

# **Supporting information**

## **Multiple and Regioselective Introduction of Protected Sulfates into Carbohydrates using Sulfuryl Imidazolium Salts**

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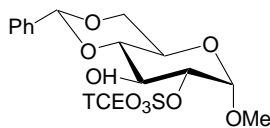
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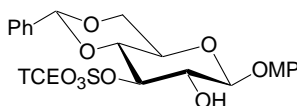
## General Information

All reactions were carried out under argon with freshly distilled solvents unless otherwise noted. Tetrahydrofuran (THF) and diethyl ether ( $\text{Et}_2\text{O}$ ) were distilled from sodium metal in the presence of benzophenone under argon.  $\text{CH}_2\text{Cl}_2$  was distilled from calcium hydride under nitrogen. Silica gel flash chromatography (flash chromatography) was performed using silica gel 60 Å (230-400 mesh). For  $^1\text{H}$  NMR in  $\text{CDCl}_3$ , chemical shifts ( $\delta$ ) are reported in ppm relative to tetramethylsilane ( $\delta$  0.0, internal standard). For  $^1\text{H}$  NMR in  $\text{DMSO}-d_6$ , chemical shifts are reported in ppm relative to the solvent residual peak ( $\delta$  2.49). For  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ , chemical shifts are reported in ppm relative to  $\text{CDCl}_3$  ( $\delta$  77.0 for the central peak). For  $^{13}\text{C}$  NMR in  $\text{DMSO}-d_6$ , chemical shifts are reported in ppm relative to  $\text{DMSO}-d_6$  ( $\delta$  39.5 for the central peak). All peak assignments were confirmed using 2D-NMR (COSY, HMQC) experiments. Optical rotations were measured at the sodium D line at ambient temperature in cells with 1 dm path length. All melting points are uncorrected.

## Selective Sulfations



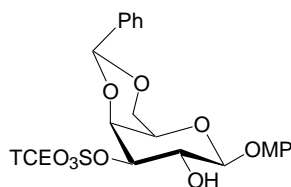
**Methyl-2-*O*-trichloroethylsulfo-4:6-*O*-benzylidene- $\alpha$ -D-glucopyranoside (20)** Prepared from carbohydrate **3**<sup>1</sup> according to the general procedures described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.4 (b, 1H, OH), 3.5-3.5 (m, 4H, OCH<sub>3</sub>, H4), 3.8-3.9 (m, 2H, H6', H5), 4.2-4.3 (m, 2H, H3, H6), 4.5 (dd, 1H,  $J$  = 9.4, 3.7 Hz, H2), 4.7, 4.8 (AB system, 2H,  $J$  = 10.7 Hz, CH<sub>2</sub>CCl<sub>3</sub>), 5.1 (d, 1H,  $J$  = 3.6 Hz, H1), 5.5 (s, 1H, CHPh), 7.4 (m, 3H, ArH), 7.4 (m, 2H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  55.7, 61.7, 68.3, 68.6, 79.7, 81.1, 81.9, 92.5, 97.2, 102.0, 126.1, 128.3, 129.4, 136.5;  $[\alpha]_D^{26}$  = -44.2 (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z$  = 492.9910, C<sub>16</sub>H<sub>20</sub>Cl<sub>3</sub>O<sub>9</sub>S (M+H)<sup>+</sup> requires 492.9894.



***p*-Methoxyphenyl-3-*O*-trichloroethylsulfo-4:6-*O*-benzylidene- $\beta$ -D-glucopyranoside (21).**

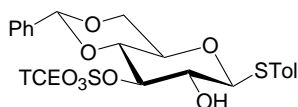
Prepared from carbohydrate **4**<sup>2</sup> according to the general procedures described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). White solid. For yields see Table 1. Mp 130-132 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.8, (d, 1H,  $J$  = 3.1 Hz, OH), 3.5 (ddd, 1H,  $J$  = 9.6, 9.5, 4.8, H5), 3.7-3.8 (m, 5H, OCH<sub>3</sub>, H6', H4), 3.9 (dt, 1H,  $J$  = 8.9, 7.5, 3.1, H2), 4.3 (dd, 1H,  $J$  = 10.5, 9.9, 4.9, H6), 4.5-4.6 (AB system, 2H,  $J$  = 10.9 Hz, CH<sub>2</sub>CCl<sub>3</sub>), 4.8, 4.9 (m, 2H, H3, H1), 5.5 (s, 1H, CHPh), 6.8 (d, 2H,  $J$  = 8.9 Hz, ArH), 7.0 (d, 2H,  $J$  = 9.0 Hz, ArH), 7.3 (m, 3H, ArH), 7.4 (m, 2H, ArH); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.8, 65.1, 68.0, 71.9, 77.5, 79.6,

86.8, 93.4, 100.9, 101.8, 115.0, 118.5, 126.6, 128.6, 129.4, 137.4, 151.2, 155.3;  $[\alpha]_D^{26} = 76.4$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 585.0154$ , C<sub>22</sub>H<sub>24</sub>Cl<sub>3</sub>O<sub>10</sub>S (M+H)<sup>+</sup> requires 585.0155.



***p*-Methoxyphenyl-3-*O*-trichloroethylsulfo-4:6-*O*-benzylidene- $\beta$ -D-galactopyranoside (22).**

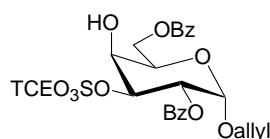
Prepared from carbohydrate **5**<sup>3</sup> according to the general procedures described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). White solid. For yields see Table 1. Mp 138-140 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.6, (d, 1H,  $J = 2.5$  Hz, OH ), 3.5 (br, 1H, H5), 3.7 (s, 3H, OCH<sub>3</sub>), 4.0 (dd, 1H,  $J = 12.5, 5.4$  Hz, H6'), 4.2-4.3 (m, 2H, H2, H6), 4.6 (d, 1H,  $J = 3.3$  Hz, H4), 4.7-4.7 (m, 2H, H3, 1H of CH<sub>2</sub>CCl<sub>3</sub>), 4.8 (d, 1H,  $J = 7.7$ , H1 ), 4.9 (d, 1H,  $J = 10.6$  Hz, the second H of CH<sub>2</sub>CCl<sub>3</sub>), 5.5 (s, 1H, CHPh) 6.8 (d, 2H,  $J = 8.9$  Hz, ArH ), 7.0 (d, 2H,  $J = 8.9$  Hz, ArH), 7.3 (m, 3H, ArH), 7.5 (m, 2H, ArH); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.8, 65.5, 67.5, 68.5, 73.4, 79.7, 85.2, 93.2, 100.0, 101.1, 114.9, 118.3, 126.5, 128.6, 129.4, 138.3, 151.3, 155.1;  $[\alpha]_D^{26} = 81.6$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 585.0168$ , C<sub>22</sub>H<sub>24</sub>Cl<sub>3</sub>O<sub>10</sub>S (M+H)<sup>+</sup> requires 585.0156.



***p*-Tolyl-3-*O*-trichloroethylsulfo-4:6-*O*-benzylidene-1-thio- $\beta$ -D-glucopyranoside (23)**

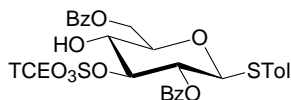
Prepared from carbohydrate **6**<sup>3</sup> according to the general procedures described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). White solid. For yields see Table 1. Mp 96-98 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.3, (s, 3H, CH<sub>3</sub>), 2.8 (s, 1H, OH ), 3.5-3.9 (m, 4H, H5, H4, H2, H6'), 4.4 (dd, 1H,  $J = 10.3, 4.5$  Hz, H6), 4.4-4.5 (m, 3H, CH<sub>2</sub>CCl<sub>3</sub>, H1), 4.8

(t, 1H,  $J = 8.9$  Hz, H3), 5.4 (s, 1H, CHPh) 7.1-7.4 (m, 9H, ArH );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.2, 68.4, 70.4, 70.7, 77.8, 79.7, 86.0, 88.7, 92.5, 102.2, 126.0, 126.2, 128.6, 129.6, 130.1, 134.3, 136.1, 139.5;  $[\alpha]_{\text{D}}^{26} = 54.3$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 584.9981$ ,  $\text{C}_{22}\text{H}_{24}\text{Cl}_3\text{O}_8\text{S}_2$   $(\text{M}+\text{H})^+$  requires 584.9978.



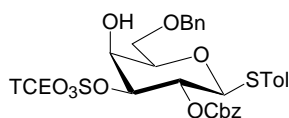
**Allyl-2,6-di-O-benzoyl-4-O-trichloroethylsulfo- $\alpha$ -D-galactopyranoside (26).**

Prepared from carbohydrate **9**<sup>4</sup> using the procedures described for compound **25** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.91 (d, 1H,  $J = 4.0$  Hz, OH), 3.99, 4.15 (dd of AB system, 2H,  $J = 13.1, 5.8$  Hz, allyl  $\text{CH}_2$ ), 4.27 (t, 1H,  $J = 6.2$  Hz, H5), 4.4-4.7 (m, 5H, H6,  $\text{CH}_2\text{CCl}_3$ , H4, H6'), 5.0- 5.3 (m, 4H, olefinic  $\text{CH}_2$ , H1, H3), 5.56 (dd, 1H,  $J = 3.3$  Hz, H2), 5.79 (m, 1H, olefinic H), 7.44 (m, 4H, ArH), 7.58 (m, 2H, ArH), 8.04 (m, 4H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  62.5, 67.6, 67.6, 68.9, 79.8, 81.6, 92.2, 95.5, 118.1, 127.5, 128.5, 128.7, 129.0, 129.2, 129.7, 129.9, 132.9, 133.5, 133.6, 165.6, 166.6;  $[\alpha]_{\text{D}}^{26} = 59.8$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 639.0261$ ,  $\text{C}_{25}\text{H}_{26}\text{Cl}_3\text{O}_{11}\text{S}$   $(\text{M}+\text{H})^+$  requires 639.0251.



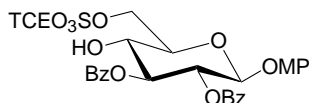
***p*-Tolyl-2,6-O-dibenzoyl-3-O-trichloroethylsulfo-1-thio- $\beta$ -D-glucopyranoside (27).** Prepared from carbohydrate **10** using the procedures described for compound **25** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.25 (s, 3H,  $\text{CH}_3$ ), 3.6-3.8 (m, 3H, OH, H5, H4),

4.53-4.6 (m, 3H, CH<sub>2</sub>CCl<sub>3</sub>, H6), 4.76-4.84 (m, 2H, H6', H1), 4.97 (t, 1H,  $J = 9.5$  Hz, H3 ), 5.19 (t, 1H,  $J = 9.5$  Hz, H2 ), 6.95, 7.34 (AB system, 4H,  $J = 7.5$  Hz, ArH), 7.4-7.6 (m, 6H, ArH), 8.0 (m, 4H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  21.1, 62.9, 68.3, 69.5, 77.9, 79.9, 85.6, 88.0, 92.3, 126.8, 128.5, 129.06, 129.1, 129.6, 130.01, 130.1, 133.66, 133.69, 134.3, 138.9, 165.1, 167.3;  $[\alpha]_D^{26} = 98.8$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 705.0177$ , C<sub>29</sub>H<sub>28</sub>Cl<sub>3</sub>O<sub>10</sub>S<sub>2</sub> (M+H)<sup>+</sup> requires 705.0189.



***p*-Tolyl-2-*O*-benzyloxycarbonyl-3-*O*-trichloroethylsulfo-6-*O*-benzyl-1-thio- $\beta$ -D-**

**galactopyranoside (28).** Prepared from carbohydrate **11** using the procedures described for compound **25** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.2 (s, 3H, CH<sub>3</sub>), 3.0 (br, 1H, OH), 3.6 (t, 1H,  $J = 8.9$  Hz, H5), 3.7 (m, 2H, H6, H6'), 4.5-4.6 (m, 6H, CH<sub>2</sub>Ph, H4, H1, H3, 1H of CH<sub>2</sub>CCl<sub>3</sub>), 4.7 (d, 1H,  $J = 10.7$  Hz, 1H of CH<sub>2</sub>CCl<sub>3</sub> ), 5.1-5.2 (m, 3H, H2, CH<sub>2</sub>Ph), 7.0 (d, 2H,  $J = 7.8$  Hz, ArH), 7.2-7.3 (m, 12H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  21.1, 68.0, 69.4, 70.4, 70.8, 73.9, 76.0, 79.9, 84.9, 86.4, 92.4, 127.5, 127.8, 128.1, 128.3, 128.6, 128.6, 128.7, 129.7, 133.8, 134.7, 137.0, 138.8, 153.9;  $[\alpha]_D^{26} = 95.8$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 721.0525$ , C<sub>30</sub>H<sub>32</sub>Cl<sub>3</sub>O<sub>10</sub>S<sub>2</sub> (M+H)<sup>+</sup> requires 721.0502.

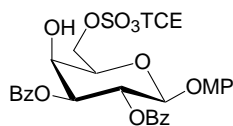


***p*-Methoxyphenyl-2,3-di-*O*-benzoyl-6-*O*-trichloroethylsulfo- $\beta$ -D-glucopyran-oside (29).**

Prepared from carbohydrate **12**<sup>5</sup> according to general procedure B described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For the yield

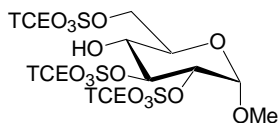


see Table 1.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.7 (s, 4H,  $\text{OCH}_3$ , OH), 4.0 (m, 2H, H5, H4), 4.6-4.8 (m, 4H, H6, H6',  $\text{CH}_2\text{CCl}_3$ ), 5.2 (d, 1H,  $J = 7.8$  Hz, H1), 5.5 (t, 1H,  $J = 9.3$  Hz, H3), 5.7 (t, 1H,  $J = 9.2$  Hz, H2), 6.7 (d, 2H,  $J = 8.8$  Hz, ArH), 6.9 (d, 2H,  $J = 8.8$  Hz, ArH), 7.4 (m, 6H, ArH), 7.9 (d, 2H,  $J = 7.3$  Hz, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.5, 68.9, 71.0, 71.8, 73.5, 76.7, 79.6, 92.3, 100.3, 114.6, 118.5, 128.4, 128.5, 128.9, 129.6, 129.9, 133.4, 133.8, 150.7, 155.8, 165., 167.6;  $[\alpha]_{\text{D}}^{26} = -36.2$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 705.0370$  ( $\text{M}+\text{H}$ ) $^+$   $\text{C}_{29}\text{H}_{28}\text{Cl}_3\text{O}_{12}\text{S}$  requires 705.0367.

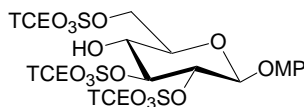


***p*-Methoxyphenyl-2,3-di-*O*-benzoyl-6-*O*-trichloroethylsulfo- $\beta$ -D-glactopyranoside (30).**

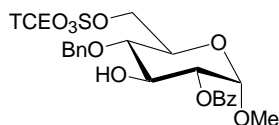
Prepared from carbohydrate **13**<sup>6</sup> according to general procedure B described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). White solid. For the yield see Table 1. Mp 71-73  $^{\circ}\text{C}$ ,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.7 (d, 1H,  $J = 4.5$  Hz, OH at C2), 3.7 (s, 3H,  $\text{OCH}_3$ ), 4.2 (t, 1H,  $J = 6.56$  Hz, H5), 4.4 (s, 1H, H4), 4.6-4.7 (m, 4H, H6, H6',  $\text{CH}_2\text{CCl}_3$ ), 5.1 (d, 1H,  $J = 7.9$  Hz, H1), 5.3- 5.4 (dd, 1H,  $J = 10.2, 2.9$  Hz, H3), 5.7 (t, 1H,  $J = 10.1, 8.2$  Hz, H2), 6.7 (d, 2H,  $J = 8.9$  Hz, ArH), 6.9 (d, 2H,  $J = 8.9$  Hz, ArH), 7.3 (m, 4H, ArH), 7.4 (t, 2H, ArH) 7.9 (m, 4H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 66.9, 69.0, 71.7, 71.9, 73.8, 76.7, 79.7, 92.3, 100.7, 114.6, 118.6, 128.4, 128.6, 129.1, 129.7, 129.9, 133.4, 133.7, 150.8, 155.8, 165.4, 165.7;  $[\alpha]_{\text{D}}^{26} = 69.2$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 705.0394$  ( $\text{M}+\text{H}$ ) $^+$   $\text{C}_{29}\text{H}_{28}\text{Cl}_3\text{O}_{12}\text{S}$  requires 705.0367.



**Methyl-2,3,6-tri-*O*-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (31).** Prepared from carbohydrate **14** according to the general procedures described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.2 (s, 1H, OH), 3.4 (s, 3H,  $\text{OCH}_3$ ), 3.9 (br, 2H, H5, H4), 4.5-4.8 (m, 9H, H6, H6', H2,  $3\text{CH}_2\text{CCl}_3$ ), 5.04 (br, 1H, H3), 5.2 (d, 1H,  $J = 2.8$  Hz, H1);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  56.1, 68., 68.6, 71.4, 78.0, 79.7, 80.2, 80.4, 83.4, 92.2, 92.2, 92.3, 96.3;  $[\alpha]_{\text{D}}^{26} = 69$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 824.7010$  ( $\text{M}+\text{H}$ ) $^+$   $\text{C}_{13}\text{H}_{18}\text{Cl}_9\text{O}_{15}\text{S}_3$  requires 824.7005.

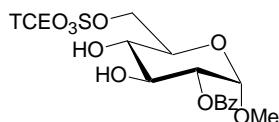


***p*-Methoxyphenyl-2,3,6-tri-*O*-trichloroethylsulfo- $\beta$ -D-glucopyranoside (32).** Prepared from carbohydrate **15** according to general procedure **A** described in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For the yield see Table 1.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.09 (br, 1H, OH), 3.75 (s, 4H,  $\text{OCH}_3$ , H5), 4.04 (t, 1H,  $J = 8.5$  Hz, H4), 4.06-4.9 (m, 10H, H6, H6', H2,  $3\text{CH}_2\text{CCl}_3$ , H3), 5.1 (d,  $J = 8.5$  Hz, 1H), 5.21 (d, 1H,  $J = 6.7$  Hz, H1), 6.81 (d, 2H,  $J = 8.9$  Hz, ArH), 6.98 (d, 2H,  $J = 8.9$  Hz, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 68.2, 70.7, 72.5, 79.8, 80.1, 80.5, 80.8, 85.5, 92.2, 92.2, 92.3, 98.6, 114.9, 118.7, 149.5, 156.4;  $[\alpha]_{\text{D}}^{26} = 77.2$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 916.7208$  ( $\text{M}+\text{H}$ ) $^+$   $\text{C}_{19}\text{H}_{23}\text{Cl}_9\text{O}_{16}\text{S}_3$  requires 916.7188.

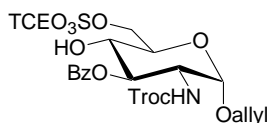


**Methyl-2-*O*-benzoyl-4-*O*-benzyl-6-*O*-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (33).**

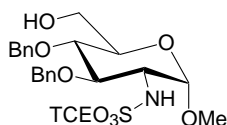
Prepared from carbohydrate **16**<sup>7</sup> using the procedures described for compound **25** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  2.4 (d, 1H,  $J$  = 3.8 Hz, OH), 3.3 (s, 3H, OCH<sub>3</sub>), 3.5 (t, 1H,  $J$  = 9.9 Hz, H4), 3.9 (m, 1H, H5), 4.3 (dt, 1H,  $J$  = 9.4, 8.6, 3.7 Hz H3), 4.5 (m, 2H, H6, H6'), 4.6-4.7 (m, 3H, CH<sub>2</sub>CCl<sub>3</sub>, 1H of CH<sub>2</sub>Ph), 4.8-4.9 (m, 2H, H2, 1H of CH<sub>2</sub>Ph), 4.9 (d, 1H,  $J$  = 3.5 Hz, H1), 7.3-7.5 (m, 8H, ArH), 8.0 (m, 2H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  55.6, 67.9, 72.3, 72.3, 73.7, 75.0, 76.9, 79.6, 92.5, 92.3, 97.0, 128.2, 128.2, 128.5, 128.7, 129.3, 129.9, 133.5, 137.5, 166.3;  $[\alpha]_D^{26}$  = 54.6 (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z$  = 599.0295 (M+H)<sup>+</sup> C<sub>23</sub>H<sub>26</sub>Cl<sub>3</sub>O<sub>10</sub>S requires 599.0312.



**Methyl-2-*O*-benzoyl-6-*O*-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (34).** Prepared from carbohydrate **17**<sup>8</sup> according to general procedure B described in the experimental section. Purified by flash chromatography (1:3, EtOAc:hexanes). Colorless syrup. For the yield see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.3 (b, OCH<sub>3</sub>, 2OH), 3.6 (t, 1H,  $J$  = 9.4 Hz, H4), 3.8 (d, 1H,  $J$  = 9.6 Hz, H5), 4.0 (t, 1H,  $J$  = 9.6 Hz, H3), 4.6 (b, 2H, H6, H6'), 4.7 (b, 2H, CH<sub>2</sub>CCl<sub>3</sub>), 4.9 (dd, 1H,  $J$  = 9.6, 2.3 Hz, H2), 4.9 (d, 1H,  $J$  = 2.3 Hz, H1); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  55.6, 68.5, 69.9, 71.8, 72.3, 73.4, 79.5, 92.4, 97.3, 128.4, 129.1, 129.8, 133.5, 166.4;  $[\alpha]_D^{26}$  = 84.1 (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z$  = 508.9836 (M+H)<sup>+</sup> C<sub>16</sub>H<sub>20</sub>Cl<sub>3</sub>O<sub>10</sub>S requires 508.9843.



**Allyl-2-deoxy-2-N-trichloroethoxyamido-3-O-benzoyl-6-O-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (35).** Prepared from carbohydrate **18**<sup>9</sup> using the procedures described for compound **24** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.1 (br, 1H, OH), 3.84 (t, 1H,  $J$ = 9.3 Hz, H4), 4.05 (m, 2H, H5, H of allyl CH<sub>2</sub>), 4.2 (m, 2H, H of allyl CH<sub>2</sub>, H2), 4.46, 4.65 (AB system, 2H,  $J$ = 12.0 Hz, H6, H6'), 4.64 (s, 2H, CH<sub>2</sub>CCl<sub>3</sub>), 4.73 (s, 2H, Troc CH<sub>2</sub>), 4.97 (d, 1H,  $J$ = 3.5 Hz, H1), 3.3 (m, 4H, olefinic CH<sub>2</sub> of allyl, H3, NH), 5.9 (m, 1H, olefinic H), 7.4 (t, 4H,  $J$ =7.6 Hz, ArH), 7.56 (t, 1H,  $J$ = 7.5 Hz, ArH), 7.99 (d, 2H,  $J$ = 7.4 Hz, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  53.3, 68.8, 69.0, 69.7, 72.1, 74.4, 75.2, 79.6, 92.5, 95.0, 96.4, 119.0, 128.5, 128.6, 130.1, 132.7, 133.8, 154.2, 168.0;  $[\alpha]_D^{26}$  = 69.2 (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z$  = 707.9204, C<sub>21</sub>H<sub>24</sub>NCl<sub>6</sub>O<sub>11</sub>S (M+H)<sup>+</sup> requires 707.9201.

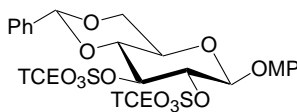


**Methyl-3,4-di-O-benzyl-2-deoxy-2-N-trichloroethoxysulfamido- $\alpha$ -D-glucopyranoside (36).** Prepared from carbohydrate **19**<sup>10</sup> using the procedures described for compound **24** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  1.7 (t, 1H,  $J$  = 6.7 Hz, OH), 3.3 (s, 3H, OCH<sub>3</sub>), 3.6-3.8 (m, 6H, H5, H4, H3, H2, H6, H6'), 4.5-4.5 (AB, 2H,  $J$  = 10.8 Hz, CH<sub>2</sub>CCl<sub>3</sub>), 4.6, 4.8 (AB, 2H,  $J$  = 10.9 Hz, CH<sub>2</sub>Ph), 4.7-5.0 (m, 4H, CH<sub>2</sub>Ph, H1, NH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  55.3, 58.2, 61.4, 71.1, 75.0, 75.6, 77.8, 78.1, 79.2, 93.3, 97.9, 128.0, 128.0, 128.5,

128.6, 137.7;  $[\alpha]_D^{26} = 69.6$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 601.0957$  ( $\text{M}+\text{NH}_4$ )<sup>+</sup>,  $\text{C}_{23}\text{H}_{32}\text{Cl}_3\text{NO}_8\text{S}$  requires 601.0945.

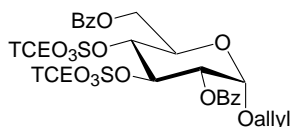
## Multiple Sulfations

**General procedure for synthesis of multiple sulfated carbohydrates.** All multiple sulfations were performed using the general procedure described for compound **40** in the experimental section. For reactions incomplete after 15h, additional equivalents of DMI and reagent **2** were added until no starting material remained by TLC, reaction time varied between 20-40 h. For yields see Table 2.

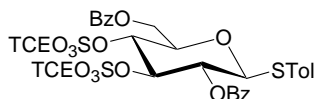


### *p*-Methoxyphenyl-2,3-di-*O*-trichloroethylsulfo-4:6-*O*-benzylidene- $\beta$ -D-glucopyranoside

**(41).** Prepared according to the general procedure. Reaction time 24 h. Flash chromatography (1:5, EtOAc:hexanes) give **41** as a white solid. Mp 132-134 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.6, (ddd, 1H,  $J = 9.4, 9.2, 4.8$  Hz, H5), 3.7 (s, 3H,  $\text{OCH}_3$ ), 3.7-3.9 (m, 2H, H4, H6'), 4.4-4.4 (m, 2H, H6, 1H of  $\text{CH}_2\text{CCl}_3$ ), 4.4, 4.5 (AB, 2H,  $J = 11.1$  Hz,  $\text{CH}_2\text{CCl}_3$ ), 4.8-4.8 (m, 2H,  $\text{CH}_2\text{CCl}_3$ ), 4.9-5.0 (m, 2H, H2, H3), 5.1 (d, 1H,  $J = 7.0$  Hz, H1), 5.5 (s, 1H,  $\text{CHPh}$ ), 6.8 (d, 2H,  $J = 9.0$  Hz, ArH), 7.0(d, 2H,  $J = 8.9$  Hz, ArH), 7.3 (m, 3H, ArH), 7.4 (m, 2H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 65.84, 68.2, 77.6, 80.1, 80.5, 81.2, 92.4, 92.6, 100.0, 102.6, 144.7, 119.1, 126.4, 128.7, 129.9, 135.6, 150.0, 156.3;  $[\alpha]_D^{26} = -48.6$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 794.8896$ ,  $\text{C}_{24}\text{H}_{25}\text{Cl}_6\text{O}_{13}\text{S}_2$  ( $\text{M}+\text{H}$ )<sup>+</sup> requires 794.8868.



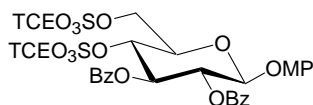
**Allyl-2,6-di-O-benzoyl-3,4-di-O-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (42).** Prepared according to the general procedure. Reaction time 30 h. Flash chromatography (5:95, EtOAc:benzene) gave **42** as a colourless syrup.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.99, 4.18 (AB, dd, 2H,  $J$  = 12.9, 7.6 Hz, allylic  $\text{CH}_2$ ), 4.32 (d, 1H,  $J$  = 9.6 Hz, H5), 4.52-4.57 (dd, 1H,  $J$  = 12.5, 3.9 Hz, H6'), 4.6-4.76 (AB, 2H,  $J$  = 11.1 Hz,  $\text{CH}_2\text{CCl}_3$ ), 4.87 (m, 3H, H6,  $\text{CH}_2\text{CCl}_3$ ), 5.06-5.12 (m, 2H, H4, H2), 5.19-5.25 (m, 3H, H1, olefinic  $\text{CH}_2$ ), 5.49 (t, 1H,  $J$  = 9.1 Hz, H3), 5.75-5.77 (ddd, 1H,  $J$  = 6 Hz, olefinic H), 7.42-7.49 (m, 4H, ArH), 7.58 (m, 2H, ArH), 8.06-8.13 (m, 4H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  61.7, 67.2, 69.4, 70.8, 78.1, 80.4, 80.6, 81.4, 92.2, 92.3, 94.7, 118.8, 128.4, 128.5, 128.6, 129.4, 129.7, 130.2, 132.3, 133.3, 133.9;  $[\alpha]_{\text{D}}^{25}$  = 56.8 (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z$  = 848.8996,  $\text{C}_{27}\text{H}_{27}\text{Cl}_6\text{O}_{14}\text{S}_2$  ( $\text{M}+\text{H}$ ) $^+$  requires 848.8973.



***p*-Tolyl-2,6-O-dibenzoyl-3,4-di-O-trichloroethylsulfo-1-thio- $\beta$ -D-glucopyranoside (43).**

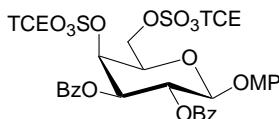
Prepared according to the general procedure. Reaction time 24 h. Flash chromatography (1:5, EtOAc:hexanes) gave **44** as a colourless syrup.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.27 (s, 3H,  $\text{CH}_3$ ), 4.02 (d, 1H,  $J$  = 8.1 Hz, H5), 4.53-4.57 (dd, 1H,  $J$  = 12.5, 4.3 Hz, H6), 4.1, 4.80 (AB system, 3H,  $J$  = 11.2 Hz,  $\text{CH}_2\text{CCl}_3$ , H1 overlapped with one proton of the  $\text{CH}_2\text{CCl}_3$ ), 4.9 (s, 2H,  $\text{CH}_2\text{CCl}_3$ ), 5.01-5.05 (m, 2H, H4, H6'), 5.23 (t, 1H,  $J$  = 9.2 Hz, H3), 5.32 (t, 1H,  $J$  = 9.4 Hz, H2), 6.9, 7.31 (AB system, 4H,  $J$  = 7.57 Hz, ArH), 7.53 (m, 4H, ArH), 7.65 (m, 2H, ArH), 8.0 (m, 4H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 61.8, 69.7, 75.5, 77.6, 80.6, 80.7, 84.1, 85.5, 92.3, 125.8,

128.5, 128.6, 128.8, 129.4, 129.7, 129.9, 130.2, 133.4, 133.9, 134.7, 139.3, 165.0, 165.7;  $[\alpha]_D^{26} = 67.8$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 914.8701$ , C<sub>32</sub>H<sub>28</sub>Cl<sub>6</sub>O<sub>13</sub>S<sub>3</sub> (M+H)<sup>+</sup> requires 914.8801.



***p*-Methoxyphenyl-2,3-di-*O*-benzoyl-4,6-di-*O*-trichloroethylsulfo- $\beta$ -D-glucopyranoside (44).**

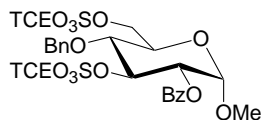
Prepared according to the general procedure. Reaction time 24 h. Flash chromatography (1:5, EtOAc:hexanes) gave **44** as a colourless syrup. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.7 (s, 3H, OCH<sub>3</sub>), 4.1, (ddd, 1H,  $J = 6.9, 5.0, 2.2$  Hz, H5), 4.5-4.6 (AB, 2H,  $J = 11.0$  Hz, CH<sub>2</sub>CCl<sub>3</sub>), 4.7 (m, 4H, H6, CH<sub>2</sub>CCl<sub>3</sub>, H6'), 5.1 (t, 1H,  $J = 9.3$  Hz, H4), 5.2 (d, 1H,  $J = 7.6$  Hz, H1), 5.6 (t, 1H,  $J = 9.0, 8.0$  Hz, H2), 5.65 (t, 1H,  $J = 9.3$  Hz, H3), 6.7 (d, 2H,  $J = 8.8$  Hz, ArH), 6.9 (m, 2H, ArH), 7.3 (m, 4H, ArH), 7.5 (m, 2H, ArH), 7.9 (m, 4H, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.6, 70.3, 71.1, 71.2, 71.6, 78.0, 79.9, 80.4, 92.0, 92.3, 100.3, 114.7, 118.9, 128.2, 128.5, 128.6, 129.8, 130.1, 133.6, 133.9, 150.4, 156.1, 164.8, 165.6;  $[\alpha]_D^{26} = 56.8$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 931.9343$ , C<sub>31</sub>H<sub>32</sub>NCl<sub>6</sub>O<sub>15</sub>S<sub>2</sub> (M+NH<sub>4</sub>)<sup>+</sup> requires 931.9345.



***p*-Methoxyphenyl-2,3-di-*O*-benzoyl-4,6-di-*O*-trichloroethylsulfo- $\beta$ -D-galactopyranoside**

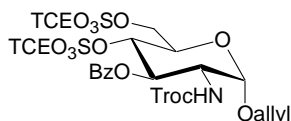
**(45).** Prepared according to the general procedure. Reaction time 24 h. Flash chromatography (1:5, EtOAc:hexanes) gave compound **45** as a colourless syrup. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.7 (s, 3H, OCH<sub>3</sub>), 4.1, (t, 1H,  $J = 6.3$  Hz, H5), 4.6-4.7 (m, 5H, H6, H6', CH<sub>2</sub>CCl<sub>3</sub>, 1H of CH<sub>2</sub>CCl<sub>3</sub>), 4.8 (the second half of the AB system, 1H,  $J = 11.0$  Hz, 1H of CH<sub>2</sub>CCl<sub>3</sub>), 5.2 (d, 1H,  $J = 8.0$  Hz, H1), 5.4-5.4 (m, 2H, H4, H3), 5.9 (t, 1H,  $J = 9.0, 8.3$  Hz, H2), 6.8 (d, 2H,  $J = 8.9$  Hz, ArH), 6.9 (d, 2H,  $J = 8.9$  Hz ArH), 7.3 (m, 4H, ArH), 7.5 (m, 2H, ArH), 7.9 (m, 4H, ArH); <sup>13</sup>C

NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.6, 68.3, 70.2, 70.7, 71.1, 78.5, 79.9, 80.3, 92.1, 92.3, 100.8, 114.7, 118.8, 128.1, 128.5, 128.7, 129.7, 129.8, 130.0, 133.6, 134.0, 150.5, 156.1, 165.1, 165.7;  $[\alpha]_D^{26} = 36.2$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 914.9109$ , C<sub>31</sub>H<sub>29</sub>Cl<sub>6</sub>O<sub>15</sub>S<sub>2</sub> [M+H]<sup>+</sup> requires 914.9079.



**Methyl-2-*O*-benzoyl-4-*O*-benzyl-3,6-di-*O*-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (46).**

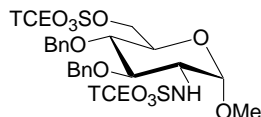
Prepared according to the general procedure. Reaction time 30 h. Flash chromatography (1:5, EtOAc:hexanes) gave compound **46** as a colourless syrup. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.3 (s, 3H, OCH<sub>3</sub>), 3.8, (t, 1H,  $J = 9.5$  Hz, H4), 3.9 (d, 1H,  $J = 10.0$  Hz, H5), 4.4-4.6 (m, 5H, H6, H6', CH<sub>2</sub>CCl<sub>3</sub>, 1H of CH<sub>2</sub>Ph), 4.7 (s, 2H, CH<sub>2</sub>CCl<sub>3</sub>), 4.9-5.1 (m, 3H, 1H of CH<sub>2</sub>Ph, H1, H2), 5.4 (t, 1H,  $J = 9.3$  Hz, H3), 7.3-7.4 (m, 7H, ArH), 7.5 (t, 1H,  $J = 7.3$  Hz, ArH), 8.1 (d, 2H,  $J = 7.4$  Hz, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.8, 68.0, 70.9, 71.3, 74.8, 75.4, 79.6, 80.0, 85.1, 92.0, 92.3, 96.9, 128.1, 128.5, 128.6, 128.8, 130.2, 130.3, 133.8, 136.2;  $[\alpha]_D^{26} = 34.6$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 808.9057$ , C<sub>25</sub>H<sub>27</sub>Cl<sub>6</sub>O<sub>13</sub>S<sub>2</sub> [M+H]<sup>+</sup> requires 808.9024.



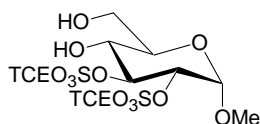
**Allyl-2-deoxy-2-*N*-trichloroethoxyamido-3-*O*-benzoyl-4,6-di-*O*-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (47).** Compound **47** prepared using the procedures described for compound **40** in the experimental section. Purified by flash chromatography (1:4, EtOAc:hexanes). Colorless syrup. For yields see Table 1. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  4.09 (m, 1H, H of allyl CH<sub>2</sub>), 4.21-4.29 (m, 3H, H of allyl CH<sub>2</sub>, H5, H2), 4.41-4.47 (m, 2H, H6, 1H of CH<sub>2</sub>CCl<sub>3</sub>), 4.59-4.73 (m, 4H, 1H of CH<sub>2</sub>CCl<sub>3</sub>, H6', CH<sub>2</sub>CCl<sub>3</sub>), 4.77 (s, 2H, Troc CH<sub>2</sub>), 4.92-5.0 (m, 2H, H4, H1), 5.28-5.37 (m, 3H, olefinic CH<sub>2</sub> of allyl, NH), 5.69 (t, 1H,  $J = 9.6$  Hz, H3), 5.91 (m, 1H, olefinic H), 7.41 (t,



4H,  $J=7.6$  Hz, ArH), 7.56 (t,  $J=7.5$  Hz, 1H, ArH), 8.03 (d, 2H,  $J=7.4$  Hz, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  54.1, 67.1, 69.6, 70.2, 70.4, 74.4, 78.4, 79.8, 80.3, 92.0, 92.4, 94.9, 96.2, 119.7, 128.3, 128.6, 130.2, 132.2, 134.0, 154.0, 166.2;  $[\alpha]_{\text{D}}^{26} = 89.2$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 917.7842$ ,  $\text{C}_{23}\text{H}_{25}\text{Cl}_9\text{NO}_{14}\text{S}$  ( $\text{M}+\text{H}$ ) $^{+}$  requires 917.7835.

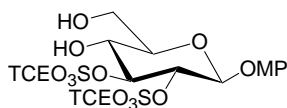


**Methyl-3,4-di-*O*-benzyl-6-*O*-trichloroethylsulfo-2-deoxy-2-*N*-trichloroethoxy-sulfamido- $\alpha$ -D-glucopyranoside (48).** Prepared according to the general procedure described from carbohydrate **19**<sup>3</sup>. Reaction time 30 h. Flash chromatography (1:4, EtOAc:hexanes) gave compound **48** as a colourless syrup.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.4 (s, 3H,  $\text{OCH}_3$ ), 3.5-3.75 (m, 3H, H6, H4, H6'), 3.83-3.87 (dd, 1H,  $J = 10, 2.4$  Hz, H5), 4.39-4.48 (m, 2H, H3, H2), 4.65-4.64 (m, 3H,  $\text{CH}_2\text{CCl}_3$ , 1H  $\text{CH}_2\text{Ph}$ ), 4.69 (s, 2H,  $\text{CH}_2\text{CCl}_3$ ), 4.85-4.9 (m, 3H,  $\text{CH}_2\text{Ph}$ , 1H of the  $\text{CH}_2\text{Ph}$ ), 4.94 (d, 1H,  $J = 3.4$  Hz, H1), 5.03 (br, 1H, NH), 7.24-7.38 (m, 10H, ArH);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  55.7, 58.1, 68.6, 72, 75.3, 75.8, 77.1, 78.2, 79.3, 79.6, 92.5, 93.3, 97.9, 128.09, 128.12, 128.17, 128.3, 128.6, 137.0, 137.3;  $[\alpha]_{\text{D}}^{26} = 72.3$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 810.9664$ ,  $\text{C}_{25}\text{H}_{33}\text{N}_2\text{Cl}_6\text{O}_{11}\text{S}_2$  [ $\text{M}+\text{NH}_4$ ] $^{+}$  requires 810.9657.

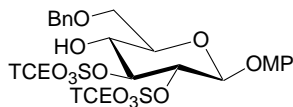


**Methyl-2,3-di-*O*-trichloroethylsulfo- $\alpha$ -D-glucopyranoside (14).** A suspension of carbohydrate **40** (0.35 g, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$ :MeOH (1:2, 2.4 mL  $\text{CH}_2\text{Cl}_2$ , 4.8 mL MeOH) in a round bottom flask equipped with a reflux condenser was heated to  $40^\circ\text{C}$  (oil bath) and stirred until all starting

material had dissolved. *p*-TsOH (0.009 g, 0.05 mmol) was added and the temperature was increased to 45°C and the reaction was stirred until no starting material remained by TLC (24 h). The reaction was neutralized with NEt<sub>3</sub> and concentrated to a yellow oil. Flash chromatography (1:3, EtOAc:hexanes) provided compound **14** as a white solid (0.26 g, 85%). Mp 48-50 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.9 (t, 1H, *J* = 5.9 Hz, OCH<sub>3</sub>, OH), 3.2 (d, 1H, *J* = 4.5 Hz, OH), 3.4 (s, 3H, OCH<sub>3</sub>), 3.7 (dd, 1H, *J* = 9.6, 5.5, 4.1 Hz, H<sub>5</sub>), 3.9-4.0 (m, 3H, H<sub>6</sub>, H<sub>6'</sub>, H<sub>4</sub>), 4.6 (dd, 1H, *J* = 9.7, 3.2 Hz, H<sub>2</sub>), 4.7-4.8 (m, 4H, 2CH<sub>2</sub>CCl<sub>3</sub>), 5.0 (t, 1H, *J* = 9.4, 9.1 Hz, H<sub>3</sub>), 5.1 (d, 1H, *J* = 2.7 Hz, H<sub>1</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 55.7, 61.3, 68.9, 70.6, 78.5, 80.2, 80.2, 84.0, 92.2, 92.4, 96.3; [α]<sub>D</sub><sup>26</sup> = 88.6 (c 1.0, CHCl<sub>3</sub>); HRMS (ESI) *m/z* = 614.8289 (M+H)<sup>+</sup> C<sub>11</sub>H<sub>17</sub>Cl<sub>6</sub>O<sub>12</sub>S<sub>2</sub> requires 614.8293.

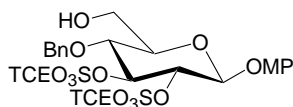


***p*-Methoxyphenyl-2,3-di-*O*-trichloroethylsulfo-β-D-glucopyranoside (15).** Compound **15** was prepared by the same procedure used for the preparation of compound **14**. Flash chromatography (1:3, EtOAc:hexanes) provided **15** as a white solid. 80% yield. Mp 62-64 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.1 (br, 1H, , OH), 3.5 (b, 2H, OH, H<sub>5</sub>), 3.8 (s, 3H, OCH<sub>3</sub>), 3.9 (m, 2H, H<sub>6</sub>, H<sub>6'</sub>), 4.1 (m, 1H, *J* = 8.8, 8.4, 4.1 Hz, H<sub>4</sub>), 4.8-4.9 (m, 6H, H<sub>3</sub>, H<sub>2</sub>, 2CH<sub>2</sub>CCl<sub>3</sub>), 5.1 (d, 1H, *J* = 7.0 Hz, H<sub>1</sub>), 6.8 (d, 2H, *J* = 8.9 Hz, ArH), 7.0 (d, 2H, *J* = 8.9 Hz, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 55.5, 61.4, 68.9, 74.8, 80.3, 80.5, 80.5, 86.0, 92.3, 92.4, 98.7, 114.7, 118.5, 149.8, 156.1; [α]<sub>D</sub><sup>26</sup> = 64.3 (c 1.0, CHCl<sub>3</sub>); HRMS (ESI) *m/z* = 723.8809 (M+NH<sub>4</sub>)<sup>+</sup> C<sub>17</sub>H<sub>24</sub>Cl<sub>6</sub>NO<sub>13</sub>S<sub>2</sub> requires 723.8820.



***p*-Methoxyphenyl-2,3-di-*O*-trichloroethylsulfo-6-*O*-benzyl- $\beta$ -D-glucopyranoside (50).**

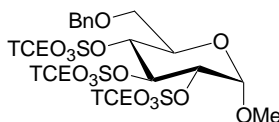
Compound **50** was prepared by the same procedure used for preparation of compound **49**. Flash chromatography (1:6, EtOAc:hexanes) provided **50** as a colourless syrup. 83% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 (br, 1H, OH), 3.60 (dd, 1H,  $J = 10.9, 4.3$  Hz, H5), 3.77 (m, 5H,  $\text{OCH}_3$ , H6, H6'), 4.03 (br, 1H, H4), 4.58 (dd, 2H,  $J = 11.3, 9.9$  Hz,  $\text{CH}_2\text{Ph}$ ), 4.89 (m, 7H,  $2\text{CH}_2\text{CCl}_3$ , H3, H2, H1), 6.81 (m, 2H, ArH), 7.0 (m, 2H, ArH), 7.31 (m, 5H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 69.2, 70.6, 73.2, 73.8, 80.3, 80.4, 80.6, 85.6, 92.5, 99.1, 114.7, 119.0, 127.9, 128.2, 128.6, 137.0, 150.0, 156.2;  $[\alpha]_{\text{D}}^{26} = 38.6$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 813.9177$ ,  $\text{C}_{24}\text{H}_{30}\text{Cl}_6\text{NO}_{13}\text{S}_2$  ( $\text{M}+\text{NH}_4$ ) $^+$  requires 813.9289.



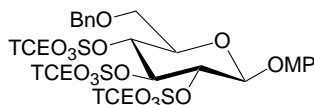
***p*-Methoxyphenyl-2,3-di-*O*-trichloroethylsulfo-4-*O*-benzyl- $\beta$ -D-glucopyranoside (52).**

Compound **52** was prepared by the same procedure used for preparation of compound **51**. Flash chromatography (1:4, EtOAc:hexanes) provided **52** as colourless syrup. 73% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.8 (br, 1H, OH), 3.4 (d, 1H,  $J = 9.1$  Hz, H5), 3.7-3.9 (m, 5H, H6',  $\text{OCH}_3$ , H6), 4.6 (d, 1H,  $J = 10.4$  Hz, 1H of  $\text{CH}_2\text{Ph}$ ), 4.7-5.0 (m, 7H,  $2\text{CH}_2\text{CCl}_3$ , 1H  $\text{CH}_2\text{Ph}$ , H2, H3), 5.0 (d, 1H,  $J = 7.3$  Hz, H1), 6.8 (d, 2H,  $J = 8.4$  Hz, ArH), 6.9 (d, 2H,  $J = 8.4$  Hz, ArH), 7.3 (m, 5H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 60.6, 74.8, 75.1, 75.2, 80.3, 80.5, 80.9, 84.8, 92.1,

92.6, 98.5, 114.8, 118.4, 128.4, 128.6, 136.5, 149.7, 156.1;  $[\alpha]_D^{26} = 87.3$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 813.9315$ , C<sub>24</sub>H<sub>30</sub>Cl<sub>6</sub>NO<sub>13</sub>S<sub>2</sub> (M+NH<sub>4</sub>)<sup>+</sup> requires 813.9290.



**Methyl-2,3,4-tri-*O*-trichloroethylsulfo-6-*O*-benzyl- $\alpha$ -D-glucopyranoside (53).** Prepared according to the general procedure described for compound **55** in the experimental section. Flash chromatography (1:5, EtOAc:hexanes) provided **53** as a colourless syrup. 84% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  3.48 (s, 3H, OCH<sub>3</sub>), 3.79-3.98 (m, 3H, H6, H6', H5), 4.5-4.62 (AB, 2H,  $J = 11.3$  Hz, CH<sub>2</sub>Ph), 4.69 (m, 1H, H2), 4.81-4.9 (m, 6H, 3CH<sub>2</sub>CCl<sub>3</sub>), 5.07-5.25 (m, 3H, H4, H3, H1), 7.34 (m, 5H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  56.1, 66.7, 68.3, 73.7, 77.3, 78.0, 79.6, 79.7, 80.1, 80.3, 80.7, 80.8, 92.2, 92.4, 92.5, 95.9, 127.9, 128.0, 128.4, 137.2;  $[\alpha]_D^{26} = 46.9$  (c 1.0, CHCl<sub>3</sub>); HRMS (ESI)  $m/z = 931.7767$ , C<sub>20</sub>H<sub>27</sub>NCl<sub>9</sub>O<sub>15</sub>S<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup> requires 931.7740.



***p*-Methoxyphenyl-2,3,4-tri-*O*-trichloroethylsulfo-6-*O*-benzyl- $\beta$ -D-glucopyranoside (54).**

Prepared according to the general procedure described for compound **55** in the experimental section. Flash chromatography (1:4, EtOAc:hexanes) provided **54** as colourless syrup. 80% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.74- 3.79 (m, 4H, H5, OCH<sub>3</sub>), 3.90 (t, 1H,  $J = 9.1$  Hz, H4), 4.37 (dd, 1H,  $J = 10.8, 4.2$  Hz, H6'), 4.49 (d, 1H,  $J = 10.9$  Hz, H6), 4.58-4.64 (m, 3H, CH<sub>2</sub>Ph, 1H of CH<sub>2</sub>CCl<sub>3</sub>), 4.79-4.95 (m, 5H, 1H of CH<sub>2</sub>CCl<sub>3</sub>, 2CH<sub>2</sub>CCl<sub>3</sub>), 5.03-5.08 (m, 2H, H2, H3), 5.13 (d, 1H,  $J = 7.3$  Hz, H1), 6.86 (d, 2H,  $J = 8.9$  Hz, ArH), 7.01 (d, 2H,  $J = 8.9$  Hz, ArH), 7.41 (m, 5H, ArH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  55.6, 70.3, 72.2, 74.6, 75.81, 79.7, 80.3, 80.5, 80.7,

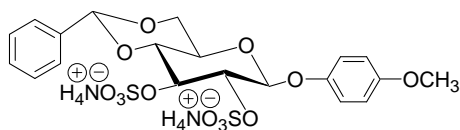
84.3, 92.2, 92.4, 92.5, 98.5, 114.9, 118.7, 128.8, 128.9, 128.9, 135.7, 149.4, 156.4;  $[\alpha]_D^{26} = 86.2$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 1006.7729$ ,  $\text{C}_{26}\text{H}_{28}\text{Cl}_9\text{NO}_{16}\text{S}_3$  ( $\text{M}+\text{H}$ )<sup>+</sup> requires 1006.7736.



***p*-Methoxyphenyl-2,3,6-tri-*O*-trichloroethylsulfo-4-*O*-benzyl- $\beta$ -D-glucopyranoside (56).**

Prepared according to the general procedure described for compound **55** in the experimental section. Flash chromatography (1:4, EtOAc:hexanes) provided **56** as colourless syrup. 71% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.7- 3.88 (m, 5H, H5,  $\text{OCH}_3$ , H4), 4.3-4.56 (m, 2H, H6, H6'), 4.57-4.73 (m, 3H,  $\text{CH}_2\text{Ph}$ , 1H of  $\text{CH}_2\text{CCl}_3$ ), 4.76-4.9 (m, 5H, 1H of  $\text{CH}_2\text{CCl}_3$ , 2 $\text{CH}_2\text{CCl}_3$ ), 4.97-5.09 (m, 2H, H3, H1), 6.8 (d, 2H,  $J = 8.8$  Hz, ArH), 6.96 (d, 2H,  $J = 8.7$  Hz, ArH), 7.36 (m, 5H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 70.3, 72.1, 74.6, 75.8, 97.7, 80.3, 80.4, 80.7, 84.4, 84.5, 92.2, 92.4, 92.5, 98.4, 114.9, 118.6, 128.8, 128.9, 135.7, 149.4, 156.4;  $[\alpha]_D^{26} = 75.1$  (c 1.0,  $\text{CHCl}_3$ ); HRMS (ESI)  $m/z = 1006.7731$ ,  $\text{C}_{26}\text{H}_{28}\text{Cl}_9\text{NO}_{16}\text{S}_3$  ( $\text{M}+\text{H}$ )<sup>+</sup> requires 1006.7736.

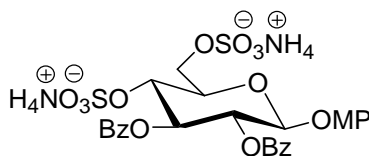
**Deprotection of the Sulfate Moiety**



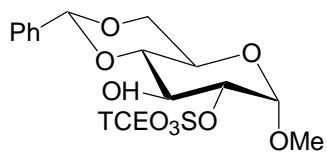
***p*-Methoxyphenyl-2,3-di-*O*-sulfo-4:6-*O*-benzylidene- $\beta$ -D-glucopyranoside (58).** Prepared

using the general procedure described for compound **57** described in the experimental section. Flash chromatography (10:2:0.5  $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$ ) afforded **58** as a white solid, which was lyophilized (3x) to yield a white powder. 89% Yield.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ )  $\delta$  3.50 (t, 1H,  $J = 10.1, 9.26$  Hz, H6'), 3.71 (m, 4H,  $\text{OCH}_3$ , H5), 4.16-4.25 (m, 2H, H6, H4), 4.32 (d, 1H,  $J$

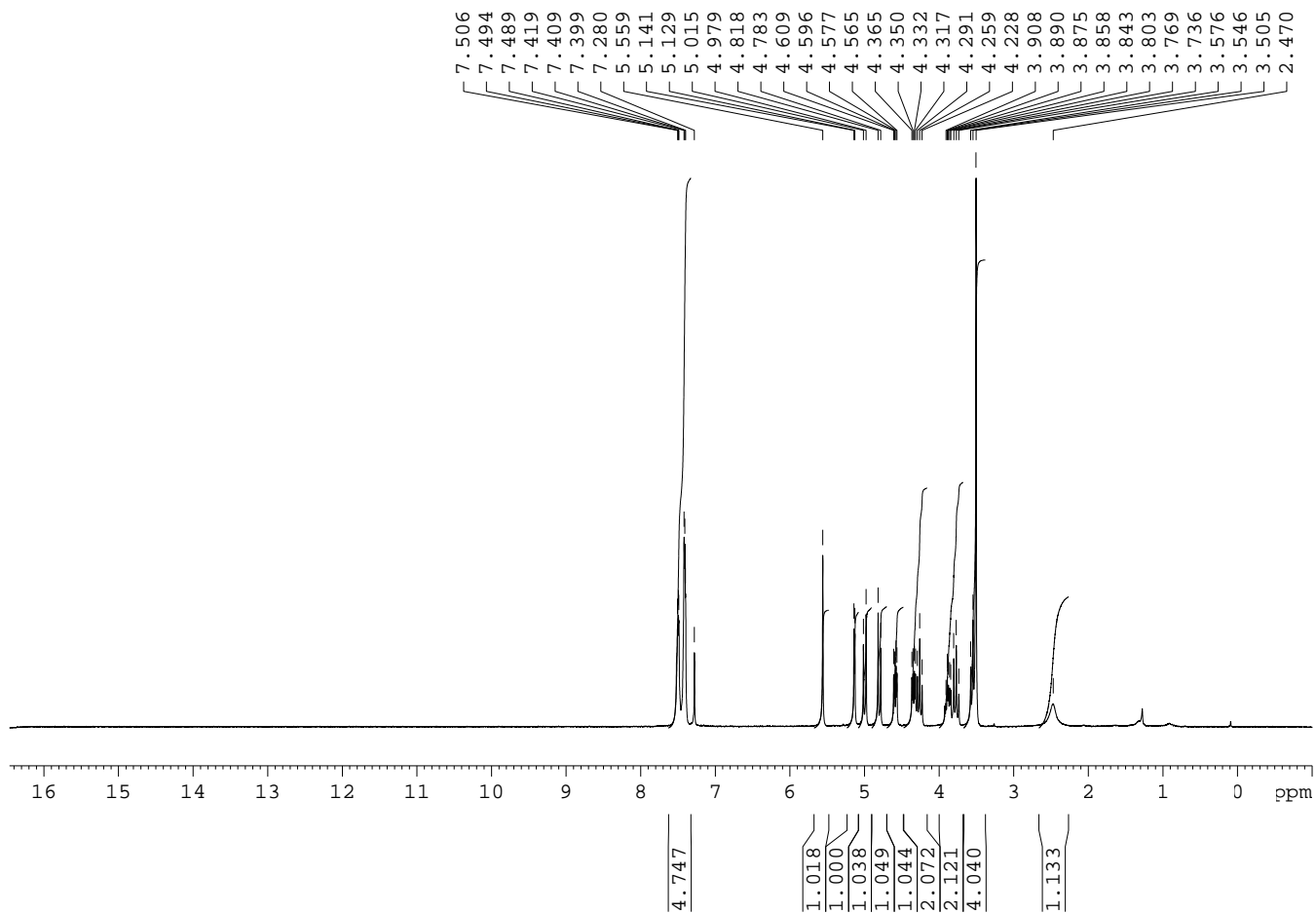
= 6.9 Hz, H3), 4.4 (s, 1H, H2), 5.58 (s, 1H, CHPh), 5.76 (s, 1H, H1), 6.84, 6.92 (AB, 4H,  $J$  = 8.6 Hz, ArH), 7.12 (s, 8H, 2NH<sub>4</sub>), 7.36 (m, 5H, ArH); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.7, 64.2, 69.5, 75.7, 76.6, 79.2, 98.0, 101.0, 115.0, 119.1, 126.8, 128.3, 129.1, 138.2, 150.8, 154.9;  $[\alpha]_D^{26}$  = 77.2 (c 1.0, H<sub>2</sub>O); HRMS (ESI)  $m/z$  = 533.0417, C<sub>20</sub>H<sub>21</sub>O<sub>13</sub>S<sub>2</sub> requires 533.0424.

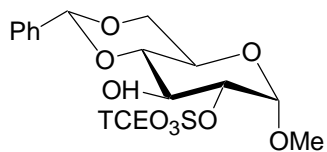


***p*-Methoxyphenyl-2,3-di-*O*-benzoyl-4,6-di-*O*-sulfo- $\beta$ -D-glucopyranoside (59).** Prepared using the general procedure described for compound **57** described in the experimental section. Flash chromatography (20:4:1 CH<sub>2</sub>Cl<sub>2</sub>/MeOH/NH<sub>4</sub>OH) afforded a white solid, which was lyophilized (3x) to yield a white powder. 88% yield. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.67 (s, 4H, OCH<sub>3</sub>, H6'), 4.01 (t, 1H,  $J$  = 9.5 Hz, H5), 4.2 (t, 1H,  $J$  = 9.4 Hz, H4), 4.36 (d, 1H,  $J$  = 11.2 Hz, H6), 5.26 (t, 1H,  $J$  = 9 Hz, H2), 5.45 (d, 1H,  $J$  = 7.8 Hz, H1), 5.66 (t, 1H,  $J$  = 9.3 Hz, H3), 6.75, 6.88 (AB, 4H,  $J$  = 8.5 Hz, ArH), 7.04 (s, 8H, 2NH<sub>4</sub>), 7.41 (m, 6H, ArH), 7.79 (d, 4H,  $J$  = 11.9 Hz, ArH); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  55.7, 66.4, 72.7, 73.2, 73.7, 74.3, 99, 114.9, 118.2, 128.5, 129.2, 129.3, 129.5, 129.9, 130.5, 133.1, 134, 151.2, 155.2, 165.1, 165.7;  $[\alpha]_D^{26}$  = 76.3 (c 1.0, H<sub>2</sub>O); HRMS (ESI)  $m/z$  = 653.0612, C<sub>27</sub>H<sub>25</sub>O<sub>15</sub>S<sub>2</sub> requires 653.0635.

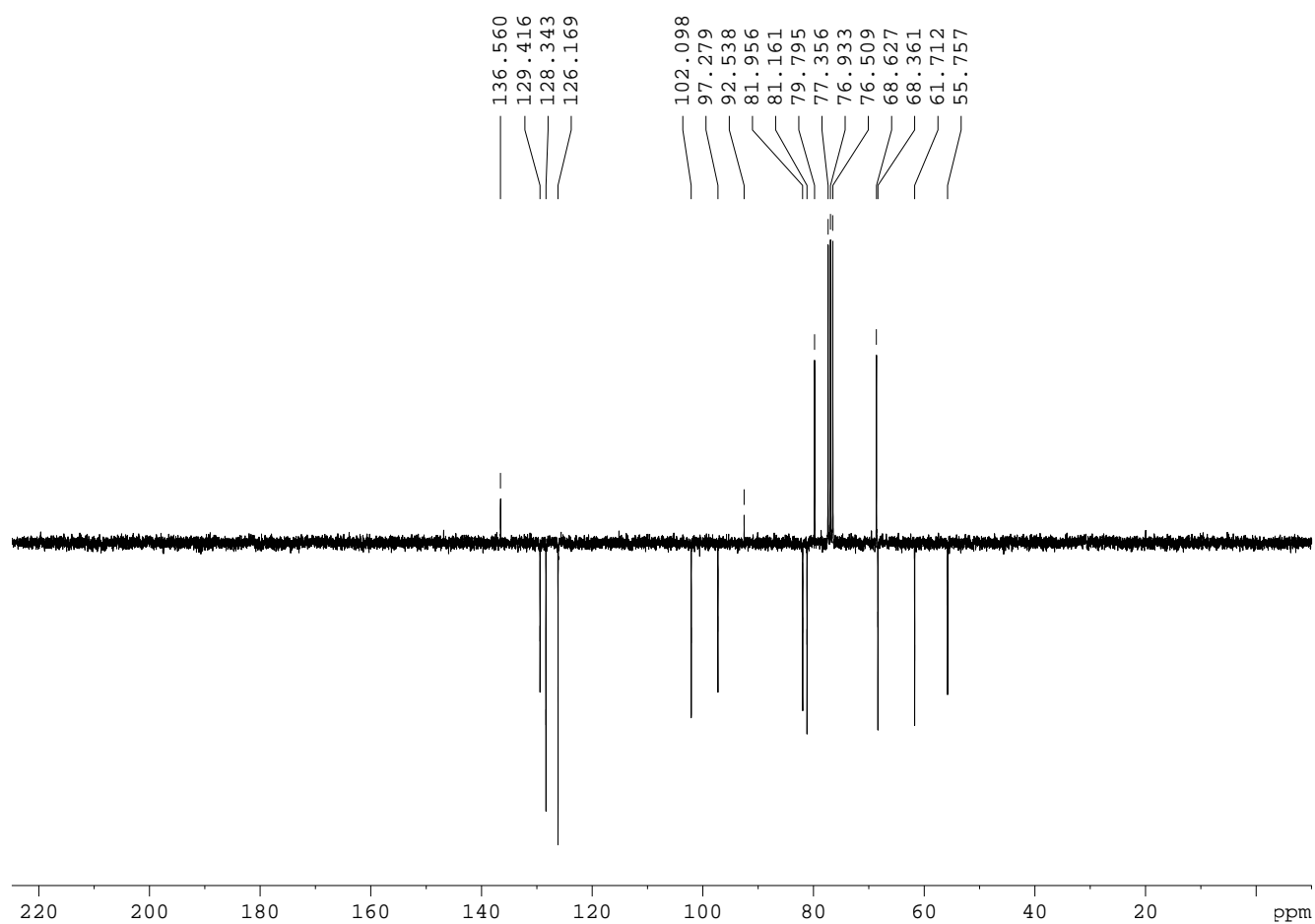


$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **20**

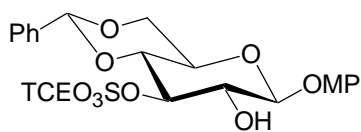




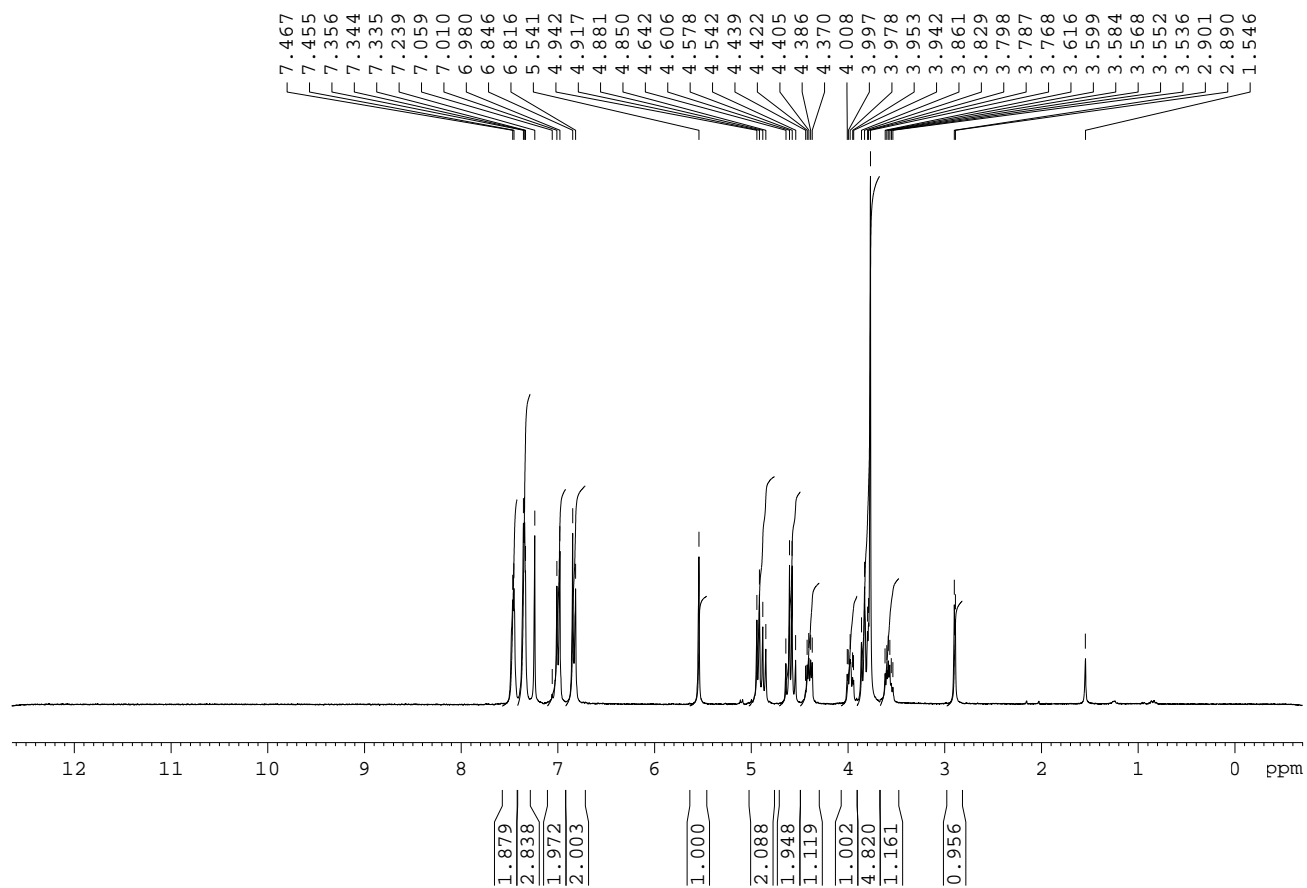
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **20**

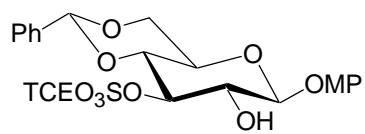




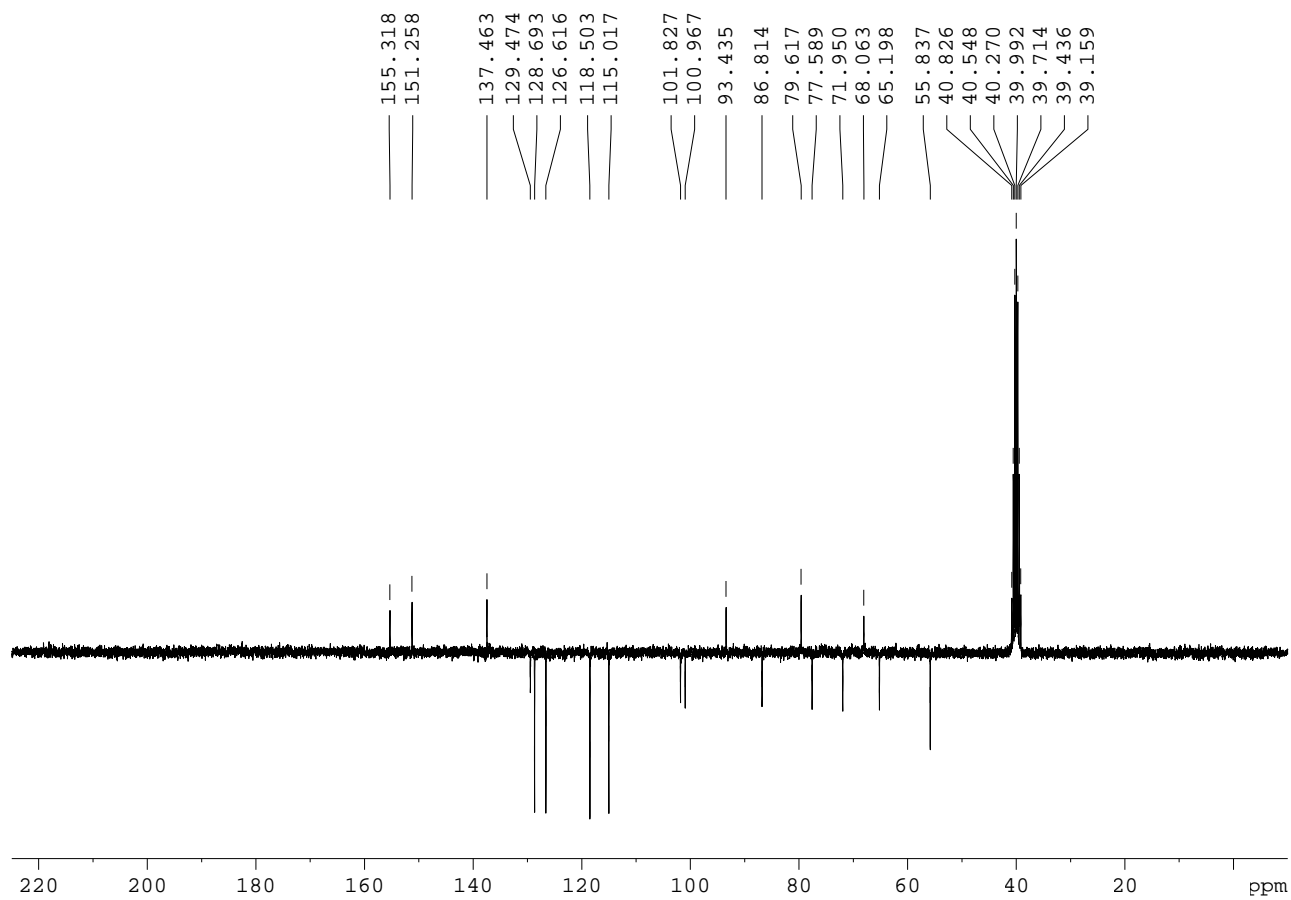


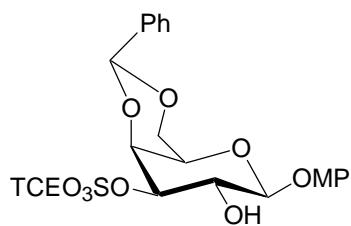
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **21**



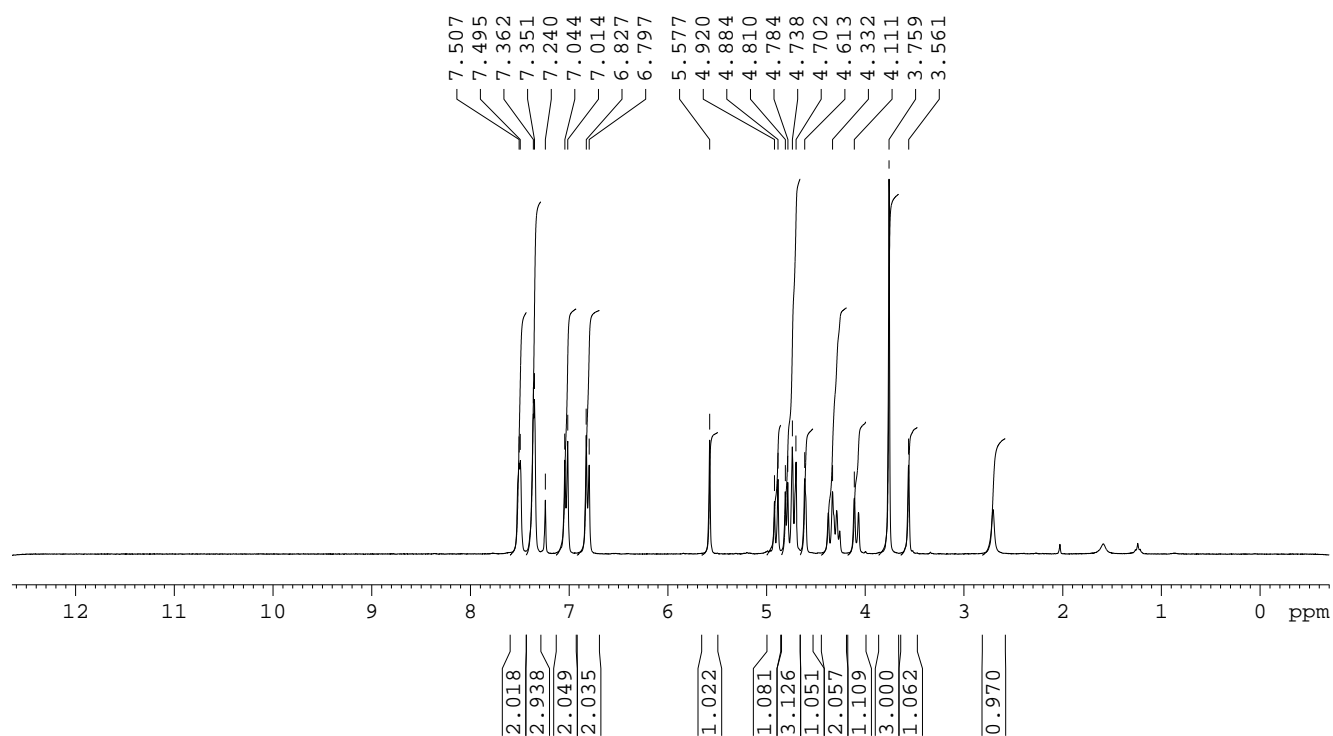


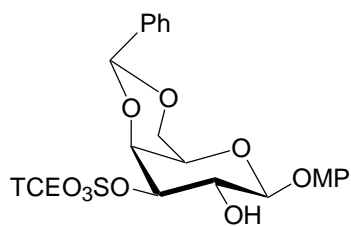
<sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>) of compound **21**



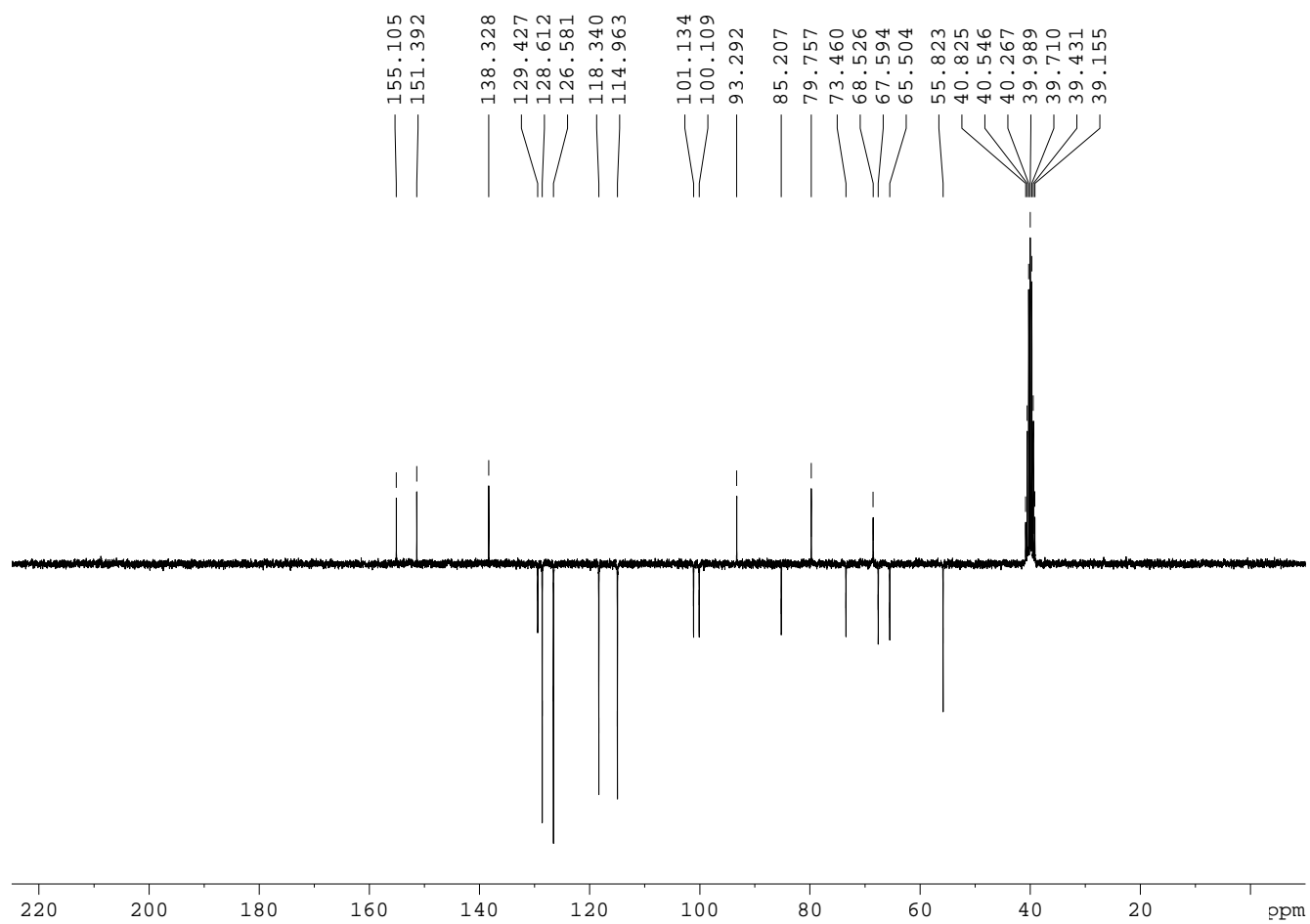


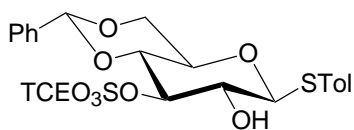
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **22**



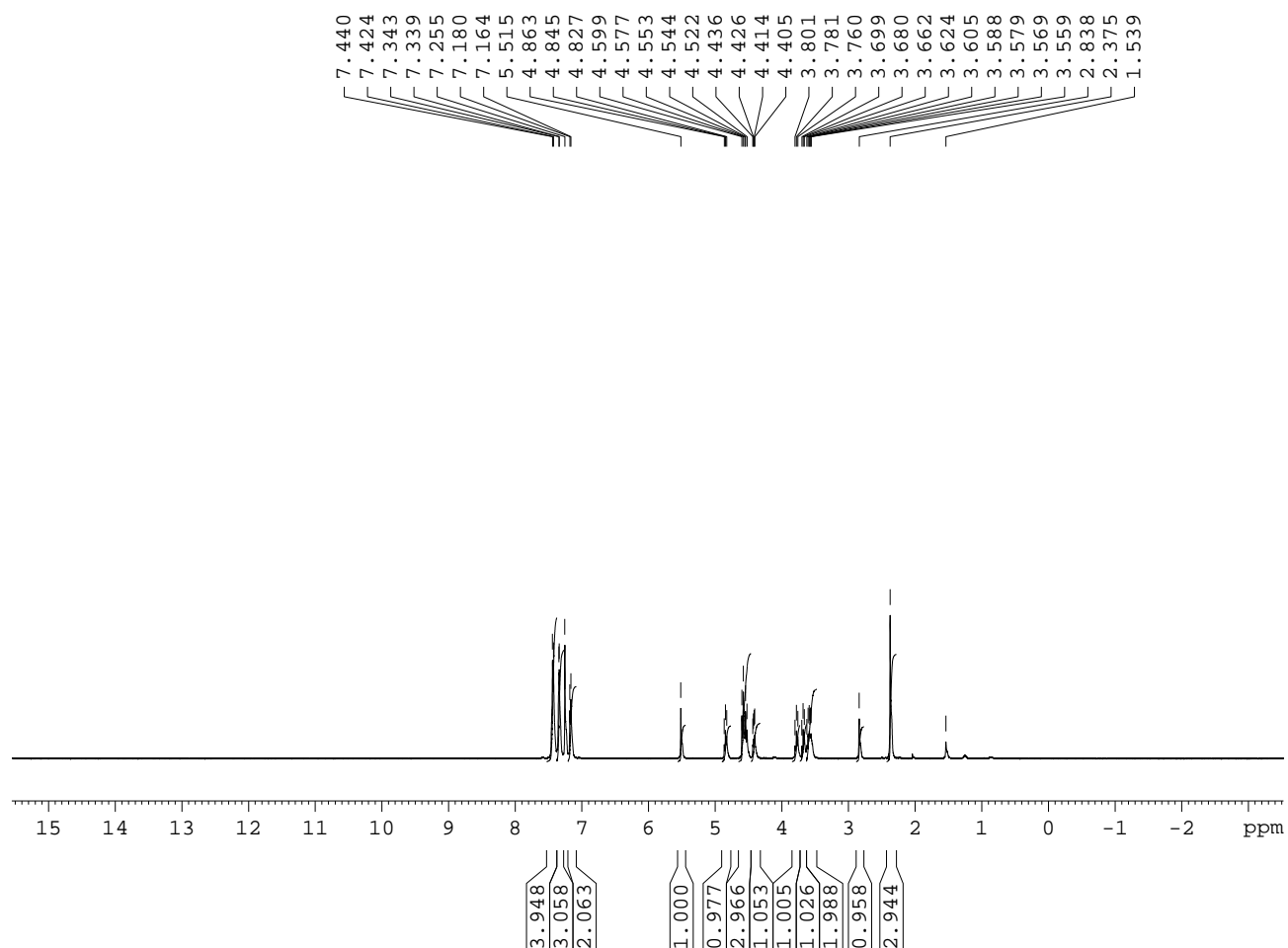


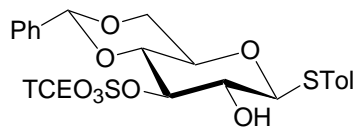
<sup>13</sup>C NMR (CDCl<sub>3</sub>) for compound **22**



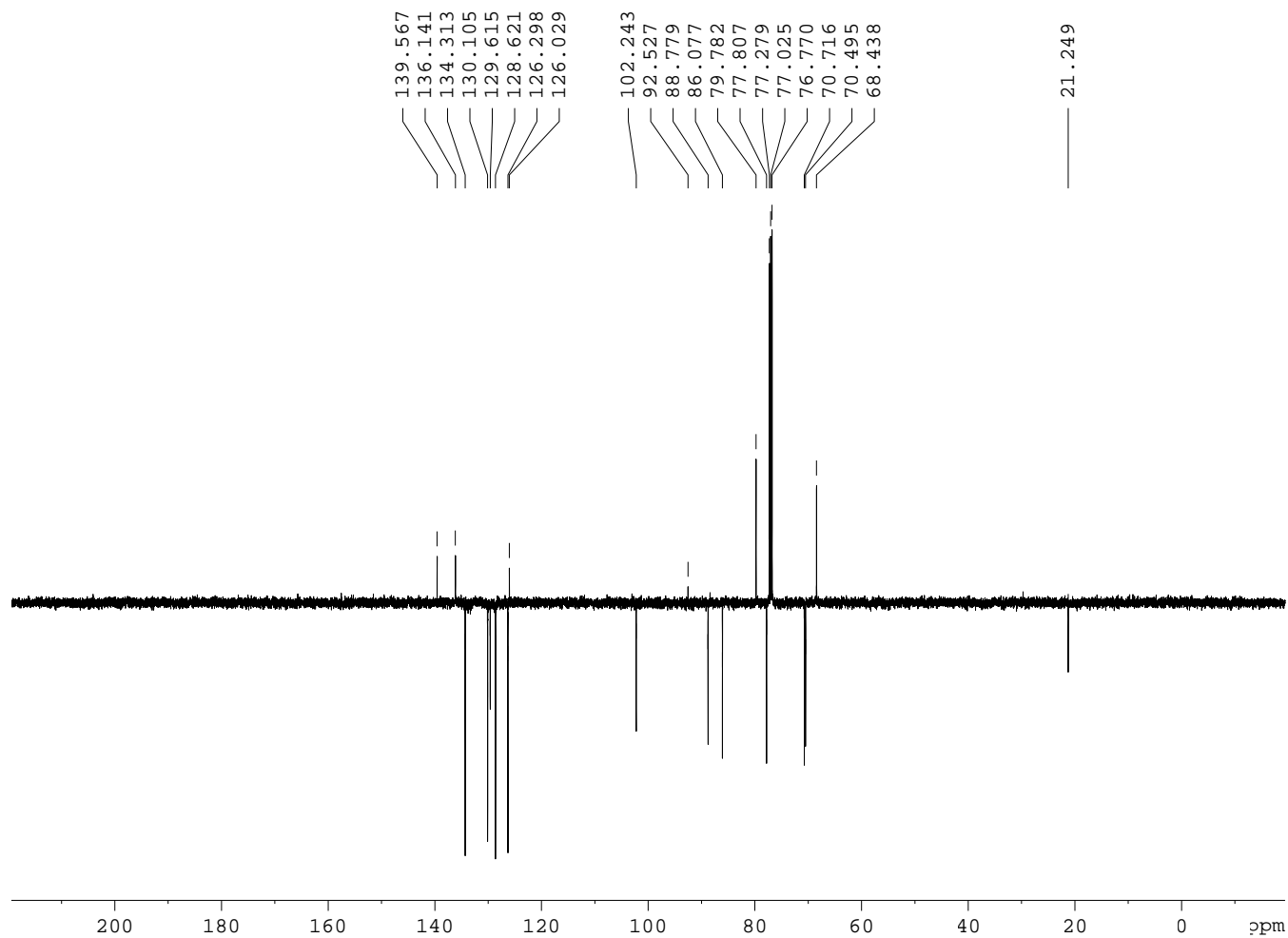


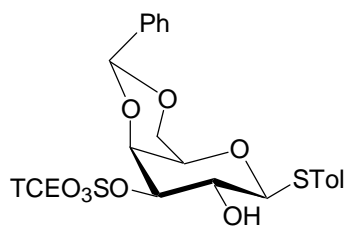
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **23**



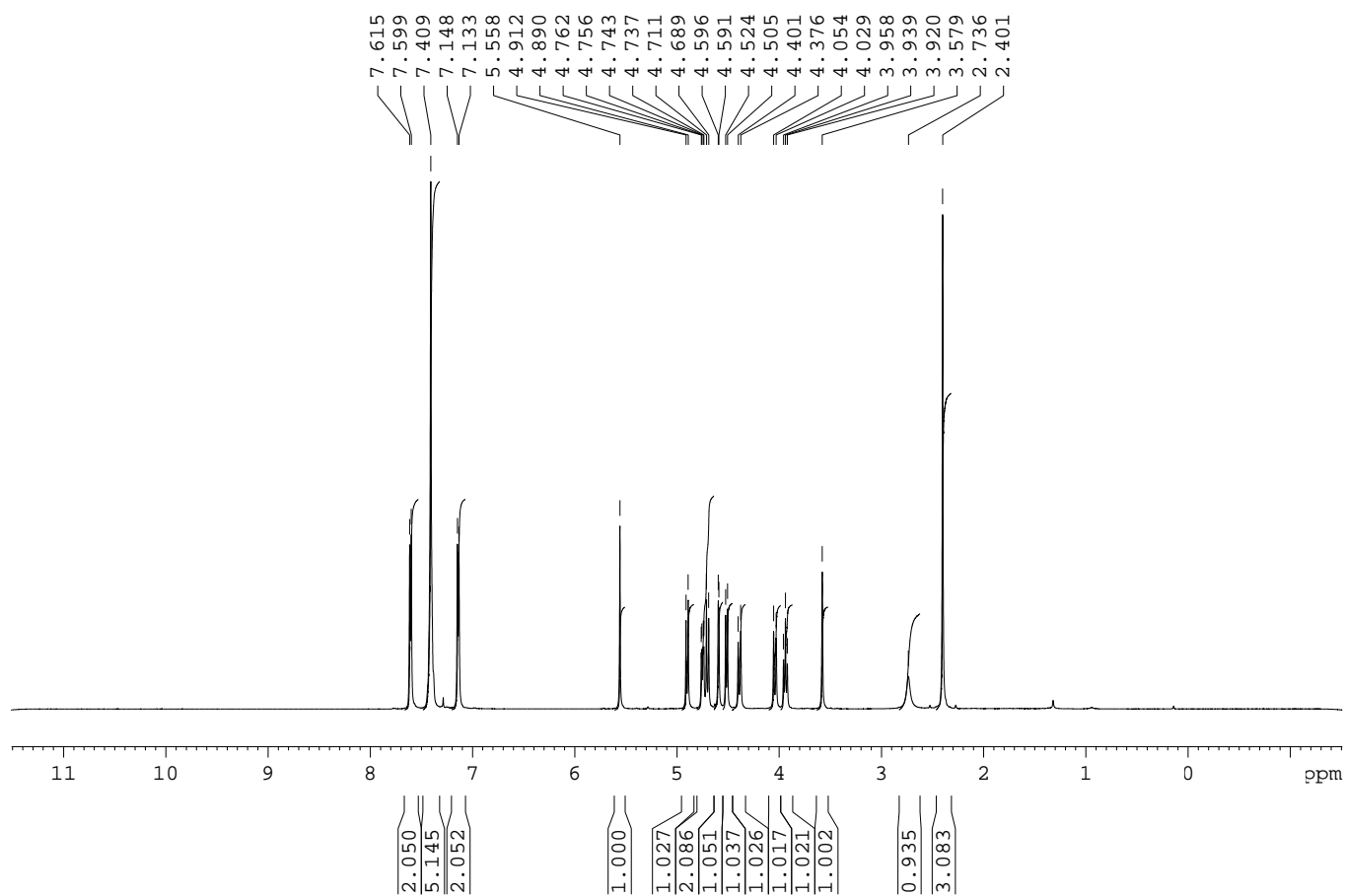


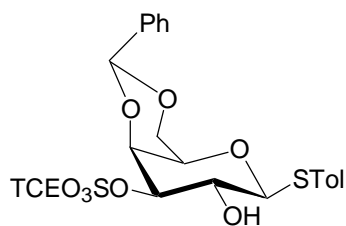
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **23**



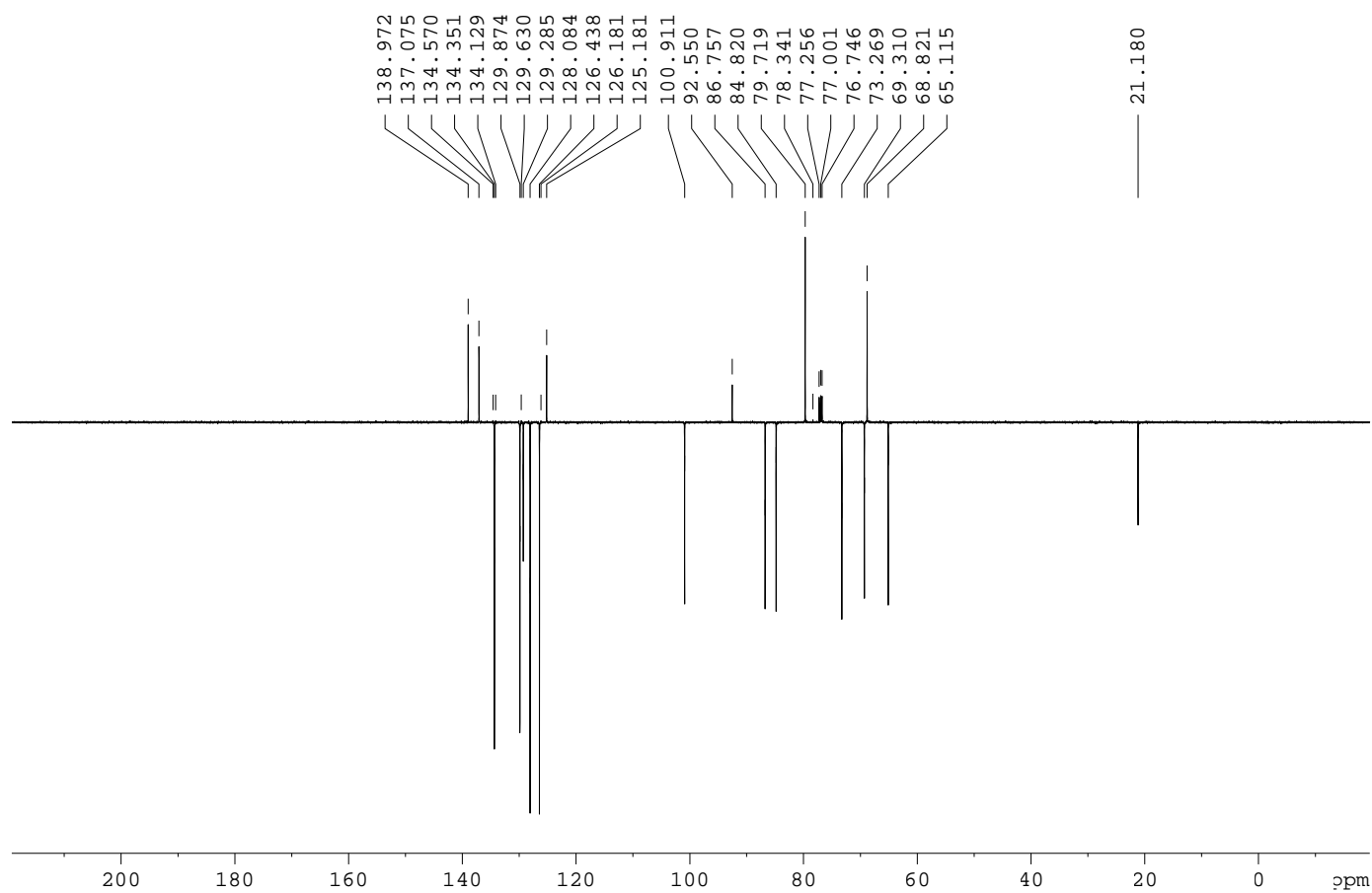


$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **24**

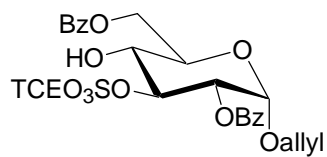




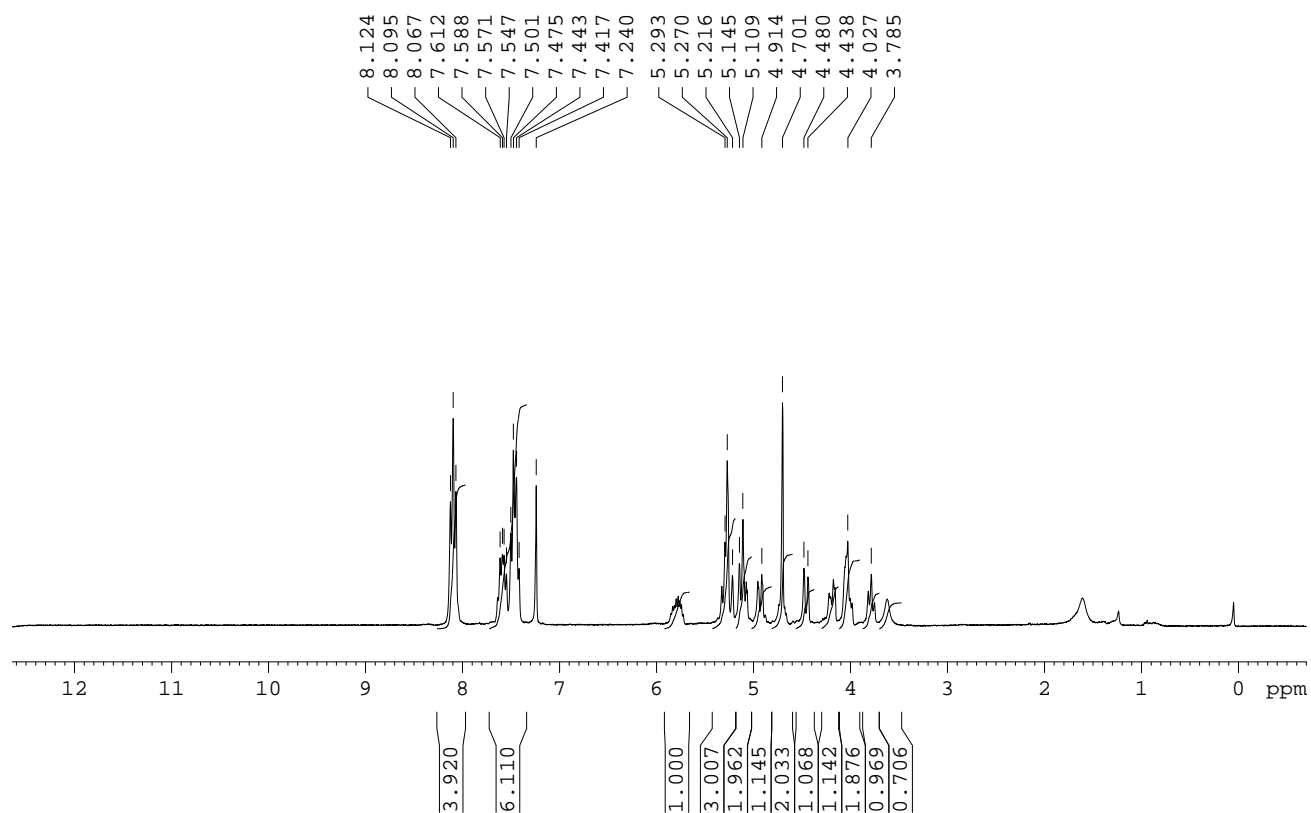
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **24**

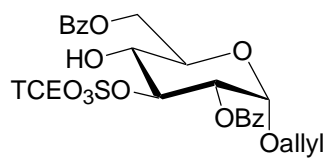




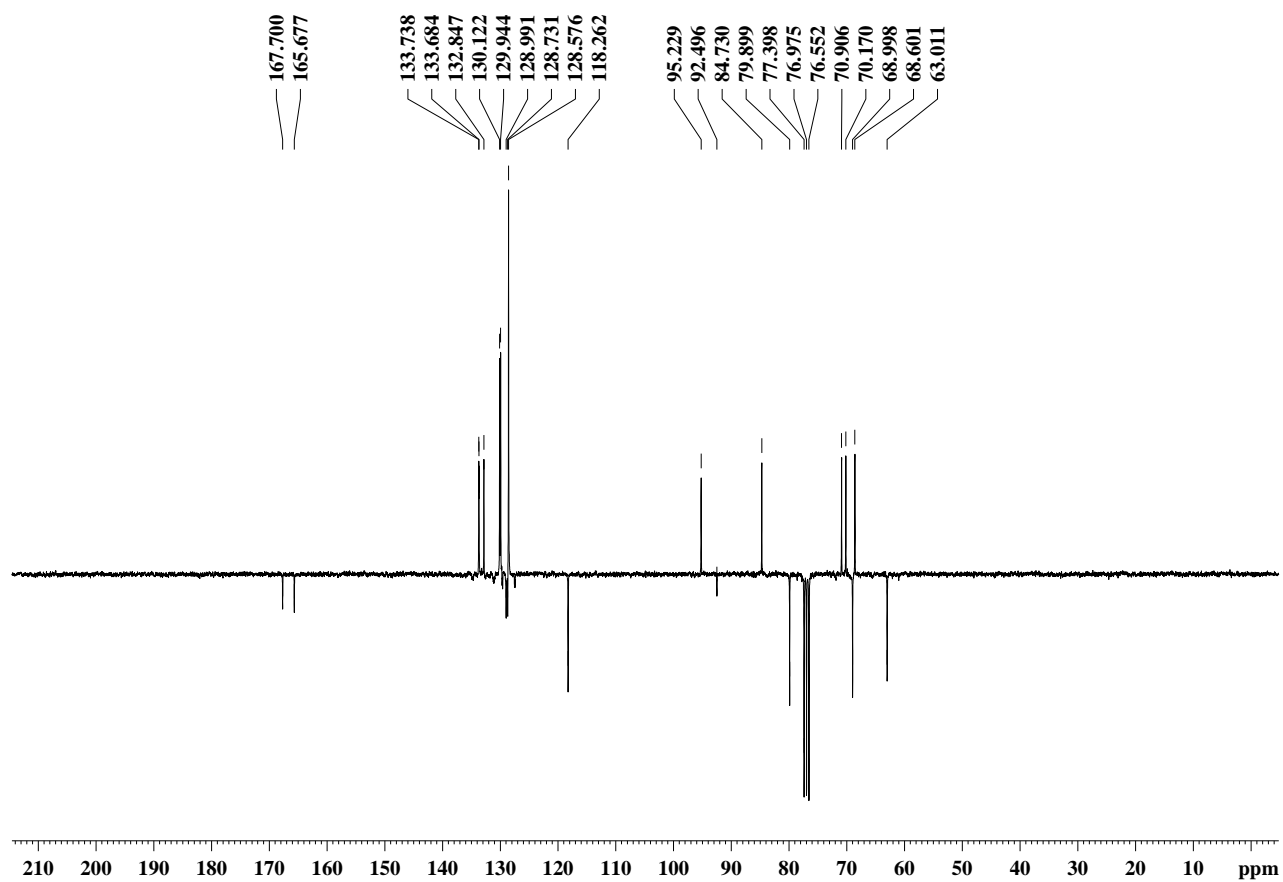


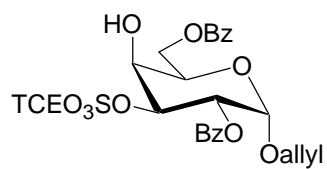
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **25**



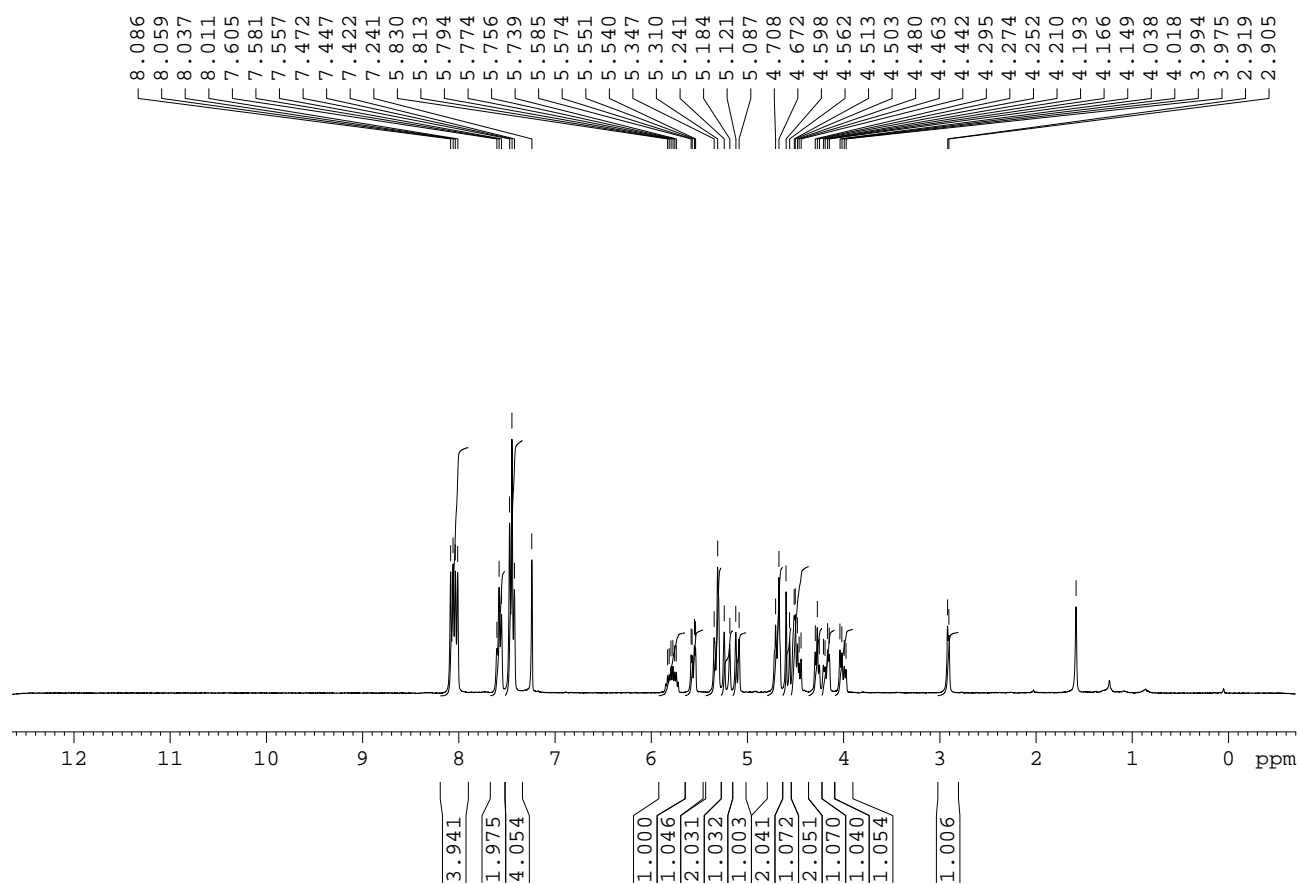


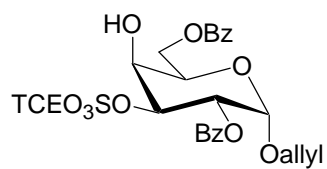
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **25**



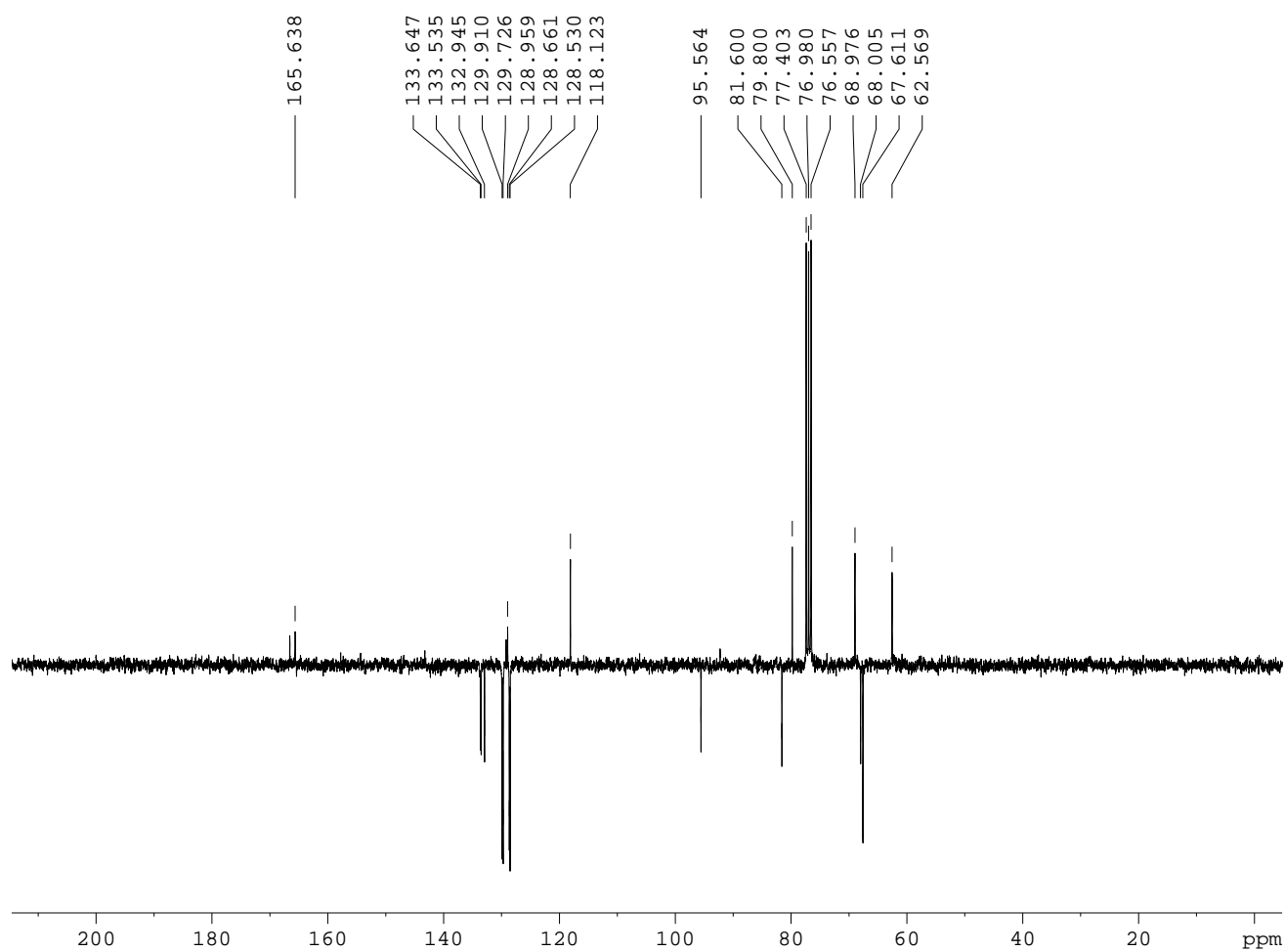


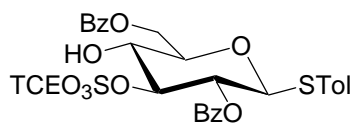
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **26**



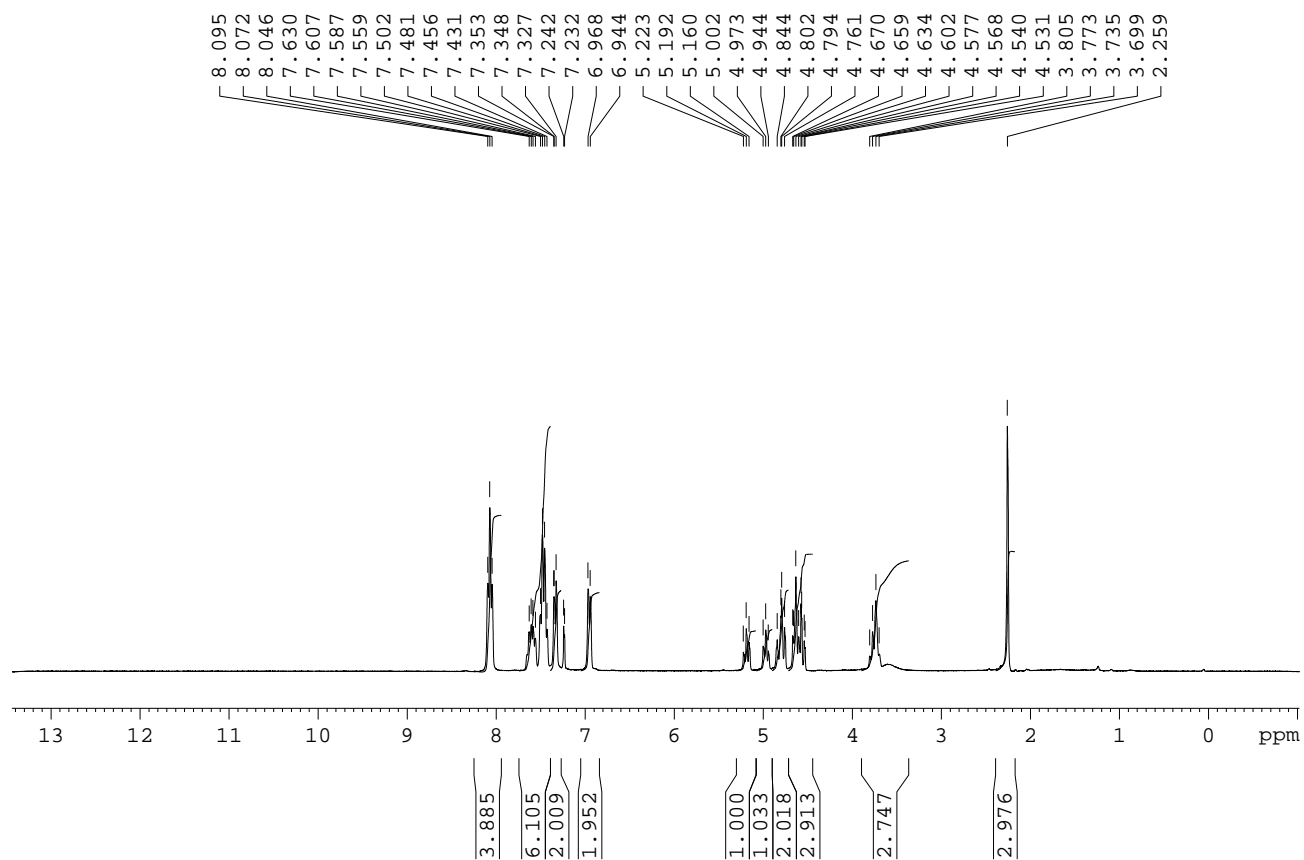


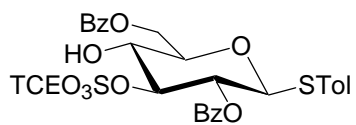
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **26**



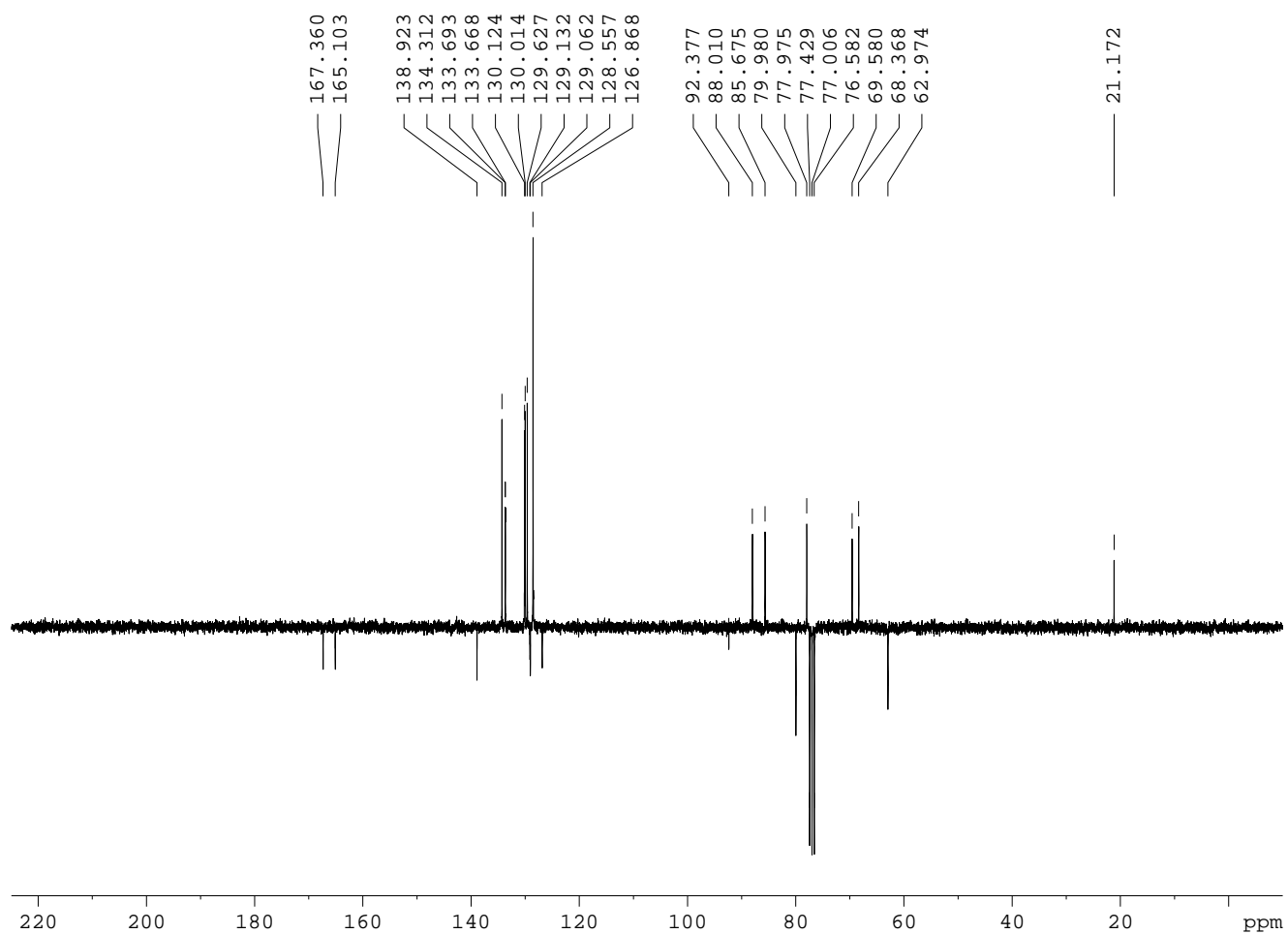


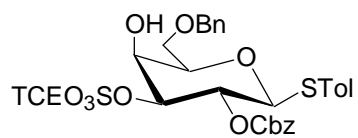
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **27**



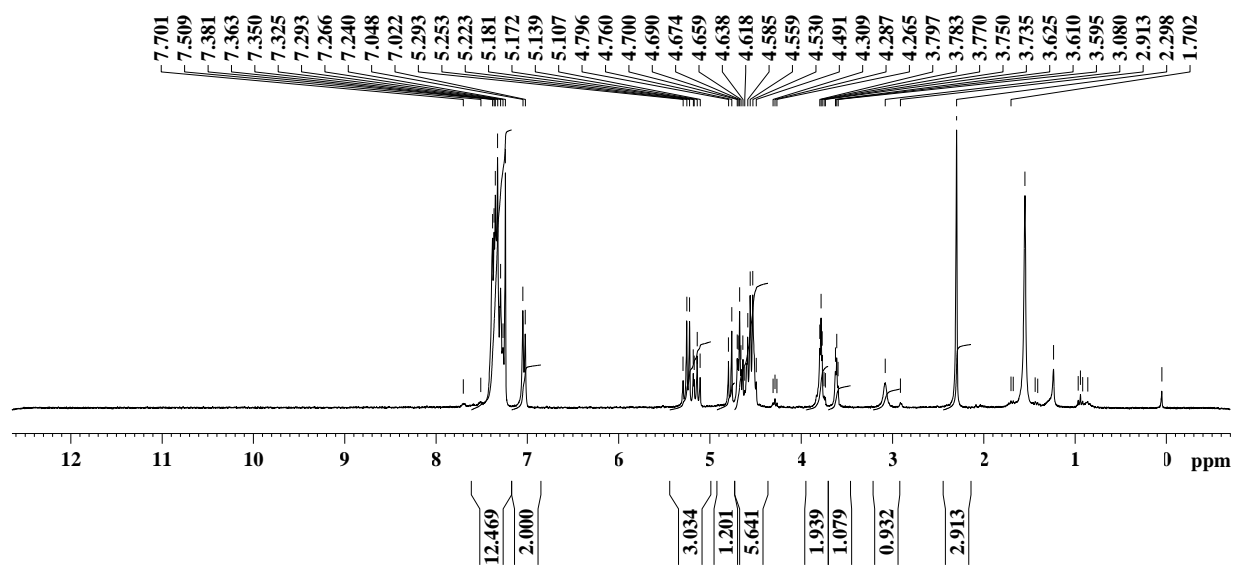


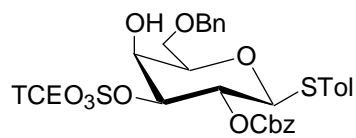
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **27**



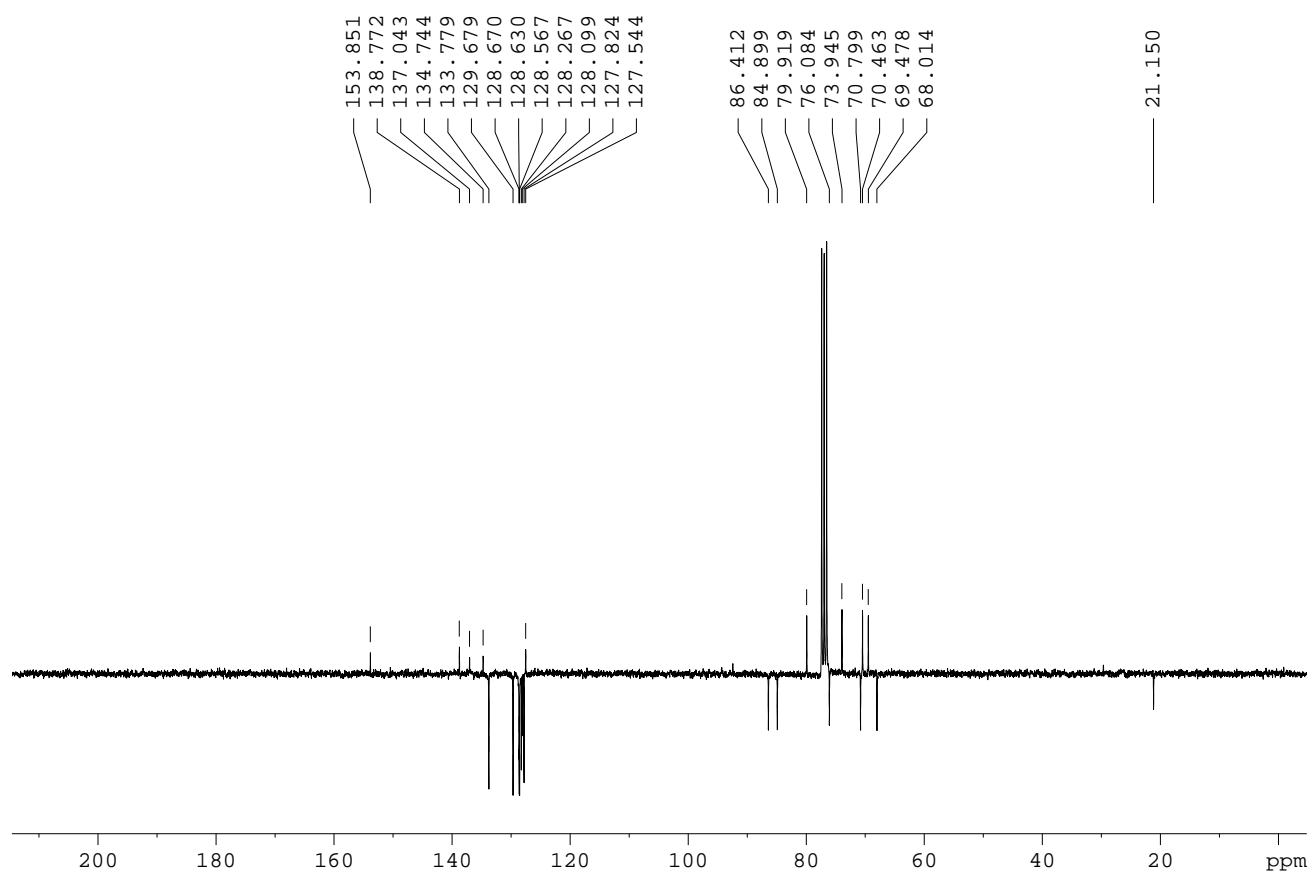


<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **28**

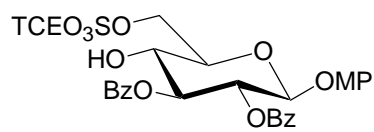




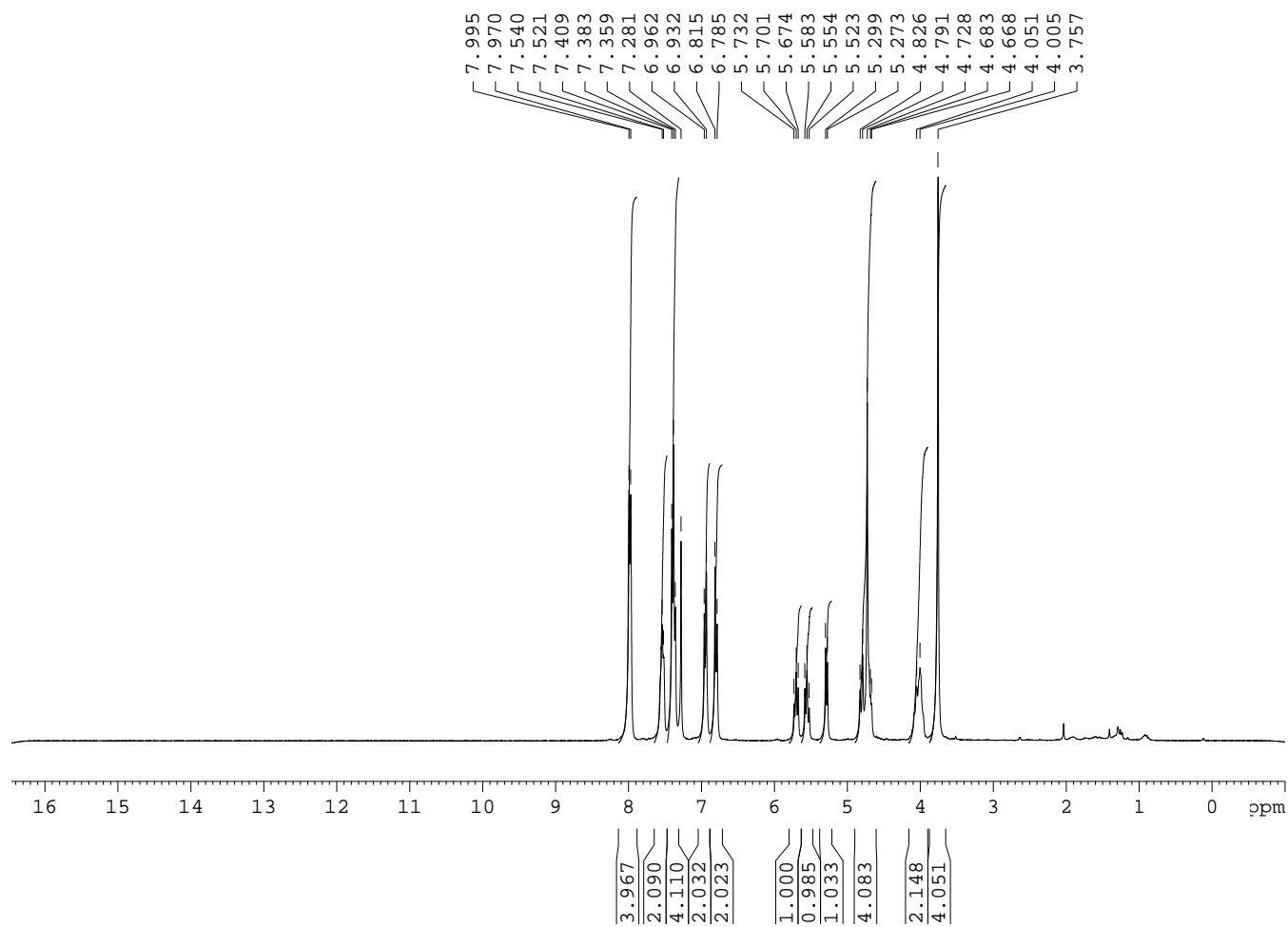
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **28**

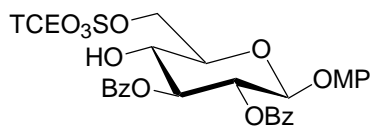




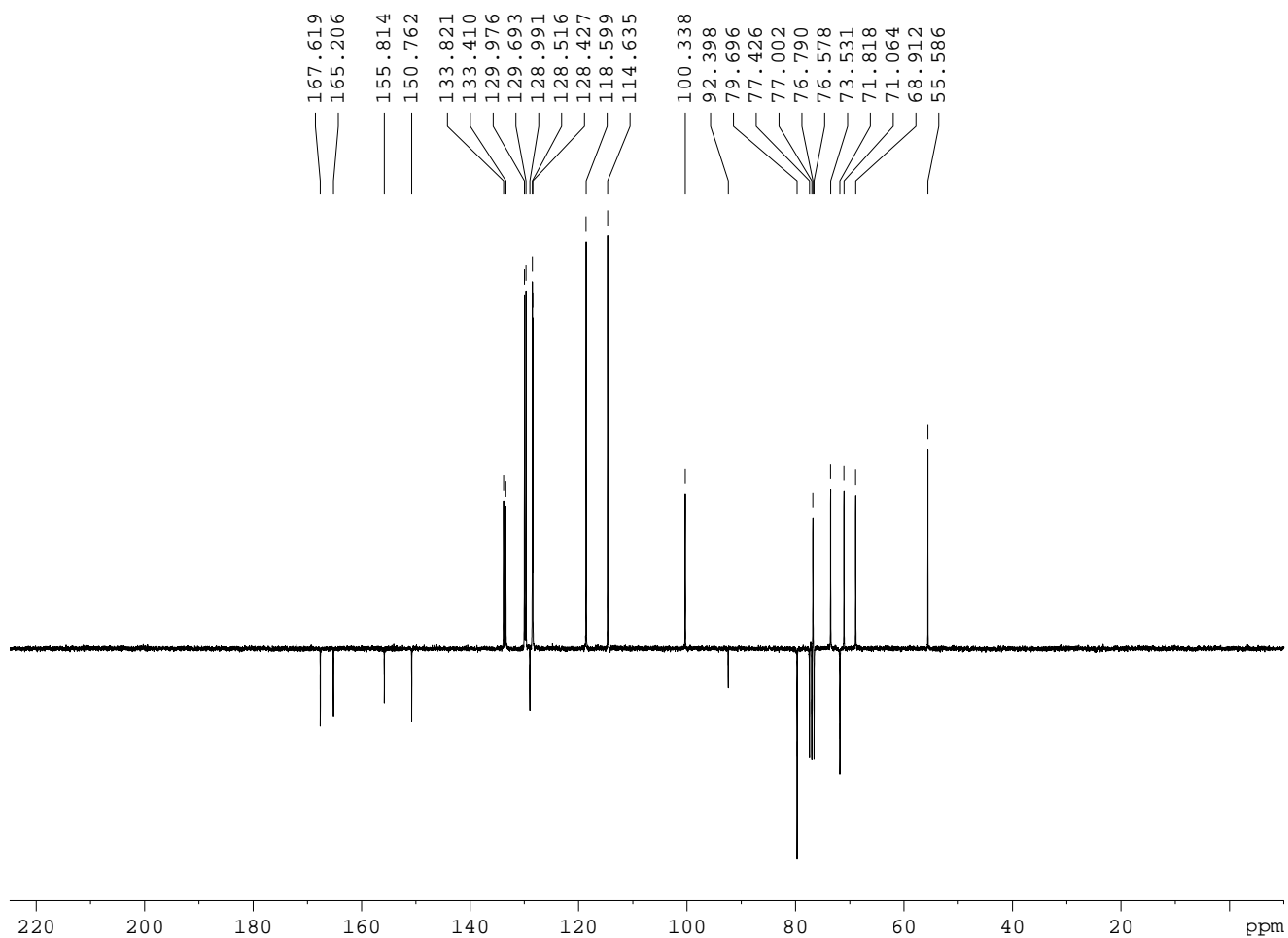


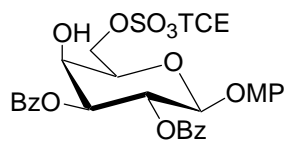
<sup>1</sup>H-MR (CDCl<sub>3</sub>) for compound **29**



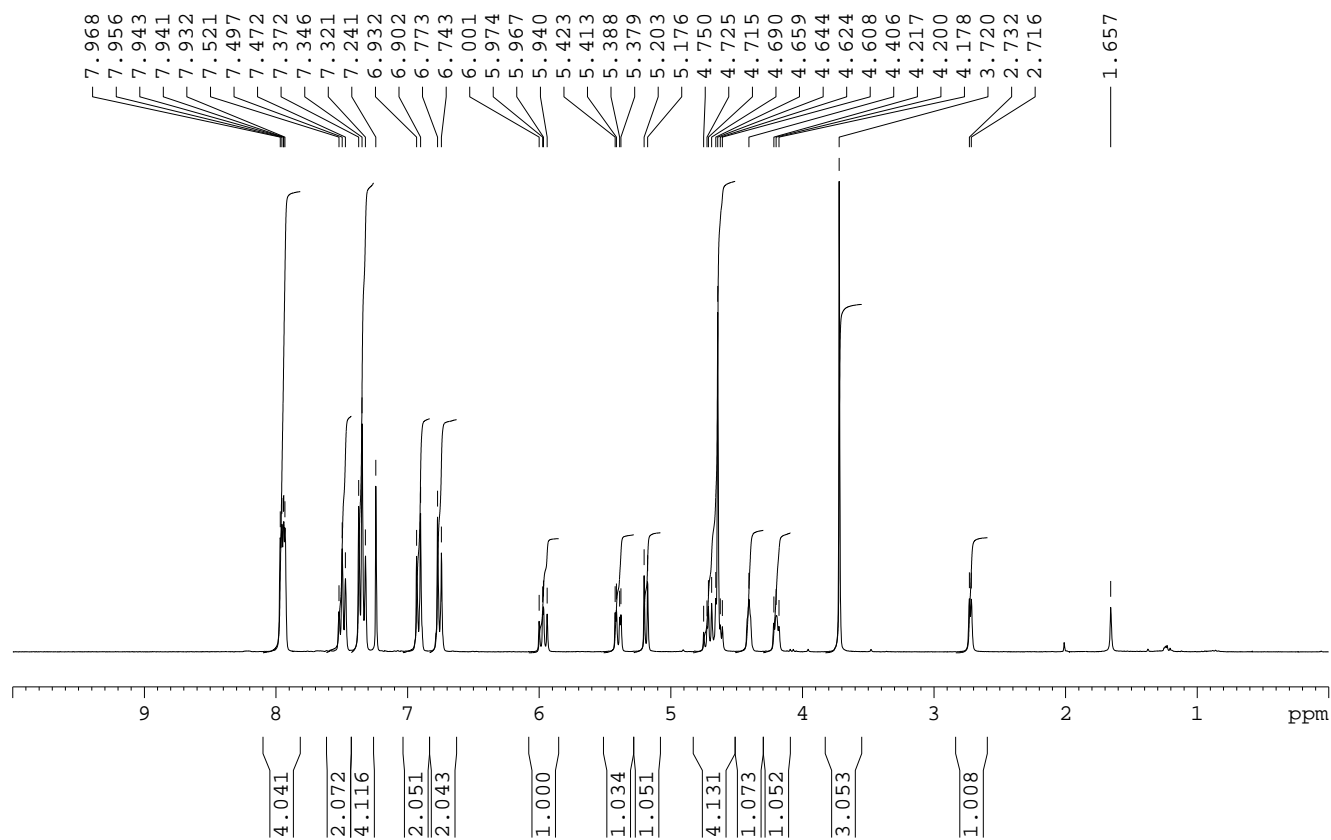


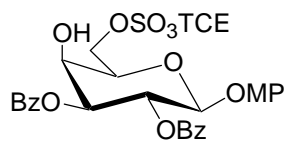
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **29**



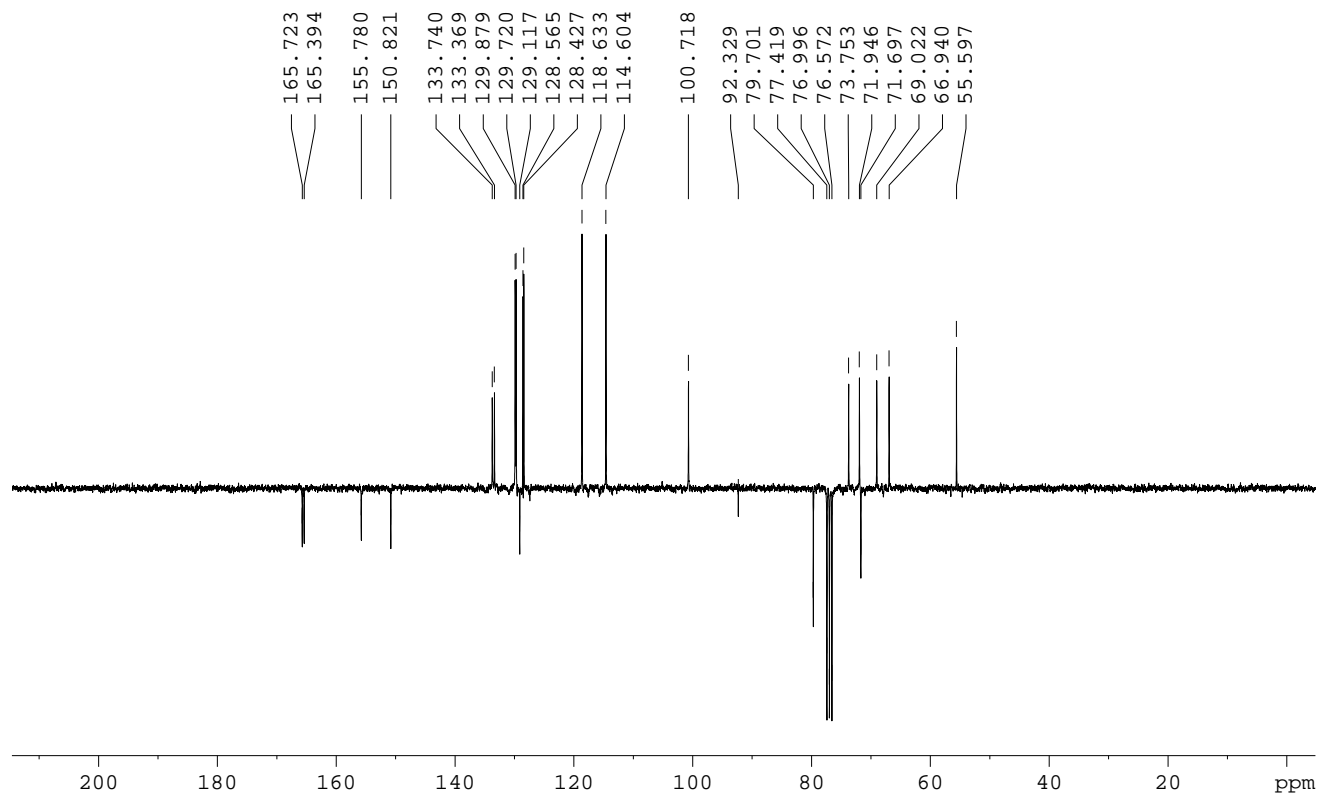


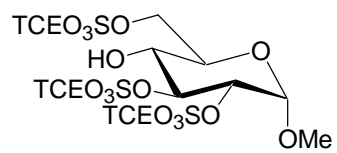
$^1\text{H}$ -MR ( $\text{CDCl}_3$ ) for compound **30**



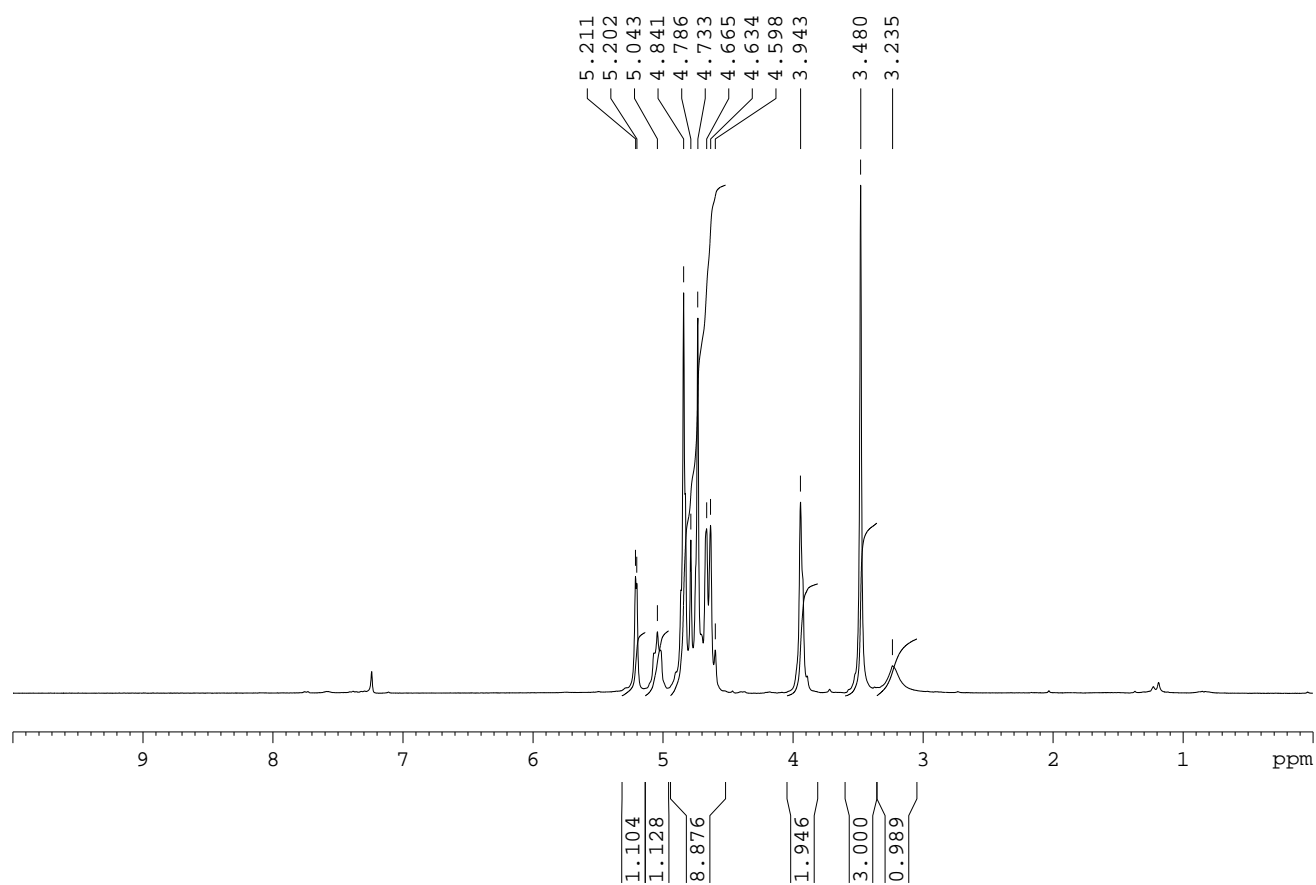


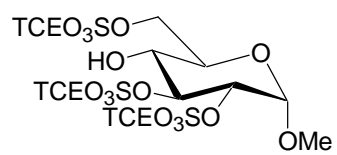
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **30**



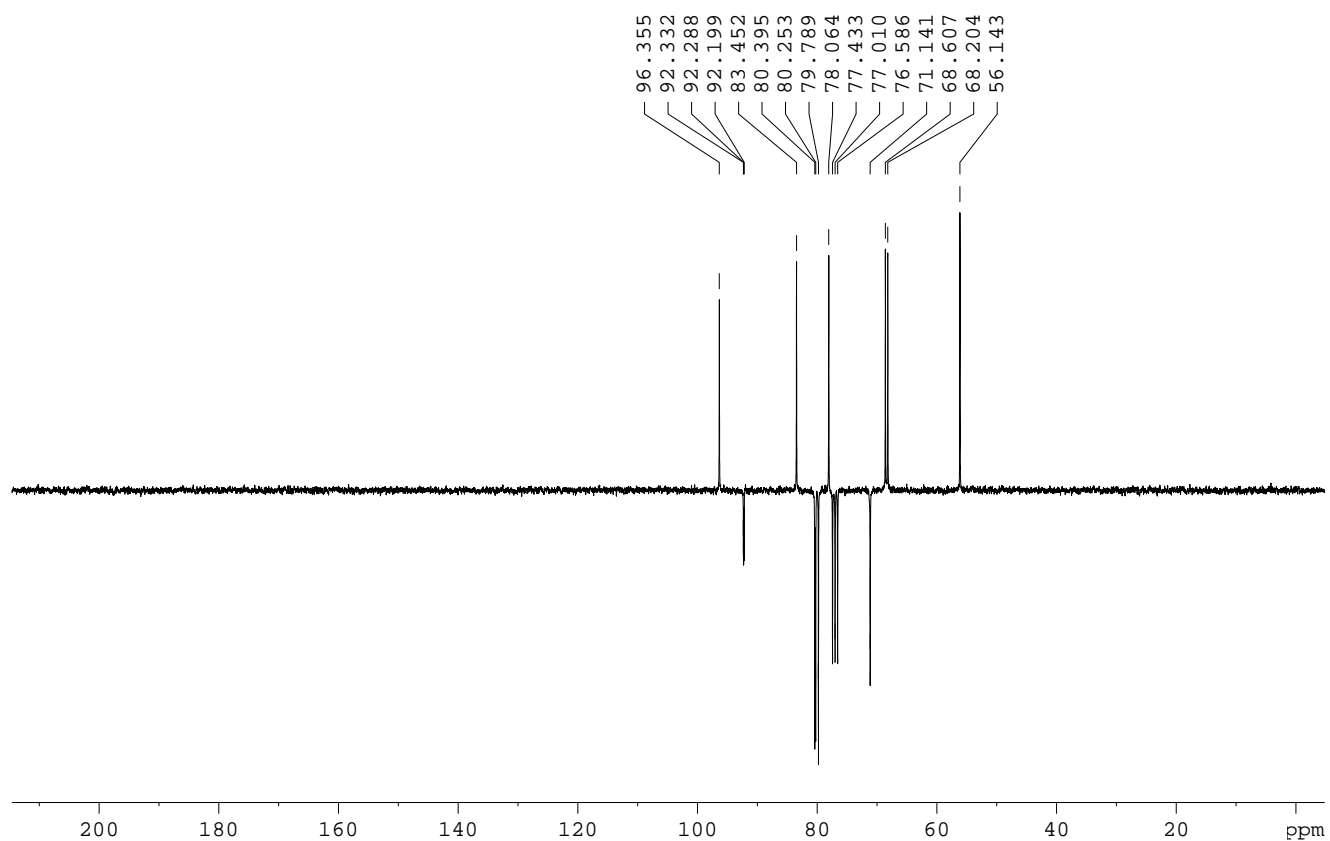


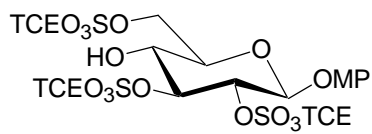
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for compound **31**



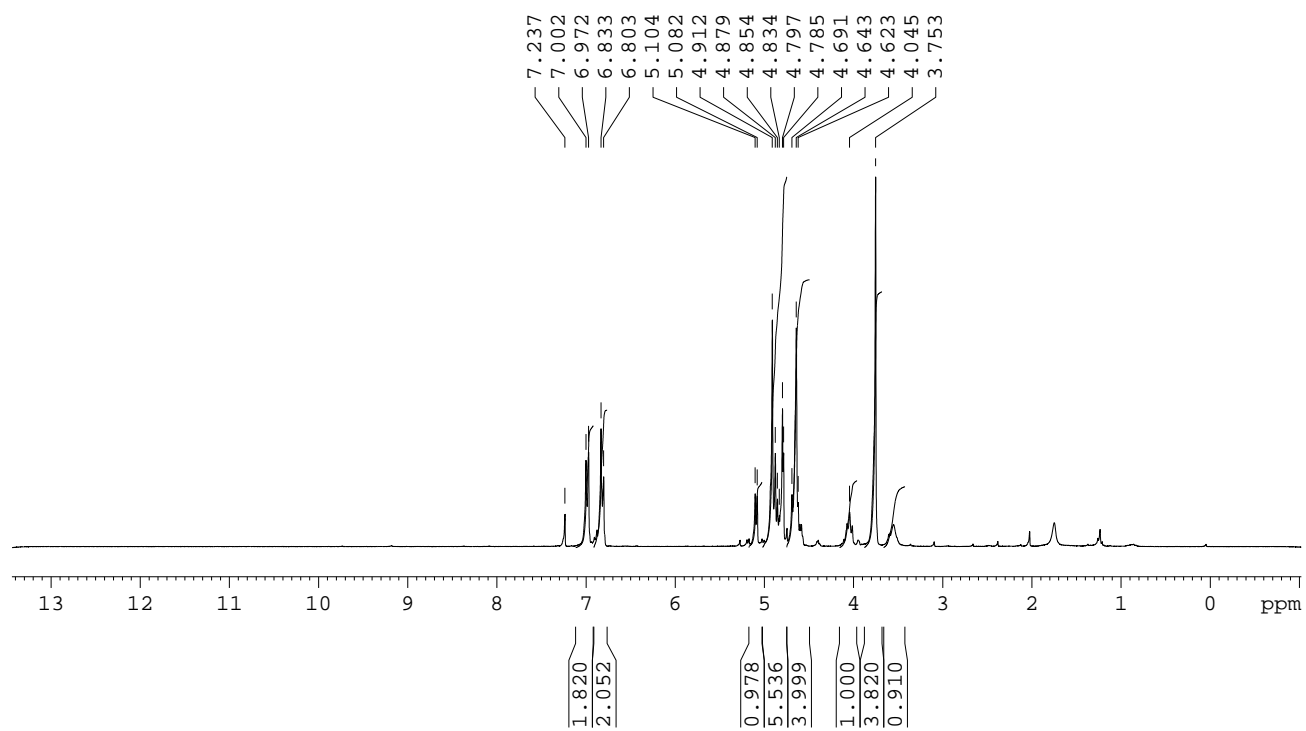


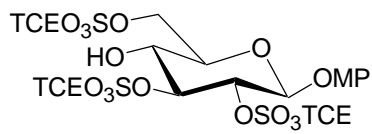
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **31**



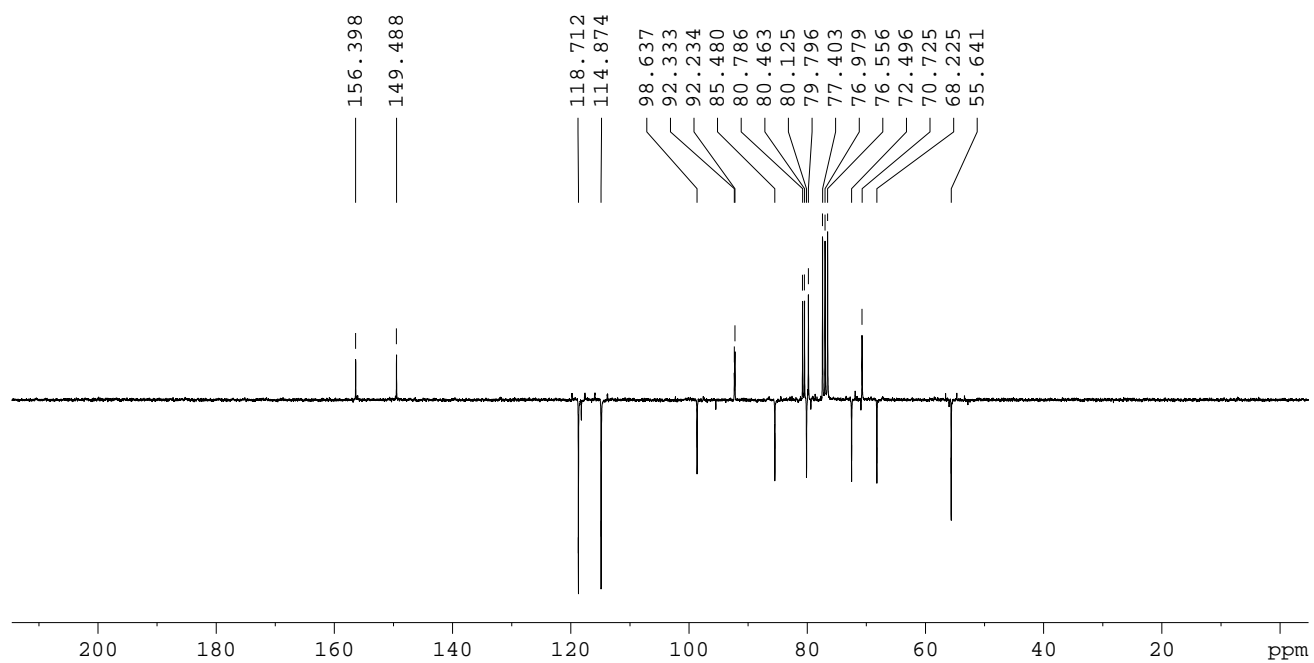


$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **32**

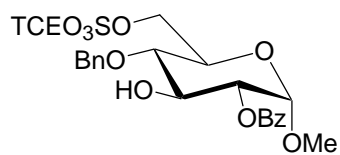




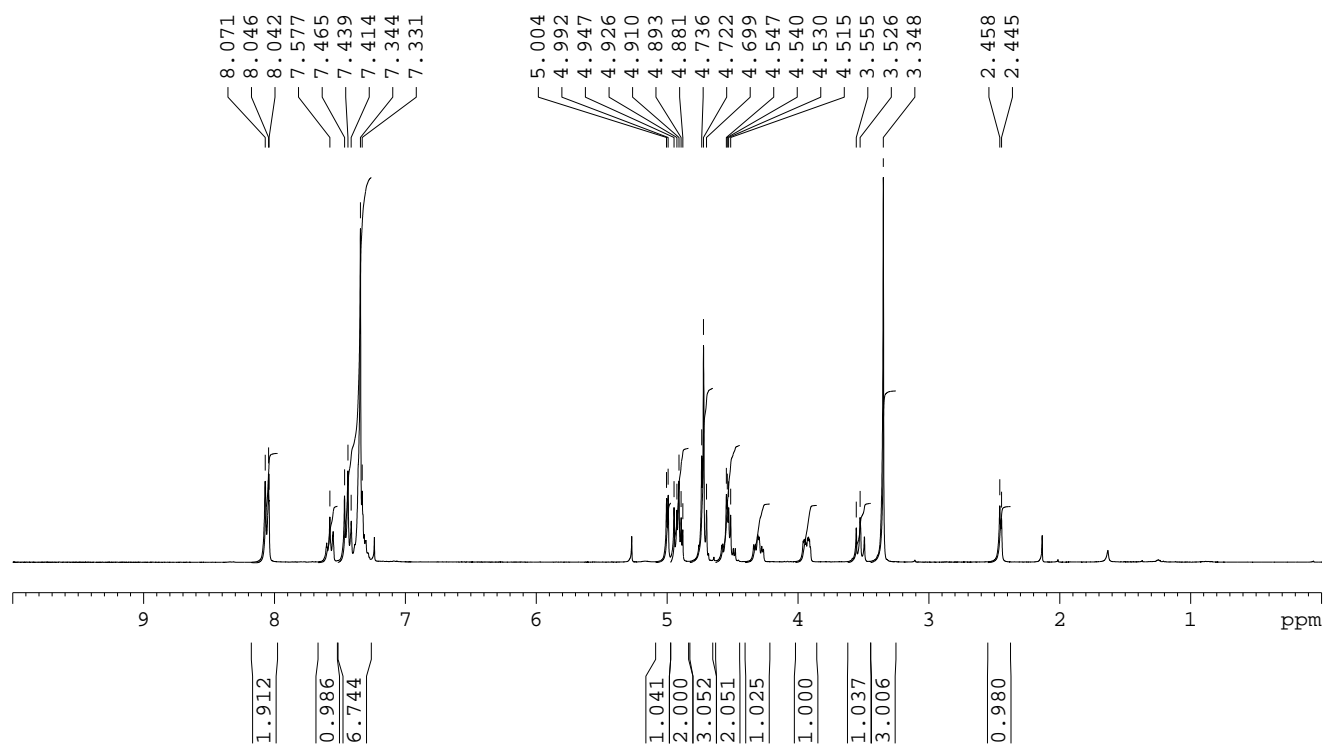
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **32**

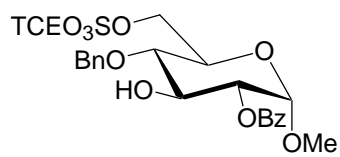




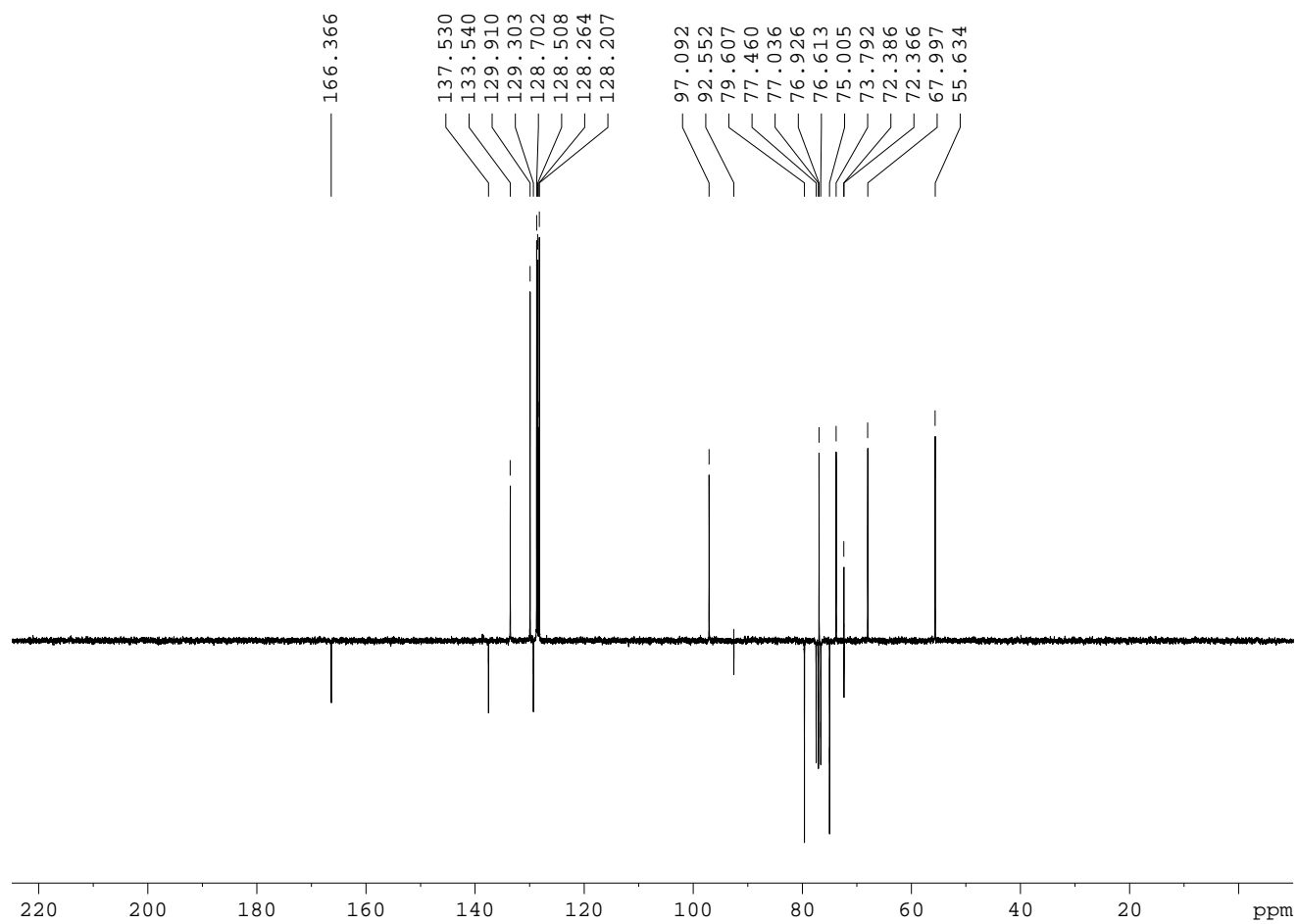


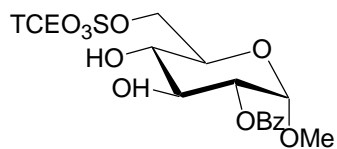
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **33**



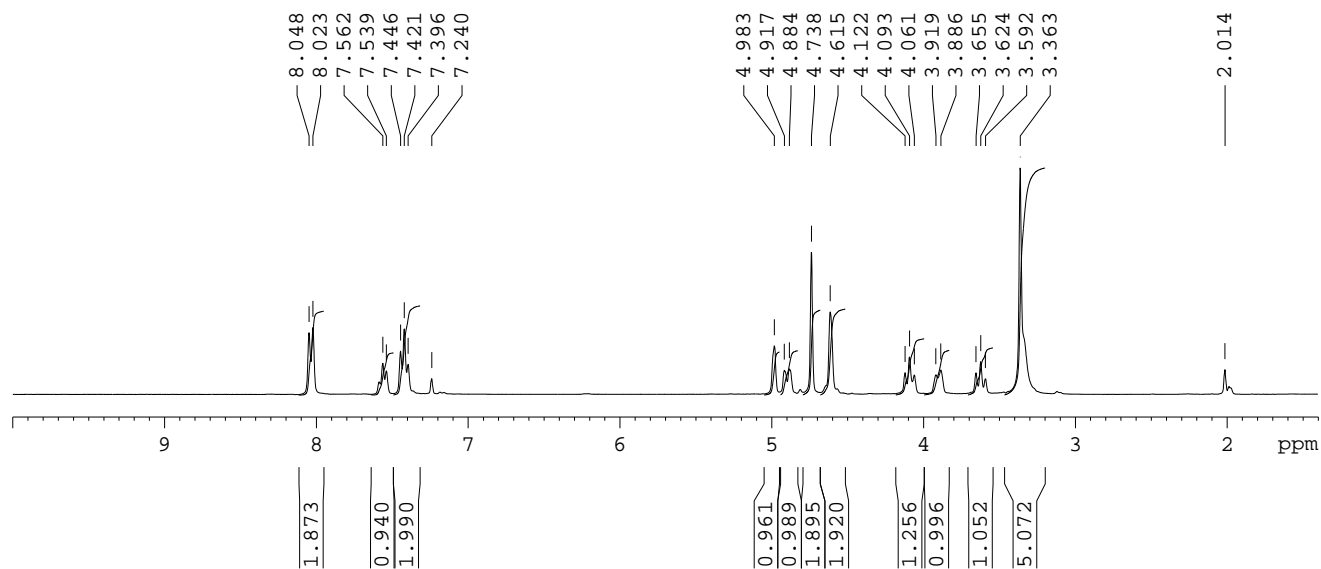


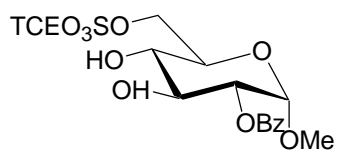
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **33**



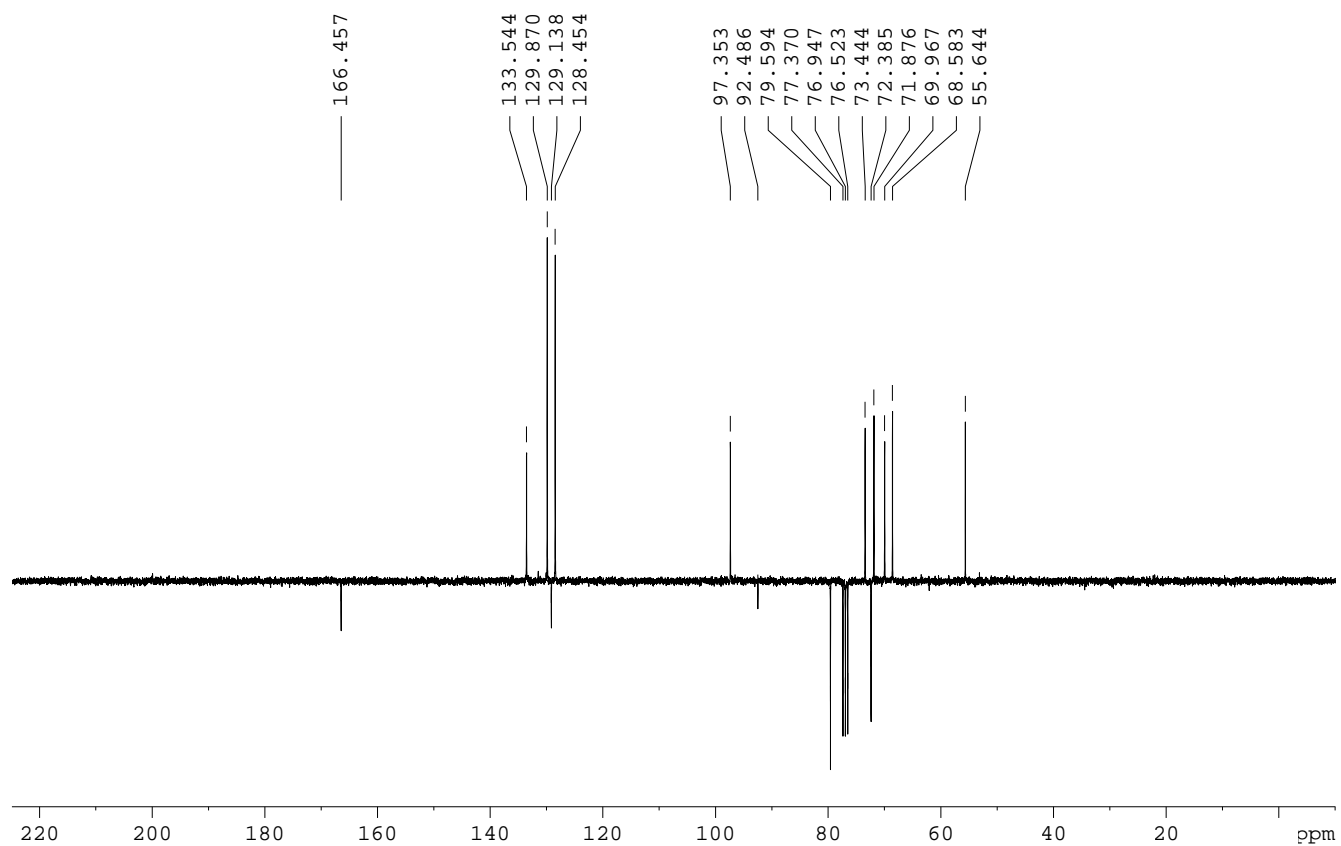


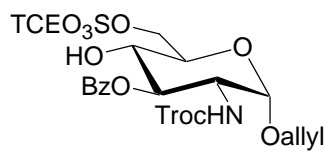
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **34**



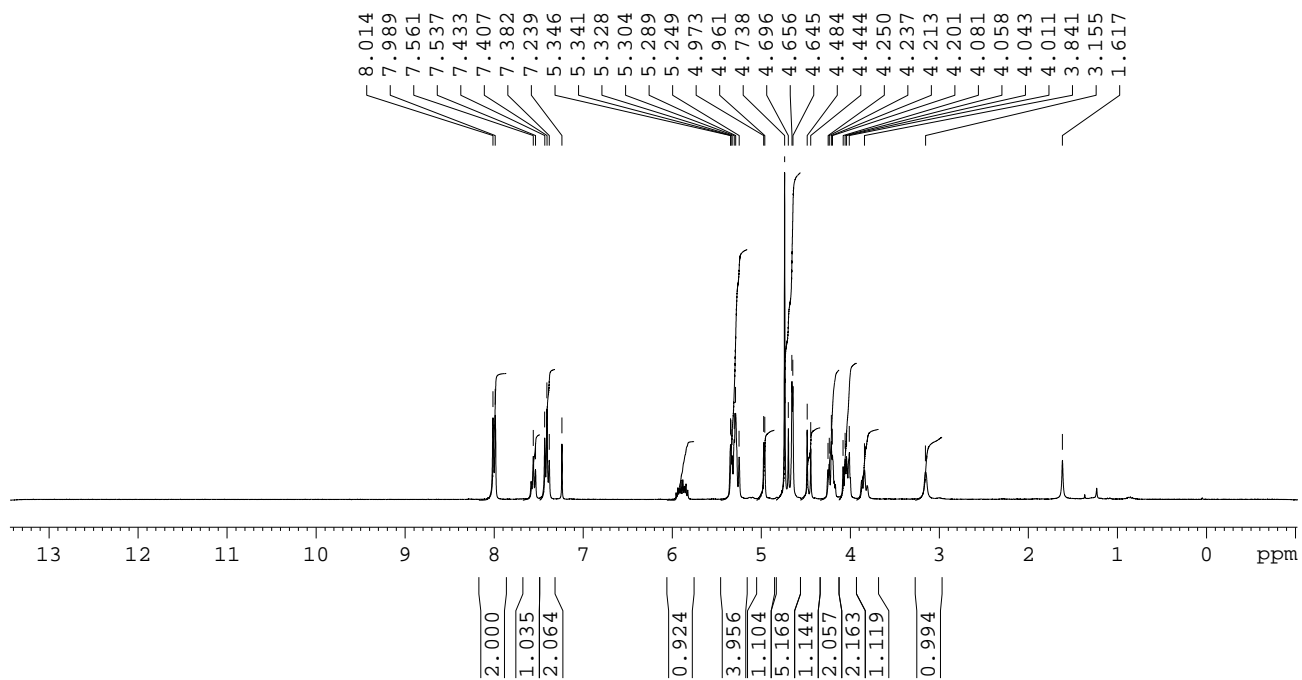


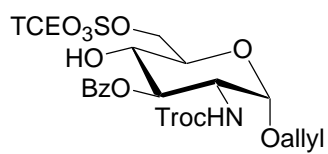
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **34**



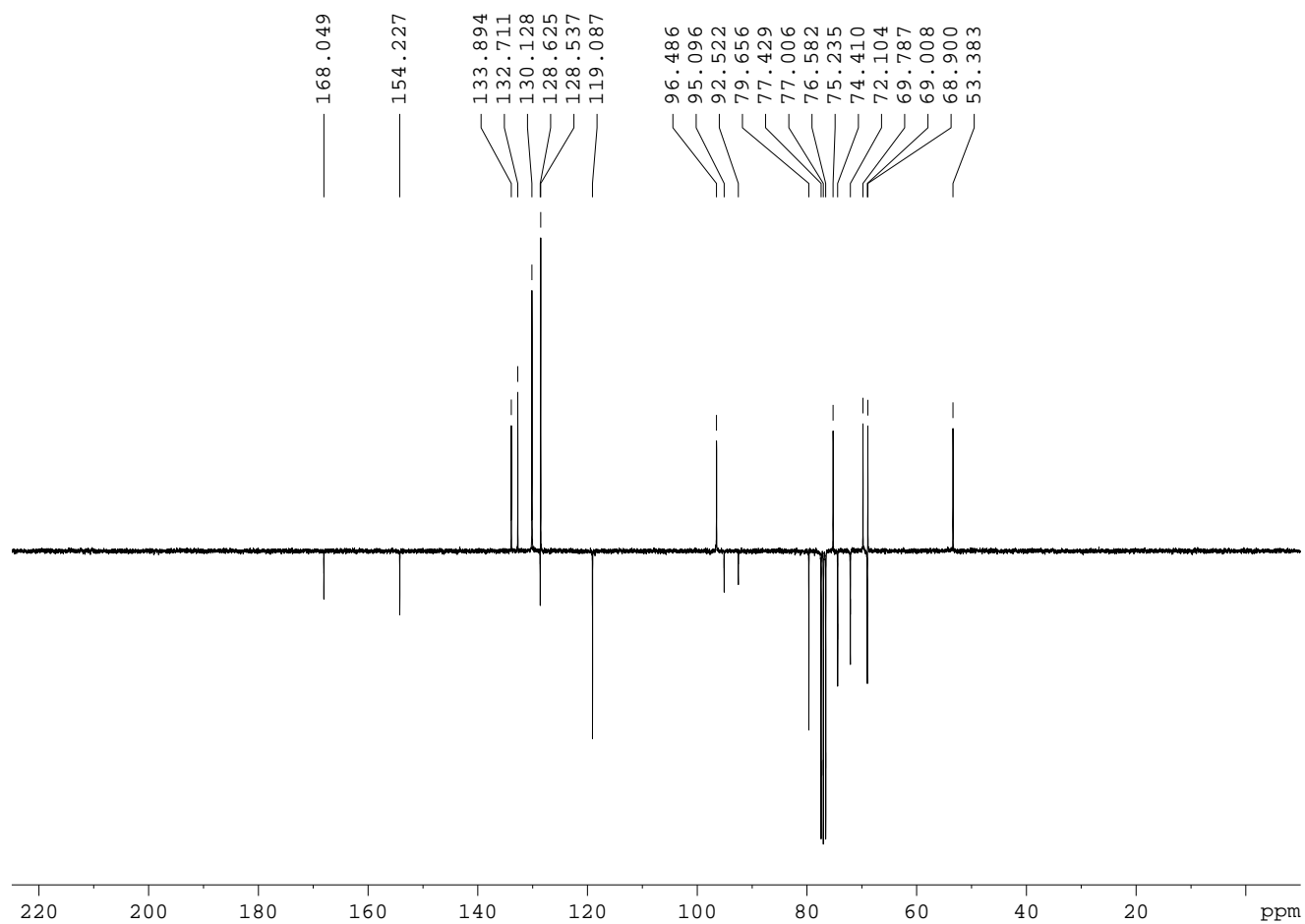


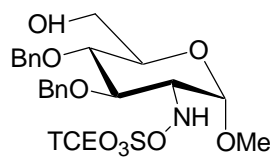
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **35**



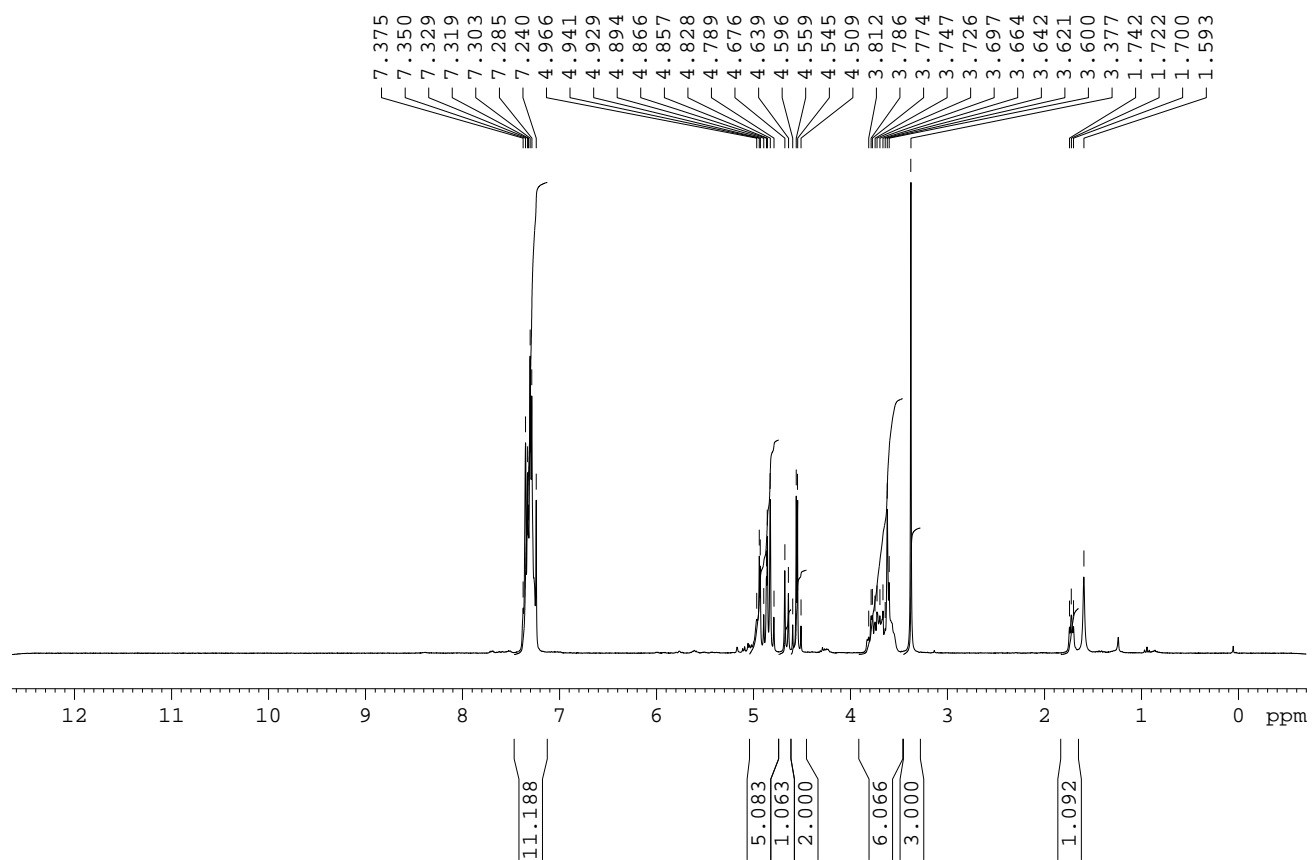


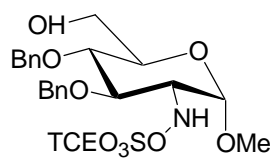
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **35**



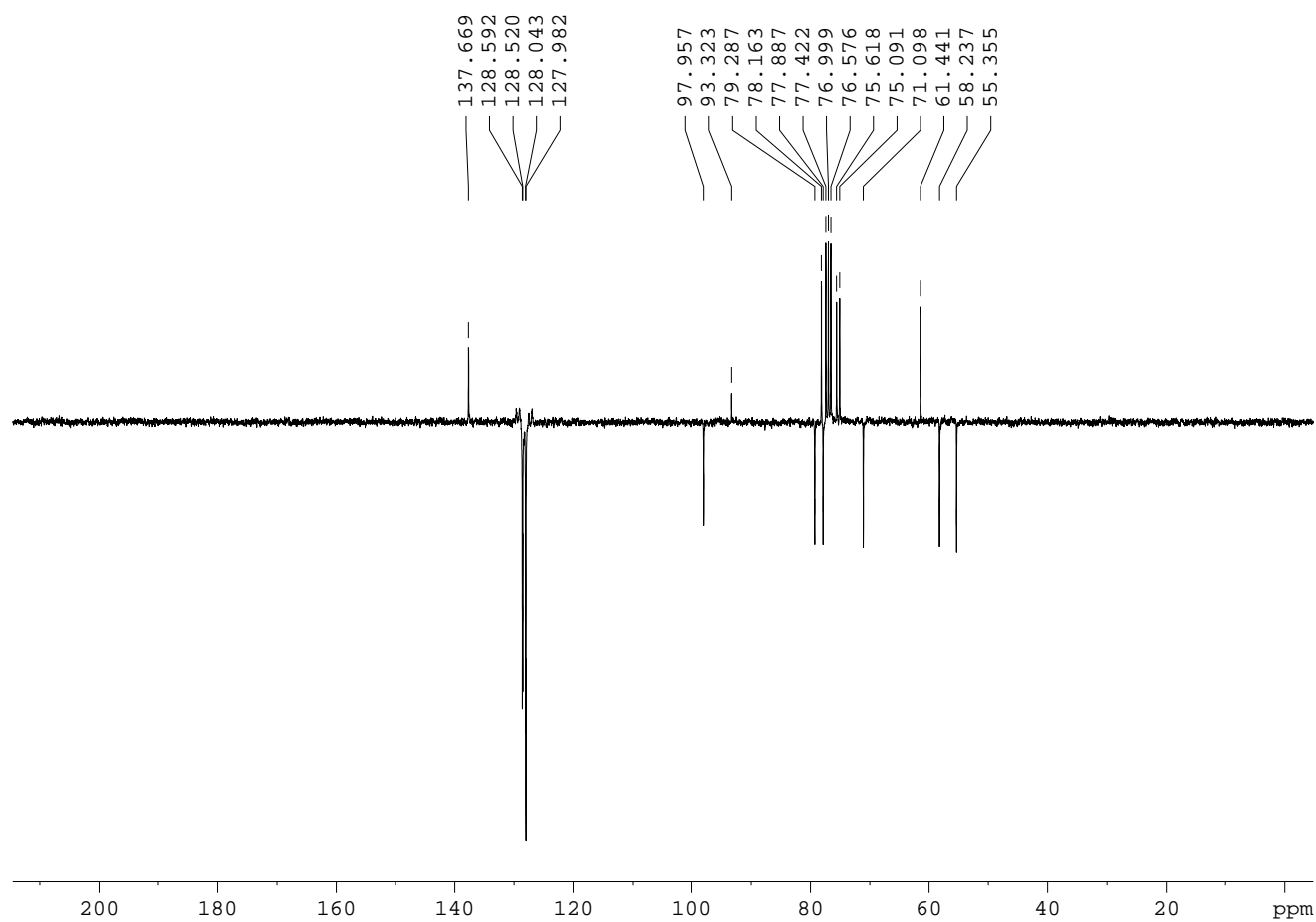


$^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) for compound **36**

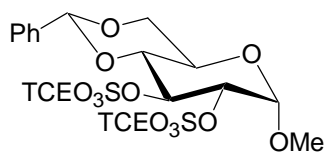




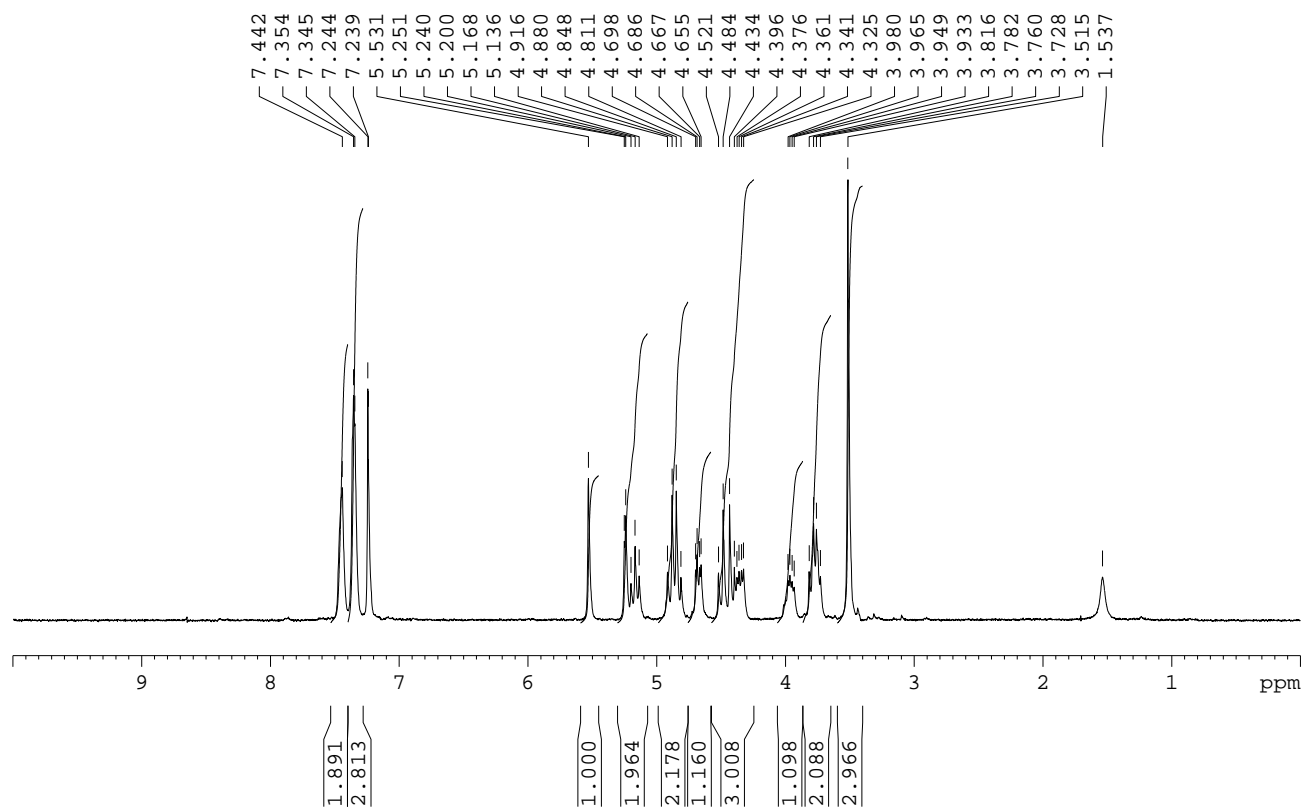
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **36**

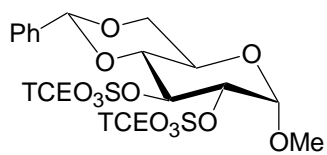




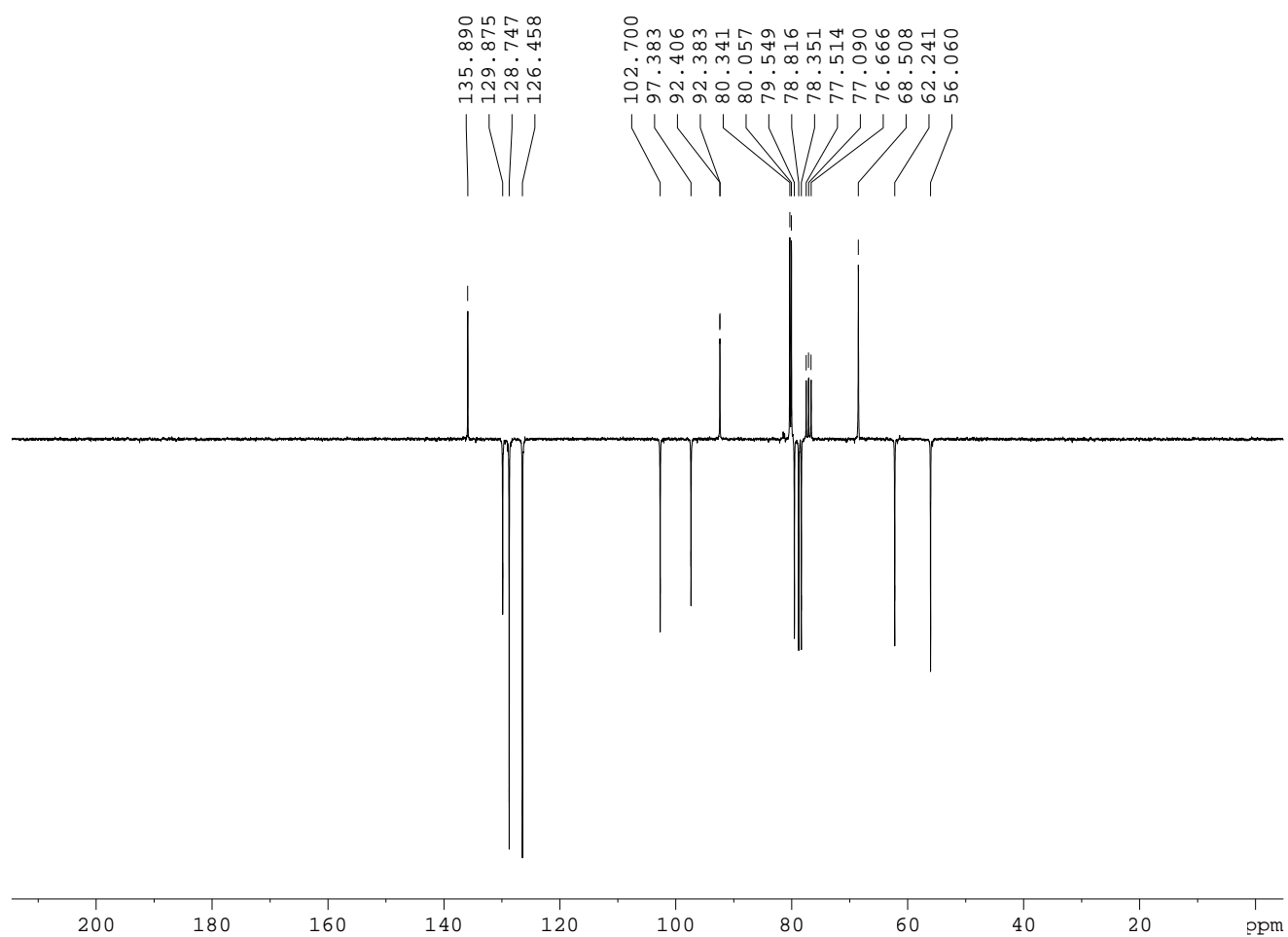


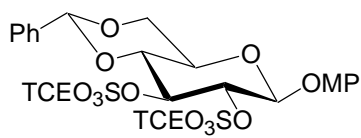
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **40**



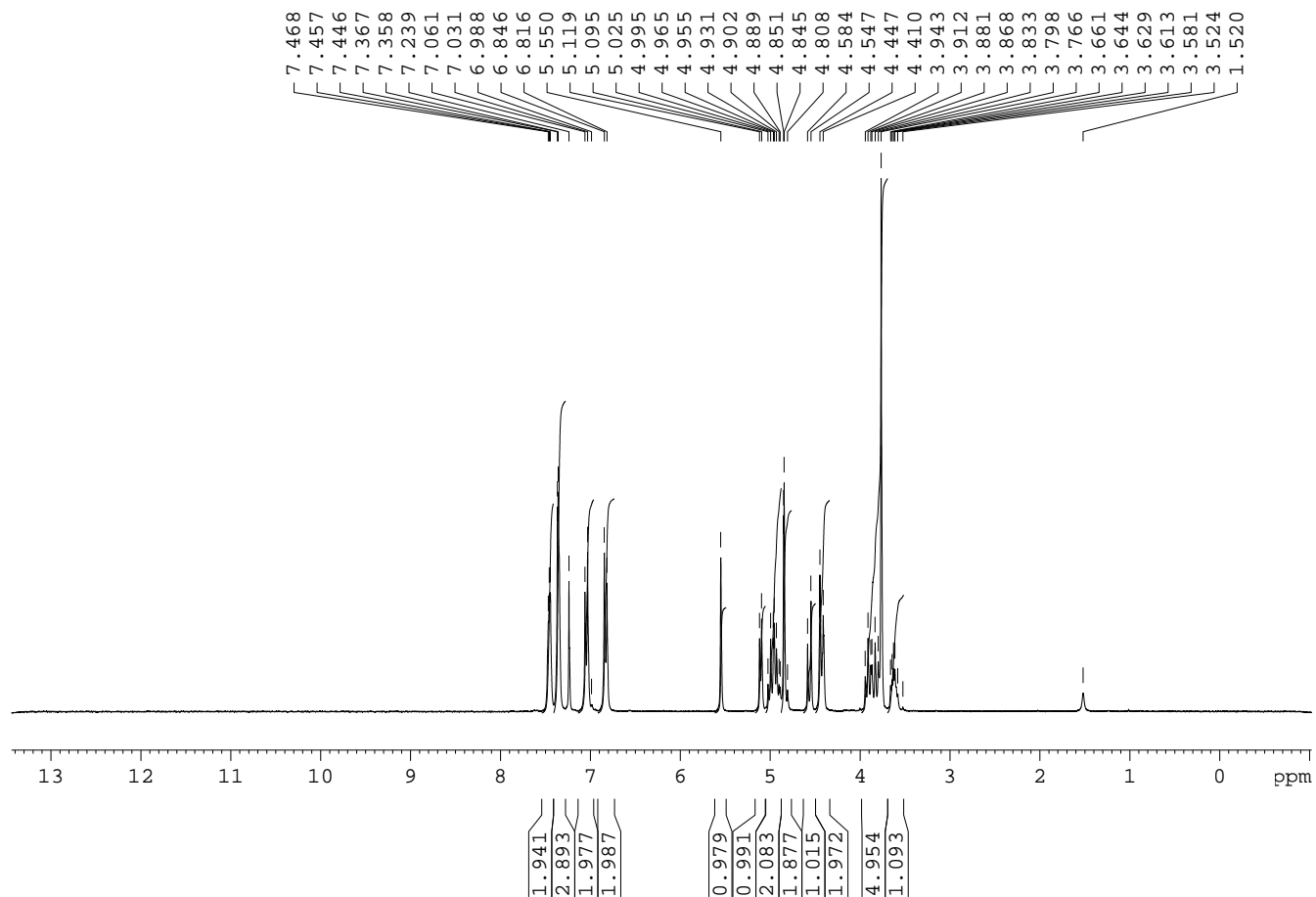


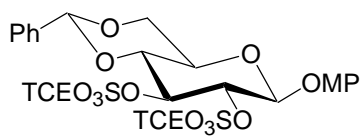
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **40**



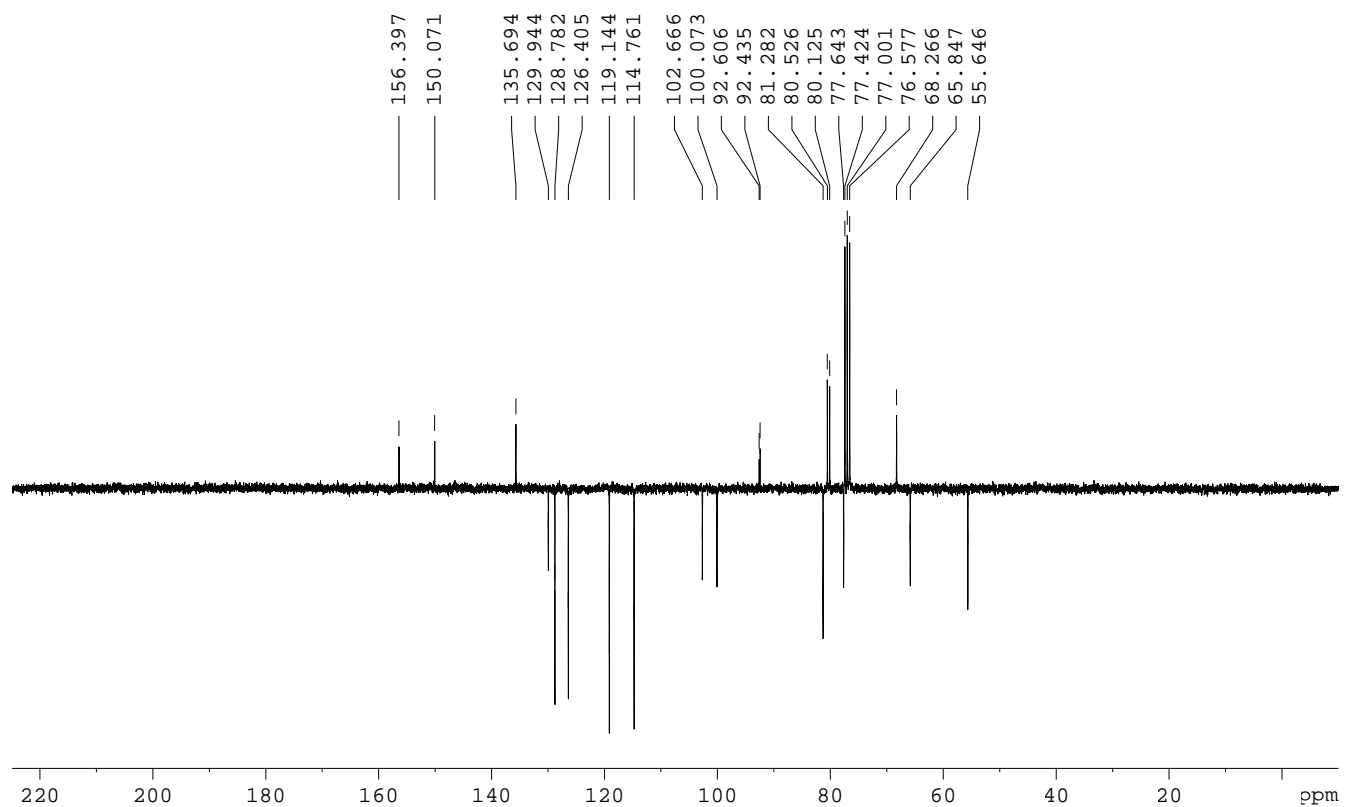


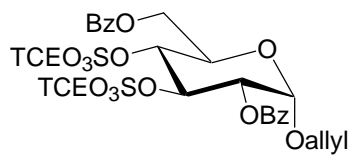
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **41**



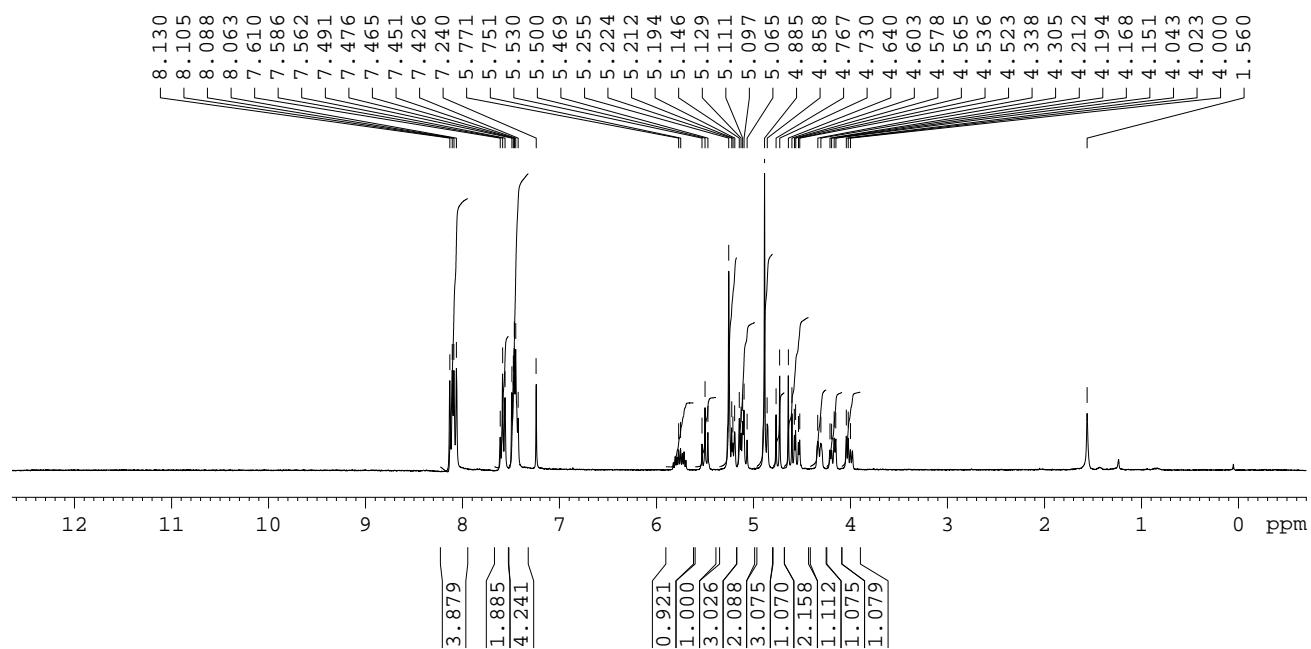


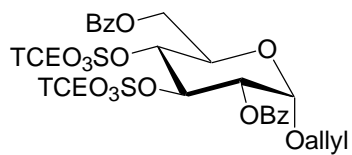
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **41**



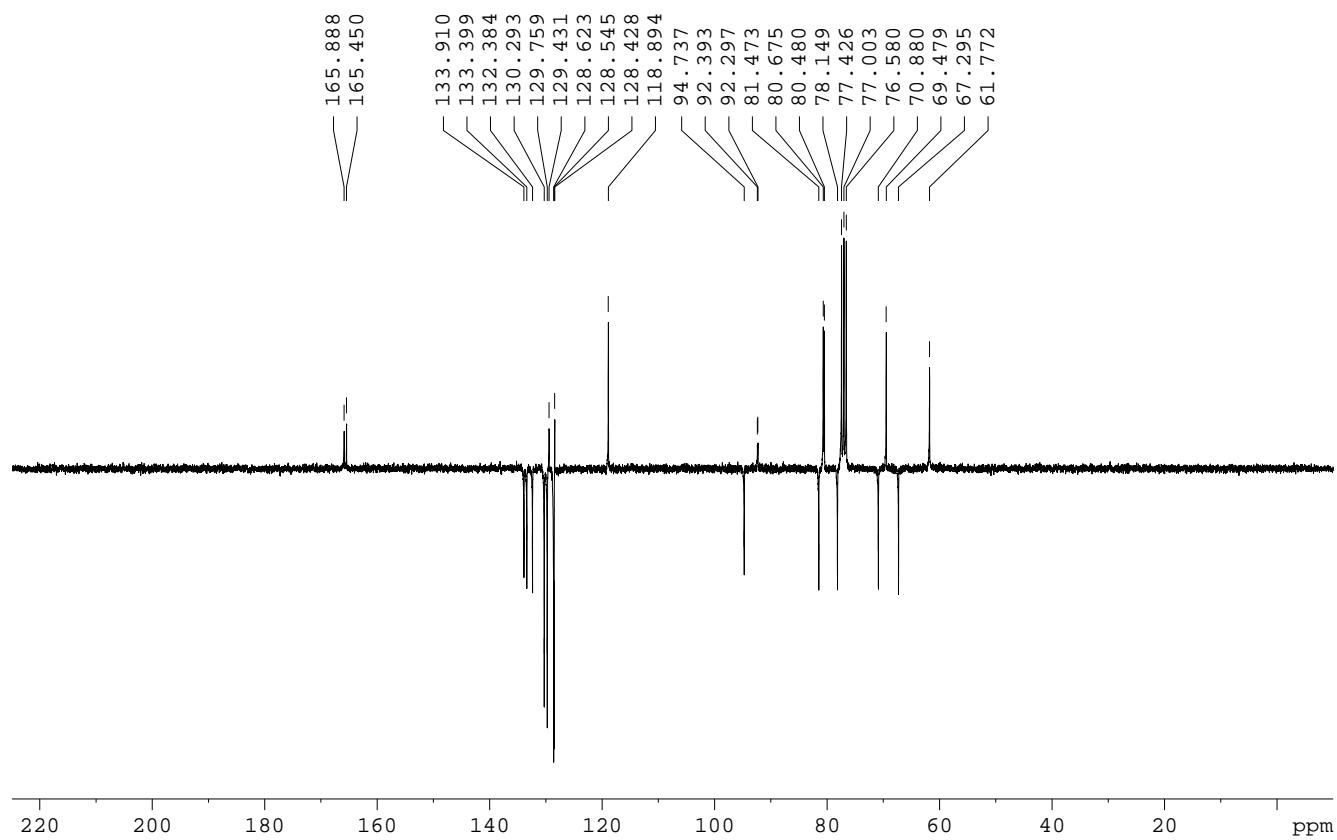


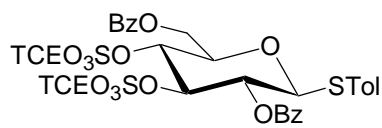
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **42**



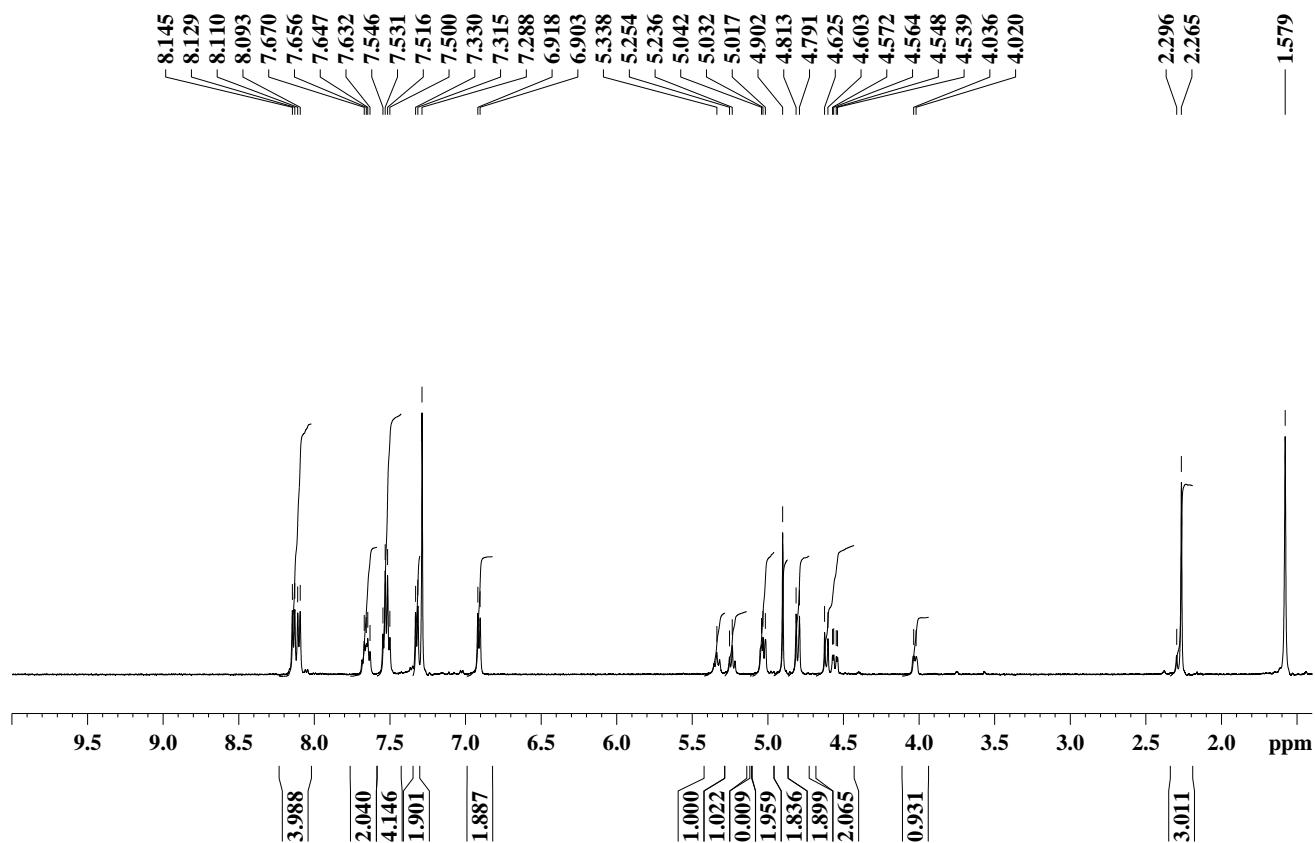


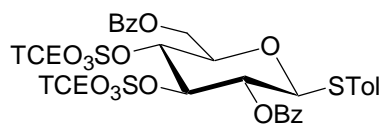
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **42**



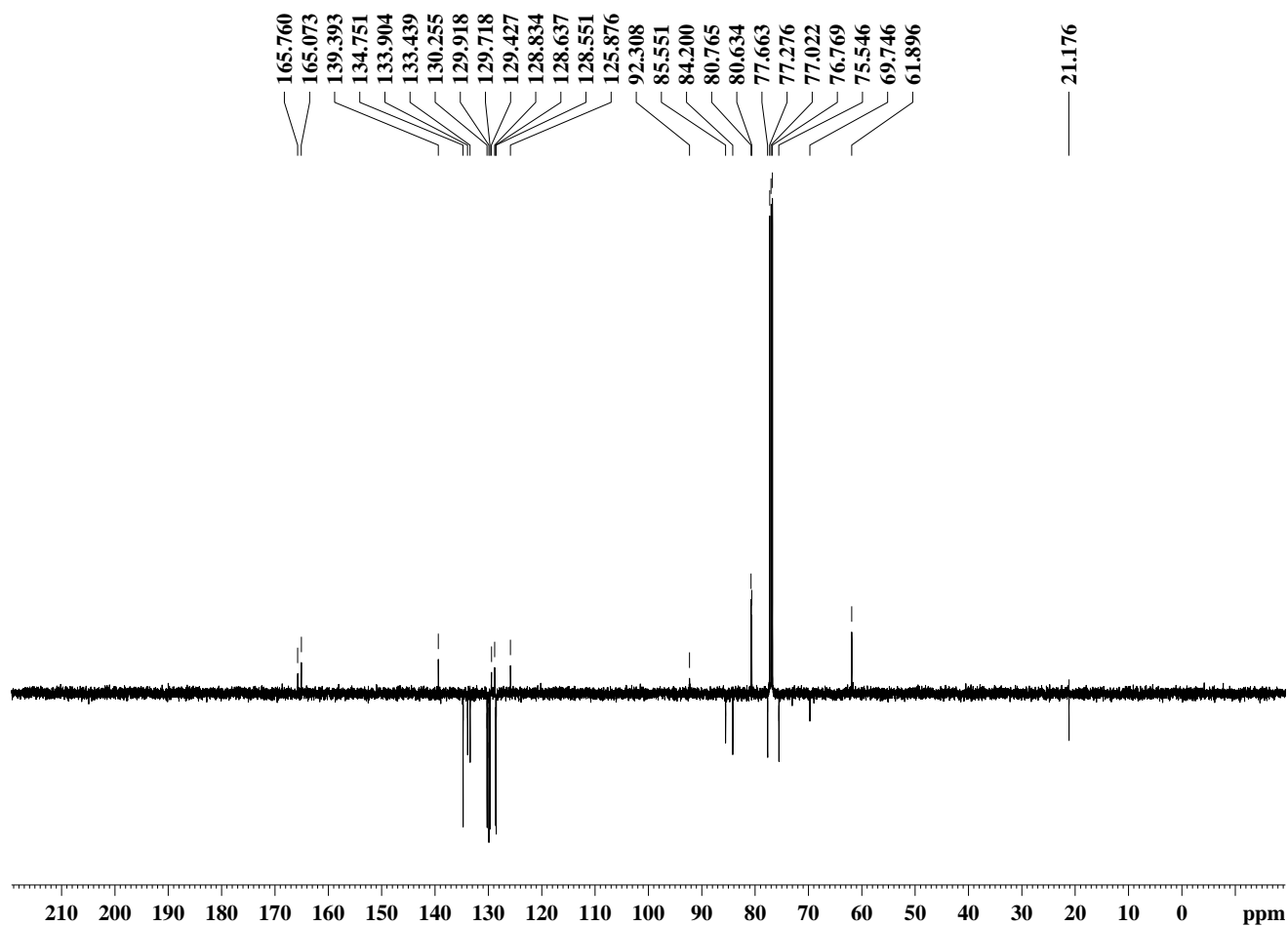


<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **43**

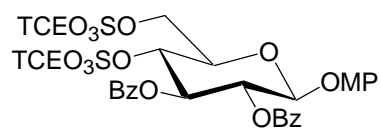




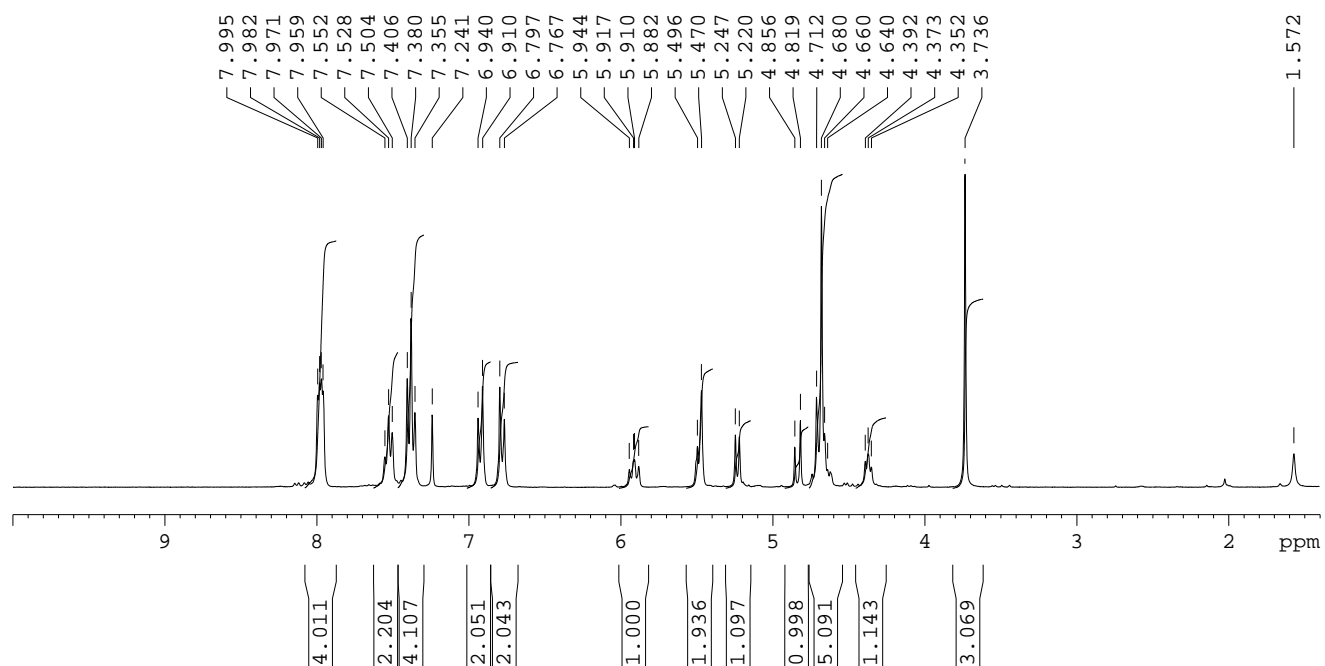
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **43**

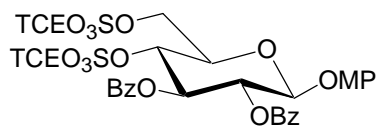




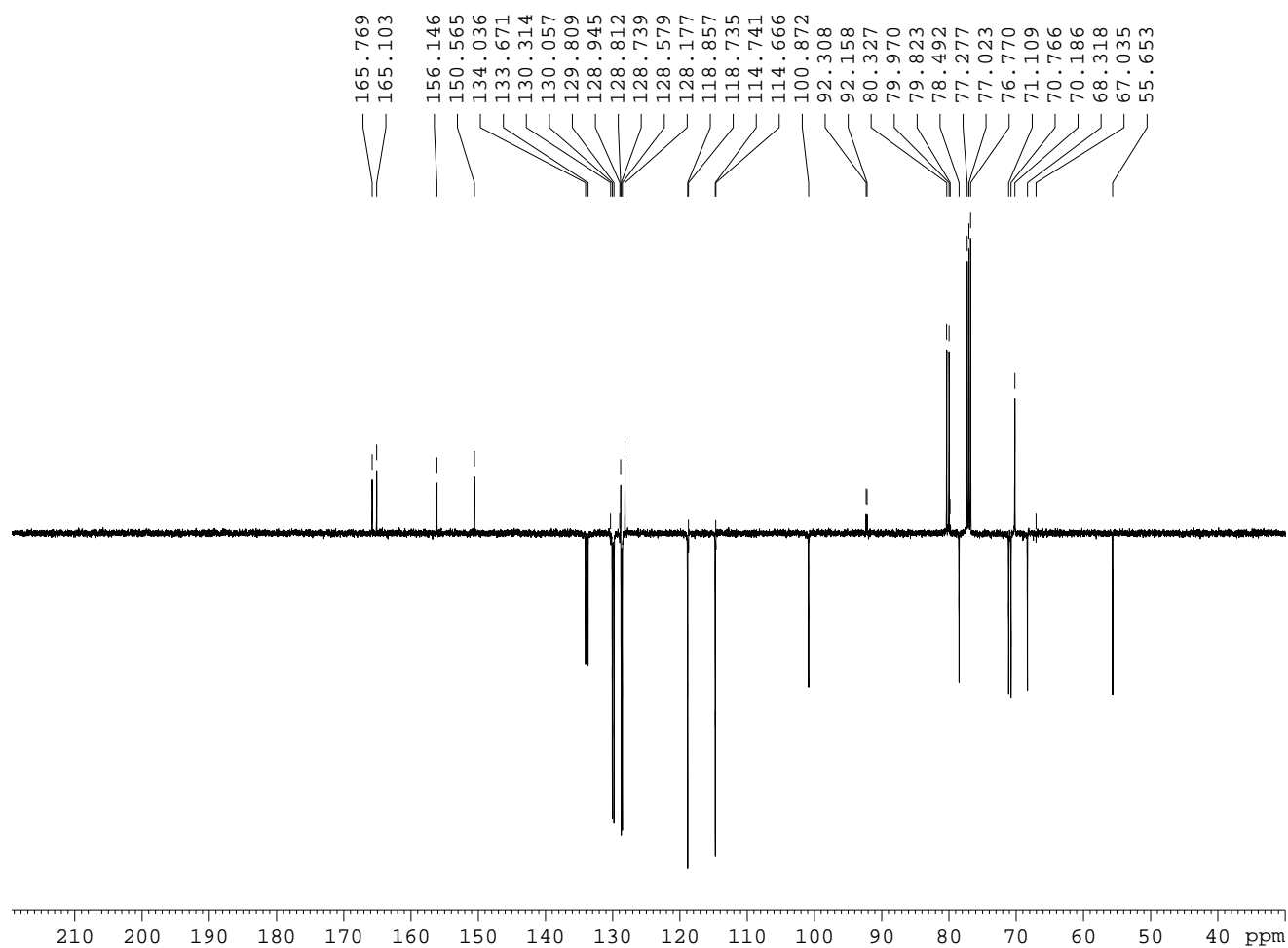


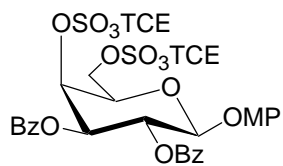
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **44**



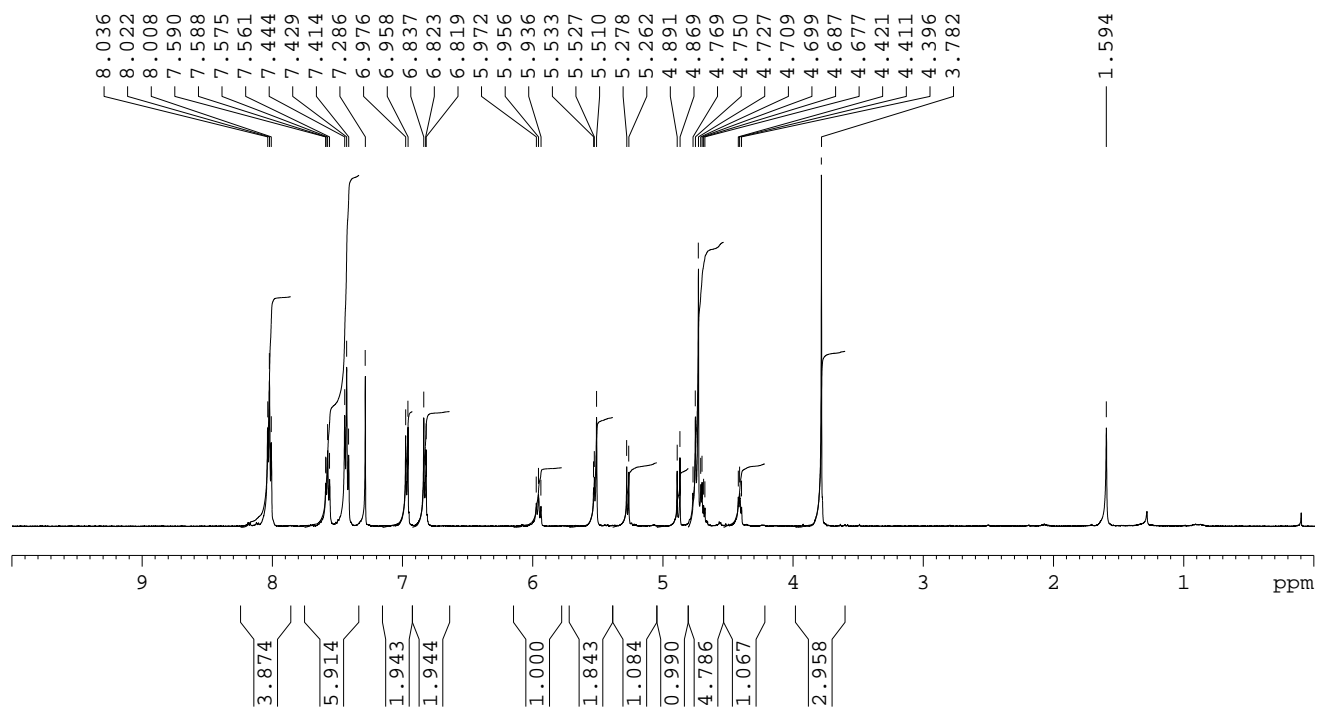


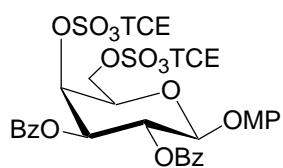
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **44**



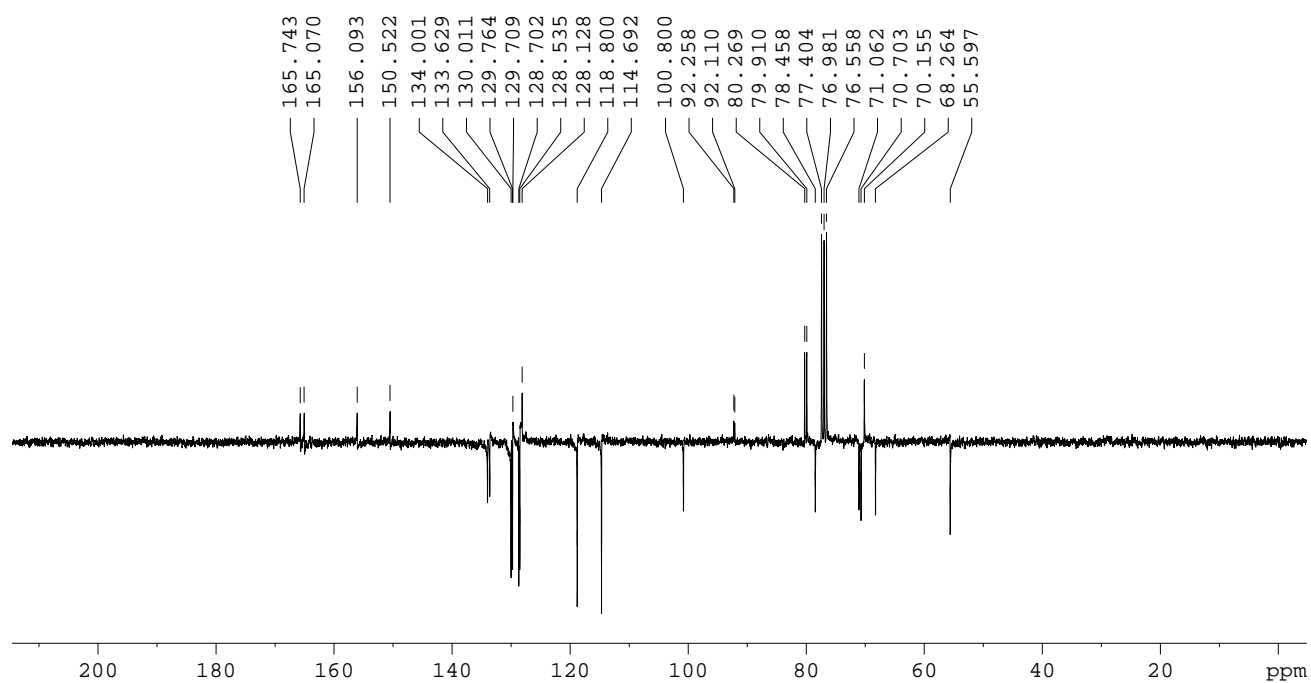


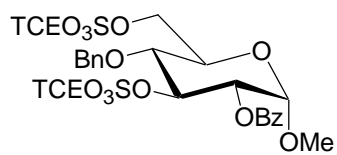
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **45**



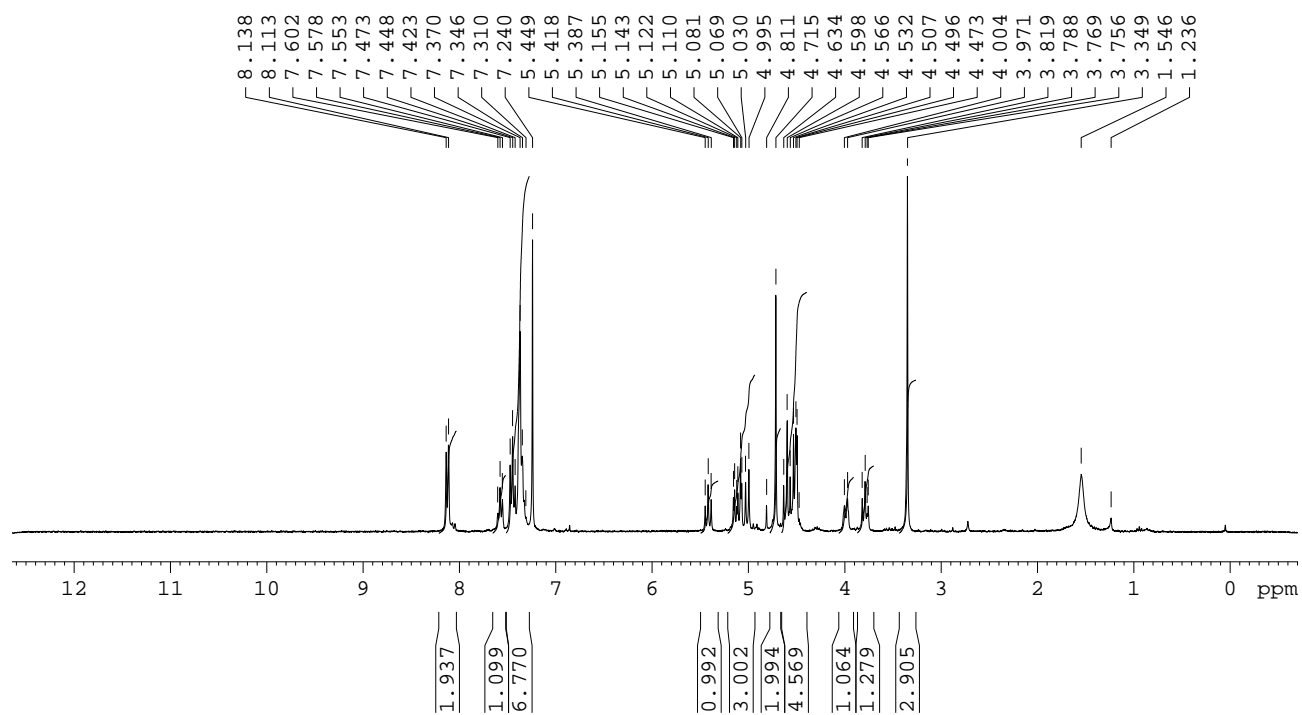


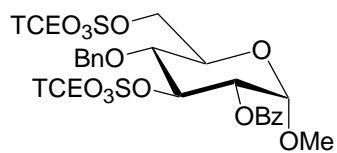
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **45**



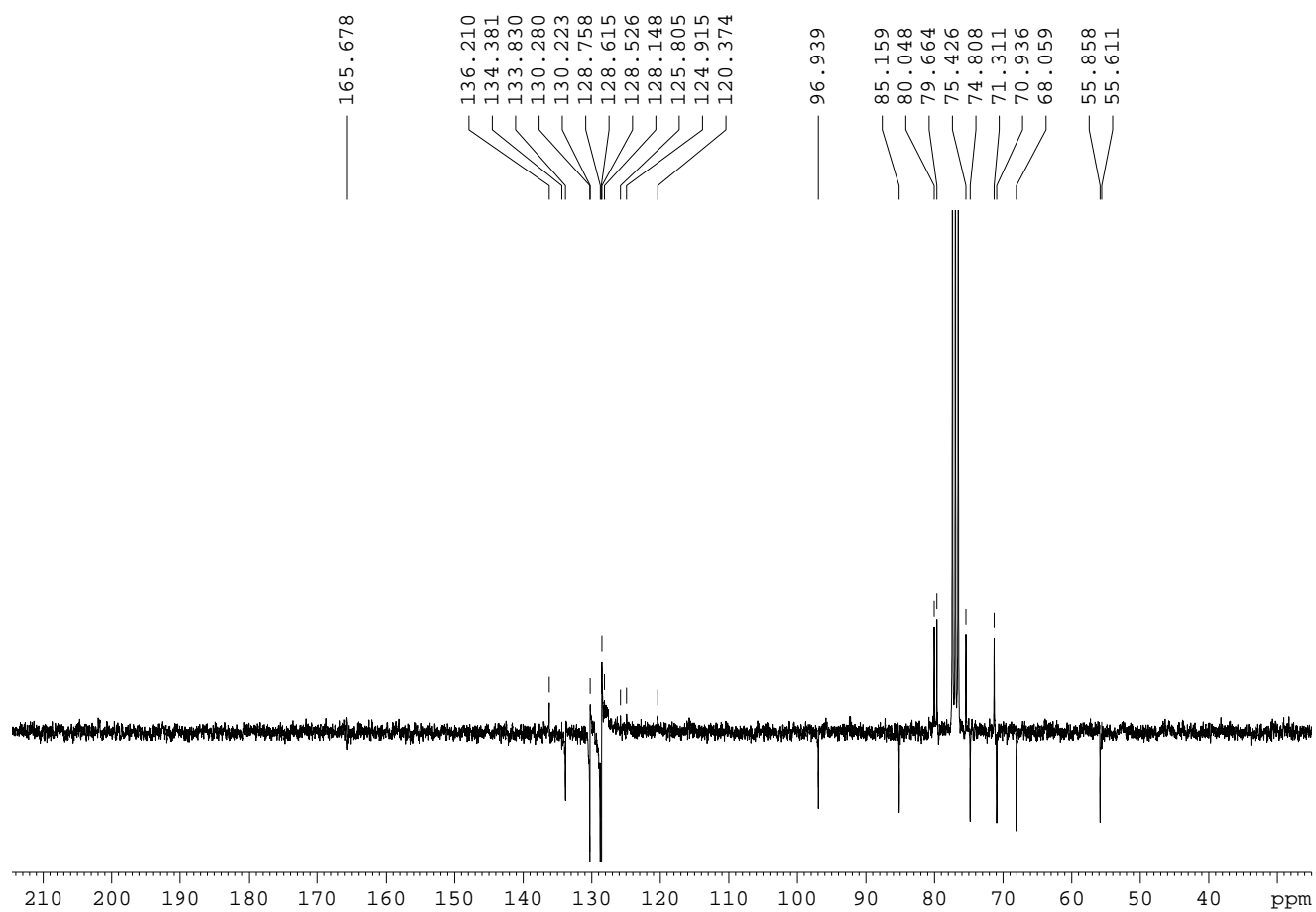


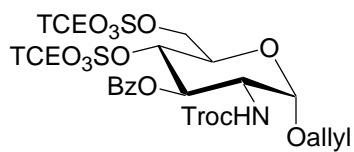
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **46**



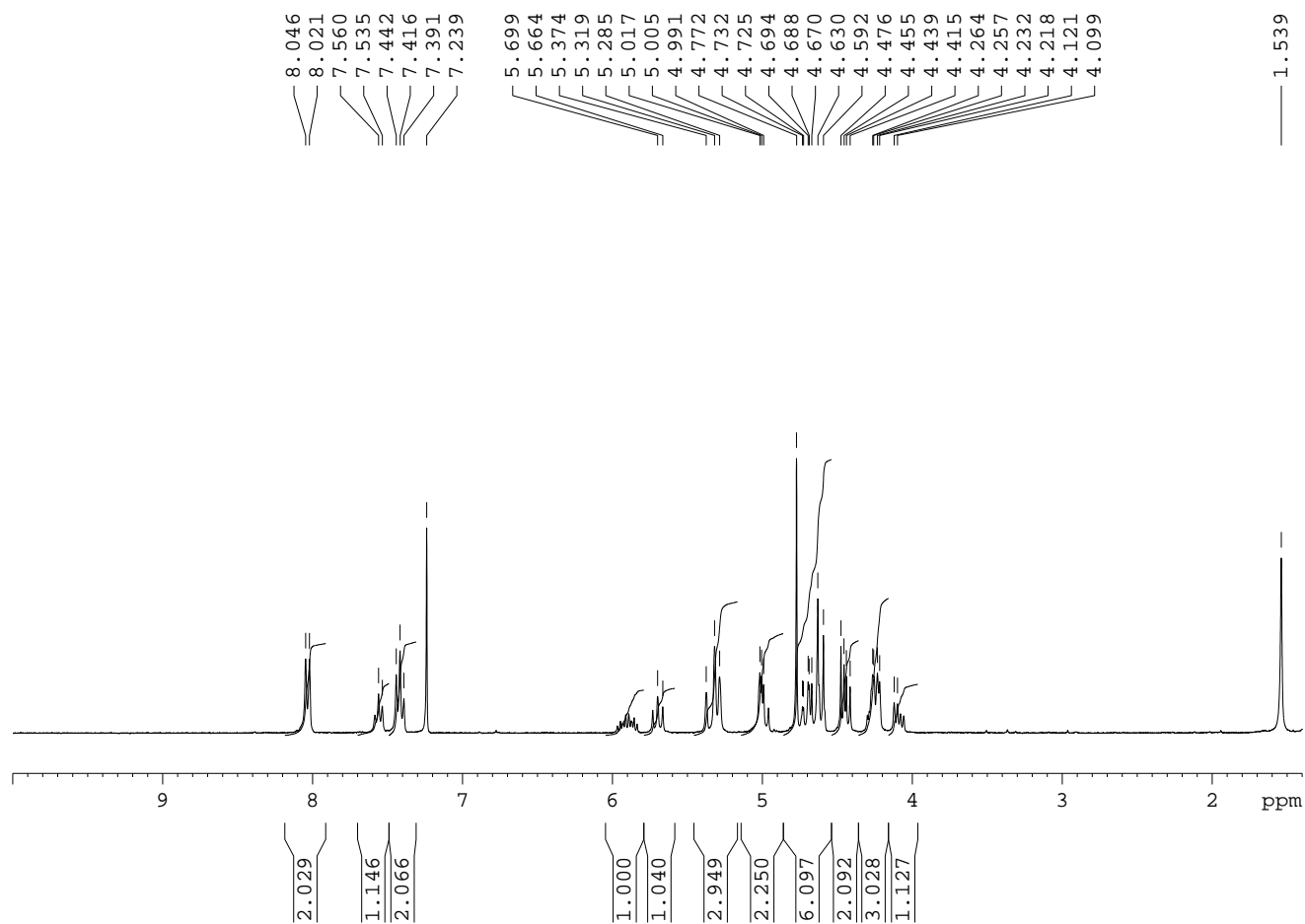


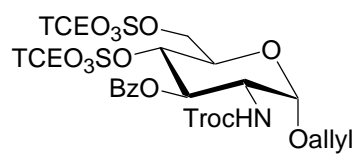
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **46**



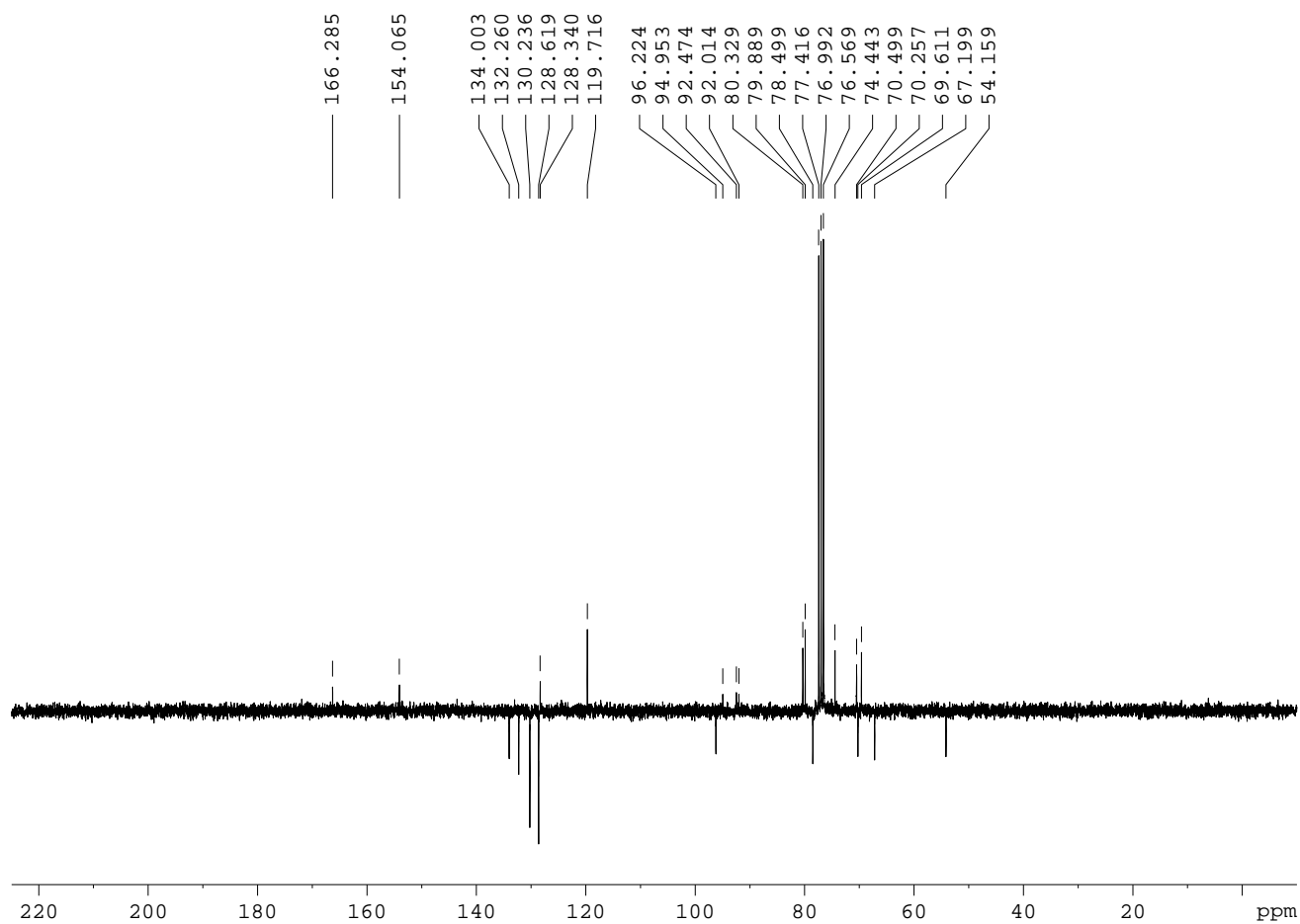


$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **47**

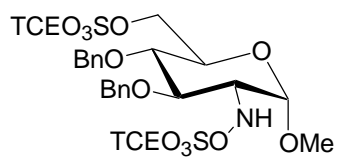




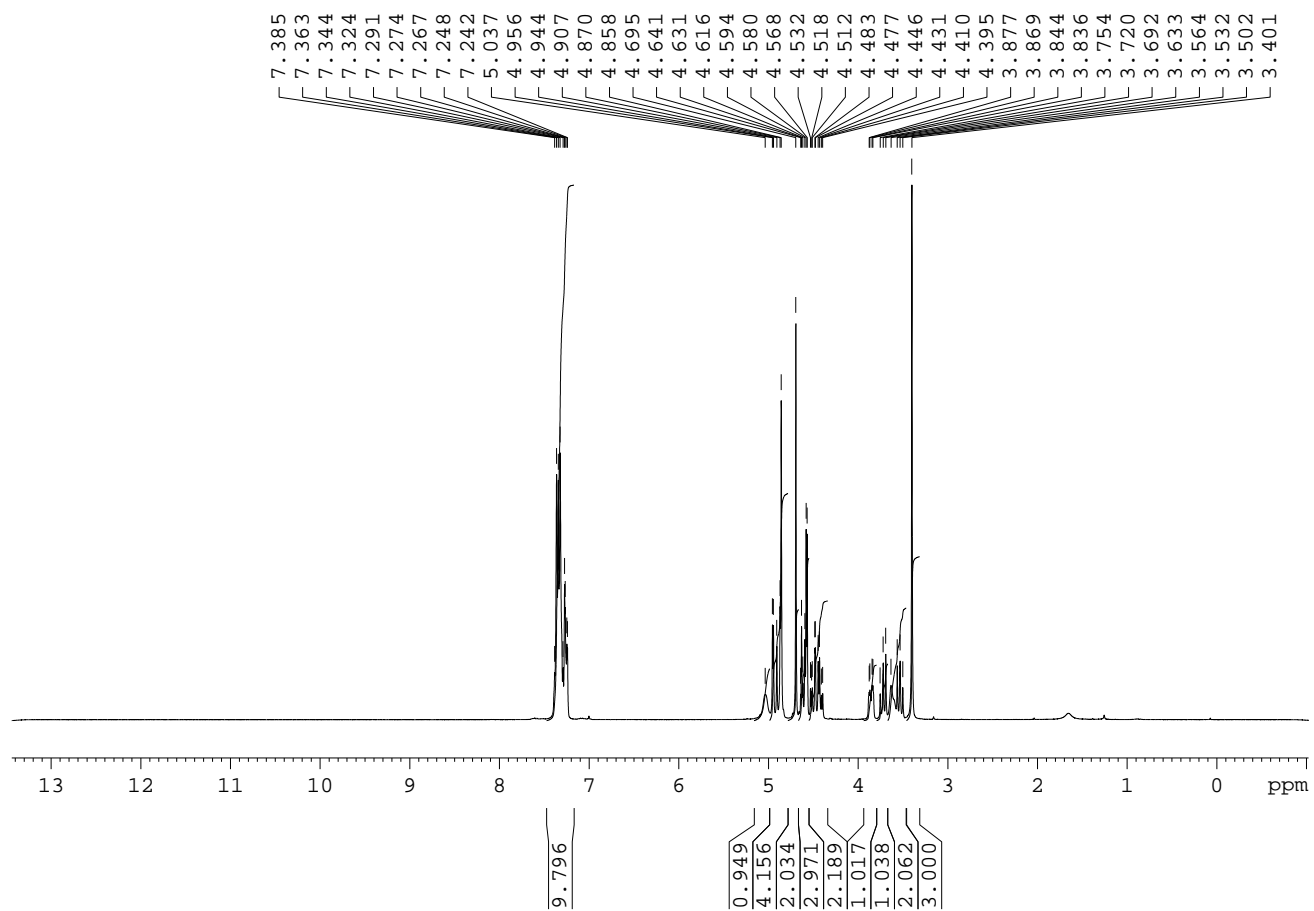
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **47**

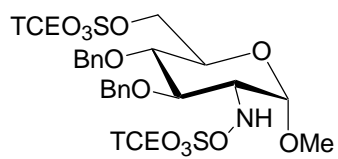




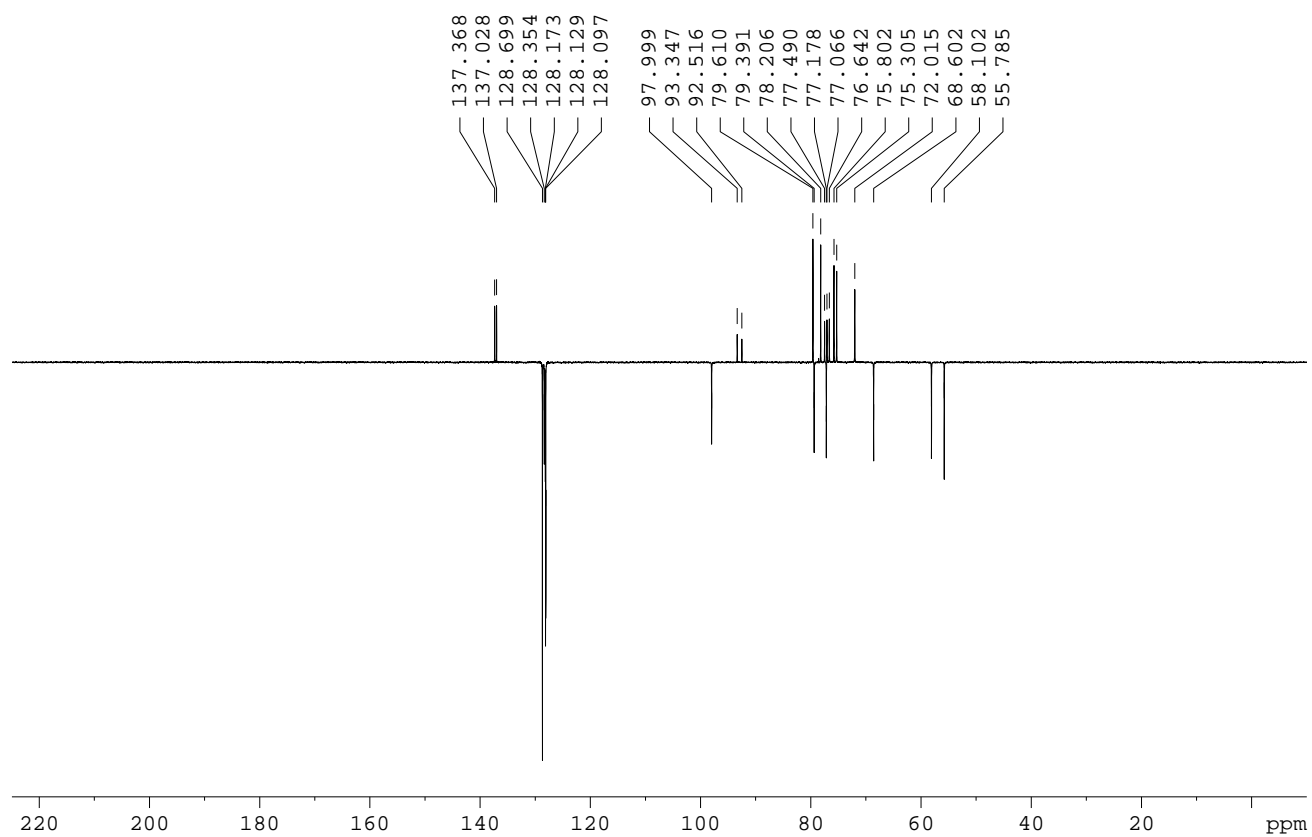


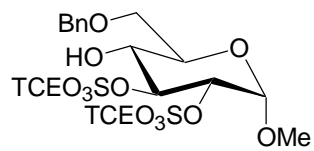
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **48**



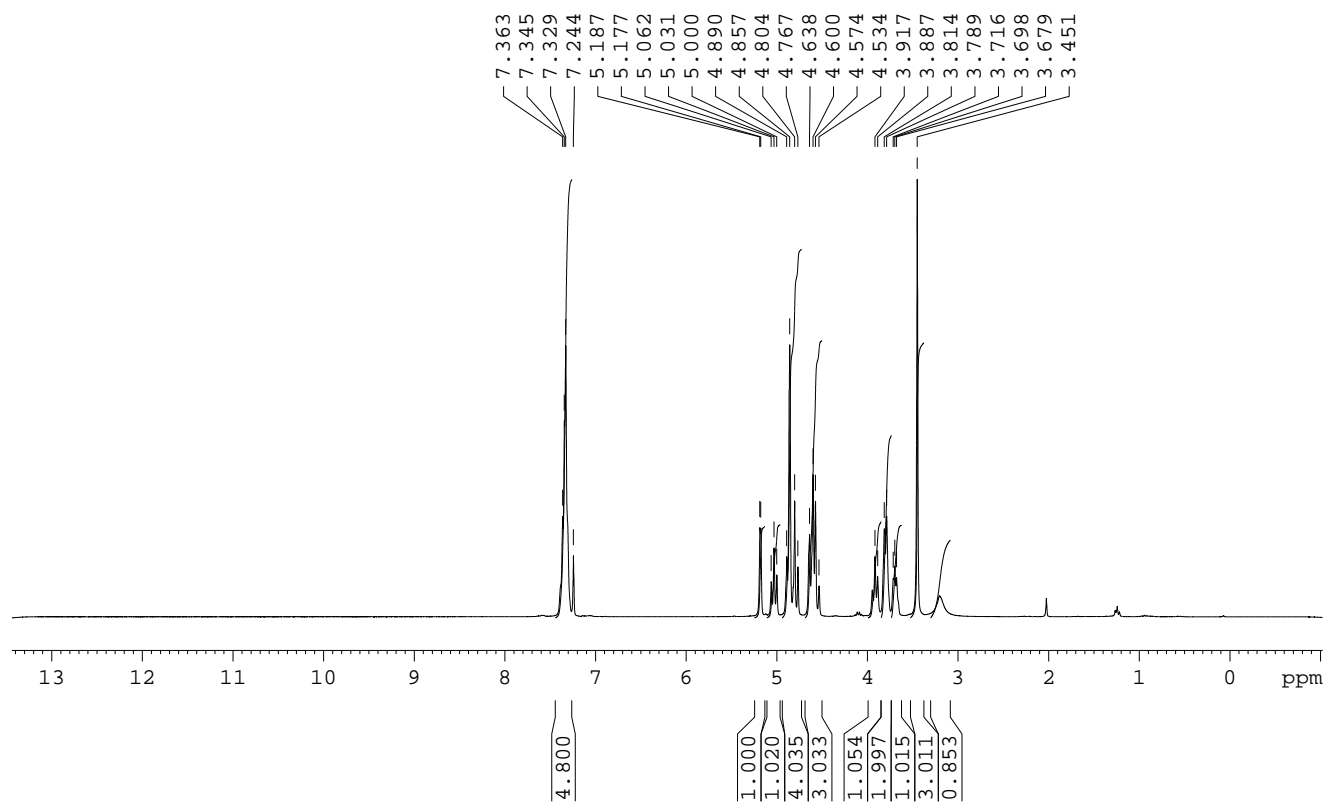


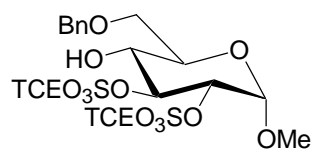
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **48**



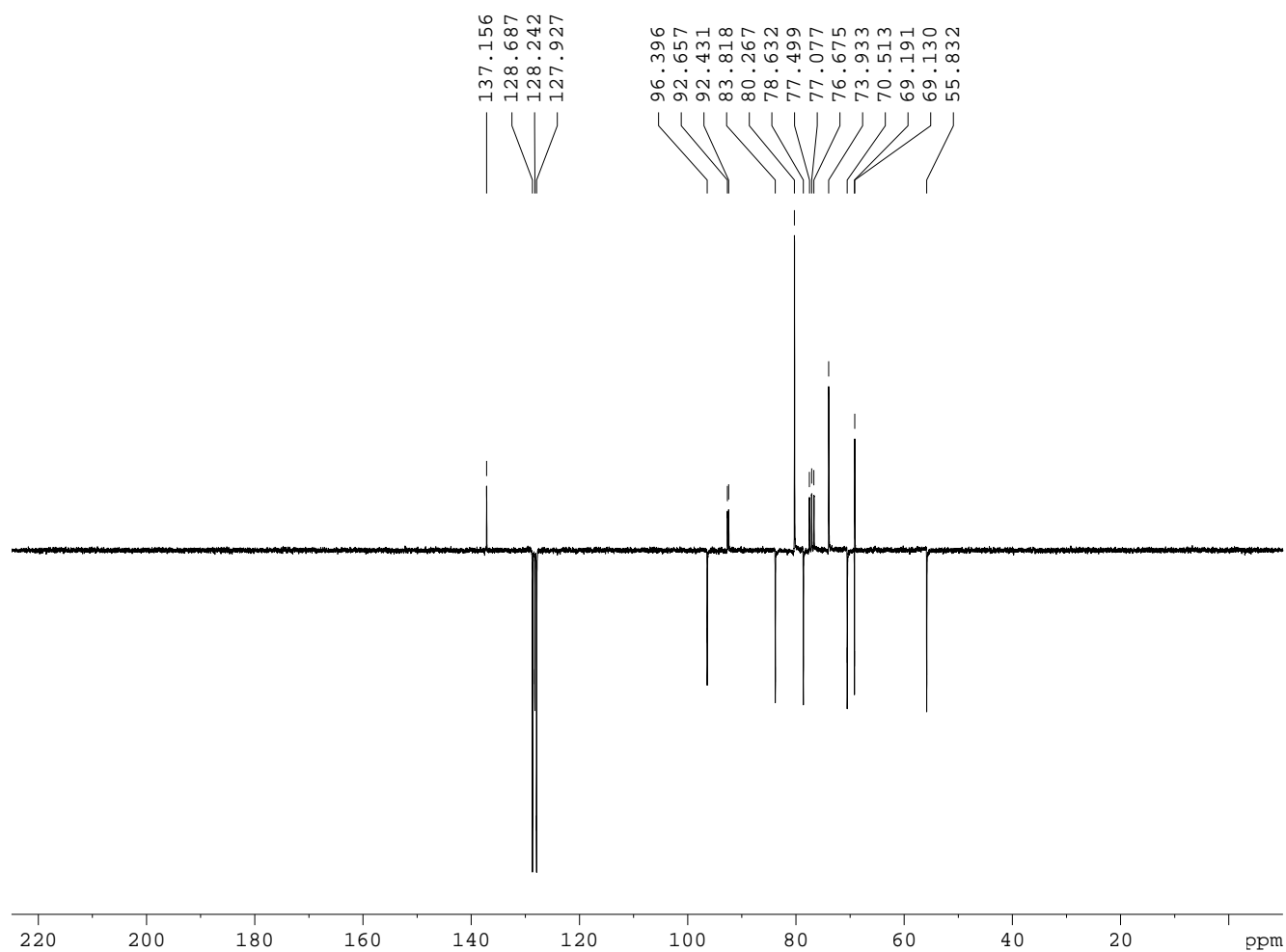


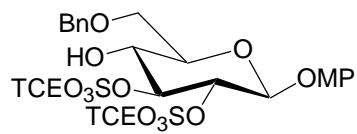
$^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) for compound **49**



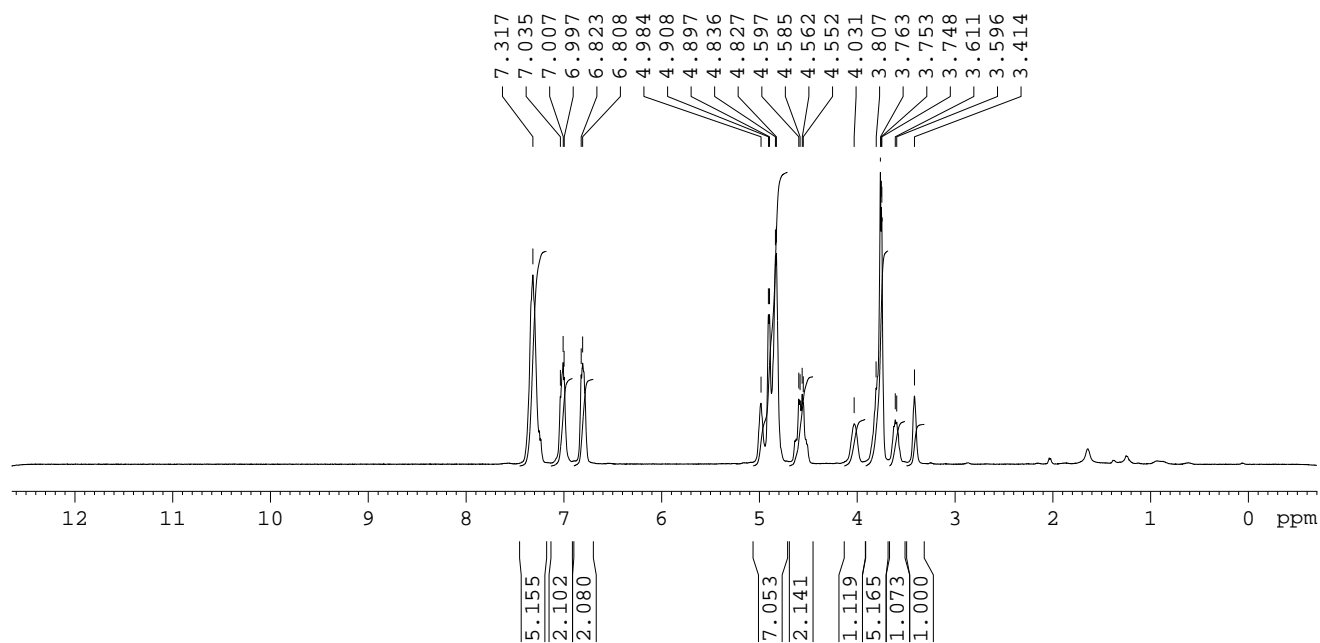


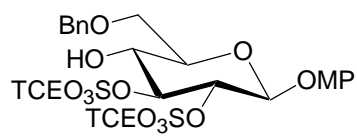
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **49**



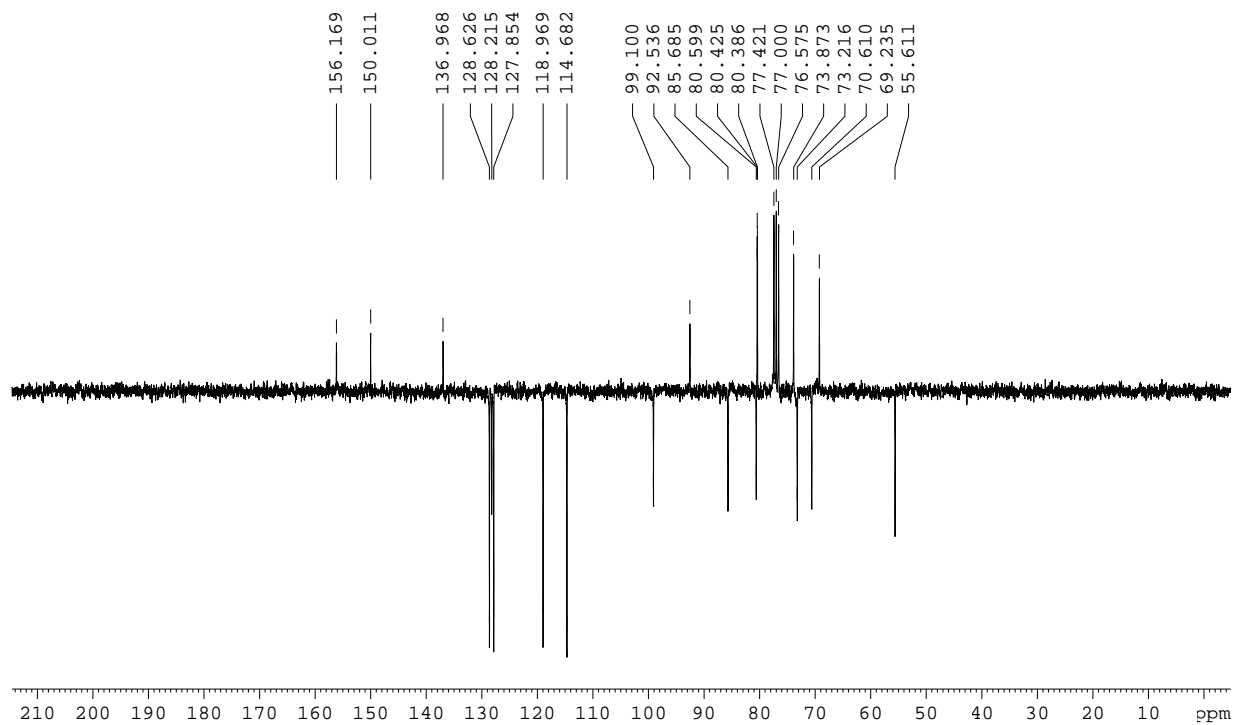


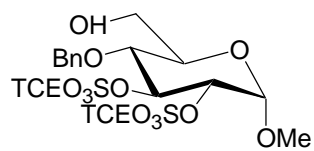
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **50**



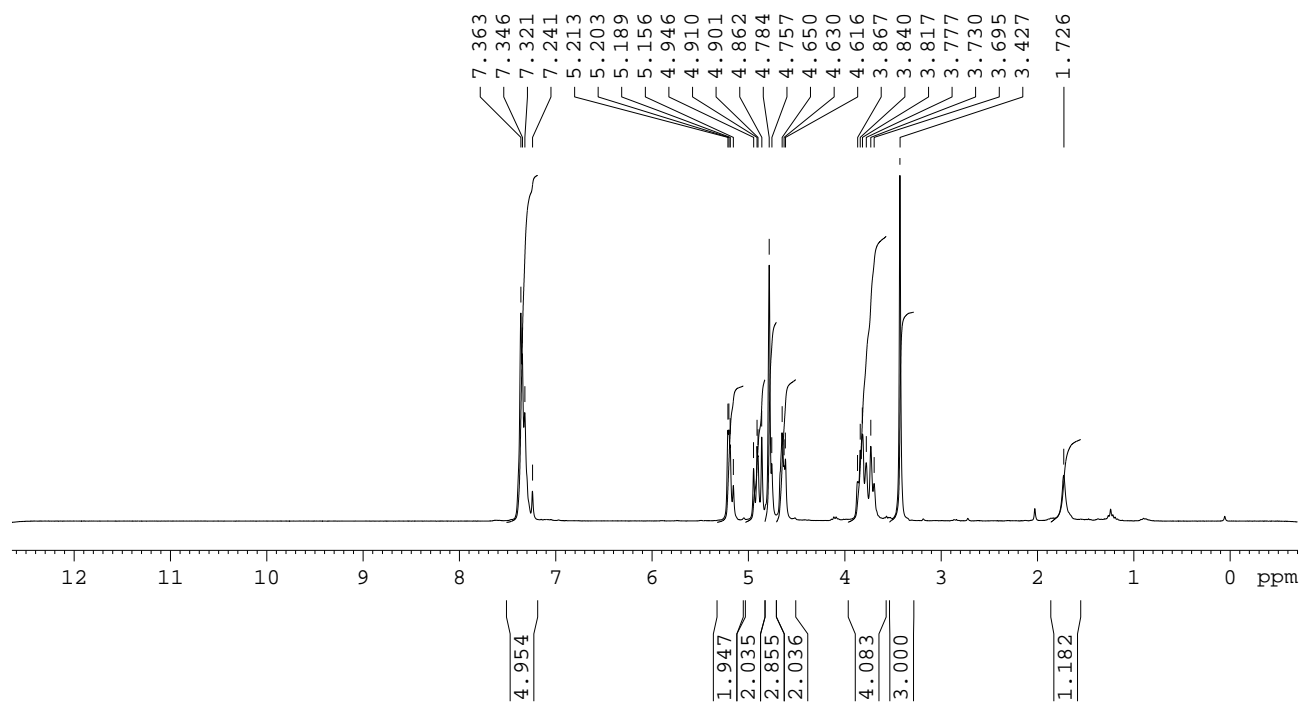


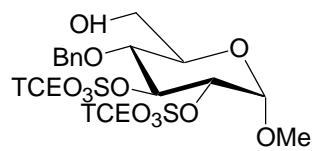
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **50**



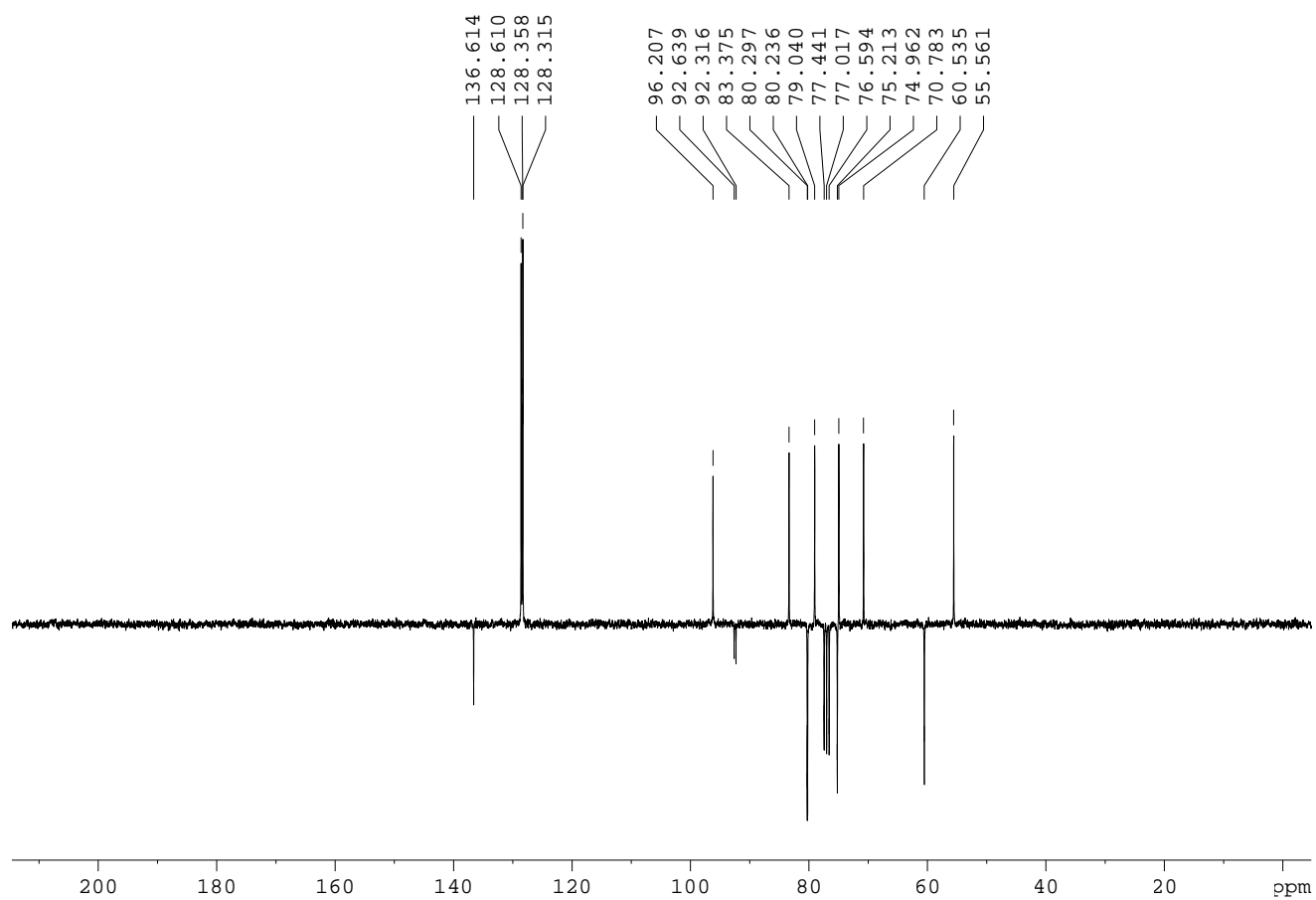


<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **51**

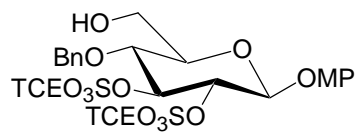




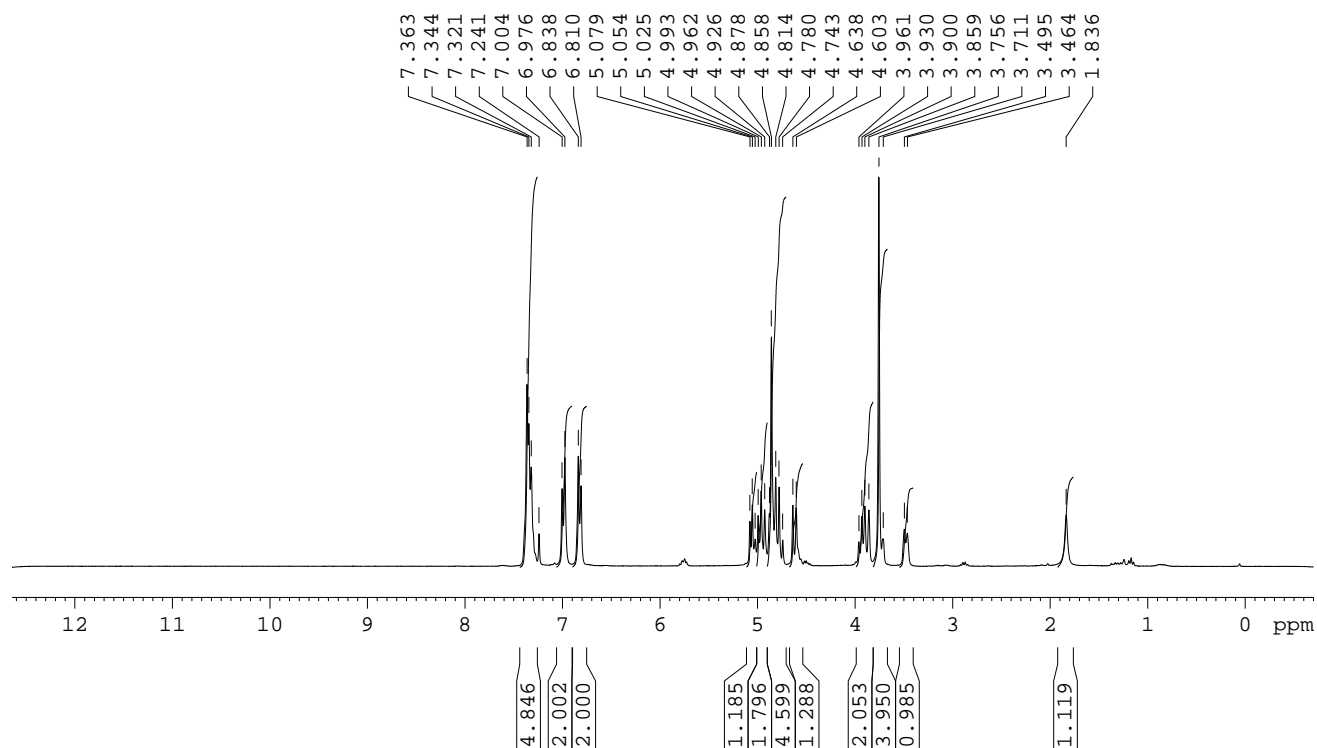
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **51**

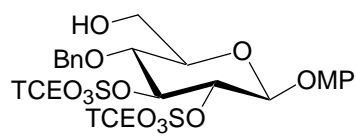




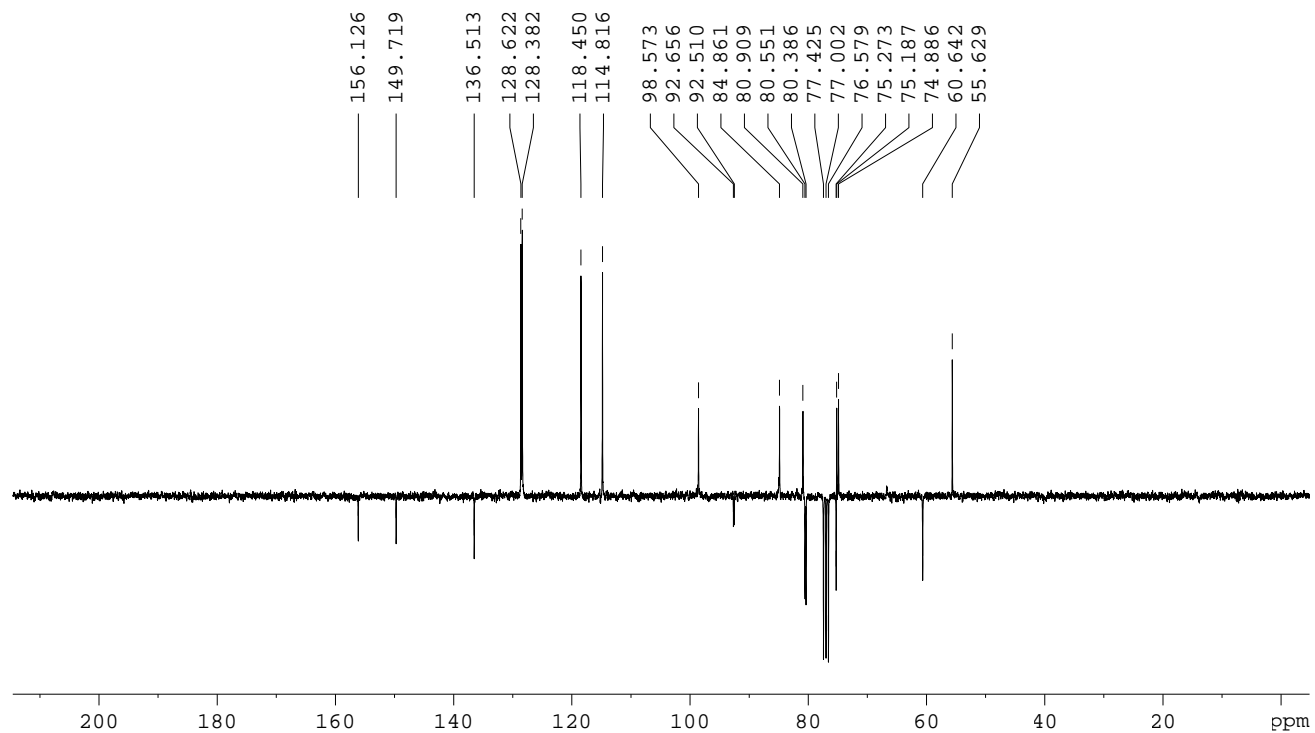


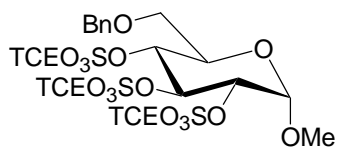
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) for compound **52**



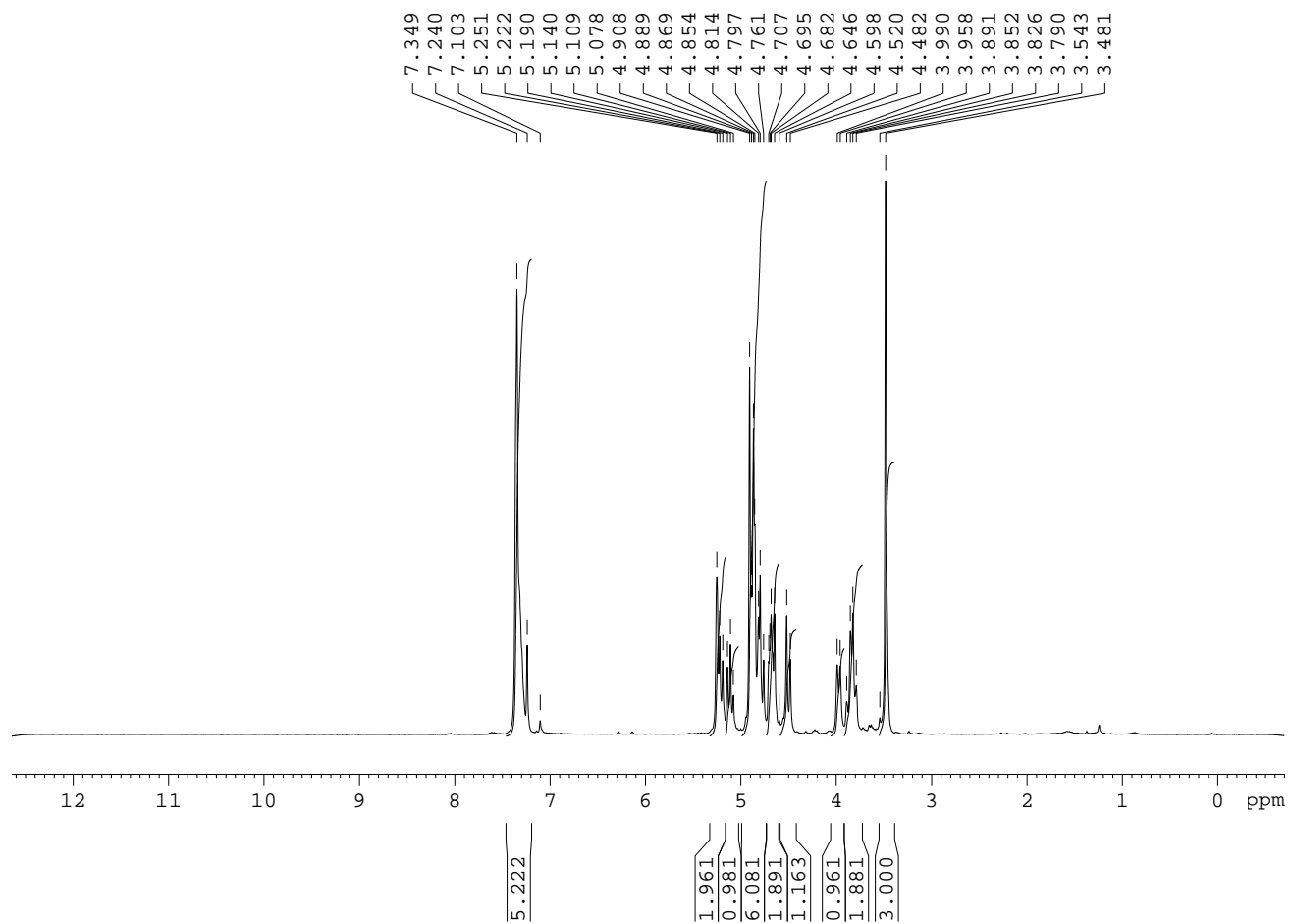


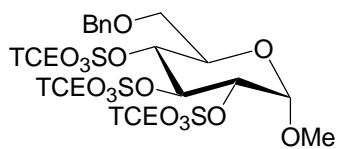
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **52**



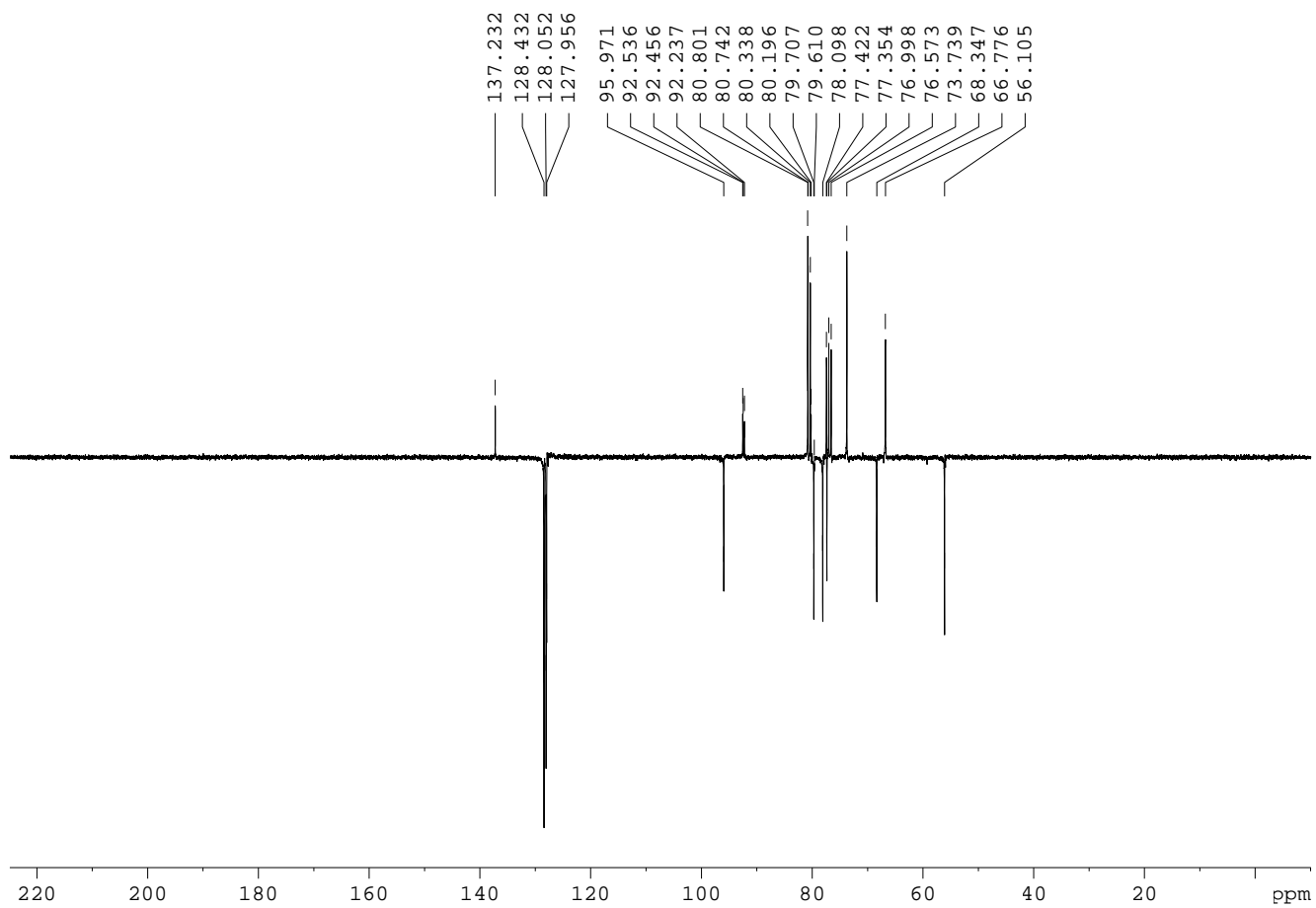


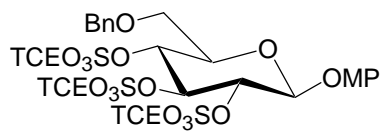
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **53**



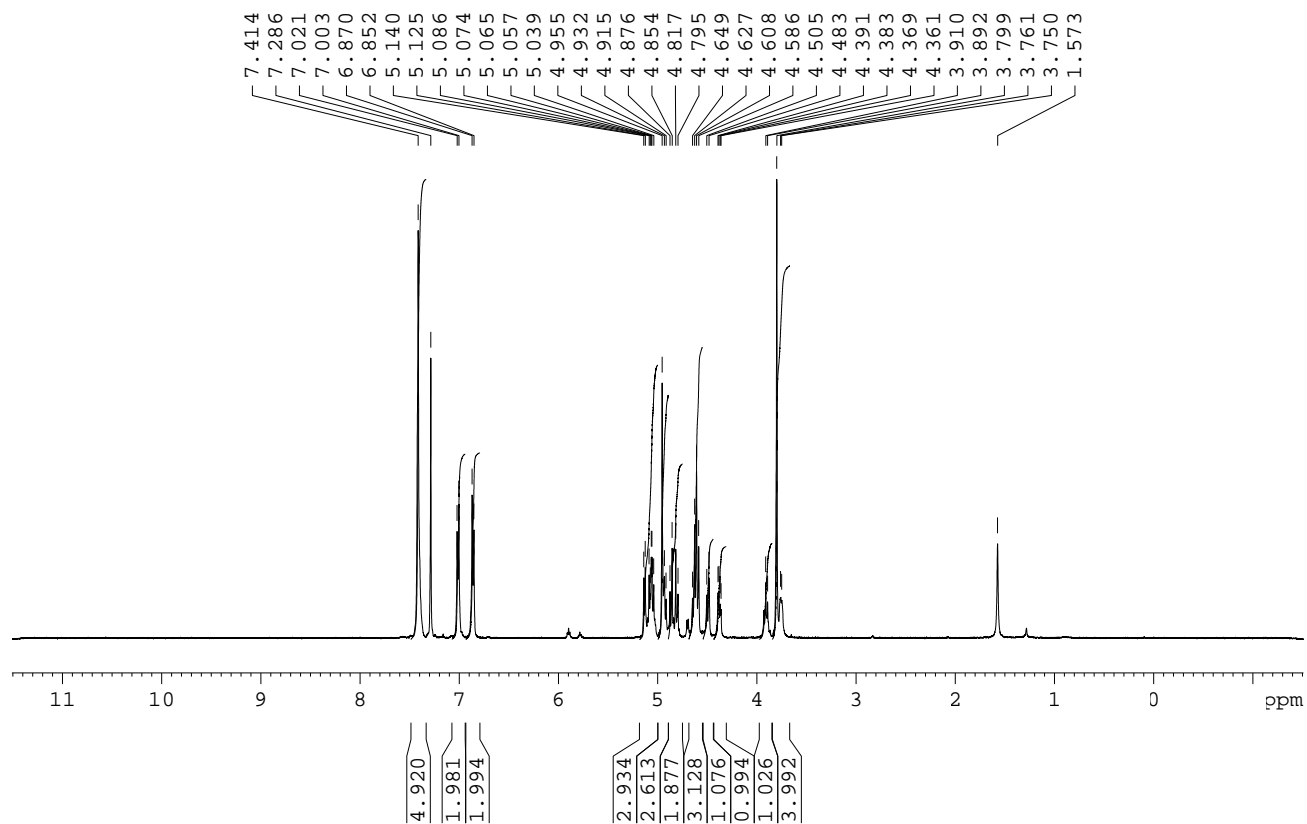


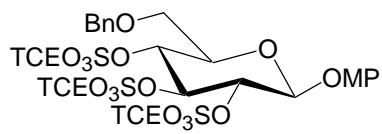
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ) for compound **53**



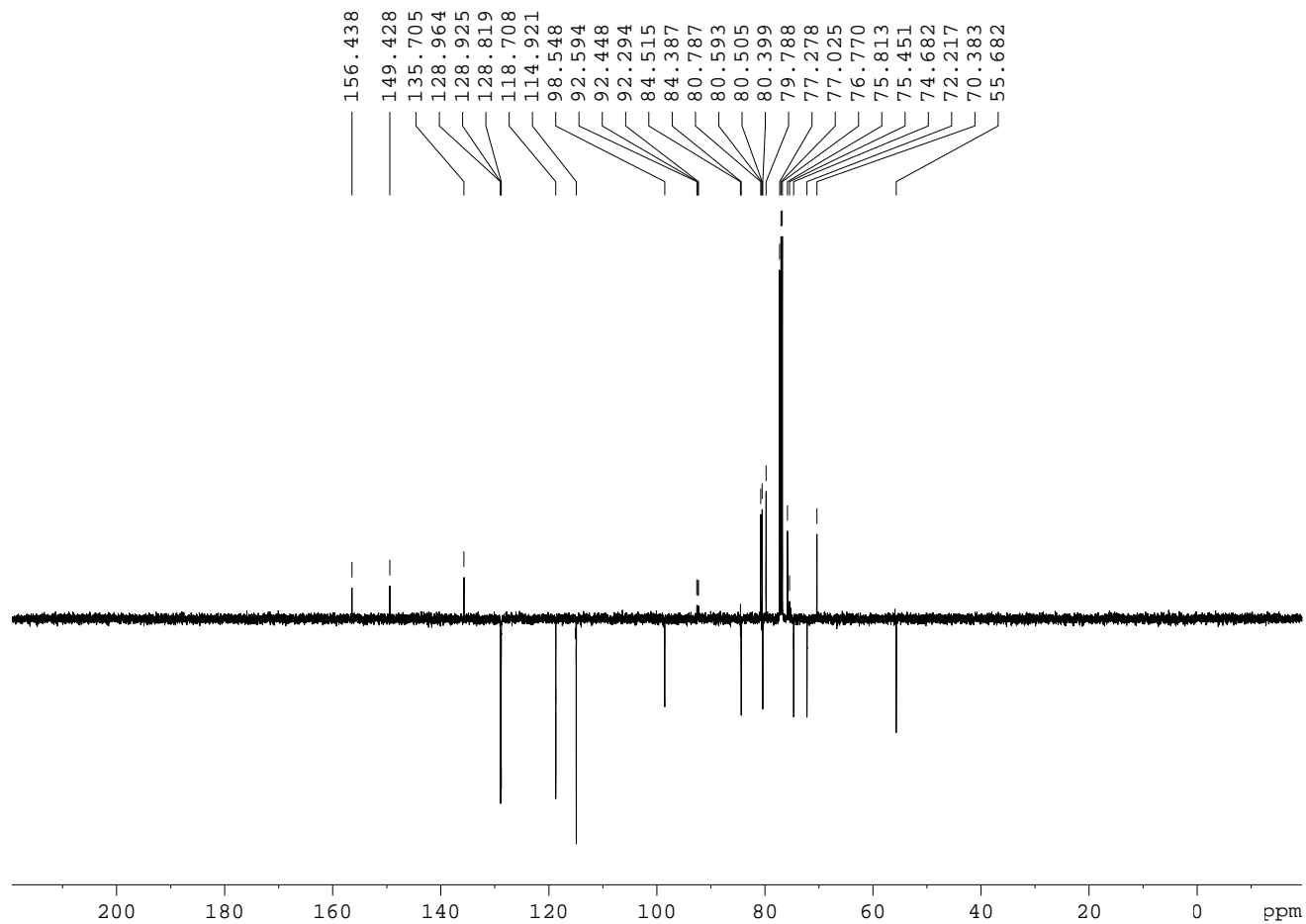


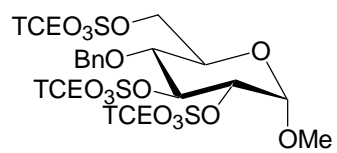
<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **54**



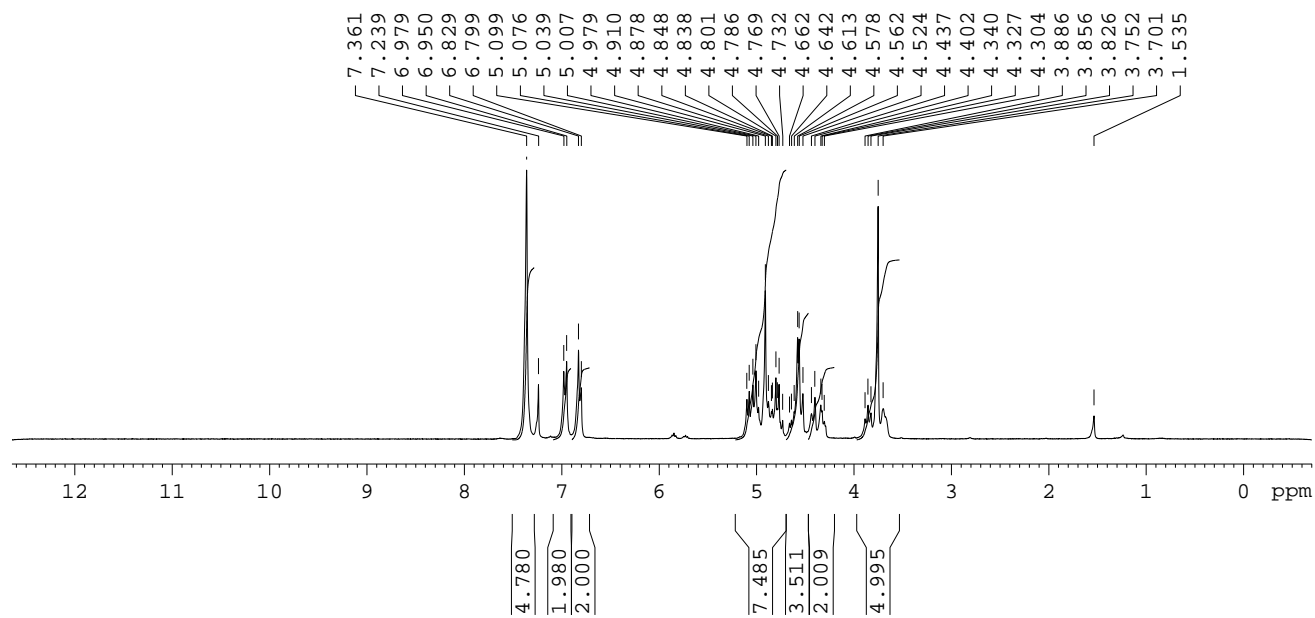


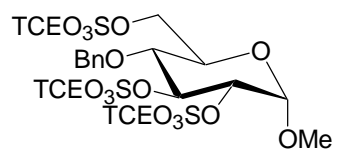
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **54**



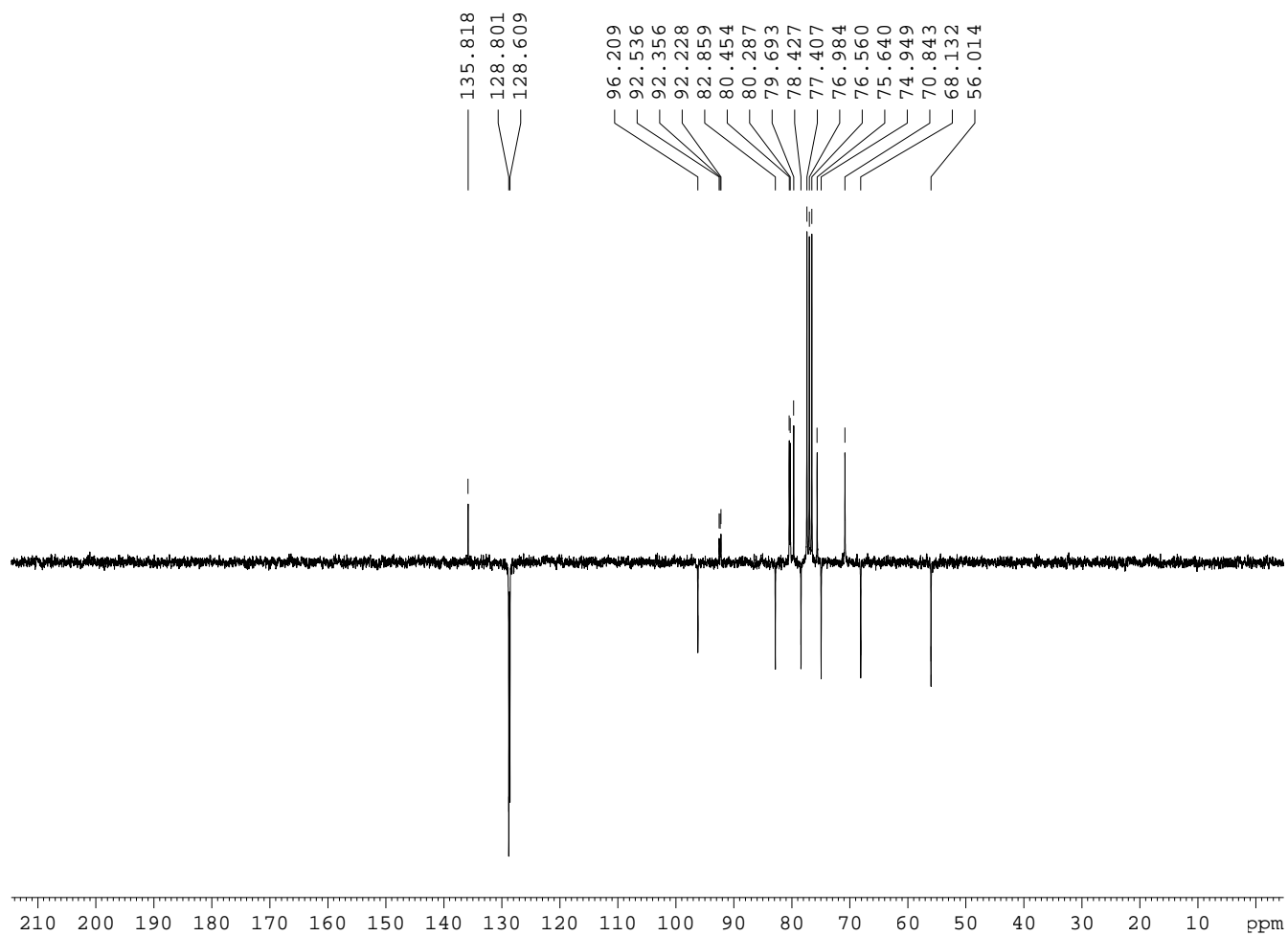


<sup>1</sup>H-NMR (CDCl<sub>3</sub>) for compound **55**

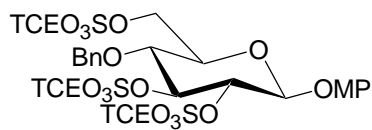




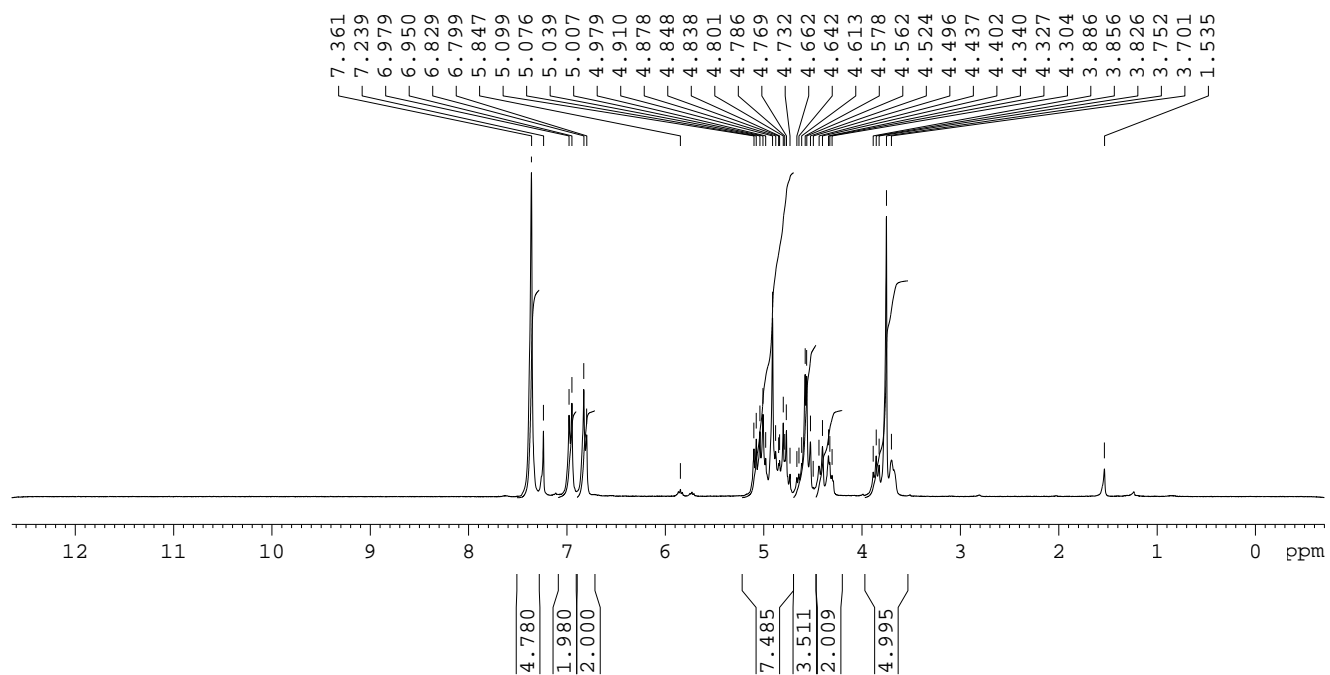
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **55**

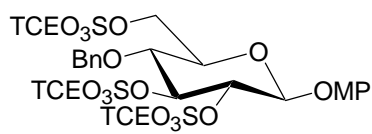




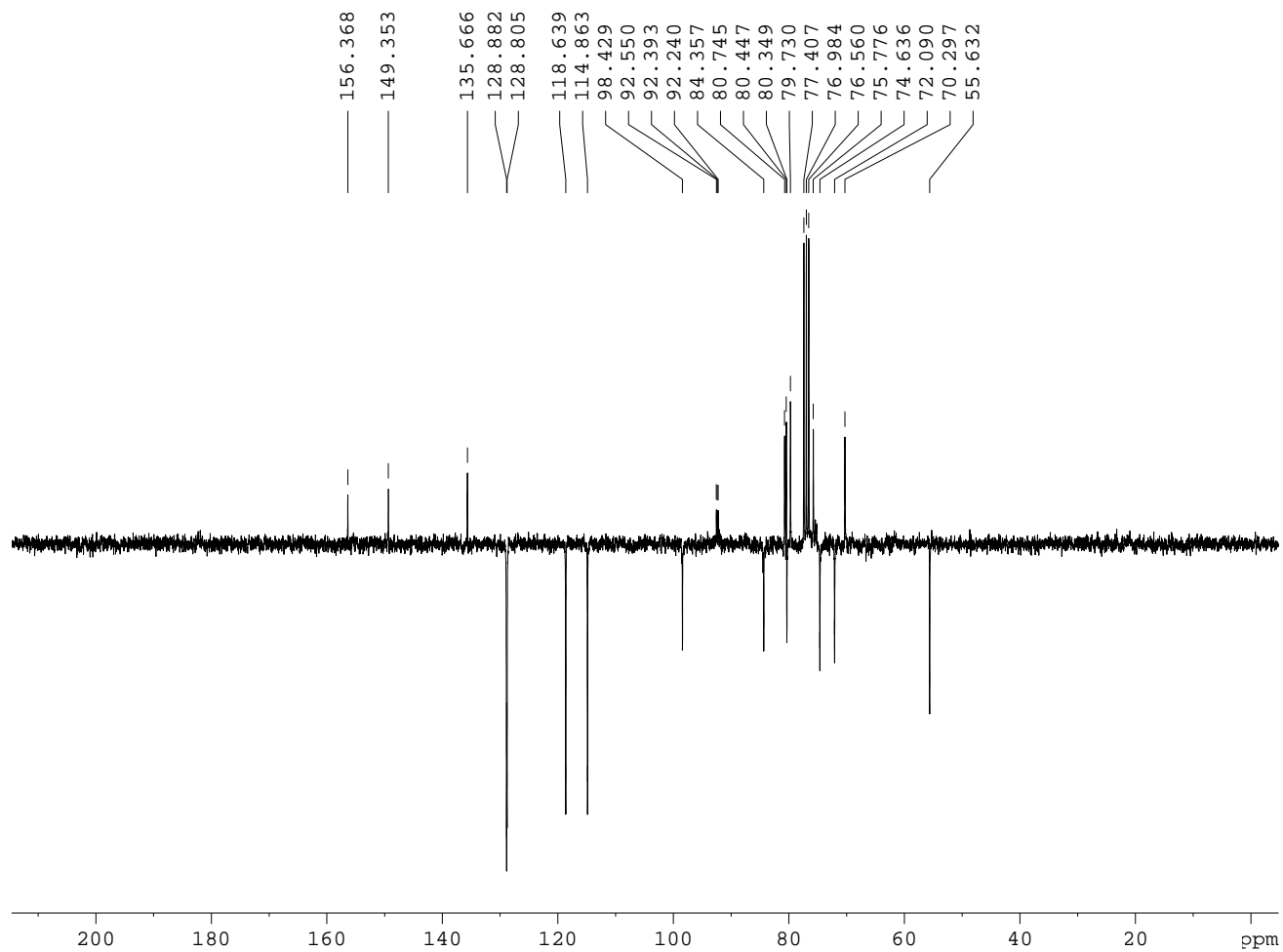


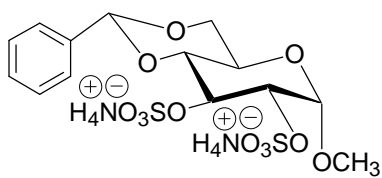
$^1\text{H}$ -NMR ( $\text{CDCl}_3$ ) for compound **56**



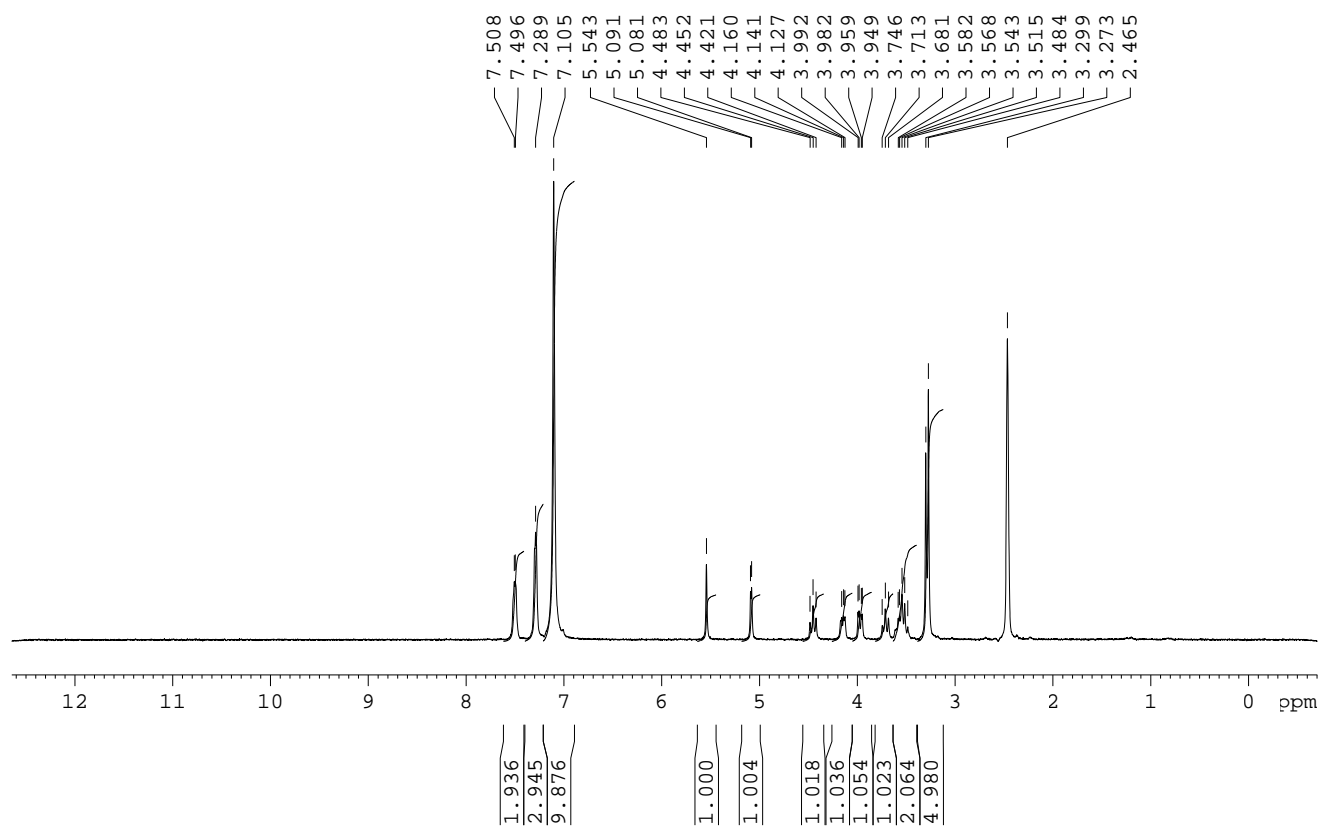


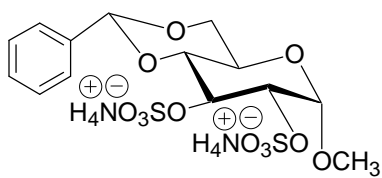
<sup>13</sup>C-NMR (CDCl<sub>3</sub>) for compound **56**



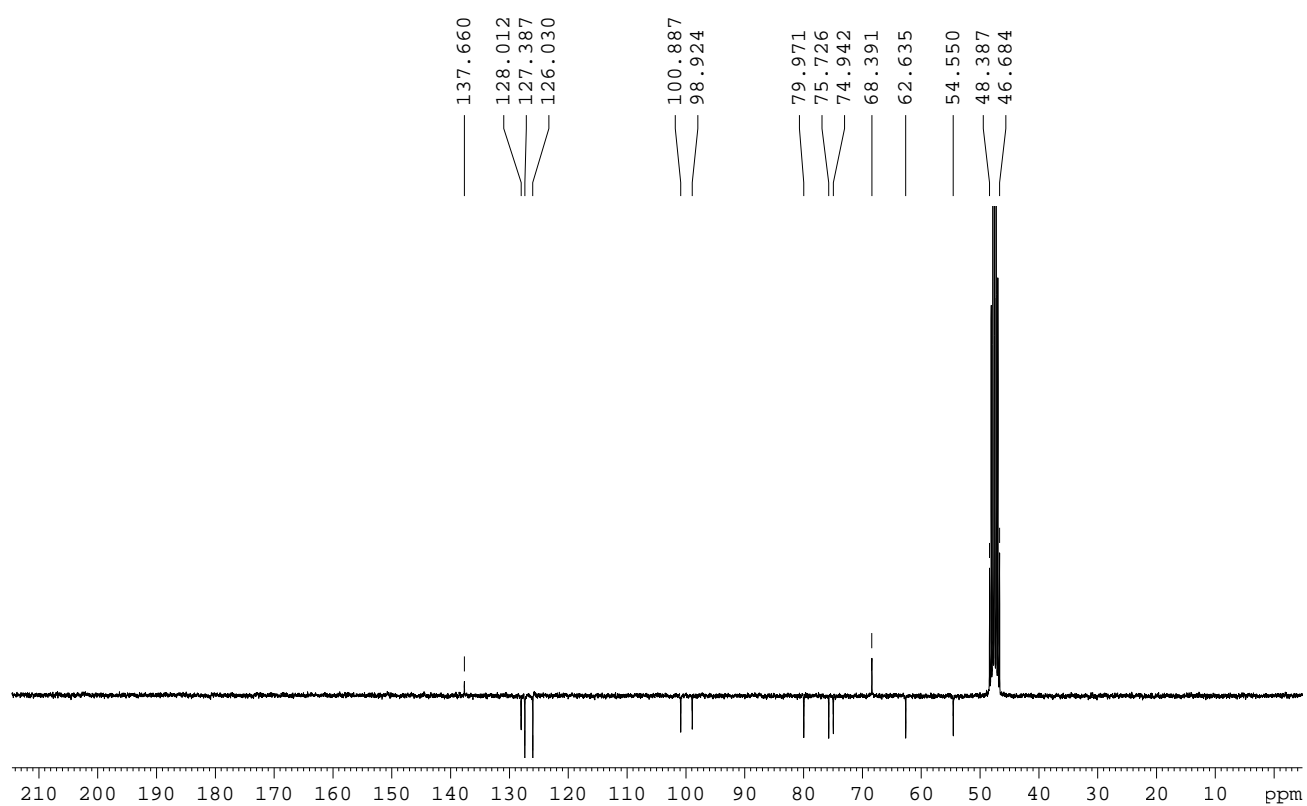


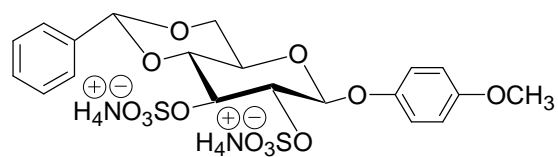
$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) for compound **57**



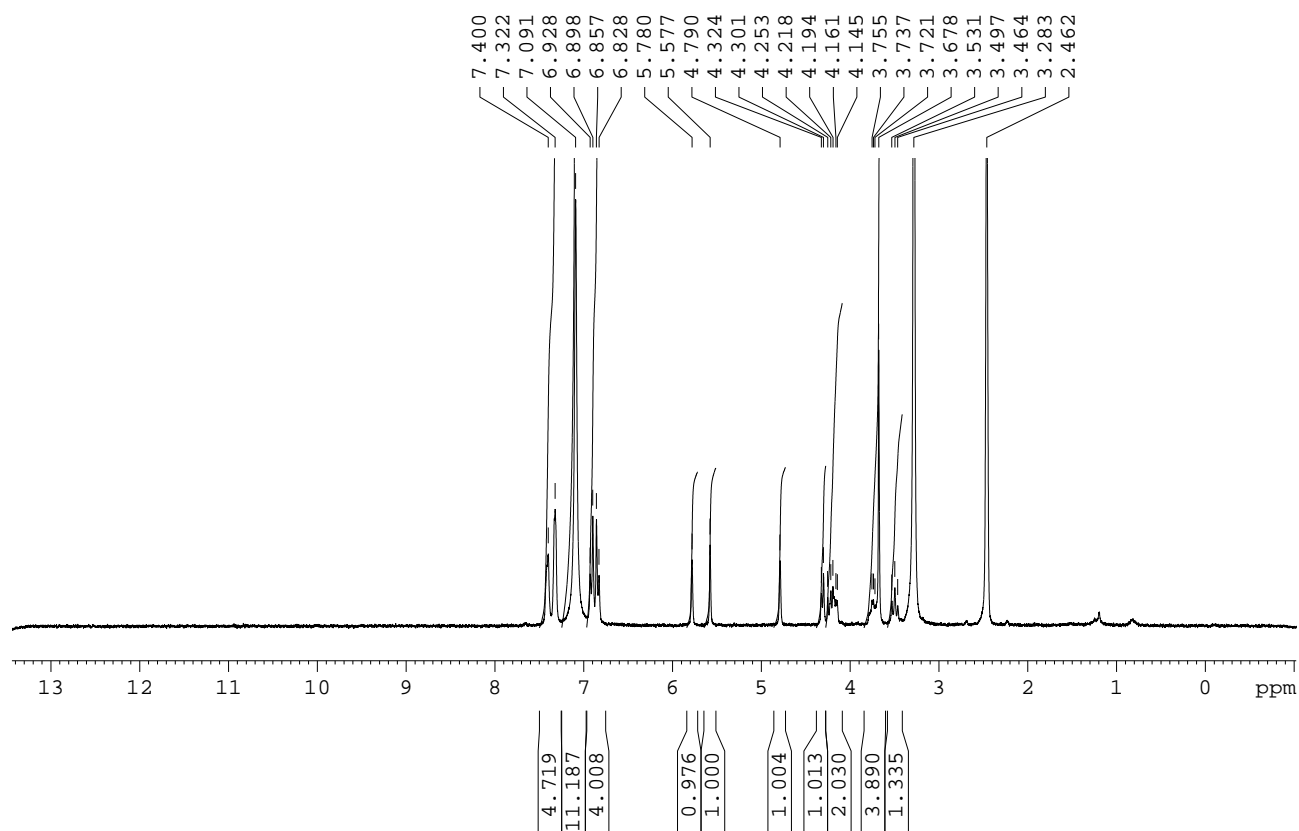


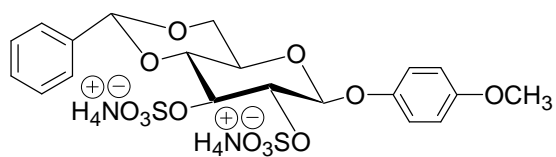
$^{13}\text{C}$ -NMR ( $\text{DMSO-}d_6$ ) for compound **57**



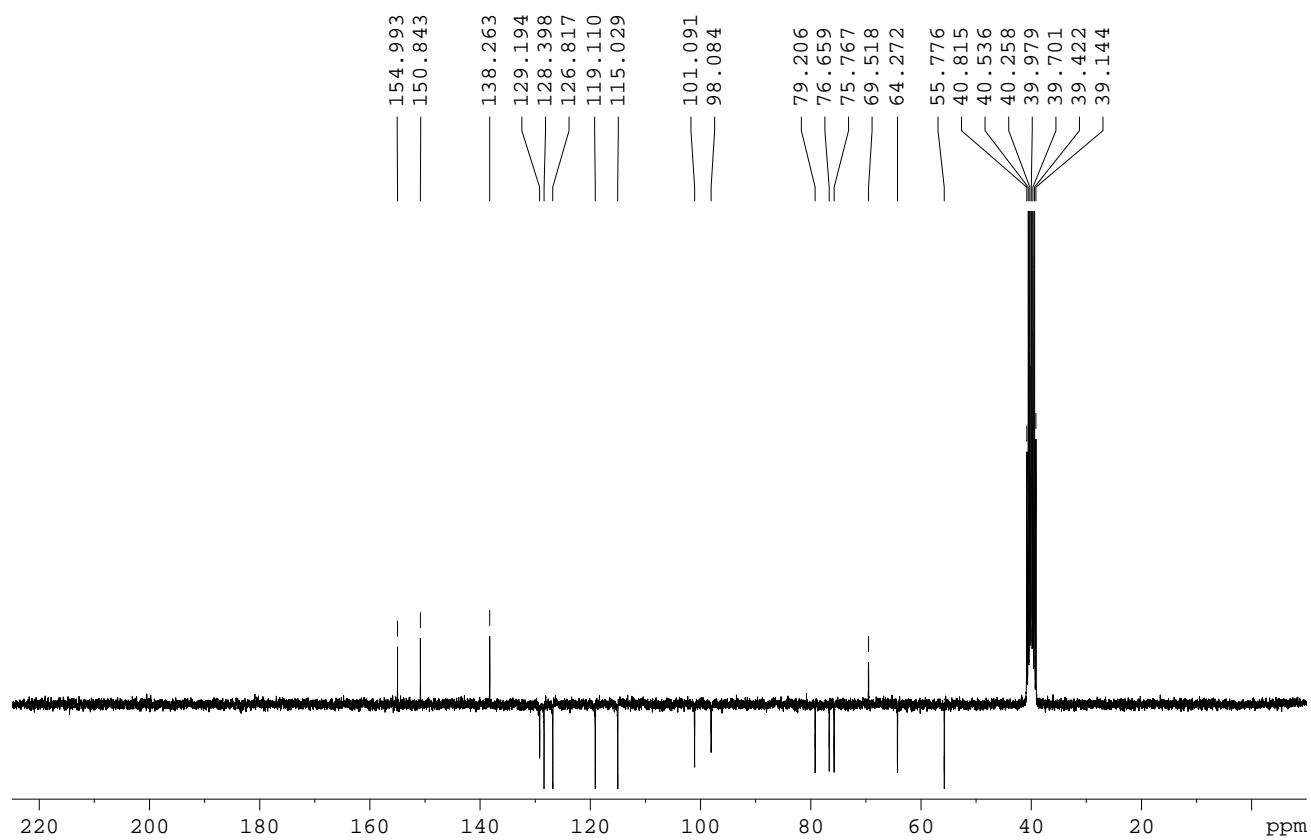


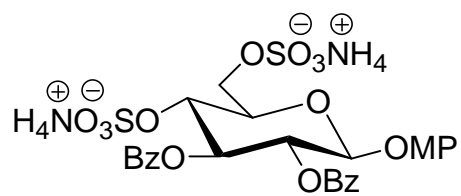
$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) for compound **58**



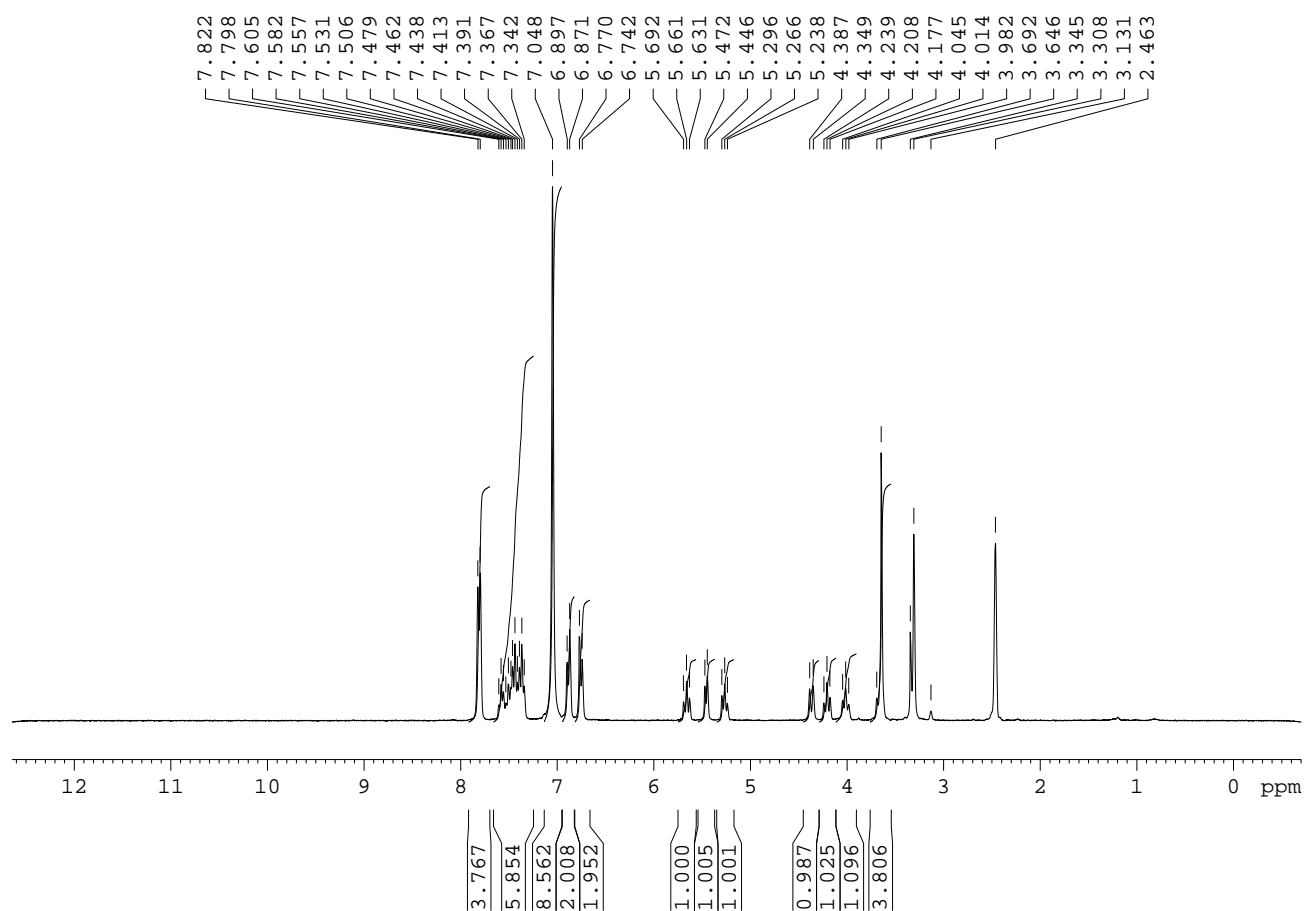


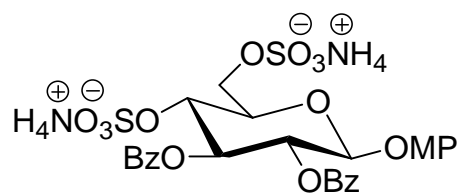
$^{13}\text{C}$ -NMR ( $\text{DMSO}-d_6$ ) for compound **58**



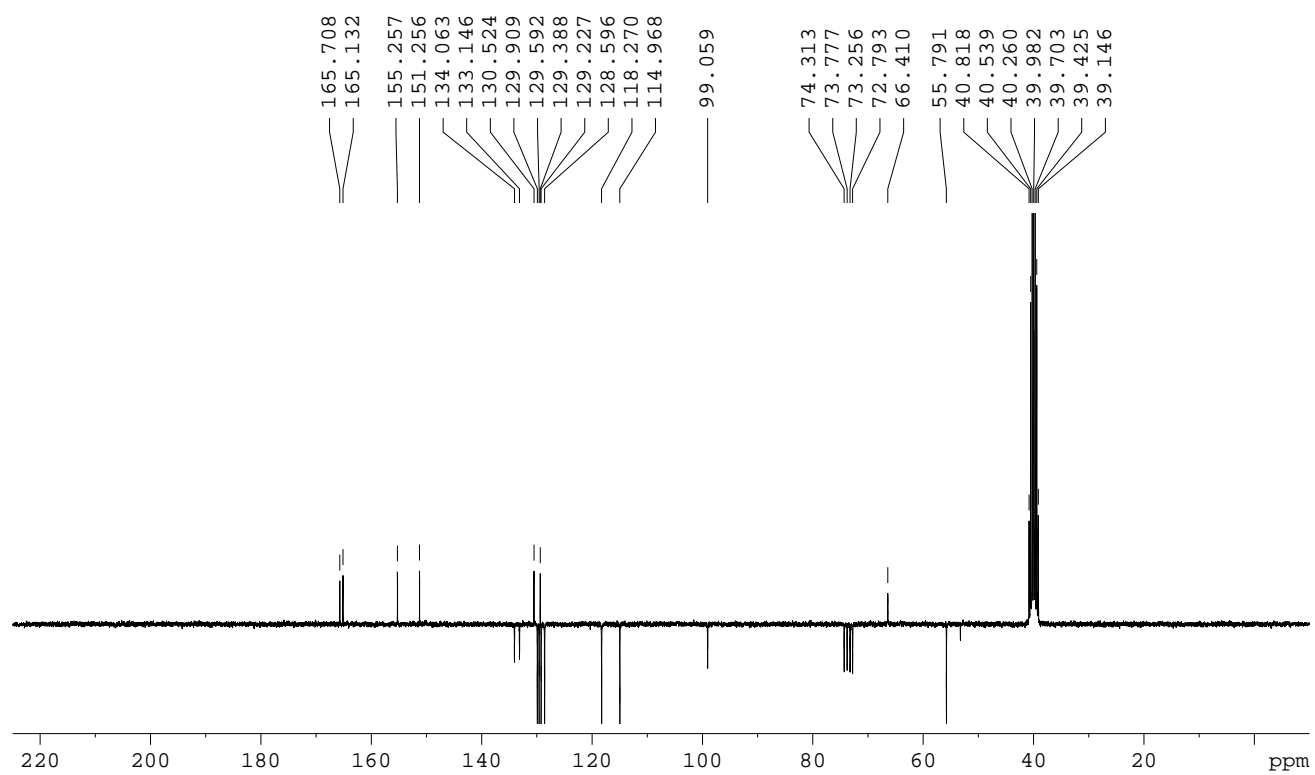


$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) for compound **59**





$^{13}\text{C}$ -NMR ( $\text{DMSO}-d_6$ ) for compound **59**





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