Supporting information

for

Perfluorophenylboronic Acid-Catalyzed Direct α-Stereoselective Synthesis of 2-Deoxygalactosides from Deactivated Peracetylated D-Galactal

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Experimental data and copies of ^{1}H and ^{13}C NMR spectra of glycosides 4a-o, 6a–11a, and 12 are provided

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1. Materials and methods

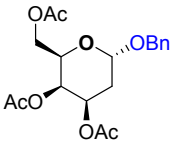
Chemical reagents were purchased from Sigma-Aldrich or Alfa Aesar and were used as received without further purification. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker Avance DPX 300. ^{13}C NMR spectra were recorded at 75.47 MHz on a Bruker Avance DPX 300. Unless stated otherwise, data refer to solutions in $CDCl_3$ with TMS as an internal reference. HRMS were recorded on a Qstar XL MS/MS system. Analytical TLC was performed using Merck 60 F254 precoated silica gel plates (0.2 mm thickness) and visualized using UV radiation (254 nm) or stained using ceric ammonium nitrate in 30% H_2SO_4 solution. Flash chromatography was performed using Merck silica gel 60 (60–120 mesh).

2 General procedure for the synthesis of 2-deoxy galactosides 4a-o and 6a-11a, and 12

General Procedure for the synthesis of compounds 4a-o, **6a-11a** and **12**

To a stirred solution of 3,4,6-tri-*O*-acetyl-D-galactal **2** (100 mg, 0.34 mmol) in anhydrous nitromethane (2 mL) was added the acceptors (1.2 eq) then perfluorophenylboronic acid (20 mol%) at room temperature. The resulting solution was stirred at 60 ^{o}C for 6 h (monitor by TLC). The reaction mixture was then evaporated under reduced pressure, and the residue was purified by column chromatography using silica gel (EtOAc:hexane).

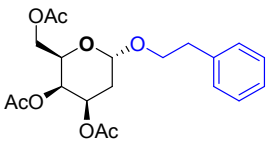
2.1 Benzyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4a)[1]



4a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and benzyl alcohol **3** (0.4 mmol, 42 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave **4a** as colorless liquid (123 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.30 (m, 5H), 5.37-5.36 (m, 2H), 5.12 (d, J = 3.1 Hz, 1H), 4.71 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 4.22 (d, J = 6.5 Hz, 1H), 4.12 (d, J = 6.5 Hz, 2H), 2.16 (s, 3H), 2.13 – 2.11 (m, 1H), 2.08 (s, 3H), 2.00 (s, 3H), 1.97 – 1.90 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.0, 137.1, 128.5,128.0,127.9, 96.5, 69.2, 66.8, 66.7, 66.2, 62.4, 30.1, 20.8, 20.76, 20.74. HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{19}H_{25}O_8$:381.1549; found: 381.1558.

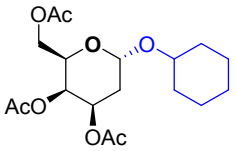
2.2 2-phenyl ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4b)



4b

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2-phenylethanol (0.4 mmol, 49 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4b** as white solid (104 mg, 72%).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.14 (m, 5H), 5.25 (t, J = 5.0 Hz, 2H), 5.00 (d, J = 2.7 Hz, 1H), 4.00 (d, J = 6.5 Hz, 2H), 3.90 – 3.74 (m, 2H), 3.68 (dd, J = 11.3, 4.8 Hz, 1H), 2.91 (t, J = 6.8 Hz, 2H), 2.13 (s, 3H), 2.09 (dd, J = 7.9, 6.1 Hz, 1H), 2.05 (s, 3H), 2.01 (d, J = 3.6 Hz, 3H), 1.91 – 1.82 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.0, 138.8, 130.0, 128.9, 128.8, 128.4, 127.4, 126.3, 97.1, 68.2, 66.7, 66.5, 66.2, 62.4, 36.1, 30.1, 20.9, 20.7 (2C). HRMS (ESI^{+}): m/z [M + H]$^{+}$ calcd for $C_{20}H_{27}O_8$:395.1706; found: 395.1736.

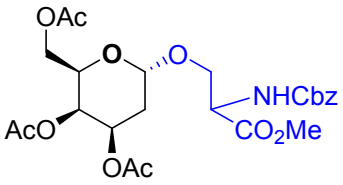
2.3 Cyclohexyl 3,4,6-tri-*O*-acyl-2-deoxy-D-galactcopyranoside (4c)[1]



4c

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and cyclohexanol (0.4 mmol, 42 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave **4c** as colorless liquid (102 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.32 (dd, *J* = 11.0, 4.2 Hz, 2H), 5.17 (d, *J* = 3.0 Hz, 1H), 4.23 (d, *J* = 6.5 Hz, 1H), 4.09 (dd, *J* = 6.5, 2.5 Hz, 2H), 3.62 – 3.47 (m, 1H), 2.14 (s, 3H), 2.08 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H), 1.91 – 1.81 (m, 2H), 1.73 (bs, 3H), 1.53 (bs, 1H), 1.41 – 1.19 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.4, 170.1, 95.5, 75.4, 66.8, 66.6, 66.4, 62.6, 33.3, 31.5, 30.74, 25.5, 24.2, 23.9, 20.8, 20.7, 20.6. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{18}H_{29}O_8$:373.1862; found: 373.1880.

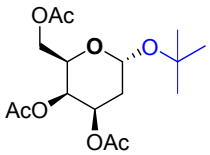
2.4 *O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-D-galactopyranosyl]-N-carbobenzyloxy-L-serine methyl ester (4d)[1]



4d

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and *N*-(tert-butoxycarbonyl)-*L*-serine methyl ester (0.4 mmol, 42 µl). Column chromatography purification using EtOAc:Hexane (4:6) gave **4d** as colorless liquid (162 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.76 (d, *J* = 8.3 Hz, 1H), 5.33 (d, *J* = 2.7 Hz, 1H), 5.26 – 5.10 (m, 4H), 4.99 (d, *J* = 3.0 Hz, 1H), 4.64 – 4.48 (m, 1H), 4.12-4.05 (m, 3H), 3.94 (bs, 2H), 3.79 (s, 3H), 2.14 (s, 3H), 2.09 – 2.06 (m, 1H), 2.04 (s, 3H), 1.99 (s, 3H), 1.84 (dd, *J* = 12.8, 5.1 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.4, 170.2, 170.0, 136.1, 128.5, 128.2, 128.1, 98.2, 68.4, 67.2, 67.1, 66.4, 65.8, 62.4, 54.3, 52.7, 29.9, 20.8, 20.6.

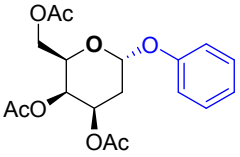
2.5 *tert*-butyl 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4e)



4e

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and *t*-butanol (0.4 mmol, 38 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave **4e** as colorless liquid (95 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35-5.32 (m, 3H), 4.33 (t, *J* = 6.4 Hz, 1H), 4.07 (dd, *J* = 6.6, 2.8 Hz, 2H), 2.14 (s, 3H), 2.08 (ddd, J = 12.6, 6.4, 2.7 Hz, 1H), 2.04 (s, 3H), 1.99 (s, 3H), 1.76 – 1.65 (m, 1H), 1.25 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.4, 170.2, 92.0, 75.0, 66.9, 66.5, 66.2, 62.5, 31.7, 28.5, 20.9, 20.75, 20.71.

2.6 phenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4f)[2]

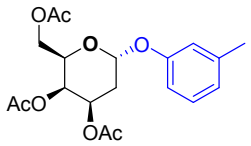


4f

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and phenol (0.4 mmol, 38 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4f** as cream solid (105mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 2H), 7.05 (m, 3H), 5.77 (d, *J* = 2.7 Hz, 1H), 5.53 (ddd, J = 12.3,

5.1, 3.1 Hz, 1H), 5.42 (d, *J* = 2.6 Hz, 1H), 4.28 (t, *J* = 6.6 Hz, 1H), 4.09 (dd, *J* = 6.6, 2.5 Hz, 2H), 2.28 (td, *J* = 12.6, 3.5 Hz, 1H), 2.18 (s, 3H), 2.16 – 2.11 (m, 1H), 2.04 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 156.3, 129.5, 122.3, 116.4, 95.8, 67.5, 66.4, 66.0, 62.0, 30.2, 20.9, 20.7, 20.6. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{18}H_{23}O_8$:367.1393; found: 367.1407.

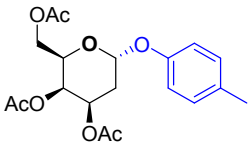
2.7 3-methylphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4g)



4g

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 136 mg) and *m*-cresol (0.4 mmol, 44 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4g** as colorless liquid (98 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.04 (m, 1H), 6.91 – 6.81 (m, 3H), 5.75 (d, *J* = 2.8 Hz, 1H), 5.52 (ddd, *J* = 12.3, 5.1, 3.1 Hz, 1H), 5.42 (d, *J* = 2.8 Hz, 1H), 4.29 (t, *J* = 6.4 Hz, 1H), 4.15 – 4.06 (m, 2H), 2.35 (s, 3H), 2.25 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.18 (s, 3H), 2.13 (d, *J* = 5.1 Hz, 1H), 2.05 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4,170.3, 170.1, 156.3, 139.5, 129.2, 123.1, 117.2, 113.3, 95.8, 67.5, 66.5, 66.0, 62.1, 30.2, 21.5, 20.9, 20.7, 20.6. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{19}H_{25}O_8$: 381.1549; found: 381.1558.

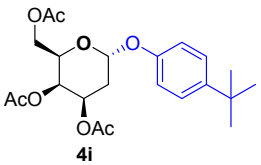
2.8 4-methylphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4h)[2]



4h

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and *p*-cresol (0.4 mmol, 44 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4h** as colorless liquid (112 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.98 (t, *J* = 5.6 Hz, 2H), 5.71 (d, *J* = 2.7 Hz, 1H), 5.52 (ddd, *J* = 12.3, 5.1, 3.1 Hz, 1H), 5.41 (d, *J* = 2.5 Hz, 1H), 4.38 – 4.21 (m, 1H), 4.19 – 3.99 (m, 2H), 2.31 (s, 3H), 2.24 (dd, *J* = 12.5, 3.5 Hz, 1H), 2.18 (s, 3H), 2.16 – 2.07 (m, 1H), 2.04 (s, 3H), 1.96 (s, 3H). 13C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 154.2, 131.7, 129.9, 116.4, 96.0, 67.4, 66.5, 66.0, 62.0, 30.3, 20.9, 20.7, 20.6, 20.5. HRMS (ESI$^+$): m/z [M+H]$^+$ calcd for $C_{19}H_{25}O_8$:381.1549; found: 381.1566.

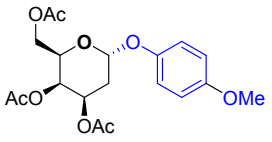
2.9 4-*tert*-butylphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4i)



4i

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 4-tert-butylphenol (0.4 mmol, 60 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4i** as white solid (133 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.74 (d, *J* = 2.8 Hz, 1H), 5.53 (ddd, *J* = 12.3, 5.1, 3.1 Hz, 1H), 5.42 (d, *J* = 2.5 Hz, 1H), 4.40 – 4.22 (m, 1H), 4.17 – 4.01 (m, 2H), 2.26 (tt, *J* = 9.4, 4.7 Hz, 1H), 2.18 (s, 3H), 2.11 (dd, *J* = 12.7, 5.1 Hz, 1H), 2.05 (s, 3H), 1.94 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 154.0, 145.1, 126.2, 115.9, 95.8, 67.4, 66.5,66.0, 62.0, 34.1, 31.4, 30.2, 20.9, 20.7, 20.6.

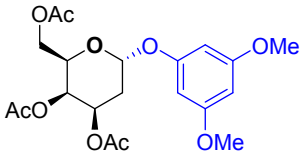
2.10 4-methoxyphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4j)[2]



4j

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 4-methoxyphenol (0.4 mmol, 50 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4j** as cream solid (102 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, *J* = 9.1 Hz, 2H), 6.84 (d, *J* = 9.1 Hz, 2H), 5.64 (d, *J* = 2.7 Hz, 1H), 5.50 (ddd, *J* = 12.2, 5.1, 3.1 Hz, 1H), 5.41 (d, *J* = 2.7 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 1H), 4.09 (dd, *J* = 6.6, 2.7 Hz, 2H), 3.78 (s, 3H), 2.25 (td, *J* = 12.6, 3.5 Hz, 1H), 2.17 (s, 3H), 2.15 – 2.07 (m, 1H), 2.04 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.0, 155.0, 150.3, 117.8 , 114.5, 96.6, 67.4, 66.5, 66.0, 62.1, 55.6, 30.3, 20.8, 20.7, 20.6. HRMS (ESI$^+$): m/z [M+H]$^+$ calcd for $C_{19}H_{24}O_9$:397.1449; found: 397.1490.

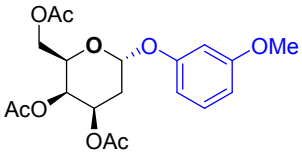
2.11 3,5-methoxyphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4k)



4k

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 3,5-dimethoxyphenol (0.4 mmol, 62 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4k** as cream solid (117 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (d, *J* = 2.2 Hz, 2H), 6.17 (d, *J* = 2.2 Hz, 1H), 5.72 (d, *J* = 2.6 Hz, 1H), 5.61 – 5.44 (m, 1H), 5.40 (d, *J* = 2.8 Hz, 1H), 4.26 (t, *J* = 6.4 Hz, 1H), 4.16 – 4.07 (m, 2H), 3.77 (s, 6H), 2.26 (td, *J* = 12.7, 3.5 Hz, 1H), 2.17 (s, 3H), 2.14 – 2.10 (m, 1H), 2.04 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 161.4, 158.1, 95.8, 95.2, 94.6, 67.5, 66.4, 66.0, 62.0, 55.3, 30.2, 20.8, 20.7, 20.5. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{20}H_{27}O_{10}$:427.1604; found: 427.1632.

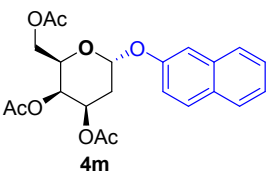
2.12 3-methoxyphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4l)



4l

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 3-methoxyphenol (0.4 mmol, 50 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4l** as cream solid (107 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.1 Hz, 1H), 6.76 – 6.53 (m, 3H), 5.75 (d, *J* = 2.7 Hz, 1H), 5.52 (ddd, *J* = 12.3, 5.1, 3.0 Hz, 1H), 5.42 (s, 1H), 4.28 (t, *J* = 6.5 Hz, 1H), 4.10 (d, *J* = 6.5 Hz, 2H), 3.81 (s, 3H), 2.27 (td, *J* = 12.6, 3.5 Hz, 1H), 2.18 (s, 3H), 2.14 – 2.08 (m, 1H), 2.10 – 2.00 (m, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 160.7, 157.5, 129.9, 108.6, 108.0, 102.8, 95.8, 67.5, 66.4, 66.0, 62.0, 55.3, 30.2, 20.9, 20.7, 20.5. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{19}H_{25}O_9$: 397.1499; found:397.1499.

2.13 Naphthalen-2-yloxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4m)[2]

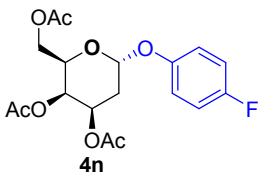


4m

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2-naphthol (0.4 mmol, 58

mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4m** as cream solid (128 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 6.0, 3.8 Hz, 1H), 7.92 – 7.76 (m, 1H), 7.59 – 7.49 (m, 3H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 5.96 (d, *J* = 2.3 Hz, 1H), 5.70 (ddd, *J* = 12.0, 5.5, 3.0 Hz, 1H), 5.48 (d, *J* = 2.7 Hz, 1H), 4.33 (t, *J* = 6.7 Hz, 1H), 4.12 (d, *J* = 6.6 Hz, 2H), 2.45–2.28 (m, 2H), 2.21 (s, 3H), 2.09 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.2, 151.9, 134.5, 127.6, 126.5, 125.74, 125.71, 122.0, 121.7, 108.3, 96.1, 67.8, 66.5, 66.2, 62.0, 30.5, 20.9, 20.7, 20.6.

2.14 4-fluorophenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4n)



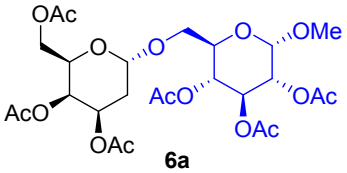
4n

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 4-fluorophenol (0.4 mmol, 45 mg). Column chromatography purification using EtOAc:Hexane (2:8) gave **4n** as cream solid (101 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 – 6.94 (m, 4H), 5.67 (d, *J* = 2.8 Hz, 1H), 5.50 (ddd, *J* = 12.3, 5.1, 3.1 Hz, 1H), 5.42 (s, 1H), 4.27 (t, *J* =6.5 Hz, 1H), 4.15 – 4.00 (m, 2H), 2.27 (td, *J* = 12.6, 3.5 Hz, 1H), 2.18 (s, 3H), 2.12 (dd, *J*=12.6, 5.7 Hz, 1H), 2.04 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 159.8, 156.6, 152.4, 150.39, 117.8, 117.7, 116.0, 115.7, 96.4, 67.6, 66.4, 65.9, 62.1, 30.2, 20.8, 20.7, 20.6. HRMS (ESI$^+$): m/z $[M + H]^+$ calcd for $C_{18}H_{22}O_8F$:385.1299; found: 385.1282.

2.15 4-formylphenoxy 3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (4o)

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 4-hydroxybenzaldehyde (0.4 mmol, 49 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **4o** as colorless gummy liquid (81 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.87 (s, 1H), 5.50 (dd, *J* = 12.1, 3.8 Hz, 1H), 5.42 (s, 1H), 4.21 (t, *J* = 6.5 Hz, 1H), 4.08 (m, 2H), 2.31 (td, *J* = 12.7, 3.2 Hz, 1H), 2.18 (s, 3H), 2.12 (bs, 1H), 2.05 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 170.2, 170.1, 161.1, 131.8, 131.1, 116.5, 95.7, 68.0, 66.1, 65.7, 61.9, 29.9, 20.8, 20.7, 20.5.

2.16 Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl)- α-D-glucopyranoside (6a)

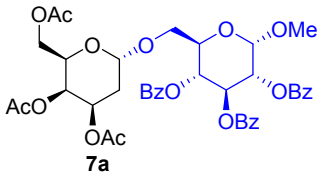


6a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2,3,4-tri-O-acetyl-methyl-α-D–glucopyranoside (0.4 mmol, 128 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **6a** as colorless liquid (126 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (t, *J* = 9.7 Hz, 1H), 5.41 – 5.22 (m, 2H), 5.05 (dd, *J* = 11.1, 8.4 Hz, 2H), 4.99 – 4.84 (m, 2H), 4.21 – 4.03 (m, 3H), 3.96 (ddd, *J* = 10.2, 5.3, 2.3 Hz, 1H), 3.72 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.53 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.43 (s, 3H), 2.17 (d, *J* = 9.9 Hz,1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.92 (dd, *J* = 12.8, 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 169.9, 169.7, 169.6, 97.3, 96.5, 70.8, 70.2, 69.1, 67.9, 66.8, 66.6, 66.0, 65.6, 62.5, 55.3,

29.9, 20.8, 20.7, 20.6. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{25}H_{37}O_{16}$: 593.2082; found: 593.2078.

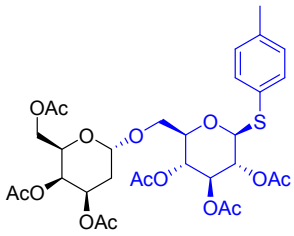
2.17 Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl)-α-D-glucopyranoside (7a)



7a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2,3,4-tri-O-benzoyl-methyl-α-D–glucopyranoside (0.4 mmol, 202 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **7a** as colorless liquid (157 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (dd, J = 10.6, 4.2 Hz, 4H), 7.92 – 7.80 (m, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.40 (m, 5H), 7.34 – 7.18 (m, 2H), 6.17 (t, *J* = 9.5 Hz, 1H), 5.64 (t, *J* = 9.9 Hz, 1H), 5.44 – 5.18 (m, 3H), 5.06 (d, *J* = 2.9 Hz, 1H), 4.34 – 4.07 (m, 3H), 3.98 (dd, *J* = 6.4, 2.8 Hz, 2H), 3.88 (dd, *J* = 11.0, 4.9 Hz, 1H), 3.64 (dd, *J* = 10.9, 2.8 Hz, 1H) 3.50 (s, 3H), 2.13 (s, 3H), 2.08 (d, *J* = 1.6 Hz, 1H), 2.00 (s, 3H), 1.92 (s, 3H), 1.89 – 1.81 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.2, 169.9, 165.7, 165.2, 133.4, 133.3, 133.1, 129.9, 129.8, 129.7, 129.2, 129.06, 129.0, 128.48, 128.42, 128.2, 97.4, 97.0, 71.9, 70.4, 69.5, 68.2, 66.7, 66.6, 66.1, 66.0, 62.6, 55.6, 29.8, 20.9, 20.7, 20.6. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{40}H_{43}O_{16}$: 779.2551; found: 779.2577.

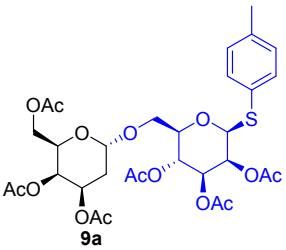
2.18 Phenyl 2,3,4-tri-*O*-acetyl-6-(3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl)-1-thio-β-D-glucopyranoside (8a)



8a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2,3,4-tri-*O*-acetyl-thio-α-D–glucopyranoside (0.4 mmol, 159 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **8a** as colorless liquid (152 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.32 – 5.16 (m, 3H), 5.02-4.92 (m, 2H), 4.71 (d, *J* = 10.0 Hz, 1H), 4.24 (d, *J* = 5.7 Hz, 1H), 4.15 – 4.03 (m, 3H), 3.80 – 3.63 (m, 2H), 3.63 – 3.53 (m, 1H), 2.36 (s,3H), 2.15 (s, 3H), 2.13 (bs, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.88 (dd, *J* = 12.6, 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.2, 169.8, 169.4, 169.3, 138.6, 133.0, 129.8, 127.7, 97.4, 85.3, 74.0, 70.0 , 68.8, 66.8, 66.6, 66.0, 62.4, 29.9, 21.1, 20.8, 20.78, 20.73, 20.63. HRMS (ESI$^+$): m/z [M + H]$^+$ calcd for $C_{31}H_{41}O_{15}S$: 685.2166; found: 685.2178.

2.19 Phenyl 2,3,4-tri-*O*-acetyl-6-(3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl)-1-thio-β-D-mannopyranoside (9a)

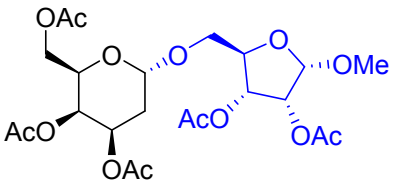


9a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2,3,4-tri-*O*-acetyl-thio-α-D–mannoside (0.4 mmol, 159 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **9a** as colorless liquid (157 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz,

2H), 7.25 – 7.13 (m, 2H), 5.66 (d, *J* = 2.9 Hz, 1H), 5.24 (m, 2H), 5.06 (dd, *J* = 12.8, 3.4 Hz, 2H), 4.94 (s, 1H), 4.10 (dt, *J* = 12.6, 6.0 Hz, 4H), 3.83 (dd, *J* = 10.8, 6.3 Hz, 1H), 3.68 (d, *J* = 6.8 Hz, 1H), 3.56 (d, *J* = 10.8 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H), 2.15 (s, 3H), 2.07 (s, 7H), 2.02 (s, 3H), 2.00 (s, 3H), 1.96 – 1.87 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 170.3, 170.1, 170.0, 169.7, 169.6, 138.3, 131.8, 129.9, 129.1, 97.2, 85.1, 71.9, 70.6, 66.9, 66.7, 66.6, 66.3, 65.9, 62.4, 60.4, 30.0, 21.0, 20.8, 20.76, 20.73, 20.6, 20.5. HRMS (ESI+): m/z $[M + H]^+$ calcd for $C_{31}H_{41}O_{15}S$: 685.2134; found: 685.2166.

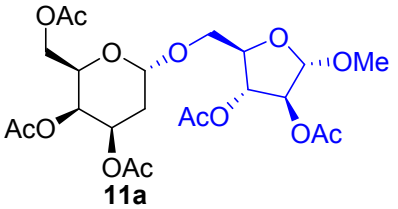
2.20 Methyl 2,3-di-*O*-acetyl-5-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl)-α-D-ribofuranoside (10a)



10a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2,3-di-*O*-acetyl-methyl-α-D–ribofuranoside (0.4 mmol, 99 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **10a** as colorless liquid (114 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38-5.35 (m, 2H), 5.38-5.35 (m, 1H) 5.22 (d, *J* = 4.9 Hz, 1H), 5.08 (d, *J* = 2.9 Hz, 1H), 4.92 (s, 1H), 4.28 – 4.18 (m, 2H), 4.11 (d, *J* = 6.5 Hz, 2H), 3.79 (dd, *J* = 10.7, 5.5 Hz, 1H), 3.62 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.40 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.09 (m, 1H),2.07 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.92 (dd, *J* = 12.7, 5.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 169.9, 169.75, 169.7, 106.2, 97.8, 79.3, 74.7, 71.8, 68.3, 66.8, 66.6, 66.0, 62.3, 55.3, 29.9, 20.8, 20.7, 20.6, 20.5. HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{22}H_{33}O_{14}$: 521.1870; found: 521.1826.

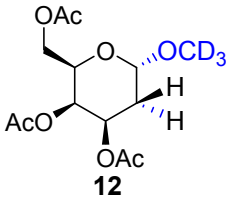
2.21 Methyl 2,3-di-*O*-acetyl-5-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranosyl)-α-D-arabinofuranoside (11a)



11a

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and 2,3-di-*O*-acetyl-methyl-α-D–arabofuranoside (0.4 mmol, 99 mg). Column chromatography purification using EtOAc:Hexane (3:7) gave **11a** as colorless liquid (124 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.36 (m, 2H), 5.10 (m, 3H), 4.93 (s, 1H), 4.27 (t, *J* = 6.5 Hz, 1H), 4.21 – 4.05 (m, 3H), 3.94 (dd, *J* = 11.1, 4.6 Hz, 1H), 3.75 (dd, *J* = 11.0, 3.3 Hz, 1H), 3.42 (s, 3H), 2.15 (s, 3H), 2.13 (br s, 1H), 2.12 (s, 3H), 2.08 (s, 6H), 2.00 (s, 3H), 1.92 (dd, *J* = 12.5, 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.2, 169.96, 169.91, 106.6, 97.7, 81.6, 81.3, 66.8, 66.6, 66.4, 66.0, 62.2, 54.9, 29.9, 20.86, 20.81, 20.7. HRMS (ESI^+): m/z $[M + H]^+$ calcd for $C_{22}H_{33}O_{14}$: 521.1870; found: 521.1871.

2.22 Trideuteromethyl-3,4,6-tri-*O*-acetyl-2-deoxy-D-galactcopyranoside (12



12

Prepared by the general procedure using 3,4,6-tri-*O*-acetyl-D-galactal **2** (0.34 mmol, 100 mg) and CD_3OD (0.4 mmol, 17 µl). Column chromatography purification using EtOAc:Hexane (2:8) gave **12** as

white solid (96 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35 – 5.21 (m, 2H), 4.90 (d, *J* = 3.2 Hz, 1H), 4.11 (m, 3H), 2.14 (s, 3H), 2.05 (s, 3H), 2.0 (dd, *J* = 12.0, 3.0 Hz, 1H), 1.98 (s, 3H), 1.88-184 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 170.0, 98.4, 66.6, 66.5, 66.1, 62.5, 30.0, 20.8, 20.7.

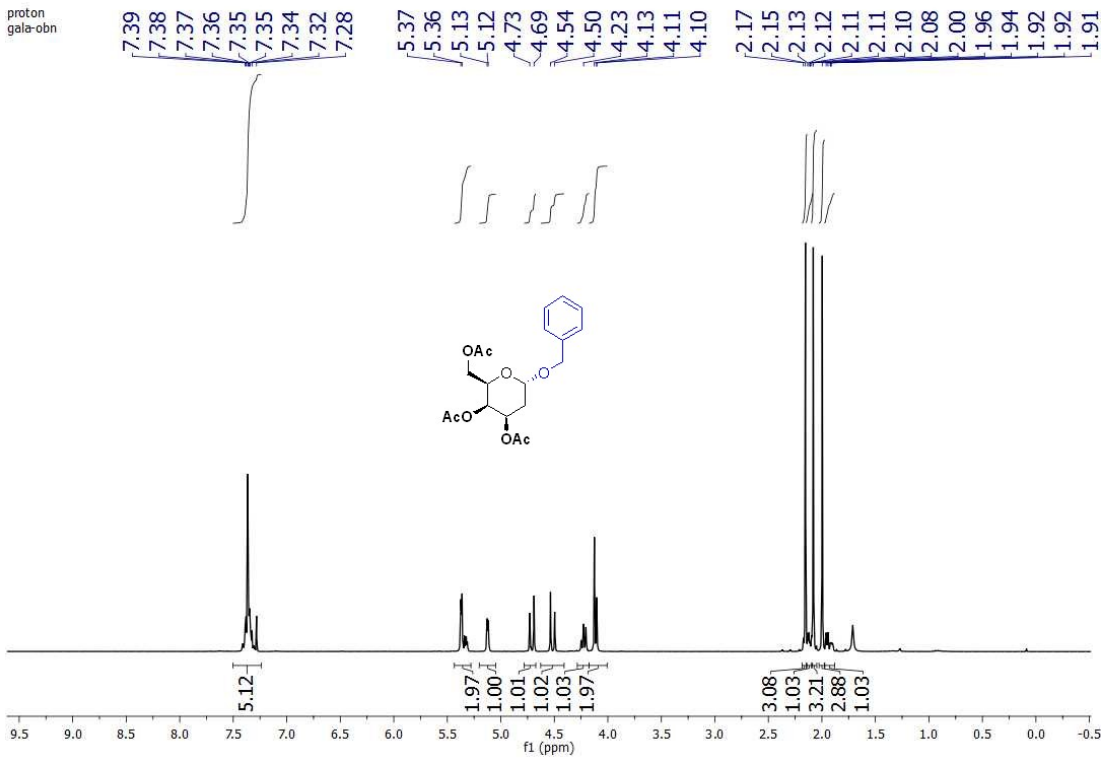
References

1) Hsu, M.-Y.; Liu, Y.-P.; Lam, S.; Lin, S.-C.; Wang, C.-C. Beilstein J. Org. Chem. 2016, 12, 1758–1764.

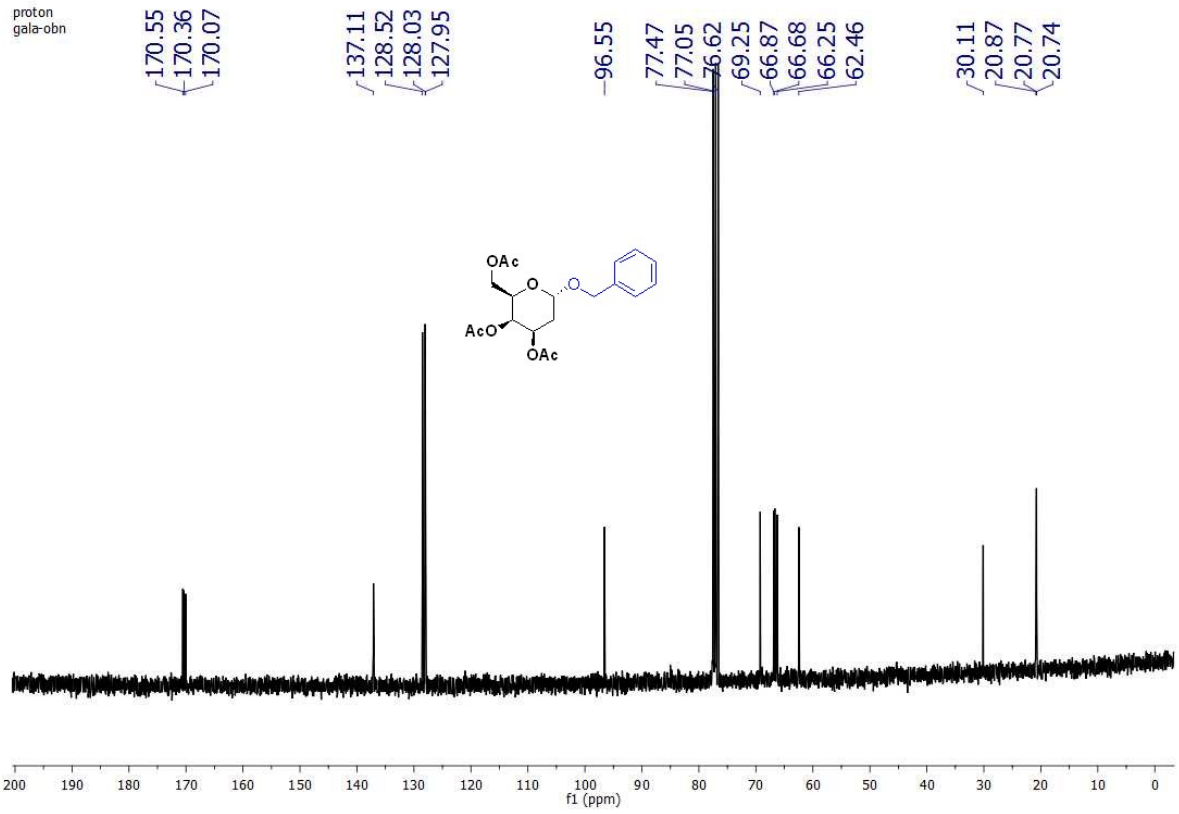
2) Williams, D. B. G.; Simelane, S. B.; Kinfe, H. H. Org. Biomol. Chem., 2012, 10, 5636–5642

3. Spectral images of compounds 4a-n, 6a-11a, and 12

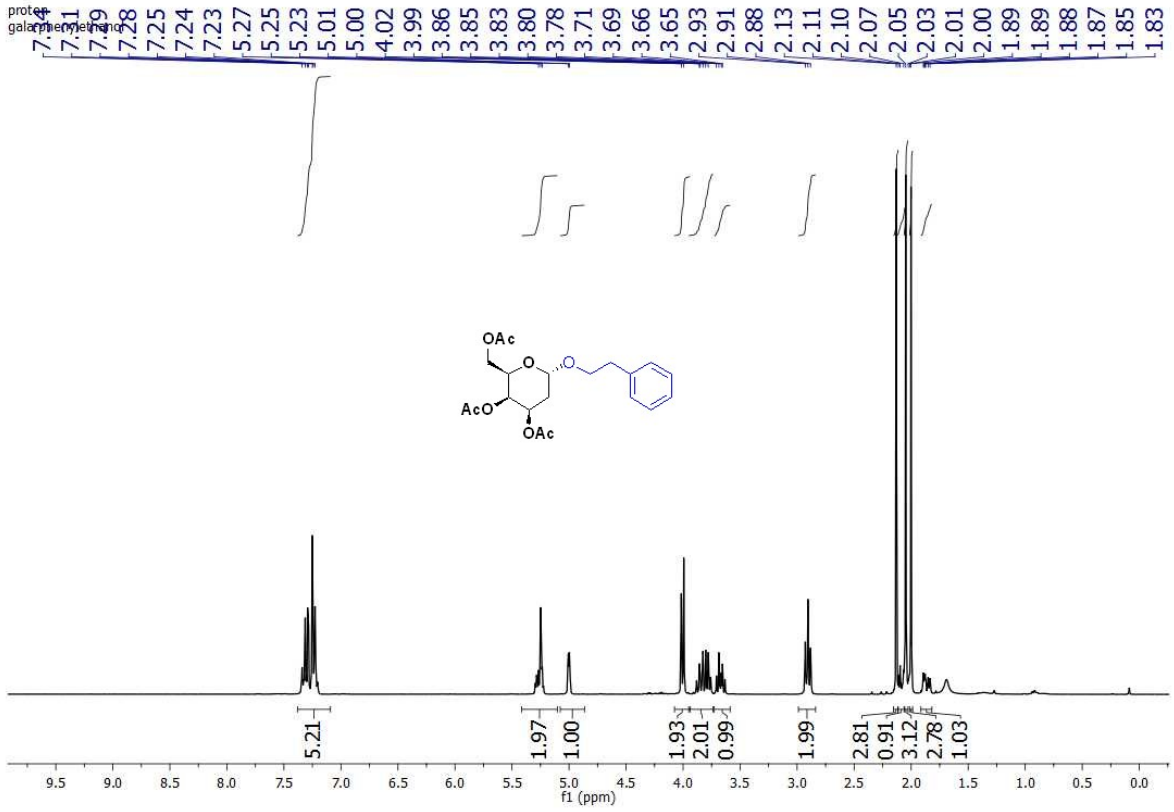
^{1}H NMR of compound **4a**



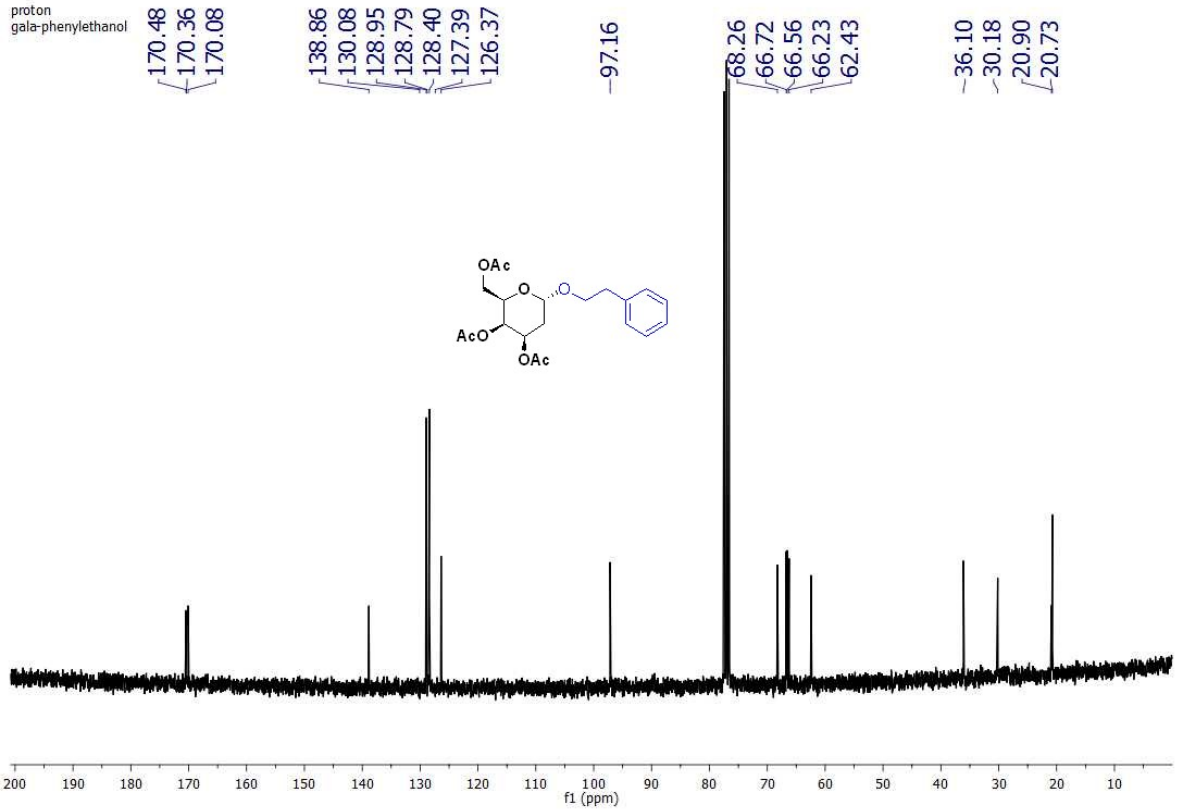
^{13}C NMR of compound **4a**



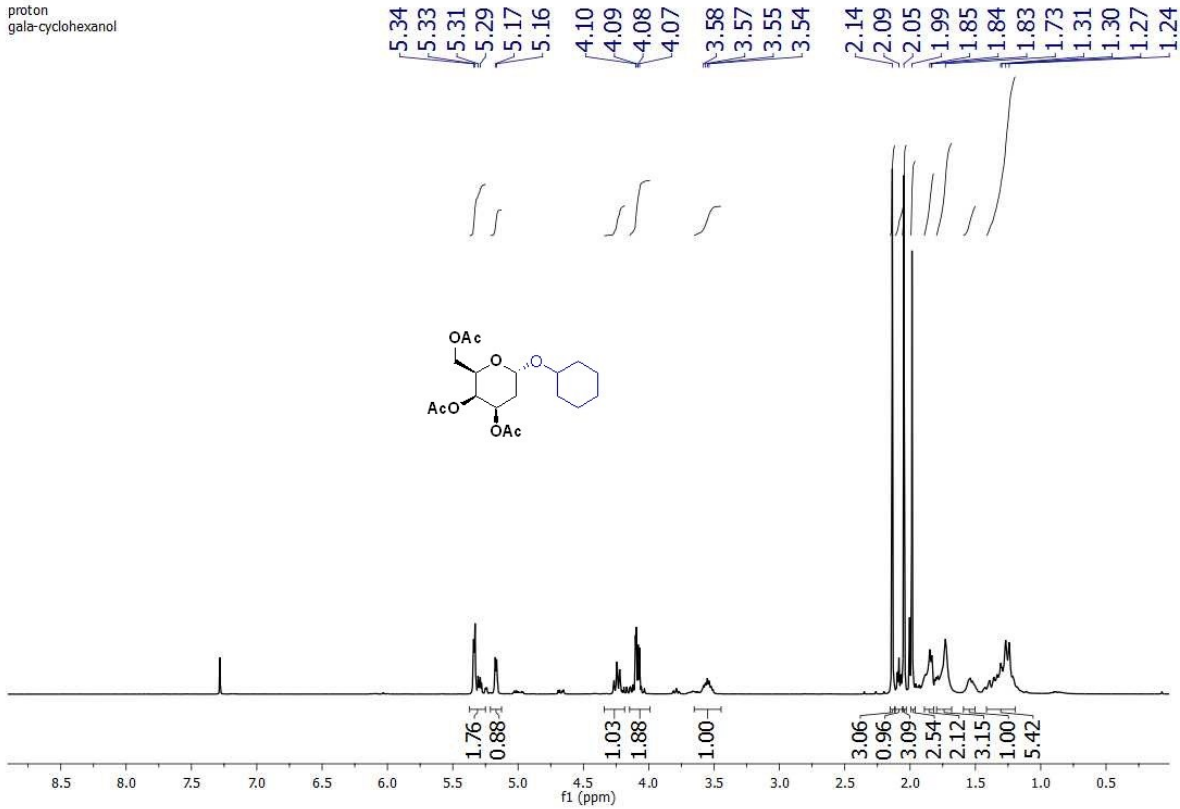
^{1}H NMR of compound **4b**



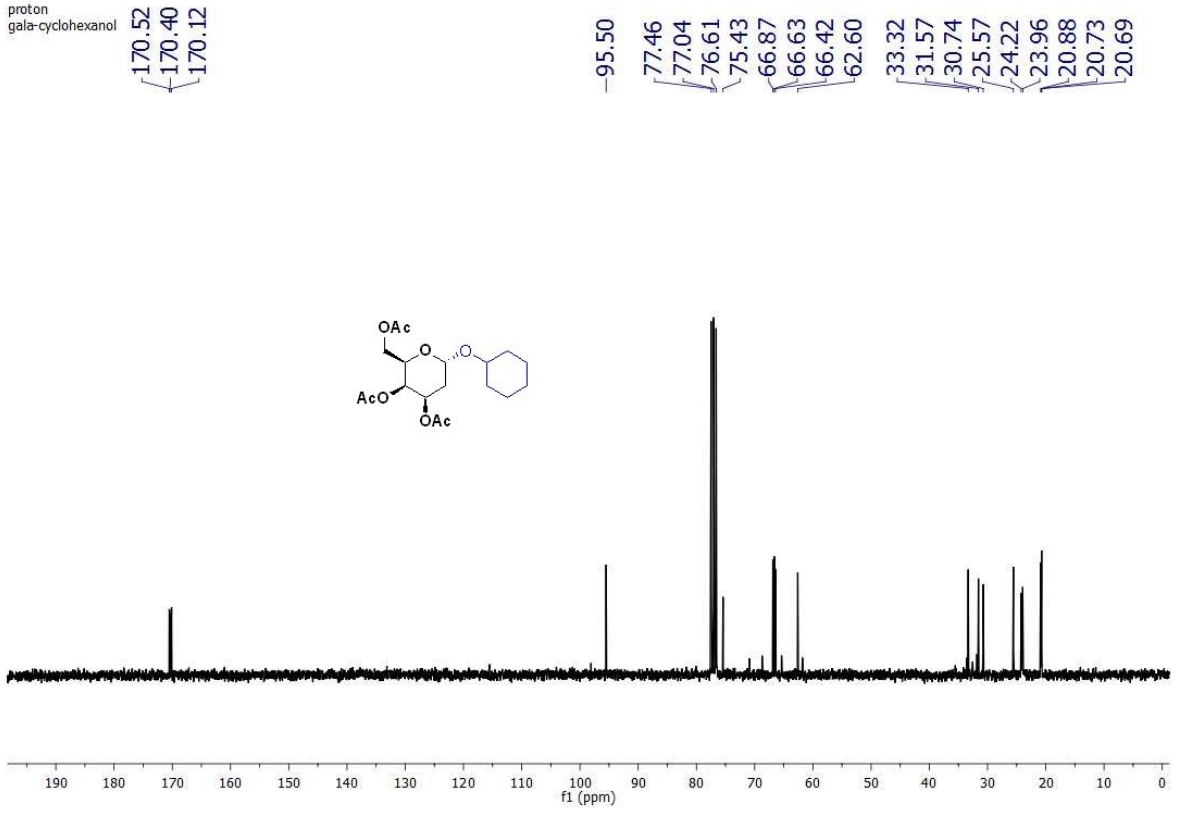
^{13}C NMR of compound **4b**



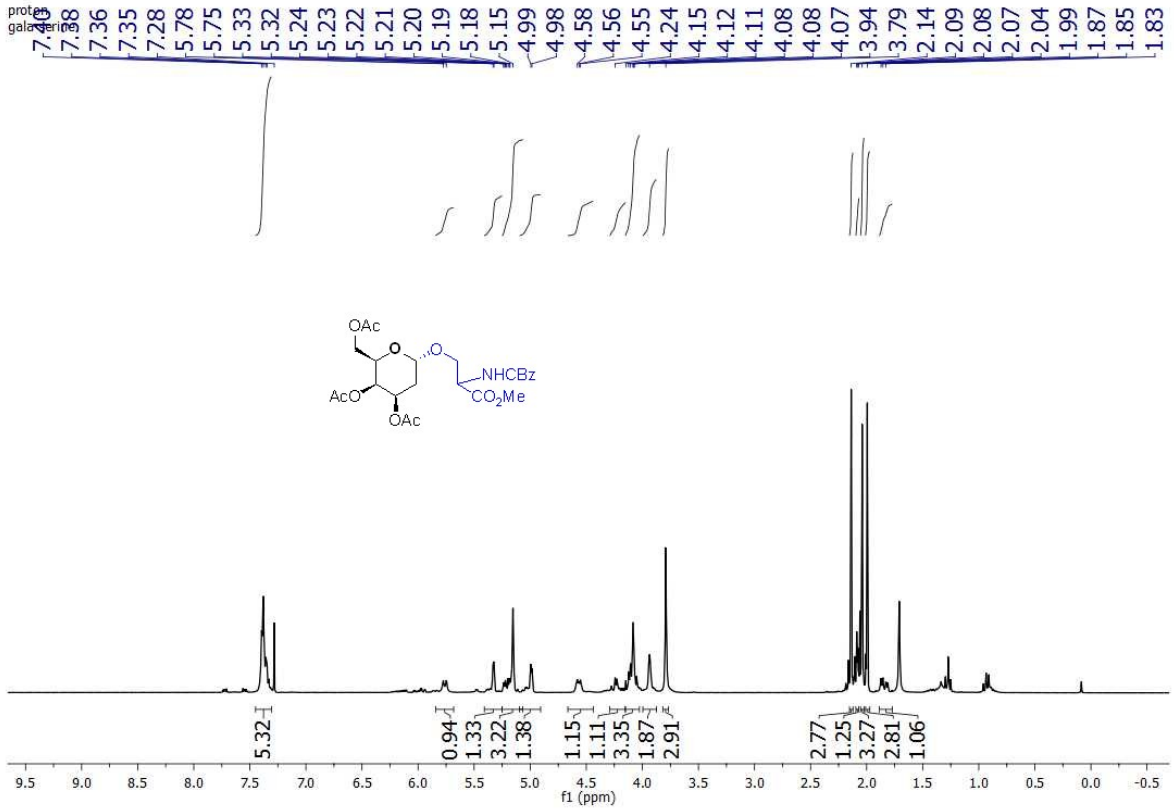
^{1}H NMR of compound **4c**



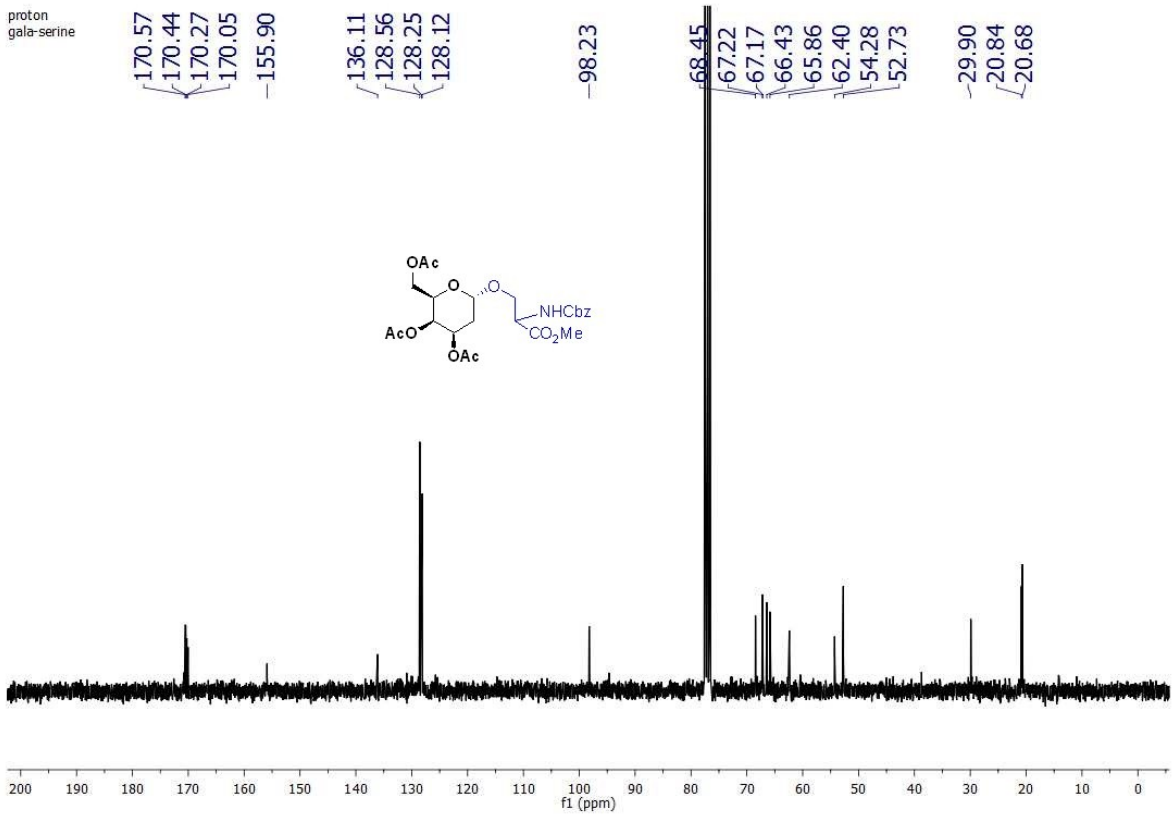
^{13}C NMR of compound **4c**



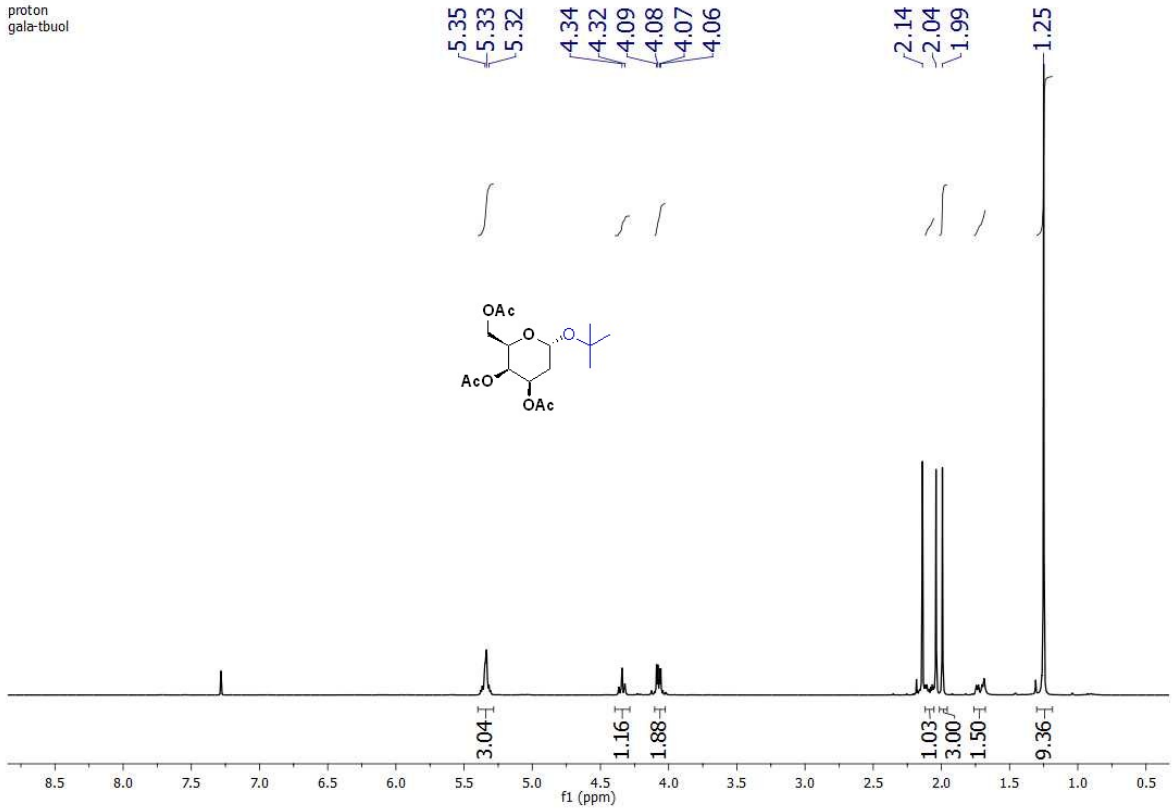
^{1}H NMR of compound **4d**



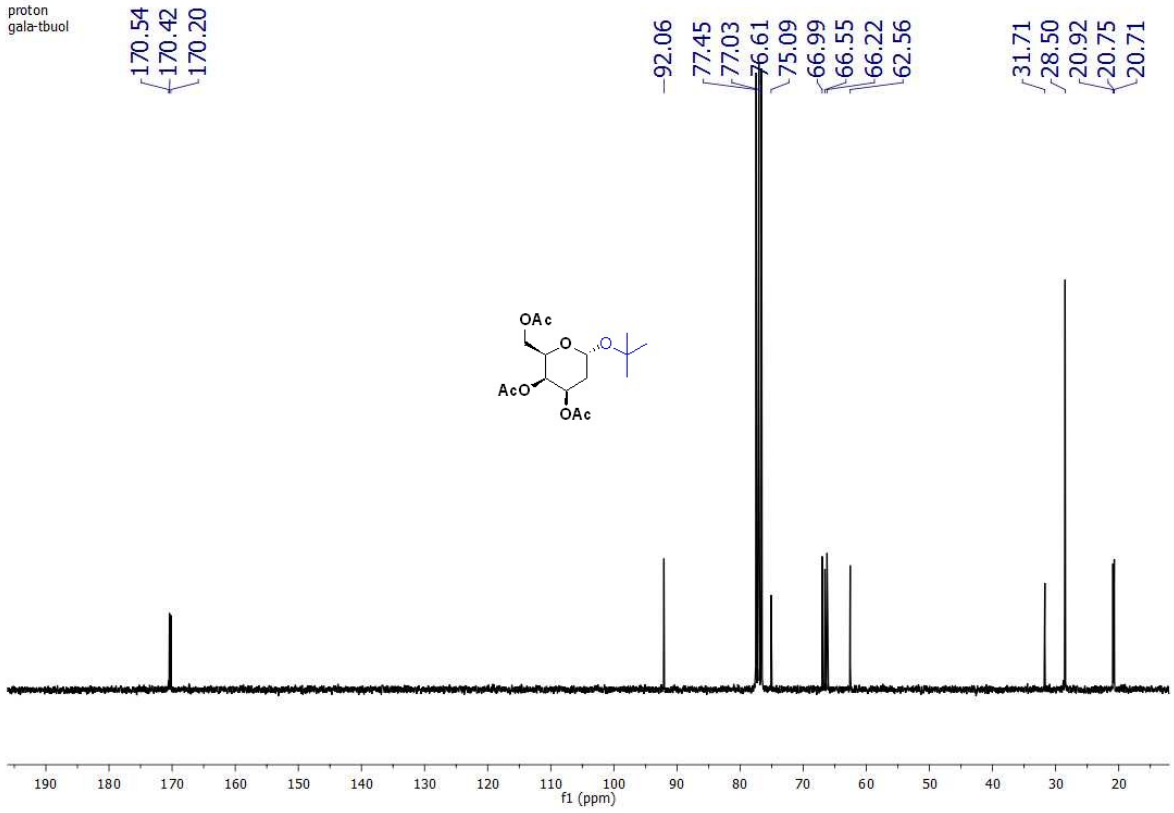
^{13}C NMR of compound **4d**



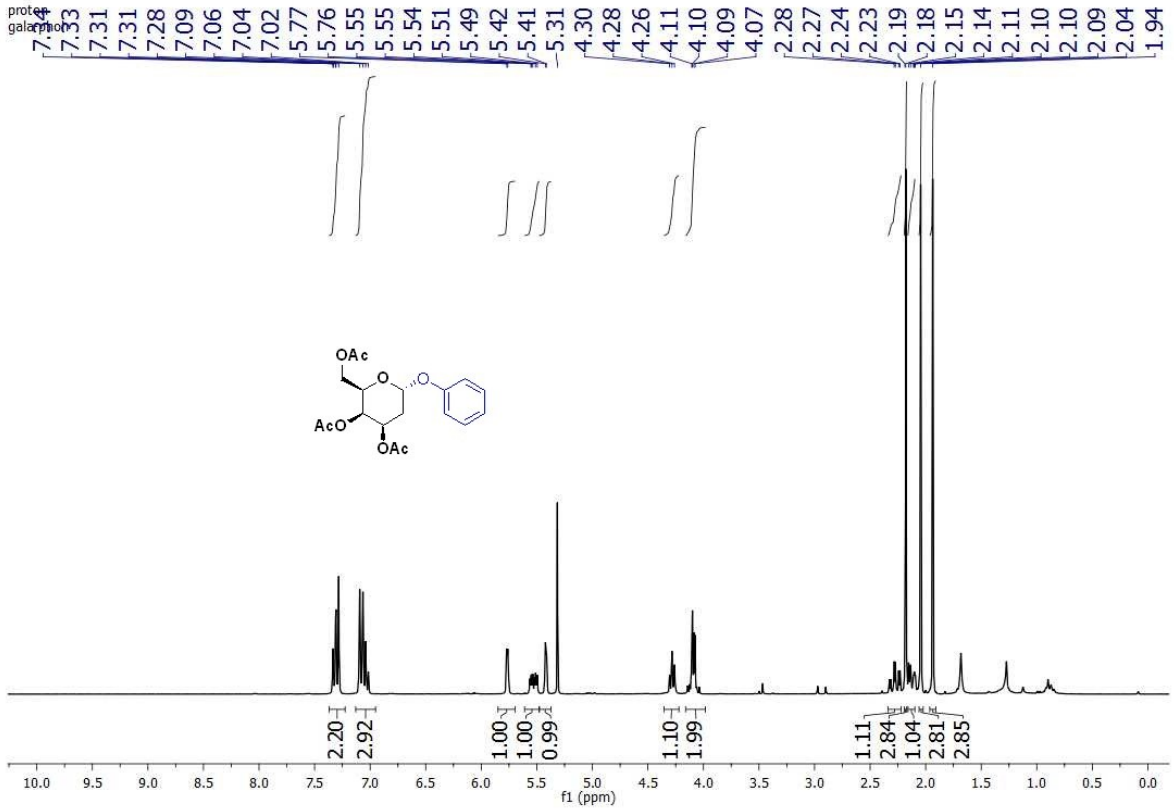
^{1}H NMR of compound **4e**



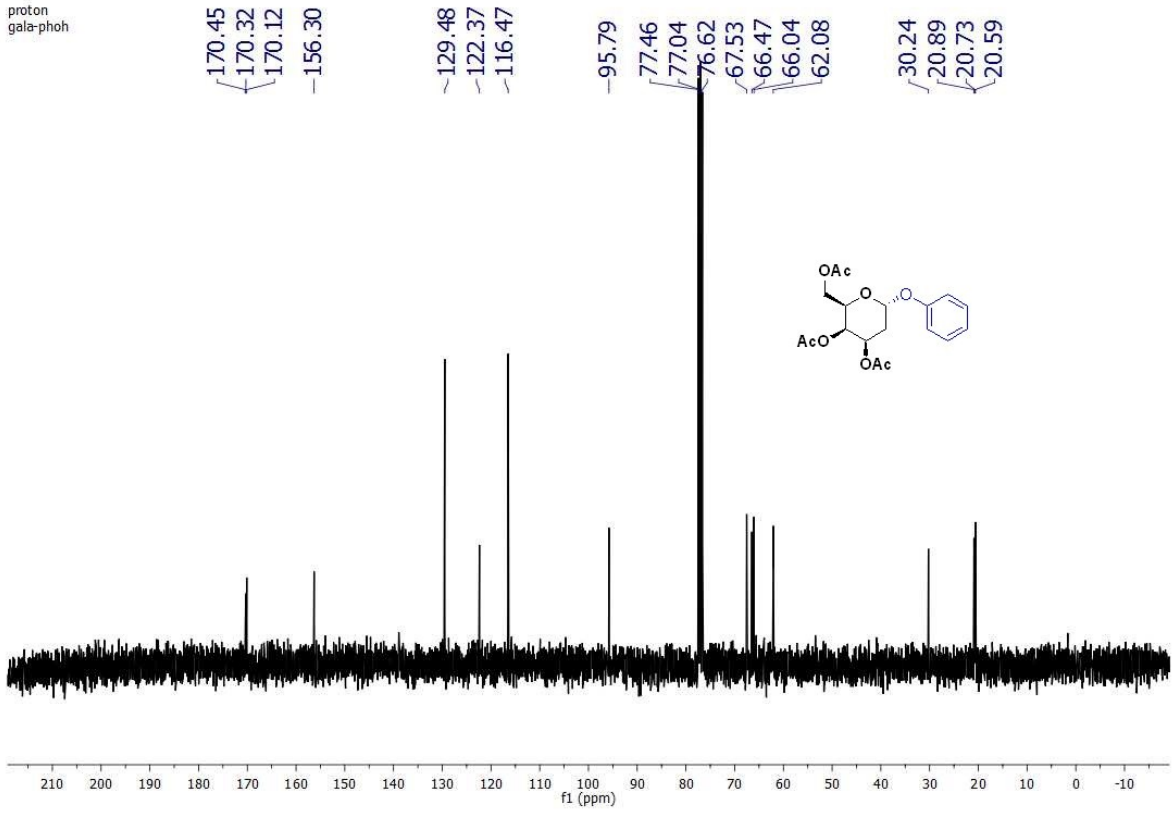
^{13}C NMR of compound **4e**



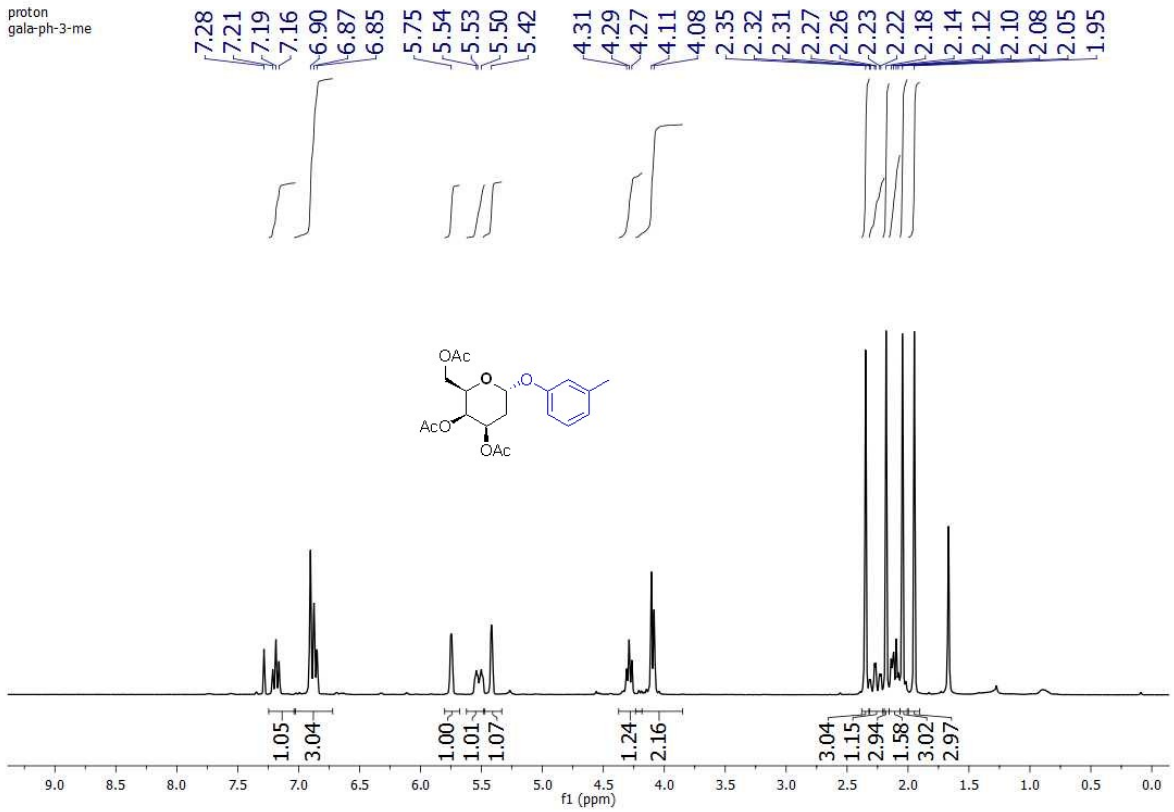
^{1}H NMR of compound **4f**



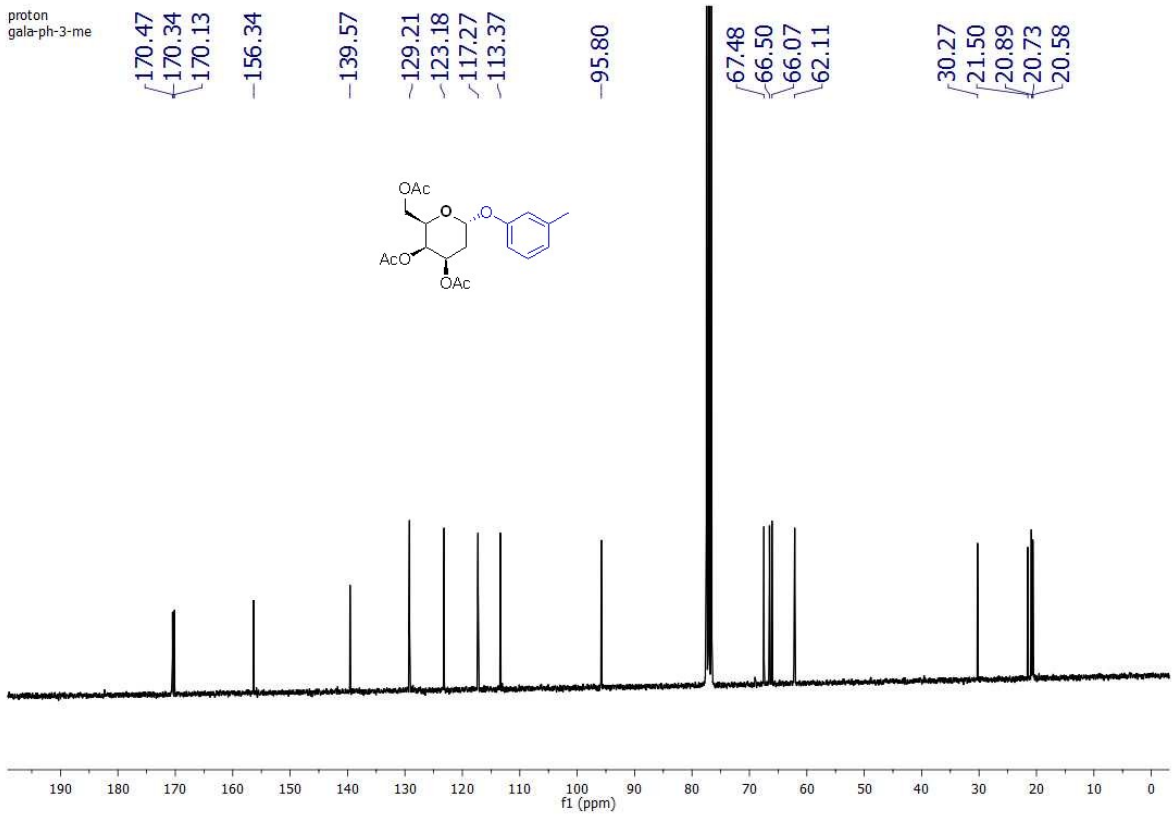
^{13}C NMR of compound **4f**



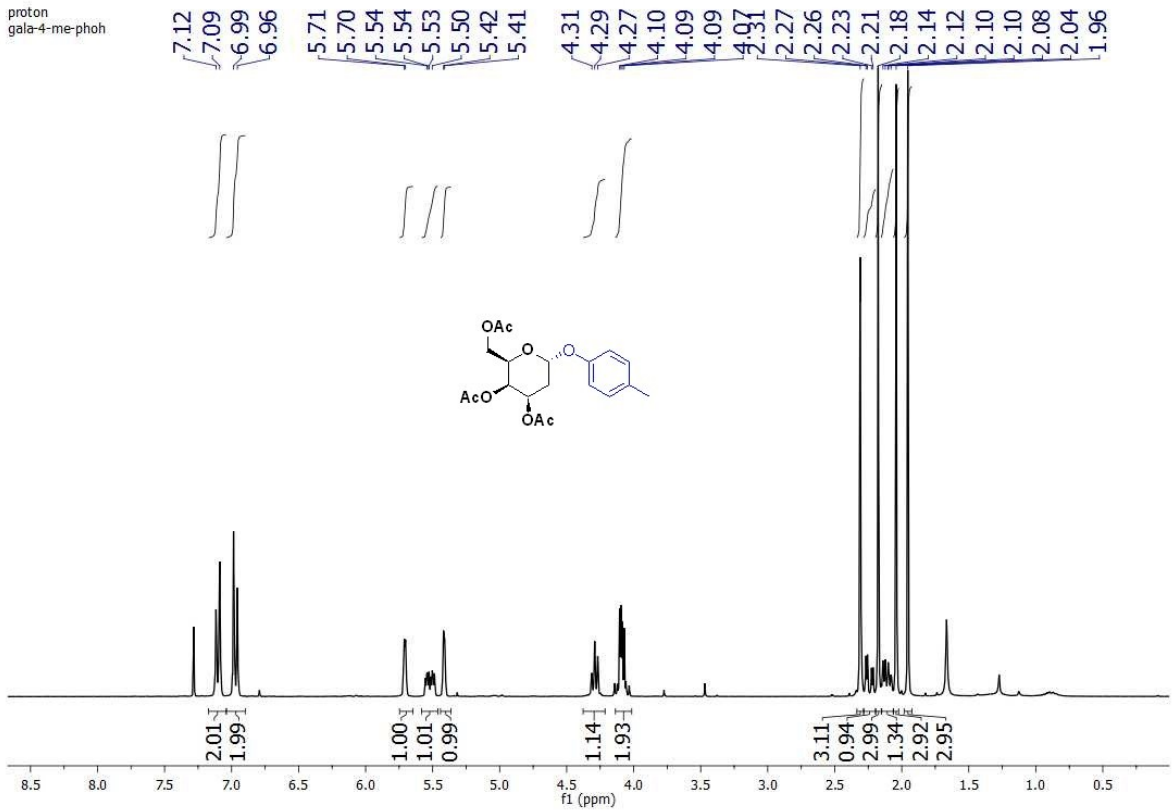
^{1}H NMR of compound **4g**



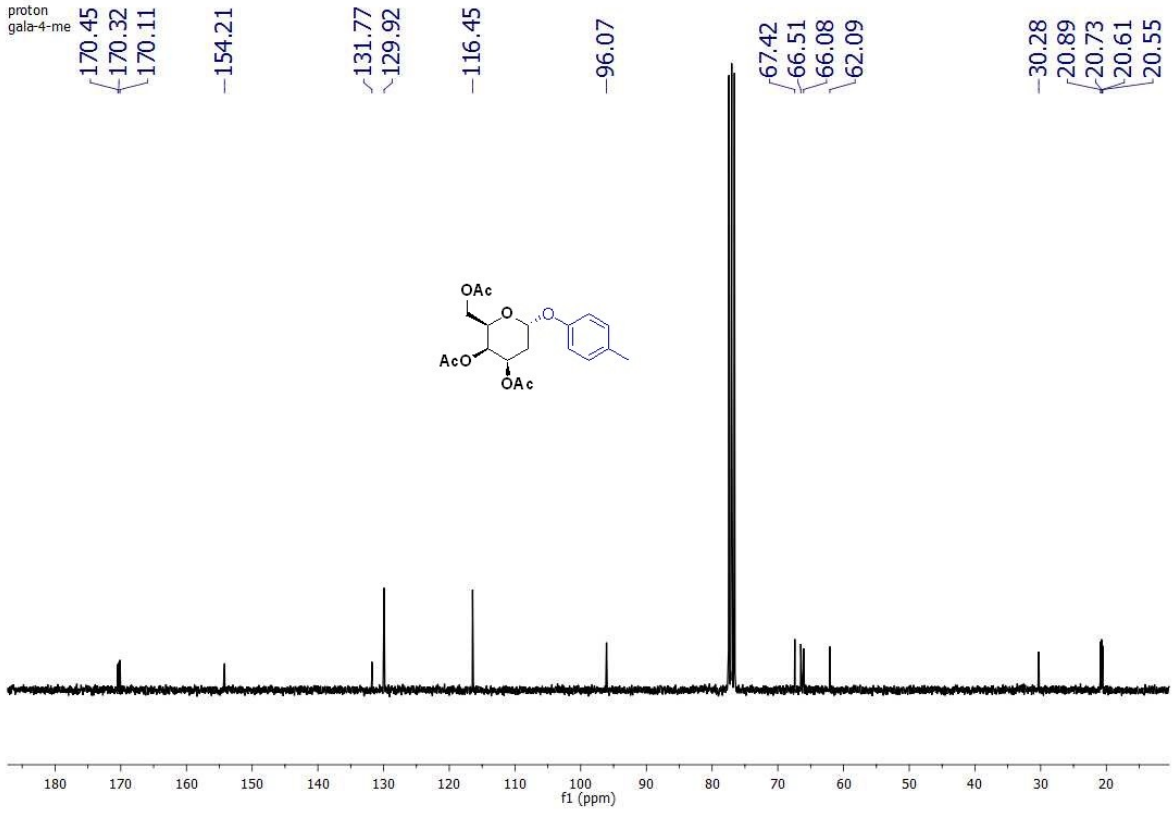
^{13}C NMR of compound **4g**



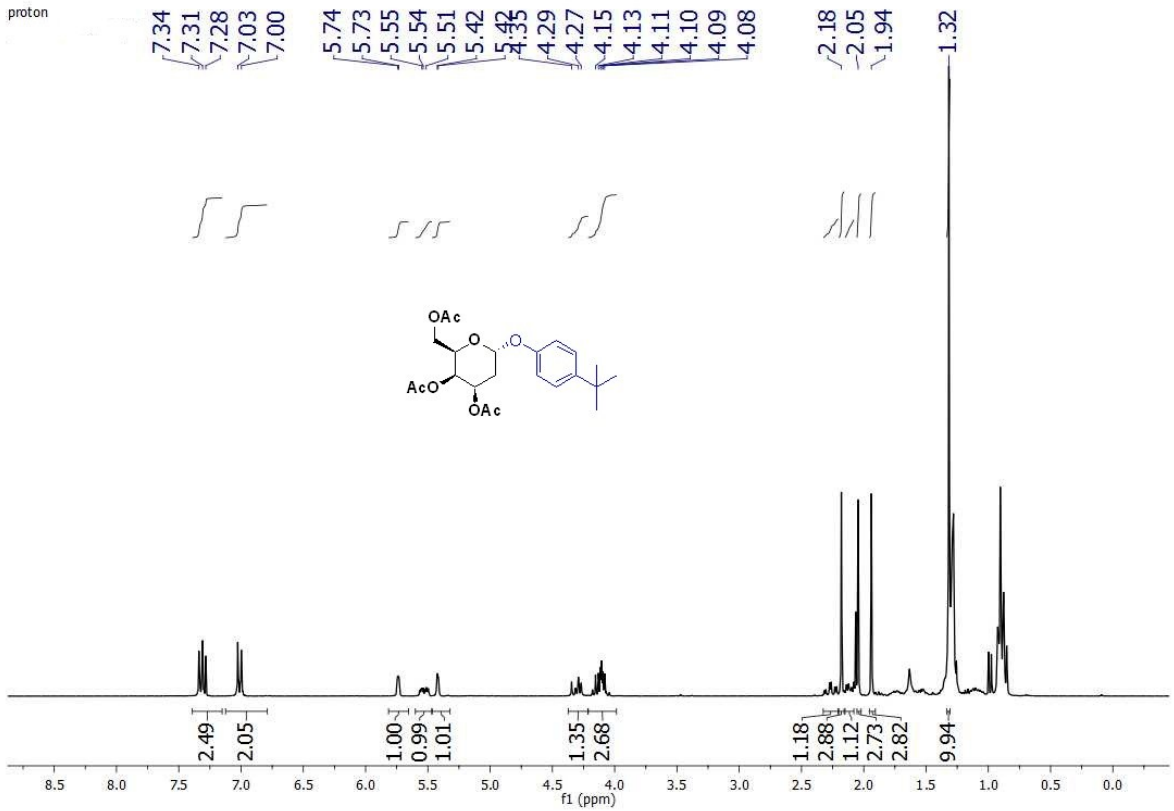
^{1}H NMR of compound **4h**



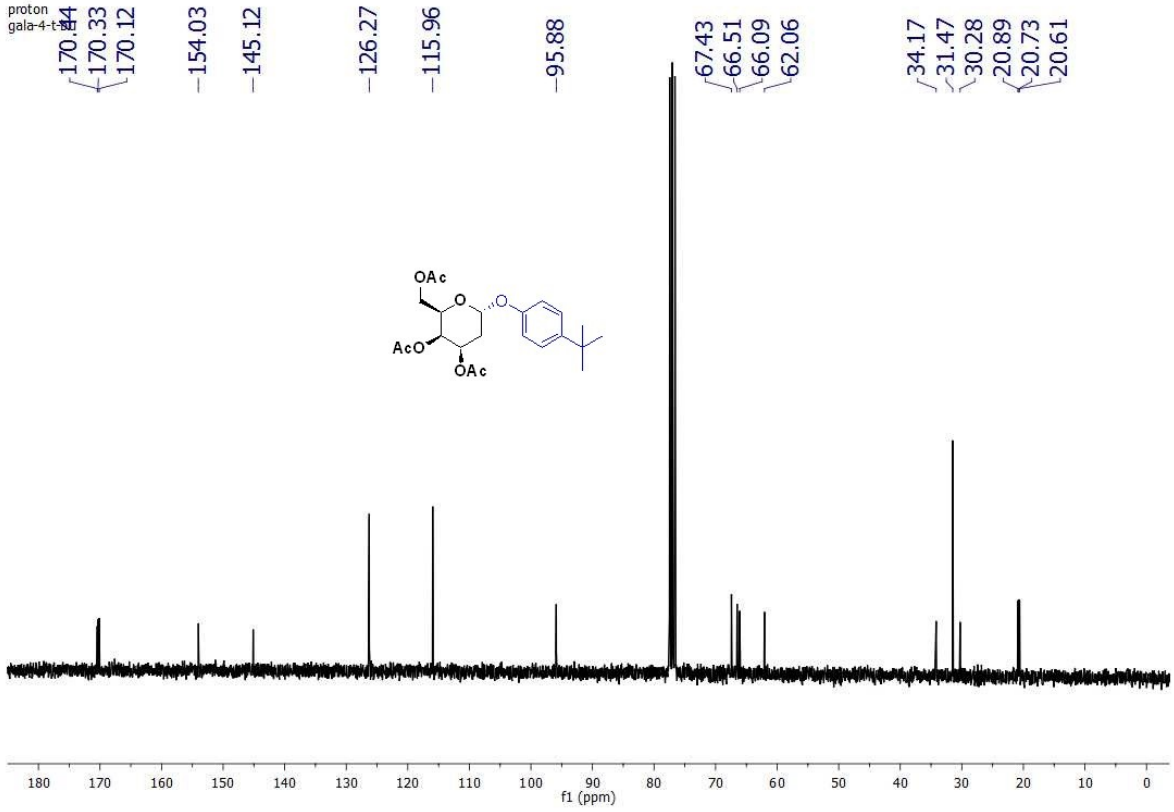
^{13}C NMR of compound **4h**



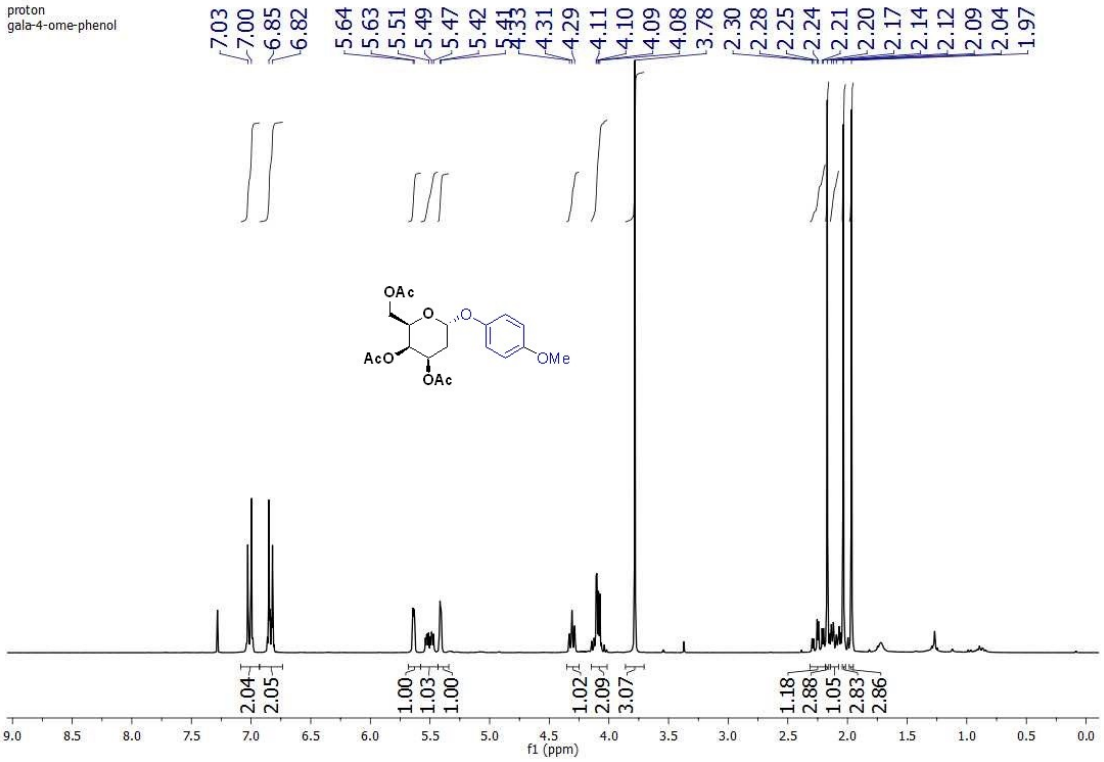
^{1}H NMR of compound **4i**



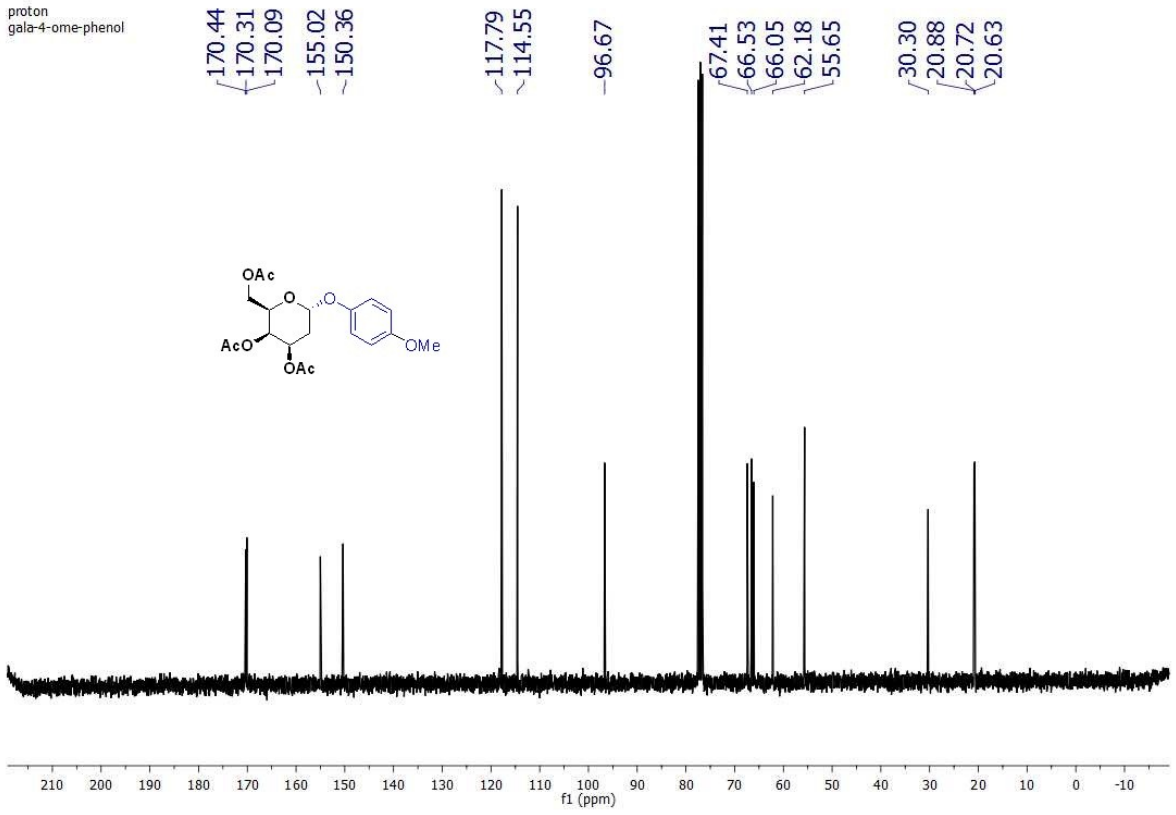
^{13}C NMR of compound **4i**



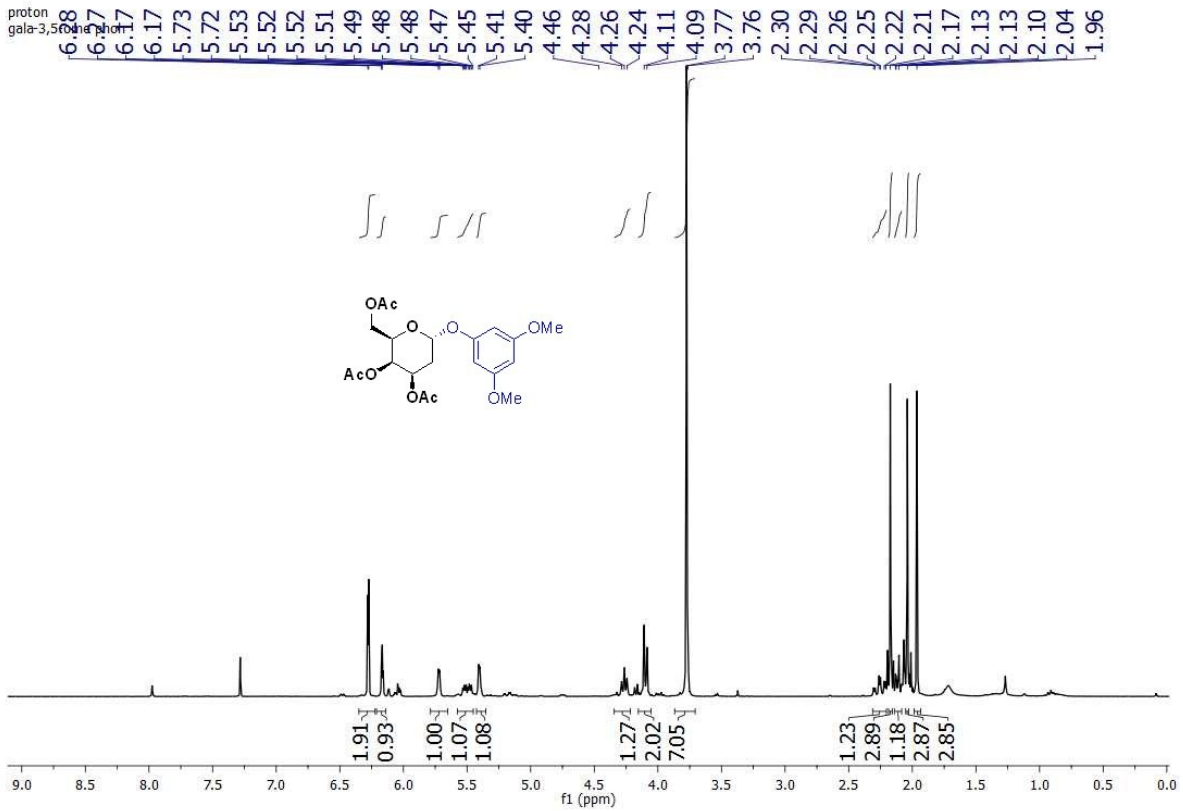
^{1}H NMR of compound **4j**



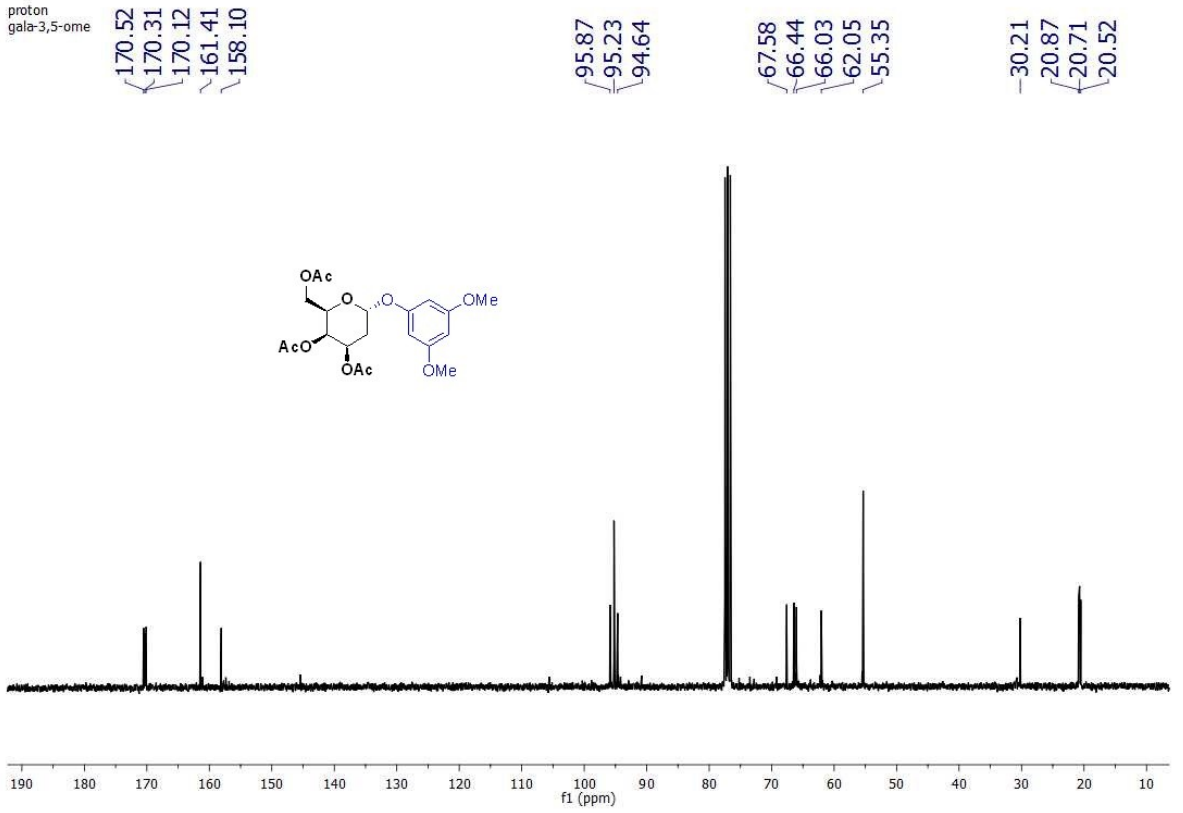
^{13}C NMR of compound **4j**



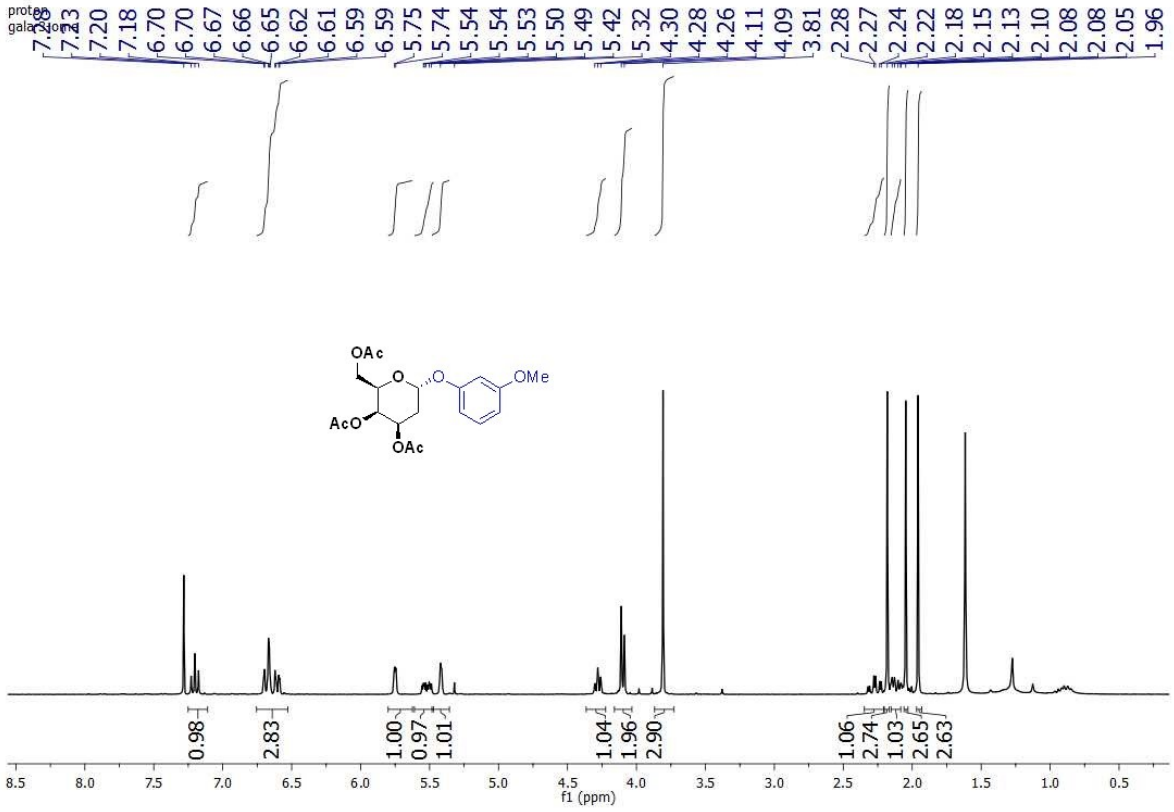
^{1}H NMR of compound **4k**



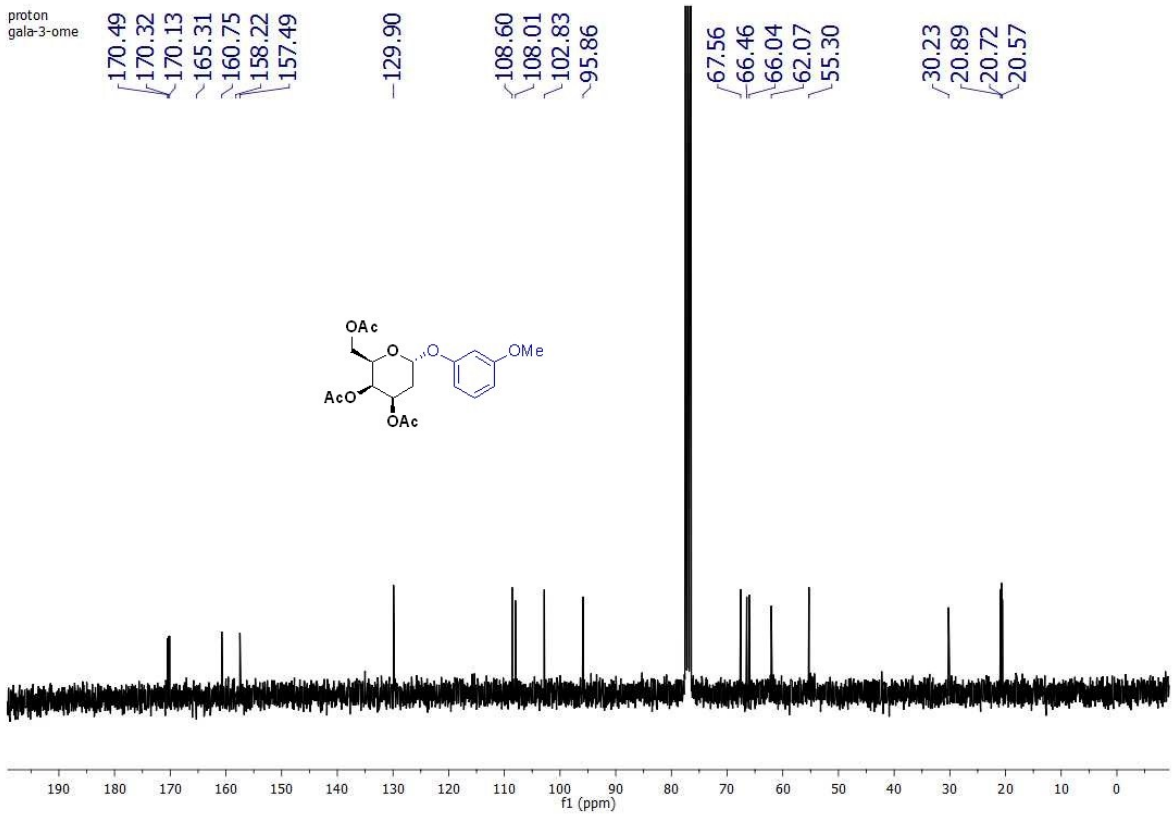
^{13}C NMR of compound **4k**



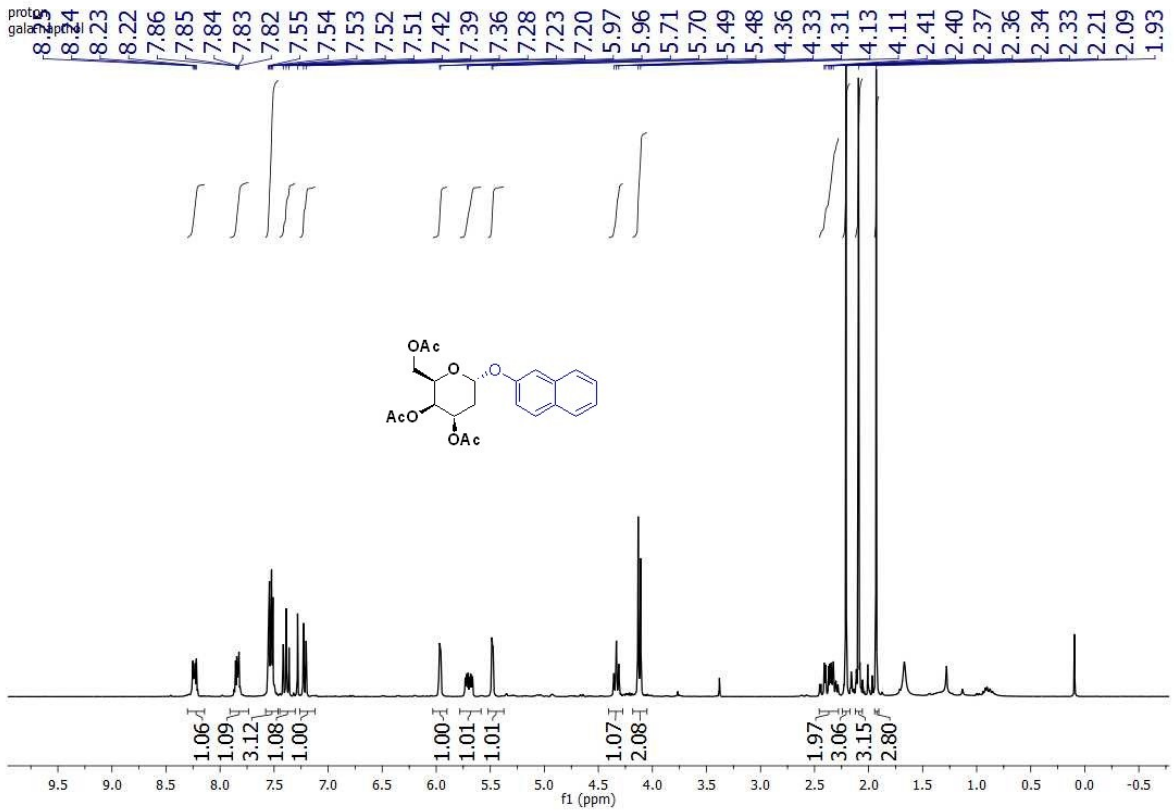
^{1}H NMR of compound **4l**



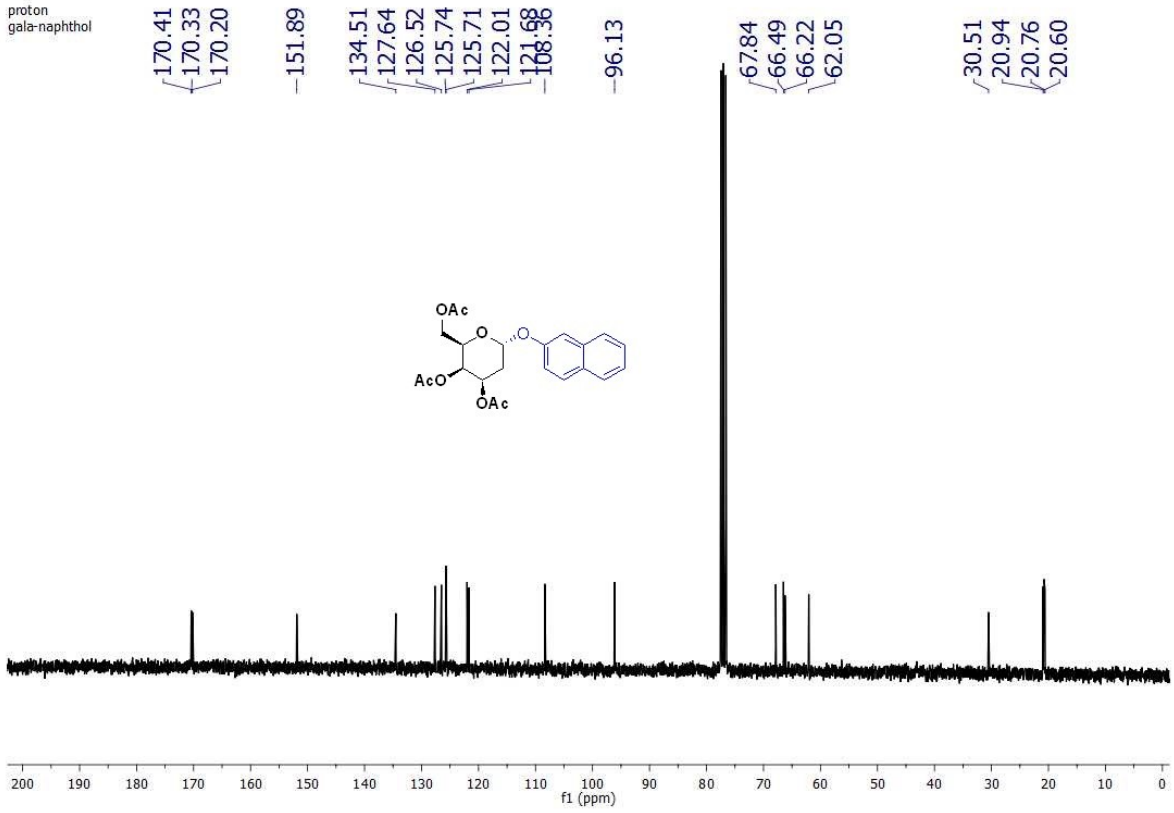
^{13}C NMR of compound **4l**



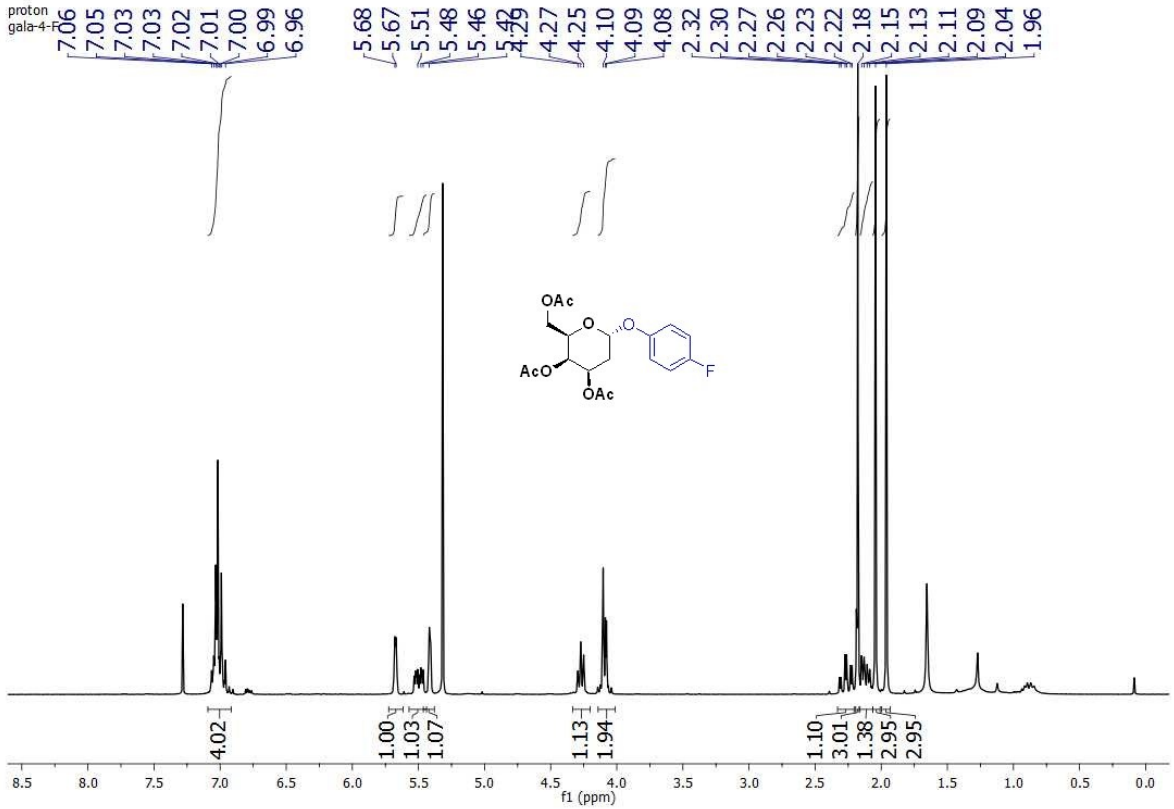
^{1}H NMR of compound **4m**



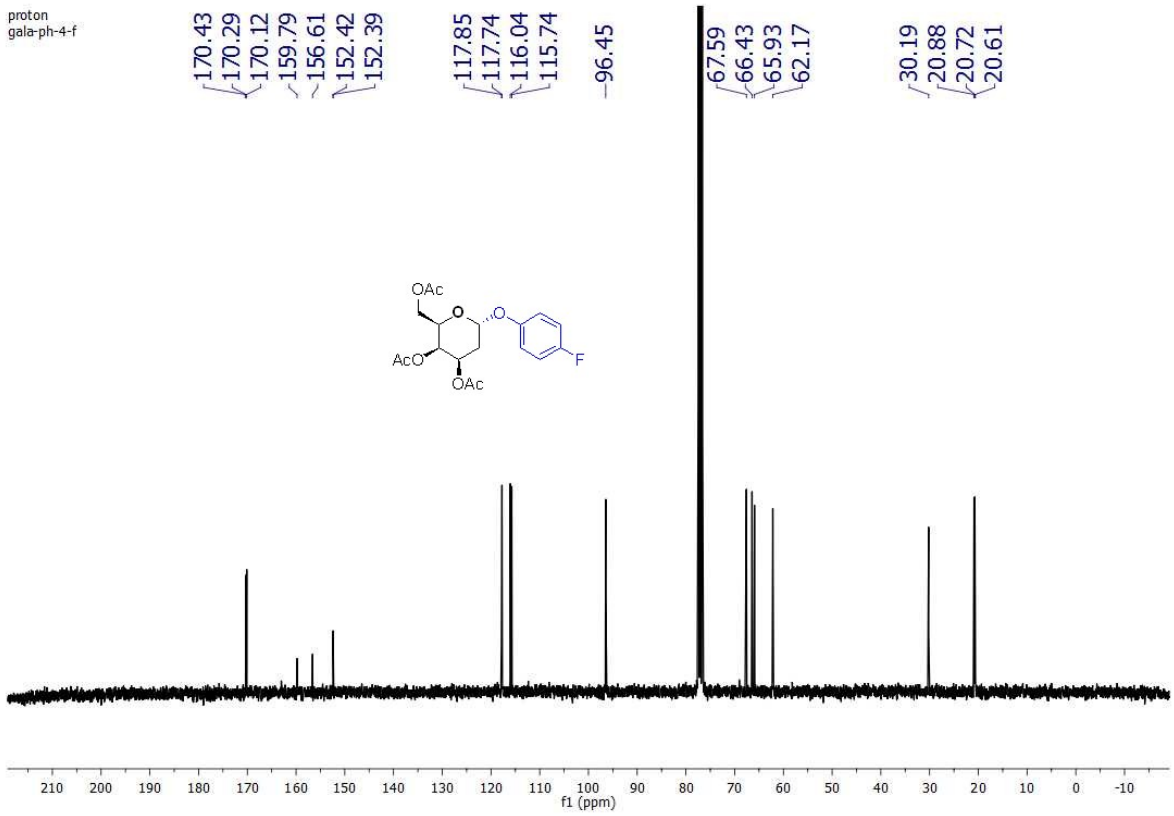
^{13}C NMR of compound **4m**



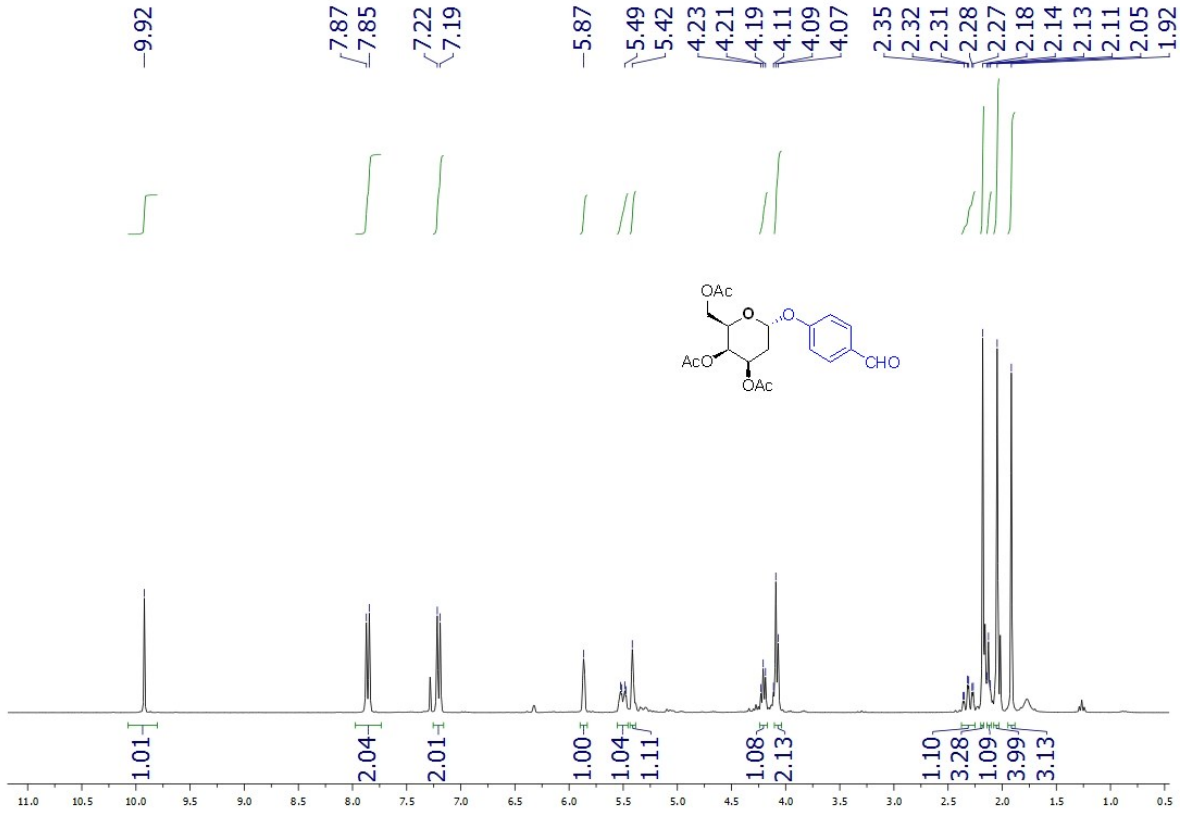
^{1}H NMR of compound **4n**



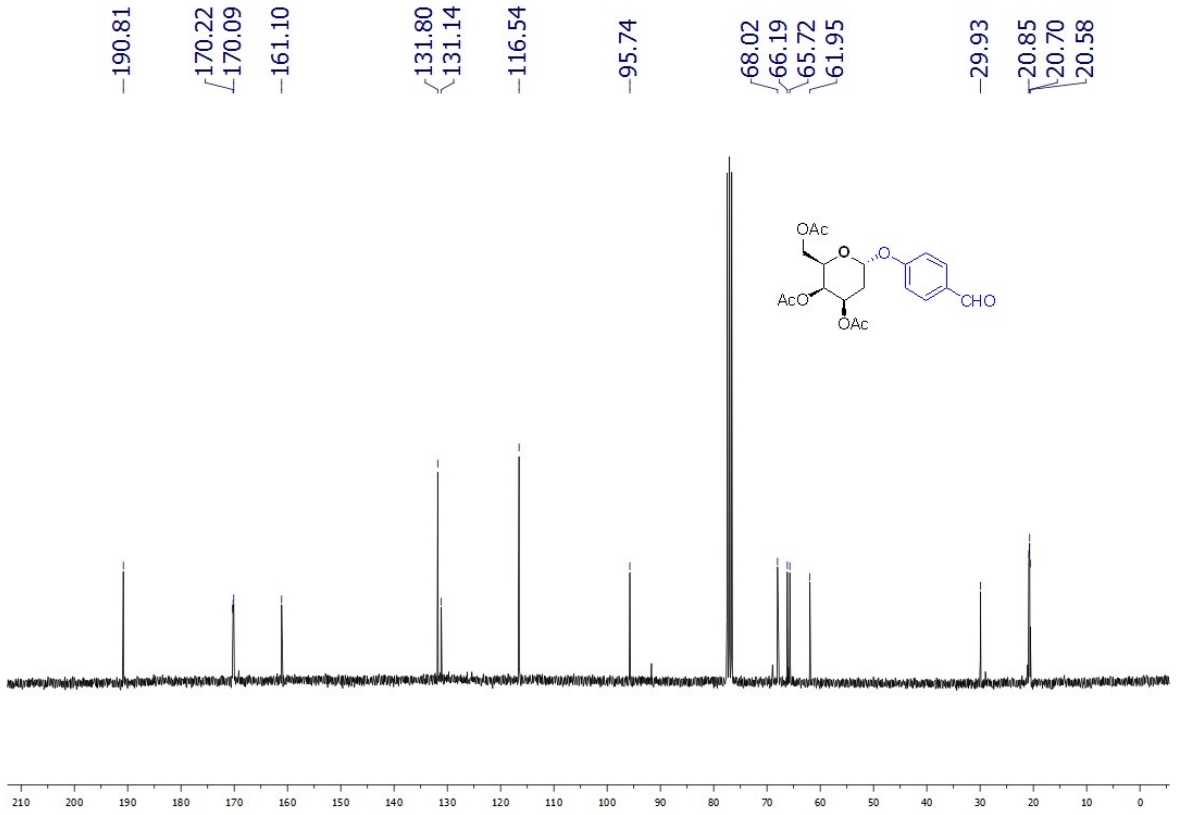
^{13}C NMR of compound **4n**



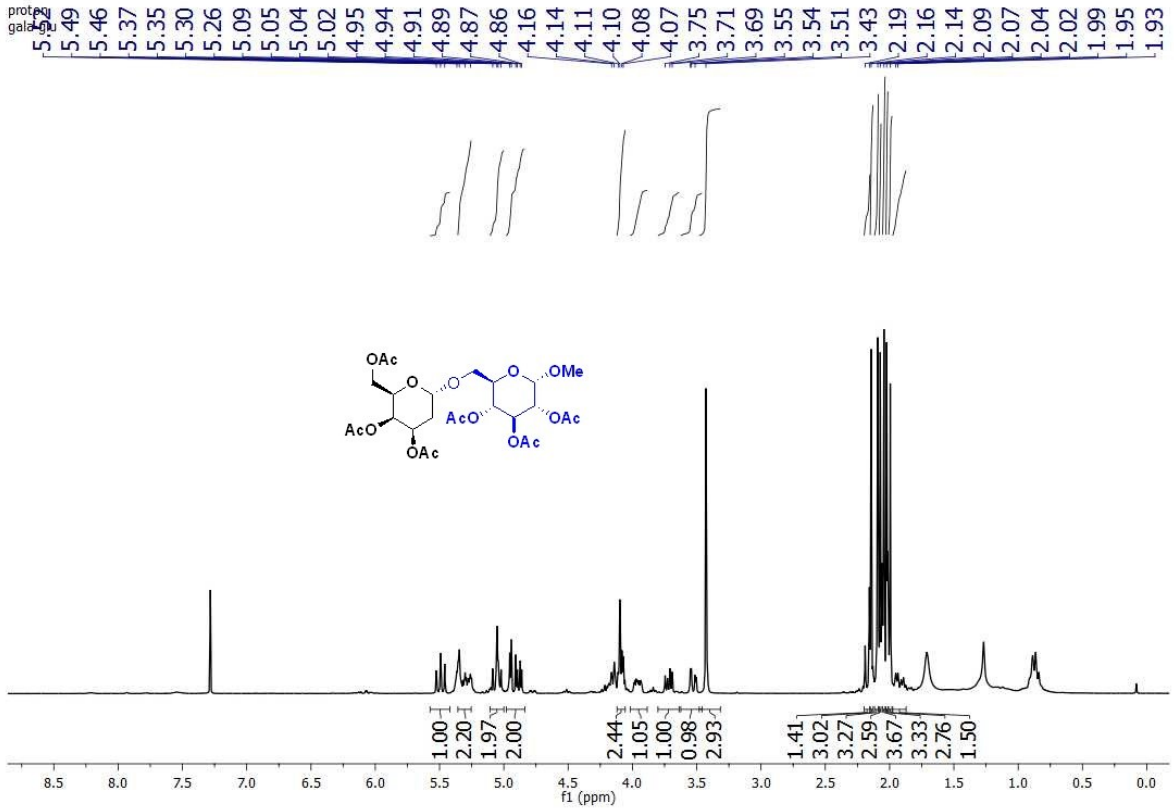
^{1}H NMR of compound **4o**



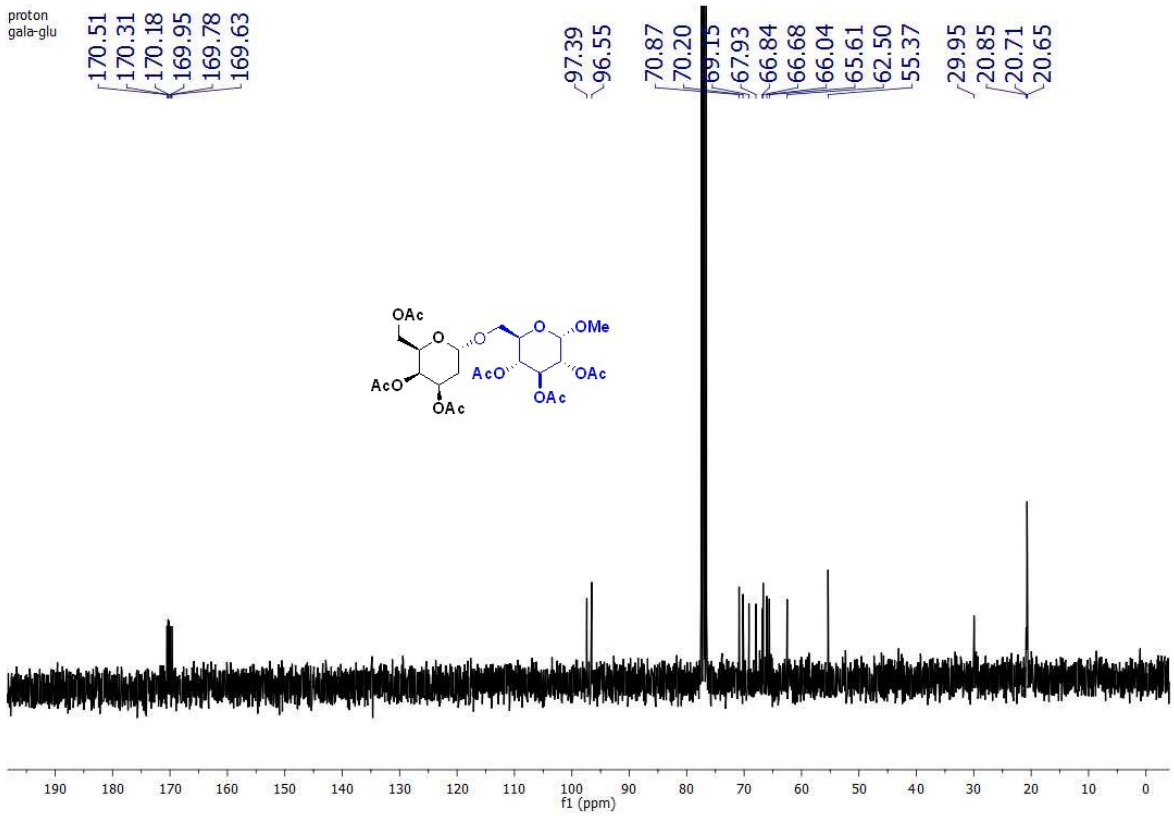
^{13}C NMR of compound **4o**



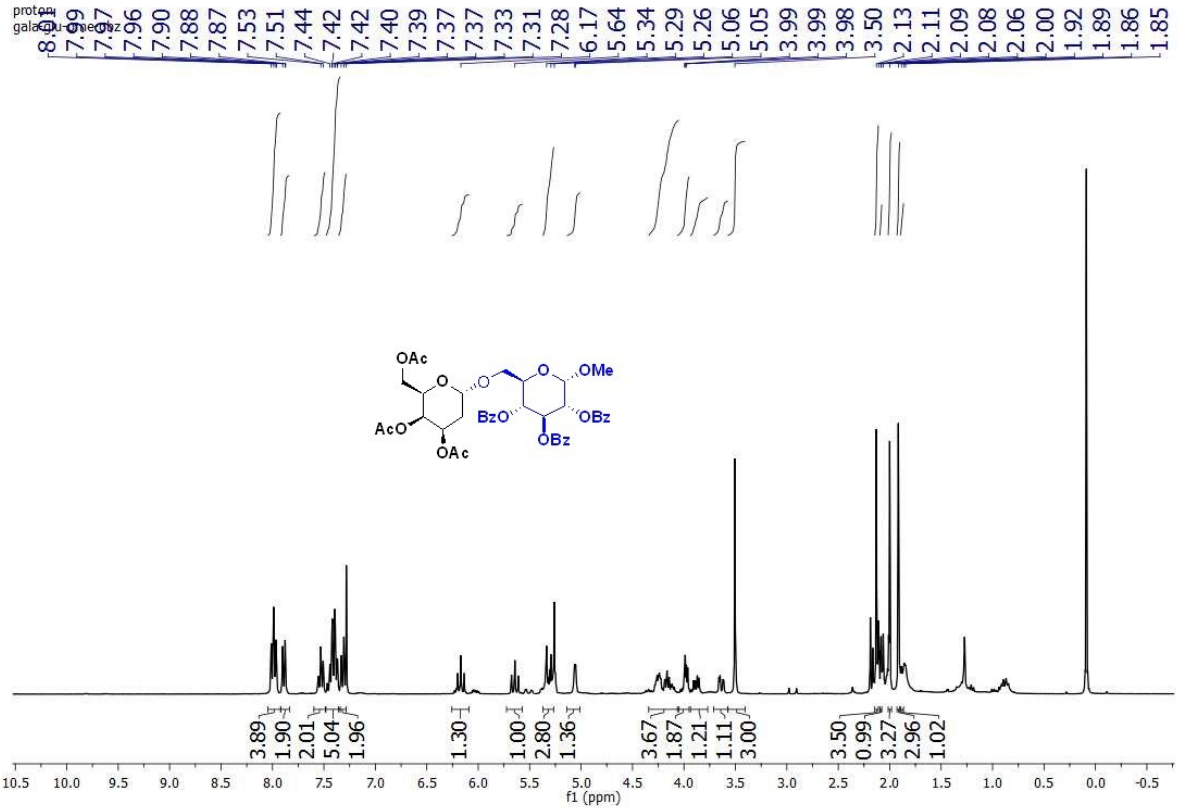
^{1}H NMR of compound **6a**



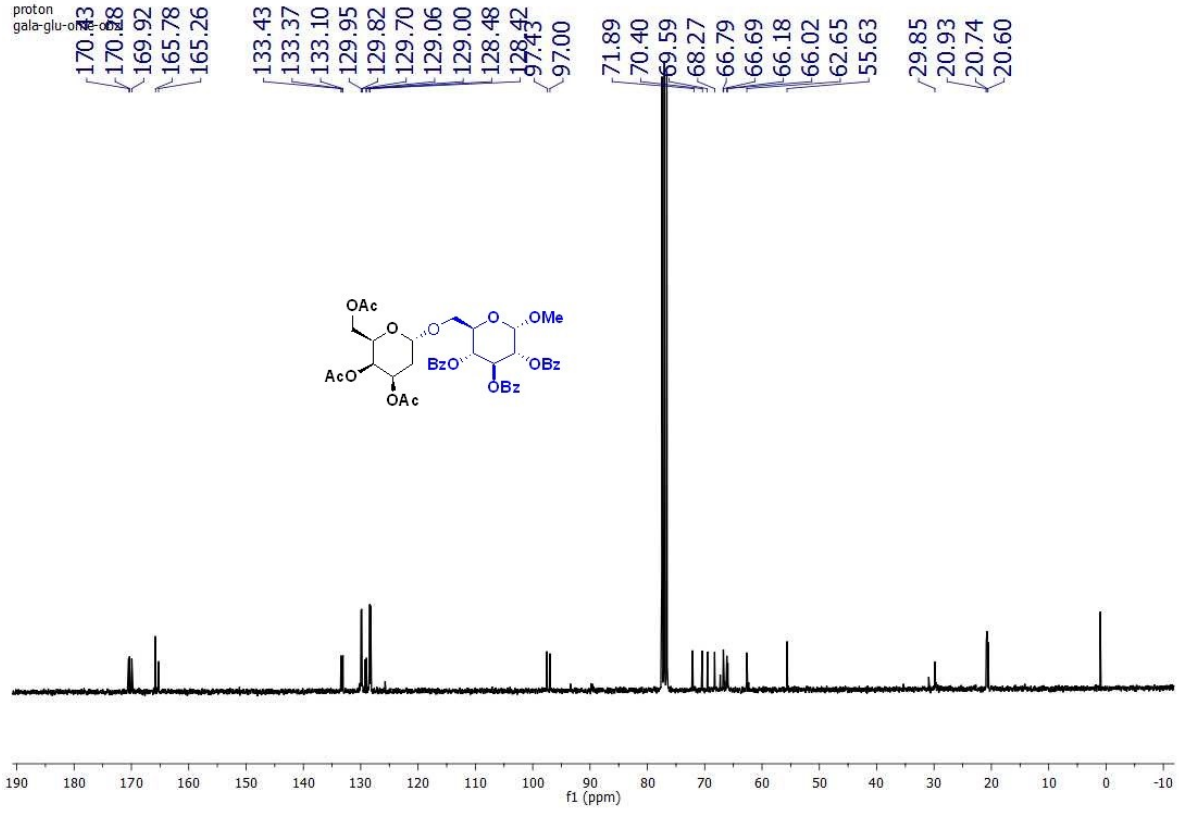
^{13}C NMR of compound **6a**



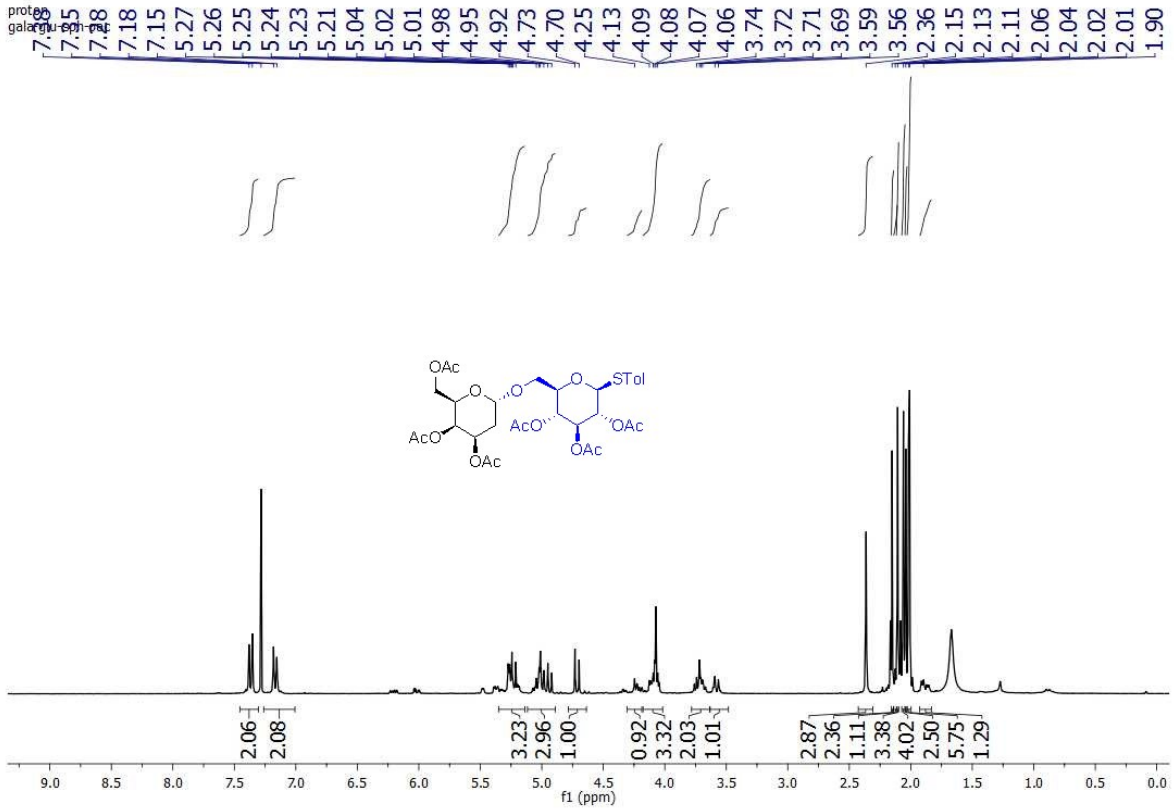
^{1}H NMR of compound **7a**



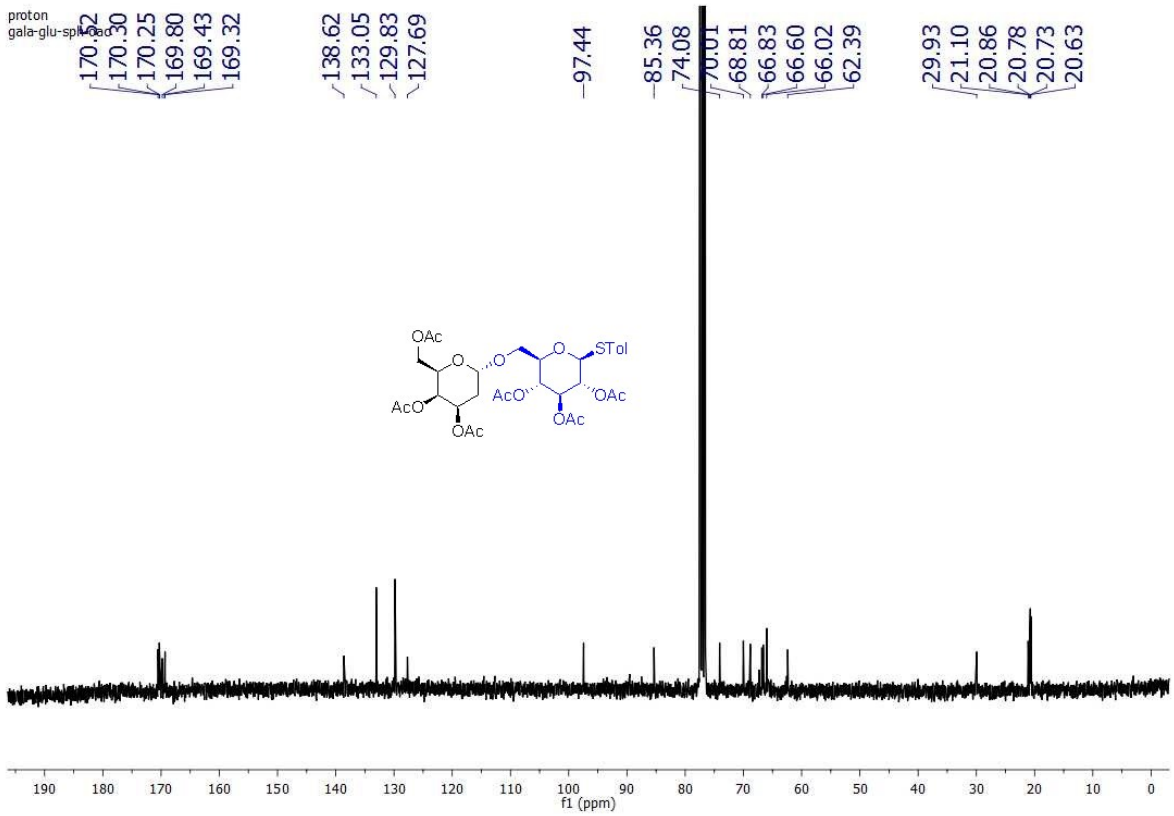
^{13}C NMR of compound **7a**



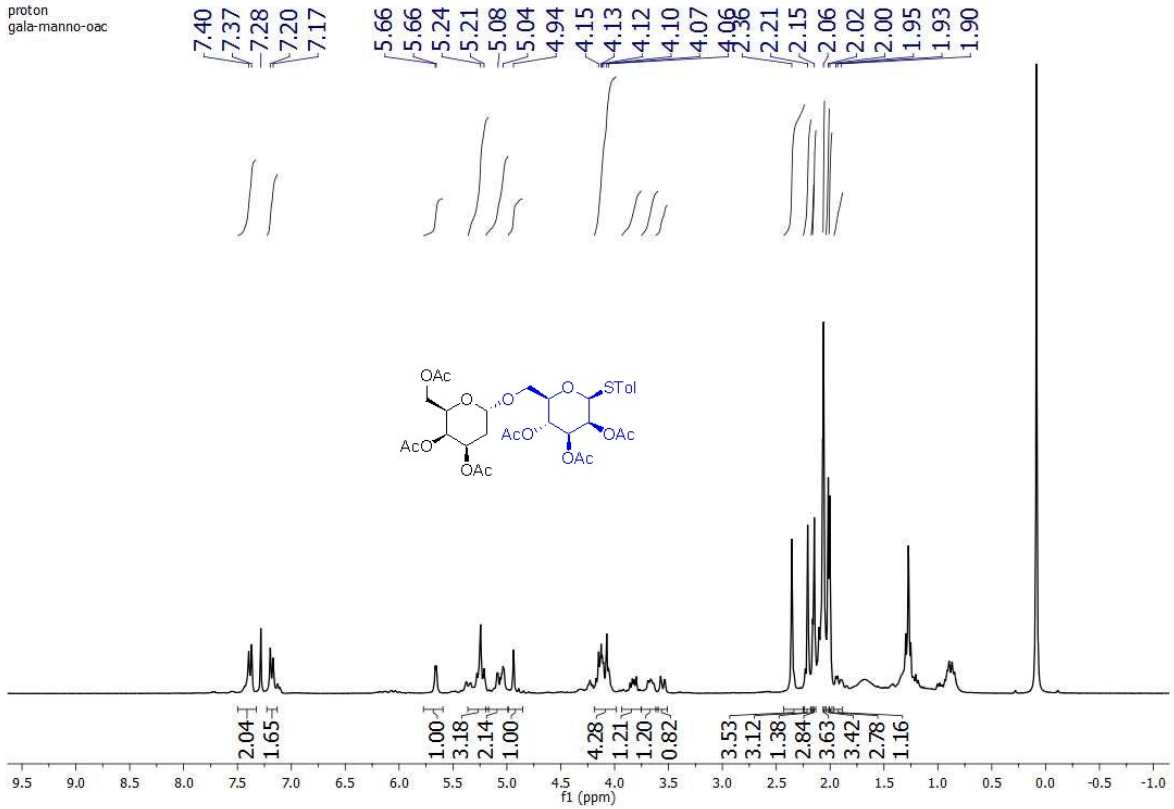
^{1}H NMR of compound **8a**



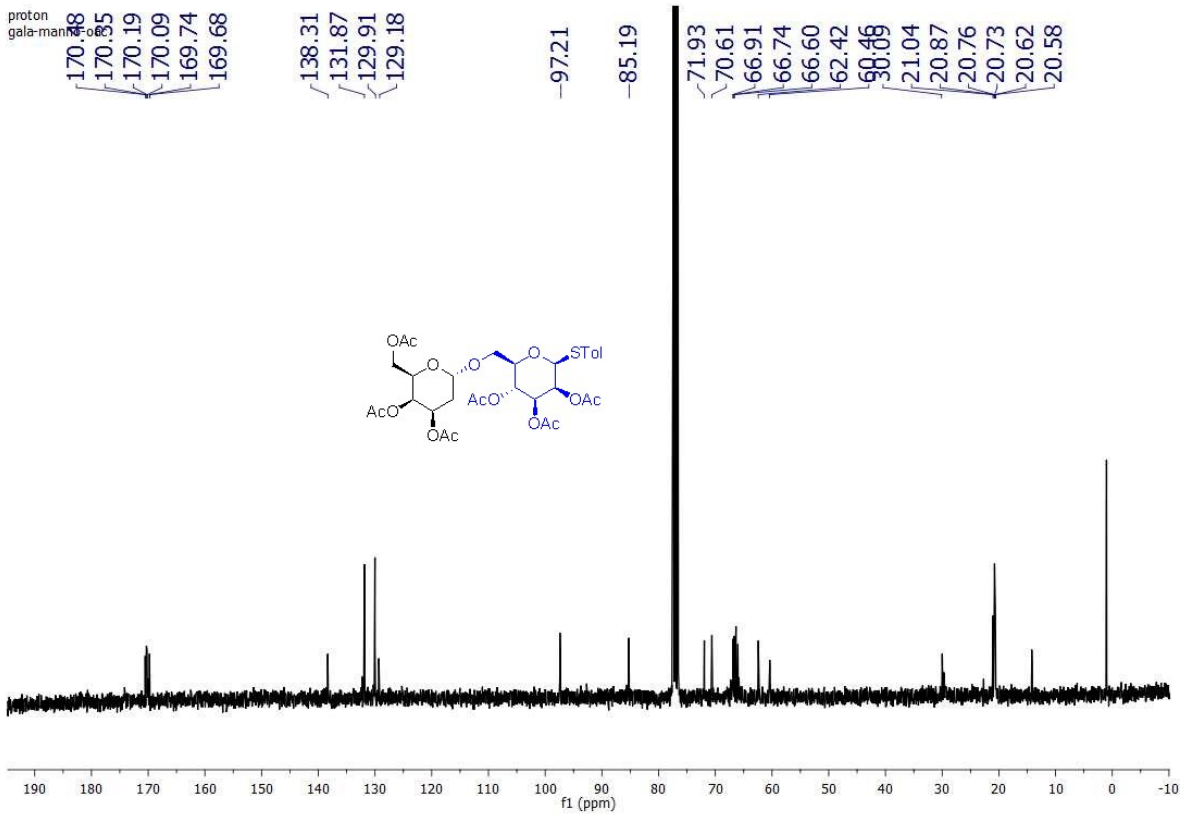
^{13}C NMR of compound **8a**



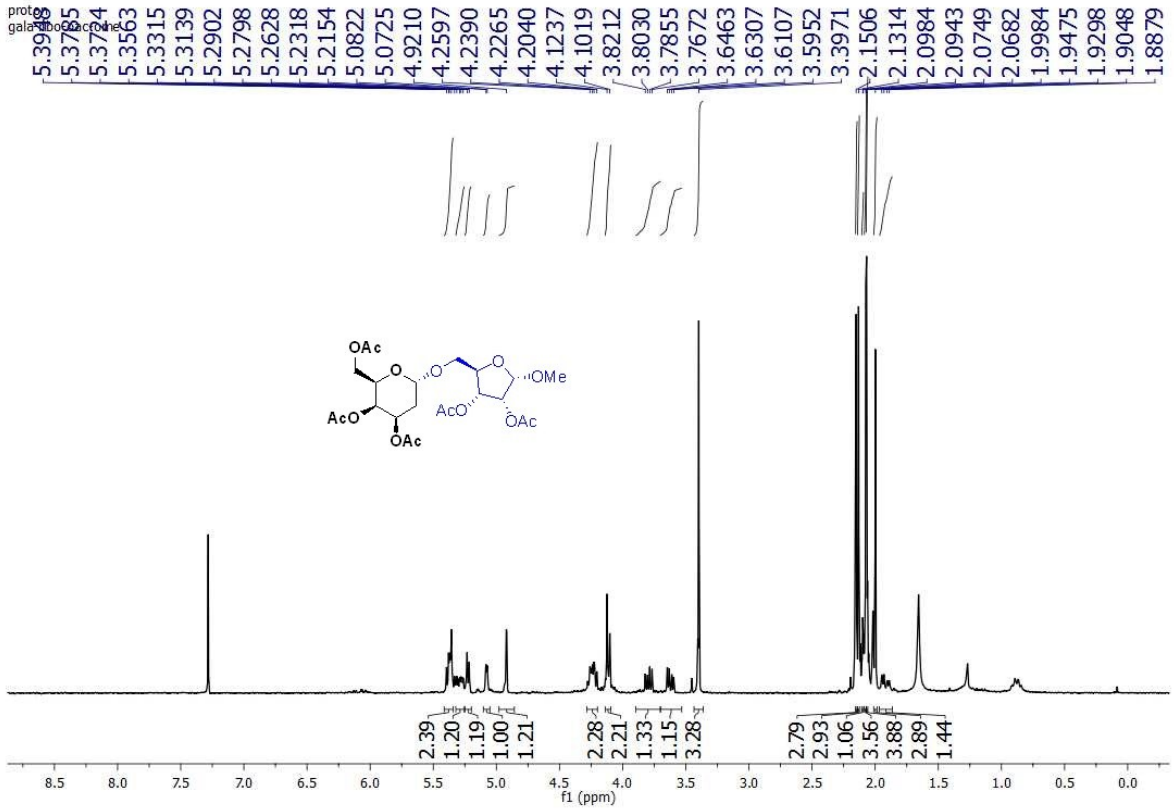
^{1}H NMR of compound **9a**



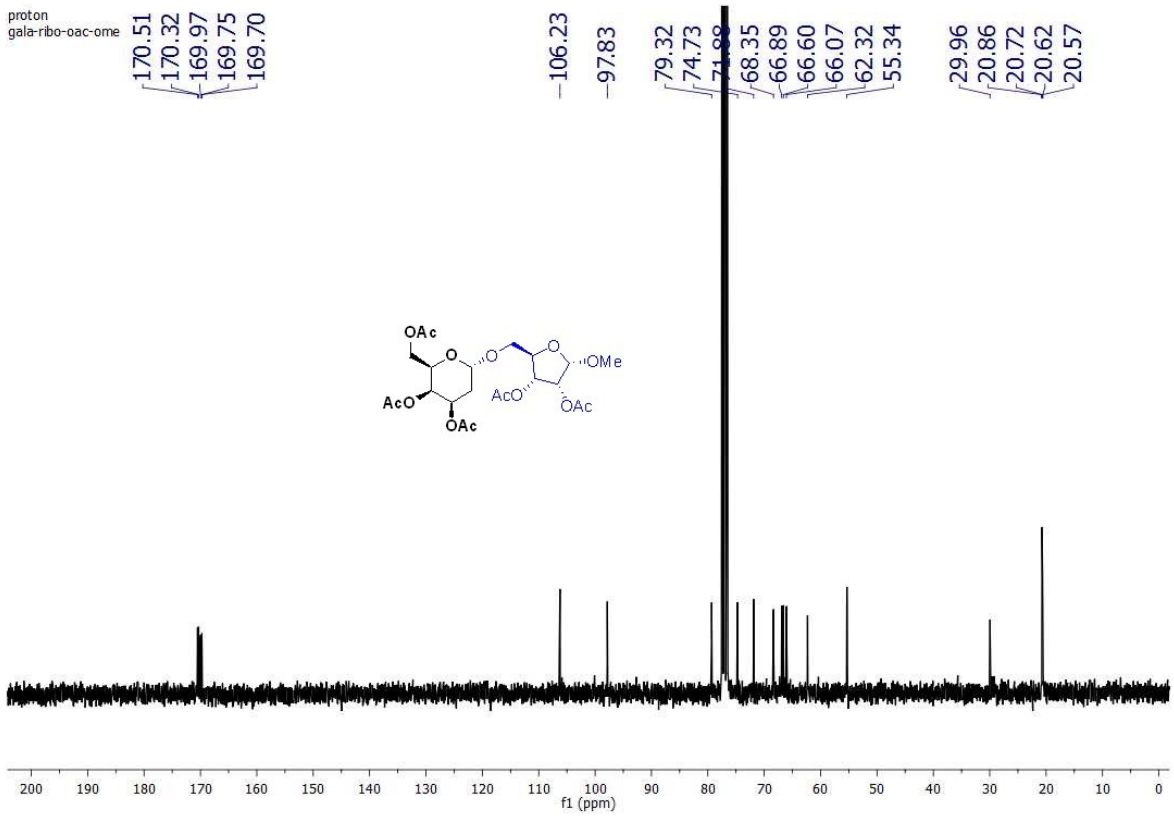
^{13}C NMR of compound **9a**



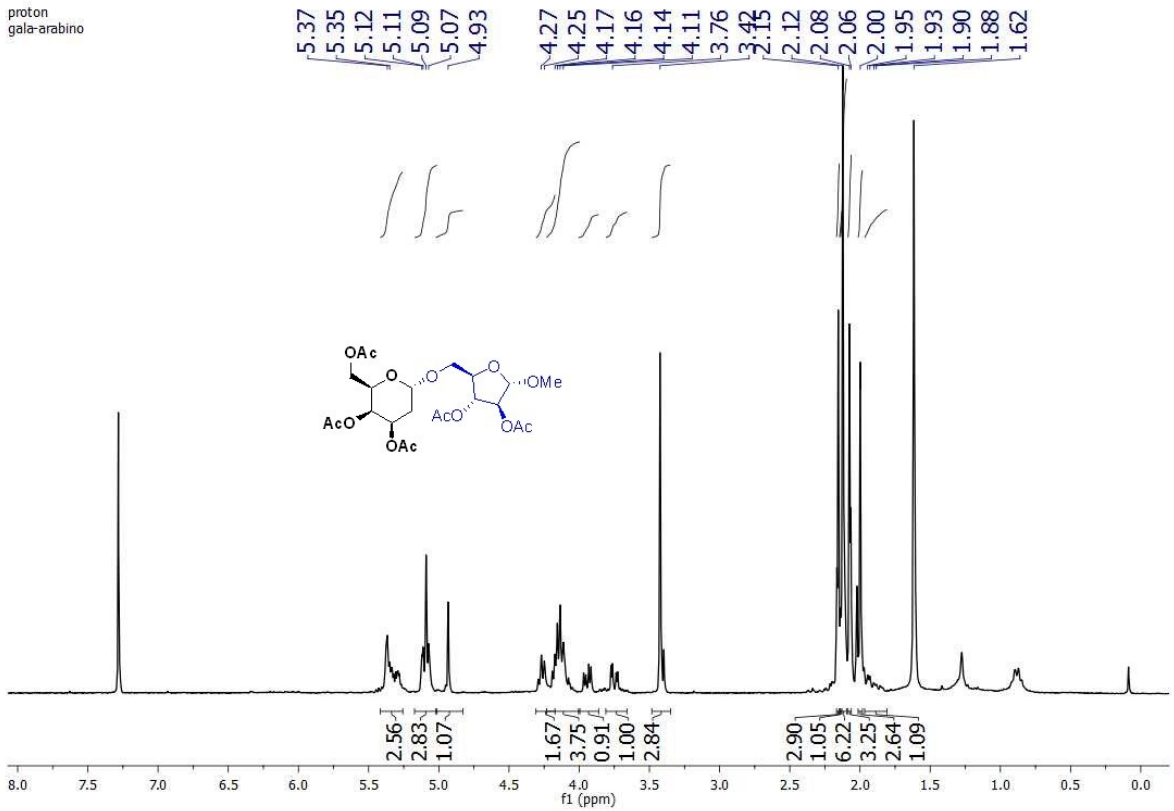
^{1}H NMR of compound **10a**



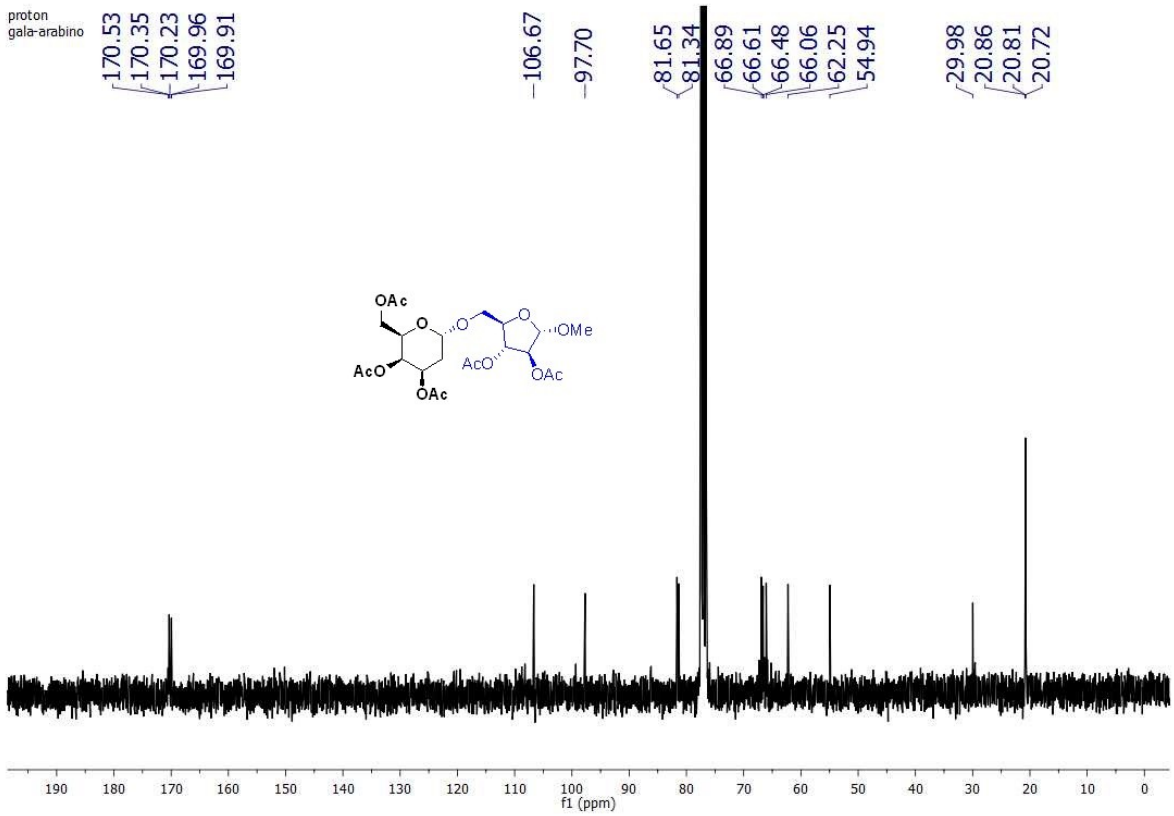
^{13}C NMR of compound **10a**



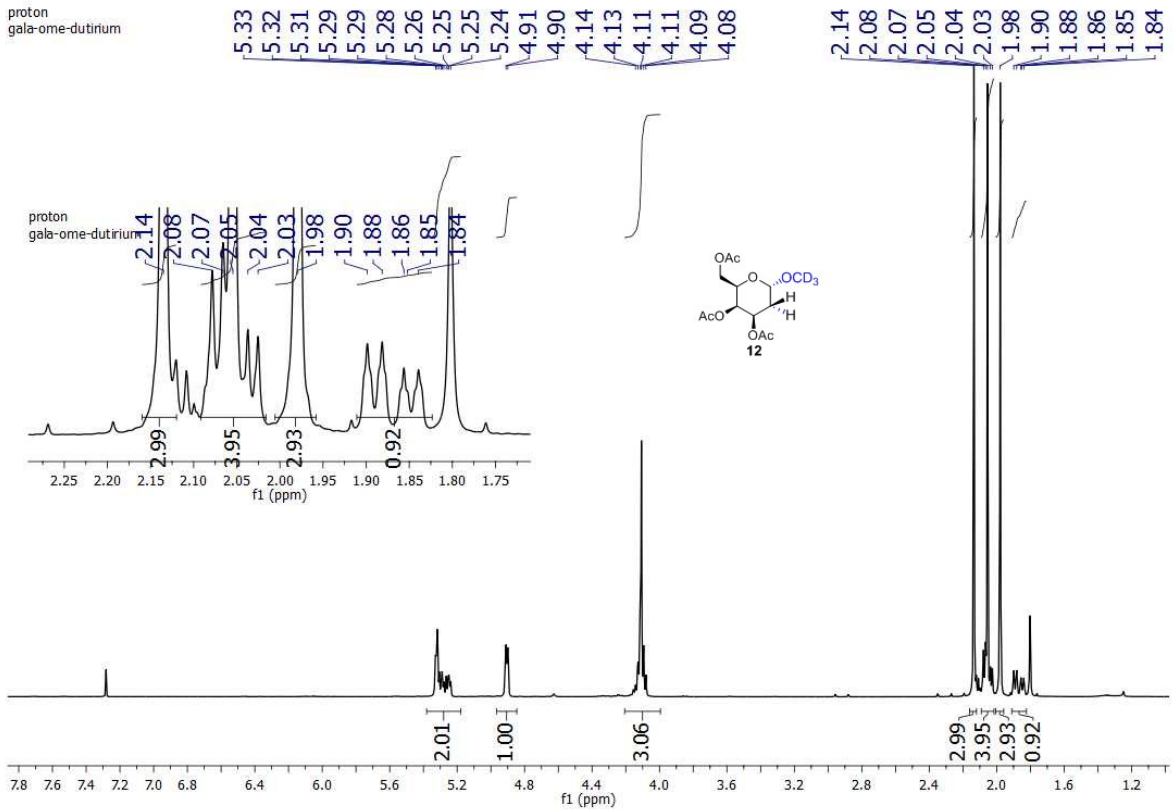
^{1}H NMR of compound **11a**



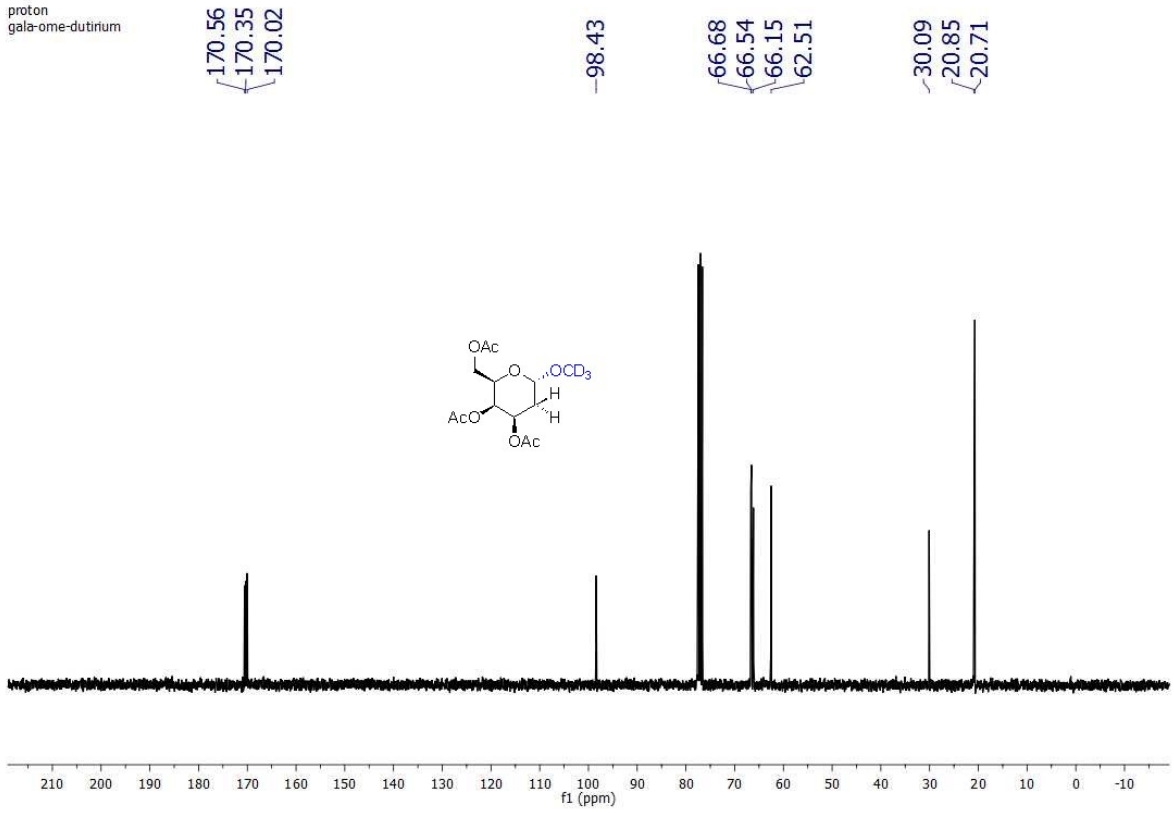
^{13}C NMR of compound **11a**



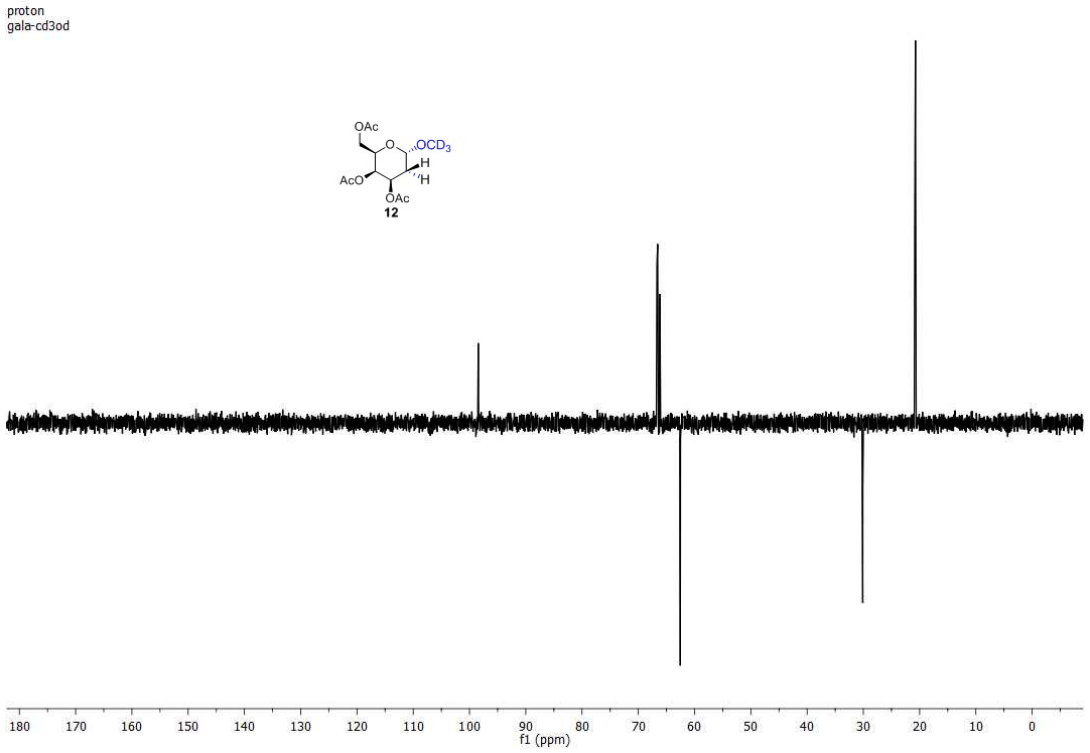
^{1}H NMR of compound **12**



^{13}C NMR of compound **12**



DEPT of compound **12**



^{1}H NMR of compound 2-deoxy methyl galactoside