Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Switchable reactivity of 2-benzoyl glycals towards stereoselective access of 1-3 and 1-1 S/O linked disaccharides

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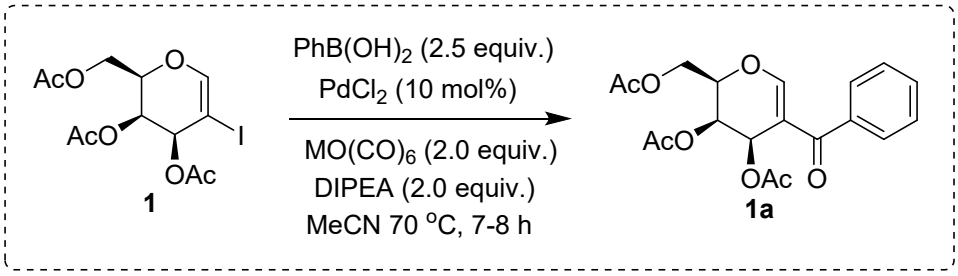
1. General Information

All compounds were characterized by spectroscopic data. The ^{1}H and ^{13}C NMR spectra were obtained using 400 and 500 MHz spectrometers with TMS as internal standard. Chemical shift (∂) is expressed in ppm, J values are given in Hz and deuterated $CDCl_3$ was used as solvent. All the reactions were monitored by thin layer chromatography (TLC). Column chromatography was performed on silica gel (60-120 mesh). All the chemicals used in experiments were purchased from commercial source mostly from sigma Aldrich and were used without further purification.

2. Experimental

2.1. General procedures

2.1.1 General procedure for the synthesis of 2-benzoyl glycals 1 (a-e)[1,2]



To a vial round bottom flask with a magnetic stirrer bar and sealed with a rubber septum connected to a deflated balloon with a needle were added the tri-O-acetylated iodoglucal **1** (1 g, 2.5 mmol, 1.0 equiv.), acetonitrile (12 mL), $PdCl_2$ (44.5 mg, 0.25 mmol, 0.1 equiv.), $MO(CO)_6$ (1.3 g, 5.02 mmol, 2.0 equiv.), phenyl boronic acid (765.6 mg, 6.3 mmol, 2.5 equiv.) and DIPEA (508.3 mg, 5.02 mmol, 2.0 equiv.). The reaction mixture was vigorously stirred at 70 ºC for 7 to 8 h. The resulting mixture was washed with water and extracted with ethyl acetate. The organic layers were then combined and evaporated. The crude products were purified by over silica gel (60-120 mesh) using petroleum ether ethyl acetate as eluent to acquire a pure product **1a** as colourless viscous liquid (90 % yield, 850 mg).[1,2]

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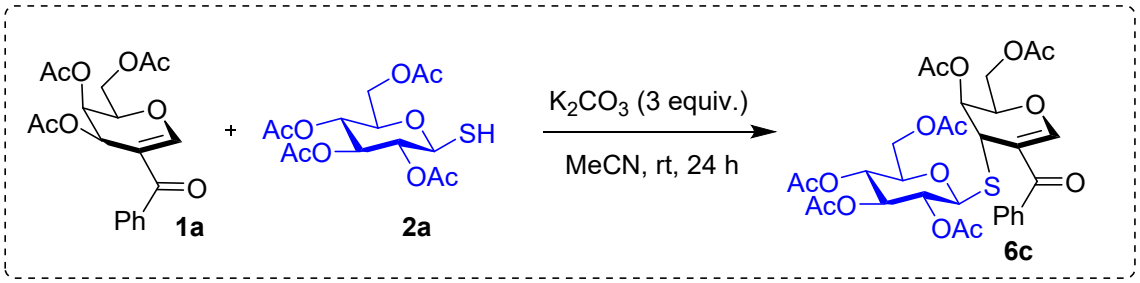
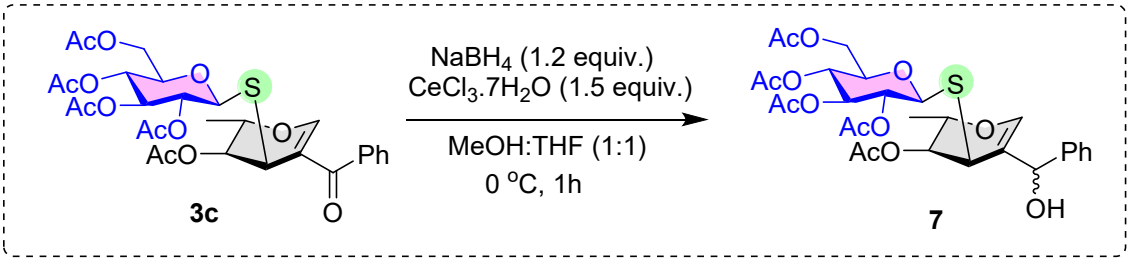
2.1.2 General procedure for the synthesis of disaccharides 3a-f, 5 a-f and 6 a-c



In an oven dried single neck round bottom flask charged with magnetic bead, 2-ketoglycal **1a** (20 mg, 0.053 mmol, 1.0 equiv.), **2a** (19.4 mg, 0.053 mmol, 1.0 equiv.), and K_2CO_3 (22.0 mg, 0.16 mmol, 3.0 equiv.), in 1 mL of acetonitrile were added and the reaction mixture was sealed with rubber septum. The resulting mixture was stirred for 24 hr at room temperature until the reaction was completed (monitored by TLC). After completion of reaction the solution was transferred into the separatory funnel and washed with ethyl acetate. The residue left was purified by column chromatography over silica gel (60-120 mesh) using petroleum ether and hexane to acquire a pure product **6c** as colourless viscous liquid (82 % yield, 30 mg).

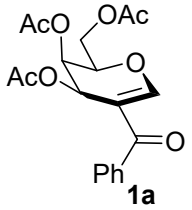
2.1.3 Procedure for the synthesis of compound 7



Compound **7** was synthesized using **3c** (20 mg, 0.032 mmol, 1.0 equiv.) in MeOH:THF (1:1), sodium borohydride (1.5 mg , 0.038 mmol, 1.2 equiv.) and $CeCl_3.7H_2O$ (18 mg, 0.048 mmol, 1.5 equiv.) were added slowly at 0 °C temperature. Stirred the reaction mixture until complete consumption of starting material was observed by TLC analysis. Then the reaction mixture was diluted with 5 mL of ethyl acetate (20 mL) and washed the reaction mixture with saturated sodium bicarbonate solution (10 mL). The organic layer was dried over sodium sulphate and evaporated in vacuo. The residue left was purified by column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (90:10) as eluent to obtain the compound **7** as gummy liquid (14.5 mg, 72%).

3. Characterization Data

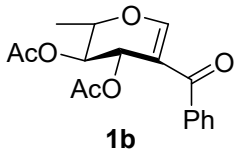
2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-3,4-diyl diacetate (1a)



1a

The compound **1a** was synthesized according to the general procedure (2.1.1) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (60:40) as eluent to obtained colorless viscous (90% yield, 850 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 7.35 (s, 1H), 6.25 (d, J = 4.5 Hz, 1H), 5.54 (dd, J = 4.4, 2.9 Hz, 1H), 4.58 – 4.48 (m, 2H), 4.34 – 4.24 (m, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 2.02 (s, 3H). ^{13}C NMR {^{1}H} {1H} (101 MHz, $CDCl_3$) δ 192.3, 170.6, 170.0, 169.9, 158.7, 138.1, 132.0, 128.9, 128.5, 114.3, 74.3, 64.4, 61.6, 61.3, 20.8, 20.6, 20.5. HRMS (ESI), m/z calcd. for $C_{19}H_{20}O_8$ $[M+Na]^+$ 399.1056, found 399.1058.

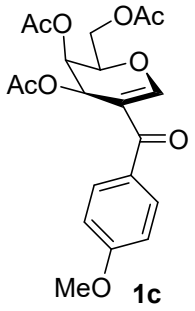
5-benzoyl-2-methyl-3,4-dihydro-2H-pyran-3,4-diyl diacetate (1b)



1b

The compound **1b** was synthesized according to the general procedure (2.1.1) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (60:40) as eluent to obtained colorless viscous (72.3% yield, 800 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.48 – 7.41 (m, 1H), 7.37 (dd, J = 12.5, 5.0 Hz, 3H), 5.93 – 5.85 (m, 1H), 5.06 (t, J = 3.8 Hz, 1H), 4.46 – 4.37 (m, 1H), 2.01 (dd, J = 1.6, 0.8 Hz, 3H), 1.97 – 1.94 (m, 3H), 1.39 (d, J = 6.9 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.5, 169.9, 169.7, 160.2, 138.4, 131.7, 128.8, 128.4, 112.9, 73.9, 70.0, 63.3, 20.9, 20.8, 16.1. HRMS (ESI), m/z calcd. for $C_{19}H_{20}O_8$ $[M+Na]^+$ 341.1001, found 341.0998.

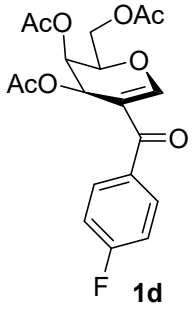
2-(acetoxymethyl)-5-(4-methoxybenzoyl)-3,4-dihydro-2H-pyran-3,4-diyl diacetate (1c)



1c

The compound **1c** was synthesized according to the general procedure (2.1.1) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (60:40) as eluent to obtained colorless viscous (95% yield, 900mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.6, 1.6 Hz, 2H), 7.21 (s, 1H), 6.85 (dd, J = 8.6, 1.5 Hz, 2H), 6.15 (s, 1H), 5.44 (s, 1H), 4.50 – 4.33 (m, 2H), 4.19 (d, J = 8.0 Hz, 1H), 3.77 (d, J = 1.5 Hz, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.89 (s, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 190.8, 170.5, 169.8, 169.6, 162.8, 157.3, 131.1, 130.5, 114.0, 113.6, 74.1, 64.5, 61.9, 61.3, 55.4, 20.7, 20.5, 20.4. HRMS (ESI), m/z calcd. for $C_{20}H_{22}O_9$ $[M+Na]^+$ 429.1162, found 429.1165.

2-(acetoxymethyl)-5-(4-fluorobenzoyl)-3,4-dihydro-2H-pyran-3,4-diyl diacetate (1d)

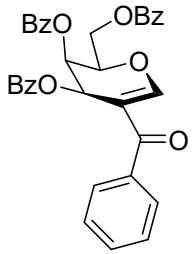


1d

The compound **1d** was synthesized according to the general procedure (2.1.1) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (60:40) as eluent to obtained colorless viscous (85% yield, 800mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.8, 5.4 Hz, 2H), 7.23 (s, 1H), 7.06 (t, J = 8.6 Hz, 2H), 6.15 (d, J = 4.5 Hz, 1H), 5.45 (dd, J = 4.1, 2.6 Hz, 1H), 4.51 – 4.41 (m, 2H), 4.19 (d, J = 8.3 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 1.92 (s, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 190.8, 170.6, 169.9, 169.6, 158.4, 134.3, 134.2, 131.4,

131.3, 115.7, 115.5, 114.2, 74.3, 64.4, 61.6, 61.2, 20.7, 20.6, 20.5. HRMS (ESI), m/z calcd. for $C_{19}H_{19}O_8$ [M+Na]+ 417.0962, found 417.0960.

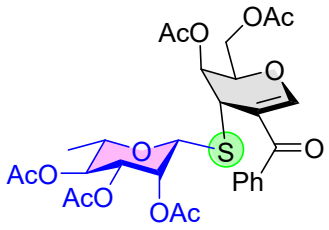
5-benzoyl-2-((benzoyloxy)methyl)-3,4-dihydro-2H-pyran-3,4-diyl dibenzoate (1e)



1e

The compound **1e** was synthesized according to the general procedure (2.1.1) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (60:40) as eluent to obtained colorless viscous (85% yield, 820mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.95 (m, 2H), 7.89 – 7.82 (m, 4H), 7.66 – 7.62 (m, 2H), 7.51 – 7.41 (m, 4H), 7.40 – 7.23 (m, 9H), 6.67 – 6.61 (m, 1H), 5.87 (t, J = 3.9 Hz, 1H), 5.03 (dd, J = 12.1, 8.6 Hz, 1H), 4.89 – 4.82 (m, 1H), 4.52 (dd, J = 12.2, 3.4 Hz, 1H). ^{13}C NMR {^{1}H} (101 MHz, CDCl3) δ 192.3, 166.3, 165.5, 165.2, 159.0, 138.2, 133.6, 133.4, 133.2, 132.0, 129.9, 129.79, 129.77, 129.4, 128.9, 128.6, 128.5, 128.5, 128.4, 114.4, 74.3, 65.8, 62.1, 62.0. HRMS (ESI), m/z calcd. for $C_{19}H_{19}O_8$ [M+Na]+ 585.1525, found 585.1525.

3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)thio)-6-methyltetrahydro-2H-pyran-3,4,5-triyl triacetate 3a

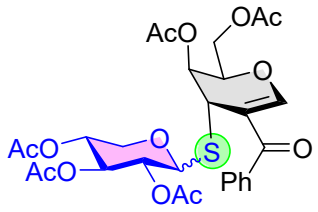


3a

The compound **3a** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (66% yield, 24 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.45 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.27 (s, 1H), 5.50 (s, 1H), 5.27 – 5.26 (m, 1H), 5.16 (s, 1H), 5.10 – 5.06 (m, 1H), 5.04 (d, *J* = 3.8 Hz, 1H), 4.67 – 4.59 (m, 1H), 4.33 – 4.26 (m, 2H), 4.22 (dd, *J* = 11.8, 5.0 Hz, 2H), 2.12 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.93 (s,

3H), 1.90 (s, 3H), 1.32 (d, J = 6.2 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.7, 170.5, 170.3, 170.1, 170.0, 169.97, 159.8, 138.5, 131.8, 129.0, 128.4, 113.2, 92.1, 80.2, 71.8, 70.9, 70.5, 69.7, 67.8, 67.4, 62.5, 21.0, 20.9, 20.79, 20.76, 20.7, 17.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{35}O_{13}S$ 623.1798; Found 623.1794.

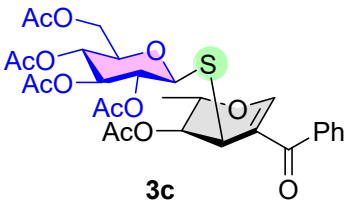
3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3b)



3b, 1.86 :1 (ax-eq:eq-eq)

The compound **3b** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (72% yield, 26 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.49 – 7.43 (m, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.27 (s, 1H), 5.24 (s, 1H), 5.19 (d, J = 1.4 Hz, 1H), 5.12 (td, J = 7.7, 2.8 Hz, 3H), 5.04 (t, J = 7.9 Hz, 2H), 4.96 (dd, J = 11.6, 7.4 Hz, 2H), 4.87 (td, J = 8.3, 4.8 Hz, 3H), 4.64 (t, J = 8.5 Hz, 3H), 4.36 (s, $1H_{major}$), 4.26 (dt, J = 12.1, 6.2 Hz, 2H), 4.21 – 4.11 (m, 3H), 3.42 (s, $0.53H_{minor}$), 3.41 – 3.34 (m, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 2.02 (s, 6H), 2.00 (s, 6H), 1.99 (s, 6H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.2, 170.4, 170.0, 169.9, 169.84, 169.76, 169.6, 169.2, 159.3, 138.2, 131.8, 129.0, 128.3, 113.3, $88.1_{(major)}$, $82.5_{(minor)}$, 71.6, 71.5, 71.3, 69.3, 69.1, 68.3, 68.1, 67.4, 65.3, 64.7, 62.4, 35.8, 20.84, 20.78, 20.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{28}H_{33}O_{13}S$ 609.1642; found 609.1638.

3-acetoxy-5-benzoyl-2-methyl-3,4-dihydro-2H-pyran-4-yl)thio)6(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3c)

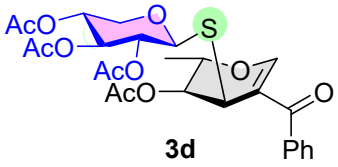


3c

The compound **3c** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (69% yield, 25 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49

(m, 2H), 7.48 – 7.43 (m, 1H), 7.40 – 7.35 (m, 2H), 7.09 (s, 1H), 5.16 (t, J = 9.3 Hz, 1H), 5.00 (dt, J = 9.6, 4.6 Hz, 2H), 4.87 (dd, J = 10.2, 9.2 Hz, 1H), 4.71 (dd, J = 10.4, 4.9 Hz, 1H), 4.47 (d, J = 4.9 Hz, 1H), 4.29 (dd, J = 12.5, 4.3 Hz, 1H), 4.11 – 4.04 (m, 1H), 4.01 (dd, J = 12.5, 1.9 Hz, 1H), 3.70 (ddd, J = 10.1, 4.3, 2.0 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.89 (s, 3H), 1.75 (s, 3H), 1.32 (d, J = 6.2 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.5, 170.8, 170.0, 169.8, 169.7, 169.6, 158.1, 138.8, 131.7, 128.5, 128.4, 117.8, 87.0, 75.8, 73.8, 72.0, 70.7, 70.4, 67.9, 61.8, 40.5, 21.0, 20.7, 20.6, 20.6, 20.5, 17.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{35}O_{13}S$ 623.1798; found 623.1799.

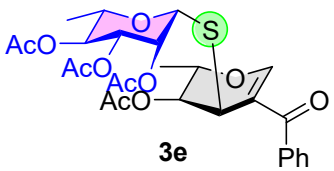
3-acetoxy-5-benzoyl-2-methyl-3,4-dihydro-2H-pyran-4-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3d)



3d

The compound **3d** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (64% yield, 23mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 7.9, 0.9 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.35 (t, J = 7.4 Hz, 2H), 7.06 (s, 1H), 5.14 (t, J = 8.8 Hz, 1H), 4.89 – 4.78 (m, 2H), 4.73 (d, J = 9.5 Hz, 1H), 4.64 (dd, J = 10.3, 4.6 Hz, 1H), 4.49 (d, J = 4.6 Hz, 1H), 4.14 (dq, J = 12.4, 6.1 Hz, 1H), 4.04 (dd, J = 11.5, 5.3 Hz, 1H), 3.34 – 3.25 (m, 1H), 2.08 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.75 (s, 3H), 1.33 (d, J = 6.2 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 192.9, 170.1, 170.0, 169.9, 169.8, 158.0, 138.8, 134.6, 131.6, 128.9, 128.6, 128.4, 116.6, 88.2, 72.5, 71.8, 71.5, 70.2, 68.8, 65.7, 42.6, 21.1, 20.9, 20.73, 20.66, 20.5.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{26}H_{31}O_{11}S$ 551.1587; found 551.1580.

3-acetoxy-5-benzoyl-2-methyl-3,4-dihydro-2H-pyran-4-yl)thio)-6-methyltetrahydro-2H-pyran-3,4,5-triyl triacetate (3e)

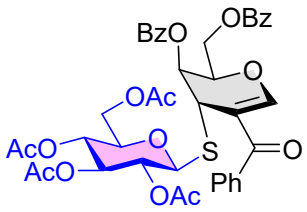


3e

The compound **3e** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as

eluent to obtained colorless viscous (51% yield, 18 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 5.50 (s, 1H), 5.35 (dd, *J* = 3.1, 1.6 Hz, 1H), 5.24 (s, 1H), 5.11 (dd, *J* = 10.0, 3.3 Hz, 1H), 5.00 (d, *J* = 9.7 Hz, 1H), 4.87 (dd, *J* = 9.7, 4.5 Hz, 1H), 4.50 (d, *J* = 4.5 Hz, 1H), 4.24 (dd, *J* = 9.8, 6.4 Hz, 1H), 4.10 (dd, *J* = 9.2, 6.1 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H), 1.90 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.11 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.2, 170.0, 169.8, 158.8, 138.6, 131.4, 128.7, 128.3, 116.8, 84.1, 77.2, 71.9, 71.3, 71.2, 69.4, 67.7, 40.0, 21.1, 20.8, 20.7, 17.4, 17.2.
HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{27}H_{33}O_{11}S$ 565.1744; found 565.1740.

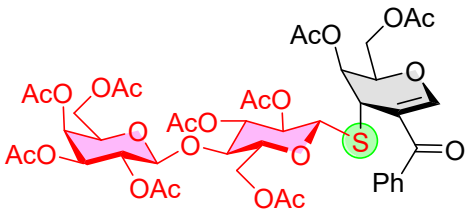
2-(acetoxymethyl)-6-((5-benzoyl-3-(benzoyloxy)-2-((benzoyloxy)methyl)-3,4-dihydro-2H-pyran-4-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3f)



3f

The compound **3f** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (55:45) as eluent to obtained colorless viscous (65% yield, 25 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 19.2, 7.6 Hz, 4H), 7.57 – 7.49 (m, 4H), 7.43 (t, J = 7.4 Hz, 1H), 7.40 – 7.31 (m, 7H), 5.59 (s, 1H), 5.25 (t, J = 9.2 Hz, 1H), 5.13 (td, J = 9.5, 4.8 Hz, 2H), 4.93 (dd, J = 12.5, 8.4 Hz, 2H), 4.60 (qd, J = 12.0, 6.1 Hz, 3H), 4.24 (dd, J = 12.5, 4.4 Hz, 1H), 3.99 (dd, J = 12.4, 1.9 Hz, 1H), 3.81 – 3.72 (m, 1H), 1.97 (s, 3H), 1.95 (d, J = 4.3 Hz, 6H), 1.91 (s, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 192.8, 170.8, 170.3, 169.5, 169.4, 166.1, 165.4, 159.4, 138.2, 133.8, 133.5, 131.8, 129.9, 129.75, 129.3, 129.0, 128.9, 128.6, 128.5, 128.3, 113.1, 83.1, 76.3, 74.2, 71.8, 69.6, 68.4, 68.1, 63.3, 61.6, 36.2, 20.7, 20.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{41}H_{40}O_{15}S$ 805.2166; found 805.2157.

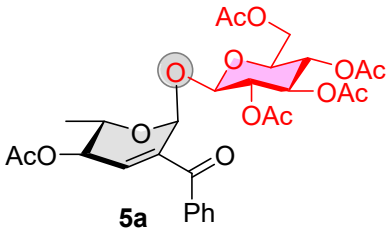
2-(acetoxymethyl)-6-((4,5-diacetoxy-6-((3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)thio)-2-(acetoxymethyl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3g)



3g

The compound **3g** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (50:50) as eluent to obtained colorless viscous (76% yield, 23 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.54 – 7.47 (m, 1H), 7.41 (dd, *J* = 10.3, 4.6 Hz, 2H), 7.35 (s, 1H), 5.39 – 5.33 (m, 2H), 5.27 (t, *J* = 9.1 Hz, 1H), 5.22 – 5.09 (m, 2H), 4.97 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.81 – 4.77 (m, 1H), 4.75 (d, *J* = 10.0 Hz, 1H), 4.55 (d, *J* = 7.9 Hz, 1H), 4.50 (dd, *J* = 12.1, 1.7 Hz, 1H), 4.40 (s, 1H), 4.38 – 4.32 (m, 2H), 4.13 (tdd, *J* = 14.4, 7.1, 3.1 Hz, 3H), 3.97 – 3.89 (m, 2H), 3.66 (ddd, *J* = 9.9, 4.5, 1.8 Hz, 1H), 2.16 (s, 3H), 2.13 (s, 3H), 2.11 – 2.09 (m, 9H), 2.08 (d, *J* = 3.2 Hz, 6H), 2.06 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 192.78, 170.46, 170.42, 170.38, 170.19, 170.07, 170.01, 169.92, 169.82, 169.12, 159.83, 138.28, 131.67, 128.90, 128.26, 112.40, 100.93, 82.75, 77.33, 75.79, 74.18, 71.33, 71.01, 70.59, 69.25, 69.10, 67.94, 66.64, 62.89, 61.75, 60.82, 60.36, 35.41, 20.81, 20.73, 20.71, 20.64, 20.63, 20.61, 20.50. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{43}H_{52}O_{23}S$ 987.2599; found 968.2604.

5-acetoxy-3-benzoyl-6-methyl-5,6-dihydro-2H-pyran-2-yl)oxy)6(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5a)

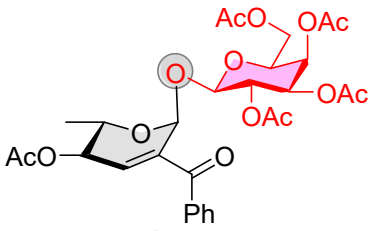


5a

The compound **5a** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (50% yield, 19 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.63 – 7.57 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.33 (dd, J = 3.4, 1.1 Hz, 1H), 5.92 (t, J = 1.2 Hz, 1H), 5.28 – 5.24 (m, 1H), 5.22 – 5.16 (m, 1H), 5.09 – 5.03 (m, 1H), 4.92 (dd, J = 9.3, 8.1

Hz, 1H), 4.86 (d, J = 8.0 Hz, 1H), 4.28 (dd, J = 12.2, 4.9 Hz, 1H), 4.14 – 4.08 (m, 1H), 3.99 (dd, J = 6.5, 5.7 Hz, 1H), 3.81 – 3.75 (m, 1H), 2.09 (d, J = 1.8 Hz, 3H), 2.04 (s, 3H), 2.01 (d, J = 1.9 Hz, 3H), 1.94 (s, 3H), 1.62 (s, 3H), 1.43 (d, J = 6.6 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 194.5, 170.7, 170.2, 169.4, 169.2, 139.4, 136.3, 134.6, 133.5, 129.6, 128.6, 101.70, 97.3, 72.7, 72.0, 71.6, 70.9, 68.3, 68.1, 62.0, 20.9, 20.8, 20.6, 20.6, 20.0, 18.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{34}O_{14}$ 624.2292; found 624.2289.

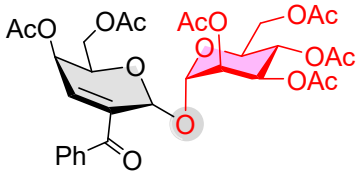
5-acetoxy-3-benzoyl-6-methyl-5,6-dihydro-2H-pyran-2-yl)oxy)6(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5b)



5b

The compound **5b** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (55% yield, 21 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.75 – 7.69 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 6.27 – 6.22 (m, 1H), 5.85 (s, 1H), 5.30 (d, J = 2.7 Hz, 1H), 5.22 (ddd, J = 6.1, 3.1, 1.6 Hz, 1H), 5.07 (dd, J = 10.5, 8.0 Hz, 1H), 4.93 (dd, J = 10.5, 3.4 Hz, 1H), 4.76 (d, J = 7.9 Hz, 1H), 4.14 – 4.01 (m, 2H), 3.93 – 3.84 (m, 2H), 2.04 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.86 (s, 3H), 1.56 (s, 3H), 1.36 (d, J = 6.5 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 194.6, 170.4, 170.3, 170.2, 170.1, 169.2, 139.5, 136.3, 135.3, 133.4, 129.7, 128.6, 102.3, 97.8, 71.6, 70.8, 68.4, 66.7, 61.1, 29.7, 20.9, 20.7, 20.7, 20.6, 20.2, 18.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. $C_{29}H_{34}O_{14}$ 624.2292; found 624.2293.

5-acetoxy-6-(acetoxymethyl)-3-benzoyl-5,6-dihydro-2H-pyran-2-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5c).

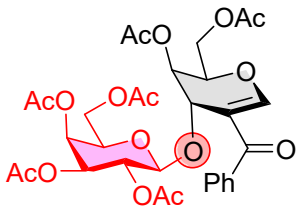


5c

The compound **5c** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as

eluent to obtained colorless viscous (64% yield, 23 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.55 (ddd, *J* = 6.9, 2.5, 1.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.62 (d, *J* = 5.4 Hz, 1H), 6.01 (s, 1H), 5.29 (dd, *J* = 5.4, 2.7 Hz, 1H), 5.27 (d, *J* = 1.5 Hz, 1H), 5.23 (t, *J* = 10.2 Hz, 1H), 5.19 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.05 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.42 (ddd, *J* = 7.4, 4.6, 2.7 Hz, 1H), 4.23 (ddd, *J* = 7.9, 4.6, 2.9 Hz, 2H), 4.19 – 4.10 (m, 2H), 3.97 – 3.90 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.00 (d, *J* = 4.3 Hz, 6H), 1.90 (d, *J* = 2.5 Hz, 6H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 194.0, 170.8, 170.8, 170.1, 169.9, 169.9, 169.8, 138.6, 136.7, 135.3, 133.1, 129.5, 128.7, 93.1, 88.5, 69.4, 69.4, 69.1, 67.3, 65.4, 62.5, 62.4, 62.0, 20.9, 20.8, 20.7, 20.6, 20.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{36}O_{16}$ 682.2347; found 682.2349.

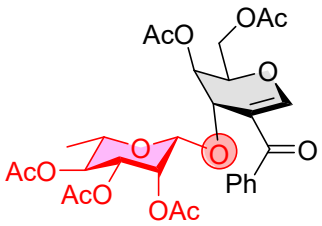
3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)oxy)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5d)



5d

The compound **5d** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (55% yield, 20 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.55 (dd, J = 8.2, 1.3 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.40 – 7.34 (m, 3H), 5.53 (d, J = 3.9 Hz, 1H), 5.39 (dd, J = 3.2, 1.0 Hz, 1H), 5.27 (dd, J = 2.5, 1.2 Hz, 1H), 5.21 – 5.17 (m, 1H), 5.05 (dd, J = 11.1, 3.8 Hz, 1H), 4.61 (d, J = 2.6 Hz, 1H), 4.41 (dd, J = 7.8, 4.5 Hz, 1H), 4.32 (dd, J = 11.9, 4.5 Hz, 1H), 4.28 – 4.20 (m, 2H), 4.18 – 4.12 (m, 1H), 4.06 – 3.99 (m, 1H), 2.07 (s, 6H), 2.02 – 1.99 (m, 6H), 1.90 (s, 3H), 1.74 (s, 3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.9, 170.7, 170.5, 170.3, 169.9, 169.3, 160.2, 138.4, 131.8, 128.8, 128.4, 114.5, 98.6, 77.2, 72.3, 68.8, 67.7, 67.4, 66.9, 65.9, 62.4, 61.8, 20.7, 20.7, 20.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{36}O_{16}$ 665.2082; found 665.2080.

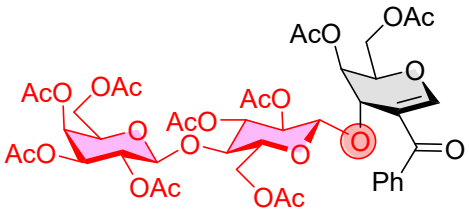
3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)oxy)6methyltetrahydro-2H-pyran-3,4,5-triyl triacetate (5e)



5e

The compound **5e** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (57% yield, 19 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.61 – 7.57 (m, 2H), 7.51 – 7.46 (m, 1H), 7.43 – 7.37 (m, 3H), 5.15 (dd, J = 3.4, 1.7 Hz, 1H), 5.12 – 5.10 (m, 1H), 5.09 – 5.06 (m, 2H), 4.98 (t, J = 10.0 Hz, 1H), 4.84 (d, J = 2.4 Hz, 1H), 4.48 – 4.42 (m, 1H), 4.30 (dd, J = 11.8, 7.4 Hz, 1H), 4.22 (dd, J = 11.8, 5.1 Hz, 1H), 3.86 – 3.78 (m, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 1.99 (s, 3H), 1.91 (d, J = 2.3 Hz, 6H), 1.15 (d, J = 6.2 Hz, 3H). ^{13}C NMR {^{1}H} (101 MHz, CDCl3) δ 194.1, 170.5, 170.3, 170.3, 170.0, 169.7, 161.3, 138.5, 131.8, 128.9, 128.4, 113.9, 95.3, 71.8, 70.7, 69.9, 69.2, 67.2, 64.3, 63.3, 62.1, 21.0, 20.81, 20.77, 20.7, 17.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{34}O_{14}$ 629.1846; found 629.1843.

2-(acetoxymethyl)-6-((-4,5-diacetoxy-6-((-3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)oxy)-2-(acetoxymethyl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (5f)

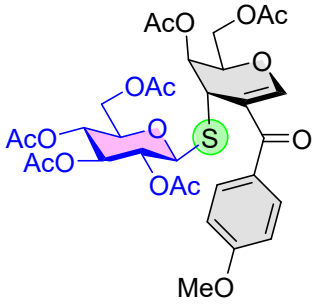


5f

The compound **5f** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (51% yield, 26 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.53 (t, J = 6.8 Hz, 1H), 7.47 – 7.41 (m, 3H), 5.48 (d, J = 3.8 Hz, 1H), 5.43 – 5.34 (m, 2H), 5.30 (s, 1H), 5.15 – 5.09 (m, 1H), 4.96 (dd, J = 10.4, 3.4 Hz, 1H), 4.78 (dd, J = 10.4, 4.0 Hz, 1H), 4.69 (d, J = 2.3 Hz, 1H), 4.48 (dd, J = 16.1, 8.0 Hz, 3H), 4.39 (dd, J = 12.1, 4.1 Hz, 1H), 4.31 – 4.19 (m, 2H), 4.11 (dt, J = 19.7, 9.8 Hz, 3H), 3.87 (t, J = 6.9 Hz, 1H), 3.73 (t, J = 9.6 Hz, 1H), 2.17 – 2.15 (m, 9H), 2.09 (d, J = 1.0 Hz, 3H), 2.06 (s, 6H), 2.02 (s, 3H), 1.97 (s, 3H), 1.80 (s,

3H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 194.0, 170.6, 170.6, 170.5, 170.4, 170.3, 170.2, 170.1, 169.7, 169.3, 160.3, 138.4, 131.879, 128.8, 128.4, 114.5, 101.4, 97.7, 77.2, 72.4, 71.1, 70.7, 70.4, 69.7, 69.14,69.1, 68.4, 66.6, 66.0, 62.6, 62.2, 60.8, 20.9, 20.8, 20.7, 20.7, 20.5, 20.4. HRMS (ESI), m/z calcd. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{43}H_{52}O_{24}$ 953.2927; found 953.2914.

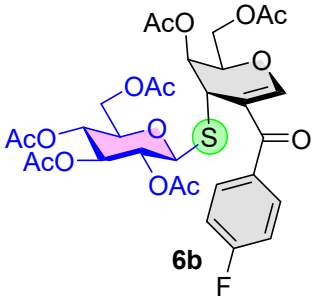
3-acetoxy-2-(acetoxymethyl)-5-(4-methoxybenzoyl)-3,4-dihydro-2H-pyran-4-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (6a)



6a

The compound **6a** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (55:45) as eluent to obtained colorless viscous (70% yield, 38 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.55 (d, J = 8.2 Hz, 2H), 7.25 (s, 1H), 6.83 (d, J = 8.2 Hz, 2H), 5.20 (dd, J = 18.0, 8.3 Hz, 2H), 5.08 (dd, J = 18.6, 9.3 Hz, 2H), 4.81 (d, J = 10.1 Hz, 1H), 4.64 (t, J = 5.7 Hz, 1H), 4.40 (s, 1H), 4.28 – 4.17 (m, 3H), 3.94 (d, J = 12.4 Hz, 1H), 3.78 (s, 3H), 3.66 (d, J = 9.4 Hz, 1H), 2.05 (s, 3H), 2.03 – 1.97 (m, 9H), 1.94 (s, 6H). ^{13}C NMR {^{1}H} 101 MHz, $CDCl_3$) δ 191.6, 170.7, 170.4, 170.3, 170.0, 169.5, 169.3, 162.7, 158.0, 131.3, 130.7, 113.5, 112.7, 83.0, 76.1, 74.0, 71.1, 69.4, 68.0, 67.7, 62.6, 61.6, 55.4, 36.2, 20.8, 20.7, 20.6, 20.6, 20.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{32}H_{38}O_{16}$ S 711.1959; found 711.1953.

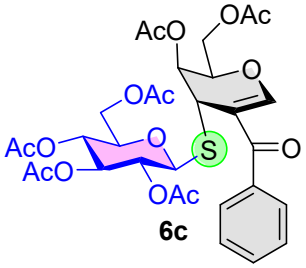
3-acetoxy-2-(acetoxymethyl)-5-(4-fluorobenzoyl)-3,4-dihydro-2H-pyran-4-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (6b)



6b

The compound **6b** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (55:45) as eluent to obtained colorless viscous (82% yield, 39 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 2H), 7.25 (s, 1H), 7.03 (t, J = 8.6 Hz, 2H), 5.27 (s, 1H), 5.24 – 5.17 (m, 1H), 5.10 (dd, J = 15.0, 5.9 Hz, 2H), 4.79 (d, J = 10.1 Hz, 1H), 4.67 (t, J = 6.1 Hz, 1H), 4.38 (s, 1H), 4.29 – 4.19 (m, 3H), 3.99 (dd, J = 12.4, 2.0 Hz, 1H), 3.74 – 3.62 (m, 1H), 2.05 (s, 3H), 2.04 – 2.01 (m, 6H), 1.99 (s, 3H), 1.95 (d, J = 0.7 Hz, 6H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 191.4, 170.7, 170.4, 170.31, 169.9, 169.5, 169.3, 166.2, 163.7, 159.1, 134.4, 134.4, 131.5, 131.4, 115.6, 115.3, 112.7, 83.0, 76.3, 74.0, 71.4, 69.4, 68.0, 67.6, 62.6, 61.7, 35.9, 20.8, 20.7, 20.6, 20.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{35}FO_{15}S$ 699.1759; found 699.1758.

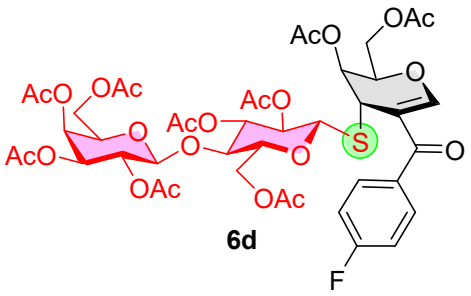
3-acetoxy-2-(acetoxymethyl)-5-benzoyl-3,4-dihydro-2H-pyran-4-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (6c)



6c

The compound **6c** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (65:35) as eluent to obtained colorless viscous (75% yield, 27mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.47 – 7.42 (m, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 5.29 – 5.25 (m, 1H), 5.23 – 5.18 (m, 1H), 5.11 (td, *J* = 9.8, 3.2 Hz, 2H), 4.80 (d, *J* = 10.1 Hz, 1H), 4.68 (t, *J* = 6.1 Hz, 1H), 4.39 (d, *J* = 1.4 Hz, 1H), 4.25 (d, *J* = 6.2 Hz, 2H), 4.24 – 4.19 (m, 1H), 3.97 (dd, *J* = 12.4, 2.2 Hz, 1H), 3.67 (ddd, *J* = 9.9, 4.2, 2.3 Hz, 1H), 2.05 (s, 3H), 2.03 (s, 6H), 1.99 (s, 3H), 1.95 (s, 6H). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 193.0, 170.7, 170.5, 170.3, 170.0, 169.5, 169.3, 159.5, 138.2, 131.8, 129.0, 128.3, 112.8, 83.1, 76.2, 74.1, 71.3, 69.4, 68.0, 67.6, 62.6, 61.7, 35.9, 20.8, 20.72, 20.67, 20.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{31}H_{37}O_{15}S$ 681.1853; Found 681.1851.

2-(acetoxymethyl)-6-((-4,5-diacetoxy-6-((-3-acetoxy-2-(acetoxymethyl)-5-(4-fluorobenzoyl)-3,4-dihydro-2H-pyran-4-yl)thio)-2-(acetoxymethyl)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (6d)

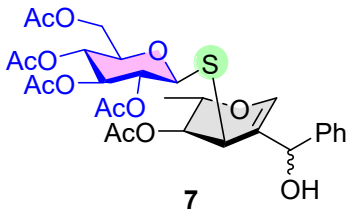


6d

The compound **6d** was synthesized according to the general procedure (2.1.2) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (50:50) as eluent to obtained colorless viscous (70% yield, 21 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 6.8, 5.5 Hz, 2H), 7.32 (s, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 5.36 (s, 2H), 5.26 (t, *J* = 9.1 Hz, 1H), 5.20 – 5.09 (m, 2H), 4.96 (dd, *J* = 10.3, 3.1 Hz, 1H), 4.76 (dd, *J* = 18.3, 8.1 Hz, 2H), 4.52 (dd, *J* = 12.4, 10.2 Hz, 2H), 4.39 (s, 1H), 4.35 (d, *J* = 4.9 Hz, 2H), 4.18 – 4.06 (m, 3H), 3.96 – 3.87 (m, 2H), 3.65 (dd, *J* = 9.9, 4.4 Hz, 1H), 2.16 (s, 3H), 2.13 (s, 3H), 2.10 (d, *J* = 3.4 Hz, 9H), 2.09 – 2.07 (m, 6H), 2.06 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 191.31, 170.49, 170.45, 170.40, 170.21, 170.11, 170.01, 169.94, 169.82, 169.14, 163.63, 159.40, 134.49, 131.44, 131.35, 115.55, 115.34, 112.43, 100.99, 82.73, 77.23, 75.84, 74.20, 71.43, 71.04, 70.65, 69.32, 69.14, 67.94, 66.64, 62.90, 61.76, 60.82, 35.45, 20.84, 20.74, 20.66, 20.63, 20.52. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{43}H_{52}O_{23}FS$ 987.2614; found 987.2604.

2-((3-acetoxy-5-(hydroxy(phenyl)methyl)-2-methyl-3,4-dihydro-2H-pyran-4-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (7)



7

The compound **7** was synthesized according to the general procedure (2.1.3) and purified using column chromatography over silica gel (60-120 mesh) using pet ether/ethyl acetate (40:60) as eluent to obtained gummy liquid (72 % yield, 14.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 7H), 7.33 (ddd, *J* = 4.5, 3.5, 2.4 Hz, 3H), 6.62 (s, 1H), 6.23 (s, 1H), 5.44 (d, *J* = 4.0 Hz, 2H), 5.18 (td, *J* = 9.3, 3.8 Hz, 2H), 5.08 – 4.95 (m, 4H),

4.74 (ddd, *J* = 9.9, 4.8, 2.3 Hz, 2H), 4.60 (d, *J* = 10.2 Hz, 1H), 4.53 (d, *J* = 10.2 Hz, 1H), 4.24 (ddd, *J* = 12.5, 10.9, 4.7 Hz, 2H), 4.09 (dd, *J* = 12.5, 2.2 Hz, 1H), 4.05 – 3.96 (m, 3H), 3.80 – 3.76 (m, 1H), 3.53 (dddd, *J* = 10.1, 6.7, 4.7, 2.2 Hz, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.08 – 2.06 (m, 9H), 2.05 (s, 3H), 2.02 (d, *J* = 0.6 Hz, 6H), 2.01 (s, 6H), 1.28 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.65, 170.22, 169.94, 169.85, 169.43, 169.40, 169.31, 169.20, 144.12, 142.86, 141.84, 141.50, 128.80, 128.50, 128.29, 127.59, 126.94, 126.05, 114.27, 113.16, 84.95, 84.69, 76.09, 73.87, 73.31, 73.01, 72.23, 71.70, 70.47, 70.41, 70.22, 69.59, 67.99, 67.78, 61.95, 61.62, 43.80, 41.91, 21.00, 20.97, 20.74, 20.70, 20.61, 20.57, 17.38, 17.20. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{36}O_{13}S$ 624.1877; found 624.1782.

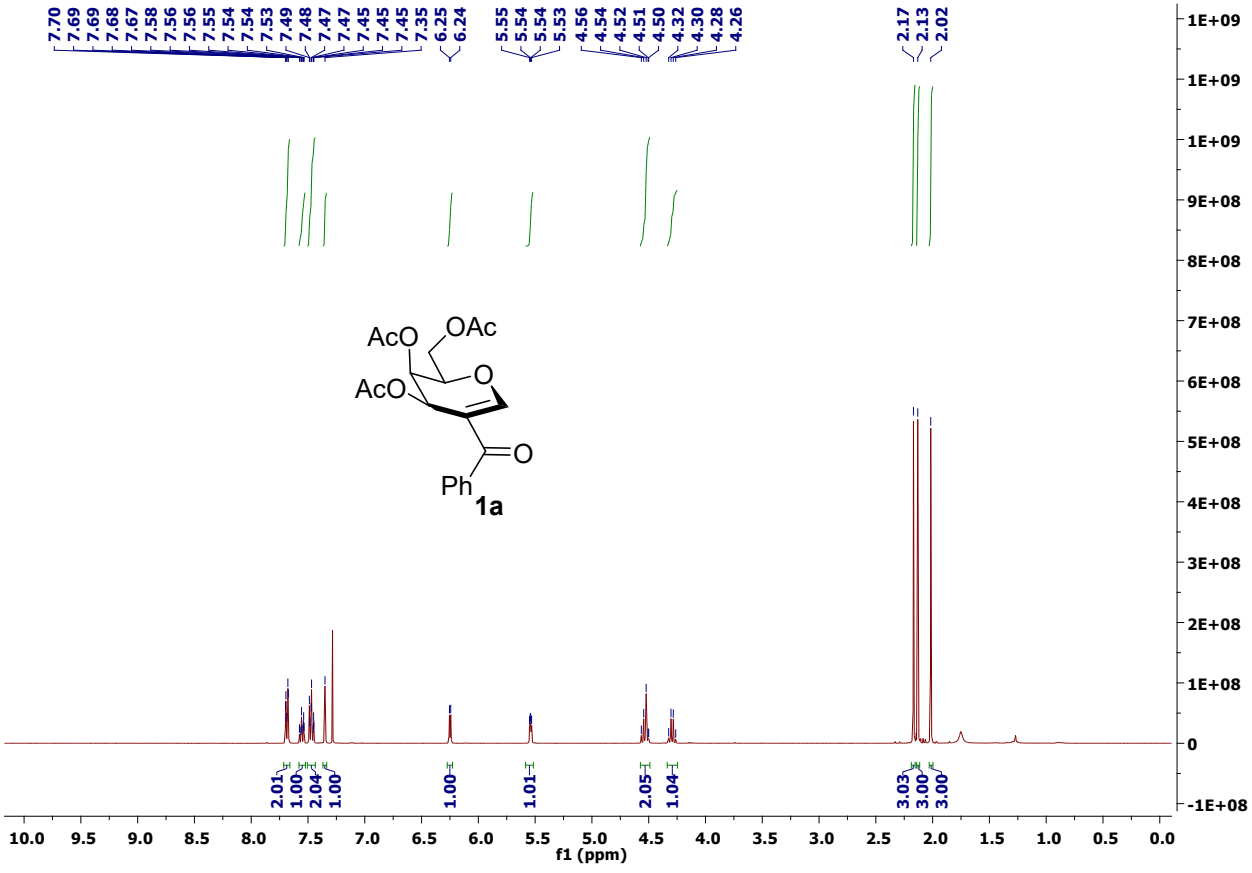
4. References

1) Darbem, M. P.; Kanno, K. S.; Oliveira, I. M. de; Esteves, C. H. A.; Pimenta, D. C.; Stefani, H. A. Synthesis of Amidoglucals and Glucal Esters via Carbonylative Coupling Reactions of 2-Iodoglucal Using $Mo(CO)_6$ as a CO Source. *New J. Chem.***2019**, *43* (2), 696–699. https://doi.org/10.1039/C8NJ04540B.

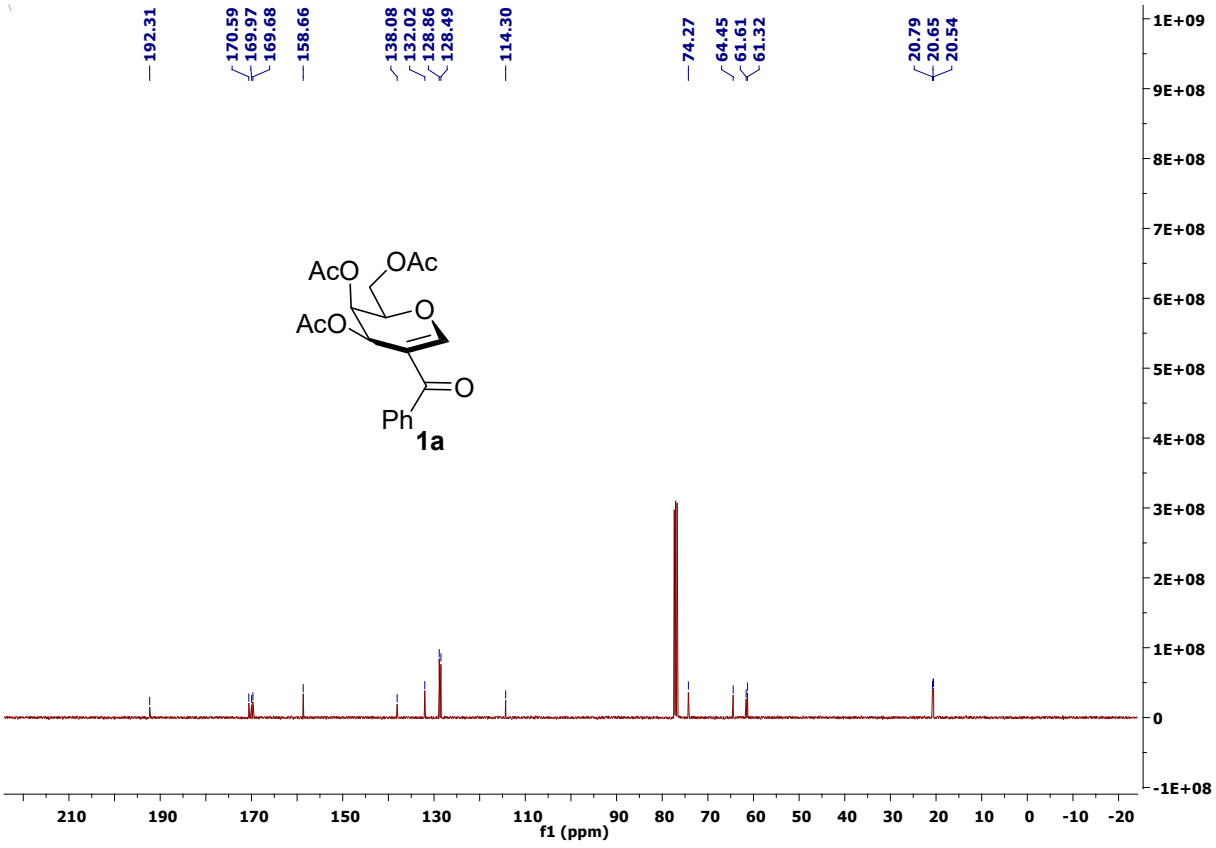
(2) Hussain, N.; Bhardwaj, M.; Ahmed, A.; Mukherjee, D. Synthesis of Sugar-Based Enones and Their Transformation into 3,5-Disubstituted Furans and 2-Acyl-Substituted 1,2,3-Trideoxy Sugars in the Presence of Lewis Acids. *Org. Lett.***2019**, *21* (9), 3034–3037. https://doi.org/10.1021/acs.orglett.9b00680.

5.NMR Spectra

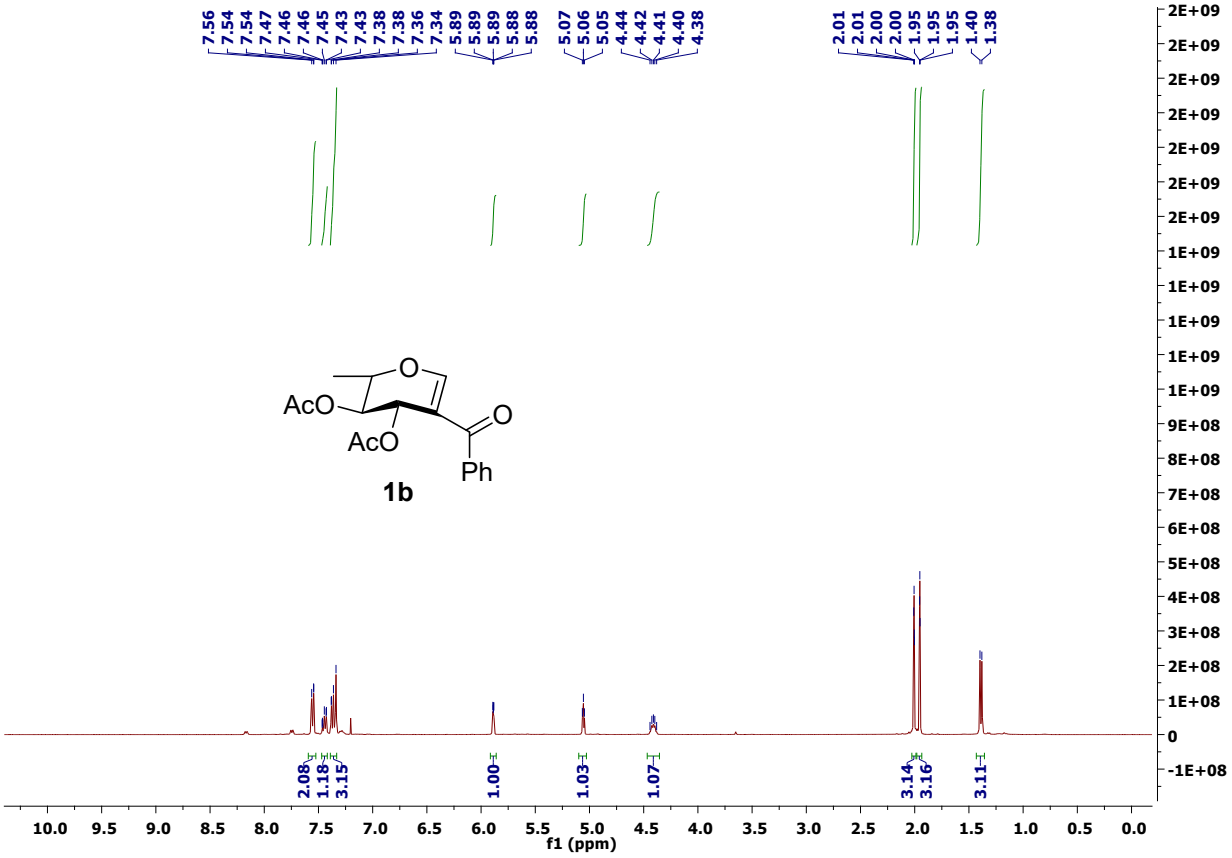
^{1}H NMR (400 MHz) of **1a** in $CDCl_3$



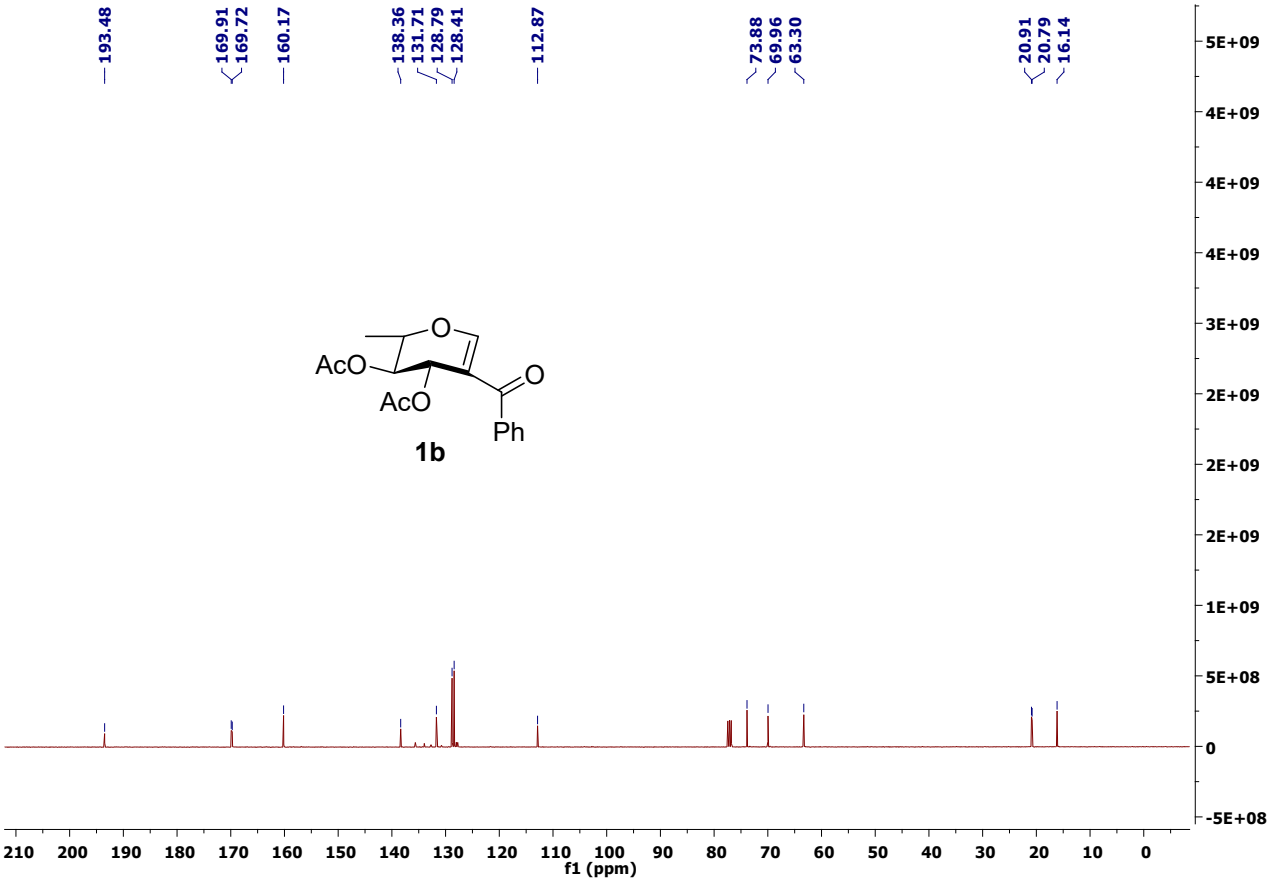
^{13}C NMR $\{^{1}H\}$ (101 MHz) of **1a** in $CDCl_3$



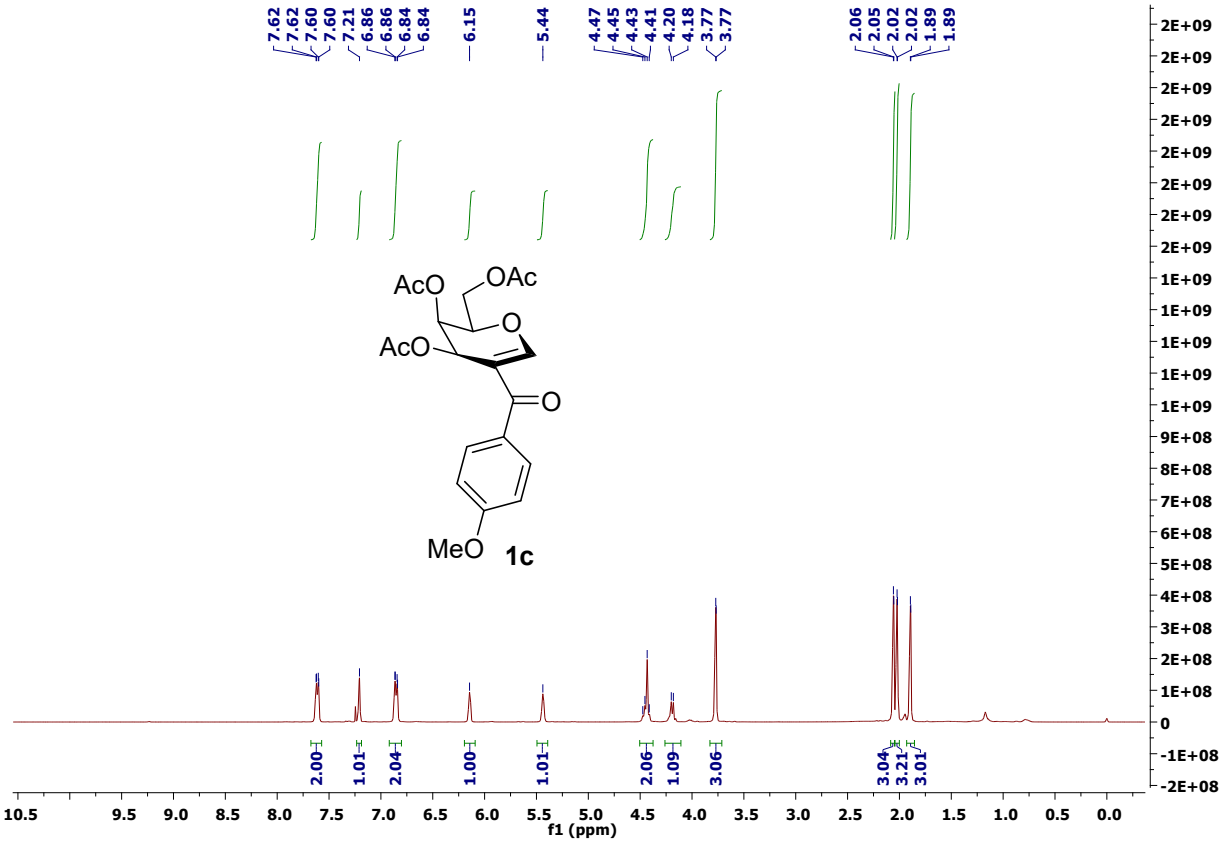
^{1}H NMR (400 MHz) of **1b** in $CDCl_3$



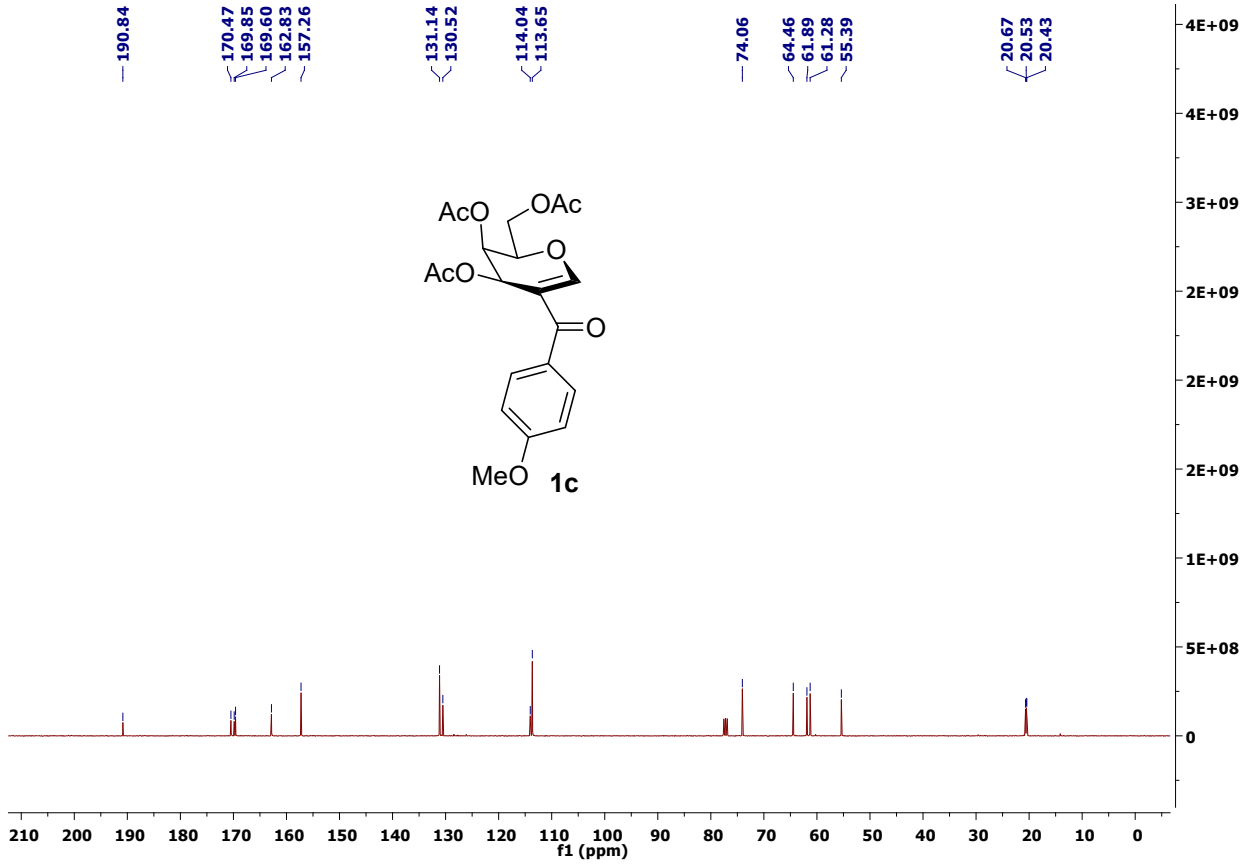
^{13}C NMR $\{^{1}H\}$ (101 MHz) of **1b** in $CDCl_3$



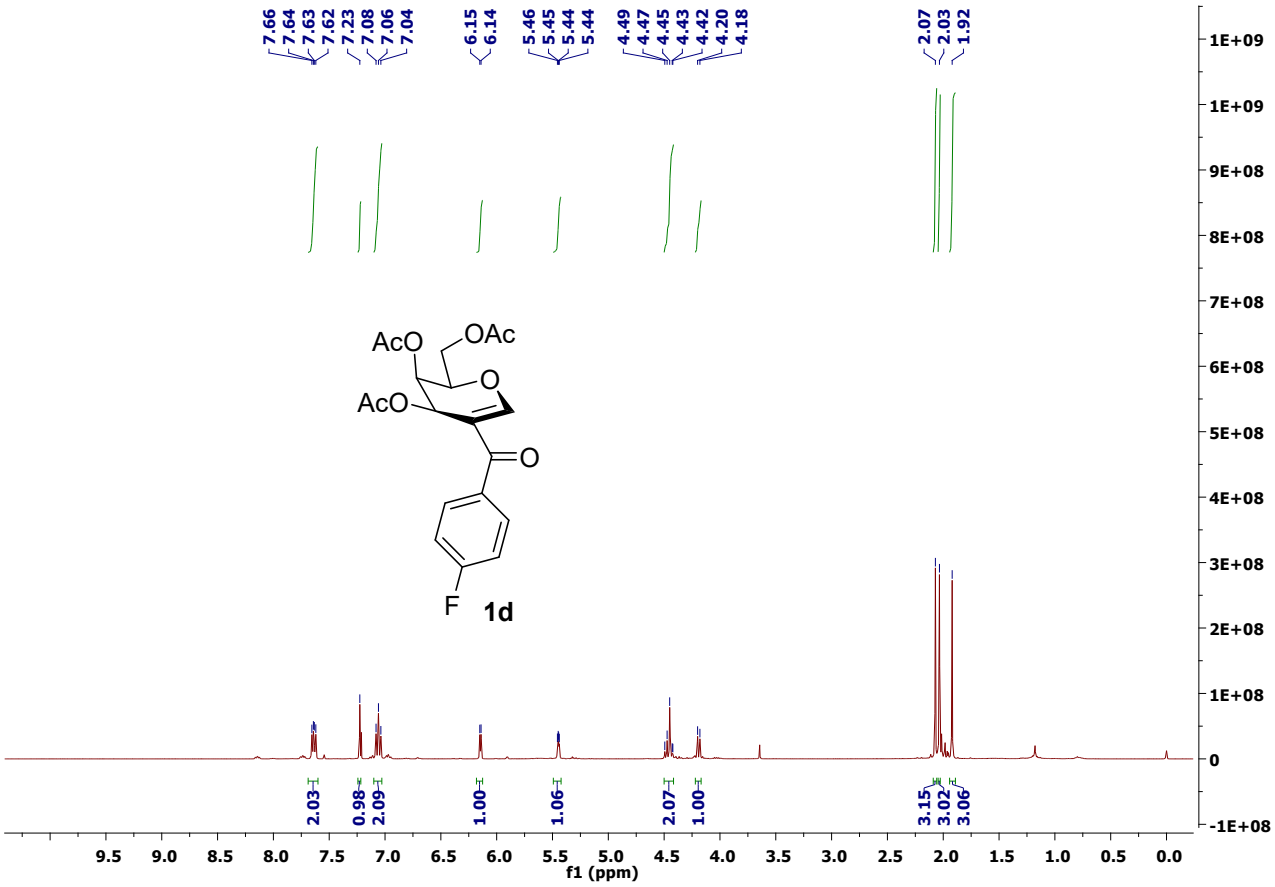
^{1}H NMR (400 MHz) of **1c** in $CDCl_3$



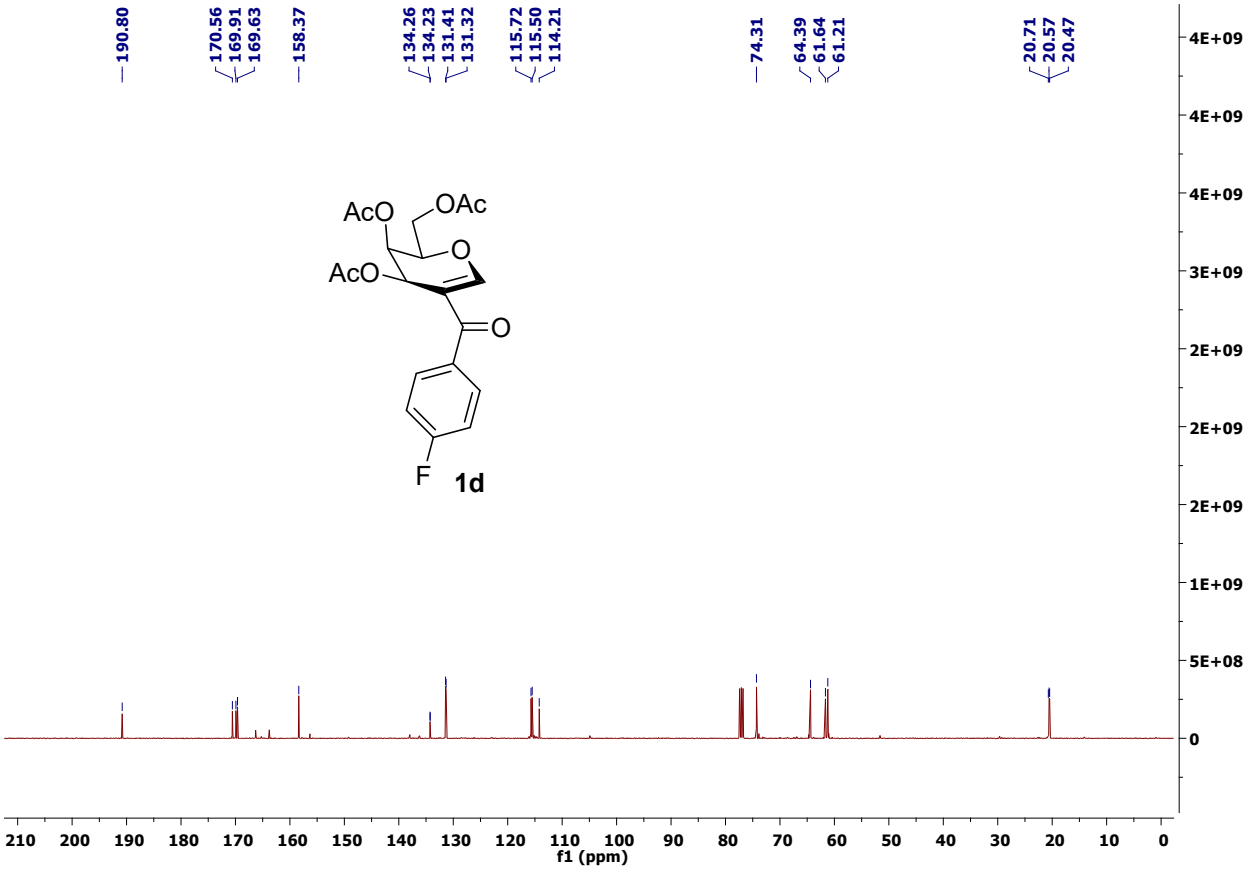
^{13}C NMR $\{^{1}H\}$ (101 MHz) of **1c** in $CDCl_3$



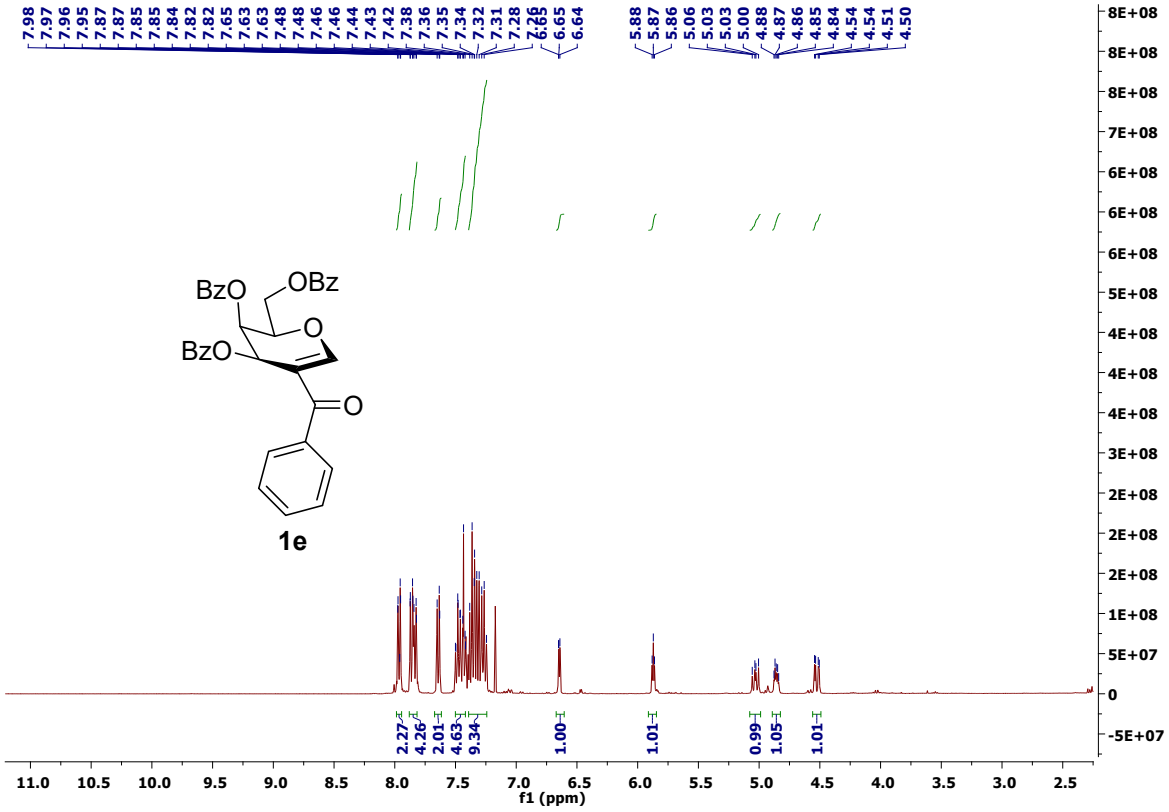
^{1}H NMR (400 MHz) of **1d** in $CDCl_3$



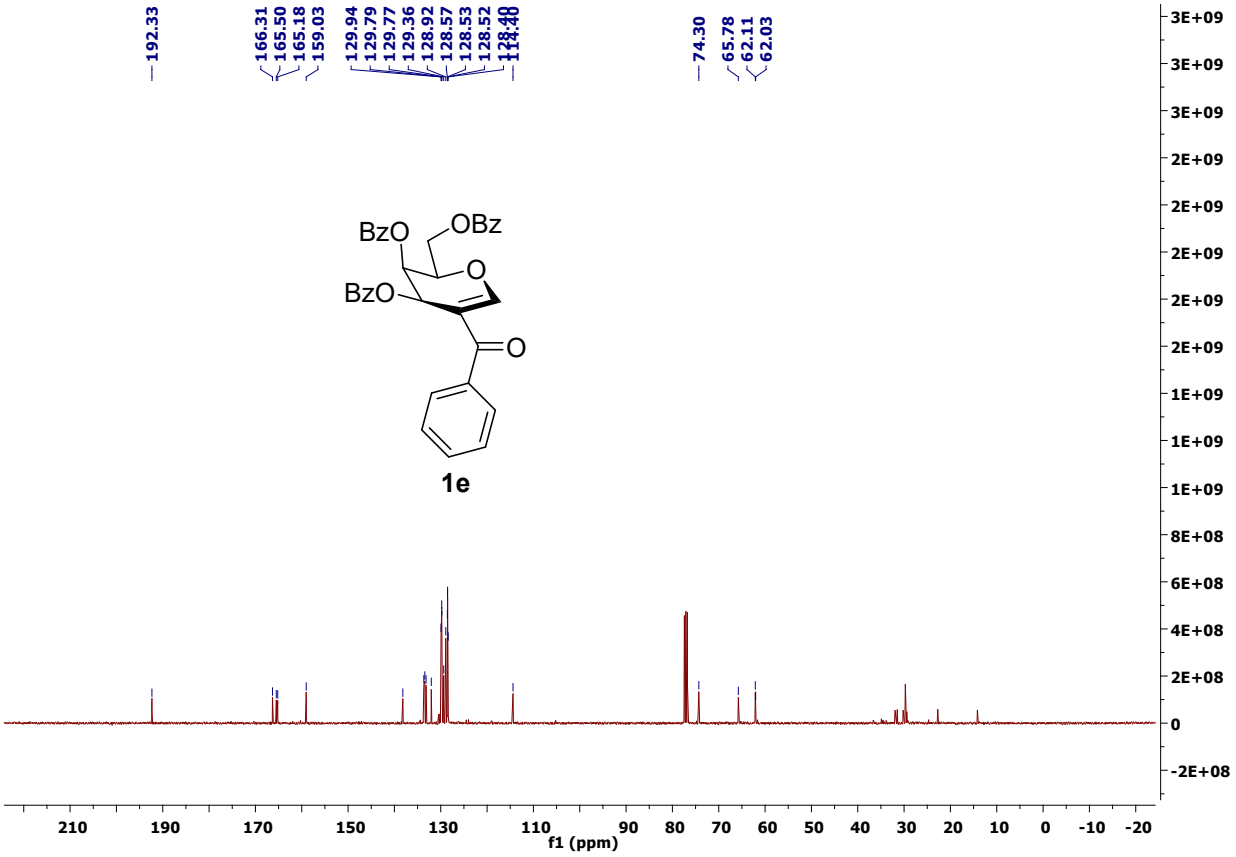
^{13}C NMR $\{^{1}H\}$ (101 MHz) of **1d** in $CDCl_3$



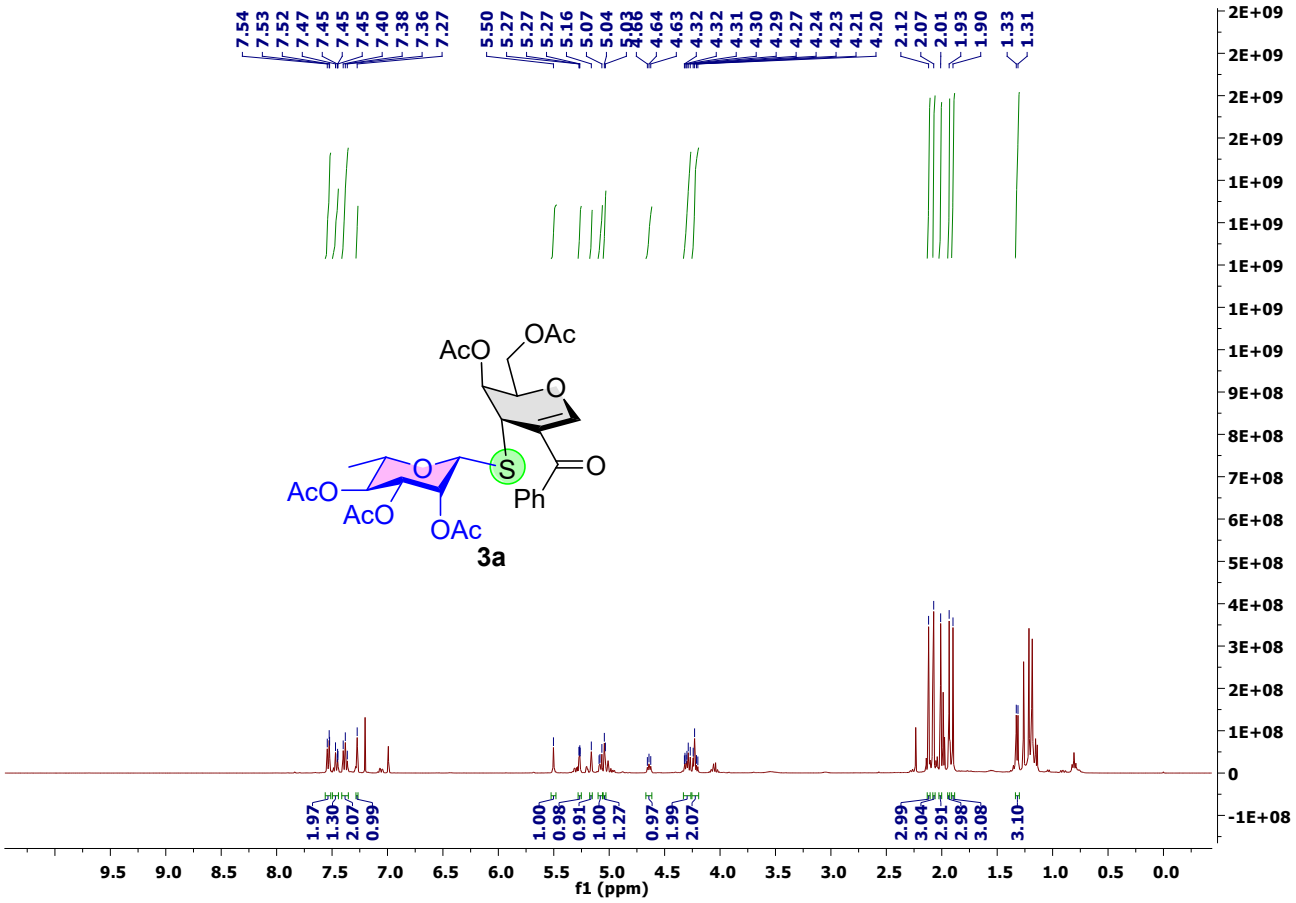
^{1}H NMR (400 MHz) of **1e** in $CDCl_3$



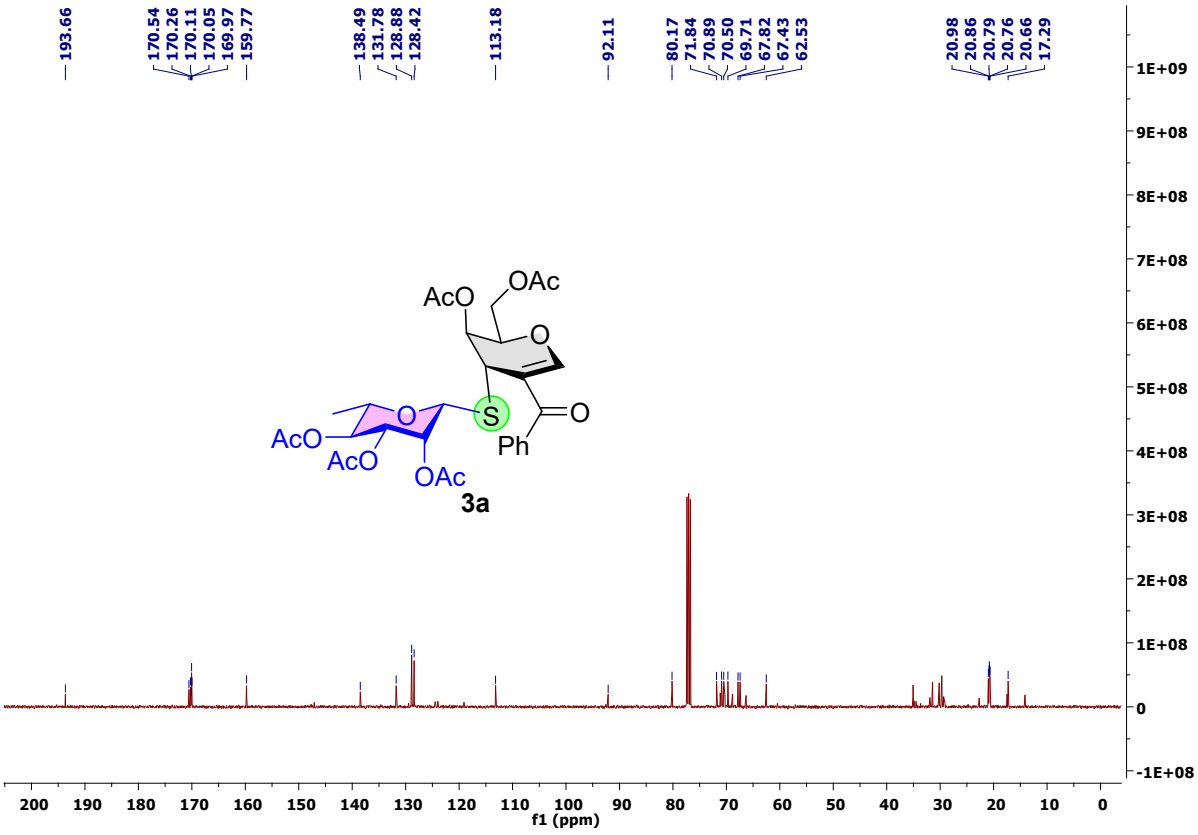
^{13}C NMR $\{^{1}H\}$ (101 MHz) of **1e** in $CDCl_3$



^{1}H NMR (400 MHz) of **3a** in $CDCl_3$



^{13}C NMR{^{1}H} (101 MHz) of **3a** in $CDCl_3$



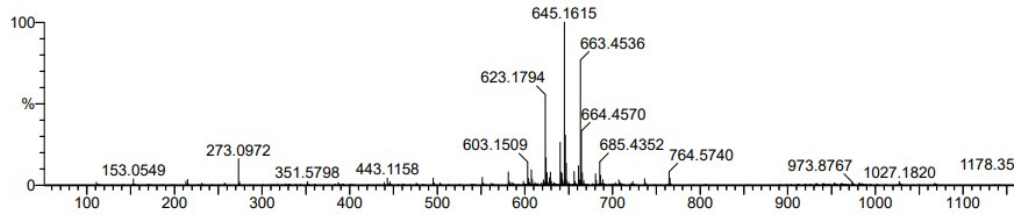
HRMS data of **3a**

Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

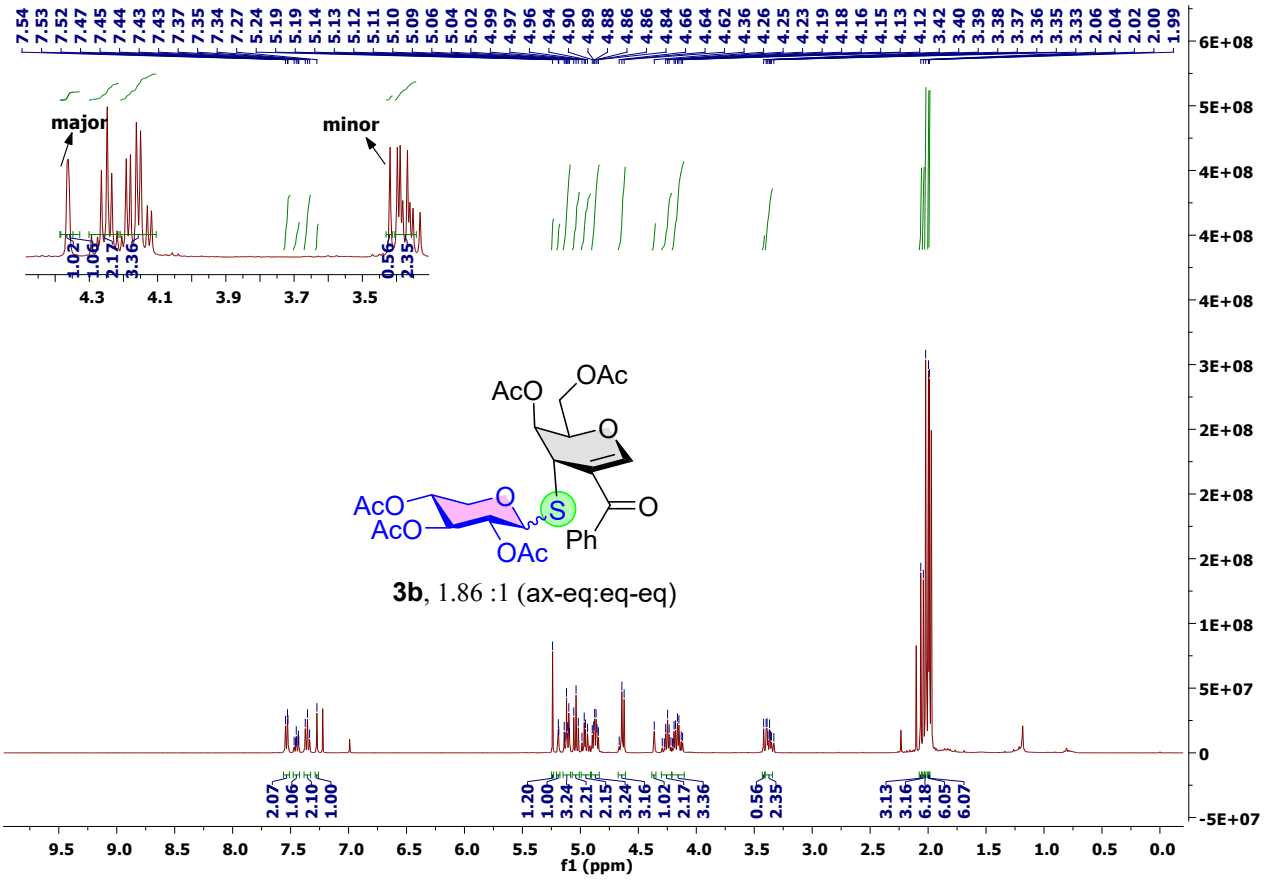
Monoisotopic Mass, Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-29 H: 0-100 O: 0-13 S: 0-1
GAL-RHAM-SH
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_03 8 (0.172)

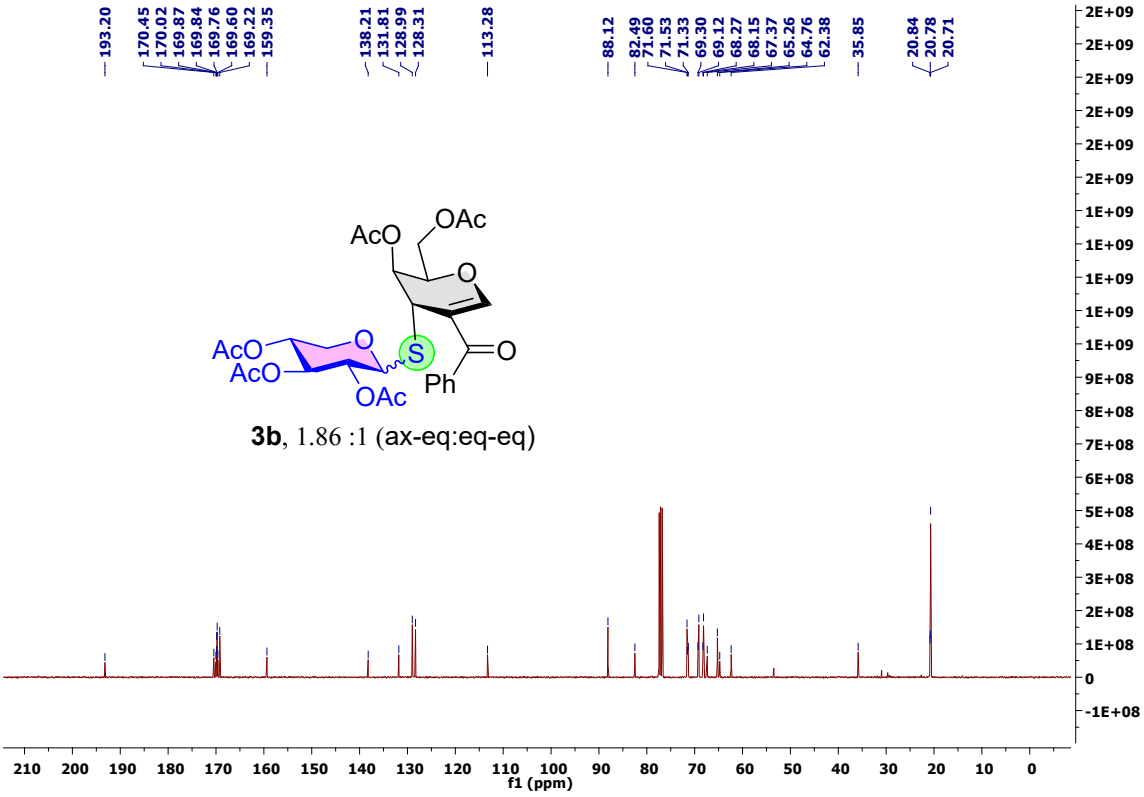


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
623.1794	623.1798	-0.4	-0.6	12.5	808.4	n/a	n/a	C29 H35 O13 S

^{1}H NMR (400 MHz) of **3b** in $CDCl_3$



^{13}C NMR{^{1}H} (101 MHz) of **3b** in $CDCl_3$



3b, 1.86 :1 (ax-eq:eq-eq)

HRMS data of **3b**

Elemental Composition Report

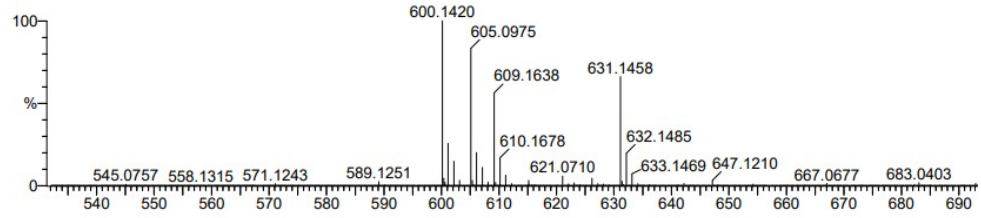
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-28 H: 0-100 O: 0-13 S: 0-1

GAL-XYL-SH

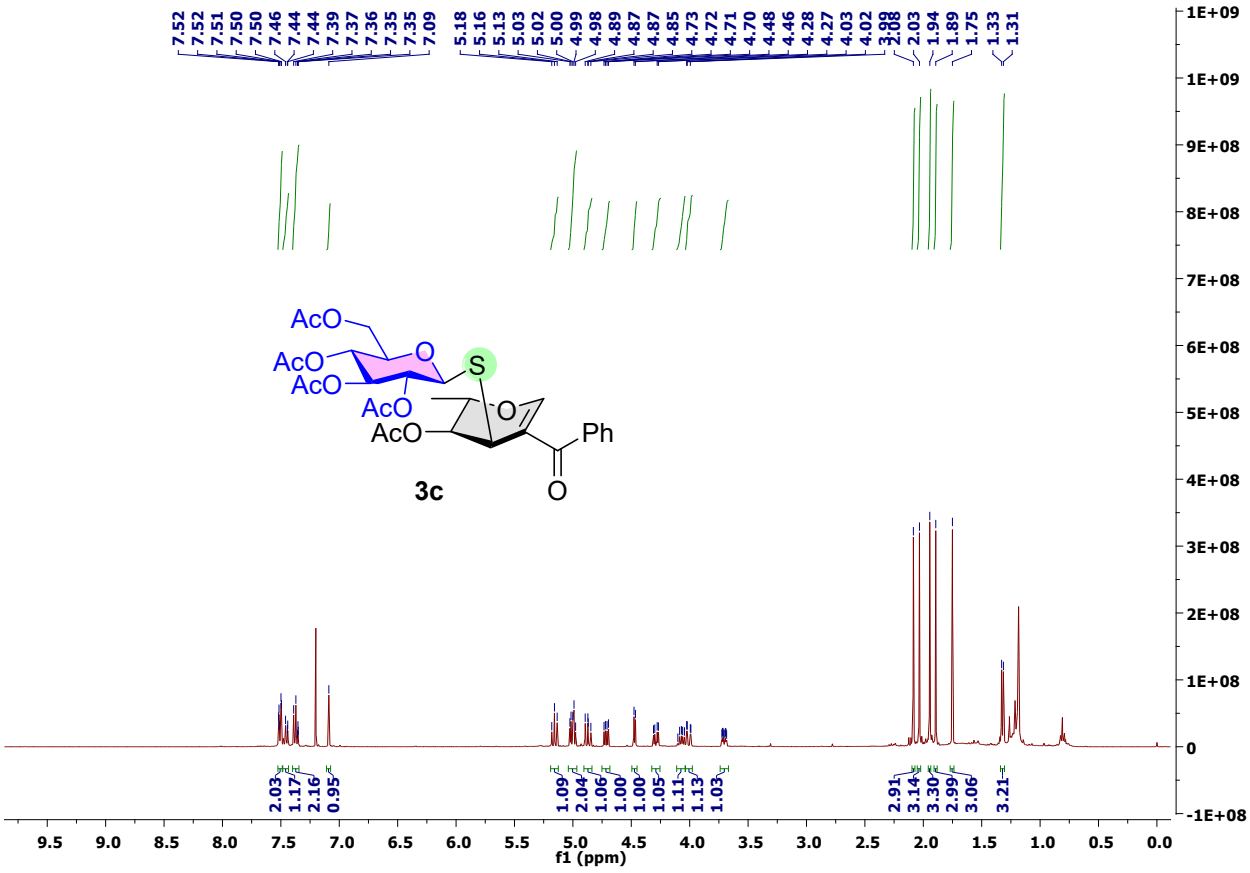
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_05 9 (0.209)

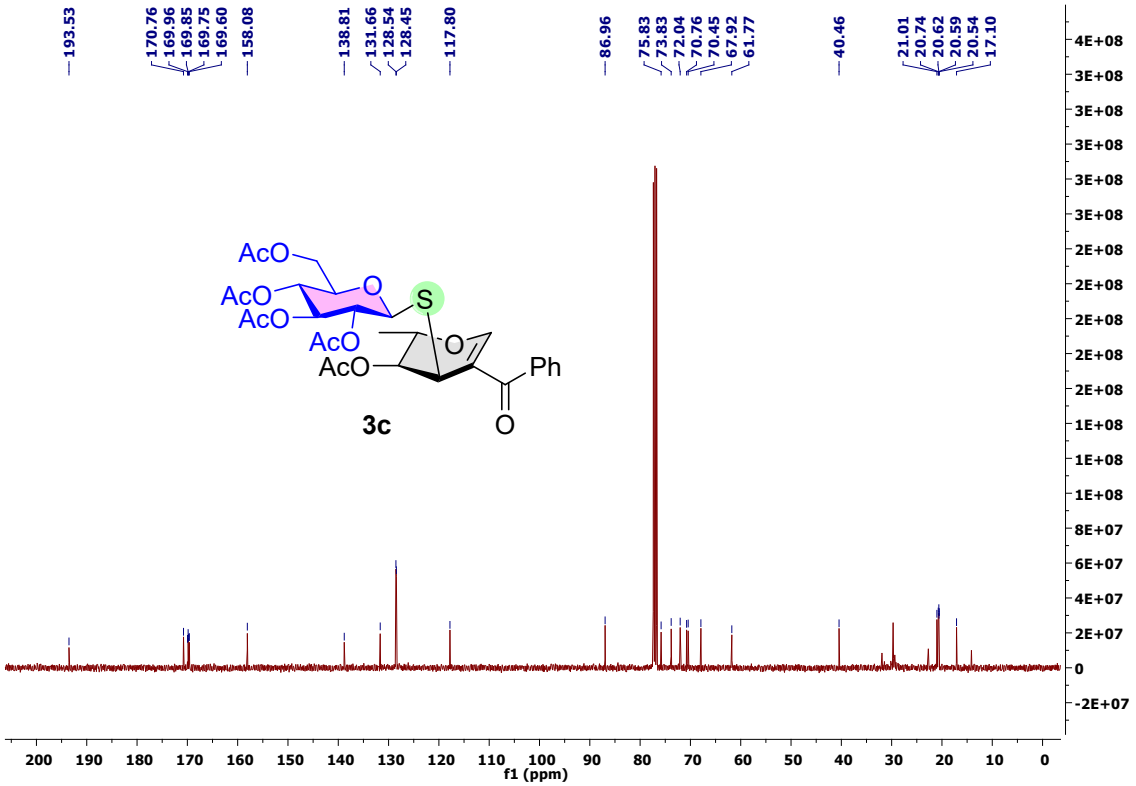


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
609.1638	609.1642	-0.4	-0.7	12.5	623.2	n/a	n/a	C28 H33 O13 S

^{1}H NMR (400 MHz) of **3c** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **3c** in $CDCl_3$



HRMS data of **3c**

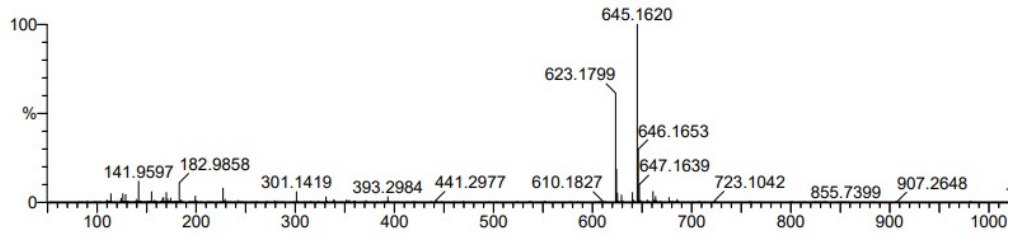
Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-29 H: 0-100 O: 0-13 S: 0-1
Rham-Glu-SH

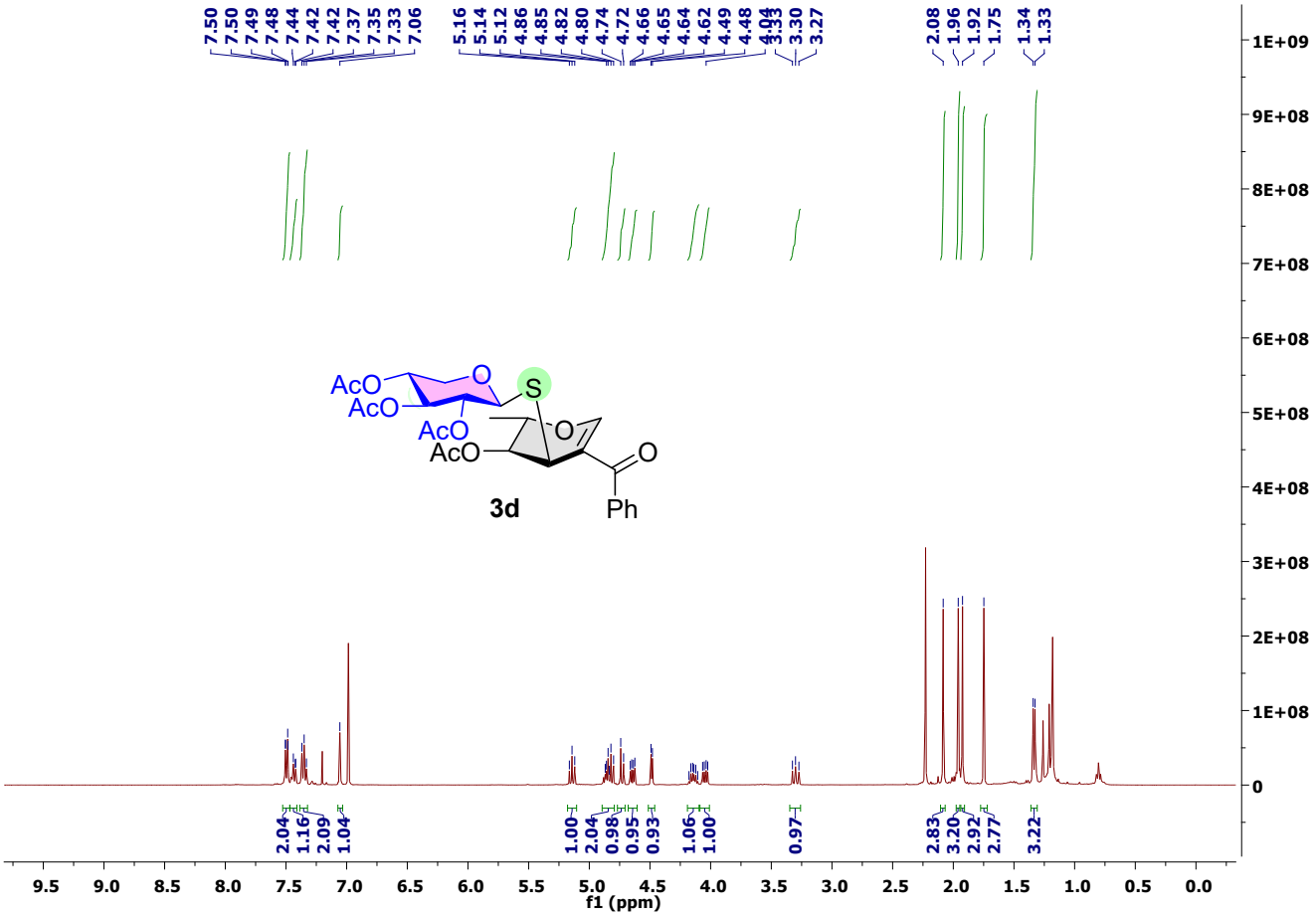
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

060423_13 12 (0.259)

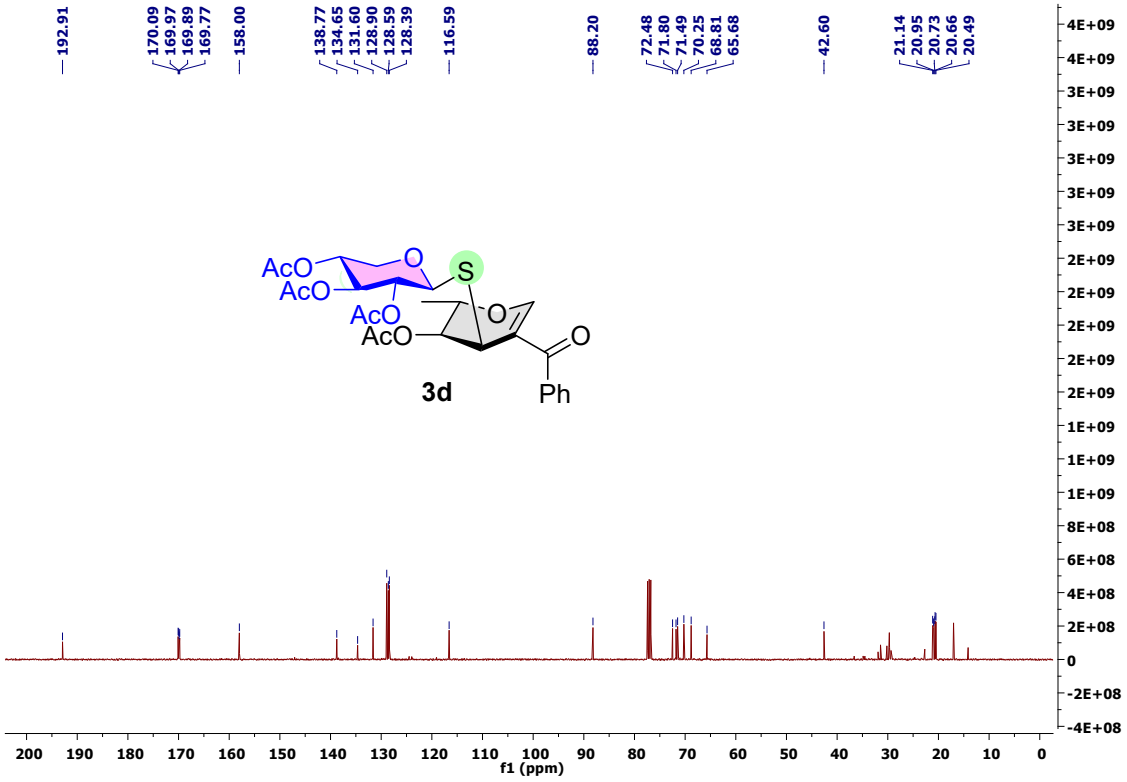


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
623.1799	623.1798	0.1	0.2	12.5	546.0	n/a	n/a	C29 H35 O13 S

^{1}H NMR (400 MHz) of **3d** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **3d** in $CDCl_3$



HRMS data of **3d**

Elemental Composition Report

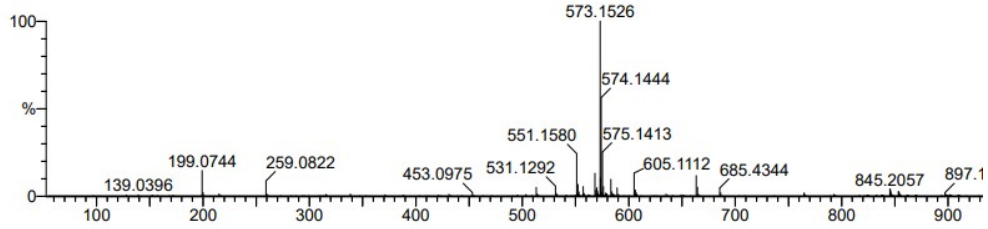
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-26 H: 0-100 O: 0-11 S: 0-1

Rham-Xyl-SH

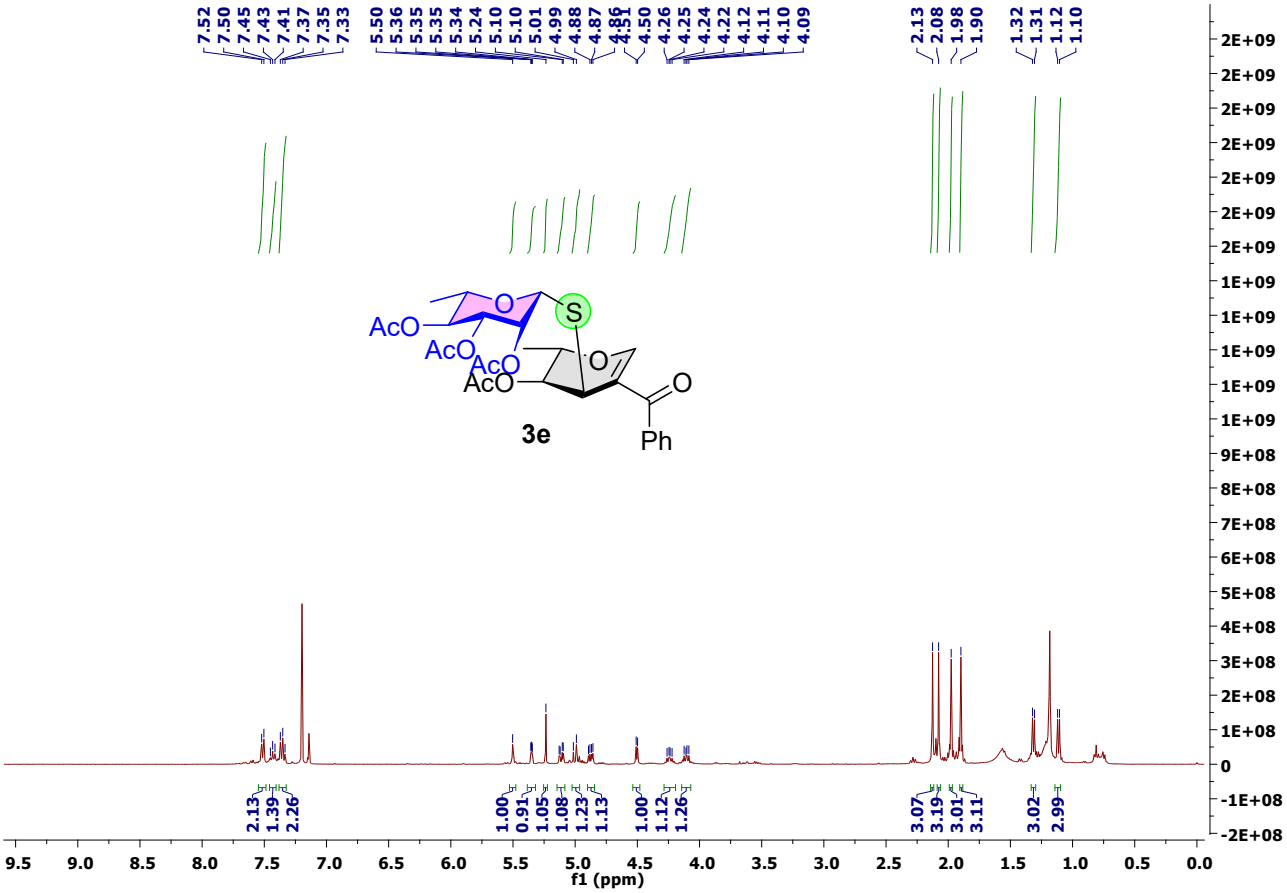
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

060423_17 6 (0.138)

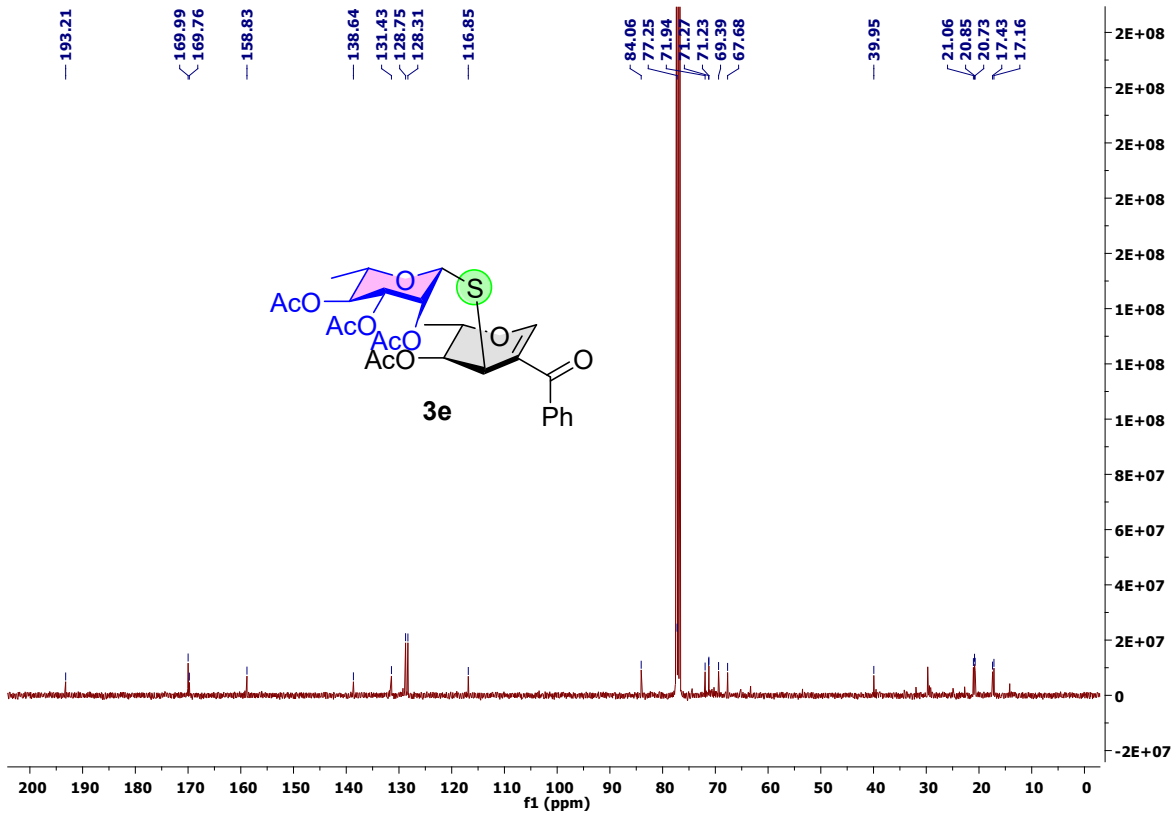


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
551.1580	551.1587	-0.7	-1.3	11.5	830.2	n/a	n/a	C26 H31 O11 S

^{1}H NMR (400 MHz) of **3e** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **3e** in $CDCl_3$



HRMS data of **3e**

Elemental Composition Report

Single Mass Analysis
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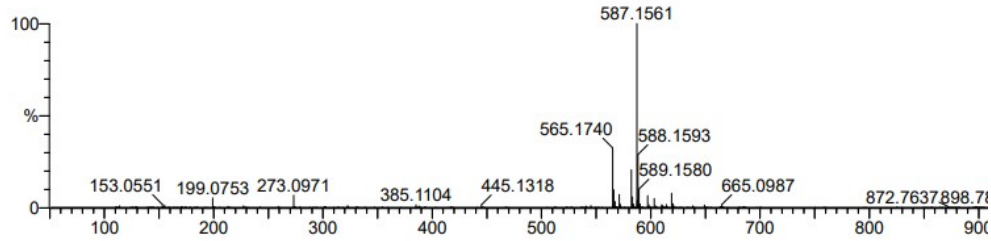
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-27 H: 0-100 O: 0-11 S: 0-1

RHAM-RHAM-SH

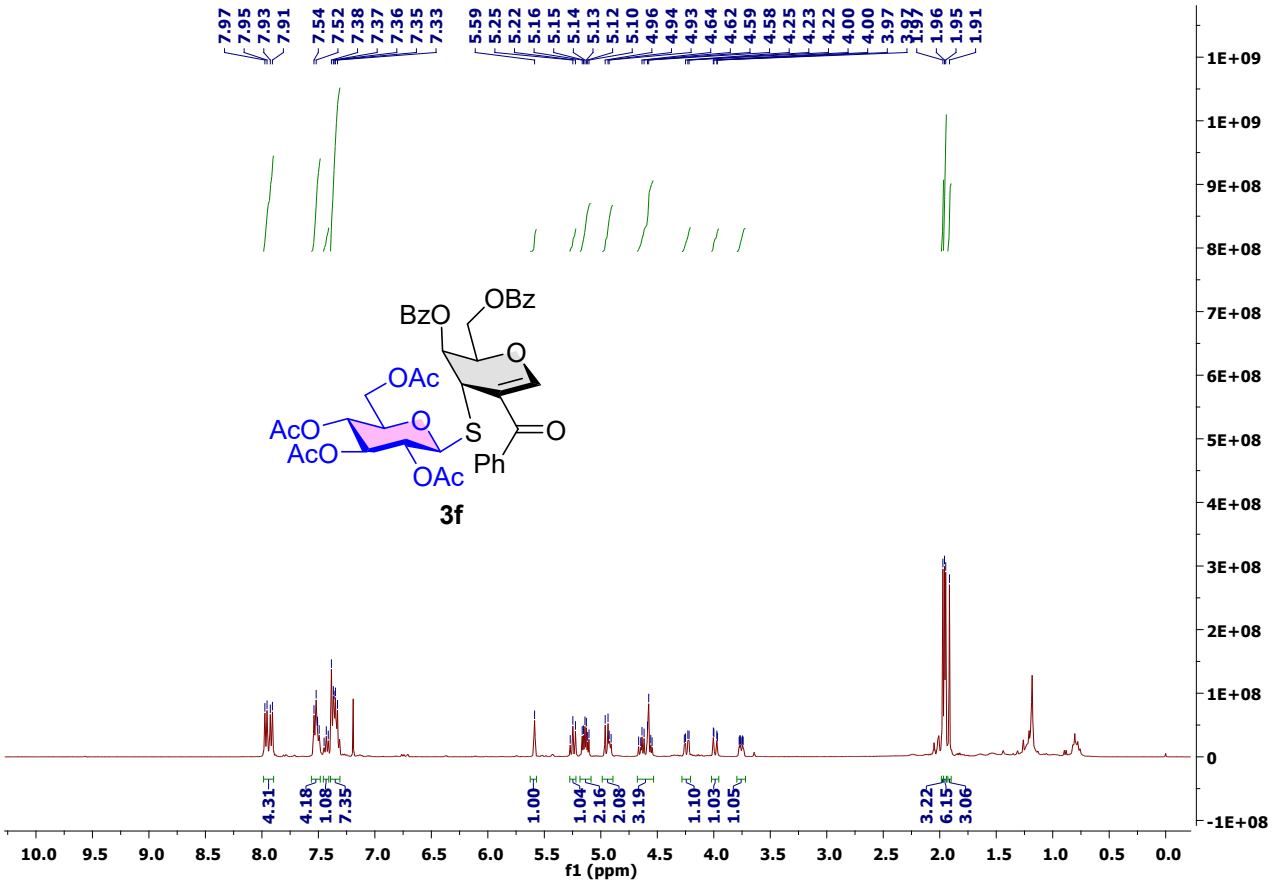
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_08 9 (0.208)

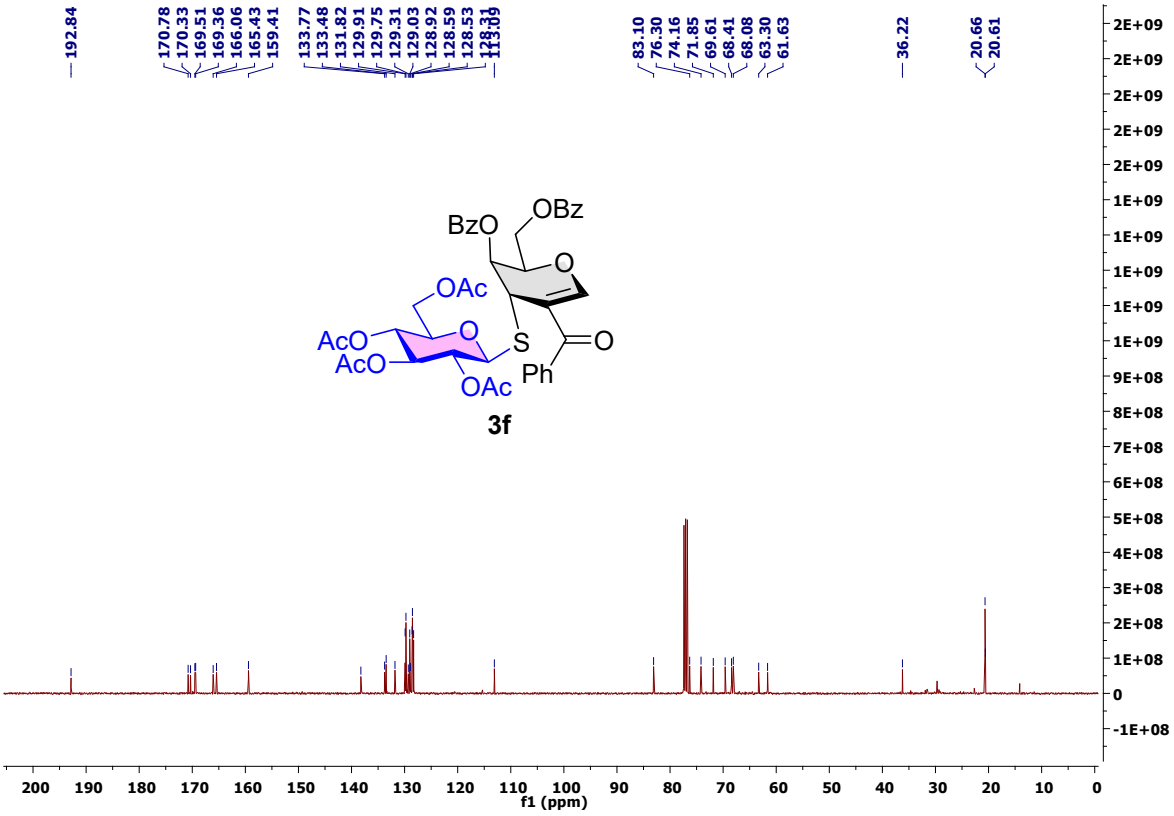


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
565.1740	565.1744	-0.4	-0.7	11.5	811.1	n/a	n/a	C27 H33 O11 S

^{1}H NMR (400 MHz) of **3f** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **3f** in $CDCl_3$



HRMS data of **3f**

Elemental Composition Report

Single Mass Analysis

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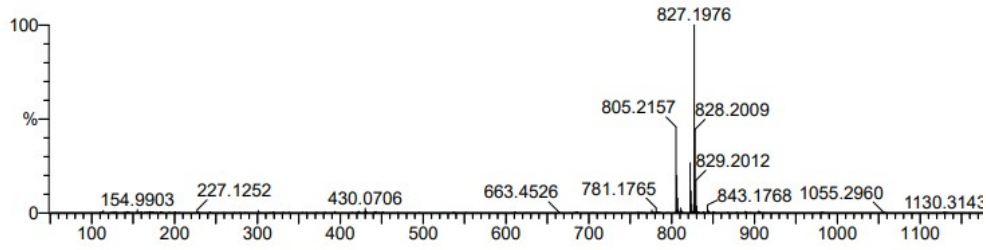
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
39 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-41 H: 0-100 O: 0-15 S: 0-1

GAL- OBZ-GLU SH

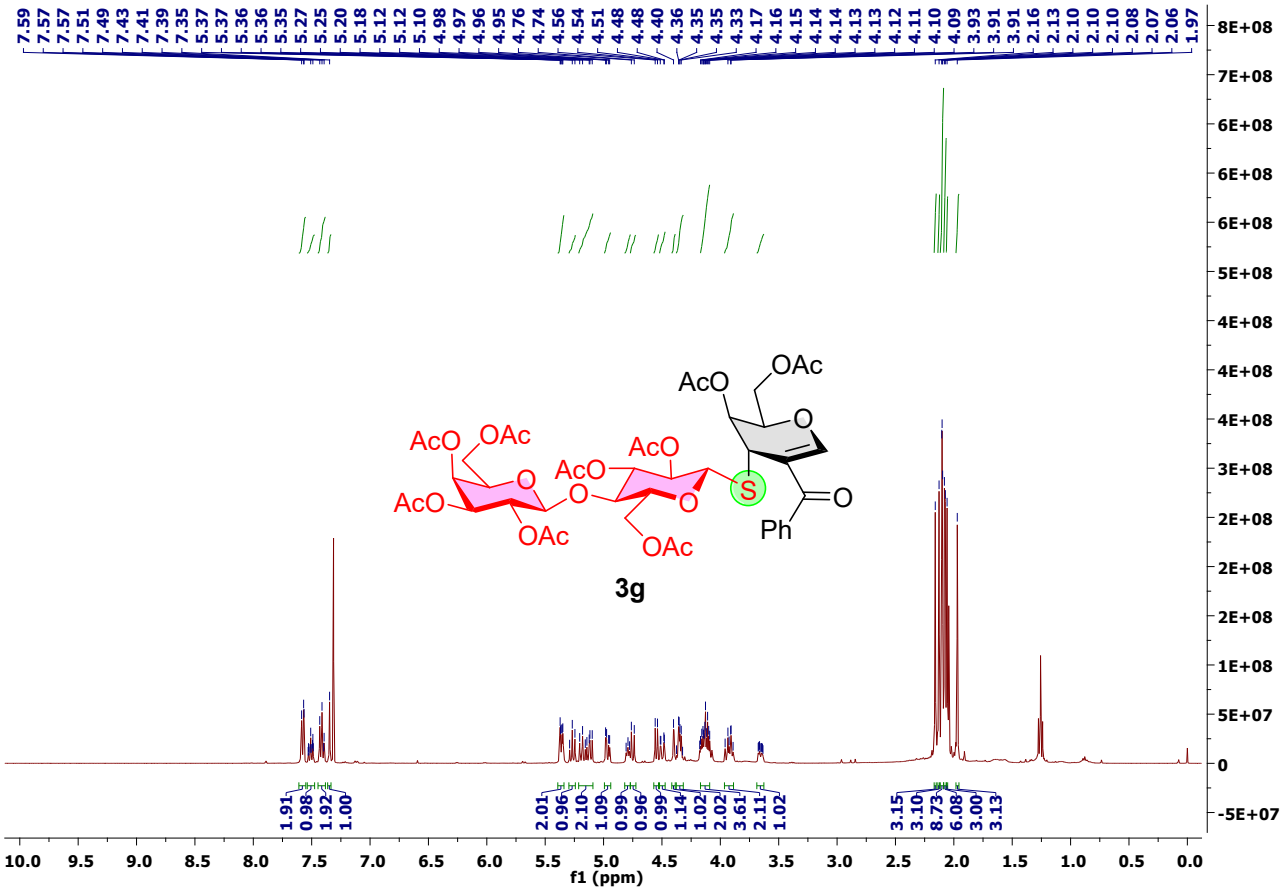
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_02 12 (0.259)

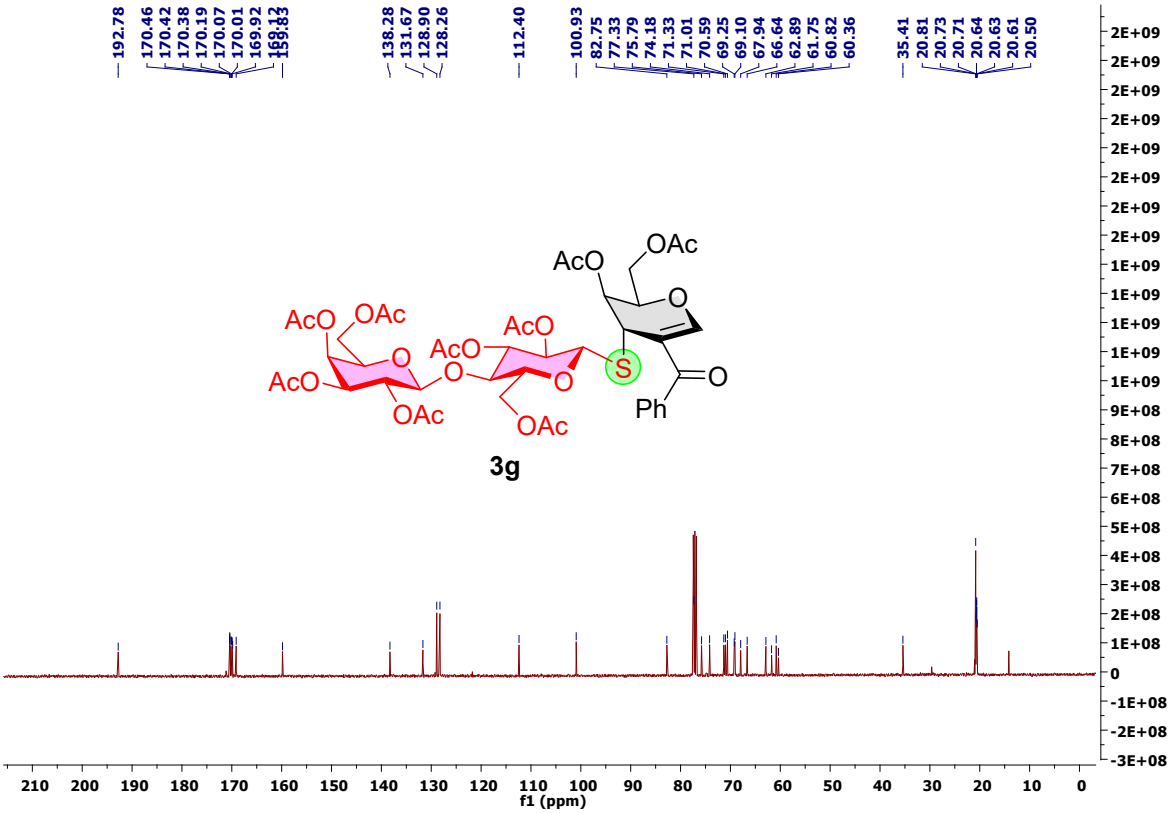


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
805.2157	805.2166	-0.9	-1.1	21.5	549.2	n/a	n/a	C41 H41 O15 S

^{1}H NMR (400 MHz) of **3g** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **3g** in $CDCl_3$



HRMS data of **3g**

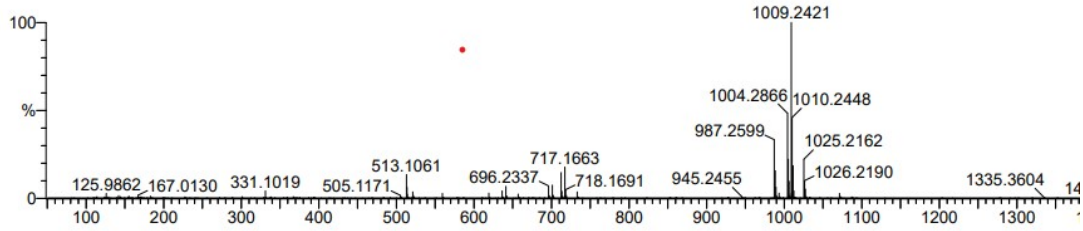
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
102 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-43 H: 0-100 O: 0-23 F: 0-1 S: 0-1
GAL-SIMPCOPH-GLU-SH

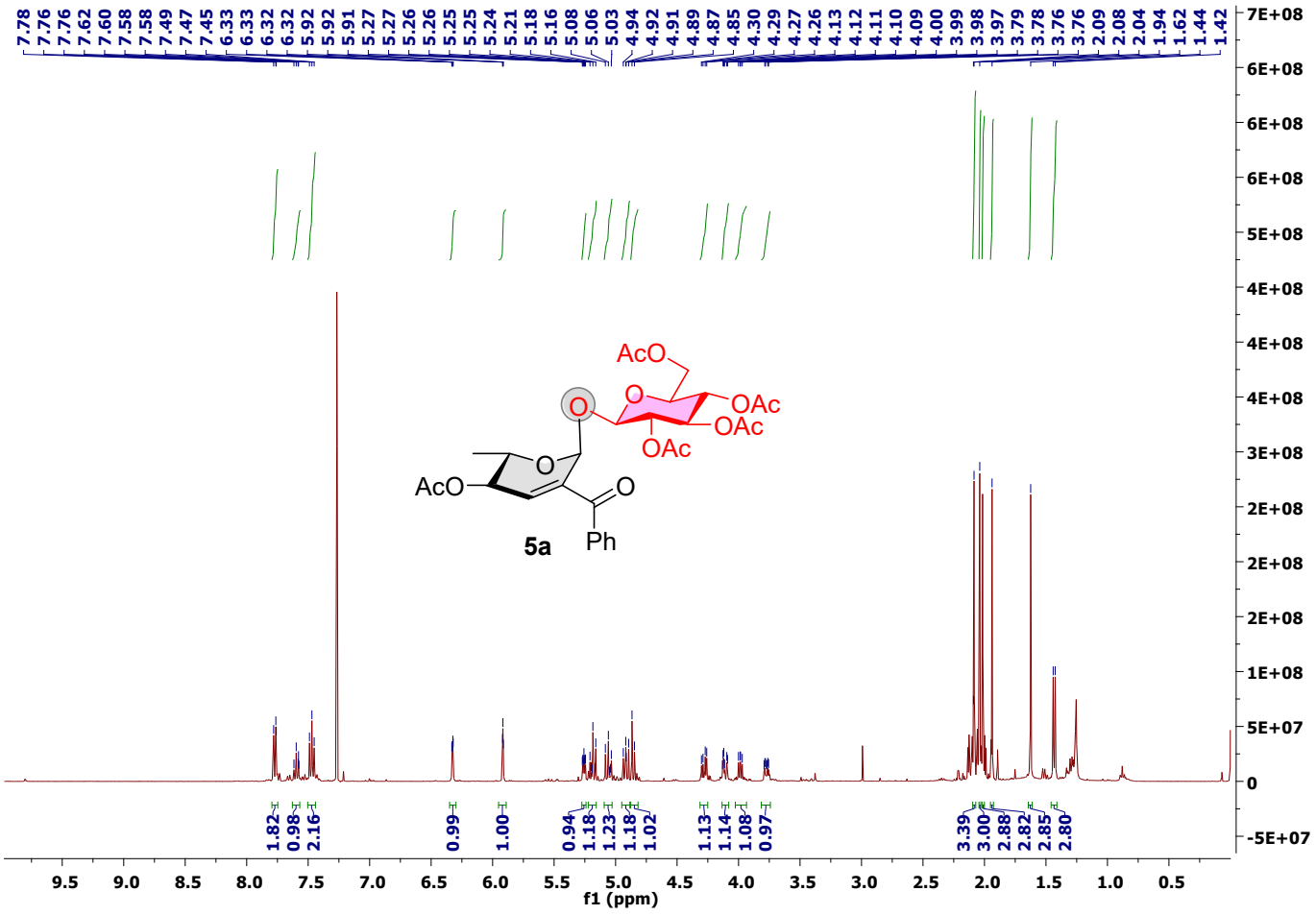
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

140723_05 9 (0.208)

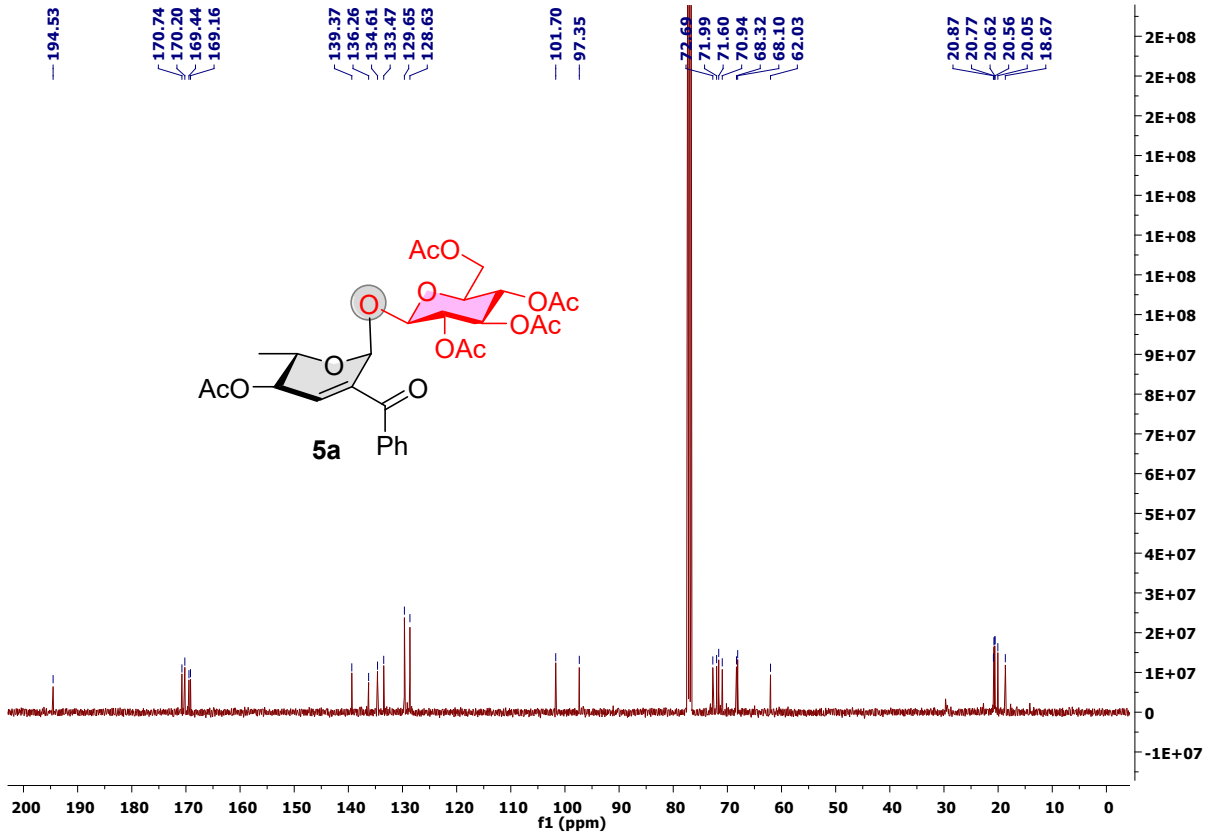


Minimum:				-1.5				
Maximum:		2.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
987.2599	987.2604	-0.5	-0.5	17.5	425.7	n/a	n/a	C43 H52 O23 F S

^{1}H NMR (400 MHz) of **5a** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5a** in $CDCl_3$



HRMS data of **5a**

Elemental Composition Report

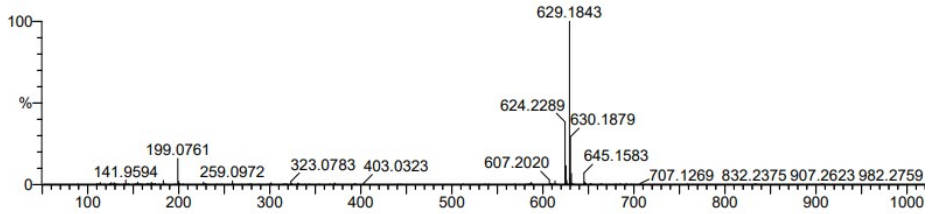
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-29 H: 0-100 N: 0-1 O: 0-14

Rham-Glu-OH

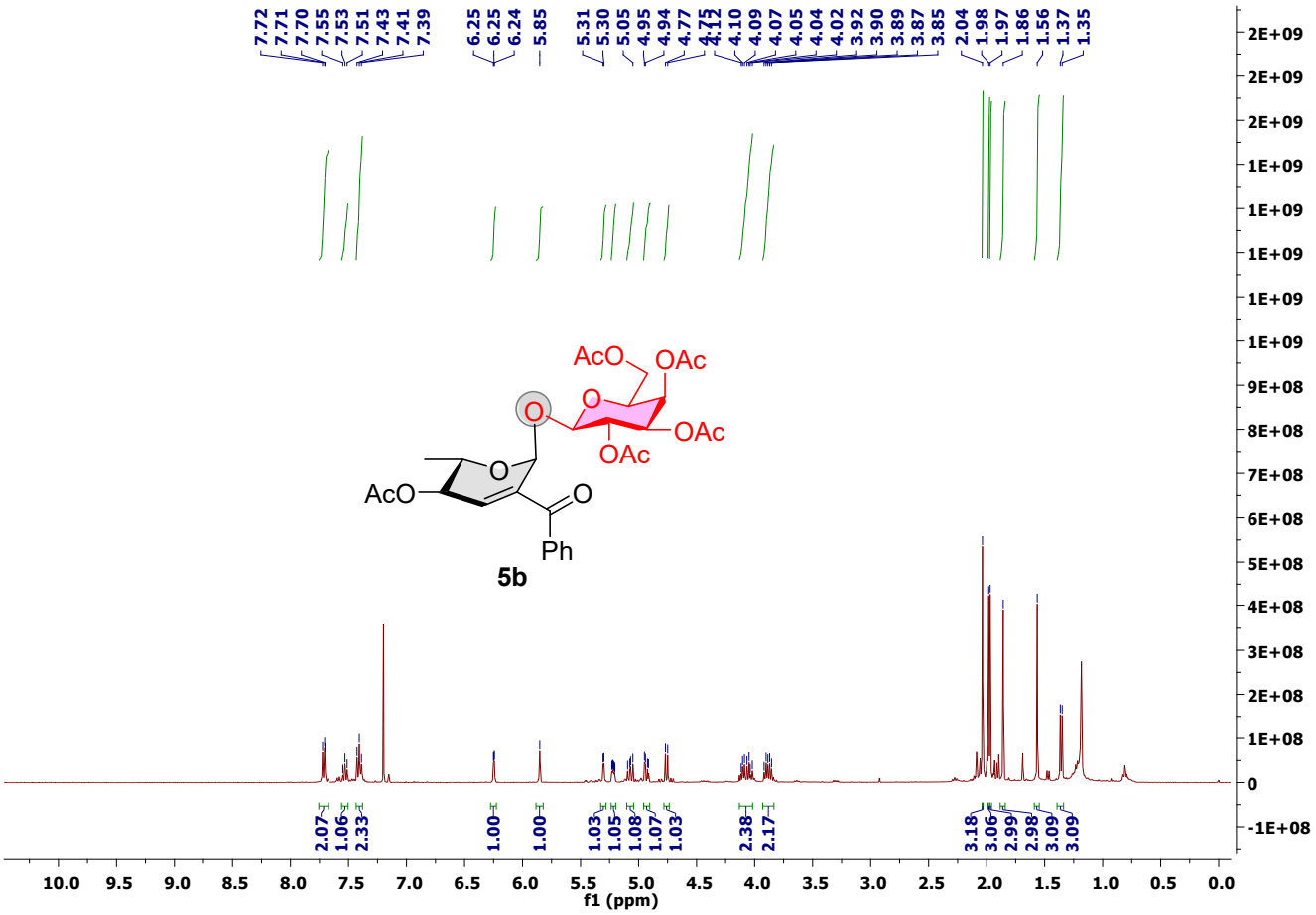
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

060423_19 12 (0.259)

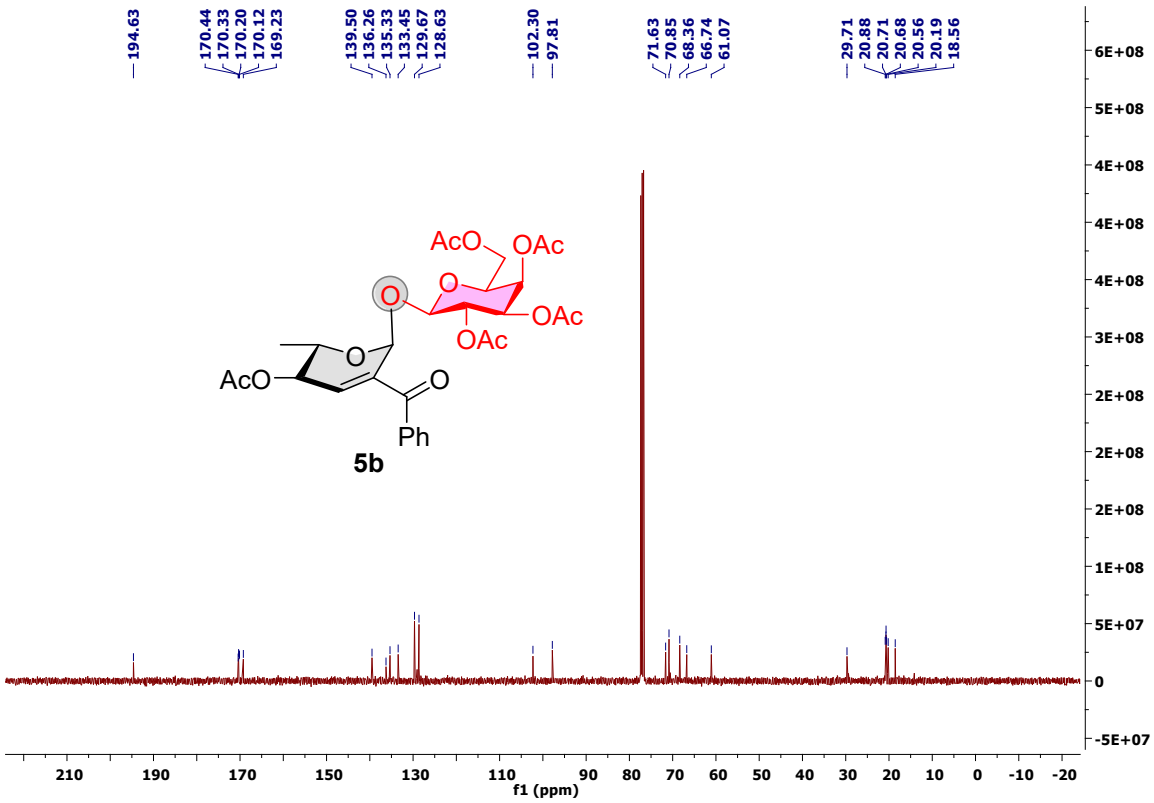


Minimum:				-1.5			
Maximum:		2.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
624.2289	624.2292	-0.3	-0.5	11.5	587.0	n/a	n/a	C29 H38 N O14

^{1}H NMR (400 MHz) of **5b** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5b** in $CDCl_3$



HRMS data of **5b**

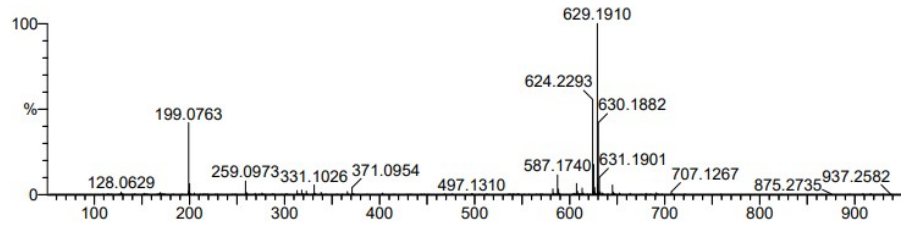
Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-29 H: 0-100 N: 0-1 O: 0-14
Rham-Gal-OH

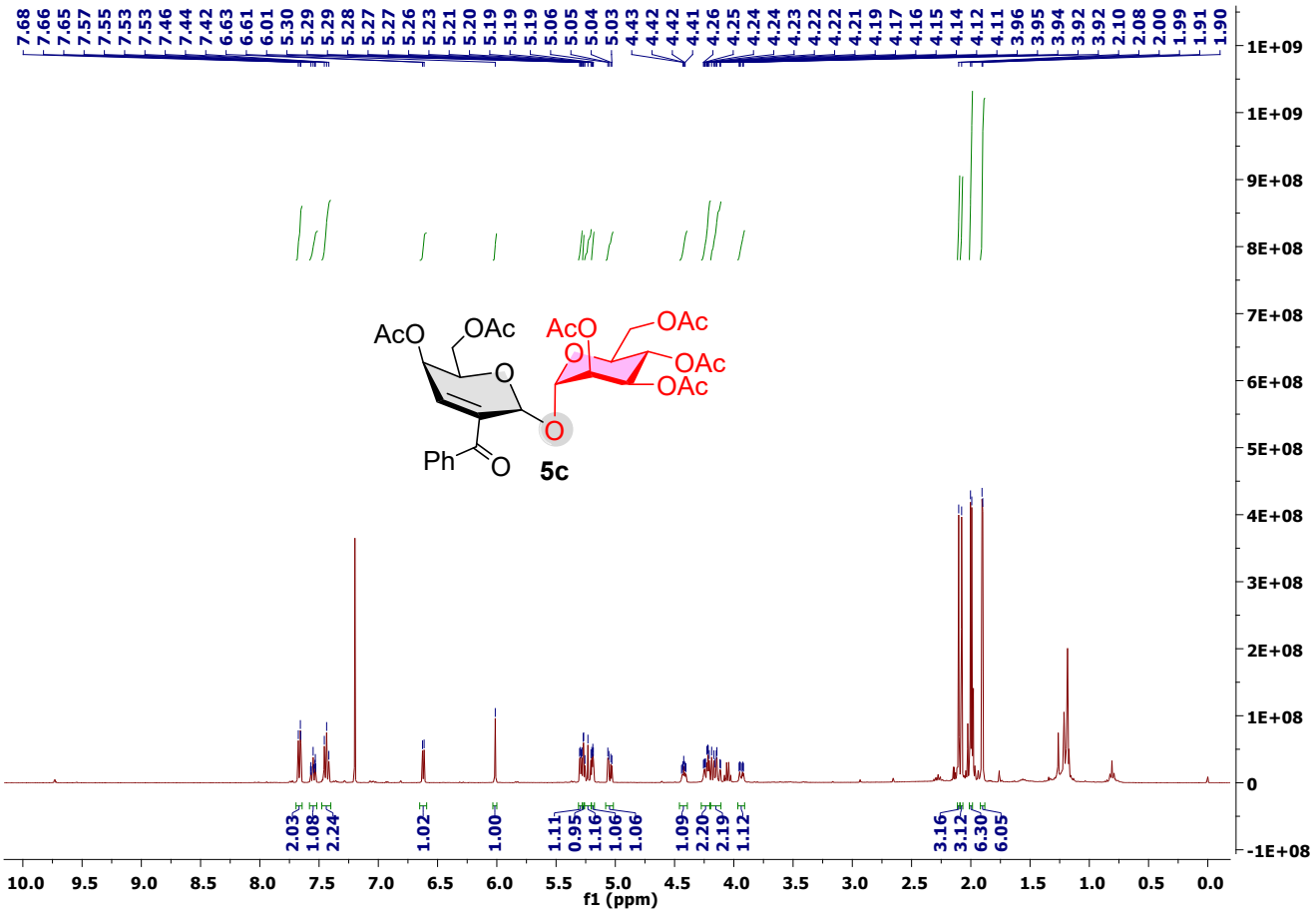
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

060423_18 7 (0.155)

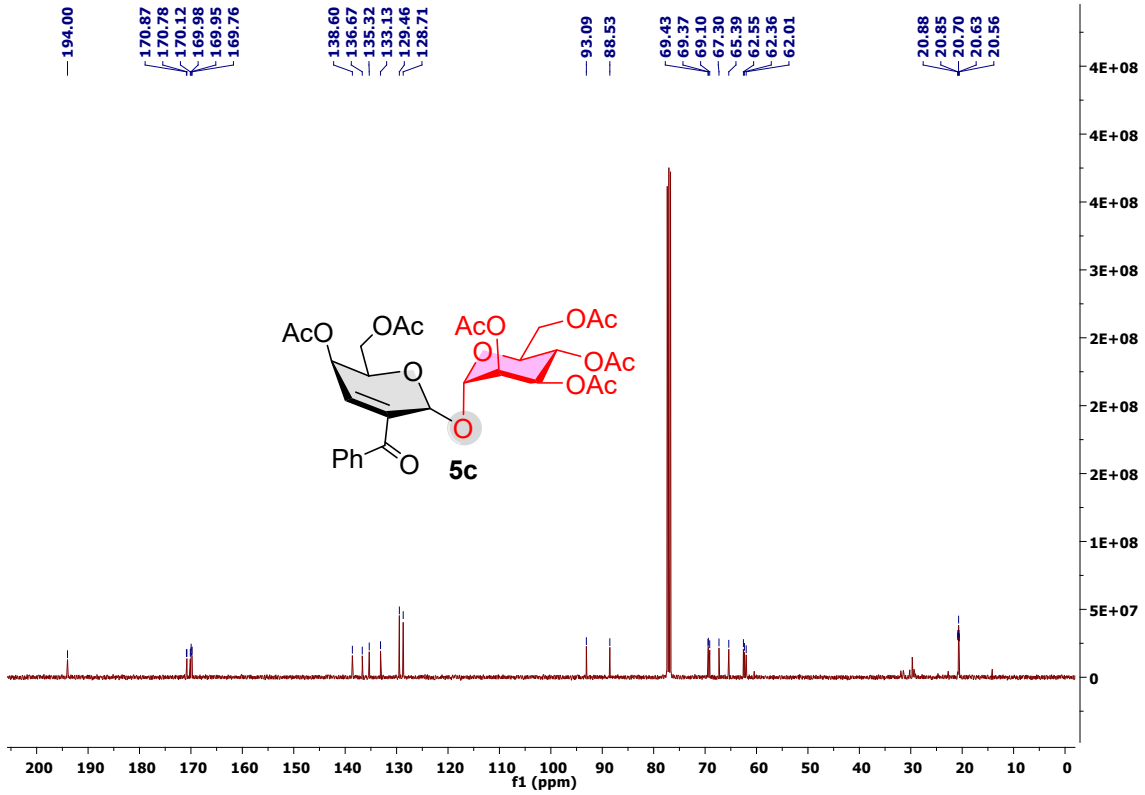


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
624.2293	624.2292	0.1	0.2	11.5	705.3	n/a	n/a	C29 H38 N O14

^{1}H NMR (400 MHz) of **5c** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5c** in $CDCl_3$



HRMS data of **5c**

Elemental Composition Report

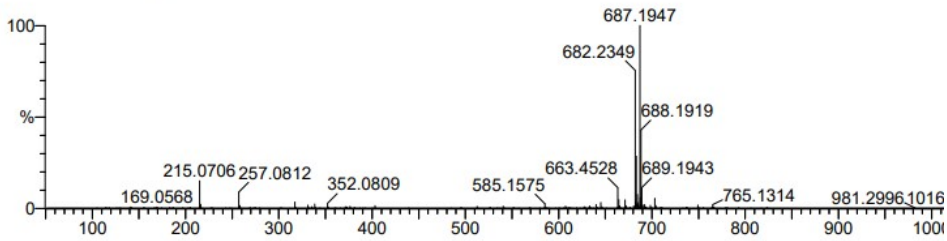
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
38 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-31 H: 0-100 N: 0-1 O: 0-16

Gal-Man-UP

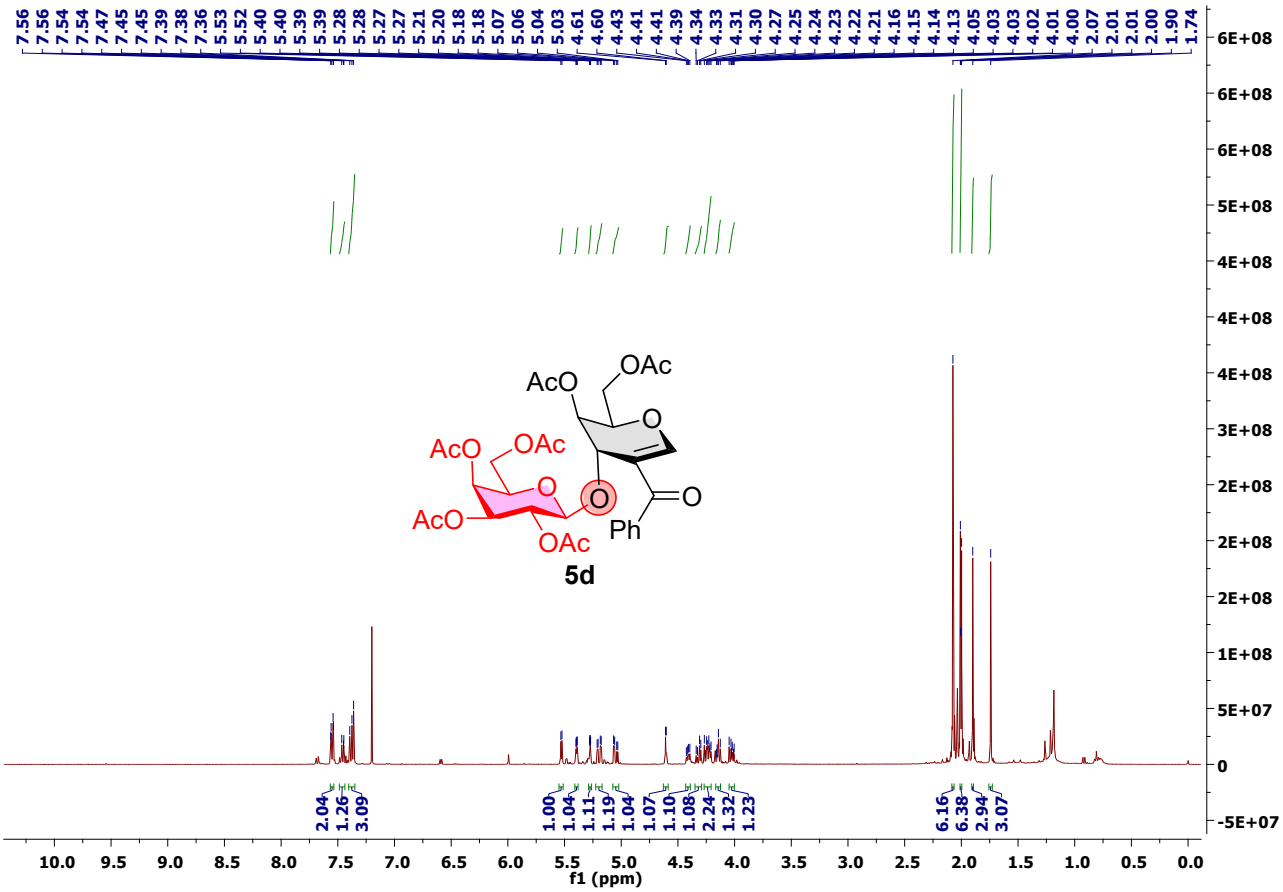
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

060423_16 7 (0.155)

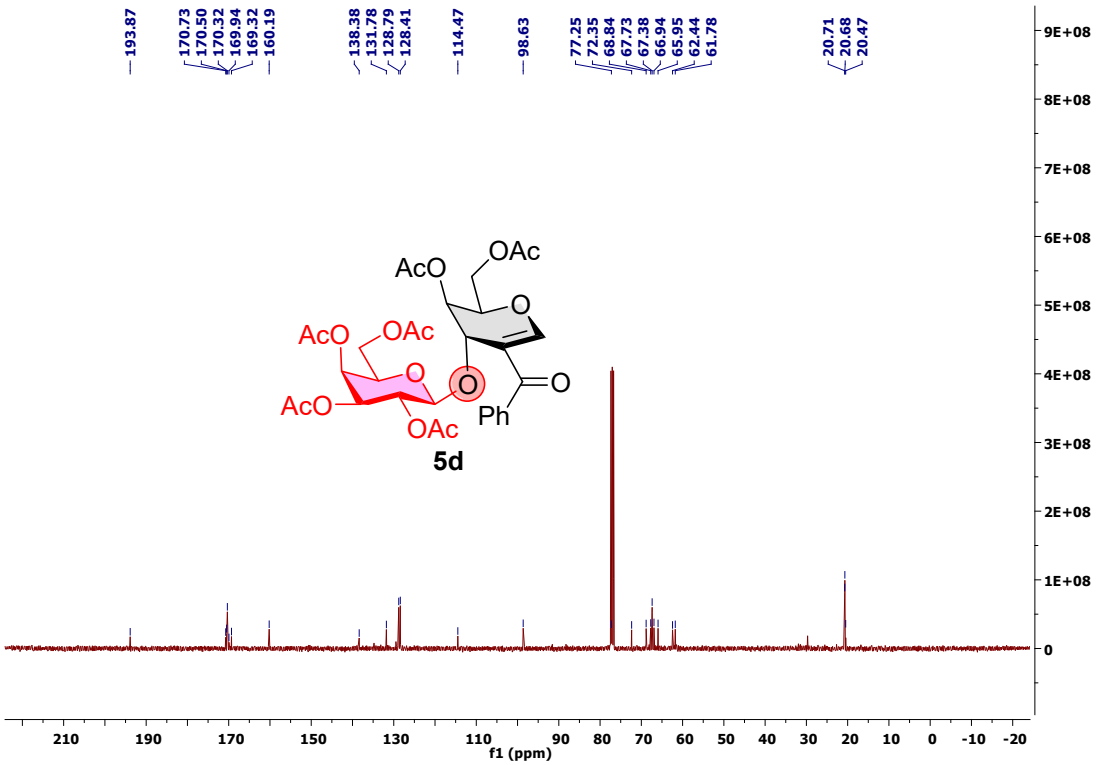


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
682.2349	682.2347	0.2	0.3	12.5	567.8	n/a	n/a	C31 H40 N O16

^{1}H NMR (400 MHz) of **5d** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5d** in $CDCl_3$



HRMS data of **5d**

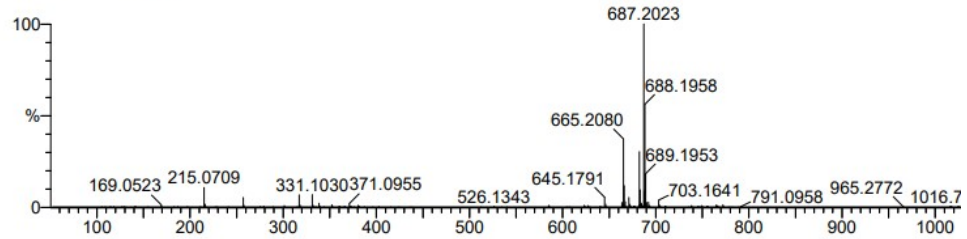
Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-31 H: 0-100 O: 0-16
Gal-Gal-OH

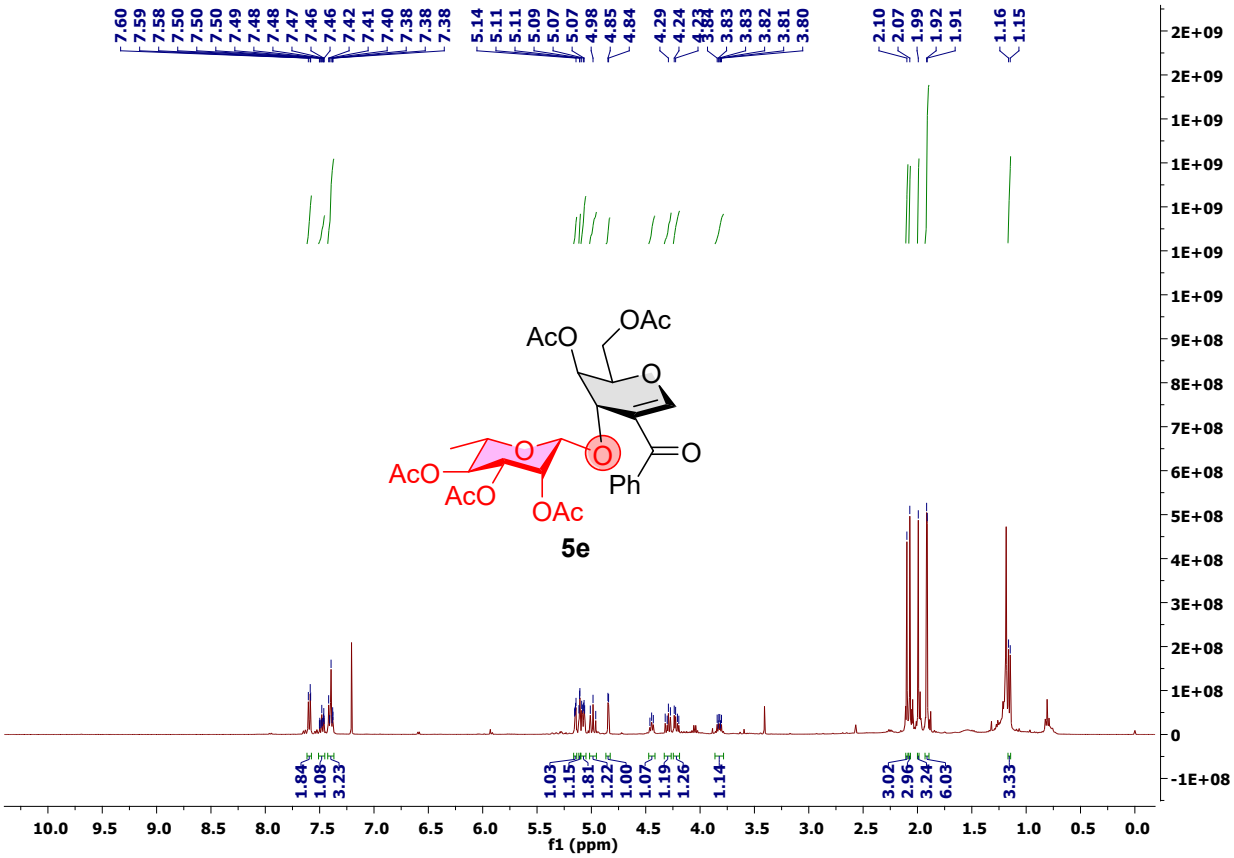
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

060423_15 5 (0.121)

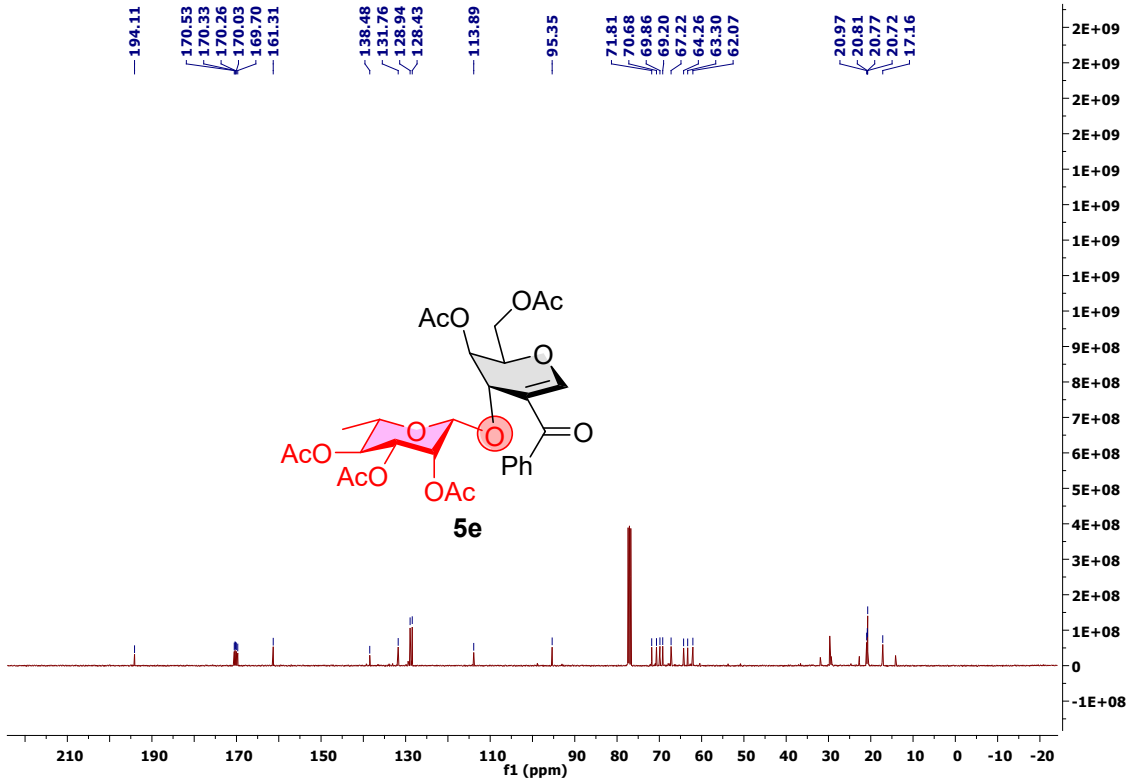


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
665.2080	665.2082	-0.2	-0.3	13.5	698.0	n/a	n/a	C31 H37 O16

^{1}H NMR (400 MHz) of **5e** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5e** in $CDCl_3$



HRMS data of **5e**

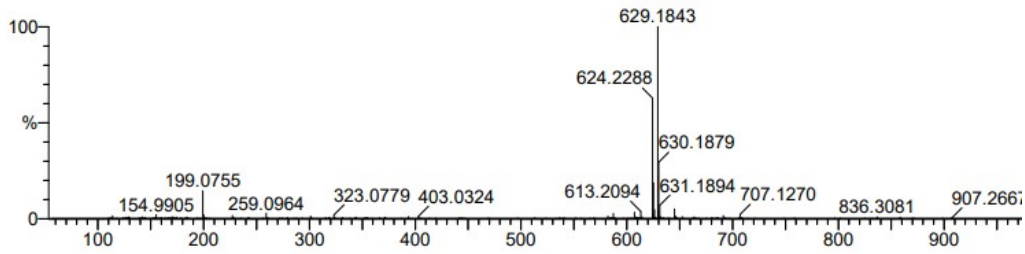
Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-29 H: 0-100 O: 0-14 Na: 0-1
GAL-RHAM- OH

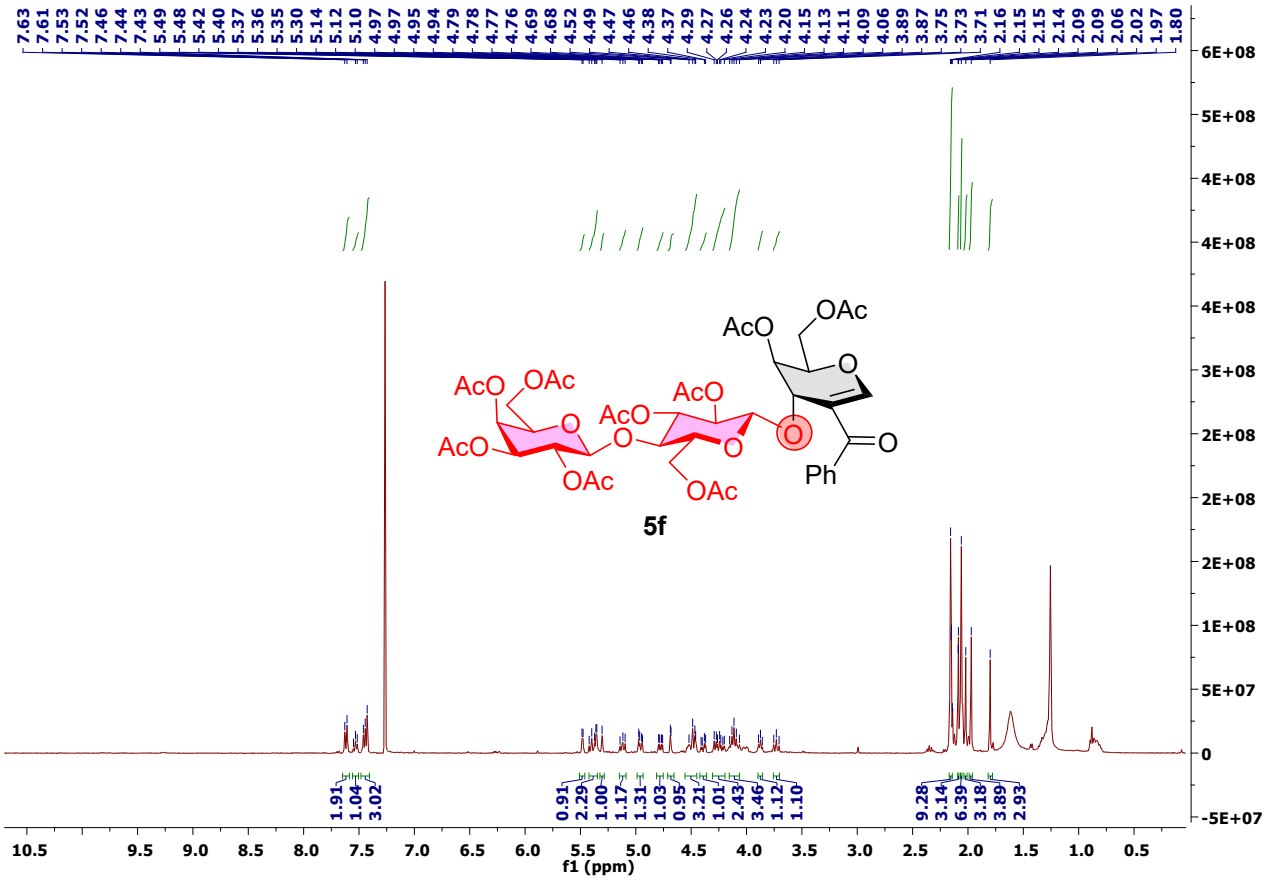
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_06 9 (0.208)

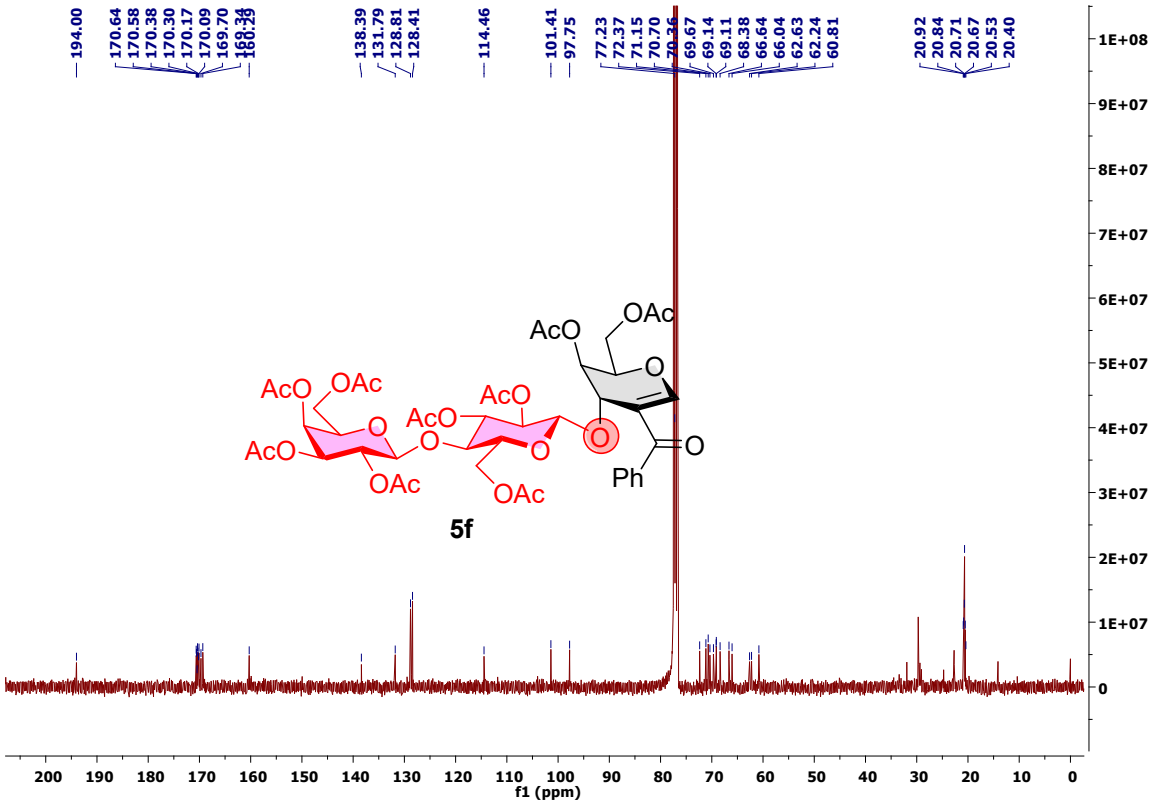


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
629.1843	629.1846	-0.3	-0.5	12.5	676.6	n/a	n/a	C29 H34 O14 Na

^{1}H NMR (400 MHz) of **5f** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **5f** in $CDCl_3$



HRMS data of **5f**

Elemental Composition Report

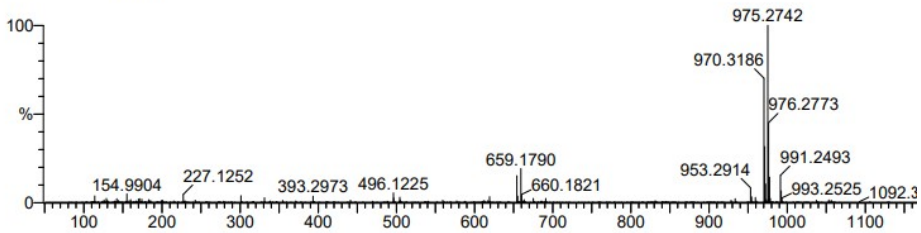
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
23 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-43 H: 0-53 O: 0-24

GAL-LAC-UP

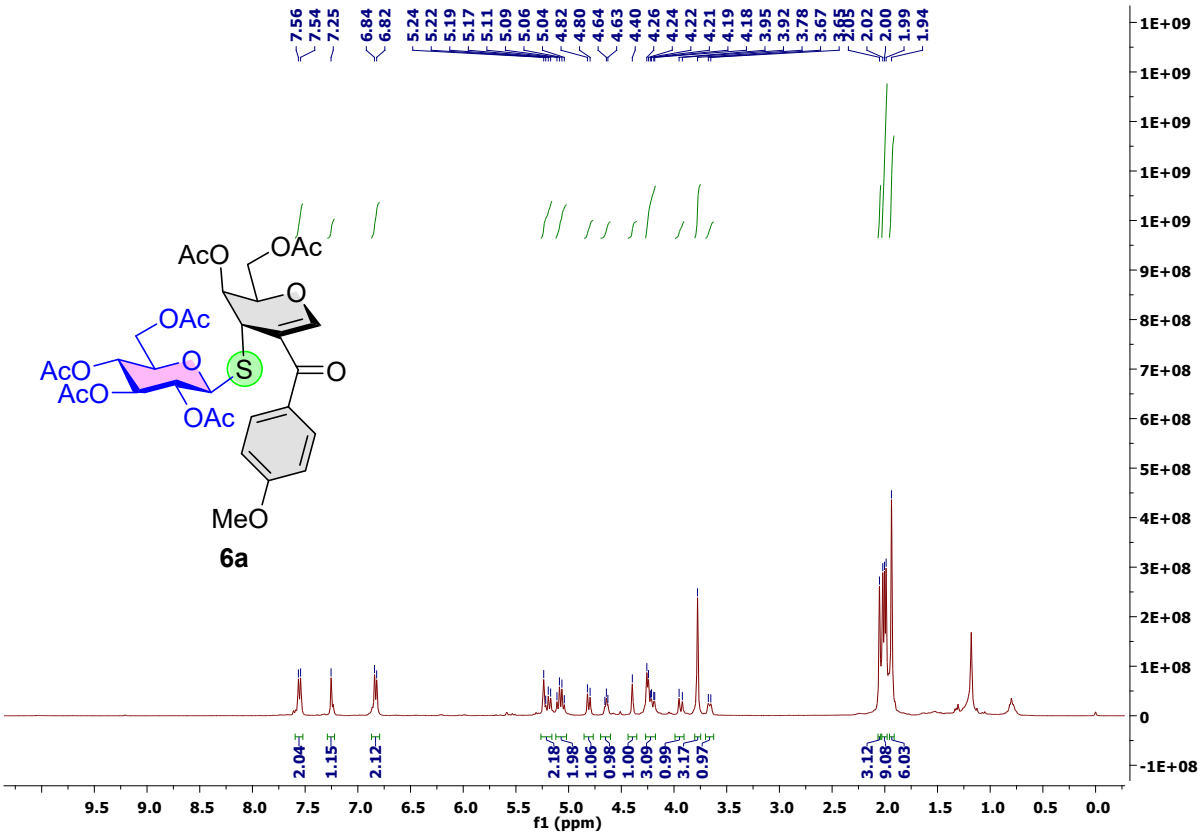
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_07 12 (0.259)

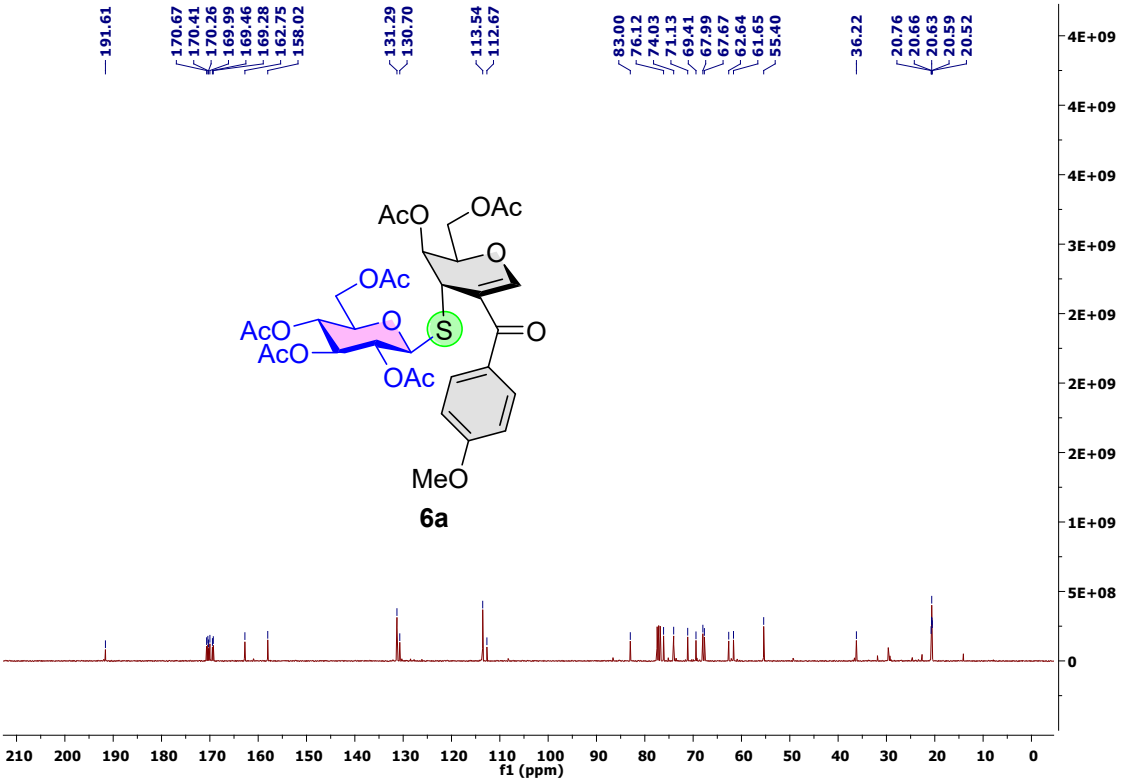


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
953.2914	953.2927	-1.3	-1.4	17.5	562.3	n/a	n/a	C43 H53 O24

^{1}H NMR (400 MHz) of **6a** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **6a** in $CDCl_3$



HRMS data of **6a**

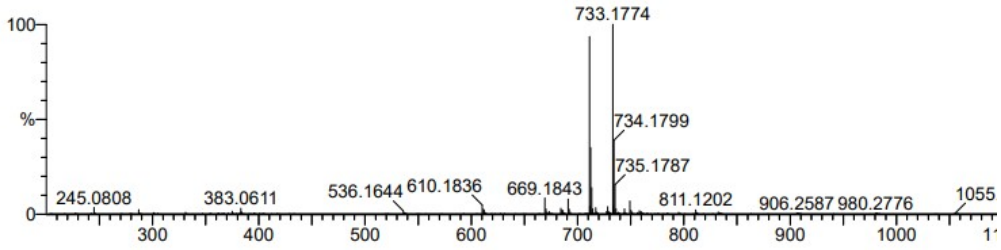
Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
37 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-32 H: 0-100 O: 0-16 S: 0-1
GAL-4 METH-GLU

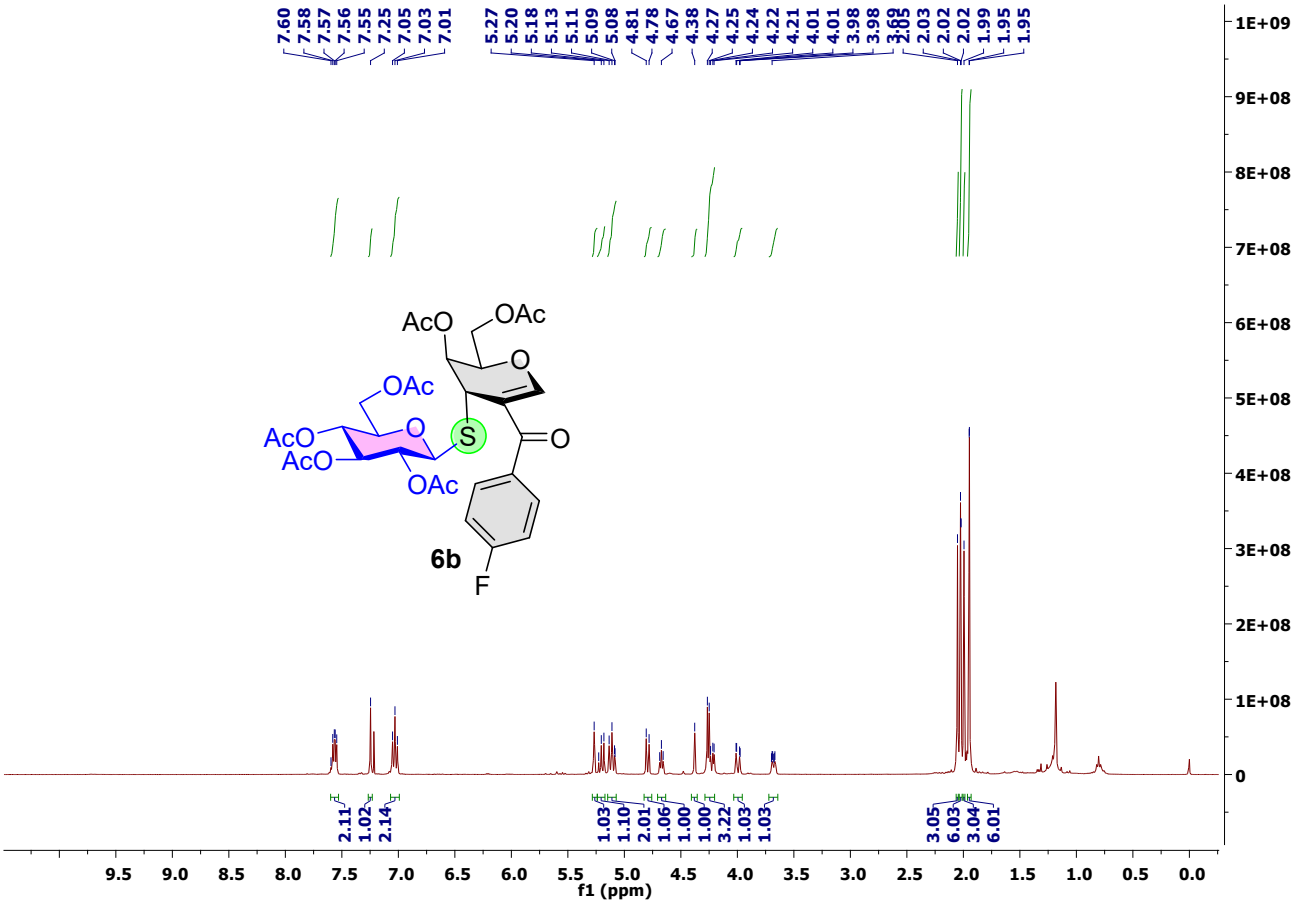
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_04 12 (0.259)

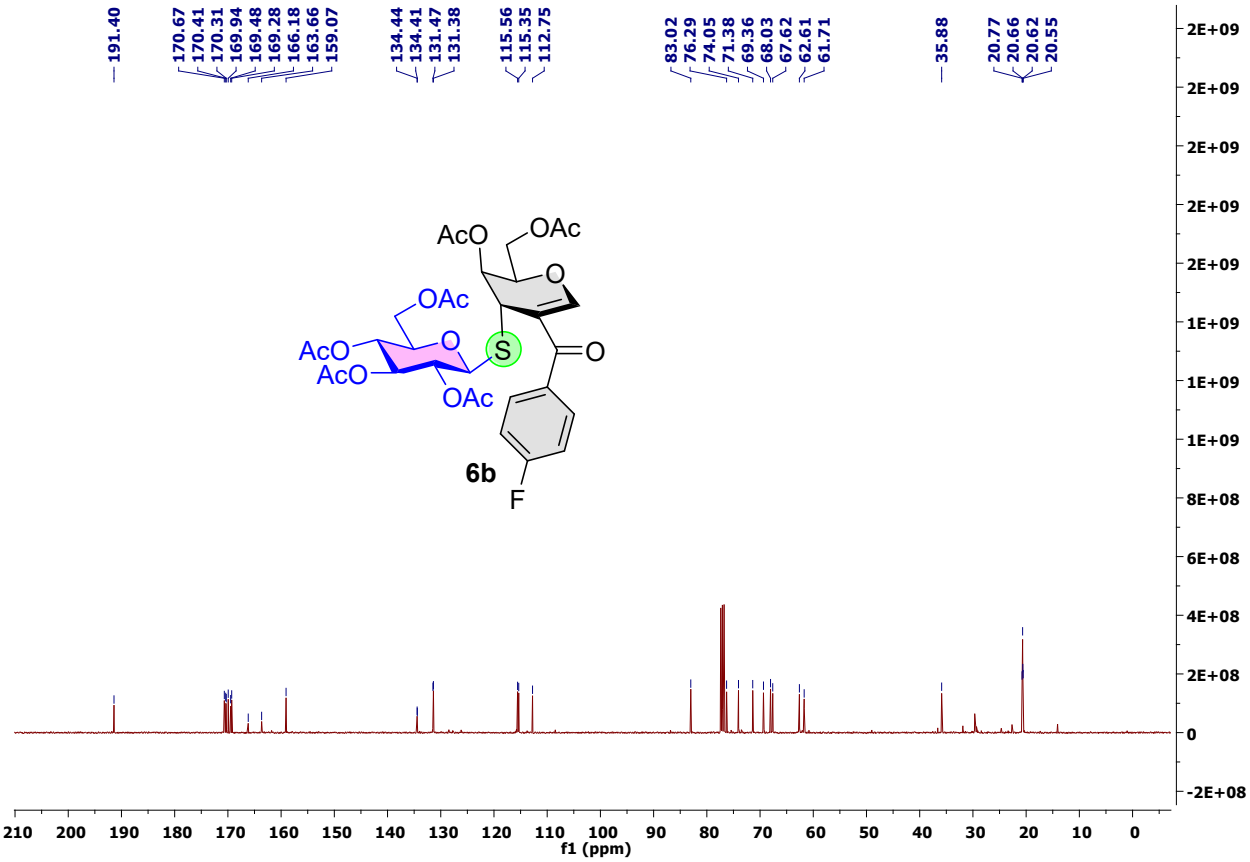


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
711.1953	711.1959	-0.6	-0.8	13.5	603.9	n/a	n/a	C32 H39 O16 S

^{1}H NMR (400 MHz) of **6b** in $CDCl_3$



^{13}C NMR {^{1}H} (101 MHz) of **6b** in $CDCl_3$



HRMS data of **6b**

Elemental Composition Report

Single Mass Analysis

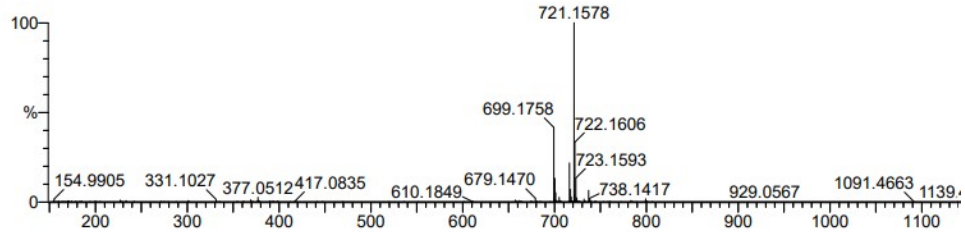
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
68 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-31 H: 0-100 O: 0-15 F: 0-1 S: 0-1

GAL-4F-GLU-SH

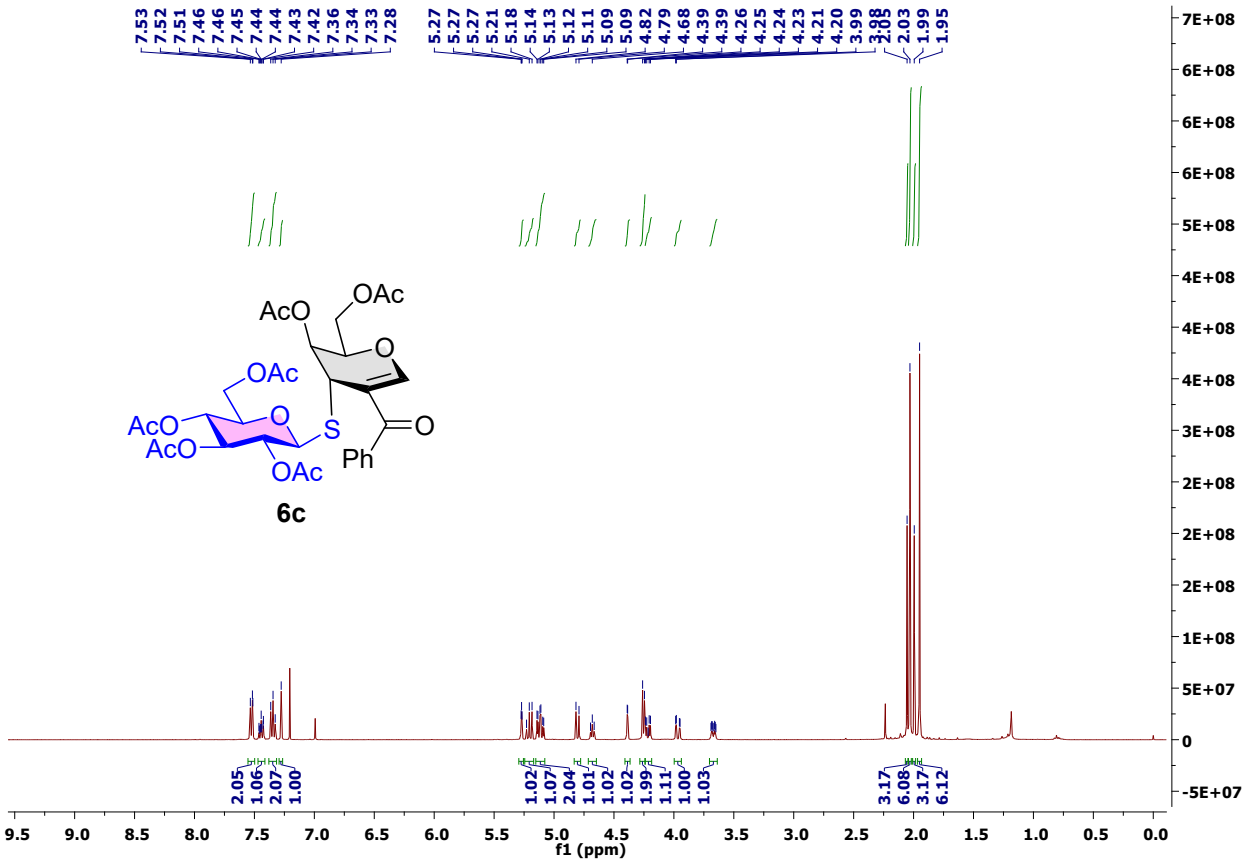
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240523_09 21 (0.431)

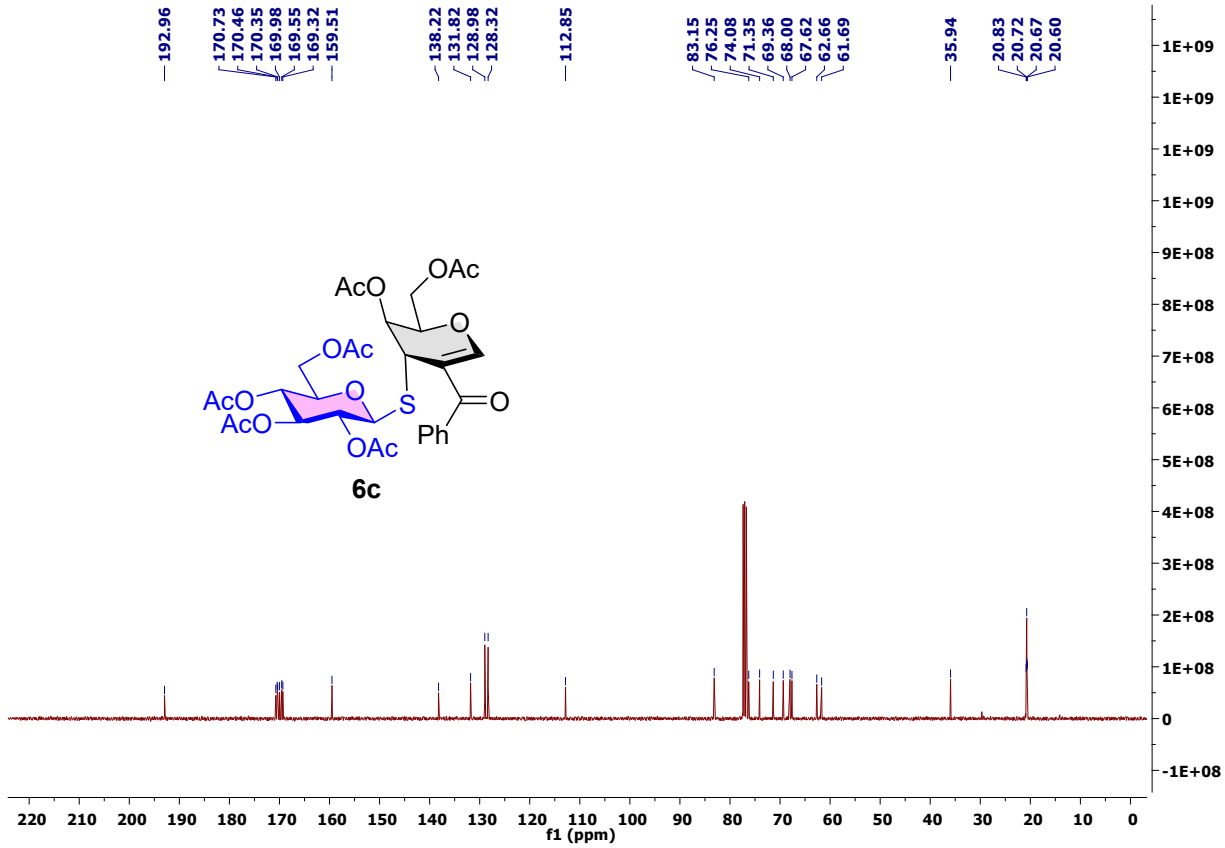


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
699.1758	699.1759	-0.1	-0.1	13.5	640.5	n/a	n/a	C31 H36 O15 F S

^{1}H NMR (400 MHz) of **6c** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **6c** in $CDCl_3$



HRMS data of **6c**

Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
35 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-31 H: 0-100 O: 0-15 S: 0-1
GAL-GLU-SH

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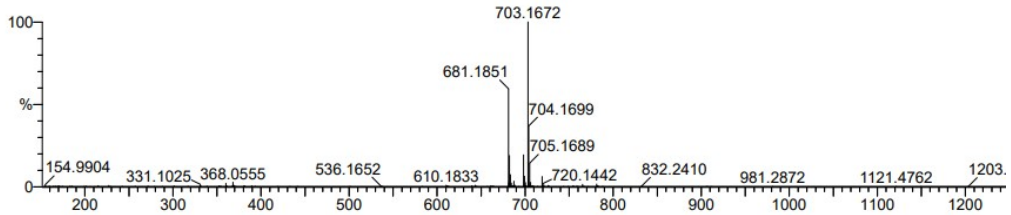
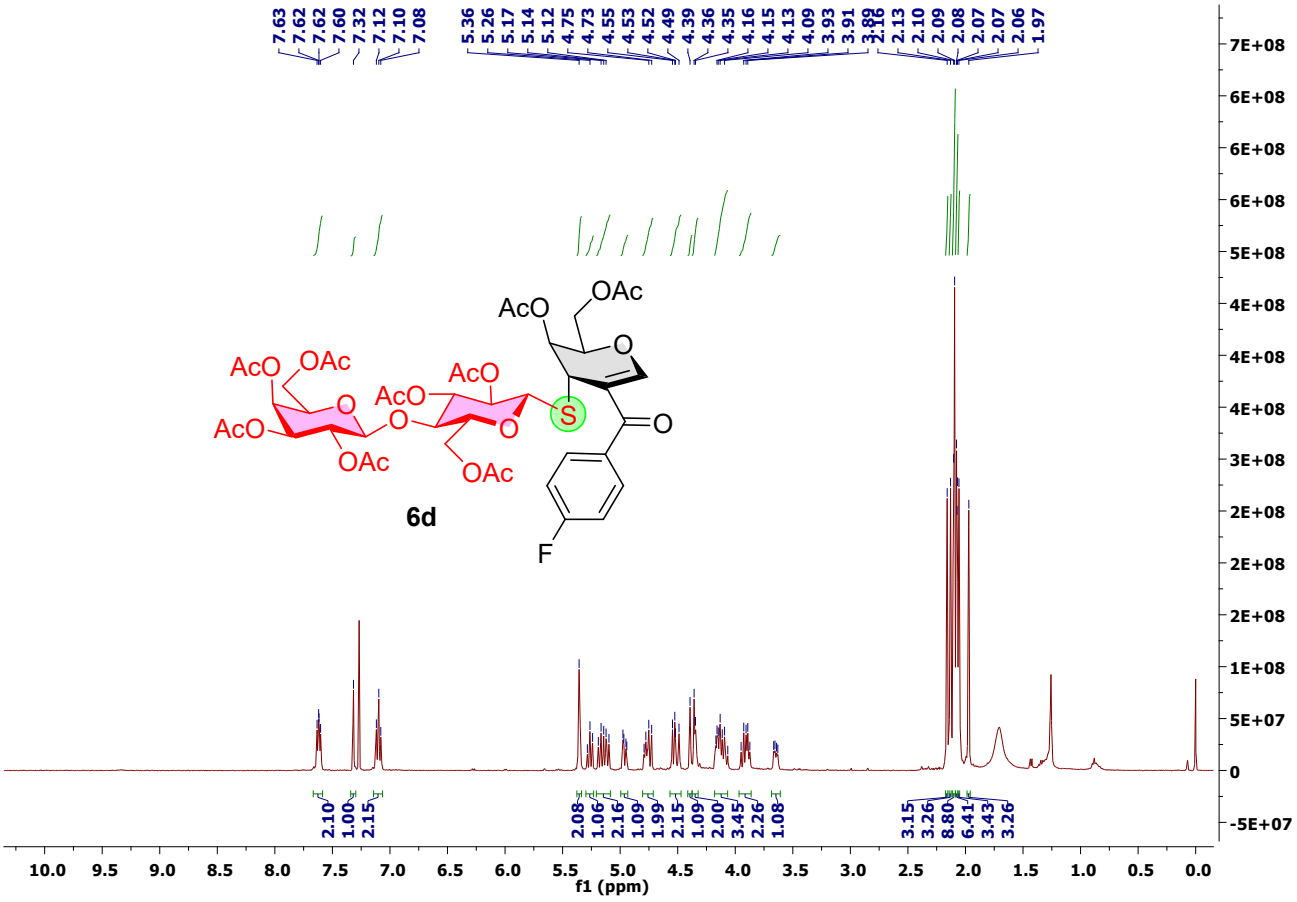
Xevo G2-XS QTOF YFC2015

240523_10 9 (0.208)

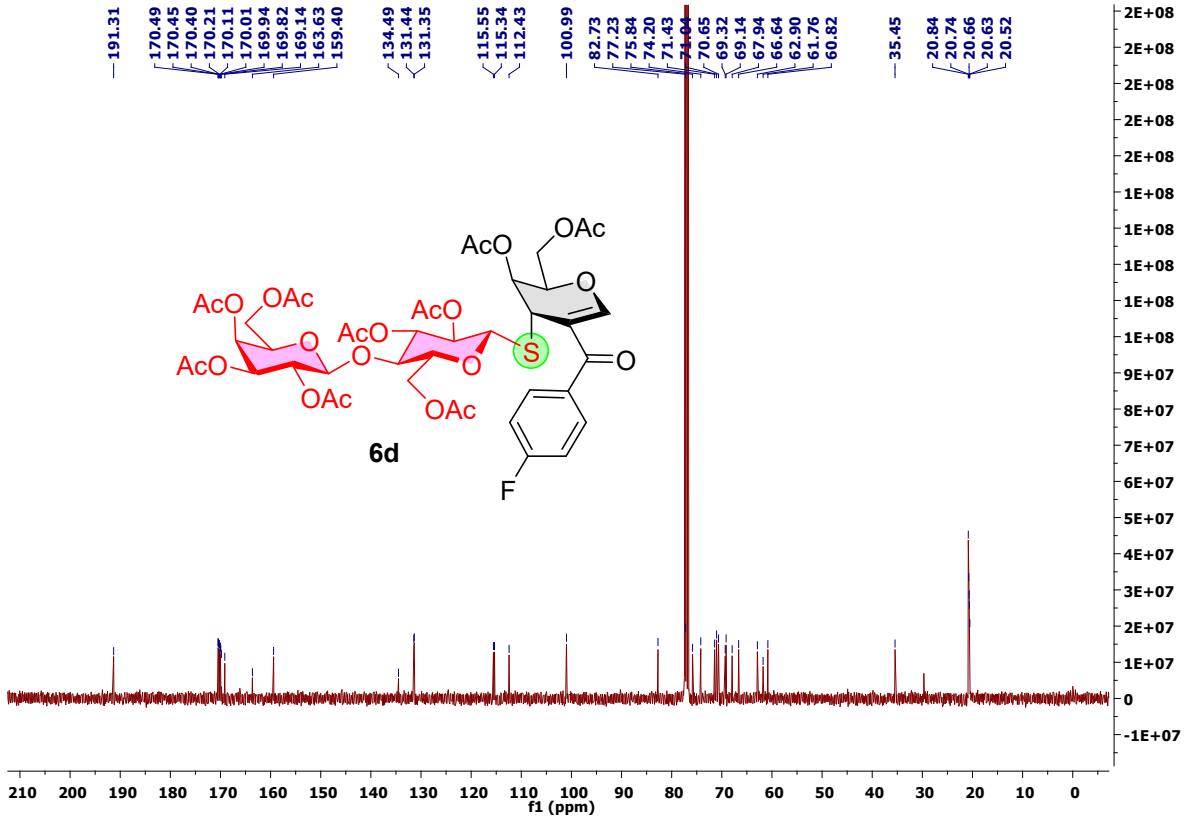


Minimum:				-1.5				
Maximum:		2.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
681.1851	681.1853	-0.2	-0.3	13.5	688.8	n/a	n/a	C31 H37 O15 S

^{1}H NMR (400 MHz) of **6d** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **6d** in $CDCl_3$



HRMS data of **6d**

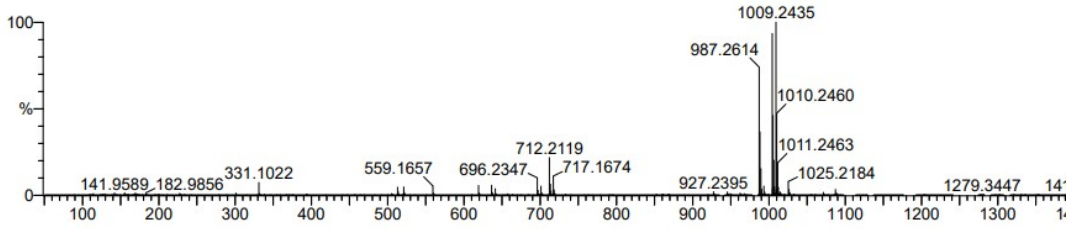
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
102 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-43 H: 0-100 O: 0-23 F: 0-1 S: 0-1
GAL-COPH-4F-GAL-SH

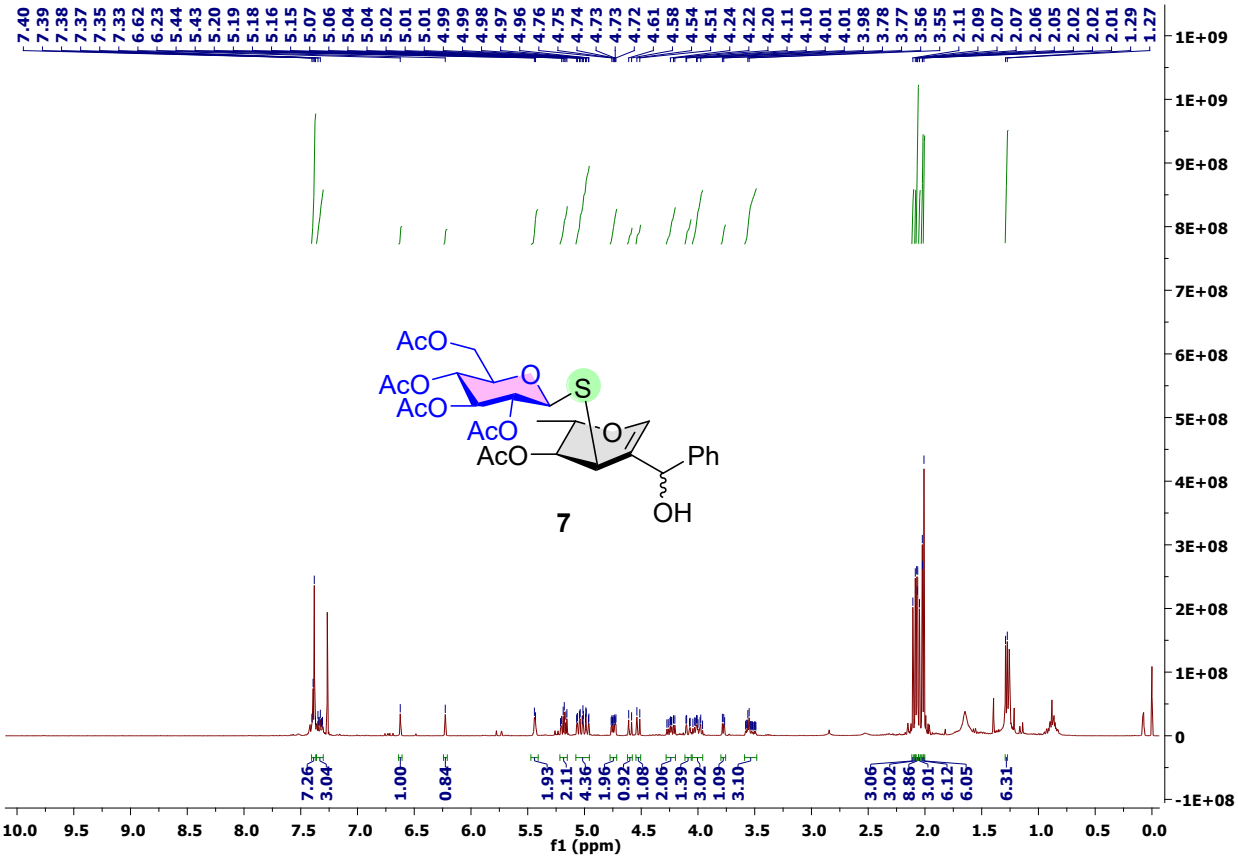
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

140723_04 4 (0.104)

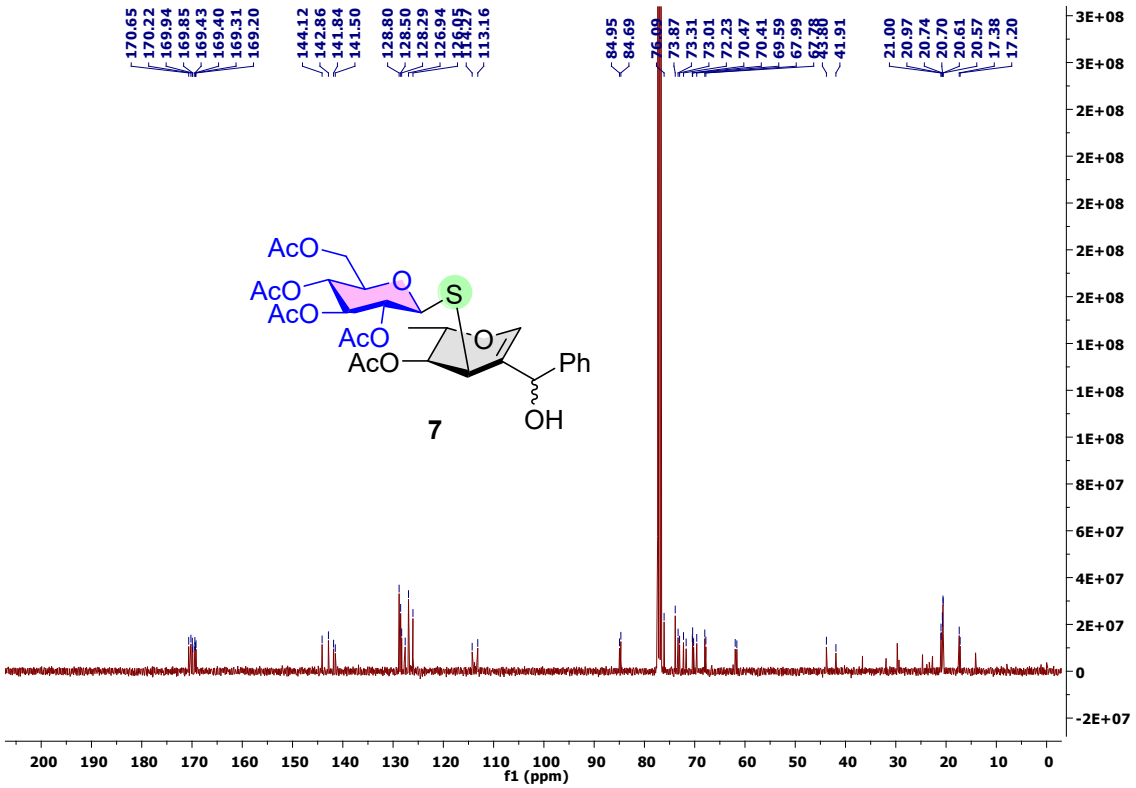


Minimum:				-1.5			
Maximum:		2.0	50.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
987.2614	987.2604	1.0	1.0	17.5	404.4	n/a	n/a	C43 H52 O23 F S

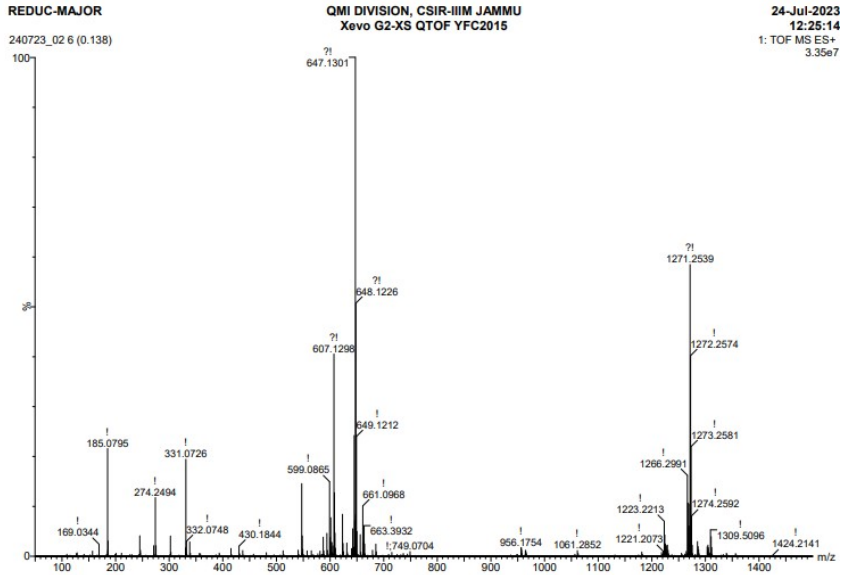
^{1}H NMR (400 MHz) of **7** in $CDCl_3$



^{13}C NMR $\{^{1}H\}$ (101 MHz) of **7** in $CDCl_3$

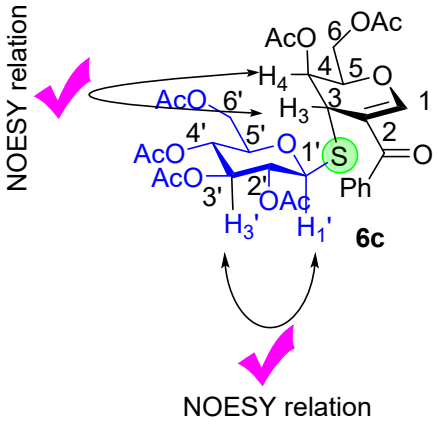


HRMS data of **7**



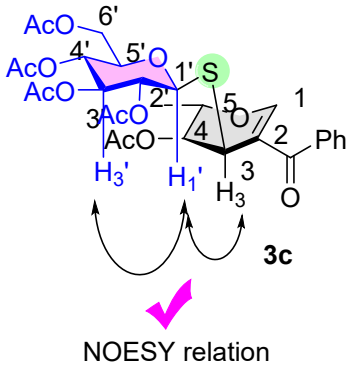
2D NMR DATA

HSQC of compound 6c



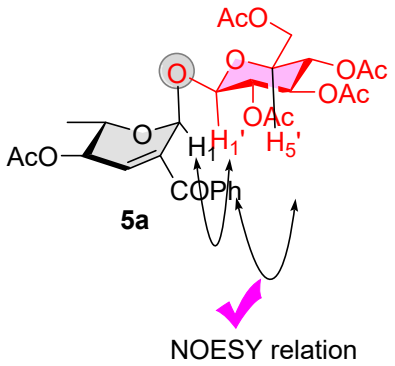
HSQC table of compound 6c

	^{1}H	^{13}C
1.	H-1= 7.28 (s, 1H)	159.6
2.	(q)	112.8
3.	H-3 = 4.39 (d, *J* = 1.4 Hz, 1H)	35.8
4.	H-4= 5.27 (m, 1H)	67.6
5.	H-5= 4.22 (dd, *J* = 12.5, 4.3 Hz, 1H)	61.5
6.	H-6= 3.97 (dd, *J* = 12.4, 2.2 Hz, 1H)	61.7
1'.	H-1'= 4.80 (d, *J* = 10.1 Hz, 1H)	83.3
2'.	H-2'= 5.20 (d, *J* = 9.2 Hz, 1H)	74.0
3'.	H-3'= 3.67 (ddd, *J* = 9.9, 4.2, 2.3 Hz, 1H)	76.3
4'.	H-2' & H-4'= 5.11 (td, *J* = 9.8, 3.2 Hz, 2H)	69.3 &67.9
5'.	H-5'= 4.68 (t, *J* = 6.1 Hz, 1H)	71.1
6'.	H-6'= 4.25 (d, *J* = 6.2 Hz, 1H)	62.7



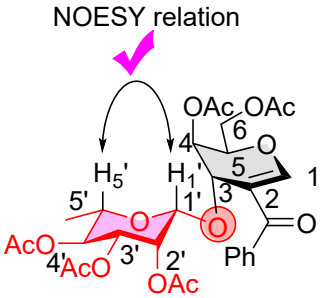
HSQC table of compound 3c

	^{1}H	**^{13}C**
1.	H-1= 7.16 (s, 1H)	158.1
2.	(q)	117.8
3.	**H-3=** 4.54 (d, *J* = 4.9 Hz, 1H)	40.5
4.	**H-4=** 4.78 (dd, *J* = 10.4, 4.9 Hz, 1H)	70.8
5.	**H-5=** 4.14 (m, 1H)	72.0
1'.	**H-1'=** 5.07 (dt, *J* = 9.6, 4.6 Hz, 1H)	87.0
2'.	**H-2'=** 5.07 (dt, *J* = 9.6, 4.6 Hz, 1H)	68.0
3'.	**H-3'=** 4.94 (dd, *J* = 10.2, 9.2 Hz, 1H)	70.5
4'.	**H-4'=** 5.23 (t, *J* = 9.3 Hz, 1H)	73.8
5'.	**H-5'=** 3.77 (ddd, *J* = 10.1, 4.3, 1.9 Hz, 1H)	75.8
6'.	**H-6'a=** 4.36 (dd, *J* = 12.5, 4.3 Hz, 1H) **H-6'a=** 4.08 (dd, *J* = 12.5, 1.9 Hz, 1H)	61.8 61.8



HSQC table of compound 5a

	^{1}H (δ)	^{13}C
1.	5.92 (t, *J* = 1.2 Hz, 1H)	97.4
2.	--	
3.	6.33 (dd, *J* = 3.4, 1.1 Hz, 1H)	134.6
4.	5.26 (m, 1H)	68.1
5.	3.99 (dd, *J* = 6.5, 5.7 Hz, 1H)	71.6
6.	--	194.3
1'.	4.86 (d, *J* = 8.0 Hz, 1H)	101.7
2'.	4.92 (dd, *J* = 9.3, 8.1 Hz, 1H)	70.9
3'.	5.18 (m, 1H)	72.7
4'.	5.05 (m, 1H)	68.3
5'.	3.77 (m, 1H)	72.0
6'.	4.28 (dd, *J* = 12.2, 4.9 Hz, 1H)	62.0

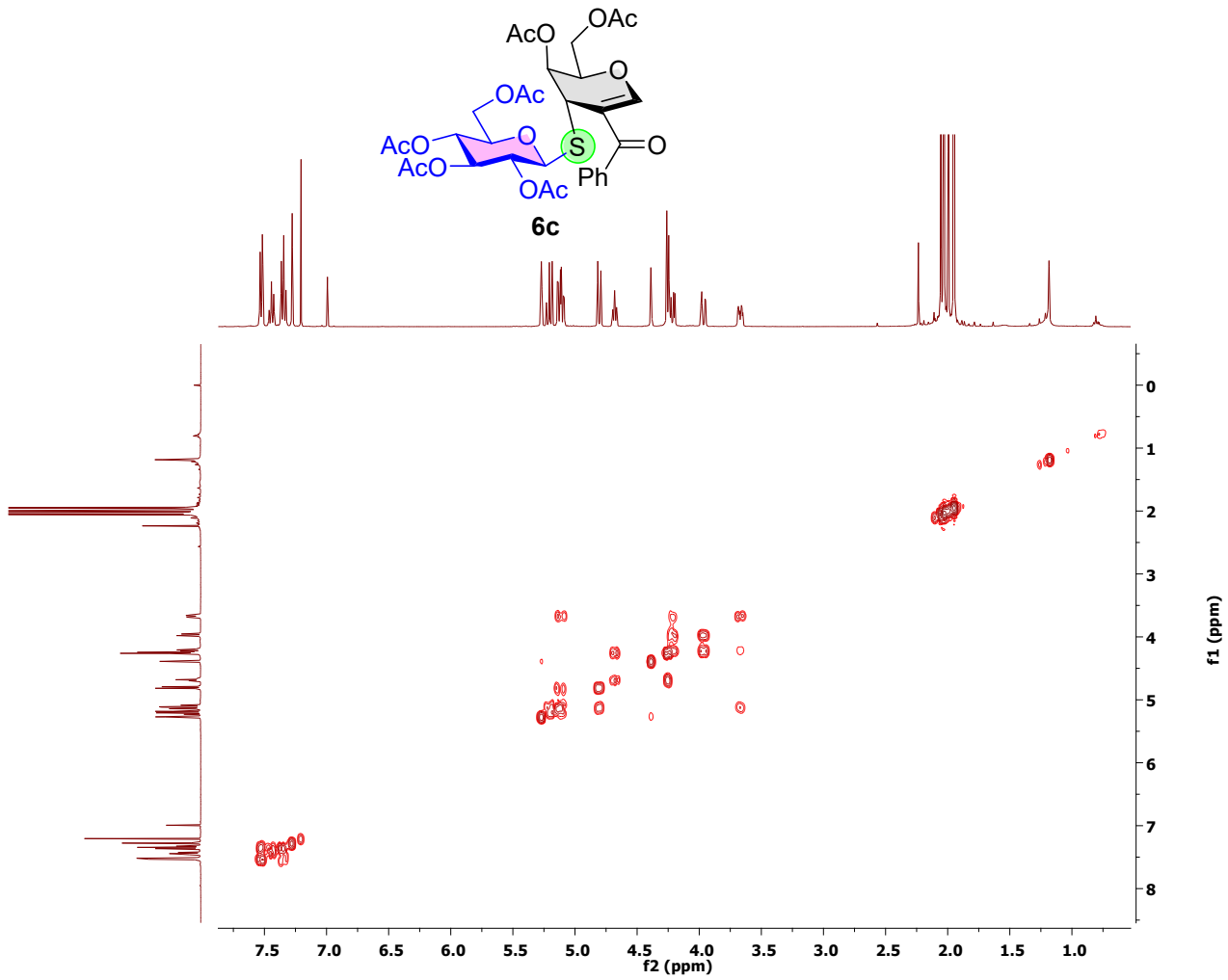


5e

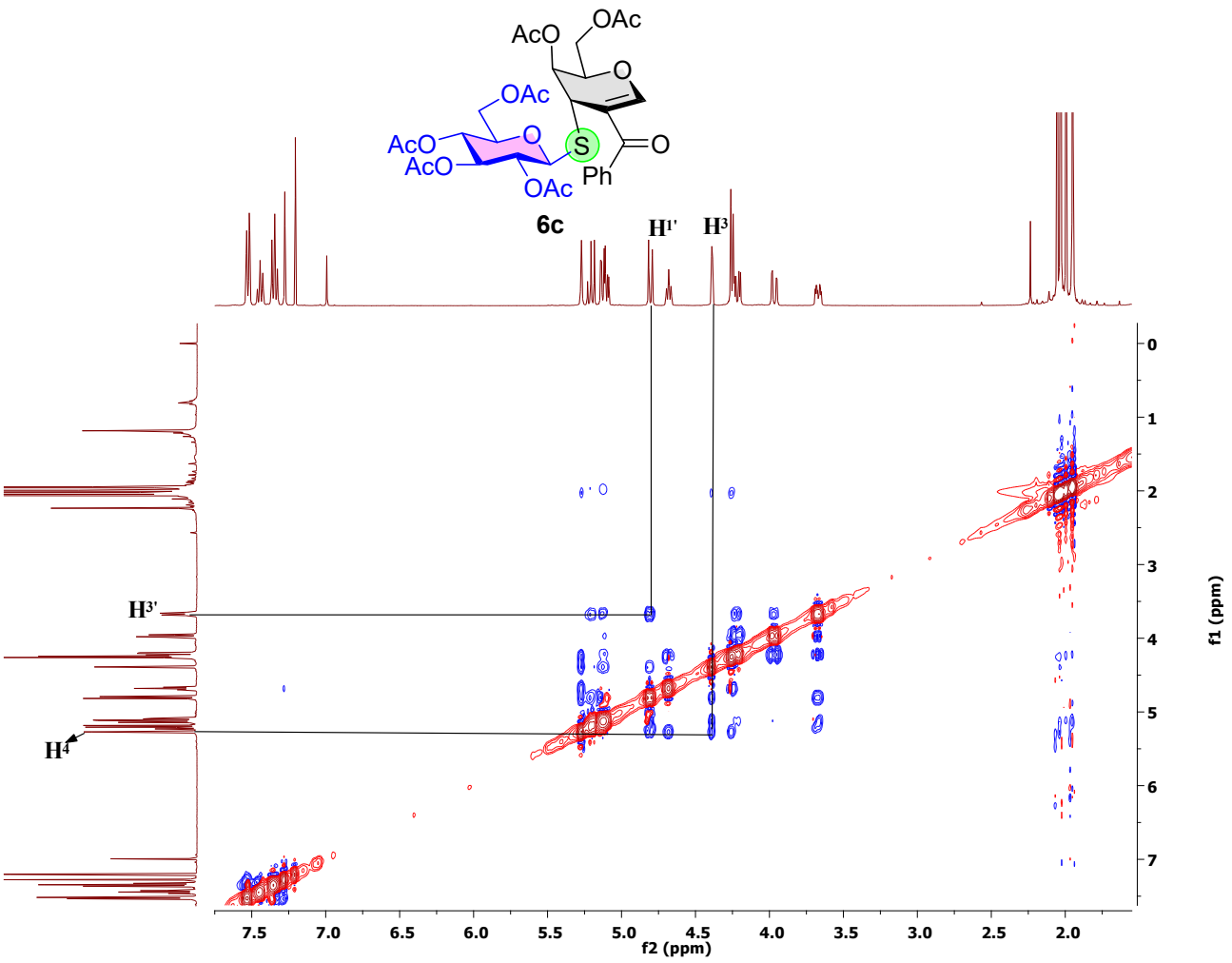
HSQC table of compound 5e

	^{1}H (δ)	**^{13}C**
1.	7.39(m, 3H)	161.3
2.	--	
3.	4.84 (d, *J* = 2.4 Hz, 1H)	63.3
4.	5.07 (m, 2H)	64.2
5.	4.48 – 4.42 (m, 1H)	71.8
6.	H_{6a}=4.30 (dd, *J* = 11.8, 7.4 Hz, 1H) and H_{6b}= 4.22 (dd, *J* = 11.8, 5.1 Hz, 1H)	62.1
1'.	5.12 – 5.10 (m, 1H)	95.53
2'.	5.15 (dd, *J* = 3.4, 1.7 Hz, 1H)	69.9
3'.	5.07 (m, 2H)	69.2
4'.	4.98 (t, *J* = 10.0 Hz, 1H)	70.7
5'.	3.82 (m, 1H)	67.2

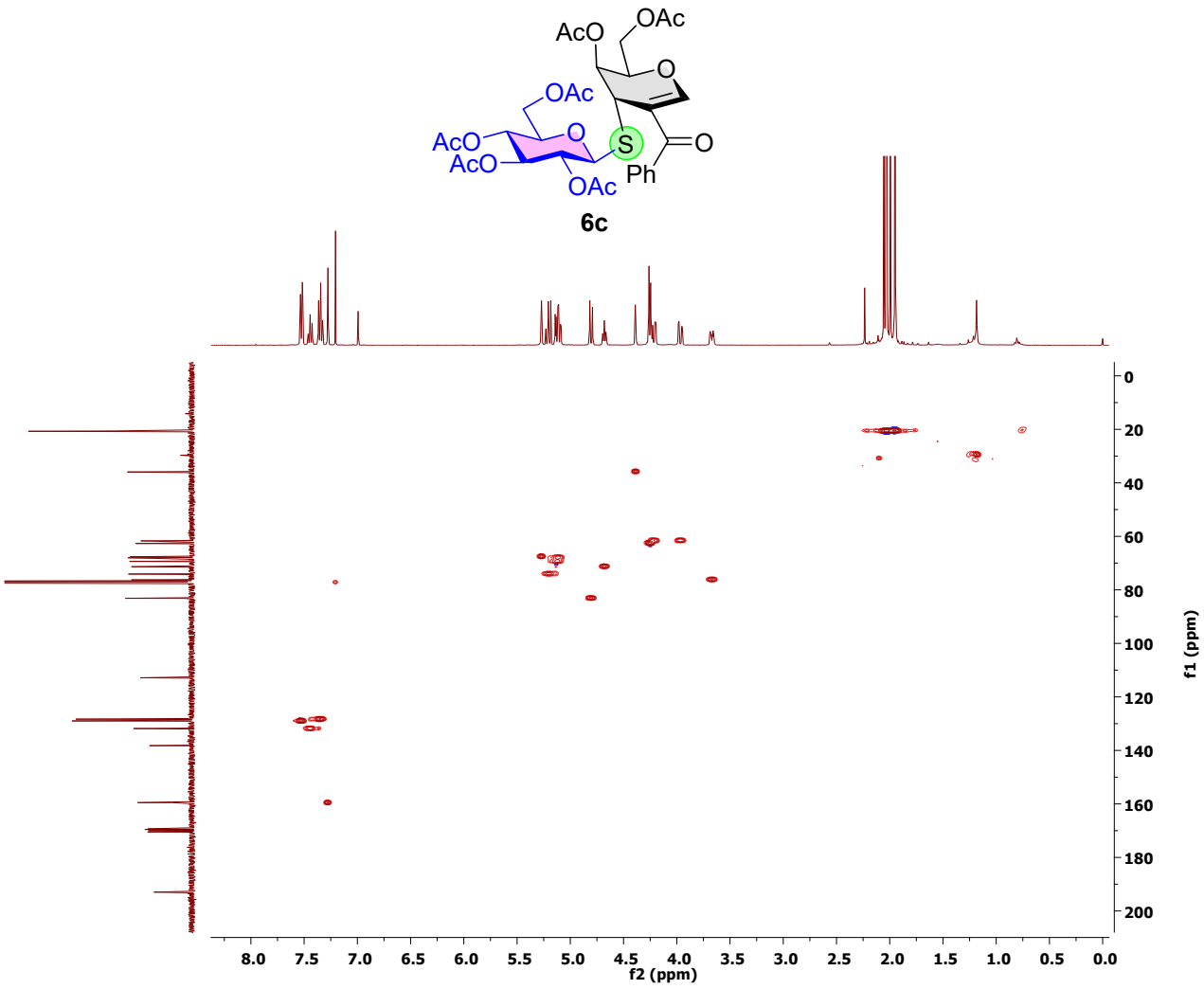
COSY of 6c



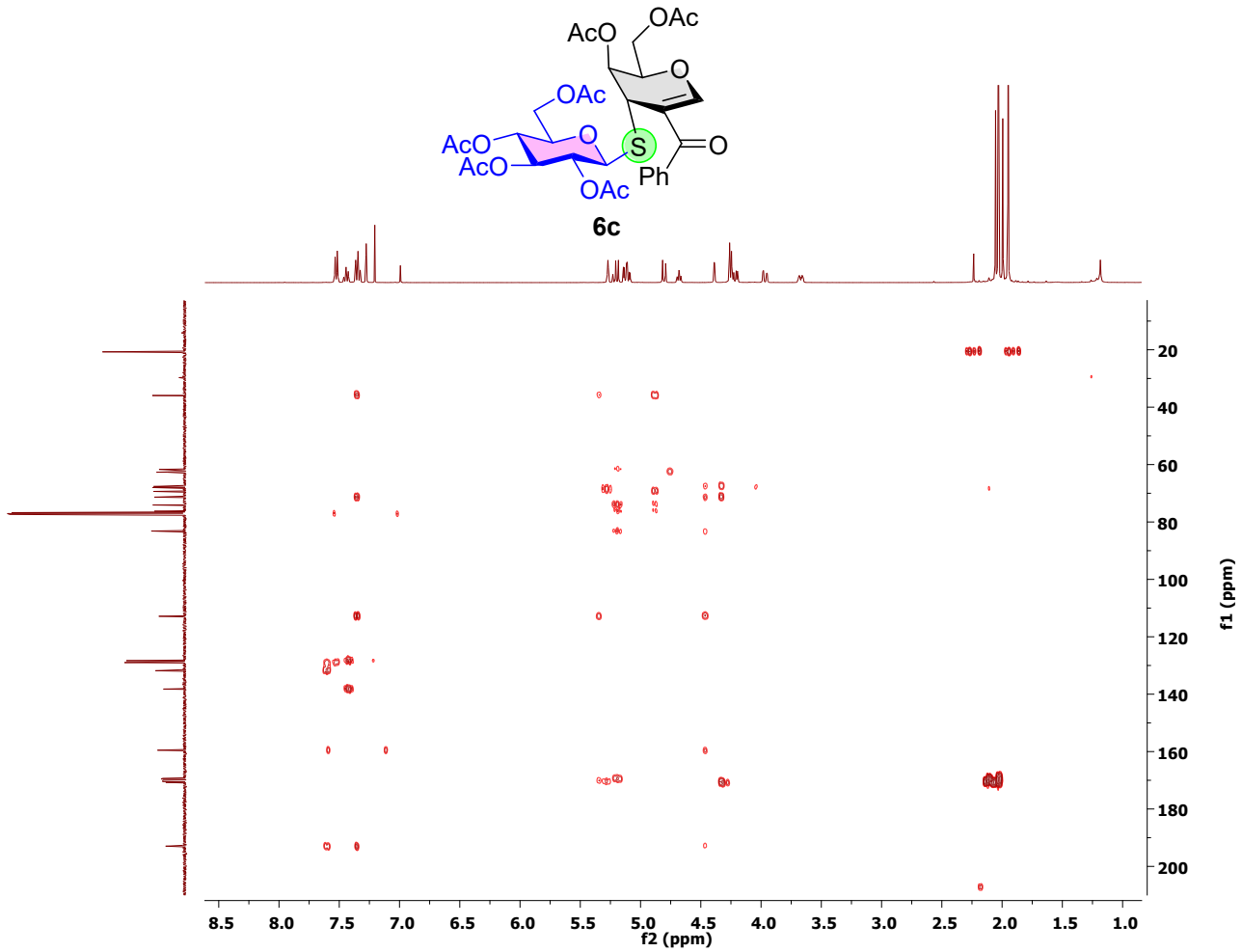
NOESY of 6c


AcO
OAc
O
OAc
AcO
O
S
O
AcO
Ph
OAc
6c
H1'
H3
H3'
H4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
0
1
2
3
4
5
6
7
f1 (ppm)

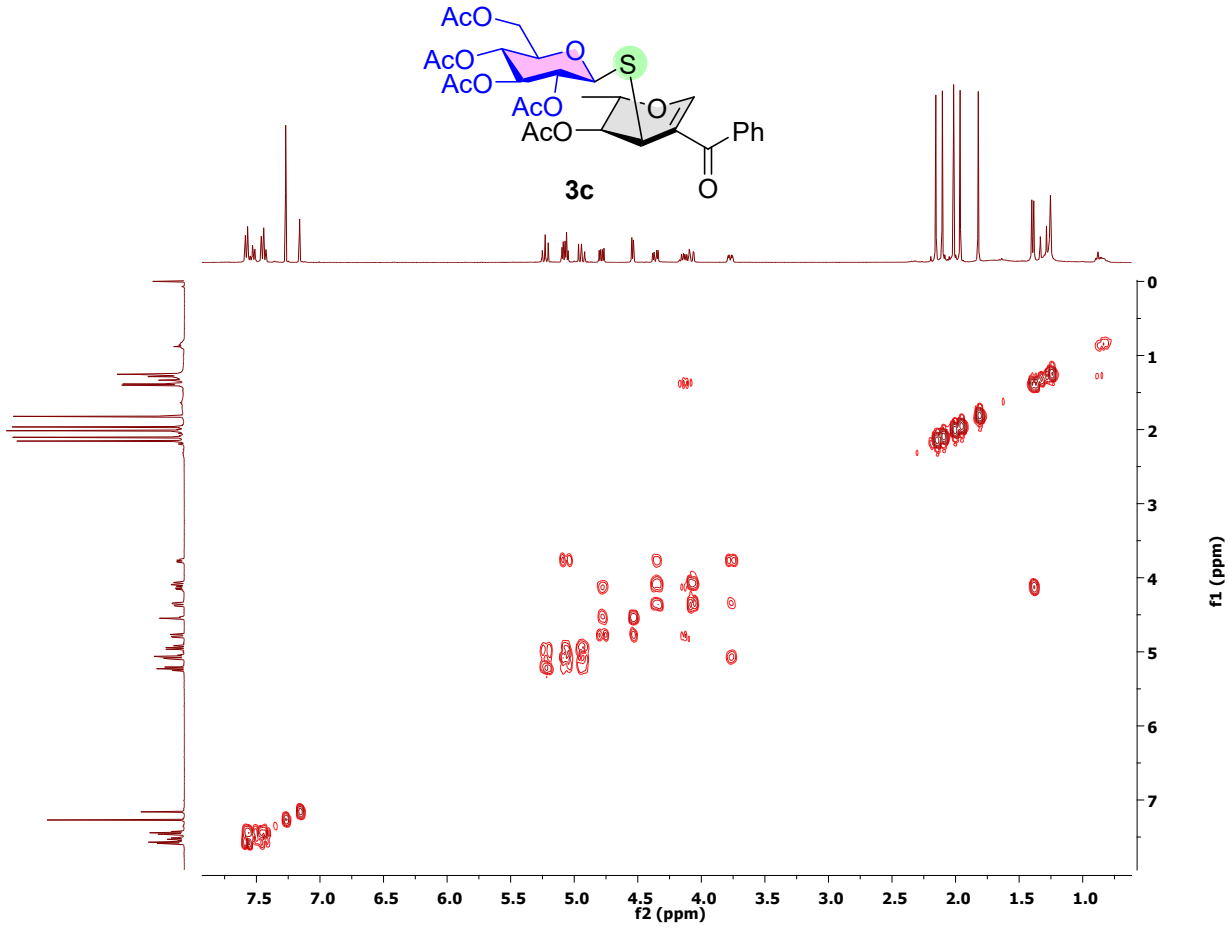
HSQC of 6c


AcO
OAc
O
OAc
AcO
O
S
O
AcO
Ph
OAc
6c
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

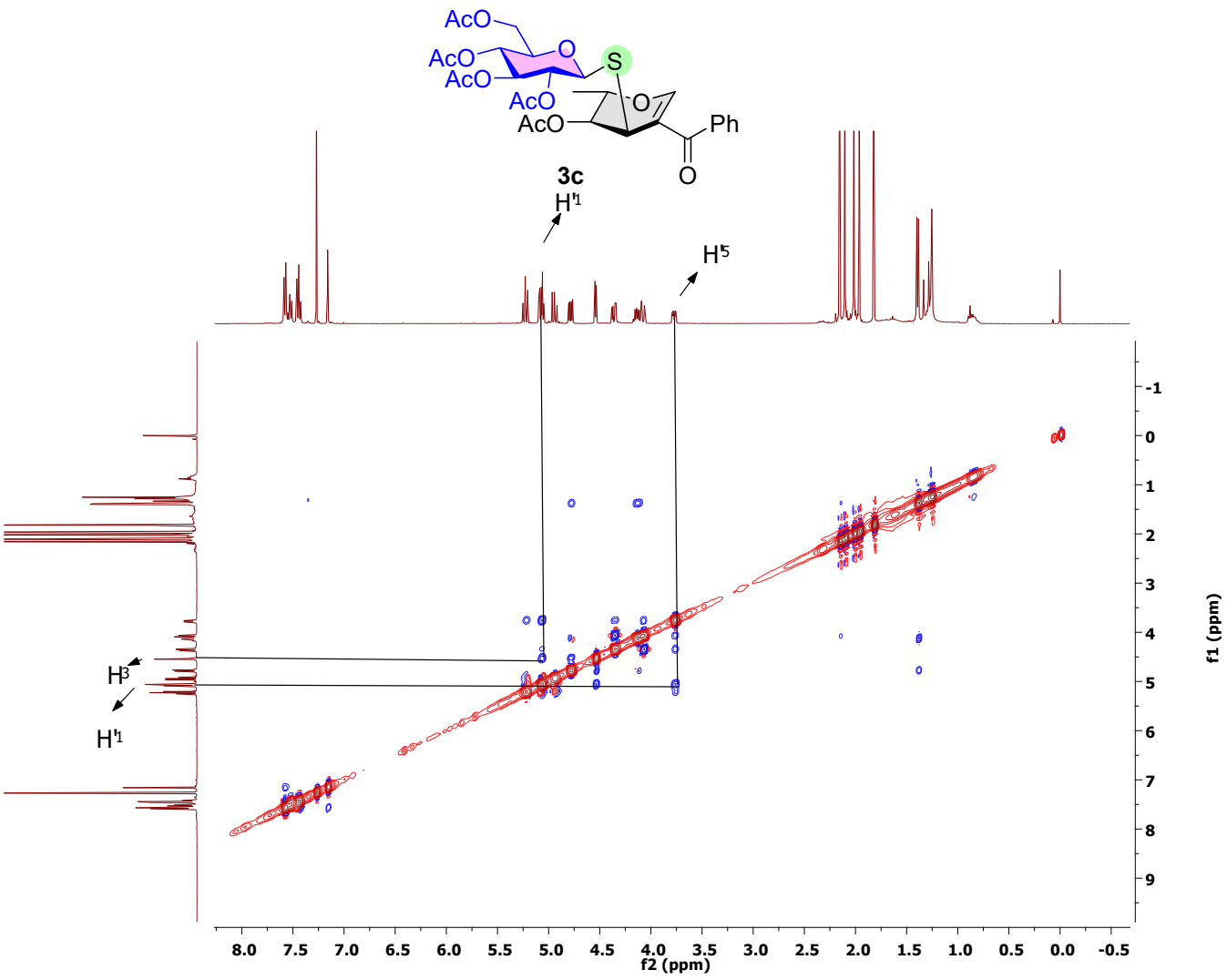
HMBC of 6c



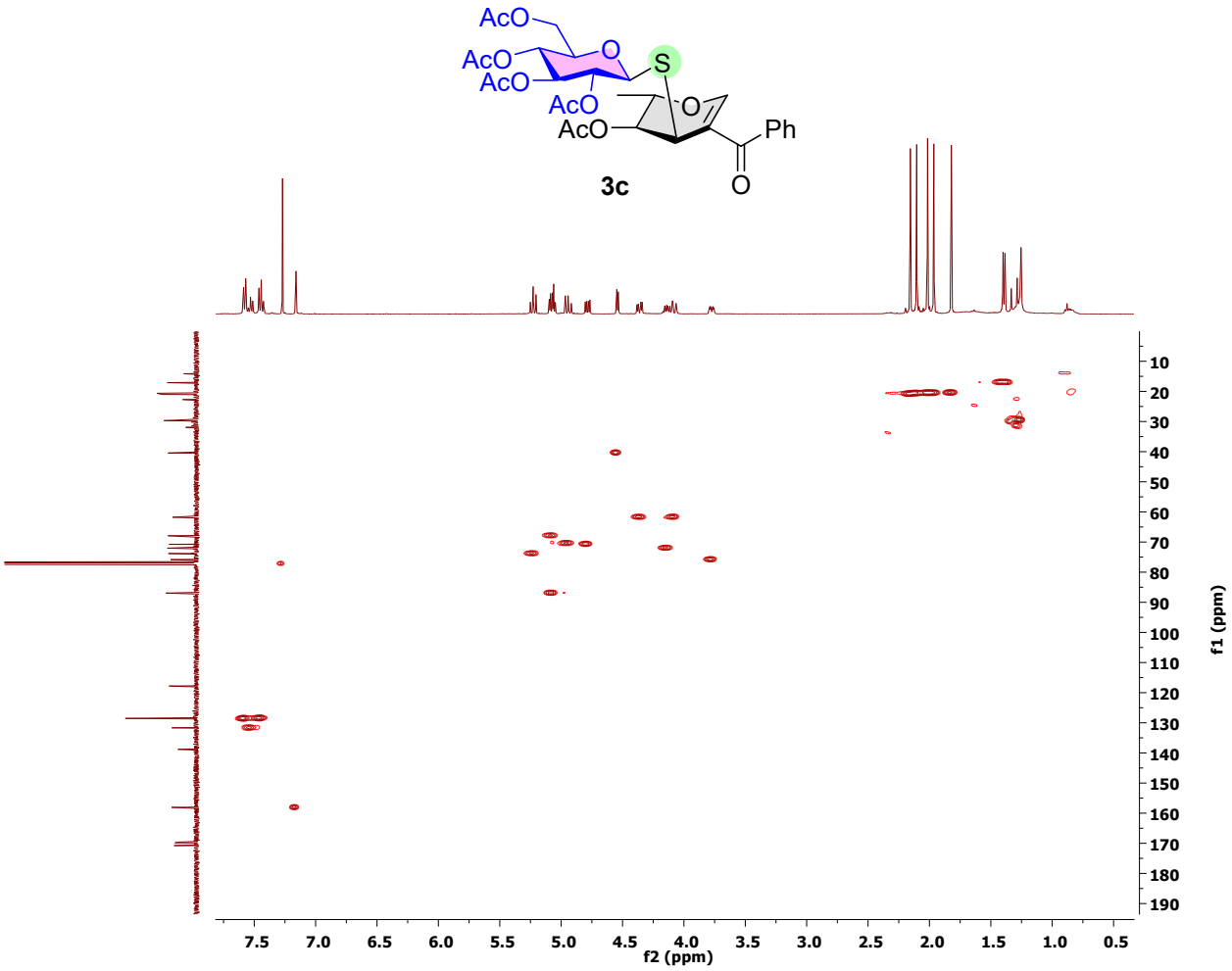
COSY of 3c


AcO
AcO
AcO
AcO
AcO
O
S
O
Ph
O
3c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0
1
2
3
4
5
6
7
f1 (ppm)

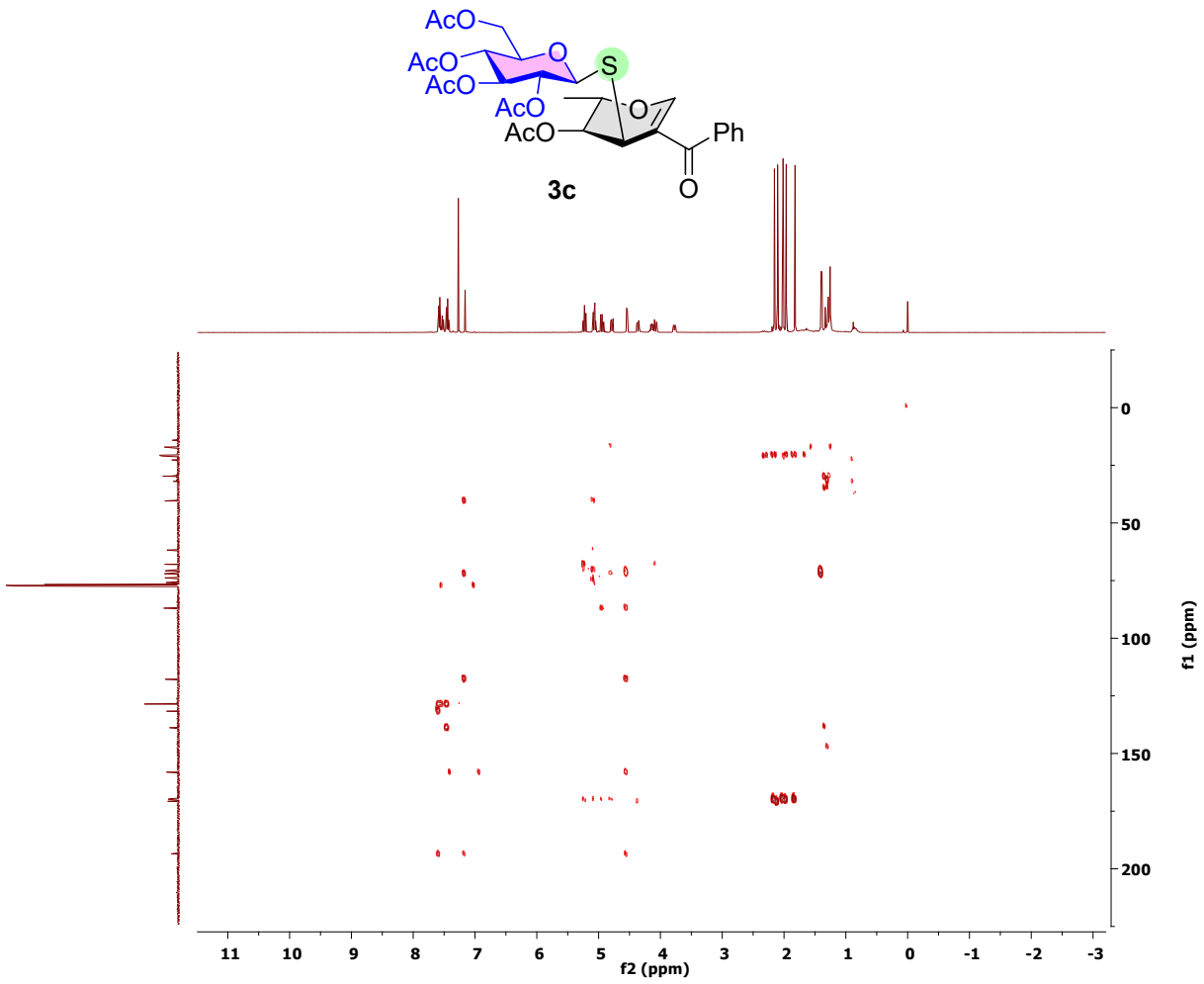
NOESY of 3c



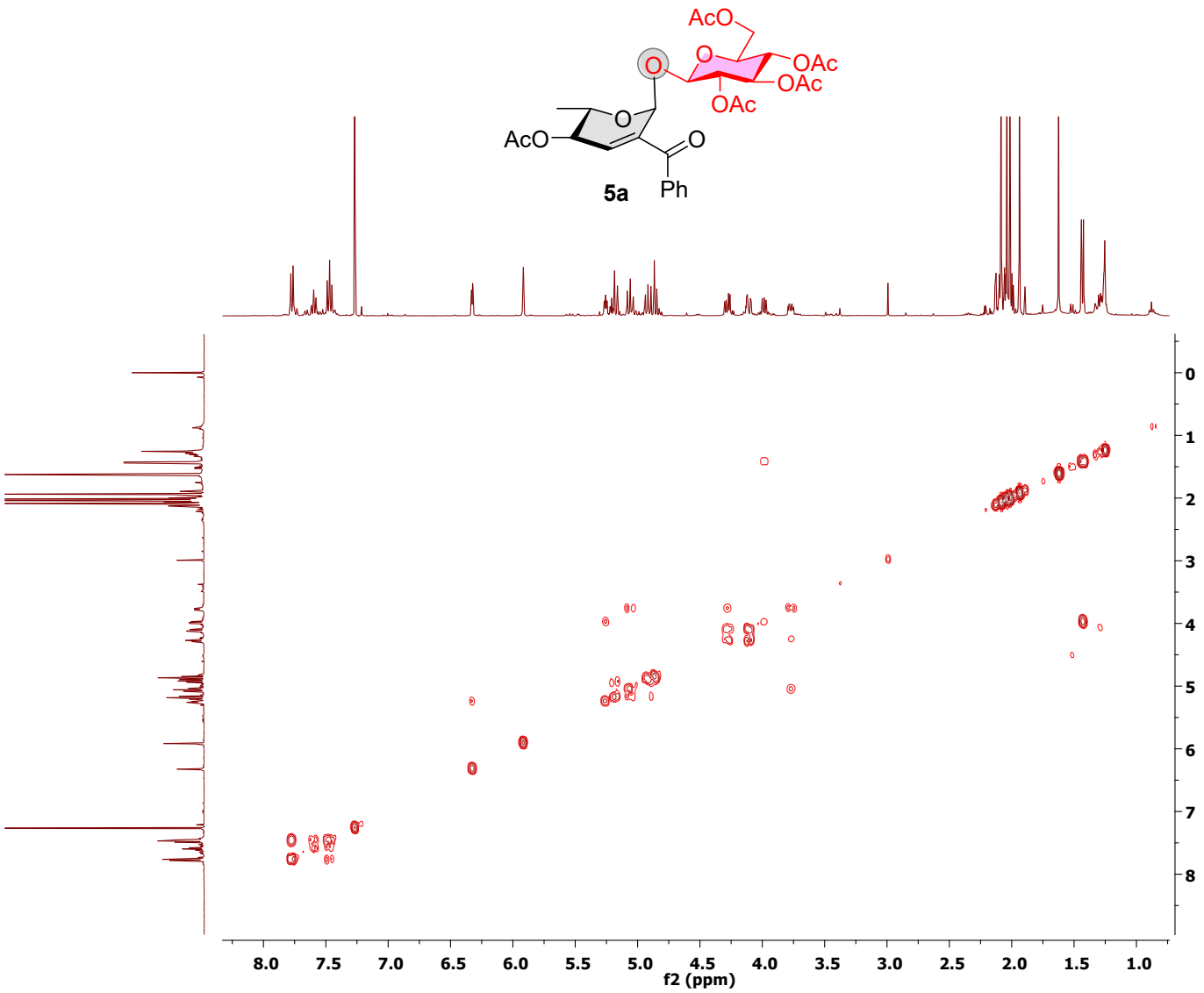
HSQC of 3c



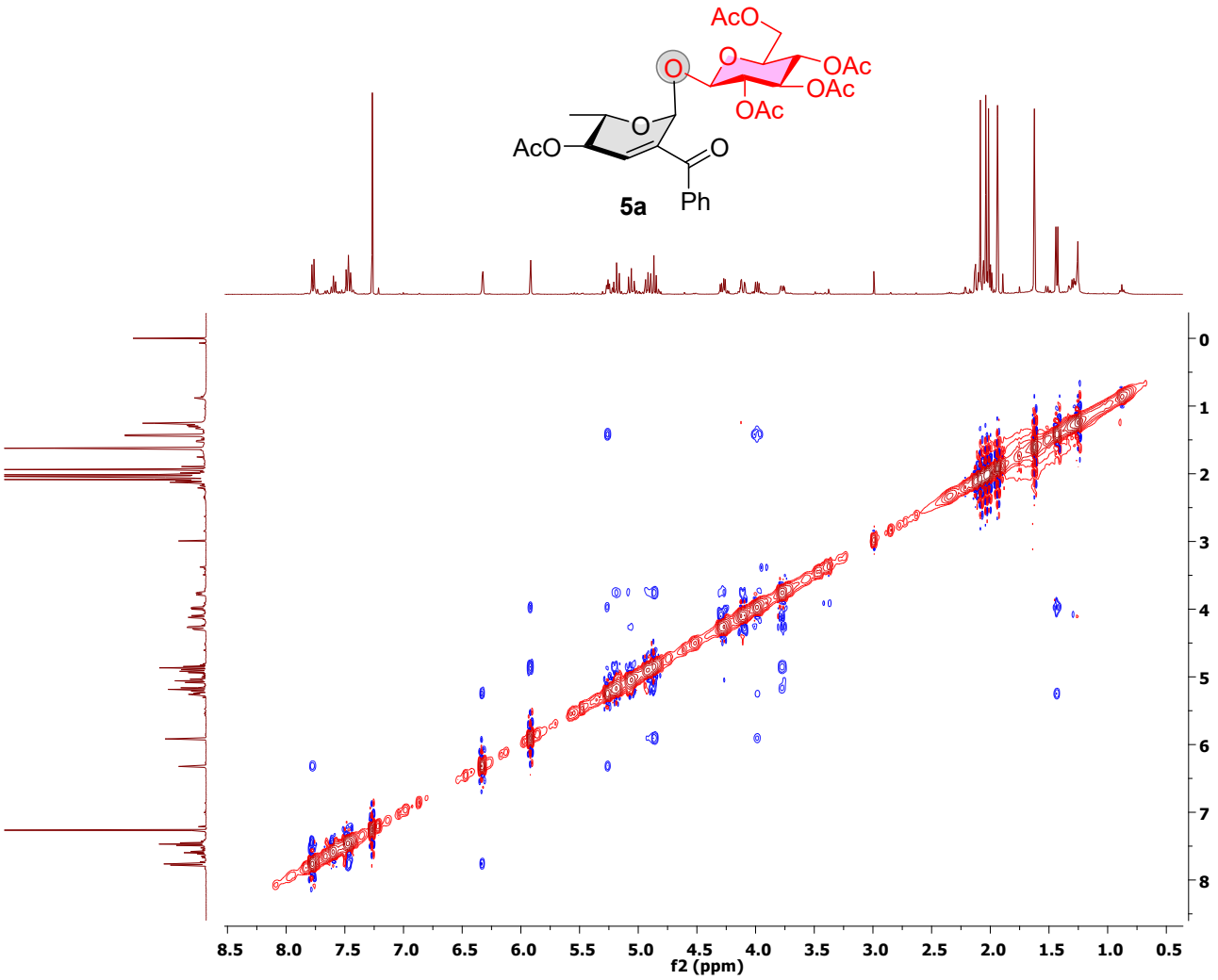
HMBC of 3c


AcO
AcO
AcO
AcO
AcO
O
S
O
Ph
O
3c
0
50
100
150
200
f1 (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f2 (ppm)

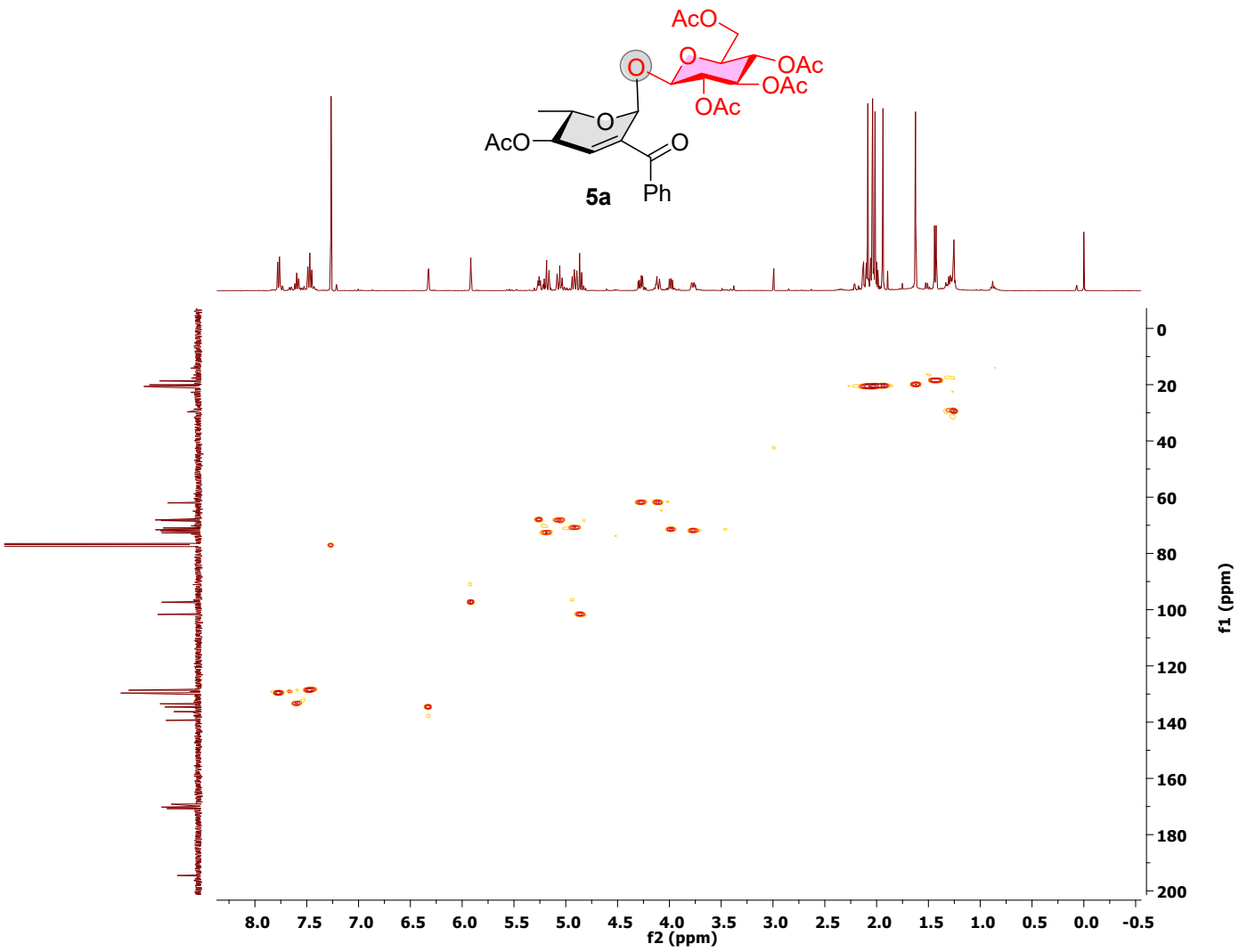
COSY of 5a


AcO
O
OAc
OAc
OAc
O
AcO
O
O
Ph
5a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0
1
2
3
4
5
6
7
8

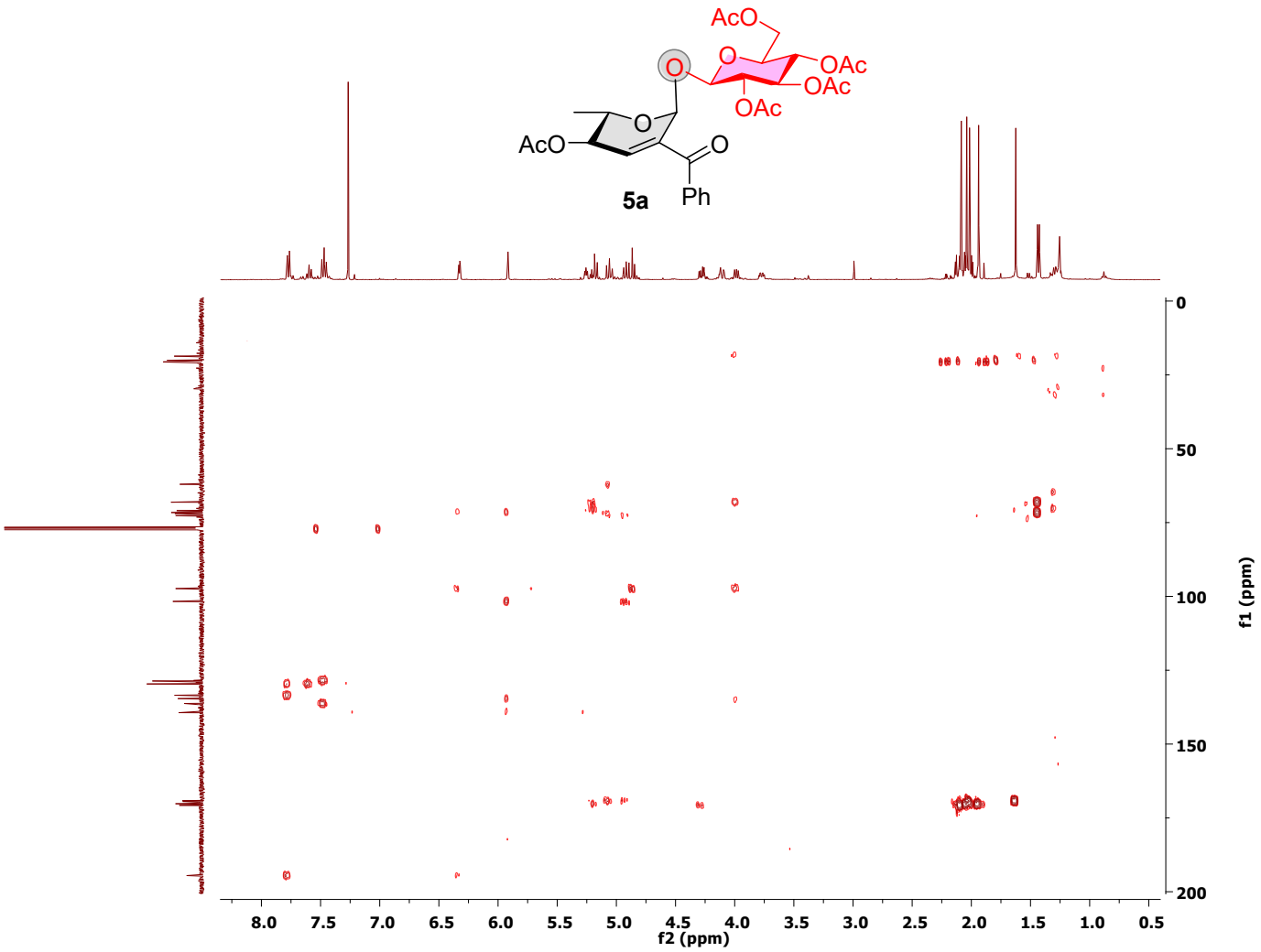
NOESY of 5a


AcO
O
OAc
OAc
OAc
O
AcO
O
Ph
5a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8

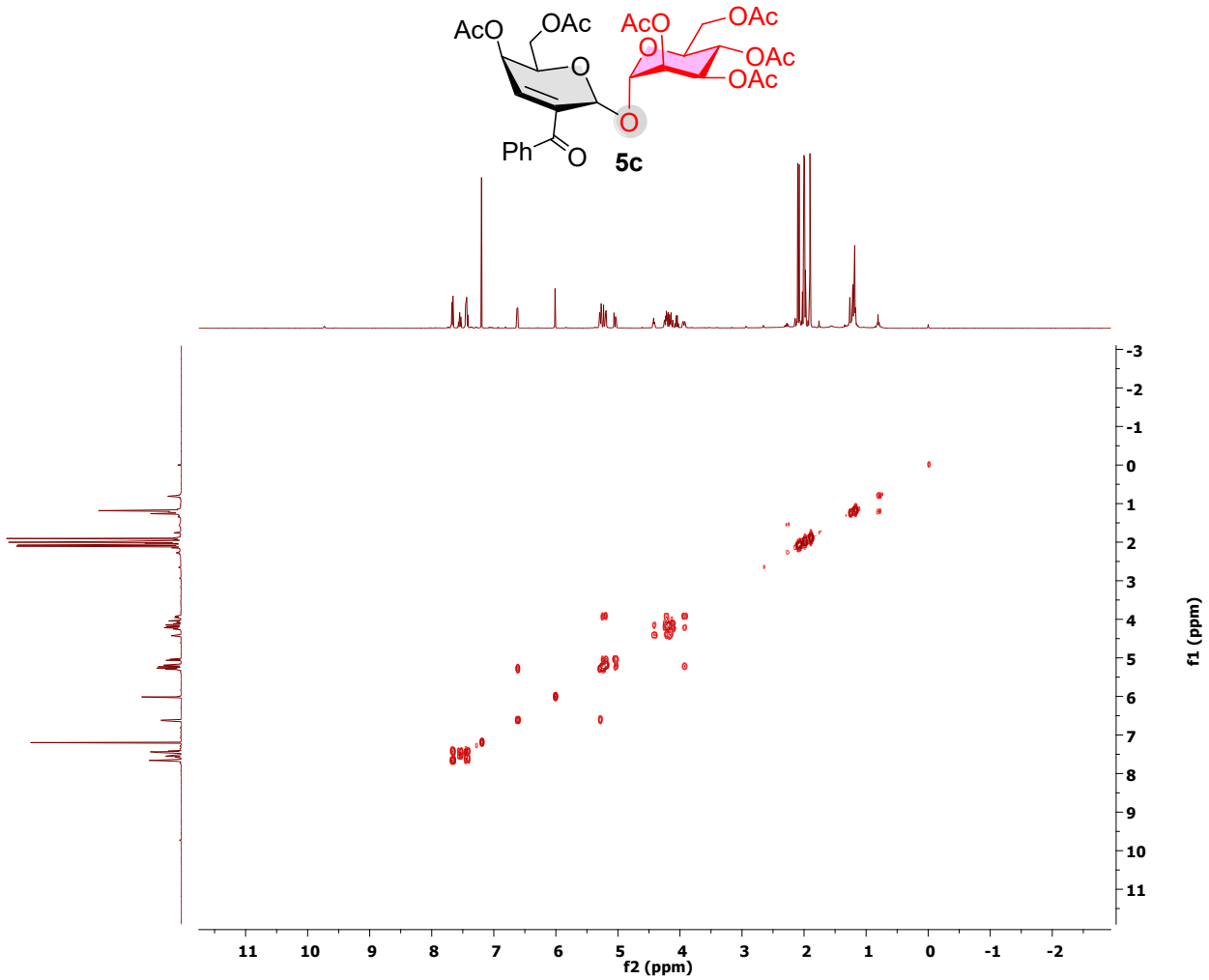
HSQC of 5a



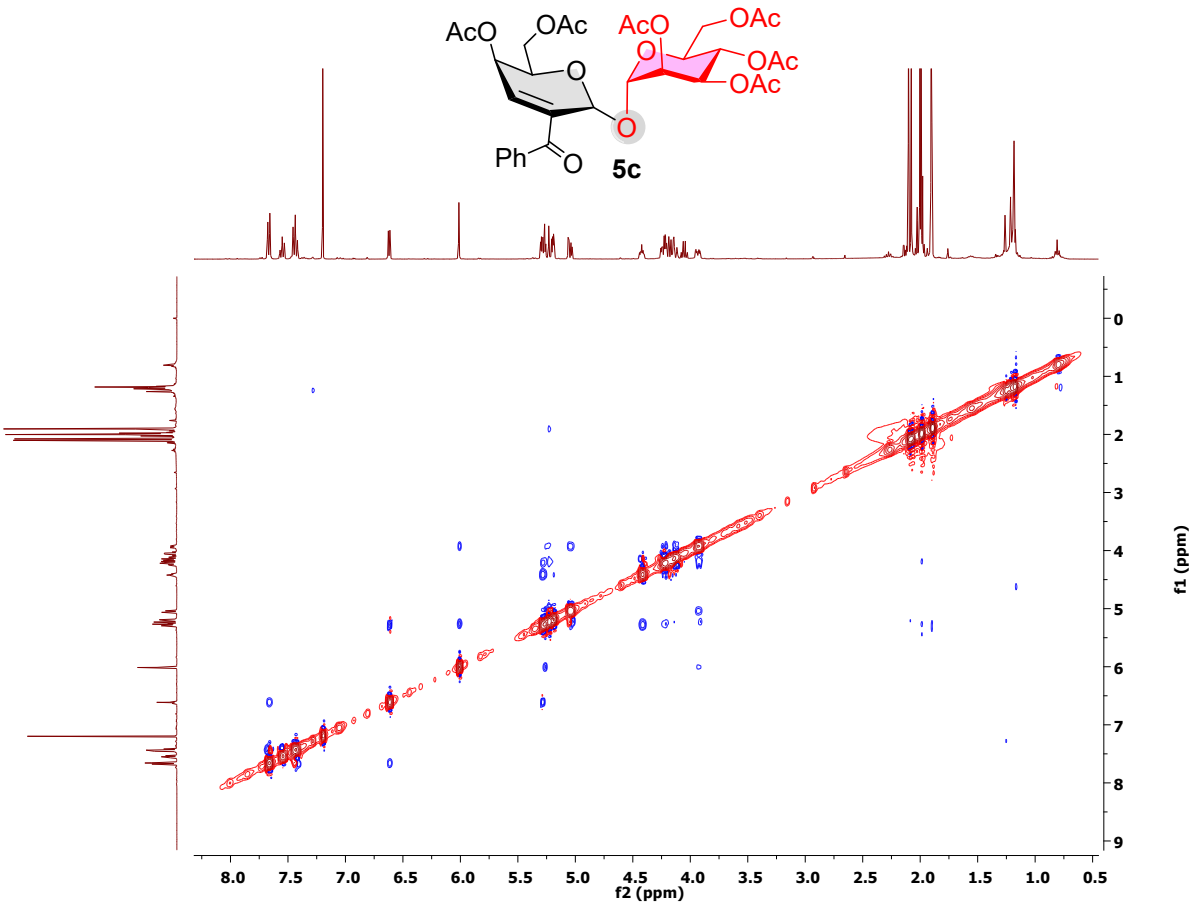
HMBC of 5a


AcO
O
OAc
OAc
OAc
O
AcO
O
Ph
5a
0
50
100
150
200
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

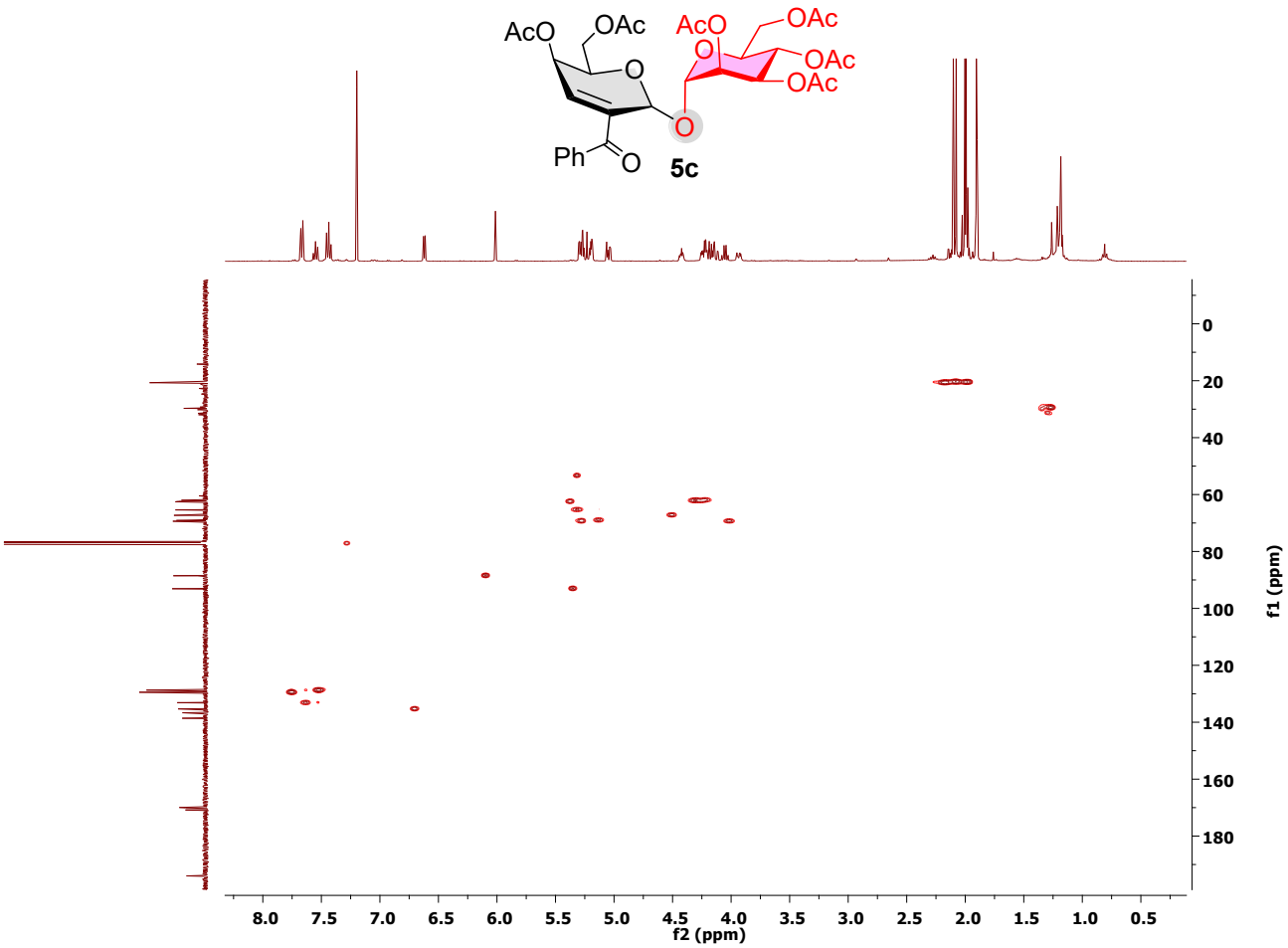
COSY of 5c



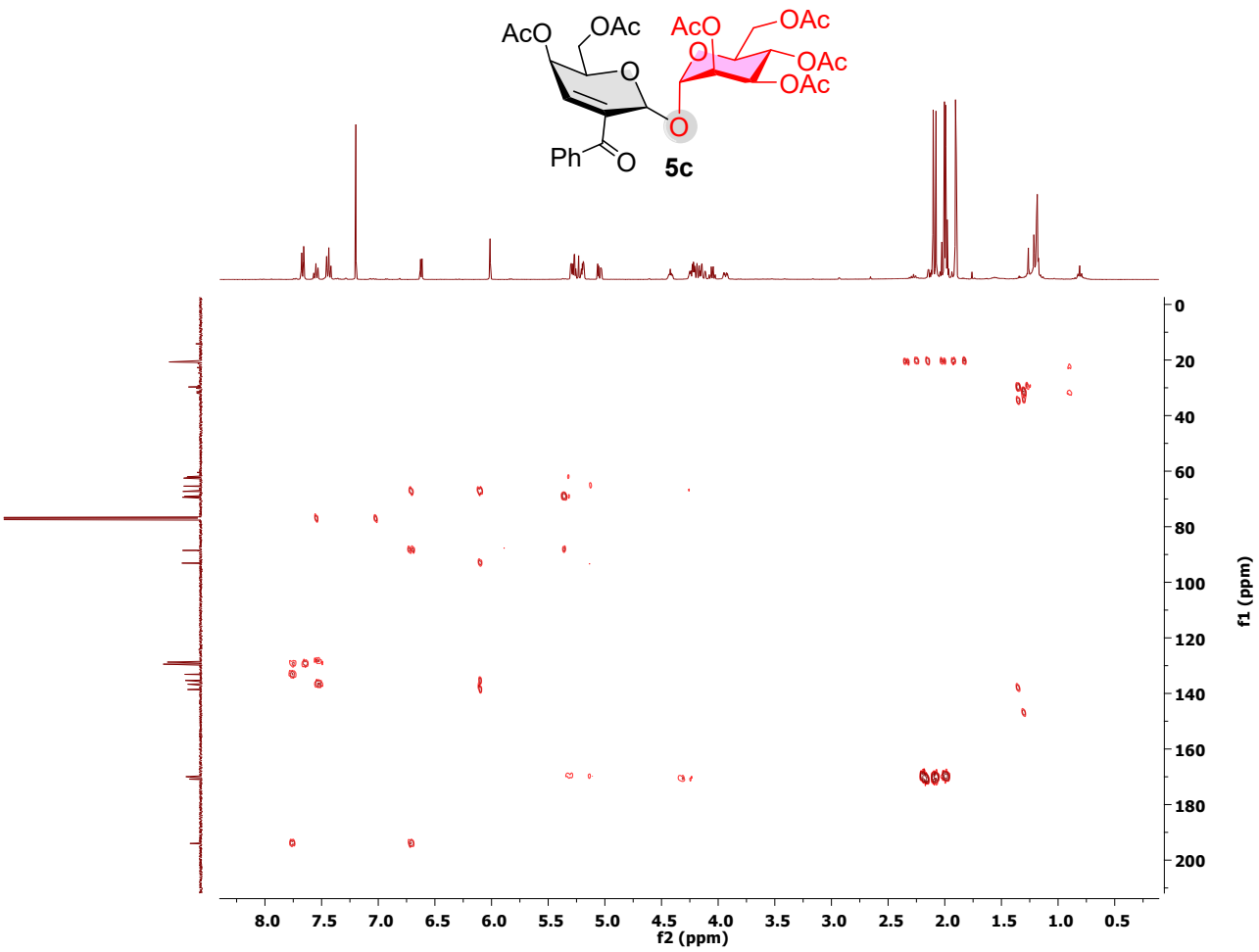
NOESY of 5c



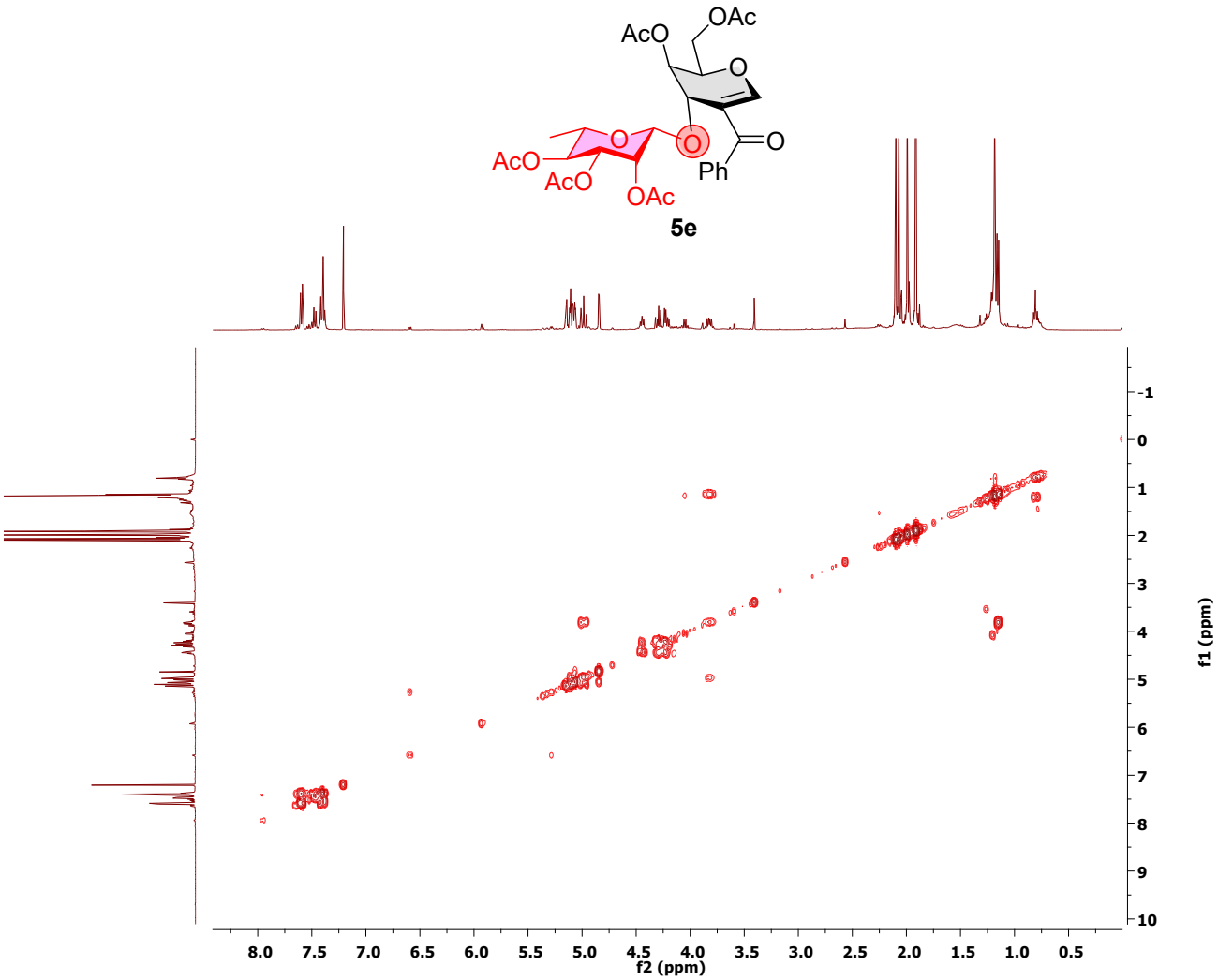
HSQC of 5c



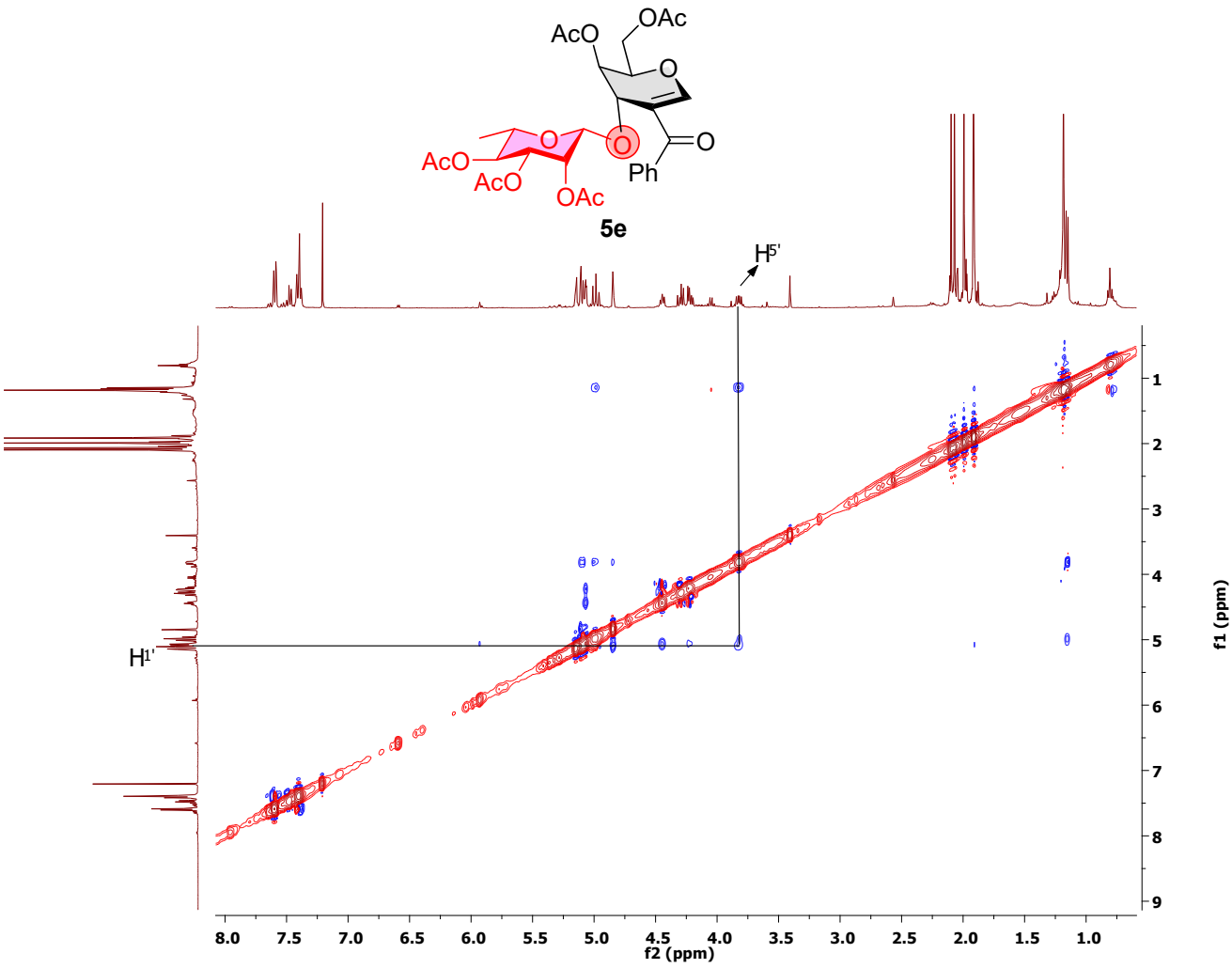
HMBC of 5c



COSY of 5e



NOESY of 5e


AcO
OAc
O
O
AcO
AcO
O
Ph
OAc
5e
H5'
H1'
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1
2
3
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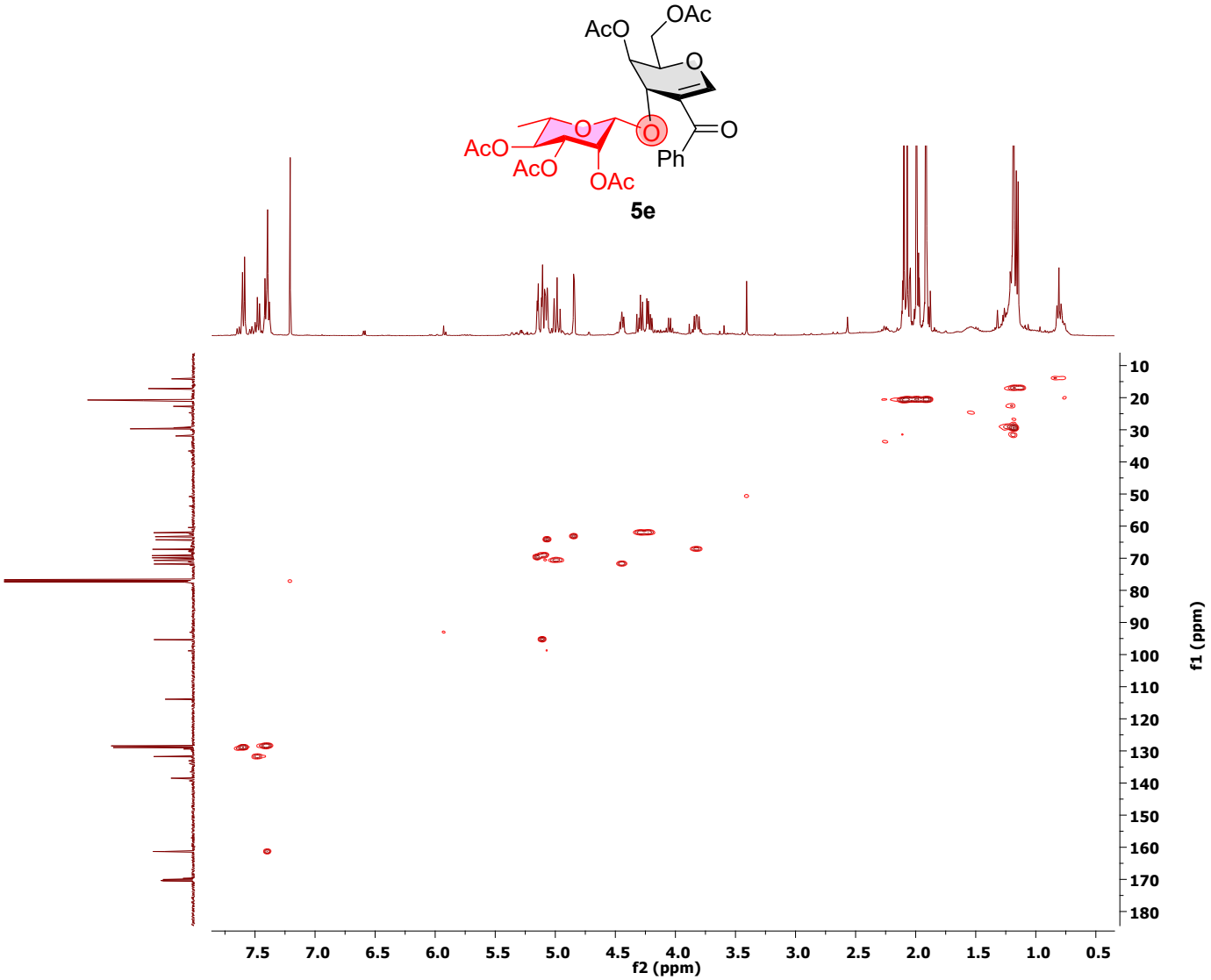
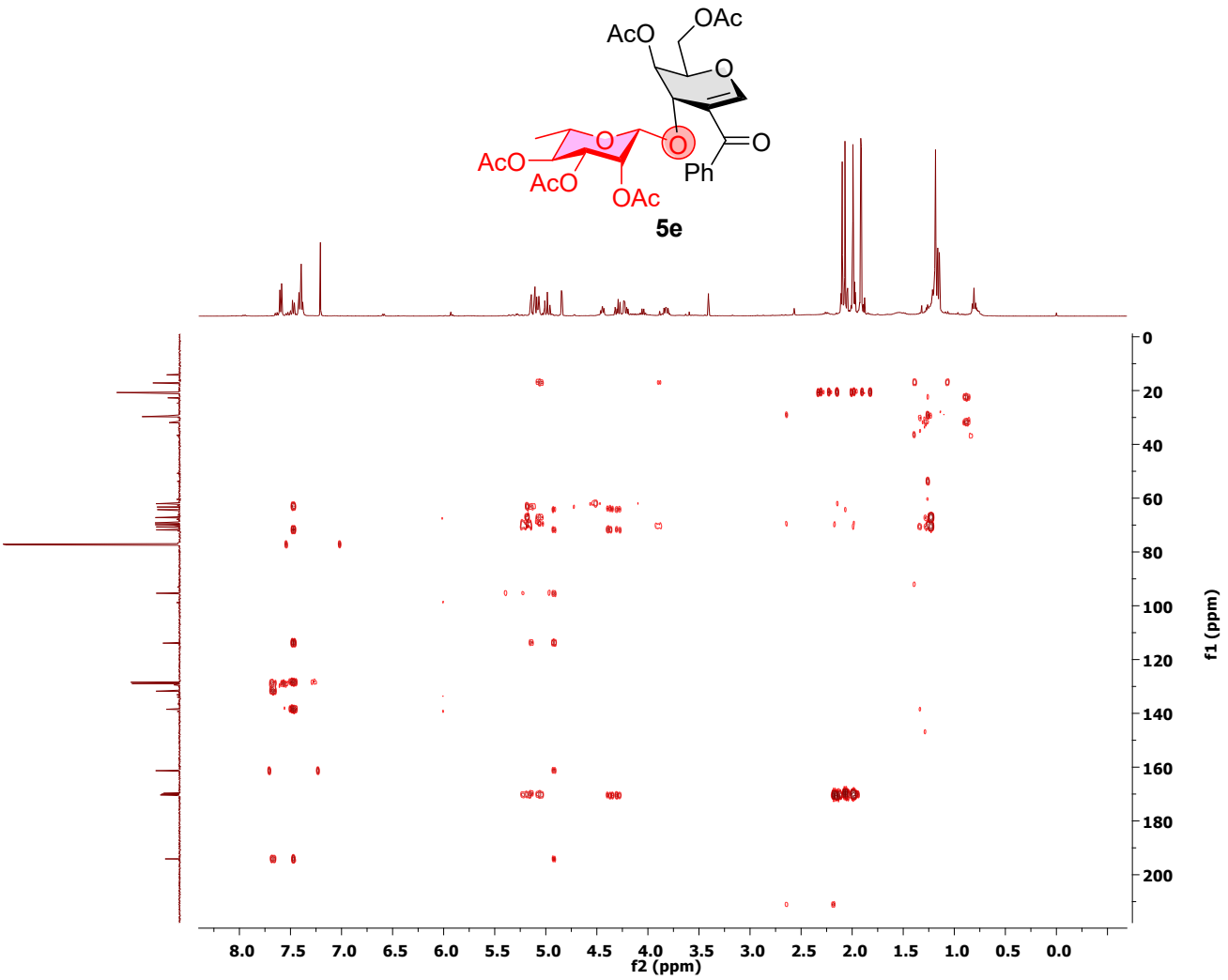
5
6
7
8
9
f1 (ppm)

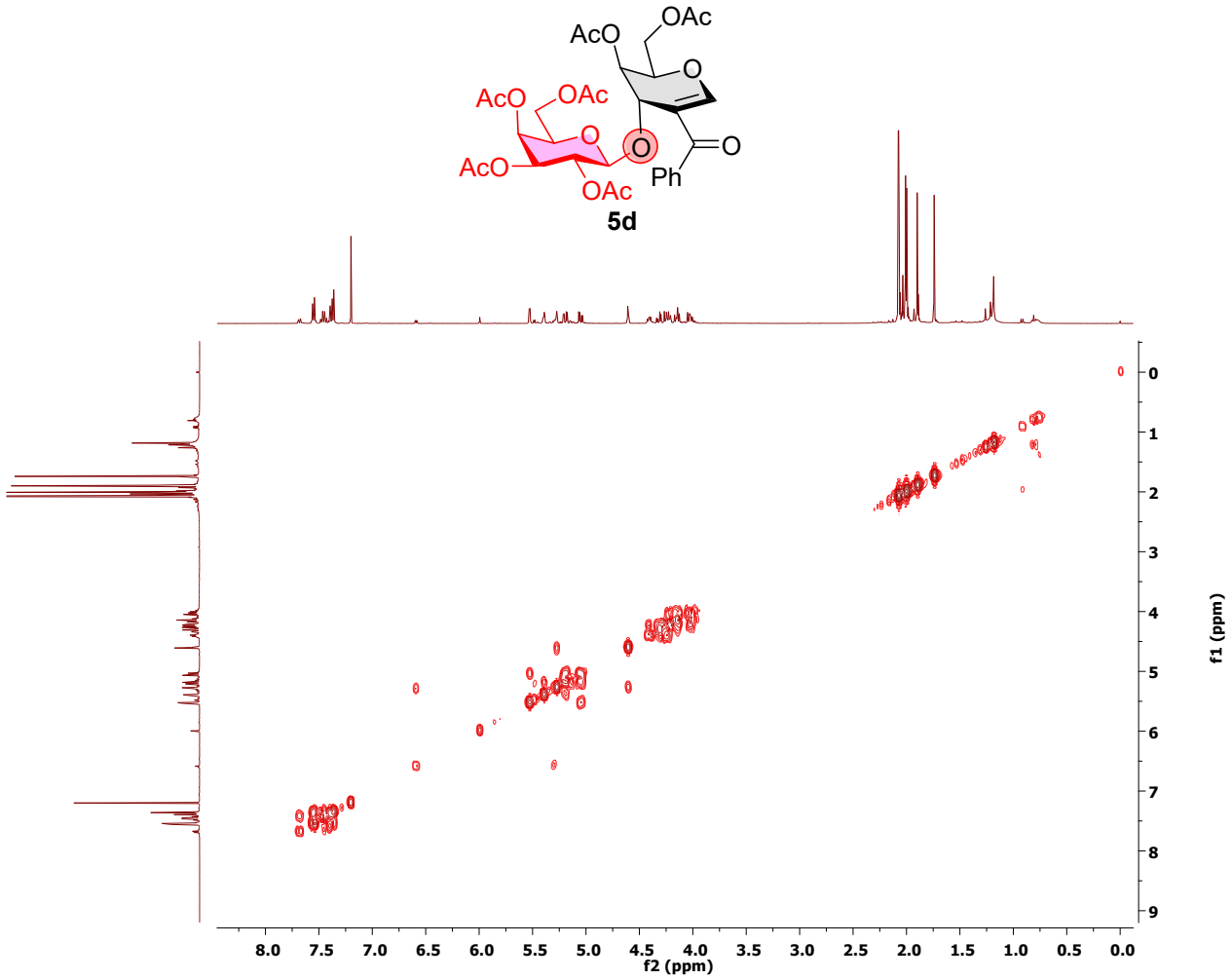
HSQC of 5e



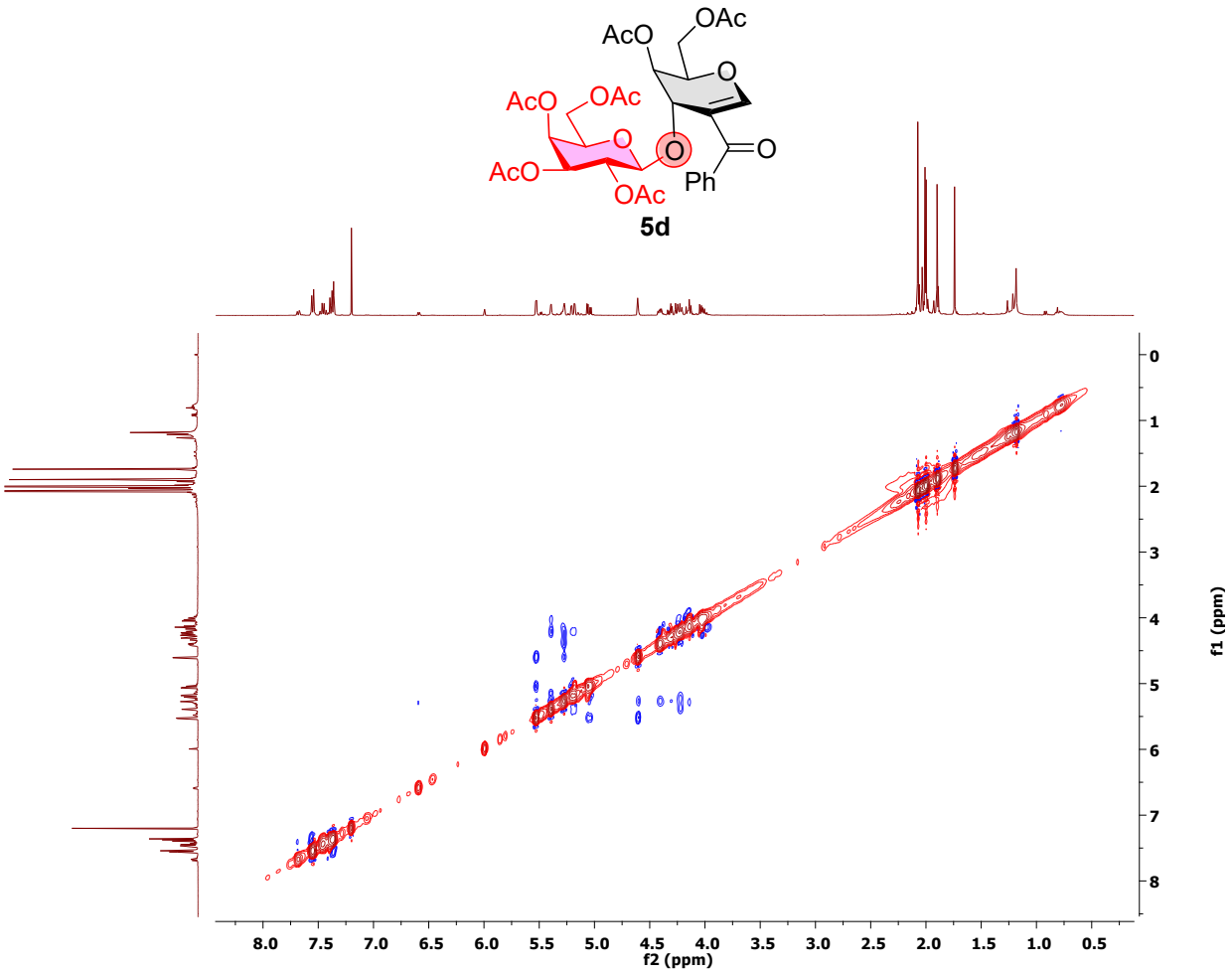
HMBC of 5e



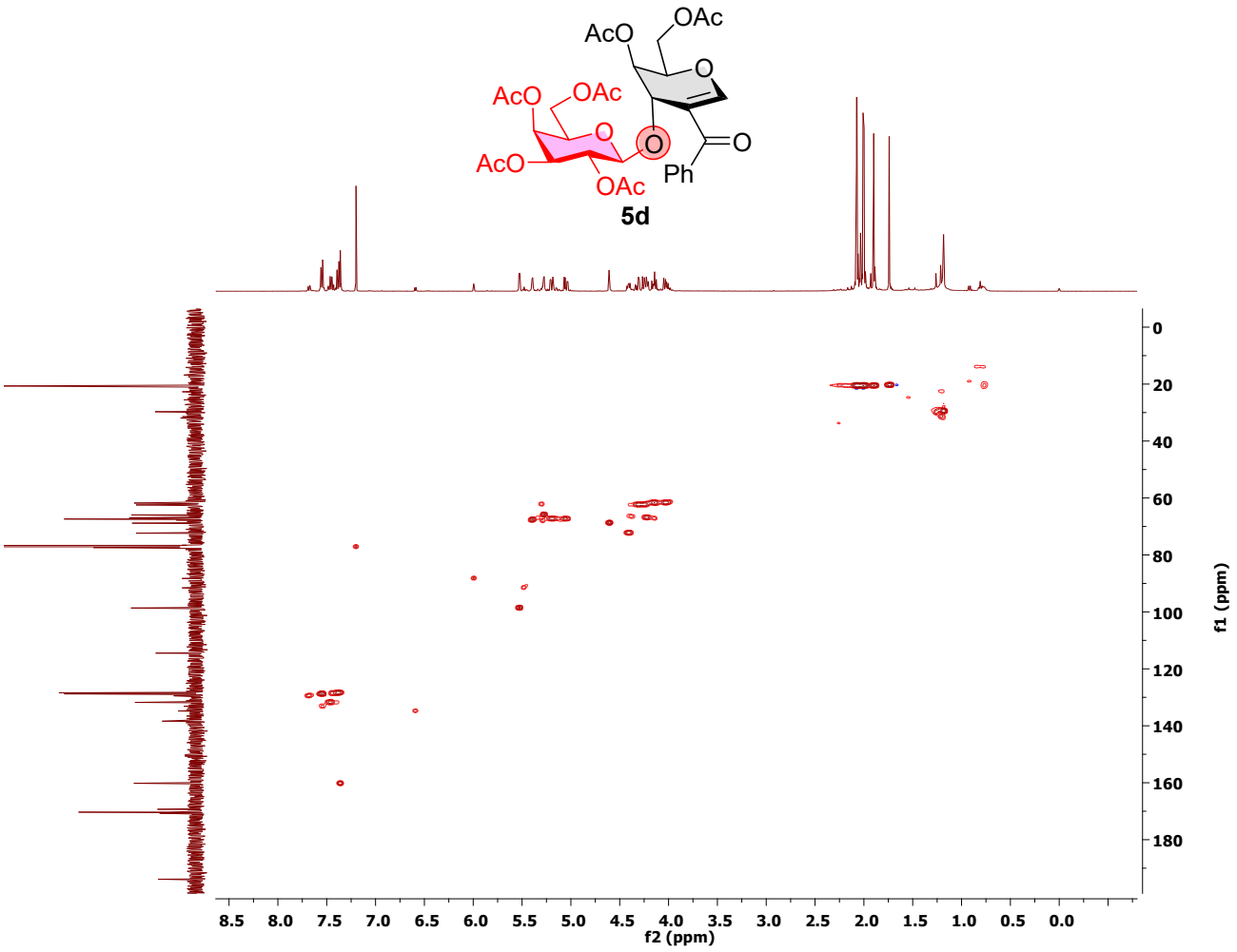
COSY of 5d



NOESY of 5d



HSQC of 5d


AcO
OAc
O
AcO
OAc
O
AcO
O
Ph
OAc
5d
0
20
40
60
80
100
120
140
160
180
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

HMBC of 5d