

Supporting Information S2

Synthesis of fluorinated glycotope mimetics derived from *Streptococcus pneumoniae* serotype 8 CPS

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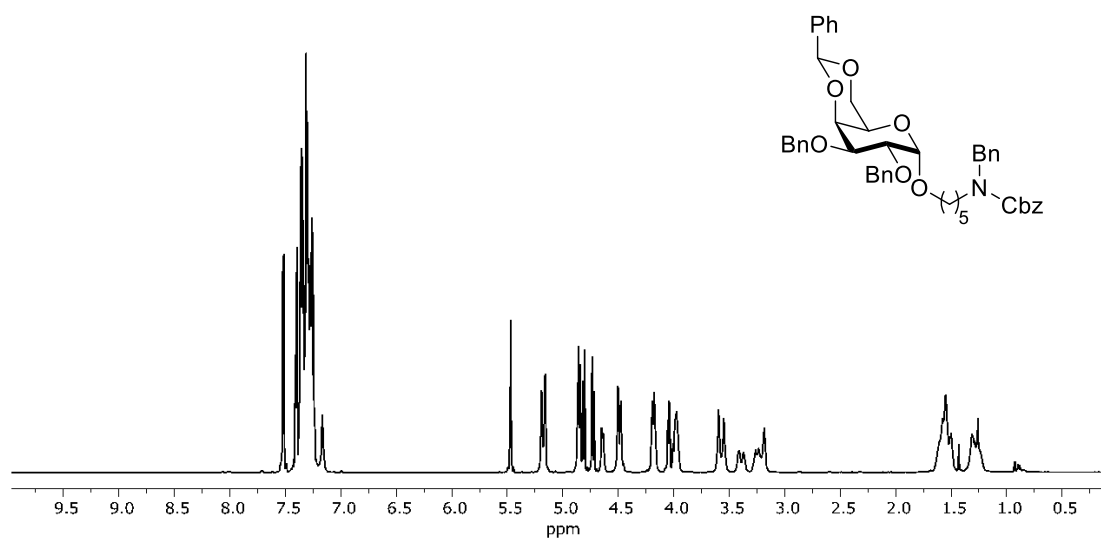
Spectroscopic Data of selected compounds

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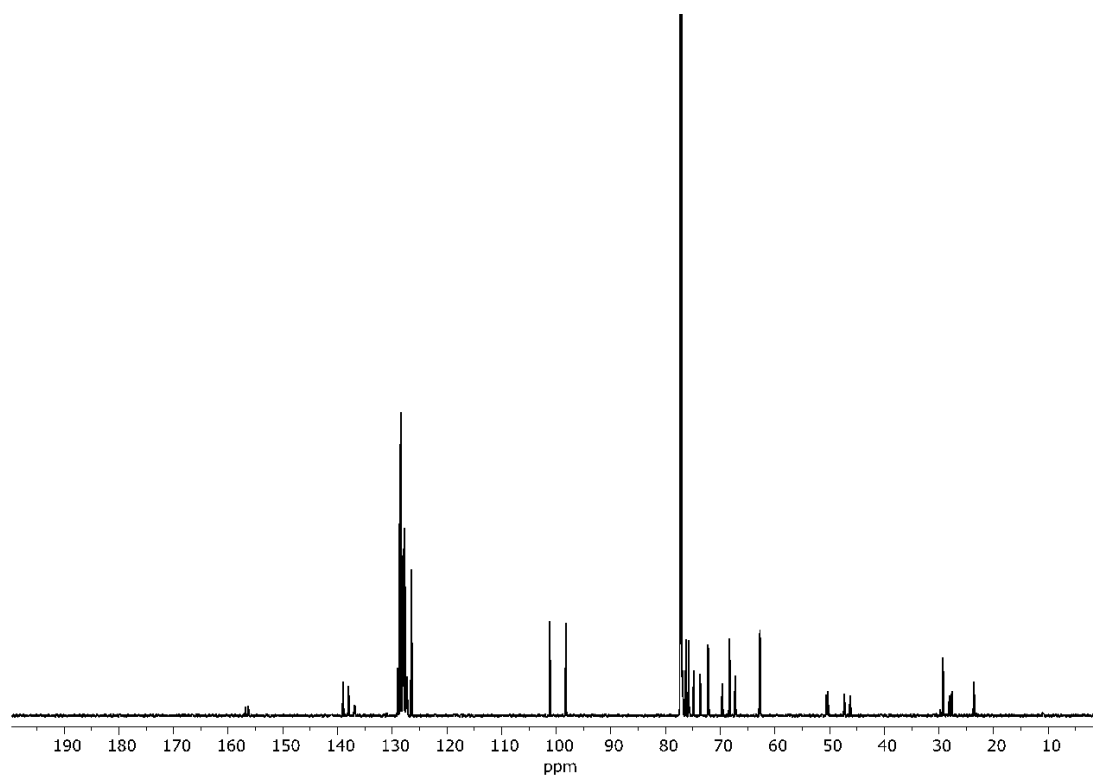
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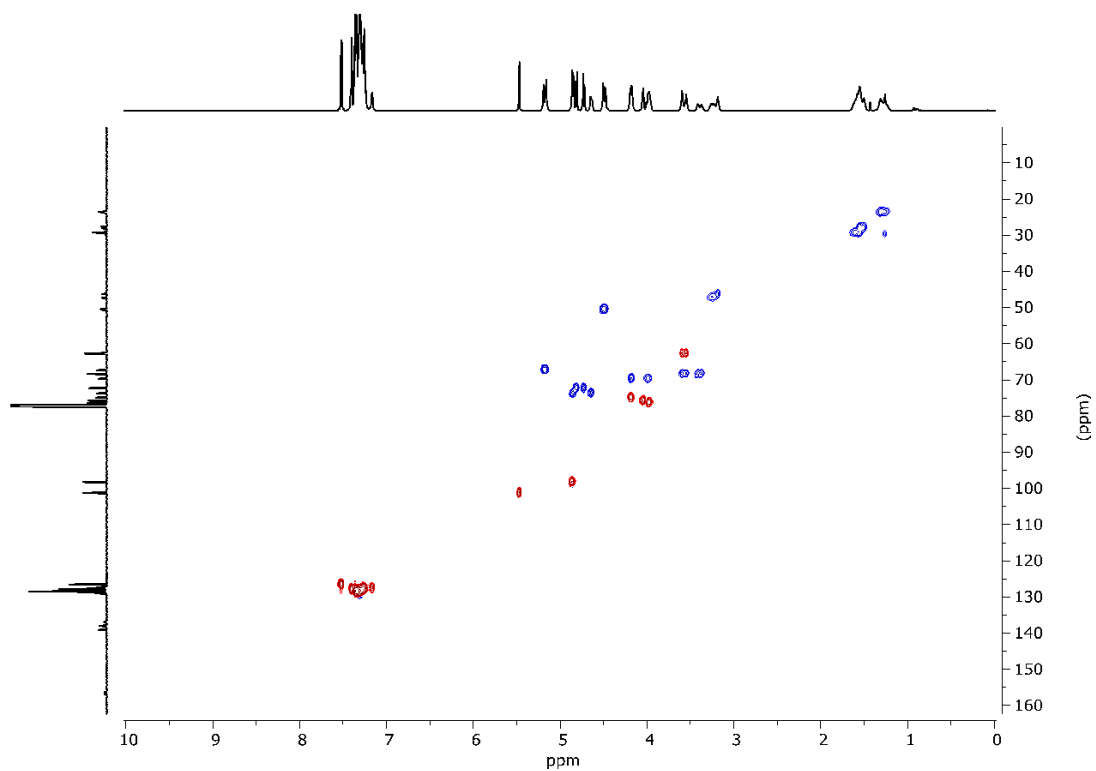
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-galactopyranoside (**24**)**



^1H NMR (800 MHz, CDCl_3) of **24**.

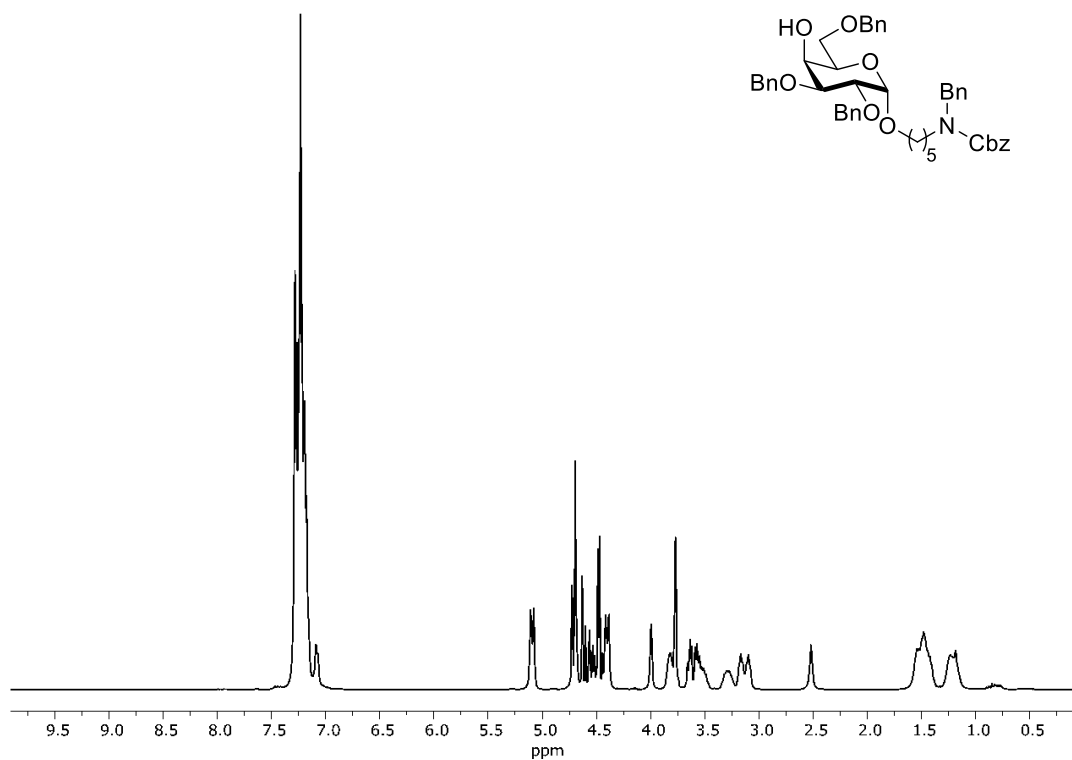


^{13}C NMR (200 MHz, CDCl_3) of **24**.

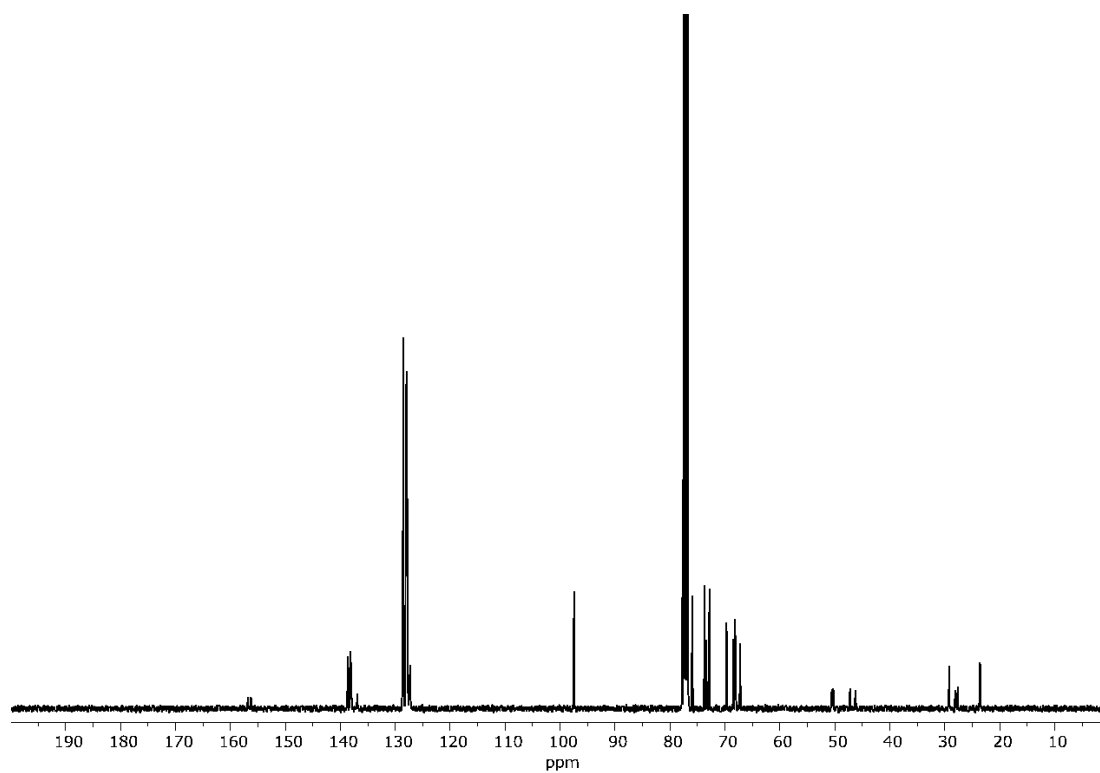


HSQC (CDCl₃) of **24**.

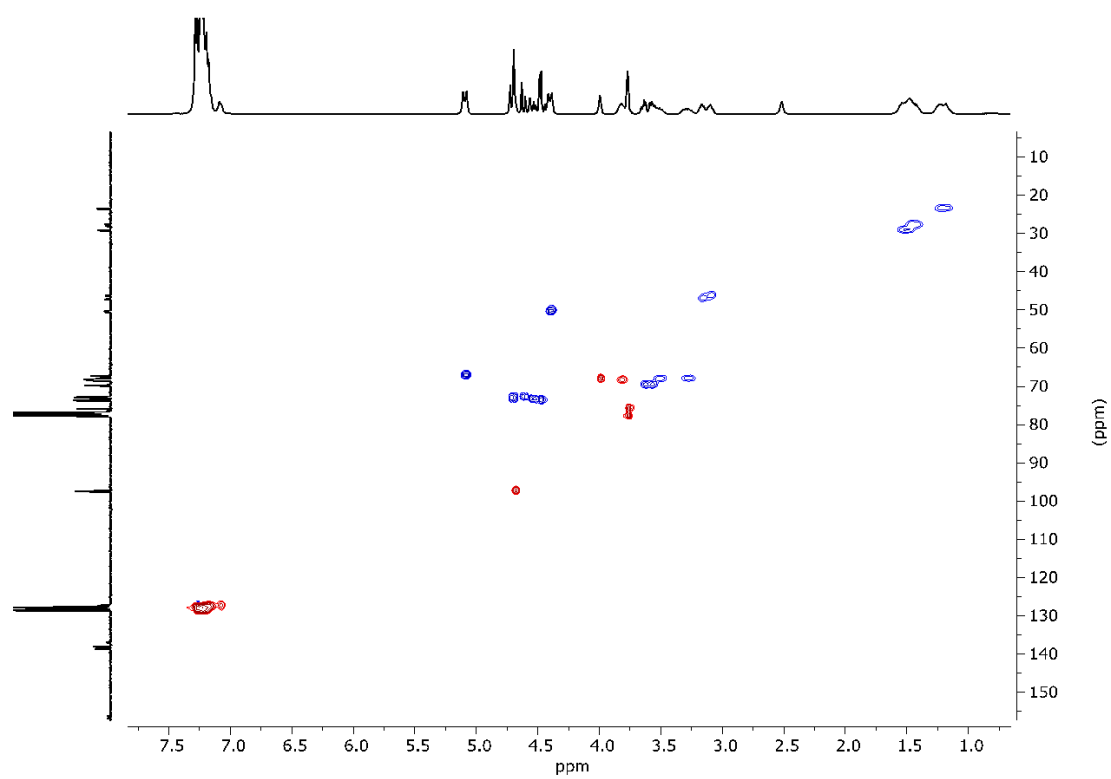
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl 2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (**18**)**



¹H NMR (600 MHz, CDCl₃) of **18**.

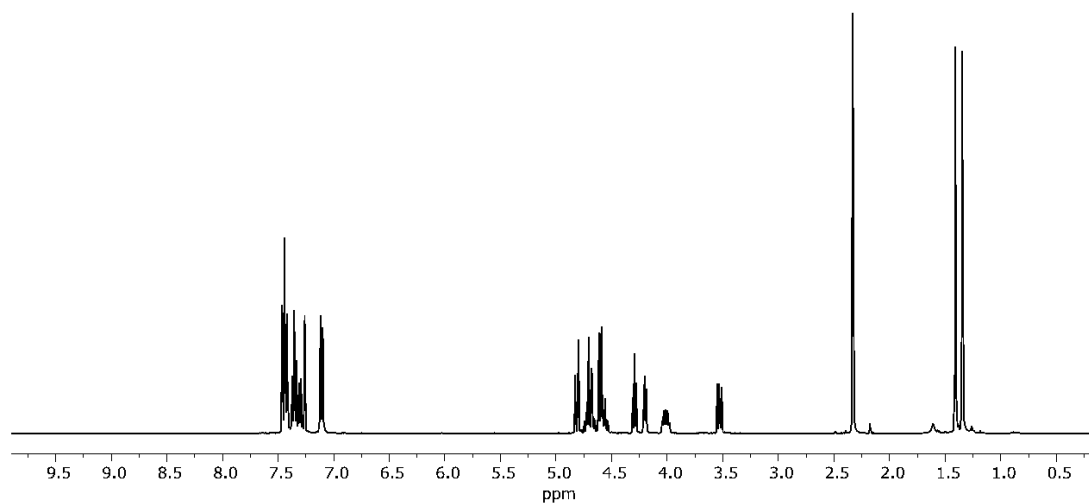
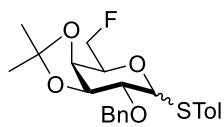


^{13}C NMR (150 MHz, CDCl_3) of **18**.

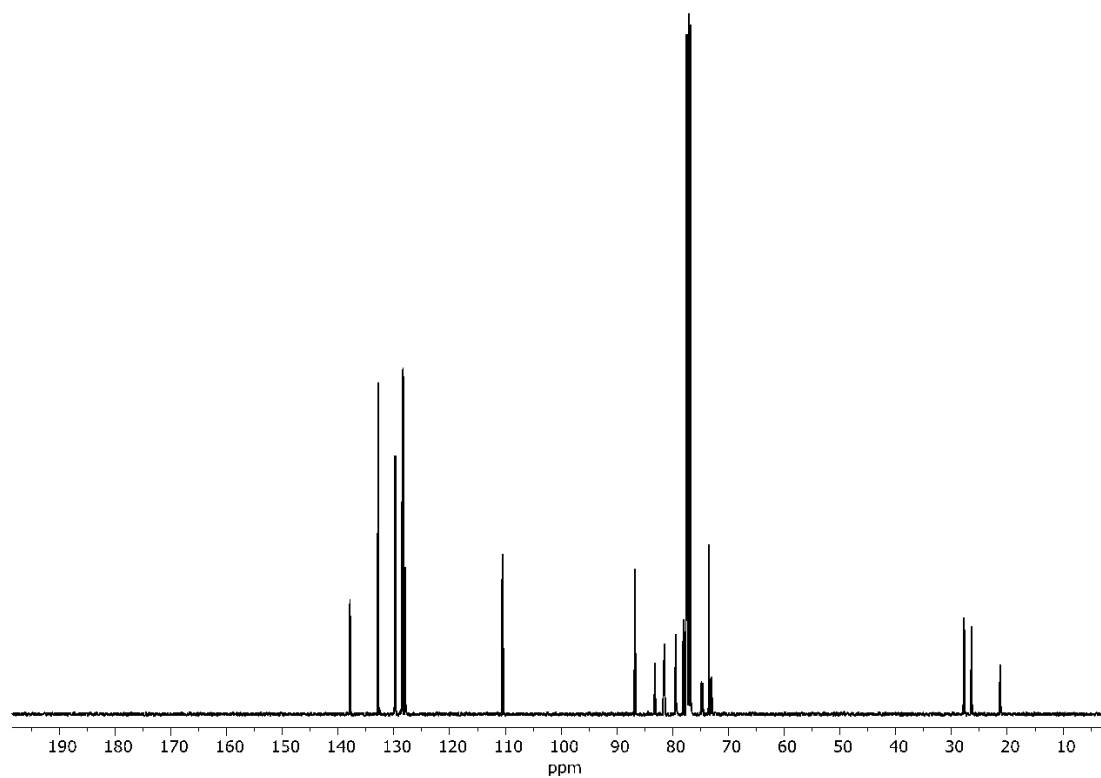


HSQC (CDCl_3) of **18**.

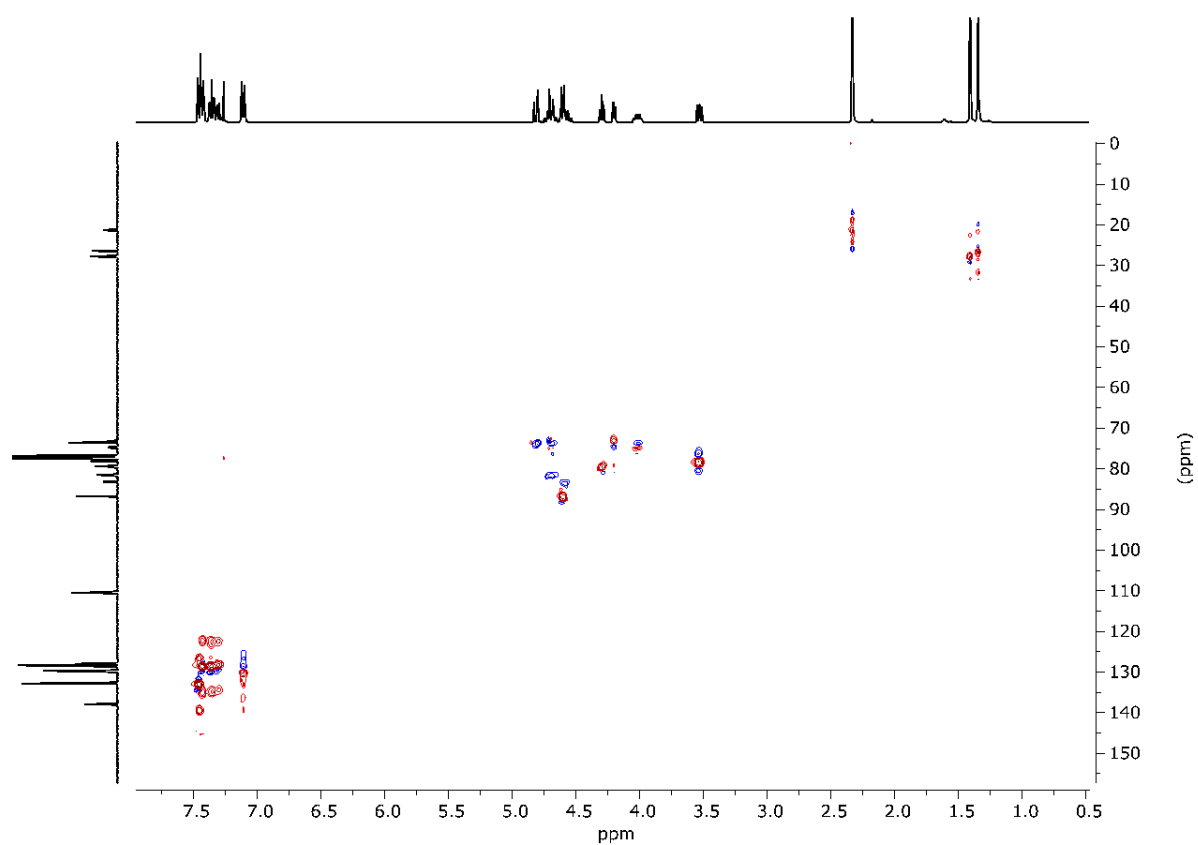
4-Methylphenyl-2-O-benzyl-3,4-O-isopropylidene-6-deoxy-6-fluoro-1-thio- α/β -D-galactopyranoside (26)



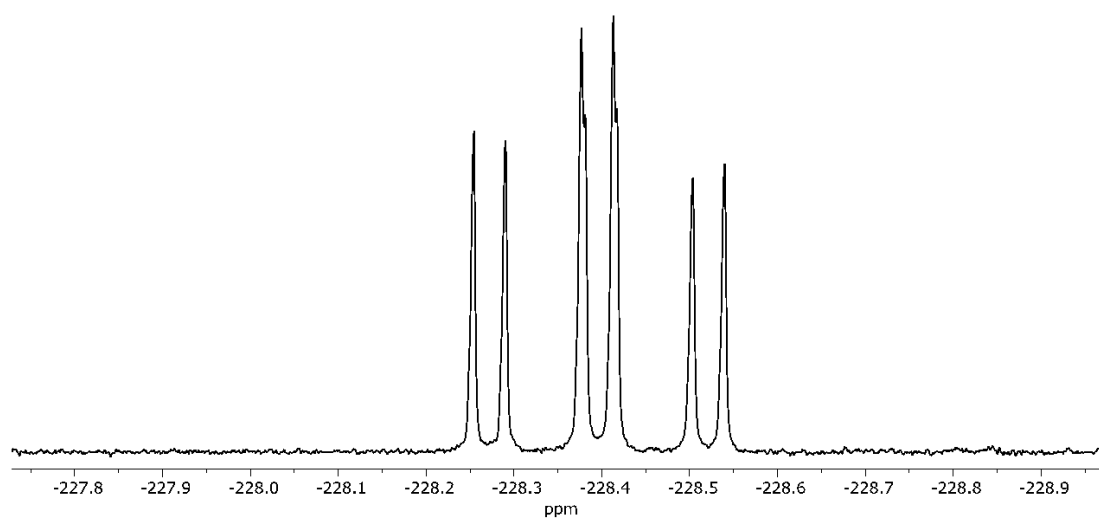
^1H NMR (400 MHz, CDCl_3) of **26**.



^{13}C NMR (100 MHz, CDCl_3) of **26**.

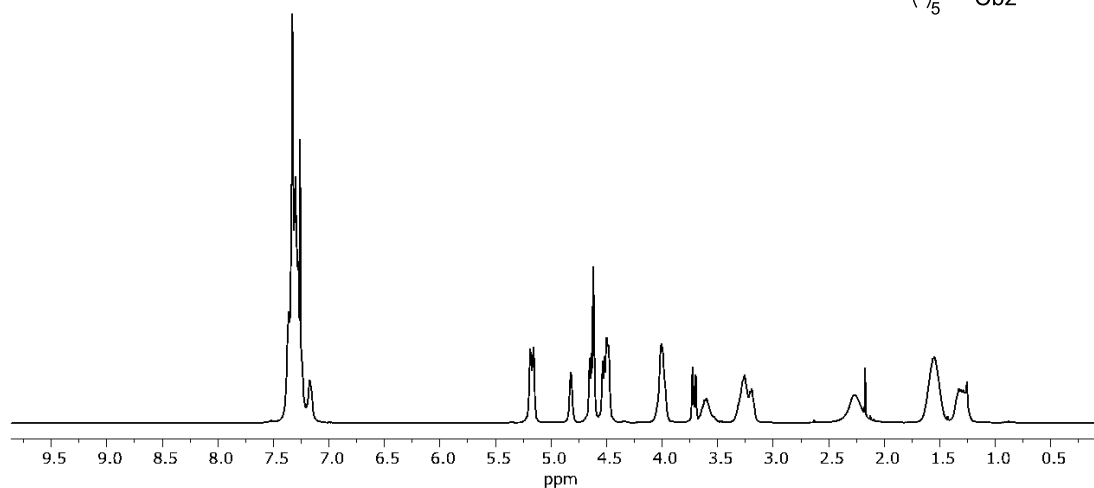
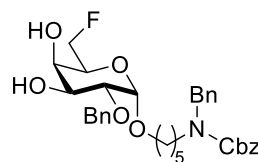


HSQC (CDCl₃) of **26**.

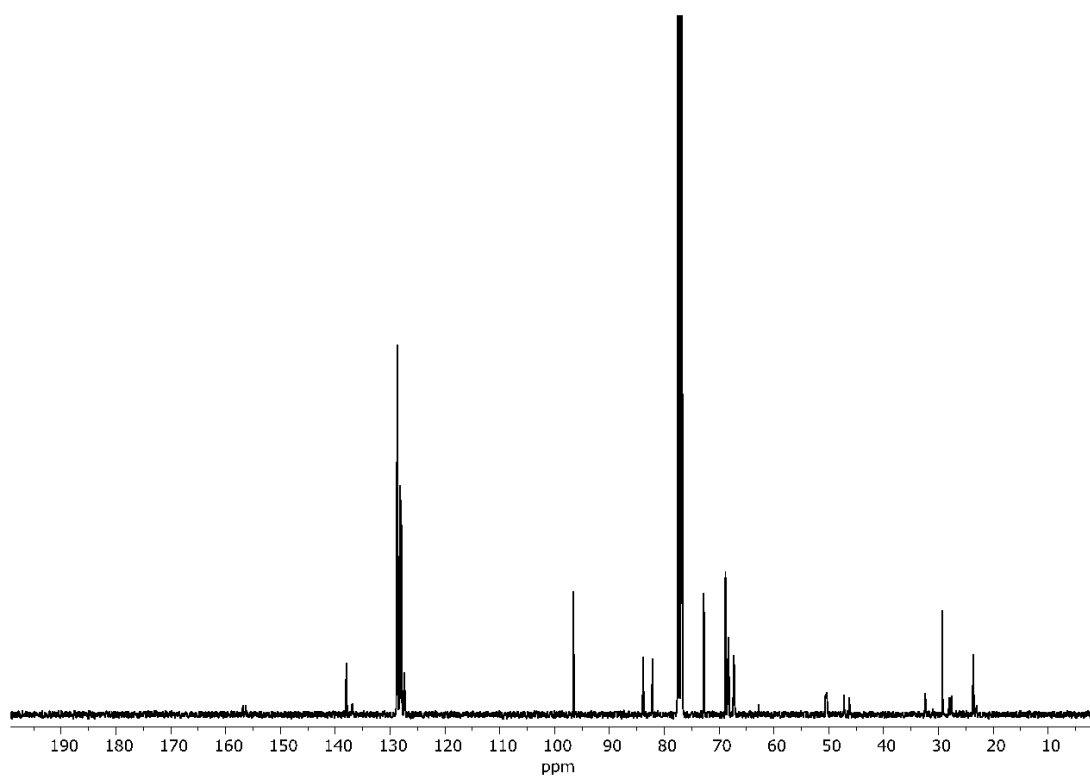


¹⁹F NMR (377 MHz, CDCl₃) of **26**.

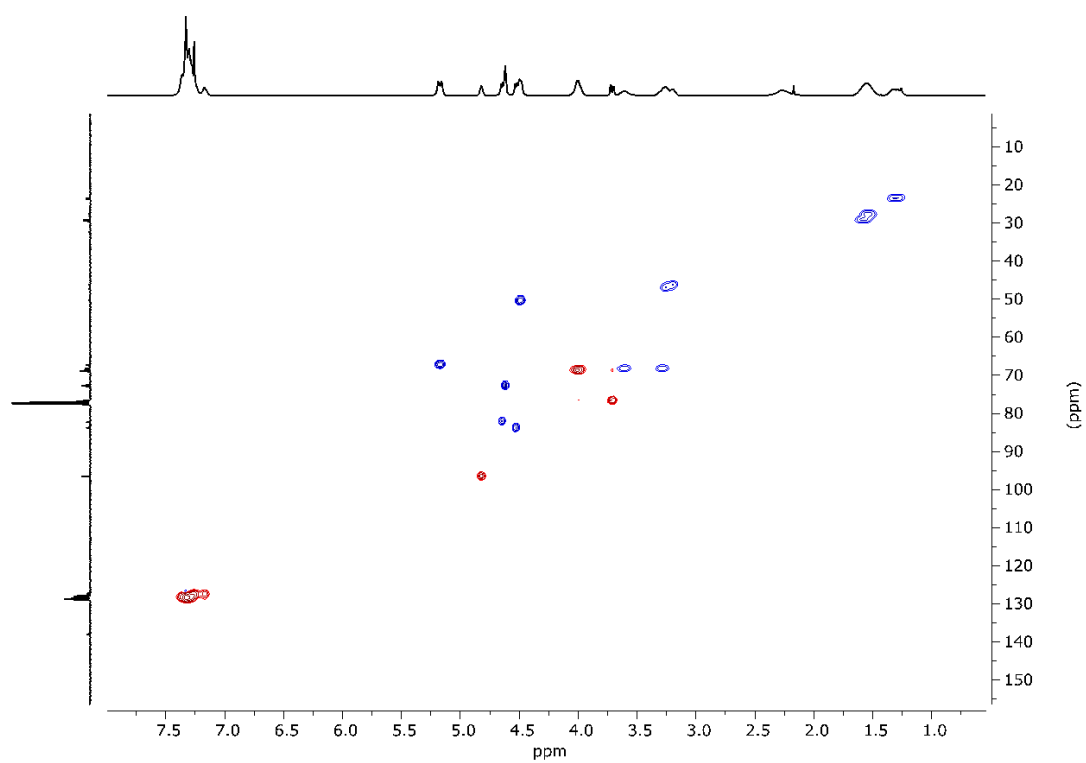
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-2-*O*-benzyl-6-deoxy-6-fluoro- α -D-galacto-pyranoside (28)**



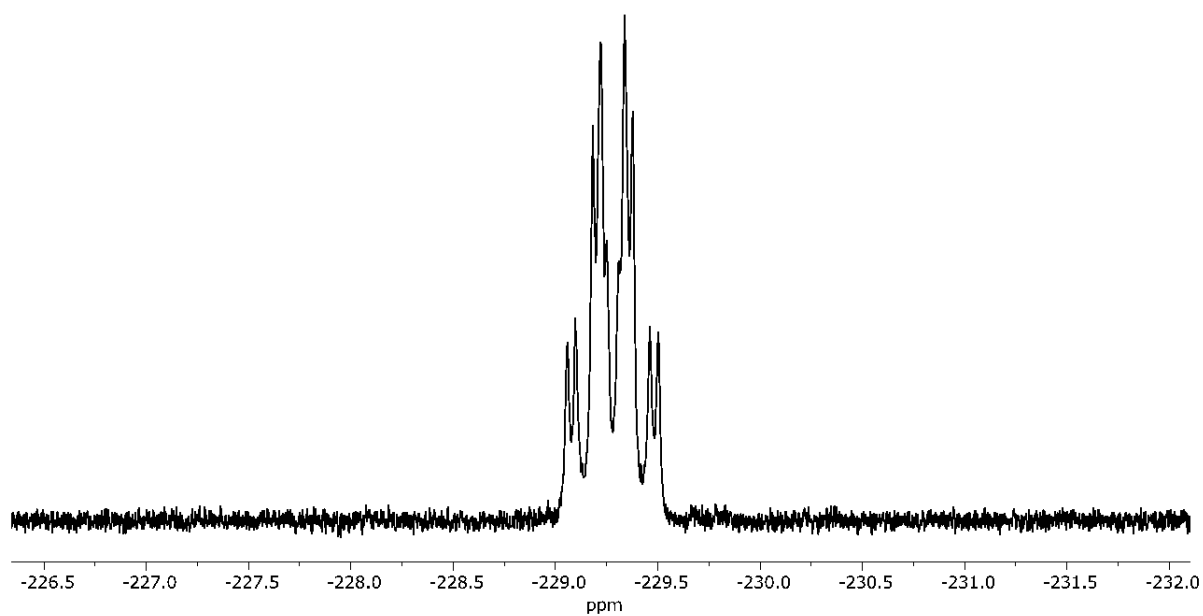
^1H NMR (400 MHz, CDCl_3) of **28**.



^{13}C NMR (100 MHz, CDCl_3) of **28**.

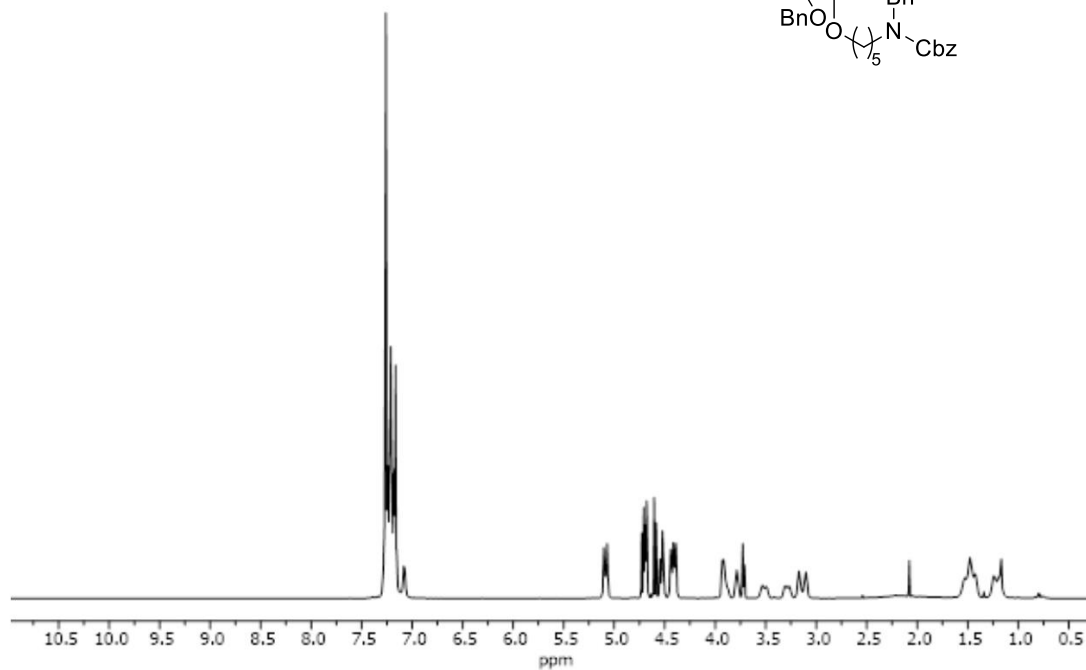
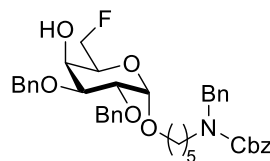


HSQC (CDCl₃) of **28**.

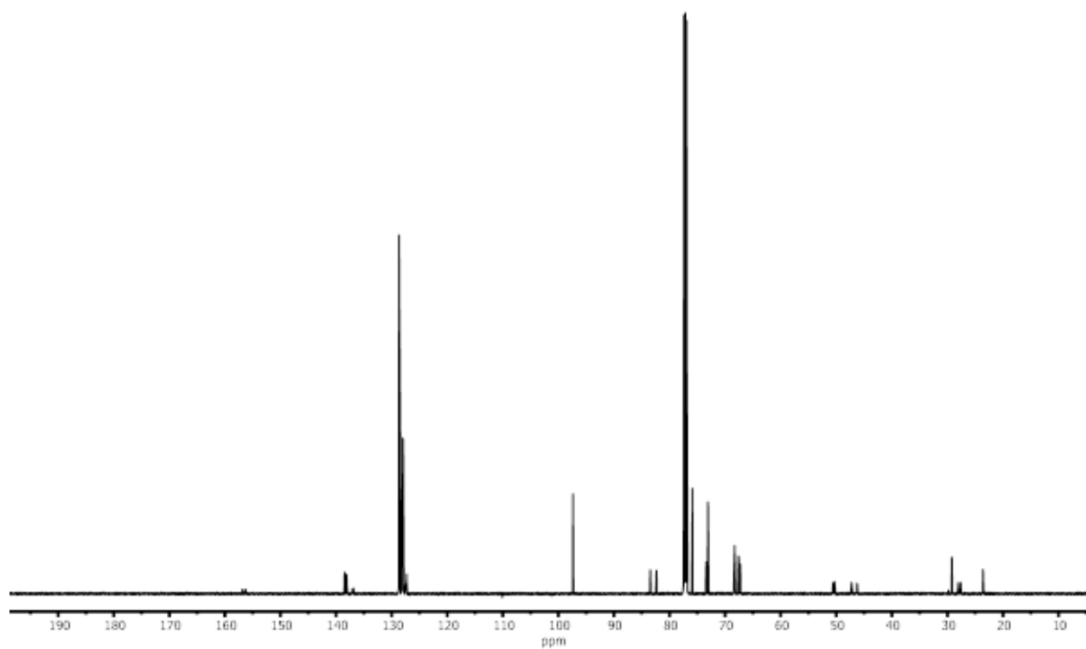


¹⁹F NMR (377 MHz, CDCl₃) of **28**.

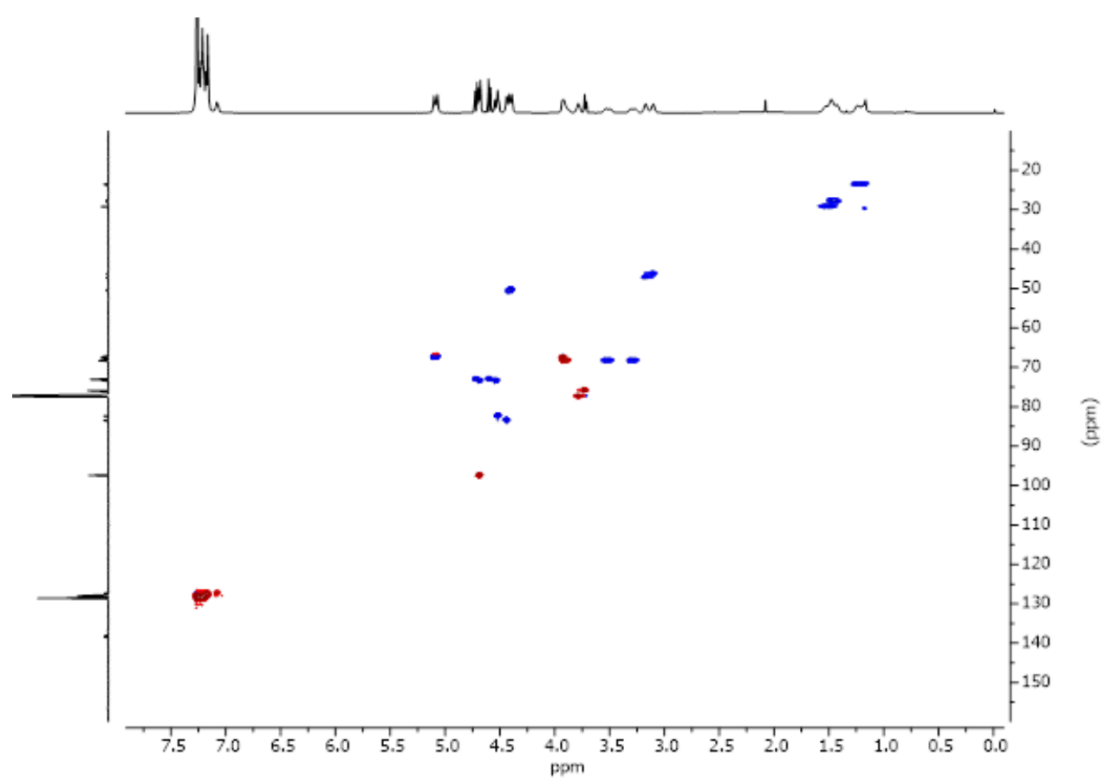
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-2,3-di-*O*-benzyl-6-deoxy-6-fluoro- α -D-galactopyranoside (19)**



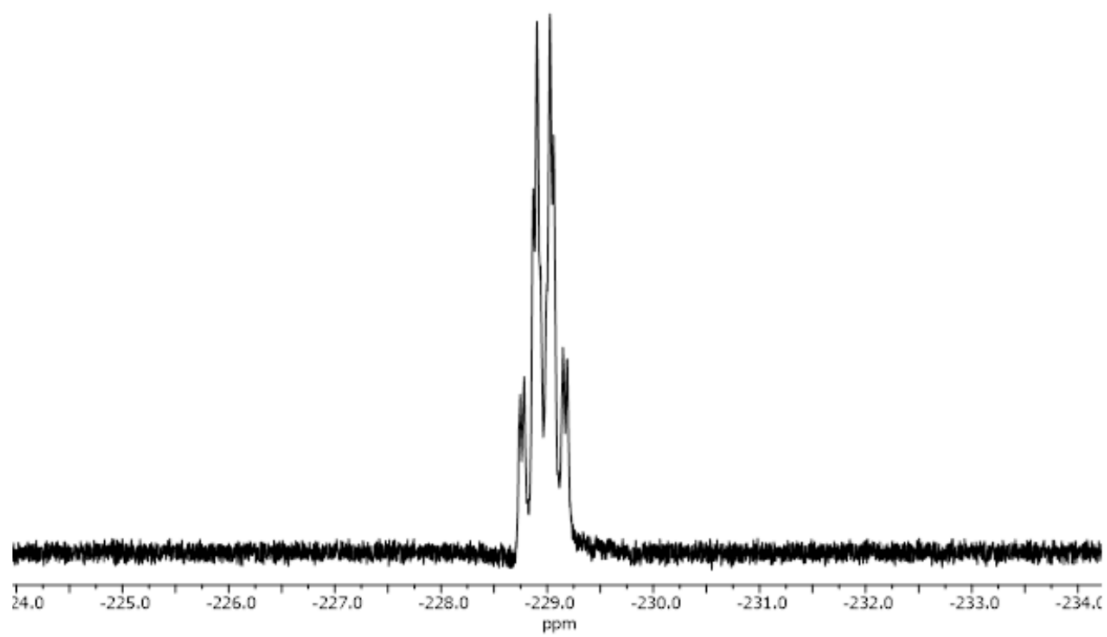
^1H NMR (600 MHz, CDCl_3) of **19**.



^{13}C NMR (150 MHz, CDCl_3) of **19**.

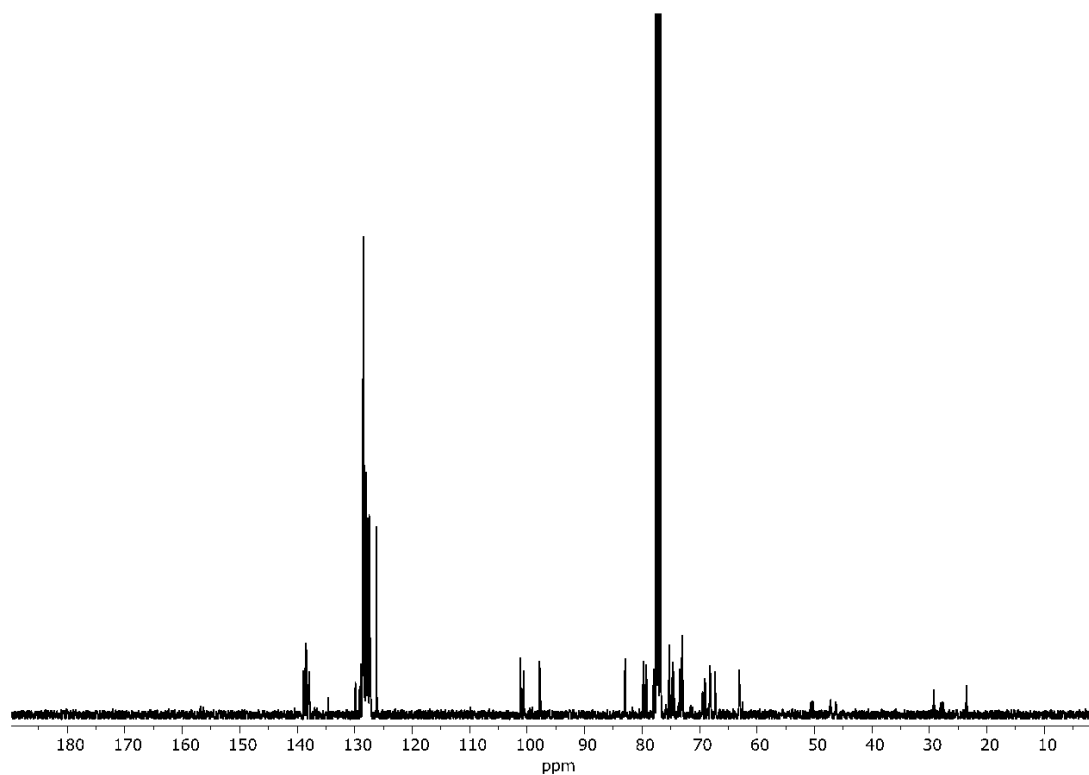
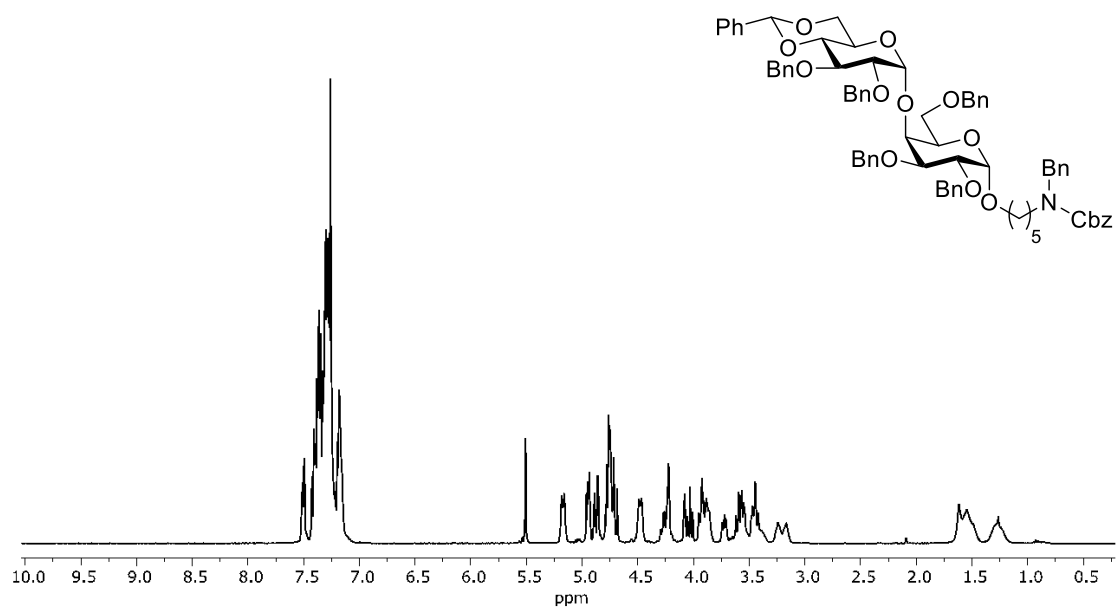


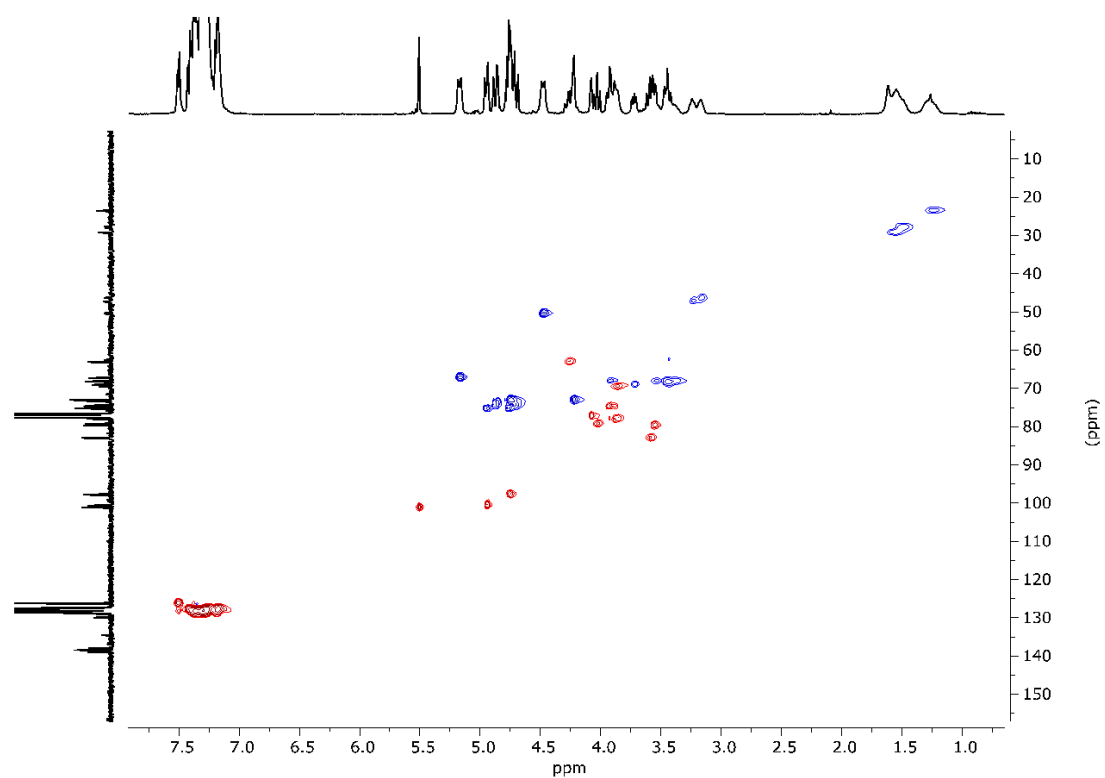
HSQC (CDCl₃) of **19**.



¹⁹F NMR (377 MHz, CDCl₃) of **19**.

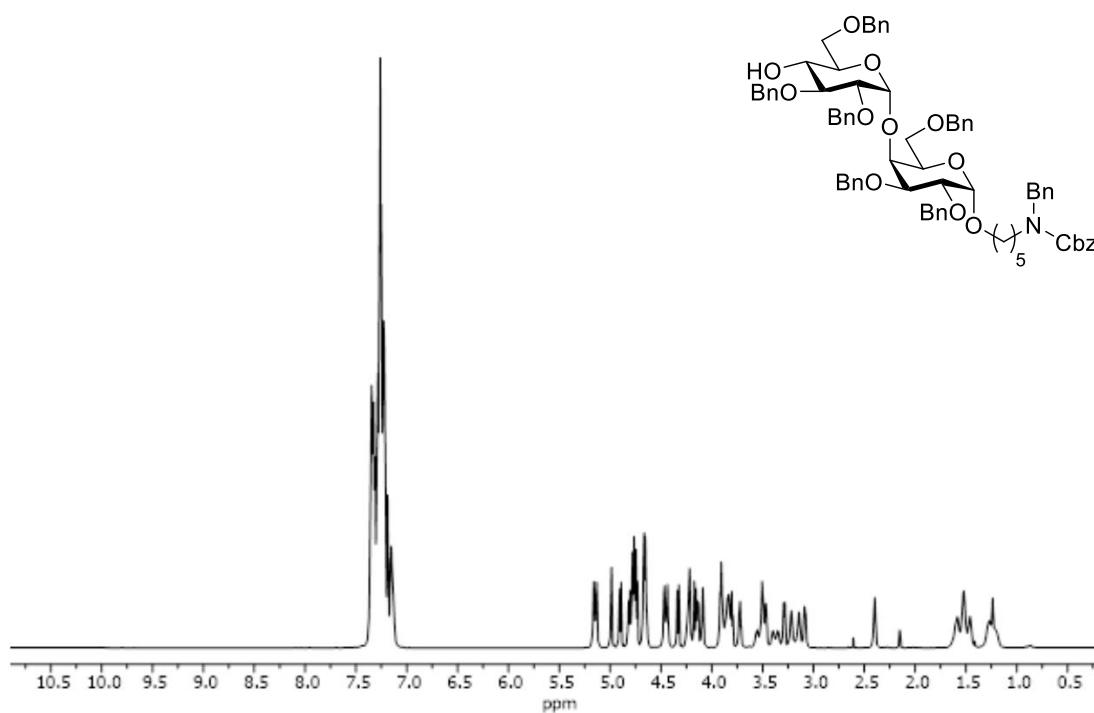
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3-di-*O*-benzyl-4,6-*O*-benzyliden- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (**29**)**



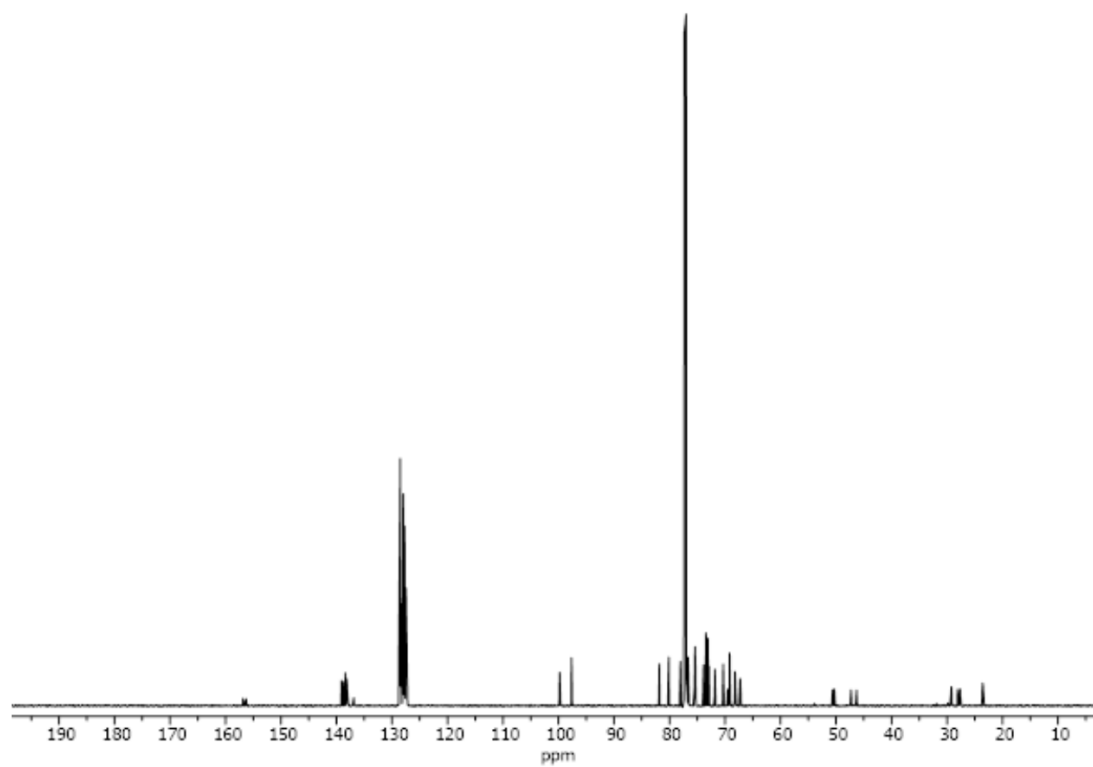


HSQC (CDCl₃) of **29**; Immediate measurement.

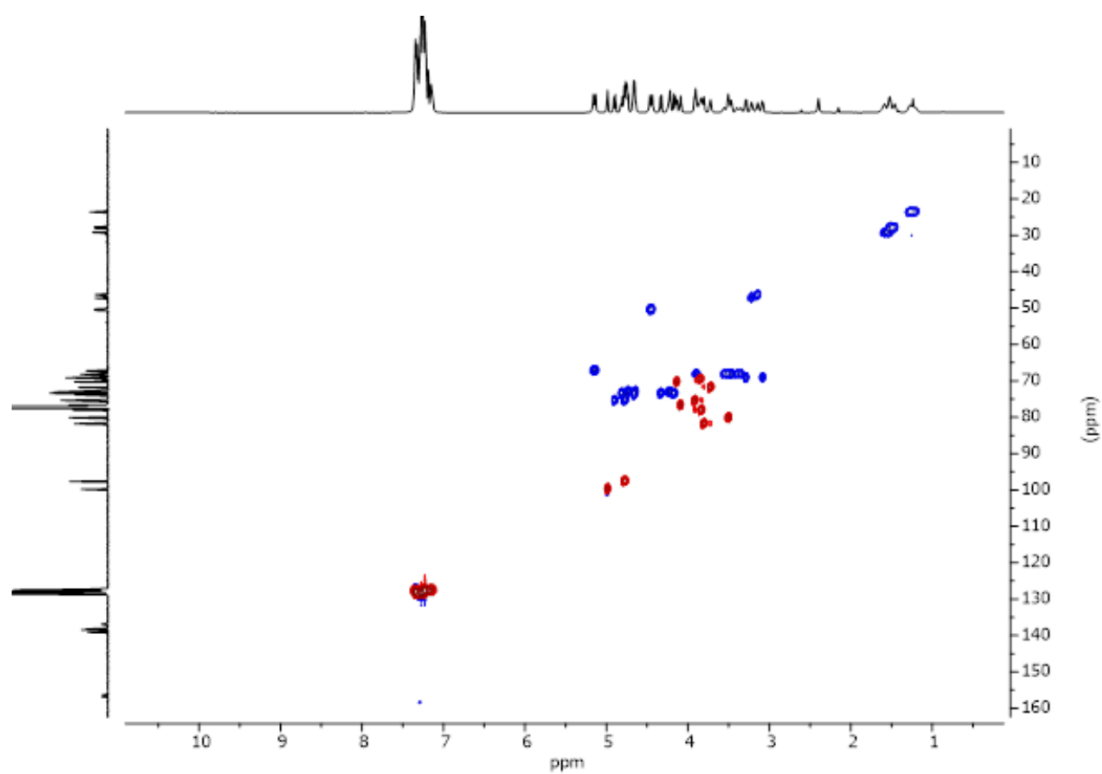
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (**10**)**



¹H NMR (600 MHz, CDCl₃) of **10**.

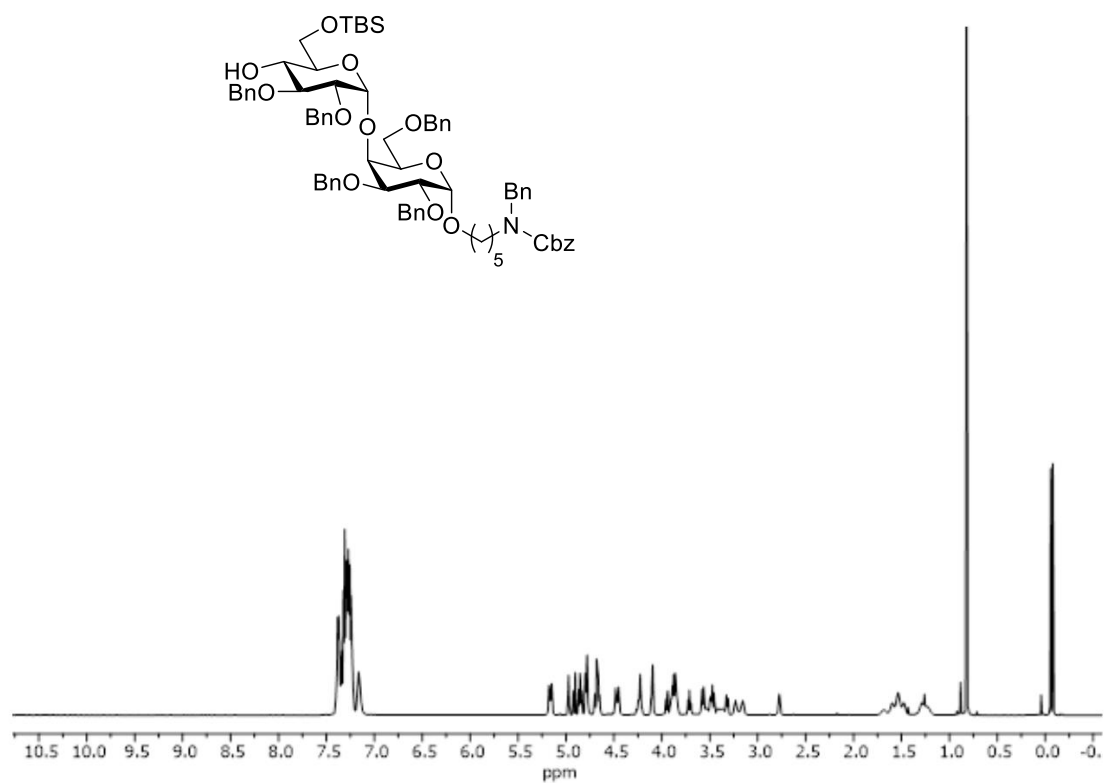


^{13}C NMR (150 MHz, CDCl_3) of 10.

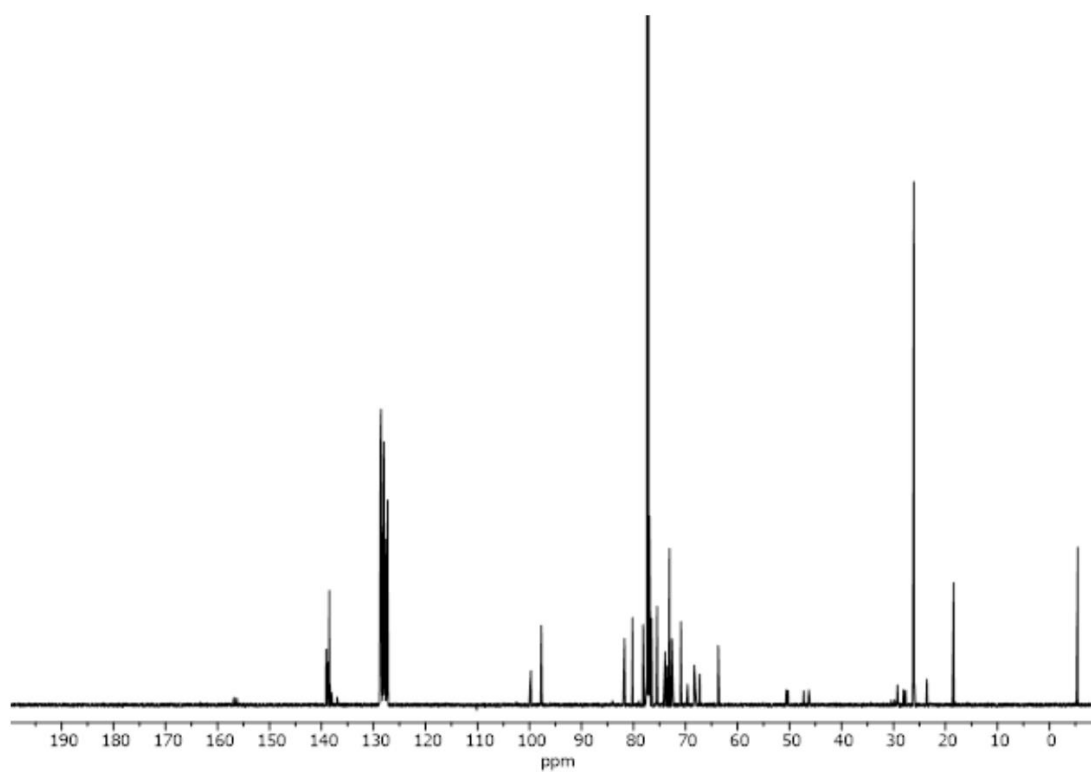


HSQC (CDCl_3) of 10.

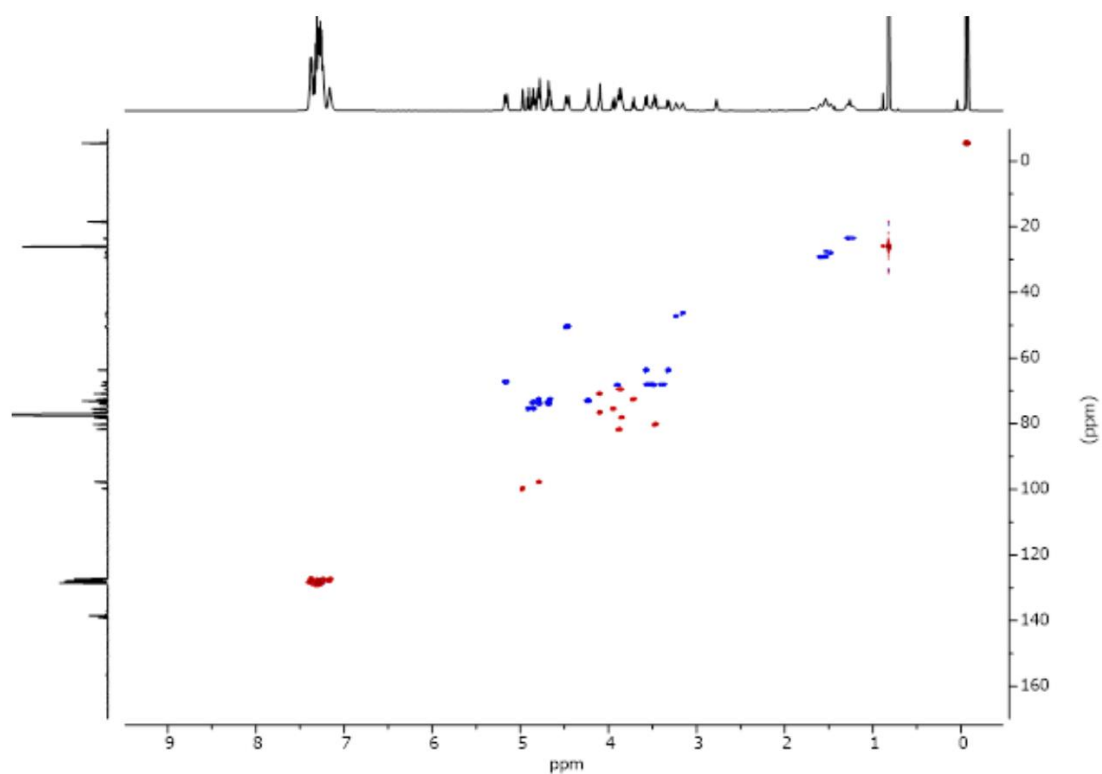
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (11)**



^1H NMR (600 MHz, CDCl_3) of 11.

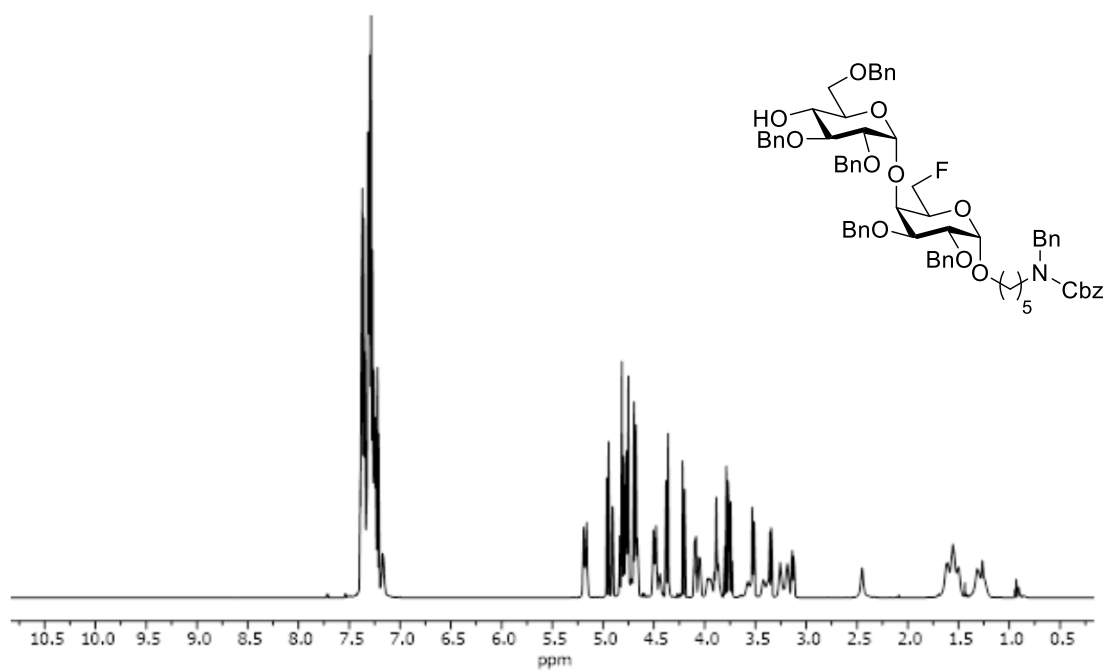


^{13}C NMR (150 MHz, CDCl_3) of 11.

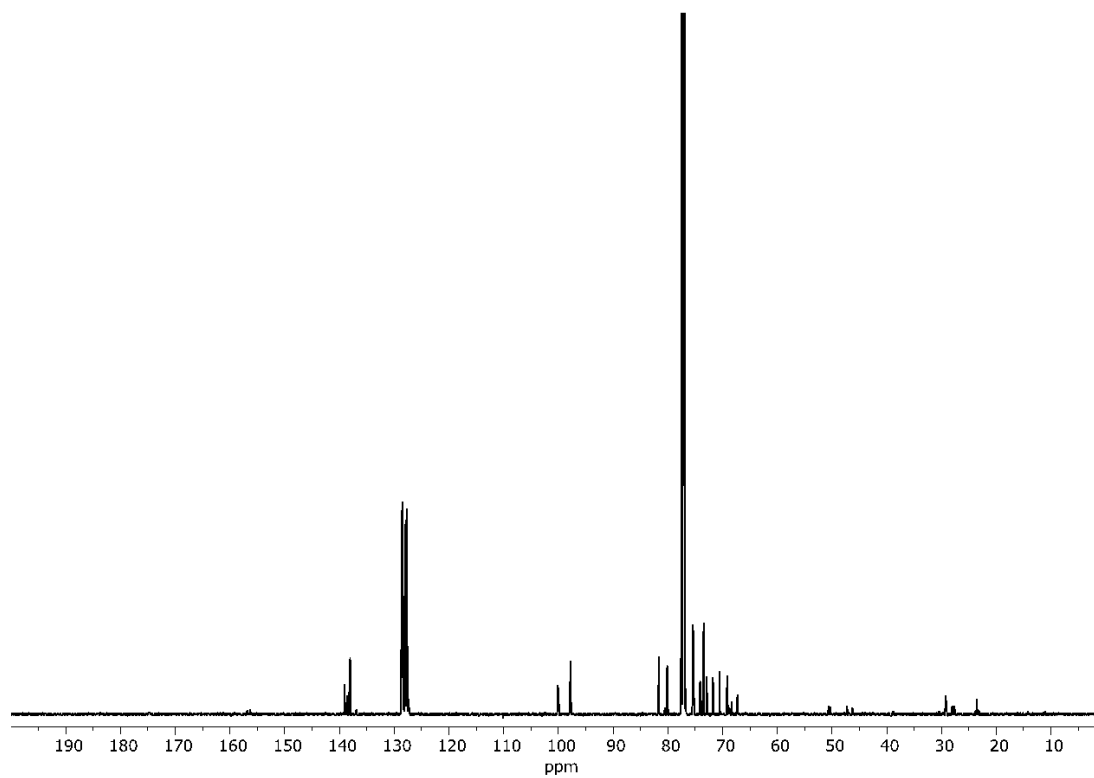


HSQC (CDCl₃) of **11**.

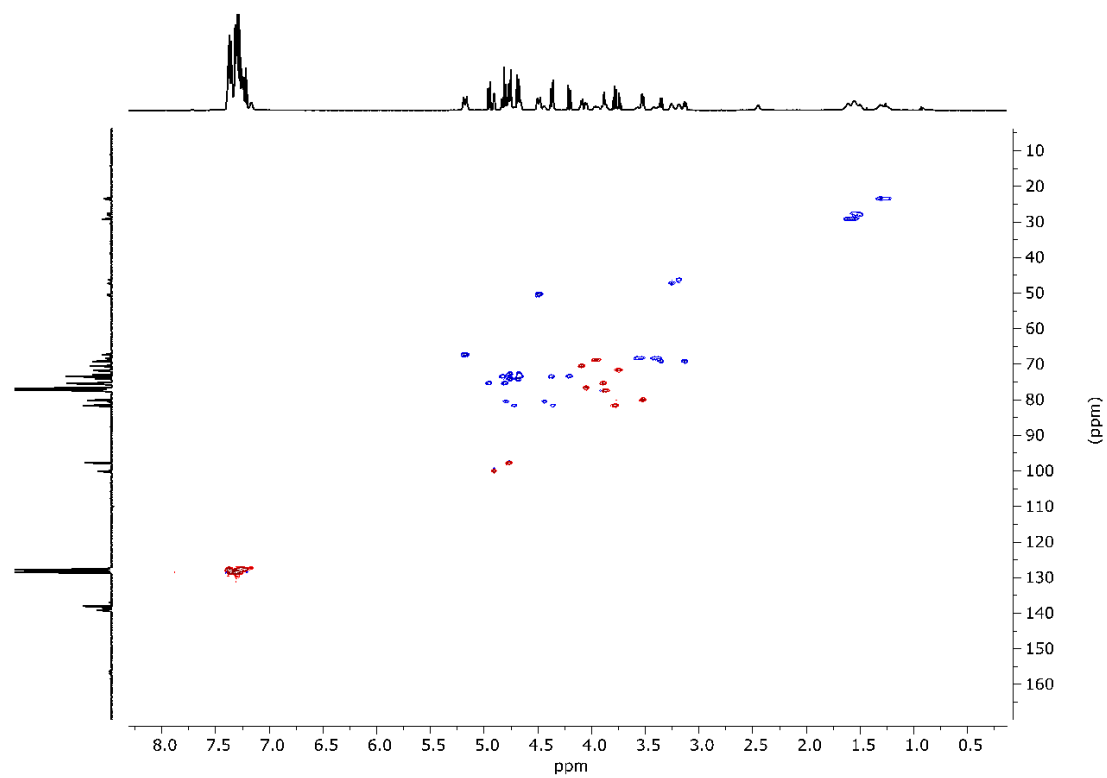
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-benzyl-6-deoxy-6-fluoro- α -D-galactopyranoside (**12**)**



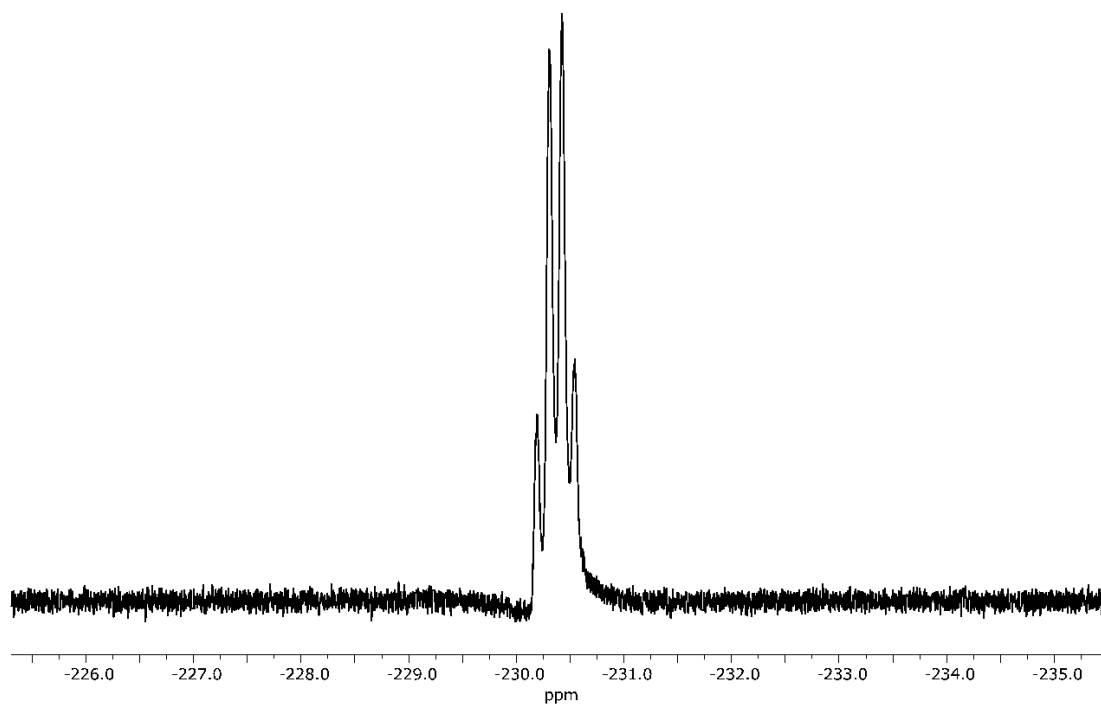
¹H NMR (600 MHz, CDCl₃) of **12**.



^{13}C NMR (150 MHz, CDCl_3) of **12**.

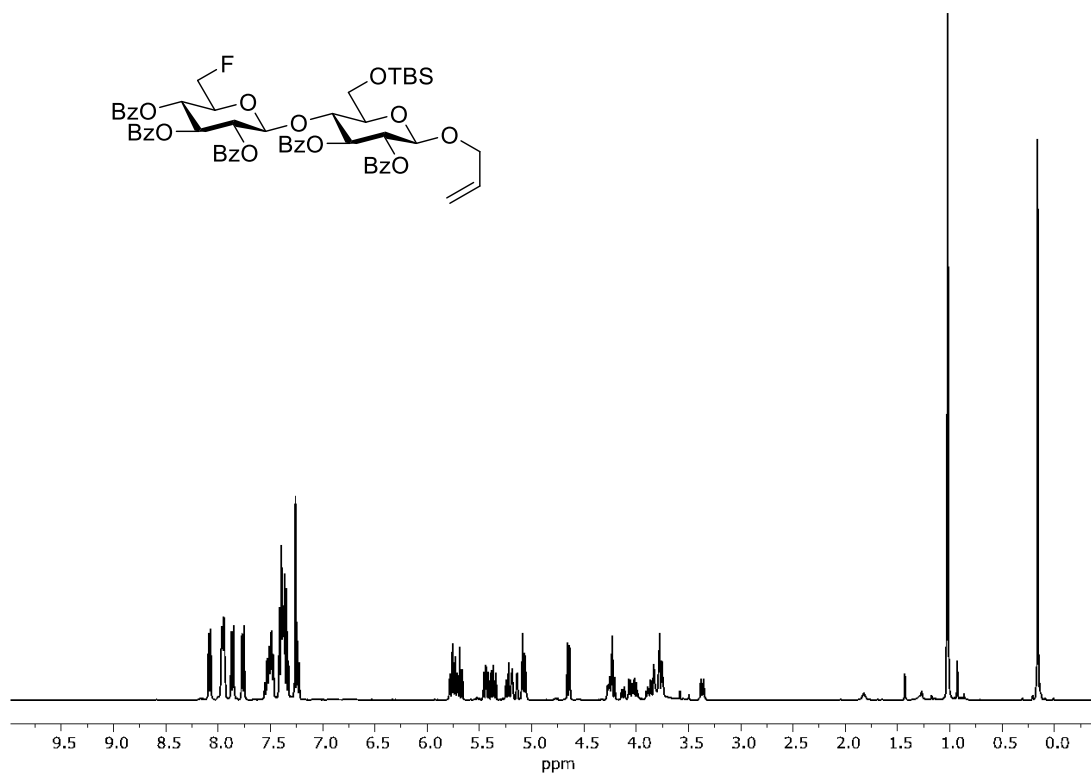
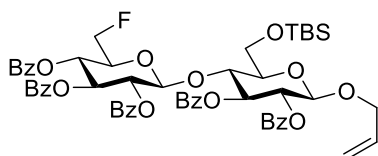


HSQC (CDCl_3) of **12**.

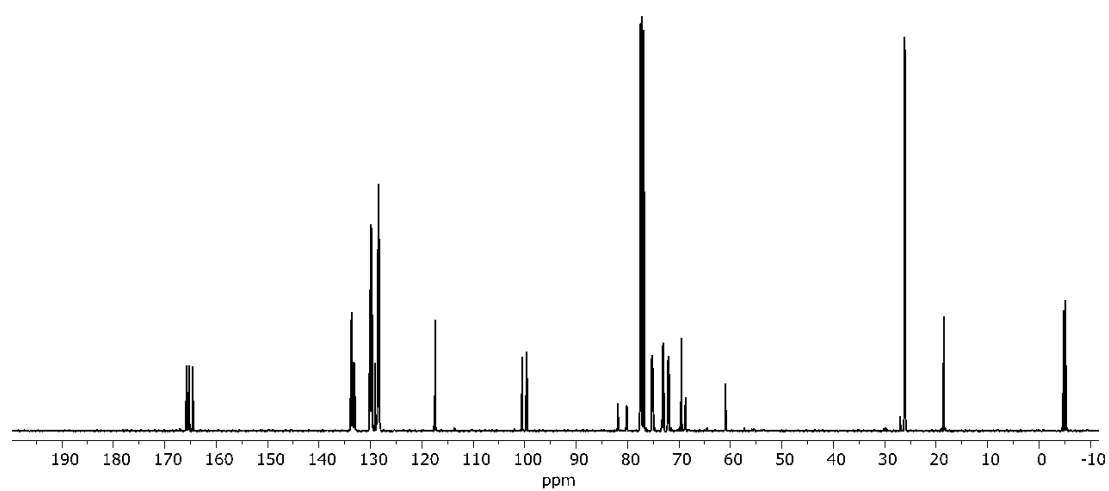


^{19}F NMR (377 MHz, CDCl_3) of **12**.

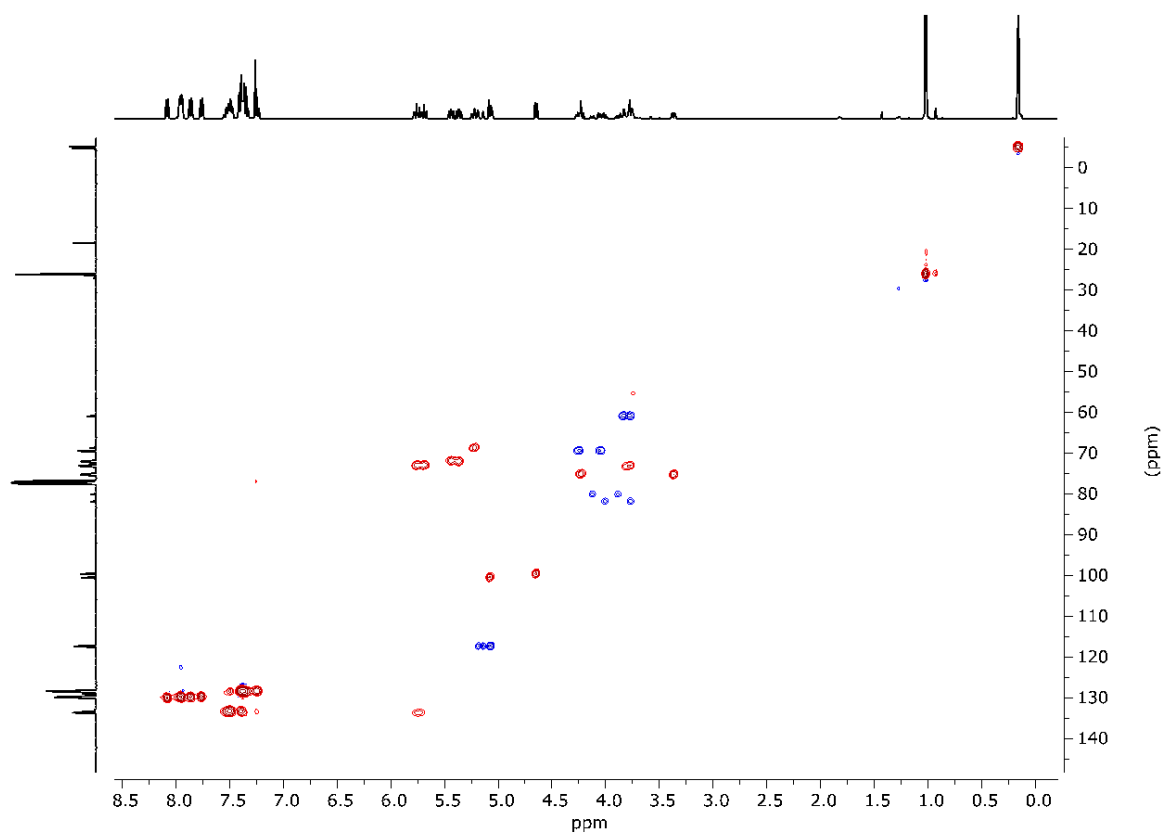
Allyl-(2,3,4-tri-*O*-benzoyl-6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl- β -D-glucopyranoside (**31**)



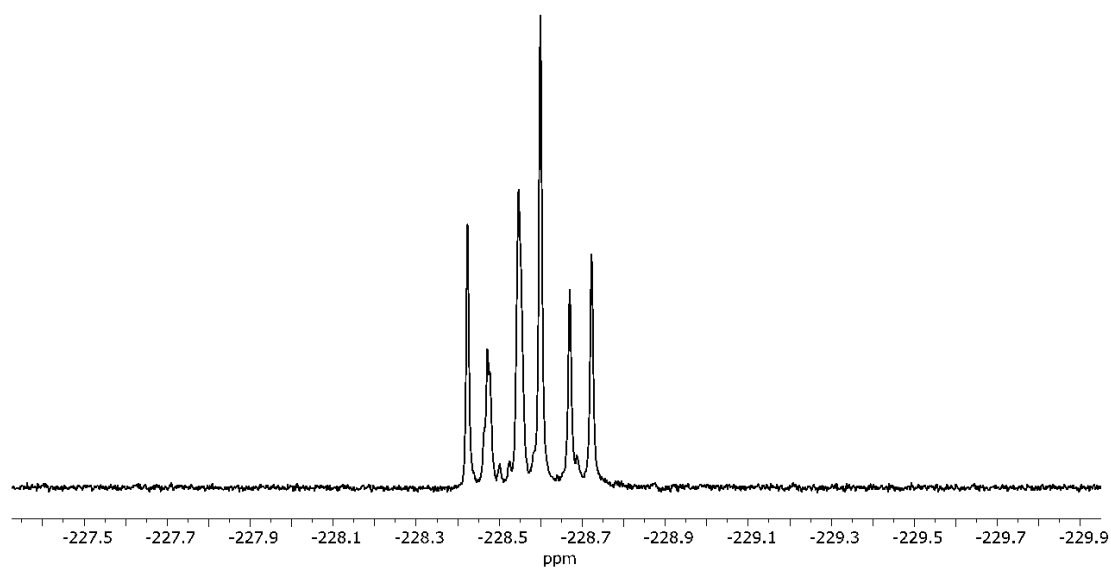
^1H NMR (400 MHz, CDCl_3) of **31**.



^{13}C NMR (100 MHz, CDCl_3) of **31**.

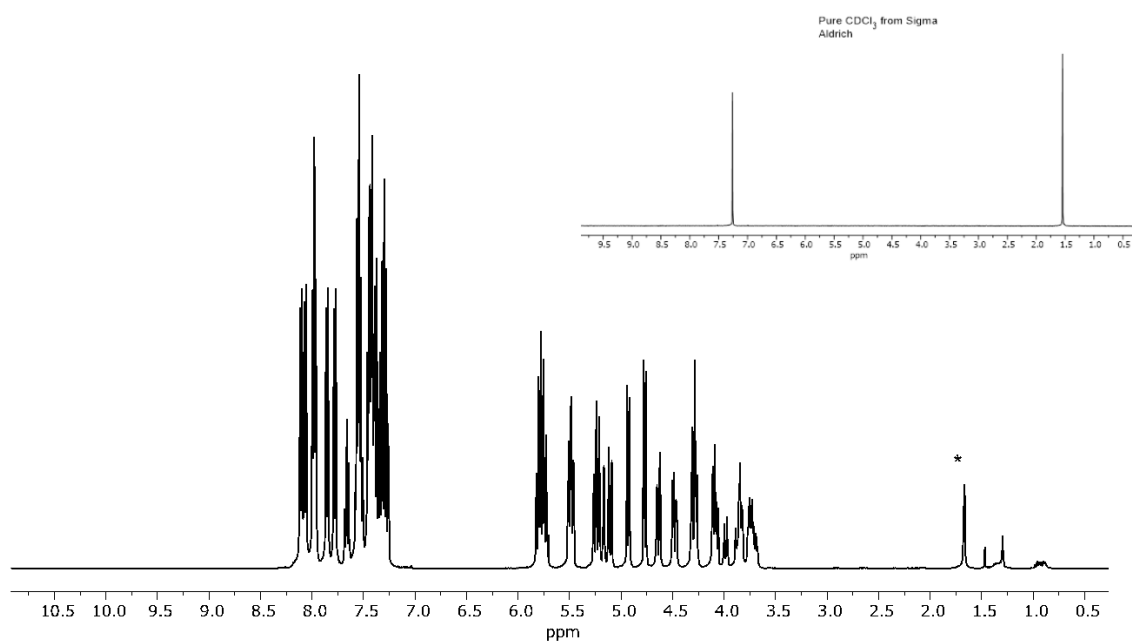
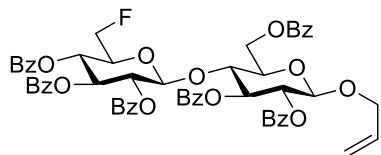


HSQC (CDCl_3) of **31**.

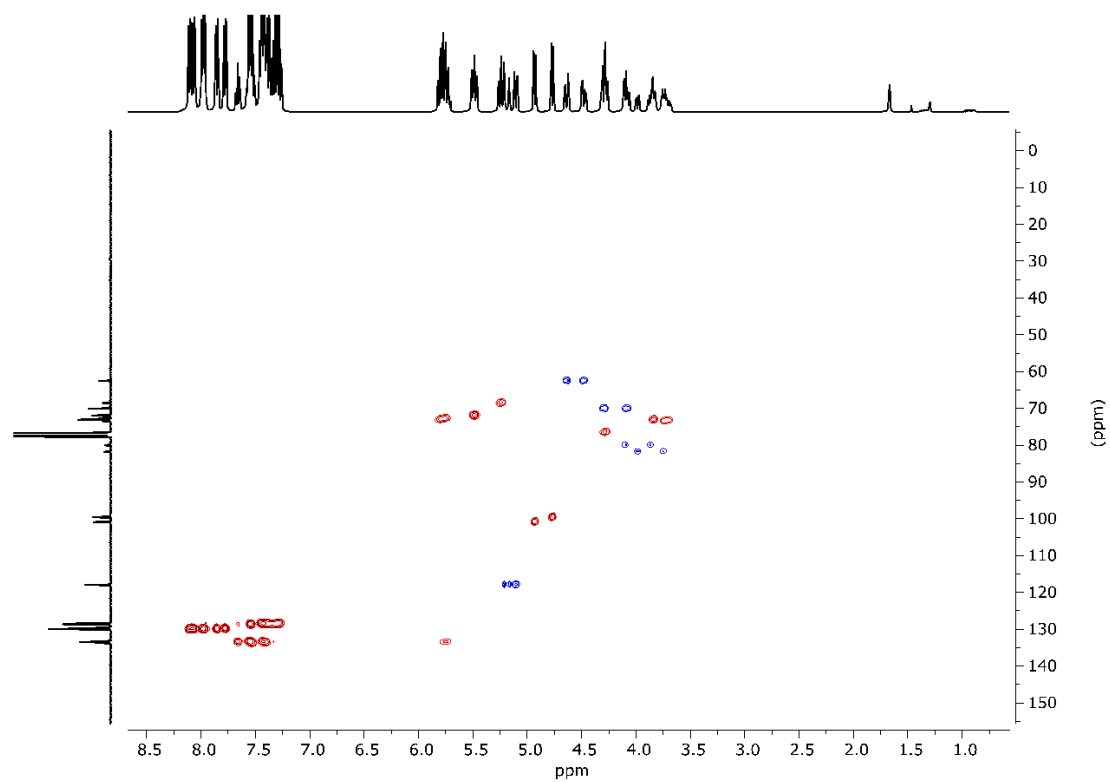
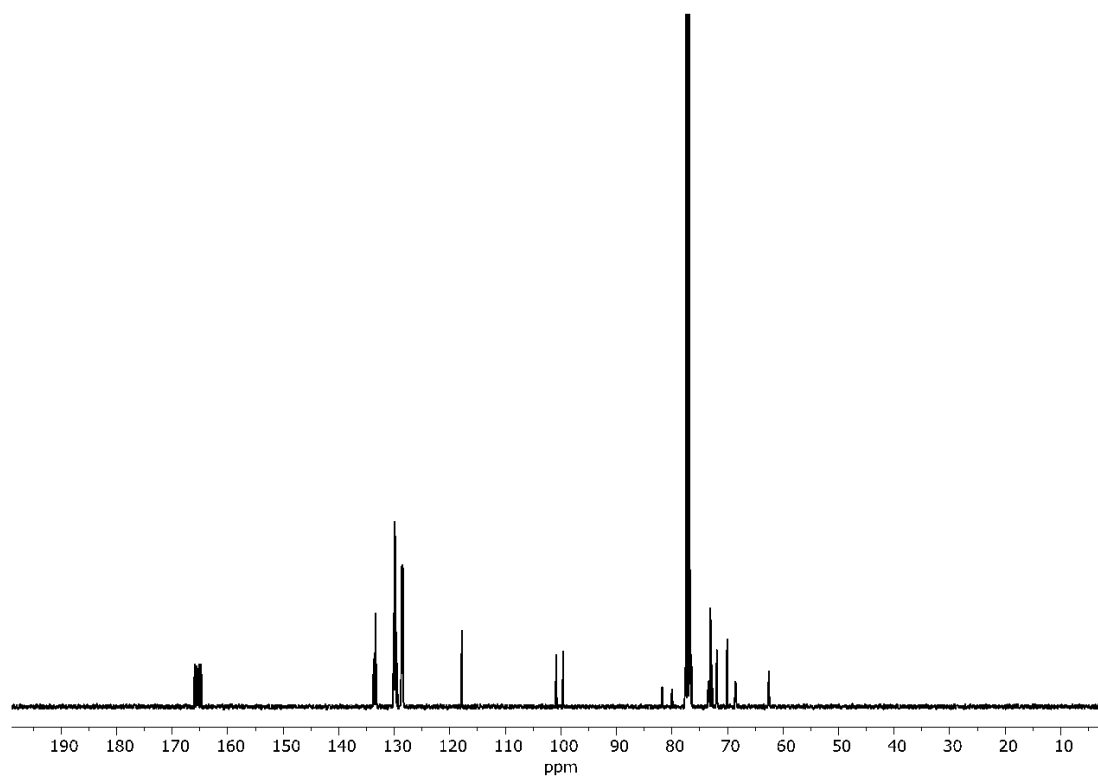


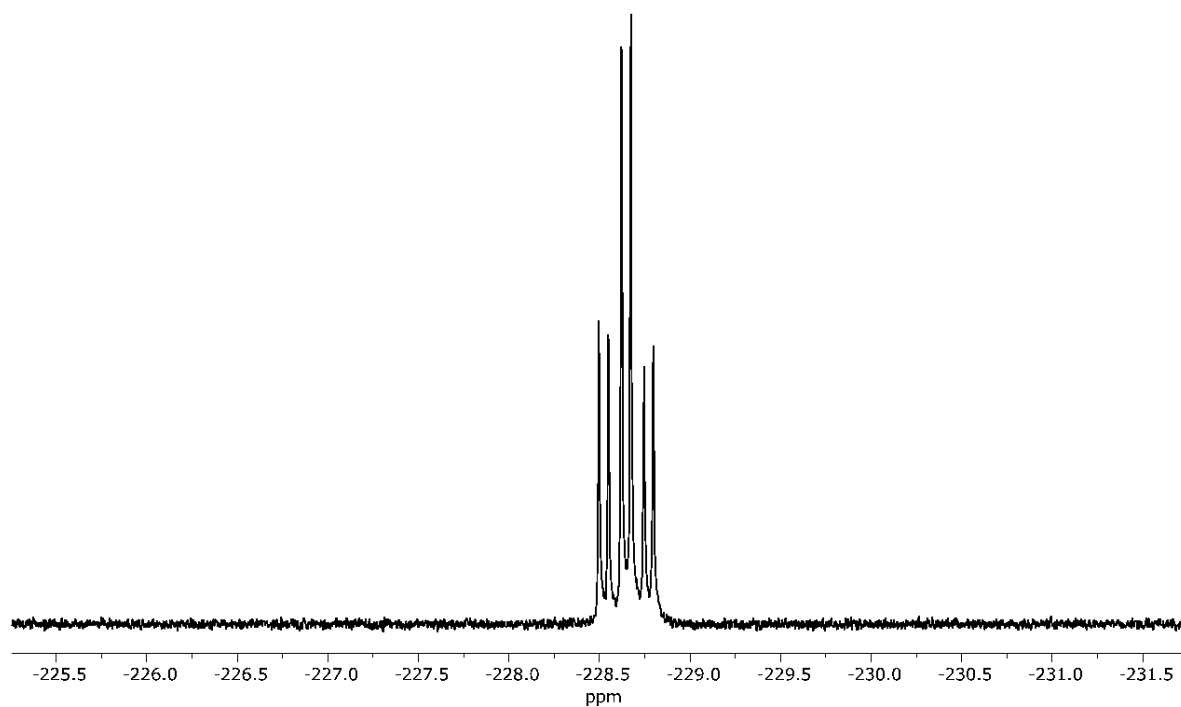
^{19}F NMR (377 MHz, CDCl_3) of **31**.

Allyl-(2,3,4-tri-*O*-benzoyl 6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzoyl- β -D-glucopyranoside (32**)**



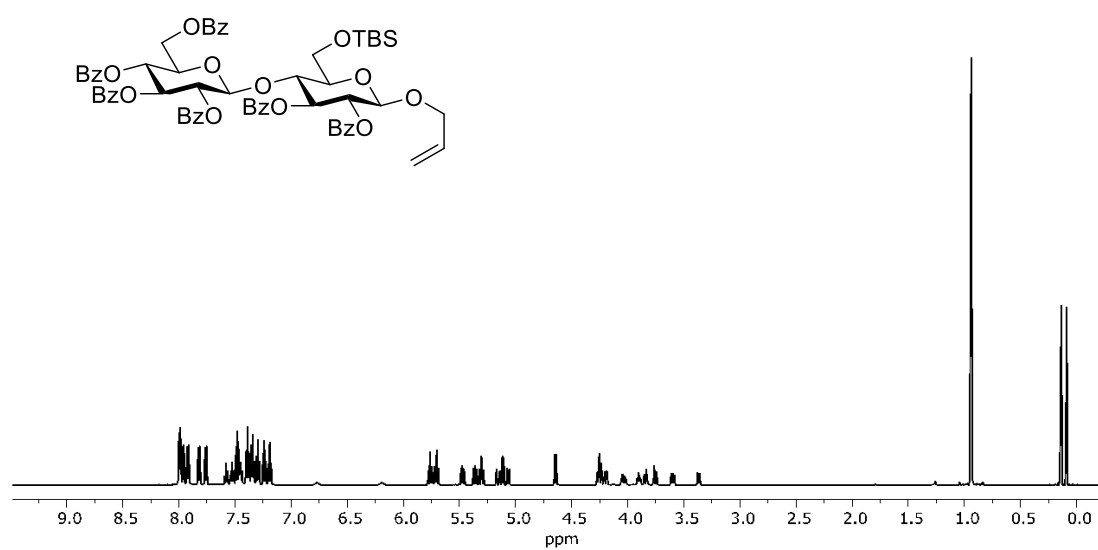
^1H NMR (400 MHz, CDCl_3) of **32**. *Water impurity from CDCl_3 solvent.



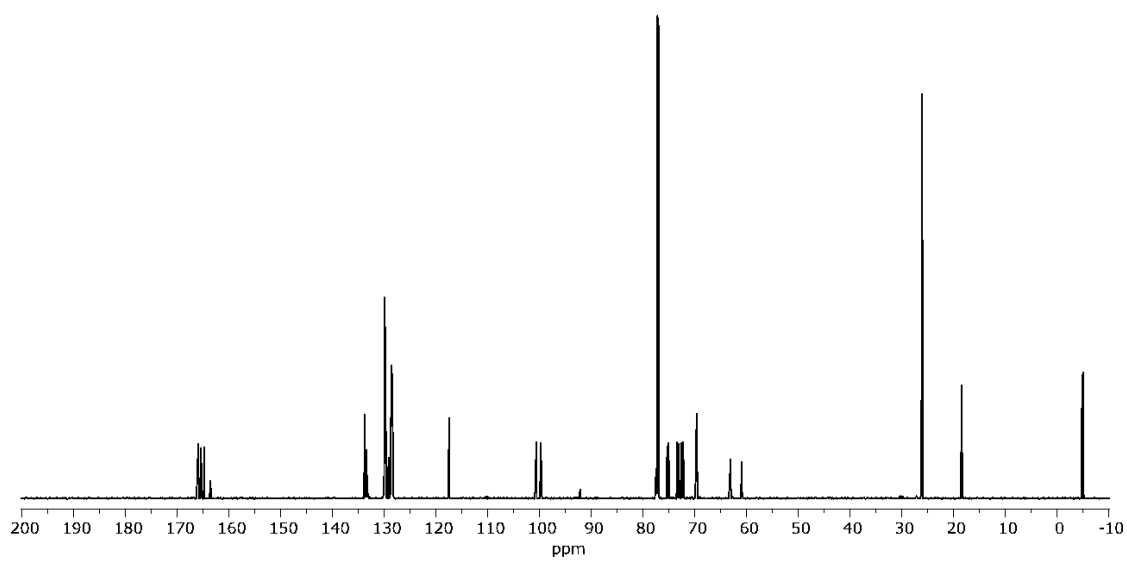


^{19}F NMR (377 MHz, CDCl_3) of **32**.

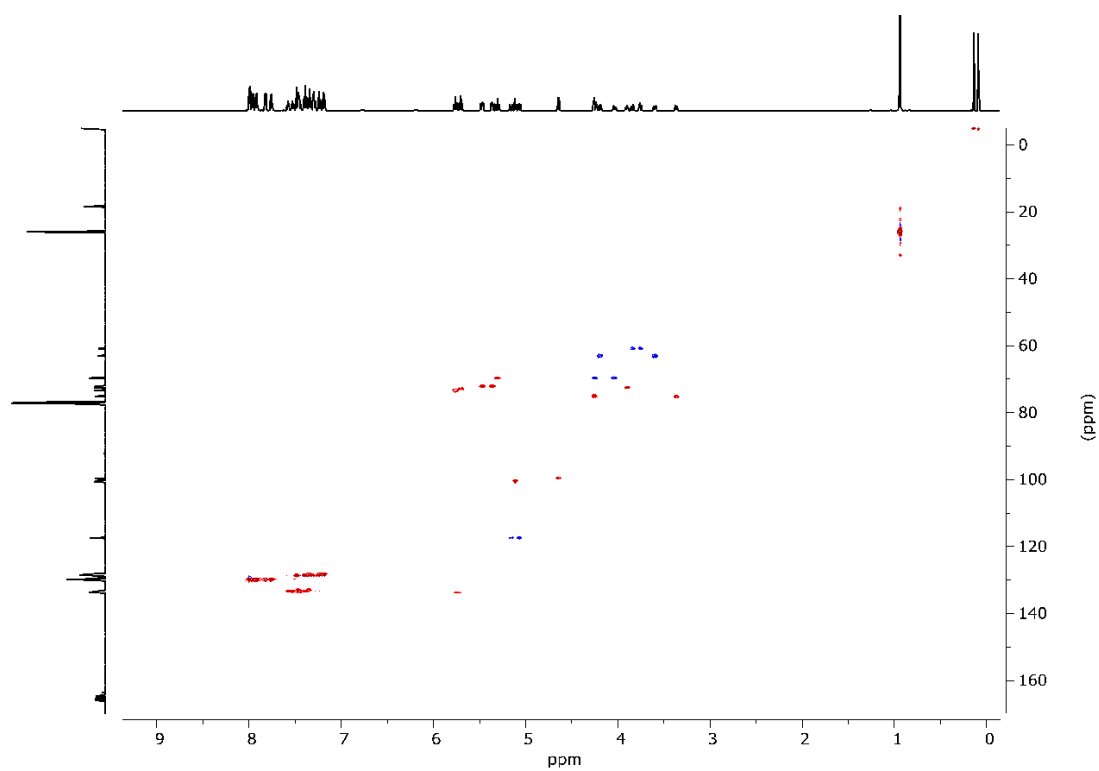
Allyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-6-*O*-tert-butyldimethylsilyl- β -D-glucopyranoside (34**)**



^1H NMR (600 MHz, CDCl_3) of **34**.

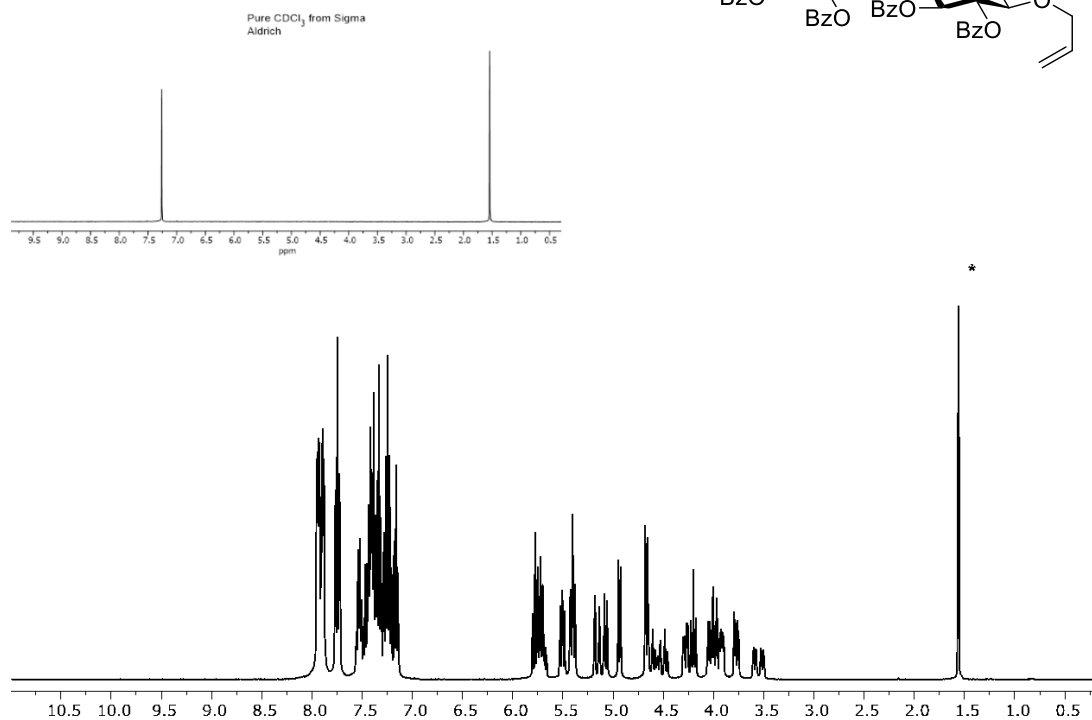
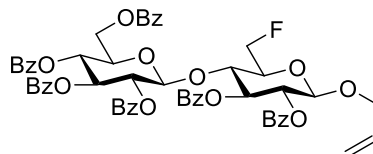


^{13}C NMR (150 MHz, CDCl_3) of **34**.

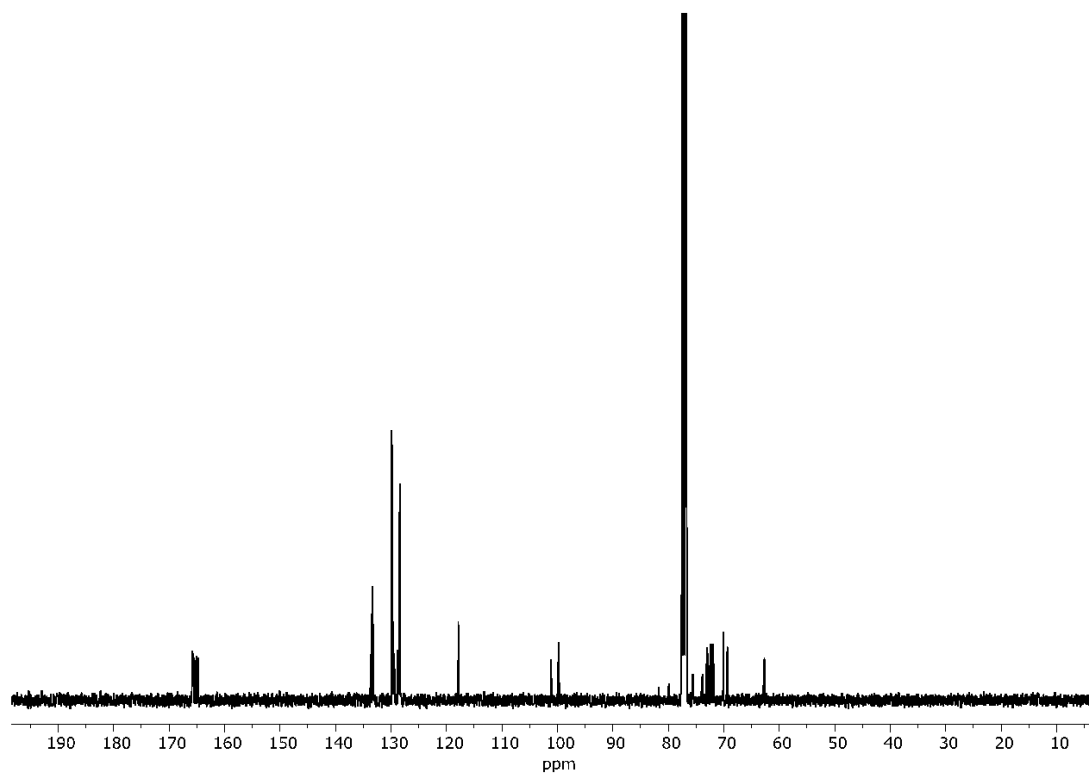


HSQC (CDCl_3) of **34**.

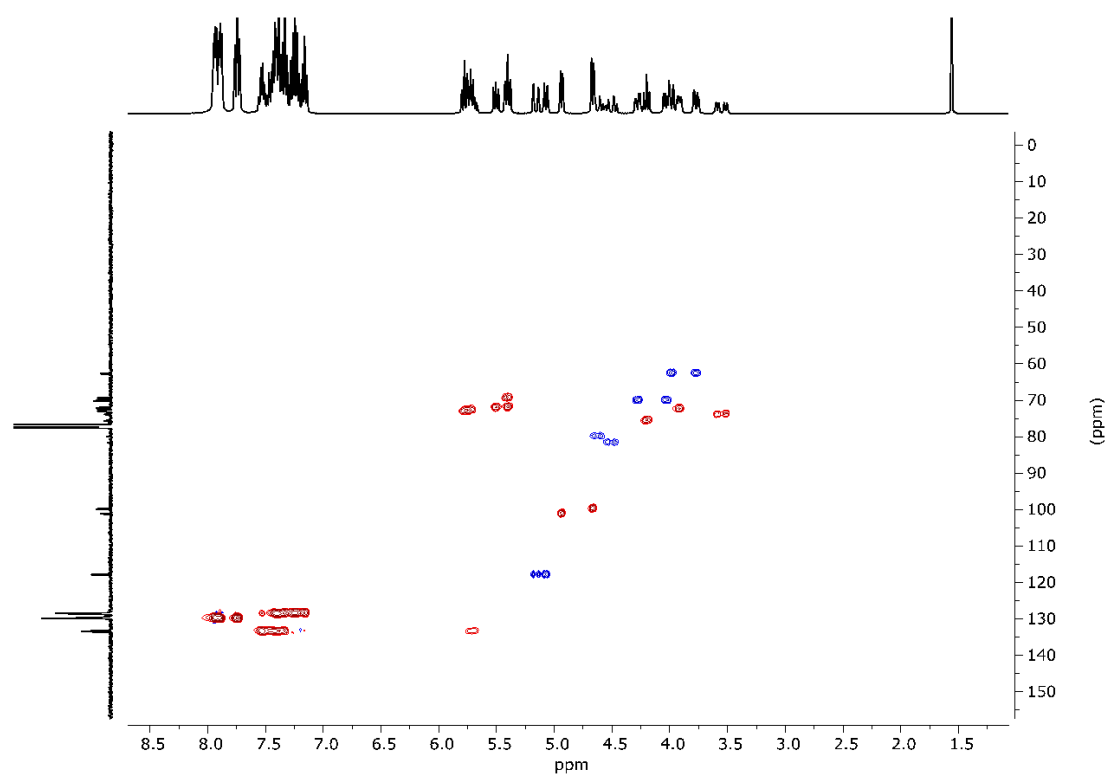
Allyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-benzoyl-6-deoxy-6-fluoro- β -D-glucopyranoside (36)



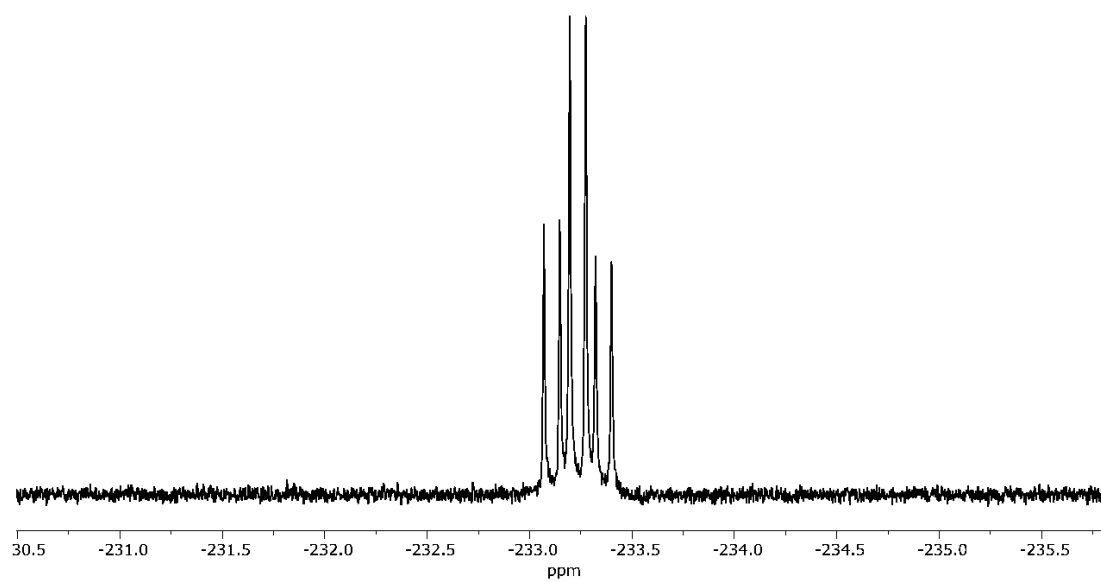
^1H NMR (400 MHz, CDCl_3) of **36**. *Water impurity from CDCl_3 solvent.



^{13}C NMR (100 MHz, CDCl_3) of **36**.

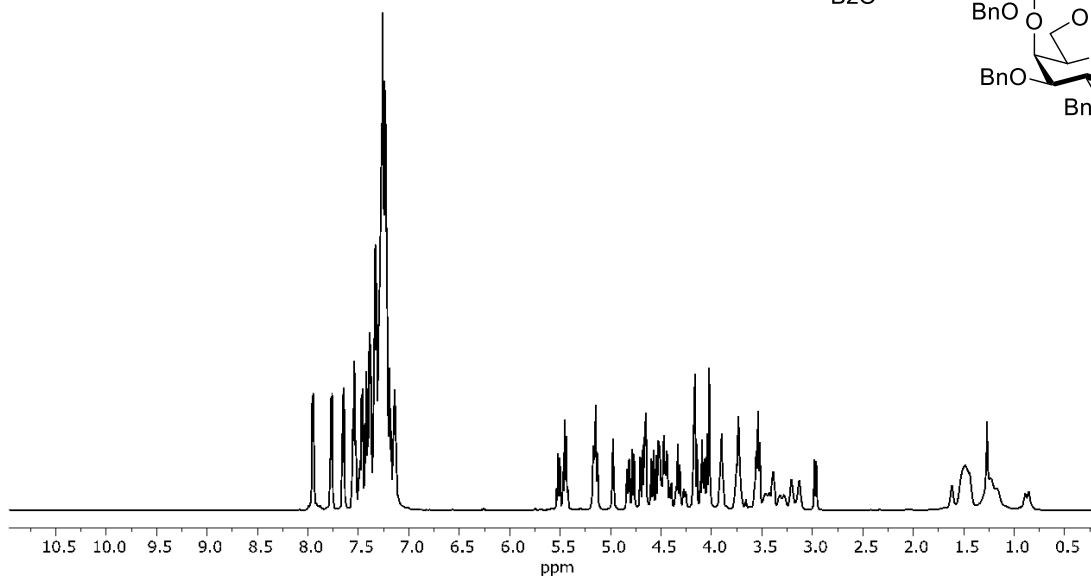
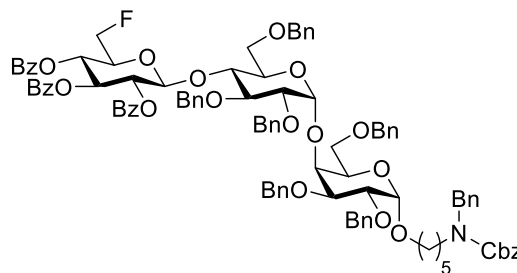


HSQC NMR (CDCl_3) of **36**.

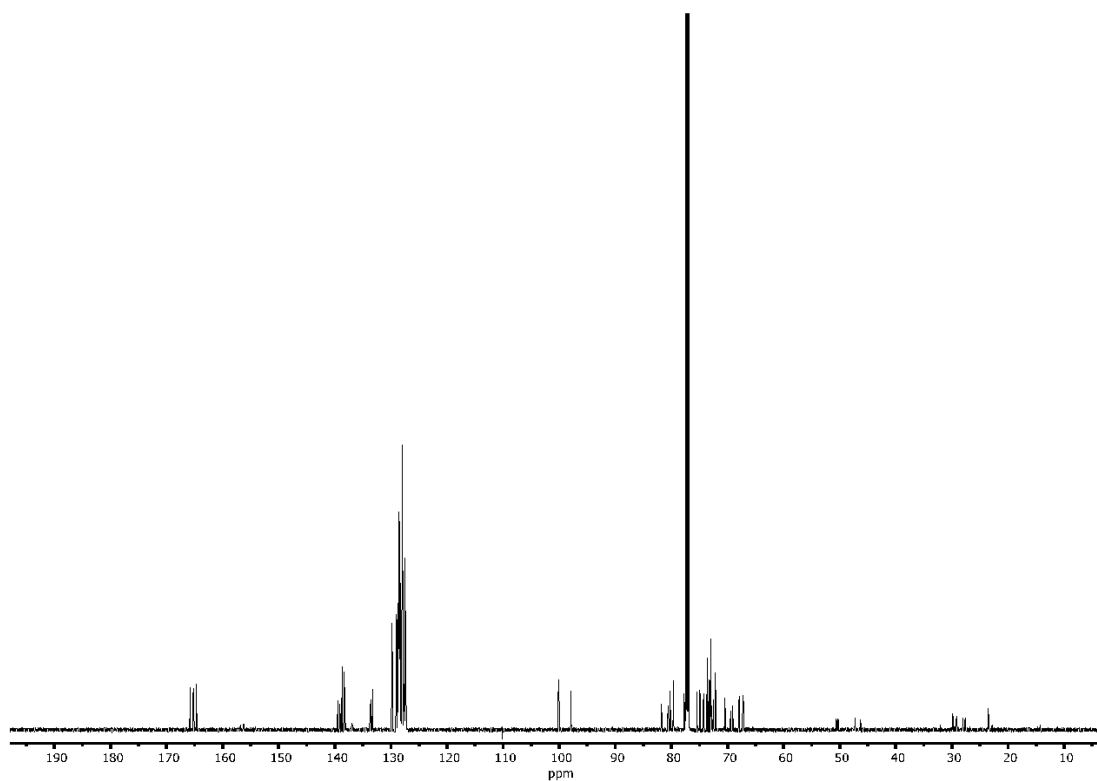


^{19}F NMR (377 MHz, CDCl_3) of **36**.

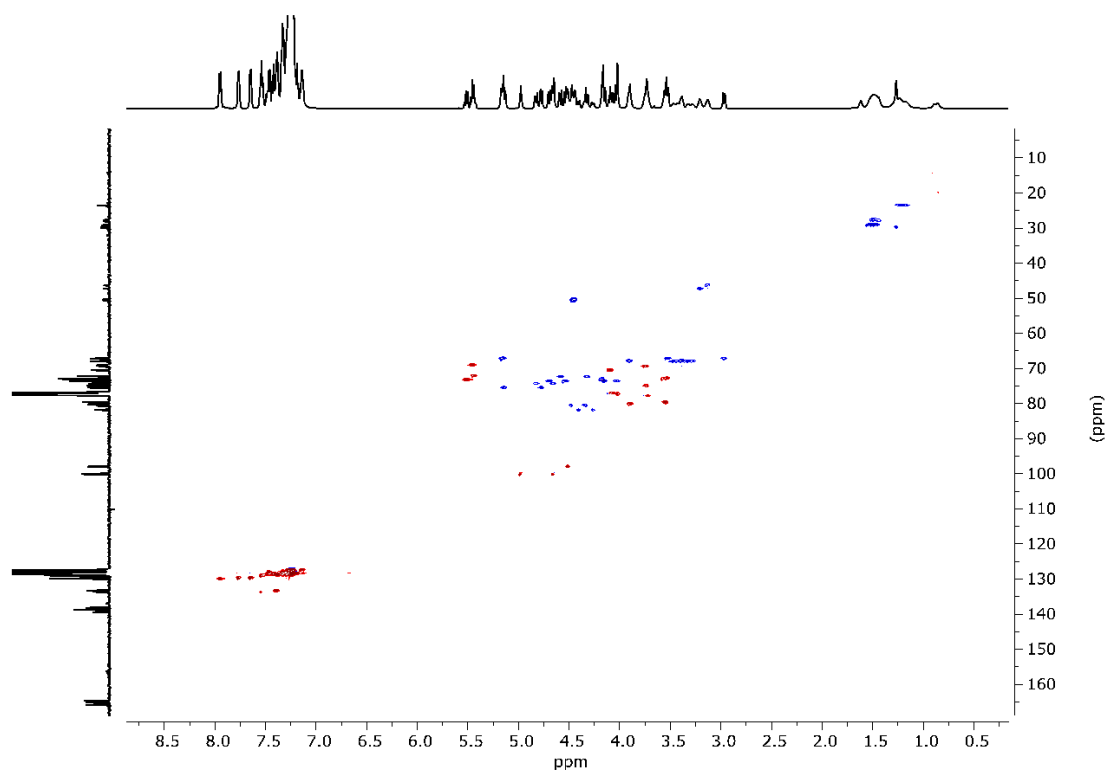
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,4-tri-*O*-benzoyl-6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (38)**



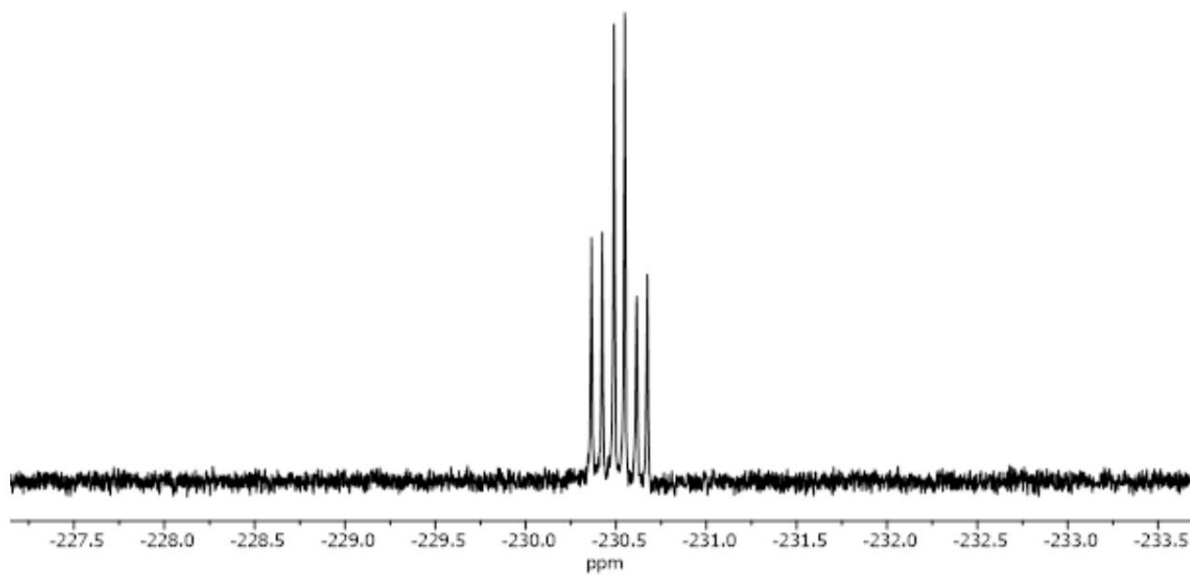
^1H NMR (600 MHz, CDCl_3) of 38.



^{13}C NMR (100 MHz, CDCl_3) of 38.

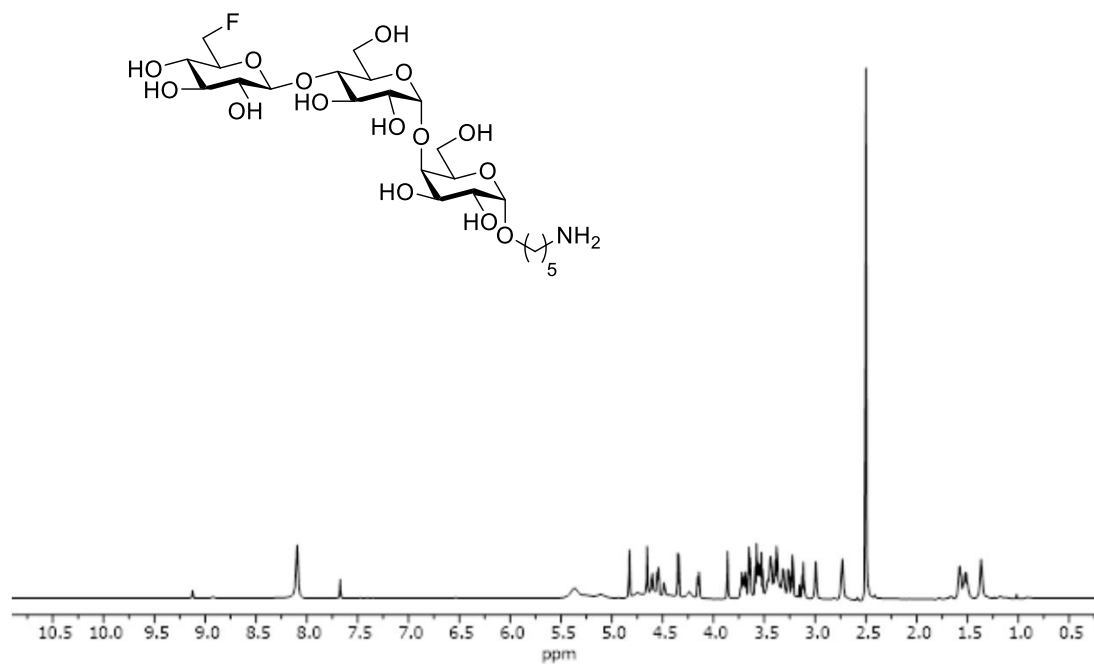


HSQC (CDCl₃) of **38**.

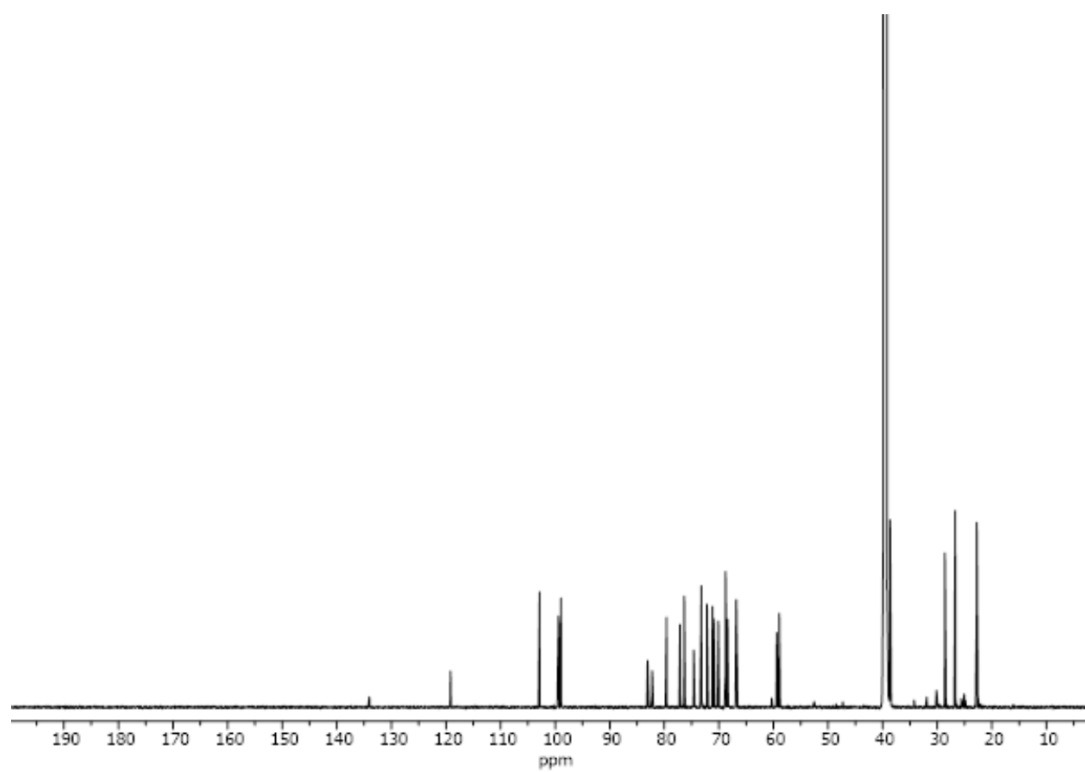


¹⁹F NMR (377 MHz, CDCl₃) of **38**.

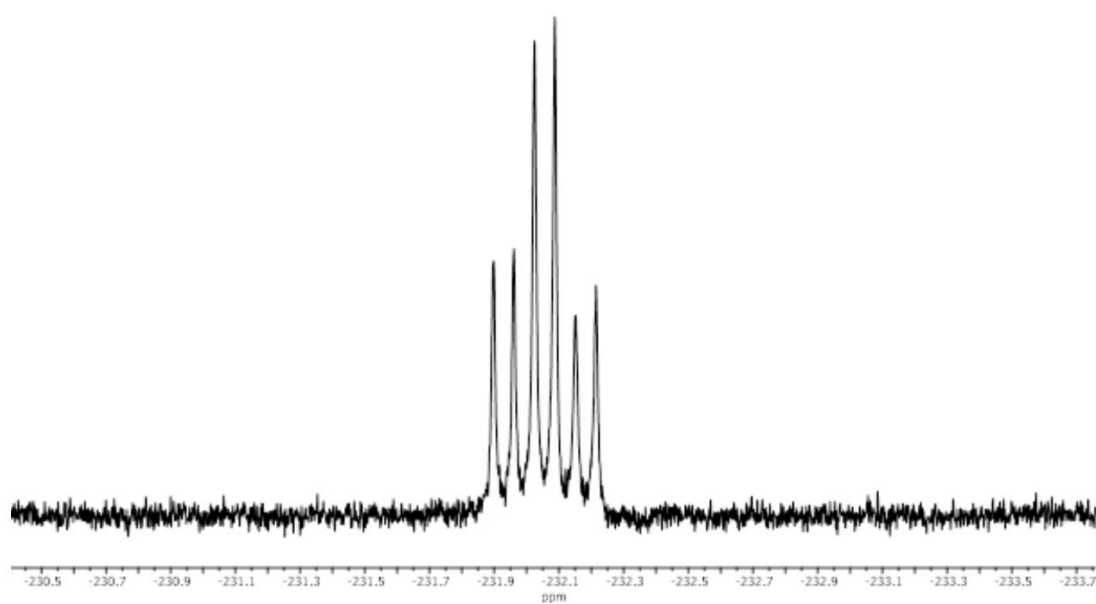
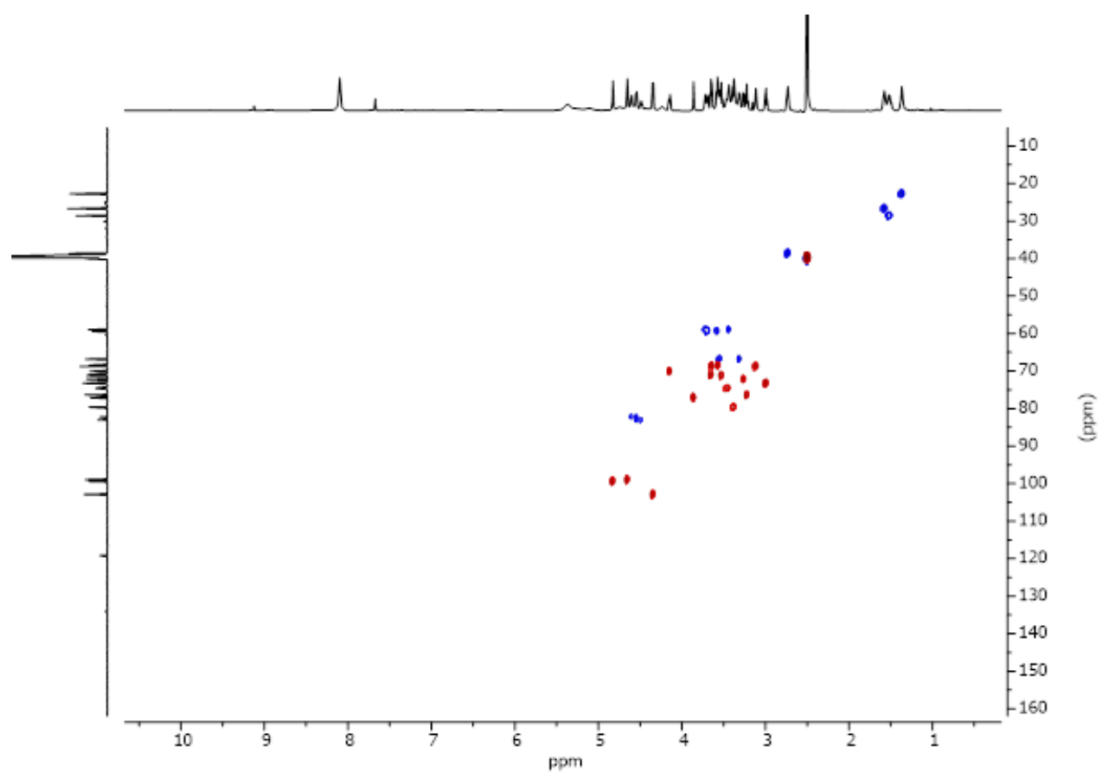
5-Aminopentyl-(6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(α -D-glucopyranosyl)-(1 $\rightarrow$ 4)- α -D-galactopyranoside (3)



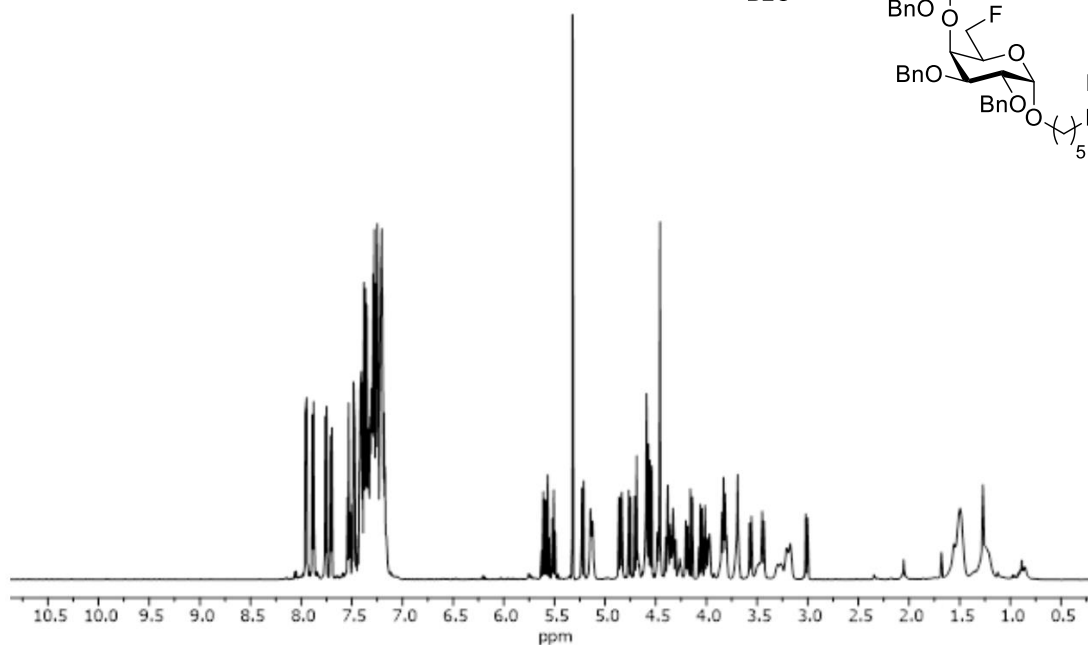
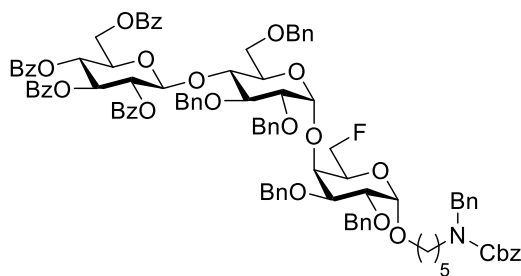
^1H NMR (800 MHz, DMSO-d_6) of 3.



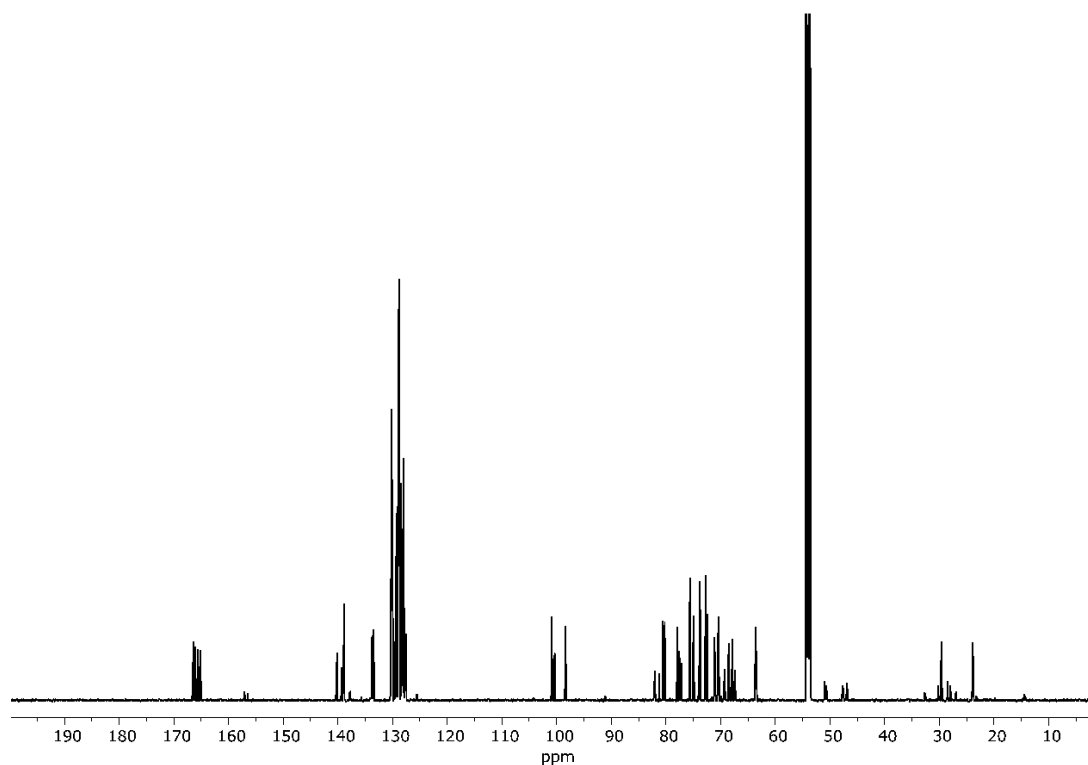
^{13}C NMR (200 MHz, DMSO-d_6) of 3.



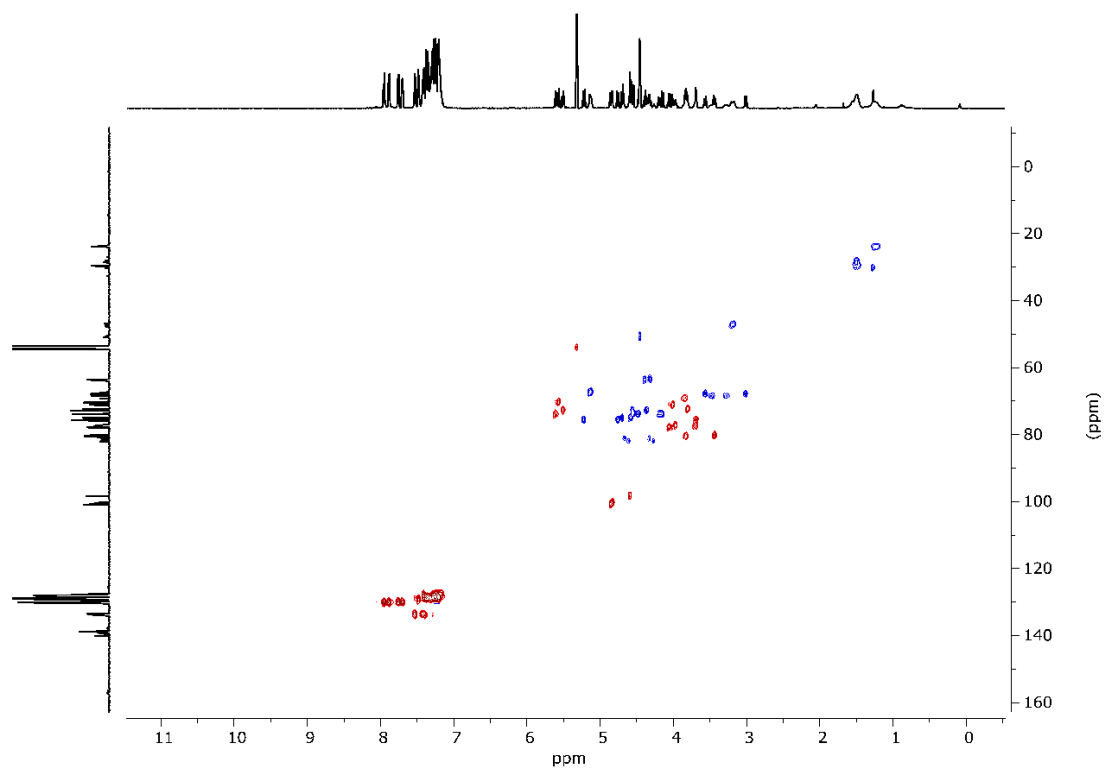
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-benzyl-6-deoxy-6-fluoro- α -D-galactopyranoside (39)**



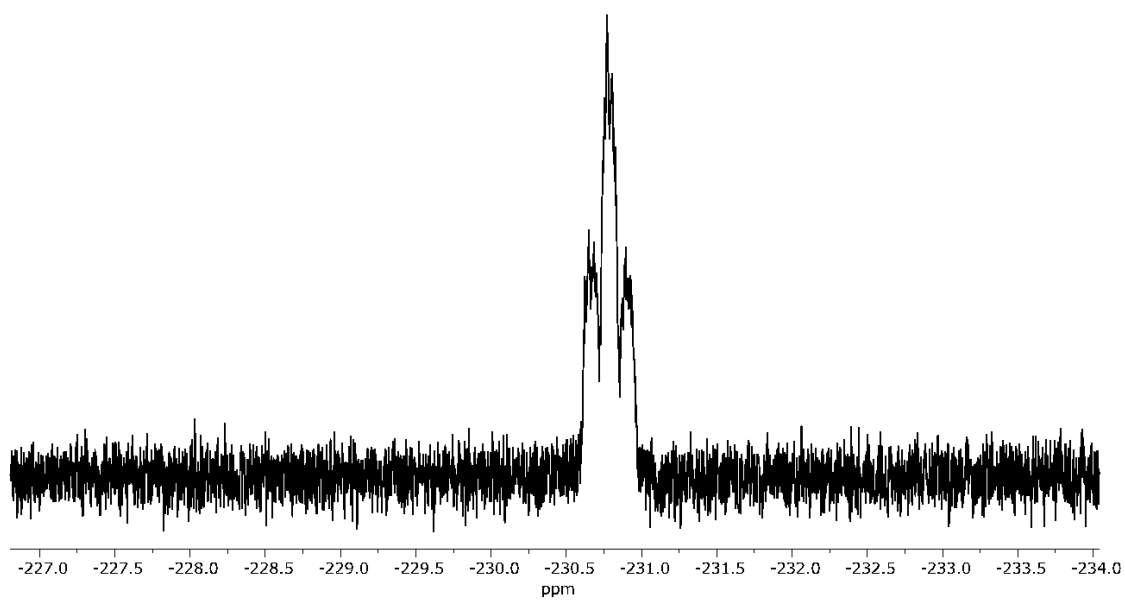
^1H NMR (800 MHz, CD_2Cl_2) of **39**.



^{13}C NMR (200 MHz, CD_2Cl_2) of **39**.

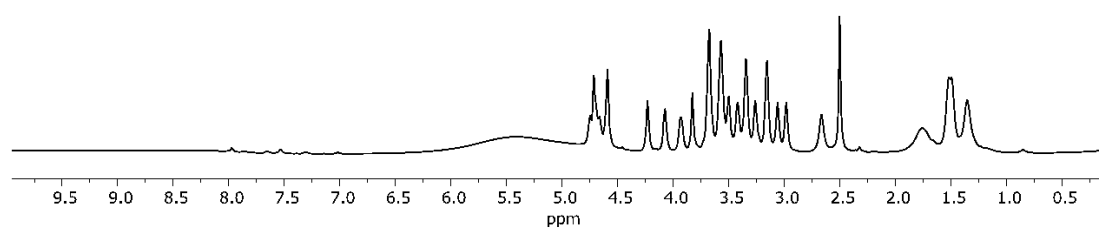
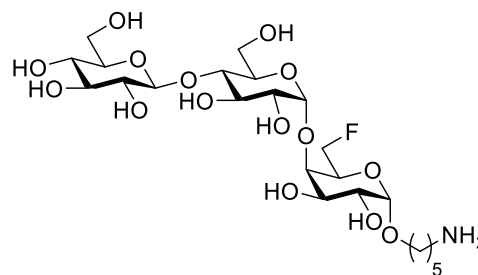


HSQC (CD₂Cl₂) of **39**.

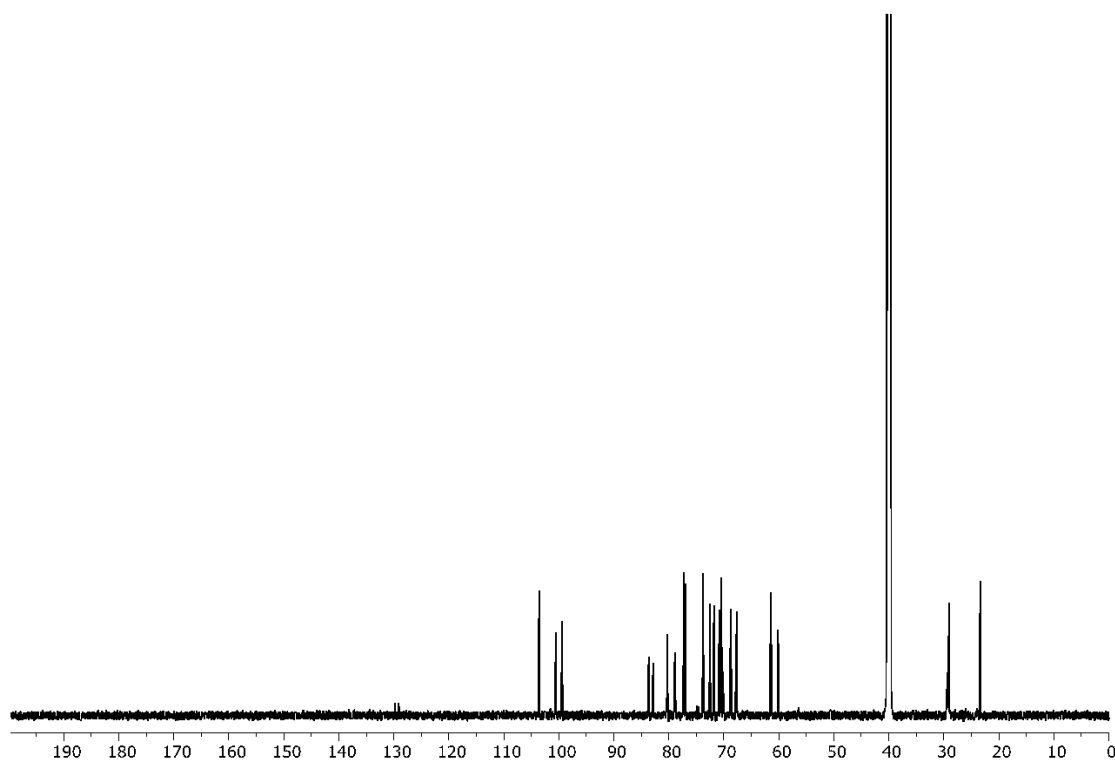


¹⁹F NMR (377 MHz, CD₂Cl₂) of **39**.

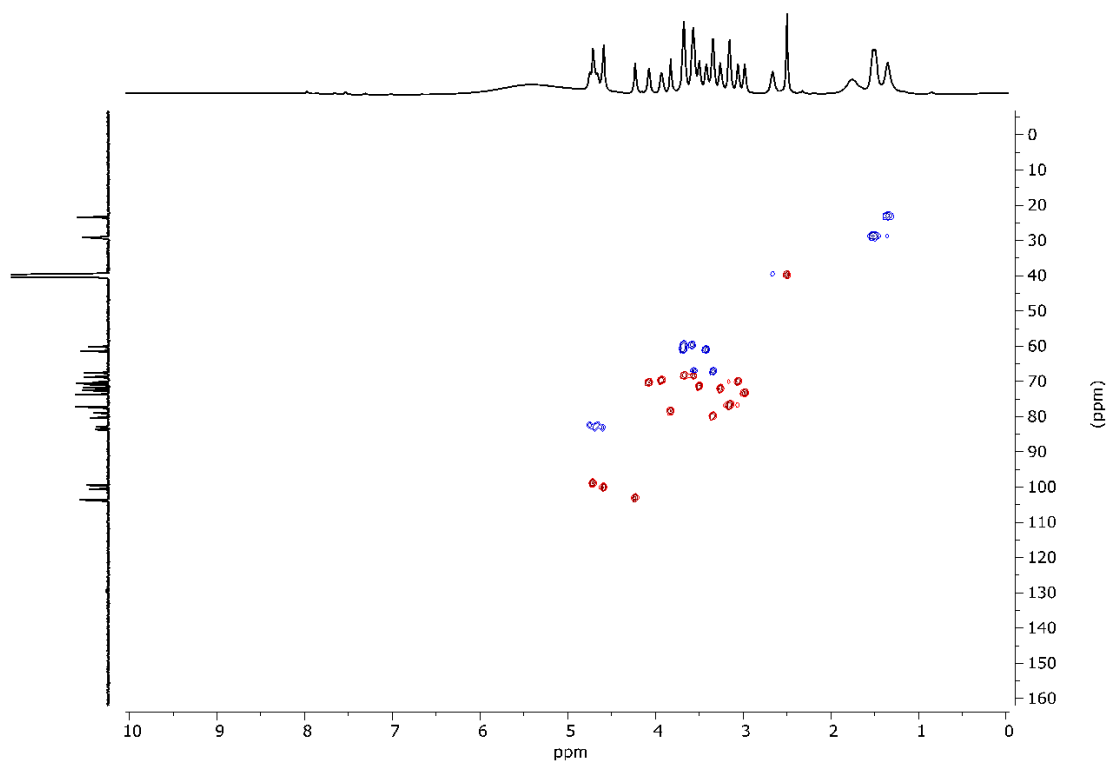
5-Aminopentyl-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-6-deoxy-6-fluoro- α -D-galactopyranoside (5)



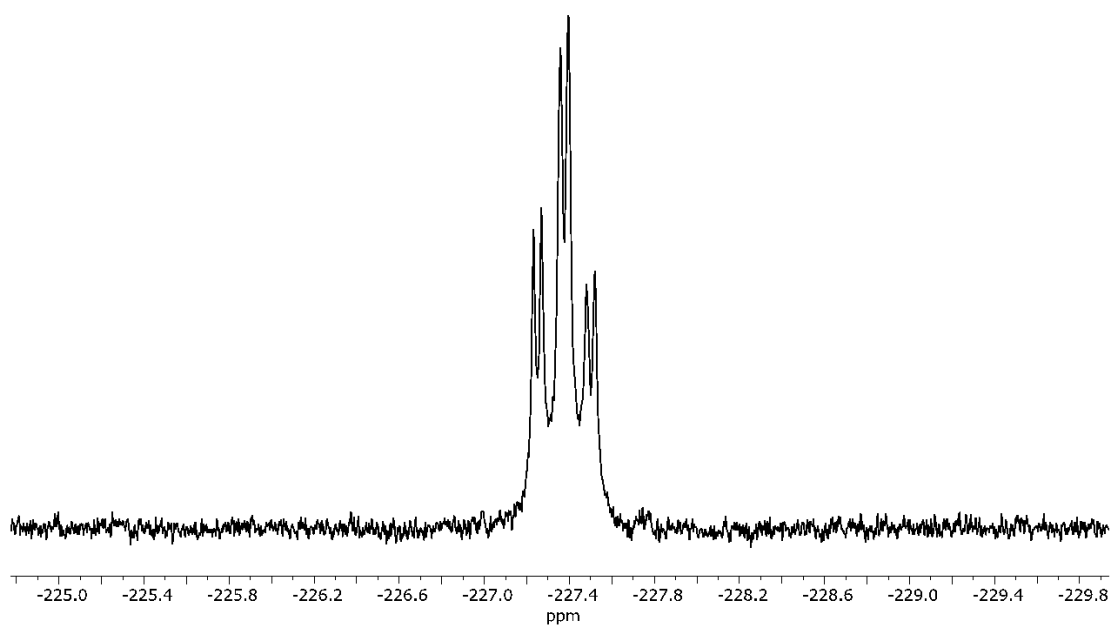
^1H NMR (800 MHz, DMSO-d_6) of 5.



^{13}C NMR (200 MHz, DMSO-d_6) of 5.

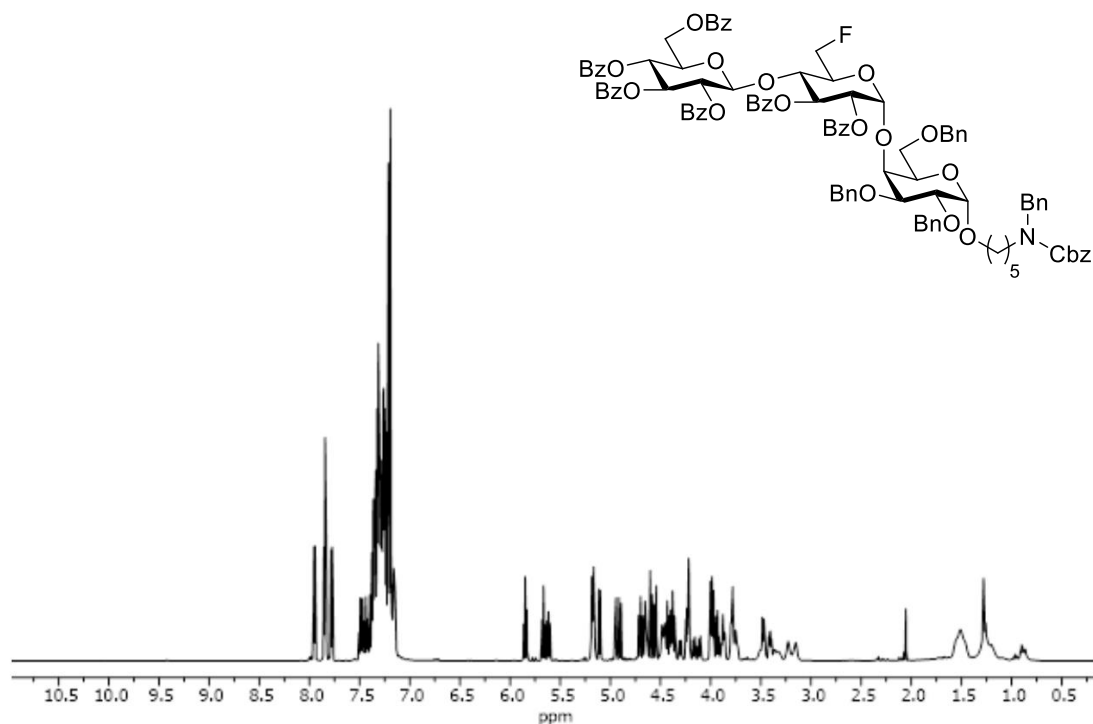


HSQC (DMSO- d_6) of 5.

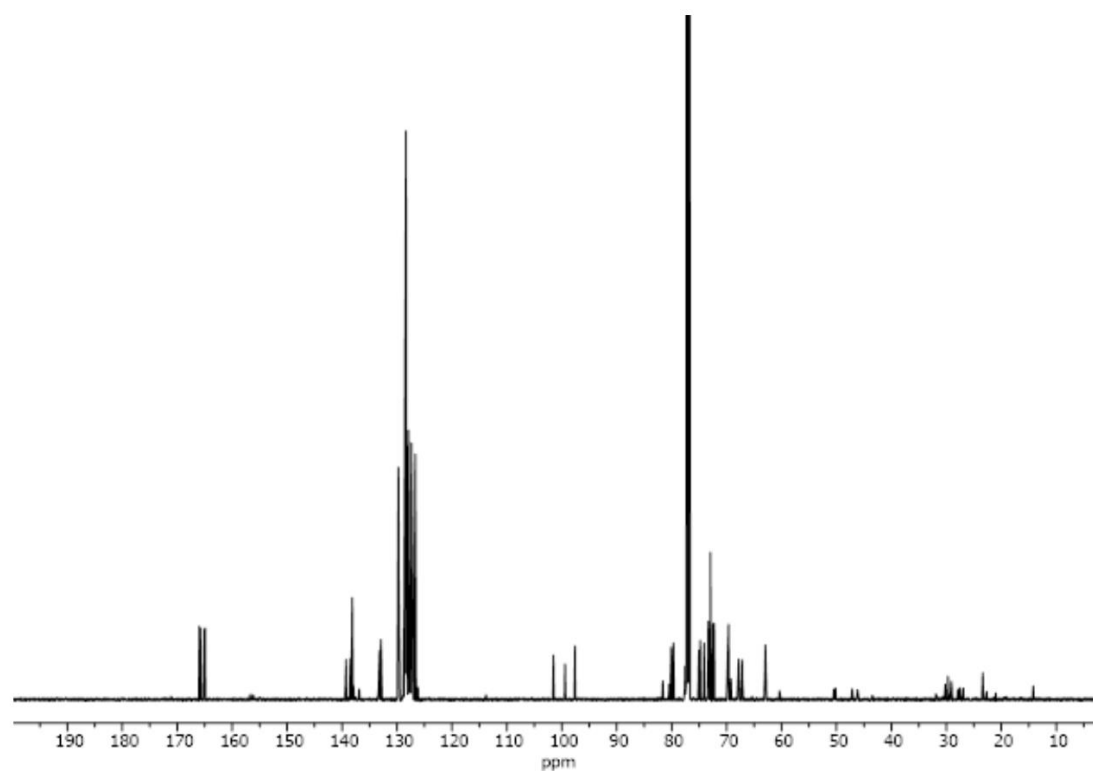


^{19}F NMR (377 MHz, DMSO- d_6) of 5.

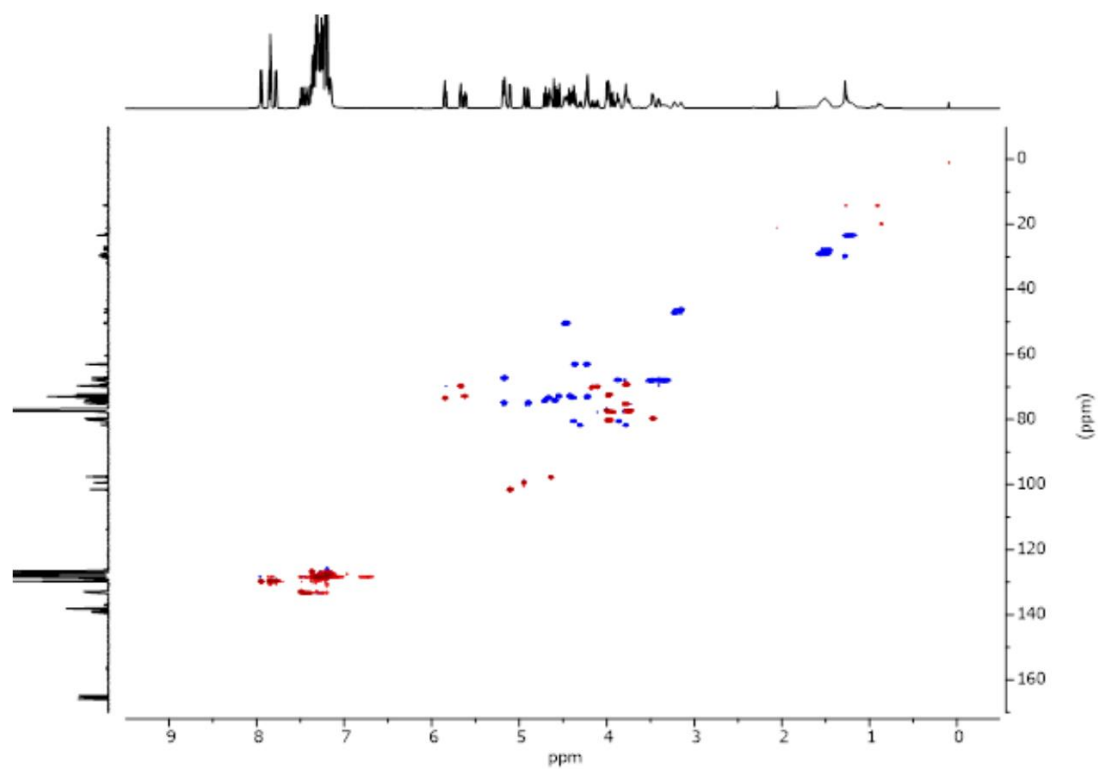
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3-di-*O*-benzyl-6-deoxy-6-fluoro- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (**42**)**



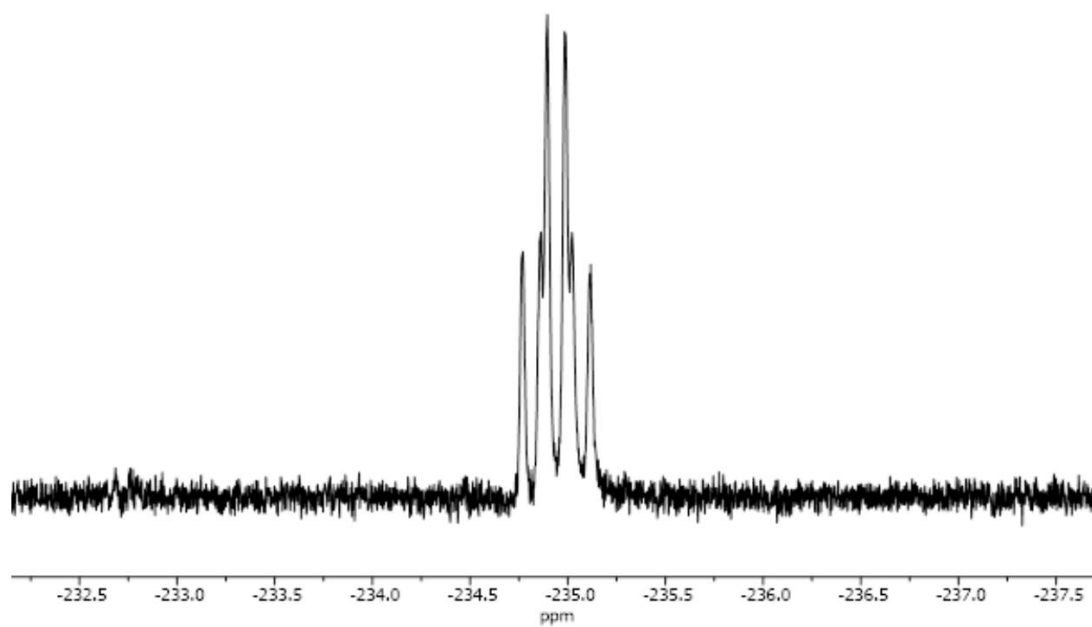
^1H NMR (800 MHz, CDCl_3) of **42**.



^{13}C NMR (200 MHz, CDCl_3) of **42**.

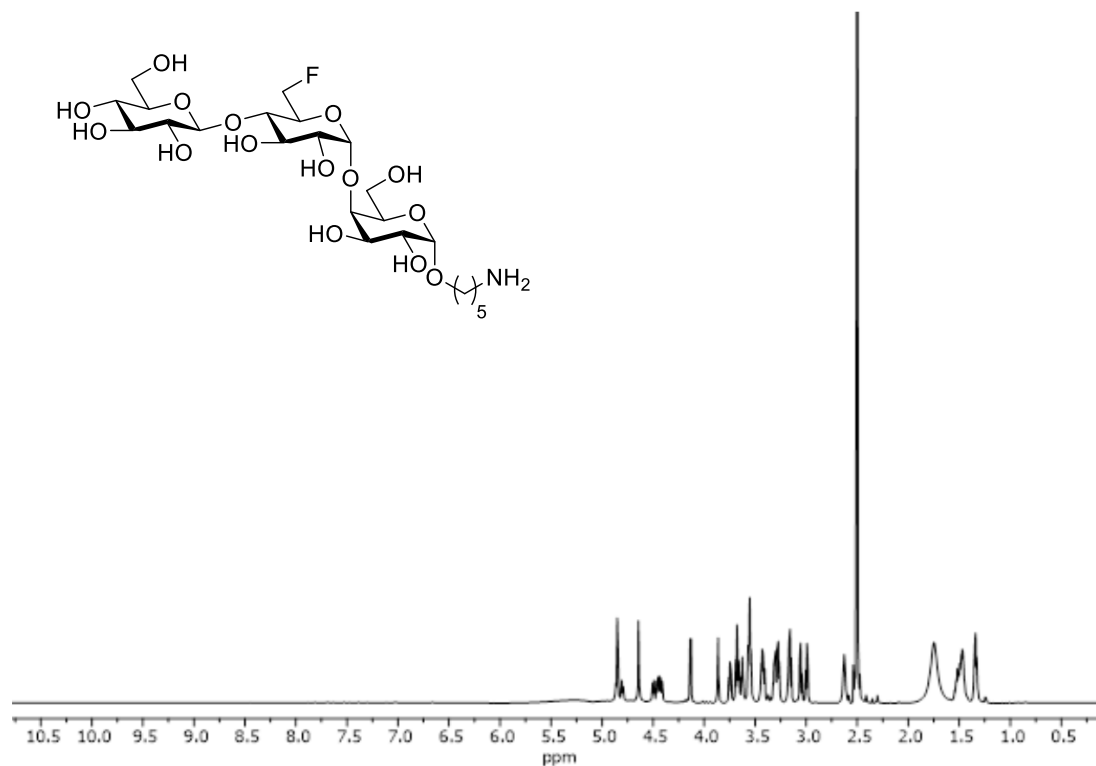


HSQC (CDCl₃) of **42**.

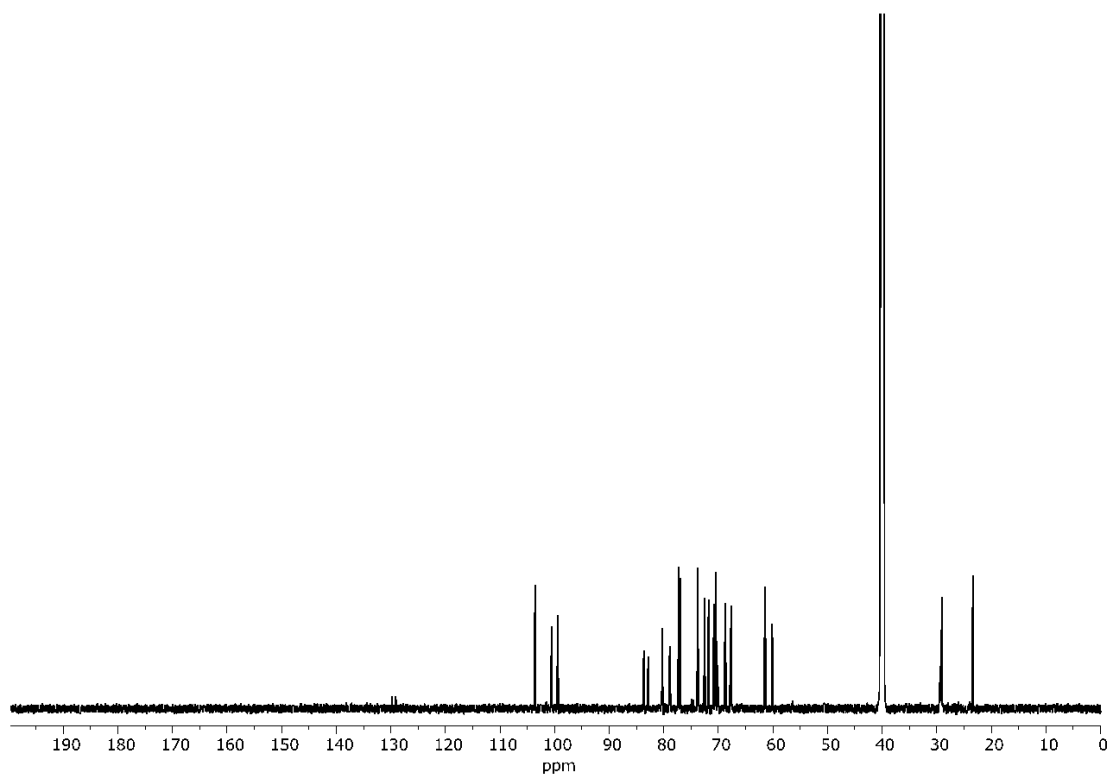


¹⁹F NMR (377 MHz, CDCl₃) of **42**.

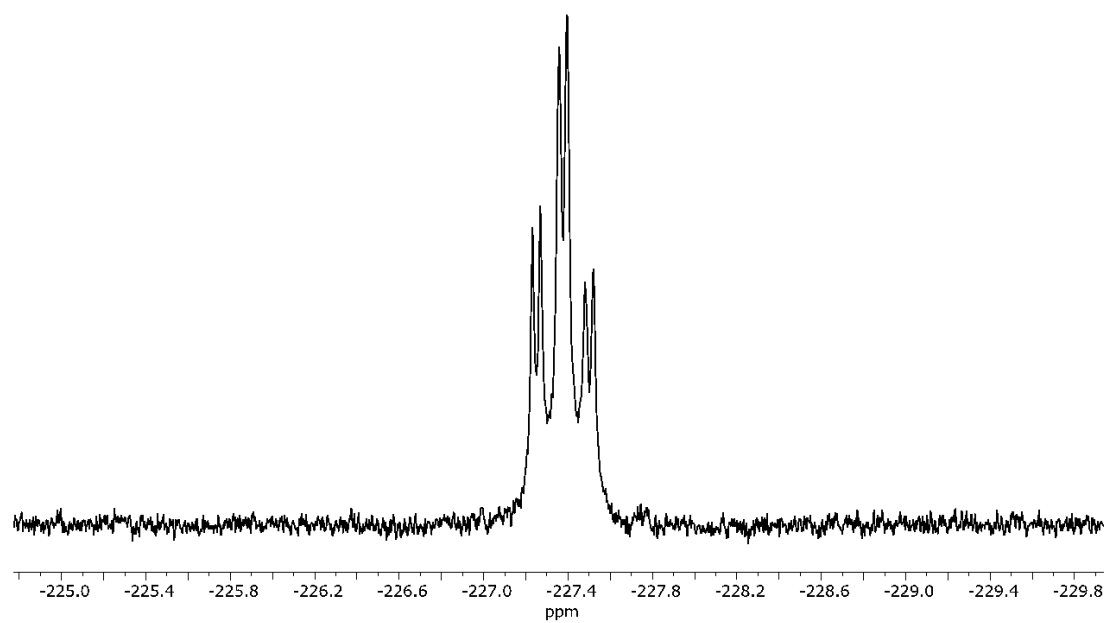
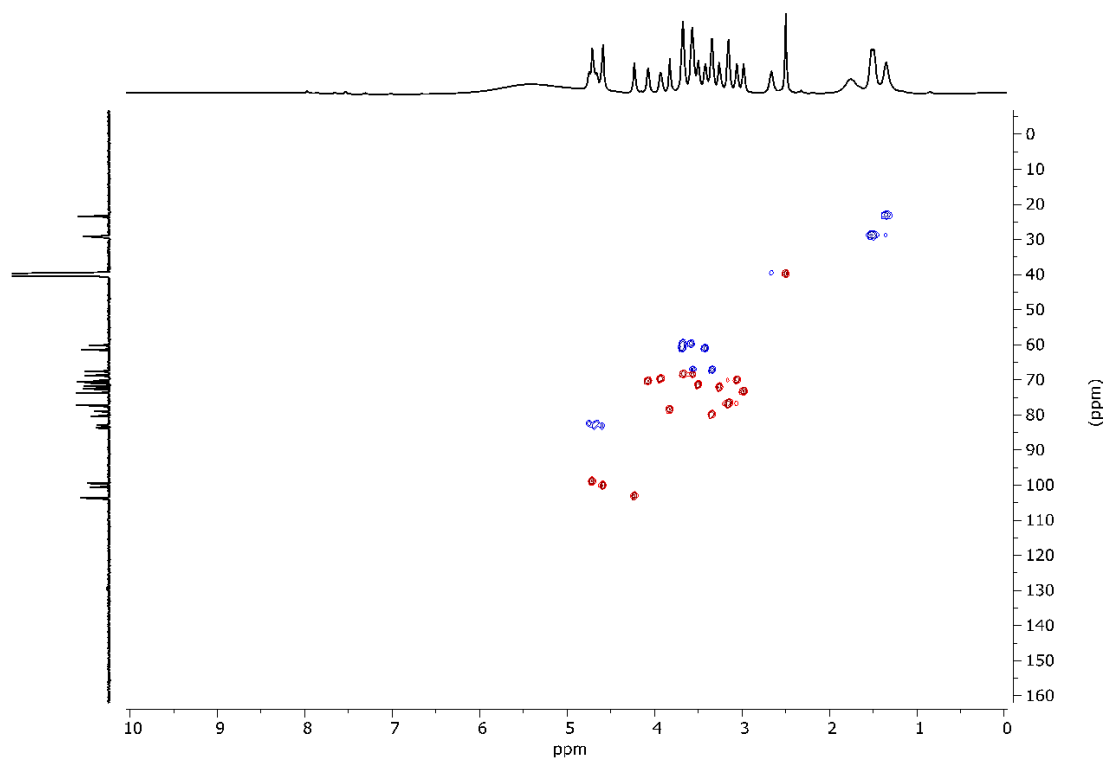
5-Aminopentyl-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(6-deoxy-6-fluoro- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)- α -D-galactopyranoside (4)



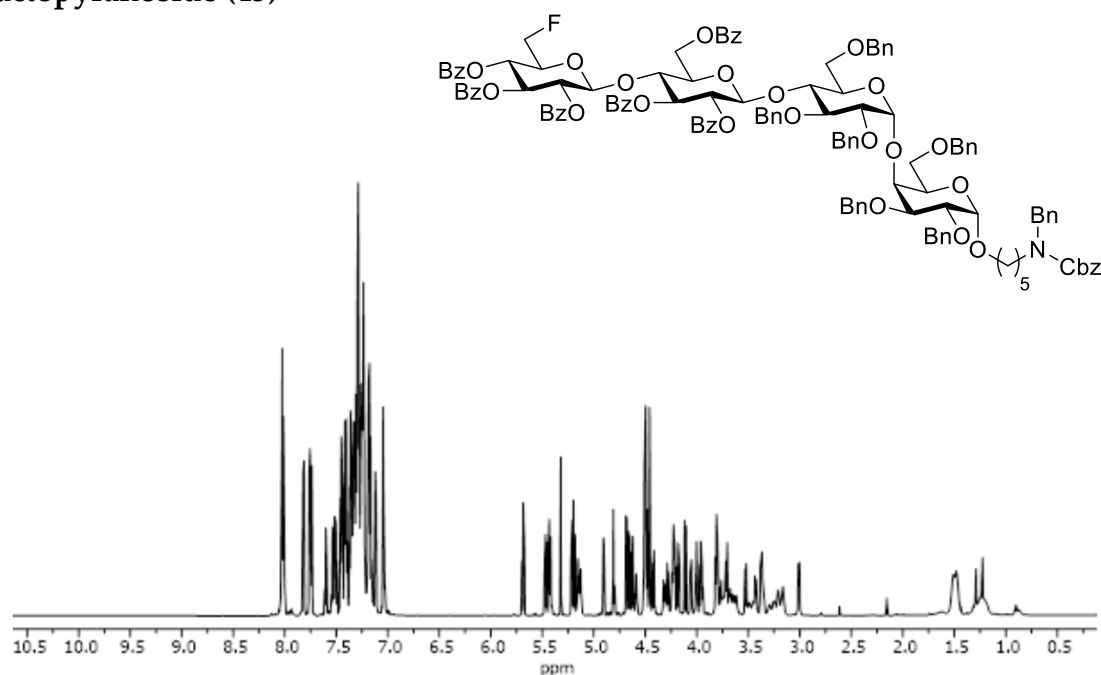
^1H NMR (800 MHz, DMSO- d_6) of 4.



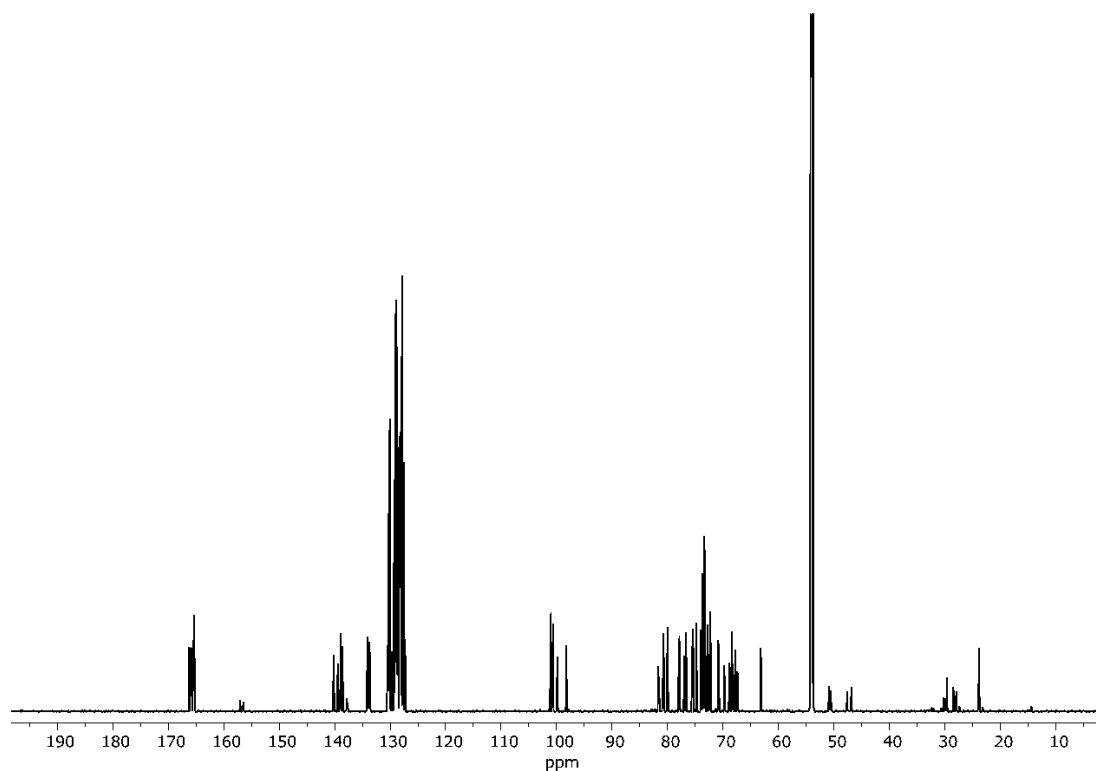
^{13}C NMR (200 MHz, DMSO- d_6) of 4.



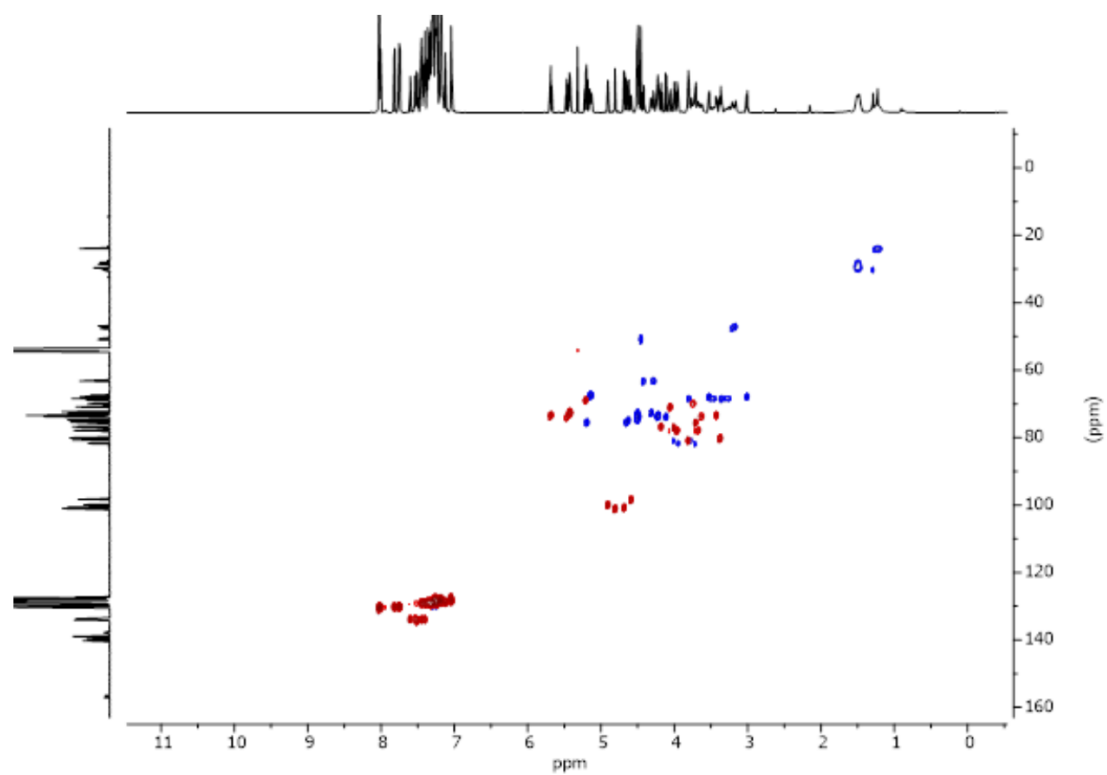
***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl-(2,3,4-tri-*O*-benzoyl-6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (**43**)**



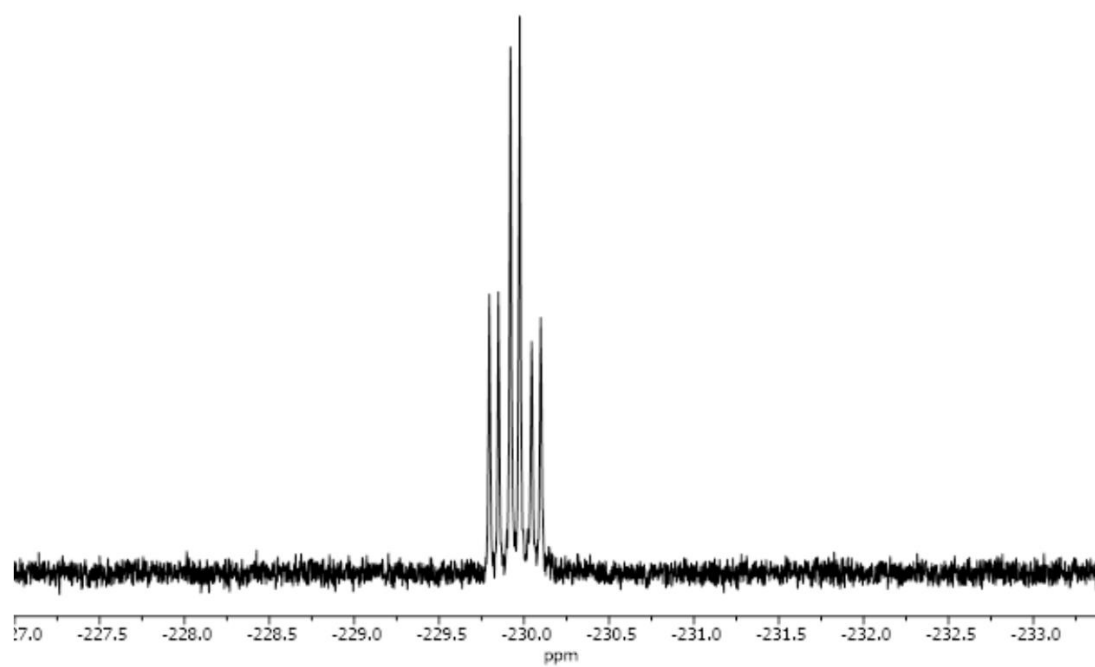
^1H NMR (800 MHz, CD_2Cl_2) of **43**.



^{13}C NMR (200 MHz, CD_2Cl_2) of **43**.

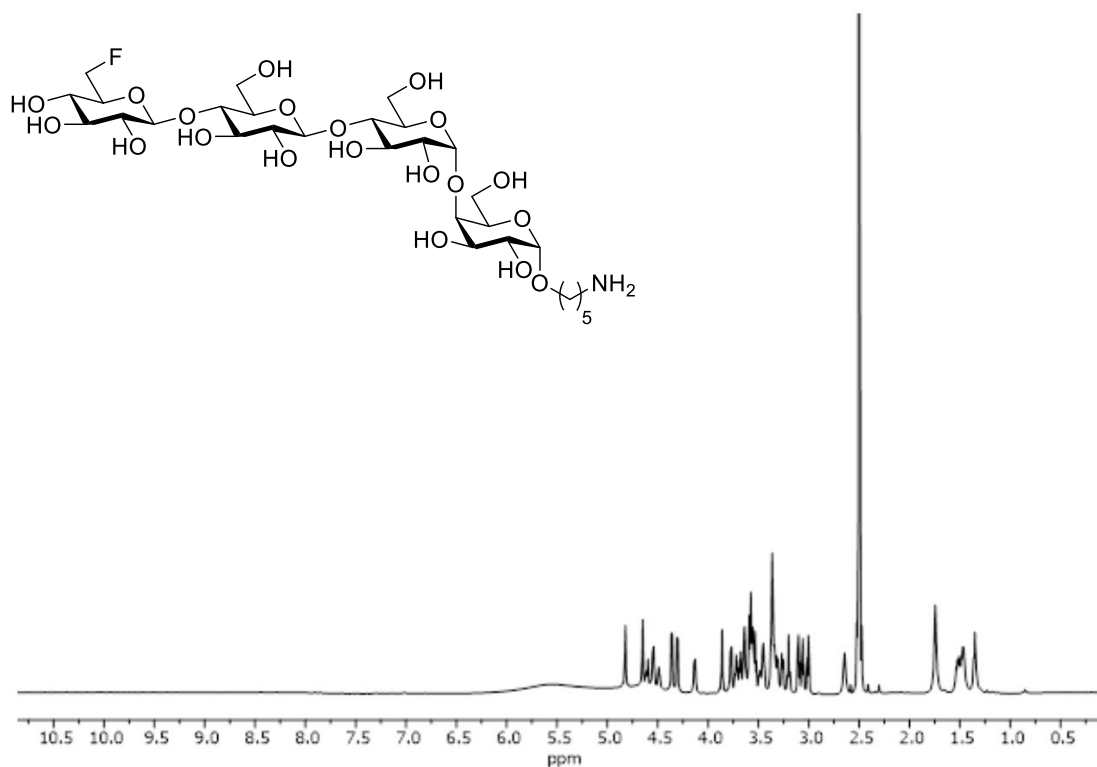


HSQC (CD₂Cl₂) of **43**.

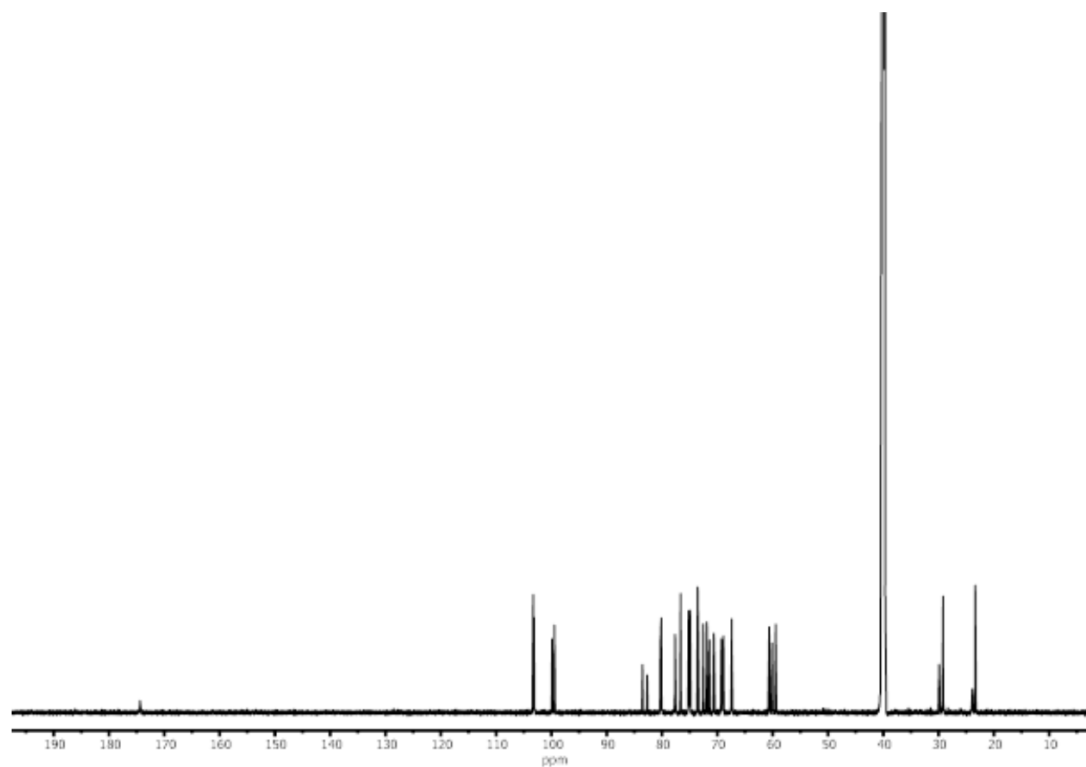


¹⁹F NMR (377 MHz, CD₂Cl₂) of **43**.

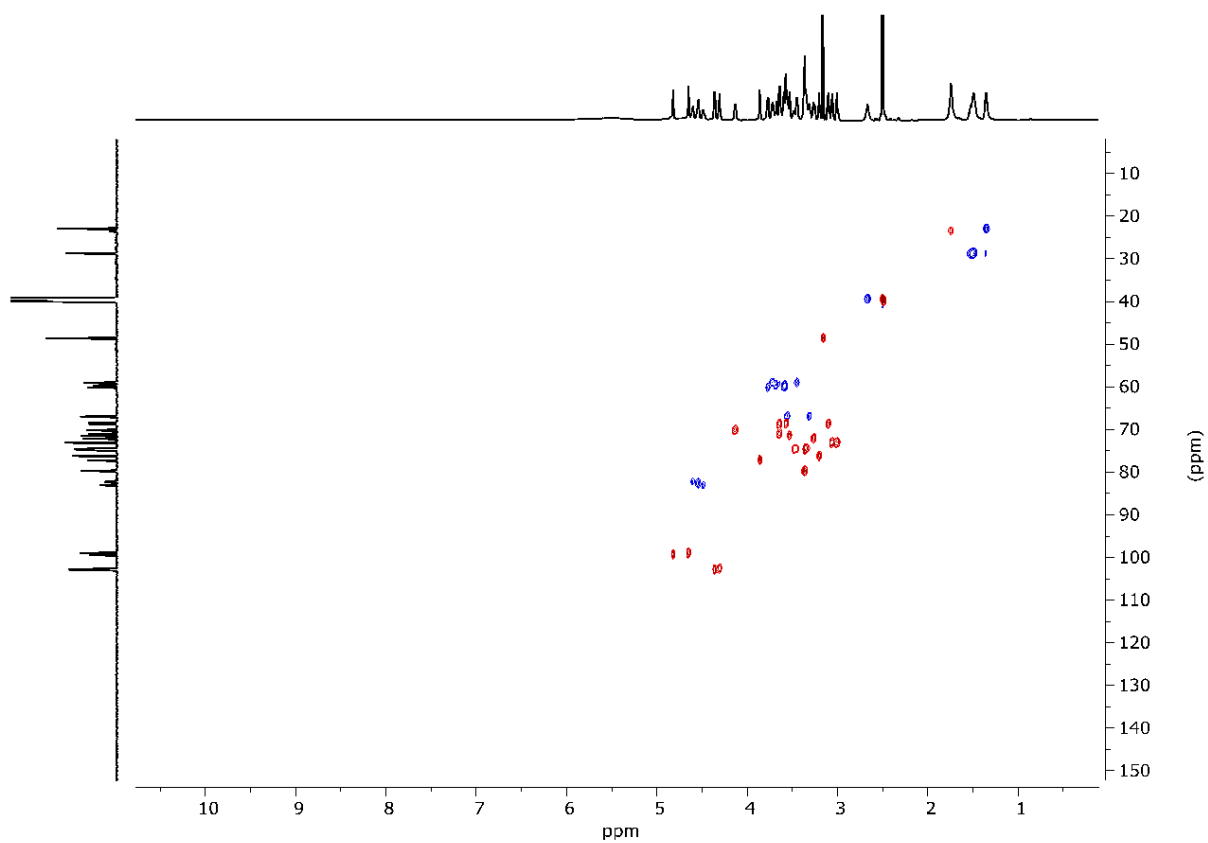
5-Aminopentyl-(6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(α -D-glucopyranosyl)-(1 $\rightarrow$ 4)- α -D-galactopyranoside (6)



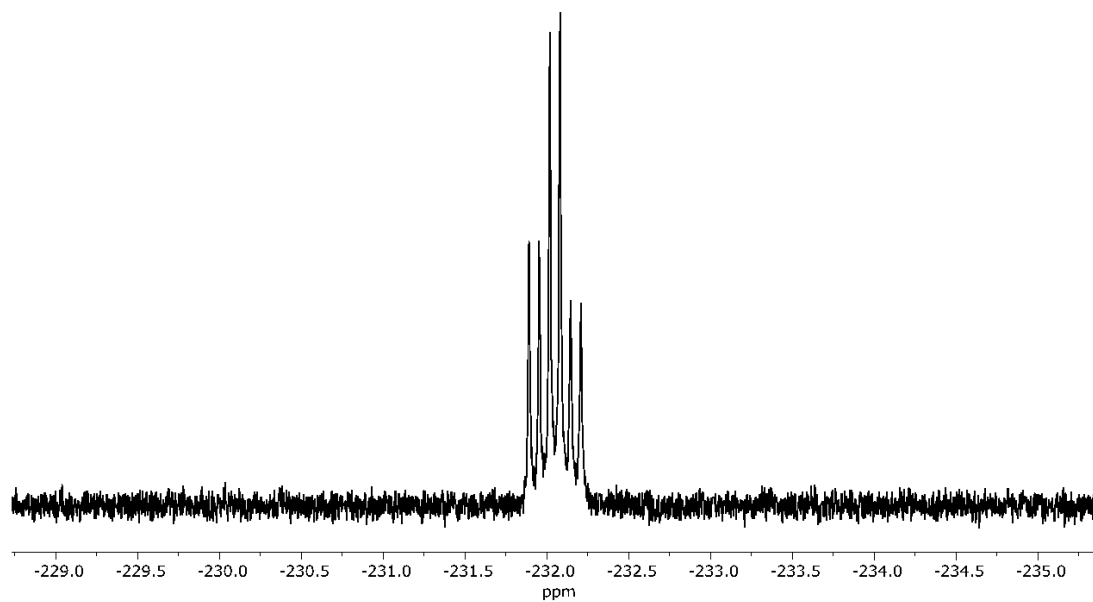
^1H NMR (800 MHz, DMSO-d_6) of 6.



^{13}C NMR (200 MHz, DMSO-d_6) of 6.

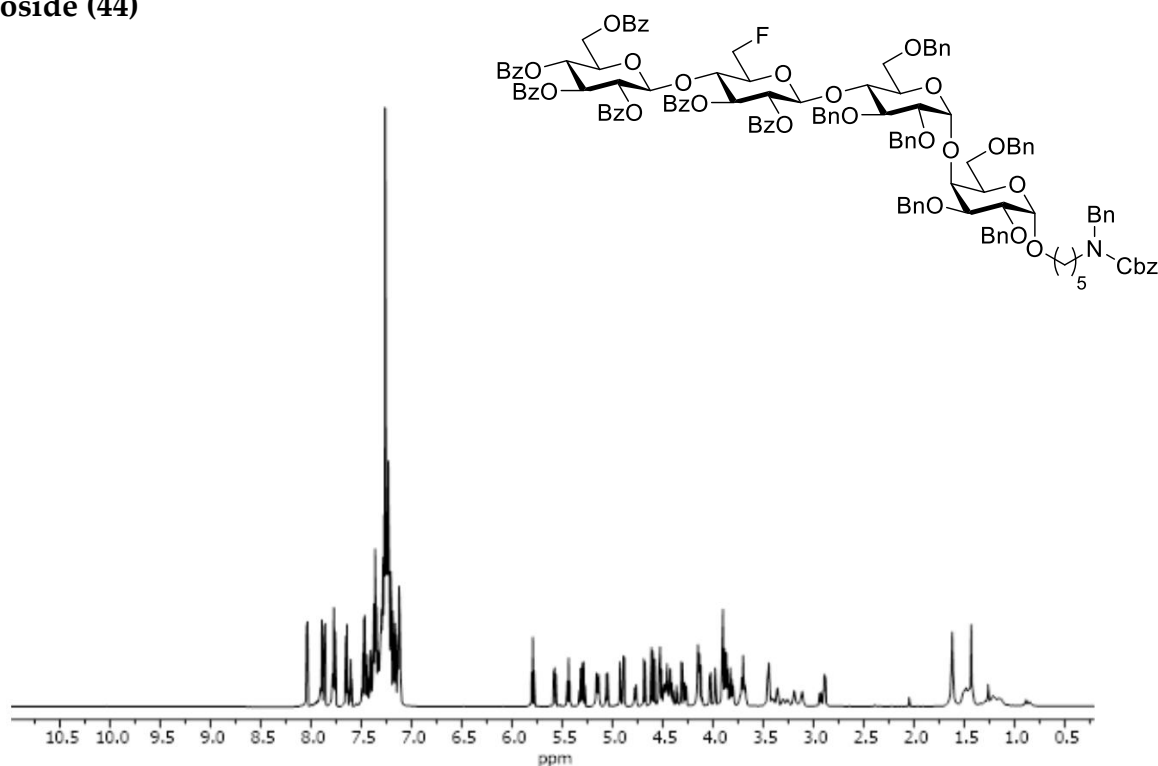


HSQC NMR (DMSO- d_6) of **6**.

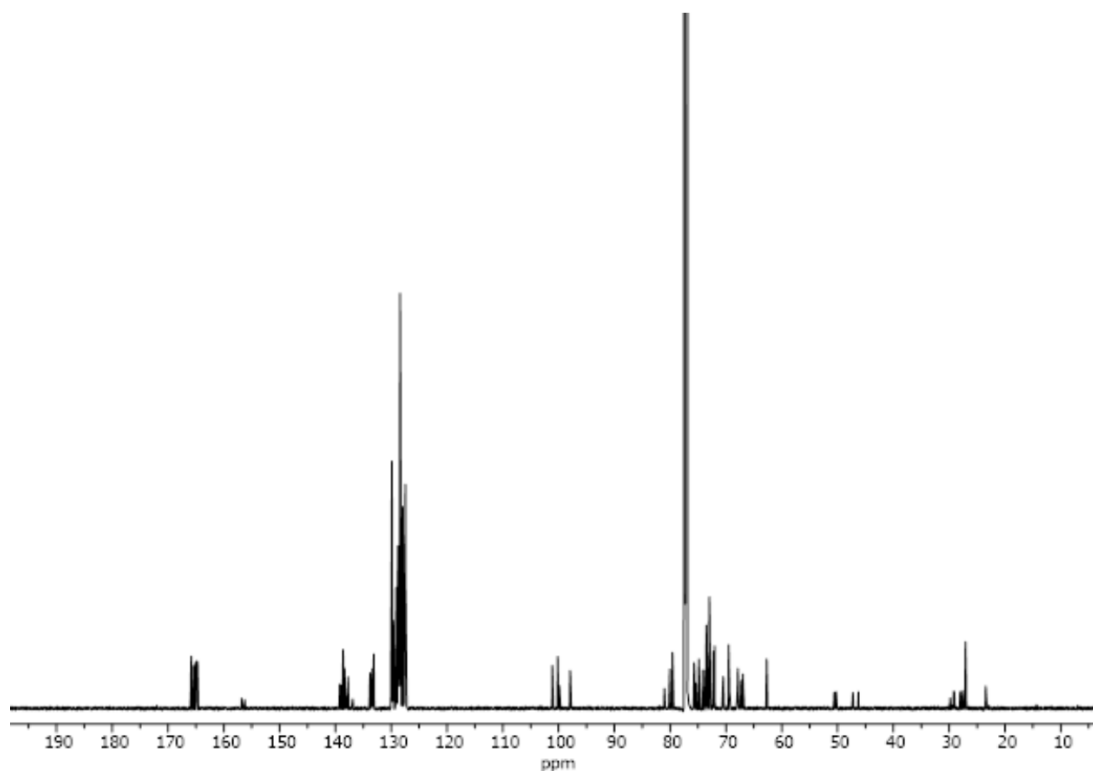


^{19}F NMR (377 MHz, DMSO- d_6) of **6**.

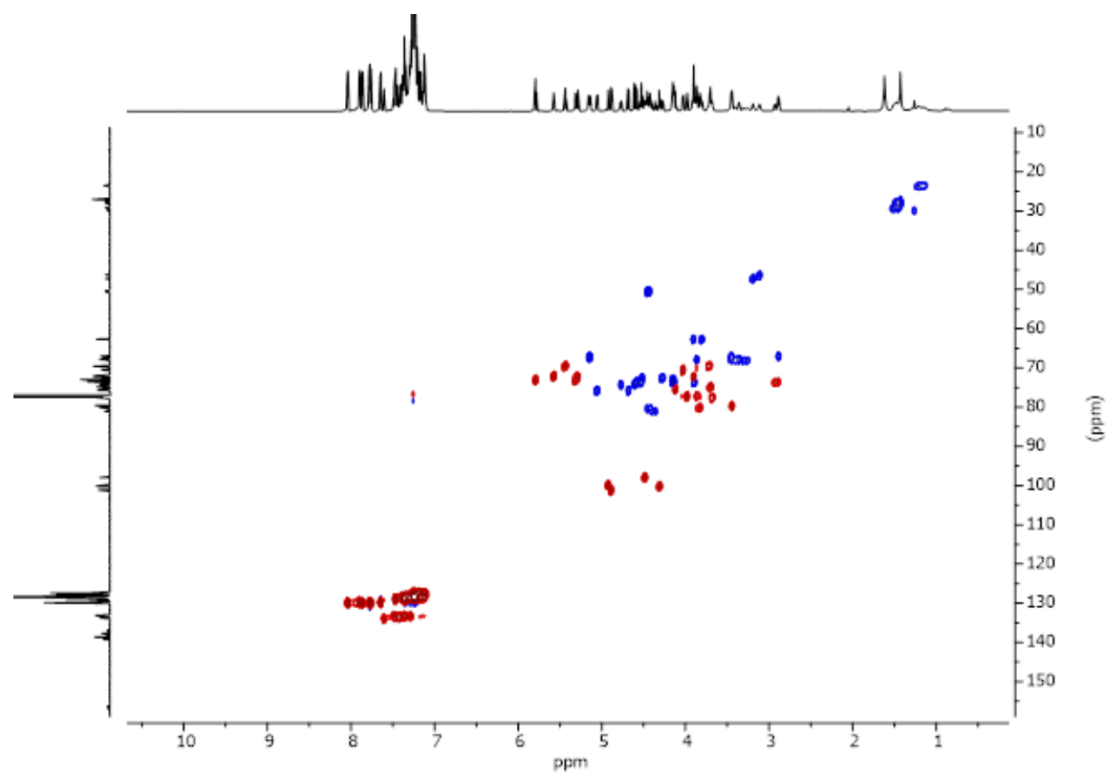
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3-di-*O*-benzoyl-6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (**44**)**



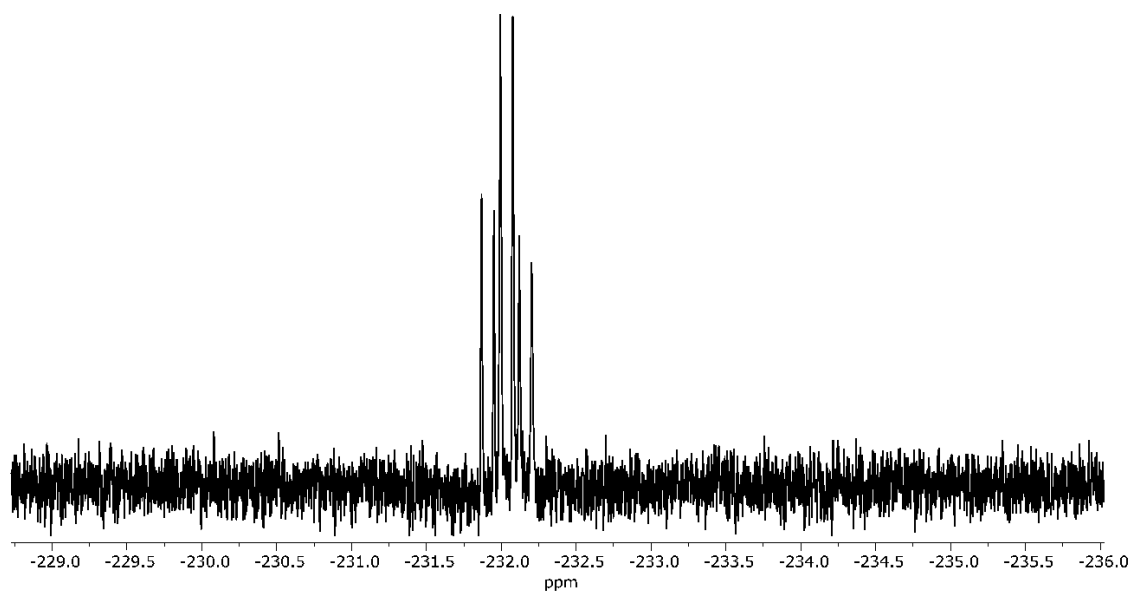
^1H NMR (800 MHz, CDCl_3) of **44**.



^{13}C NMR (200 MHz, CDCl_3) of **44**.

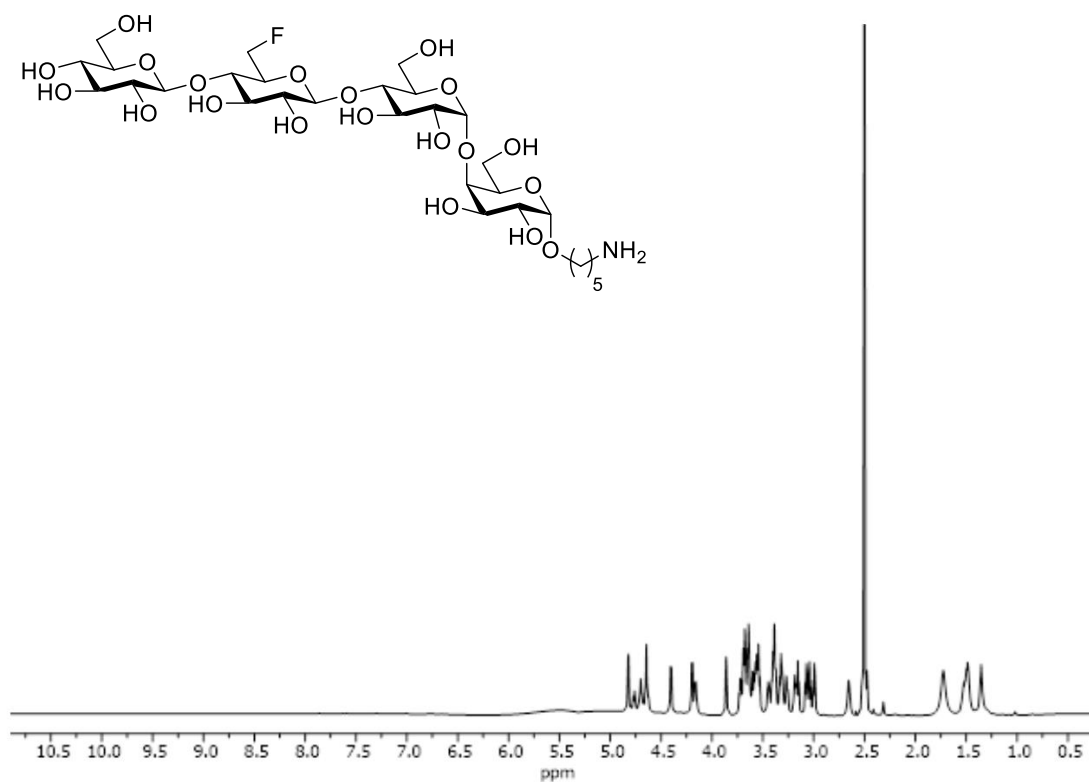


HSQC (CDCl₃) of **44**.

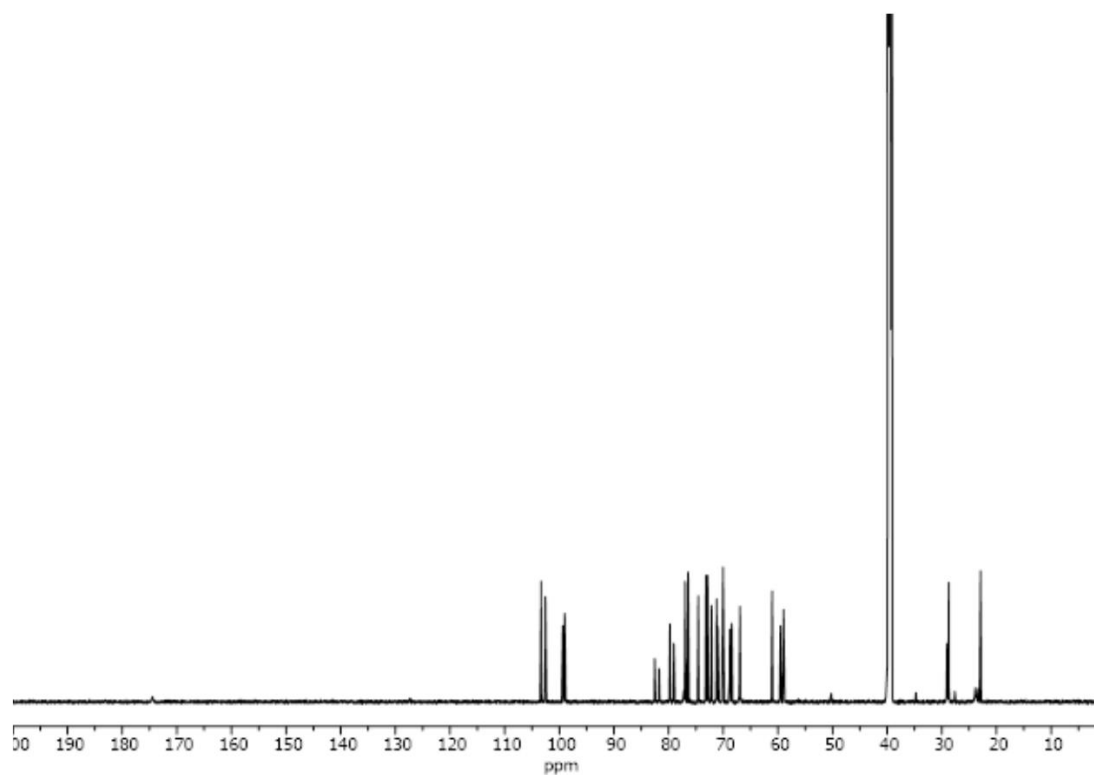


¹⁹F NMR (377 MHz, CDCl₃) of **44**.

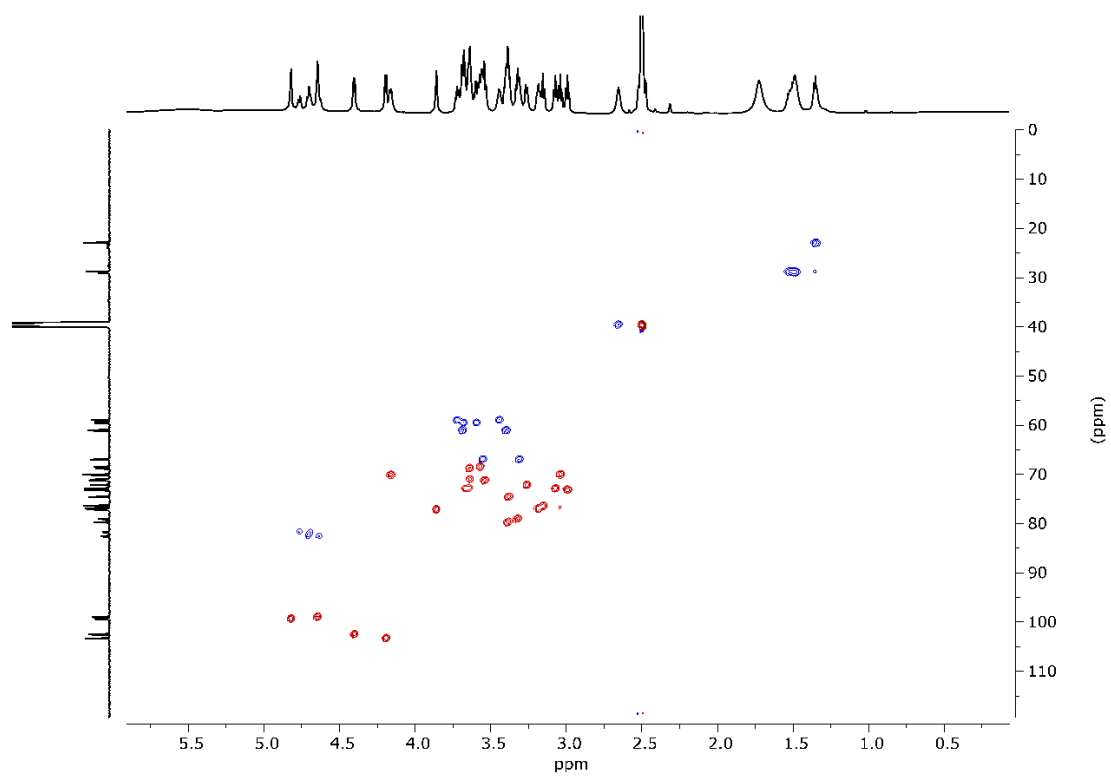
5-Aminopentyl-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(6-deoxy-6-fluoro- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(α -D-glucopyranosyl)-(1 $\rightarrow$ 4)- α -D-galactopyranoside (7)



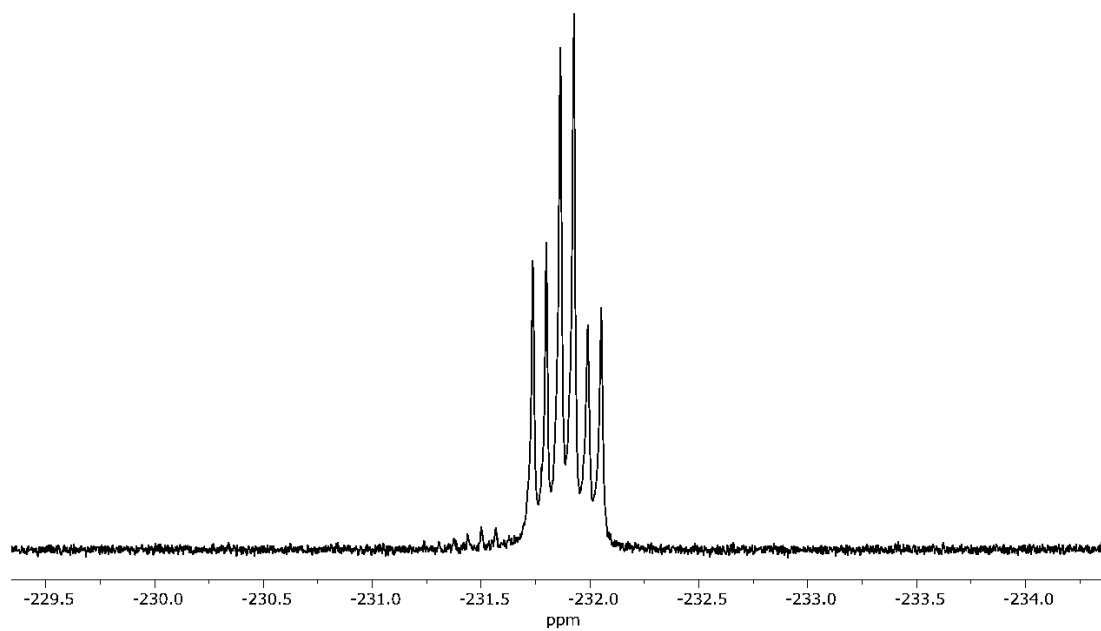
^1H NMR (800 MHz, DMSO- d_6) of 7.



^{13}C NMR (200 MHz, DMSO- d_6) of 6.

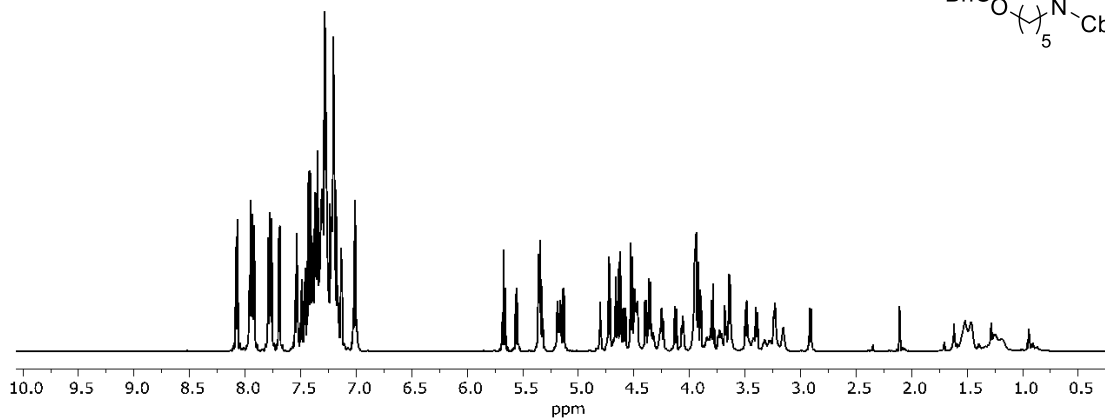
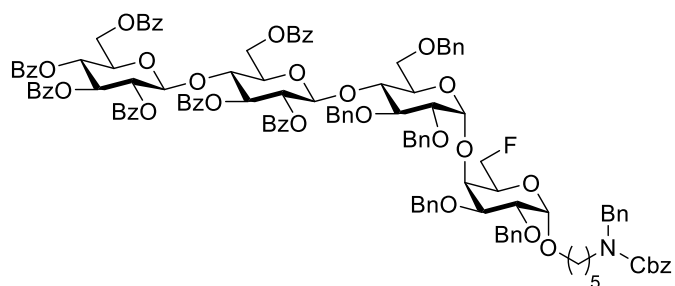


HSQC NMR (DMSO- d_6) of 7.

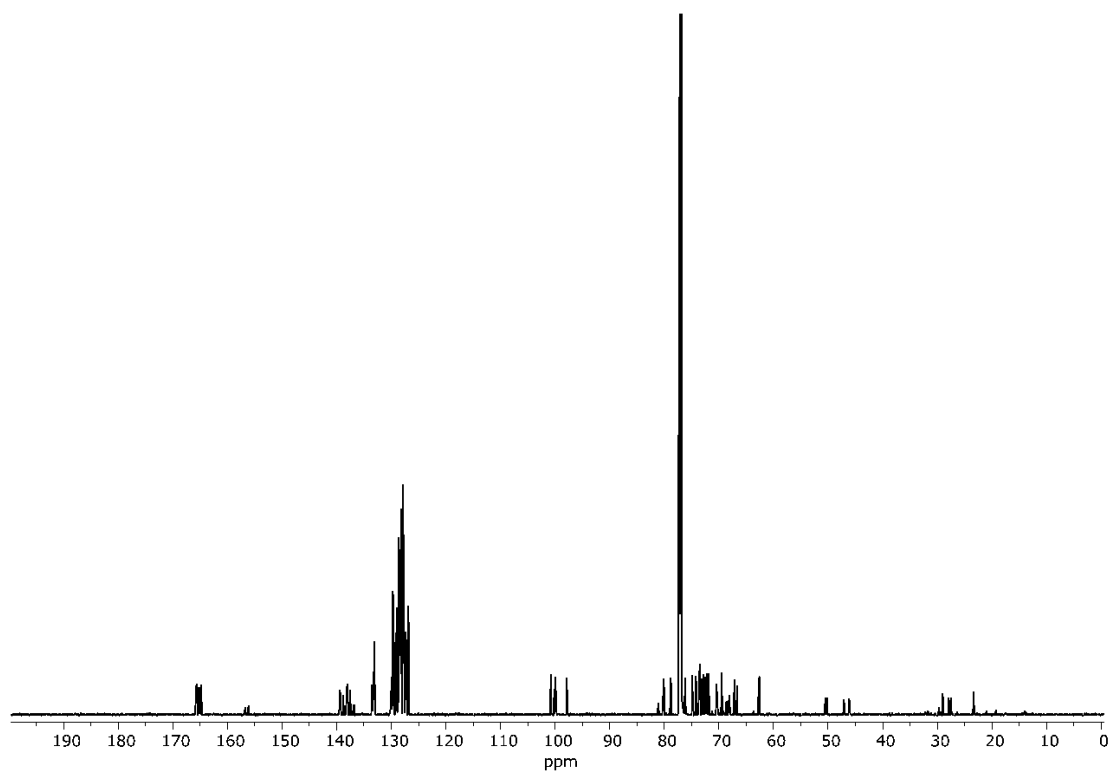


^{19}F NMR (377 MHz, DMSO- d_6) of 7.

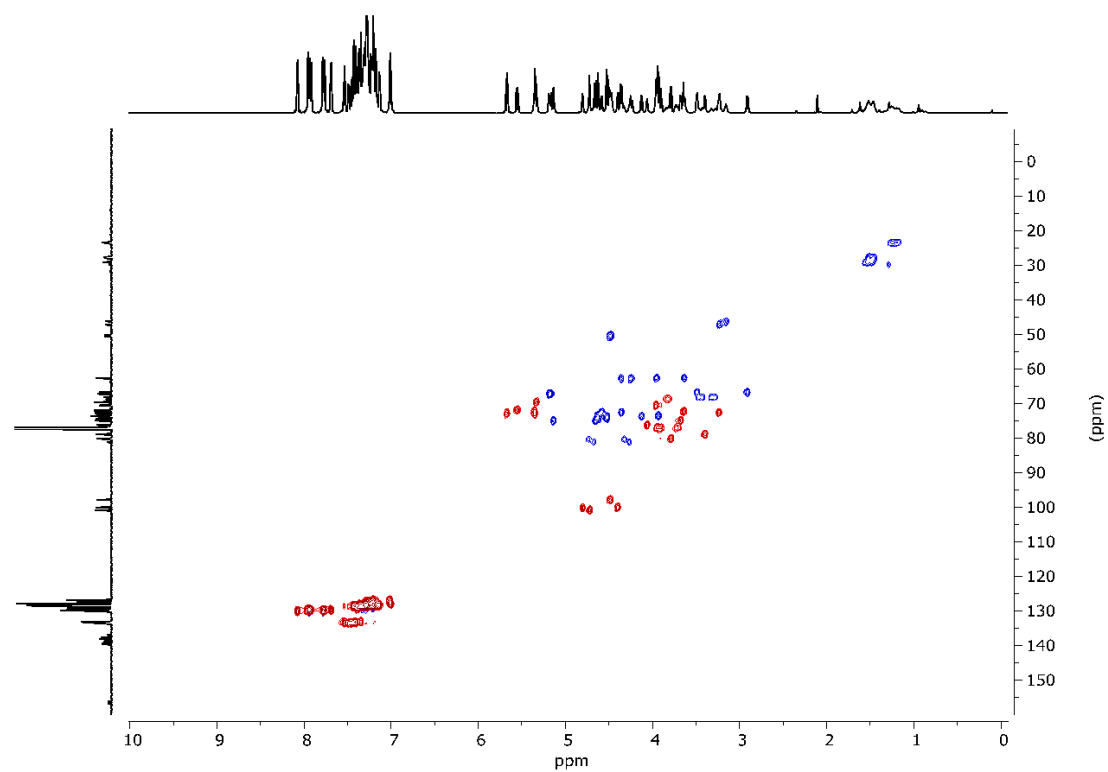
***N*-(Benzyl)benzyloxycarbonyl-5-aminopentyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-benzyl-6-deoxy-6-fluoro- α -D-galactopyranoside (45)**



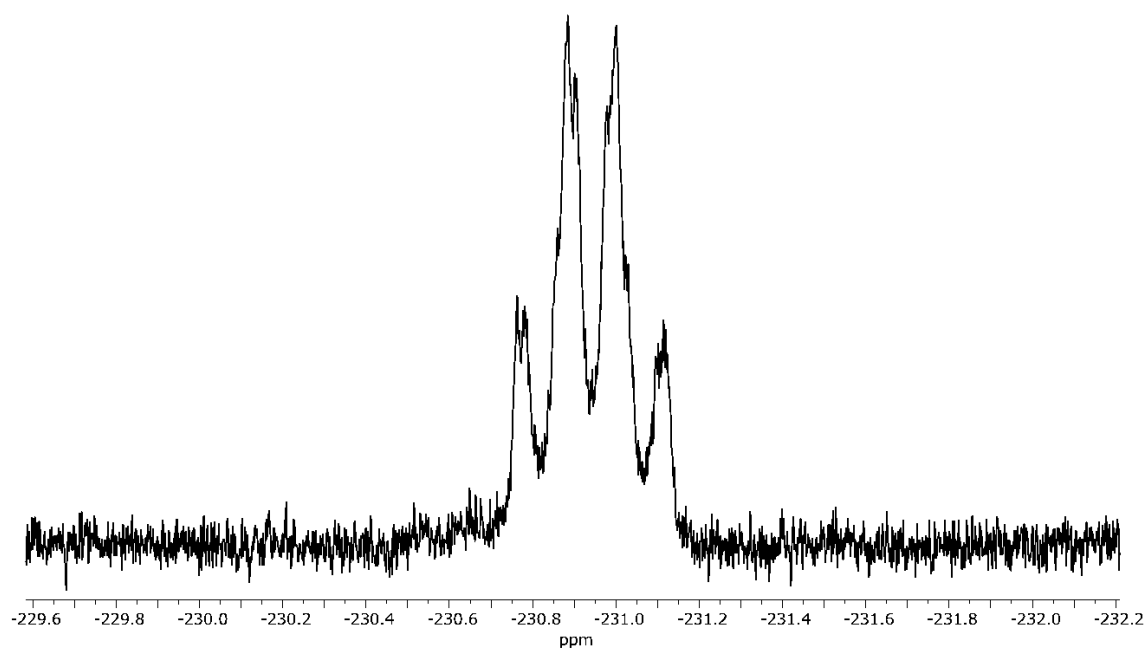
^1H NMR (800 MHz, CDCl_3) of **45**.



^{13}C NMR (200 MHz, CDCl_3) of **45**.

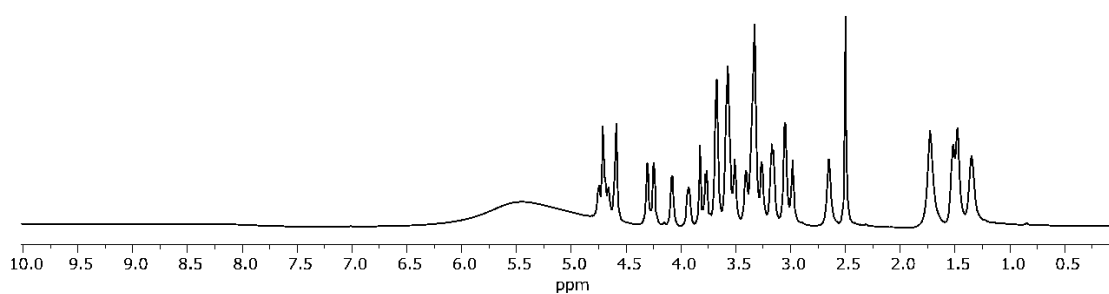
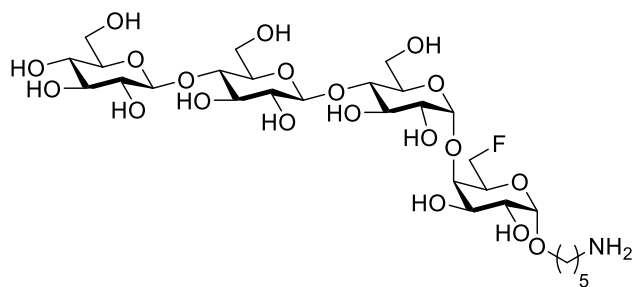


HSQC (CDCl₃) of **45**.

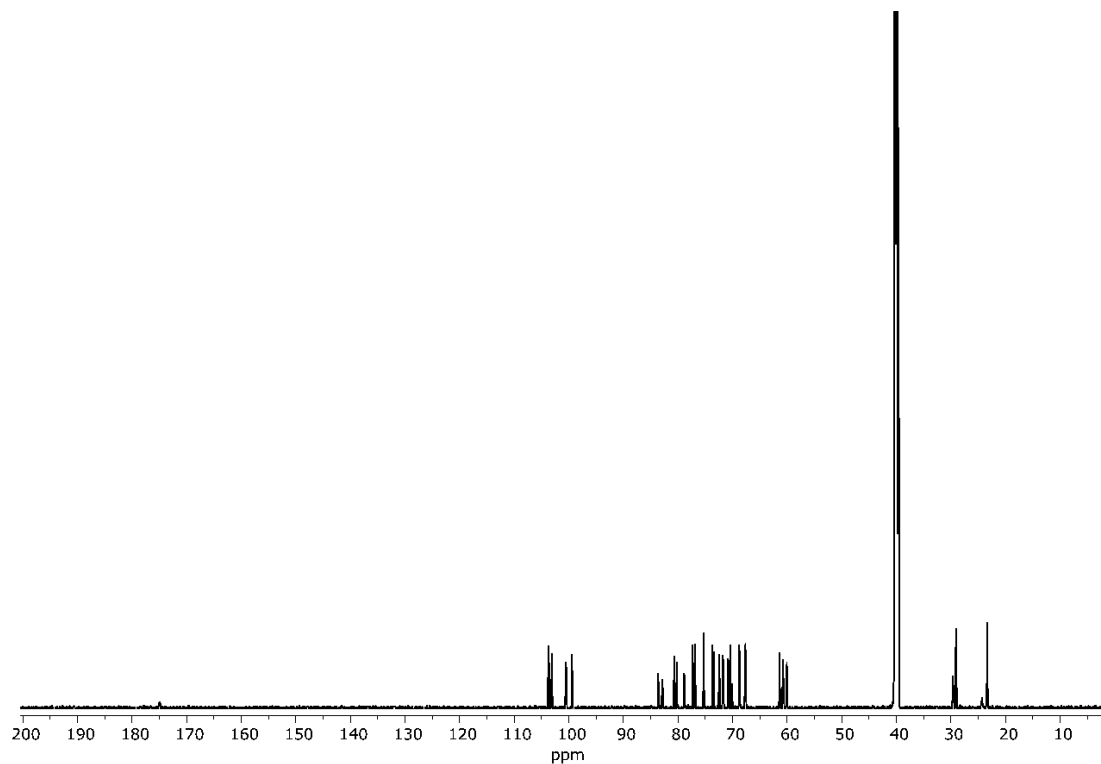


¹⁹F NMR (377 MHz, CDCl₃) of **45**.

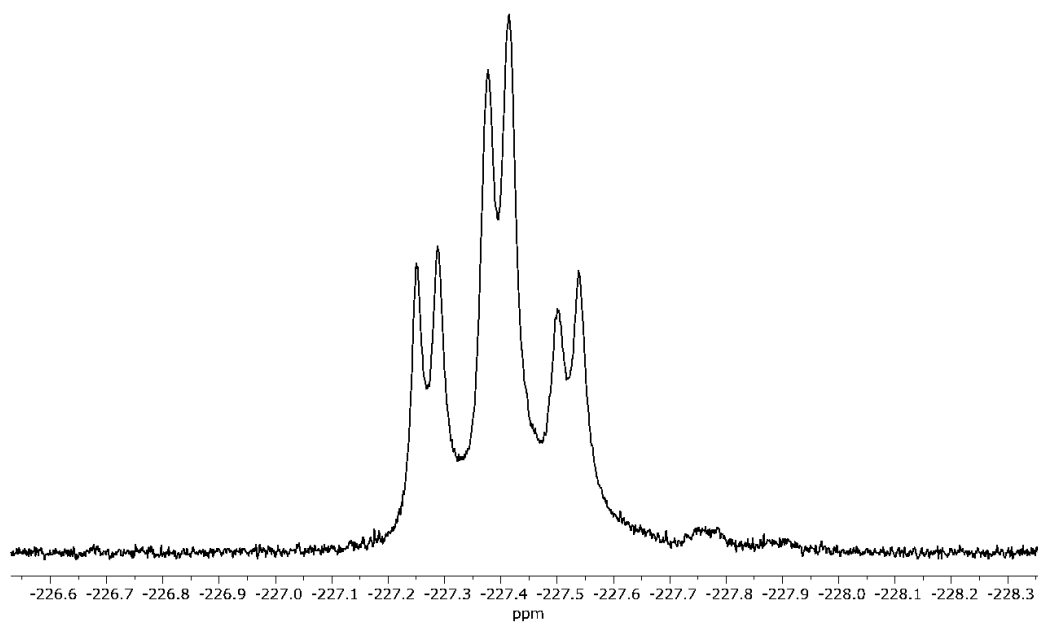
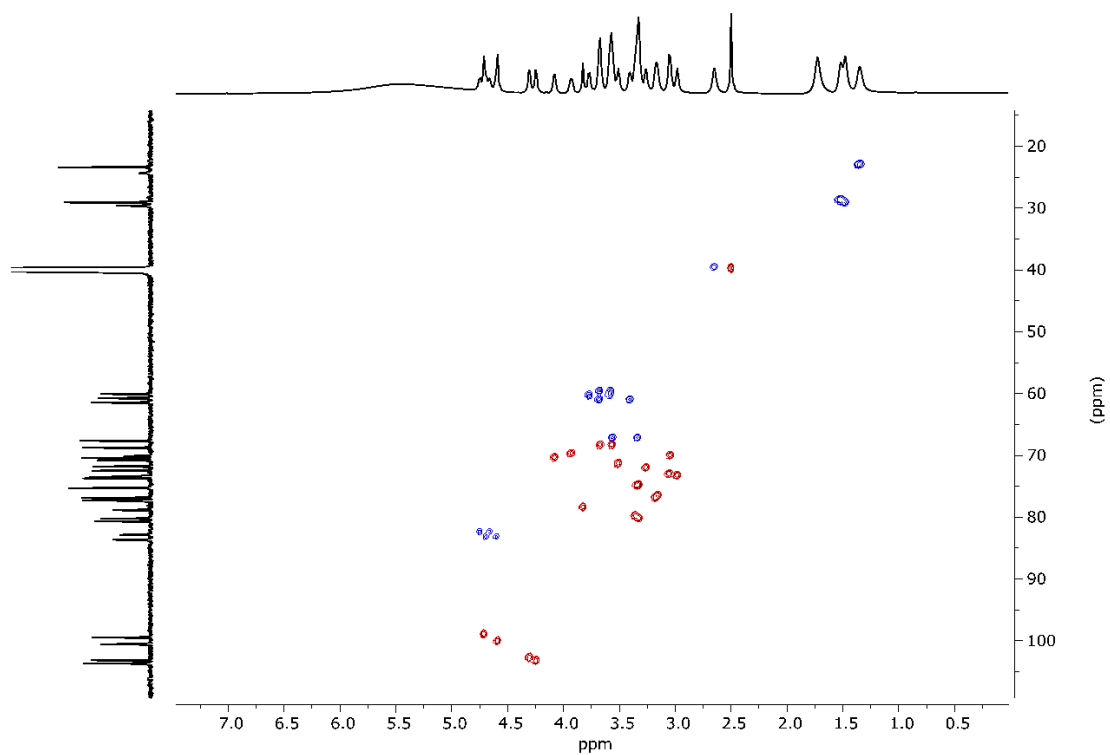
5-Aminopentyl-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-6-deoxy-6-fluoro- α -D-galactopyranoside (9)



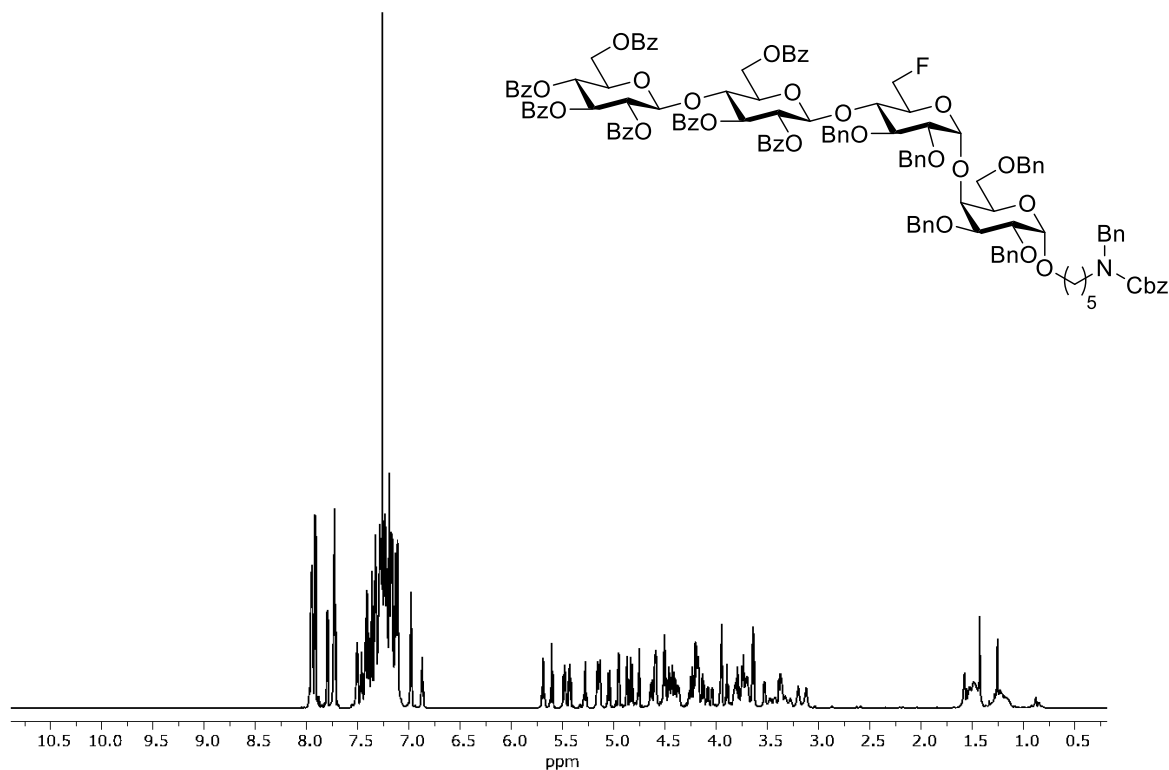
^1H NMR (800 MHz, DMSO-d_6) of **9**.



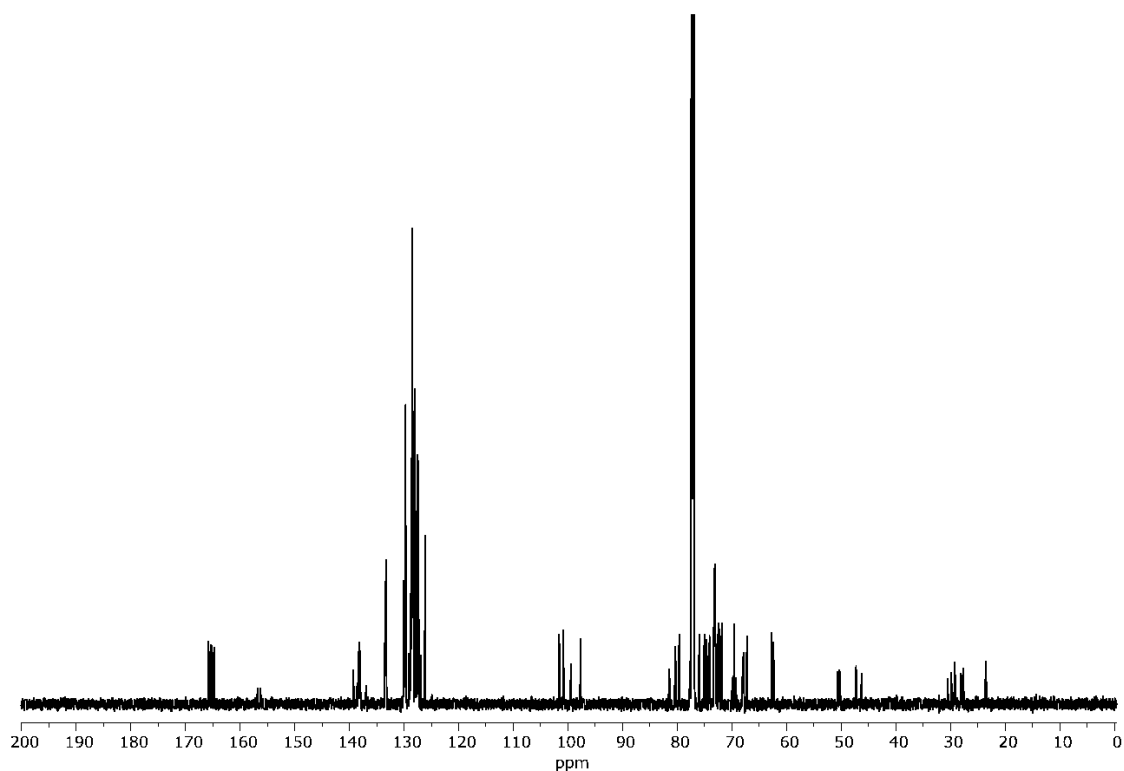
^{13}C NMR (200 MHz, DMSO-d_6) of **9**.



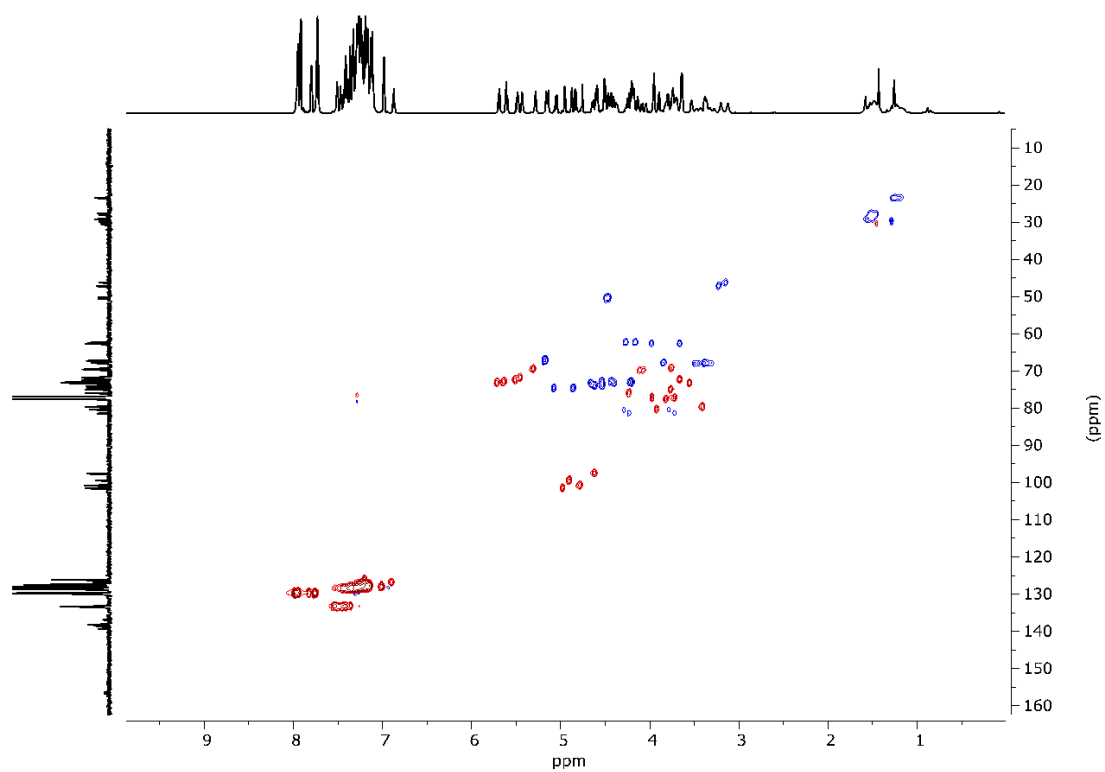
***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-(2,3,4,6-tetra-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3,6-tri-*O*-benzoyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(2,3-di-*O*-benzyl-6-deoxy-6-fluoro- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-galactopyranoside (48)**



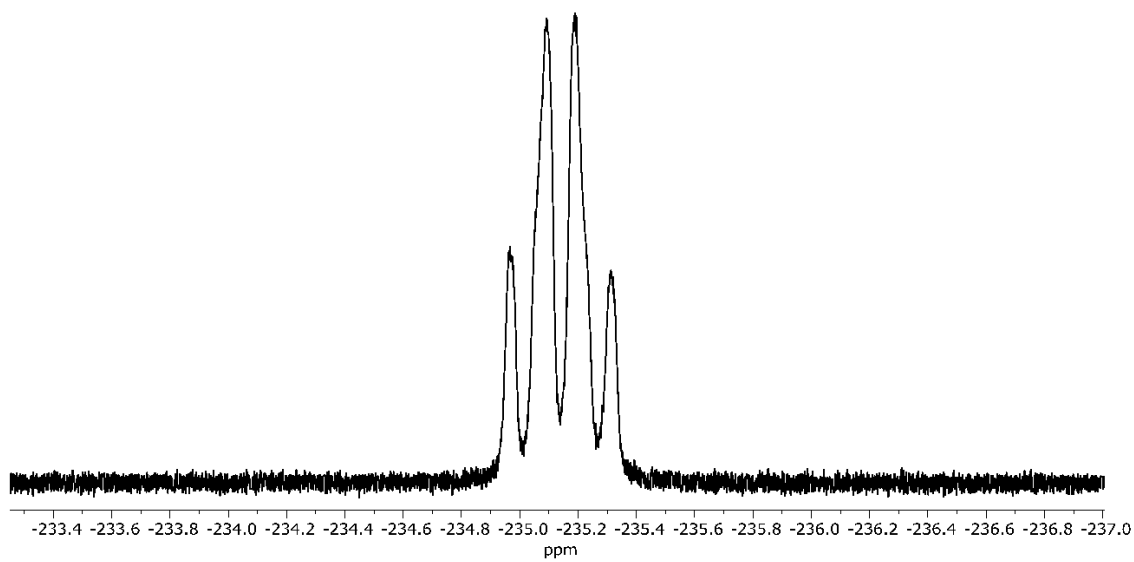
^1H NMR (800 MHz, CDCl_3) of 48.



^{13}C NMR (200 MHz, CDCl_3) of 48.

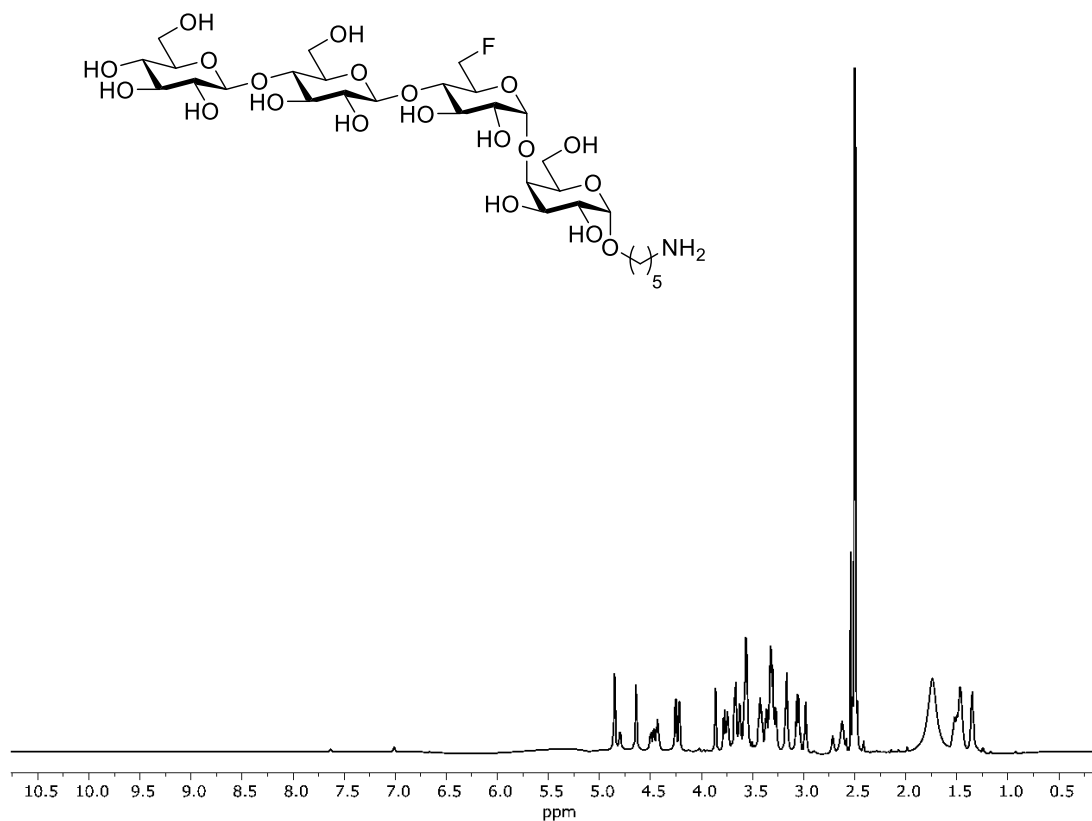


HSQC (CDCl_3) of **48**.

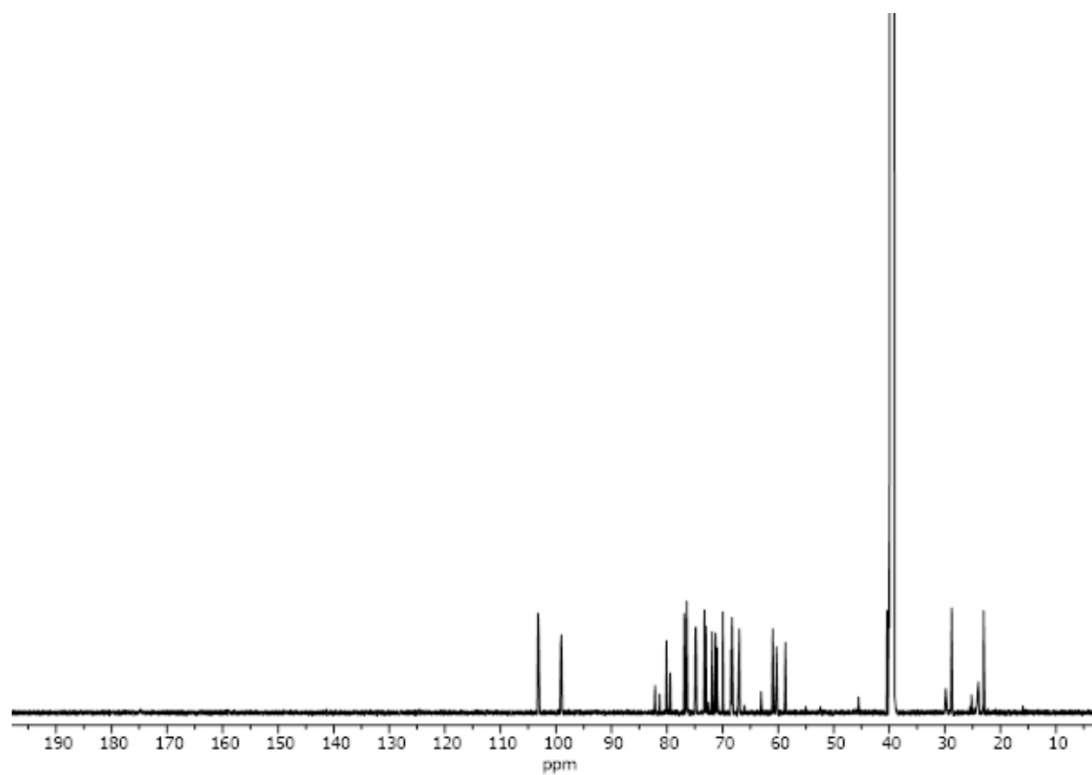


^{19}F NMR (377 MHz, CDCl_3) of **48**.

5-Aminopentyl-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-(6-deoxy-6-fluoro- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)- α -D-galactopyranoside (8)



^1H NMR (800 MHz, DMSO- d_6) of 8.



^{13}C NMR (200 MHz, DMSO- d_6) of 8.

