

## **Supporting information**

### **O-Benzoxazolyl imidates as versatile glycosyl donors for chemical glycosylation**

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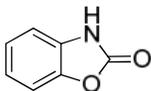
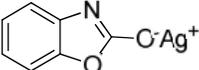
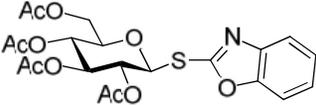
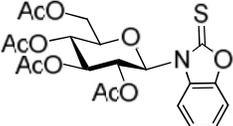
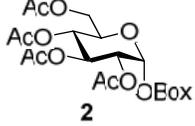
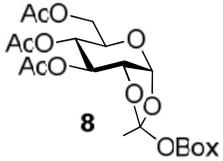
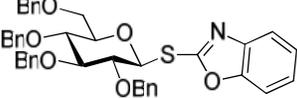
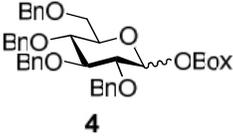
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**Table 1S.** Comparative UV data for O, N and S-linked derivatives

Entry	Compound	Band 1 max (nm)	Band 2 max (nm)	Ref.
1		275	-	This work
2		274	280	This work
3		280	290	1
4		300	--	1
5		273	279	This work
6		274	280	This work
7		280	290	2
8		270	276	This work

### Synthesis of oligosaccharides:

**Methyl 6-O-(2,3,4,6-tetra-O-benzyl- -D-glucopyranosyl)-2,3,4-tri-O-benzyl- -D-glucopyranoside (19).** The title compound was obtained from donor **4** and acceptor **15** by Method C in 95% yield ( / = 1/4.0) as a white amorphous solid. The analytical data for the title compound **19** was in accordance to that reported previously.<sup>3</sup>

**Methyl 4-O-(2,3,4,6-tetra-O-benzyl- -D-glucopyranosyl)-2,3,6-tri-O-benzyl- -D-glucopyranoside (20).** The title compound was obtained from donor **4** and acceptor **16** by Method C in 89% yield ( / = 1/1.5) as a white amorphous solid. The analytical data for the title compound was in accordance to that reported previously.<sup>4</sup>

**Methyl 3-O-(2,3,4,6-tetra-O-benzyl- -D-glucopyranosyl)-2,4,6-tri-O-benzyl- -D-glucopyranoside (21).** The title compound was obtained from donor **4** and acceptor **17** by Method C in 95% yield ( / = 1/1.0) as a white amorphous solid. The analytical data for the title compound was in accordance to that reported previously.<sup>5</sup>

**Methyl 2-O-(2,3,4,6-tetra-O-benzyl- -D-glucopyranosyl)-3,4,6-tri-O-benzyl- -D-glucopyranoside (22).** The title compound was obtained from donor **4** and acceptor **18** by Method C in 92% yield ( / = 1/2.4) as a white amorphous solid. The analytical data for the title compound was in accordance to that reported previously.<sup>6</sup>

**Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-D-mannopyranosyl)- -D-glucopyranoside (23).** The title compound was obtained from donor **4** and acceptor **15** by Method C in 93% yield ( / = 2.9/1) as a white amorphous solid. The title compound was reported previously<sup>7</sup> and its spectra is provided below

**Methyl 2,3,6-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl- -D-mannopyranosyl)- -D-glucopyranoside (24).** The title compound was obtained from donor **4** and acceptor **16** by Method C in 91% yield ( only) as a white amorphous solid. The title compound was reported previously<sup>8</sup> and its spectra is provided below

**Methyl 2,4,6-tri-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl- -D-mannopyranosyl)- -D-glucopyranoside (25).** The title compound was obtained from donor **4** and acceptor **17** by Method C in 90% yield ( only) as a white amorphous solid. Compound **25** was reported previously<sup>9</sup> and its spectra is provided below.

**Methyl 3,4,6-tri-O-benzyl-2-O-(2,3,4,6-tetra-O-benzyl- -D-mannopyranosyl)- -D-glucopyranoside (26).** The title compound was obtained from donor **4** and acceptor **18** by Method C in 94% yield ( only) as a white amorphous solid. The title compound was reported previously<sup>6</sup> and its spectra is provided below

**Methyl 6-O-(2,3,4,6-tetra-O-acetyl- -D-glucopyranosyl)-2,3,4-tri-O-benzyl- -D-glucopyranoside (27).** The title compound was obtained from donor **2** and acceptor **15** by Method D in 97% yield ( only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>6</sup>

**Methyl 4-O-(2,3,4,6-tetra-O-acetyl- -D-glucopyranosyl)-2,3,6-tri-O-benzyl- -D-glucopyranoside (28).** The title compound was obtained from donor **2** and acceptor **16** by Method D in 97% yield ( only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>10</sup>

**Methyl 6-O-(2,3,4,6-tetra-O-benzoyl- -D-glucopyranosyl)-2,3,4-tri-O-benzyl- -D-glucopyranoside (29).** The title compound was obtained from donor **10** and acceptor **15** by

Method C in 89% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>11</sup>

**Methyl 4-O-(2,3,4,6-tetra-O-benzoyl- -D-glucopyranosyl)-2,3,6-tri-O-benzyl- -D-glucopyranoside (30).** The title compound was obtained from donor **10** and acceptor **16** by Method C in 88% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>11</sup>

**Methyl 3-O-(2,3,4,6-tetra-O-benzoyl- -D-glucopyranosyl)-2,4,6-tri-O-benzyl- -D-glucopyranoside (31).** The title compound was obtained from donor **10** and acceptor **17** by Method C in 88% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>12</sup>

**Methyl 2-O-(2,3,4,6-tetra-O-benzoyl- -D-glucopyranosyl)-3,4,6-tri-O-benzyl- -D-glucopyranoside (32).** The title compound was obtained from donor **10** and acceptor **18** by Method C in 87% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>13</sup>

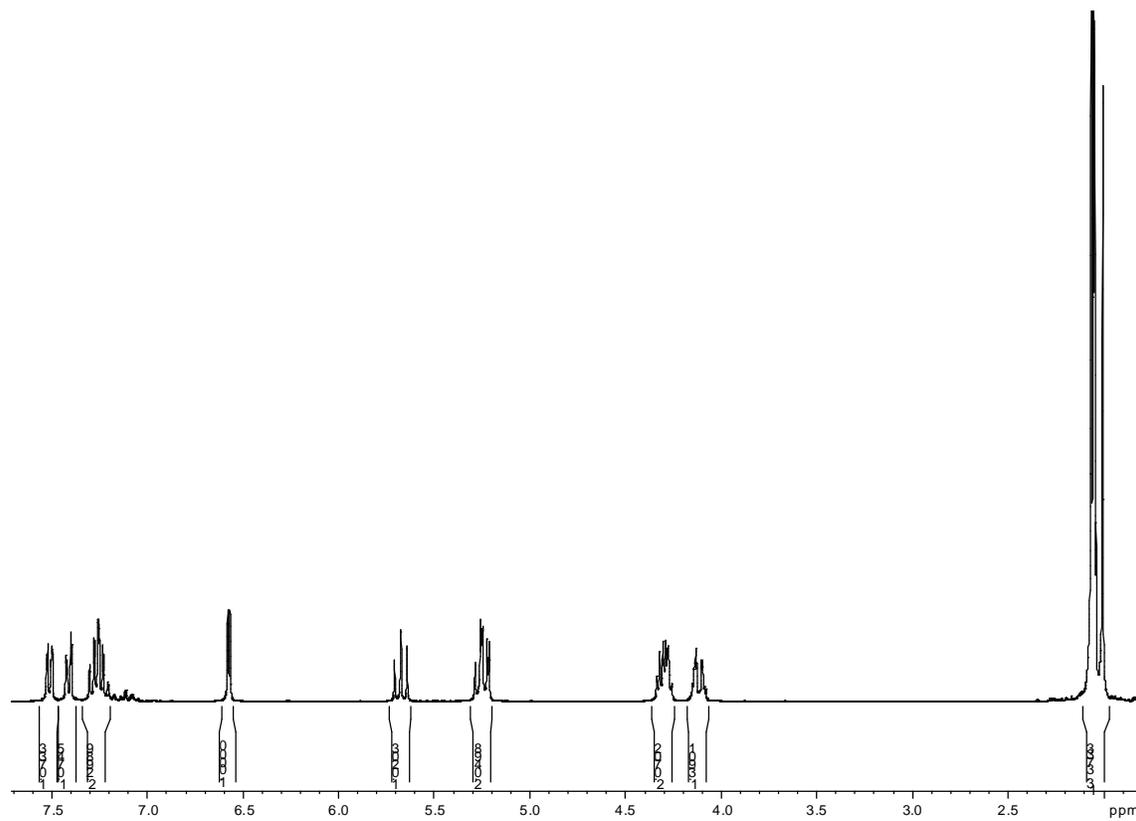
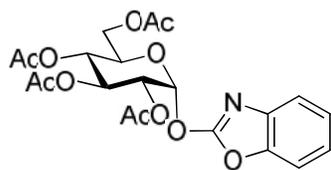
**Methyl 6-O-(2,3,4,6-tetra-O-benzoyl- -D-galactopyranosyl)-2,3,4-tri-O-benzyl- -D-glucopyranoside (33).** The title compound was obtained from donor **12** and acceptor **15** by Method C in 83% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>14</sup>

**Methyl 4-O-(2,3,4,6-tetra-O-benzoyl- -D-galactopyranosyl)-2,3,6-tri-O-benzyl- -D-glucopyranoside (34).** The title compound was obtained from donor **12** and acceptor **16** by Method C in 78% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>15</sup>

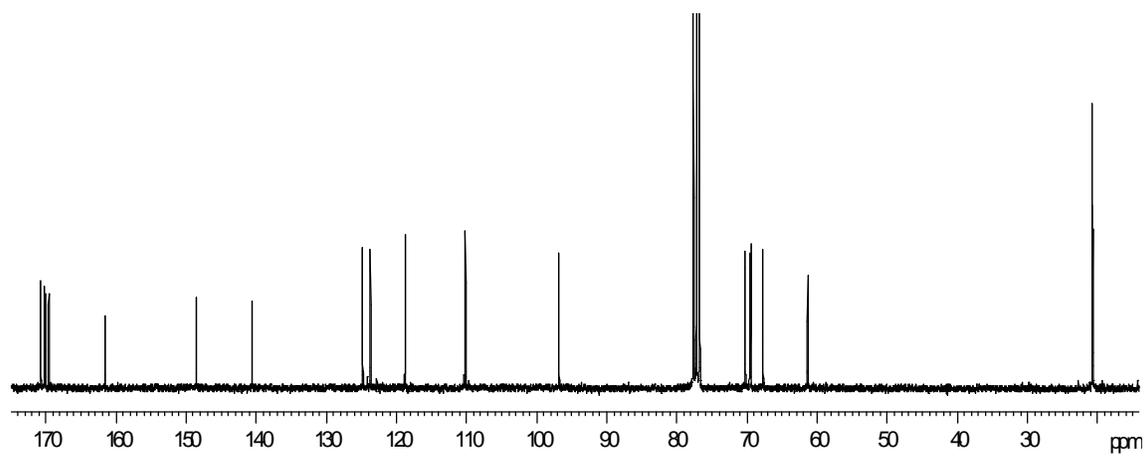
**Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl- -D-mannopyranosyl)- -D-glucopyranoside (35).** The title compound was obtained from donor **14** and acceptor **15** by Method C in 95% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>15</sup>

**Methyl 2,3,6-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl- -D-mannopyranosyl)- -D-glucopyranoside (36).** The title compound was obtained from donor **14** and acceptor **16** by Method C in 97% yield (only) as a white amorphous solid. The analytical data for the title compound was essentially the same as reported previously.<sup>11</sup>

**Benzoxazolyl 2,3,4,6-tetra-O-acetyl-  $\beta$ -D-glucofuranoside (2).**

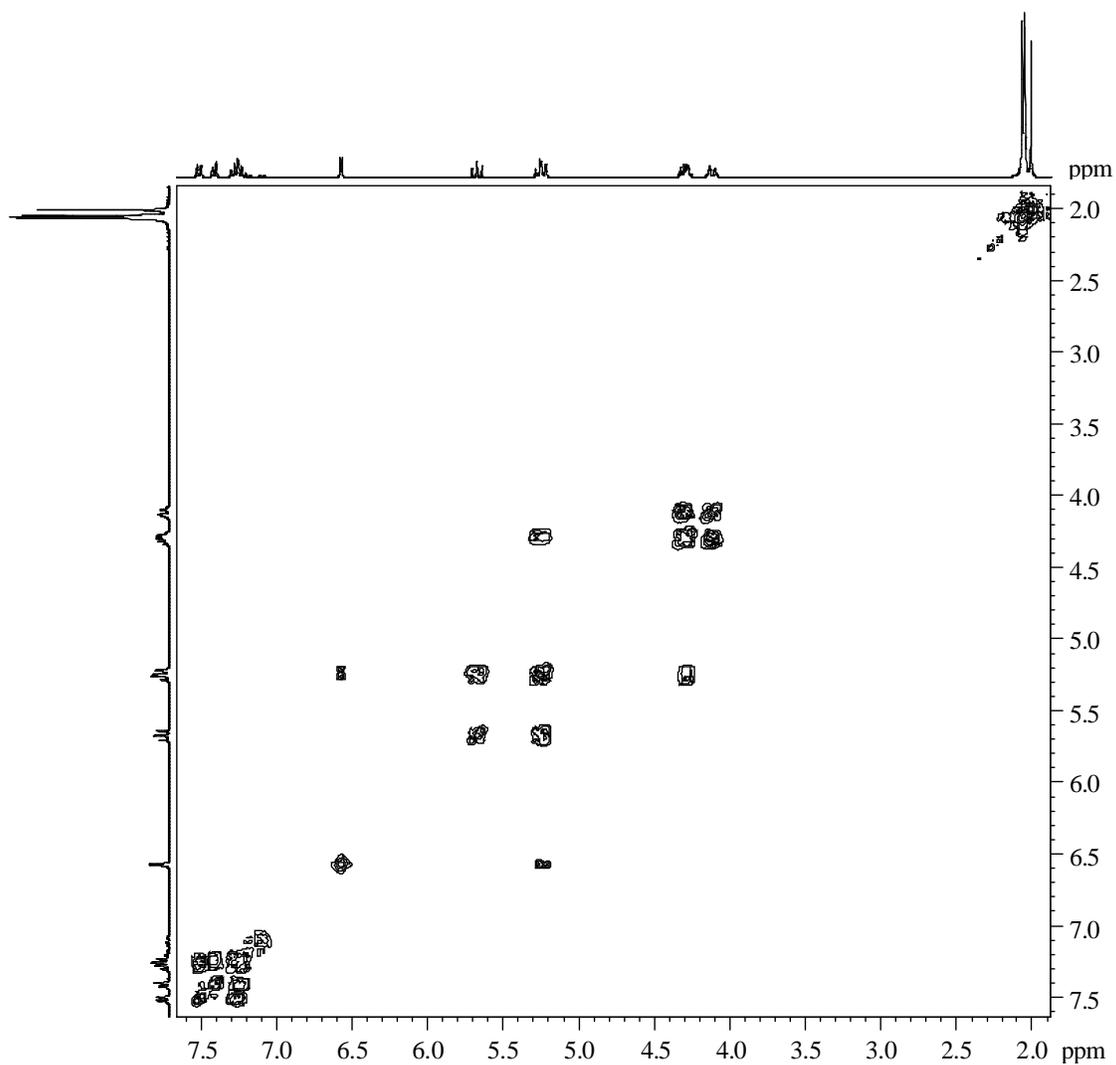
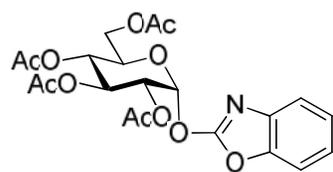


$(^1\text{H NMR 300 MHz, CDCl}_3)$

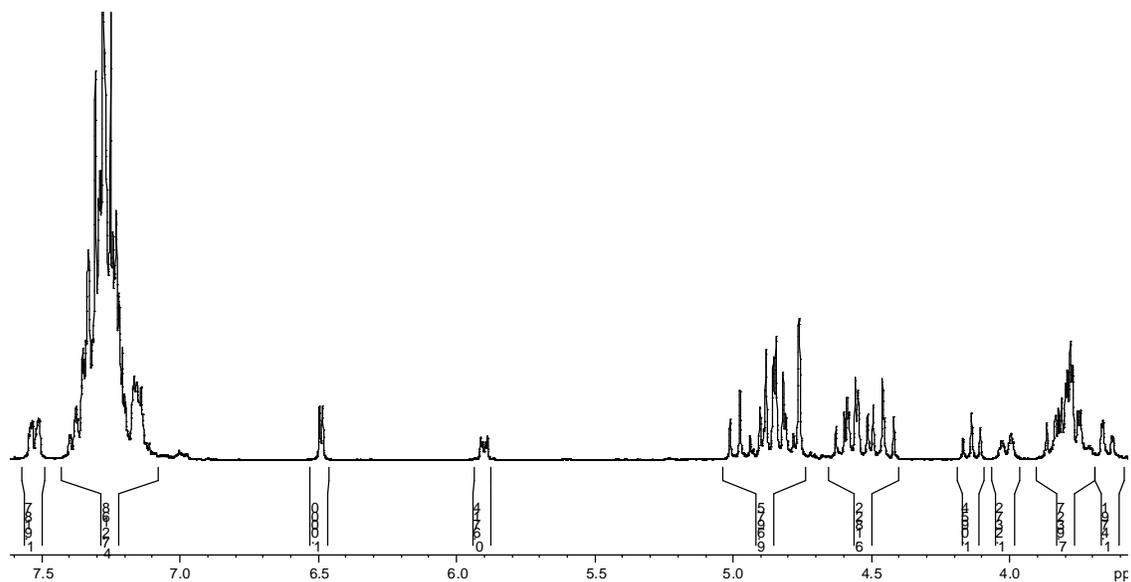
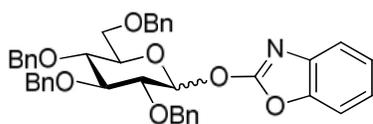


$(^{13}\text{C NMR 75 MHz, CDCl}_3)$

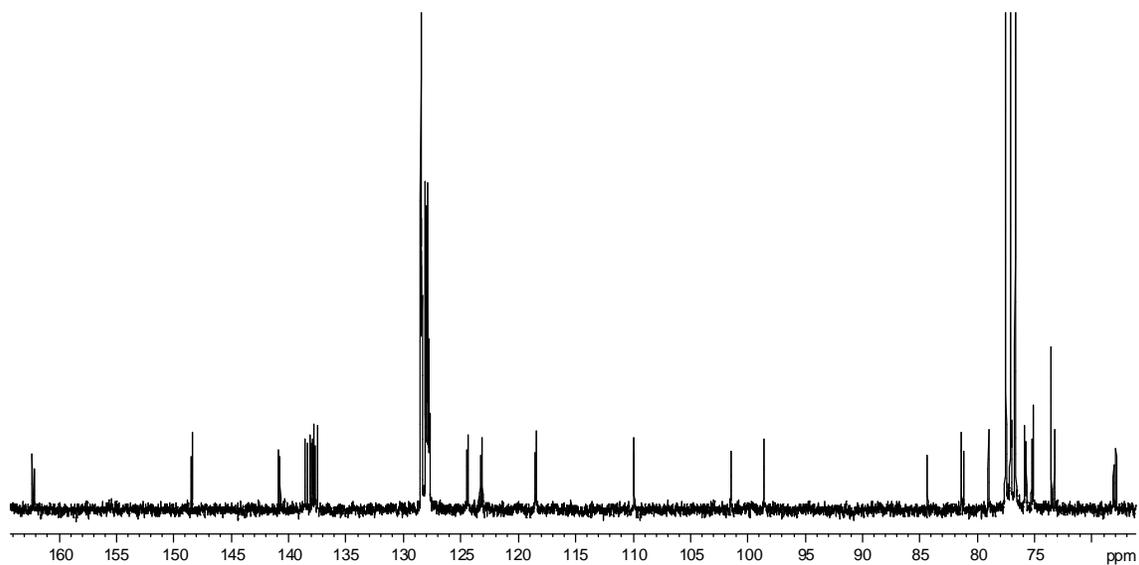
**Benzoxazolyl 2,3,4,6-tetra-O-acetyl-  $\beta$ -D-glucofuranoside (2).**



**Benzoxazolyl 2,3,4,6-tetra-O-benzyl- / -D-glucopyranoside (4)**

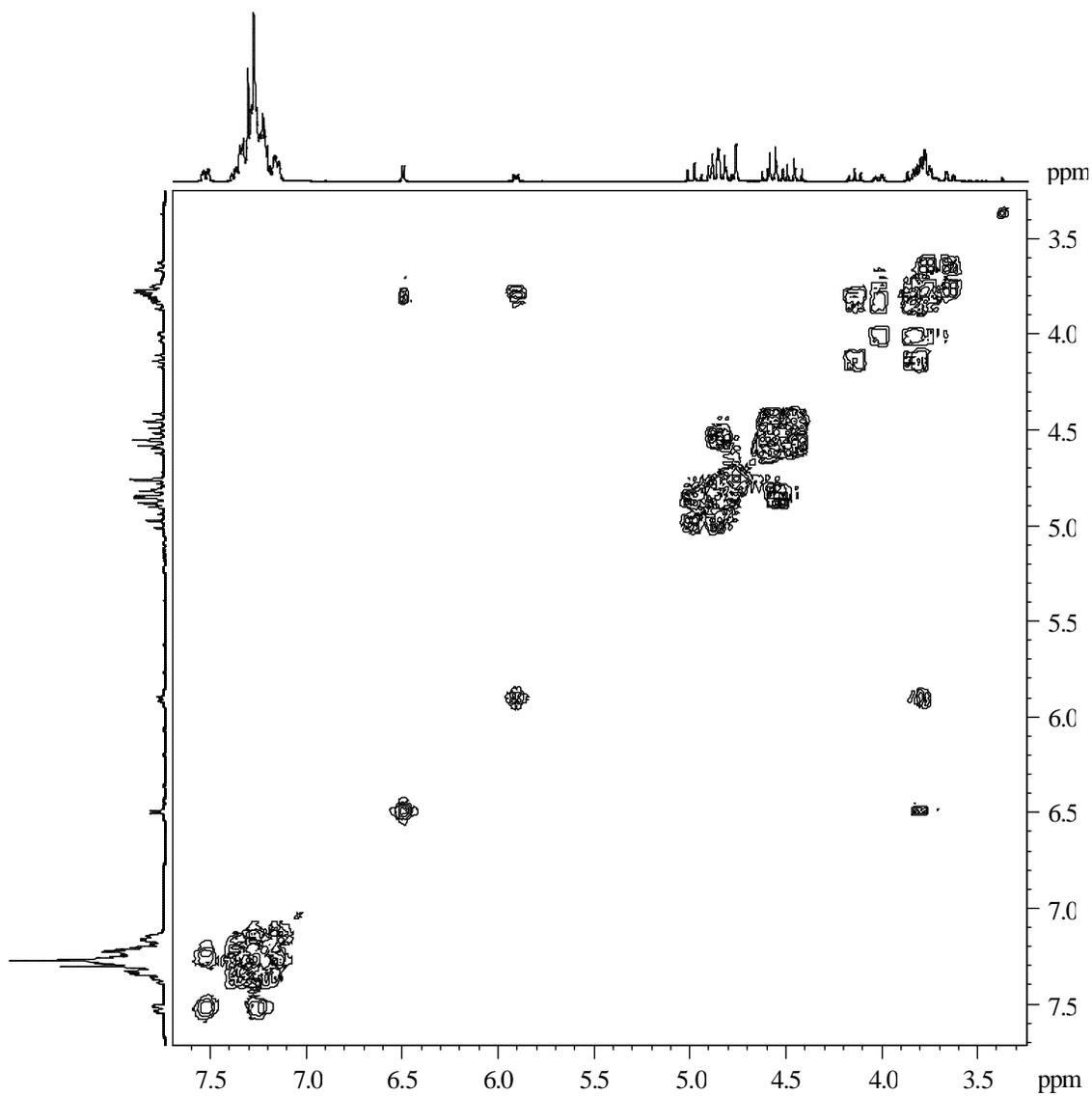
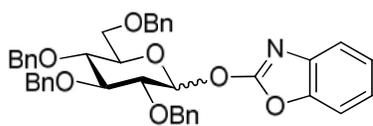


**(<sup>1</sup>H NMR 300 MHz, CDCl<sub>3</sub>)**



**(<sup>13</sup>C NMR 75 MHz, CDCl<sub>3</sub>)**

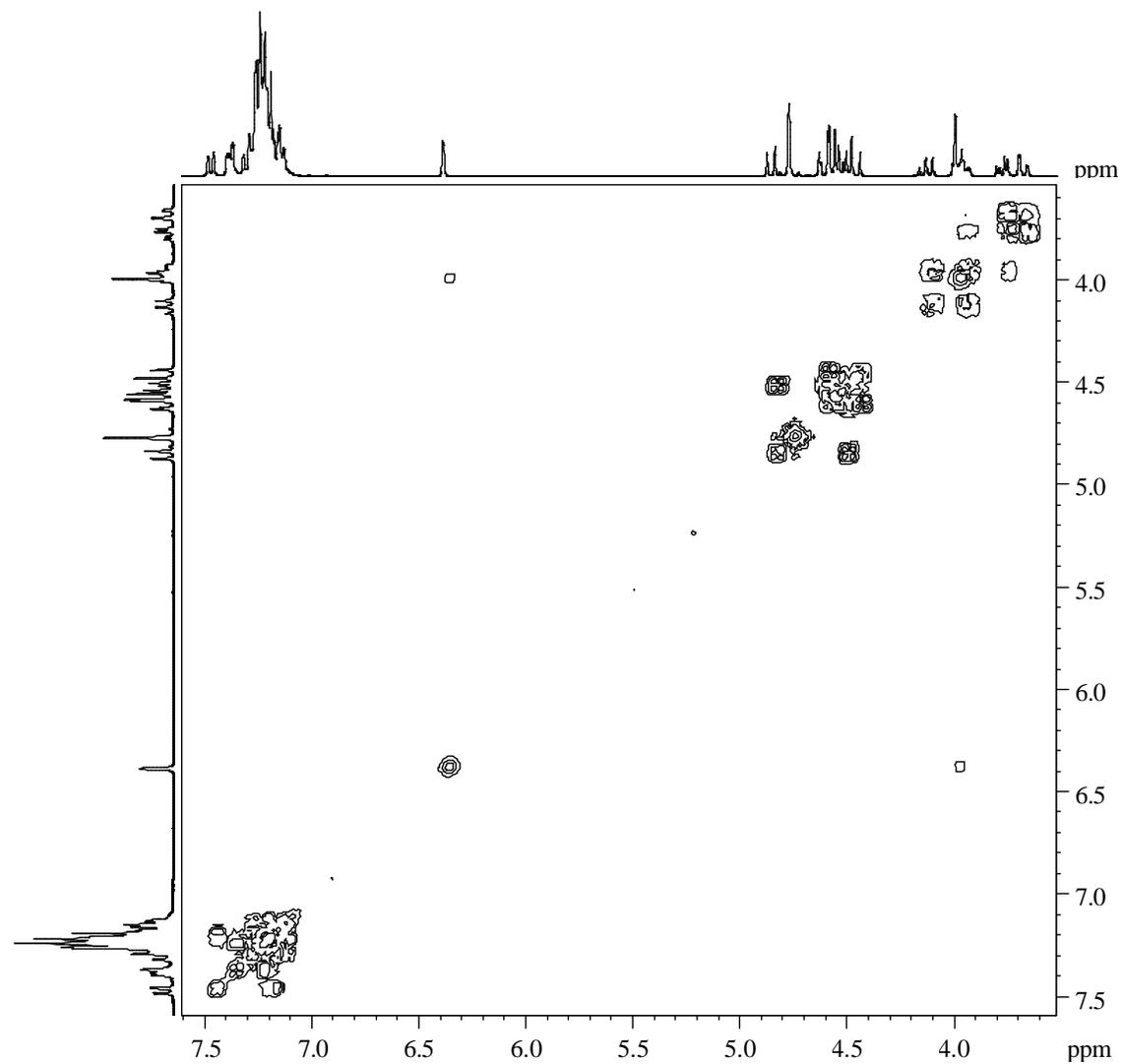
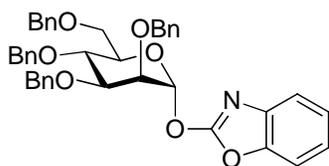
**Benzoxazolyl 2,3,4,6-tetra-O-benzyl- / -D-glucopyranoside (4)**



(2D NMR 300 MHz, CDCl<sub>3</sub>)

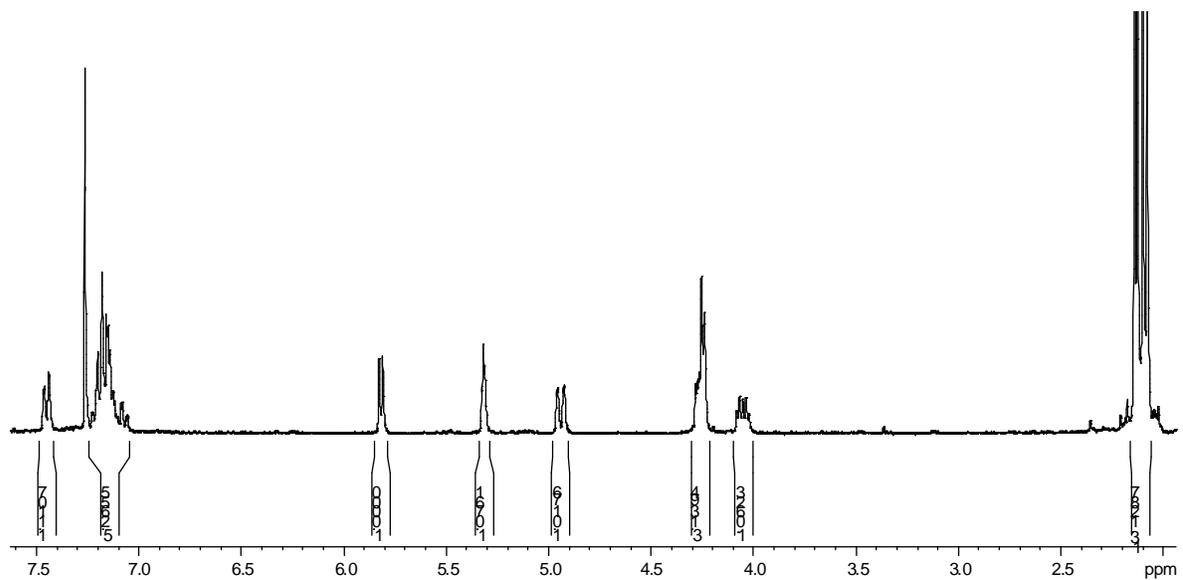
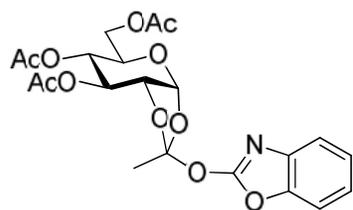


**Benzoxazolyl 2,3,4,6-tetra-O-benzyl-  $\alpha$ -D-mannopyranoside (6).**

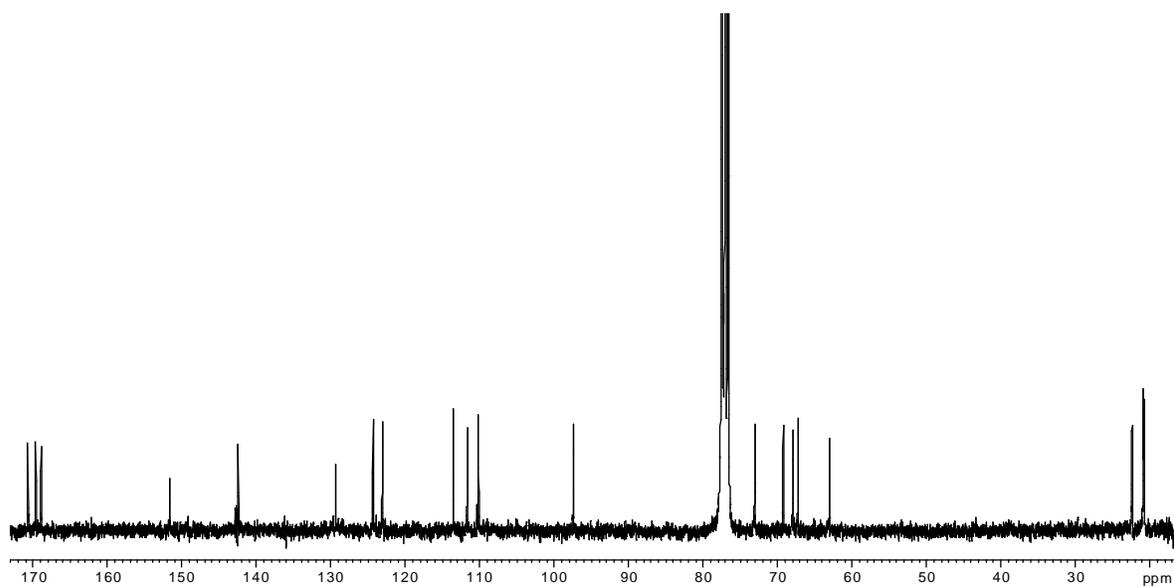


(2D NMR 300 MHz,  $\text{CDCl}_3$ )

**3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-benzoxazolonyloxyethylidene)-*-D*-glucopyranose (8).**

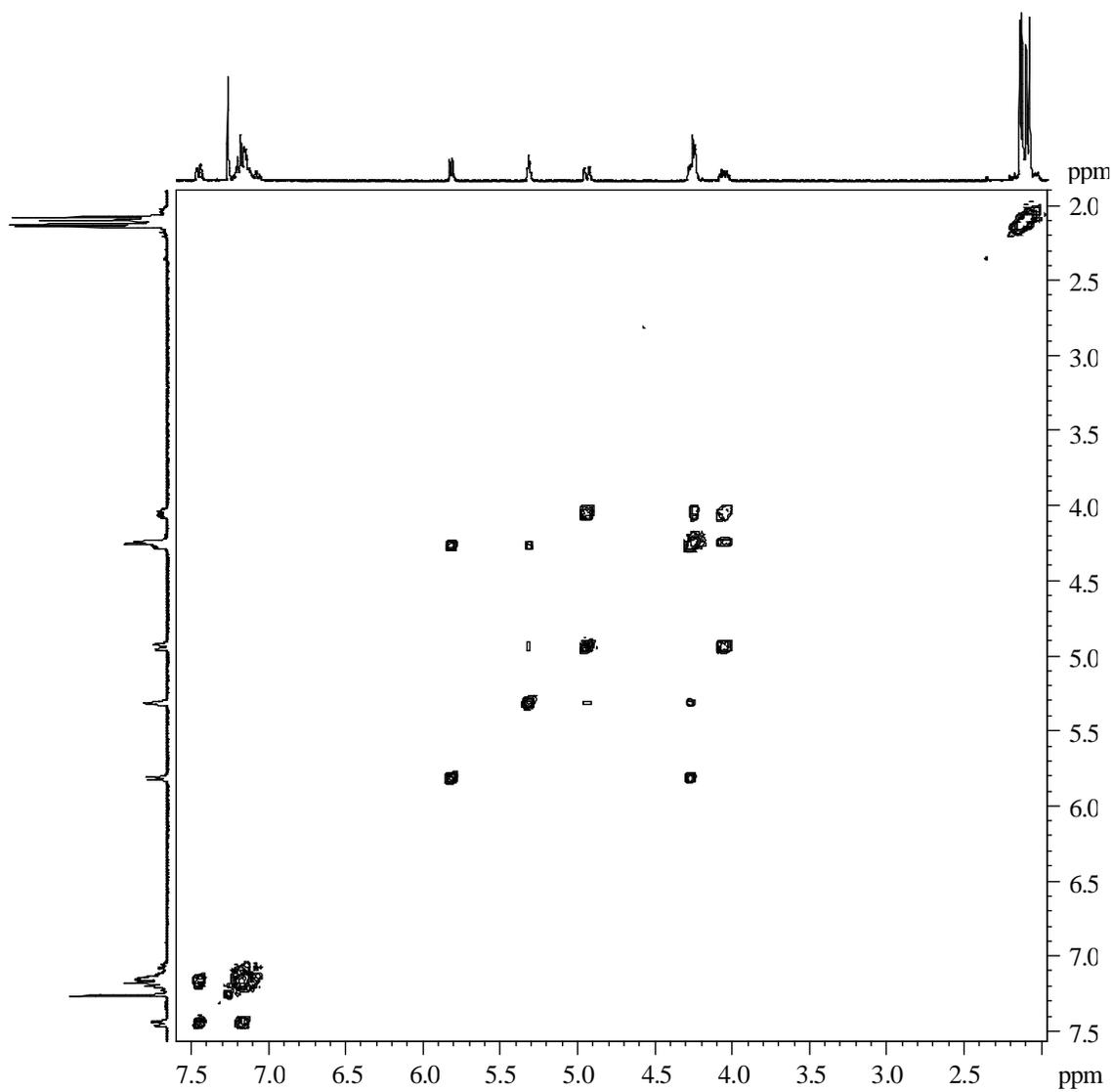
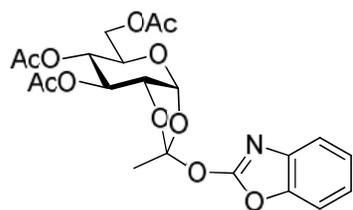


**(<sup>1</sup>H NMR 300 MHz, CDCl<sub>3</sub>)**



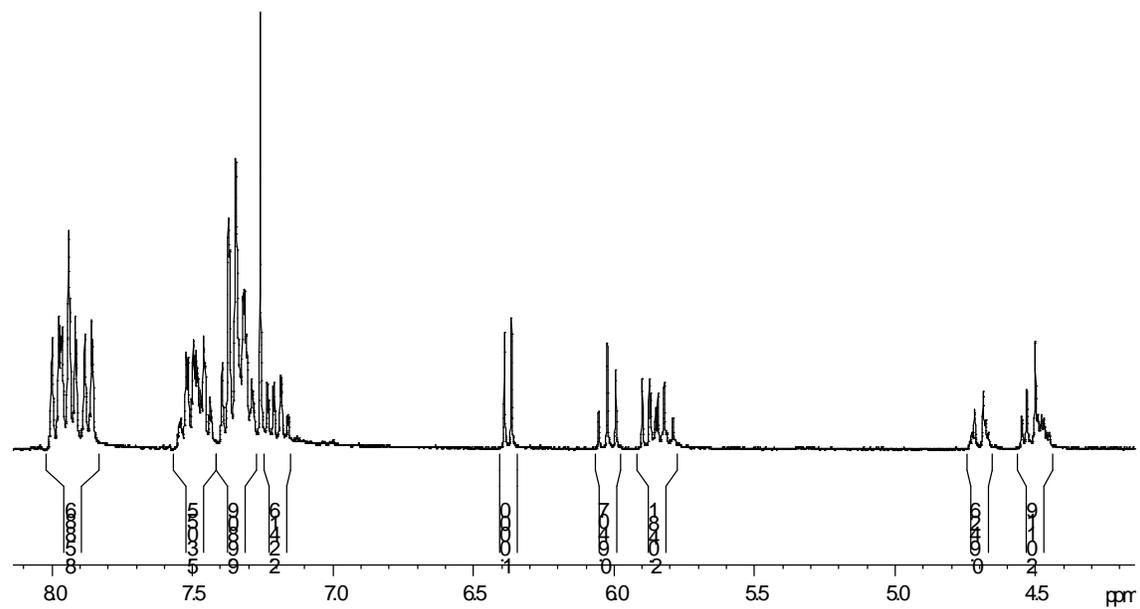
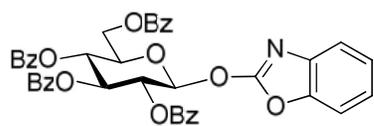
**(<sup>13</sup>C NMR 75 MHz, CDCl<sub>3</sub>)**

**3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-benzoxazolonyloxyethylidene)- $\beta$ -D-glucopyranose (8).**

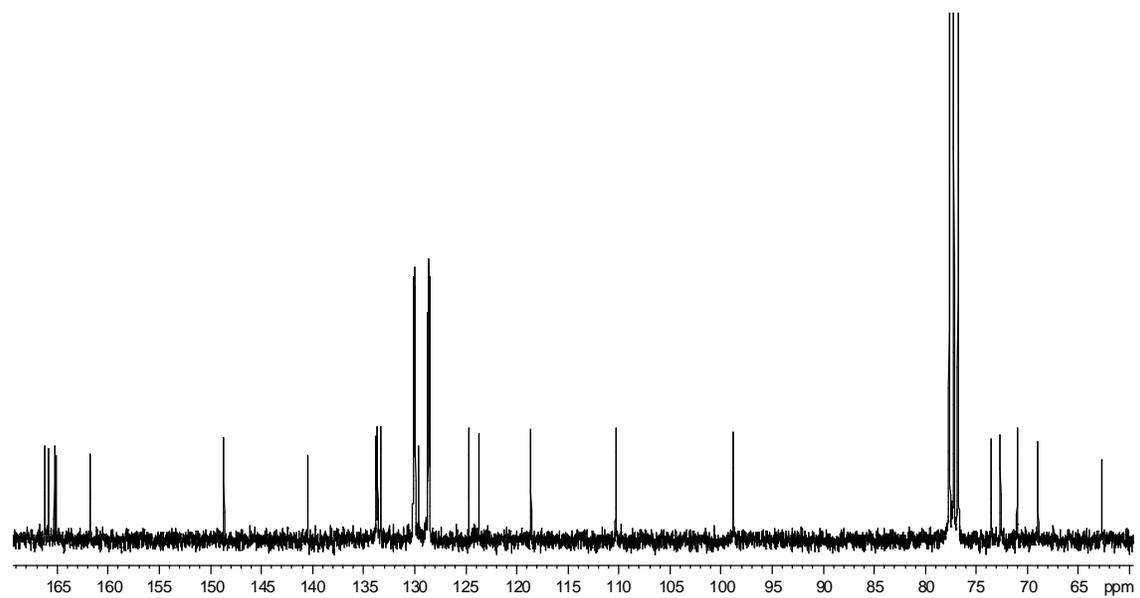


(2D NMR 300 MHz, CDCl<sub>3</sub>)

**Benzoxazolyl 2,3,4,6-tetra-O-benzoyl-  $\beta$ -D-glucopyranoside (10).**



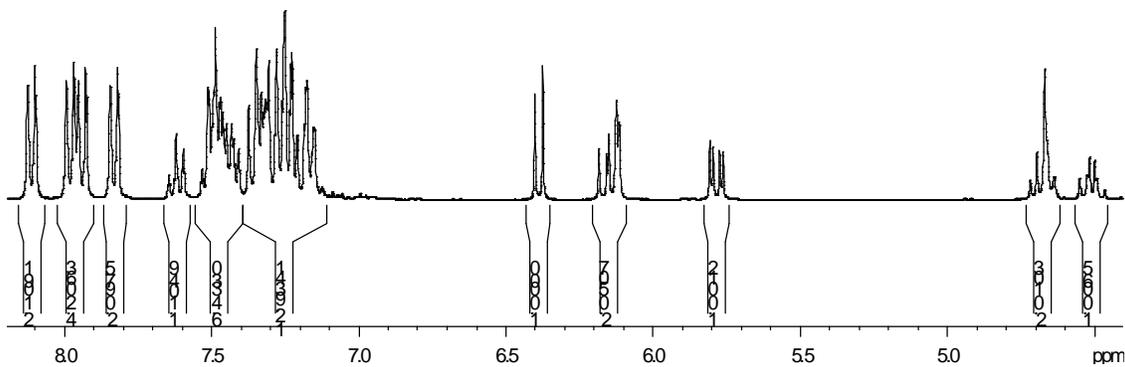
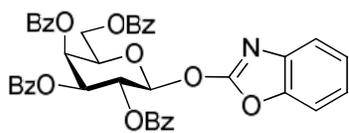
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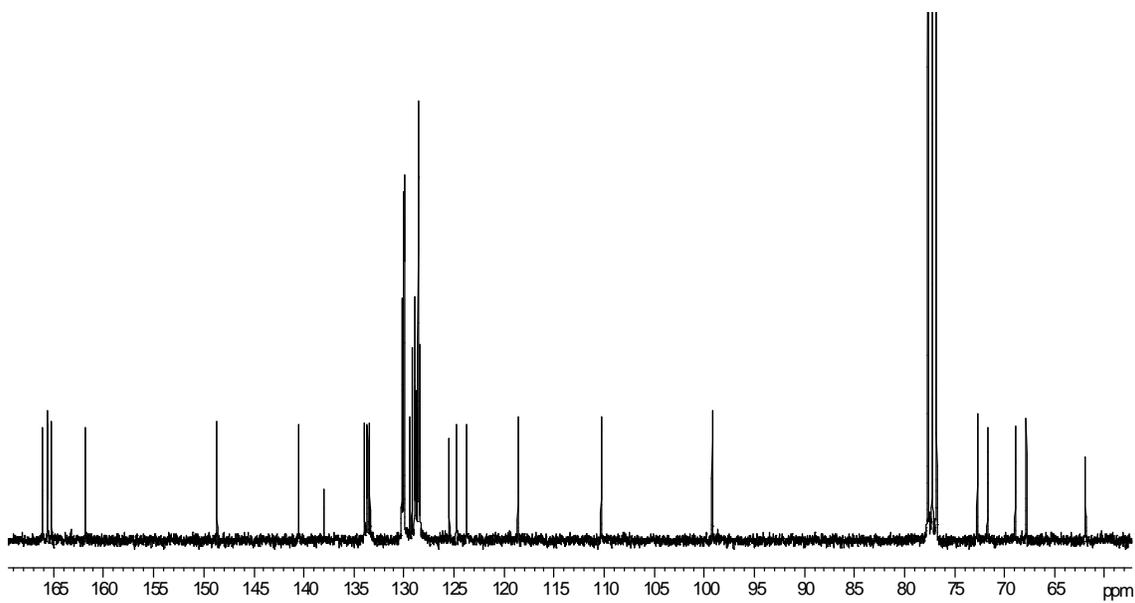
( $^{13}\text{C}$  NMR 75 MHz,  $\text{CDCl}_3$ )



**Benzoxazolyl-2,3,4,6-tetra-O-benzoyl-  $\beta$ -D-galactopyranoside (12).**

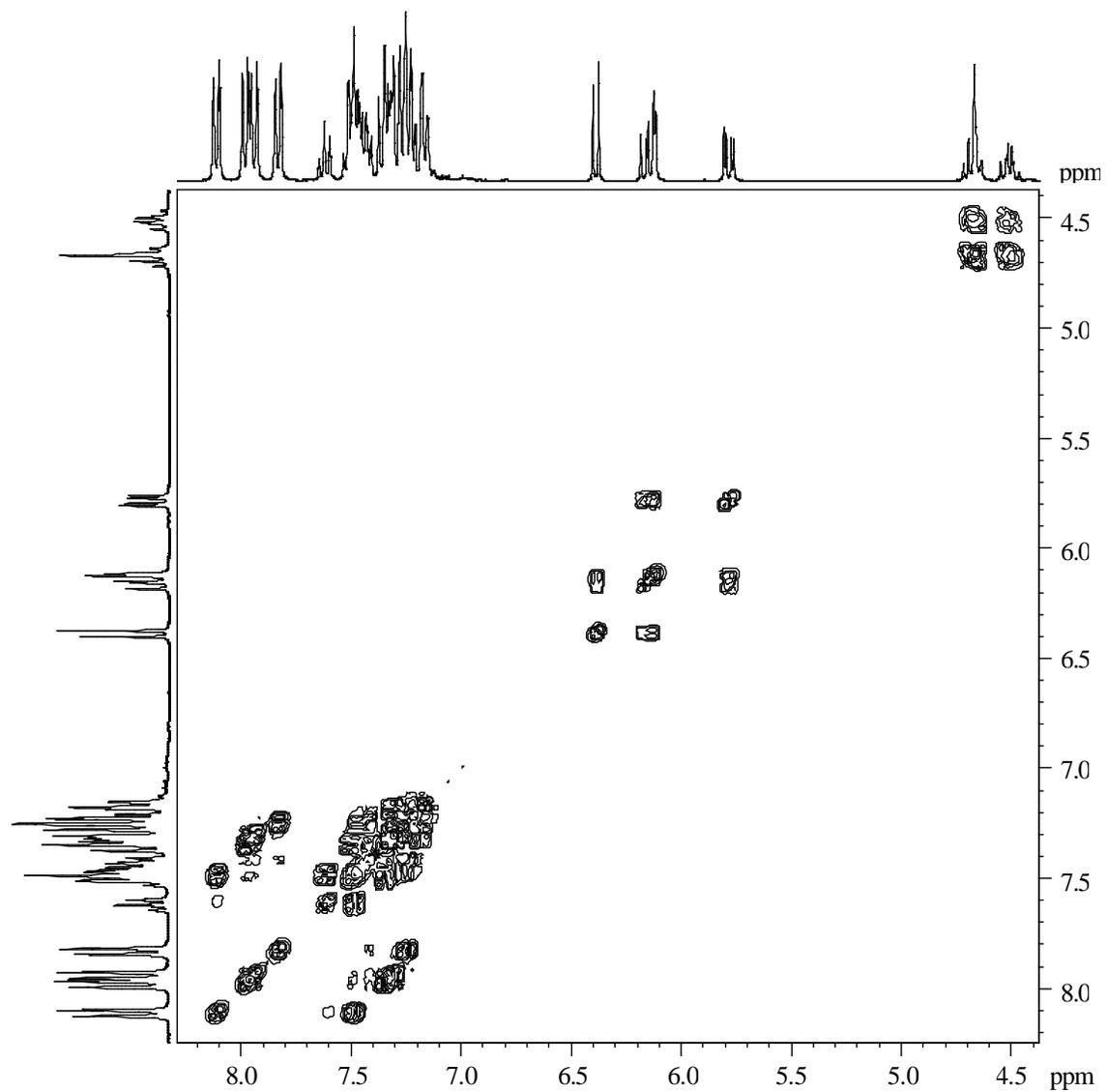
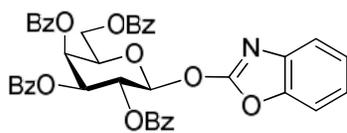


**( $^1\text{H}$  NMR 300 MHz,  $\text{CDCl}_3$ )**



**( $^{13}\text{C}$  NMR 75 MHz,  $\text{CDCl}_3$ )**

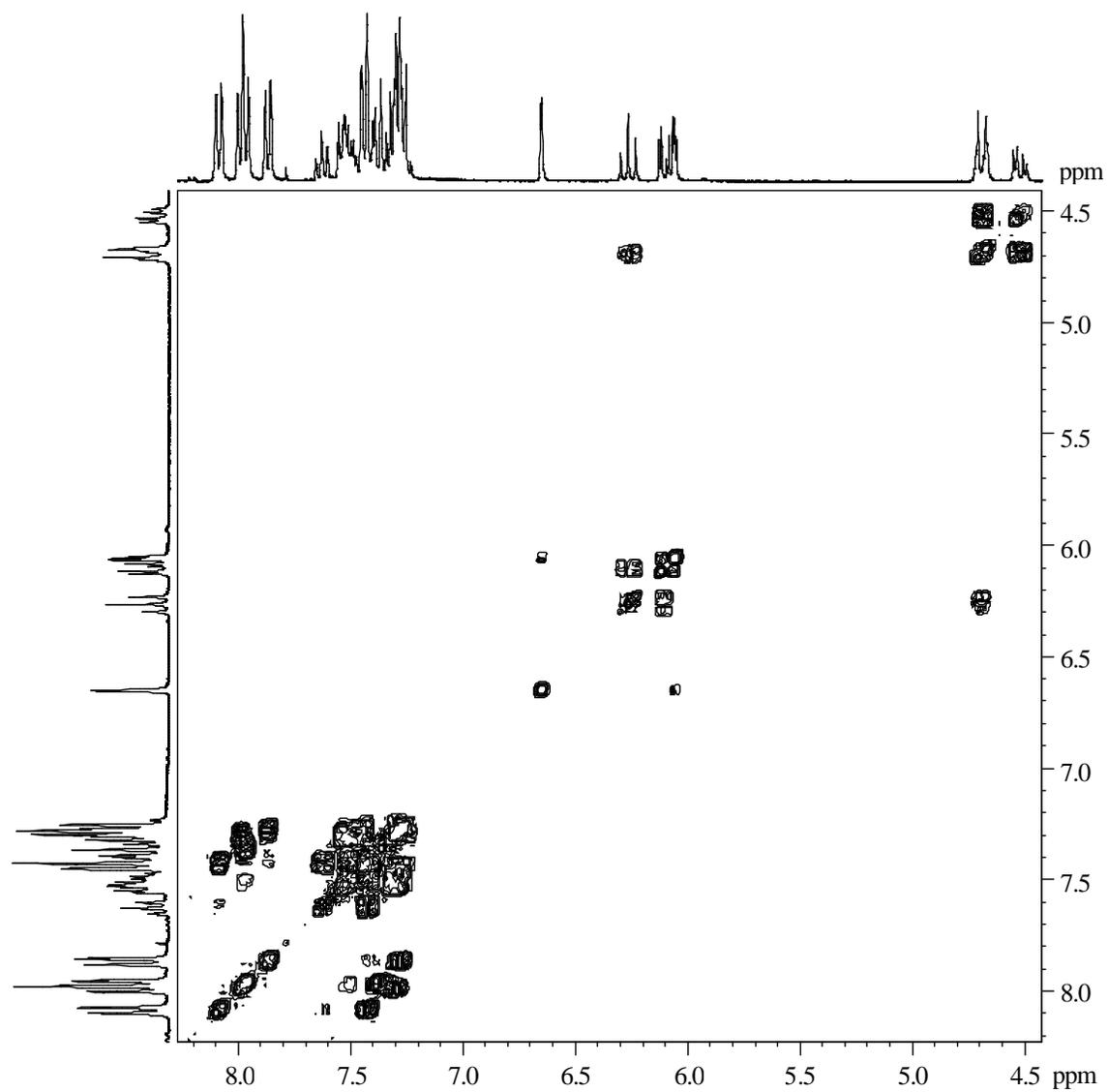
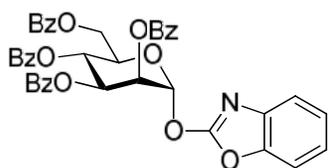
**Benzoxazolyl-2,3,4,6-tetra-O-benzoyl-  $\beta$ -D-galactopyranoside (12).**



(2D NMR 300 MHz,  $\text{CDCl}_3$ )

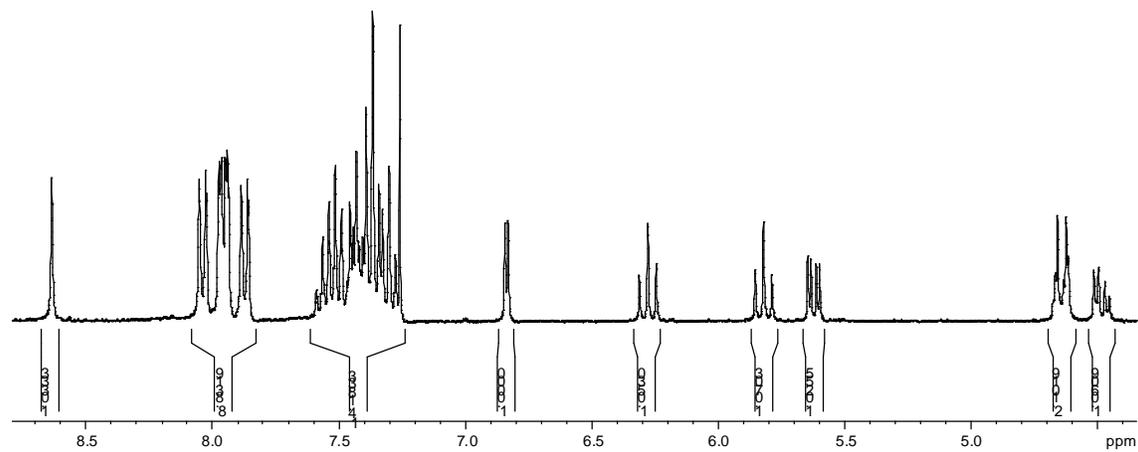
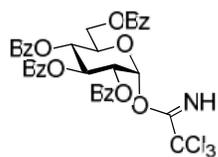


**Benzoxazolyl 2,3,4,6-tetra-O-benzoyl- $\alpha$ -D-mannopyranoside (14).**

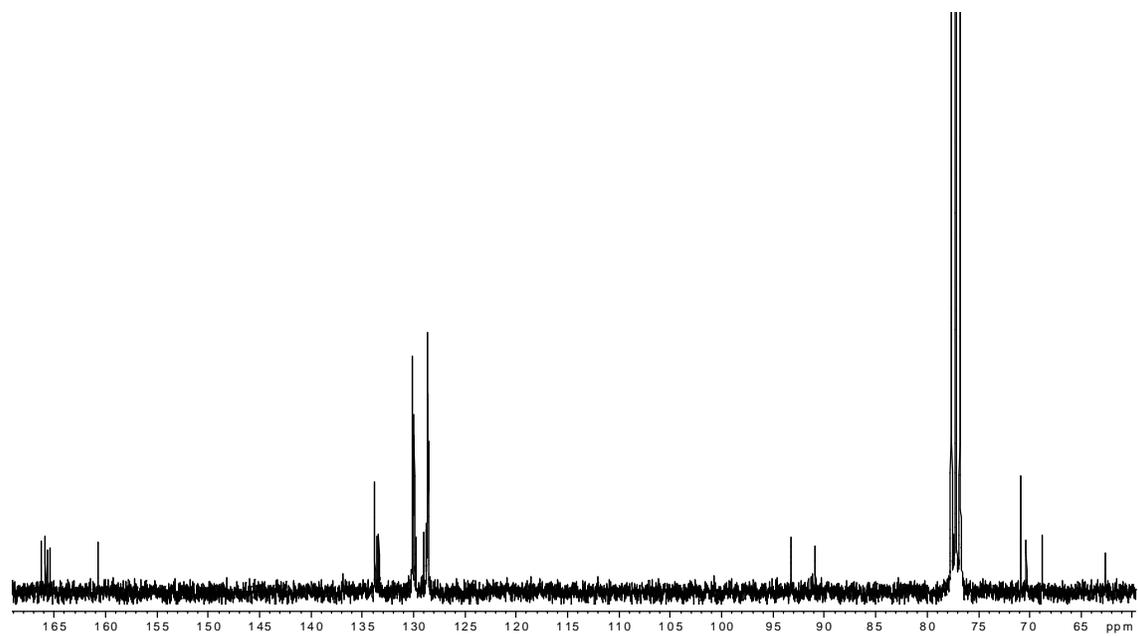


(2D NMR 300 MHz, CDCl<sub>3</sub>)

**2,3,4,6-tetra-*O*-benzyl-  $\beta$ -D-glucopyranosyl trichloroacetimidate (38)**

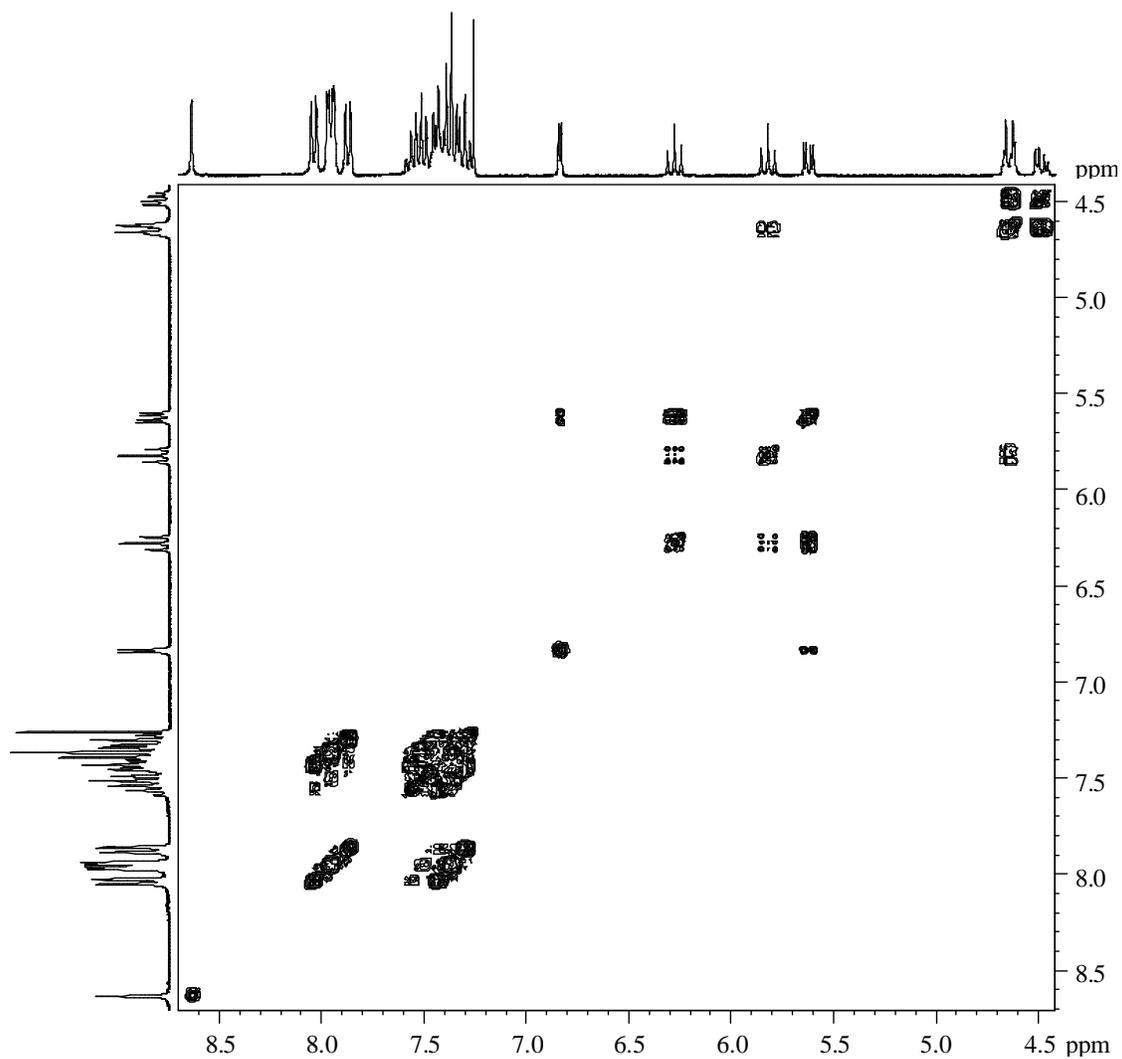
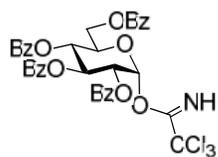


$(^1\text{H NMR 300 MHz, CDCl}_3)$

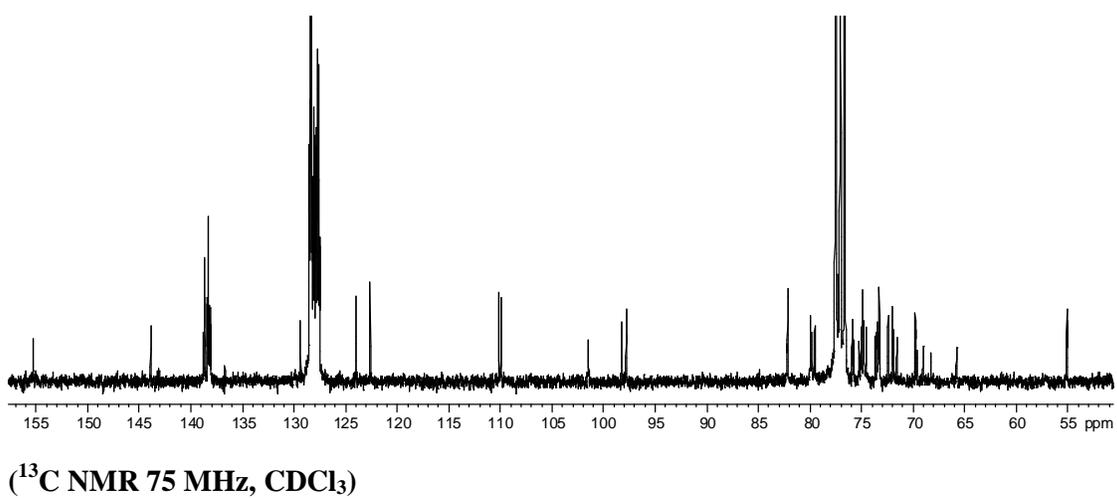
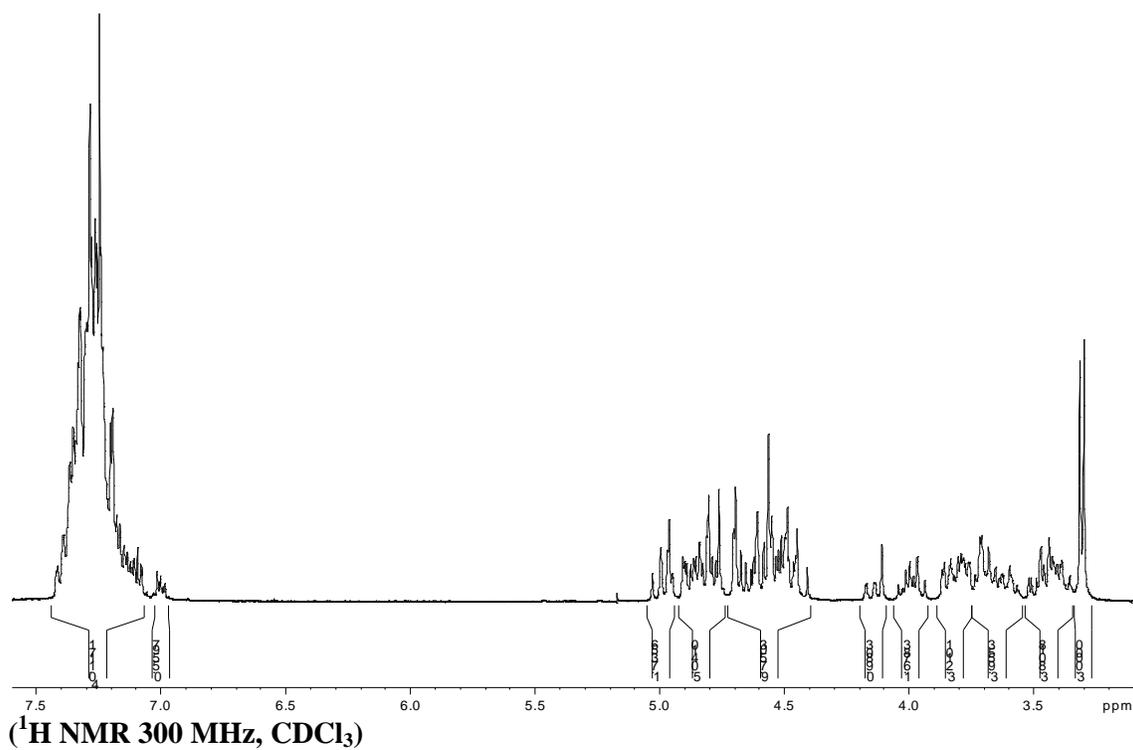
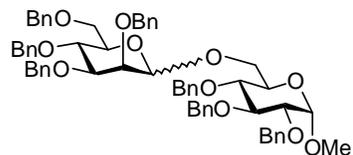


$(^{13}\text{C NMR 75 MHz, CDCl}_3)$

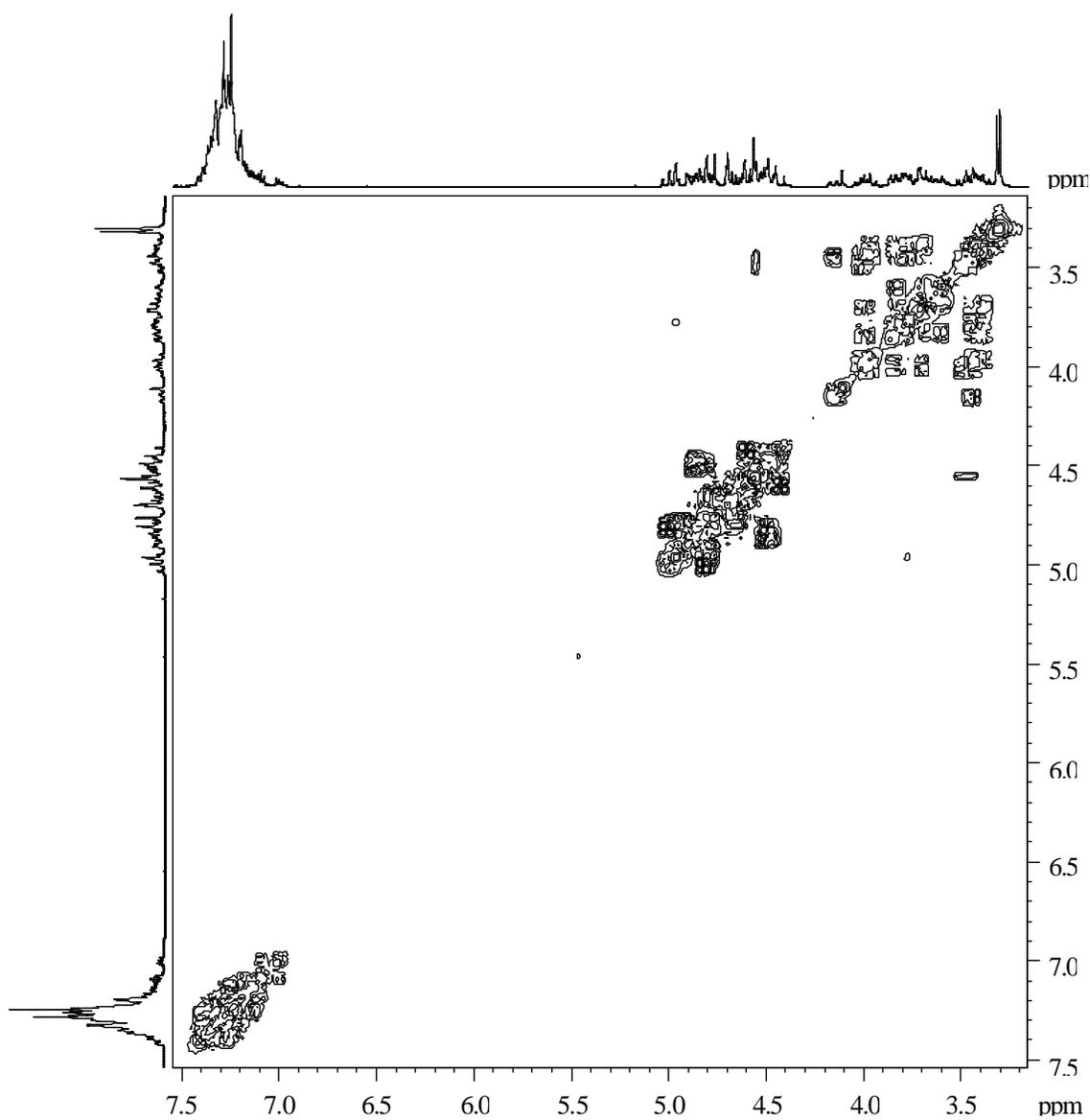
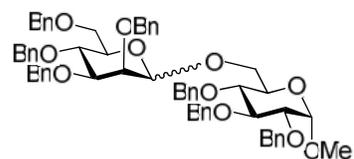
2,3,4,6-tetra-*O*-benzyl-  $\beta$ -D-glucopyranosyl trichloroacetimidate (38)



**Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-D-mannopyranosyl)-D-glucopyranoside (23)**



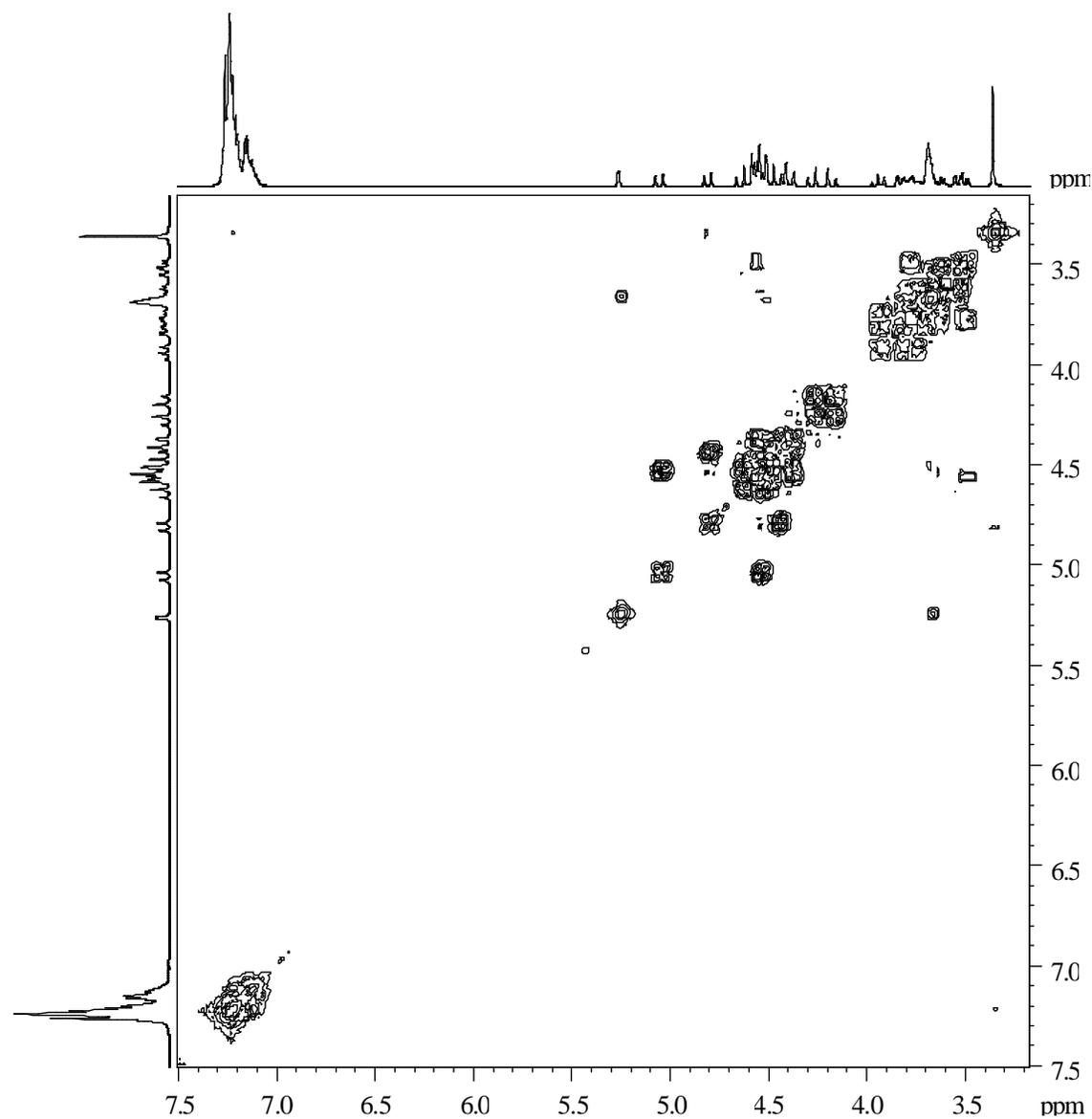
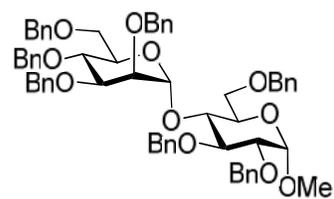
**Methyl 2,3,4-tri-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-D-mannopyranosyl)-D-glucopyranoside (23)**



(2D NMR 300 MHz, CDCl<sub>3</sub>)

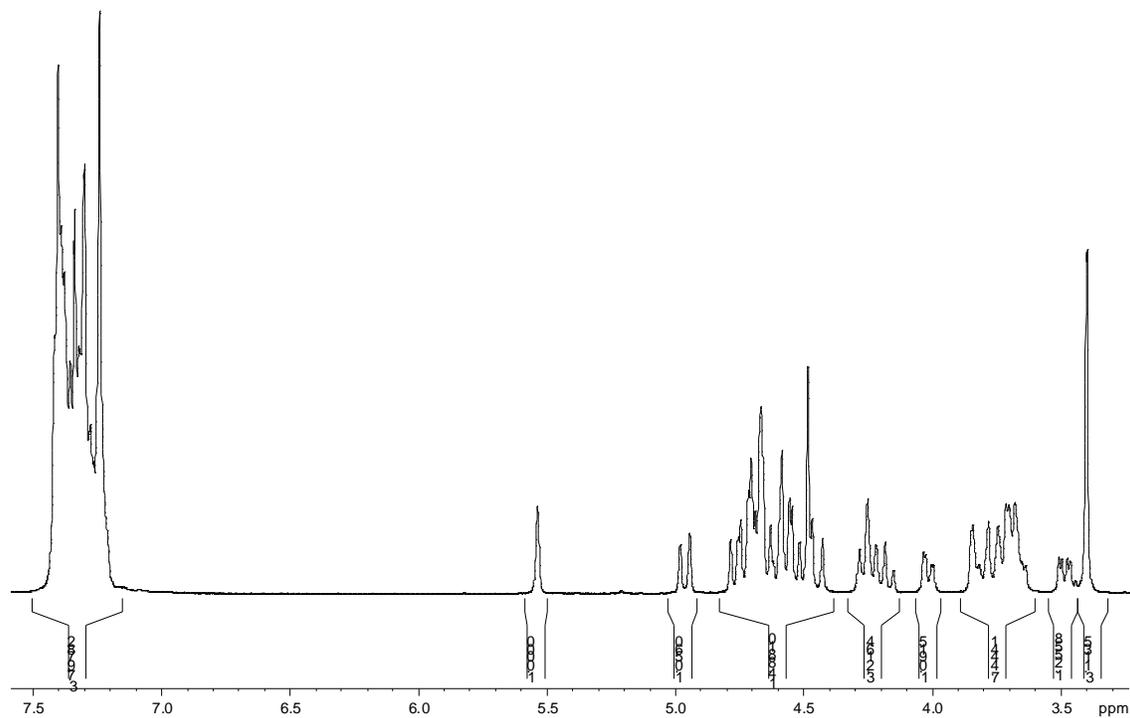
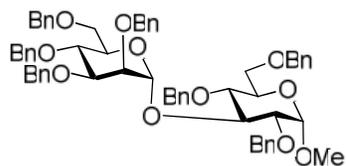


**Methyl 2,3,6-tri-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl- $\beta$ -D-mannopyranosyl)- $\beta$ -D-glucopyranoside (24)**

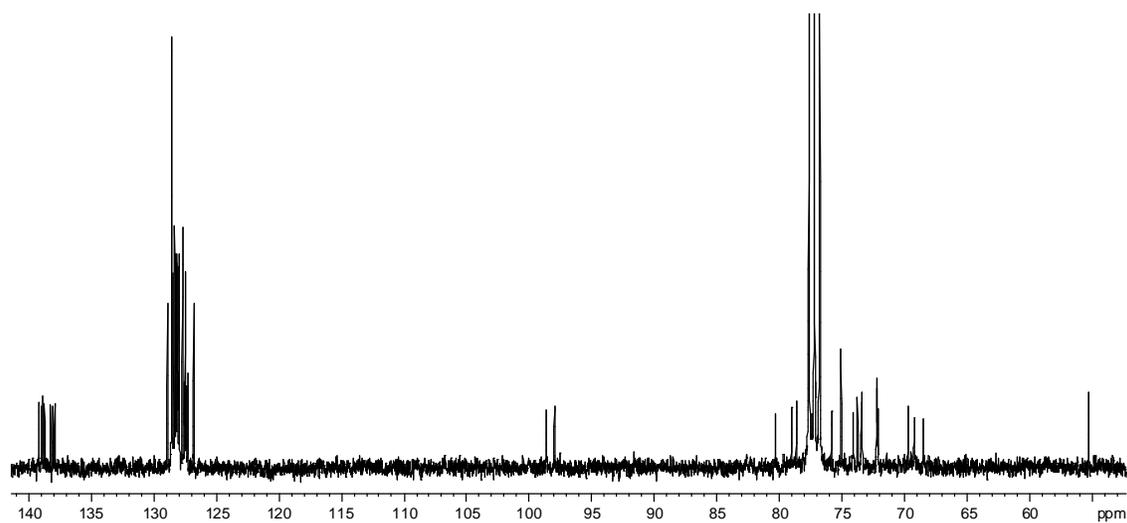


(2D NMR 300 MHz,  $\text{CDCl}_3$ )

**Methyl 2,4,6-tri-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl- $\beta$ -D-mannopyranosyl)- $\beta$ -D-glucopyranoside (25).**

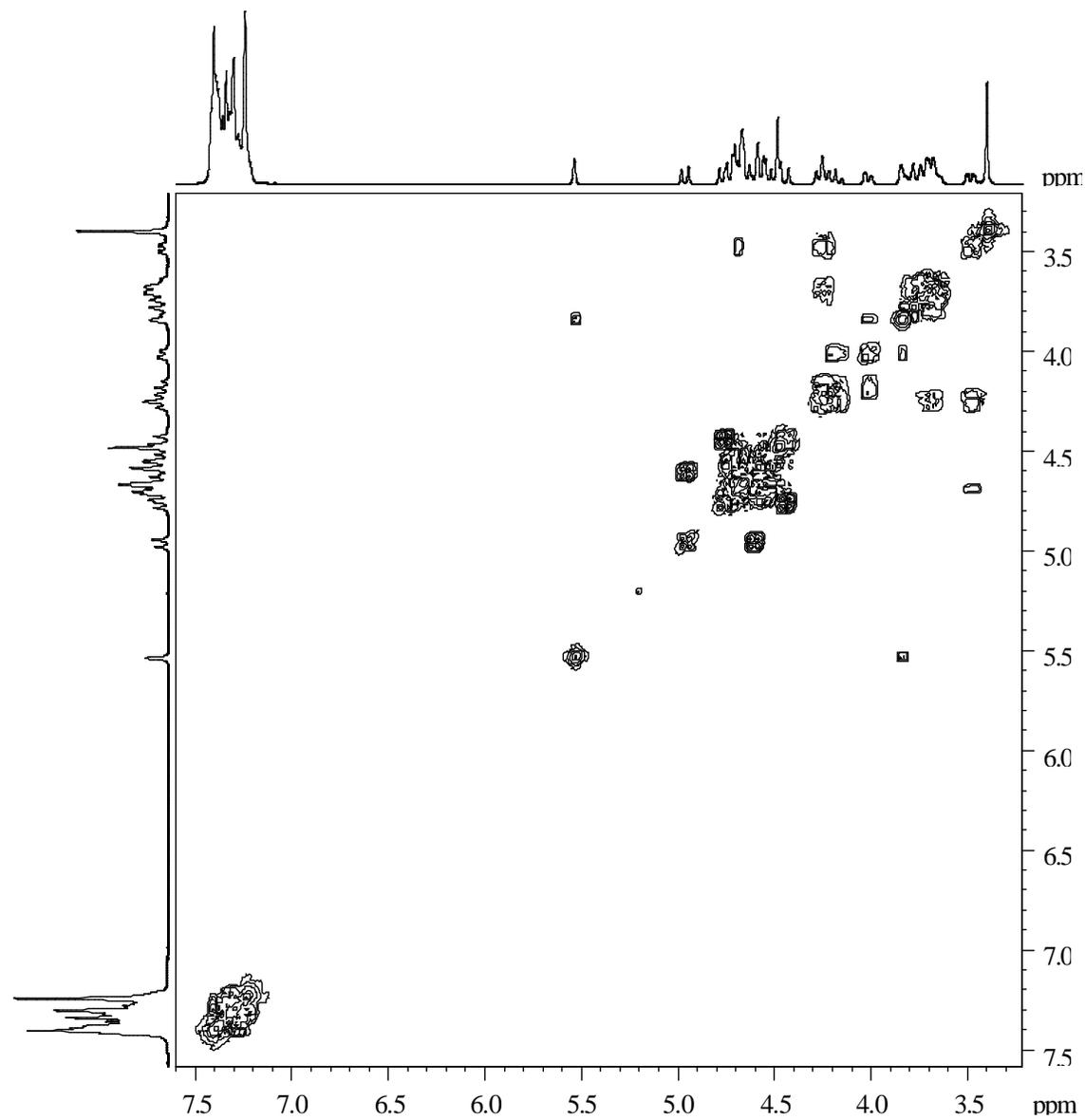
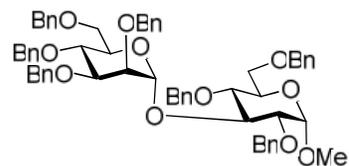


( $^1\text{H}$  NMR 300 MHz,  $\text{CDCl}_3$ )



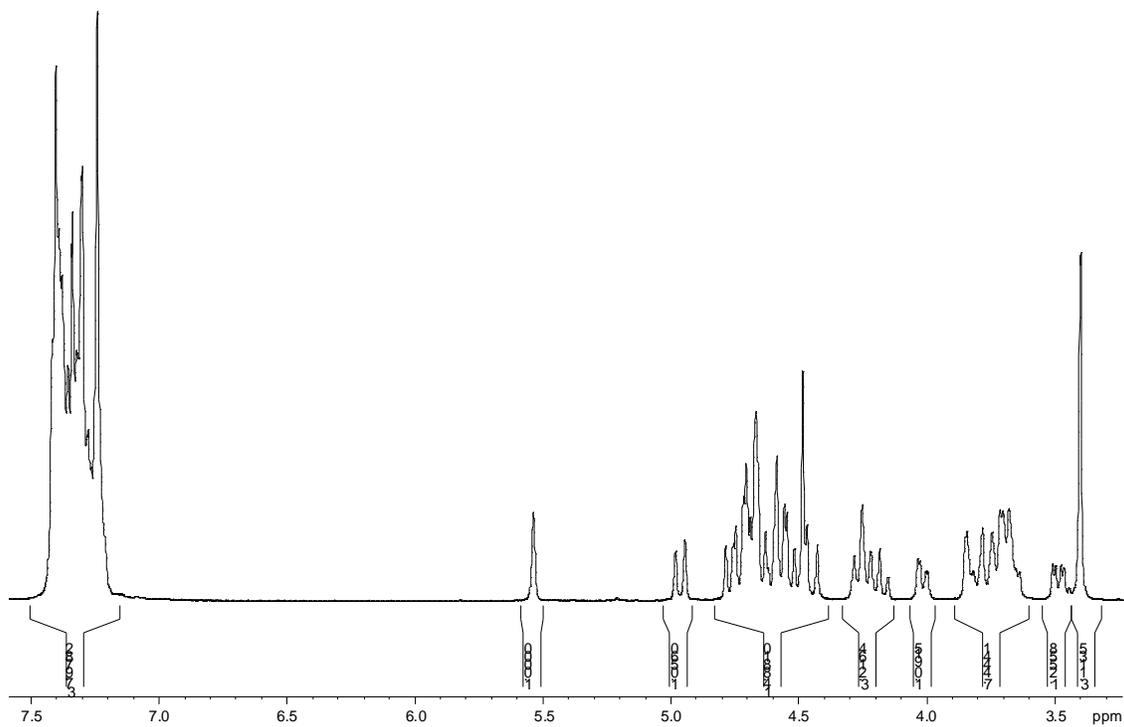
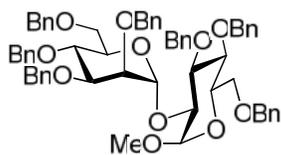
( $^{13}\text{C}$  NMR 75 MHz,  $\text{CDCl}_3$ )

**Methyl 2,4,6-tri-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl- $\beta$ -D-mannopyranosyl)- $\beta$ -D-glucopyranoside (25).**

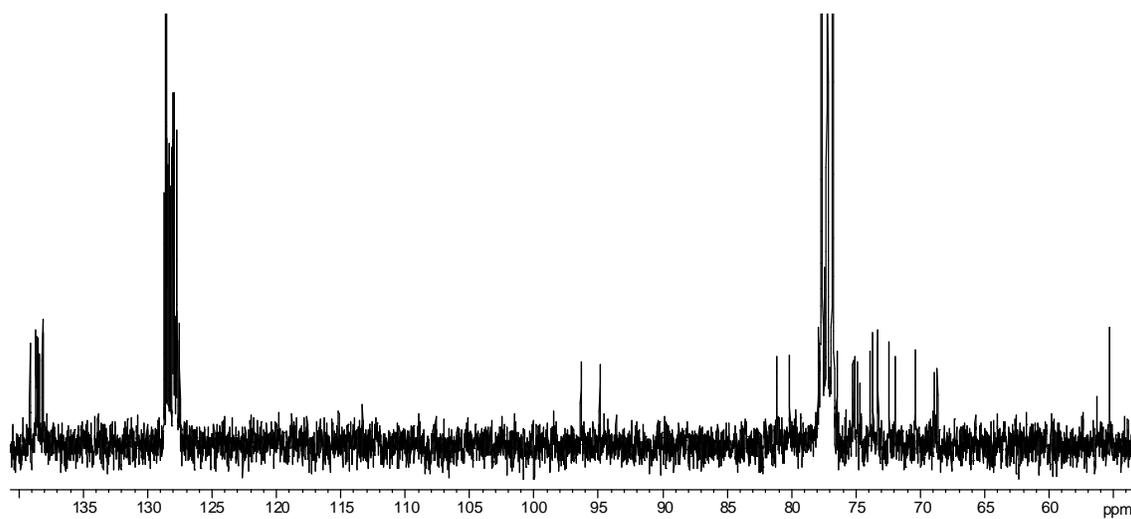


(2D NMR 300 MHz,  $\text{CDCl}_3$ )

**Methyl 3,4,6-tri-O-benzyl-2-O-(2,3,4,6-tetra-O-benzyl- $\beta$ -D-mannopyranosyl)- $\beta$ -D-glucopyranoside (26)**

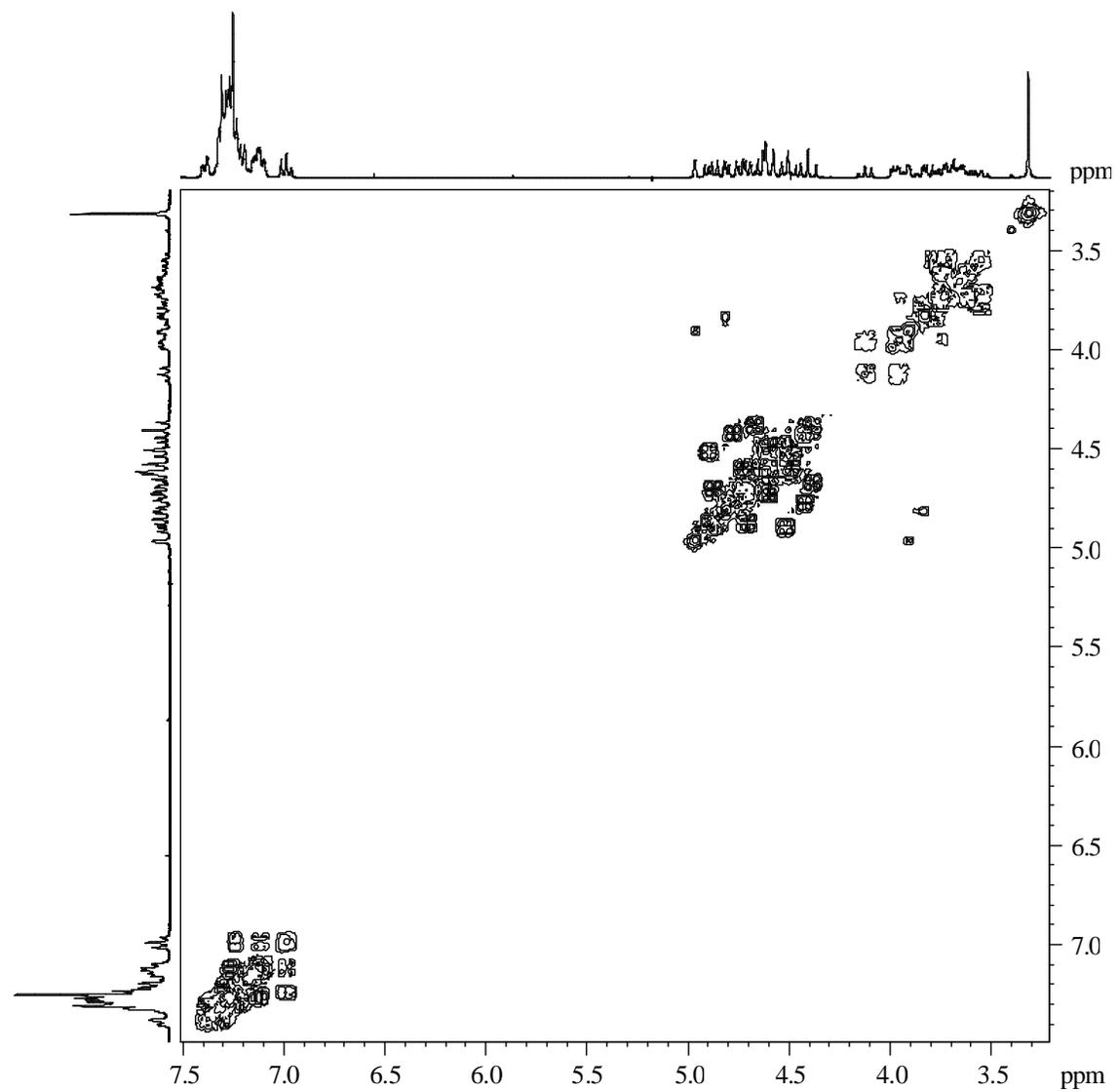
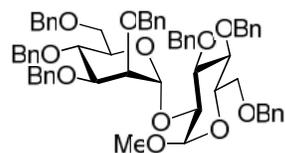


**( $^1\text{H}$  NMR 300 MHz,  $\text{CDCl}_3$ )**



**( $^{13}\text{C}$  NMR 75 MHz,  $\text{CDCl}_3$ )**

**Methyl 3,4,6-tri-O-benzyl-2-O-(2,3,4,6-tetra-O-benzyl- $\beta$ -D-mannopyranosyl)- $\beta$ -D-glucopyranoside (26)**



(2D NMR 300 MHz,  $\text{CDCl}_3$ )

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