

## Supplementary Information for:

### Synthesis of Arabinofuranose Branched Galactofuran Tetrasaccharides Constituents of Mycobacterial Arabinogalactan

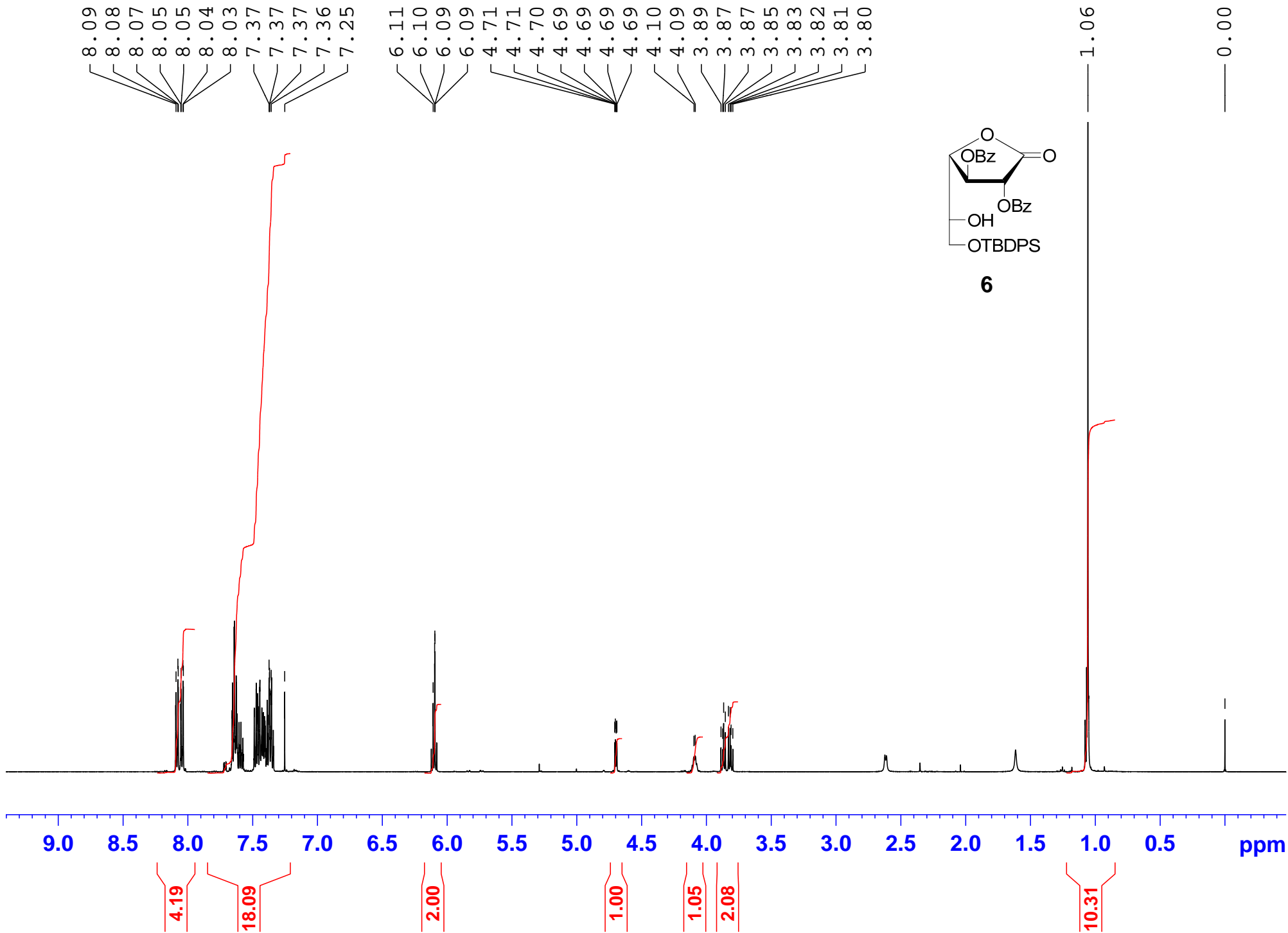
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#### Table of Contents

Compound	Spectra
2,3-Di- <i>O</i> -benzoyl-6- <i>O</i> -tert-butyldiphenylsilyl-D-galactono-1,4-lactone ( <b>6</b> )	S3-S4
2,3-Di- <i>O</i> -benzoyl-6- <i>O</i> -tert-butyldimethylsilyl-D-galactono-1,4-lactone ( <b>12</b> )	S5-S6
2,3,5-Tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)-2,3-di- <i>O</i> -benzoyl-6- <i>O</i> -tert-butyldiphenylsilyl-D-galactono-1,4-lactone ( <b>15</b> )	S7-S8
2,3,5-Tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)-2,3-di- <i>O</i> -benzoyl-D-galactono-1,4-lactone ( <b>4</b> )	S9-S10
2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl-D-galactono-1,4-lactone ( <b>16</b> )	S11-S14
2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl-D-galactofuranose ( <b>18</b> )	S15-S18
<i>O</i> -(2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl-D-galactofuranosyl) trichloroacetimidate ( <b>19</b> )	S19-S20
9-Decenyl 2,3,5,6-tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl- $\beta$ -D-galactofuranoside ( <b>20</b> )	S21-S23
9-Decenyl $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[ $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]- $\beta$ -D-galactofuranoside ( <b>1</b> )	S24-S27
2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl-D-galactono-1,4-lactone ( <b>21</b> )	S28-S29

2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl-D-galactofuranose ( <b>22</b> )	S30-S33
<i>O</i> -(2,3,5,6- <i>O</i> -(tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl-D-galactofuranosyl) trichloroacetimidate ( <b>7</b> )	S34-S35
2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-2,6-di- <i>O</i> -pivaloyl-D-galactono-1,4-lactone ( <b>23</b> )	S36-S37
2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl-D-galactono-1,4-lactone ( <b>24</b> )	S38-S41
2,3,5,6-Tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\alpha,\beta$ -D-galactofuranose ( <b>25</b> )	S42-S45
<i>O</i> -(2,3,5,6-tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\beta$ -D-galactofuranosyl) trichloroacetimidate ( <b>26</b> )	S46
Decenyl 2,3,5,6-tetra- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[2,3,5-tri- <i>O</i> -benzoyl- $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]-2,3-di- <i>O</i> -benzoyl- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)-3- <i>O</i> -acetyl-2,6-di- <i>O</i> -pivaloyl- $\beta$ -D-galactofuranoside ( <b>27</b> )	S47-S50
9-Decenyl $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 6)-[ $\alpha$ -D-arabinofuranosyl-(1 $\rightarrow$ 5)]- $\beta$ -D-galactofuranosyl-(1 $\rightarrow$ 5)- $\beta$ -D-galactofuranoside ( <b>2</b> )	S51-S54



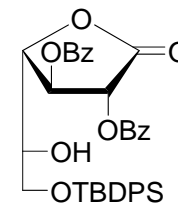
<sup>1</sup>H NMR spectrum of compound **6** (CDCl<sub>2</sub>; 500 MHz).

168.7  
165.6  
165.2

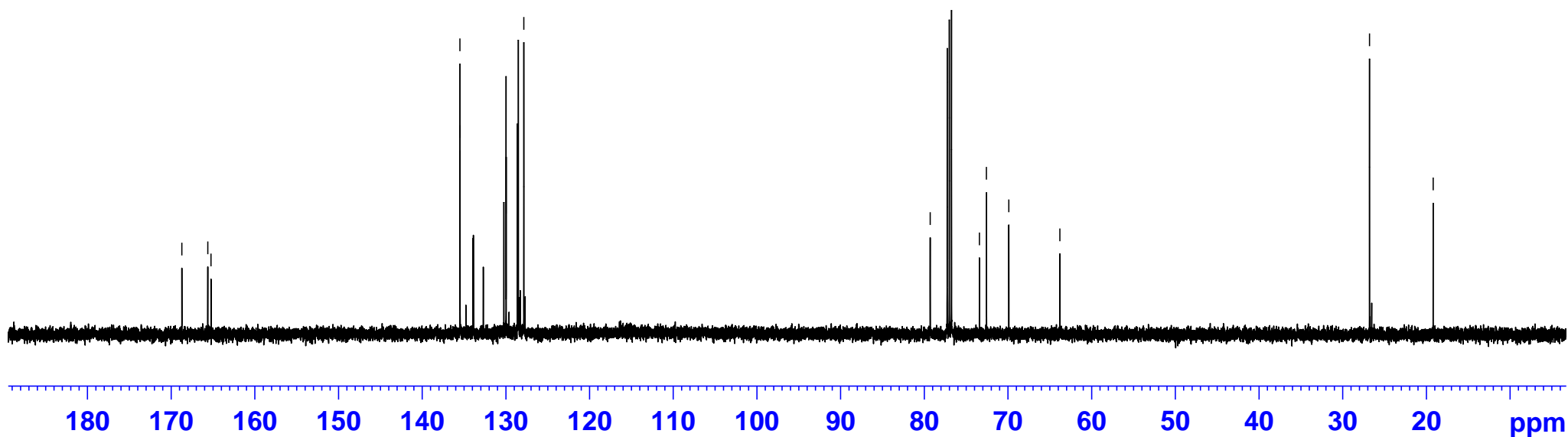
135.5  
135.5  
127.8

79.3  
73.4  
72.6  
69.9  
63.8

26.8  
19.2

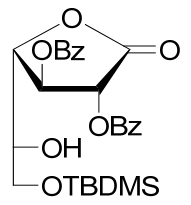


**6**

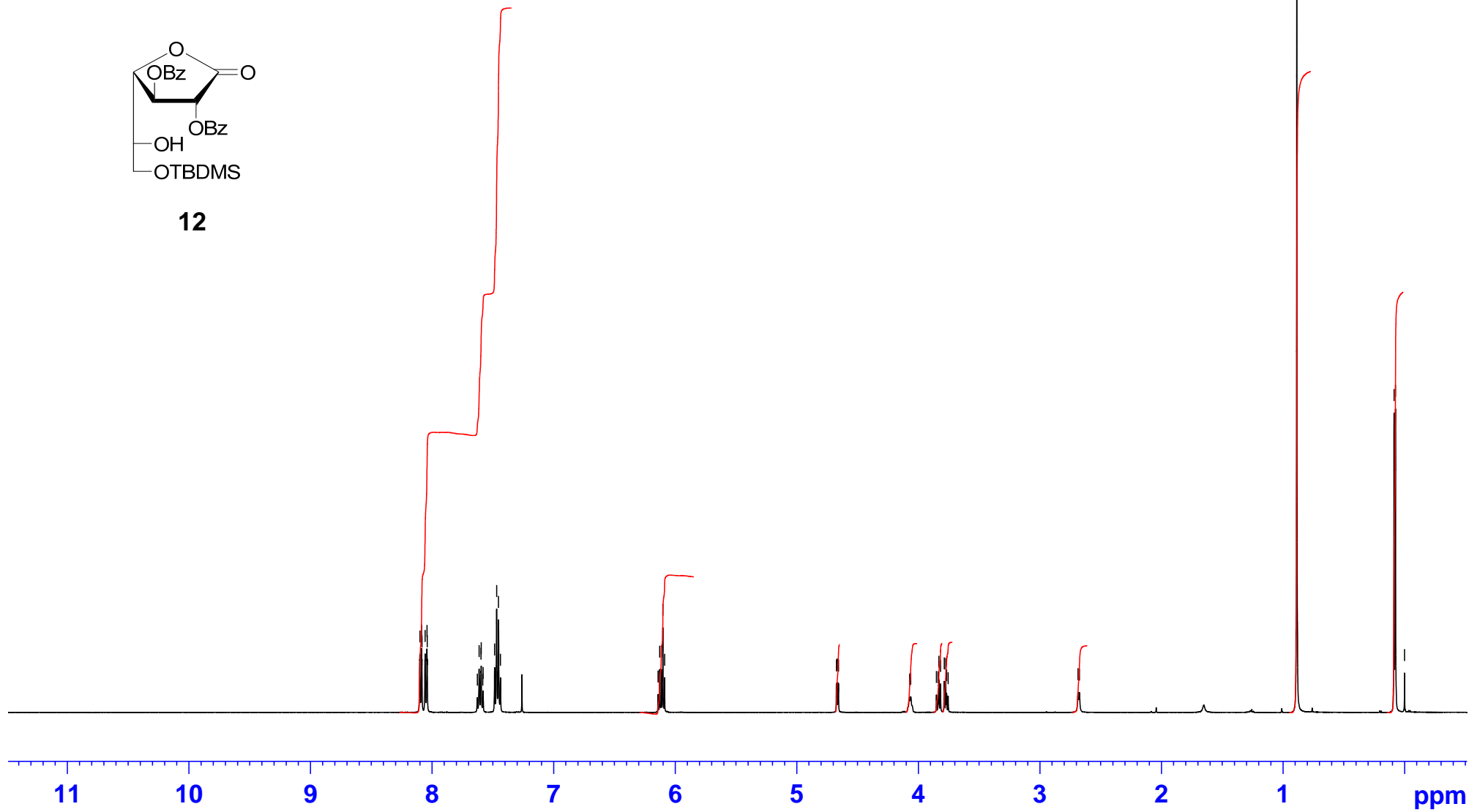


$^{13}\text{C}$  NMR spectrum of compound **6** (CDCl<sub>3</sub>; 125.8 MHz).

8.10  
8.09  
8.08  
8.06  
8.04  
8.04  
7.63  
7.61  
7.60  
7.60  
7.58  
7.58  
7.49  
7.47  
7.45  
7.44  
6.14  
6.13  
6.11  
6.10  
6.09  
4.67  
4.67  
4.66  
4.66  
4.07  
4.06  
3.85  
3.84  
3.83  
3.82  
3.79  
3.77  
3.77  
3.75  
2.69  
2.67



**12**



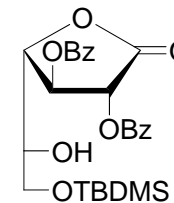
10.41  
2.00  
1.00  
1.01  
1.02  
1.04  
0.98  
9.47  
6.21

<sup>1</sup>H NMR spectrum of compound **12** (CDCl<sub>3</sub>, 500 MHz).

168.8  
165.7  
165.2

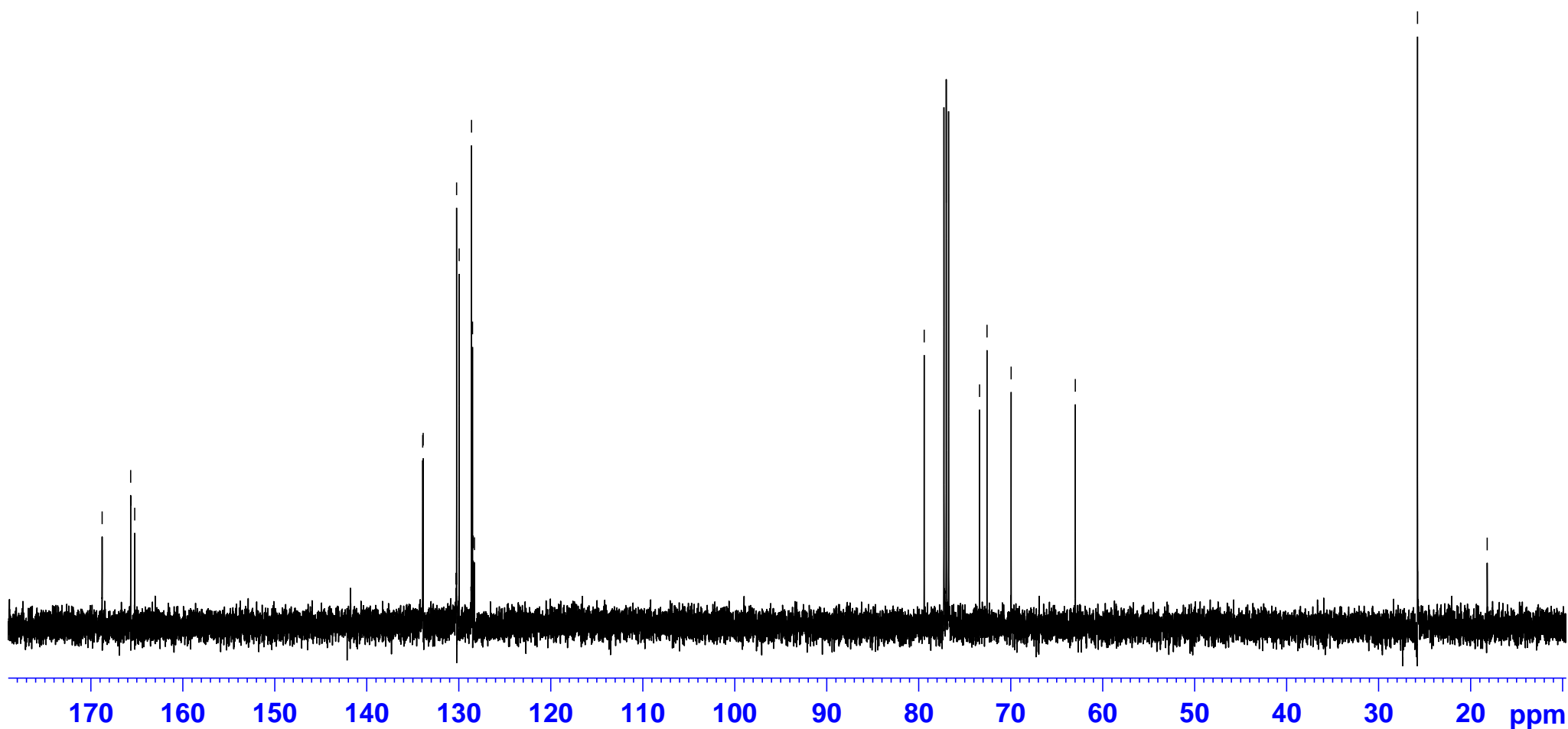
133.9  
133.9  
130.2  
130.0  
128.6  
128.5  
128.4  
128.3

79.4  
73.4  
72.6  
69.9  
63.0

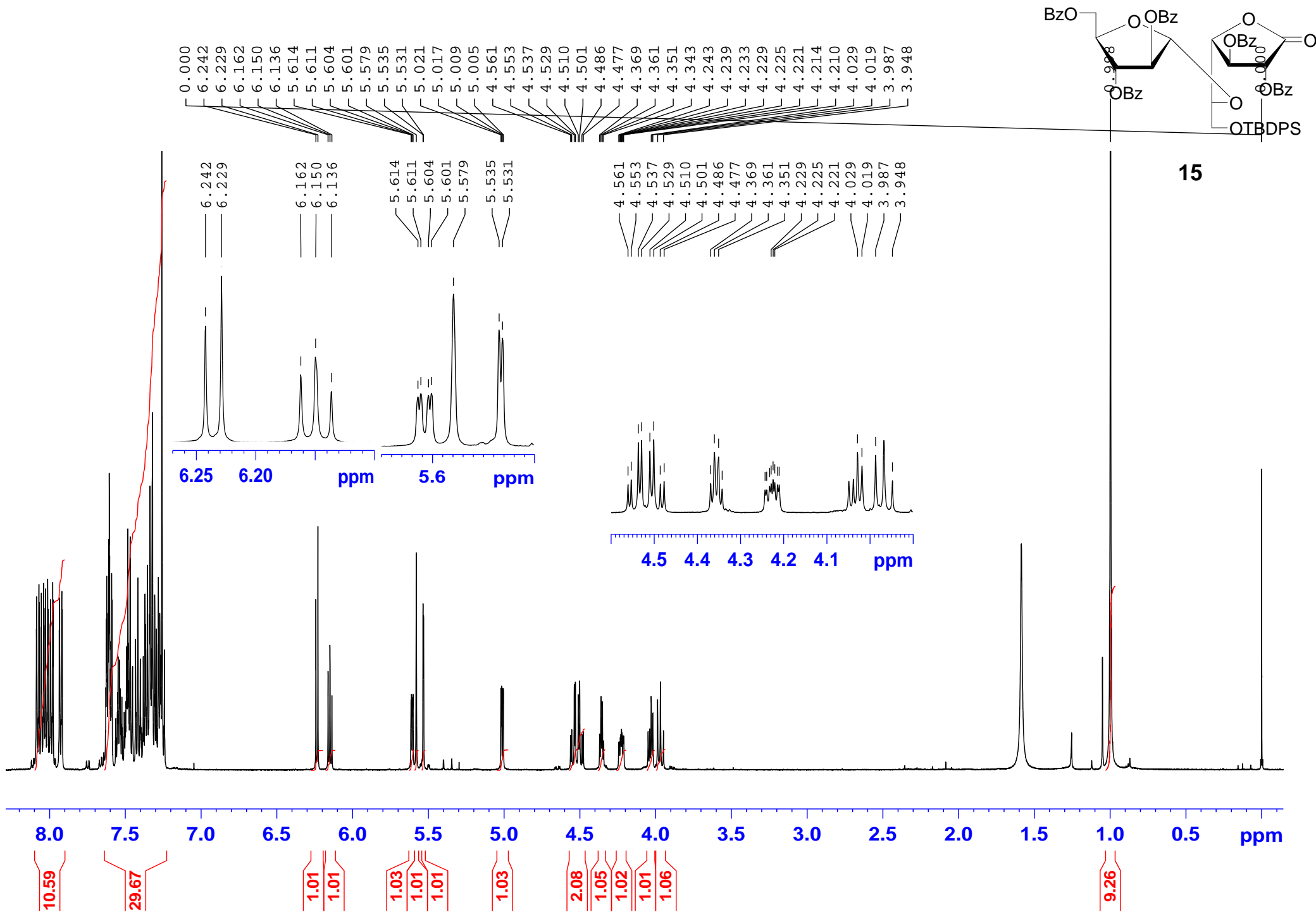


**12**

25.8  
18.2



$^{13}\text{C}$  NMR spectrum of compound **12** ( $\text{CDCl}_3$ ; 125.8 MHz).



<sup>1</sup>H NMR spectrum of compound **15** (CDCl<sub>3</sub>, 500 MHz)

168.8  
166.1  
165.7  
165.4  
165.2

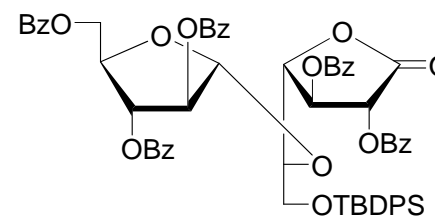
135.4  
135.4  
133.8  
127.8

107.5

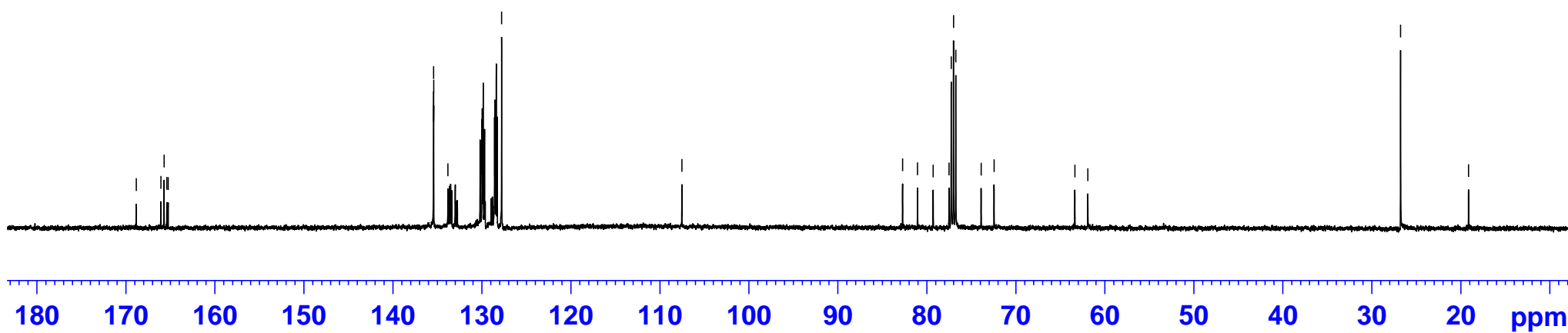
82.7  
81.0  
79.3  
77.5  
77.3  
77.0  
76.7  
73.9  
72.4  
63.4  
61.9

26.8

19.1

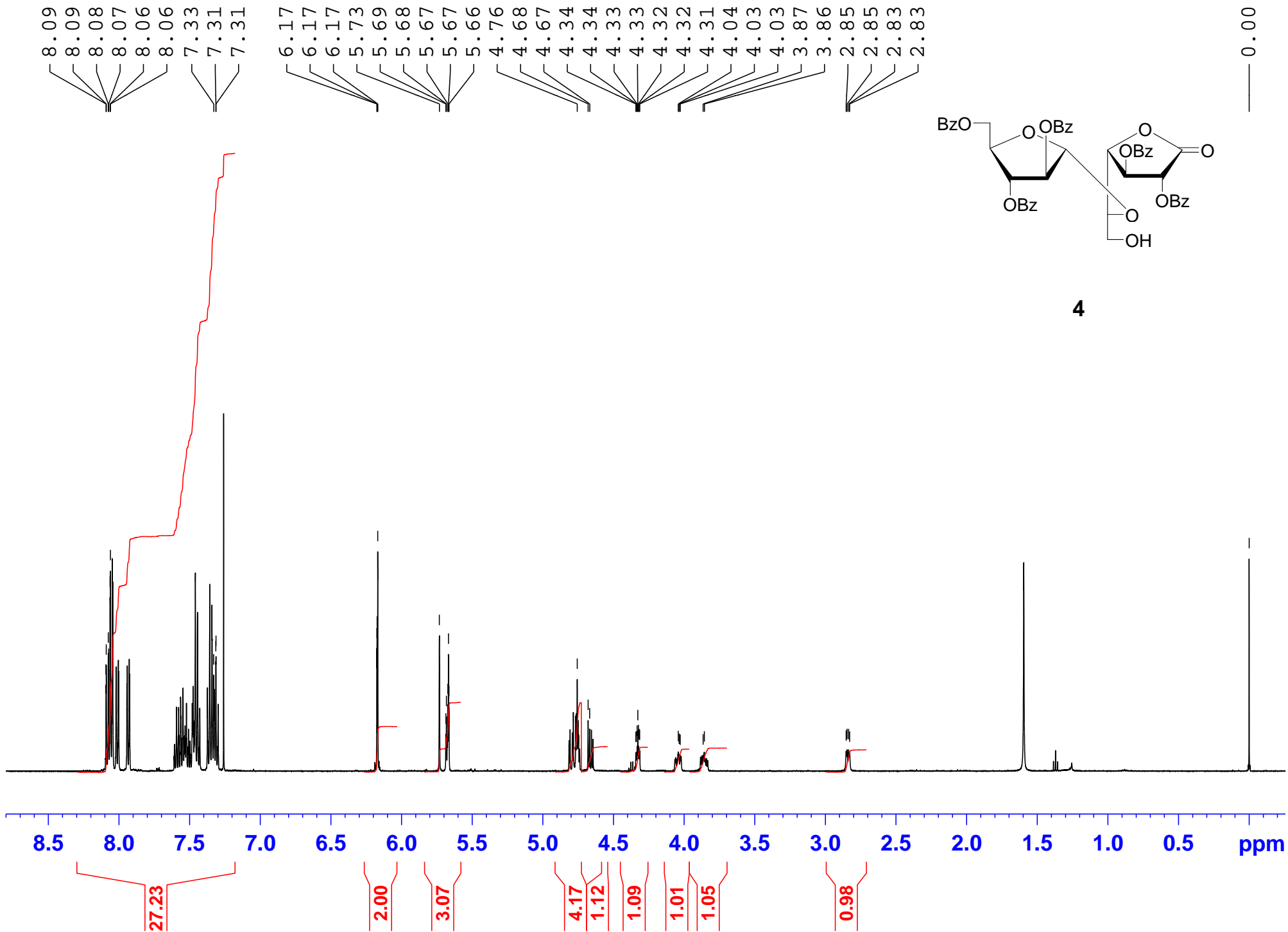


**15**

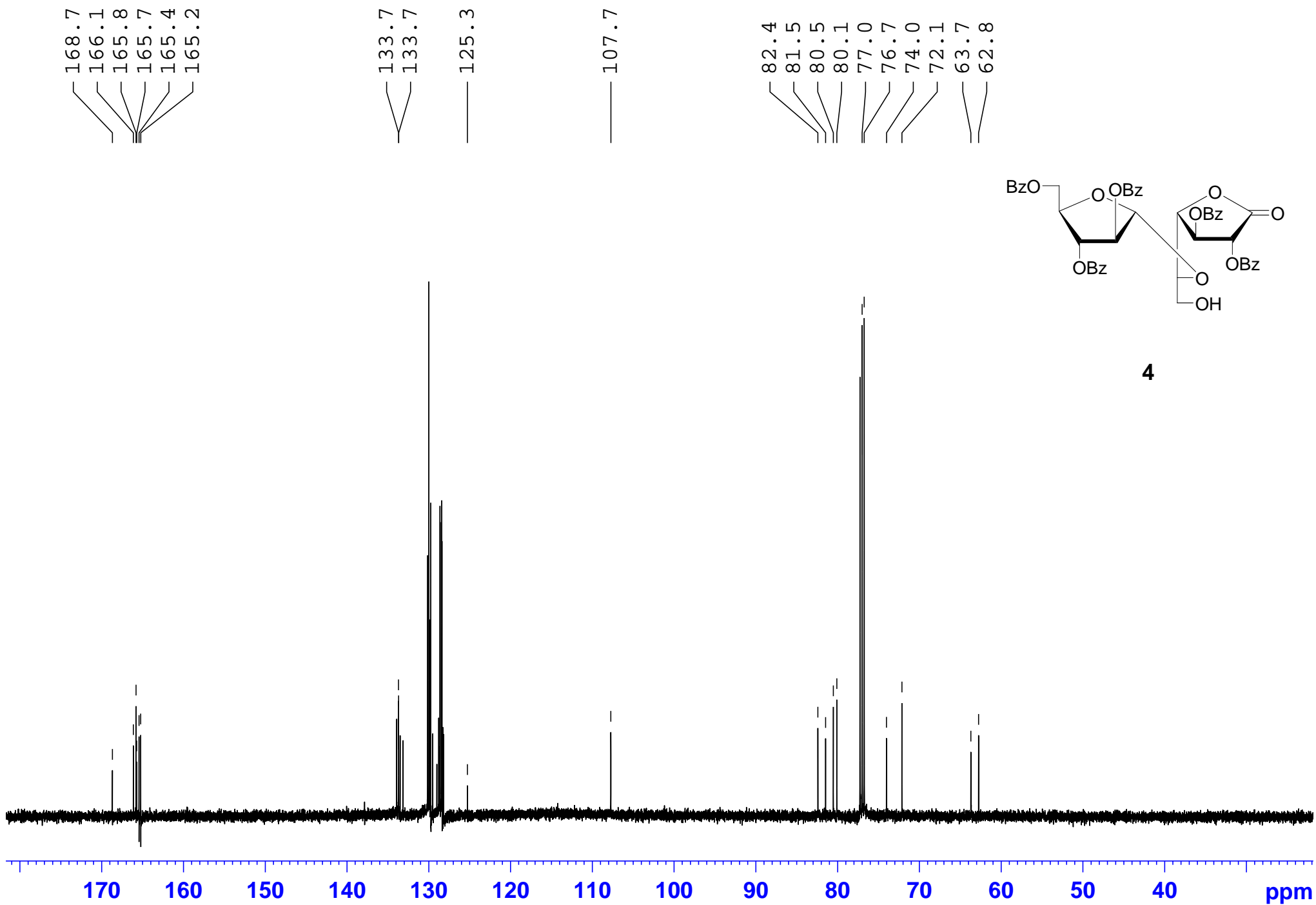


$^{13}\text{C}$  NMR spectrum of compound **15** ( $\text{CDCl}_3$ , 125.8 MHz)



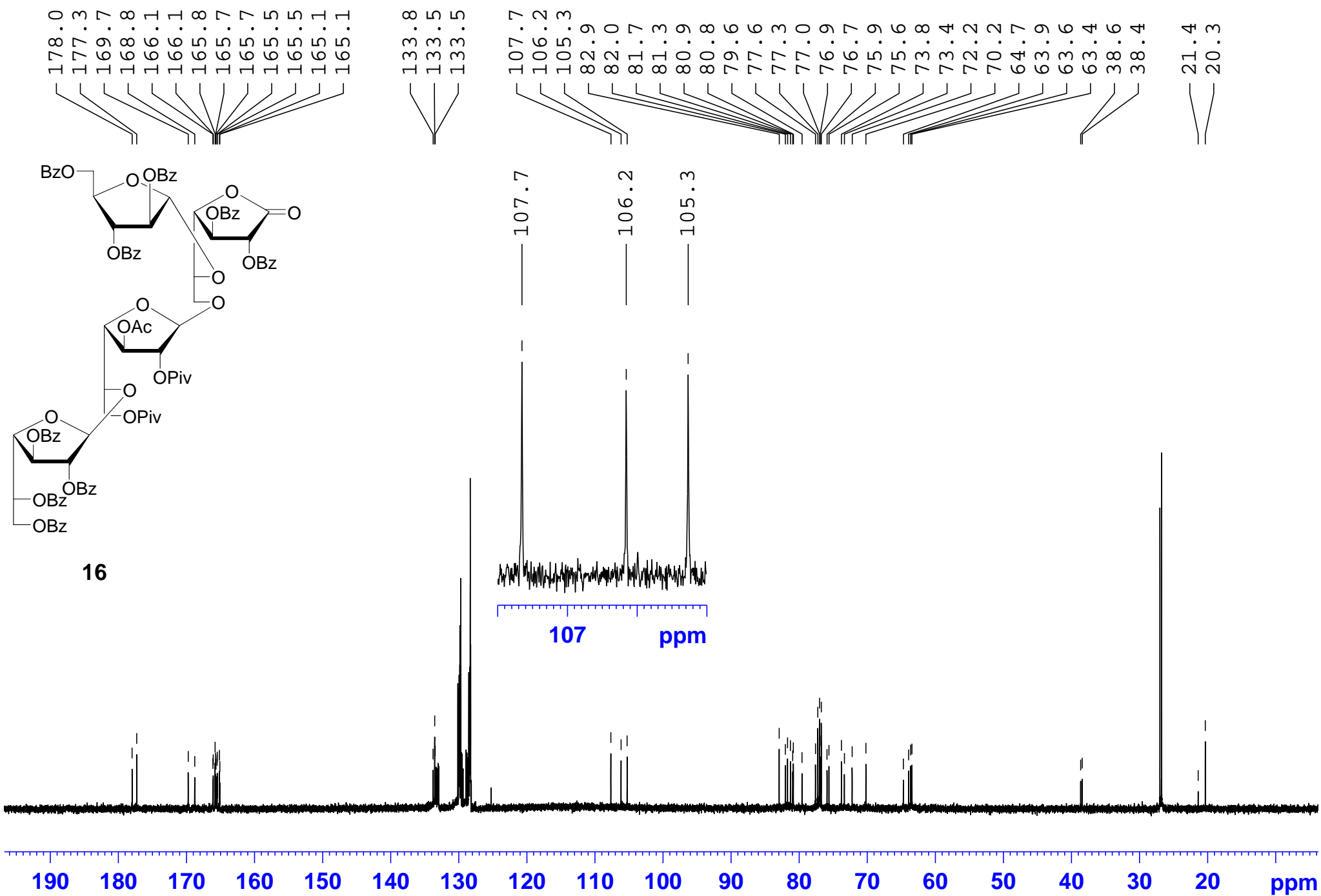


**<sup>1</sup>H NMR spectrum of compound 4 (CDCl<sub>3</sub>; 500 MHz).**

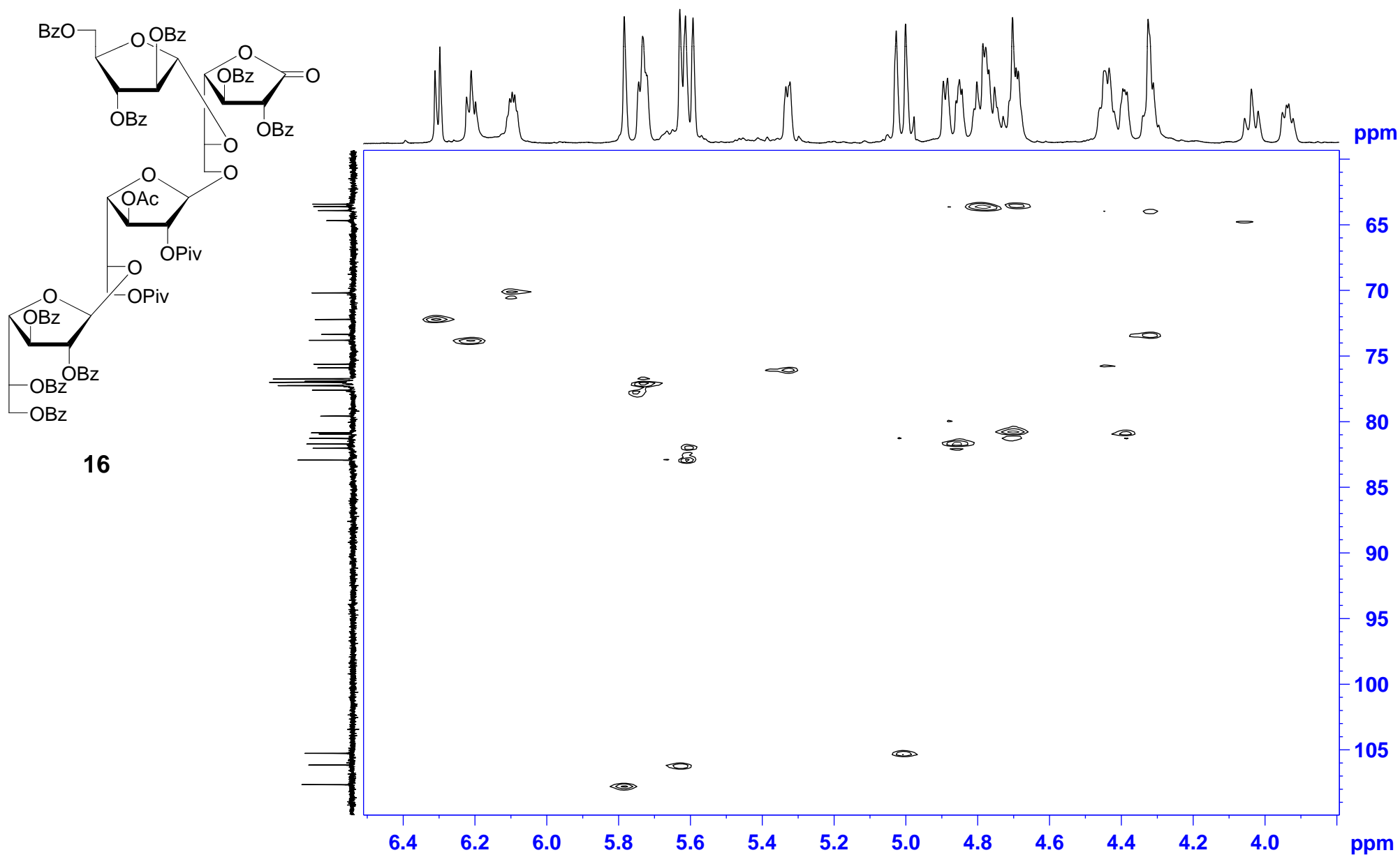


**<sup>13</sup>C NMR spectrum of compound 4 (CDCl<sub>3</sub>; 125.8 MHz).**

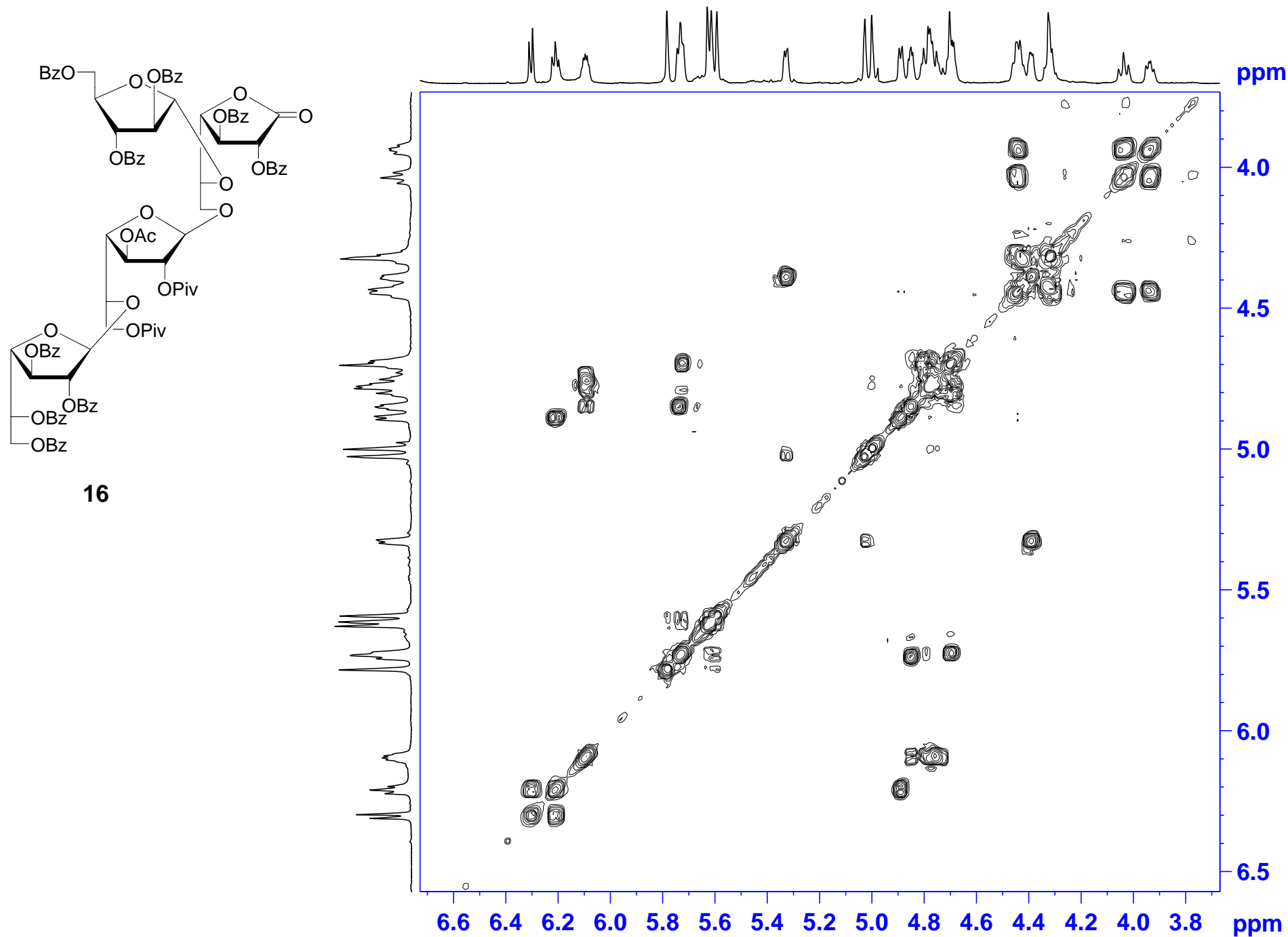




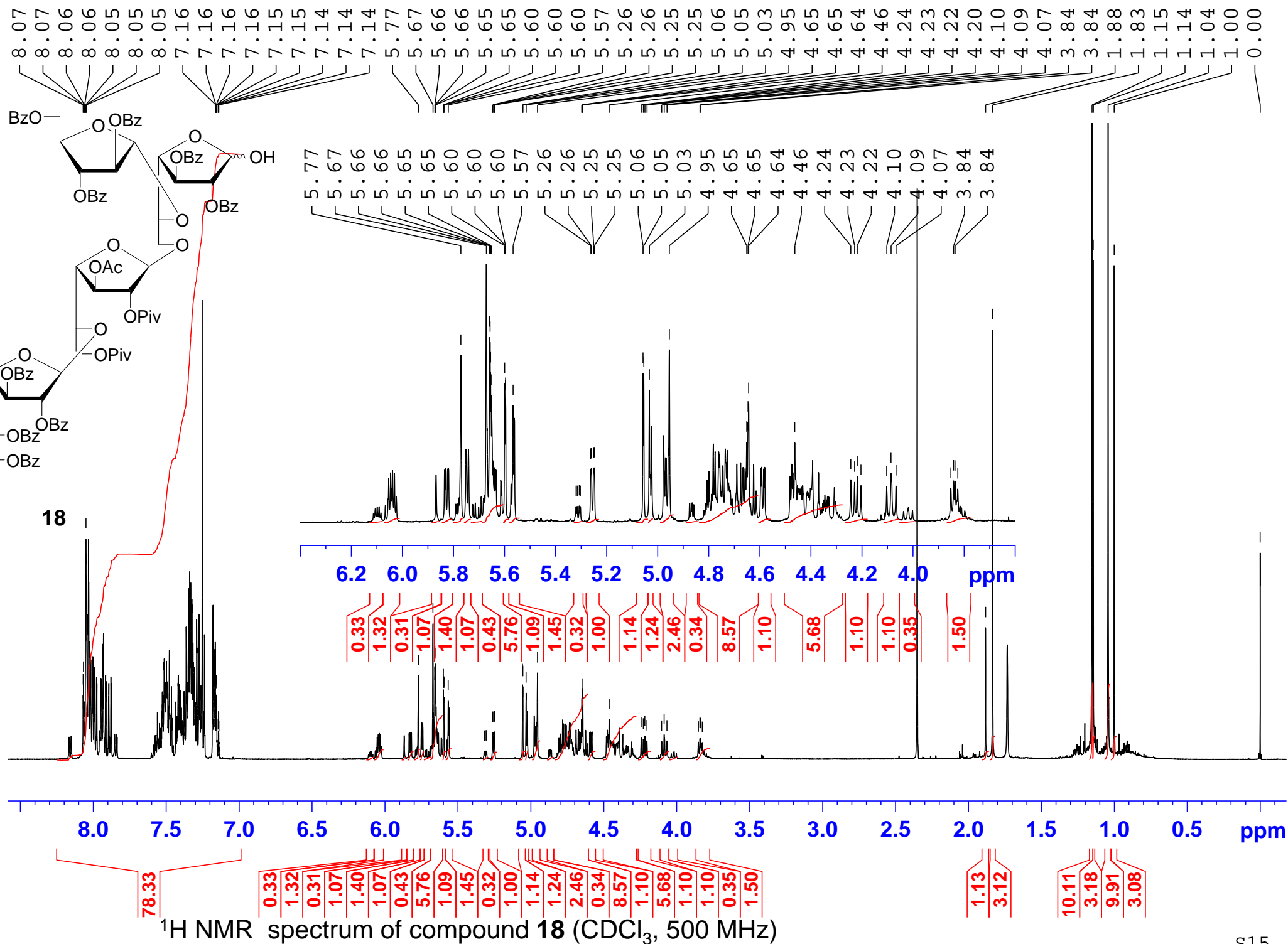
$^{13}\text{C}$  NMR spectrum of compound **16** (CDCl<sub>3</sub>, 125.8 MHz)

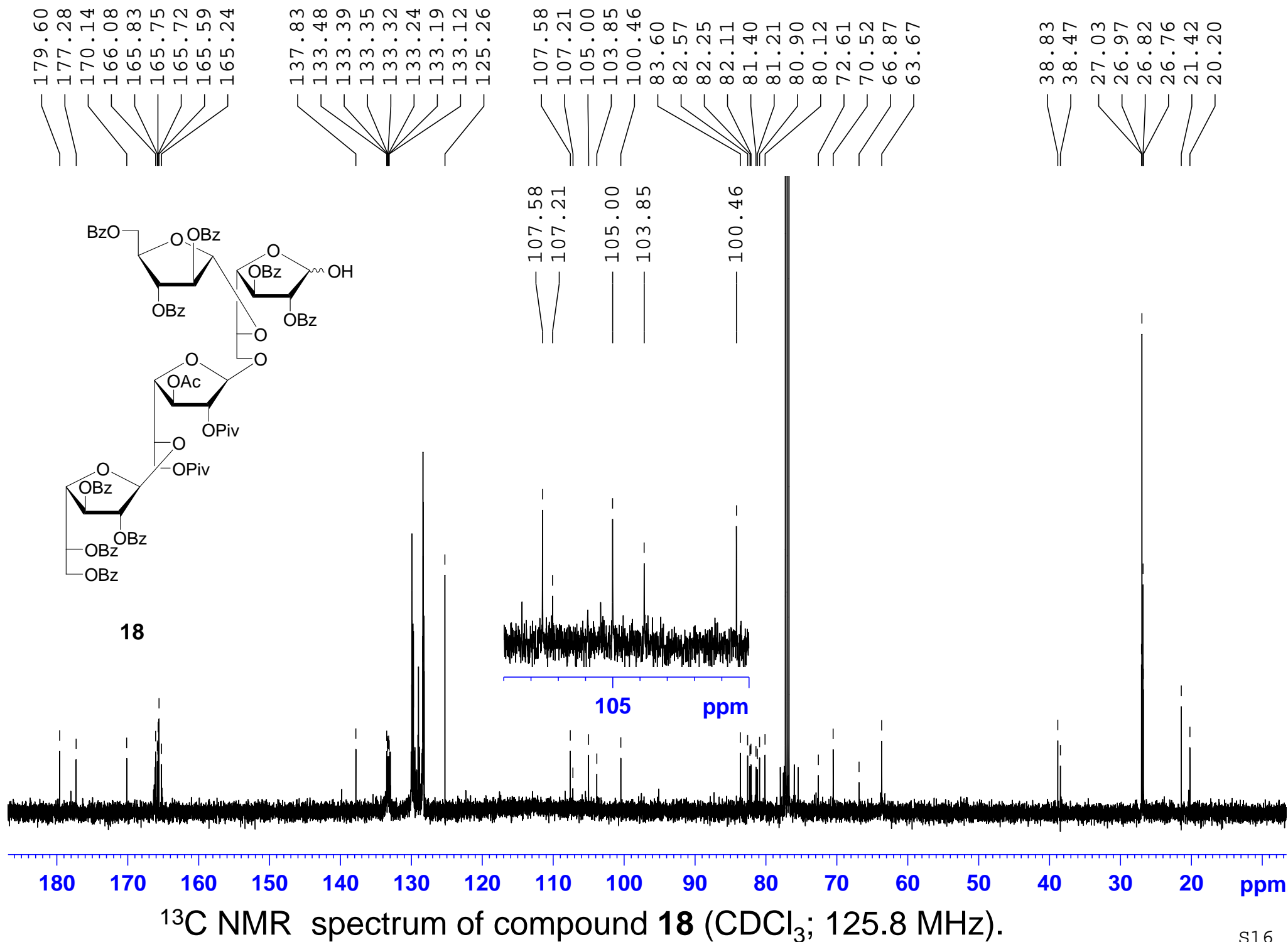


HSQC spectrum of compound **16** (CDCl<sub>3</sub>, 125.8 MHz)

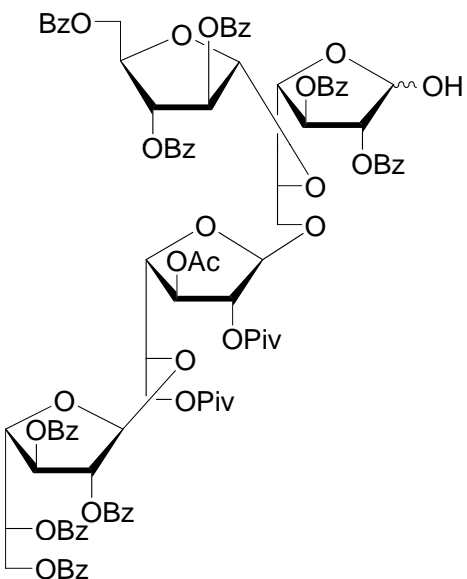
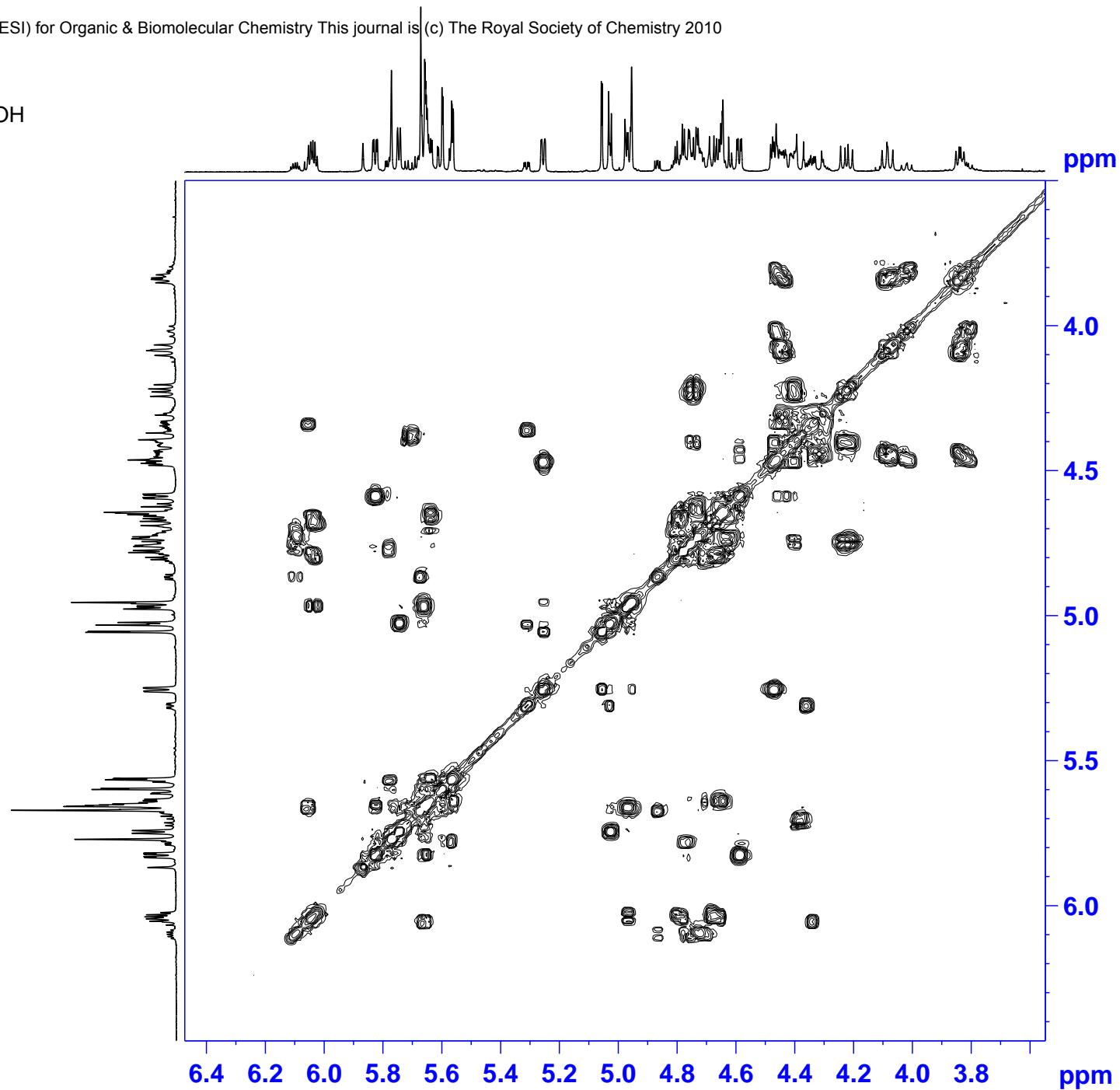


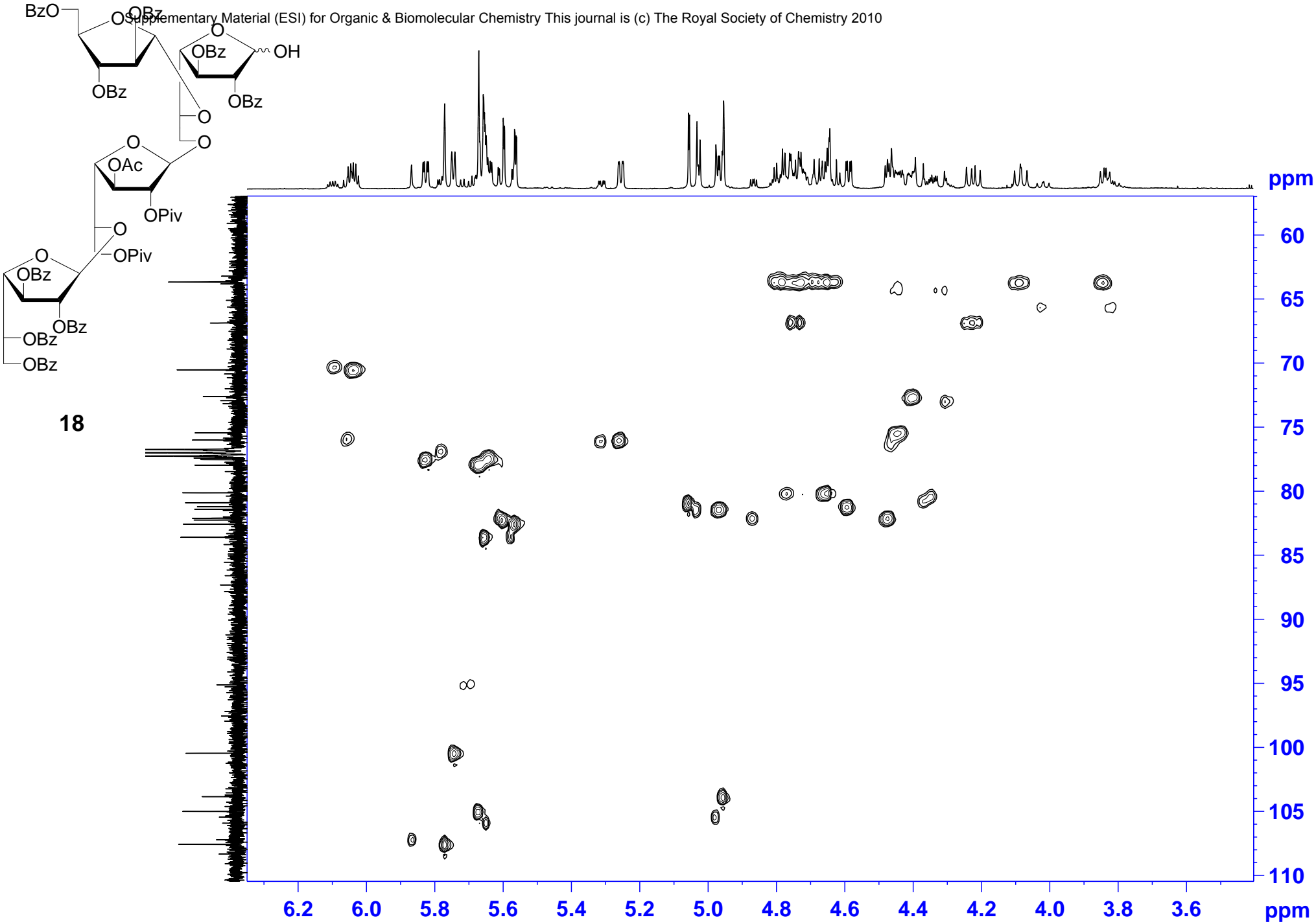
COSY spectrum of compound **16** (CDCl<sub>3</sub>, 500 MHz)



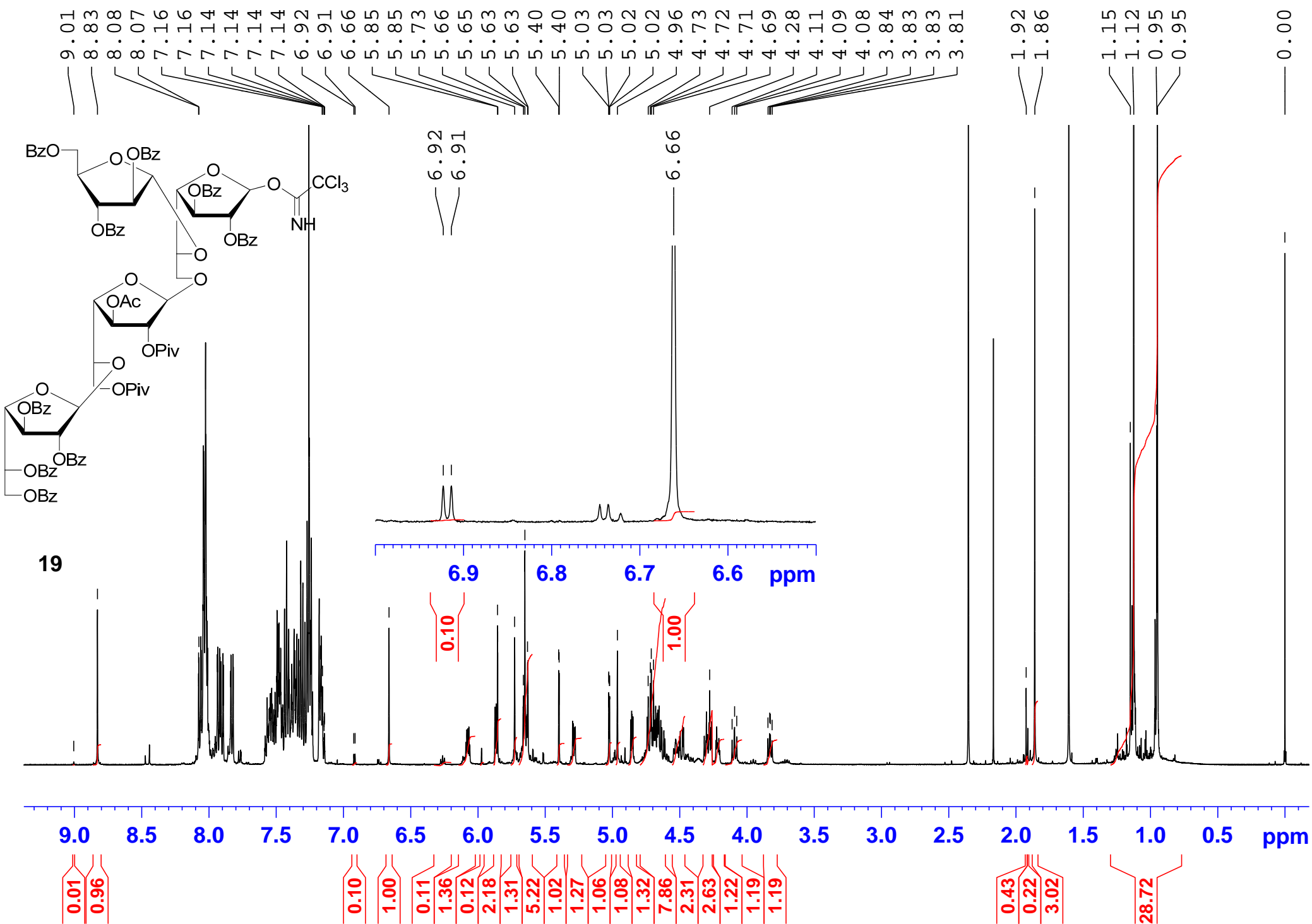




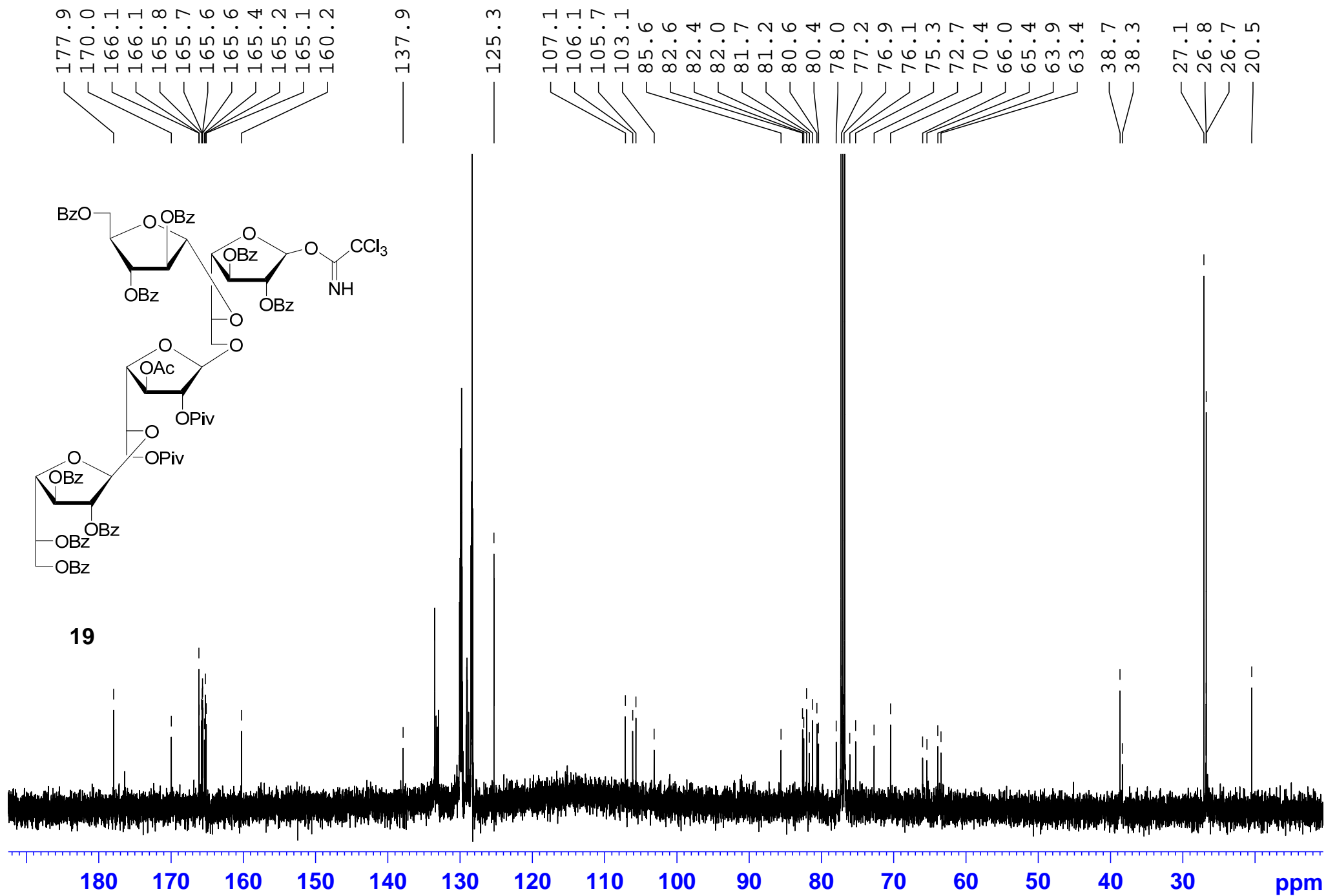
**18**COSY spectrum of compound **18** (CDCl<sub>3</sub>, 125.8 MHz)



HSQC spectrum of compound **18** ( $\text{CDCl}_3$ , 125.8 MHz)

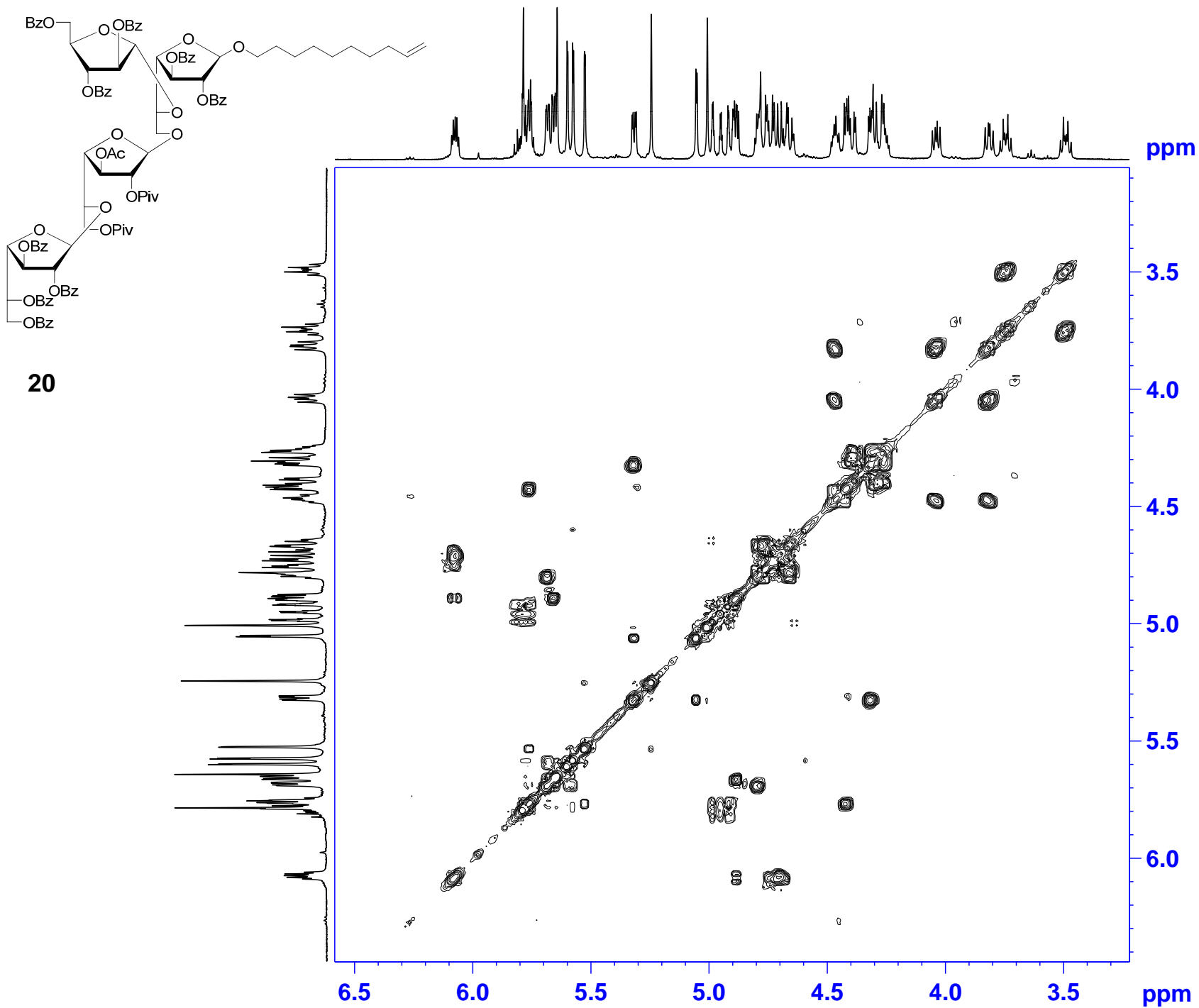


**1H NMR spectrum of compound 19 (CDCl<sub>3</sub>, 500 MHz).**

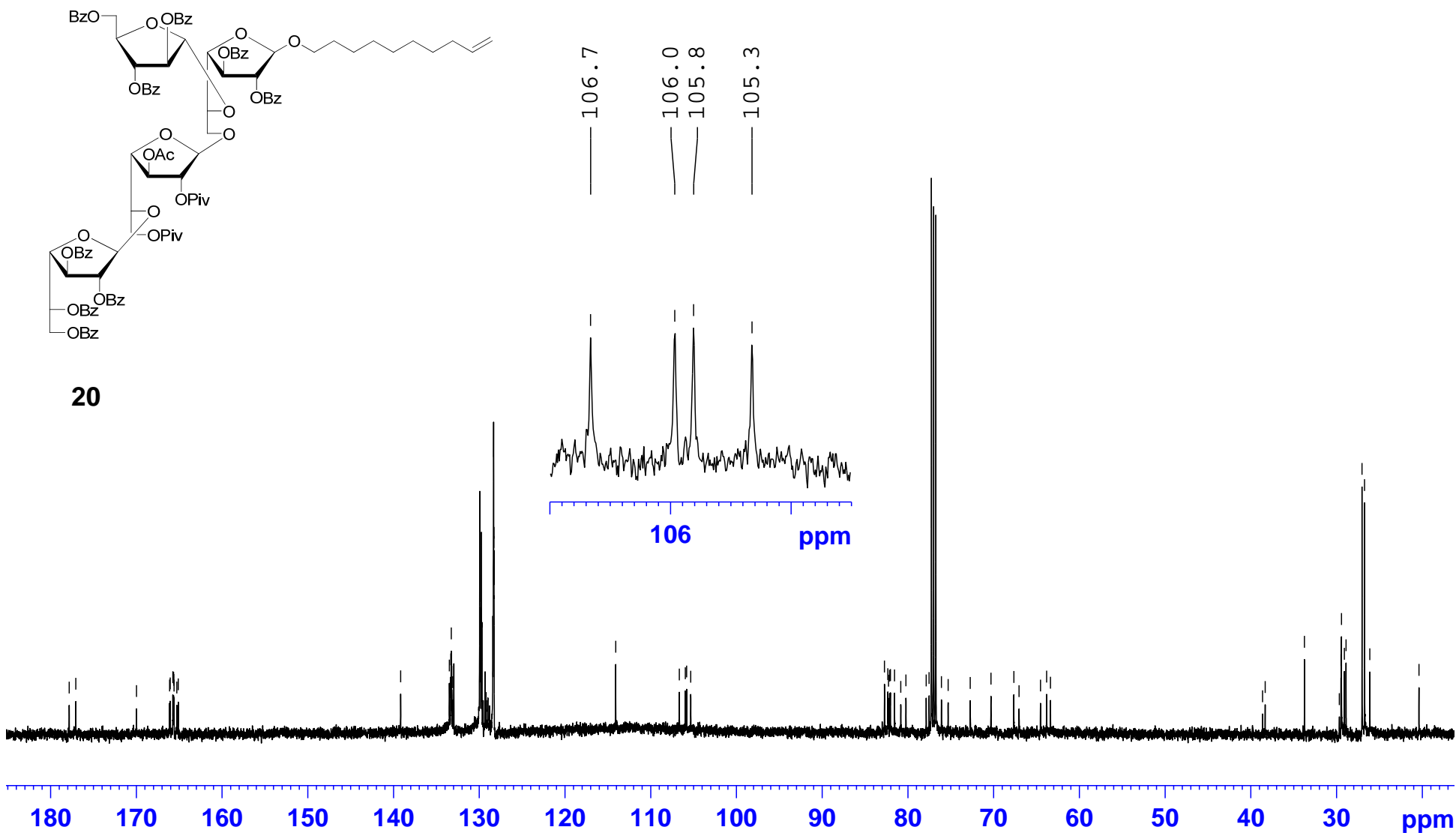
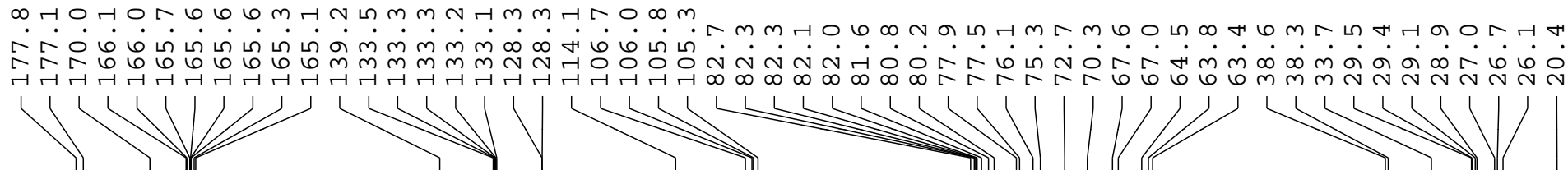


$^{13}\text{C}$  NMR spectrum of compound **19** ( $\text{CDCl}_3$ , 125.8 MHz)

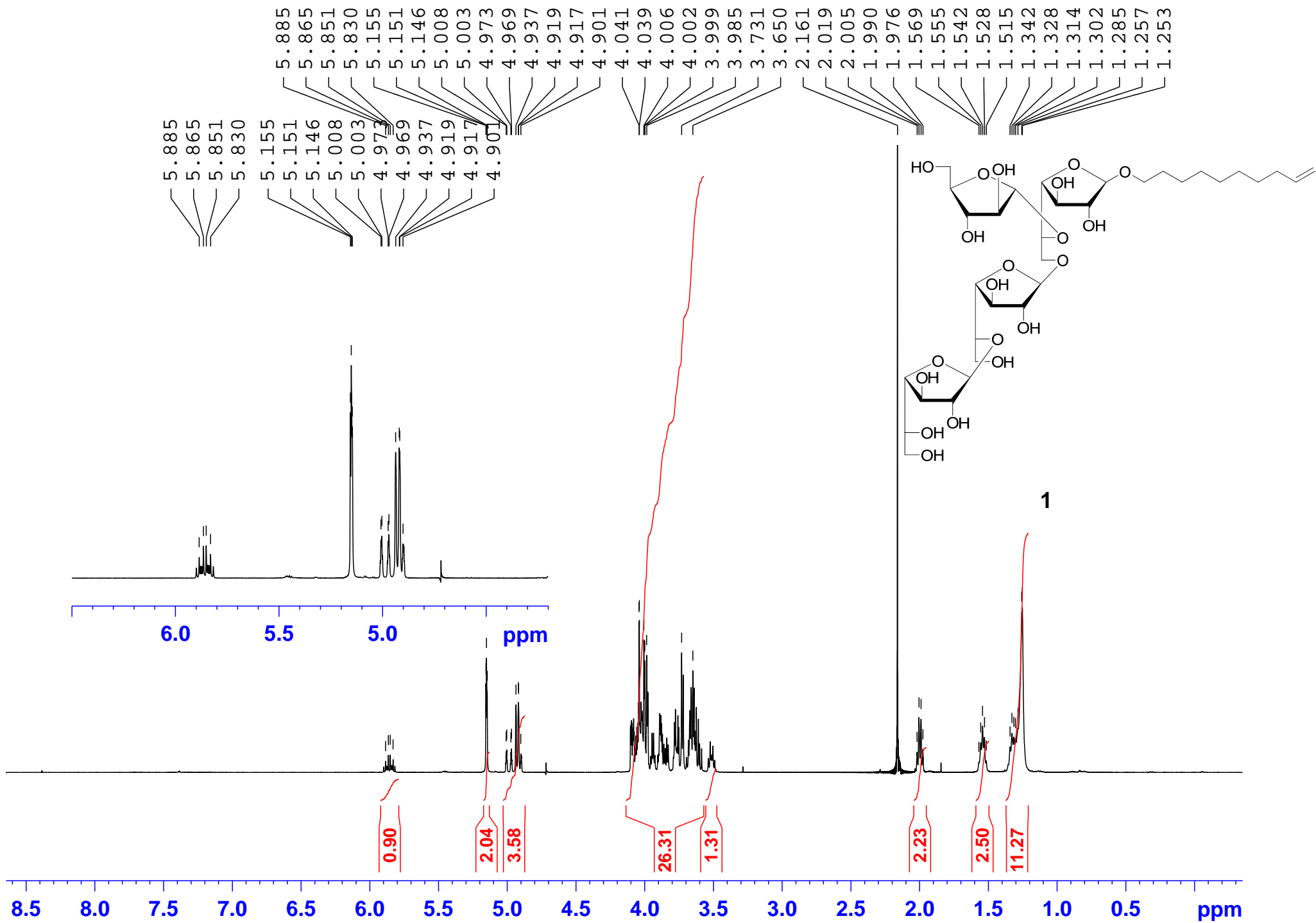




COSY spectrum of compound **20** (CDCl<sub>3</sub>, 500 MHz)

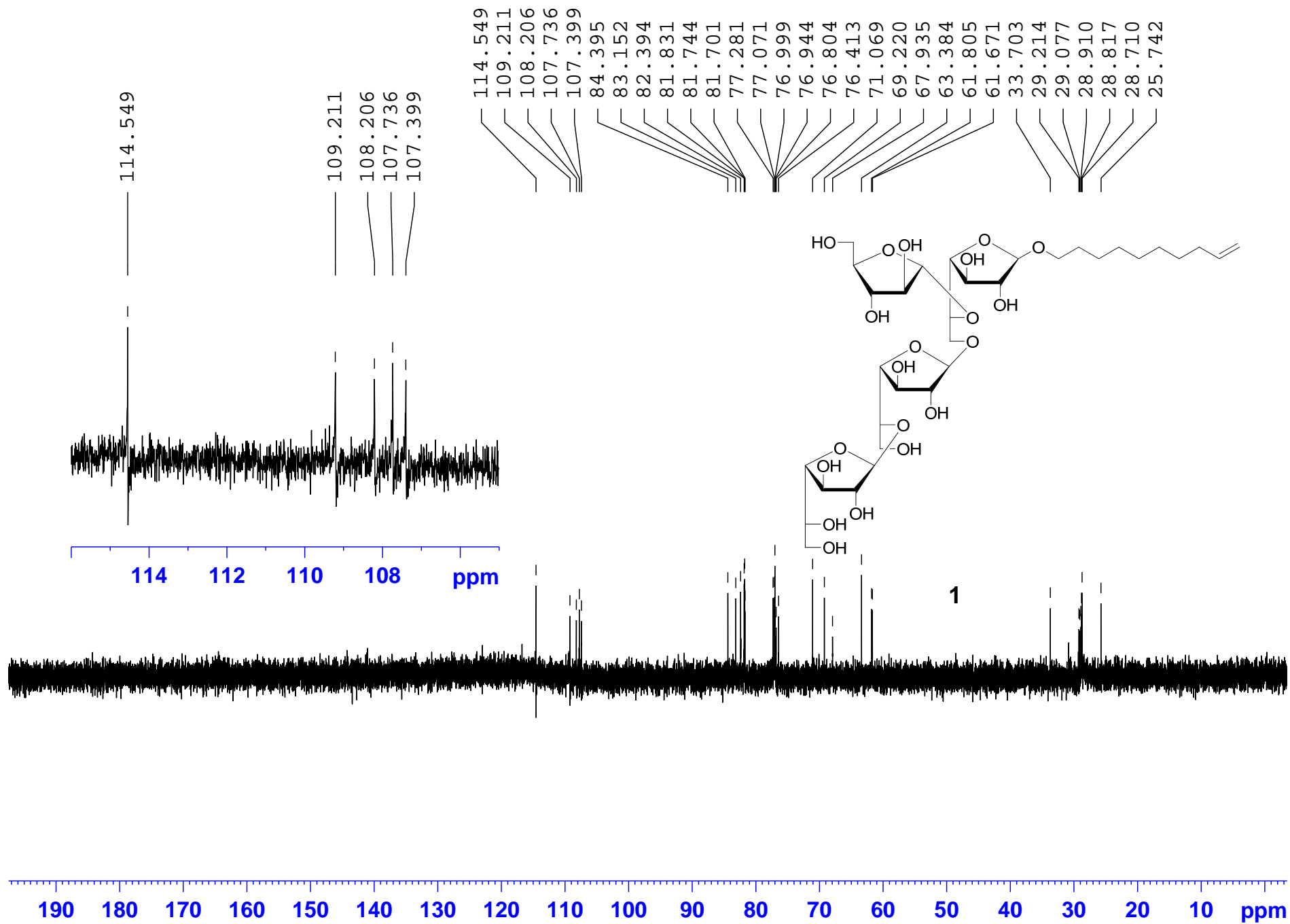


<sup>13</sup>C NMR spectrum of compound **20** (CDCl<sub>3</sub>, 125.8 MHz)

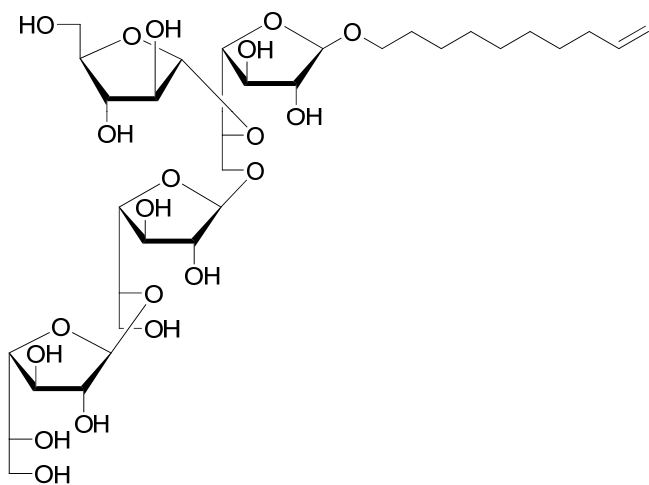


$^1\text{H}$  NMR spectrum of compound 1 ( $\text{D}_2\text{O}$ ; 500 MHz).

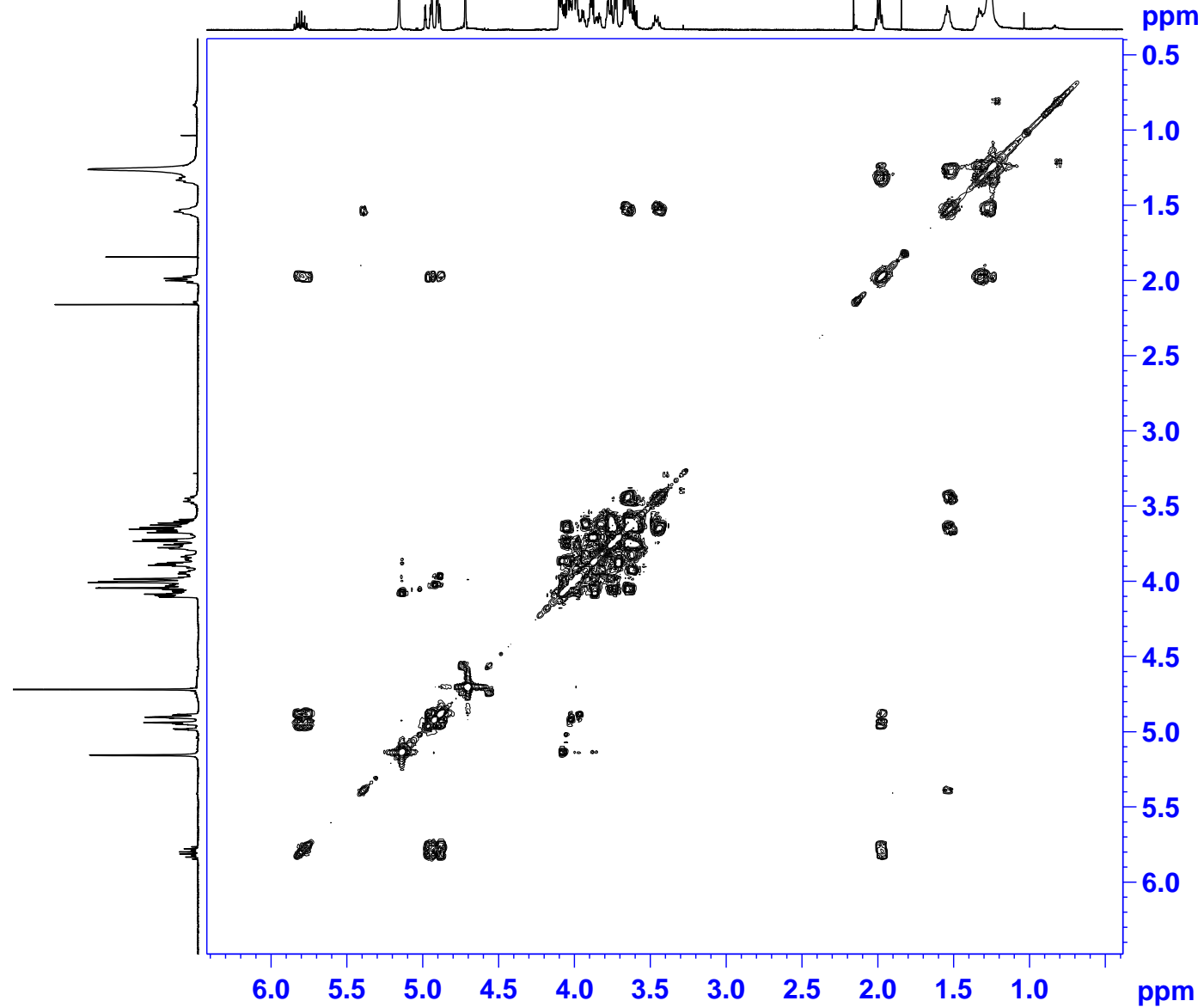




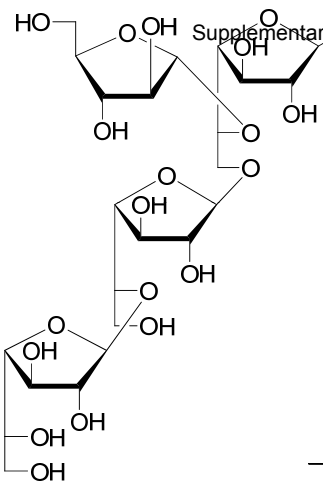
$^{13}\text{C}$  NMR spectrum of compound **1** ( $\text{D}_2\text{O}$ , 125.8 MHz)



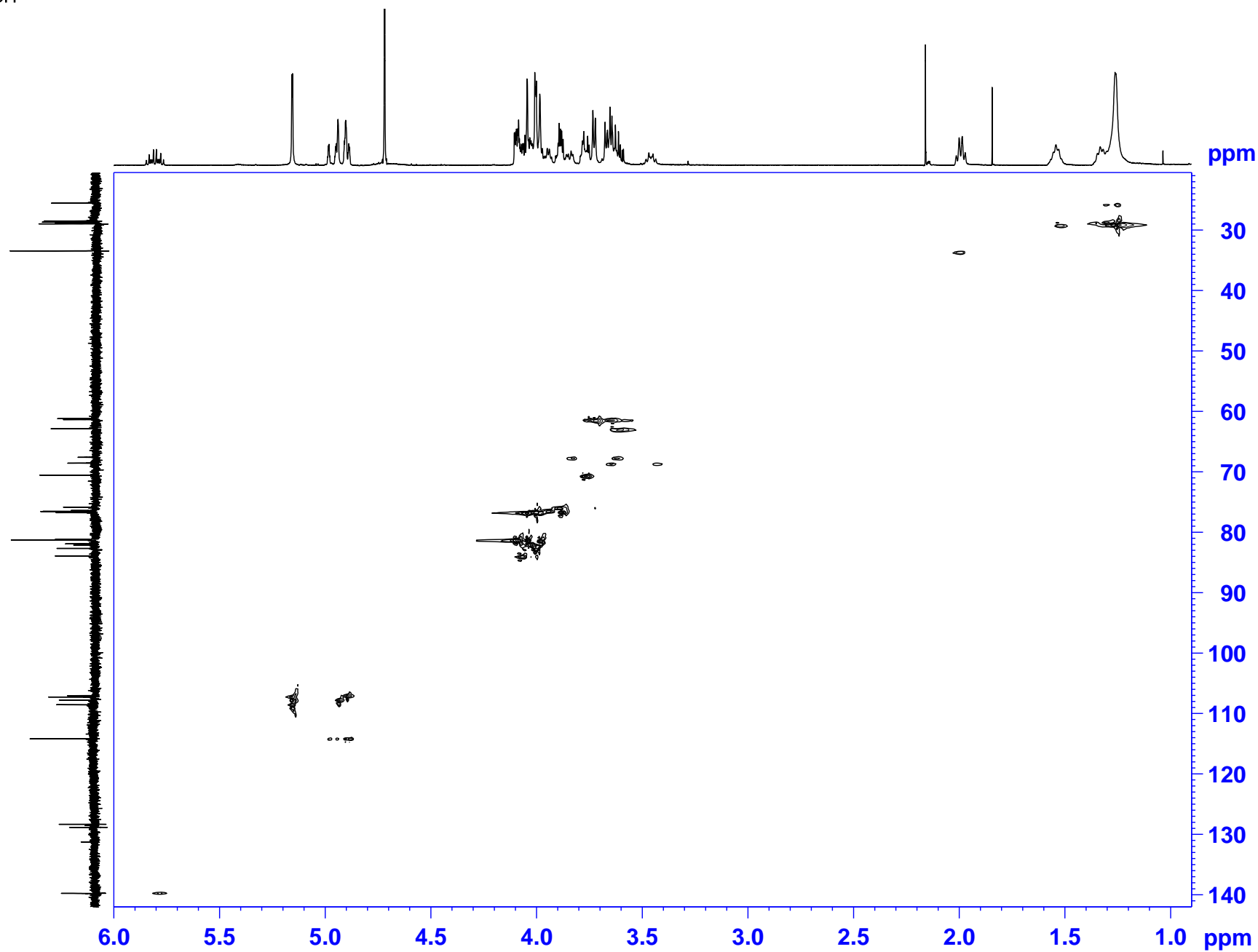
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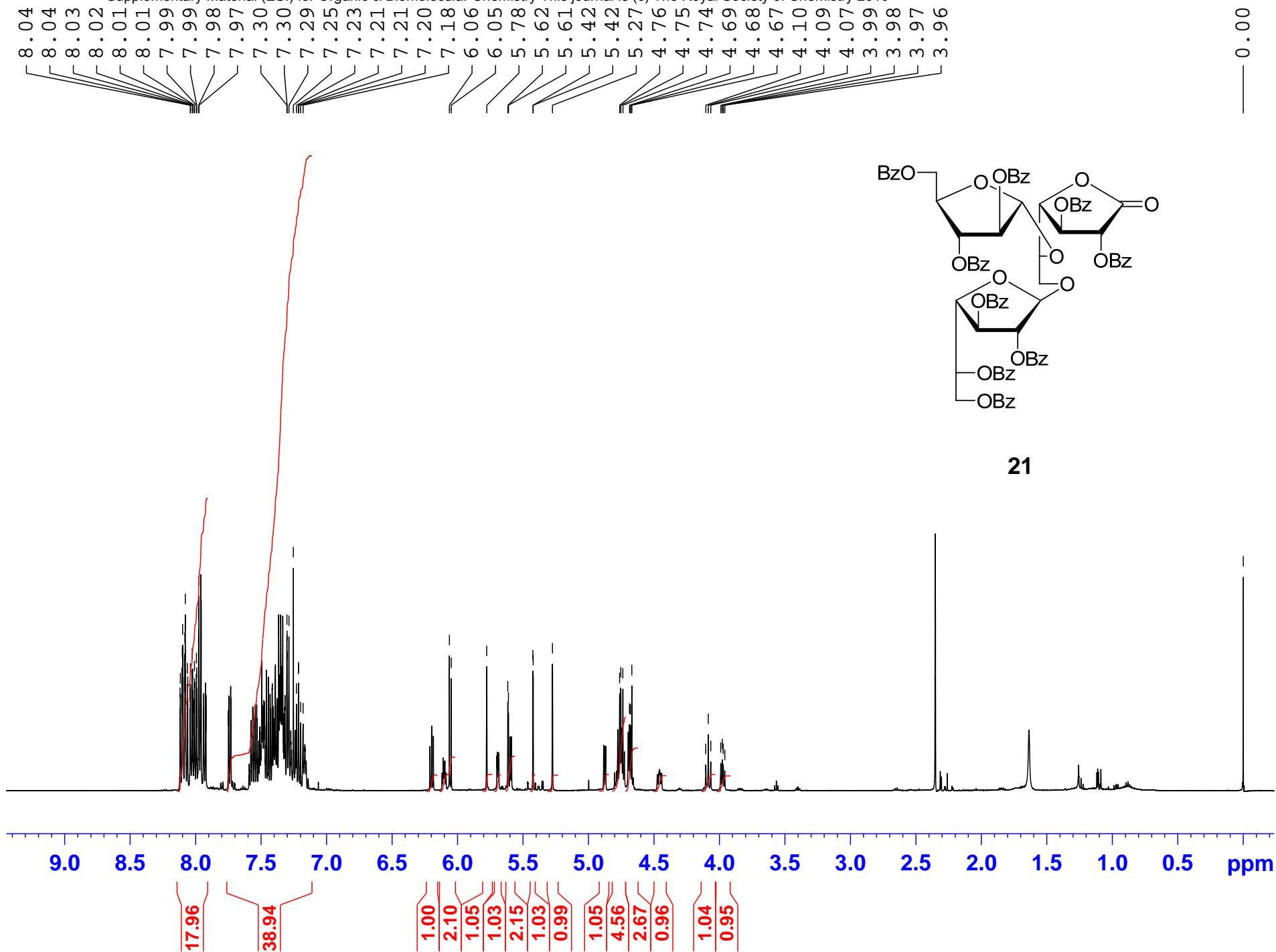
COSY NMR spectrum of compound 1 (D<sub>2</sub>O, 500 MHz)



1

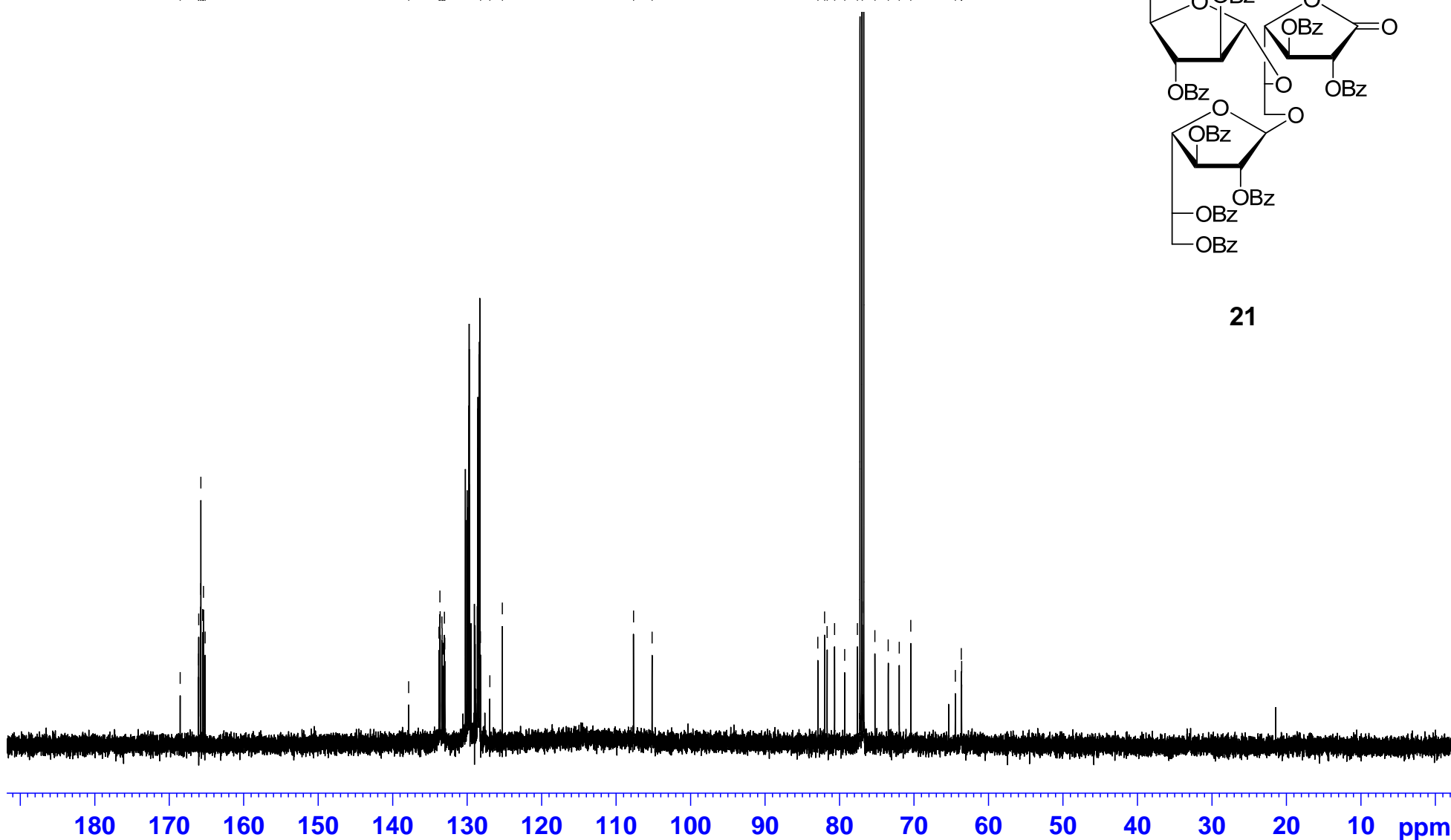


HSQC spectrum of compound 1 (D<sub>2</sub>O, 125.8 MHz)

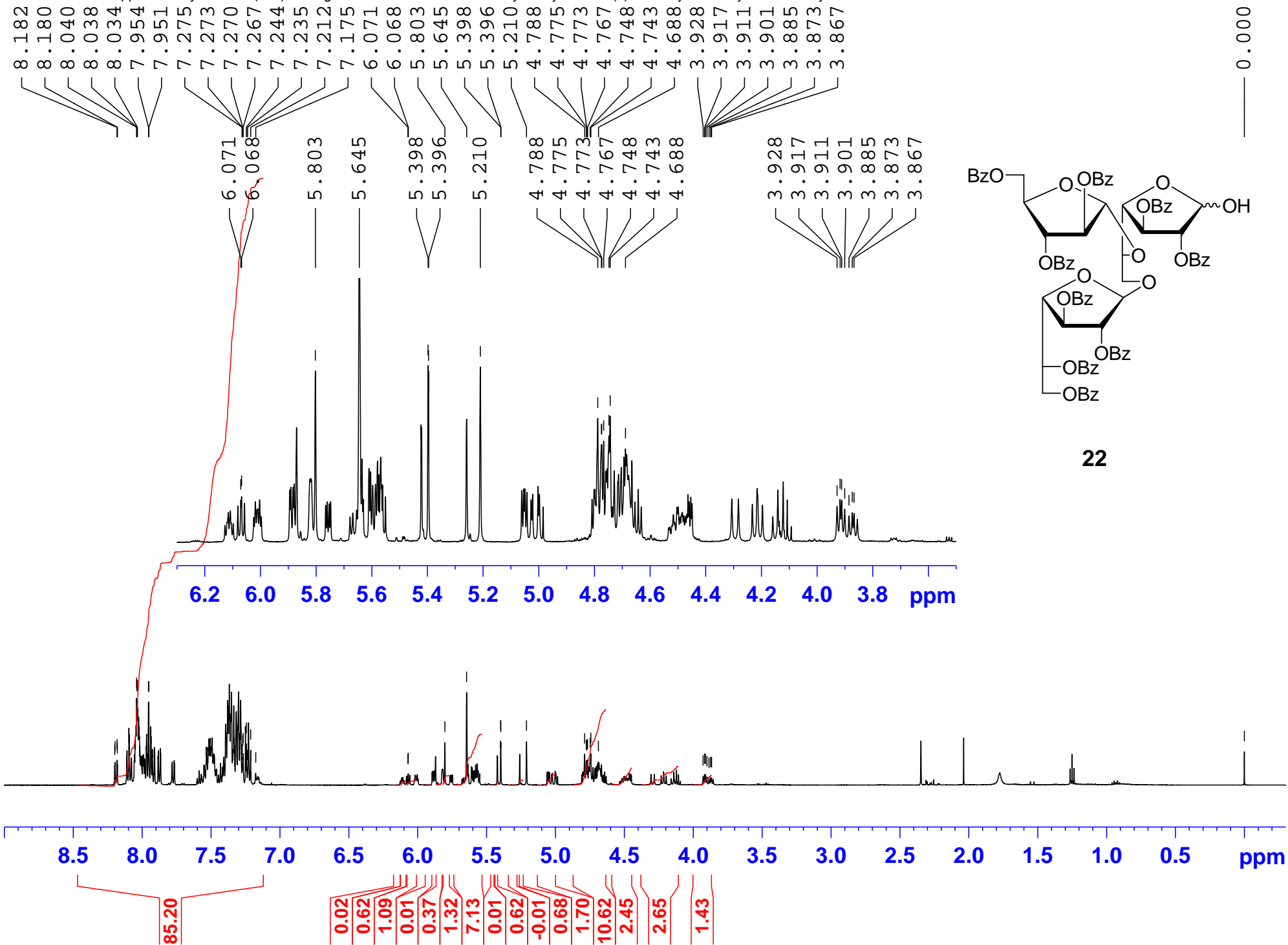


<sup>1</sup>H NMR spectrum of compound **21** (CDCl<sub>3</sub>, 500 MHz)

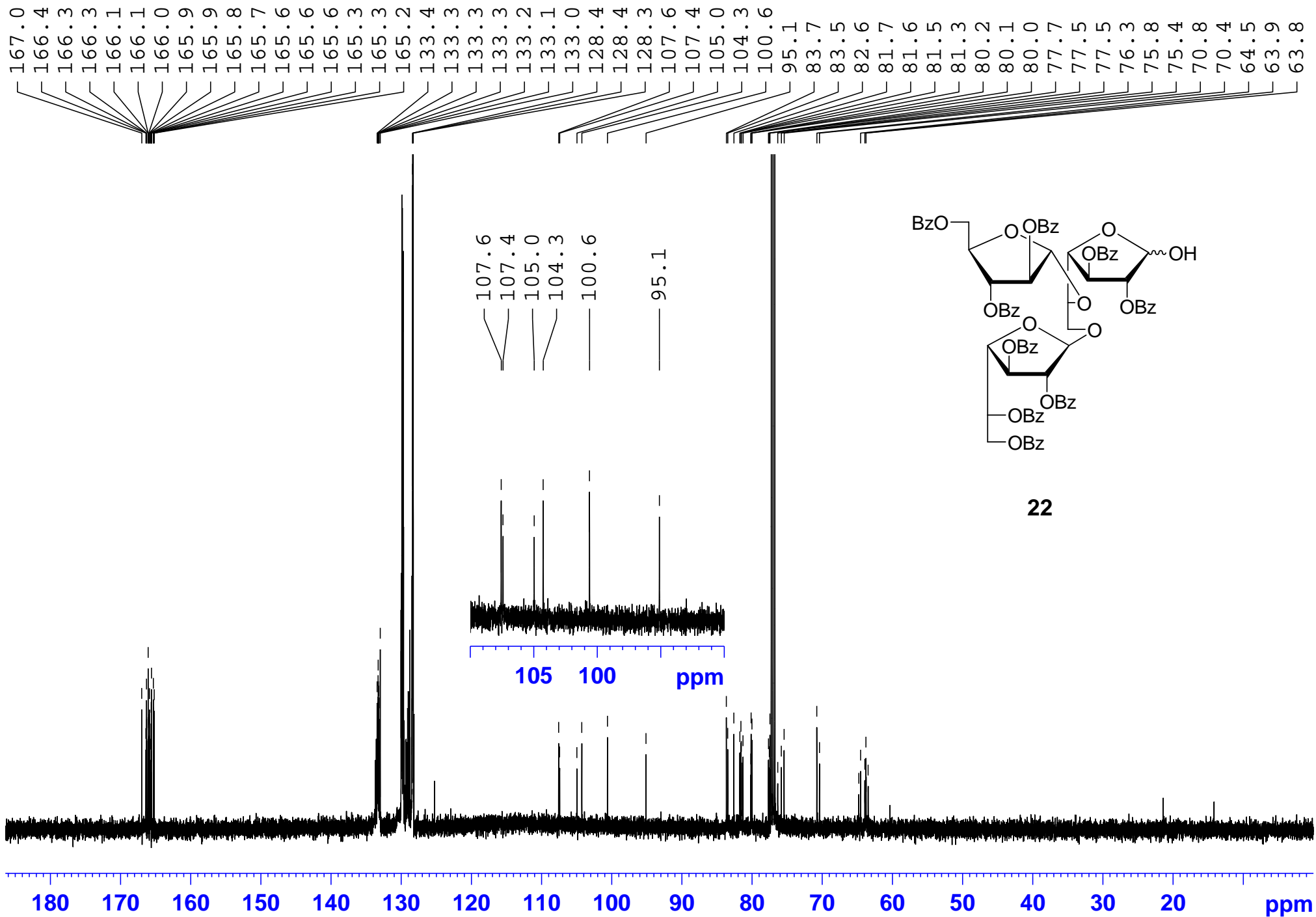
168.526  
166.051  
166.037  
165.763  
165.741  
165.502  
165.488  
165.394  
165.170  
137.841  
133.774  
133.656  
133.616  
133.377  
133.342  
133.203  
133.037  
132.991  
128.200  
126.950  
125.266  
107.659  
105.161  
82.905  
81.997  
81.659  
80.661  
79.302  
77.599  
76.943  
75.244  
73.456  
71.976  
70.429  
64.448  
63.652  
63.605



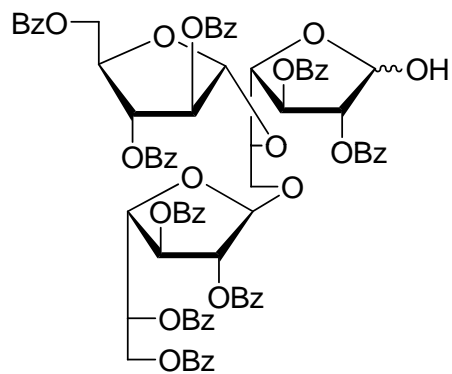
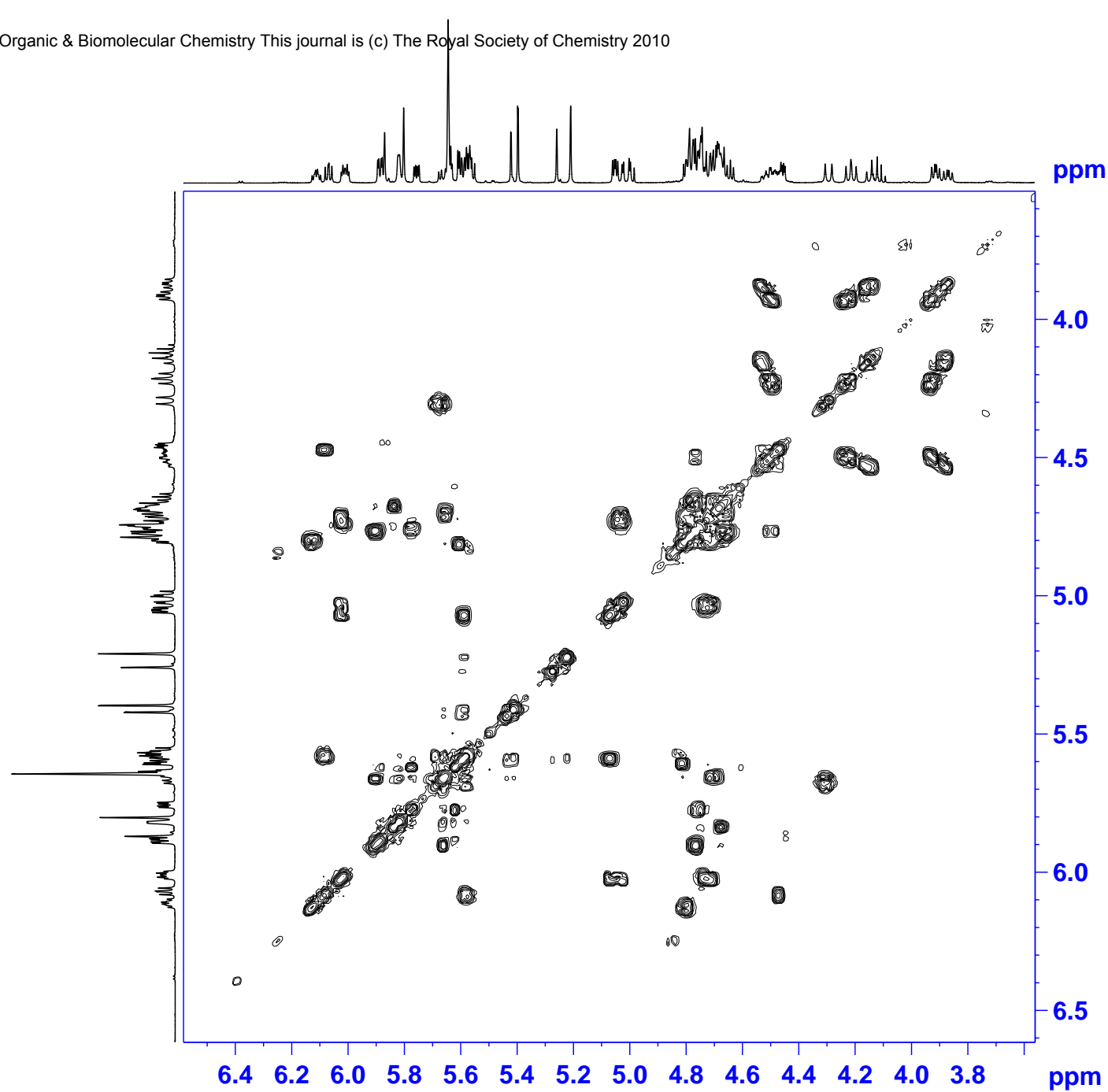
$^{13}\text{C}$  NMR spectrum of compound **18** ( $\text{CDCl}_3$ , 125.8 MHz)



<sup>1</sup>H NMR spectrum of compound **22** (CDCl<sub>3</sub>, 500 MHz)

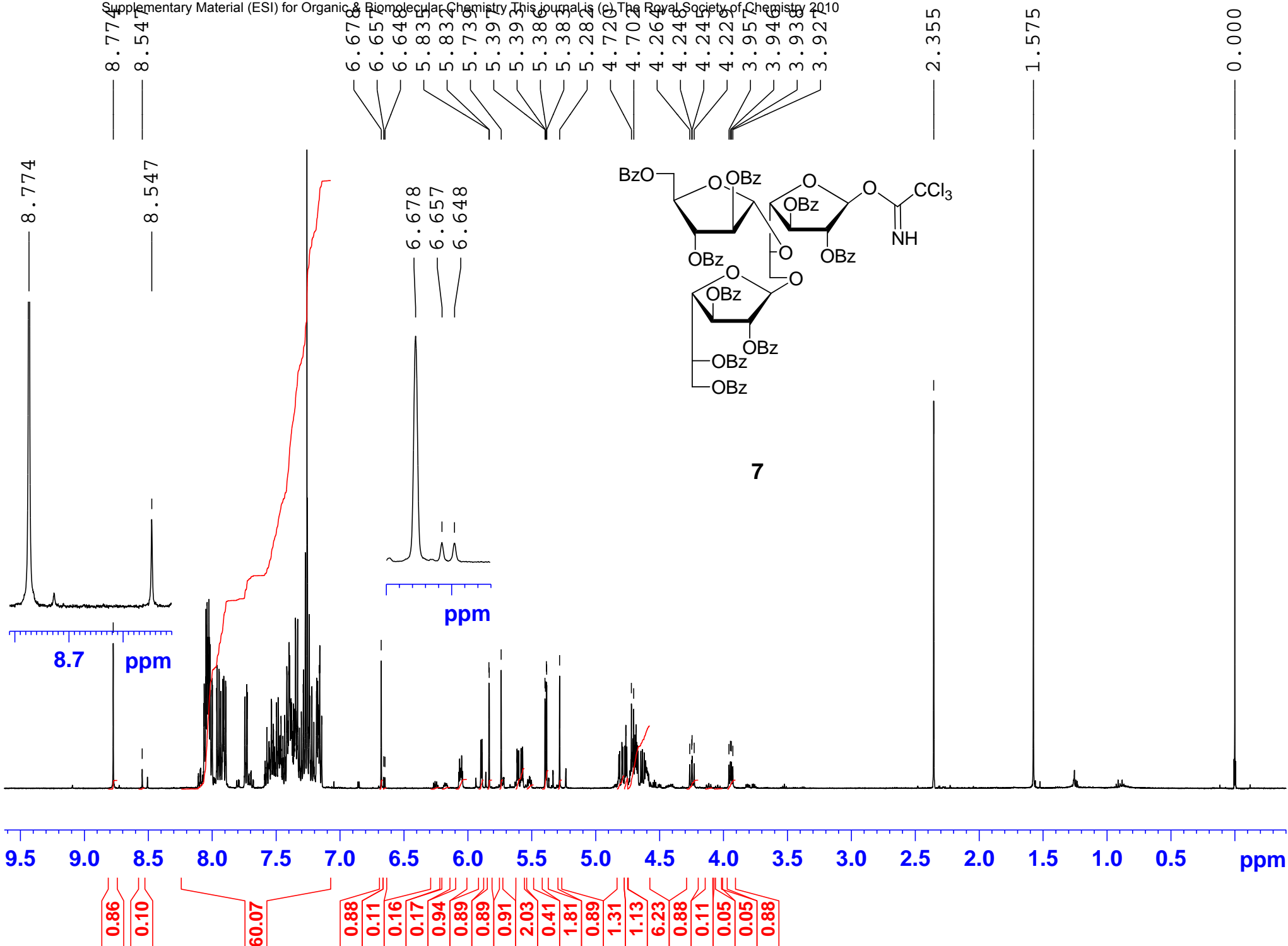


$^{13}\text{C}$  NMR spectrum of compound **22** ( $\text{CDCl}_3$ , 125.8 MHz)

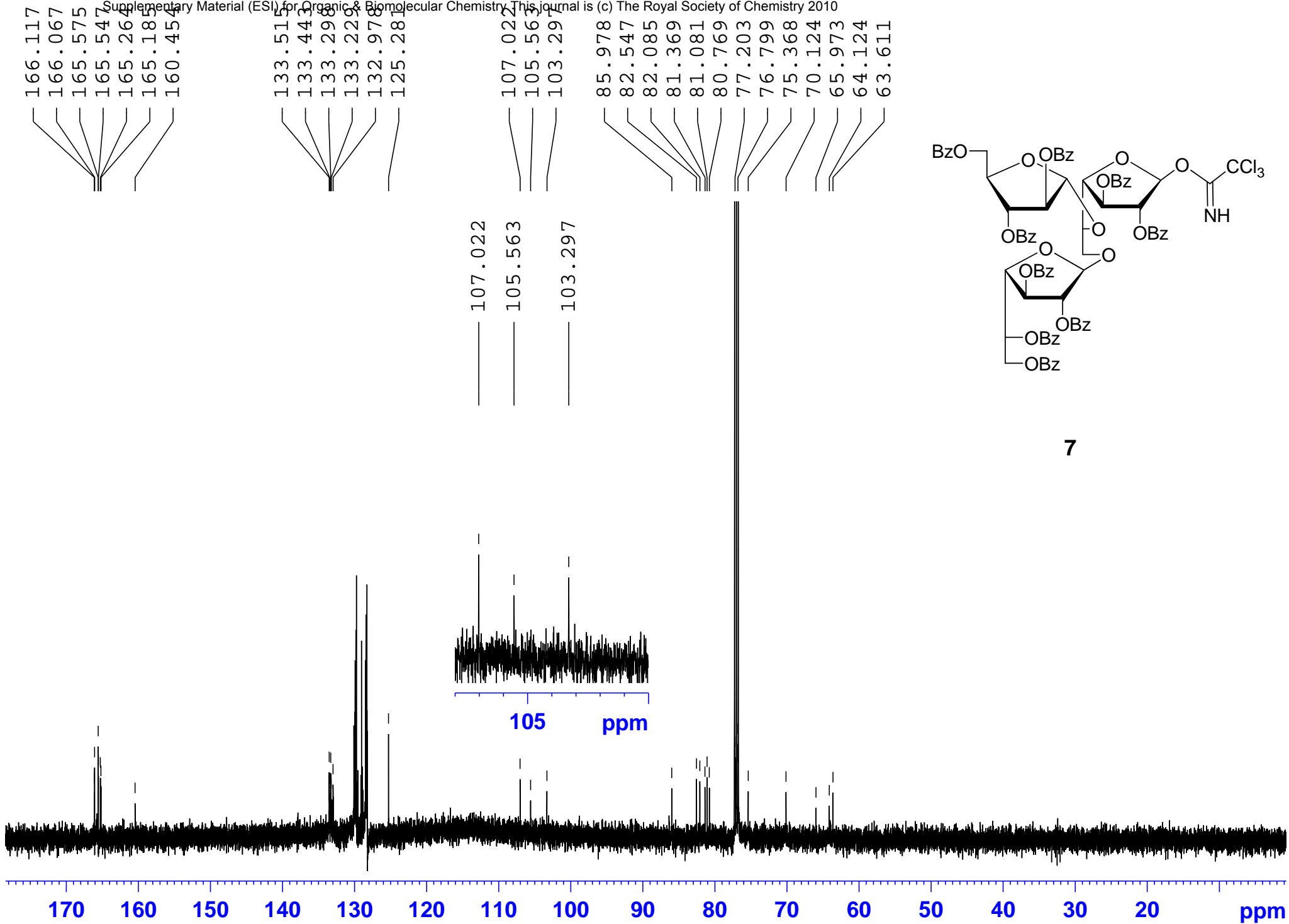
**22**COSY spectrum of compound **22** ( $\text{CDCl}_3$ , 500 MHz)





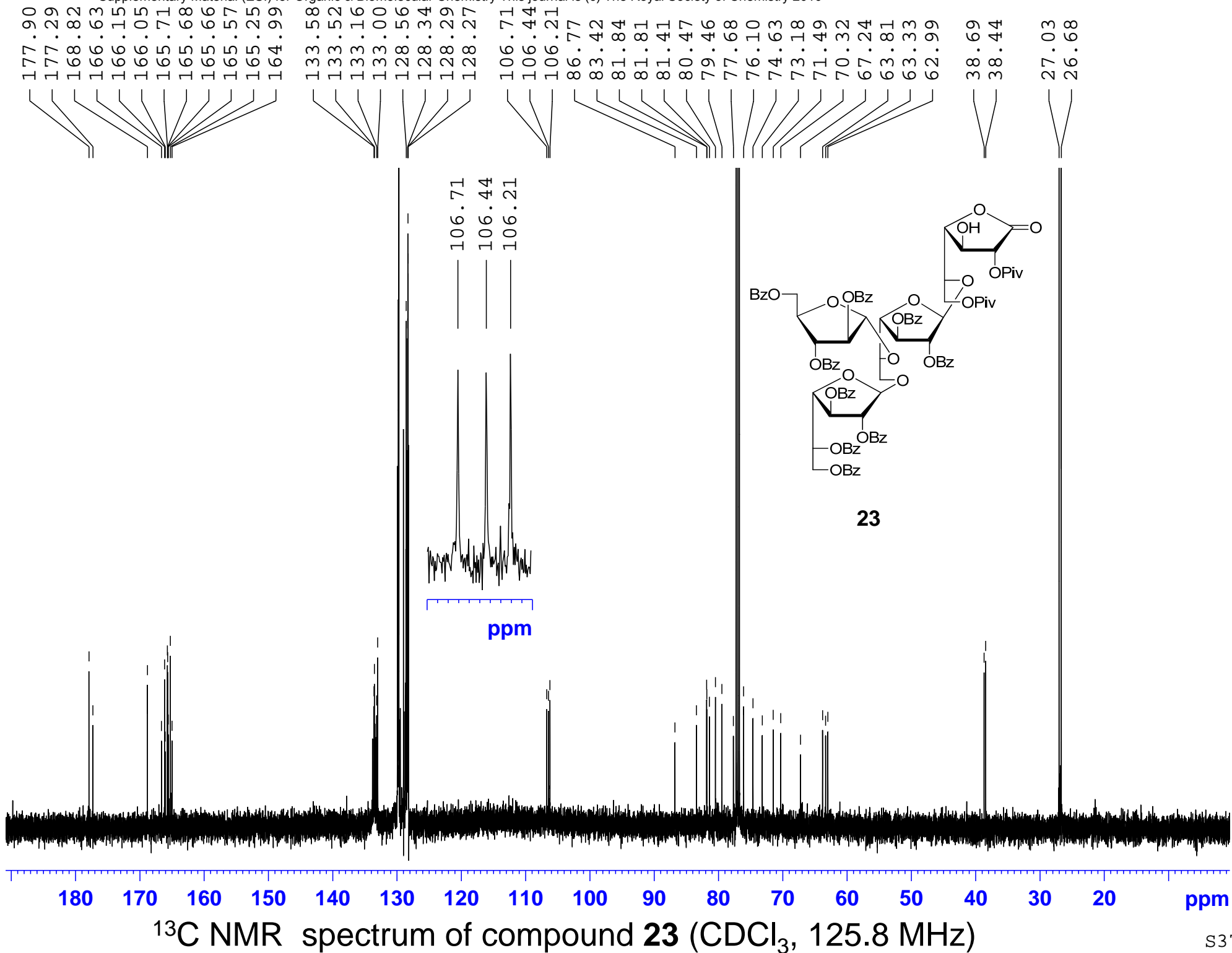


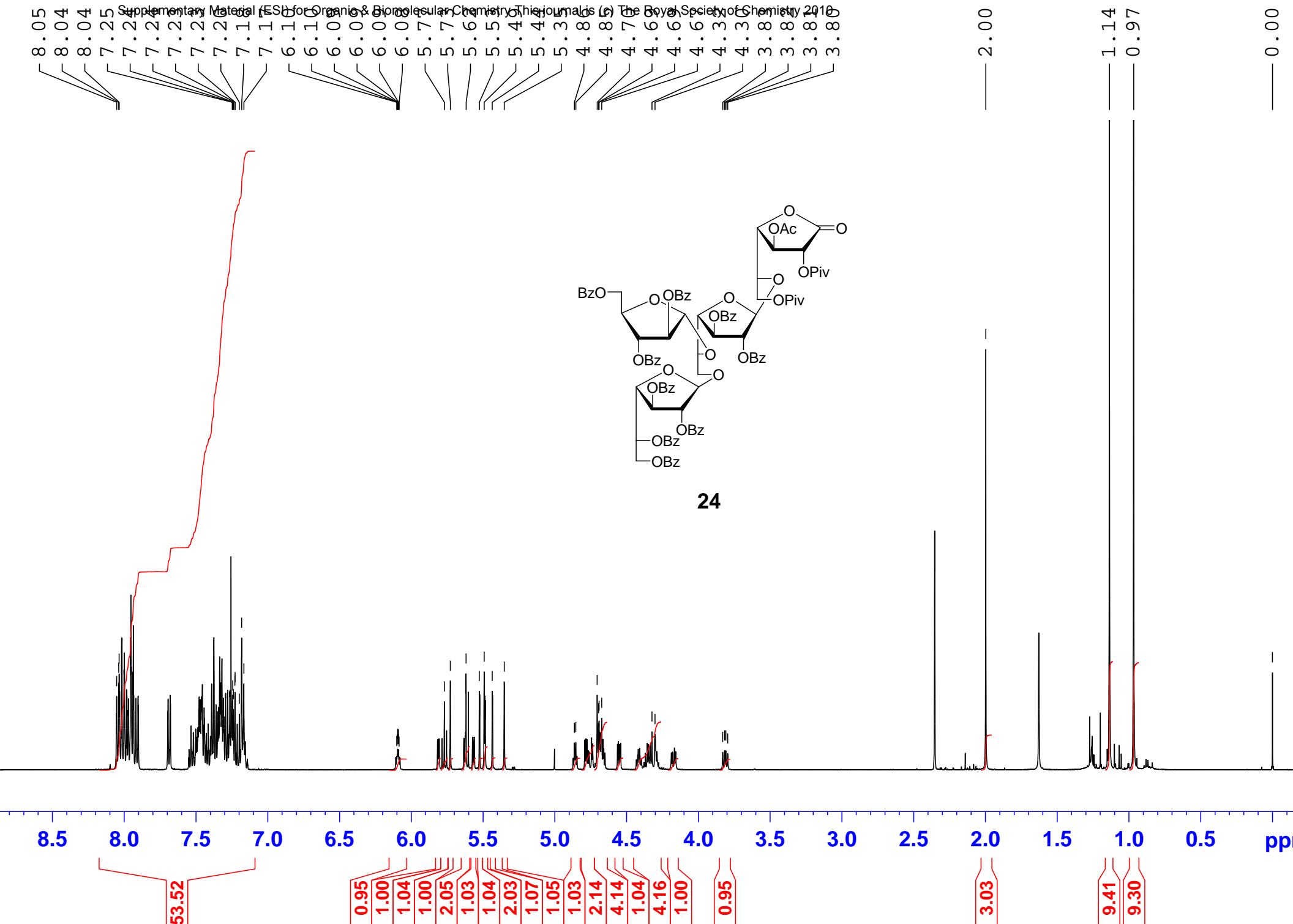
<sup>1</sup>H NMR spectrum of compound 7 (CDCl<sub>3</sub>, 500 MHz)



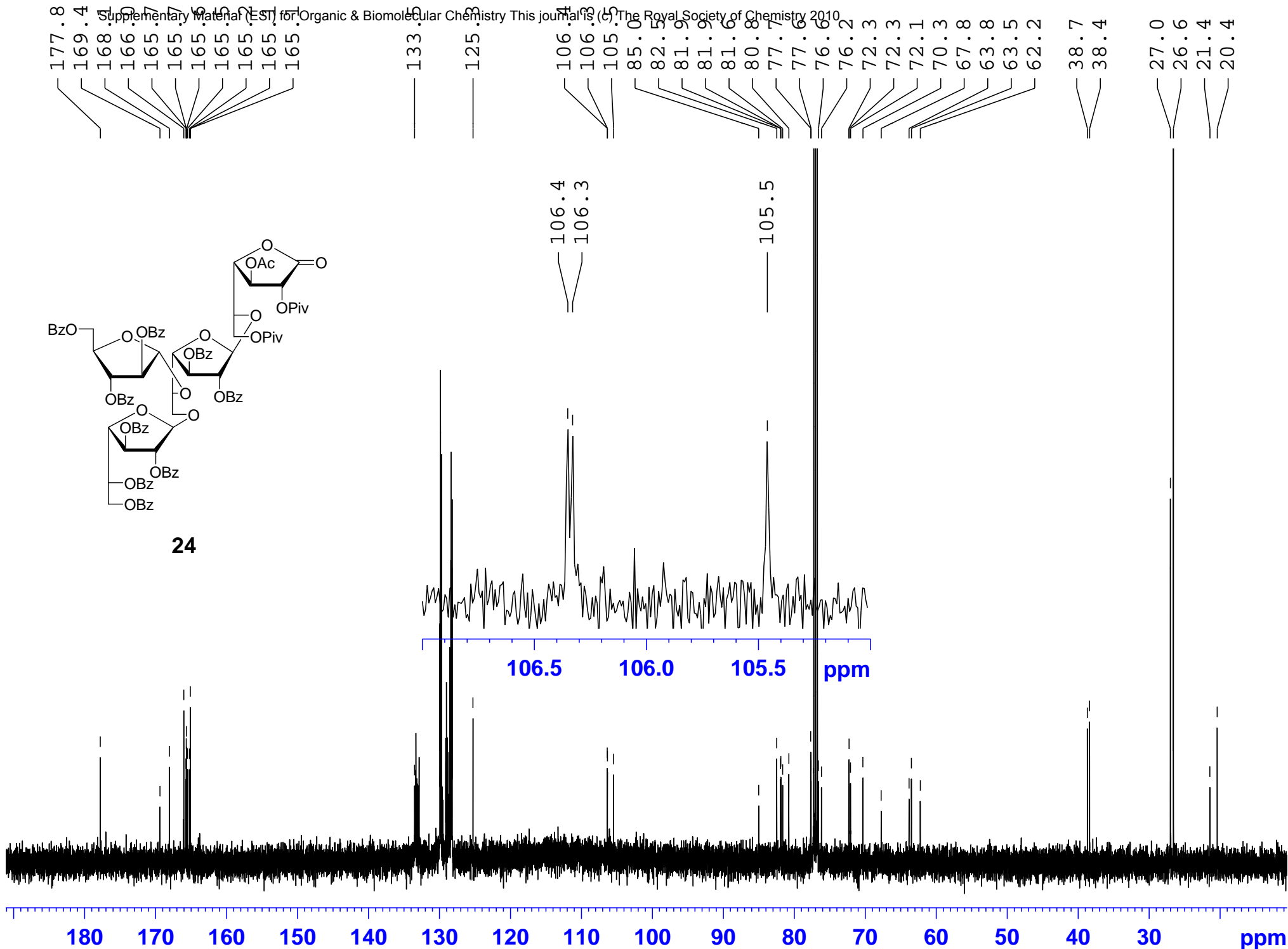
$^{13}\text{C}$  NMR spectrum of compound **7** ( $\text{CDCl}_3$ , 125.8 MHz)



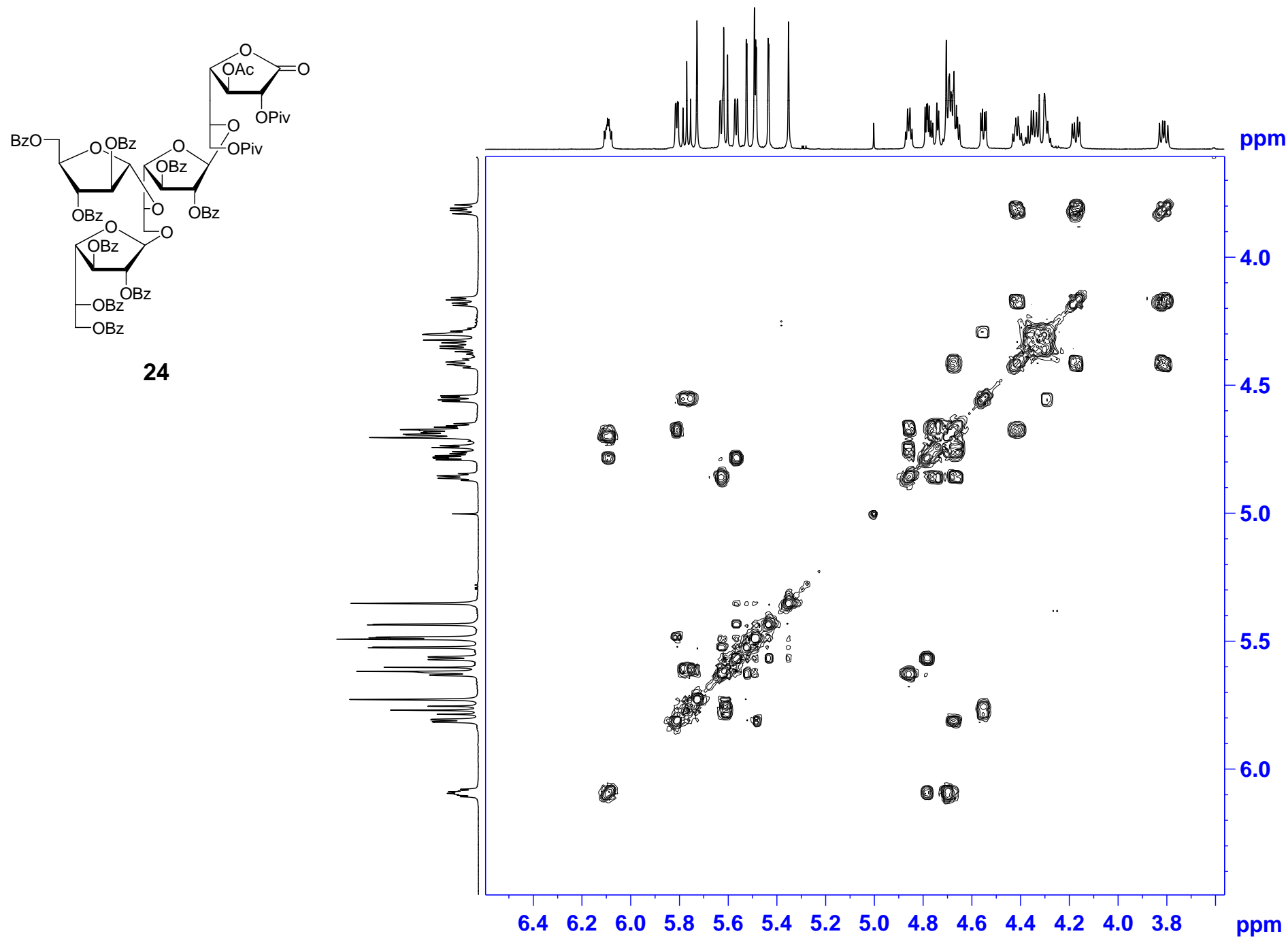




<sup>1</sup>H NMR spectrum of compound **24** (CDCl<sub>3</sub>, 500 MHz)

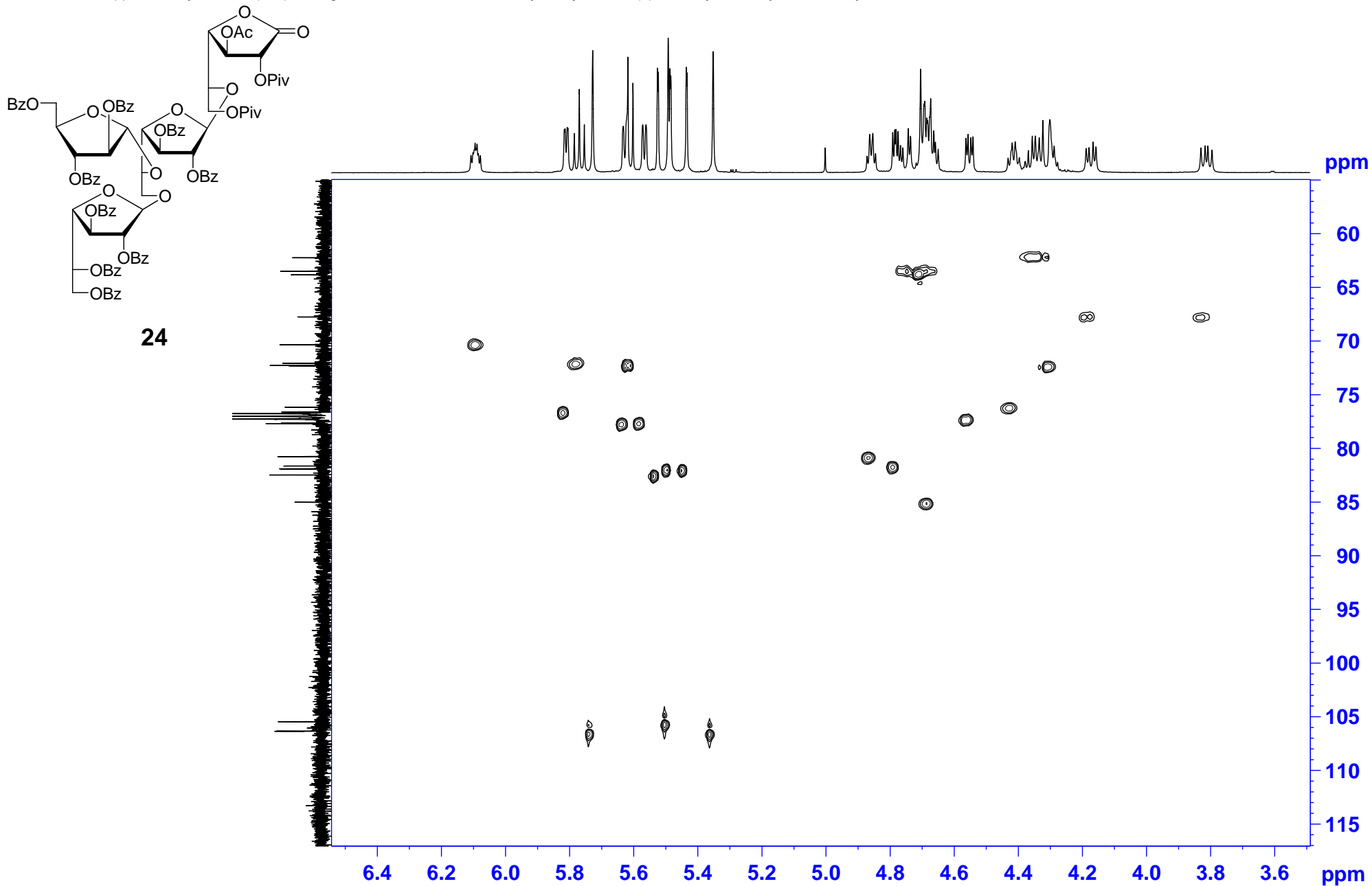


**13C NMR spectrum of compound 24 (CDCl<sub>3</sub>, 125.8 MHz)**

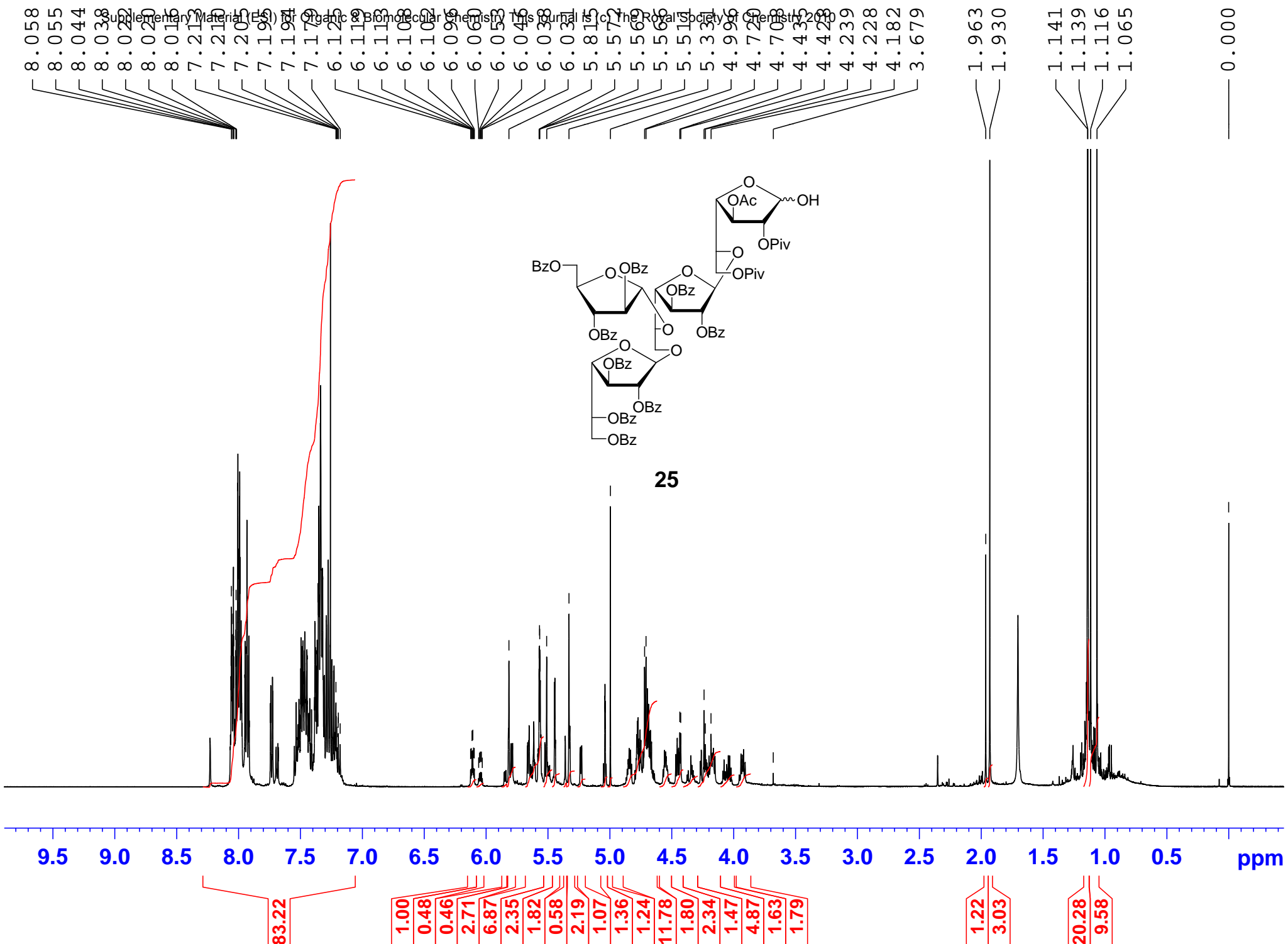


COSY spectrum of compound **24** (CDCl<sub>3</sub>, 500 MHz)

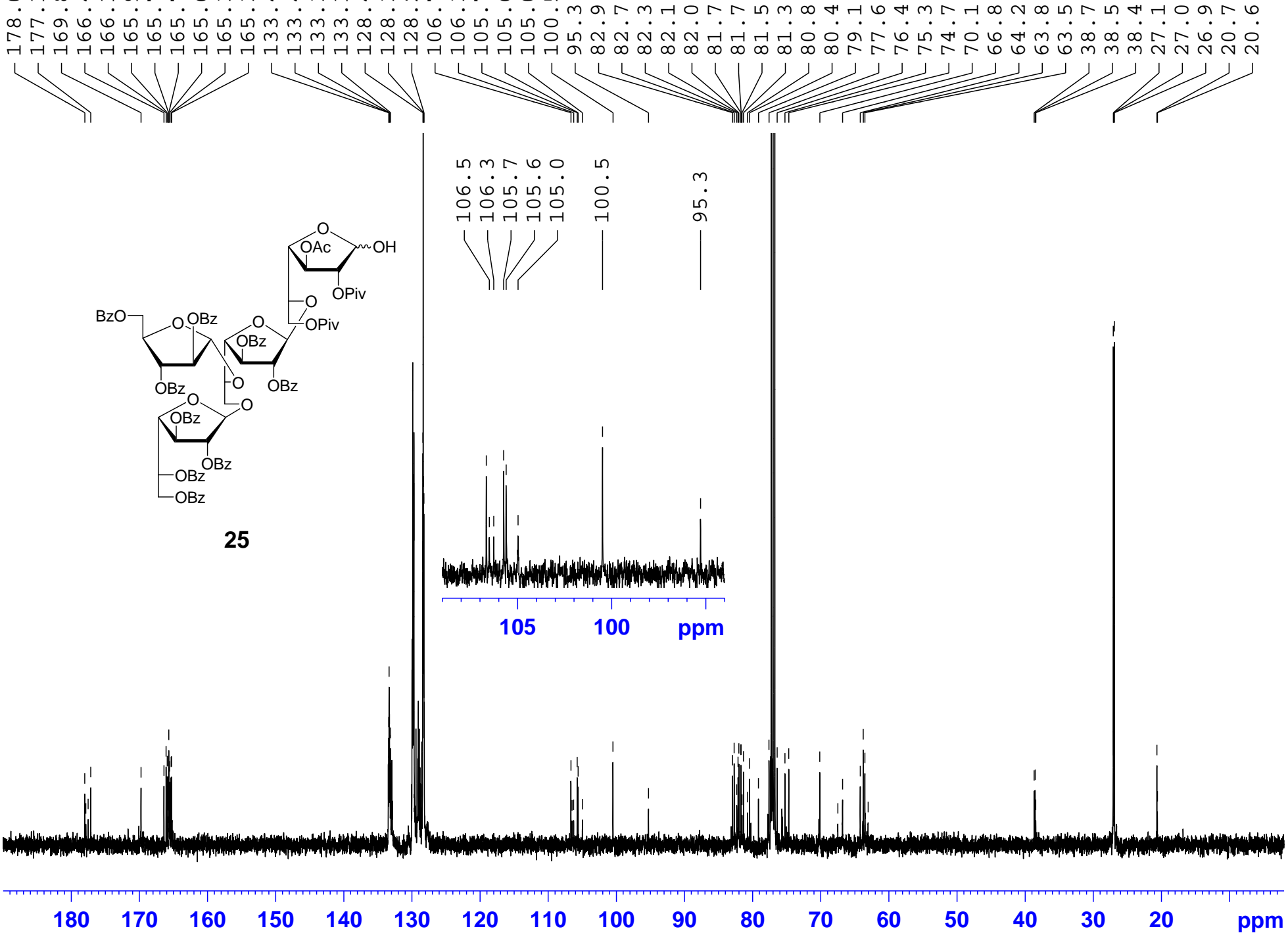




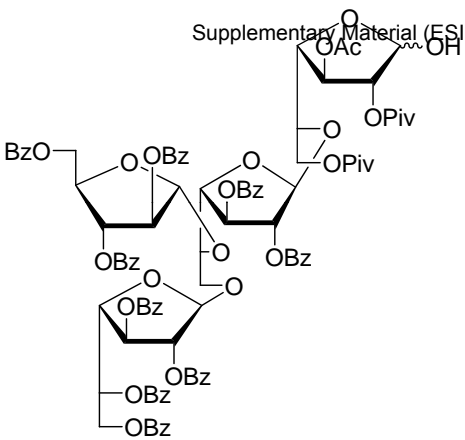
HSQC spectrum of compound **24** (CDCl<sub>3</sub>, 125.8 MHz)



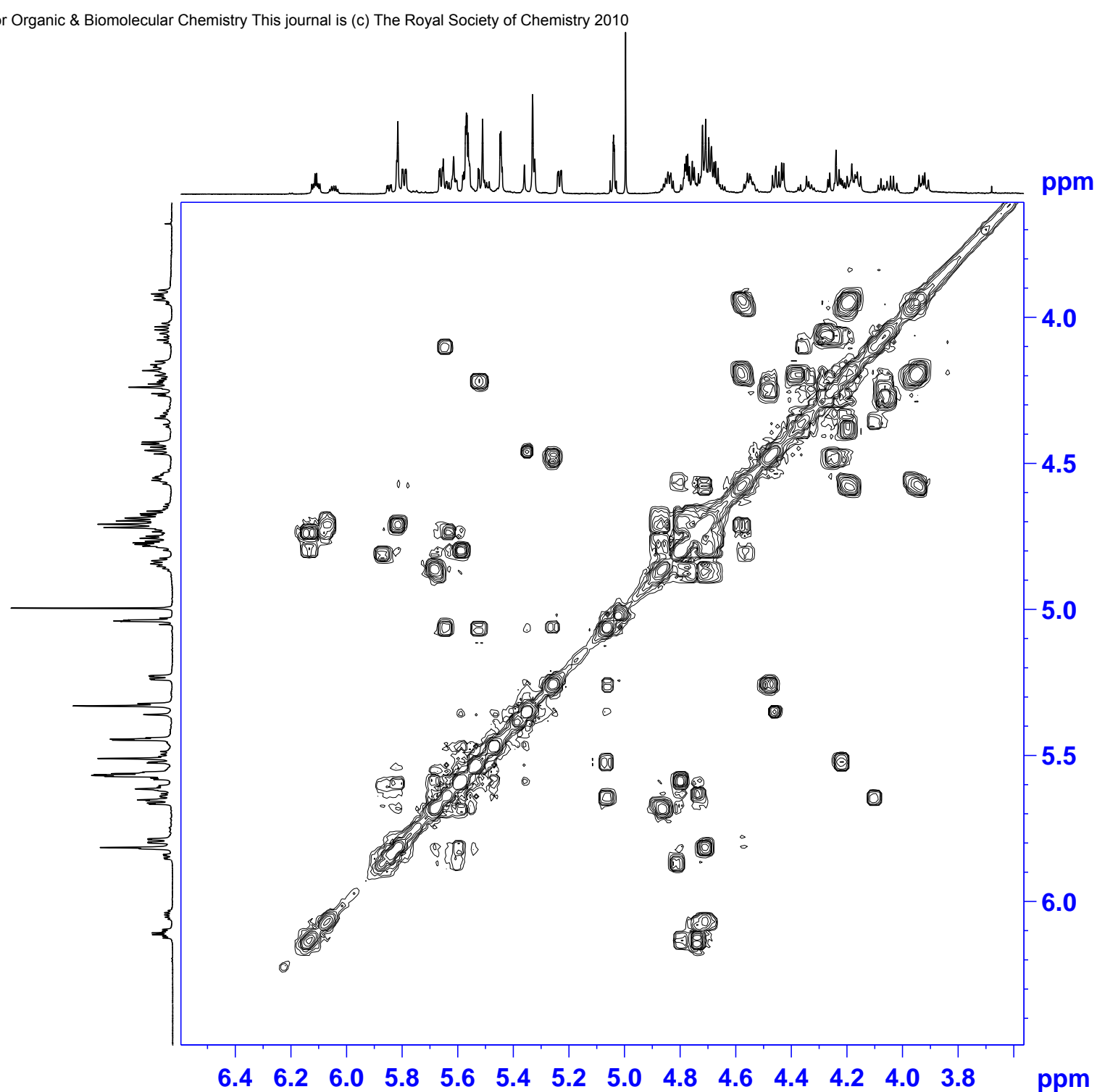
<sup>1</sup>H NMR spectrum of compound **25** (CDCl<sub>3</sub>, 500 MHz)



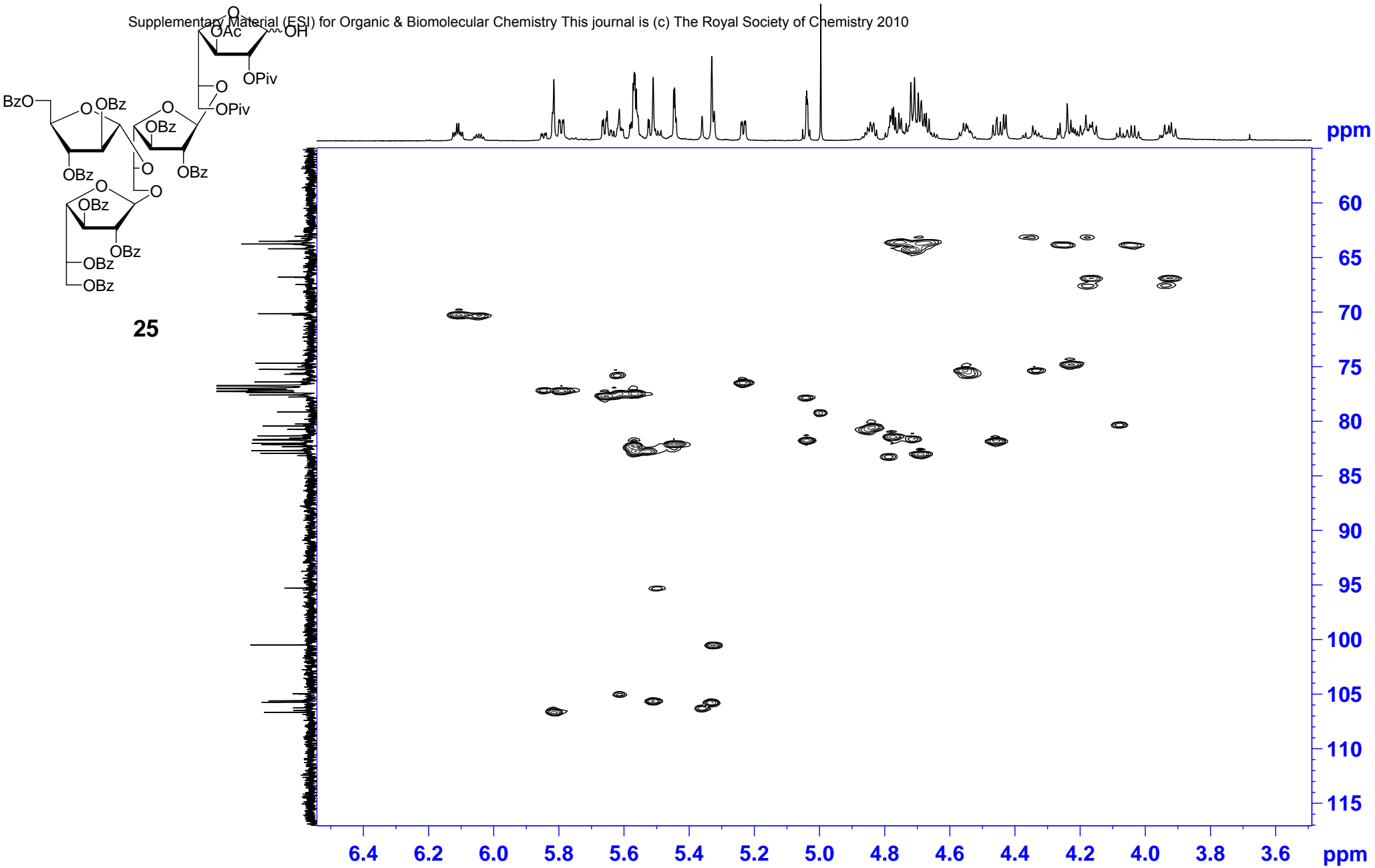
$^{13}\text{C}$  NMR spectrum of compound **25** (CDCl<sub>3</sub>, 125.8 MHz)



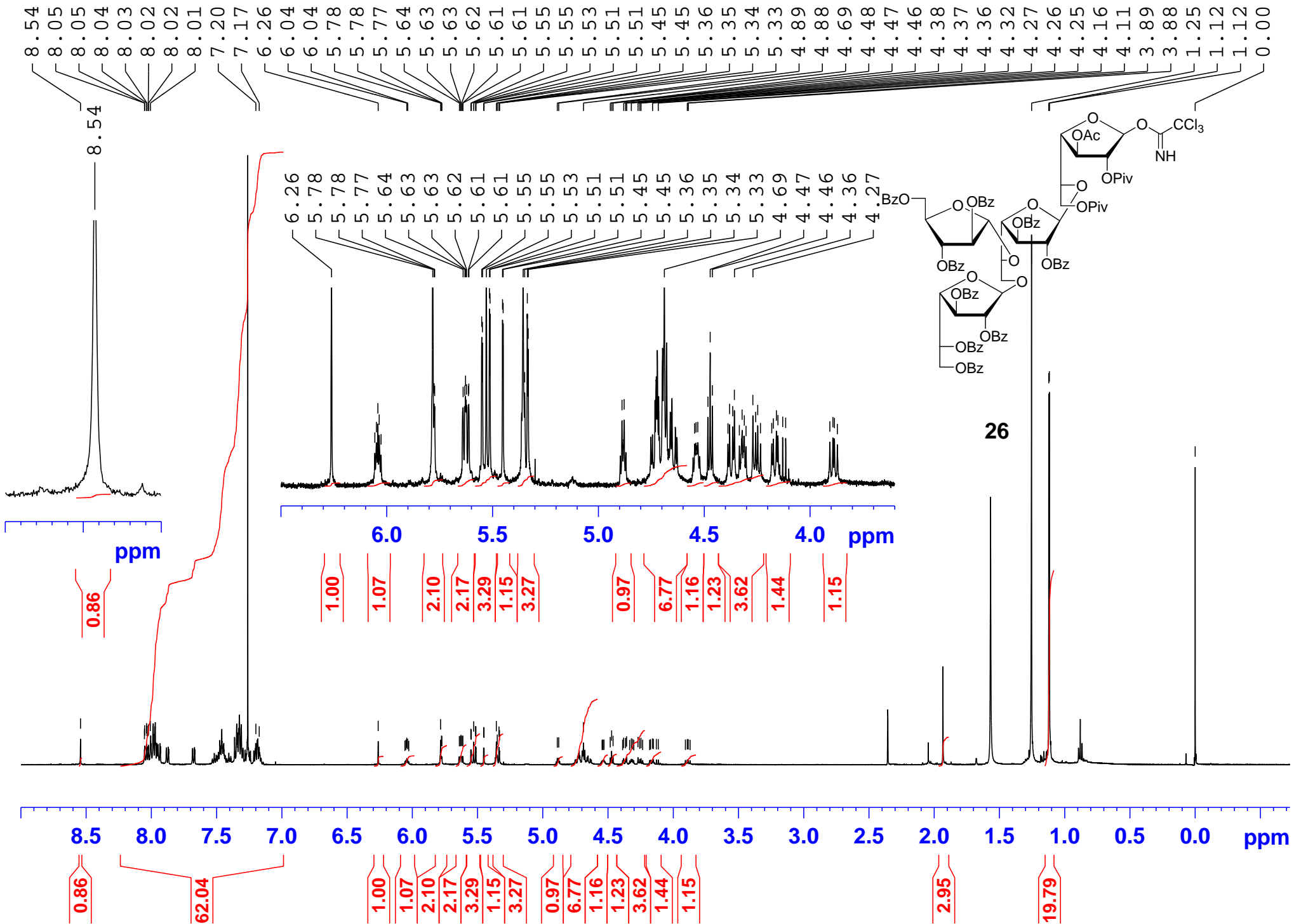
**25**



COSY spectrum of compound **25** (CDCl<sub>3</sub>, 500 MHz)

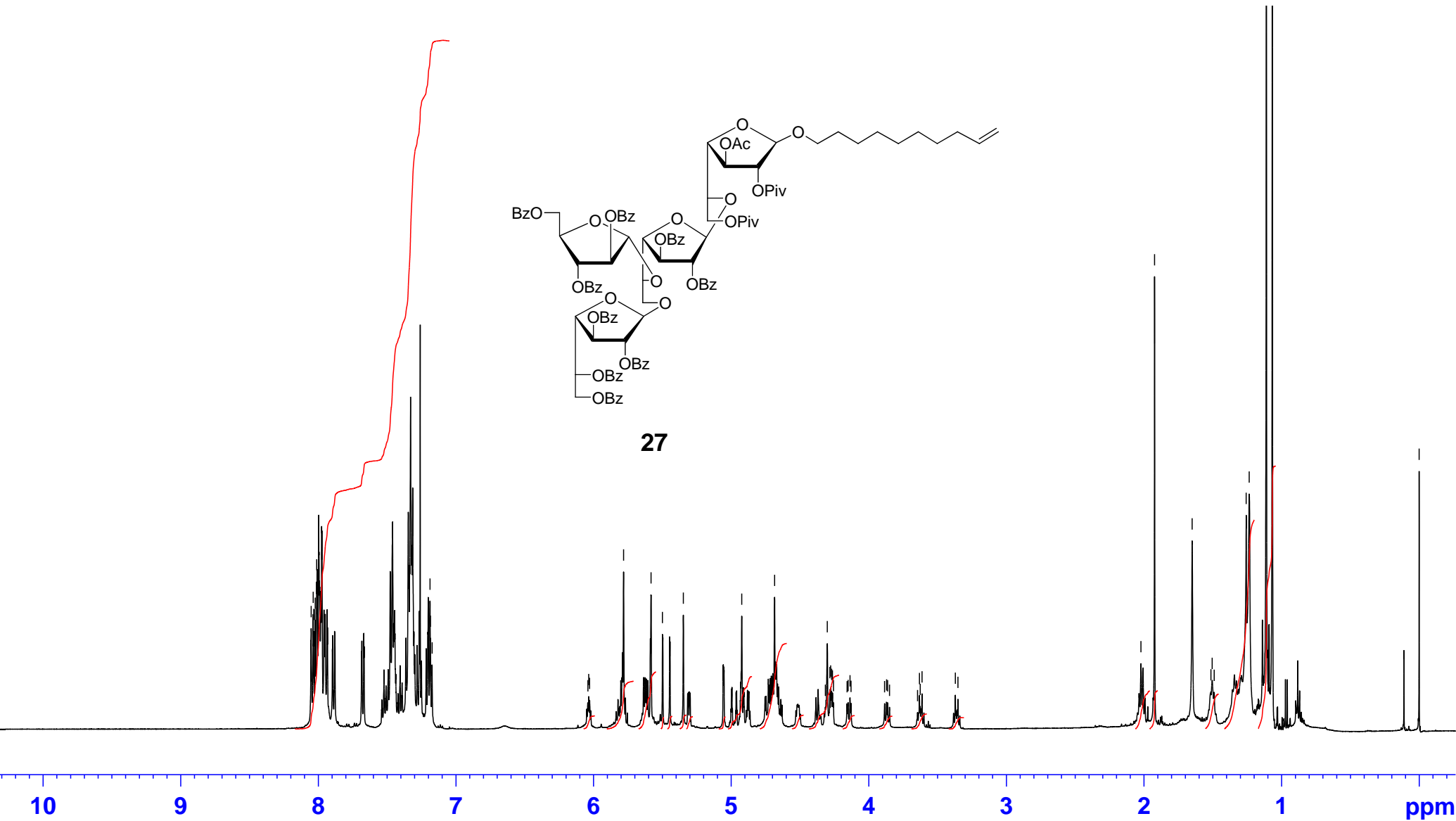


HSQC spectrum of compound **25** (CDCl<sub>3</sub>, 125.8 MHz)



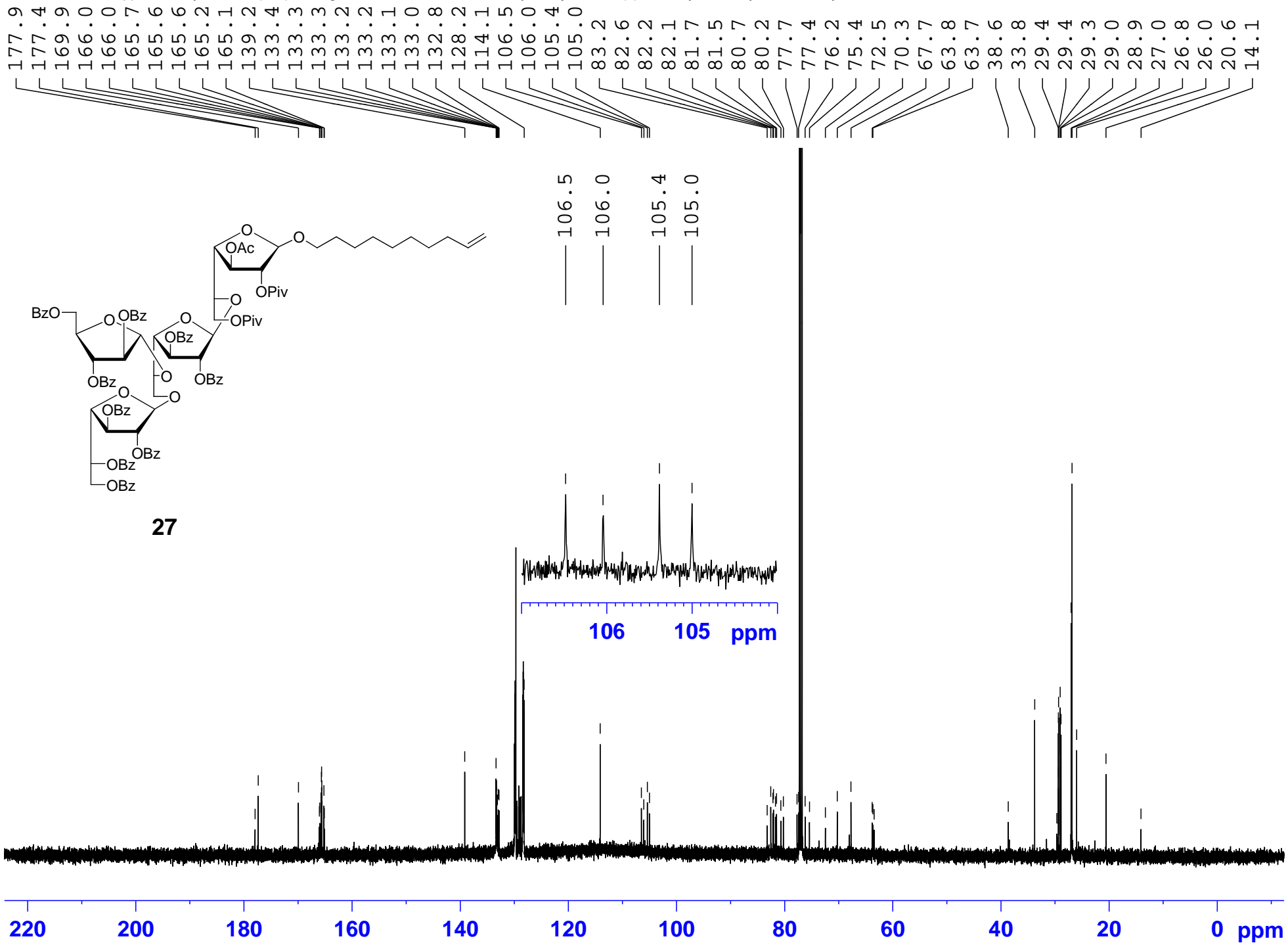
<sup>1</sup>H NMR spectrum of compound **26** (CDCl<sub>3</sub>, 500 MHz)

8.05  
8.04  
8.03  
8.02  
8.02  
8.01  
7.19  
7.18  
7.17  
6.04  
6.03  
6.03  
5.78  
5.58  
5.50  
5.35  
4.92  
4.68  
4.32  
4.30  
4.28  
4.28  
4.27  
4.26  
4.26  
4.16  
4.15  
4.14  
4.13  
3.88  
3.87  
3.86  
3.85  
3.65  
3.63  
3.63  
3.61  
3.37  
3.35  
2.02  
1.92  
1.65  
1.51  
1.50  
1.49  
1.26  
1.24  
1.11  
1.07  
0.00



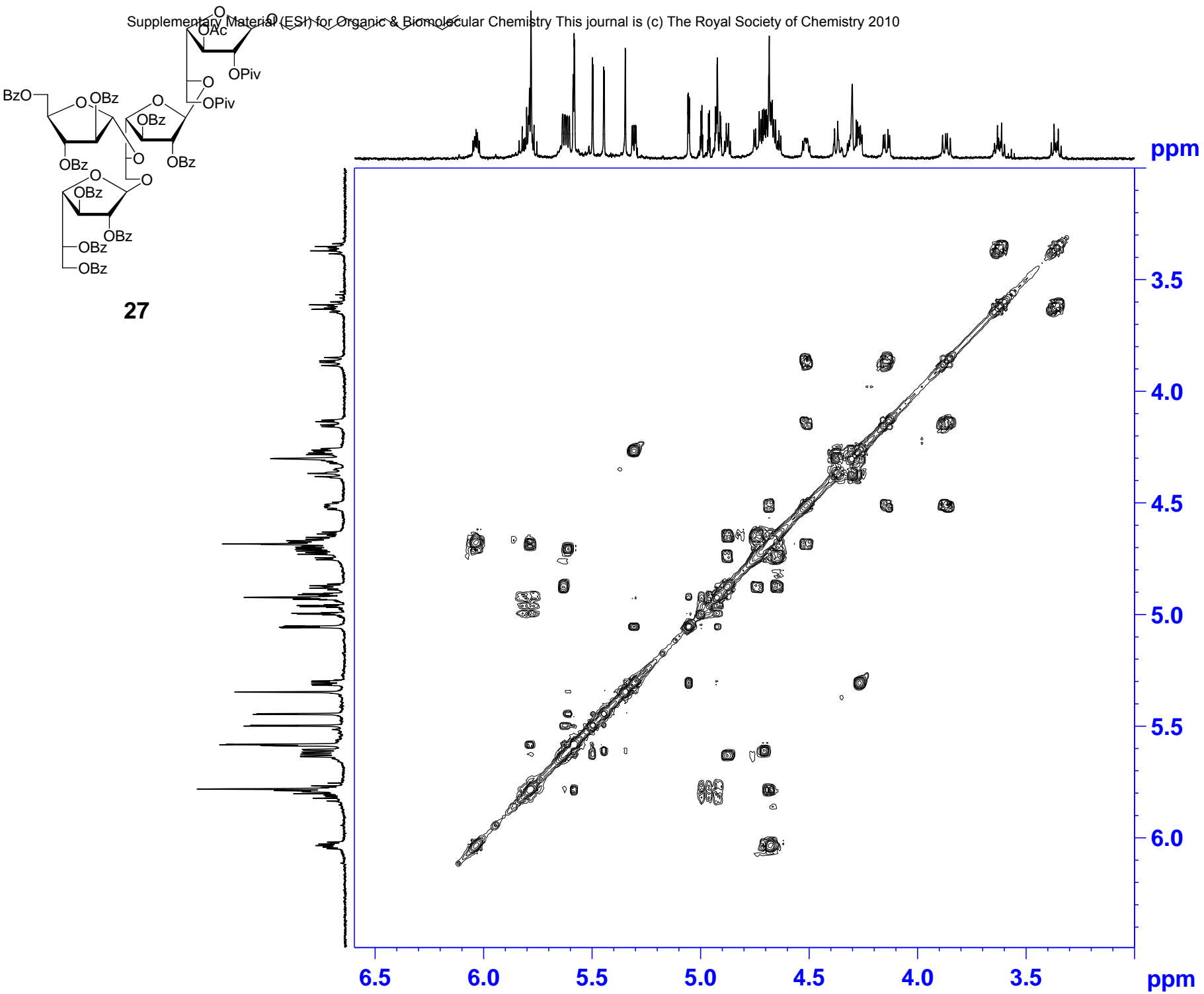
52.80  
1.00  
3.66  
4.38  
0.88  
0.97  
1.08  
0.94  
0.92  
4.02  
6.56  
1.06  
4.13  
1.02  
0.98  
1.15  
0.86  
2.93  
2.94  
2.69  
16.04  
20.16

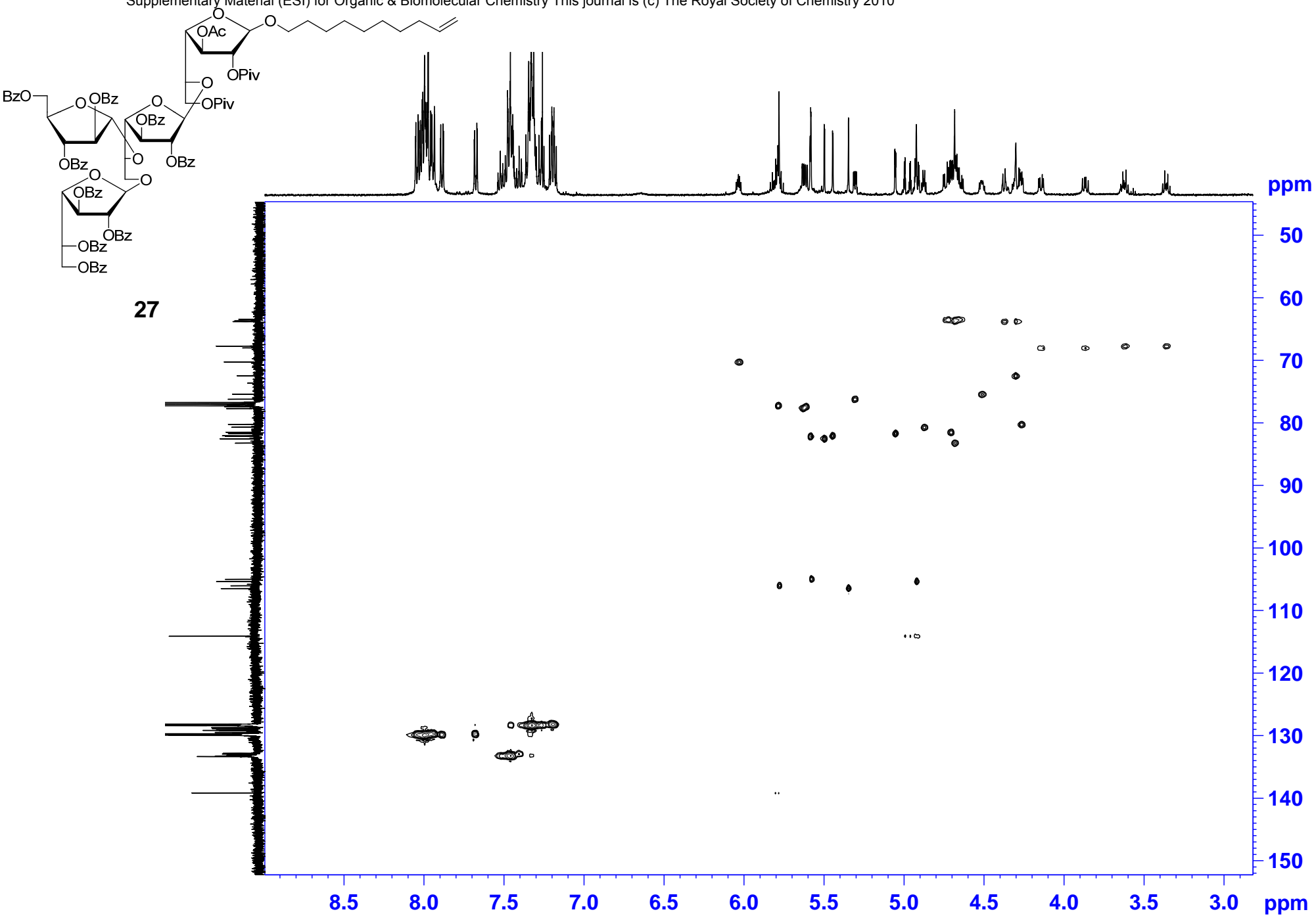
<sup>1</sup>H NMR spectrum of compound **27** (CDCl<sub>3</sub>, 500 MHz)



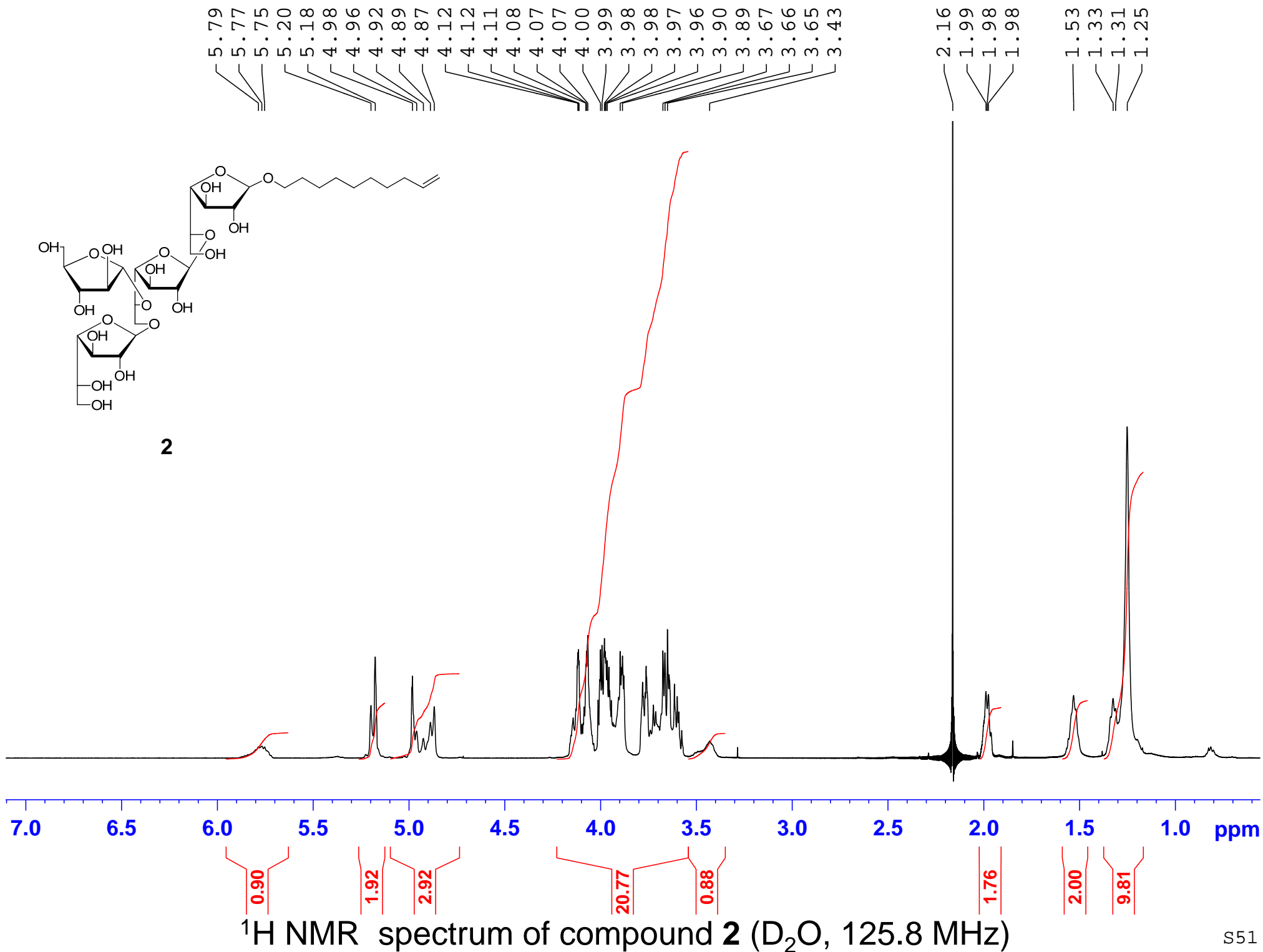
**13**C NMR spectrum of compound **27** (CDCl<sub>3</sub>, 125.8 MHz)

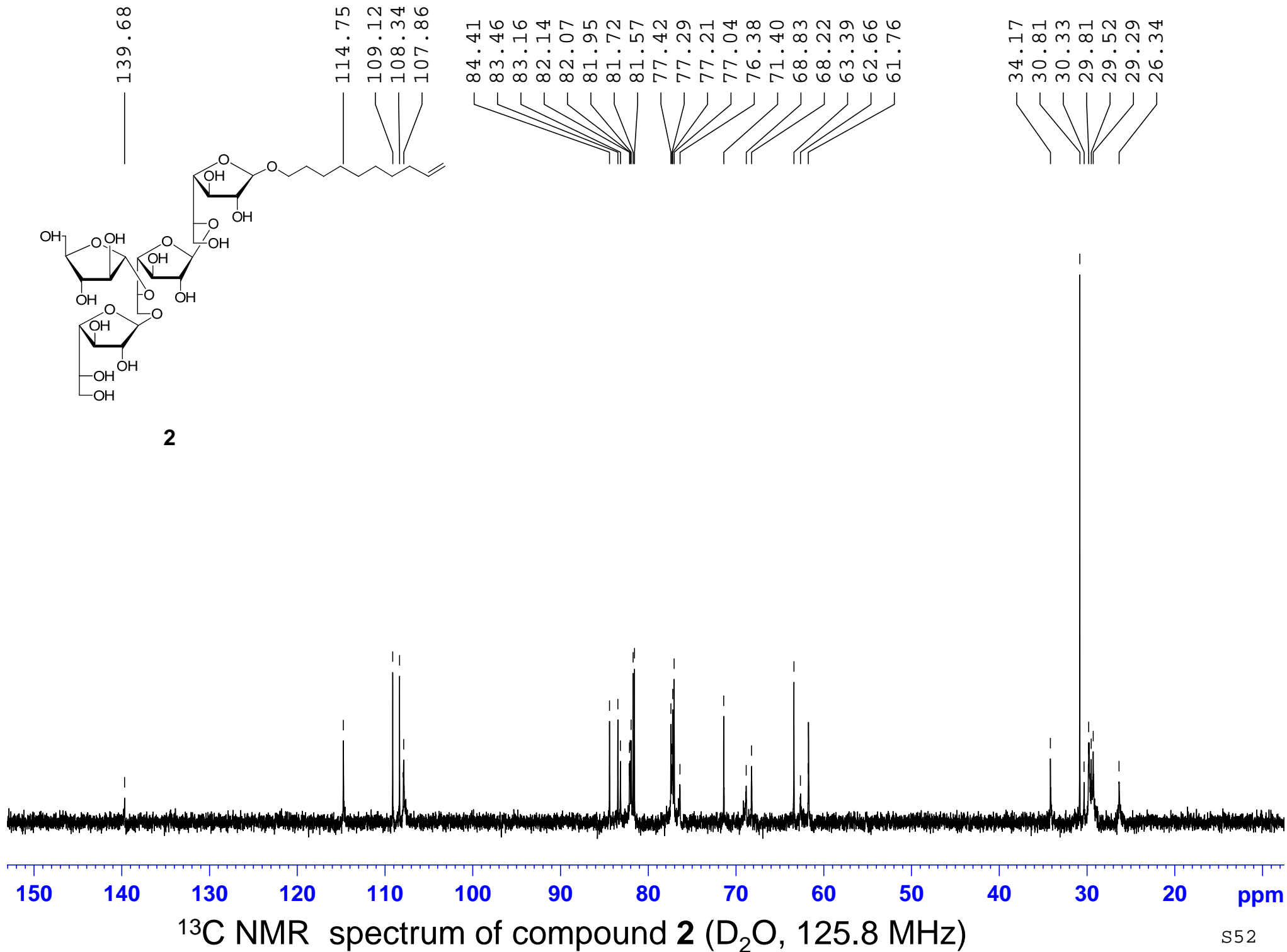


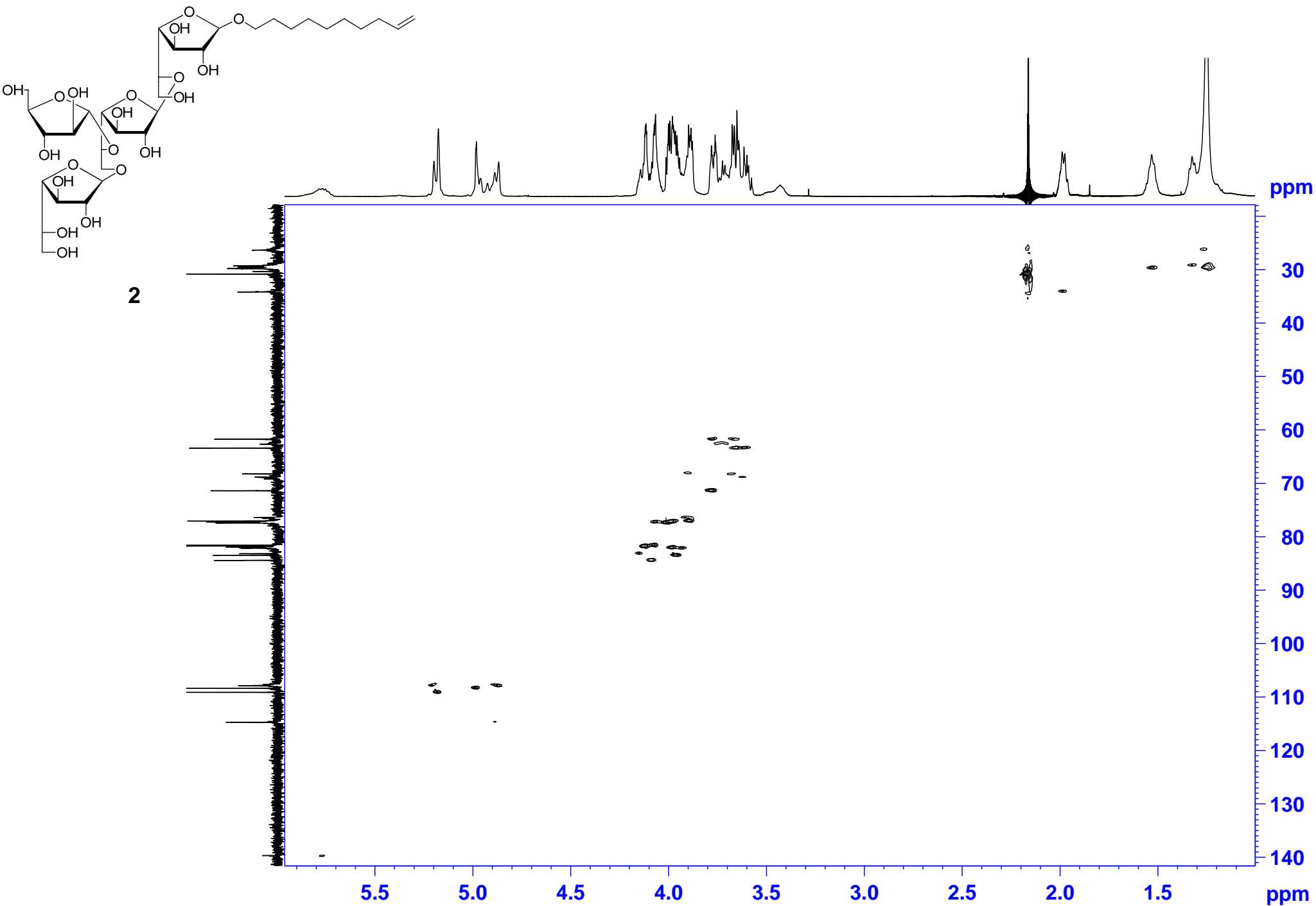
COSY spectrum of compound **27** (CDCl<sub>3</sub>, 500 MHz)



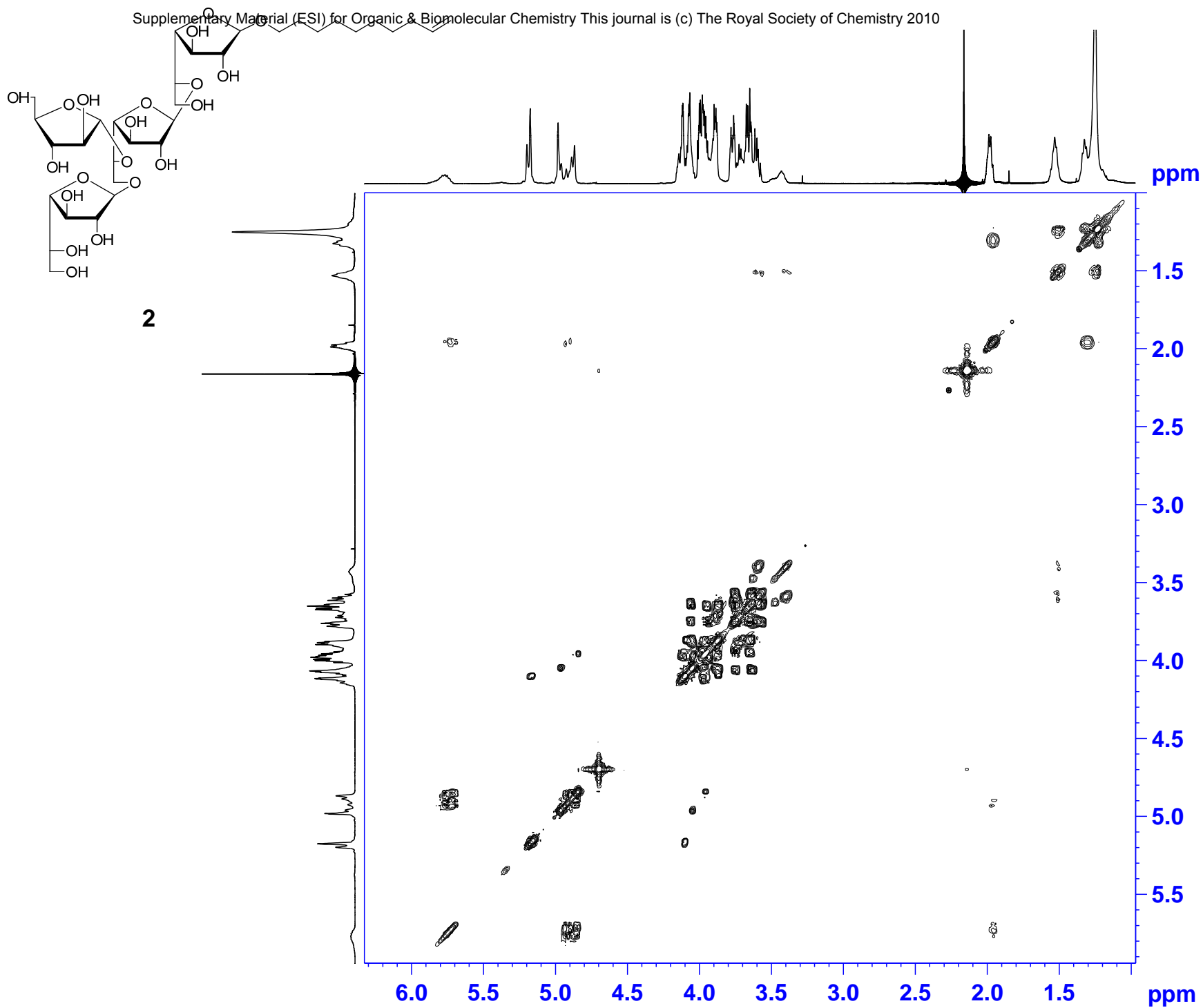
HSQC spectrum of compound **27** ( $\text{CDCl}_3$ , 125.8 MHz)







HSQC spectrum of compound **2** ( $\text{D}_2\text{O}$ , 125.8 MHz)



COSY spectrum of compound **2** (D<sub>2</sub>O, 500 MHz)