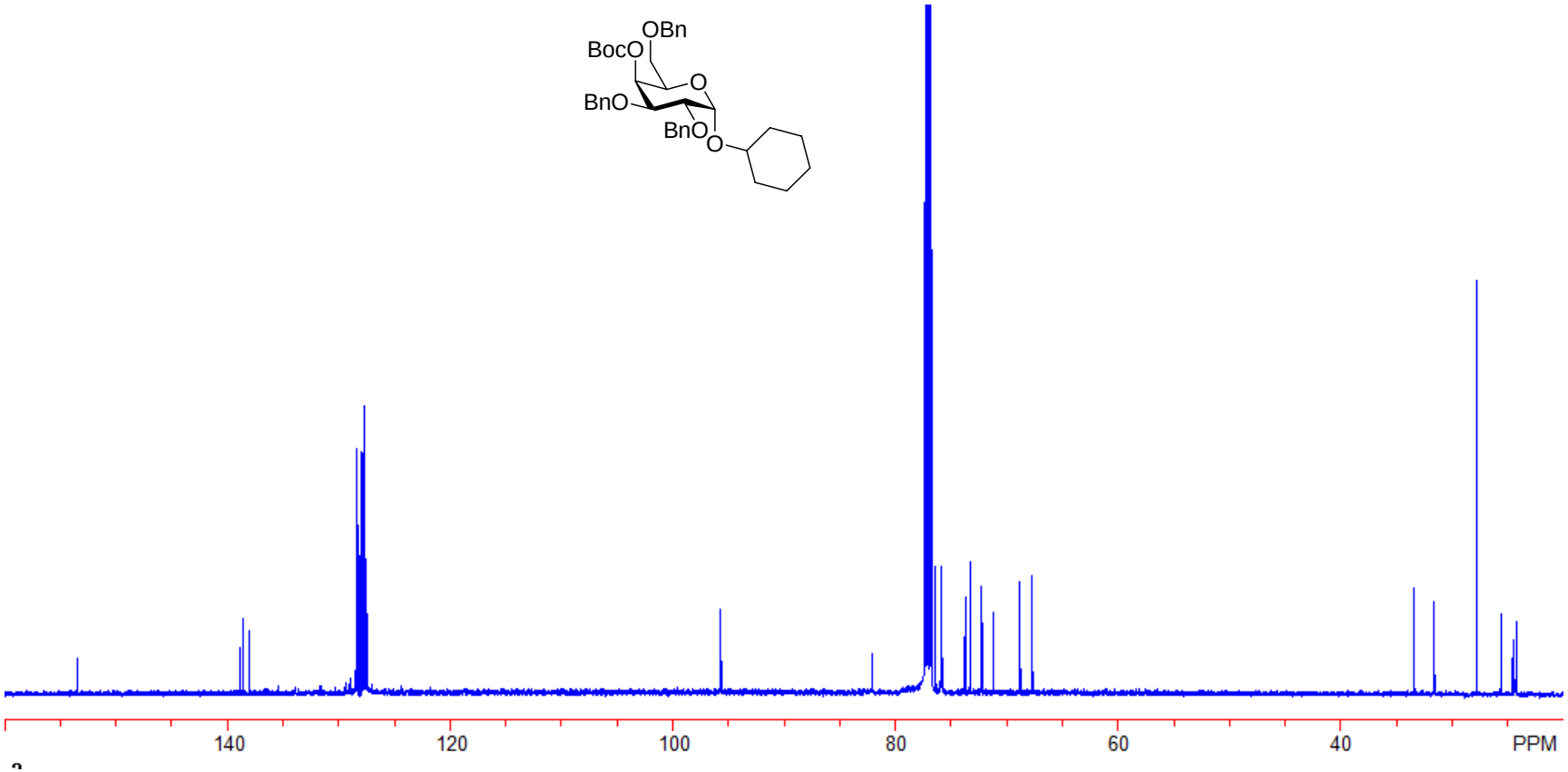
4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-β-D-galactopyranosyl acetate (**25β**).



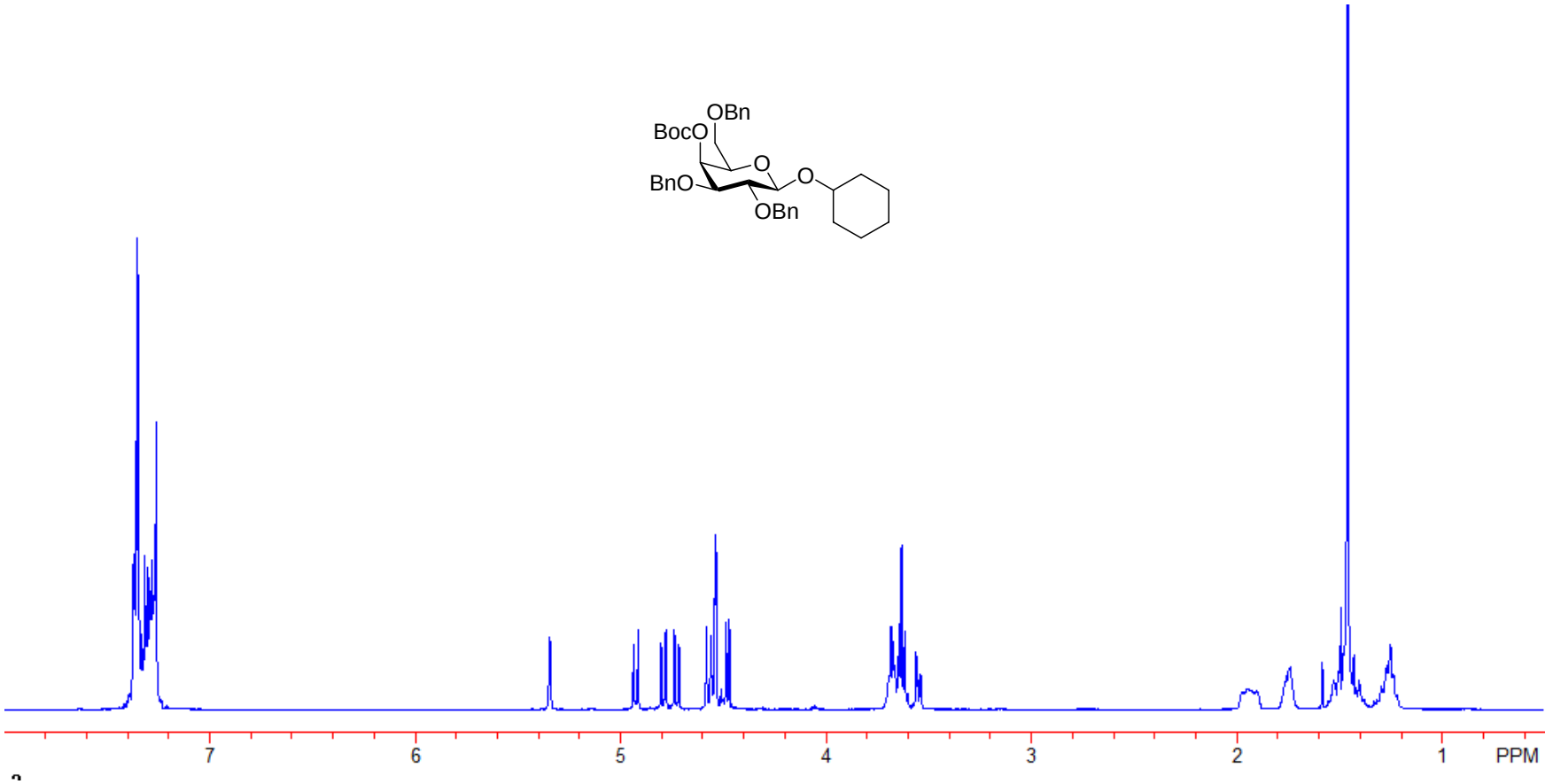
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-D-galactopyranoside (**26α**).



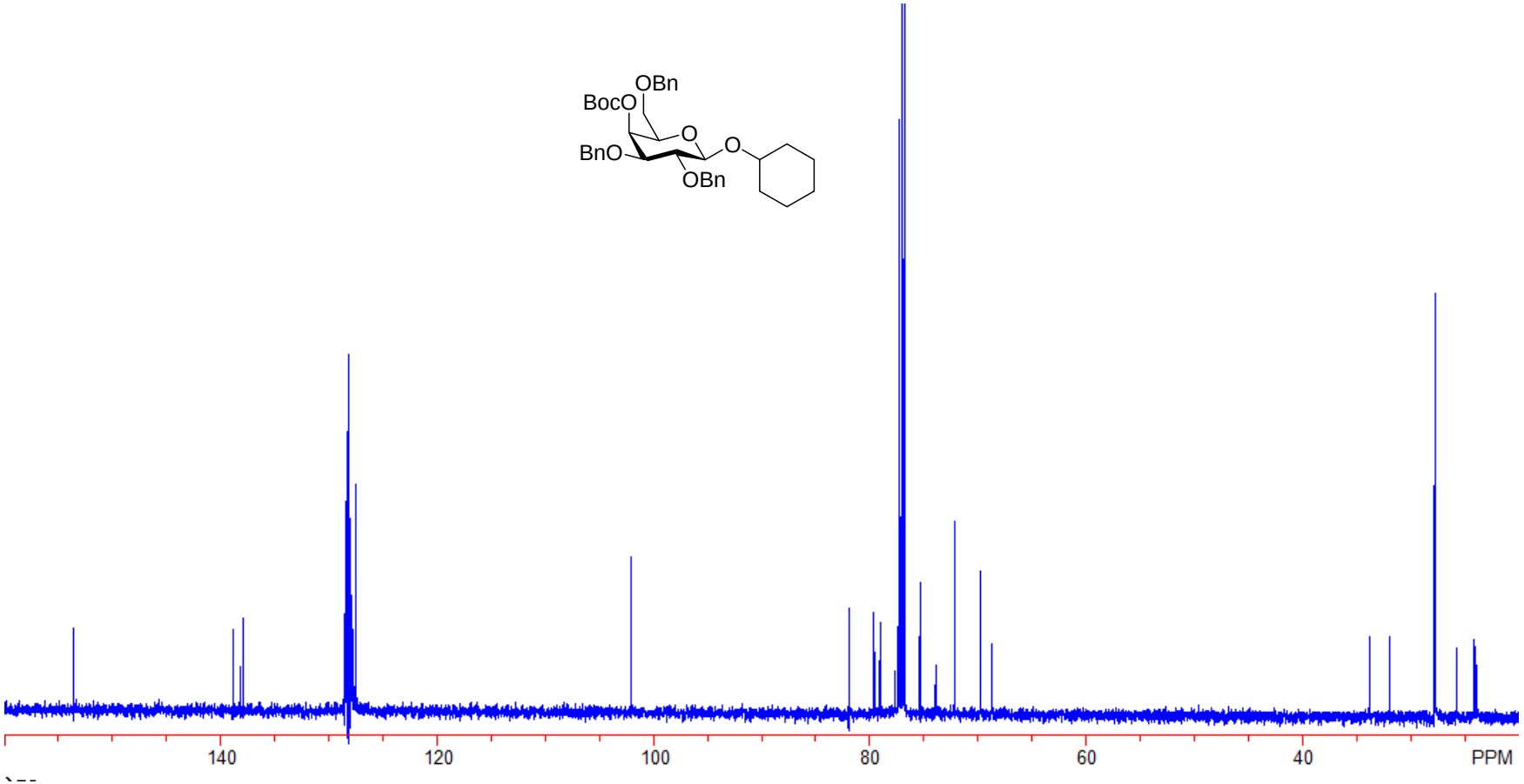
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-D-galactopyranoside (**26α**).



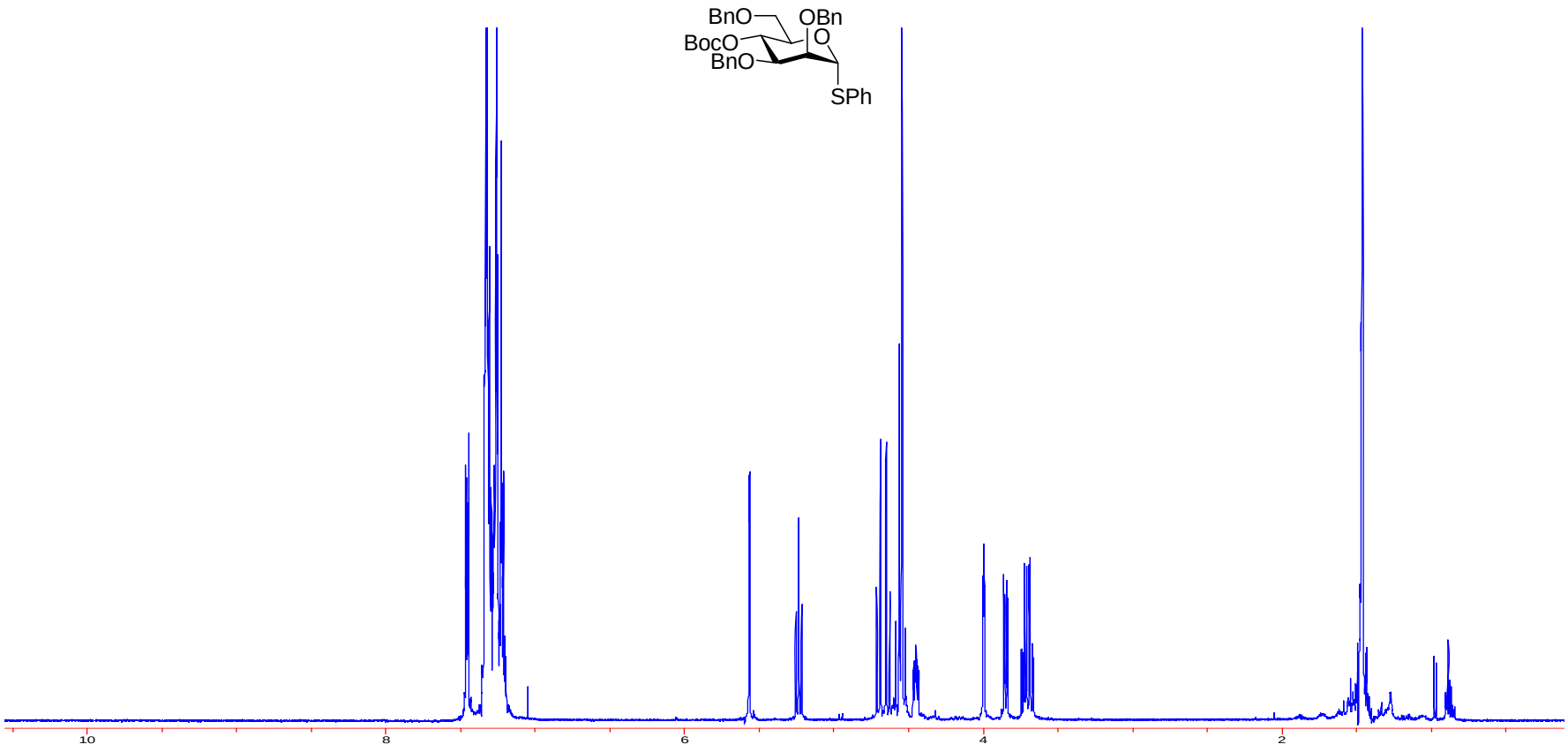
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-β-D-galactopyranoside (**26β**).



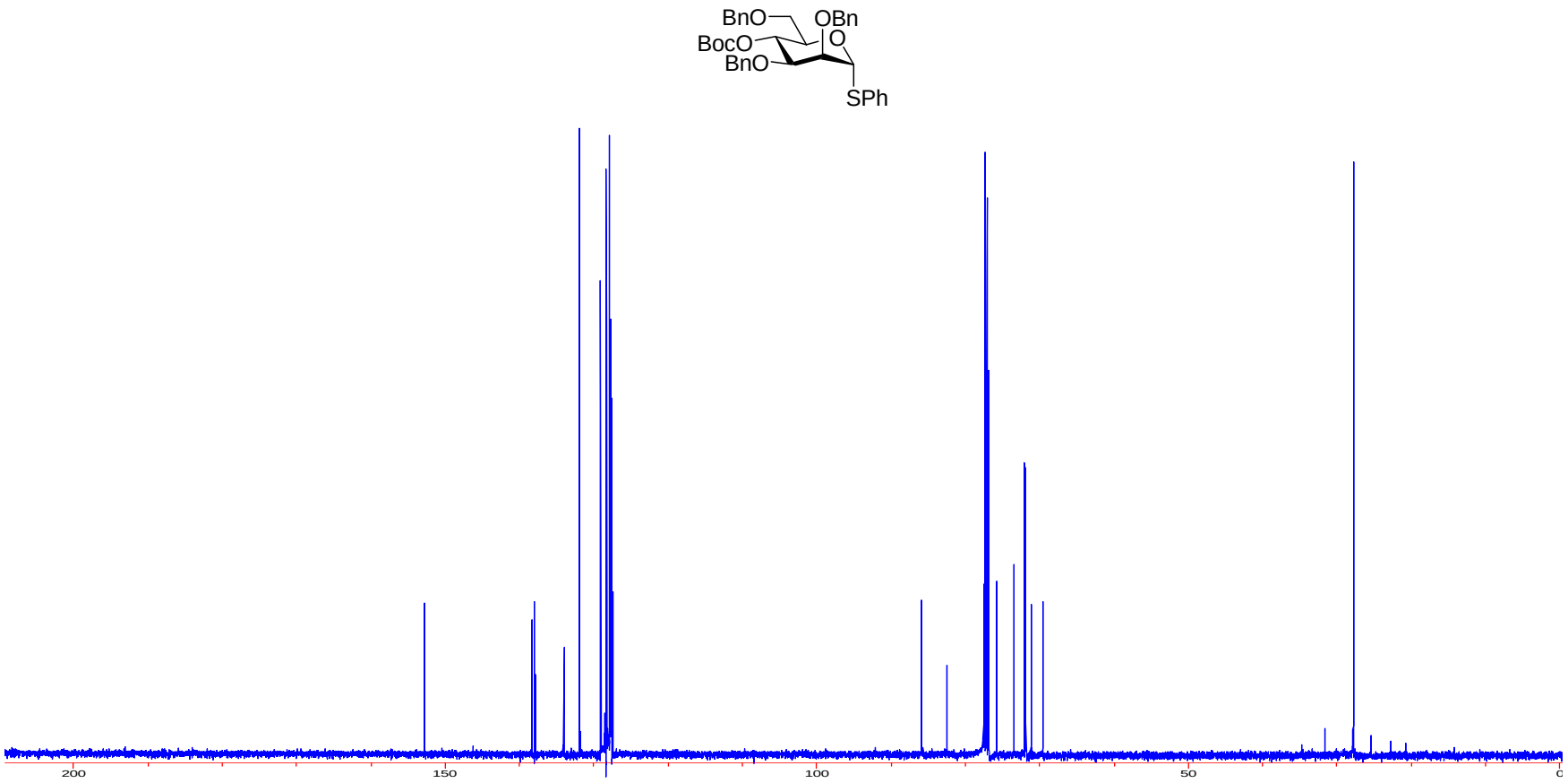
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-2,3,6-*O*-benzyl-β-D-galactopyranoside (**26β**).



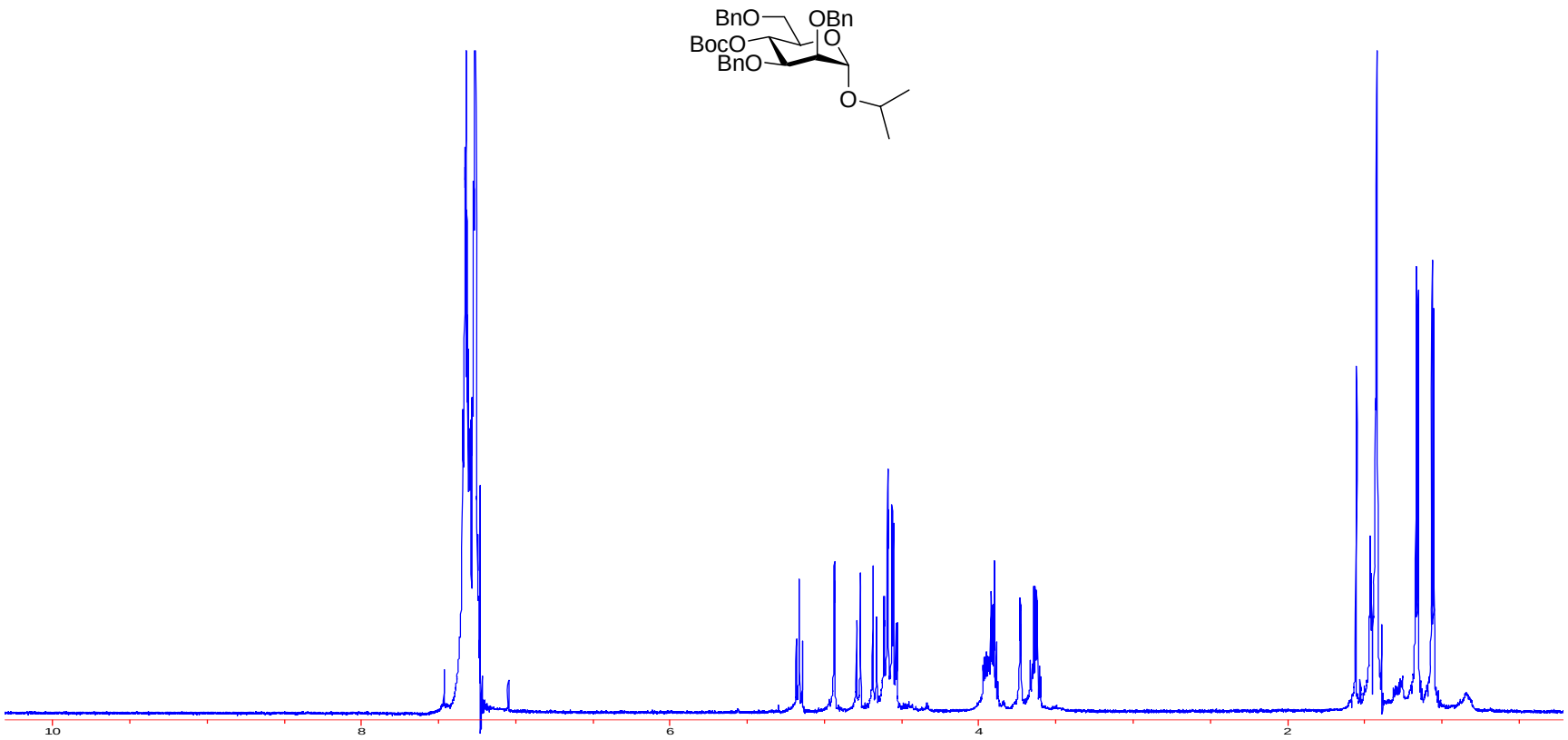
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl-1-thio-*α*-D-mannopyranoside (**27**)



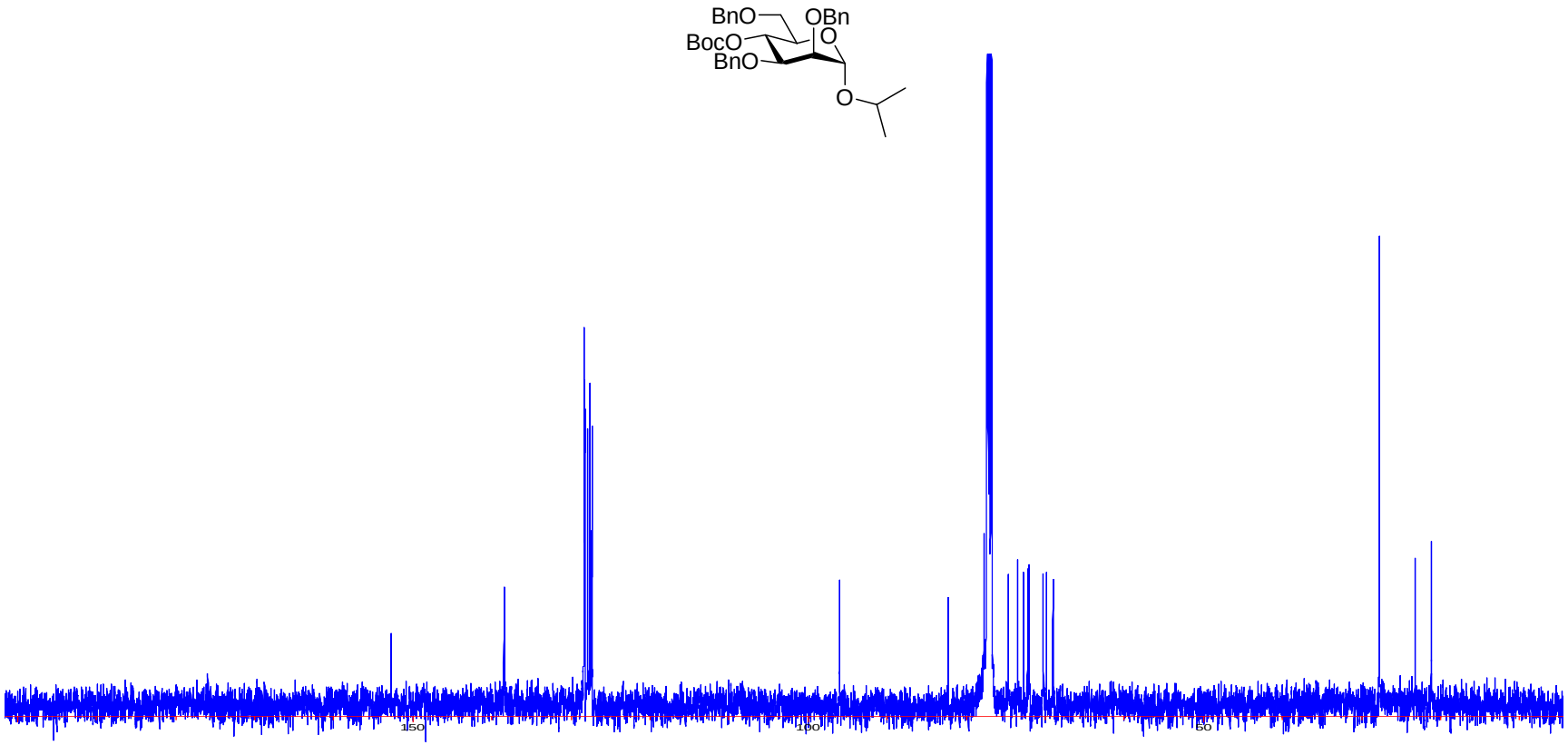
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-*tert*-butyloxycarbonyl-1-thio-*α*-D-mannopyranoside (**27**)



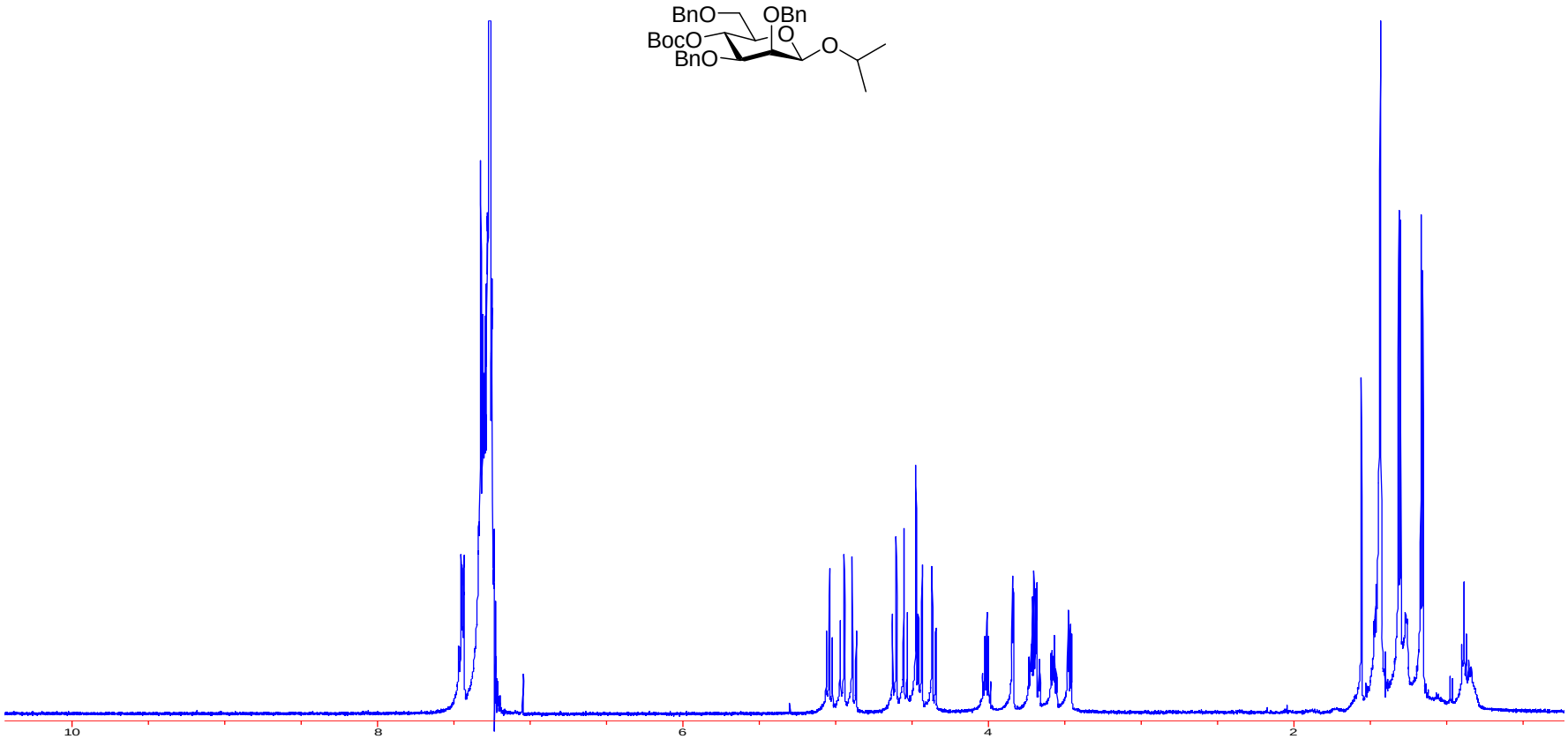
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*- *tert*-butyloxycarbonyl-*α*-D-mannopyranoside (**28α**)



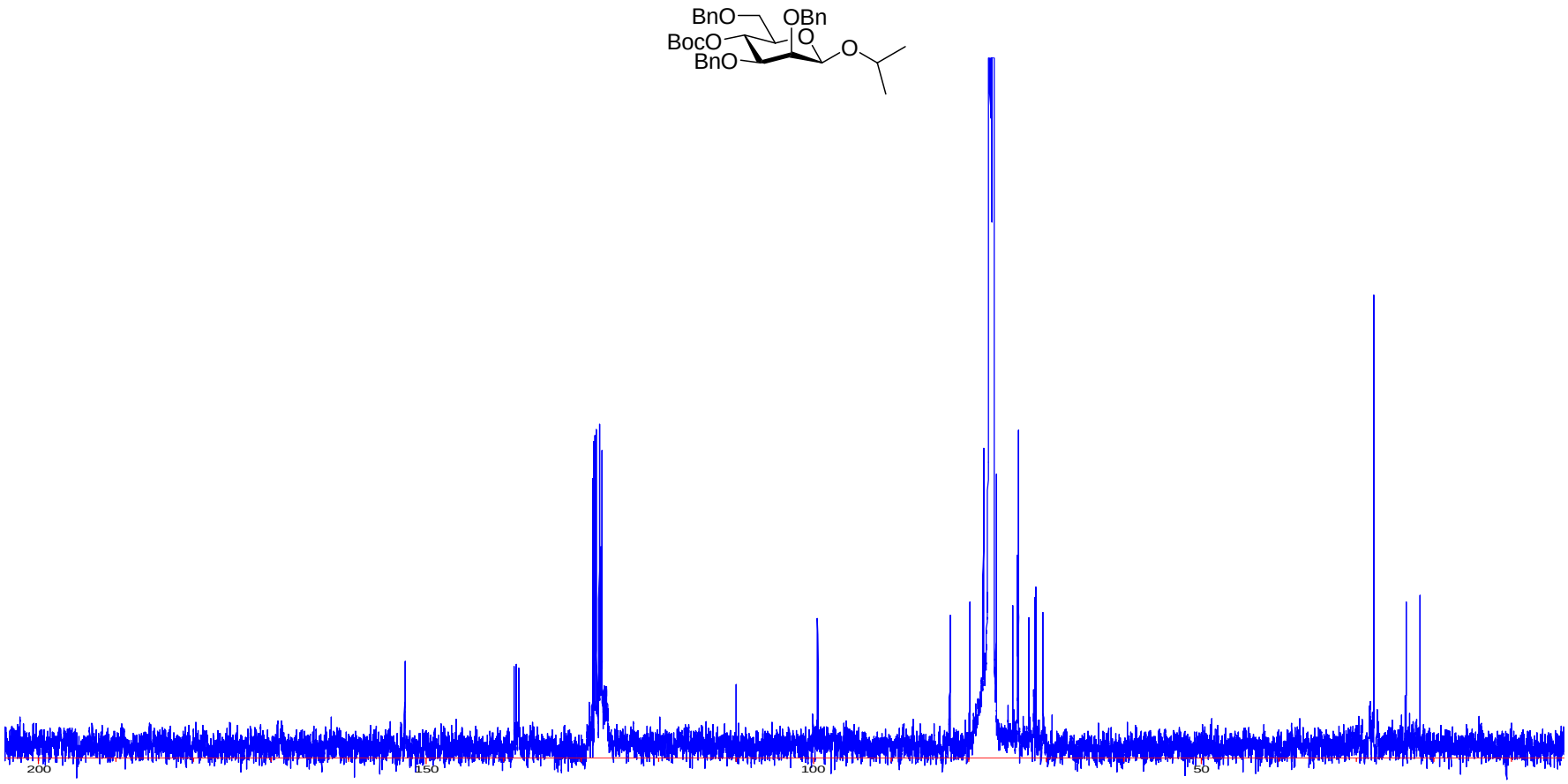
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*- *tert*-butyloxycarbonyl-*α*-D-mannopyranoside (**28α**)



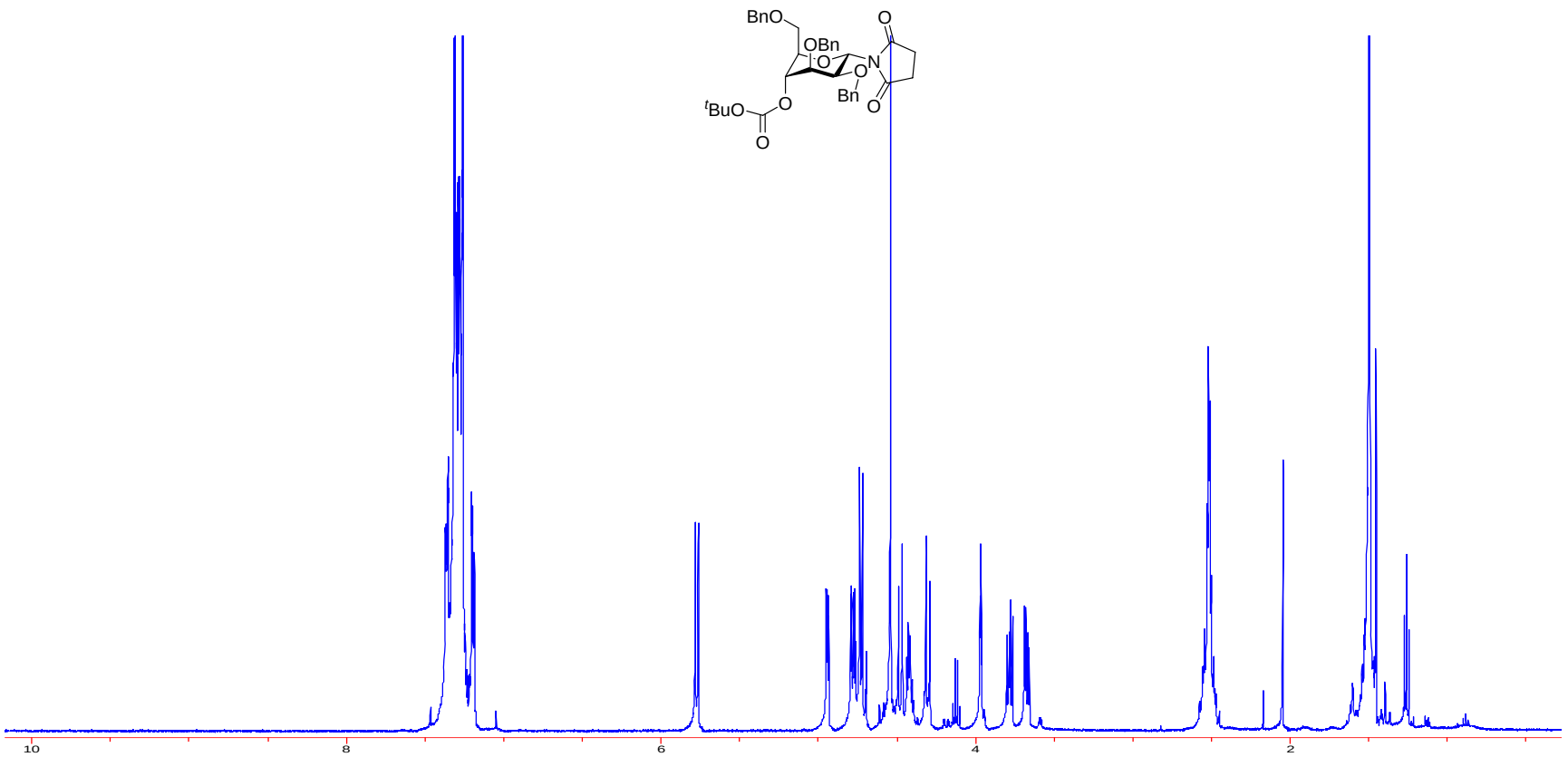
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*- *tert*-butyloxycarbonyl-*β*-D-mannopyranoside (**28β**)



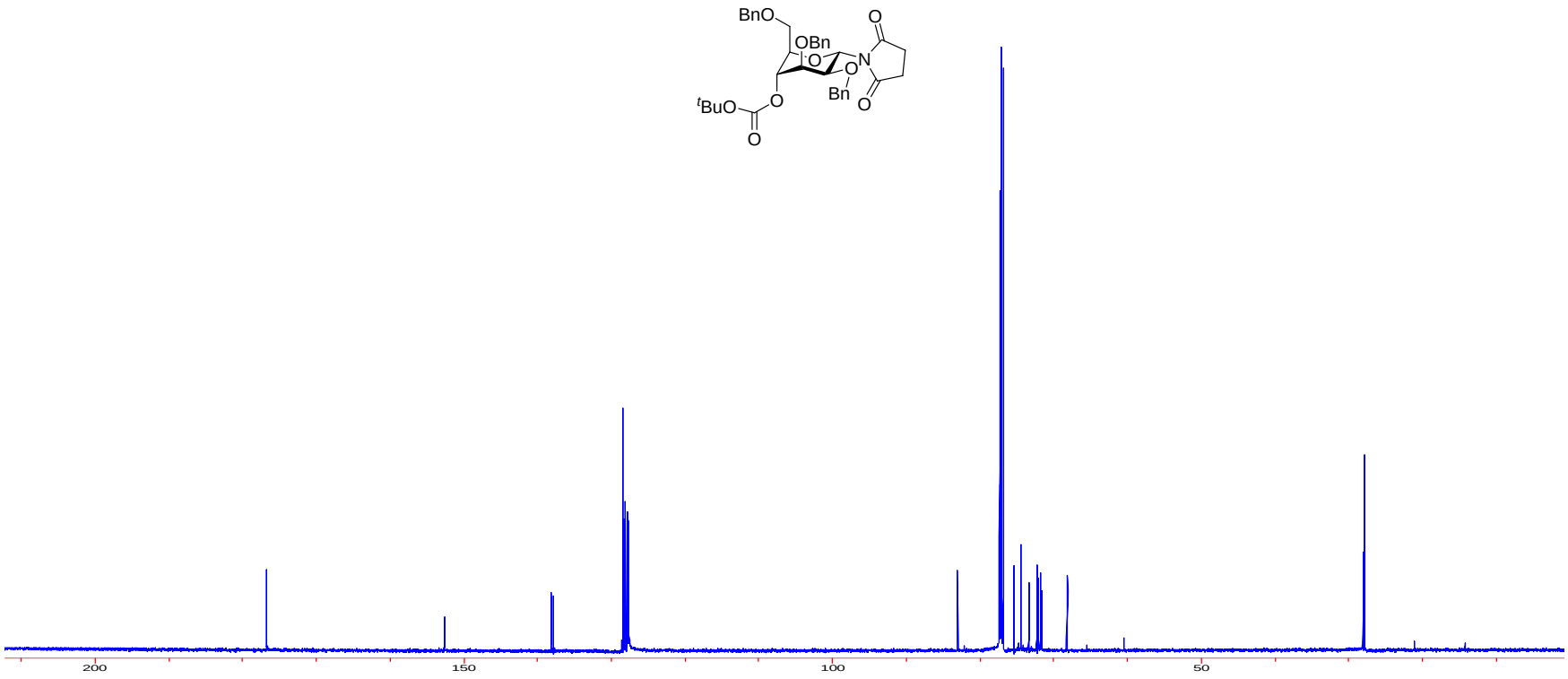
Isopropyl 2,3,6-tri-*O*-benzyl-4-*O*- *tert*-butyloxycarbonyl-*β*-D-mannopyranoside (**28β**)



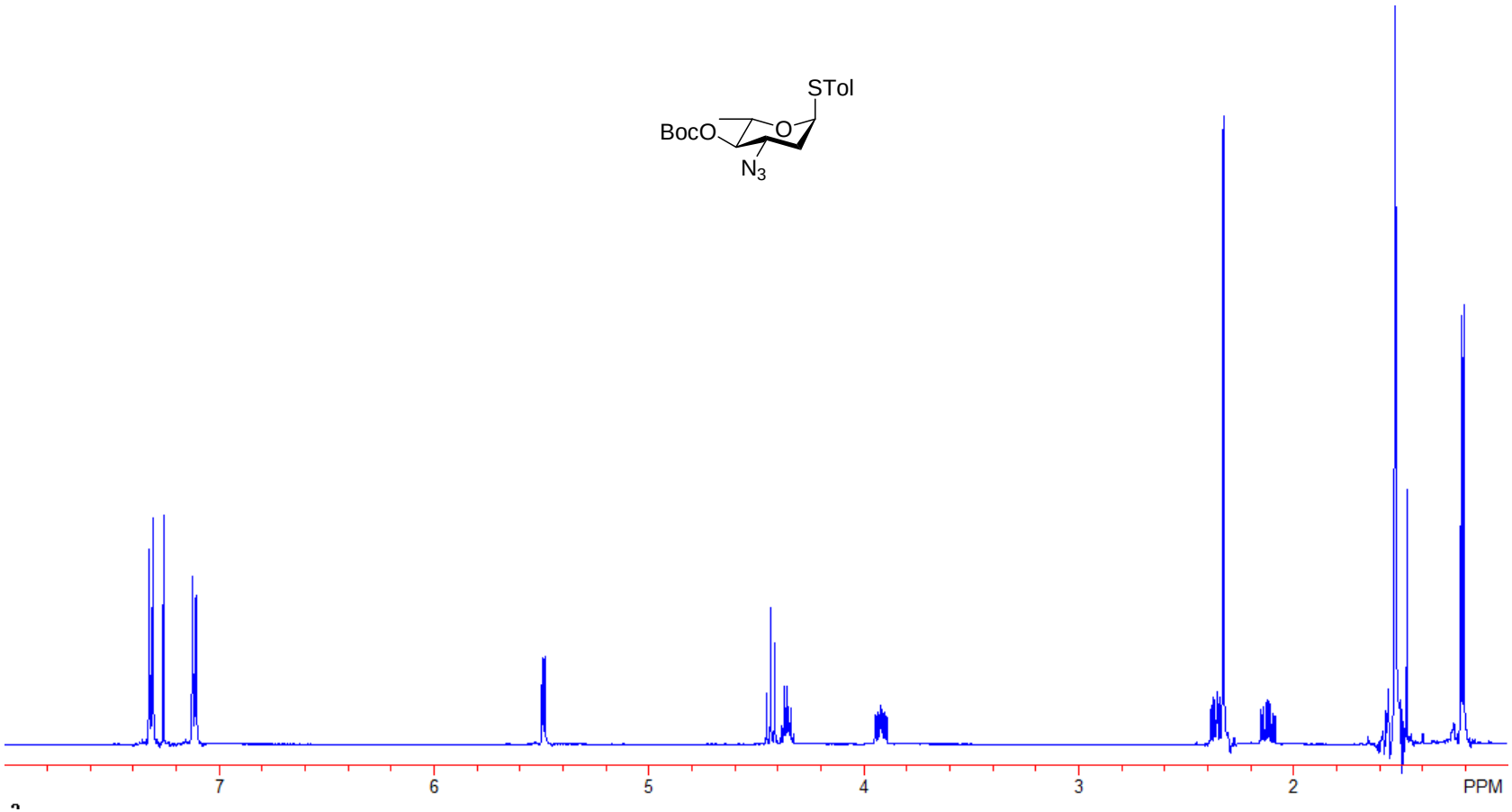
N-(2’,3’,6’-tri-*O*-benzyl-4’-*O*-*tert*-butyloxycarbonyl-*α*-D-mannopyranosyl)- succinimide (**29**).



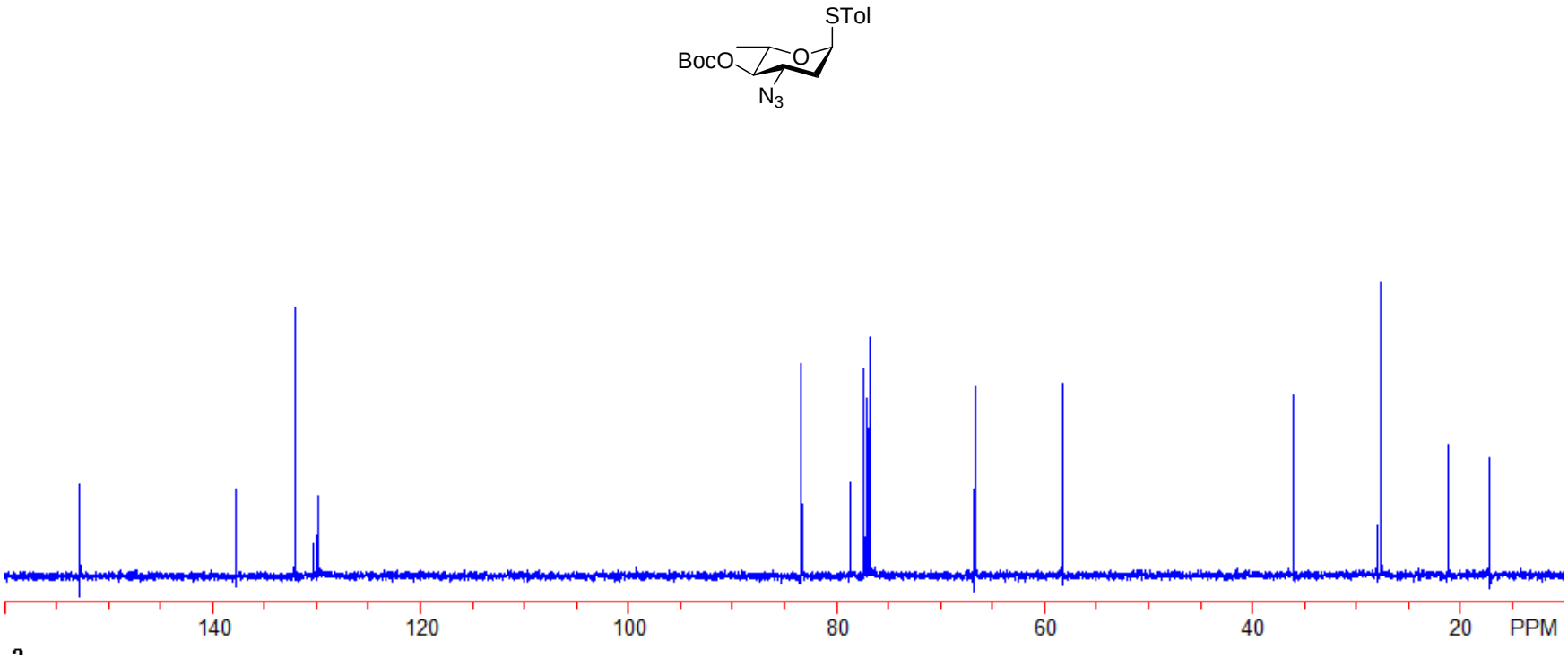
N-(2’,3’,6’-tri-*O*-benzyl-4’-*O*-*tert*-butyloxycarbonyl-*α*-D-mannopyranosyl)- succinimide (**29**).



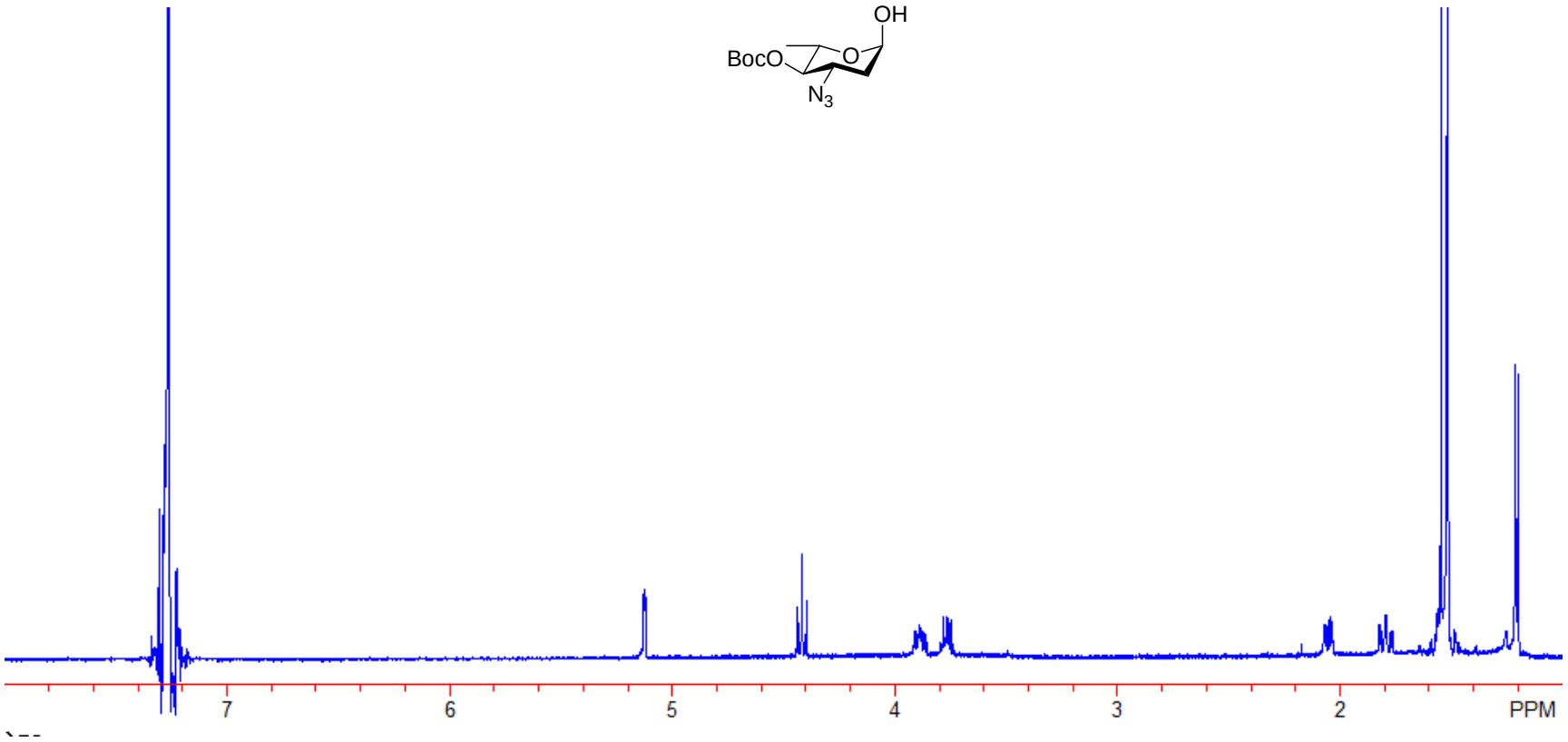
p-Tolyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-thio-α-L-*lyxo*-hexopyranoside (**30**).



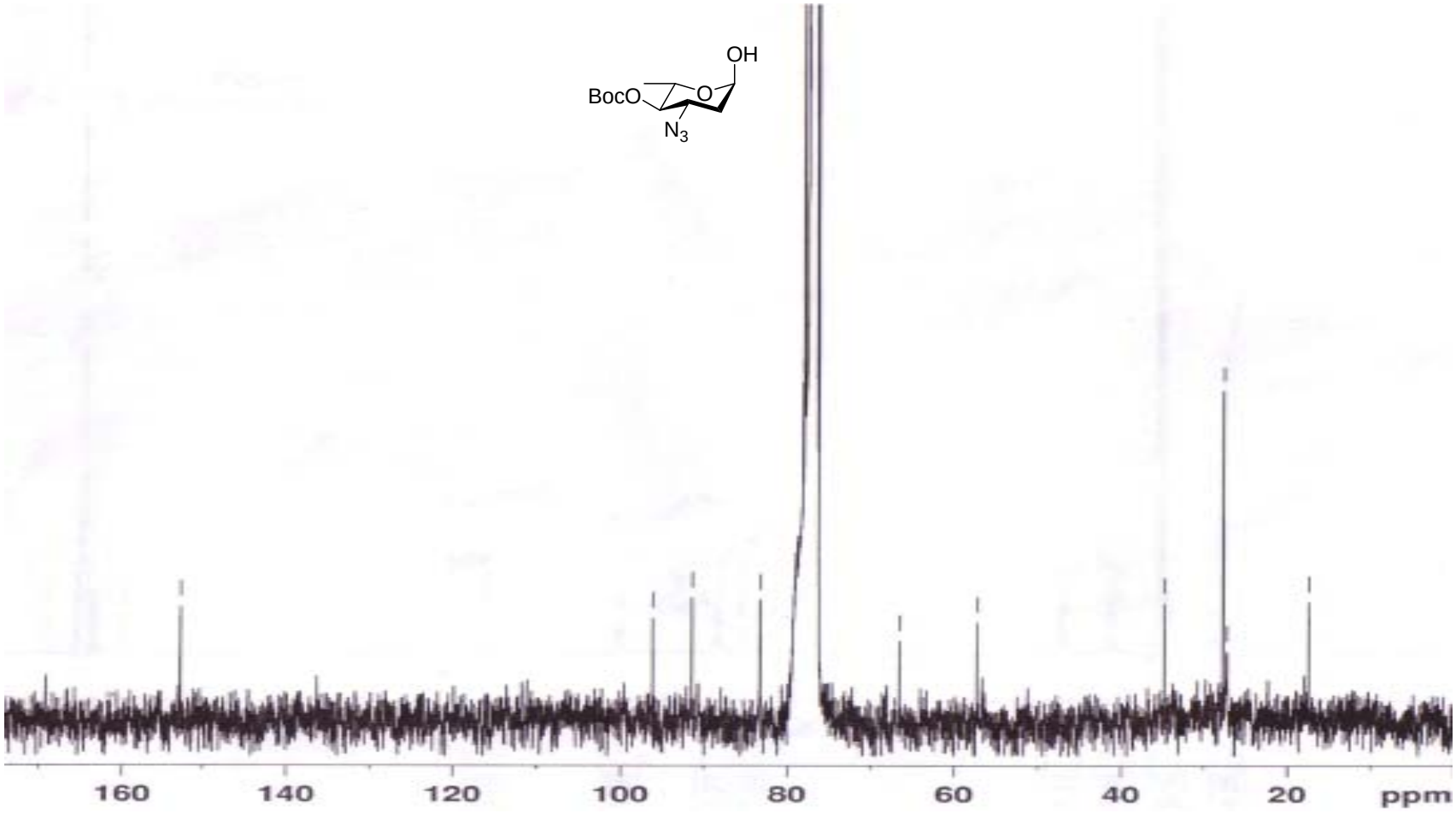
p-Tolyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-thio-α-L-*lyxo*-hexopyranoside (**30**).



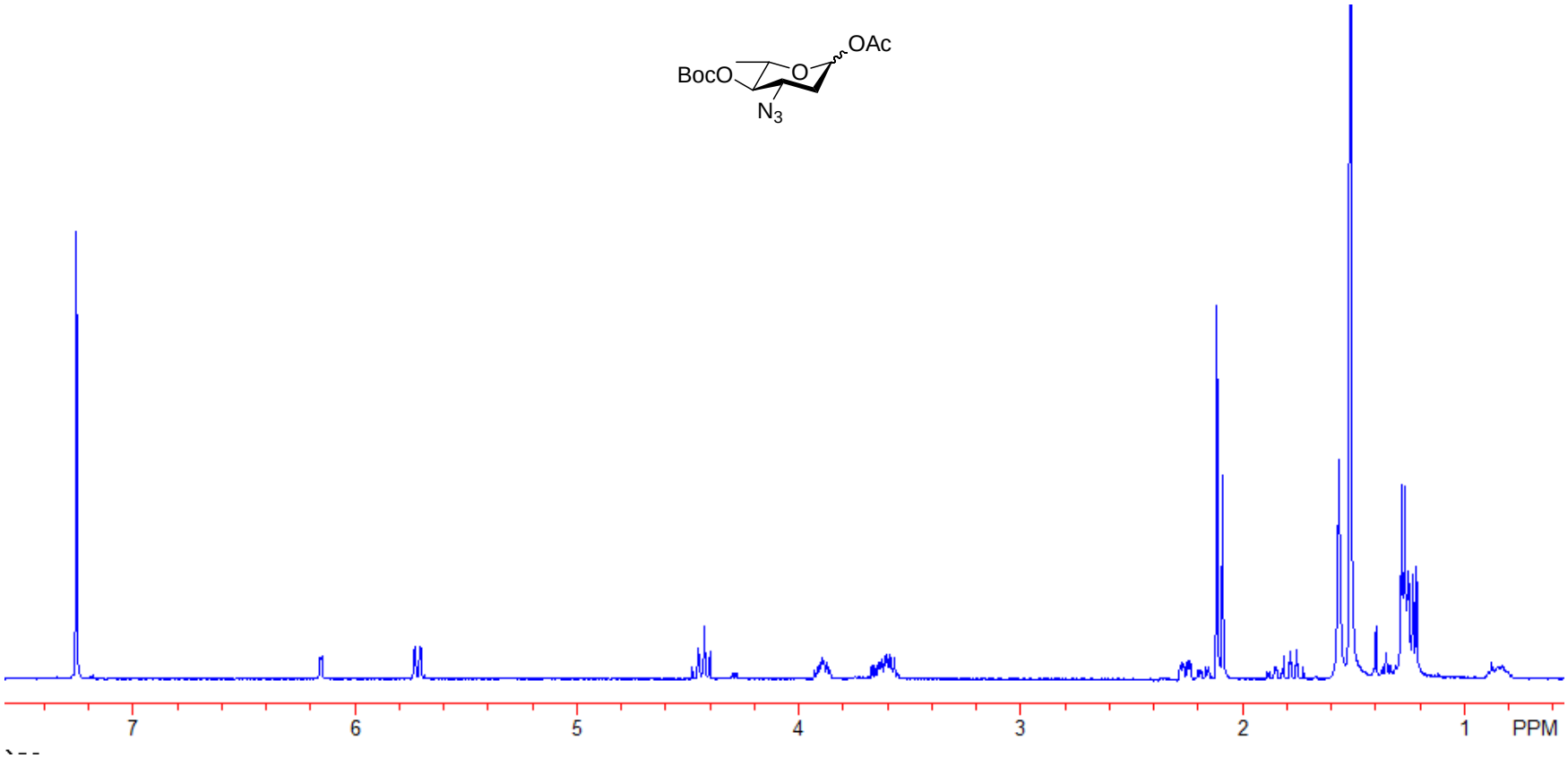
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-α-L-*lyxo*-hexopyranoside.



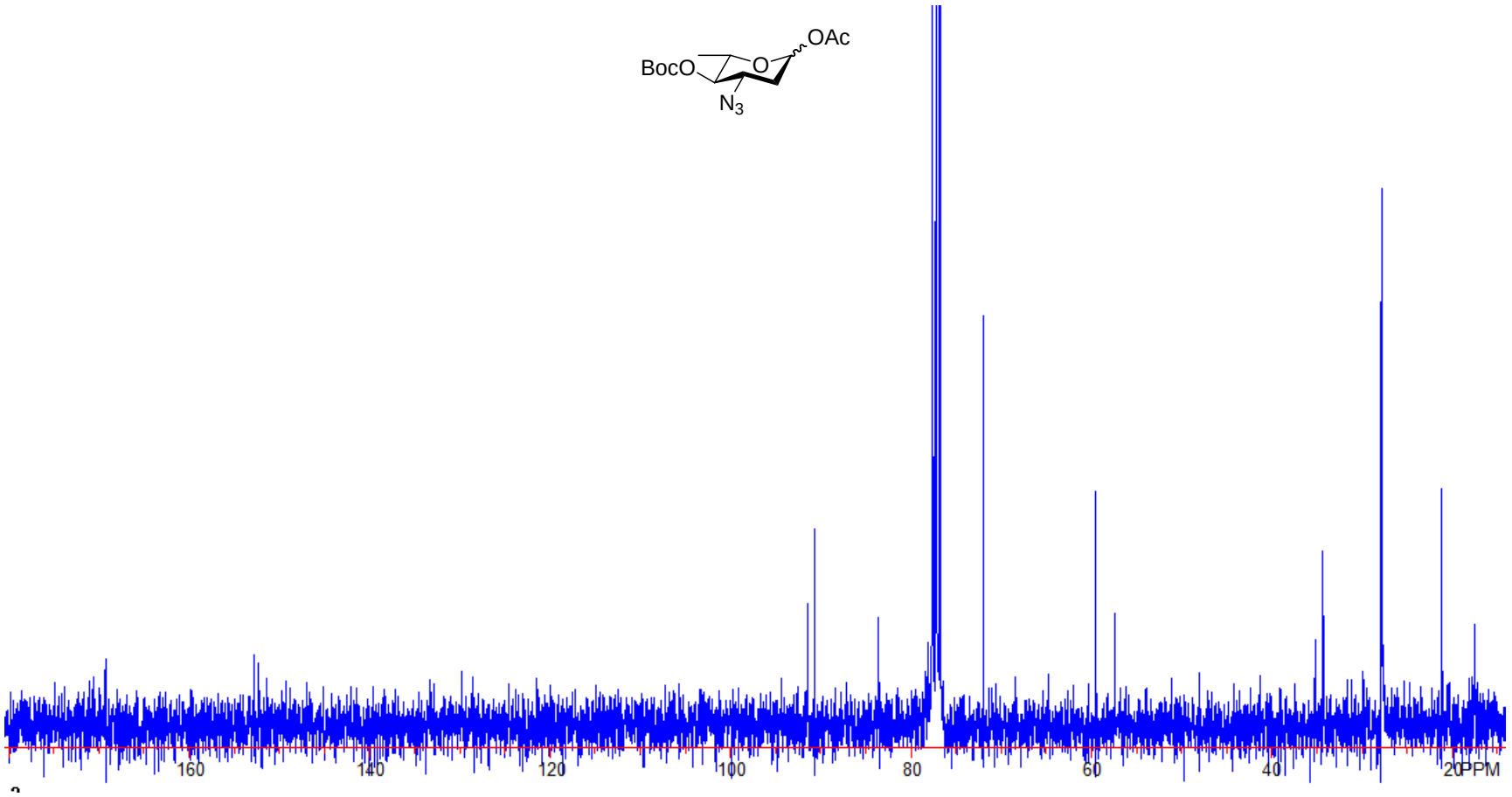
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-α-L-*lyxo*-hexopyranoside.



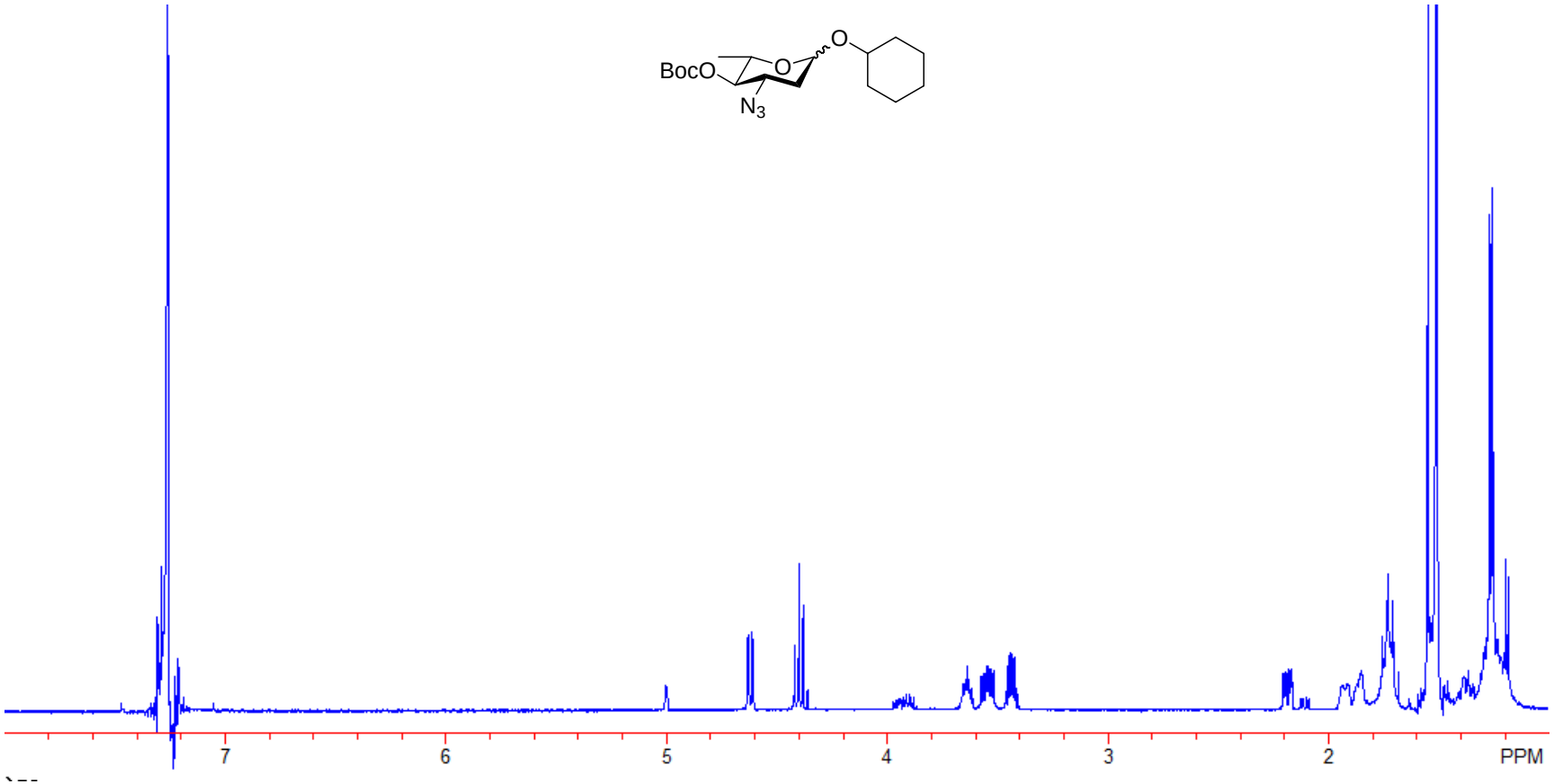
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranosyl acetate (**31**).



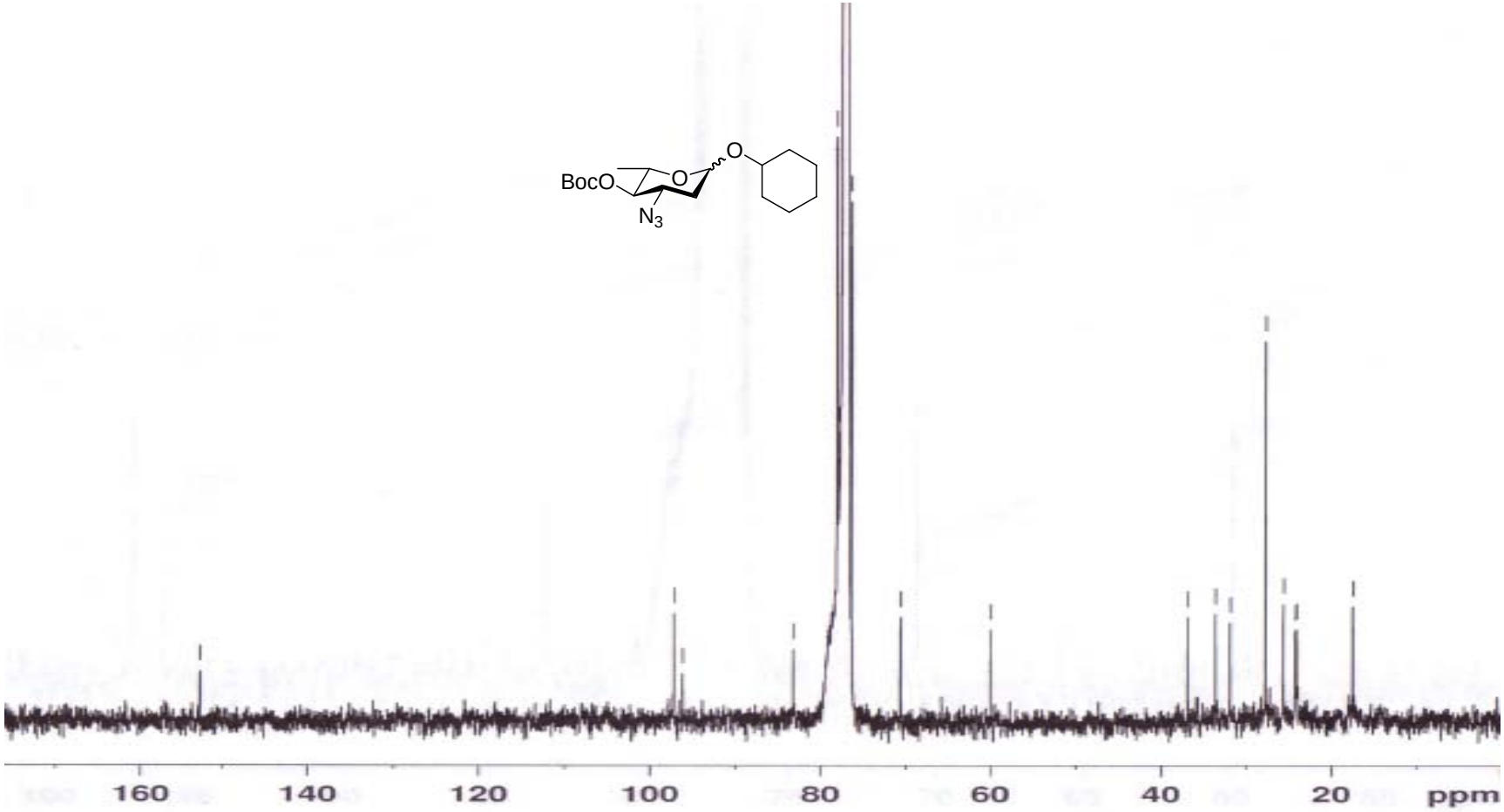
4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranosyl acetate (**31**).



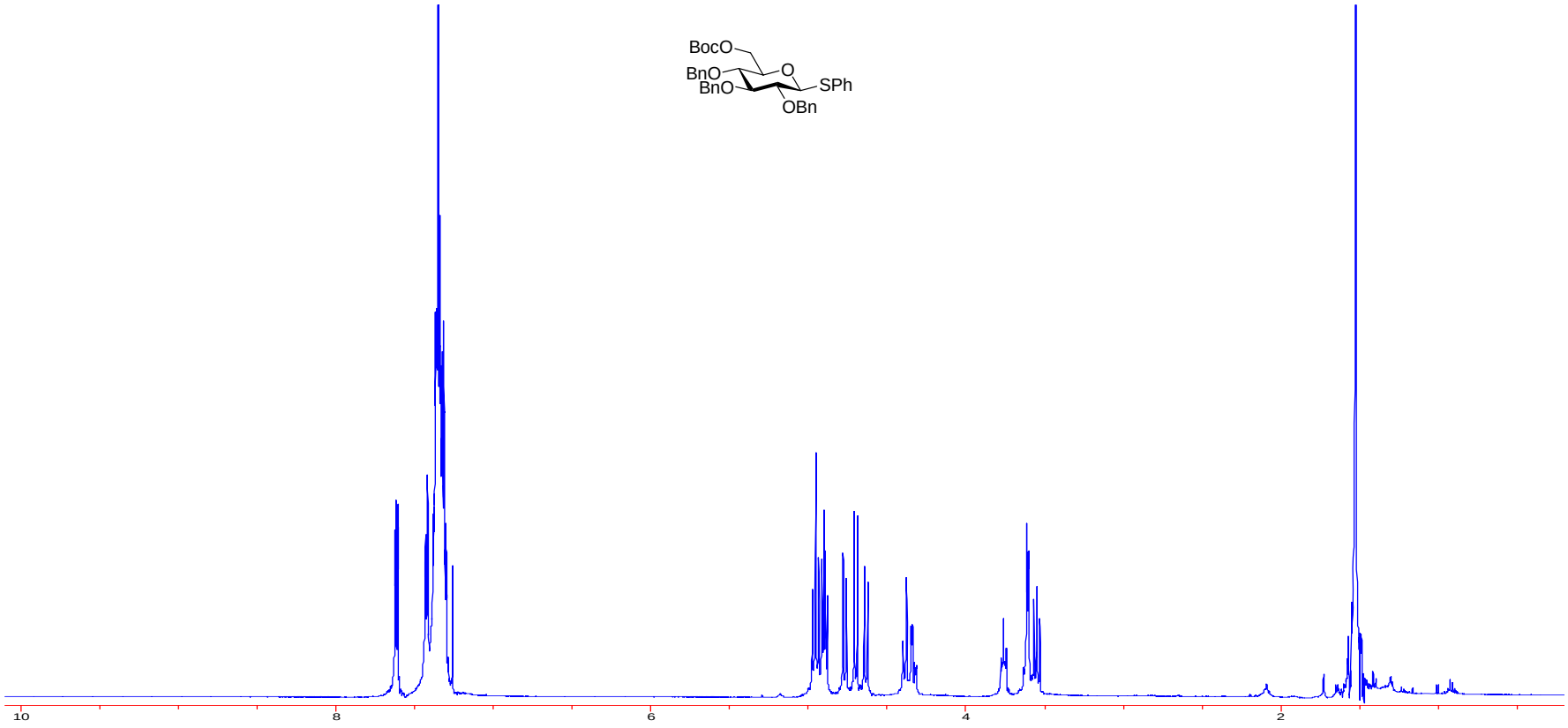
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranoside (**32**).



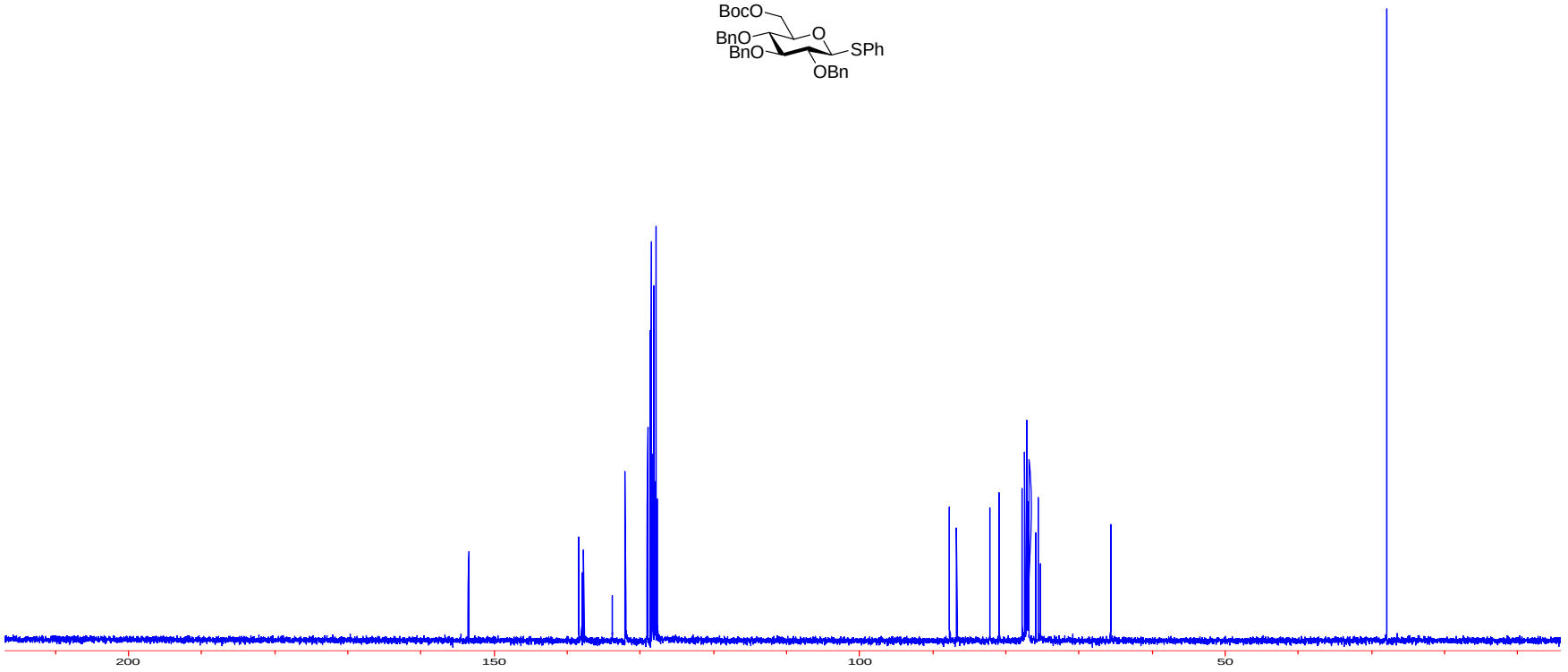
Cyclohexyl 4-*O*-*tert*-butoxycarbonyl-3-azido-2,3,6-trideoxy-1-L-*lyxo*-hexopyranoside (**32**).



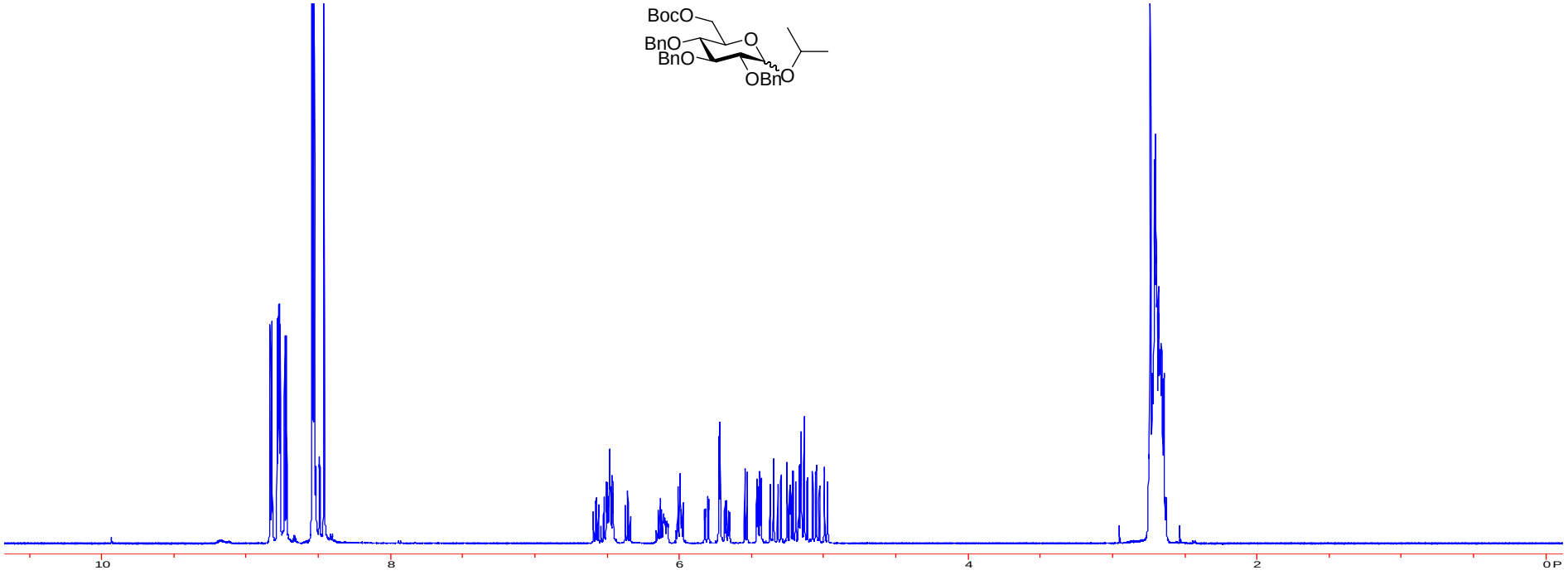
Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-glucopyranoside (**33**)



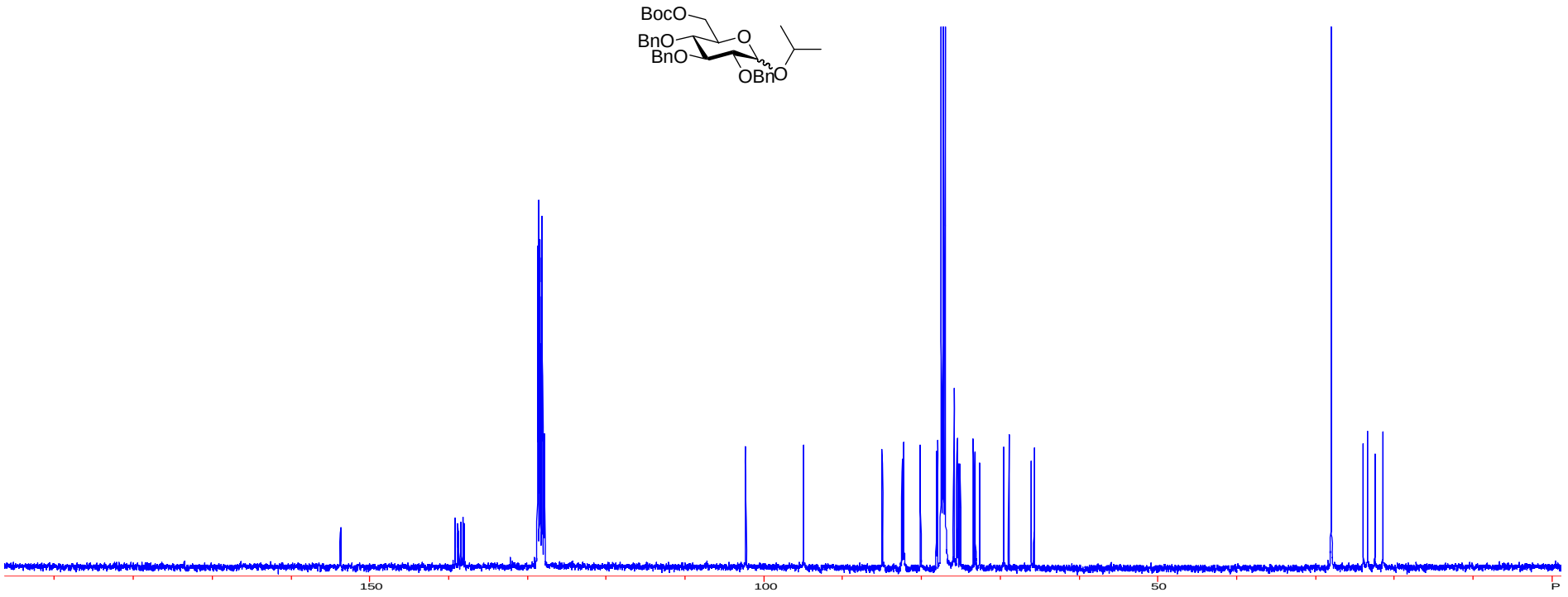
Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-1-thio-*β*-D-glucopyranoside (**33**)



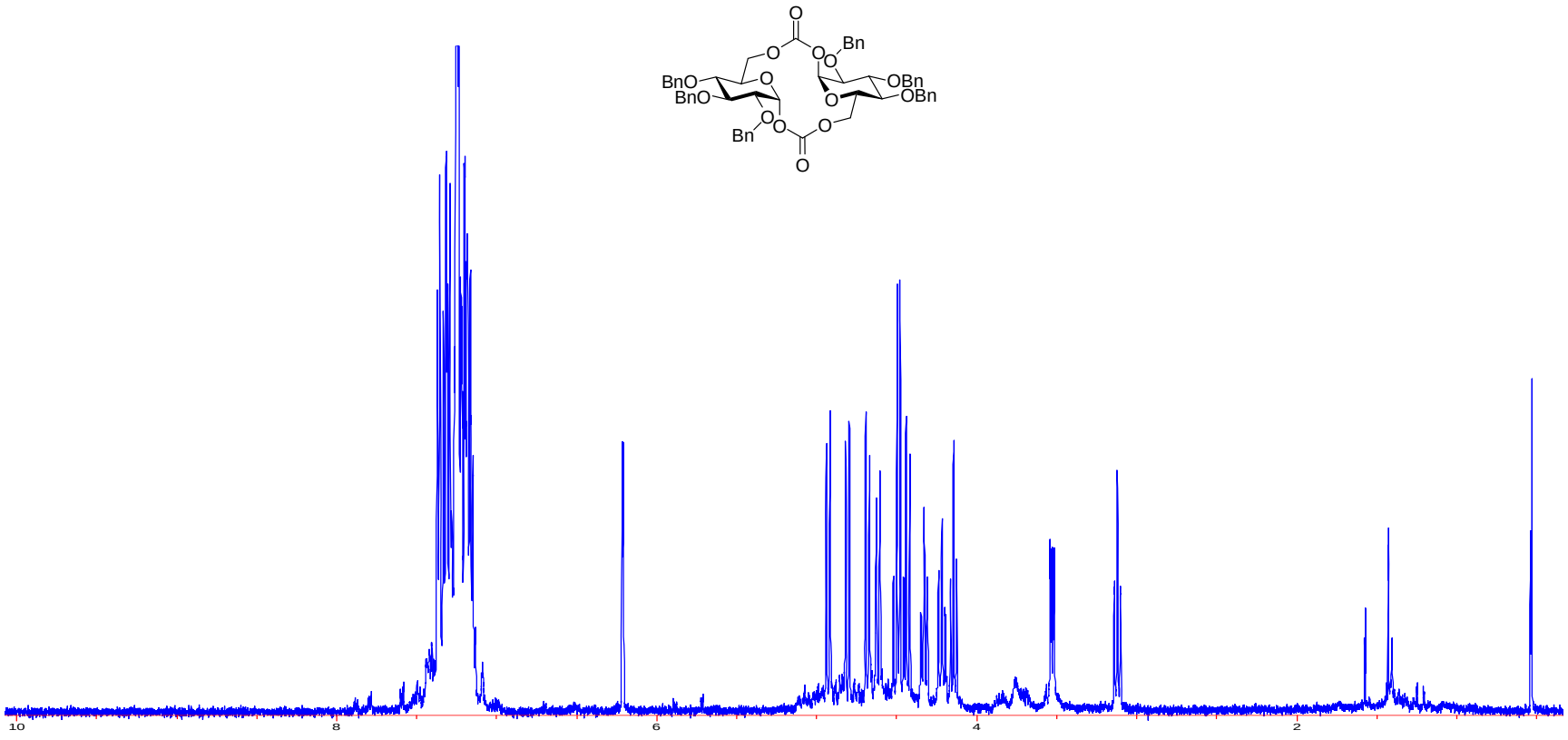
Isopropyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-D-glucopyranoside (**34α** and **34β**).



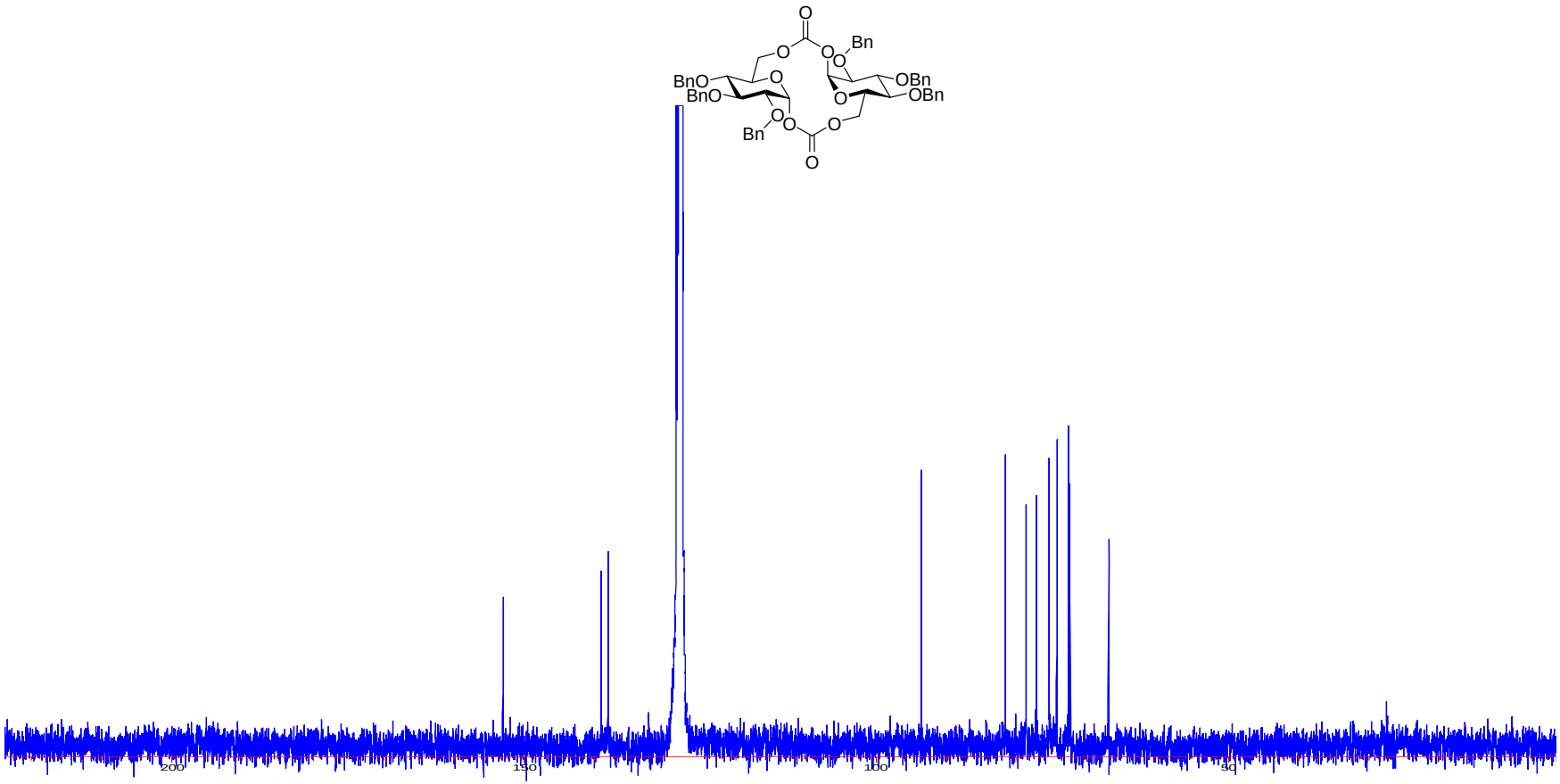
Isopropyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyloxycarbonyl-D-glucopyranoside (**34α** and **34β**).



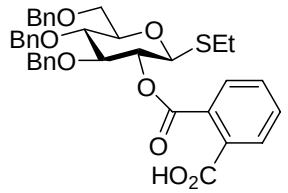
Di-(2,3,4-tri-*O*-benzyl-D-glucopyranoside)-(1,6), (6,1)-dicarbonate (**35**).

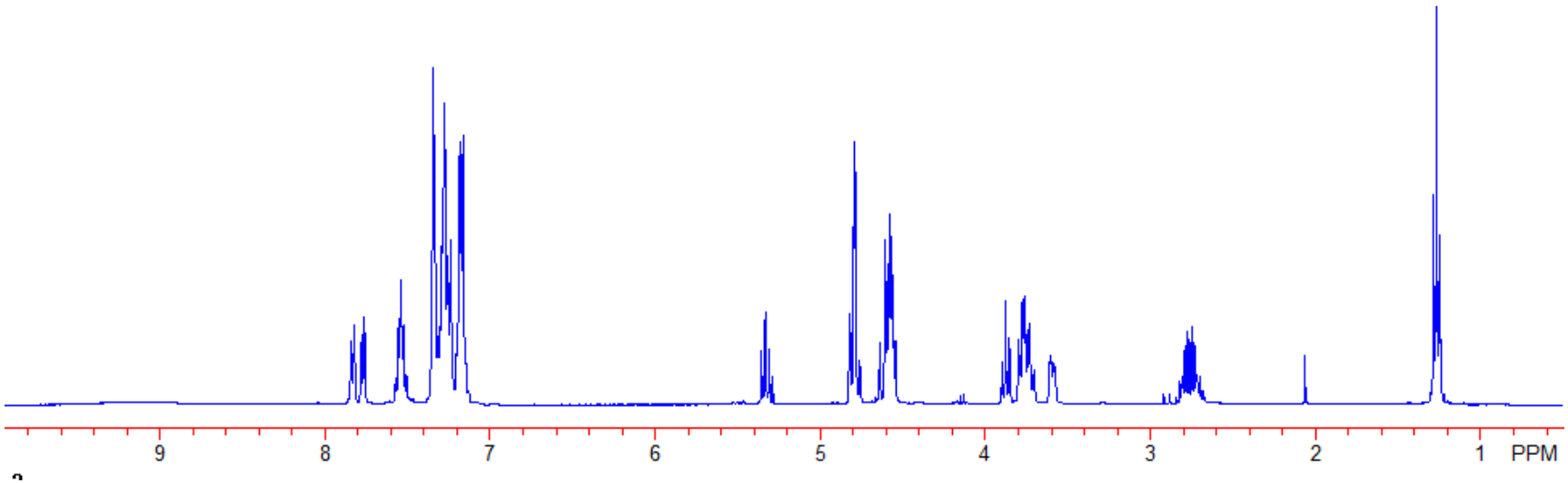


Di-(2,3,4-tri-o-benzyl-D-glucopyranoside)-(1,6), (6,1)-dicarbonate (**35**).

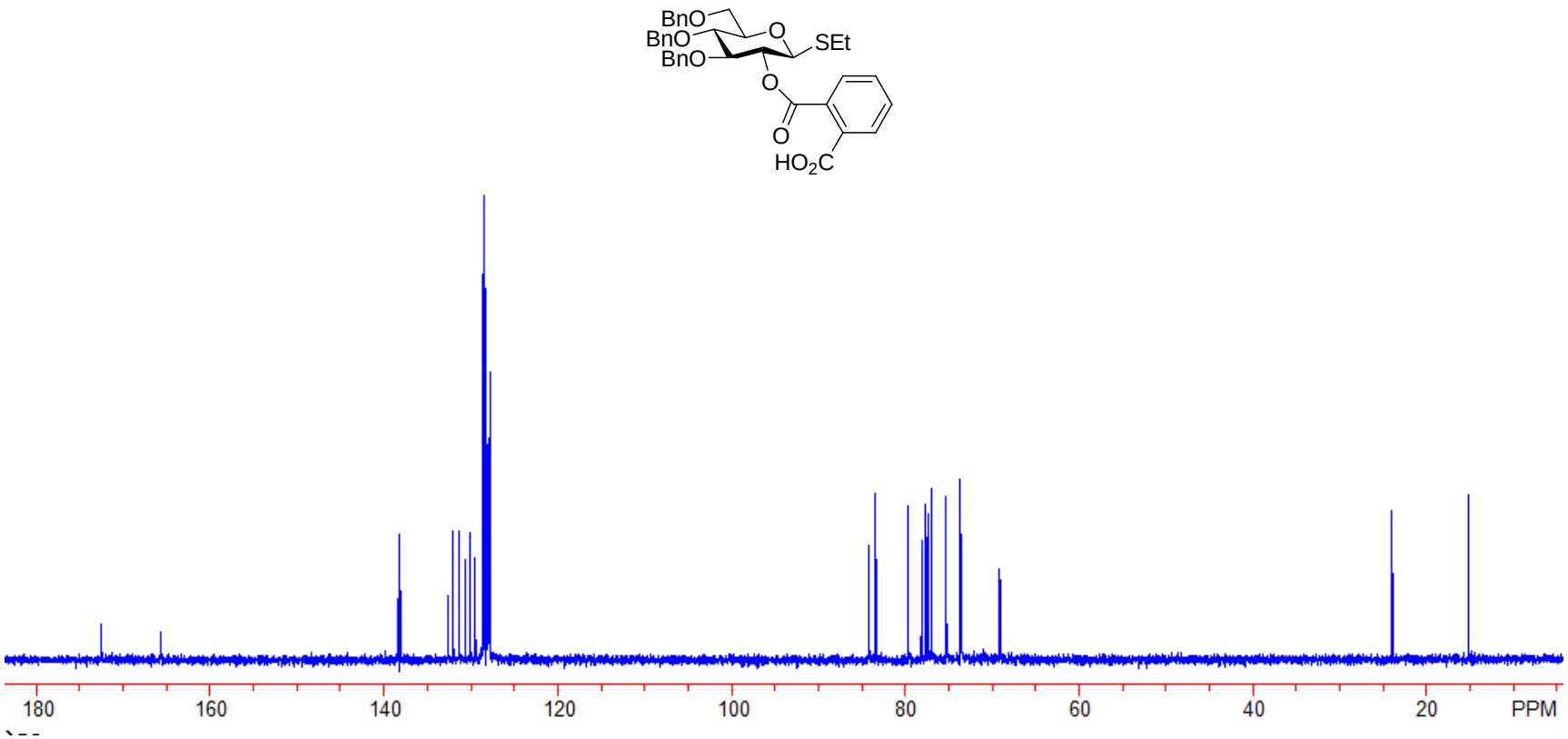


Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-carboxybenzoyl)-1-thio-β-D-glucopyranoside (**36**).

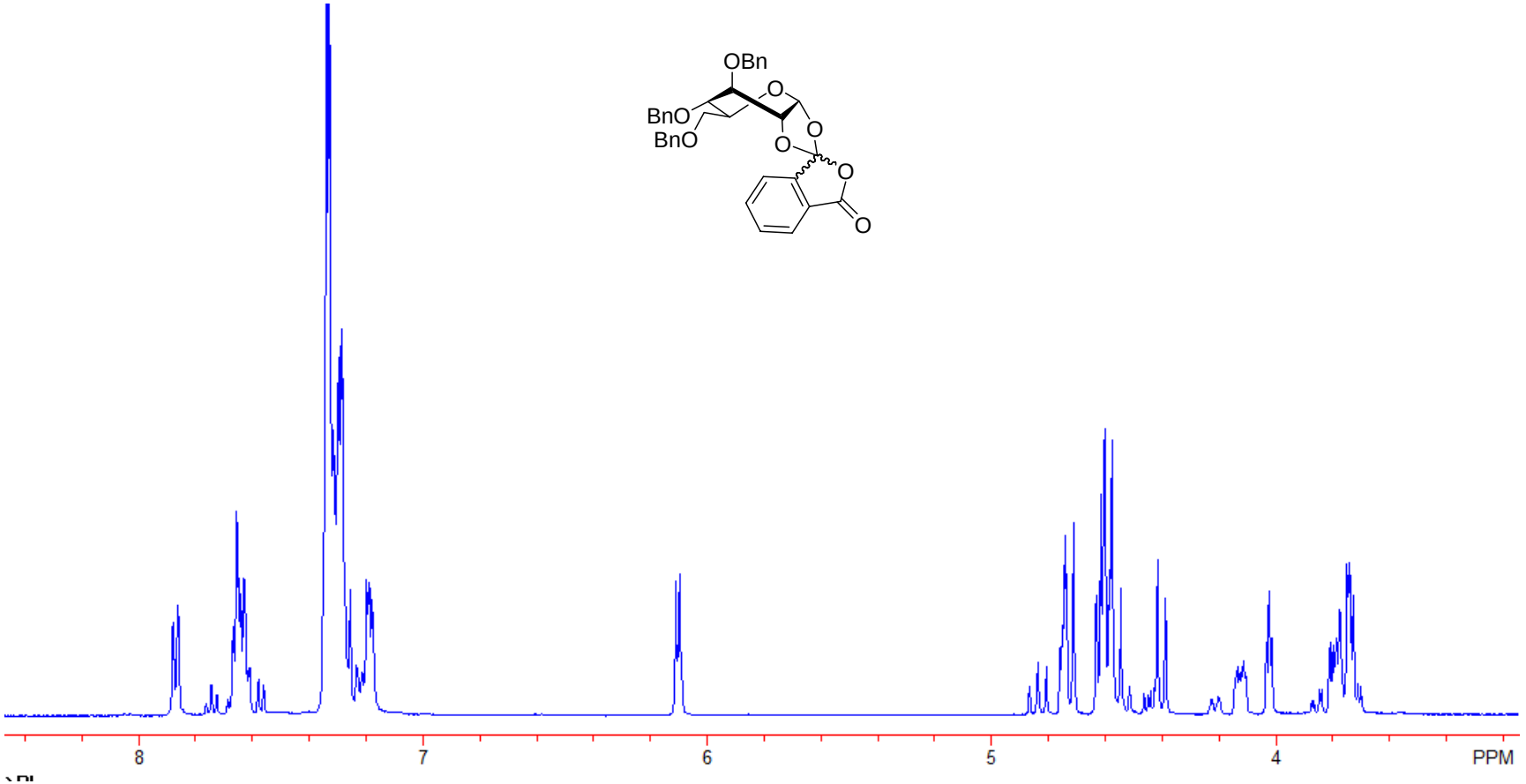




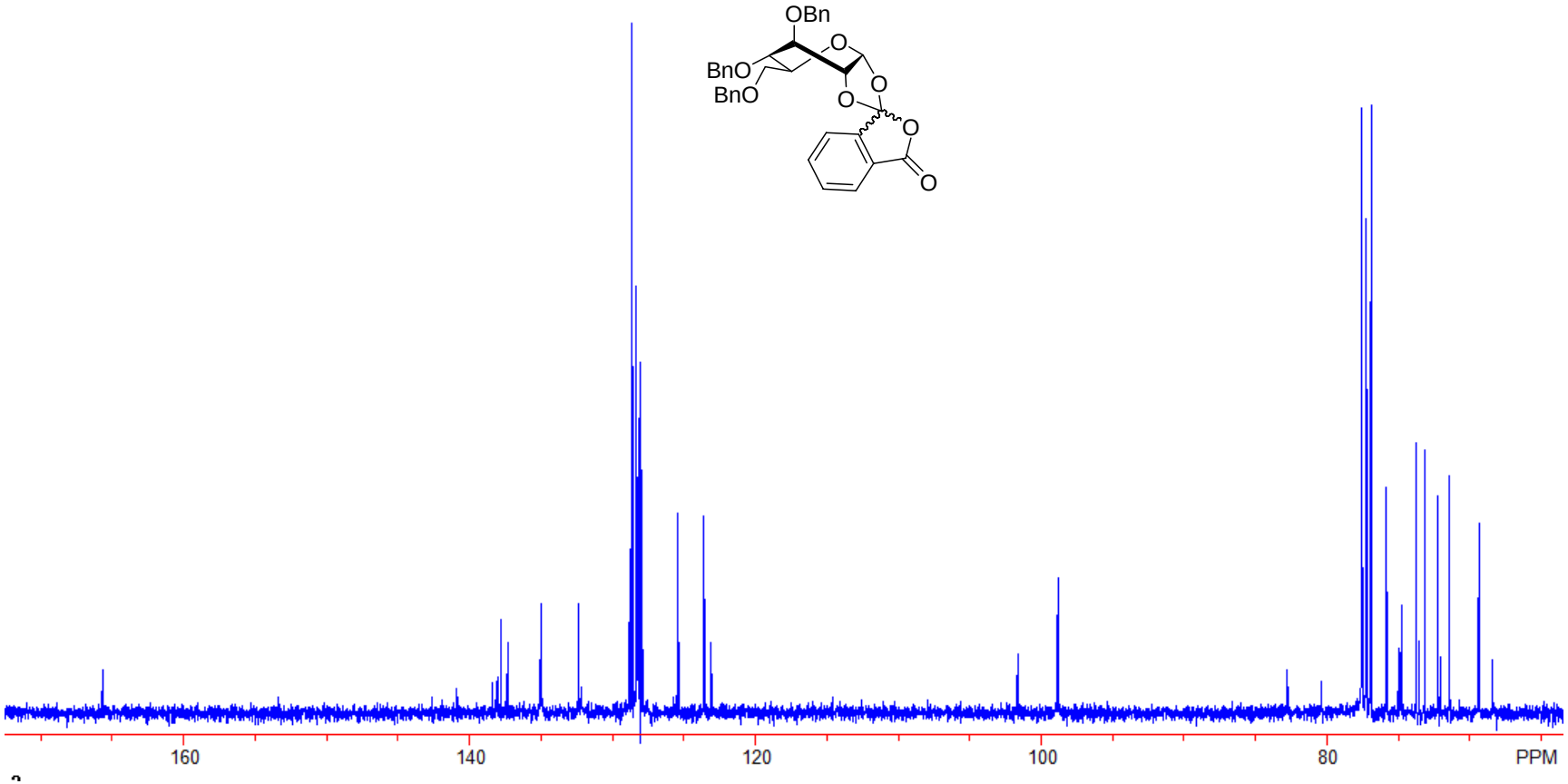
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-(2-carboxybenzoyl)-1-thio-β-D-glucopyranoside (**36**).



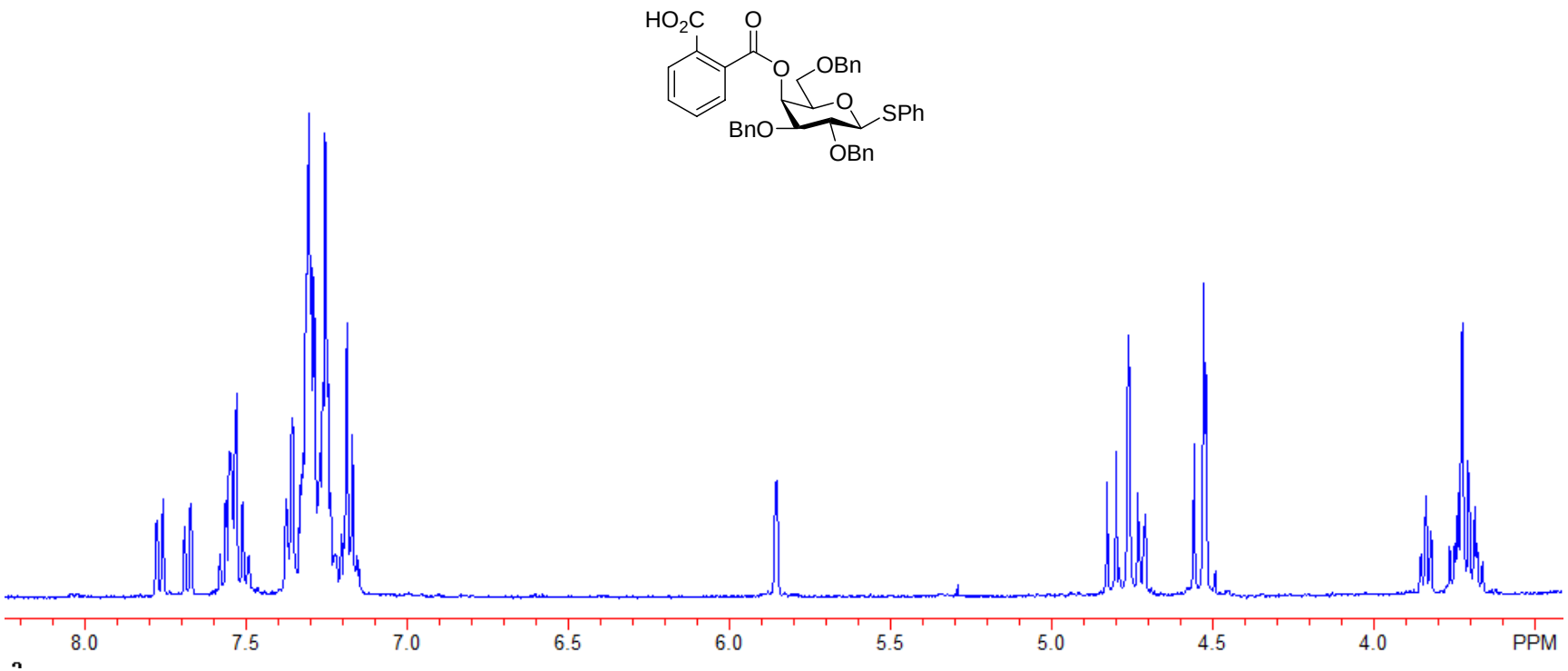
3,4,6-*Tri*-O-benzyl-1,2-O-phthalidylidene-α-D-glucopyranose (**37**).



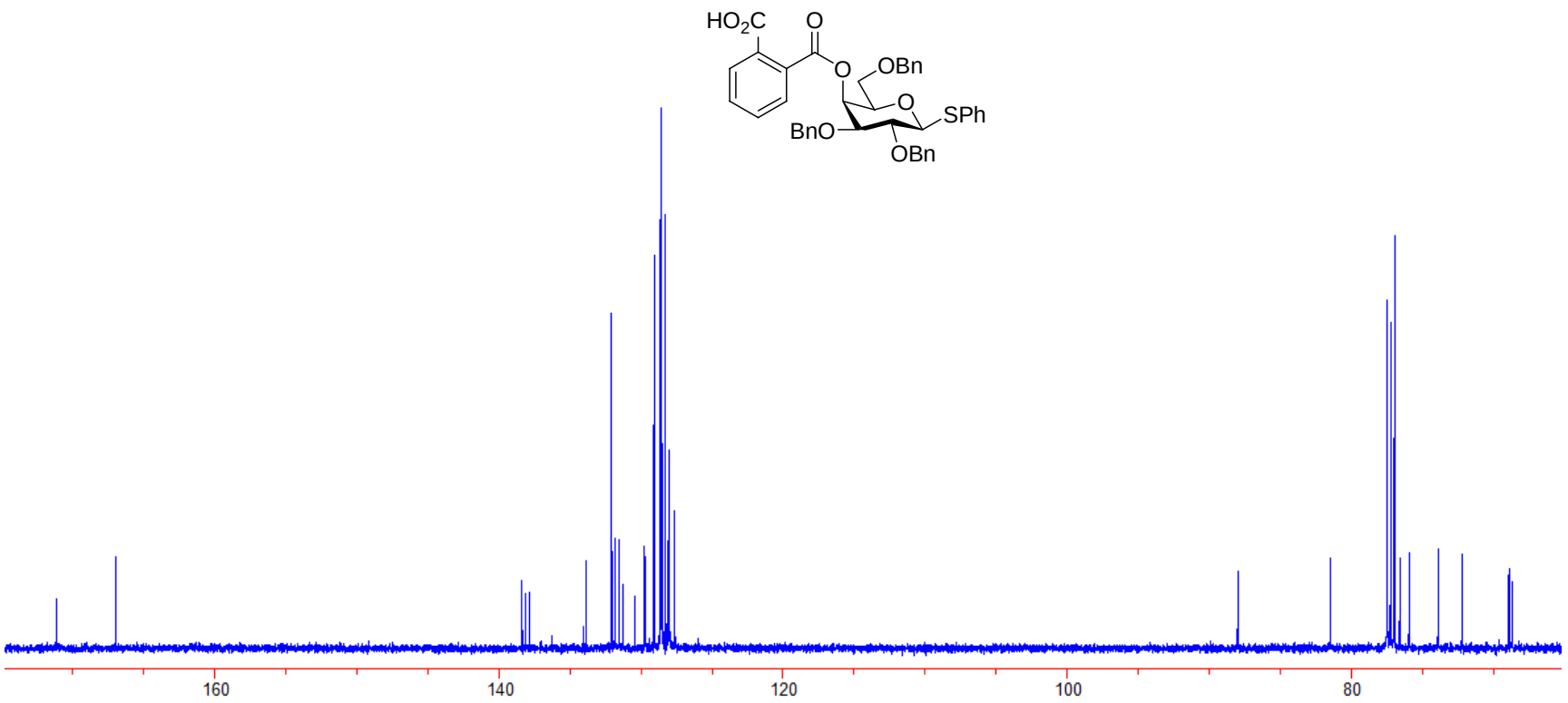
3,4,6-*Tri*-O-benzyl-1,2-O-phthalidylidene-α-D-glucopyranose (**37**).



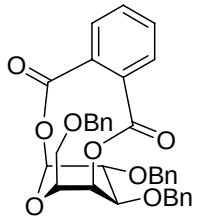
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-carboxybenzoyl)-1-thio-β-D-galactopyranoside (**38**).

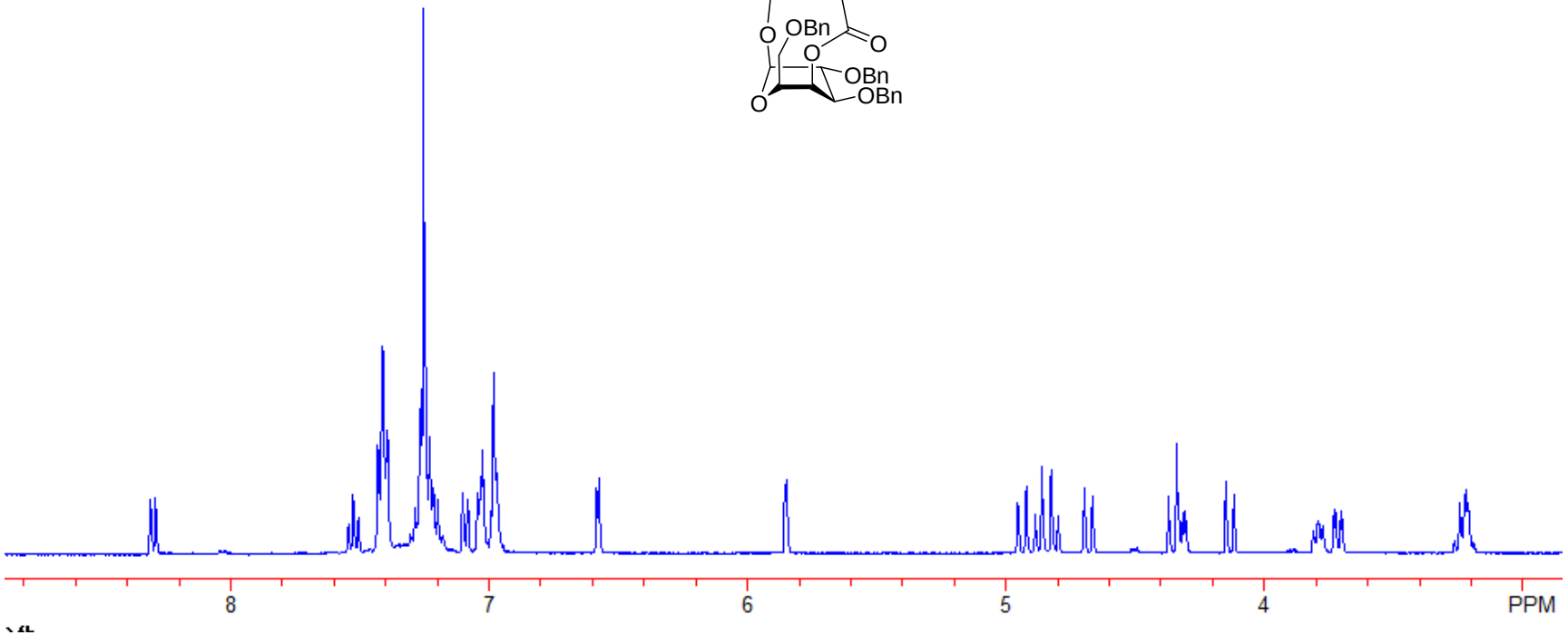


Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-carboxybenzoyl)-1-thio-β-D-galactopyranoside (**38**).

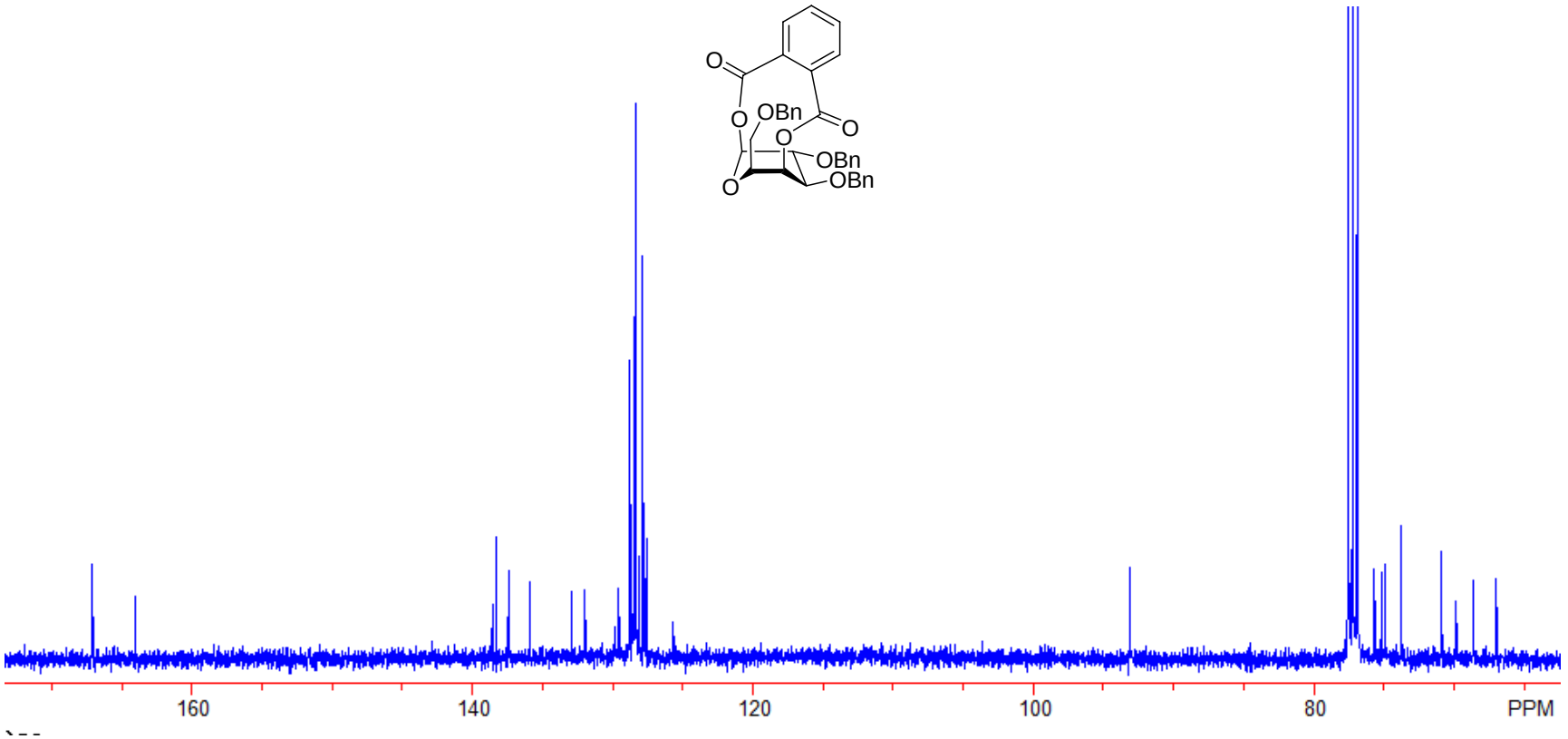


3,4,6-Tri-*O*-benzyl-1,2-*O*-phthaloyl-β-D-galactopyranoside (**40**).

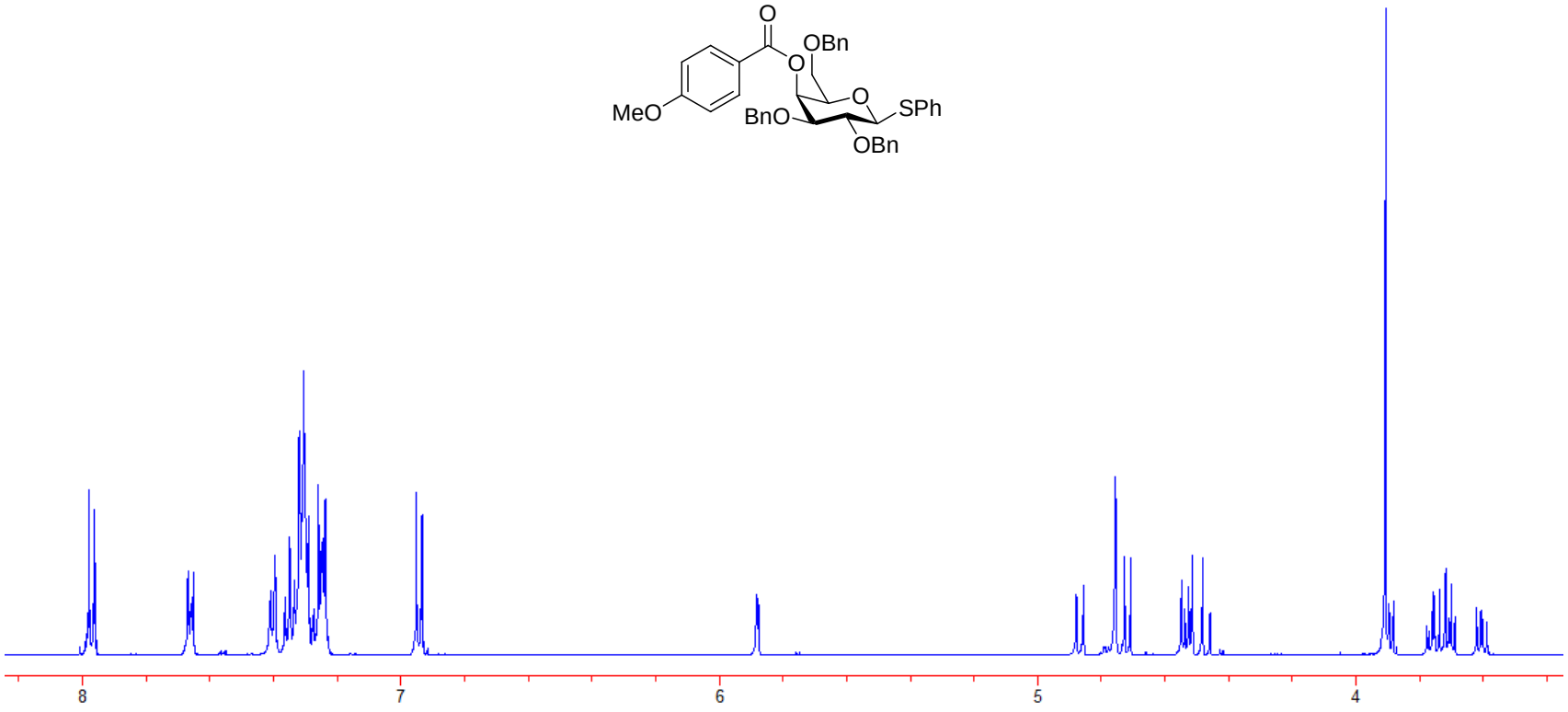




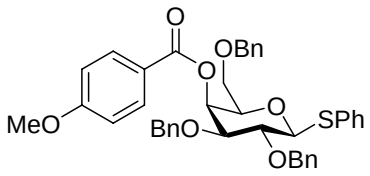
3,4,6-Tri-*O*-benzyl-1,2-*O*-phthaloyl-β-D-galactopyranoside (**40**).

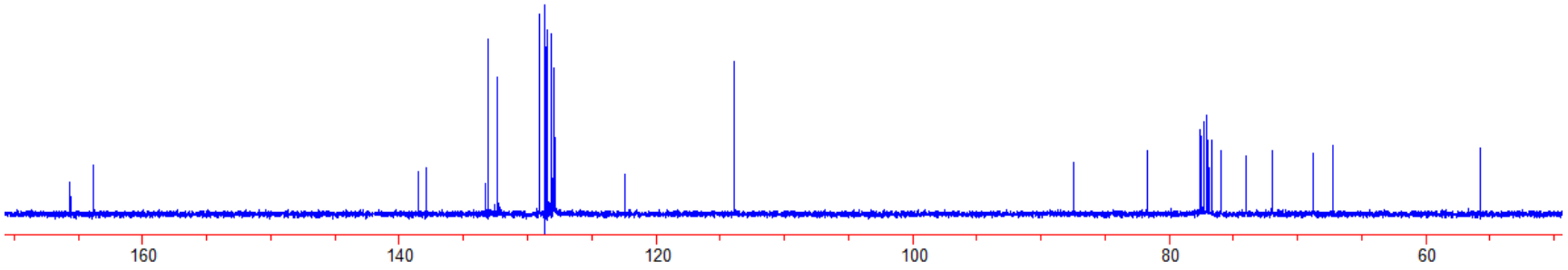


Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-1-thio-β-D-galactopyranoside (**41**).

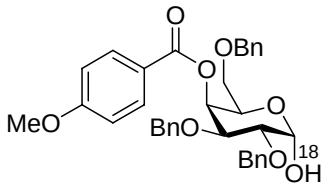


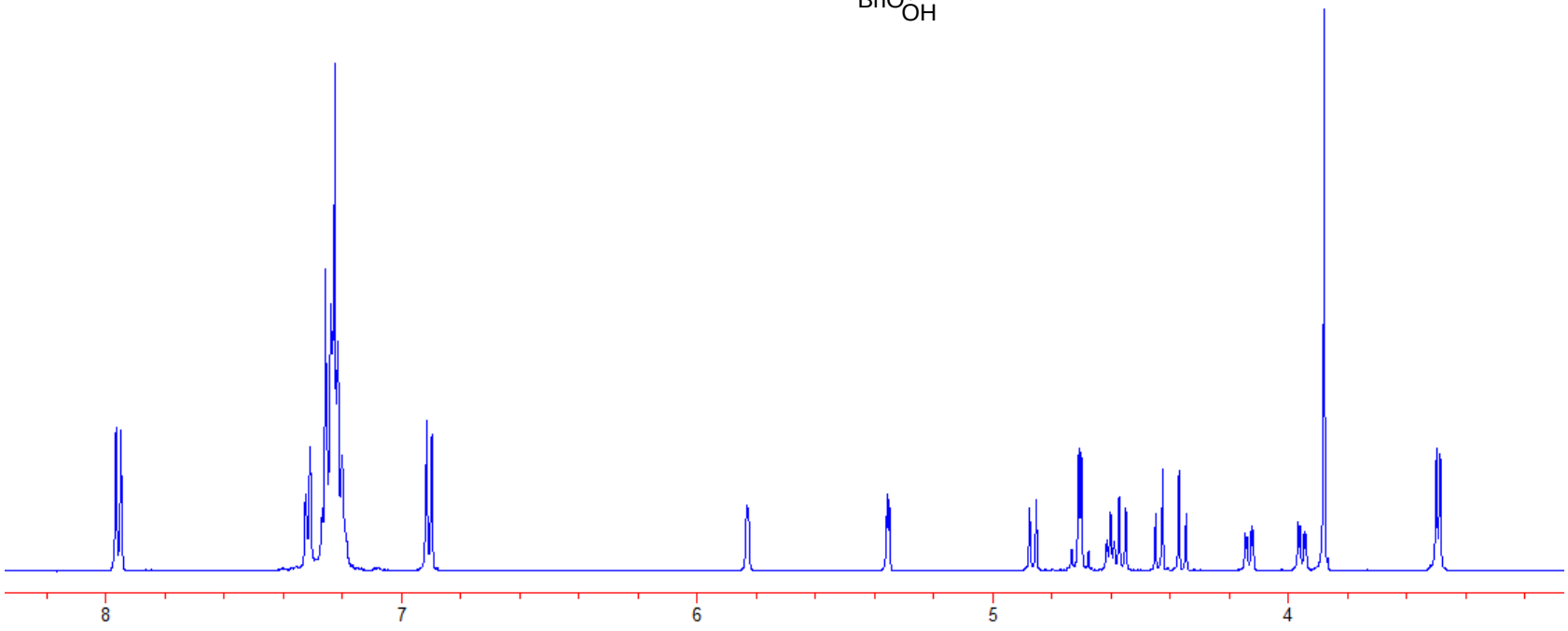
Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-1-thio-β-D-galactopyranoside (**41**).



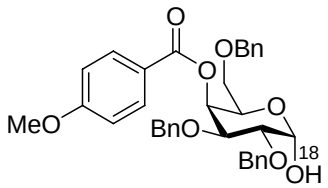


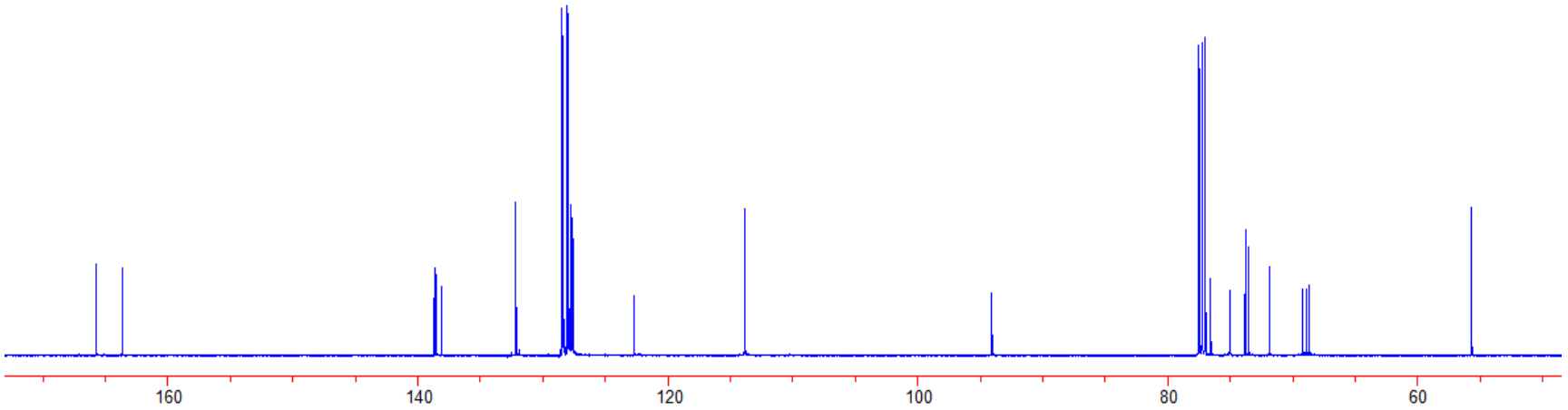
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-α-D-[1-$^{16/18}$*O*]-galactopyranoside (**43**).



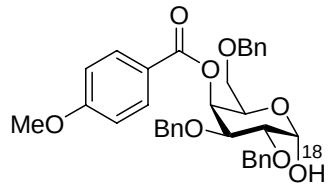


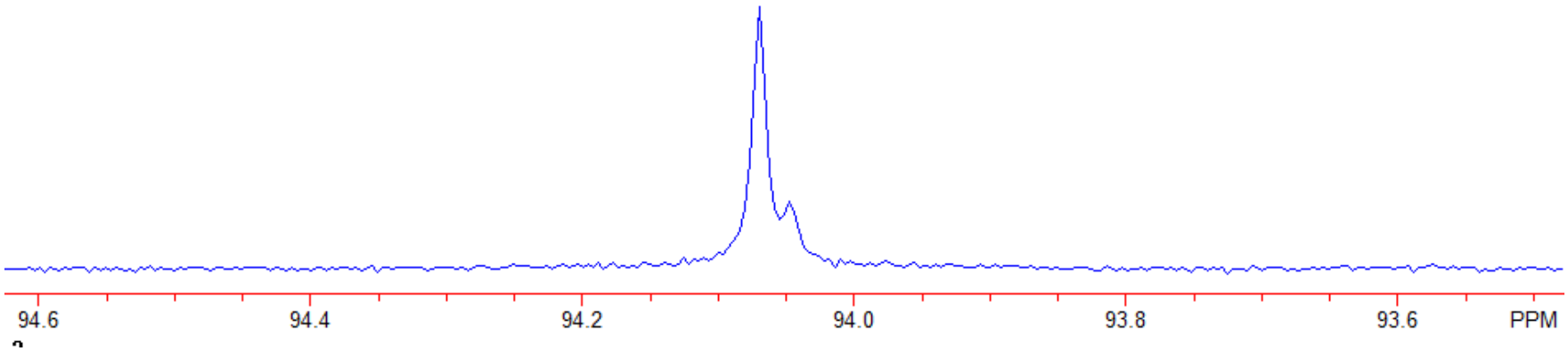
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-α-D-[1-$^{16/18}$*O*]-galactopyranoside (**43**).



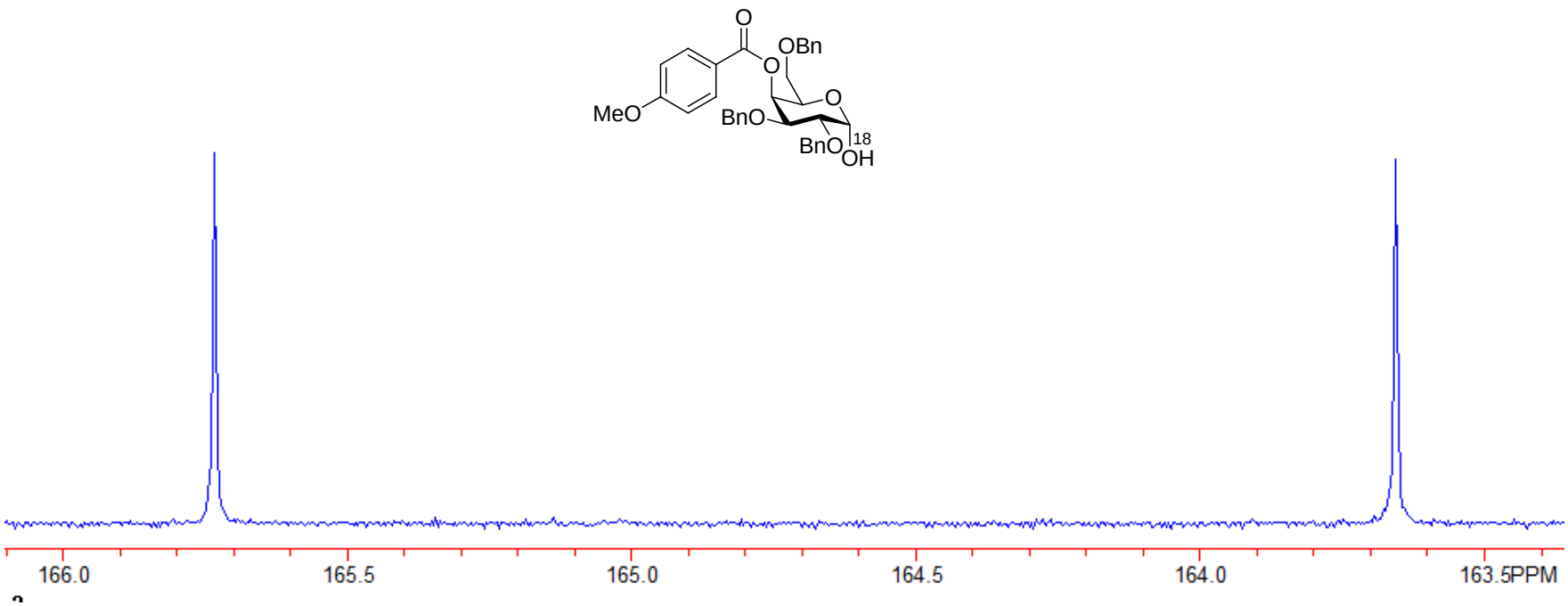


2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-α-D-[1-$^{16/18}$*O*]-galactopyranoside (**43**, expansion).

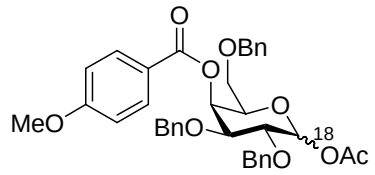


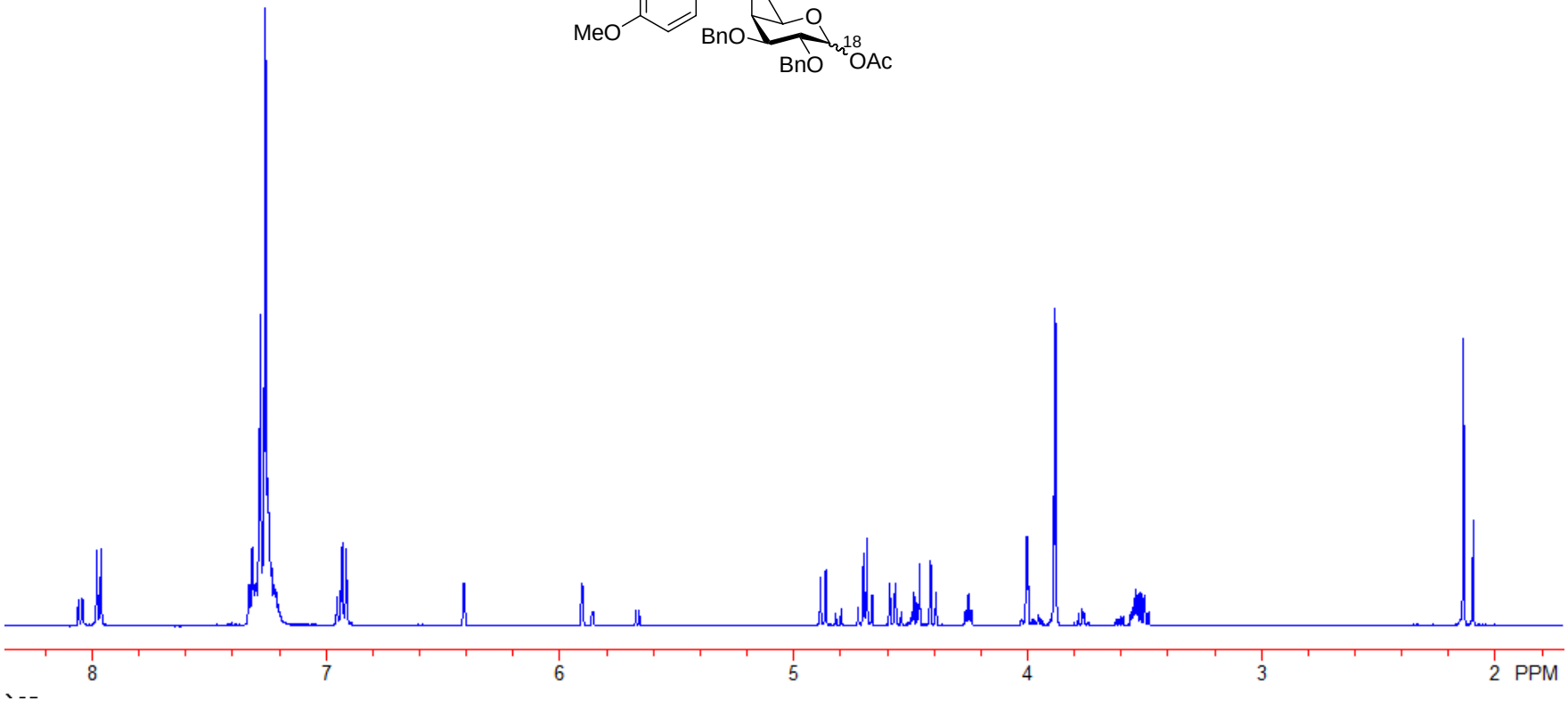


2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-α-D-[1-$^{16/18}$*O*]-galactopyranoside (**43**, expansion).

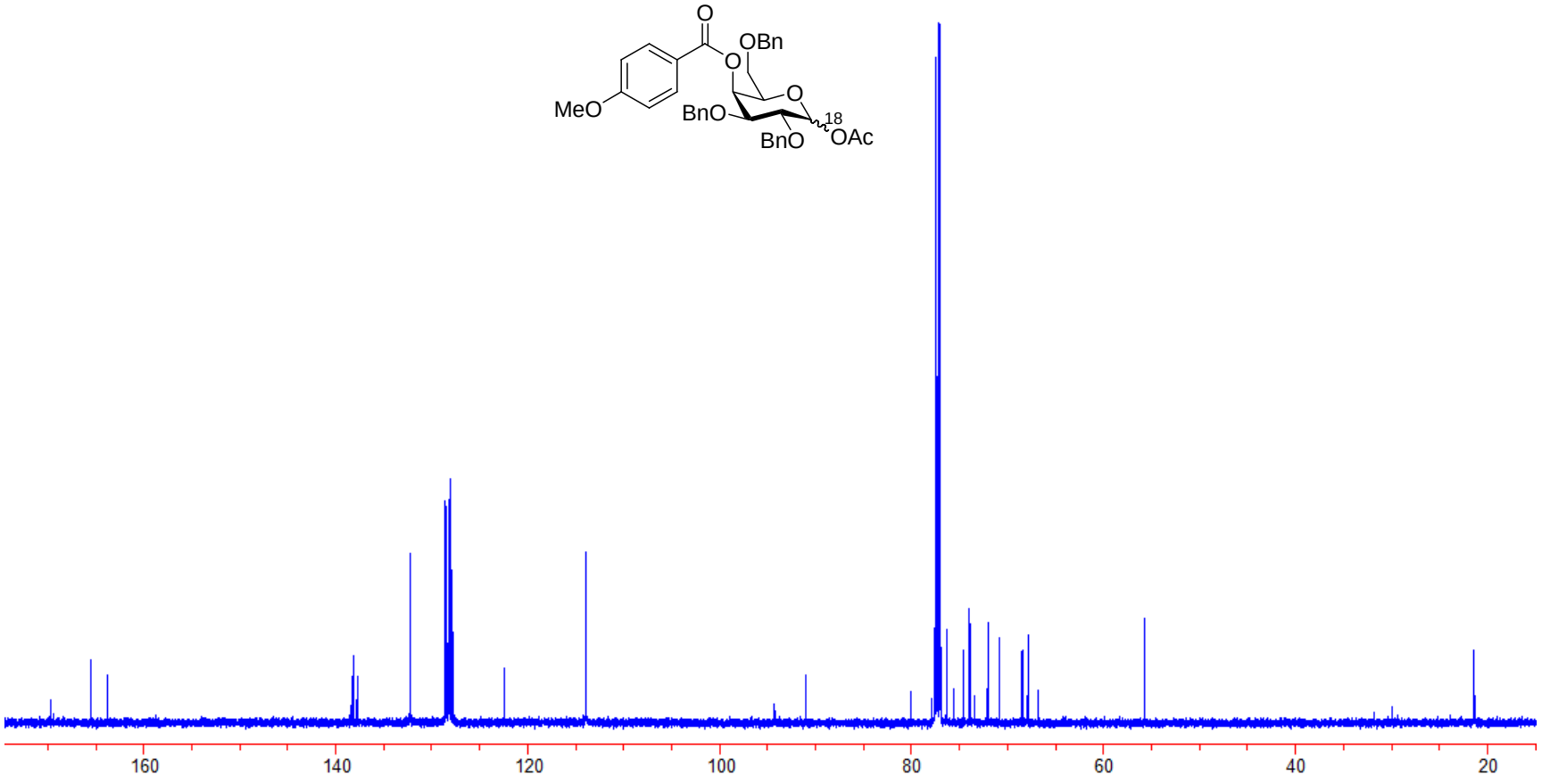


2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-$^{16/18}$*O*]-galactopyranosyl acetate (**47**).

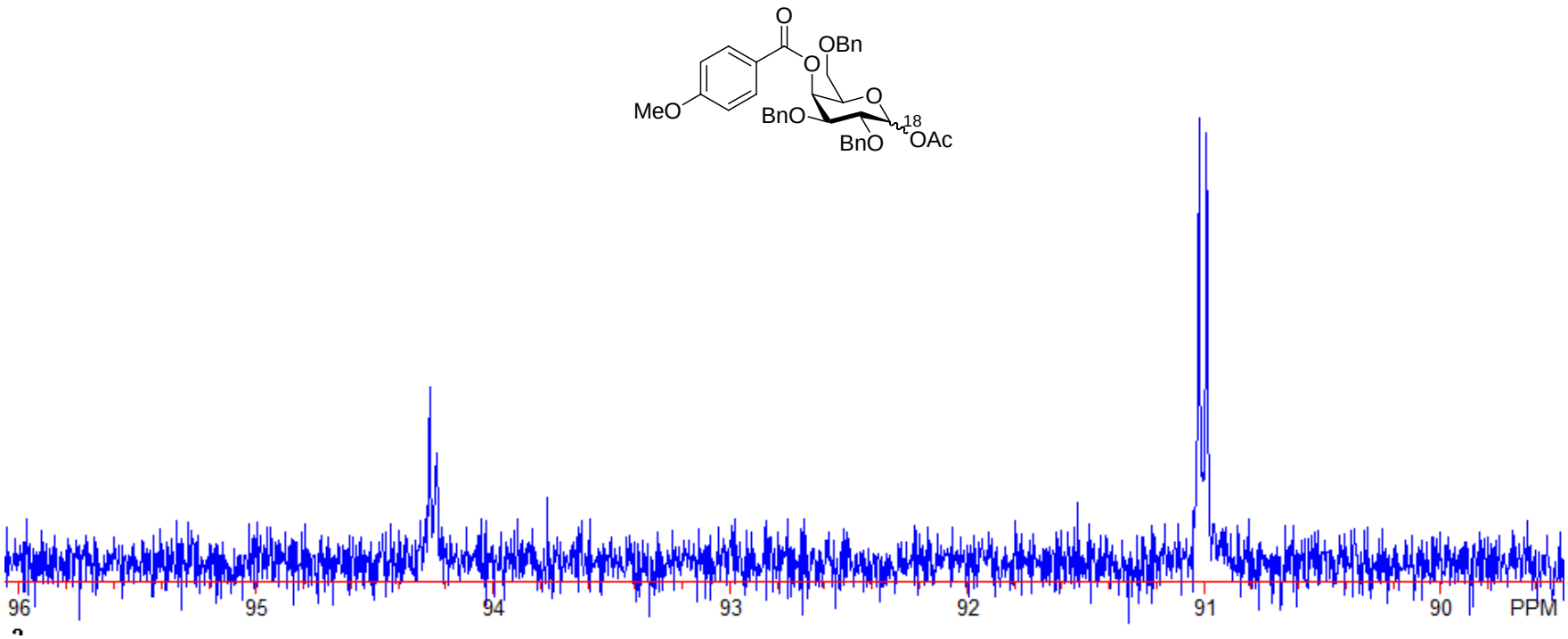




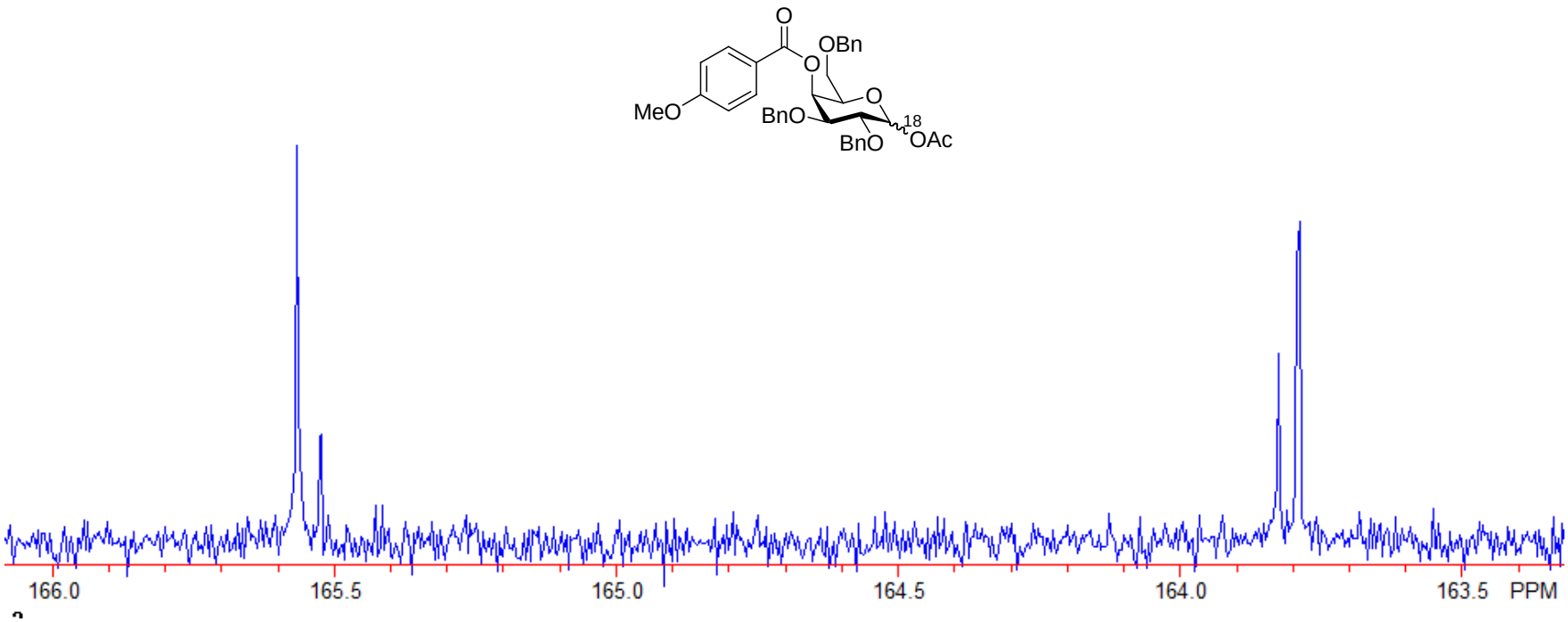
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-$^{16/18}$*O*]-galactopyranosyl acetate (**47**).



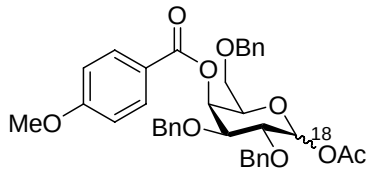
2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-$^{16/18}$*O*]-galactopyranosyl acetate (**47**, expansion).

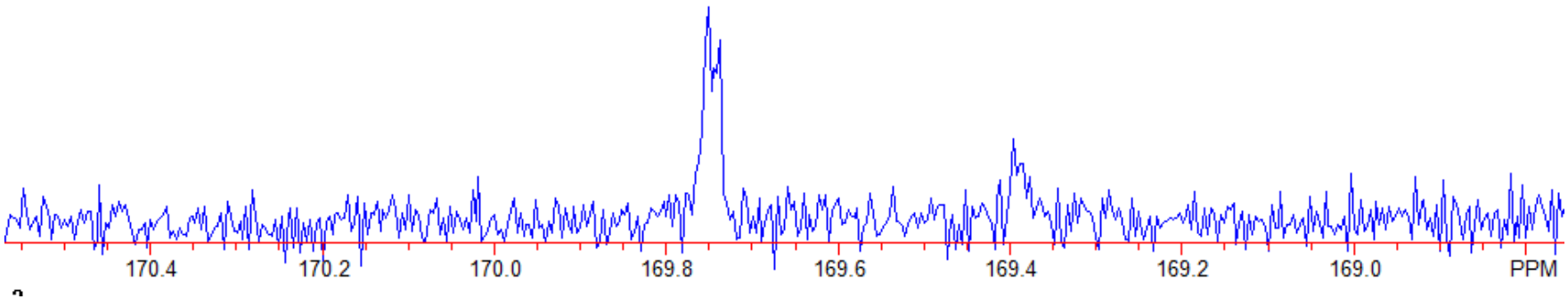


2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-$^{16/18}$*O*]-galactopyranosyl acetate (**47**, expansion).

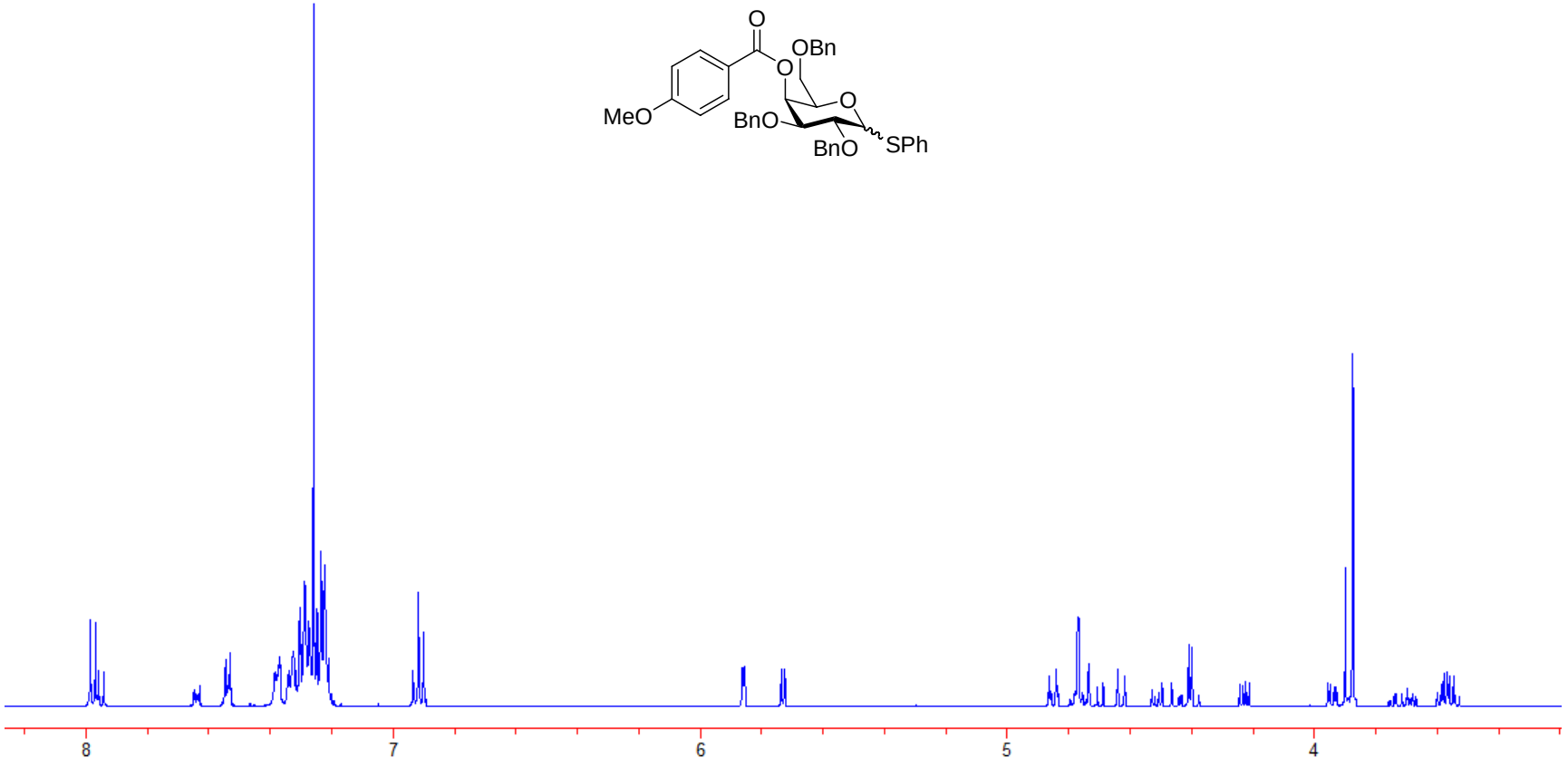


2,3,6-Tri-*O*-benzyl-4-*O*-(4-methoxybenzoyl)-D-[1-$^{16/18}$*O*]-galactopyranosyl acetate (**47**, expansion).





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**).