

## **Supporting Information**

### **A Diastereoselective Ni-Catalyzed Negishi Cross-Coupling Approach to Saturated, Fully Oxygenated C-Alkyl and C-Aryl Glycosides**

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### **Table of Contents**

I.	Experimental Section .....	S-2-S-15
II.	Spectral Data for New Compounds.....	S-16-S-44

## Experimental Section

**General.** All reagents were reagent grade quality and used as received from Aldrich unless otherwise indicated. All reactions were carried out under an atmosphere of argon or nitrogen unless otherwise indicated. Anhydrous THF was distilled from sodium/ benzophenone ketyl prior to use. All other solvents were technical grade unless noted. Anhydrous *N,N*-dimethylacetamide (DMA), anhydrous *N,N*-dimethylimidazolidinone (DMI; Fluka), anhydrous DMF (Acros), NiCl<sub>2</sub>·glyme, Ni(COD)<sub>2</sub> (Strem), terpyridine, and 4, 4', 4''-tri-*tert*-butyl-2,2',6,2''-terpyridine ('Bu-terpy) were used as received. The unsubstituted Py-Box was prepared according to a literature procedure. EtO-Terpy and Pyrrolidine-Terpy were prepared according to literature procedures. Acetobromo- $\alpha$ -D-glucose (1% CaCO<sub>3</sub>) and acetobromo- $\alpha$ -D-galactose (1% CaCO<sub>3</sub>) were purified by passing through a silica column prior to use. Acetobromo- $\alpha$ -D-mannose, benzylchloro- $\alpha$ -D-glucose, benzylchloro- $\alpha$ -D-mannose were prepared according to reported procedures. 2,3,4,6-tetra-O-benzyl-D-mannopyranose was purchased from TRC Biomedical Research Chemicals. 2,3,5-Tri-O-benzyl- $\alpha$ -D-arabinofuranosyl bromide (Fluka), tri-O-acetyl- $\beta$ -D-arabinosyl bromide and  $\alpha$ -D-glucopyranosyl bromide tetrabenzoate were used as received. 2-Deoxy-triacetyl D-arabino-Hexopyranosyl chloride was prepared according to the literature procedures. 2,3,5-Tri-O-acetyl-D-ribofuranosyl chloride was prepared from  $\beta$ -D-ribofuranose 1,2,3,5-tetraacetate (Alfa Aesar). 3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-D-glucopyranosyl bromide was prepared from D-(+)-glucosamine hydrochloride (sigma) according to the reported procedures. Aryl iodides and bromides were used as received, or prepared according to the known procedures ((*E*)-2-iodovinylbenzene, 2-(5-Iodofuran-2-yl)-[1,3]dioxolane, 5-Iodo-2,3-dimethoxybenzoic acid methyl ester). Arylzinc reagents in DMI, DMA and DMF were prepared based on a literature procedure. Column chromatography was performed using Merck silica gel 60 as the solid support. All NMR spectra were recorded on Bruker Avance 400 MHz or 300 MHz spectrometer at STP unless otherwise indicated. Deuterated solvents were used as received from Cambridge

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  - 2) (a) Johansson, O. *Synthesis* **2006**, *15*, 2585-2589. (b) Lowe, G.; Droz, A. S.; Vilaivan, T.; Weaver, G. W.; Tweedale, L.; Pratt, J. M.; Rock, P.; Yardley, V.; Croft, S. L. *J. Med. Chem.* **1999**, *42*, 999-1006.
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  - 11) (a) Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 6040-6044. (b) Ho, S. *Org. Lett.* **2003**, *4*, 423-425.

Isotope Laboratories, Inc.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts are reported in  $\delta$  units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were set at 7.24 ppm and 77.0 ppm, respectively; For methanol the reference peaks in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were set at 3.30 ppm and 49.0 ppm, respectively; For dichloromethane, the reference peaks in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were set at 5.33 ppm and 53.5 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker Biotof-II instrument. Melting point was recorded on Uni-melt (Thoms Hoover) capillary melting point apparatus.

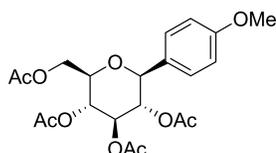
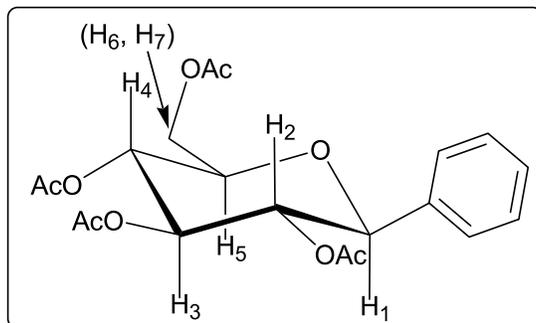
*Preparation of aryl zinc reagents:* To a flame-dried Schlenk flask equipped with a magnetic stir bar was added Zn (0.98 g, 150 mol%, 15.0 mmol) and LiCl (0.42 g, 100 mol%, 10 mmol) in a glove box. After the flask was moved out of the glove box, it was heated at 70 °C for 30 min in vacuo. A solution of  $\text{I}_2$  (0.13 g, 5 mol%, 0.5 mmol) in DMF was then added to the flask via syringe, followed by the addition of aryl halides (for the liquid aryl halides, addition was carried out through a syringe; for the solid aryl halides, addition was performed under argon atmosphere). The resultant mixture was allowed to stir for 12 h at 70 °C. For 4-methoxyphenylzinc iodide, 1,2-dibromoethane and  $\text{Me}_3\text{SiCl}$  were used to activate the Zn powder.<sup>11a</sup> The concentration of organozinc reagents were determined to be ~0.5 M by titration with  $\text{I}_2$ .

*General Procedure for Negishi Coupling.* To a flame-dried Schlenk tube equipped with a stir bar was loaded  $t\text{Bu-Terpy}$  (0.015 g, 0.037 mmol, 15 mol%). The tube was moved to a dry glove box, at which point  $\text{Ni}(\text{COD})_2$  (0.007 g, 0.024 mmol, 10 mol%) was added. After the tube was moved out of the glove box, DMF (0.5 mL) was then added through a syringe. The mixture was allowed to stir for 15 min, and a typical dark blue solution formed along with trace of  $t\text{Bu-Terpy}$  suspension. Under argon atmosphere, acetobromo- $\alpha$ -D-glucose (100.0 mg, 0.243 mmol, 100 mol%) was added in one portion followed by the addition of corresponding organozinc reagent (~0.5 M in DMF, 0.75 mL, 150 mol%) *via* syringe. After the resulting mixture was stirred for 12 h at 25 °C, it was directly loaded onto a silica column without work-up (the residue was rinsed with small amount of DCM). Flash column chromatography provided the product as white solids or colorless oil after removal of solvents. Recrystallization in diethyl ether was performed to obtain the pure  $\beta$ -anomer for NMR spectroscopy studies.

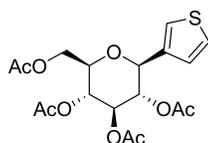
*Proton labeling:* For the purpose of spectral assignment, the proton labeling outlined in the following box was used throughout the text (including mannosides).

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(12) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890-891.

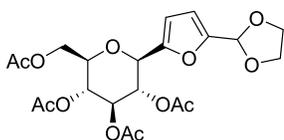


(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 4,5-diacetoxy-2-acetoxymethyl-6-(4-methoxy-phenyl)-tetrahydro-pyran-3-yl ester. This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 4-methoxyphenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (10:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (60 mg, 0.14 mmol, 58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.30 (t, *J* = 9.6 Hz, 1H; *H*3), 5.20 (t, *J* = 9.6 Hz, 1H; *H*4), 5.12 (t, *J* = 9.6 Hz, 1H; *H*2), 4.33 (d, *J* = 10.0 Hz, 1H; *H*1), 4.25 (dd, *J* = 12.4 and 4.8 Hz, 1H; *H*6), 4.12 (dd, *J* = 12.4 and 2.0 Hz, 1H; *H*7), 3.80 (ddd, *J* = 10.0, 4.8 and 2.0 Hz, 1H; *H*5), 3.77 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.78 (s, 3H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  170.7, 170.4, 169.5, 168.9, 160.0, 128.5, 128.3, 80.0, 76.1, 74.4, 72.6, 68.7, 62.4, 55.2, 20.7, 20.6, 20.4. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> found 461.141, calcd 461.142 for C<sub>21</sub>H<sub>26</sub>O<sub>10</sub>Na. MP = 103-105 °C.

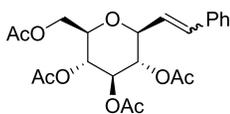


(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 4,5-diacetoxy-6-acetoxymethyl-2-thiophen-3-yl-tetrahydro-pyran-3-yl ester. This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 3-thiophenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (16:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (83.6 mg, 0.202 mmol, 83% yield). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.27 (m, 2H), 7.06 (d,  $J$  = 3.6 Hz, 1H), 5.28 (t,  $J$  = 9.2 Hz, 1H; *H3*), 5.19 (t,  $J$  = 9.2 Hz, 1H; *H4*), 5.14 (t,  $J$  = 9.2 Hz, 1H; *H2*), 4.52 (d,  $J$  = 9.6 Hz, 1H; *H1*), 4.25 (dd,  $J$  = 12.4 and 4.8 Hz, 1H; *H6*), 4.13 (dd,  $J$  = 12.4 and 1.6 Hz; *H7*), 3.80 (ddd,  $J$  = 9.2, 4.4 and 2.0 Hz, 1H; *H5*), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.84 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.8, 170.4, 169.5, 169.0, 137.2, 126.4, 126.0, 123.7, 76.2, 76.1, 74.2, 72.2, 68.5, 62.3, 20.8, 20.7, 20.67, 20.5. HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> found 437.086, calcd 437.088 for C<sub>18</sub>H<sub>22</sub>O<sub>9</sub>Na. MP = 147-149 °C.



**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 3,4,5-triacetoxy-6-(5-[1,3]dioxolan-2-yl-furan-2-yl)-tetrahydro-pyran-2-ylmethyl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and [1,3]Dioxolan-2-furanylzinc iodide/LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (>10:1  $\beta$  to  $\alpha$  anomers based on NMR) as syrup (91.4 mg, 0.19 mmol, 80% yield). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  6.42 (d,  $J$  = 2.0 Hz, 2H), 5.88 (s, 1H), 5.39 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.32 (t,  $J$  = 9.6 Hz, 1H; *H4*), 5.18 (t,  $J$  = 9.6 Hz, 1H; *H2*), 4.58 (d,  $J$  = 10.0 Hz, 1H; *H1*), 4.27 (dd,  $J$  = 12.4 and 4.8 Hz, 1H; *H6*), 4.07-4.20 (m, 3H), 4.07-4.00 (m, 2H), 3.88 (ddd,  $J$  = 10.0, 4.8 and 2.0 Hz, 1H; *H5*), 2.09 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.90 (s, 3H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  170.5, 170.0, 169.4, 169.0, 152.2, 149.7, 110.0, 109.3, 97.38, 75.9, 74.0, 73.2, 69.7, 68.2, 65.2, 65.1, 62.2, 20.5, 20.4, 20.2. HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> found 493.131, calcd 493.132 for C<sub>21</sub>H<sub>26</sub>O<sub>12</sub>Na. MP = 82-84 °C.

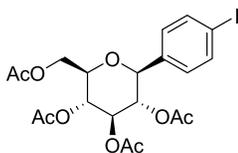


**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 3,5-diacetoxy-2-acetoxymethyl-6-*E*-styryl-tetrahydro-pyran-4-yl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and *E*-phenyl-2-vinylzinc iodide/LiCl (0.75 mL, ~0.5 M, 150 mmol, 300 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (~1:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (63.3 mg, 0.146 mmol, 60% yield).

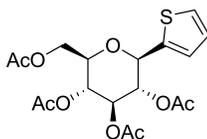
*Characterization data for the  $\alpha$ -anomer:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.20-7.40 (m, 5H), 6.76 (d,  $J$  = 16.0 Hz, 1H), 6.36 (dd,  $J$  = 16.0 and 6.0 Hz, 1H), 5.38 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.13 (dd,  $J$  = 10.0

and 6.0 Hz, 1H; *H2*), 5.07 (t, *J* = 9.6 Hz, 1H; *H4*), 4.90 (t, *J* = 5.6 Hz, 1H; *H1*), 4.23 (dd, *J* = 12.0 and 4.4 Hz, 1H; *H6*), 4.10 (dd, *J* = 12.0 and 1.6 Hz, 1H; *H7*), 4.03 (ddd, *J* = 10.0, 4.8 and 2.0 Hz, 1H; *H5*), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.7, 170.2, 169.8, 169.6, 137.1, 135.8, 128.7, 128.6, 126.7, 120.6, 73.13, 70.8, 70.5, 69.3, 69.0, 62.3, 20.8, 20.7, 20.6. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> found 457.147, calcd 457.147 for C<sub>22</sub>H<sub>26</sub>O<sub>9</sub>Na. MP = 132-135 °C.

*Characterization data for the β-anomer:* Residual α-anomer is present in this partially purified product. Additional purification was not possible. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.15-7.45 (m, 5H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.36 (dd, *J* = 16.0 and 8.0 Hz, 1H), 5.26 (t, *J* = 9.6 Hz, 1H; *H3*), 5.11 (t, *J* = 9.6 Hz, 1H; *H4*), 5.01 (t, *J* = 9.6 Hz, 1H; *H2*), 4.26 (dd, *J* = 12.4 and 4.4 Hz, 1H; *H6*), 4.12 (dd, *J* = 12.4 and 2.0 Hz, 1H; *H7*), 4.01 (dd, *J* = 9.2 and 8.0 Hz, 1H; *H1*), 3.74 (ddd, *J* = 10.0, 4.8 and 2.0 Hz, 1H; *H5*), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.8, 170.4, 169.5, 135.6, 135.3, 128.6, 128.4, 126.8, 124.0, 79.8, 74.1, 75.7, 73.8, 73.1, 71.4, 70.8, 69.4, 69.0, 68.5, 62.3, 20.8, 20.7, 20.6. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> found 457.147, calcd 457.147 for C<sub>22</sub>H<sub>26</sub>O<sub>9</sub>Na.

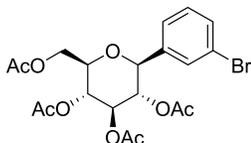


**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 4,5-diacetoxy-2-acetoxymethyl-6-(4-iodo-phenyl)-tetrahydro-pyran-3-yl ester.** This compound was prepared according to the General Procedure using acetobromo-α-D-glucose (100 mg, 0.24 mmol, 100 mol%) and 4-iodophenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (14:1 β to α anomers based on NMR) as a white solid (39.0 mg, 0.073 mmol, 30% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 5.29 (t, *J* = 9.6 Hz, 1H; *H3*), 5.19 (t, *J* = 9.6 Hz, 1H; *H4*), 5.06 (t, *J* = 9.6 Hz, 1H; *H2*), 4.32 (d, *J* = 9.6 Hz, 1H; *H1*), 4.25 (dd, *J* = 12.4 and 4.4 Hz, 1H; *H6*), 4.12 (dd, *J* = 12.4 and 1.6 Hz, 1H; *H7*), 3.80 (ddd, *J* = 9.6, 4.4 and 2.0 Hz, 1H; *H5*), 2.06 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.81 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.7, 170.4, 169.5, 168.8, 137.6, 135.9, 128.0, 94.8, 79.6, 74.1, 72.4, 68.4, 62.2, 20.8, 20.64, 20.63, 20.4. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> found 557.031, calcd 557.028 for C<sub>20</sub>H<sub>23</sub>IO<sub>9</sub>Na. MP = 135-138 °C.

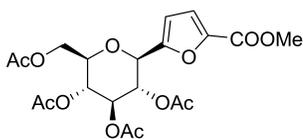


**(2*R*, 3*R*, 4*S*, 5*R*, 6*R*)- Acetic acid 3,4,5-triacetoxy-6-thiophen-2-yl-tetrahydro-pyran-2-ylmethyl ester.** This compound was prepared according to the General Procedure using acetobromo-α-D-glucose (100 mg, 0.24 mmol, 100 mol%) and 2-thiophenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (16:1 β to α anomers based on NMR) as a white solid (78.6 mg, 0.190 mmol, 78% yield). <sup>1</sup>H

NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.28 (dd,  $J = 5.1, 0.9$  Hz, 1H), 7.03 (d,  $J = 3.0$  Hz, 1H), 6.94 (dd,  $J = 5.1$  and 3.6 Hz, 1H), 5.29 (t,  $J = 9.3$  Hz, 1H; *H3*), 5.20 (t,  $J = 9.3$  Hz, 1H; *H4*), 5.16 (t,  $J = 9.3$  Hz, 1H; *H2*), 4.90 (d,  $J = 9.6$  Hz, 1H; *H1*), 4.25 (dd,  $J = 12.3$  and 4.5 Hz, 1H; *H6*), 4.15 (dd,  $J = 12.3$  and 2.4 Hz; *H7*), 3.82 (ddd,  $J = 9.6, 4.8$  and 2.4 Hz, 1H; *H5*), 2.07 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.8, 170.4, 169.5, 169.0, 138.6, 126.6, 126.3, 126.2, 76.2, 76.0, 74.2, 72.8, 68.4, 62.2, 20.8, 20.69, 20.66, 20.5. HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> found 437.089, calcd 437.088 for C<sub>18</sub>H<sub>22</sub>O<sub>9</sub>SNa. MP = 122-124 °C.

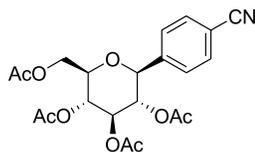


**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 3,4,5-triacetoxy-6-(3-bromo-phenyl)-tetrahydro-pyran-2-ylmethyl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 3-bromophenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (14:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (91.2 mg, 0.187 mmol, 77% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.46 (s, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.19 (t,  $J = 7.6$  Hz, 1H), 5.30 (t,  $J = 9.6$  Hz, 1H; *H3*), 5.19 (t,  $J = 9.6$  Hz, 1H; *H4*), 5.04 (t,  $J = 9.6$  Hz, 1H; *H2*), 4.33 (d,  $J = 9.6$  Hz, 1H; *H1*), 4.25 (dd,  $J = 12.4$  and 4.4 Hz, 1H; *H6*), 4.13 (d,  $J = 12.4$  and 2.0 Hz, 1H; *H7*), 3.80 (ddd,  $J = 10.0, 4.8$  and 2.0 Hz, 1H; *H5*), 2.06 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.6, 170.2, 169.4, 168.7, 138.6, 131.9, 130.2, 130.0, 125.4, 122.3, 79.3, 77.0, 74.0, 72.6, 68.5, 62.2, 20.7, 20.6, 20.3. HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> found 509.047, calcd 509.042 for C<sub>20</sub>H<sub>23</sub>BrO<sub>9</sub>SNa. MP = 132-133 °C.

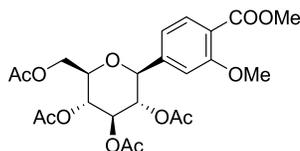


**(2*R*, 3*R*, 4*S*, 5*R*, 6*R*)-5-(3,4,5-Triacetoxy-6-acetoxymethyl-tetrahydro-pyran-2-yl)-furan-2-carboxylic acid methyl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 5-methoxycarbonylfuranylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (14:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (72 mg, 0.16 mmol, 65% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.08 (d,  $J = 3.6$  Hz, 1H), 6.49 (d,  $J = 3.6$  Hz, 1H), 5.34 (t,  $J = 9.6$  Hz, 1H; *H3*), 5.27 ( $J = 9.6$  Hz, 1H; *H4*), 5.14 (t,  $J = 9.6$  Hz, 1H; *H2*), 4.56 (d,  $J = 9.6$  Hz, 1H; *H1*), 4.23 (dd,  $J = 12.4$  and 4.8 Hz, 1H; *H6*), 4.10 (dd,  $J = 12.4$  and 2.0 Hz, 1H; *H7*), 3.85 (s, 3H), 3.79 (ddd,  $J = 10.0, 4.8$  and 2.0 Hz, 1H; *H5*), 2.05 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.91 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.6, 170.2, 169.3, 169.2, 158.7, 153.5, 144.8, 118.5, 110.6, 76.2, 74.0, 73.2, 70.0,

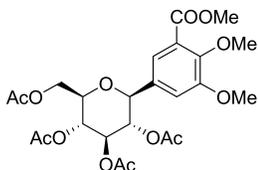
68.2, 62.0, 51.9, 20.7, 20.6, 20.4. HRMS (ESI):  $m/z$   $[M+Na]^+$  found 479.113, calcd 479.117 for  $C_{20}H_{24}O_{12}Na$ . MP = 136-140 °C.



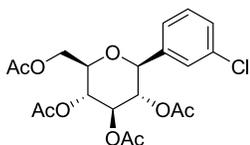
**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-Acetic acid 4,5-diacetoxy-2-acetoxymethyl-6-(4-cyano-phenyl)-tetrahydro-pyran-3-yl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 4-cyanophenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (>12:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (83.2 mg, 0.192 mmol, 79% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d,  $J$  = 8.4 Hz, 2H), 7.40 (d,  $J$  = 8.4 Hz, 1H), 5.31 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.19 ( $J$  = 9.6 Hz, 1H; *H4*), 5.02 (t,  $J$  = 9.6 Hz, 1H; *H2*), 4.43 (d,  $J$  = 9.6 Hz, 1H; *H1*), 4.27 (dd,  $J$  = 12.3 and 4.8 Hz, 1H; *H6*), 4.13 (dd,  $J$  = 12.3 and 2.1 Hz, 1H; *H7*), 3.82 (ddd,  $J$  = 9.9, 4.8 and 2.1 Hz, 1H; *H5*), 2.06 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.81 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.7, 170.3, 169.5, 168.7, 141.5, 132.3, 127.8, 118.4, 112.8, 79.2, 76.3, 73.9, 72.4, 68.3, 62.2, 20.8, 20.6, 20.4. HRMS (ESI):  $m/z$   $[M+Na]^+$  found 456.124, calcd 456.127 for  $C_{21}H_{23}NO_9Na$ . MP = 144-146 °C.



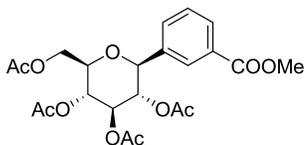
**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)- 2-Methoxy-4-(3,4,5-triacetoxy-6-acetoxymethyl-tetrahydro-pyran-2-yl)-benzoic acid methyl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 3-methoxy-4-methoxycarbonylphenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (13:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (98.9 mg, 0.199 mmol, 82% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d,  $J$  = 8.0 Hz, 1H), 6.95 (s, 1H), 6.91 (d,  $J$  = 8.0 Hz, 1H), 5.30 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.21 ( $J$  = 9.6 Hz, 1H; *H4*), 5.11 (t,  $J$  = 9.6 Hz, 1H; *H2*), 4.40 (d,  $J$  = 10.0 Hz, 1H; *H1*), 4.27 (dd,  $J$  = 12.4 and 4.8 Hz, 1H; *H6*), 4.15 (dd,  $J$  = 12.4 and 1.6 Hz, 1H; *H7*), 3.89 (s, 3H), 3.85 (s, 3H), 3.82 (ddd,  $J$  = 10.0, 4.8 and 2.0 Hz, 1H; *H5*), 2.06 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.81 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.5, 170.2, 169.4, 168.6, 166.1, 159.1, 141.9, 131.6, 120.4, 119.0, 79.6, 76.2, 74.1, 72.3, 68.5, 62.2, 56.0, 51.9, 20.6, 20.5, 20.3. HRMS (ESI):  $m/z$   $[M+Na]^+$  found 519.148, calcd 519.148 for  $C_{23}H_{28}O_{12}Na$ . MP = 135-138 °C.



**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)- 2,3-Dimethoxy-5-(3,4,5-triacetoxy-6-acetoxymethyl-tetrahydro-pyran-2-yl)-benzoic acid methyl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 4,5-dimethoxy-3-methoxycarbonylphenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 25% ethyl acetate in hexanes) gave a mixture of diastereomers (13:1  $\beta$  to  $\alpha$  anomers based on NMR) as a colorless oil (88.3 mg, 0.168 mmol, 69% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.24 (s, 1H), 7.05 (d,  $J$  = 1.2 Hz, 1H), 5.29 (t,  $J$  = 9.6 Hz, 1H; *H*3), 5.20 ( $J$  = 9.6 Hz, 1H; *H*4), 5.12 (t,  $J$  = 9.6 Hz, 1H; *H*5), 4.35 (d,  $J$  = 10.0 Hz, 1H; *H*1), 4.25 (dd,  $J$  = 12.4 and 4.8 Hz, 1H; *H*6), 4.14 (dd,  $J$  = 12.4 and 1.6 Hz, 1H; *H*7), 3.87 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.81 (ddd,  $J$  = 9.6, 4.8 and 2.0 Hz, 1H; *H*5), 2.05 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.82 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.6, 170.2, 169.5, 168.9, 166.2, 153.8, 149.7, 131.8, 125.5, 121.7, 114.0, 79.6, 77.2, 76.3, 74.2, 72.3, 68.7, 62.4, 61.5, 56.2, 52.2, 20.7, 20.6, 20.4. HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> found 549.154, calcd 549.158 for C<sub>24</sub>H<sub>30</sub>O<sub>13</sub>Na.

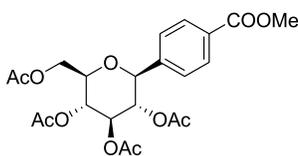


**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)- Acetic acid 4,5-diacetoxy-2-acetoxymethyl-6-(3-chloro-phenyl)-tetrahydro-pyran-3-yl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (100 mg, 0.24 mmol, 100 mol%) and 3-chlorophenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (13:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (80.7 mg, 0.182 mmol, 75% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.33 (s, 1H), 7.20-7.30 (m, 3H), 5.33 (t,  $J$  = 9.3 Hz, 1H; *H*3), 5.22 (t,  $J$  = 9.6 Hz, 1H; *H*4), 5.07 (t,  $J$  = 9.6 Hz, 1H; *H*2), 4.38 (d,  $J$  = 9.9 Hz, 1H; *H*1), 4.29 (dd,  $J$  = 12.3 and 4.8 Hz, 1H; *H*6), 4.16 (dd,  $J$  = 12.3 and 2.1 Hz; *H*7), 3.83 (ddd,  $J$  = 9.9, 4.8 and 2.1 Hz, 1H; *H*5), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.8, 170.4, 169.5, 168.9, 138.3, 134.3, 129.8, 129.1, 127.4, 125.1, 79.4, 76.2, 74.1, 72.6, 68.4, 62.3, 20.8, 20.7, 20.4. HRMS (ESI):  $m/z$  [M+Na]<sup>+</sup> found 465.091, calcd 465.093 for C<sub>20</sub>H<sub>23</sub>ClO<sub>9</sub>Na. MP = 142-145 °C.

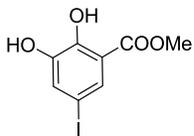


**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)- 3-(3,4,5-Triacetoxy-6-acetoxymethyl-tetrahydro-pyran-2-yl)-benzoic acid methyl ester.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -

D-glucose (100 mg, 0.24 mmol, 100 mol%) and 3-methoxycarbonylphenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (14:1 β to α anomers based on NMR) as a white solid (81.6 mg, 0.175 mmol, 72% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 5.33 (t, *J* = 9.6 Hz, 1H; *H3*), 5.22 (t, *J* = 9.6 Hz, 1H; *H4*), 5.09 (t, *J* = 9.6 Hz, 1H; *H2*), 4.44 (d, *J* = 9.6 Hz, 1H; *H1*), 4.27 (dd, *J* = 12.8 and 4.8 Hz, 1H; *H6*), 4.16 (dd, *J* = 12.8 and 2.4 Hz, 1H; *H7*), 3.89 (s, 3H), 3.83 (ddd, *J* = 10.0, 4.8 and 2.4 Hz, 1H; *H5*), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.79 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.7, 170.3, 169.5, 168.8, 166.6, 136.9, 131.3, 130.3, 130.0, 128.7, 128.5, 79.7, 76.3, 74.1, 72.7, 68.6, 62.3, 52.2, 20.7, 20.6, 20.3. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> found 489.136, calcd 489.137 for C<sub>22</sub>H<sub>26</sub>O<sub>11</sub>Na. MP = 134-135 °C.

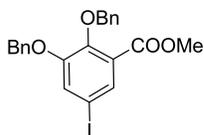


**(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)- 4-(3,4,5-Triacetoxy-6-acetoxymethyl-tetrahydro-pyran-2-yl)-benzoic acid methyl ester.** This compound was prepared according to the General Procedure using acetobromo-α-D-glucose (100 mg, 0.24 mmol, 100 mol%) and 4-methoxycarbonylphenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (10:1 β to α anomers based on NMR) as a white solid (74.8 mg, 0.160 mmol, 66% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.32 (t, *J* = 9.6 Hz, 1H; *H3*), 5.21 (t, *J* = 9.6 Hz, 1H; *H4*), 5.07 (t, *J* = 9.6 Hz, 1H; *H2*), 4.43 (d, *J* = 10.0 Hz, 1H; *H1*), 4.28 (dd, *J* = 12.4 and 4.8 Hz, 1H; *H1*), 4.15 (dd, *J* = 12.4 and 2.4 Hz, 1H; *H7*), 3.88 (s, 3H), 3.83 (ddd, *J* = 10.0, 4.8 and 2.4 Hz, 1H; *H5*), 2.07 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.79 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.6, 170.3, 169.4, 168.7, 166.6, 141.2, 130.7, 129.7, 127.1, 79.7, 76.3, 74.1, 72.6, 68.6, 62.3, 52.1, 20.7, 20.6, 20.3. HRMS (ESI): *m/z* [M+Na]<sup>+</sup> found 489.136, calcd 489.137 for C<sub>22</sub>H<sub>26</sub>O<sub>11</sub>Na. MP = 126-128 °C.

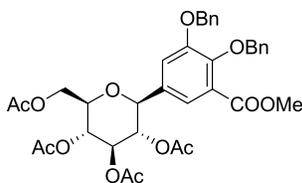


**2,3-Dihydroxy-5-iodo-benzoic acid methyl ester 3.** To an oven-dried round bottom flask charged with 2,2-dihydroxybenzoic acid methyl ester (1.1 g, 100 mol%, 3.6 mmol) was added BBr<sub>3</sub> solution in DCM (1M, 200 mol%, 7.2 mL) at -78 °C under argon. The reaction was allowed to stir for 30 min, and was warmed to rt for additional 20 min. The reaction mixture was quenched with ice water (30 mL), and extracted with DCM two times (2×20 mL). The combined organic layer was dried (MgSO<sub>4</sub>) and filtered. The crude material was dried onto silica gel under reduced pressure. Flash column chromatography (SiO<sub>2</sub>: 3% ethyl acetate in hexanes) gave the title compound as a white solid (0.70 g, 2.38 mmol, 67% yield). <sup>1</sup>H

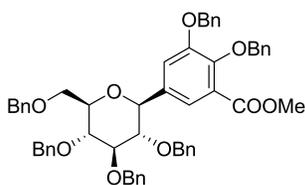
NMR (400 MHz, CDCl<sub>3</sub>): 10.72 (s, 1H), 7.54 (s, 1H), 7.53 (s, 1H), 5.49 (s, 1H), 3.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 169.2, 148.5, 145.6, 128.8, 128.0, 113.7, 79.7, 52.5. HRMS (ESI): *m/z* [M+H]<sup>+</sup> found 294.944, calcd 294.947 for C<sub>8</sub>H<sub>8</sub>IO<sub>4</sub>. MP = 133-134 °C.



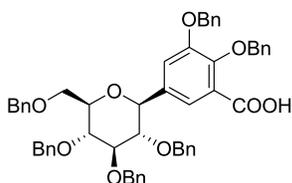
**2,3-Bis-benzyloxy-5-iodo-benzoic acid methyl ester.** To a flask equipped with a magnetic stir bar was loaded K<sub>2</sub>CO<sub>3</sub> (750 mg, 400 mol%, 5.43 mmol) and NaI (12.0 mg, 6 mol%, 0.08 mmol). The mixture was flame-dried for 3 min under vacuum. After the flask was cooled to rt, **3** (385 mg, 100 mol%, 1.31 mmol) was added, followed by the addition of DMF (2.8 mL) and BnBr (0.33 mL, 210 mol%, 2.75 mmol). The reaction mixture was allowed to stir for 12 h at rt, at which point water (30 mL) was added. The mixture was extracted with EtOAc (2×60 mL). The combined organic solution was dried (MgSO<sub>4</sub>), and filtered. The crude material was dried onto silica gel. Flash column chromatography (SiO<sub>2</sub>: 5% ethyl acetate in hexanes) gave the title compound as a white solid (600 mg, 1.27 mmol, 97% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.61 (s, 1H), 7.23-7.36 (m, 11H), 5.04 (s, 2H), 4.99 (s, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.9, 153.4, 148.1, 136.9, 135.7, 131.3, 128.42, 128.4, 128.3, 128.1, 127.8, 127.4, 126.4, 86.1, 75.5, 71.3, 52.1. HRMS (ESI): *m/z* [M+Cs]<sup>+</sup> found 606.940, calcd 606.938 for C<sub>22</sub>H<sub>19</sub>IO<sub>4</sub>Cs. MP = 105-106 °C.



**(2R, 3R, 4S, 5S, 6S)-2,3-bis-benzyloxy-5-(3,4,5-triacetoxy-6-acetoxymethyl-tetrahydropyran-2-yl)-benzoic acid methyl ester 4.** This compound was prepared according to the General Procedure using acetobromo- $\alpha$ -D-glucose (500 mg, 1.22 mmol, 100 mol%) and 1-methoxycarboxy-2,3-dibenzyloxyphenyl zinc iodide-LiCl (3.65 mL, ~0.5 M, 1.83 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (20:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (455 mg, 0.67 mmol, 55% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.19-7.44 (m, 12H), 5.30 (t, *J* = 9.6 Hz, 1H, *H3*), 5.21 (t, *J* = 9.6 Hz, 1H, *H4*), 5.12 (s, 2H), 5.04 (s, 2H), 5.04 (t, *J* = 9.6 Hz, 1H, *H2*), 4.35 (d, 10 Hz, 1H, *H1*), 4.28 (dd, *J* = 12.4 Hz, 4.8 Hz, 1H, *H6*), 4.14 (d, *J* = 12.0 Hz, 1H, *H7*), 3.80 (s, 3H), 3.80-3.90 (m, 1H, *H5*), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.79 (s, 3H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>): 170.7, 170.3, 169.5, 169.0, 166.3, 153.1, 148.6, 137.2, 136.3, 132.1, 128.6, 128.3, 128.2, 128.0, 127.7, 126.3, 122.2, 115.8, 79.5, 76.2, 75.6, 74.1, 72.3, 71.3, 68.6, 62.4, 52.2, 20.8, 20.7, 20.4. HRMS (ESI): *m/z* [M+Cs]<sup>+</sup> found 811.142, calcd 811.137 for C<sub>36</sub>H<sub>38</sub>O<sub>13</sub>Cs. MP = 128-129 °C.

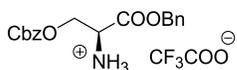


**(2R, 3R, 4S, 5S, 6S)-2,3-Bis-benzyloxy-5-(3,4,5-tris-benzyloxy-6-benzyloxymethyl-tetrahydro-pyran-2-yl)-benzoic acid methyl ester 5.** To an oven-dried round bottom flask equipped with a magnetic bar was added **4** (100 mg, 100 mol%, 0.15 mmol), Na<sub>2</sub>CO<sub>3</sub> (78 mg, 500 mol%, 0.74 mmol) and anhydrous MeOH (4 mL). The reaction was allowed to stir for 3 h at rt. The solid was filtered through a pipette filled with glass whirl, and washed with MeOH (4×5 mL). The mother liquid was collected. After the solvent was removed, it was dried in vacuo. The crude polyol was dissolved in anhydrous DMF (1 mL). The resulting solution was added dropwise at 0 °C to a suspension of NaH (28 mg, 60% in mineral oil, 476 mmol, 0.7 mmol) in DMF (0.5 mL). After 20 min BnBr (0.11 mL, 600 mol%, 0.88 mmol) in DMF (0.5 mL) and Bu<sub>4</sub>NI (5 mg 10 mol%, 0.015 mmol). After the reaction mixture was warmed to rt and stirred for 15 h, it was portioned with water (5 mL) and extracted with EtOAc (10 mL). The aqueous layer was washed two times with EtOAc (2×5 mL). The combined organic layer was dried (MgSO<sub>4</sub>), filtered. The crude material was dried onto silica gel. Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) provided the perbenzylated aryl C-glycosides as benzyl (28.4 mg, 0.03 mmol, 20%) and methyl (69.7 mg, 0.08 mmol, 53%) benzoic acid esters as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55 (d, *J* = 1.2 Hz, 1H), 7.22-7.49 (m, 29H) 7.00 (m, 2H), 5.16 (s, 2H), 5.02 (s, 2H), 4.90-5.03 (m, 3H), 4.60-4.71 (m, 3H), 4.49 (d, *J* = 10.4Hz, 1H), 4.26 (d, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 3.82-3.86 (m, 5H), 3.61-3.66 (m, 1H), 3.46 (t, *J* = 8.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.3, 152.5, 147.9, 138.6, 138.2, 138.0, 137.3, 137.2, 136.4, 135.1, 128.7, 128.5, 128.4, 128.3, 128.26, 128.2, 128.0, 127.9, 127.7, 127.6, 127.57, 127.54, 17.5, 86.6, 83.9, 80.8, 79.2, 78.1, 75.6, 75.55, 75.1, 75.0, 73.3, 70.9, 68.9, 52.0. HRMS (ESI): *m/z* [M+C<sub>s</sub>]<sup>+</sup> found 1003.289, calcd 1003.282 for C<sub>56</sub>H<sub>54</sub>O<sub>9</sub>C<sub>s</sub>. MP = 111-113 °C.

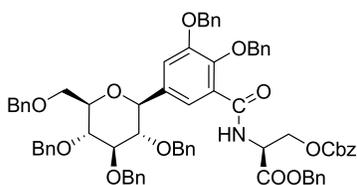


**(2R, 3R, 4S, 5S, 6S)-2,3-Bis-benzyloxy-5-(3,4,5-tris-benzyloxy-6-benzyloxymethyl-tetrahydro-pyran-2-yl)-benzoic acid.** To a solution of **5** (500 mg, 100 mol%, 0.57 mmol) in THF/ MeOH (4 mL, 3:1) was added NaOH solution (1.0 mL, 5.5 M, 1000 mol%, 5.5 mmol). The reaction mixture was stirred at rt for 4 h, at which point HCl (1M, 0.3 mL) was added. The resulting mixture was extracted with DCM (3×10 mL). The combined organic layer was dried (MgSO<sub>4</sub>), and filtered. The crude material was dried onto silica gel. Flash column chromatography (SiO<sub>2</sub>: 40% ethyl acetate in hexanes) gave the acid as white solid (400.0 mg, 4.67 mmol, 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 1H), 6.95-7.43 (m, 29H), 6.95 (s, 2H), 5.26

(s, 2H), 4.99 (s, 2H), 4.95 (d,  $J = 3.3$  Hz, 2H), 4.80-4.90 (m, 1H), 4.56-4.67 (m, 3H), 4.49 (d,  $J = 10.5$  Hz, 1H), 4.25 (d,  $J = 9.0$  Hz, 1H), 3.70-3.86 (m, 5H), 3.51-3.52 (m, 1H), 3.44 (t,  $J = 8.7$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.8, 151.1, 146.9, 138.3, 138.2, 137.6, 136.4, 136.0, 135.0, 129.1, 129.0, 128.6, 128.31, 128.28, 128.1, 128.0, 127.9, 127.7, 127.6, 127.54, 127.50, 126.8, 123.0, 117.9, 86.8, 83.9, 80.7, 79.5, 78.4, 75.7, 75.2, 75.0, 73.5, 71.4, 69.2. HRMS (ESI):  $m/z$   $[\text{M}+\text{Cs}]^+$  found 989.273, calcd 989.267 for  $\text{C}_{55}\text{H}_{52}\text{O}_9\text{Cs}$ . MP = 94-96 °C.

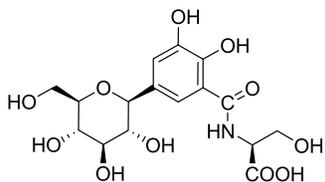


**Ser(Ocbz)Bn trifluoroacid salt.** A solution of Boc-Ser(Ocbz)Bn (g, mmol) in TFA (0.5 mL) was allowed to stir for 30 min at 0 °C, at which point TFA was removed under reduced pressure. The crude mixture was used without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.8 (s, 3H), 7.30-7.43 (m, 4H), 5.12-5.20 (m, 2H), 5.06 (q,  $J = 12$  Hz, 2H), 4.65 (d,  $J = 11.2$  Hz, 1H), 4.55 (dd,  $J = 12$  and 4 Hz, 1H), 4.38 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.4, 154.1, 134.5, 134.0128.9, 128.7, 128.6, 128.56, 128.5, 127.1, 70.6, 69.0, 64.5, 52.6. HRMS (ESI):  $m/z$   $[\text{M}]^+$  found 330.1337, calcd 330.1341 for  $\text{C}_{18}\text{H}_{20}\text{O}_5^+$ .

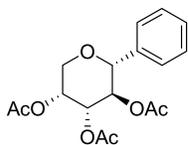


**Perbenzylated C-glucosyl Serine(Cbz)OBn 7.** To a solution of benzoic acid **6** (80 mg, 100 mol %, 0.093 mmol) in anhydrous DCM (2 mL) was added DMF (0.02 mL) and  $\text{SOCl}_2$  (50  $\mu\text{L}$ , 400 mol%, 0.248 mmol). The reaction was stirred for 3 h at rt. After the solvent and excess  $\text{SOCl}_2$  were removed under reduce pressure, the acyl chloride was redissolved in DCM (2 mL). At 0 °C, a solution of *S*-COOBnCH(Ocbz)NH $_2$ -CF $_3$ COOH salt (60 mg, 150 mol%, 0.014 mmol) in DCM (1 mL) was added, followed by Et $_3$ N (19.5  $\mu\text{L}$ , 150 mol%, 0.014 mmol). The reaction mixture was allowed to warm to rt, and stirred for 30 min, at which point it was dried over silica gel. Flash column chromatography ( $\text{SiO}_2$ : 20% EtOAc in hexanes) gave the triamide **7** as foam (95 mg, 0.081 mmol, 88%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ): 8.89 (d,  $J = 7.8$  Hz, 1H), 7.88 (d,  $J = 1.8$  Hz, 1H), 7.26-7.39 (m, 29H), 7.13-7.19 (m, 7H), 7.08 (t,  $J = 7.2$  Hz, 2H), 6.95 (t,  $J = 3.6$  Hz, 2H), 5.17 (t,  $J = 12$  Hz, 1H), 5.14 (dd,  $J = 10.8, 1.2$  Hz, 2H), 5.09 (quint,  $J = 3.6$  Hz, 1H), 5.04 (t,  $J = 12$  Hz, 1H), 5.01 (dd,  $J = 10.8$  and 4.2 Hz, 2H), 4.90-4.96 (m, 4H), 4.86 (d,  $J = 10.8$  Hz, 1H), 4.63 (d,  $J = 4.2$  Hz, 1H), 4.62 (s, 1H), 4.56 (s, 1H), 4.56-4.59 (m, 1H), 4.45 (dd,  $J = 11.4, 4.8$  Hz, 1H), 4.42 (d,  $J = 10.2$  Hz, 1H), 4.23 (d,  $J = 9.0$  Hz, 1H), 3.81 (d,  $J = 9.6$  Hz, 1H), 3.79 (d,  $J = 8.4$  Hz, 1H), 3.76 (d,  $J = 1.8$  Hz, 2H), 3.73 (t,  $J = 3.6$  Hz, 1H), 3.61 (dt,  $J = 9.6$  and 3.6 Hz, 1H), 3.47 (t,  $J = 9.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.9, 164.7, 154.5, 151.5, 146.5, 138.7, 138.3, 138.1, 137.6, 136.1, 135.9, 135.5, 135.1, 134.9, 129.1, 128.6, 128.5, 128.4, 128.3, 128.27, 128.23, 128.21, 128.0, 127.9,

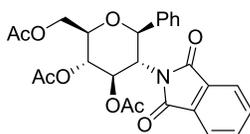
127.7, 127.6, 127.5, 126.1, 122.1, 116.4, 86.7, 83.9, 81.0, 79.3, 78.3, 76.1, 75.6, 75.1, 74.9, 73.4, 71.1, 69.8, 69.1, 67.5, 67.2, 52.2. HRMS (ESI):  $m/z$   $[M+H]^+$  found 1168.479, calcd 1168.485 for  $C_{73}H_{70}NO_{13}$ .



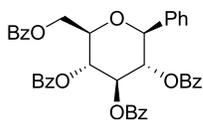
**Salmoachelin SX.** To a flame-dried round bottom flask (10 mL) equipped with a magnetic stir bar was loaded **7** (90 mg, 0.077 mmol) followed by the addition of MeOH/ EtOAc (2 mL, 1:1) and Pd(OH)<sub>2</sub> (30 mg, 20% weight on carbon, wet). The reaction mixture was first purged with argon for 3 min, and then hydrogen for 3 min. After the reaction mixture was stirred for 18 h under hydrogen, it was filtered and washed with dry MeOH (3×5 mL). The organic solution was collected, and the solvent was removed under reduced pressure to give a white solid (29 mg, 0.072 mmol, 93%). <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD): 7.41 (s, 1H), 7.00 (s, 1H), 4.68 (s, 1H), 4.00(d,  $J$  = 9.0 Hz, 2H), 3.92 (dd,  $J$  = 11.4 and 3.6 Hz, 1H), 3.82 (d,  $J$  = 10.8 Hz, 1H), 3.67 (dd,  $J$  = 11.4 and 4.8 Hz, 1H), 3.38-3.44 (m, 2H), 3.30-3.34 (m, 2H), 3.26 (d,  $J$  = 1.2 Hz). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD):  $\delta$  173.4, 170.7, 150.0, 146.8, 131.4, 119.5, 119.0, 116.5, 83.1, 82.0, 79.7, 76.3, 71.7, 62.9, 56.3, 49.9. HRMS (ESI):  $m/z$   $[M+H]^+$  found 404.1188, calcd 404.1193 for  $C_{16}H_{22}NO_{11}$ . MP: 147 °C (decomposed).



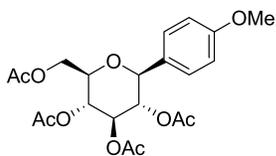
**(2R, 3R, 4R, 5R)-Acetic acid 3,5-diacetoxy-2-phenyl-tetrahydro-pyran-4-yl ester.** This compound was prepared according to the General Procedure using tri-O-acetyl- $\beta$ -D-arabinosylbromide (164.8 mg, 0.48 mmol, 100 mol%) and phenylzinc iodide/ LiCl (1.5 mL, ~0.5 M, 1.46 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (2.6:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (73.3 mg, 0.10 mmol, 45% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.37 (m, 5H), 5.36-5.41 (m, 2H;  $H_2$ ,  $H_4$ ), 5.17 (dd,  $J$  = 10.2 and 3.6 Hz, 1H;  $H_3$ ), 4.25 (d,  $J$  = 9.6 Hz, 1H;  $H_1$ ), 4.12 (dd,  $J$  = 13.2 and 1.8 Hz, 1H;  $H_5$ ), 3.79 (dd,  $J$  = 13.2 and 0.6 Hz, 1H;  $H_6$ ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.5, 170.3, 169.0, 136.8, 128.9, 128.4, 127.3, 81.5, 71.9, 70.2, 69.0, 68.5, 21.1, 20.8, 20.5. HRMS (ESI):  $m/z$   $[M+Na]^+$  found 359.111, calcd 359.111 for  $C_{17}H_{20}O_7Na$ . MP = 98-100 °C.



**(2R, 3S, 4R, 5S, 6S)-Acetic acid 3-acetoxy-2-acetoxymethyl-5-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-6-phenyl-tetrahydro-pyran-4-yl ester.** This compound was prepared according to the General Procedure using triaceto  $\alpha$ -D-ribofuranosyl chloride (72 mg, 0.24 mmol, 100 mol%) and phenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (>20:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (48 mg, 0.10 mmol, 41% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.80 (d,  $J$  = 7.2 Hz, 1H), 7.65 (d,  $J$  = 6.8 Hz, 1H), 7.62 (s, 2H), 7.21-7.29 (m, 5H), 5.92 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.34 (d,  $J$  = 10.4 Hz, 1H; *H1*), 5.31 (t,  $J$  = 9.6 Hz, 1H; *H4*), 4.52 (t,  $J$  = 10.4 Hz, 1H; *H2*), 4.32 (dd,  $J$  = 12.4 and 4.8 Hz, 1H; *H6*), 4.17 (dd,  $J$  = 12.4 and 2.0 Hz, 1H; *H7*), 4.04 (ddd,  $J$  = 10.0, 4.4 and 2.0 Hz, 1H; *H5*), 2.10 (s, 3H), 2.05 (s, 3H), 1.83 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.8, 170.1, 169.6, 169.2, 136.4, 134.3, 134.1, 129.0, 128.6, 127.1, 123.5, 77.8, 76.3, 71.9, 69.3, 62.5, 55.9, 20.8, 20.7, 20.5. HRMS (ESI):  $m/z$  [M+Cs]<sup>+</sup> found 628.064, calcd 628.058 for C<sub>26</sub>H<sub>25</sub>NO<sub>9</sub>Cs. MP = 130-132 °C.

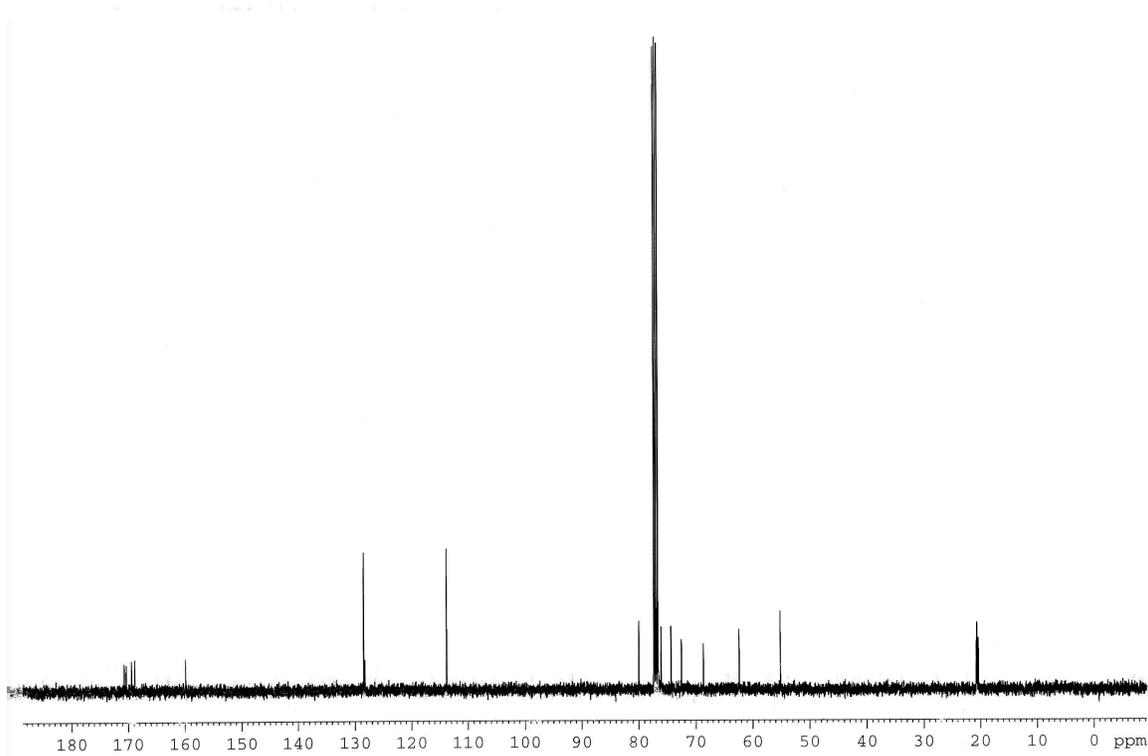
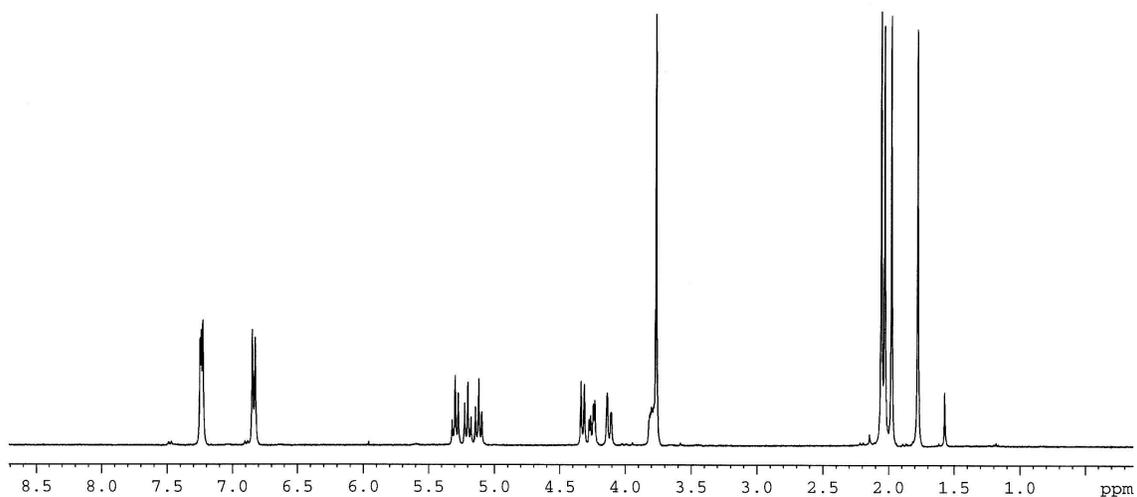


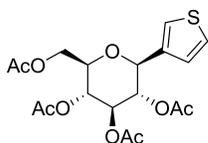
**(2R, 3R, 4R, 5S, 6S)-Benzoic acid 3,4,5-tribenzoyloxy-6-phenyl-tetrahydro-pyran-2-ylmethyl ester.** This compound was prepared according to the General Procedure using 1-bromo-D-glucose precursor (121 mg, 0.24 mmol, 100 mol%) and phenylzinc iodide/ LiCl (0.75 mL, ~0.5 M, 0.73 mmol, 150 mol%). Flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate in hexanes) gave a mixture of diastereomers (10:1  $\beta$  to  $\alpha$  anomers based on NMR) as a white solid (60 mg, 0.14 mmol, 58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.03 (d,  $J$  = 7.6 Hz, 2H), 7.92 (d,  $J$  = 7.6 Hz, 2H), 7.74 (dd,  $J$  = 17.6, 7.6 Hz, 4H), 7.2-7.6 (m, 17H), 6.02 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.84 (t,  $J$  = 9.6 Hz, 1H; *H4*), 5.65 (t,  $J$  = 9.6 Hz, 1H; *H2*), 4.76 (d,  $J$  = 9.6 Hz, 1H; *H1*), 4.68 (dd,  $J$  = 12.0 and 2.4 Hz, 1H; *H6*), 4.52 (dd,  $J$  = 12.0 and 4.8 Hz, 1H; *H7*), 4.29 (ddd,  $J$  = 12.0, 4.8 and 2.0 Hz, 1H; *H5*). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  170.7, 170.4, 169.5, 168.9, 160.0, 128.5, 128.3, 80.0, 76.1, 74.4, 72.6, 68.7, 62.4, 55.2, 20.7, 20.6, 20.4. HRMS (ESI):  $m/z$  [M+Cs]<sup>+</sup> found 789.116, calcd 789.110 for C<sub>40</sub>H<sub>32</sub>O<sub>9</sub>Cs. MP = 180-181 °C.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.30 (t, *J* = 9.6 Hz, 1H; *H*3), 5.20 (t, *J* = 9.6 Hz, 1H; *H*4), 5.12 (t, *J* = 9.6 Hz, 1H; *H*2), 4.33 (d, *J* = 10.0 Hz, 1H; *H*1), 4.25 (dd, *J* = 12.4 and 4.8 Hz, 1H; *H*6), 4.12 (dd, *J* = 12.4 and 2.0 Hz, 1H; *H*7), 3.80 (ddd, *J* = 10.0, 4.8 and 2.0 Hz, 1H; *H*5), 3.77 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.78 (s, 3H).

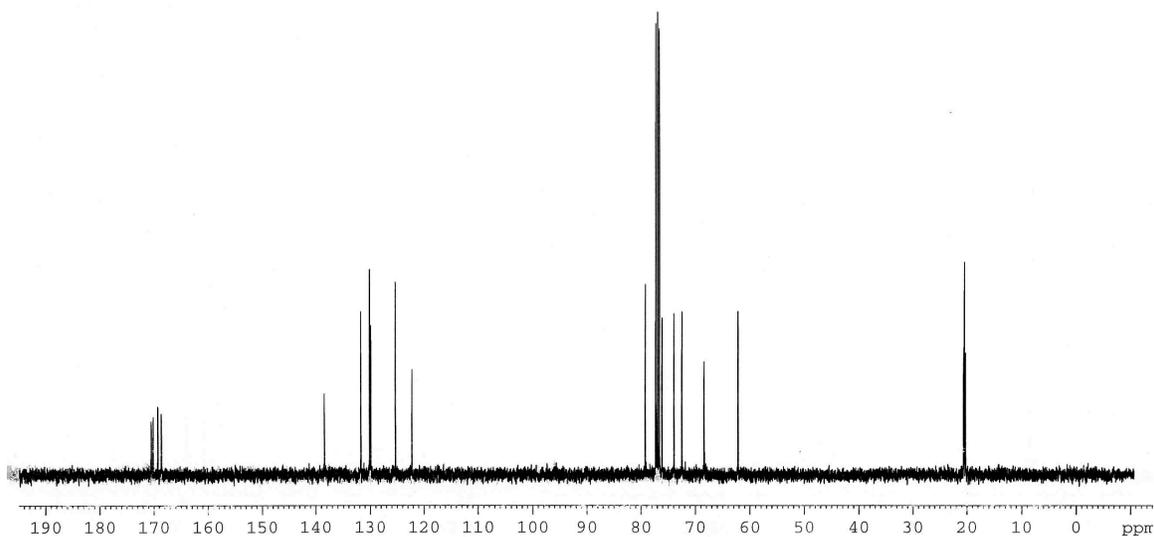
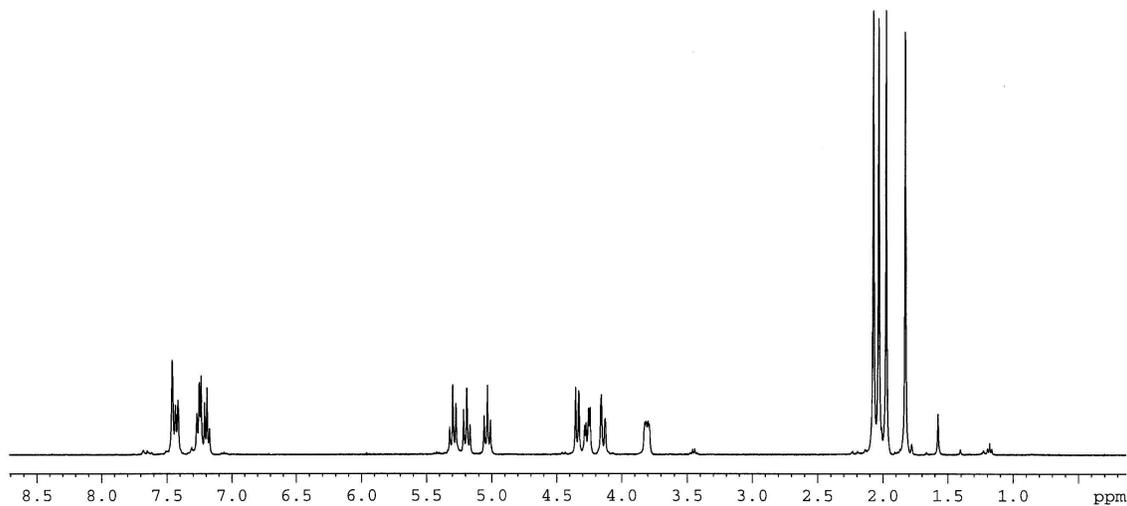
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.7, 170.4, 169.5, 168.9, 160.0, 128.5, 128.3, 80.0, 76.1, 74.4, 72.6, 68.7, 62.4, 55.2, 20.7, 20.6, 20.4.

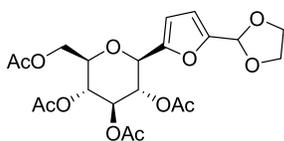




**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.27 (m, 2H), 7.06 (d,  $J = 3.6$  Hz, 1H), 5.28 (t,  $J = 9.2$  Hz, 1H;  $H_3$ ), 5.19 (t,  $J = 9.2$  Hz, 1H;  $H_4$ ), 5.14 (t,  $J = 9.2$  Hz, 1H;  $H_2$ ), 4.52 (d,  $J = 9.6$  Hz, 1H;  $H_1$ ), 4.25 (dd,  $J = 12.4$  and 4.8 Hz, 1H;  $H_6$ ), 4.13 (dd,  $J = 12.4$  and 1.6 Hz;  $H_7$ ), 3.80 (ddd,  $J = 9.2, 4.4$  and 2.0 Hz, 1H;  $H_5$ ), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.84 (s, 3H).

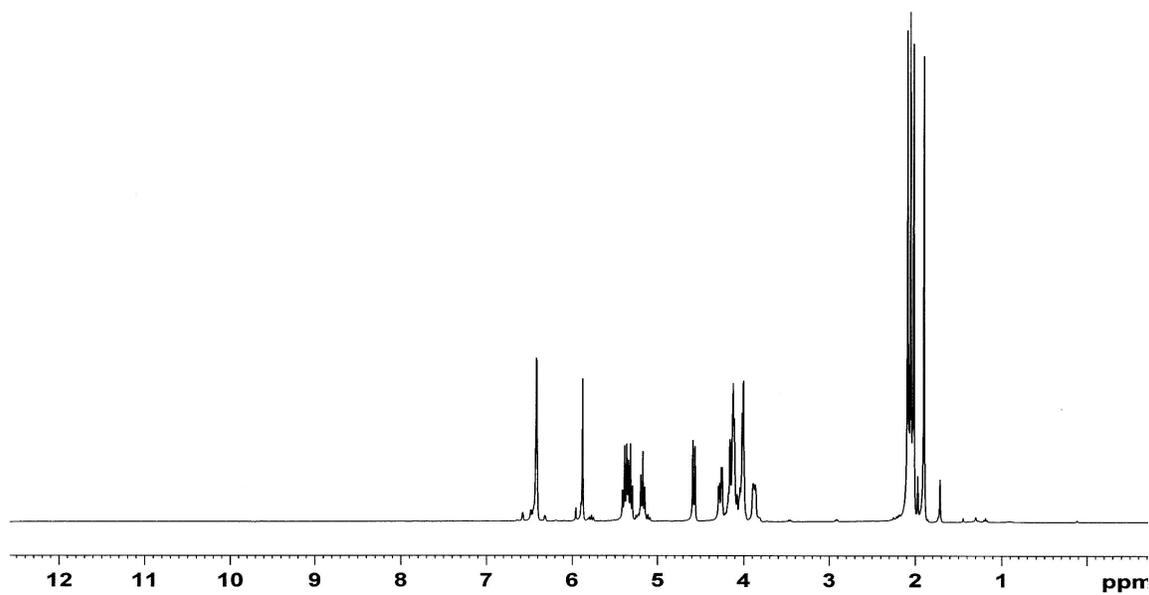
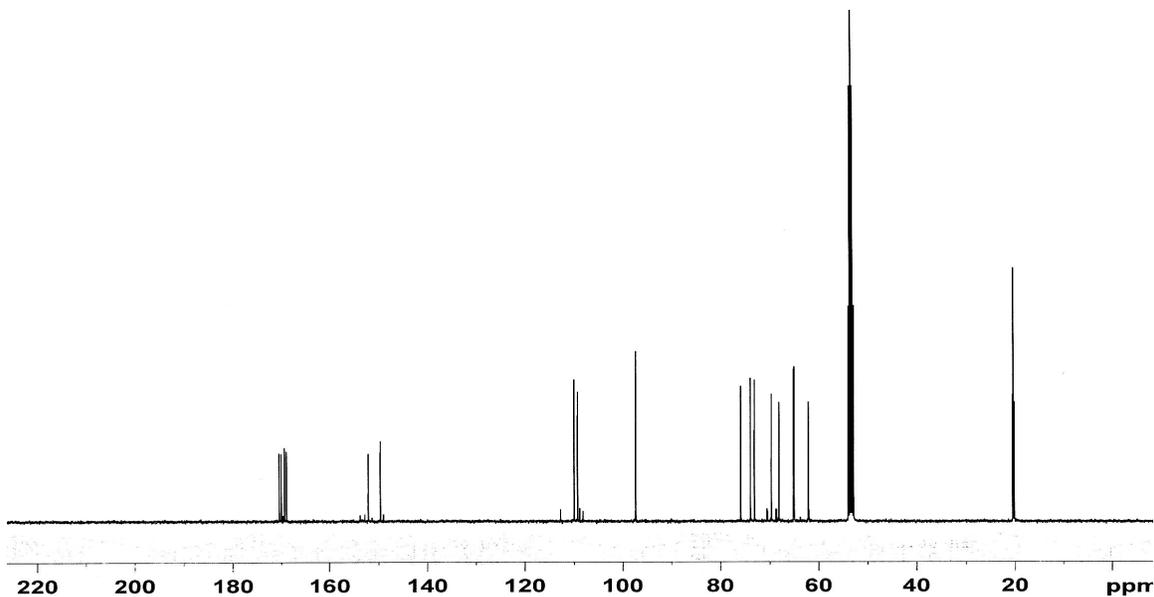
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.8, 170.4, 169.5, 169.0, 137.2, 126.4, 126.0, 123.7, 76.2, 76.1, 74.2, 72.2, 68.5, 62.3, 20.8, 20.7, 20.67, 20.5.

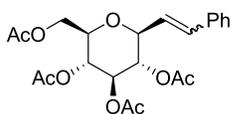




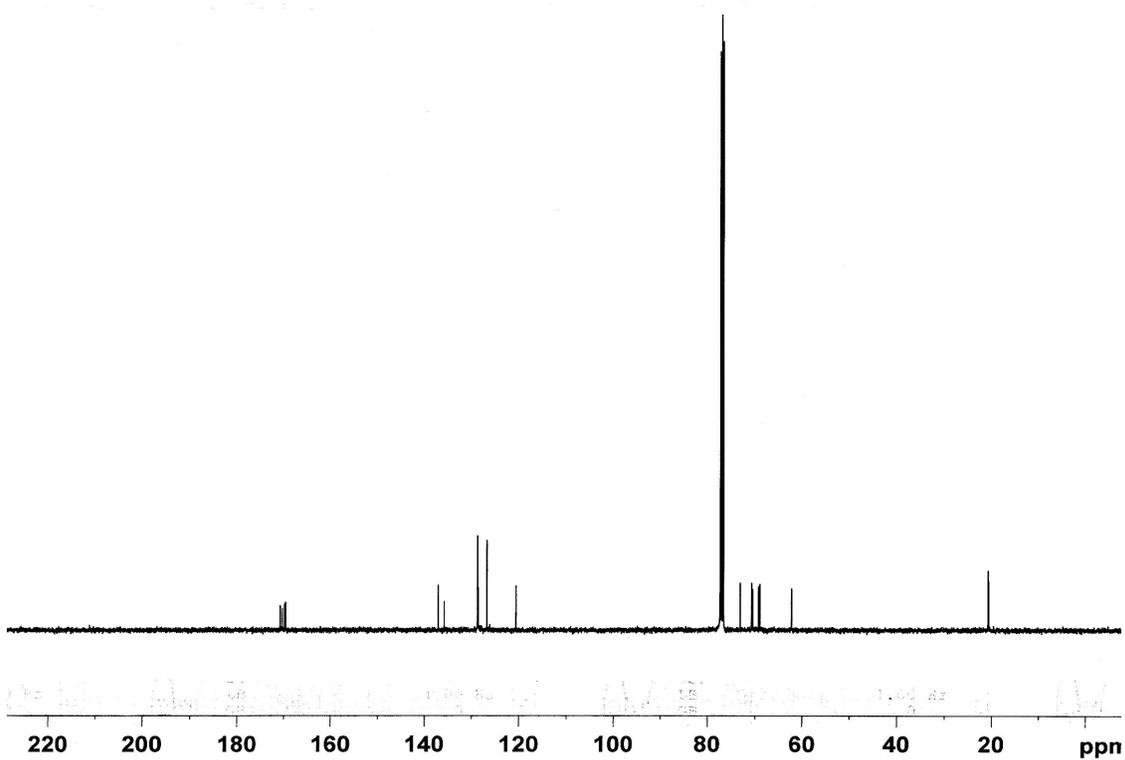
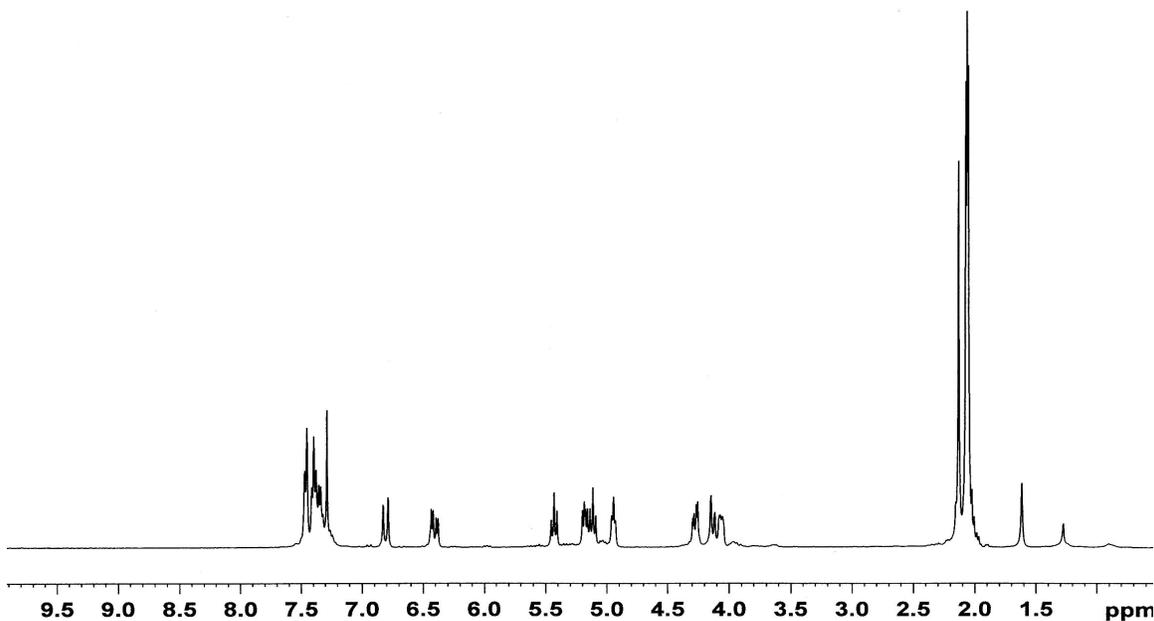
**$^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  6.42 (d,  $J = 2.0$  Hz, 2H), 5.88 (s, 1H), 5.39 (t,  $J = 9.6$  Hz, 1H;  $H_3$ ), 5.32 (t,  $J = 9.6$  Hz, 1H;  $H_4$ ), 5.18 (t,  $J = 9.6$  Hz, 1H;  $H_2$ ), 4.58 (d,  $J = 10.0$  Hz, 1H;  $H_1$ ), 4.27 (dd,  $J = 12.4$  and 4.8 Hz, 1H;  $H_6$ ), 4.07-4.20 (m, 3H), 4.07-4.00 (m, 2H), 3.88 (ddd,  $J = 10.0, 4.8$  and 2.0 Hz, 1H;  $H_5$ ), 2.09 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.90 (s, 3H).

**$^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):**  $\delta$  170.5, 170.0, 169.4, 169.0, 152.2, 149.7, 110.0, 109.3, 97.38, 75.9, 74.0, 73.2, 69.7, 68.2, 65.2, 65.1, 62.2, 20.5, 20.4, 20.2.

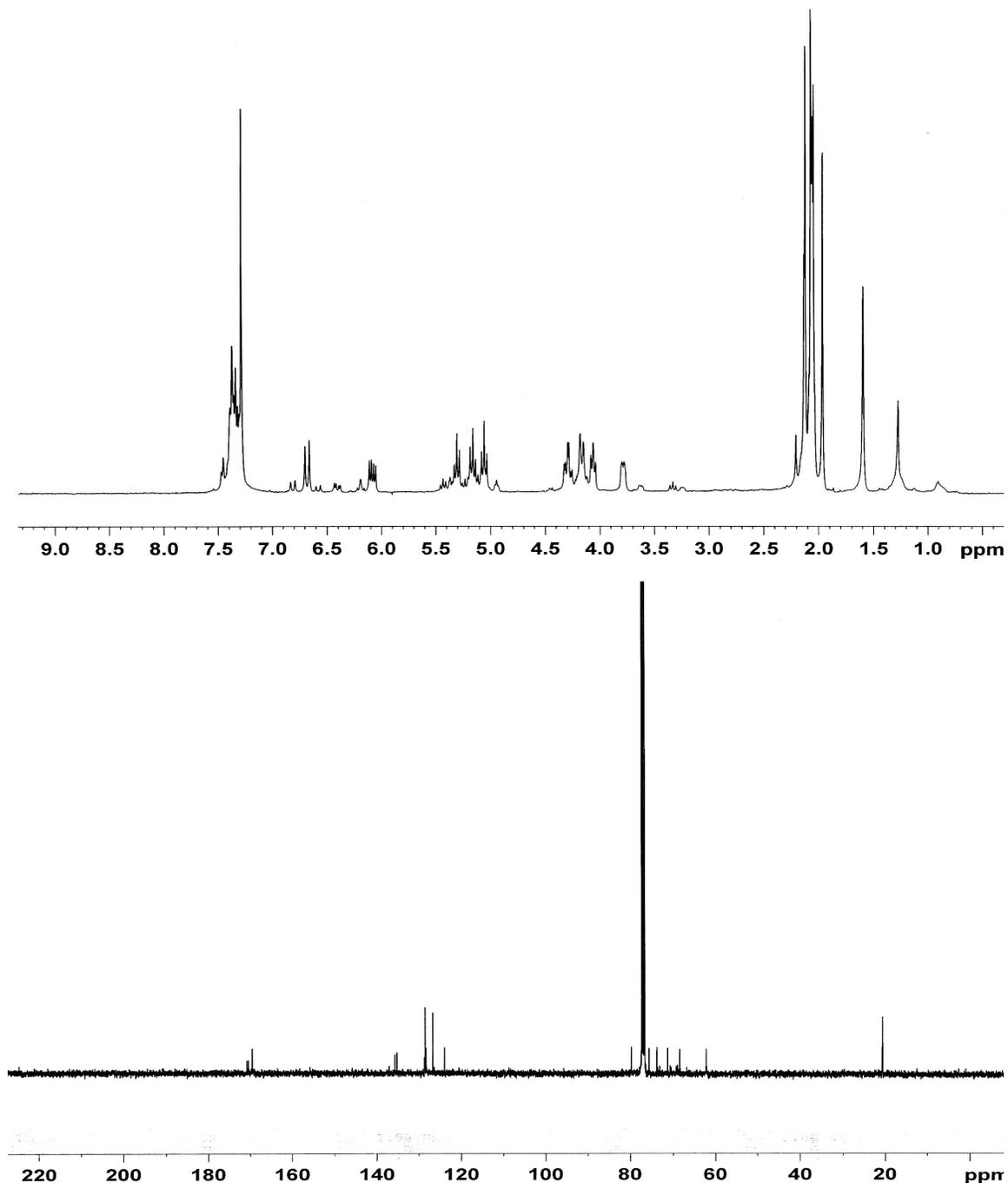


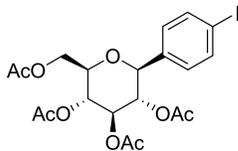


Characterization data for the  $\alpha$ -anomer:  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.20-7.40 (m, 5H), 6.76 (d,  $J = 16.0$  Hz, 1H), 6.36 (dd,  $J = 16.0$  and 6.0 Hz, 1H), 5.38 (t,  $J = 9.6$  Hz, 1H;  $H3$ ), 5.13 (dd,  $J = 10.0$  and 6.0 Hz, 1H;  $H2$ ), 5.07 (t,  $J = 9.6$  Hz, 1H;  $H4$ ), 4.90 (t,  $J = 5.6$  Hz, 1H;  $H1$ ), 4.23 (dd,  $J = 12.0$  and 4.4 Hz, 1H;  $H6$ ), 4.10 (dd,  $J = 12.0$  and 1.6 Hz, 1H;  $H7$ ), 4.03 (ddd,  $J = 10.0$ , 4.8 and 2.0 Hz, 1H;  $H5$ ), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.7, 170.2, 169.8, 169.6, 137.1, 135.8, 128.7, 128.6, 126.7, 120.6, 73.13, 70.8, 70.5, 69.3, 69.0, 62.3, 20.8, 20.7, 20.6.



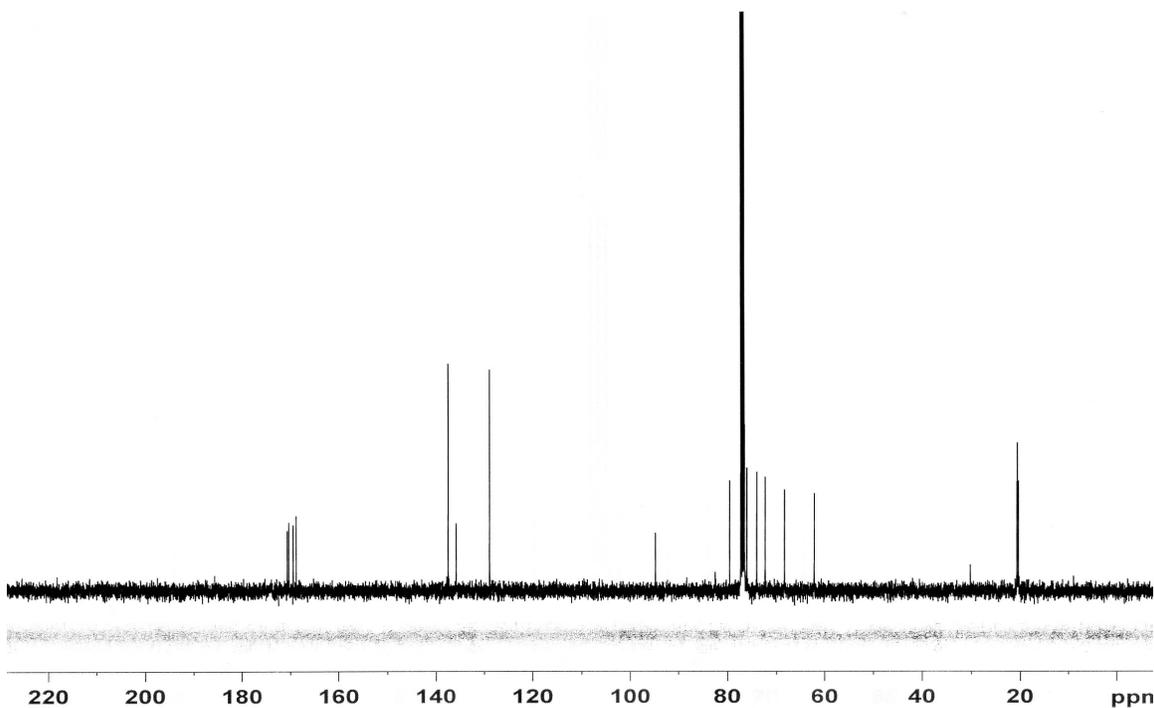
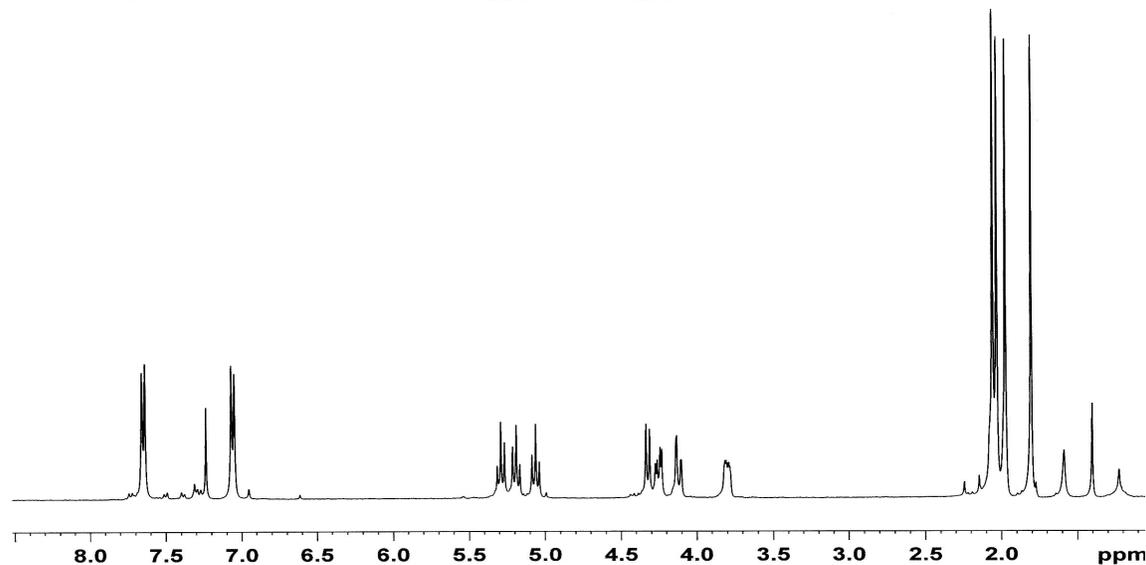
Characterization data for the  $\beta$ -anomer:  **$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.15-7.45 (m, 5H), 6.63 (d,  $J = 16.0$  Hz, 1H), 6.36 (dd,  $J = 16.0$  and 8.0 Hz, 1H), 5.26 (t,  $J = 9.6$  Hz, 1H;  $H3$ ), 5.11 (t,  $J = 9.6$  Hz, 1H;  $H4$ ), 5.01 (t,  $J = 9.6$  Hz, 1H;  $H2$ ), 4.26 (dd,  $J = 12.4$  and 4.4 Hz, 1H;  $H6$ ), 4.12 (dd,  $J = 12.4$  and 2.0 Hz, 1H;  $H7$ ), 4.01 (dd,  $J = 9.2$  and 8.0 Hz, 1H;  $H1$ ), 3.74 (ddd,  $J = 10.0$ , 4.8 and 2.0 Hz, 1H;  $H5$ ), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H).  **$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.8, 170.4, 169.5, 135.6, 135.3, 128.6, 128.4, 126.8, 124.0, 79.8, 74.1, 75.7, 73.8, 73.1, 71.4, 70.8, 69.4, 69.0, 68.5, 62.3, 20.8, 20.7, 20.6. Residual alpha anomer is present in this partially purified product. Additional purification was not possible.

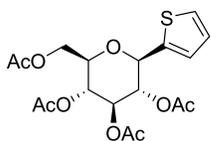




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 5.29 (t, *J* = 9.6 Hz, 1H; *H*3), 5.19 (t, *J* = 9.6 Hz, 1H; *H*4), 5.06 (t, *J* = 9.6 Hz, 1H; *H*2), 4.32 (d, *J* = 9.6 Hz, 1H; *H*1), 4.25 (dd, *J* = 12.4 and 4.4 Hz, 1H; *H*6), 4.12 (dd, *J* = 12.4 and 1.6 Hz, 1H; *H*7), 3.80 (ddd, *J* = 9.6, 4.4 and 2.0 Hz, 1H; *H*5), 2.06 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.81 (s, 3H).

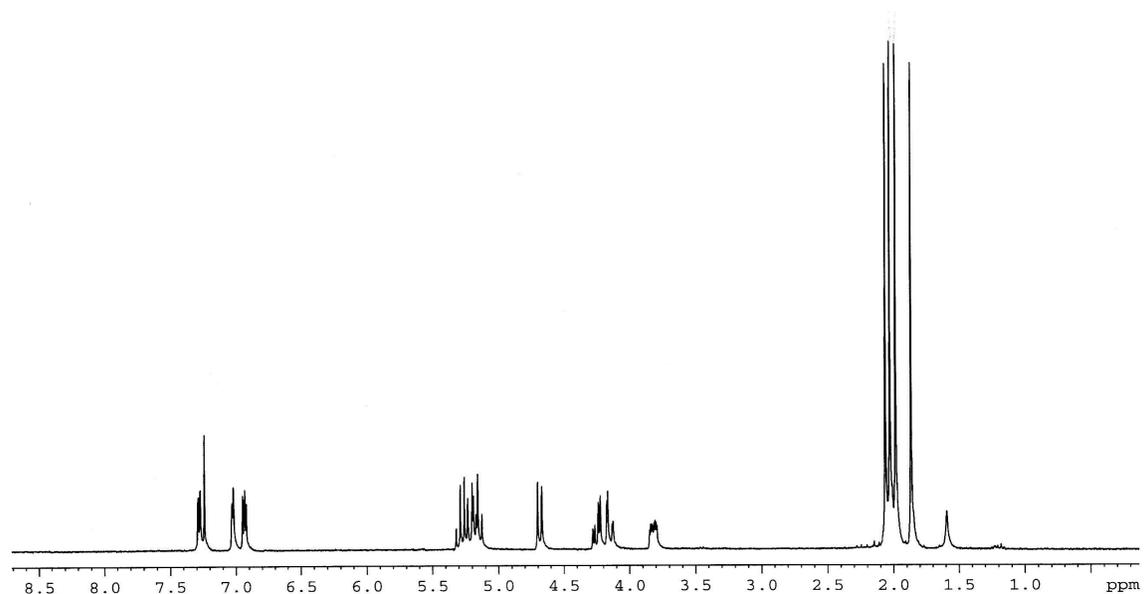
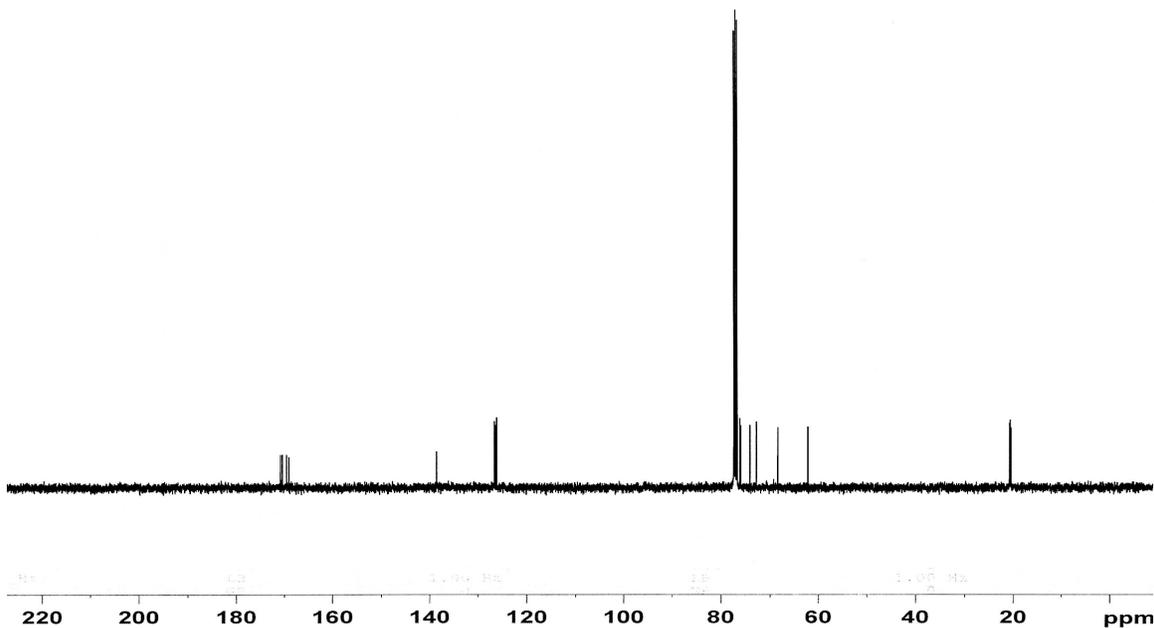
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.7, 170.4, 169.5, 168.8, 137.6, 135.9, 128.0, 94.8, 79.6, 74.1, 72.4, 68.4, 62.2, 20.8, 20.64, 20.63, 20.4.

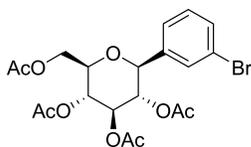




**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.28 (dd,  $J = 5.1, 0.9$  Hz, 1H), 7.03 (d,  $J = 3.0$  Hz, 1H), 6.94 (dd,  $J = 5.1$  and 3.6 Hz, 1H), 5.29 (t,  $J = 9.3$  Hz, 1H;  $H3$ ), 5.20 (t,  $J = 9.3$  Hz, 1H;  $H4$ ), 5.16 (t,  $J = 9.3$  Hz, 1H;  $H2$ ), 4.90 (d,  $J = 9.6$  Hz, 1H;  $H1$ ), 4.25 (dd,  $J = 12.3$  and 4.5 Hz, 1H;  $H6$ ), 4.15 (dd,  $J = 12.3$  and 2.4 Hz;  $H7$ ), 3.82 (ddd,  $J = 9.6, 4.8$  and 2.4 Hz, 1H;  $H5$ ), 2.07 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.87 (s, 3H).

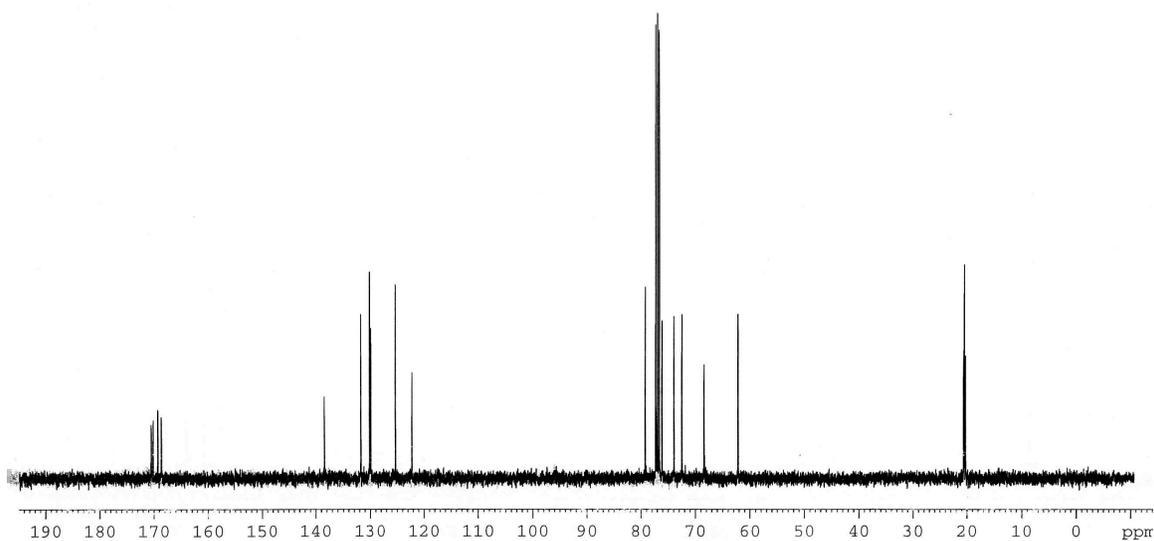
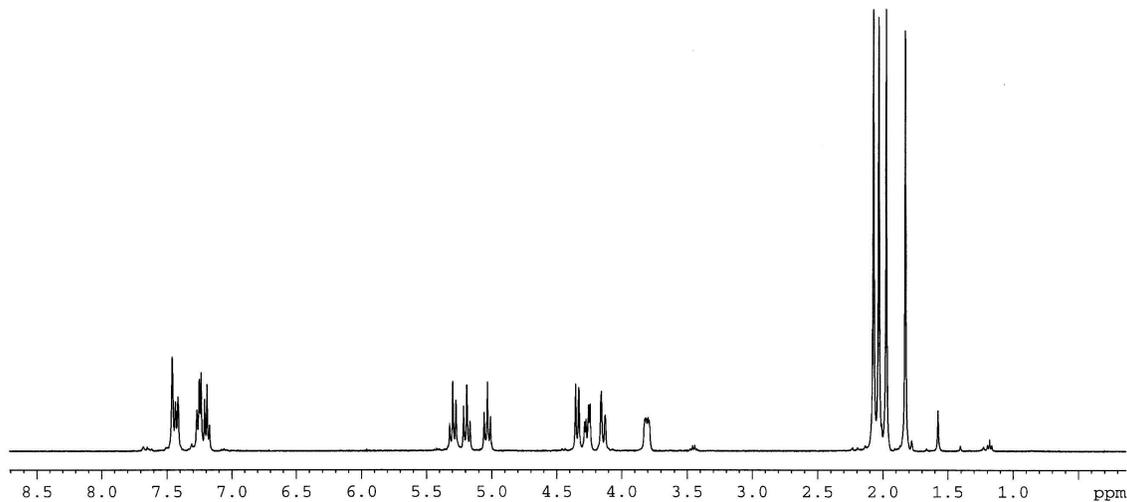
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.8, 170.4, 169.5, 169.0, 138.6, 126.6, 126.3, 126.2, 76.2, 76.0, 74.2, 72.8, 68.4, 62.2, 20.8, 20.69, 20.66, 20.5.

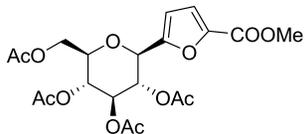




**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.46 (s, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.19 (t,  $J = 7.6$  Hz, 1H), 5.30 (t,  $J = 9.6$  Hz, 1H;  $H_3$ ), 5.19 (t,  $J = 9.6$  Hz, 1H;  $H_4$ ), 5.04 (t,  $J = 9.6$  Hz, 1H;  $H_2$ ), 4.33 (d,  $J = 9.6$  Hz, 1H;  $H_1$ ), 4.25 (dd,  $J = 12.4$  and 4.4 Hz, 1H;  $H_6$ ), 4.13 (d,  $J = 12.4$  and 2.0 Hz, 1H;  $H_7$ ), 3.80 (ddd,  $J = 10.0$ , 4.8 and 2.0 Hz, 1H;  $H_5$ ), 2.06 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.82 (s, 3H).

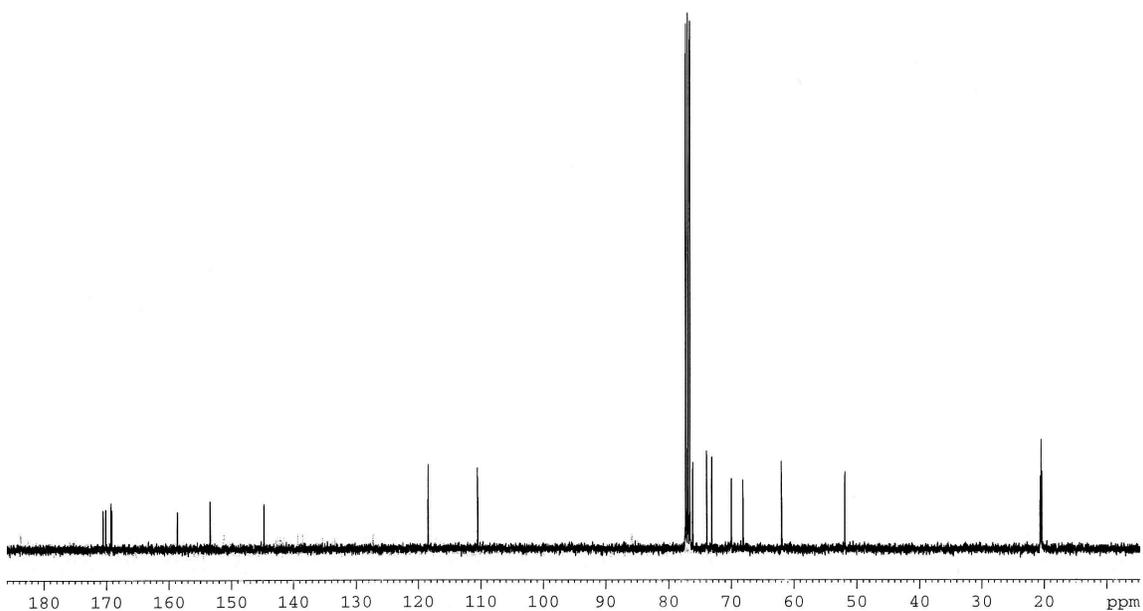
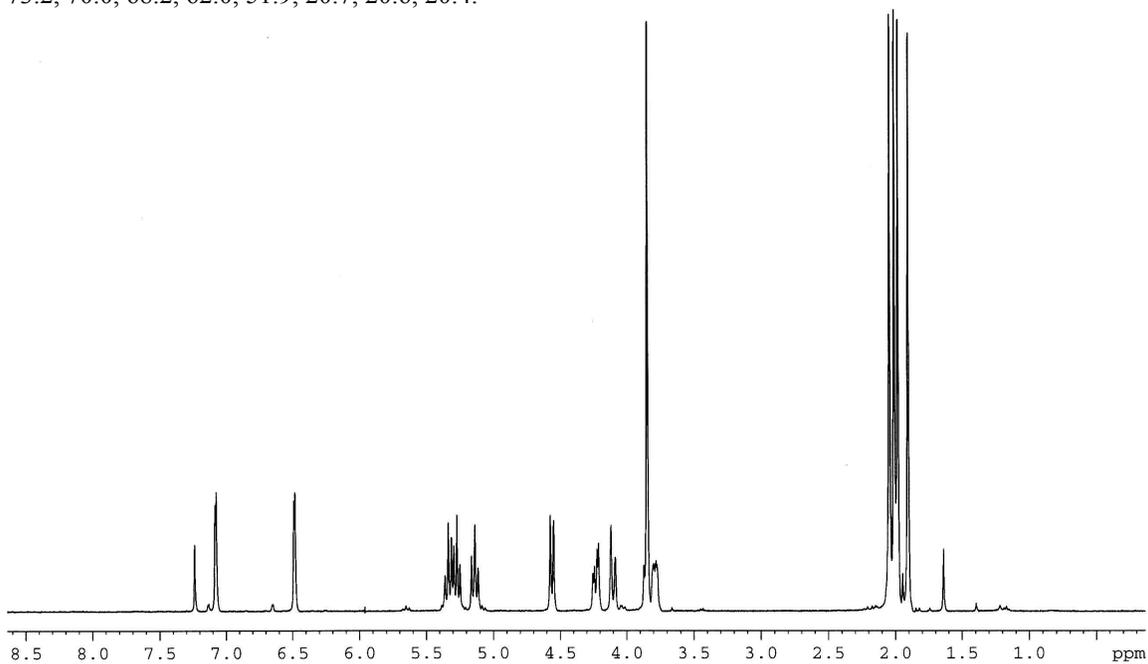
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.6, 170.2, 169.4, 168.7, 138.6, 131.9, 130.2, 130.0, 125.4, 122.3, 79.3, 77.0, 74.0, 72.6, 68.5, 62.2, 20.7, 20.6, 20.3.

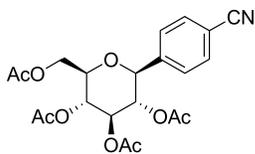




**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.08 (d,  $J = 3.6$  Hz, 1H), 6.49 (d,  $J = 3.6$  Hz, 1H), 5.34 (t,  $J = 9.6$  Hz, 1H;  $H3$ ), 5.27 ( $J = 9.6$  Hz, 1H;  $H4$ ), 5.14 (t,  $J = 9.6$  Hz, 1H;  $H2$ ), 4.56 (d,  $J = 9.6$  Hz, 1H;  $H1$ ), 4.23 (dd,  $J = 12.4$  and 4.8 Hz, 1H;  $H6$ ), 4.10 (dd,  $J = 12.4$  and 2.0 Hz, 1H;  $H7$ ), 3.85 (s, 3H), 3.79 (ddd,  $J = 10.0$ , 4.8 and 2.0 Hz, 1H;  $H5$ ), 2.05 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.91 (s, 3H).

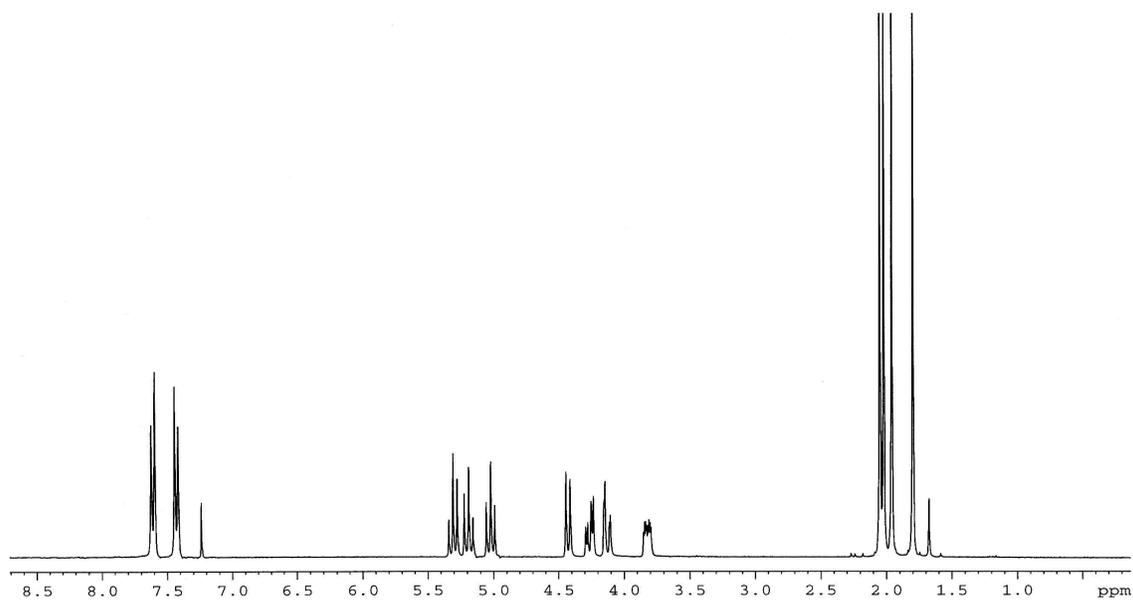
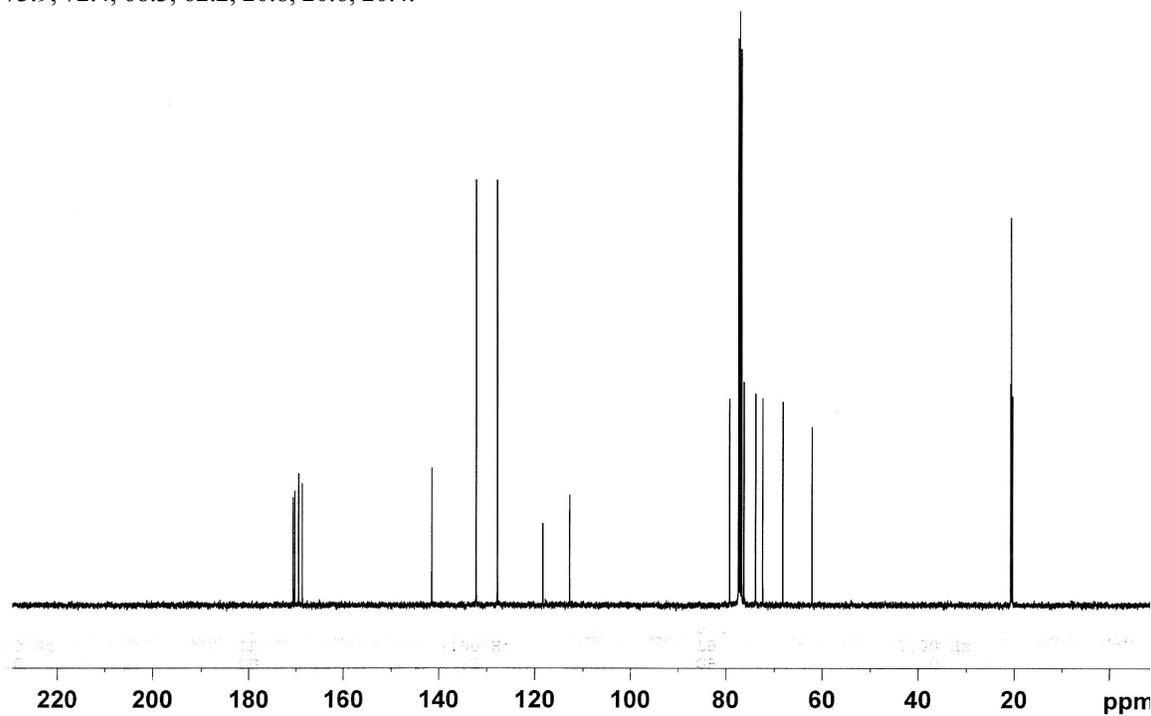
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.6, 170.2, 169.3, 169.2, 158.7, 153.5, 144.8, 118.5, 110.6, 76.2, 74.0, 73.2, 70.0, 68.2, 62.0, 51.9, 20.7, 20.6, 20.4.

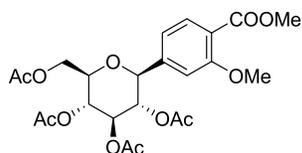




**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  7.61 (d,  $J$  = 8.4 Hz, 2H), 7.40 (d,  $J$  = 8.4 Hz, 1H), 5.31 (t,  $J$  = 9.6 Hz, 1H; *H3*), 5.19 ( $J$  = 9.6 Hz, 1H; *H4*), 5.02 (t,  $J$  = 9.6 Hz, 1H; *H2*), 4.43 (d,  $J$  = 9.6 Hz, 1H; *H1*), 4.27 (dd,  $J$  = 12.3 and 4.8 Hz, 1H; *H6*), 4.13 (dd,  $J$  = 12.3 and 2.1 Hz, 1H; *H7*), 3.82 (ddd,  $J$  = 9.9, 4.8 and 2.1 Hz, 1H; *H5*), 2.06 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.81 (s, 3H).

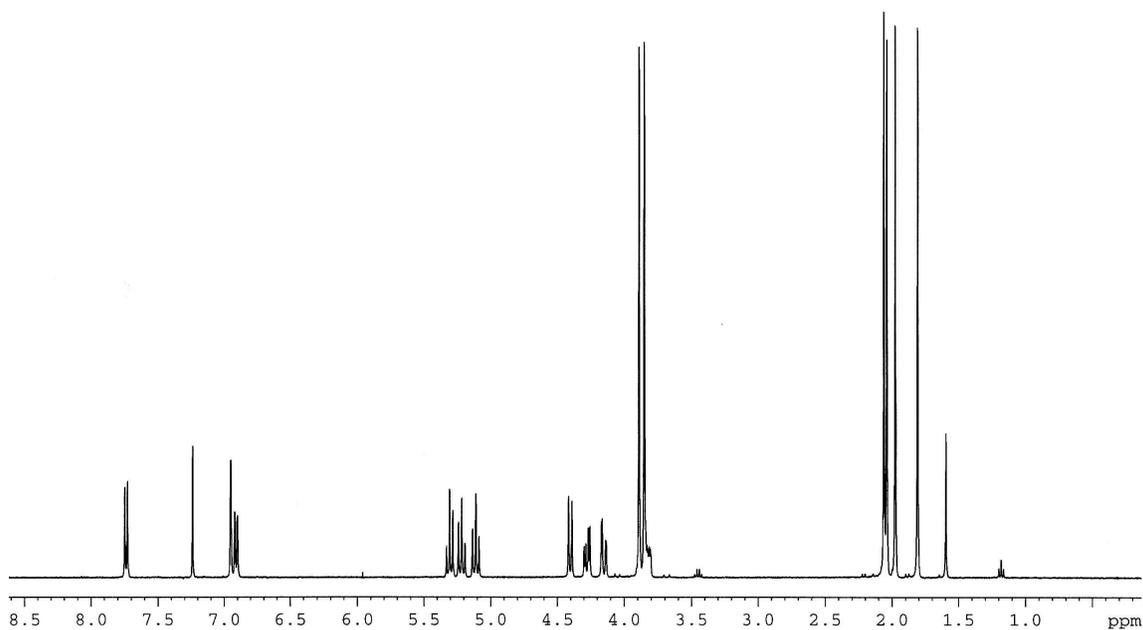
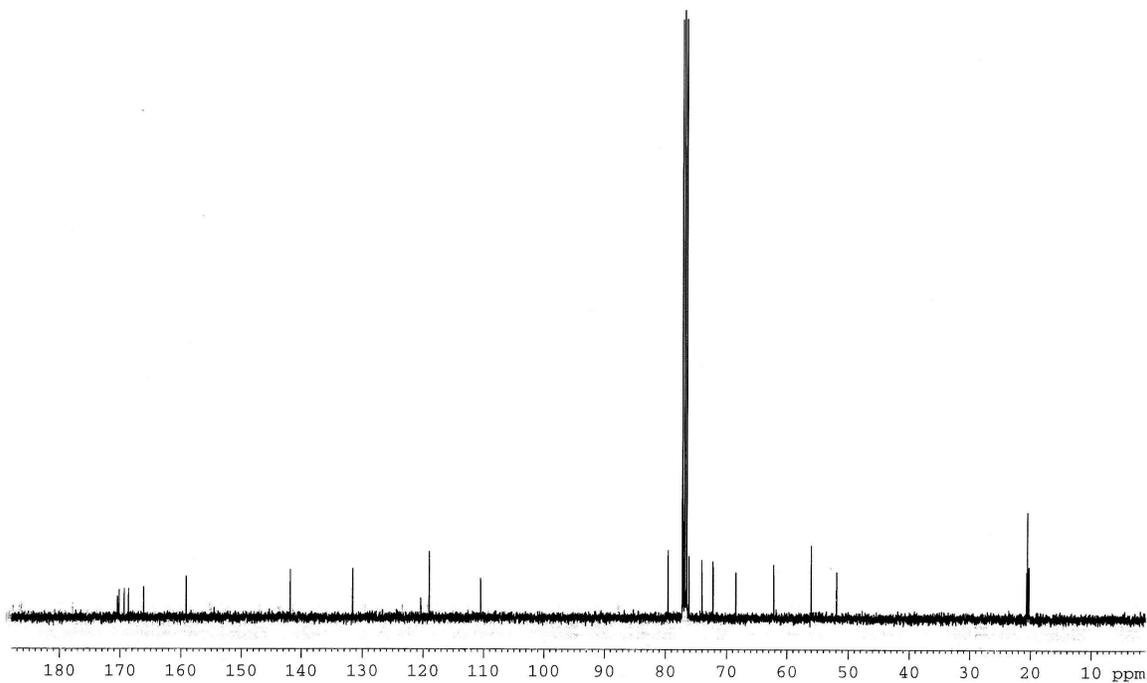
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  170.7, 170.3, 169.5, 168.7, 141.5, 132.3, 127.8, 118.4, 112.8, 79.2, 76.3, 73.9, 72.4, 68.3, 62.2, 20.8, 20.6, 20.4.

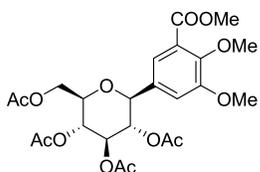




**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.74 (d,  $J = 8.0$  Hz, 1H), 6.95 (s, 1H), 6.91 (d,  $J = 8.0$  Hz, 1H), 5.30 (t,  $J = 9.6$  Hz, 1H;  $H3$ ), 5.21 ( $J = 9.6$  Hz, 1H;  $H4$ ), 5.11 (t,  $J = 9.6$  Hz, 1H;  $H2$ ), 4.40 (d,  $J = 10.0$  Hz, 1H;  $H1$ ), 4.27 (dd,  $J = 12.4$  and 4.8 Hz, 1H;  $H6$ ), 4.15 (dd,  $J = 12.4$  and 1.6 Hz, 1H;  $H7$ ), 3.89 (s, 3H), 3.85 (s, 3H), 3.82 (ddd,  $J = 10.0$ , 4.8 and 2.0 Hz, 1H;  $H5$ ), 2.06 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.81 (s, 3H).

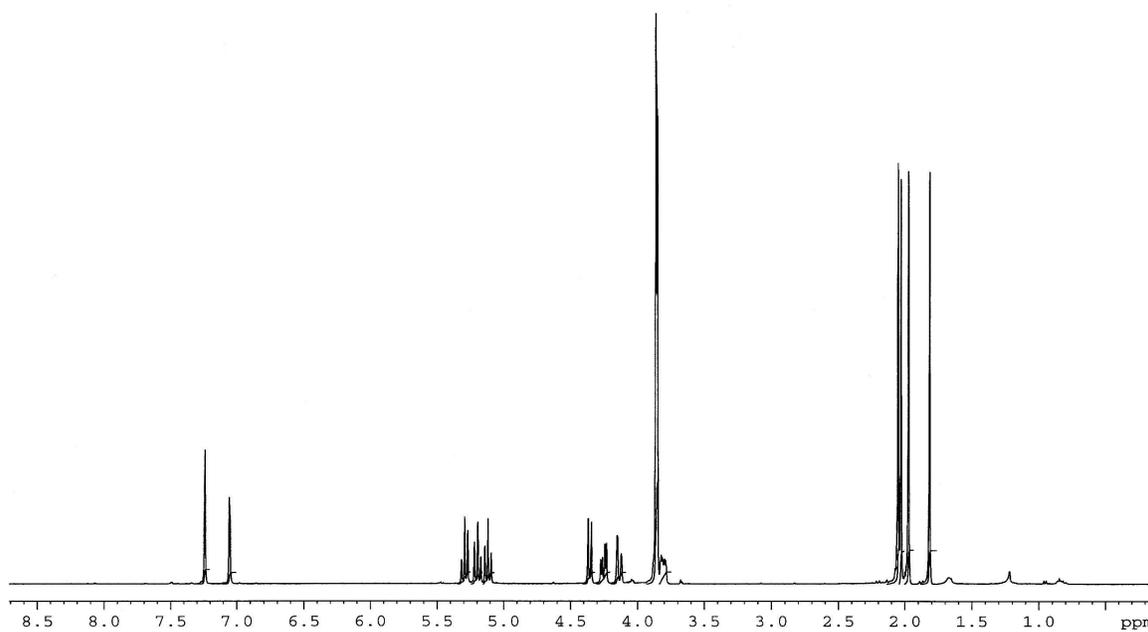
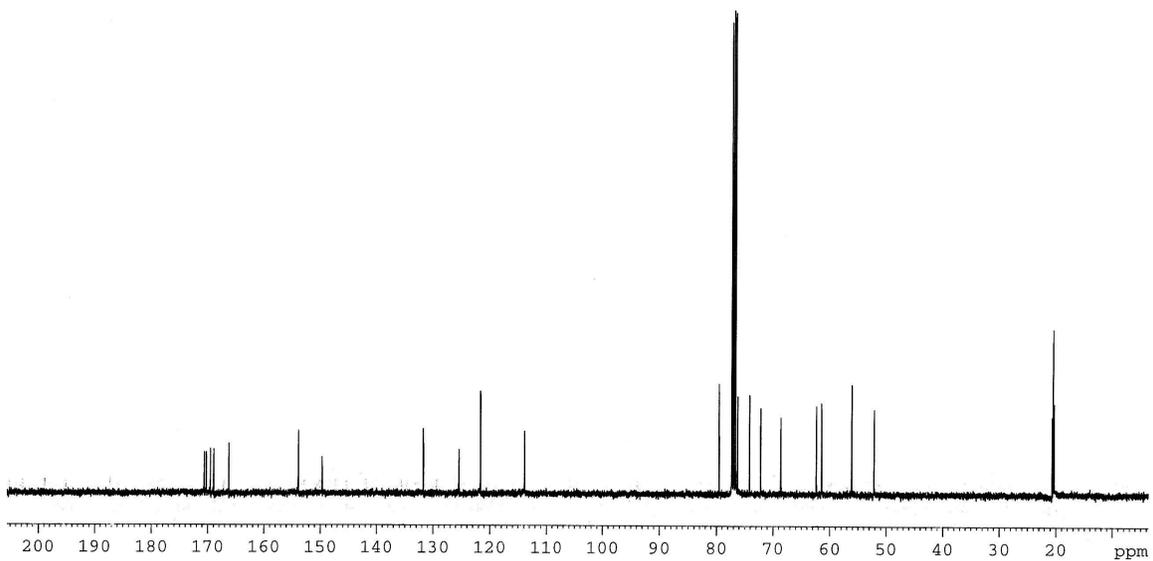
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.5, 170.2, 169.4, 168.6, 166.1, 159.1, 141.9, 131.6, 120.4, 119.0, 79.6, 76.2, 74.1, 72.3, 68.5, 62.2, 56.0, 51.9, 20.6, 20.5, 20.3.

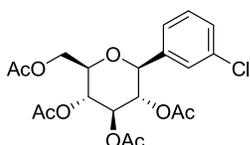




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.24 (s, 1H), 7.05 (d, *J* = 1.2 Hz, 1H), 5.29 (t, *J* = 9.6 Hz, 1H; *H*3), 5.20 (*J* = 9.6 Hz, 1H; *H*4), 5.12 (t, *J* = 9.6 Hz, 1H; *H*5), 4.35 (d, *J* = 10.0 Hz, 1H; *H*1), 4.25 (dd, *J* = 12.4 and 4.8 Hz, 1H; *H*6), 4.14 (dd, *J* = 12.4 and 1.6 Hz, 1H; *H*7), 3.87 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.81 (ddd, *J* = 9.6, 4.8 and 2.0 Hz, 1H; *H*5), 2.05 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.82 (s, 3H).

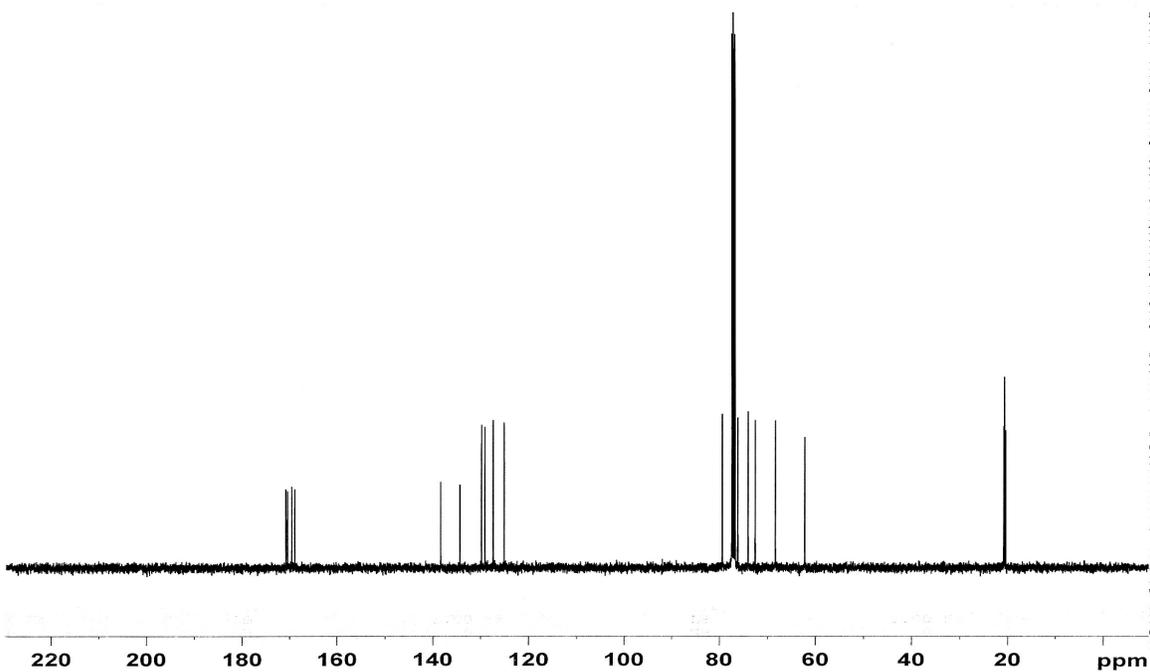
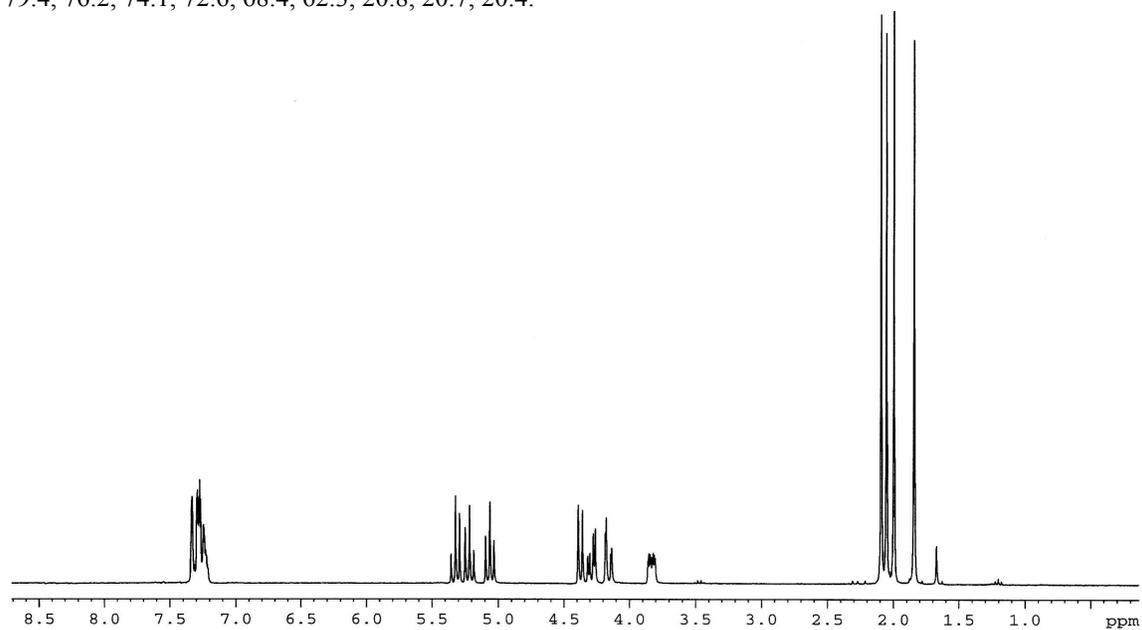
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.6, 170.2, 169.5, 168.9, 166.2, 153.8, 149.7, 131.8, 125.5, 121.7, 114.0, 79.6, 77.2, 76.3, 74.2, 72.3, 68.7, 62.4, 61.5, 56.2, 52.2, 20.7, 20.6, 20.4.

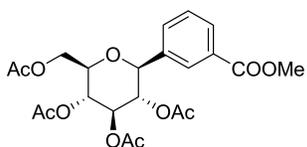




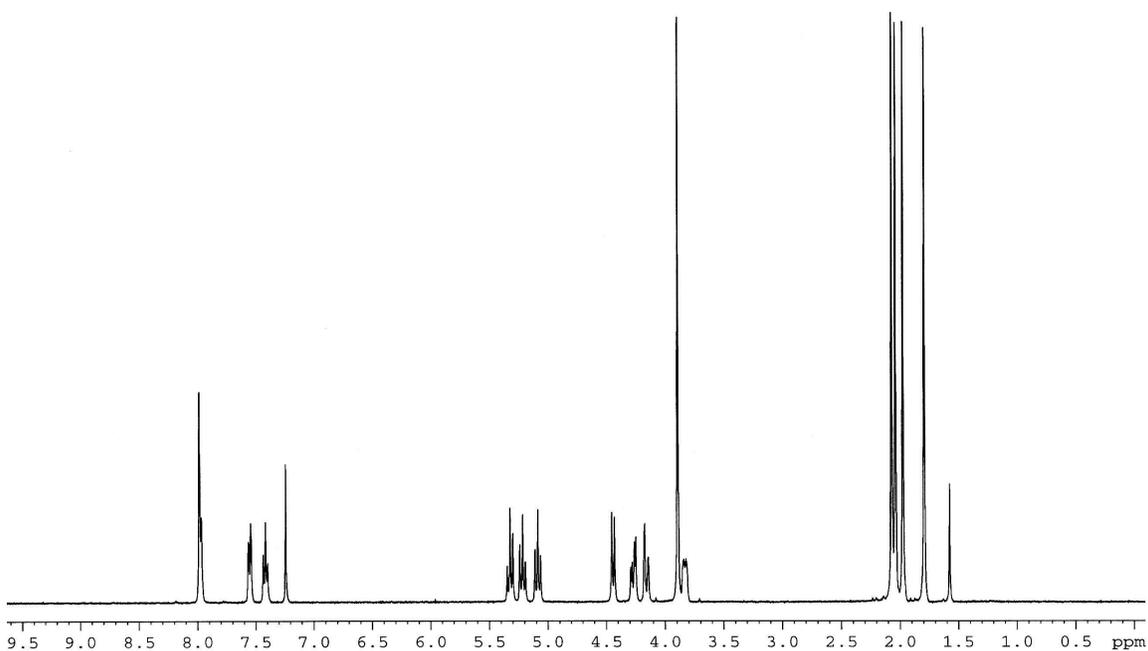
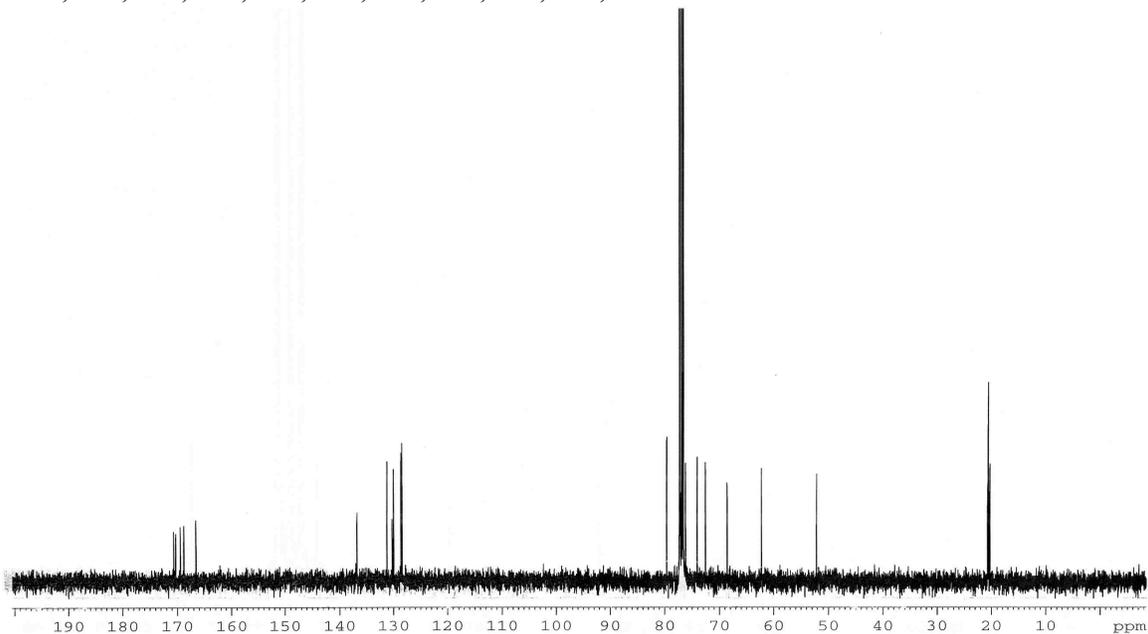
**$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.33 (s, 1H), 7.20-7.30 (m, 3H), 5.33 (t,  $J = 9.3$  Hz, 1H;  $H_3$ ), 5.22 (t,  $J = 9.6$  Hz, 1H;  $H_4$ ), 5.07 (t,  $J = 9.6$  Hz, 1H;  $H_2$ ), 4.38 (d,  $J = 9.9$  Hz, 1H;  $H_1$ ), 4.29 (dd,  $J = 12.3$  and 4.8 Hz, 1H;  $H_6$ ), 4.16 (dd,  $J = 12.3$  and 2.1 Hz;  $H_7$ ), 3.83 (ddd,  $J = 9.9, 4.8$  and 2.1 Hz, 1H;  $H_5$ ), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.85 (s, 3H).

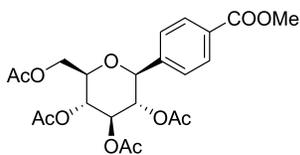
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  170.8, 170.4, 169.5, 168.9, 138.3, 134.3, 129.8, 129.1, 127.4, 125.1, 79.4, 76.2, 74.1, 72.6, 68.4, 62.3, 20.8, 20.7, 20.4.





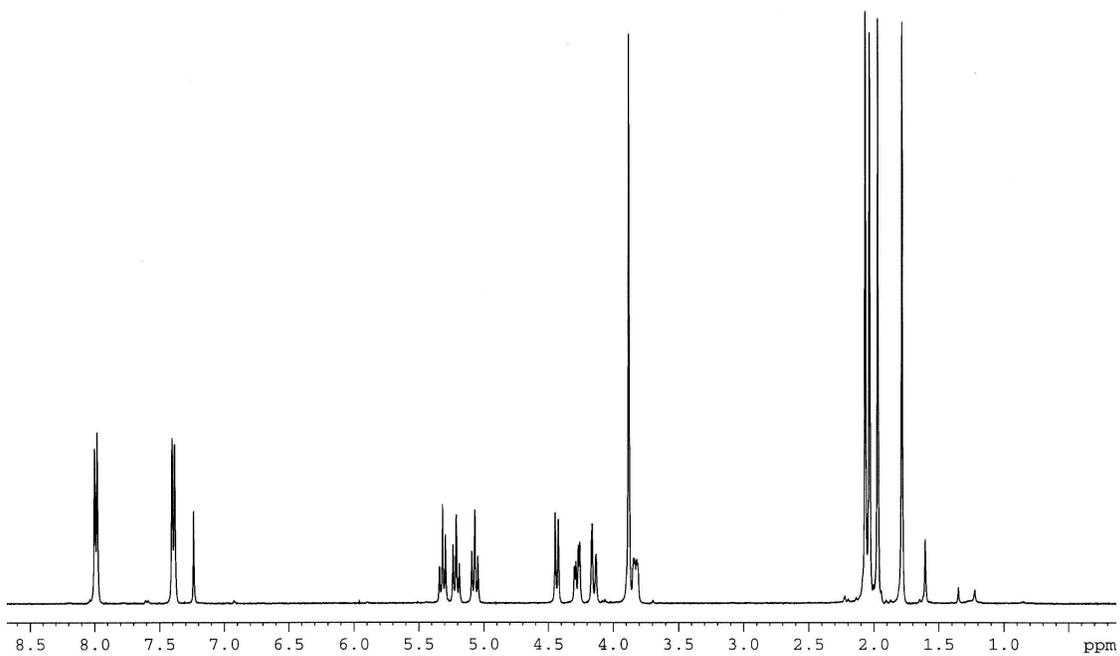
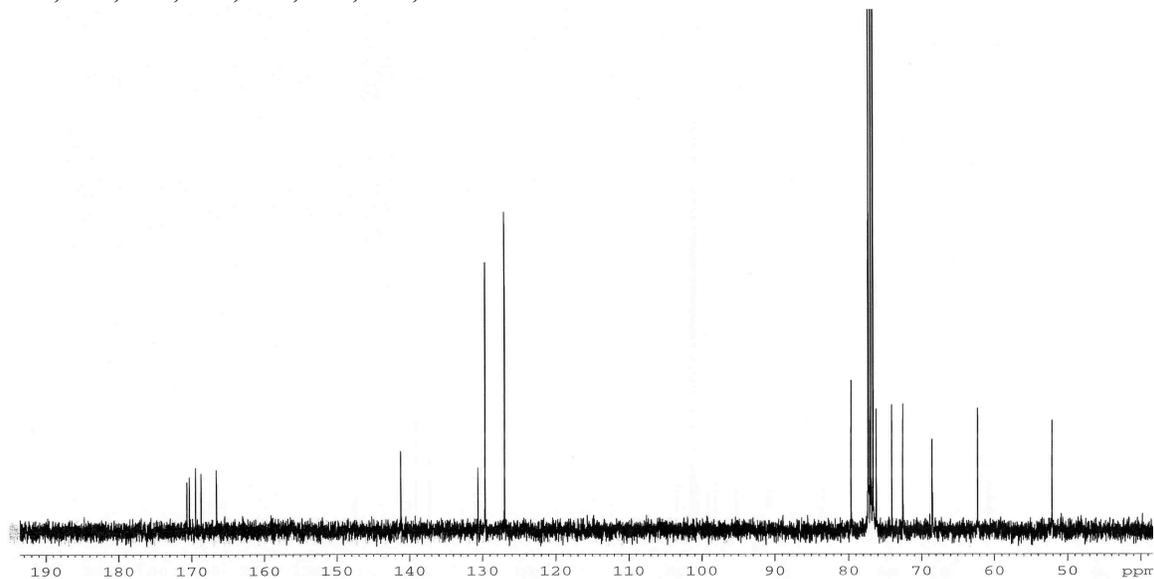
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.98 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 5.33 (t, *J* = 9.6 Hz, 1H; *H*3), 5.22 (t, *J* = 9.6 Hz, 1H; *H*4), 5.09 (t, *J* = 9.6 Hz, 1H; *H*2), 4.44 (d, *J* = 9.6 Hz, 1H; *H*1), 4.27 (dd, *J* = 12.8 and 4.8 Hz, 1H; *H*6), 4.16 (dd, *J* = 12.8 and 2.4 Hz, 1H; *H*7), 3.89 (s, 3H), 3.83 (ddd, *J* = 10.0, 4.8 and 2.4 Hz, 1H; *H*5), 2.07 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.79 (s, 3H). **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.7, 170.3, 169.5, 168.8, 166.6, 136.9, 131.3, 130.3, 130.0, 128.7, 128.5, 79.7, 76.3, 74.1, 72.7, 68.6, 62.3, 52.2, 20.7, 20.6, 20.3.

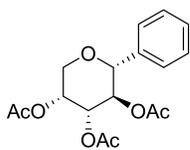




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  7.99 (d,  $J = 8.0$  Hz, 2H), 7.39 (d,  $J = 8.0$  Hz, 2H), 5.32 (t,  $J = 9.6$  Hz, 1H; *H3*), 5.21 (t,  $J = 9.6$  Hz, 1H; *H4*), 5.07 (t,  $J = 9.6$  Hz, 1H; *H2*), 4.43 (d,  $J = 10.0$  Hz, 1H; *H1*), 4.28 (dd,  $J = 12.4$  and 4.8 Hz, 1H; *H1*), 4.15 (dd,  $J = 12.4$  and 2.4 Hz, 1H; *H7*), 3.88 (s, 3H), 3.83 (ddd,  $J = 10.0, 4.8$  and 2.4 Hz, 1H; *H5*), 2.07 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H), 1.79 (s, 3H).

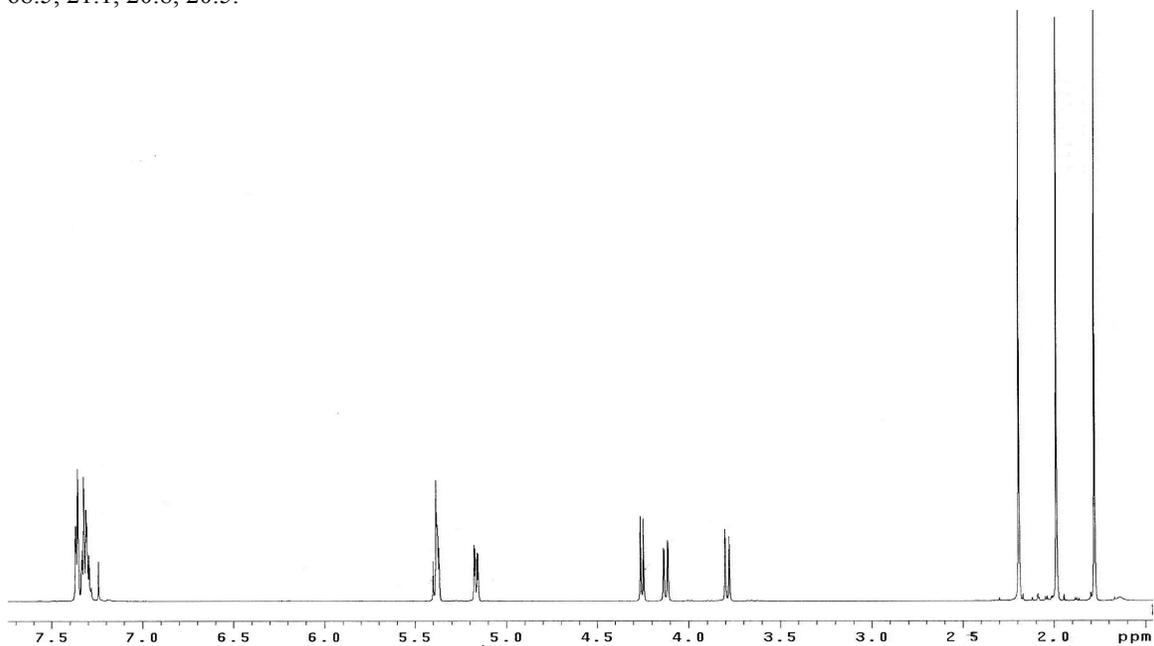
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  170.6, 170.3, 169.4, 168.7, 166.6, 141.2, 130.7, 129.7, 127.1, 79.7, 76.3, 74.1, 72.6, 68.6, 62.3, 52.1, 20.7, 20.6, 20.3.

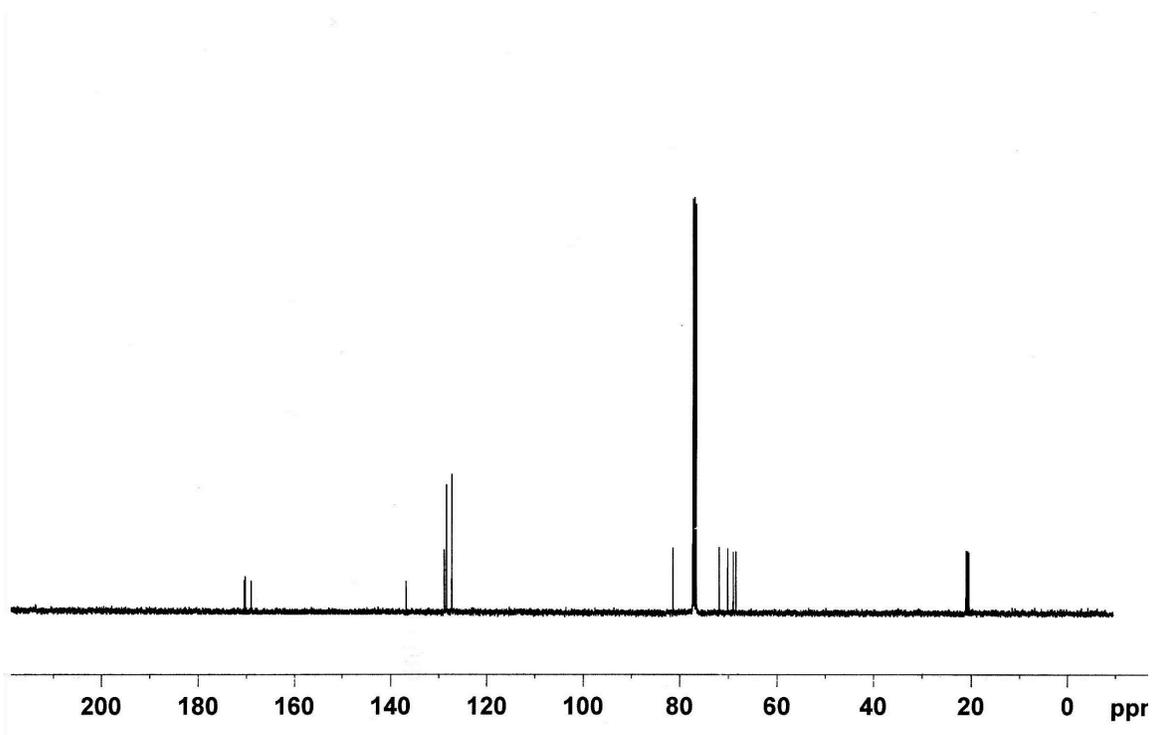




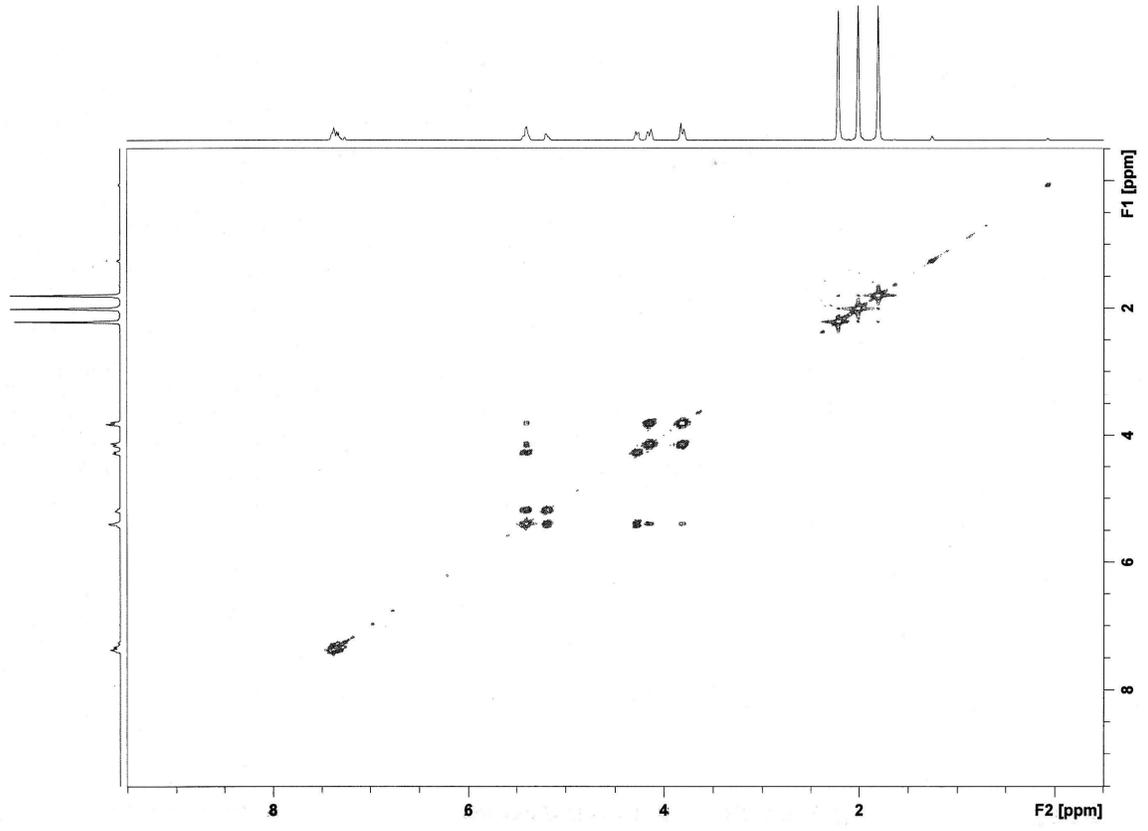
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.30-7.37 (m, 5H), 5.36-5.41 (m, 2H; *H*2, *H*4), 5.17 (dd, *J* = 10.2 and 3.6 Hz, 1H; *H*3), 4.25 (d, *J* = 9.6 Hz, 1H; *H*1), 4.12 (dd, *J* = 13.2 and 1.8 Hz, 1H; *H*5), 3.79 (dd, *J* = 13.2 and 0.6 Hz, 1H; *H*6).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.5, 170.3, 169.0, 136.8, 128.9, 128.4, 127.3, 81.5, 71.9, 70.2, 69.0, 68.5, 21.1, 20.8, 20.5.

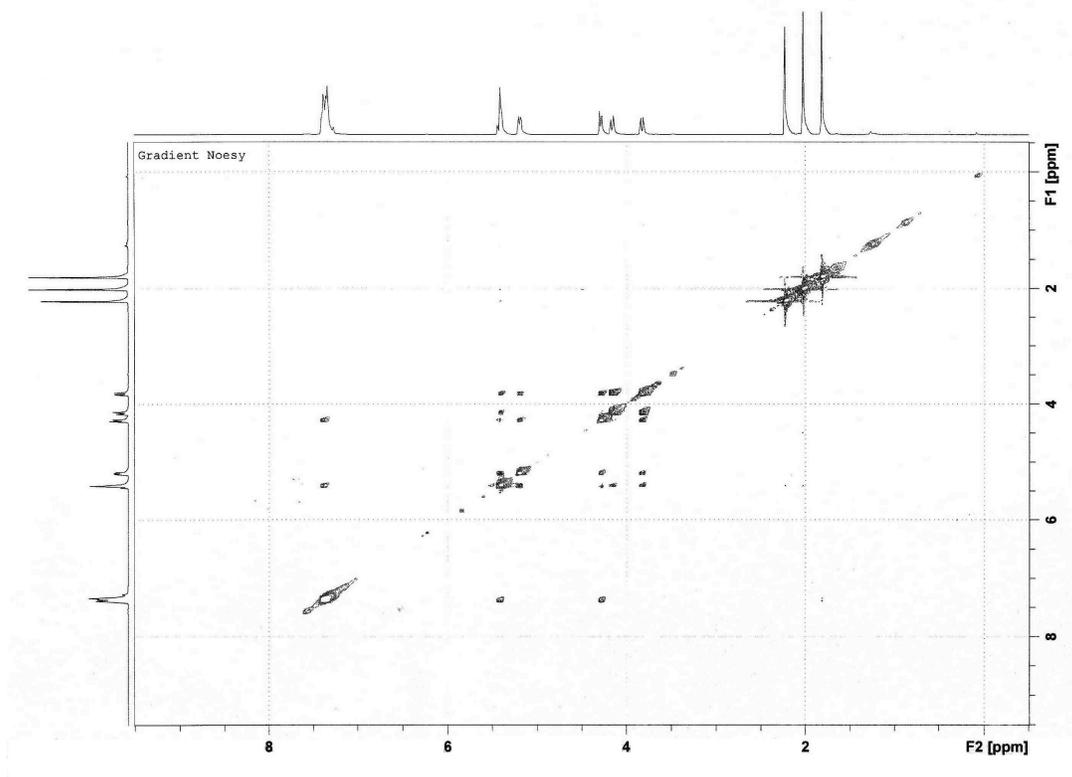


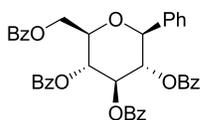


**2D-COSY:**



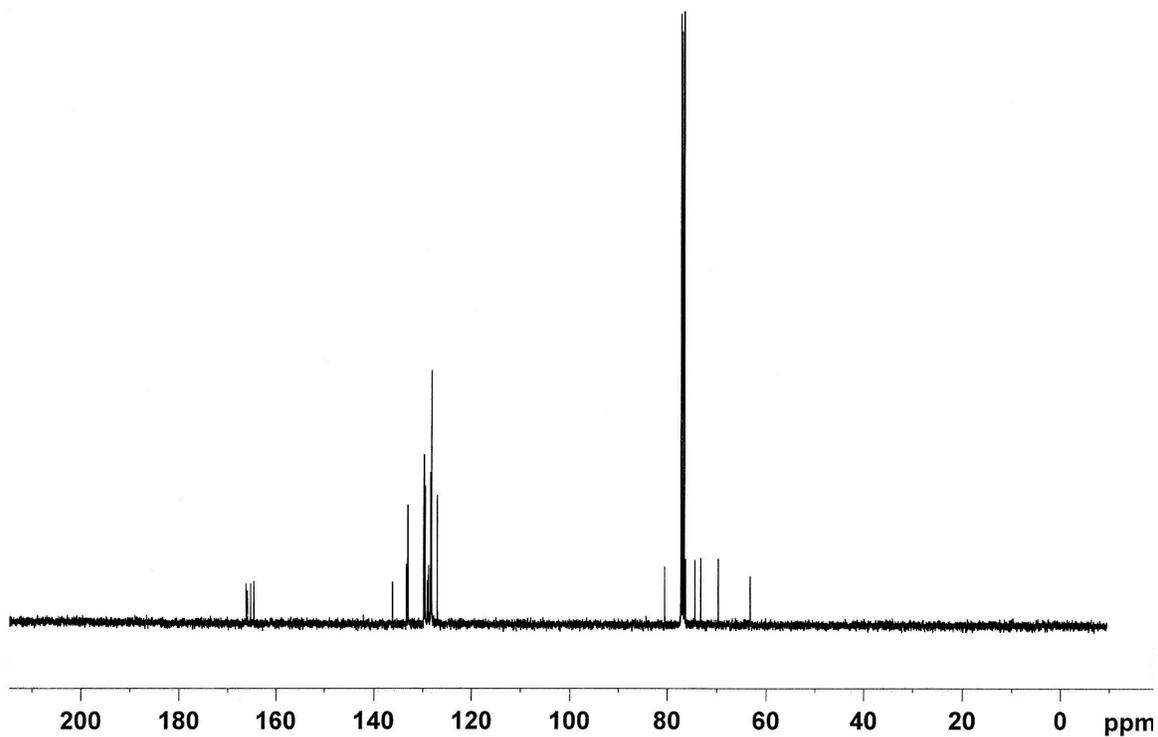
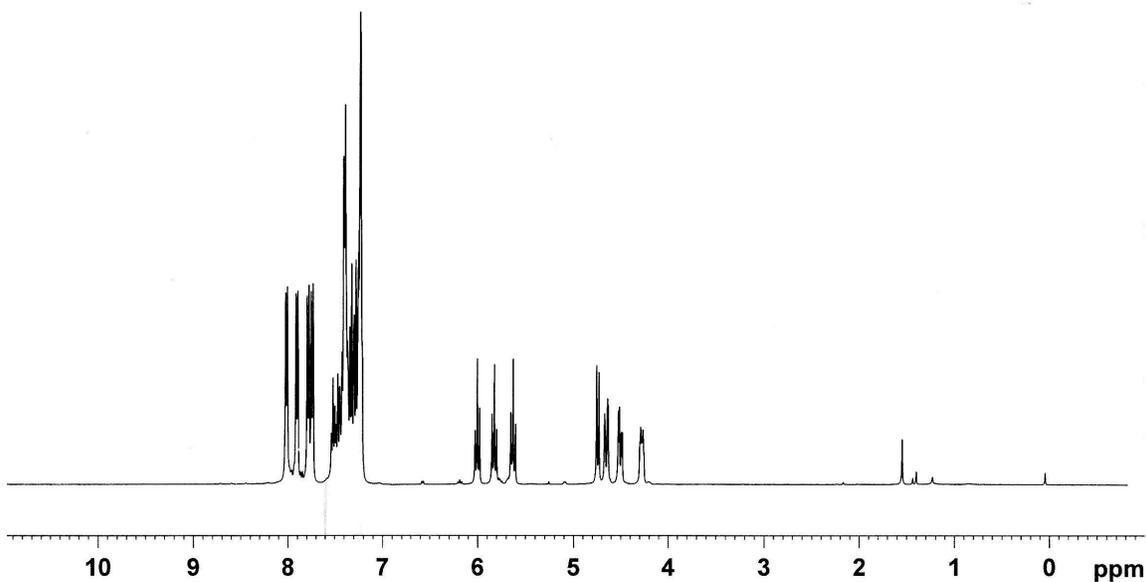
**2D-NOESY:**

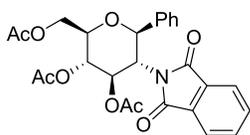




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.74 (dd, *J* = 17.6, 7.6 Hz, 4H), 7.2-7.6 (m, 17H), 6.02 (t, *J* = 9.6 Hz, 1H; *H3*), 5.84 (t, *J* = 9.6 Hz, 1H; *H4*), 5.65 (t, *J* = 9.6 Hz, 1H; *H2*), 4.76 (d, *J* = 9.6 Hz, 1H; *H1*), 4.68 (dd, *J* = 12.0 and 2.4 Hz, 1H; *H6*), 4.52 (dd, *J* = 12.0 and 4.8 Hz, 1H; *H7*), 4.29 (ddd, *J* = 12.0, 4.8 and 2.0 Hz, 1H; *H5*).

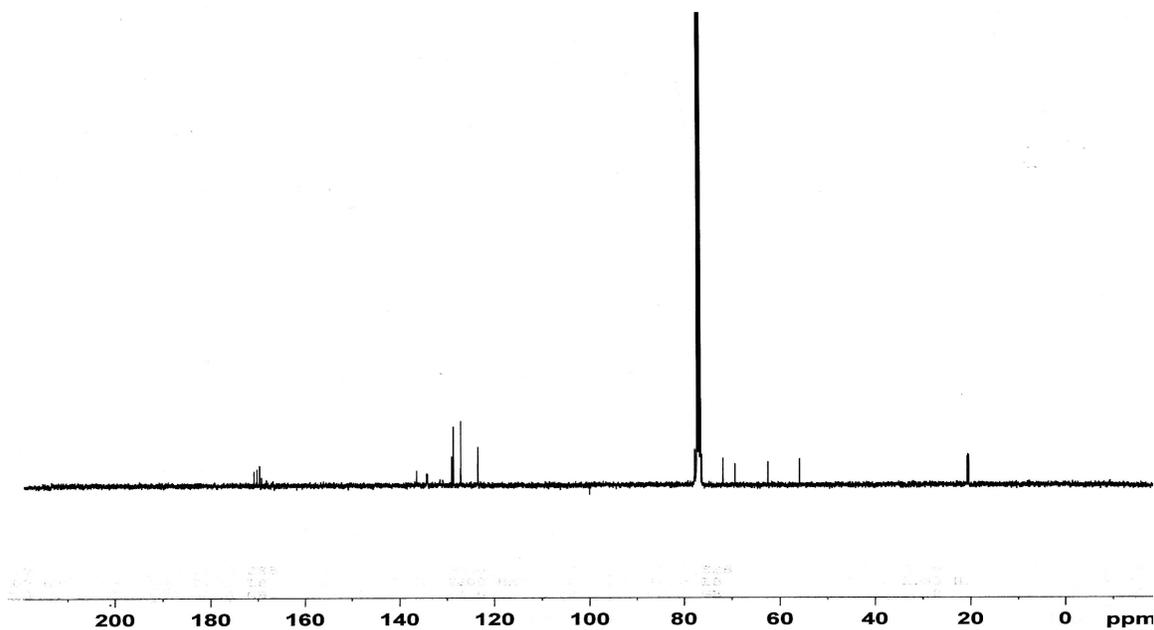
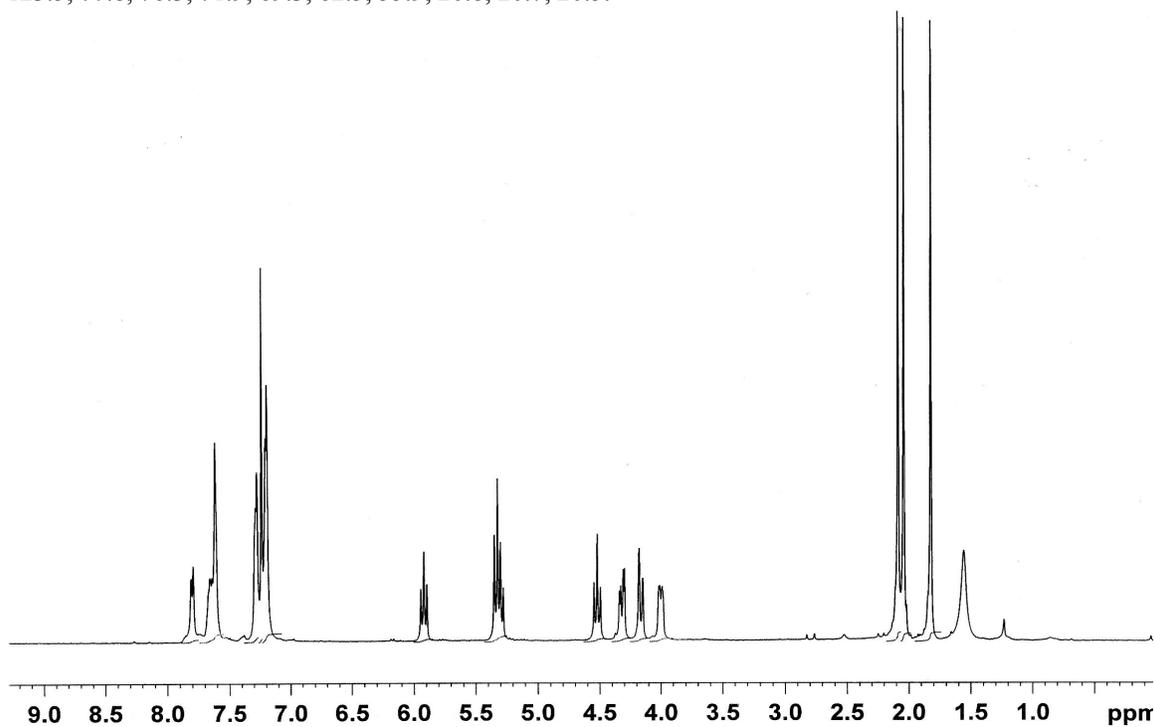
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.7, 170.4, 169.5, 168.9, 160.0, 128.5, 128.3, 80.0, 76.1, 74.4, 72.6, 68.7, 62.4, 55.2, 20.7, 20.6, 20.4.



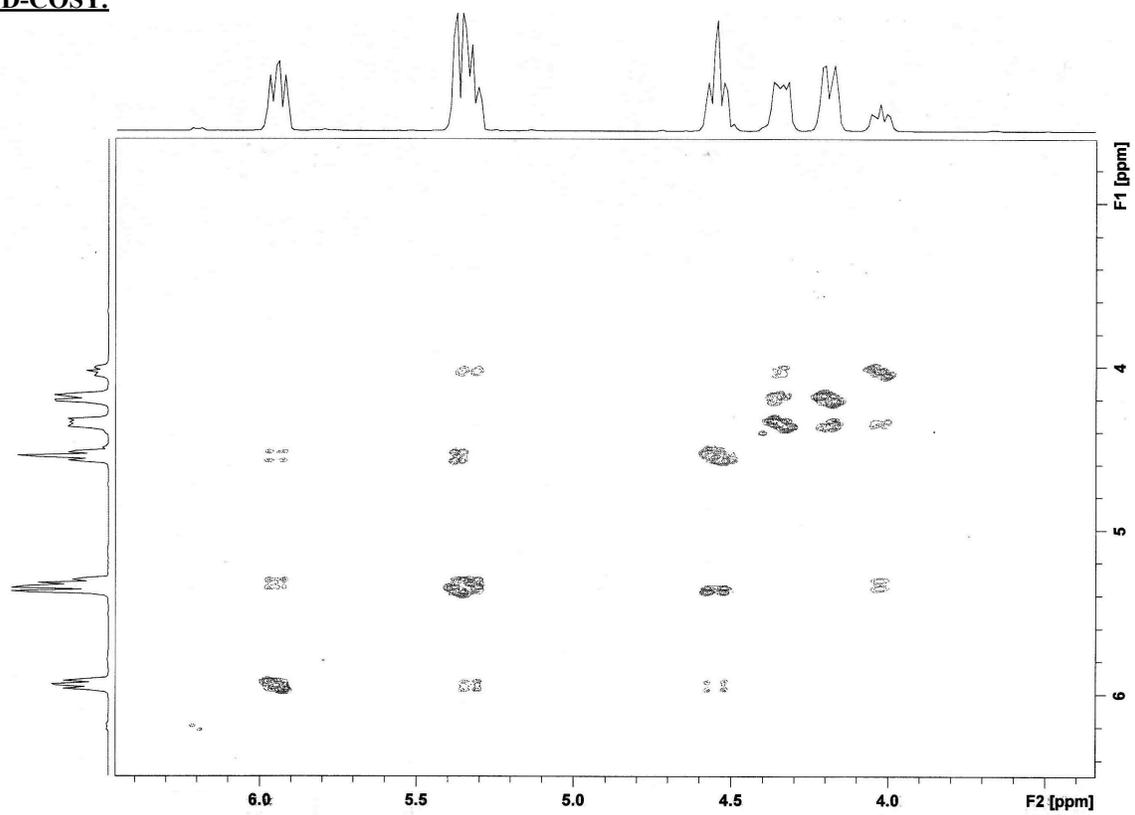


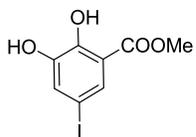
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.80 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.62 (s, 2H), 7.21-7.29 (m, 5H), 5.92 (t, *J* = 9.6 Hz, 1H; *H3*), 5.34 (d, *J* = 10.4 Hz, 1H; *H1*), 5.31 (t, *J* = 9.6 Hz, 1H; *H4*), 4.52 (t, *J* = 10.4 Hz, 1H; *H2*), 4.32 (dd, *J* = 12.4 and 4.8 Hz, 1H; *H6*), 4.17 (dd, *J* = 12.4 and 2.0 Hz, 1H; *H7*), 4.04 (ddd, *J* = 10.0, 4.4 and 2.0 Hz, 1H, *H5*), 2.10 (s, 3H), 2.05 (s, 3H), 1.83 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 170.8, 170.1, 169.6, 169.2, 136.4, 134.3, 134.1, 129.0, 128.6, 127.1, 123.5, 77.8, 76.3, 71.9, 69.3, 62.5, 55.9, 20.8, 20.7, 20.5.



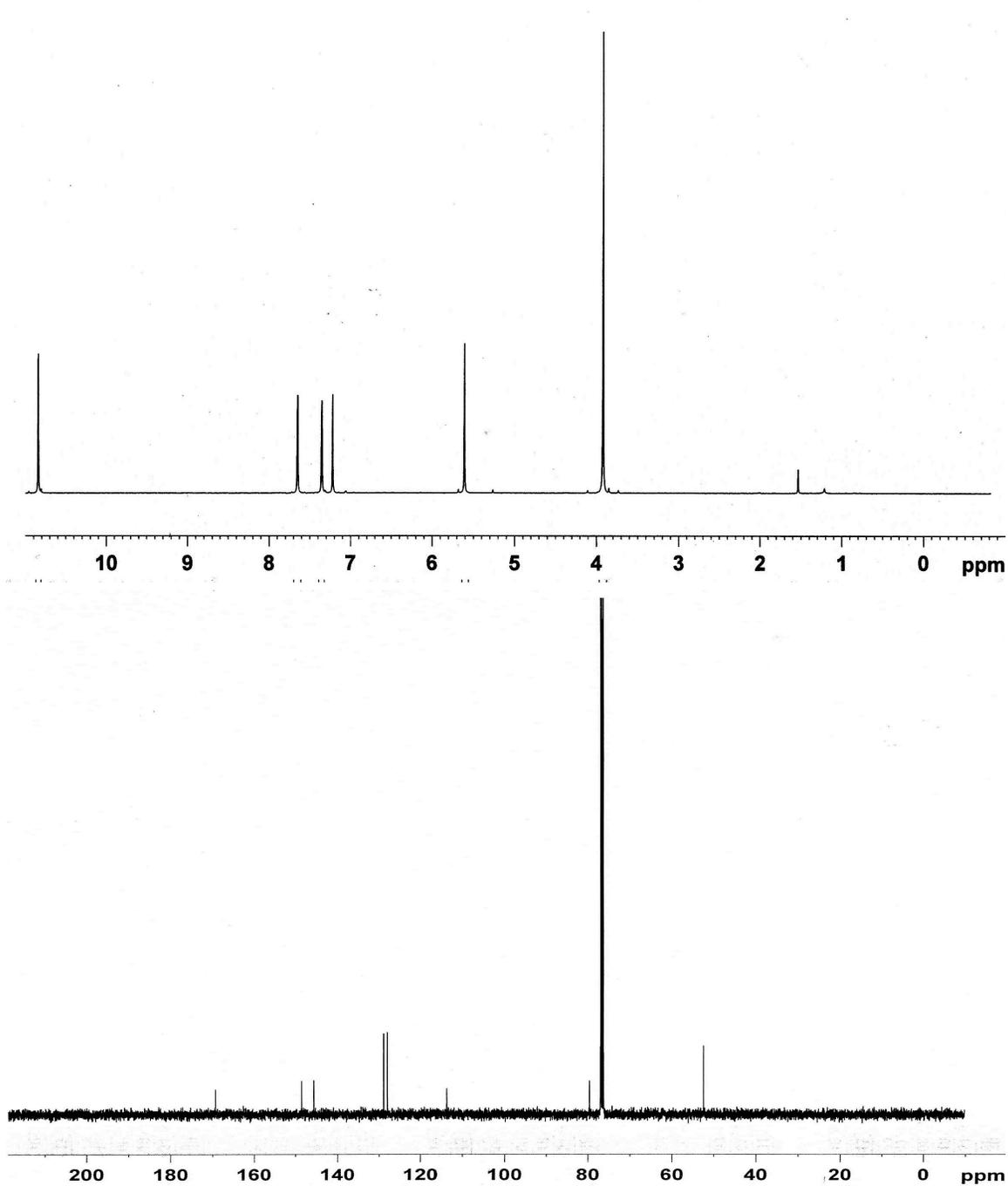
**2D-COSY:**

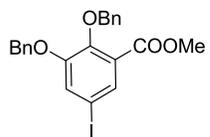




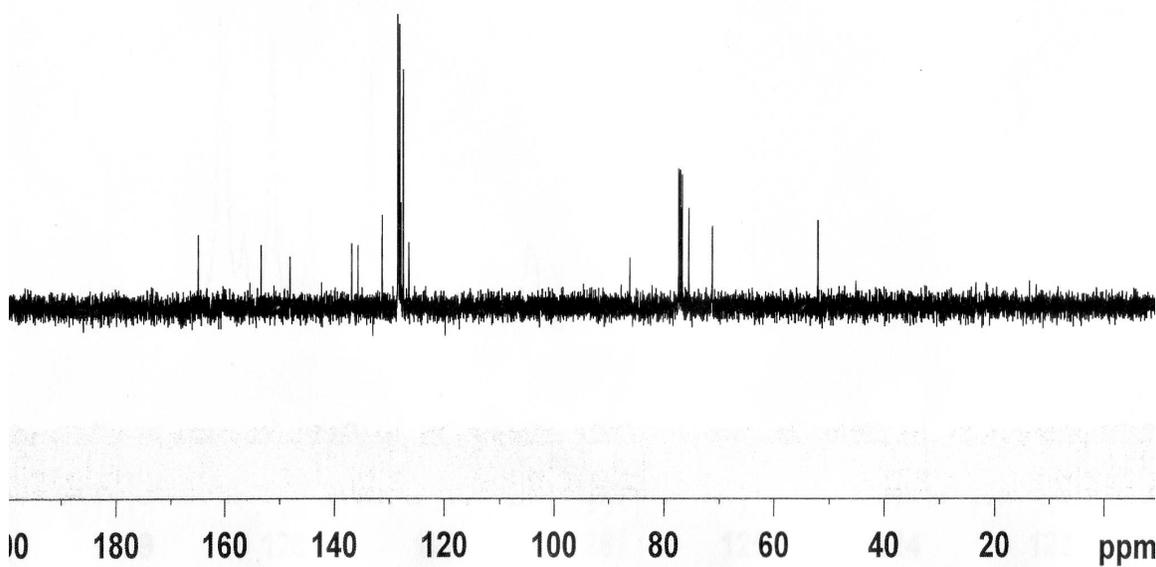
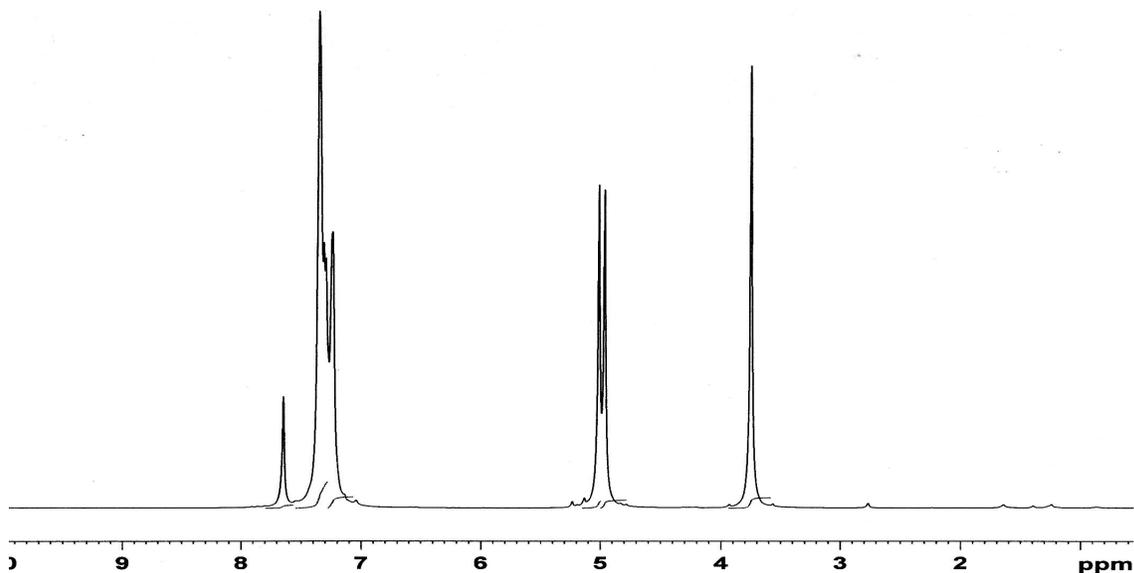
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** 10.72 (s, 1H), 7.54 (s, 1H), 7.53 (s, 1H), 5.49 (s, 1H), 3.80 (s, 3H).

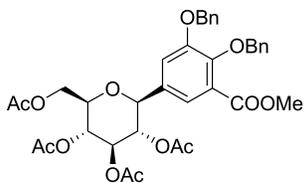
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** 169.2, 148.5, 145.6, 128.8, 128.0, 113.7, 79.7, 52.5.





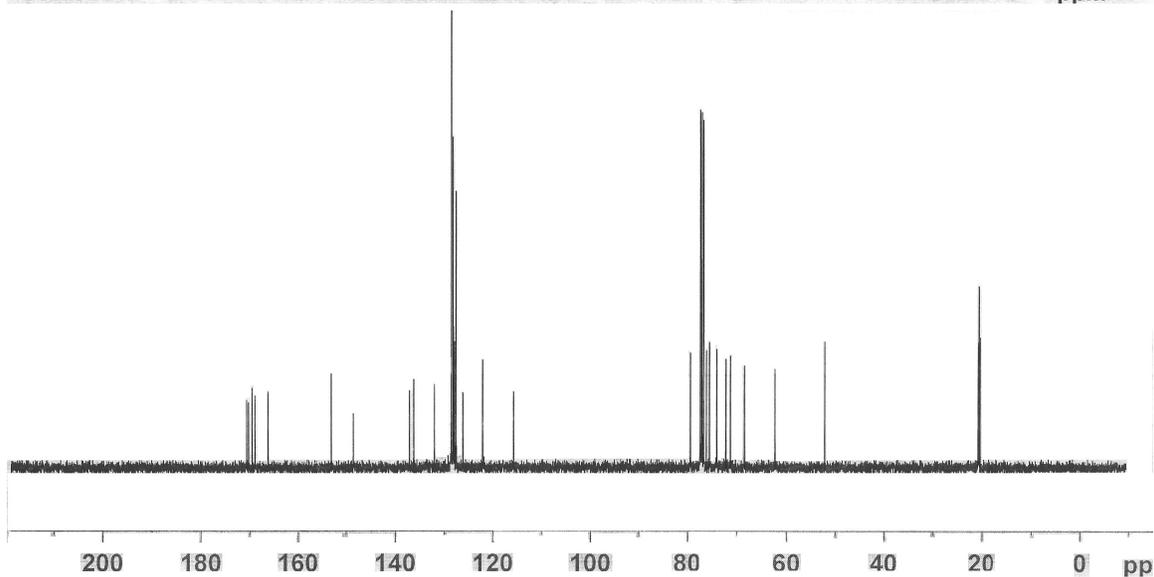
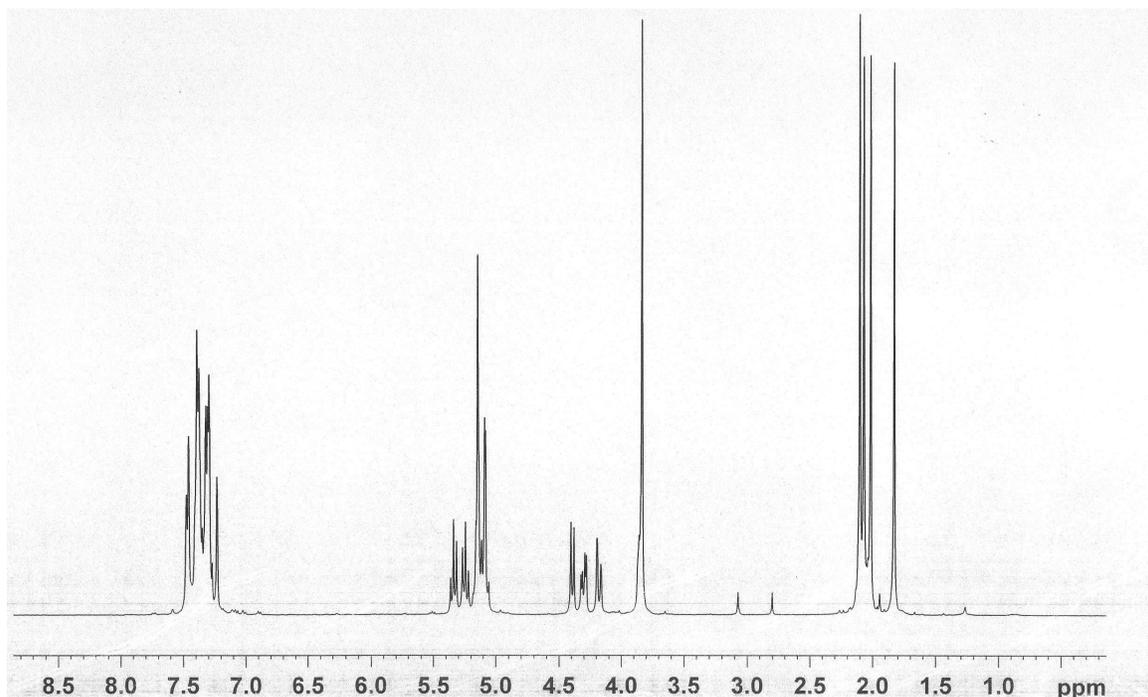
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** 7.61 (s, 1H), 7.23-7.36 (m, 11H), 5.04 (s, 2H), 4.99 (s, 2H), 3.77 (s, 3H).  
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** 164.9, 153.4, 148.1, 136.9, 135.7, 131.3, 128.42, 128.4, 128.3, 128.1, 127.8, 127.4, 126.4, 86.1, 75.5, 71.3, 52.1.

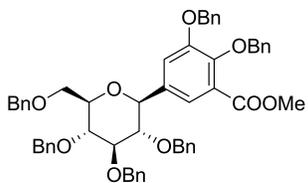




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** 7.19-7.44 (m, 12H), 5.30 (t,  $J = 9.6$  Hz, 1H, *H*3), 5.21 (t,  $J = 9.6$  Hz, 1H, *H*4), 5.12 (s, 2H), 5.04 (s, 2H), 5.04 (t,  $J = 9.6$  Hz, 1H, *H*2), 4.35 (d, 10 Hz, 1H, *H*1), 4.28 (dd,  $J = 12.4$  Hz, 4.8 Hz, 1H, *H*6), 4.14 (d,  $J = 12.0$  Hz, 1H, *H*7), 3.80 (s, 3H), 3.80-3.90 (m, 1H, *H*5), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.79 (s, 3H).

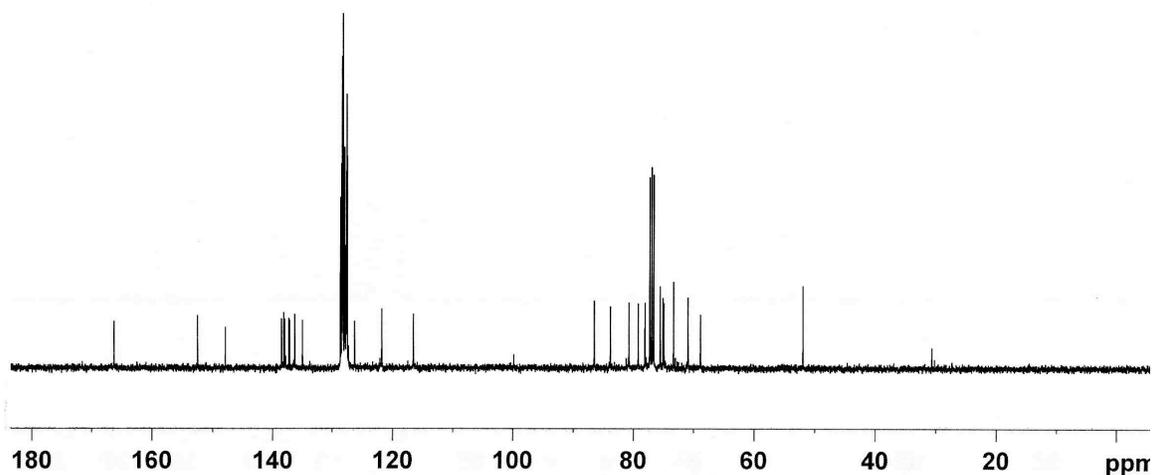
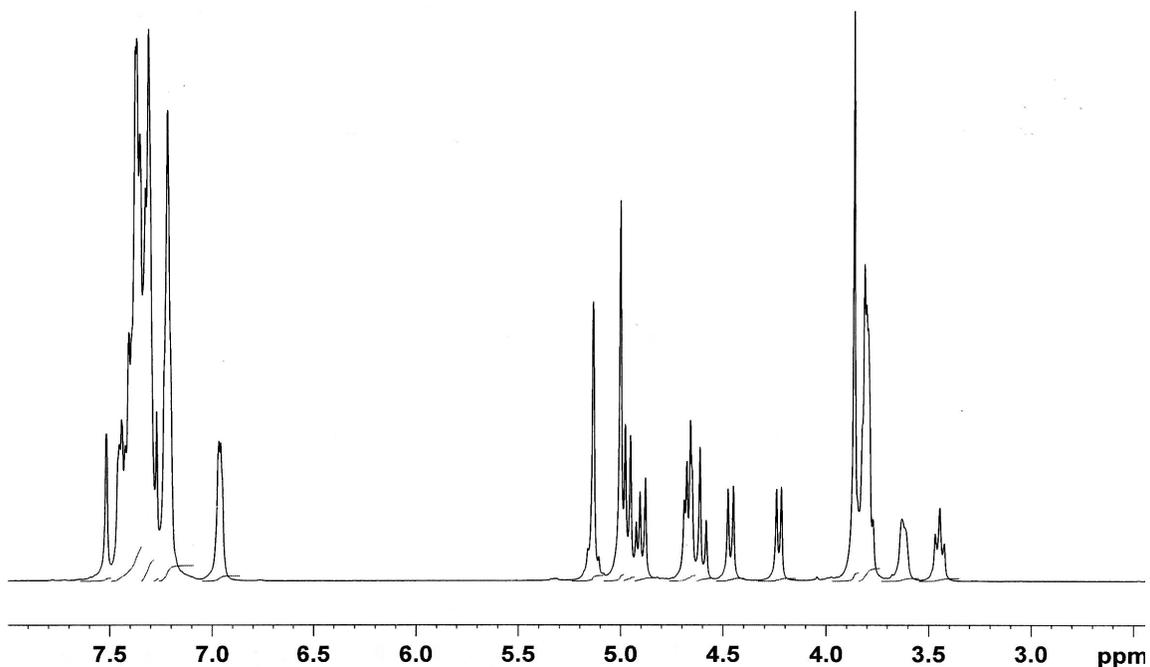
**<sup>13</sup>C (100 MHz, CDCl<sub>3</sub>):** 170.7, 170.3, 169.5, 169.0, 166.3, 153.1, 148.6, 137.2, 136.3, 132.1, 128.6, 128.3, 128.2, 128.0, 127.7, 126.3, 122.2, 115.8, 79.5, 76.2, 75.6, 74.1, 72.3, 71.3, 68.6, 62.4, 52.2, 20.8, 20.7, 20.4.

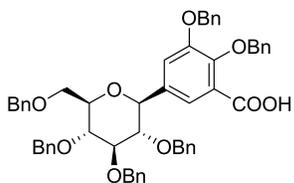




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.55 (d, *J* = 1.2 Hz, 1H), 7.22-7.49 (m, 29H) 7.00 (m, 2H), 5.16 (s, 2H), 5.02 (s, 2H), 4.90-5.03 (m, 3H), 4.60-4.71 (m, 3H), 4.49 (d, *J* = 10.4Hz, 1H), 4.26 (d, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 3.82-3.86 (m, 5H), 3.61-3.66 (m, 1H), 3.46 (t, *J* = 8.8 Hz, 1H).

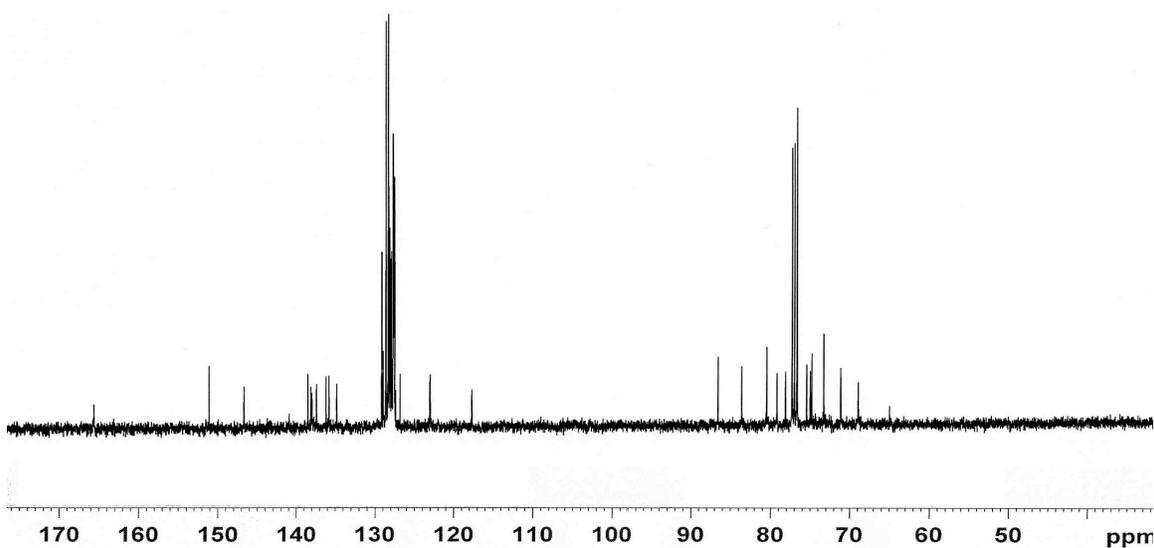
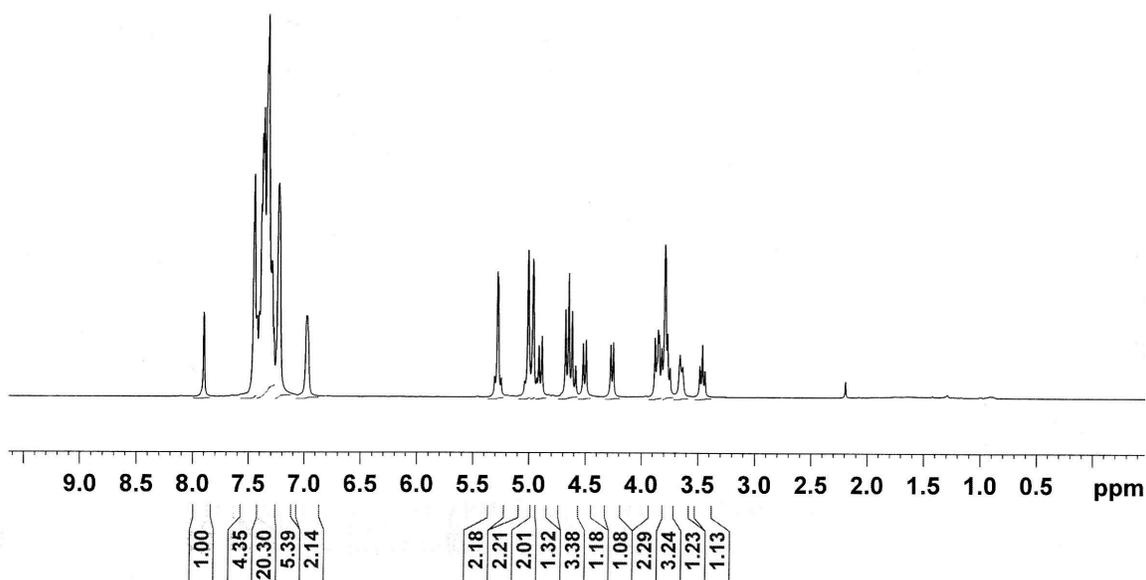
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 166.3, 152.5, 147.9, 138.6, 138.2, 138.0, 137.3, 137.2, 136.4, 135.1, 128.7, 128.5, 128.4, 128.3, 128.26, 128.2, 128.0, 127.9, 127.7, 127.6, 127.57, 127.54, 17.5, 86.6, 83.9, 80.8, 79.2, 78.1, 75.6, 75.55, 75.1, 75.0, 73.3, 70.9, 68.9, 52.0.

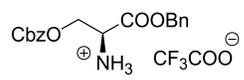




**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.89 (s, 1H), 6.95-7.43 (m, 29H), 6.95 (s, 2H), 5.26 (s, 2H), 4.99 (s, 2H), 4.95 (d, *J* = 3.3 Hz, 2H), 4.80-4.90 (m, 1H), 4.56-4.67 (m, 3H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.25 (d, *J* = 9.0 Hz, 1H), 3.70-3.86 (m, 5H), 3.51-3.52 (m, 1H), 3.44 (t, *J* = 8.7 Hz, 1H).

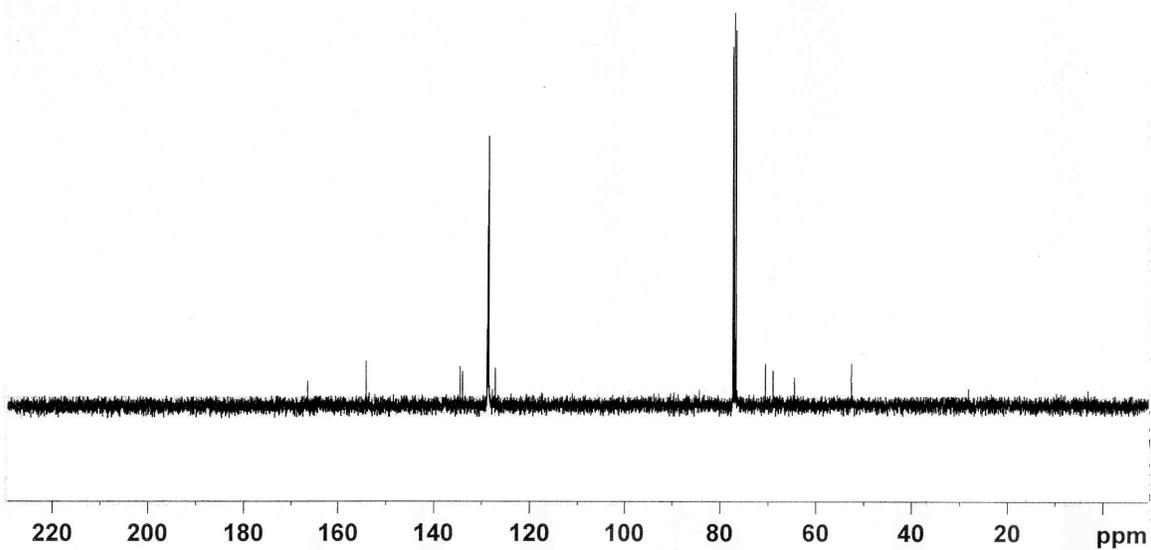
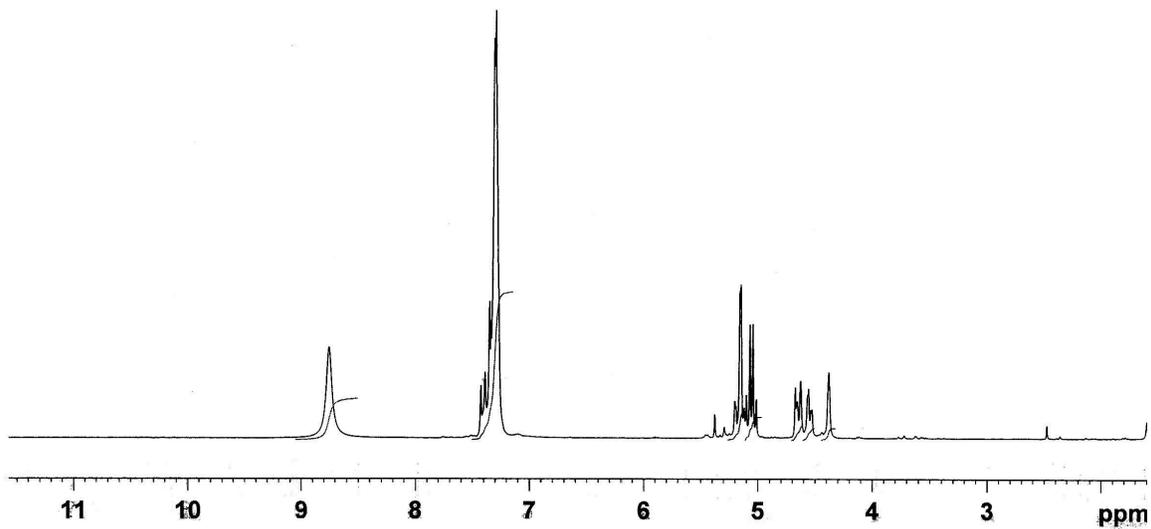
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 165.8, 151.1, 146.9, 138.3, 138.2, 137.6, 136.4, 136.0, 135.0, 129.1, 129.0, 128.6, 128.31, 128.28, 128.1, 128.0, 127.9, 127.7, 127.6, 127.54, 127.50, 126.8, 123.0, 117.9, 86.8, 83.9, 80.7, 79.5, 78.4, 75.7, 75.2, 75.0, 73.5, 71.4, 69.2.

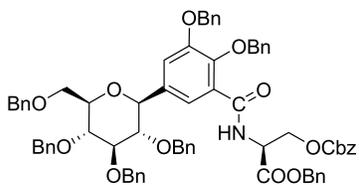




**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta$  8.8 (s, 3H), 7.30-7.43 (m, 4H), 5.12-5.20 (m, 2H), 5.06 (q,  $J = 12$  Hz, 2H), 4.65 (d,  $J = 11.2$  Hz, 1H), 4.55 (dd,  $J = 12$  and 4 Hz, 1H), 4.38 (s, 1H).

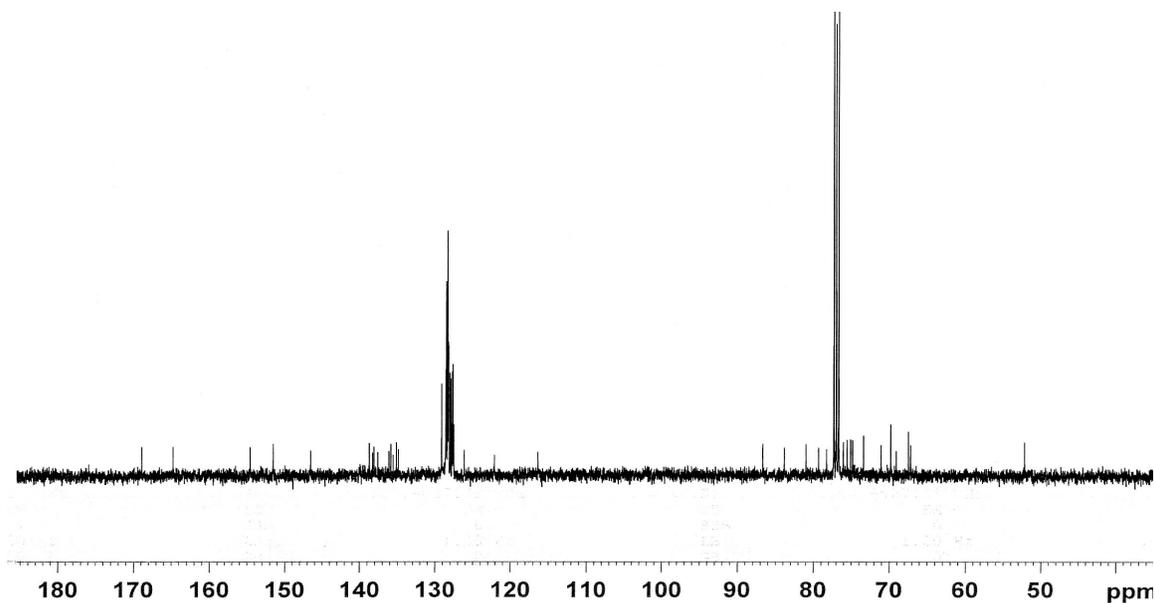
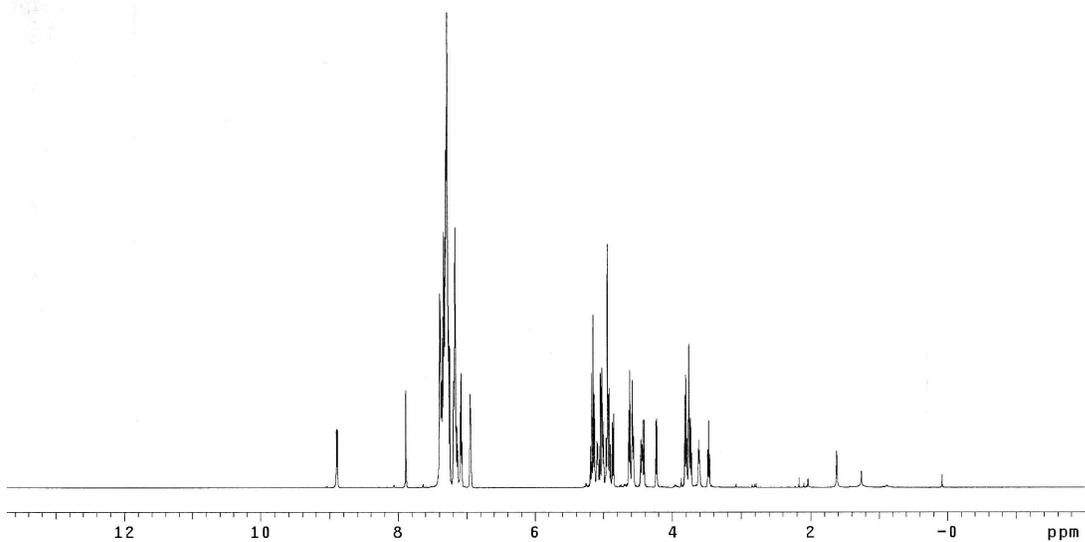
**$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):**  $\delta$  166.4, 154.1, 134.5, 134.0, 128.9, 128.7, 128.6, 128.56, 128.5, 127.1, 70.6, 69.0, 64.5, 52.6.

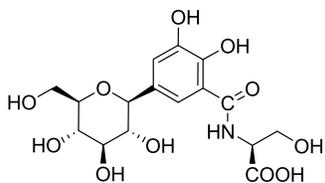




**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** 8.89 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 1.8 Hz, 1H), 7.26-7.39 (m, 29H), 7.13-7.19 (m, 7H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.95 (t, *J* = 3.6 Hz, 2H), 5.17 (t, *J* = 12 Hz, 1H), 5.14 (dd, *J* = 10.8, 1.2 Hz, 2H), 5.09 (quint, *J* = 3.6 Hz, 1H), 5.04 (t, *J* = 12 Hz, 1H), 5.01 (dd, *J* = 10.8 and 4.2 Hz, 2H), 4.90-4.96 (m, 4H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 4.2 Hz, 1H), 4.62 (s, 1H), 4.56 (s, 1H), 4.56-4.59 (m, 1H), 4.45 (dd, *J* = 11.4, 4.8 Hz, 1H), 4.42 (d, *J* = 10.2 Hz, 1H), 4.23 (d, *J* = 9.0 Hz, 1H), 3.81 (d, *J* = 9.6 Hz, 1H), 3.79 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 1.8 Hz, 2H), 3.73 (t, *J* = 3.6 Hz, 1H), 3.61 (dt, *J* = 9.6 and 3.6 Hz, 1H), 3.47 (t, *J* = 9.0 Hz, 1H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 168.9, 164.7, 154.5, 151.5, 146.5, 138.7, 138.3, 138.1, 137.6, 136.1, 135.9, 135.5, 135.1, 134.9, 129.1, 128.6, 128.5, 128.4, 128.3, 128.27, 128.23, 128.21, 128.0, 127.9, 127.7, 127.6, 127.5, 126.1, 122.1, 116.4, 86.7, 83.9, 81.0, 79.3, 78.3, 76.1, 75.6, 75.1, 74.9, 73.4, 71.1, 69.8, 69.1, 67.5, 67.2, 52.2.





**<sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>OD):** 7.41 (s, 1H), 7.00 (s, 1H), 4.68 (s, 1H), 4.00(d, *J* = 9.0 Hz, 2H), 3.92 (dd, *J* = 11.4 and 3.6 Hz, 1H), 3.82 (d, *J* = 10.8 Hz, 1H), 3.67 (dd, *J* = 11.4 and 4.8 Hz, 1H), 3.38-3.44 (m, 2H), 3.30-3.34 (m, 2H), 3.26 (d, *J* = 1.2 Hz).

**<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD):** δ 173.4, 170.7, 150.0, 146.8, 131.4, 119.5, 119.0, 116.5, 83.1, 82.0, 79.7, 76.3, 71.7, 62.9, 56.3, 49.9.

