Supplementary Material (ESI) for Green Chemistry

Supporting Information

Green glycosylation promoted by reusable biomass carbonaceous solid acid: An easy access to β-stereoselective terpene galactosides

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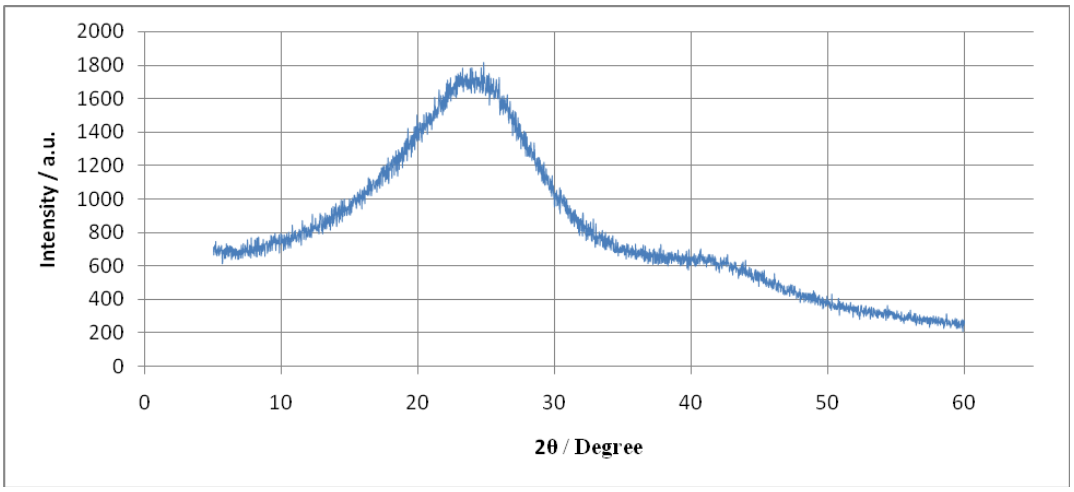
Experimental section:

General: All reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise stated. Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 mm). Chromatograms were visualized by staining using base solution of potassium permanganate. Technical grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded at room temperature on 400 MHz Bruker DPX 400 spectrometers. The residual solvent signals were taken as the reference (7.26 ppm and 4.78 ppm for ^{1}H NMR spectra and 77.0 ppm and 49.1 ppm for ^{13}C NMR spectra in $CDCl_3$ and methanol-d_4 respectively. Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved. HRMS (ESI) spectra were recorded on a Waters Q-Tof premier^{TM} mass spectrometer. Elemental analysis was measured on Perkin Elmer Series II CHNS/O Analyzer 2400. Powder X-ray diffraction (XRD) was collected from Shimadzu 6000 diffractometer. Carbonization of D-glucose was carried out on Carbolite 1200 °C three zone tube furnace.

Preparation of carbon-based solid acid catalyst (1a):

D-Glucose powder (2 g) was heated at 400 °C for 15 h under N_2 flow to produce a black carbon solid. The solid was ground to fine powder and heated in 20 mL of conc. H_2SO_4 (>96%) at 150 °C under N_2. After heating for 15 h and then cooling to room temperature, the mixture was diluted with 100 mL of distilled water. The black precipitate was collected by filtration and washed repeatedly with hot distilled water (>80 °C) until pH 7 was observed in filtrate. The resulting black solid was then washed with methanol (30 mL) followed by diethyl ether (30 mL). It was further dried at 60 °C *in vacuo* prior to use. Elemental analysis revealed that sulfur content is 1.13 wt% which is equivalent to 0.35 mmol SO_3H per gram of catalyst.

Figure S1. XRD profile for the sulfonated carbon based solid acid.



A typical procedure for neat glycosylation of monosaccharides wih aglycones:

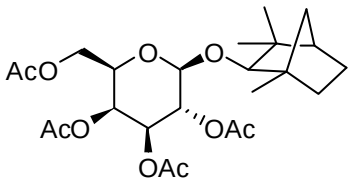
To a mixture of monosaccharide (1 eq) and aglycone (10 eq) was added 5 mol% solid acid catalyst and the reaction mixture was heated at 80 °C and stirred for 8 hrs. When the monosaccharide is completely consumed (TLC monitored), the reaction mixture was diluted with ethyl acetate and subjected to centrifugation. After the centrifugation, the remaining supernatant solution was decanted and this process is repeated for 3 times. The combined organic solutions were removed under reduced pressure followed by purification of the residue by silica gel chromatography to give the desired glycosides. The remaining solid acid catalyst was dried under reduced pressure to remove all the volatile components, and then reused in the next run. The NMR data of all the glycosides is in accordance with the reported literature data.

A typical procedure for glycosylation of galactosyl trichloroacetimidates with acceptors:

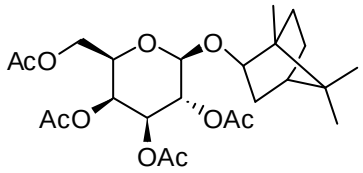
To a mixture of galactosyl trichloroacetimidate (1 eq) and acceptor (1.5 eq) in toluene (3 mL) was added 5 mol% solid acid catalyst and the reaction mixture was heated at 80 °C and stirred for appropriate amount of time (table 2) and the extent of reaction was monitored by TLC analysis. The reaction mixture was diluted with ethyl acetate

and subjected to centrifugation. After the centrifugation, the remaining supernatant solution was decanted and this process is repeated for 3 times. The combined organic solutions were removed under reduced pressure followed by purification of the residue by silica gel chromatography to give the desired β-galactosides. The remaining solid acid catalyst was dried under reduced pressure to remove all the volatile components, and then reused in the next run.

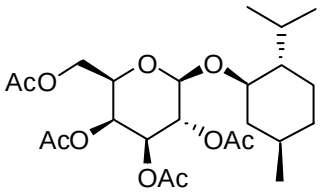
Characterization of galactosides:



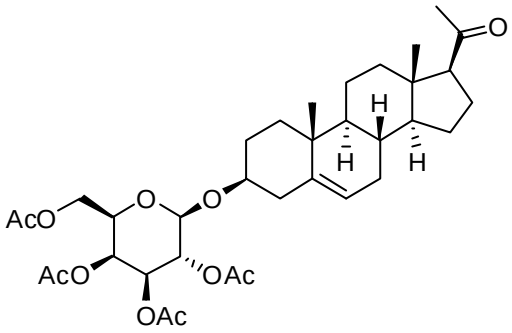
Fenchyl-2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.46; $[\alpha]_D^{24}$ –7.3 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (d, *J* = 2.7 Hz, 1H), 5.21 (dd, *J* = 8.0, 10.3 Hz, 1H), 5.00 (dd, *J* = 3.3, 10.3 Hz, 1H), 4.32 (d, *J* = 8.0 Hz, 1H), 4.09-4.14 (m, 2H), 3.85 (t, *J* = 6.3 Hz, 1H), 3.03 (s, 1H), 2.16 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.66-1.59 (m, 4H), 1.26-1.43 (m, 3H), 0.96 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ 170.5, 70.4, 170.3, 169.4, 103.0, 94.6, 71.0, 70.4, 69.2, 67.3, 61.7, 49.1, 48.0, 41.0, 39.2, 29.7, 26.1, 25.6, 21.6, 20.9 20.7, 20.6, 19.4; IR (neat) ν_{max}/cm^{-1} 1718, 1367, 1217, 1097; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{36}O_{10}Na$ 507.2206, found 507.2200.



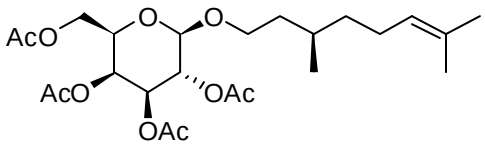
Bornyl-2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.46; $[\alpha]_D^{24}$ –14.5 (*c* = 0.1, $CHCl_3$); 1H NMR (400 MHz, CDCl3): δ 5.19 (t, *J* = 9.4 Hz, 1H), 5.08 (t, *J* = 9.6 Hz, 1H), 5.00 (dd, *J* = 8.1, 10.5 Hz, 1H), 4.45 (d, *J* = 8.1 Hz, 1H), 4.26 (dd, *J* = 4.8, 12.1 Hz, 1H), 4.11 (dd, *J* = 2.5, 12.1 Hz, 1H), 3.95 (d, *J* = 9.4 Hz, 1H), 3.63-3.66 (m, 1H), 2.00-2.17 (m, 12 H), 1.85-1.88 (m, 1H), 1.60-1.70 (m, 2H), 1.17-1.25 (m, 2H), 1.05-1.07 (m, 1H), 0.81-0.94 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.4, 169.5, 169.2, 99.7, 84.1, 72.8, 71.6, 71.4, 68.8, 62.2, 49.1, 48.0, 44.9, 36.1, 28.3, 26.4, 20.7, 20.7, 20.6, 19.7, 18.9, 13.3. IR (neat) ν_{max}/cm^{-1} 1755, 1367, 1222, 1039; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{36}O_{10}Na$ 507.2206, found 507.2190.



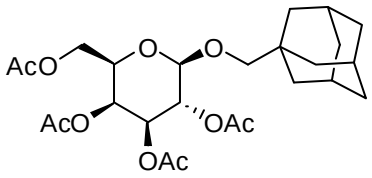
Menthyl-2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.40; $[\alpha]_D^{24}$ –240.2 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.20 (t, *J* = 9.5 Hz, 1H), 5.04 (t, *J* = 9.7 Hz, 1H), 4.93 (dd, *J* = 8.0, 9.6 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.18 (dd, *J* = 5.5, 12.0 Hz, 1H), 4.11 (dd, *J* = 2.7, 12.0 Hz, 1H), 3.67 (ddd, *J* = 2.7, 5.5, 9.9 Hz, 1H), 3.38 (dt, *J* = 4.3, 10.7 Hz, 1H), 2.21-2.23 (m, 1H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.93-1.96 (m, 1H), 1.60-1.64 (m, 2H), 1.58 (s, 3H), 1.31-1.35 (m, 1H), 1.17-1.25 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 4 H), 0.86 (d = 6.6 Hz, 3H), 0.77-0.81 (m, 2H), 0.72 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.4, 169.5, 169.3, 98.8, 79.1, 77.2, 73.1, 71.6, 71.5, 68.9, 62.5, 47.4, 40.8, 34.2, 31.5, 25.0, 23.0, 22.3, 20.9, 20.7, 20.7, 20.6, 20.6, 15.4; IR (neat) ν_{max}/cm^{-1} 1749, 1367, 1226, 1037; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{38}O_{10}Na$ 509.2328, found 509.2332.



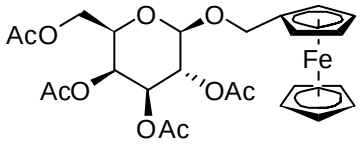
Pregnenolonyl-2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.42; $[\alpha]_D^{24}$ +46.96 (*c* = 0.1, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.36 (m, 2H), 5.18 (dd, *J* = 8.0, 10.4 Hz, 1H), 5.01 (dd, *J* = 3.4, 10.4 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.18 (dd, *J* = 6.6, 11.2 Hz, 1H), 4.10 (dd, *J* = 7.1, 11.2 Hz, 1H), 3.88 (t, *J* = 6.6 Hz, 1H), 3.54-3.55 (m, 1H), 2.52 (t, *J* = 9.6 Hz, 1H), 2.19-2.25 (m, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.85-1.91 (m, 2H), 1.60-1.67 (m, 3H), 1.43-1.52 (m, 3H), 1.21-1.29 (m, 4H), 1.03-1.19 (m, H), 0.93-1.01 (m containing s, 4H), 0.89 (t, *J* = 7.0 Hz, 1H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 209.5, 170.4, 170.4, 170.2, 169.4, 140.3, 121.9, 100.3, 80.2, 71.0, 70.6, 69.1, 67.0, 63.7, 61.3, 56.9, 50.0, 44.0, 38.9, 38.8, 37.2, 36.7, 31.8, 31.8, 31.6, 29.5, 24.5, 22.8, 21.1, 20.8, 20.7, 20.6, 19.4, 13.2. IR (neat) ν_{max}/cm^{-1} 1749, 1367, 1217, 1055; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{35}H_{50}O_{11}Na$ 669.3251, found 669.3242.



Citronellyl-2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.37; $[\alpha]_D^{24}$ +3.9 (*c* = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (t, *J* = 9.5 Hz, 1H), 5.08 (t, *J* = 9.6 Hz, 2H), 4.97 (dd, *J* = 8.0, 9.5 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.26 (dd, *J* = 4.7, 12.3 Hz, 1H), 4.13 (dd, *J* = 2.3, 12.3 Hz, 1H), 3.89-3.94 (m, 1H), 3.68 (ddd, *J* = 2.3, 4.7, 9.9 Hz, 1H), 3.46-3.52 (m, 1H), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.9-1.99 (m, 2H), 1.49-1.67 (m containing s, 5H), 1.25-1.37 (m, 2H), 1.11-1.18 (m, 1H), 0.86 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.4, 169.4, 169.3, 131.3, 124.6, 101.0, 72.9, 71.7, 71.3, 68.5, 68.5, 62.0, 37.2, 36.3, 29., 25.7, 25.4, 20.7, 20.6, 20.6, 19.1, 17.6; IR (neat) ν_{max}/cm^{-1} 1749, 1371, 1226, 1056; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{24}H_{38}O_{10}Na$ 509.2363, found 509.152352.

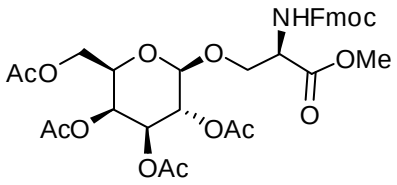


Adamentanemethanyl-2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.55; $[\alpha]_D^{24}$ –86.16 (*c* = 0.2, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.37 (d, *J* = 3.2 Hz, 1H), 5.21 (dd, *J* = 8.2, 10.4 Hz, 1H), 5.00 (dd, *J* = 3.2, 10.4 Hz, 1H), 4.37 (d, *J* = 7.9 Hz, 1H), 4.12-4.17 (m, 2H), 3.86 (t, *J* = 6.8 Hz, 1H), 3.50 (d, *J* = 9.5 Hz, 1H), 2.97 (d, *J* = 9.6 Hz, 1H), 2.14 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.94 (m, 2H), 1.69-1.72 (m, 3H), 1.60-1.62 (m, 4H), 1.46-1.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.4, 170.2, 169.3, 102.5, 81.1, 70.9, 70.5, 69.0, 67.1, 61.2, 39.3, 37.1, 33.9, 28.1, 20.8, 20.7, 20.6; IR (neat) ν_{max}/cm^{-1} 1751, 1369, 1224, 1053; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{25}H_{36}O_{10}Na$ 519.2206, found 519.2198.

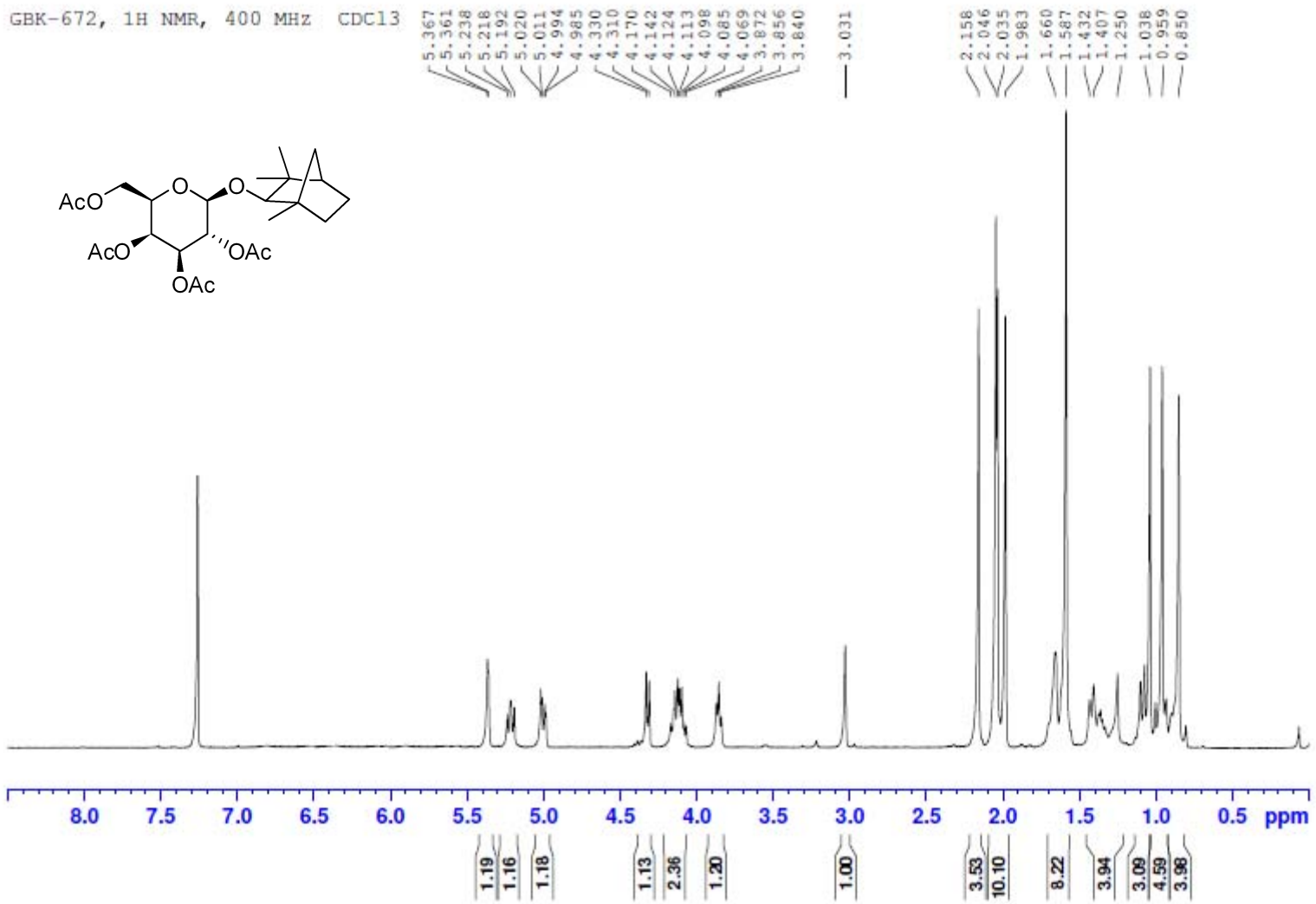


Ferrocenemethyl 2,3,4,6-tetraacetyl-*O*-β-D-galactopyranoside: *Rf* (50% EtOAc/Hexane) 0.42; $[\alpha]_D^{24}$ +22.9 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36 (d, *J* = 3.2 Hz, 1H), 5.18 (dd, *J* = 8.0, 10.2 Hz, 1H), 4.96 (dd, *J* = 3.2, 10.2 Hz, 1H), 4.63 (d, *J* = 11.8, 1H), 4.49 (d, *J* = 7.9 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 4.11-4.19 (m, 9H), 3.86 (t, *J* = 6.4 Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 1.96 (s 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.2, 169.4, 99.4,

82.0, 71.0, 70.6, 69.3, 69.0, 68.9, 68.8, 68.6, 68.5, 68.5, 67.4, 67.1, 61.3, 20.8, 20.7, 20.7, 20.6; IR (neat) ν_{max}/cm^{-1} 1749, 1369, 1222, 1053; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{27}H_{36}FeO_{10}Na$ 599.1556, found 599.1558.



N-9-fluorenylmethoxycarbonyl-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-serine methyl ester: R_f (50% EtOAc/Hexane) 0.25; $[\alpha]_D^{24}$ –7.3 (*c* = 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.71 (m, 2H), 7.40 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 5.74 (d, *J* = 4.7 Hz, 1H), 5.63 (d, *J* = 8.6 Hz, 1H), 5.42 (s. 1H), 5.02 (dd, *J* = 3.0, 6.7 Hz), 4.53 (d, *J* = 8.6 Hz, 1H), 4.30-4.41 (m, 2H), 4.22-4.29 (m, 3H), 4.08-4.14 (m, 2H), 4.0 (dd, *J* = 2.2, 9.6 Hz, 1H), 3.78 (s, 3H), 2.04-2.10 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.4, 170.0, 169.7, 155.9, 143.8, 143, 141.3, 127.7, 125.1, 121.0, 95.5, 73.9, 71.4, 69.2, 67.3, 65.8, 63.1, 61.3, 53.9, 52.7, 47.1, 23.5, 20.7, 20.5; IR (neat) ν_{max}/cm^{-1} 1747, 1367, 1217, 1060; HRMS (ESI) m/z $[M + Na]^+$ calcd for $C_{33}H_{37}NO_{14}Na$ 694.2112, found 694.2082.


GBK-672, 1H NMR, 400 MHz CDCl3
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5.238
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5.020
5.011
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4.310
4.170
4.142
4.124
4.113
4.098
4.085
4.069
3.872
3.856
3.840
3.031
2.158
2.046
2.035
1.983
1.660
1.587
1.432
1.407
1.250
1.038
0.959
0.850
AcO
AcO
OAc
OAc
O
O
8.0
7.5
7.0
6.5
6.0
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2.0
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ppm
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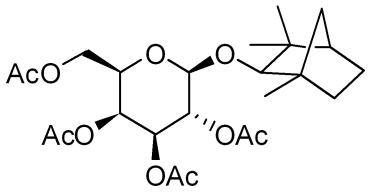
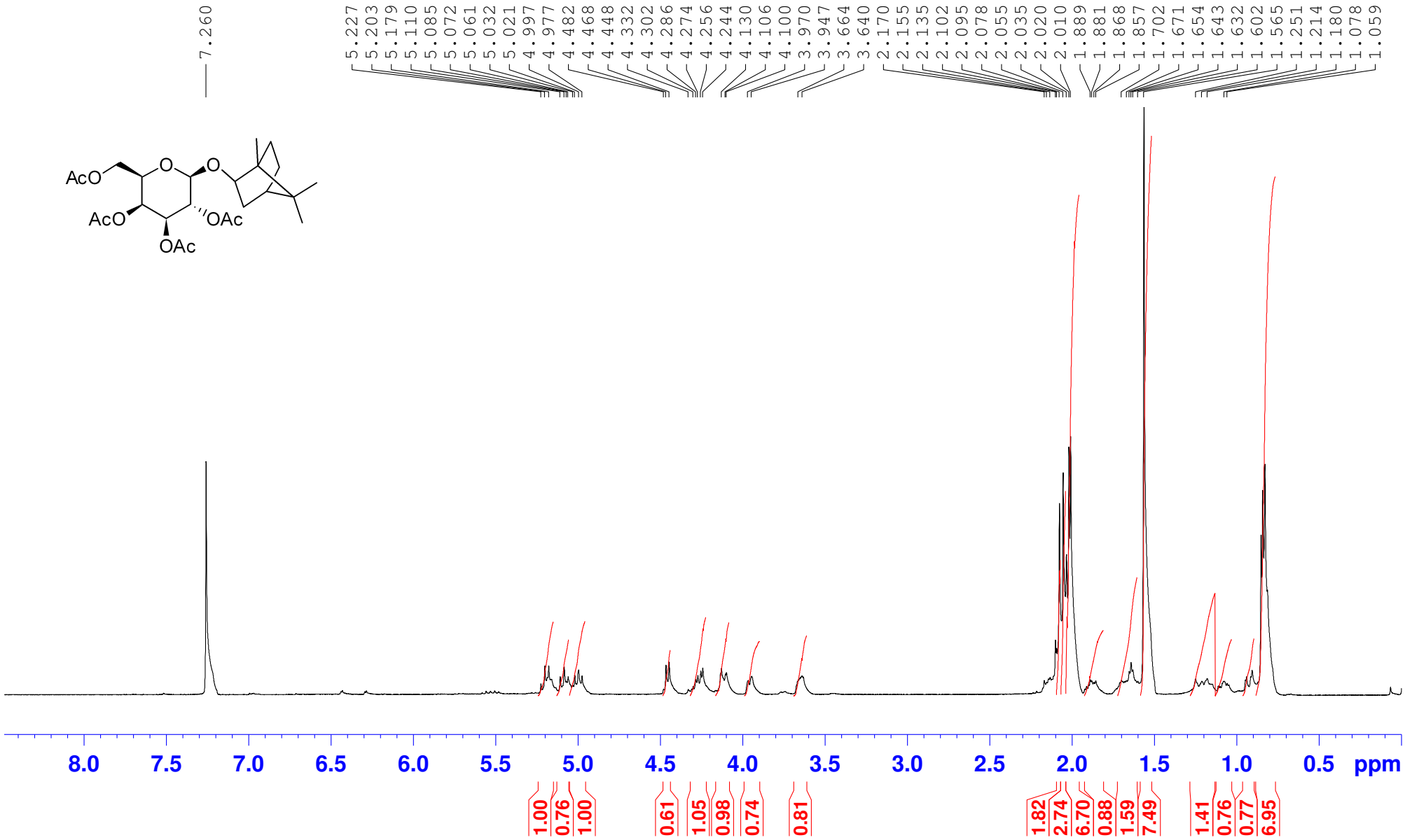
1.18
1.13
2.36
1.20
1.00
3.53
10.10
8.22
3.94
3.09
4.59
3.98

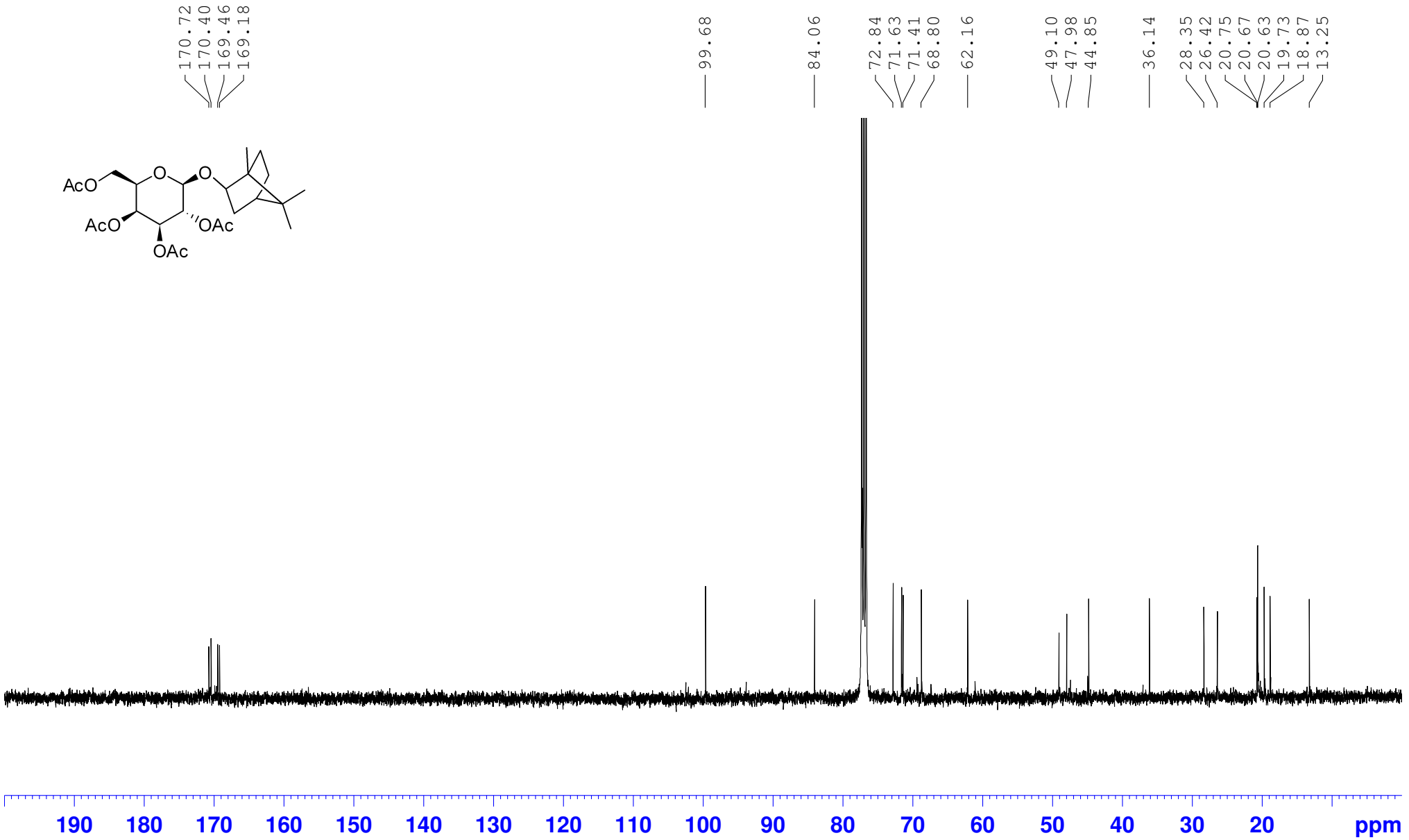
GBK-E-Fenchol-Carbon, 13C NMR, 400 MHz CDCl3



GBK-760, 1HNMR, AV400mHz, CDCL3

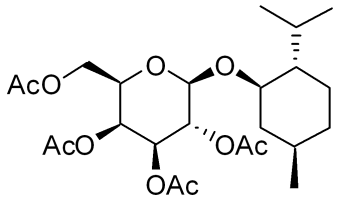


GBK-760-A, 13C NMR, AV400mHz, CDCL3

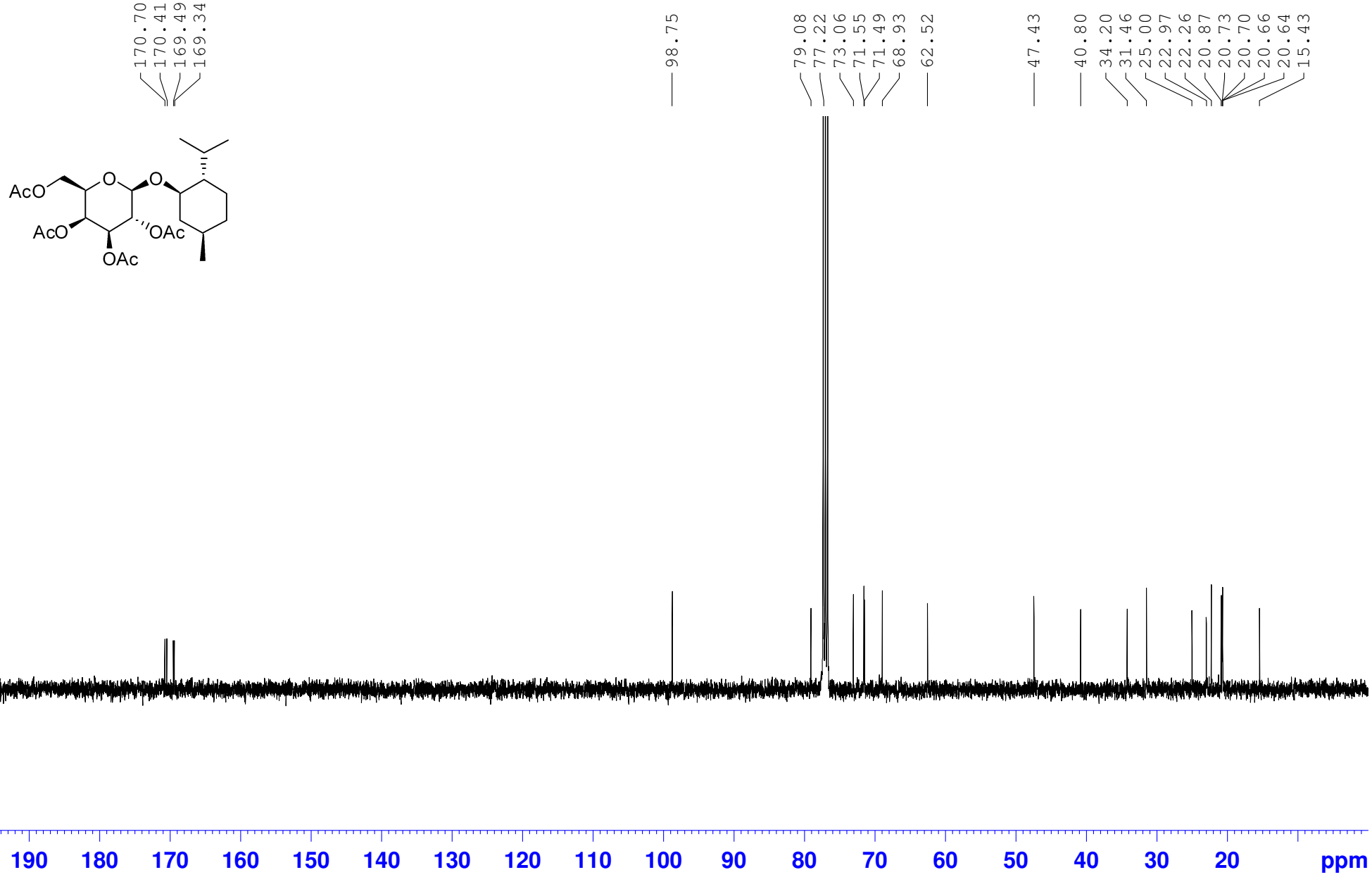


GBK-759, 1HNMR, AV400mHz, CDCL3

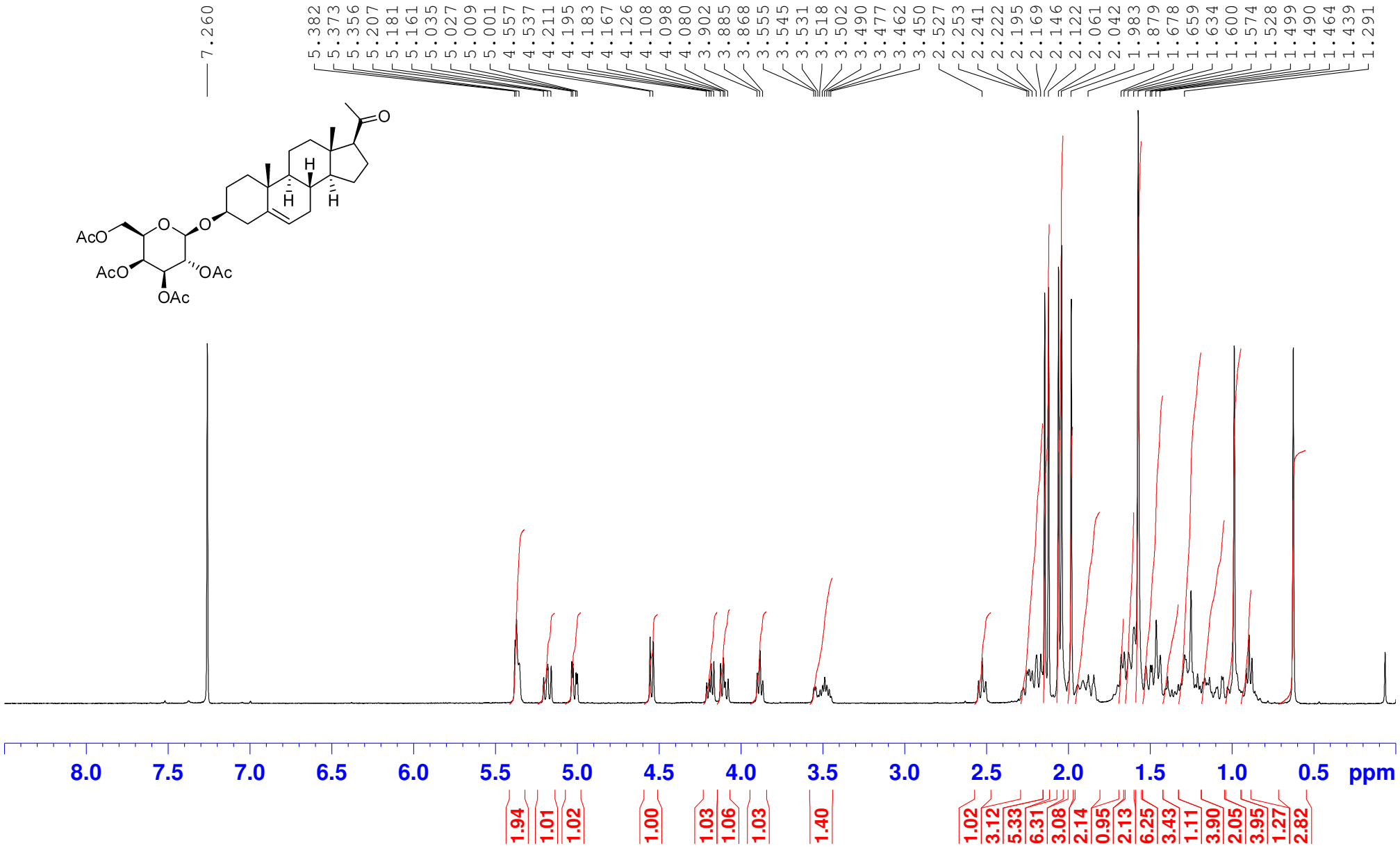
7.260 5.225 5.201 5.177 5.068 5.044 5.020 4.952 4.931 4.927 4.907 4.558 4.538 4.209 4.196 4.179 4.165 4.132 4.125 4.102 4.095 3.689 3.682 3.675 3.668 3.664 3.657 3.650 3.643 3.404 3.388 3.378 3.362 2.239 2.233 2.221 2.216 2.204 2.198 2.058 2.049 2.032 2.025 2.000 1.958 1.928 1.648 1.640 1.622 1.615 1.607 1.579 1.345 1.336 1.330 1.252 1.227 1.200 1.171 0.964 0.958 0.921 0.905 0.871 0.854 0.832 0.803 0.773 0.734 0.717



GBK-759, 13CNMR, AV400mHz, CDCL3



GBK-Preg, 1H NMR, 400 MHz CDCl3



GBK-Preg-Carbon 1 1 D:\spms\cbc\DrLiu\Nov10 GBK

GBK-Preg, 13C NMR, 400 MHz CDCl3

209.5259
170.4291
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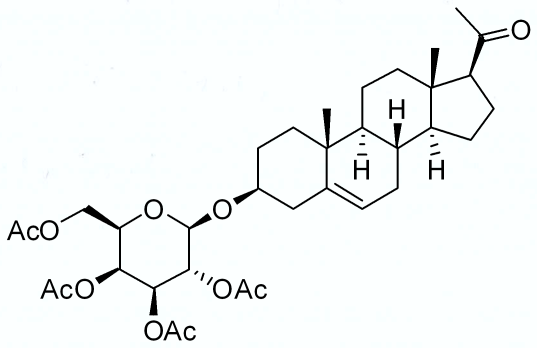
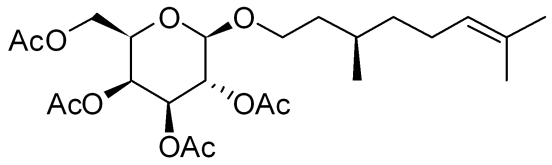
170.2411
169.4091
140.3245
121.8822
100.2820
80.1628
71.0114
70.5569
69.0796
67.0249
63.7044
61.2748
56.8980
50.0099
43.9980
38.9082
38.8175
37.1998
36.7370
31.8254
31.7992
31.5509
29.4946
24.4877
22.8217
21.0627
20.8376
20.7128
20.6262
19.3523
13.2300

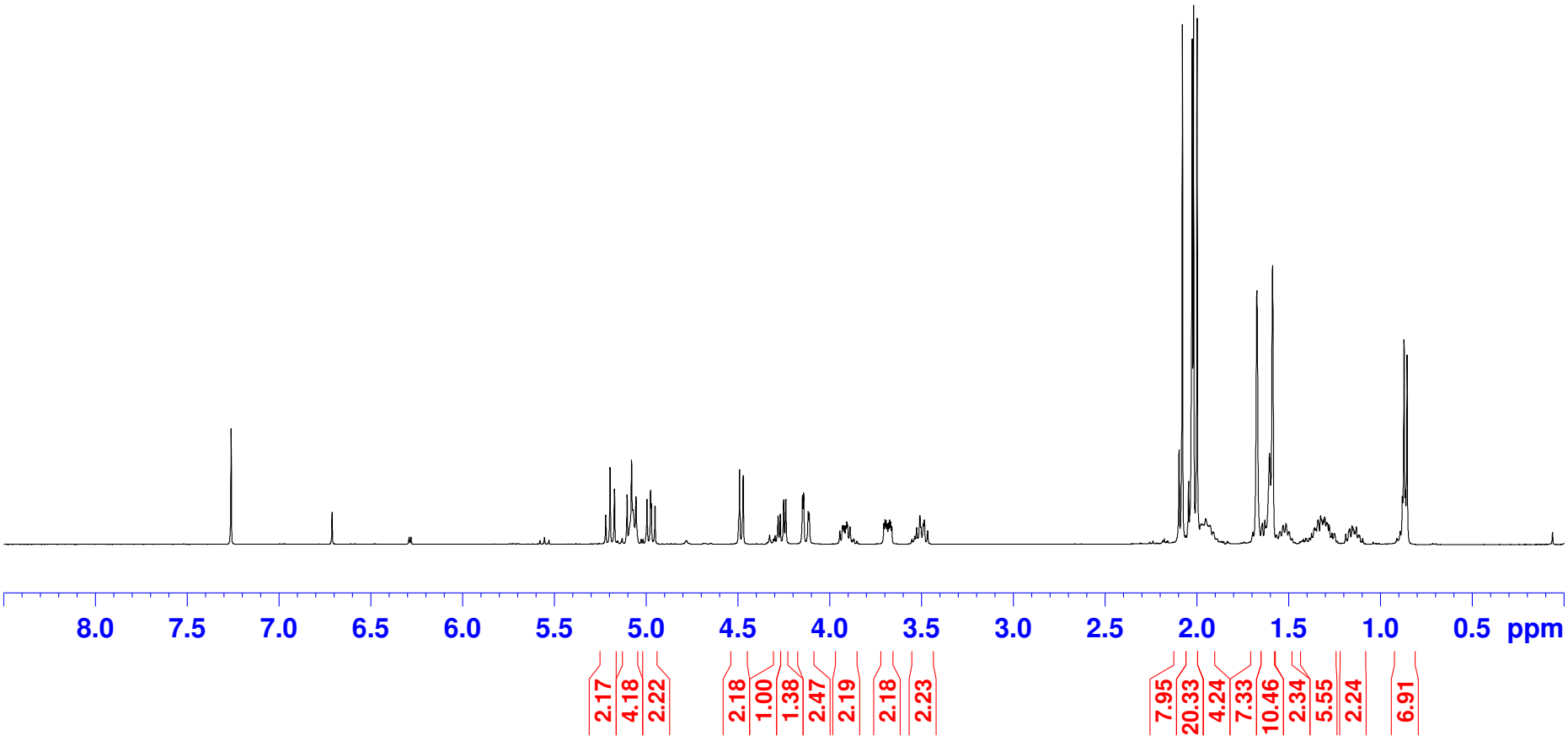


200
150
100
50
[ppm]

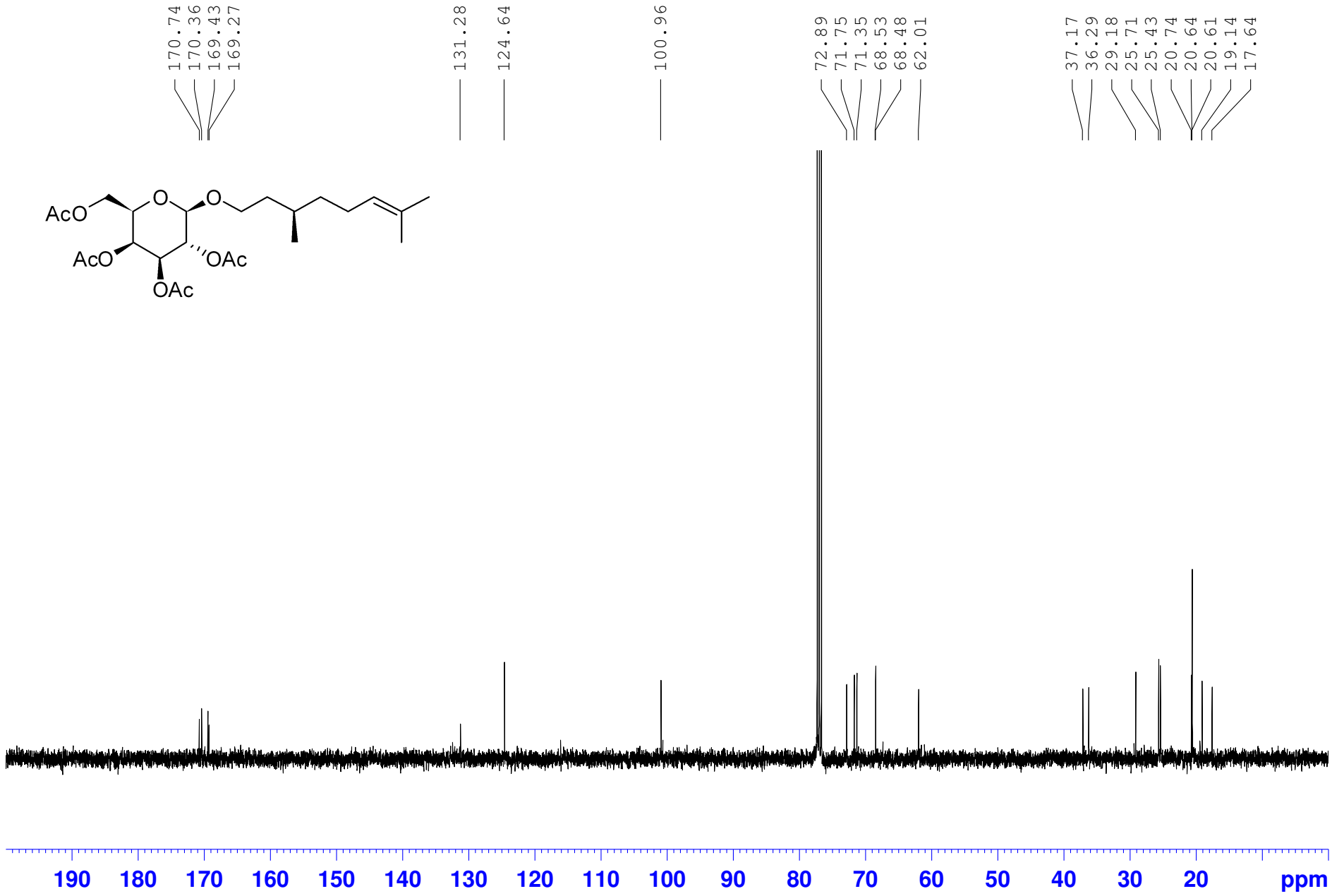
GBK-740, 1NMR AV400 MHz CDCl3

6.710 5.222 5.198 5.174 5.105 5.081 5.072 5.057 4.997 4.977 4.973 4.953 4.492 4.473 4.283 4.271 4.252 4.240 4.149 4.143 4.119 4.113 3.928 3.922 3.914 3.909 3.904 3.706 3.700 3.694 3.688 3.681 3.675 3.669 3.510 3.491 3.486 2.098 2.080 2.046 2.026 2.019 1.999 1.976 1.952 1.929 1.674 1.644 1.630 1.605 1.589 1.531 1.515 1.342 1.326 1.312 1.304 1.294 1.288 1.280 1.155 0.881 0.872 0.865 0.856

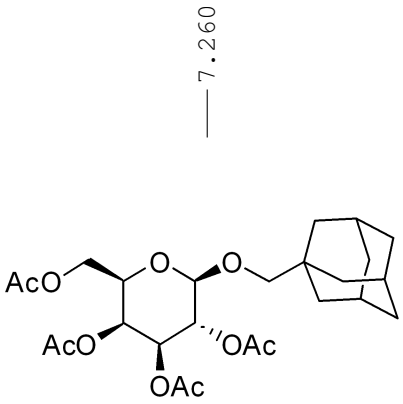




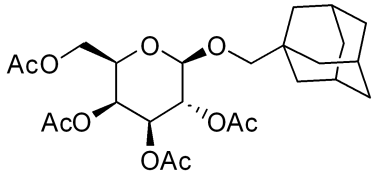
GBK-740, 13C NMR AV400 MHz CDCl3



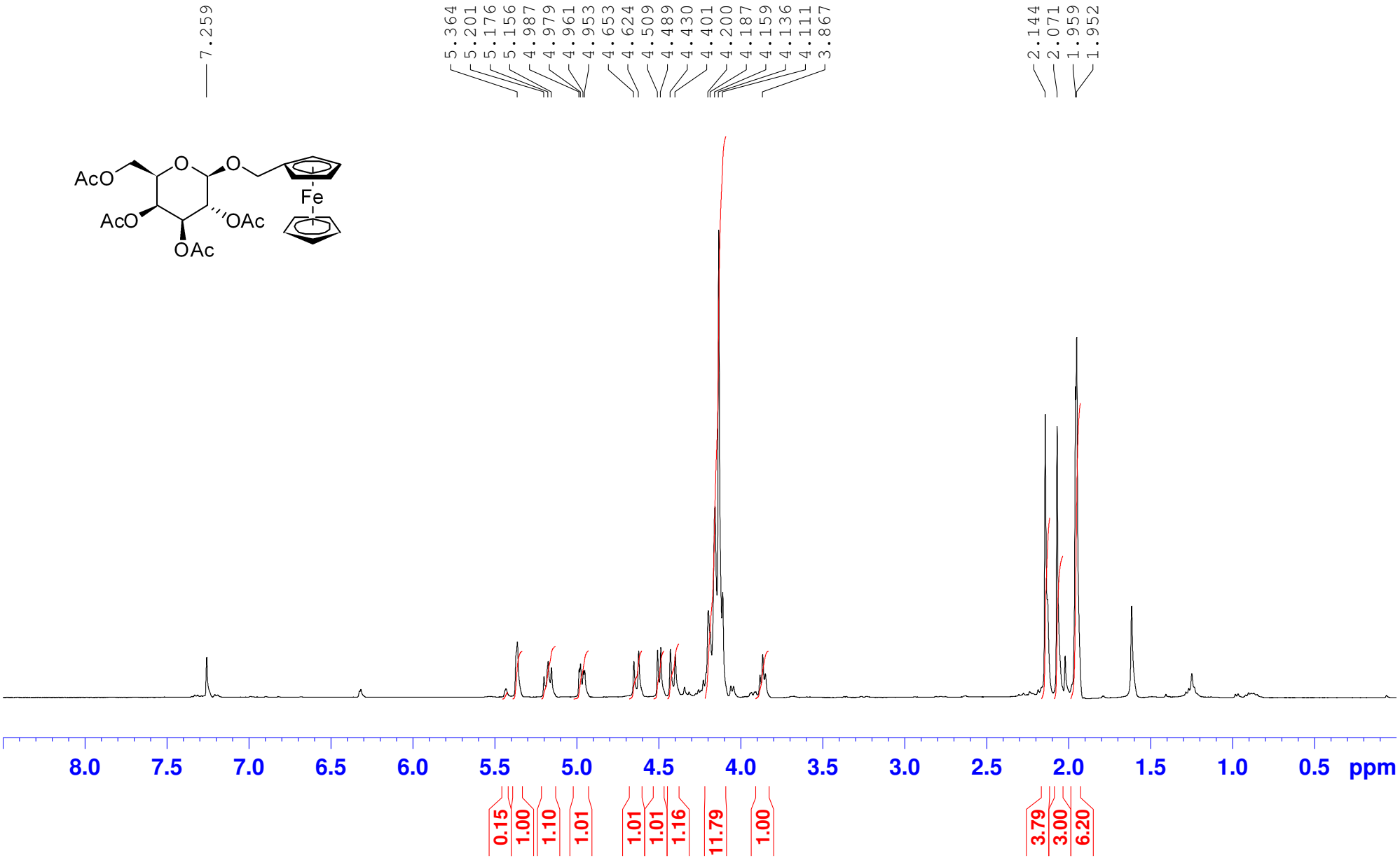
GBK-766, 1H NMR, 400 MHz CDCl3



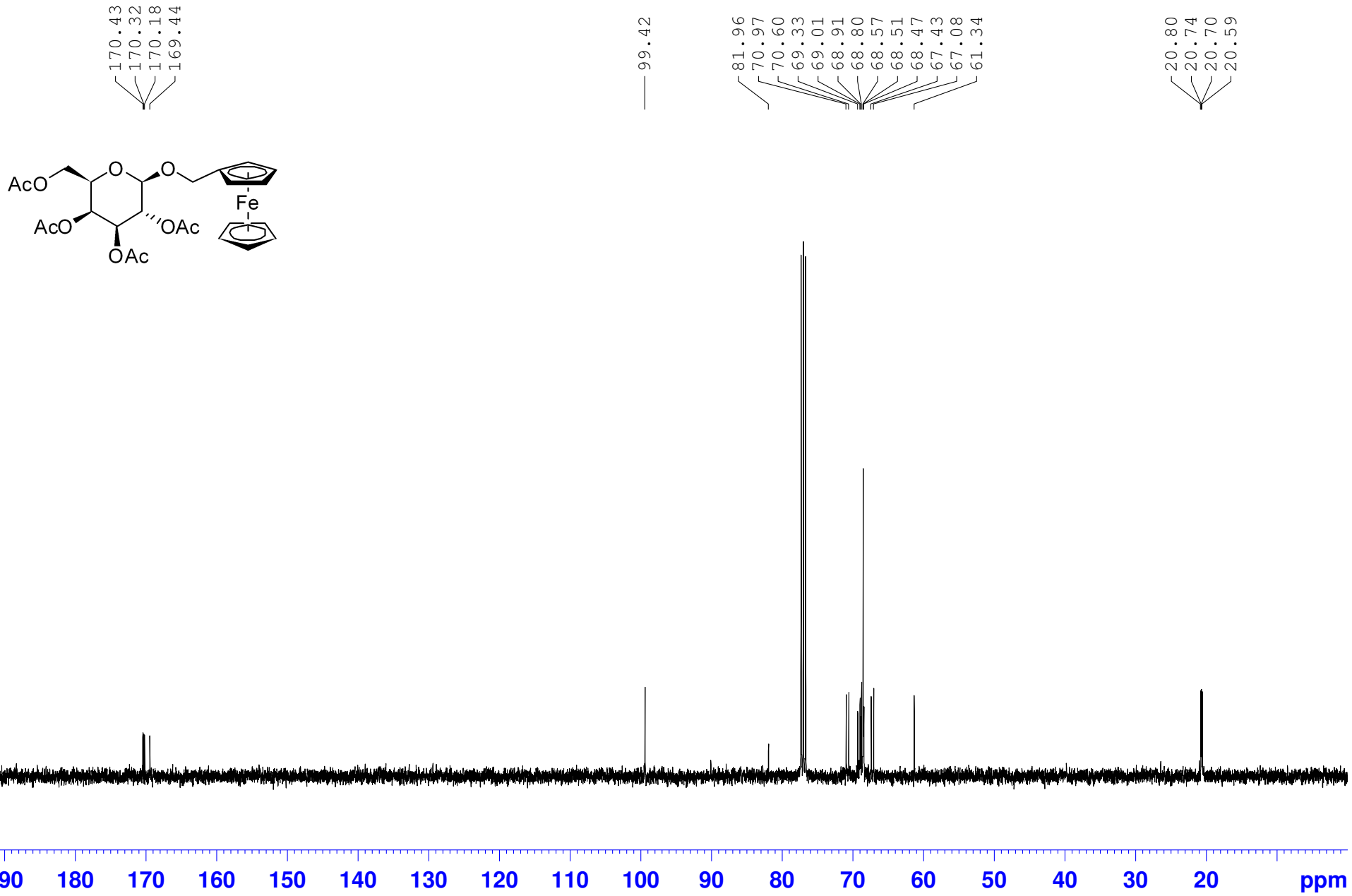
GBK-766, 13C NMR, 400 MHz CDCl3



GBK-767, 1H NMR, 400 MHz CDCl3

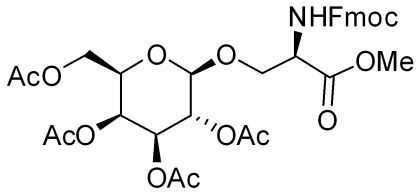


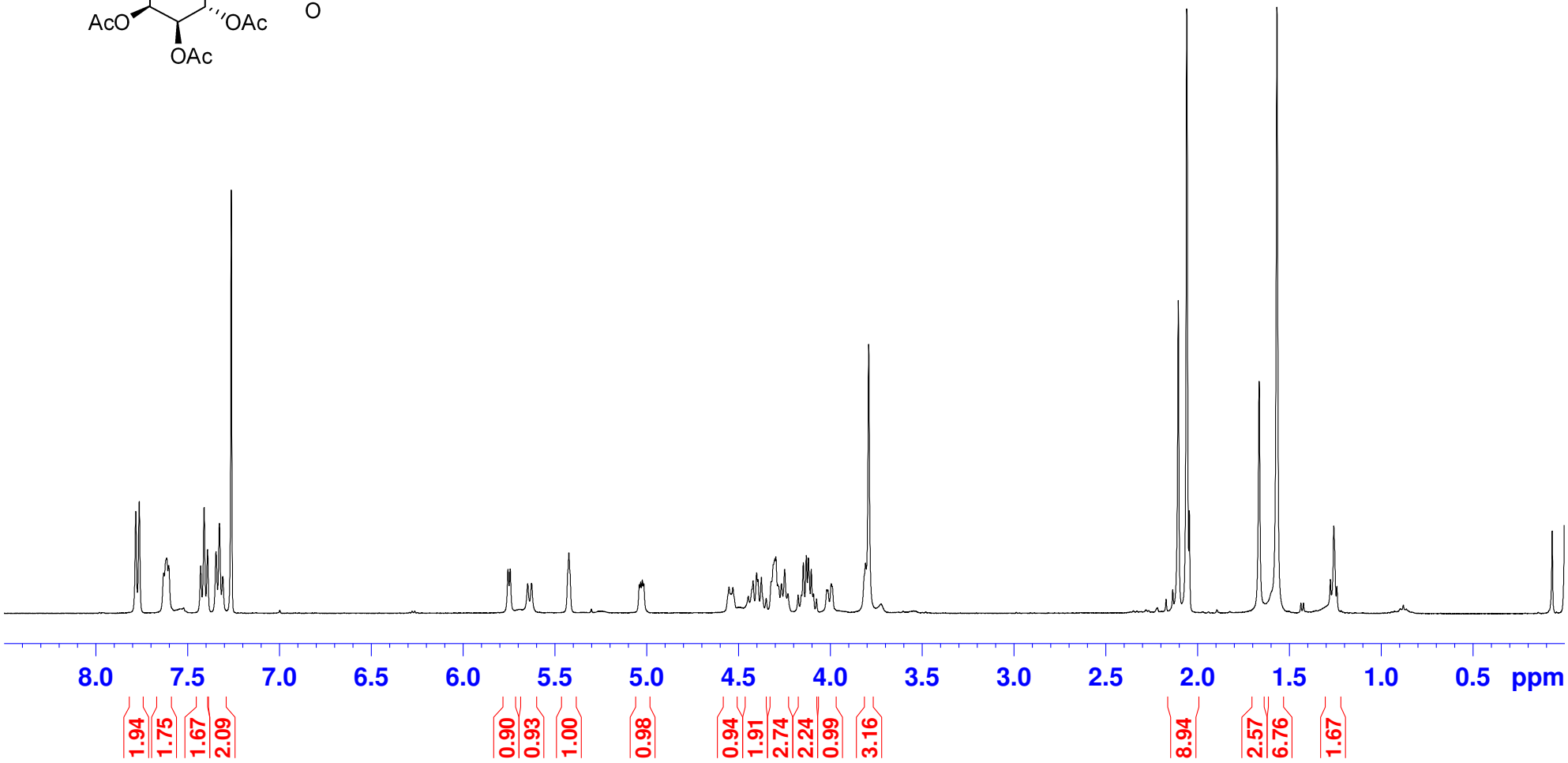
GBK-767, 13C NMR, 400 MHz CDCl3



GBK-768, 1H NMR, 400 MHz CDCl3

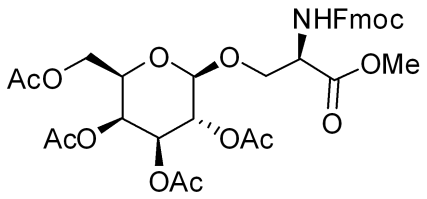
7.780 7.762 7.629 7.612 7.601 7.426 7.408 7.389 7.343 7.325 7.306 7.260 5.753 5.741 5.646 5.624 5.421 5.038 5.030 5.021 5.014 4.550 4.528 4.418 4.399 4.391 4.373 4.300 4.294 4.284 4.264 4.246 4.228 4.145 4.128 4.117 4.101 4.089 4.017 4.011 3.993 3.805 3.789 2.105 2.059 2.045 1.664 1.567 1.258



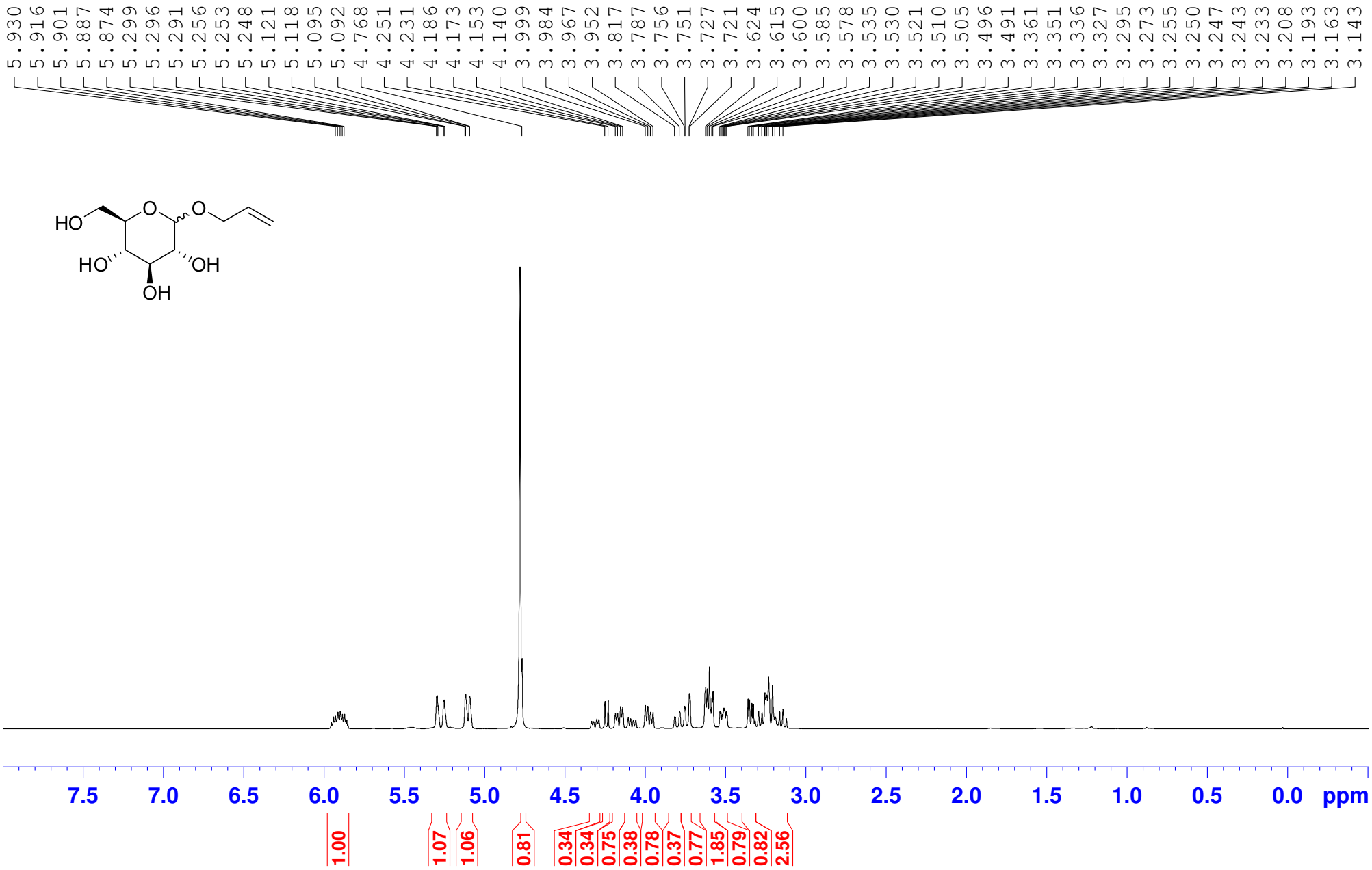


GBK-768, 13C NMR, 400 MHz CDCl3

170.48
170.40
170.05
169.79
155.94
143.84
143.74
141.30
127.76
127.10
125.13
121.09
120.02
97.53
73.98
71.41
69.29
67.31
65.90
63.16
61.32
54.00
52.71
47.10
23.58
20.72
20.57

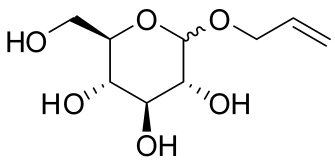


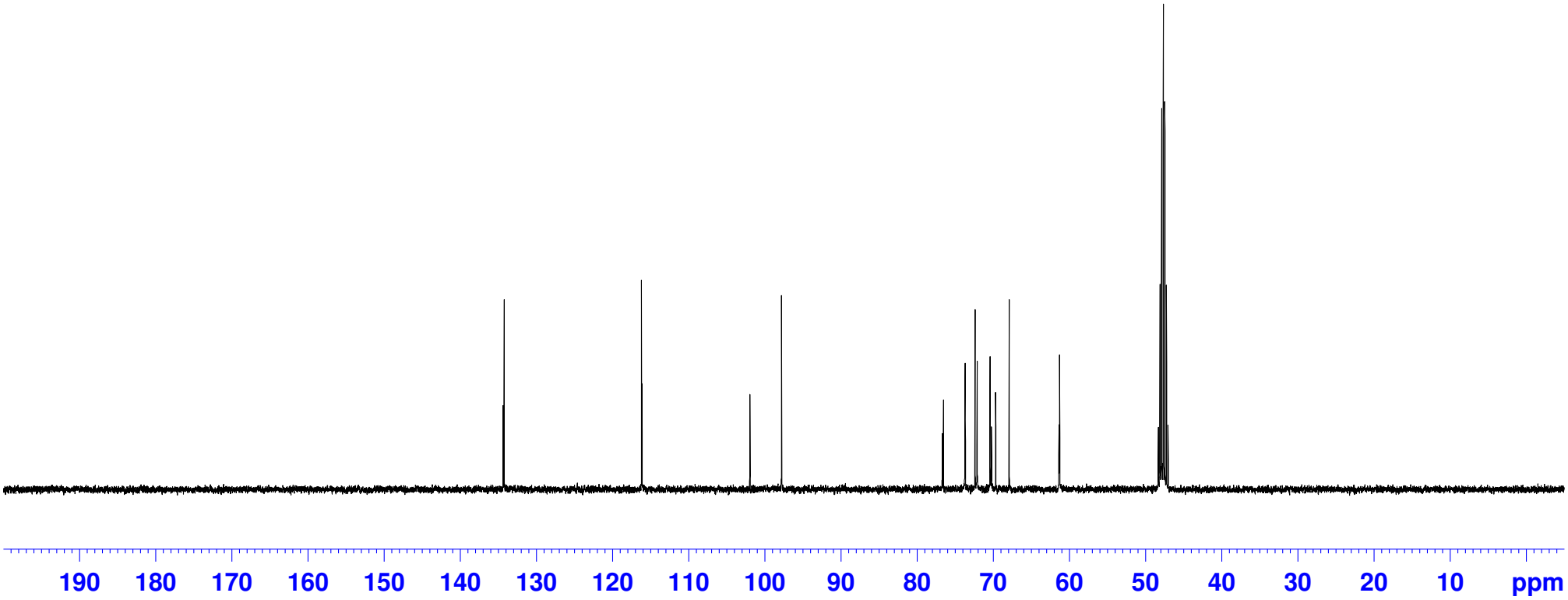
GBK-539, 1HNMR, 400NMR MEOD



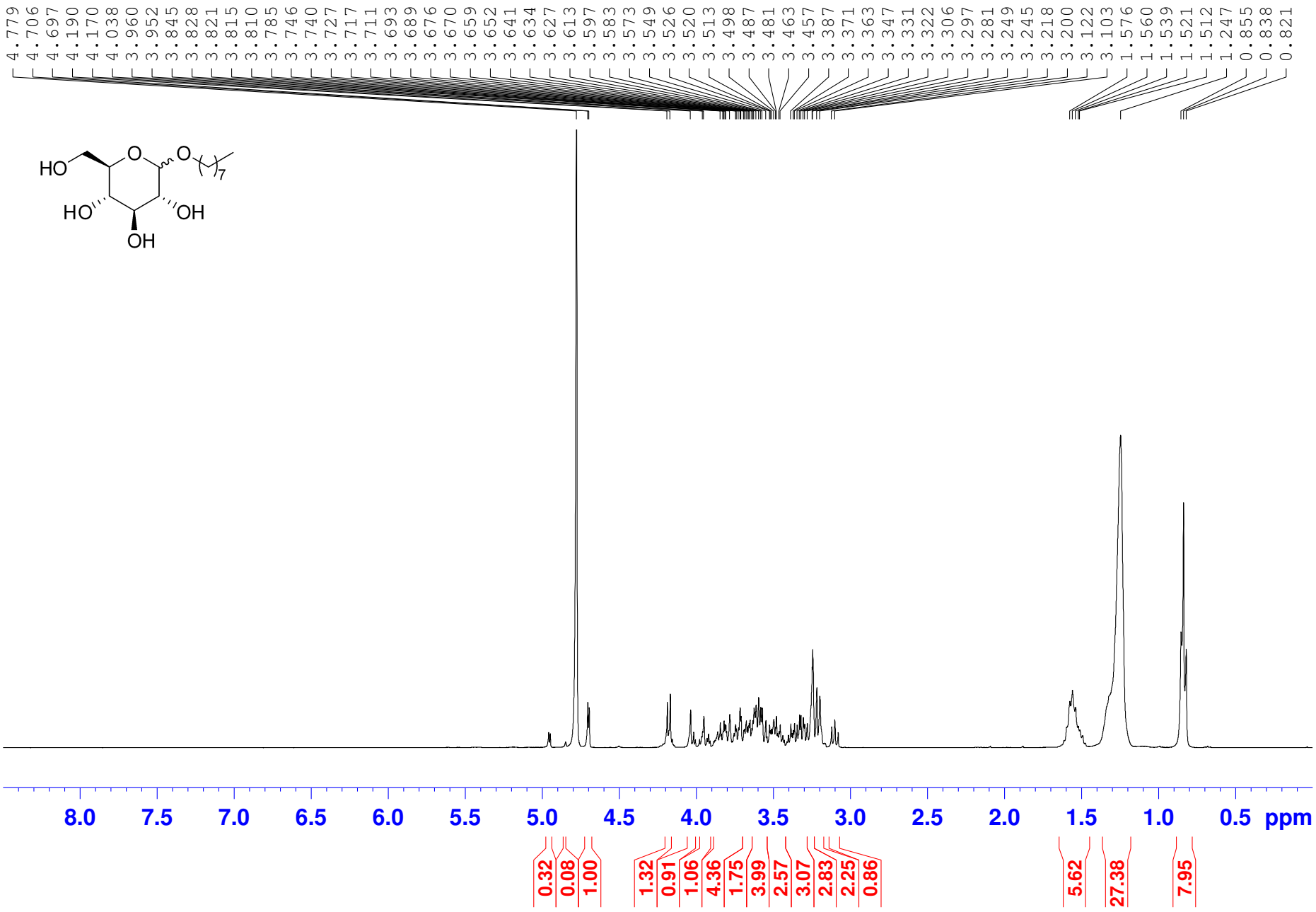
GBK-539, 13C NMR, 400NMR MEOD

134.36
134.23
116.17
116.12
101.95
97.79
76.67
76.53
73.69
73.66
72.37
72.11
70.40
70.22
69.67
67.90
61.36
61.27
48.30
48.09
47.88
47.66
47.45
47.24
47.03

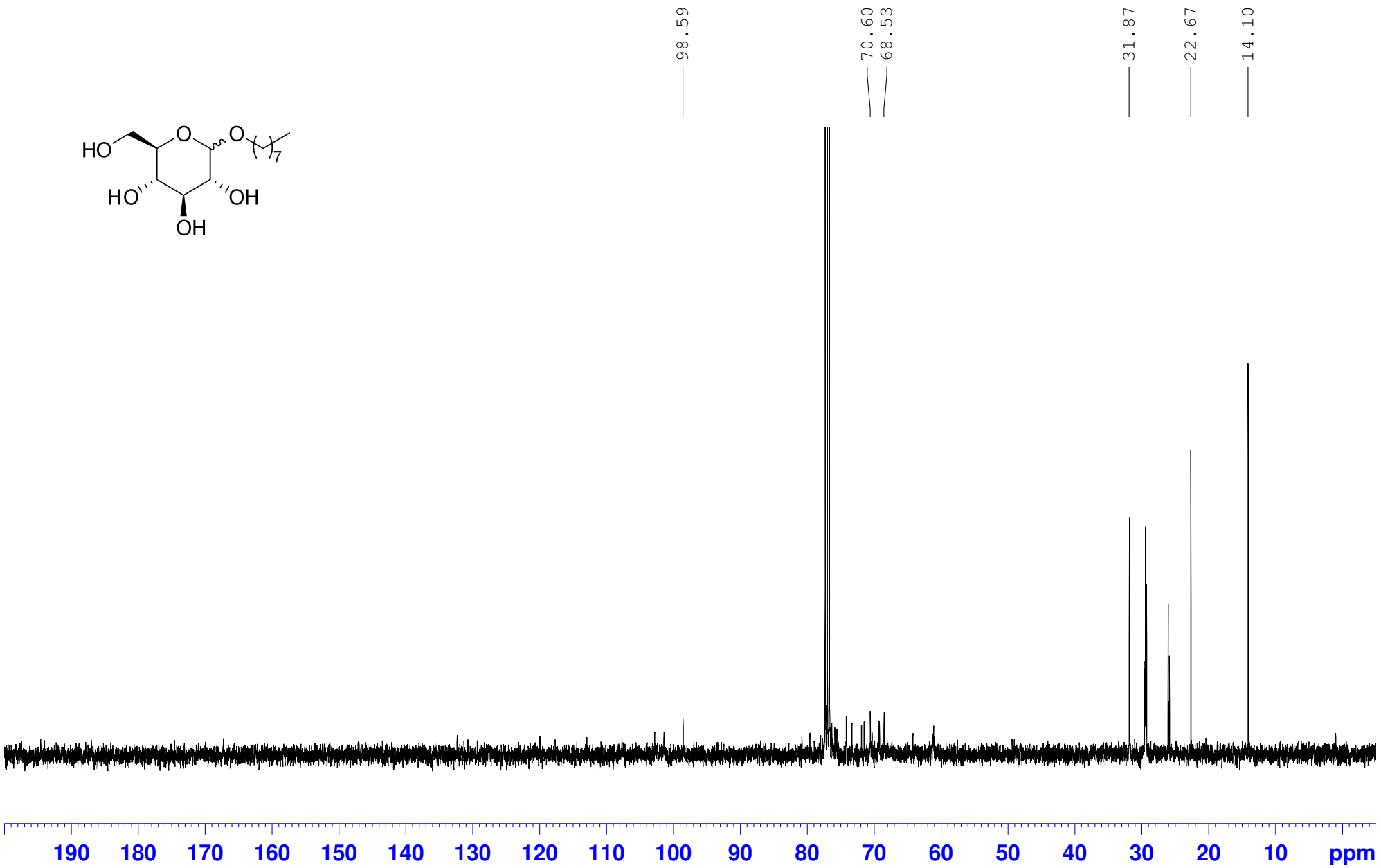




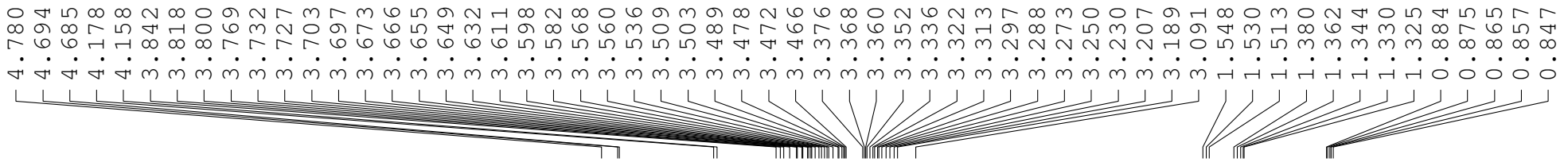
GBK-octanol, Av400 MEOD, 01-Dec-10

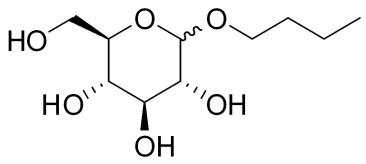


GBK-554, 400NMR CDCl3 13C NMR

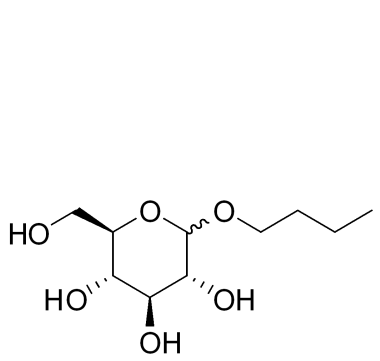


GBK-556, 400NMR MEOD 1H NMR

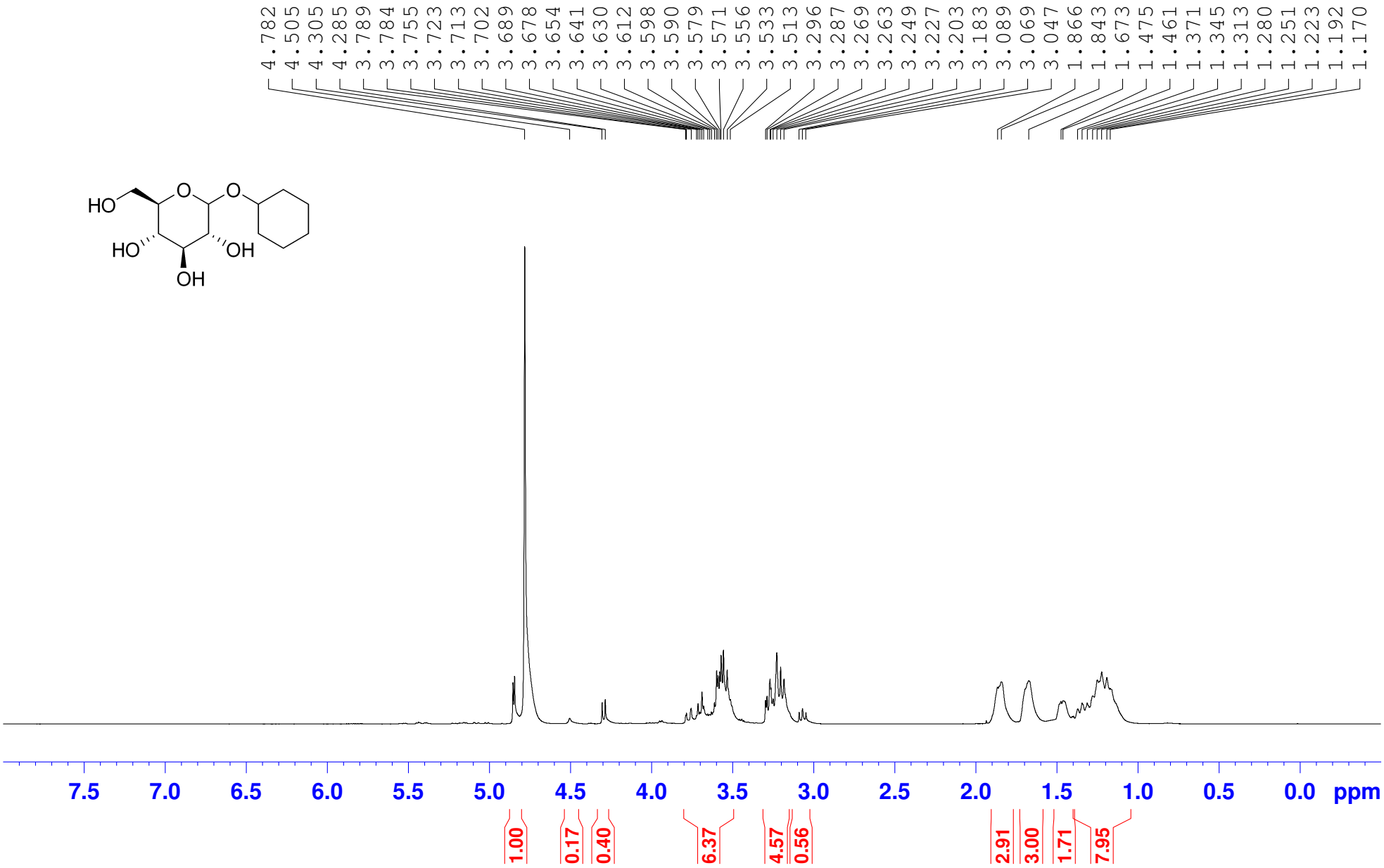




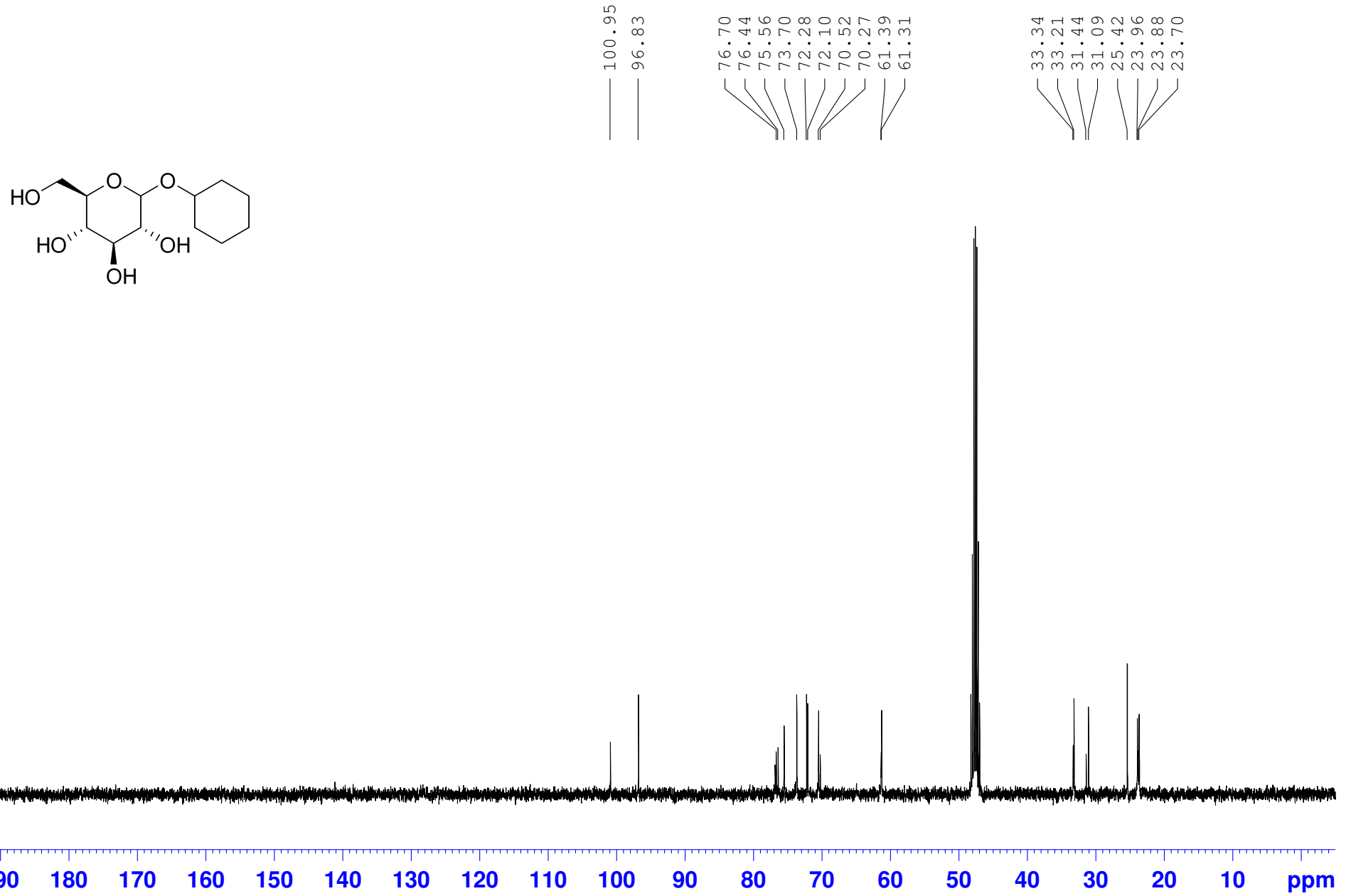
GBK-556, 400NMR MEOD 13C NMR



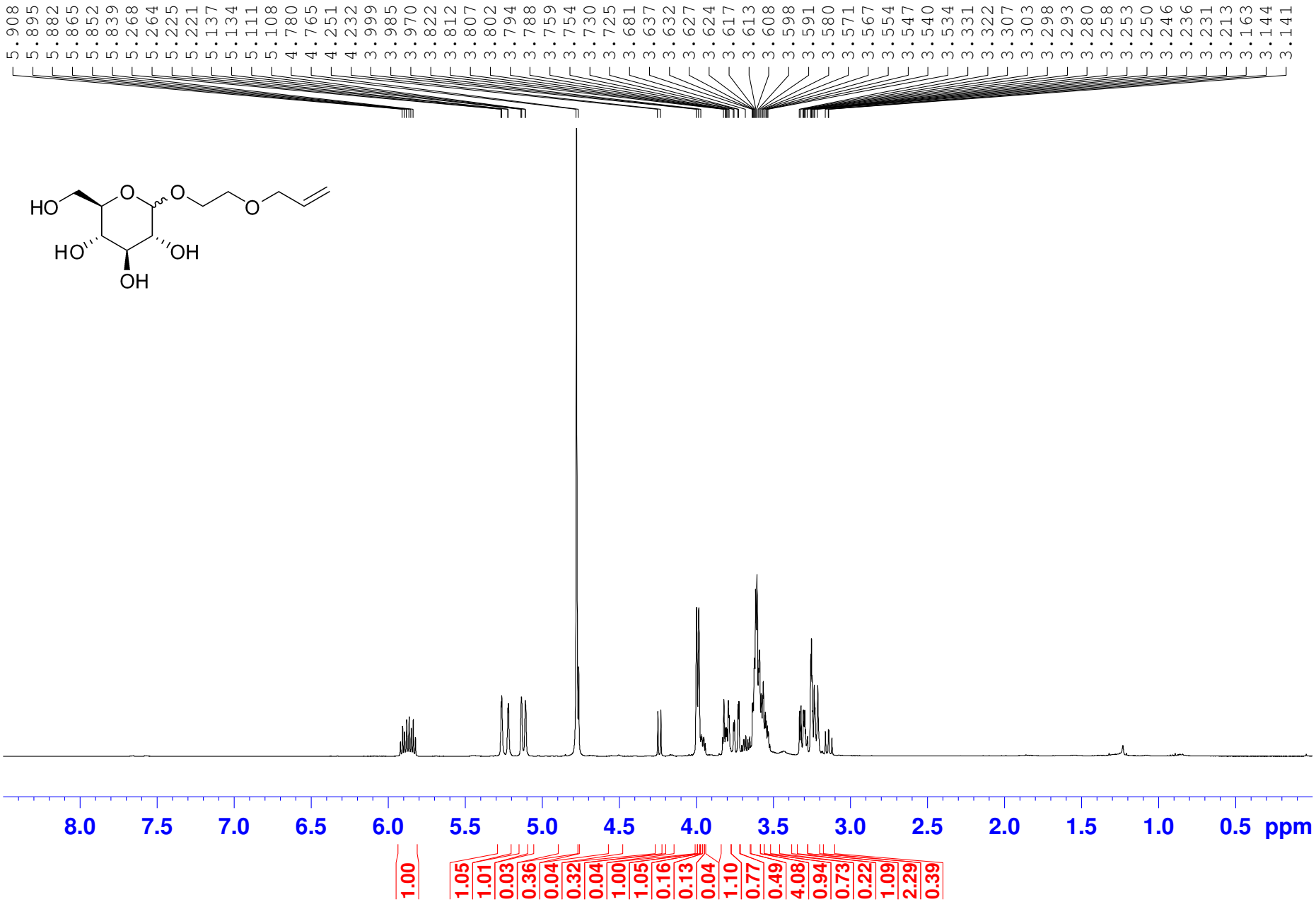
GBK-568, 1H AV400MHz, MEOD



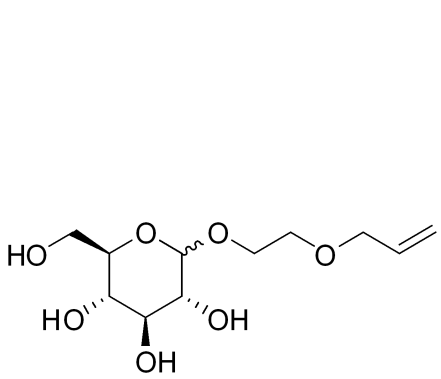
GBK-568, 13C AV400MHz, MEOD



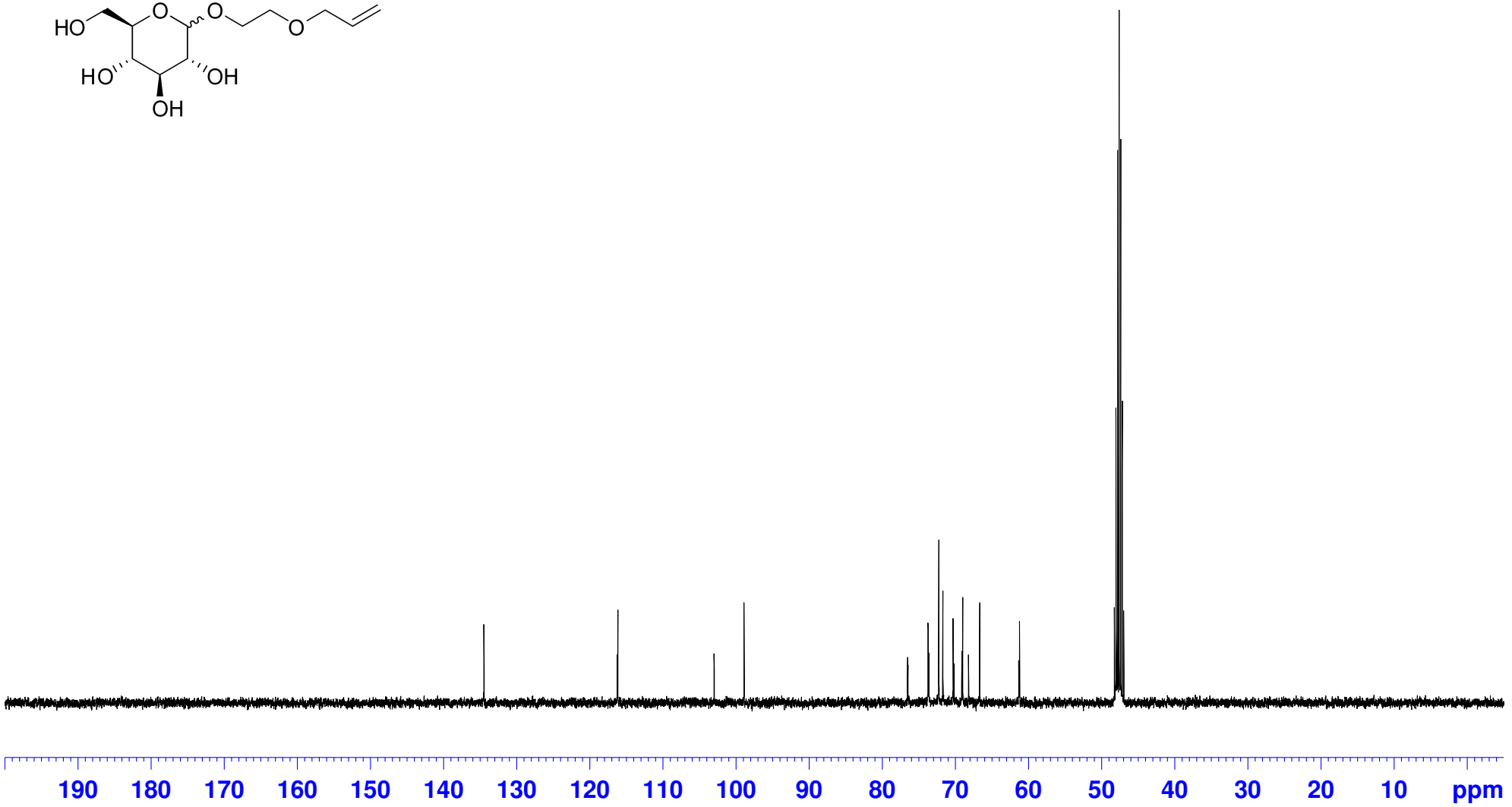
GBK-569-allyloxyethanol, Av400 MeOD, 01-Dec-10



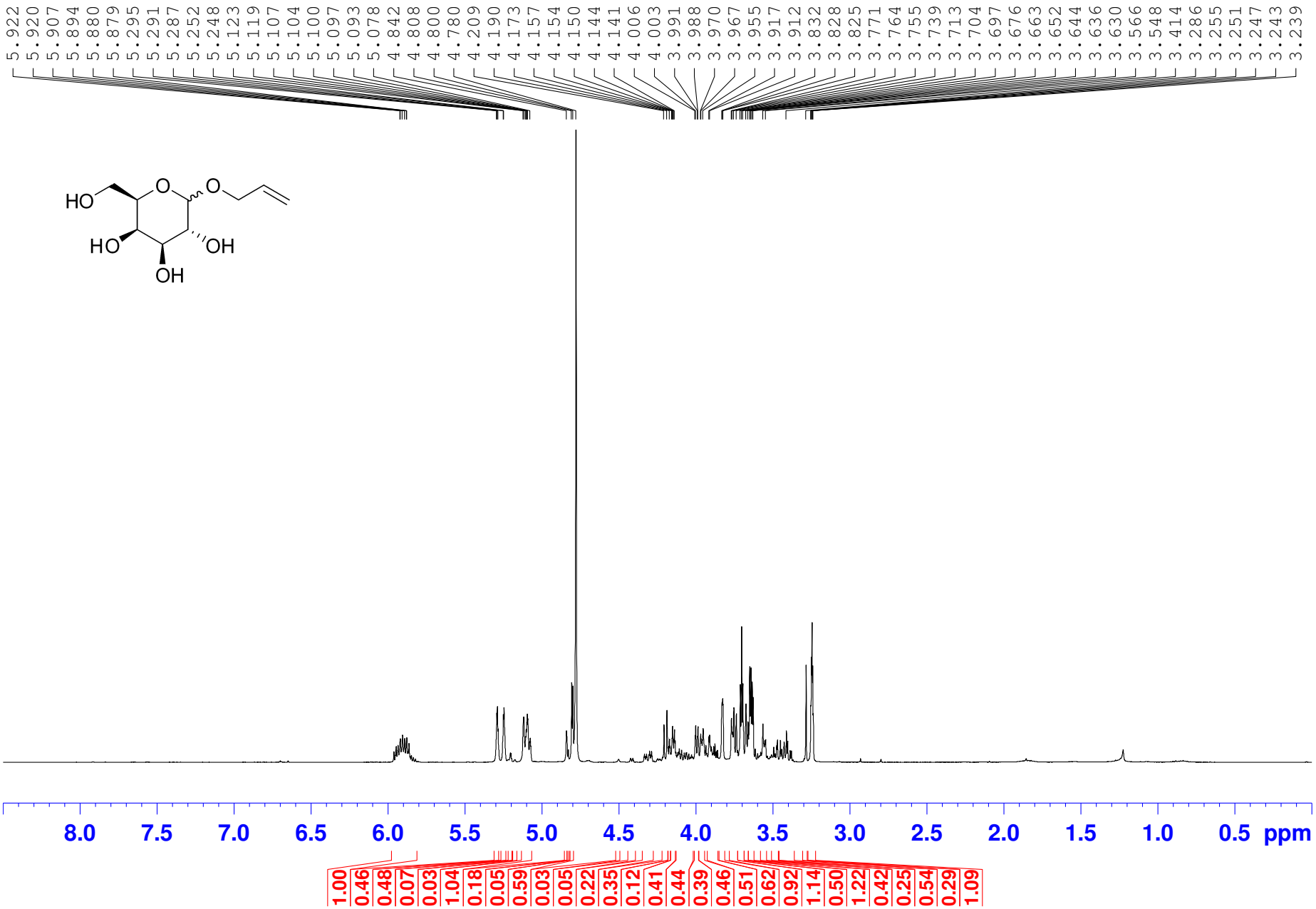
GBK-569, 13C AV400MHz, MEOD



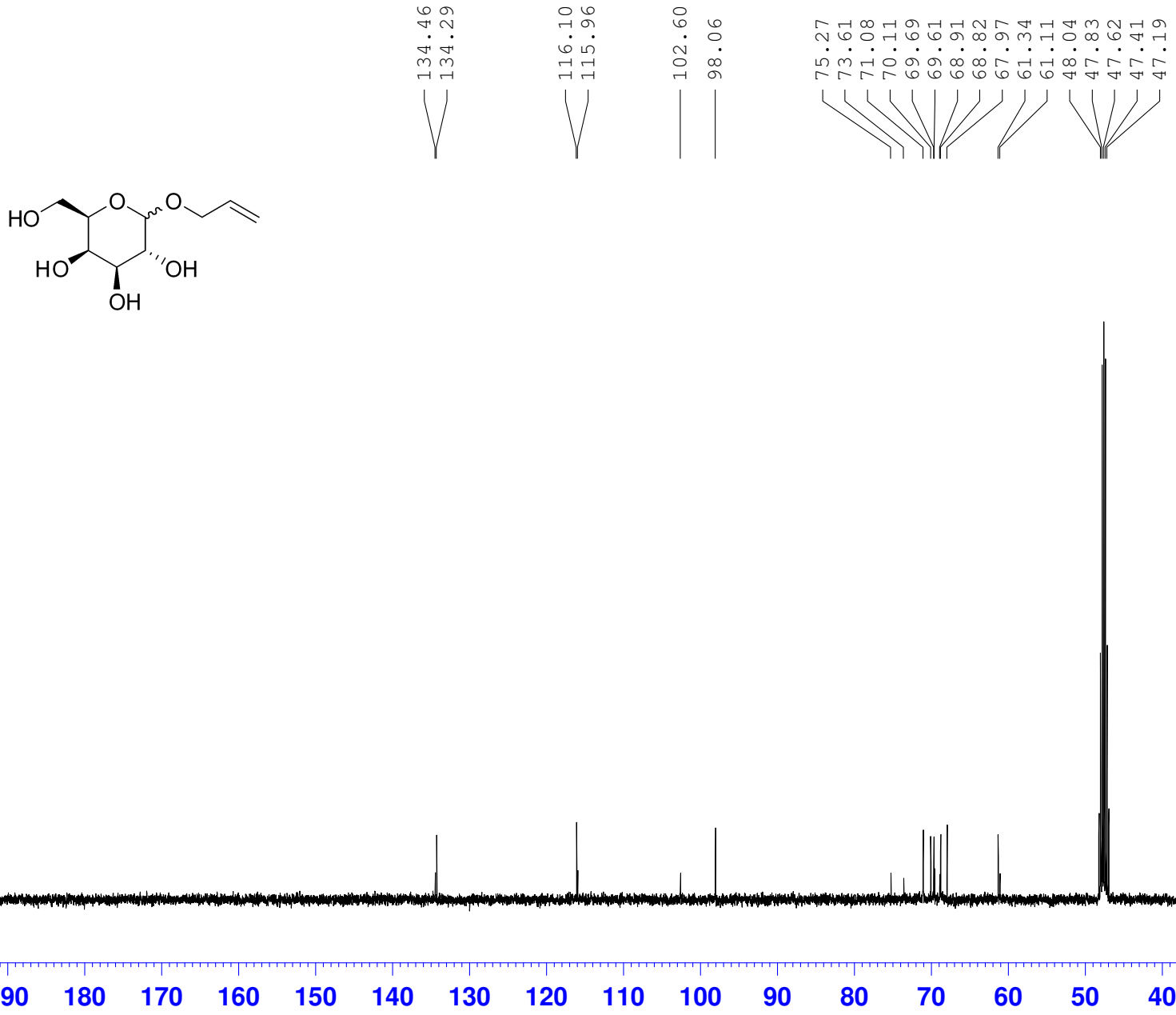
134.52
134.47
116.28
116.19
103.02
98.93
76.56
76.51
73.75
73.66
72.29
71.75
71.72
70.34
70.19
69.14
69.01
68.22
66.70
61.36
61.25
47.84
47.63
47.42



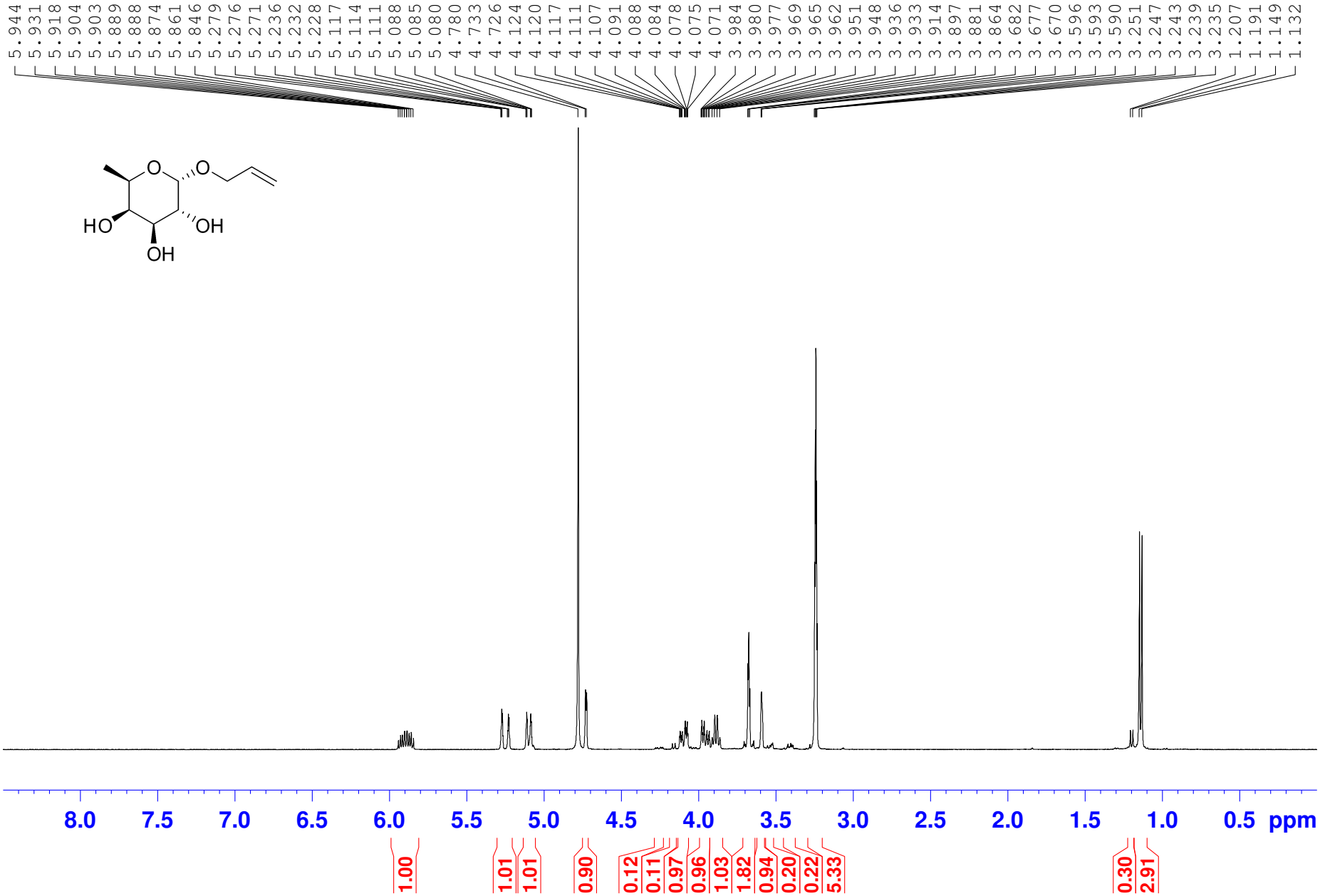
GBK-543-galactose, Av400 MeOD, 01-Dec-10



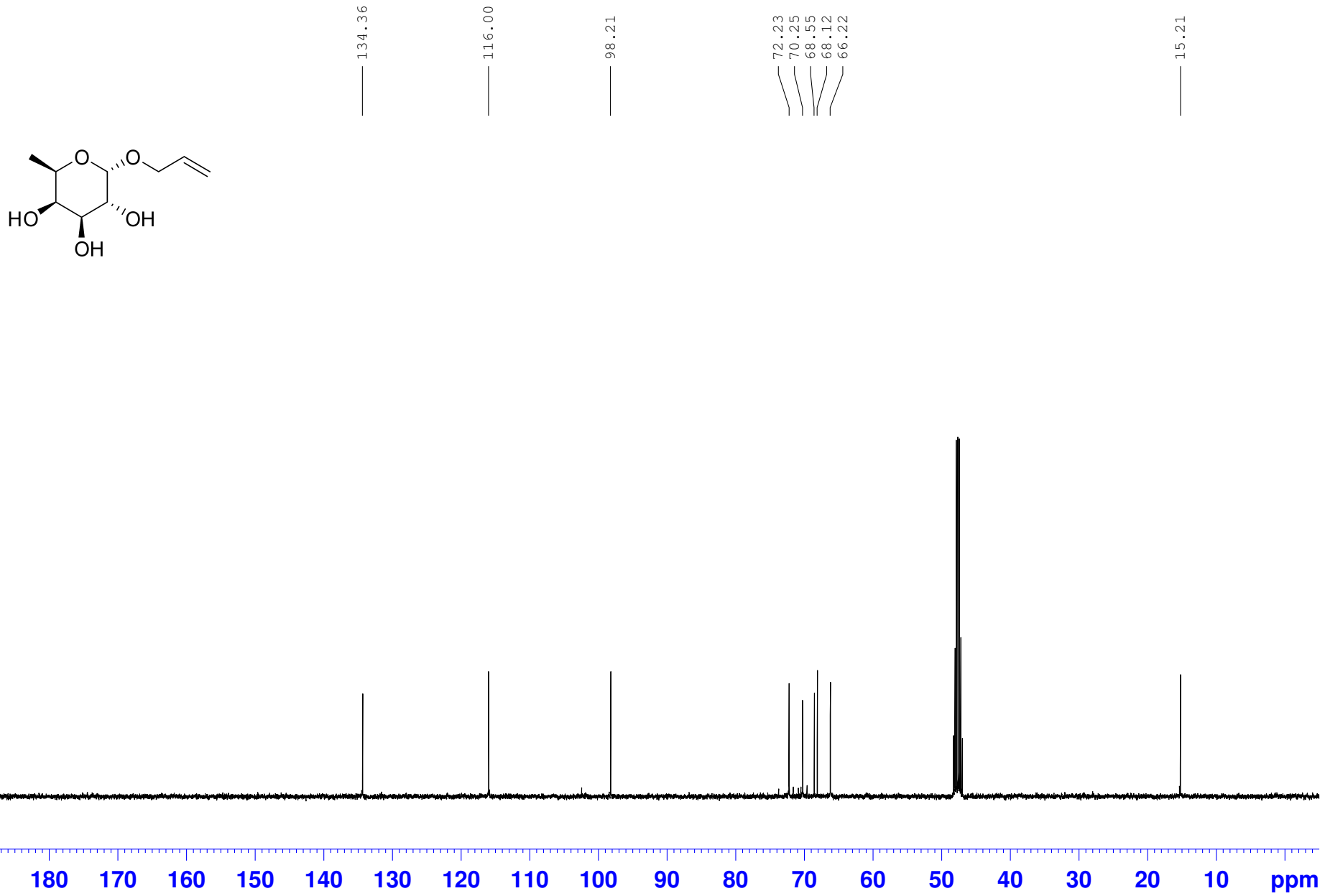
GBK-543B, 13C NMR, 400NMR MEOD

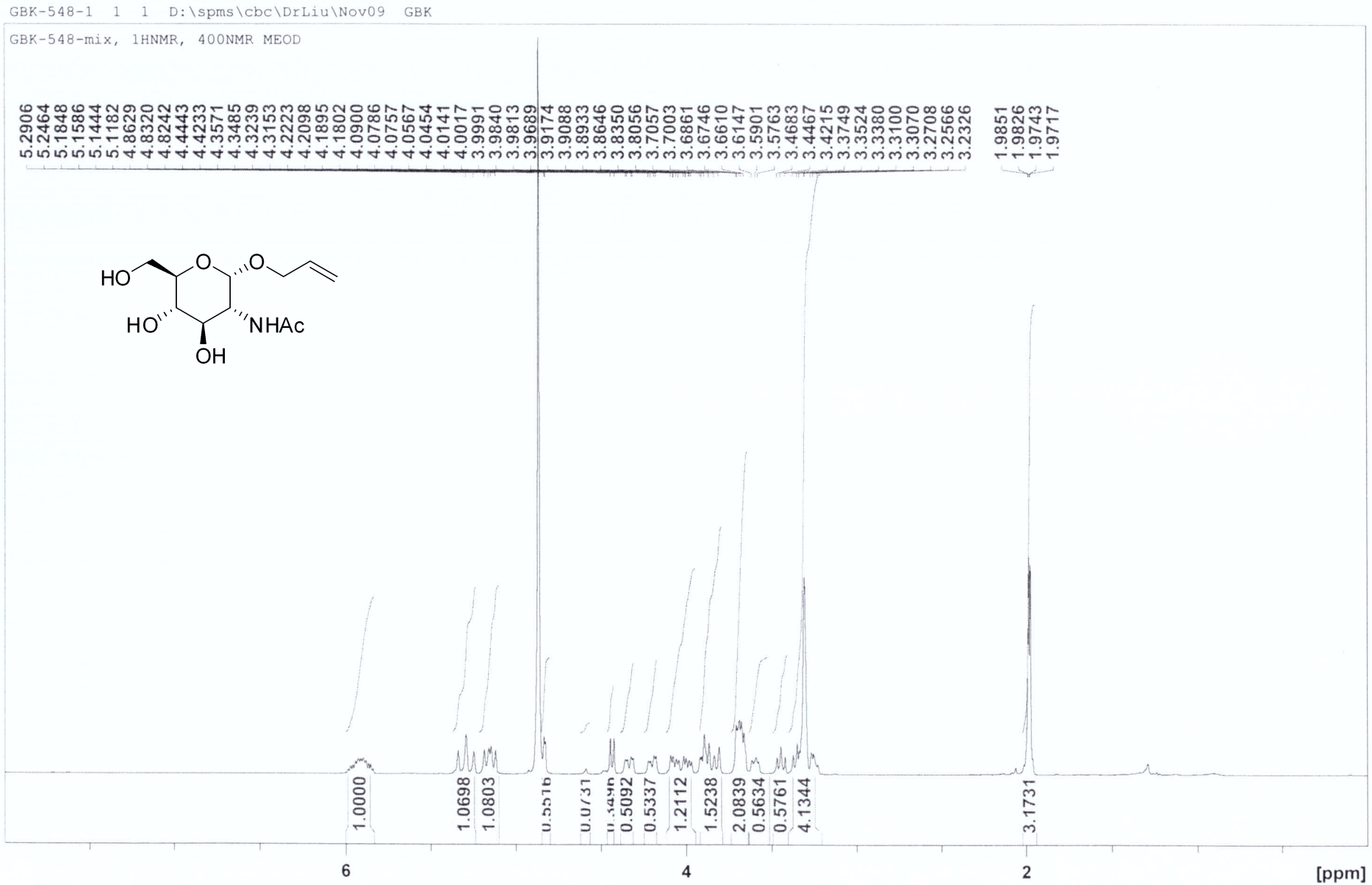


GBK-546-fucose, Av400 MeOD, 01-Dec-10

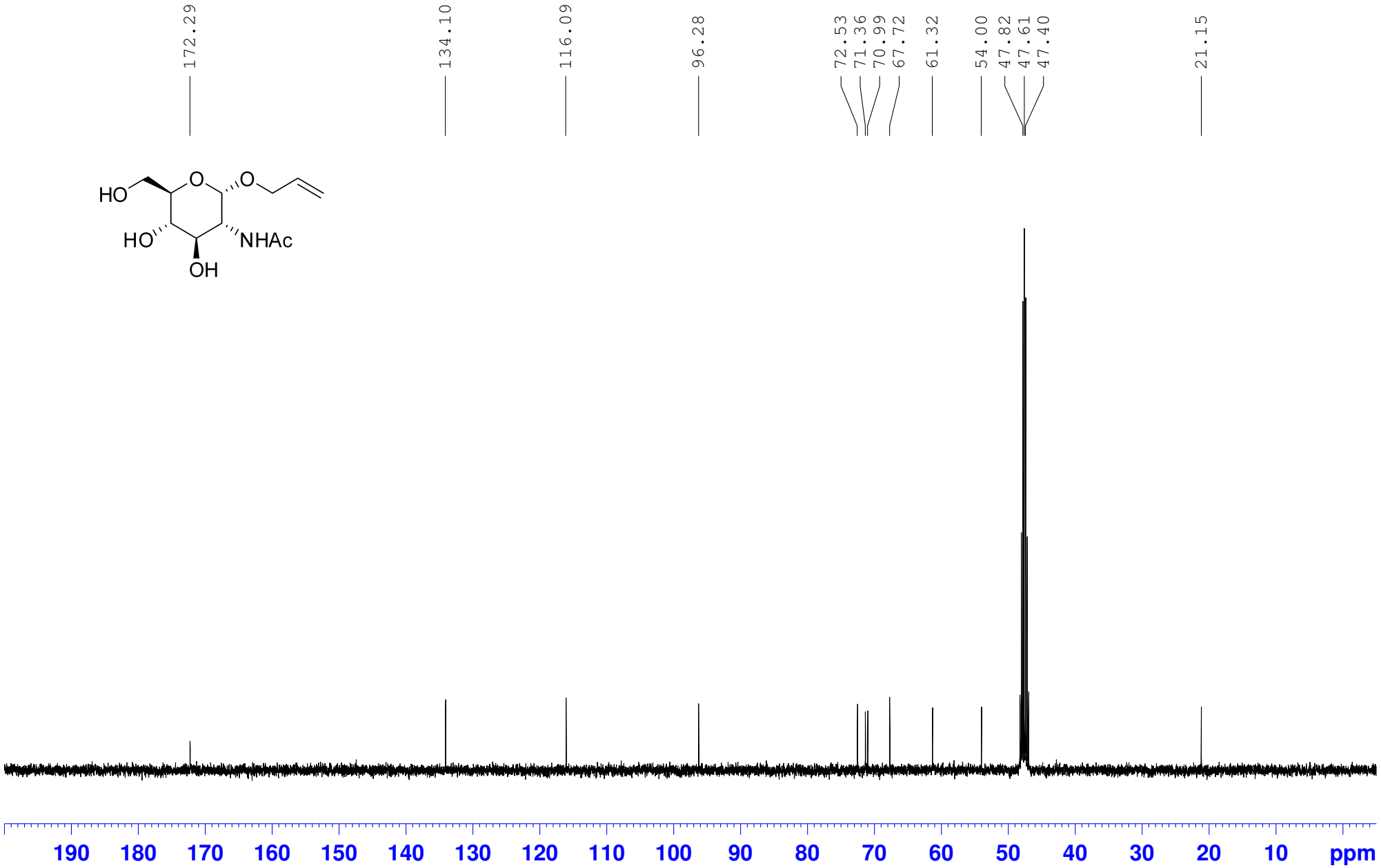


GBK-546pure, 13C NMR, 400NMR MEOD



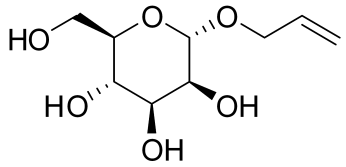

GBK-548-1 1 1 D:\spms\cbc\DrLiu\Nov09 GBK
GBK-548-mix, 1HNMR, 400NMR MEOD
5.2906
5.2464
5.1848
5.1586
5.1444
5.1182
4.8629
4.8320
4.8242
4.4443
4.4233
4.3571
4.3485
4.3239
4.3153
4.2223
4.2098
4.1895
4.1802
4.0900
4.0786
4.0757
4.0567
4.0454
4.0141
4.0017
3.9991
3.9840
3.9813
3.9689
3.9174
3.9088
3.8933
3.8646
3.8350
3.8056
3.7057
3.7003
3.6861
3.6746
3.6610
3.6147
3.5901
3.5763
3.4683
3.4467
3.4215
3.3749
3.3524
3.3380
3.3100
3.3070
3.2708
3.2566
3.2326
1.9851
1.9826
1.9743
1.9717
HO
O
O
HO
NHAc
OH
1.0000
1.0698
1.0803
0.5092
0.5337
1.2112
1.5238
2.0839
0.5634
0.5761
4.1344
3.1731
6
4
2
[ppm]

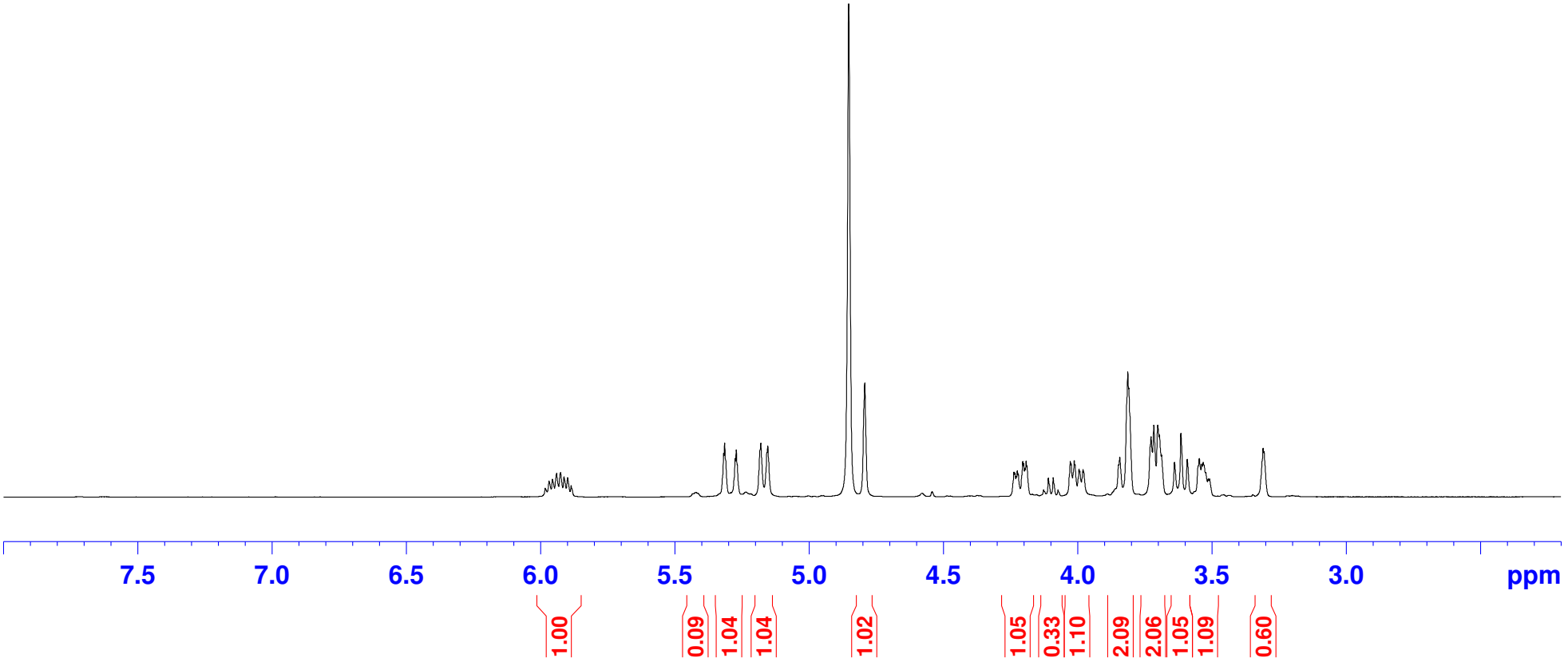
GBK-548, 13C NMR, 400NMR MEOD



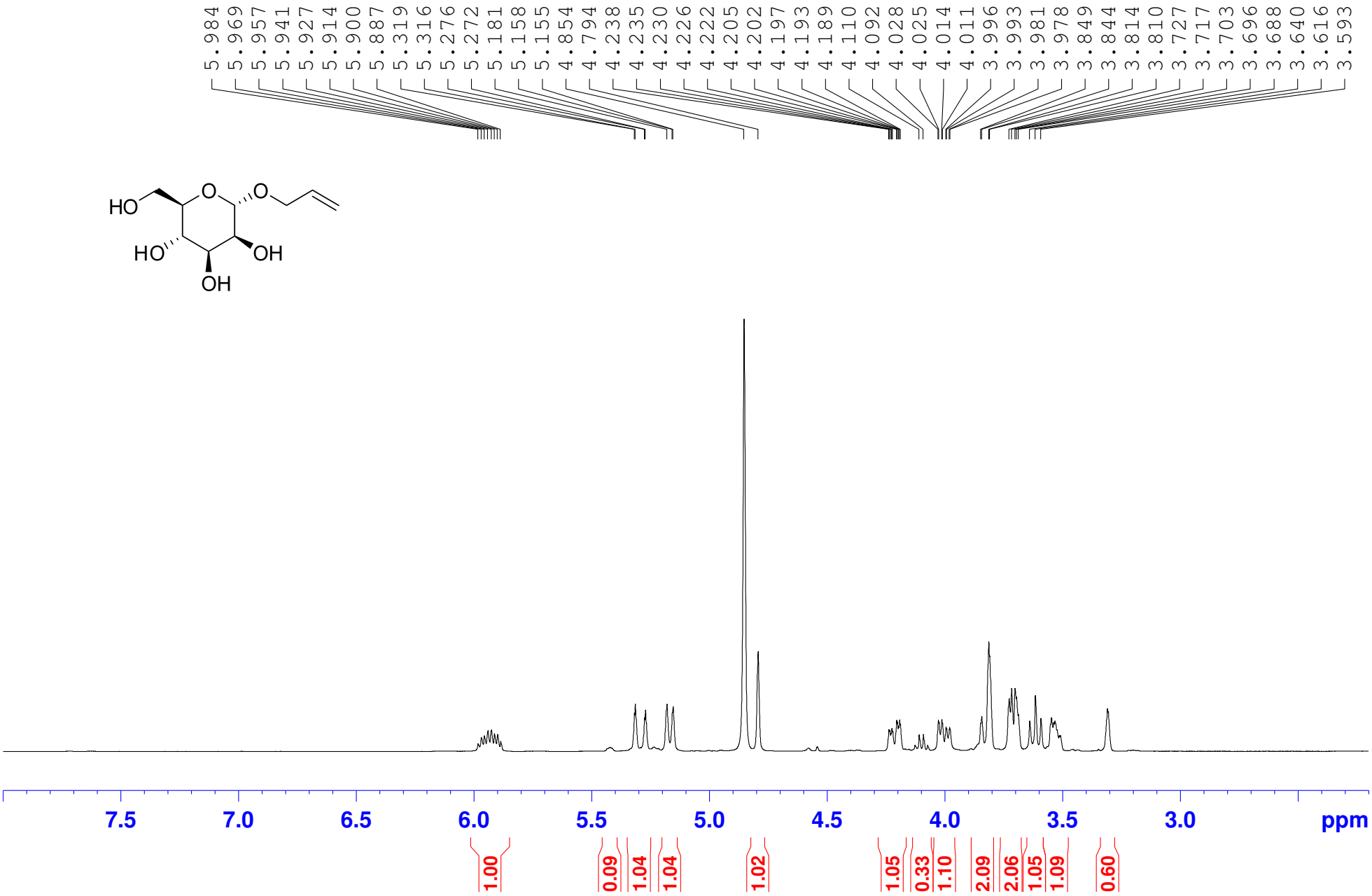
GBK-550, 1HNMR, 400NMR MEOD

5.984
5.969
5.957
5.941
5.927
5.914
5.900
5.887
5.319
5.316
5.276
5.272
5.181
5.158
5.155
4.854
4.794
4.238
4.235
4.230
4.226
4.222
4.205
4.202
4.197
4.193
4.189
4.110
4.092
4.028
4.025
4.014
4.011
3.996
3.993
3.981
3.978
3.849
3.844
3.814
3.810
3.727
3.717
3.703
3.696
3.688
3.640
3.616
3.593

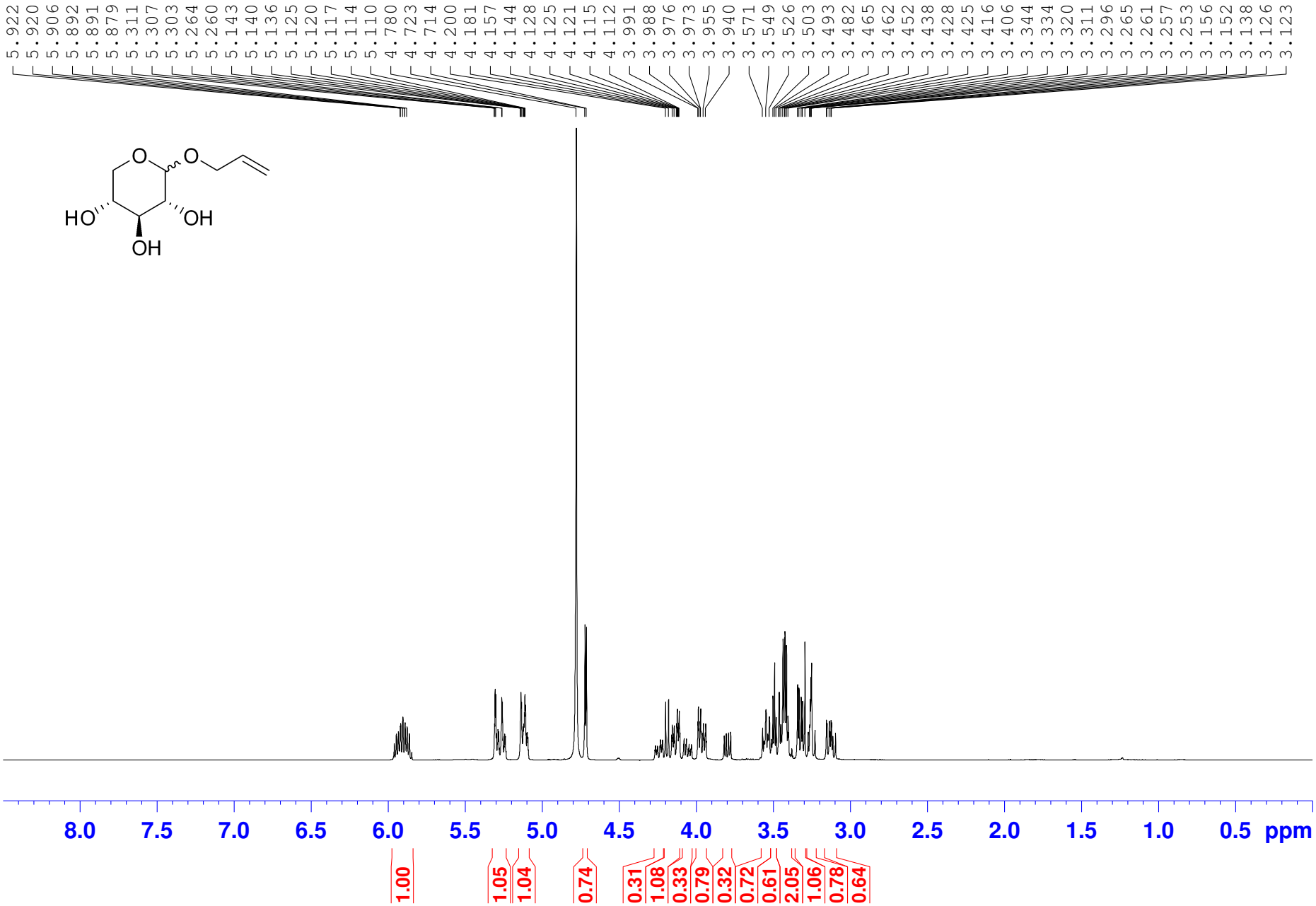




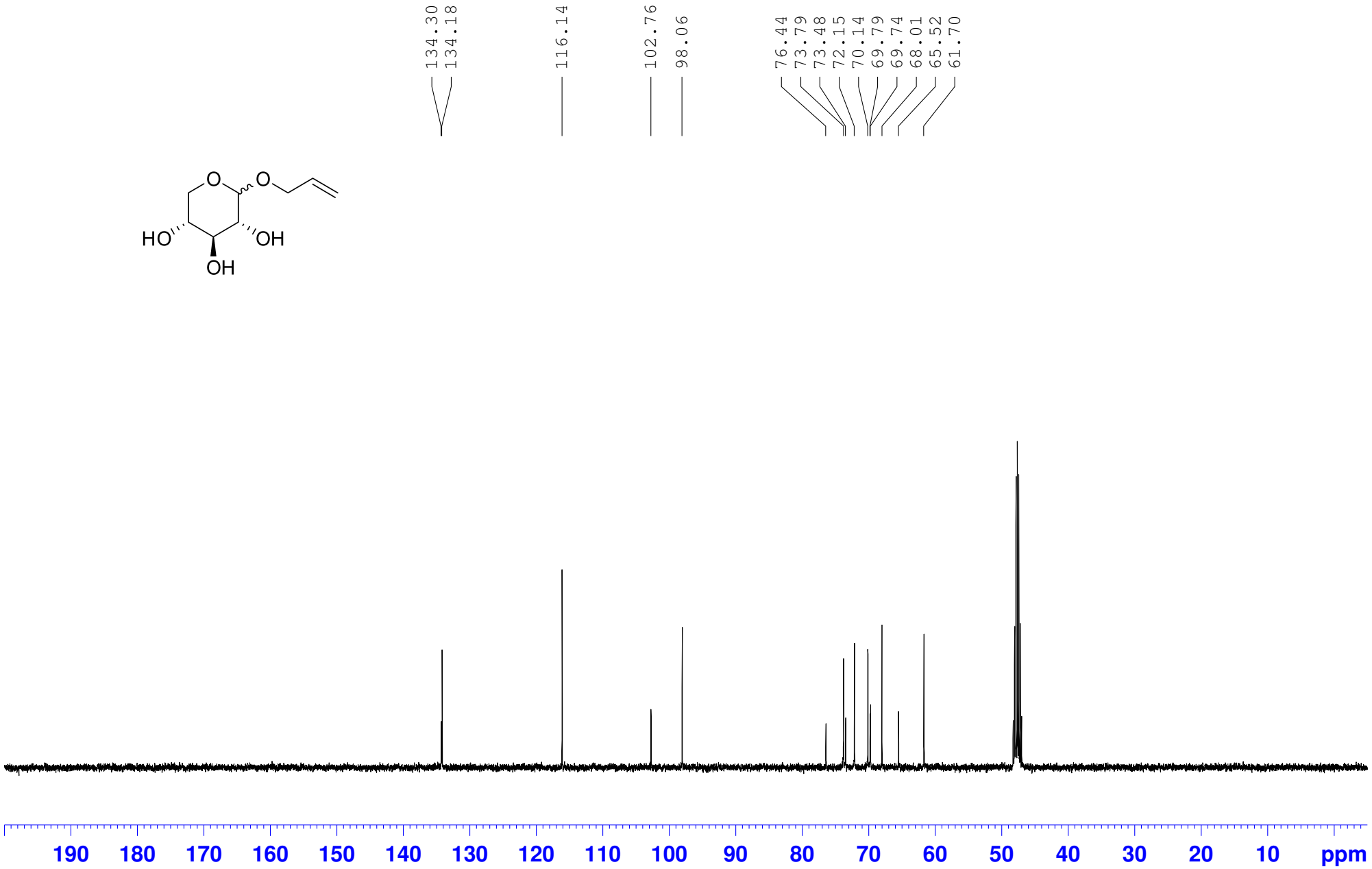
GBK-550, 1HNMR, 400NMR MEOD



GBK-551, Av400 MeOD, 01-Dec-10

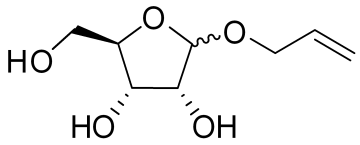


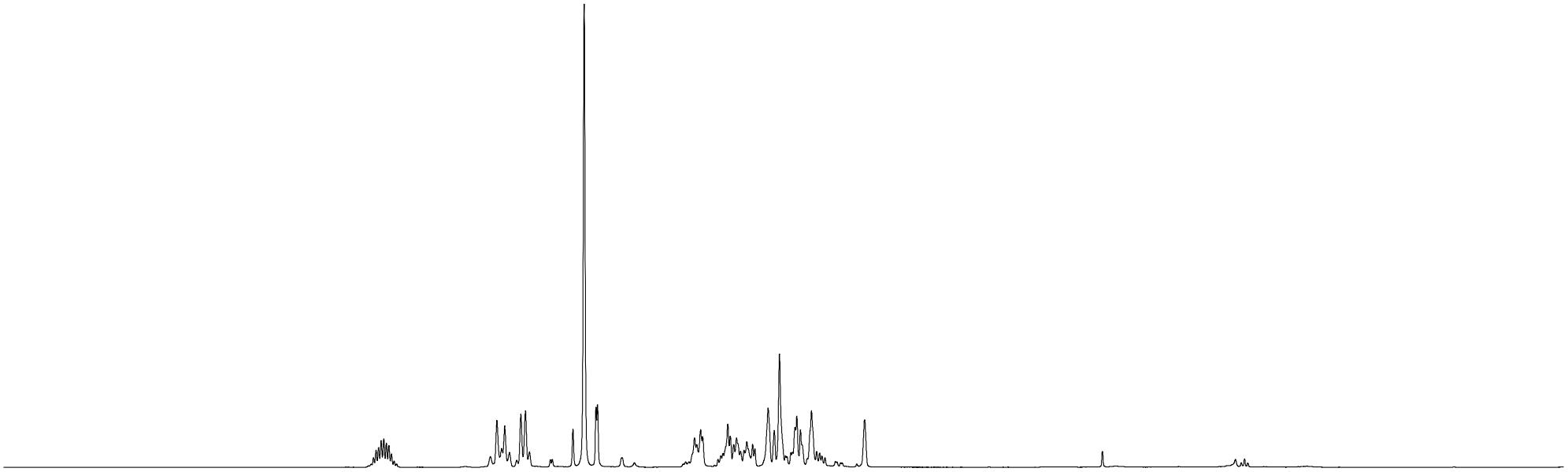
GBK-551, 13C NMR, 400NMR MEOD



GBK-552, 1HNMR, 400NMR MEOD

5.958
5.944
5.929
5.915
5.902
5.888
5.348
5.313
5.287
5.270
5.244
5.205
5.183
5.157
5.135
4.899
4.773
4.765
4.631
4.236
4.226
4.203
4.193
4.093
4.082
4.055
4.042
4.023
4.007
3.986
3.967
3.952
3.920
3.908
3.835
3.802
3.774
3.741
3.733
3.711
3.703
3.689
3.680
3.659
3.599
3.571
3.555
3.542
3.310

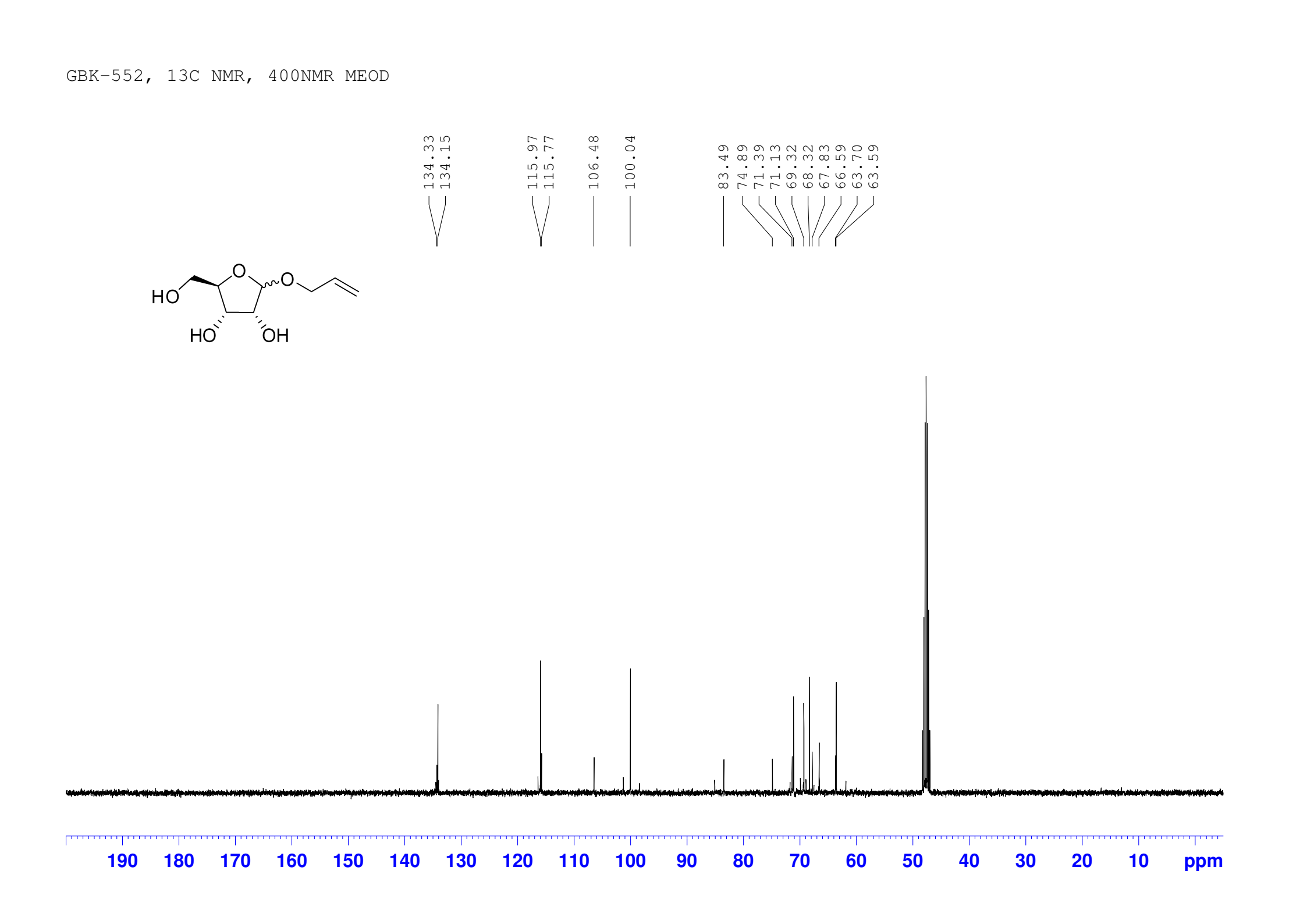




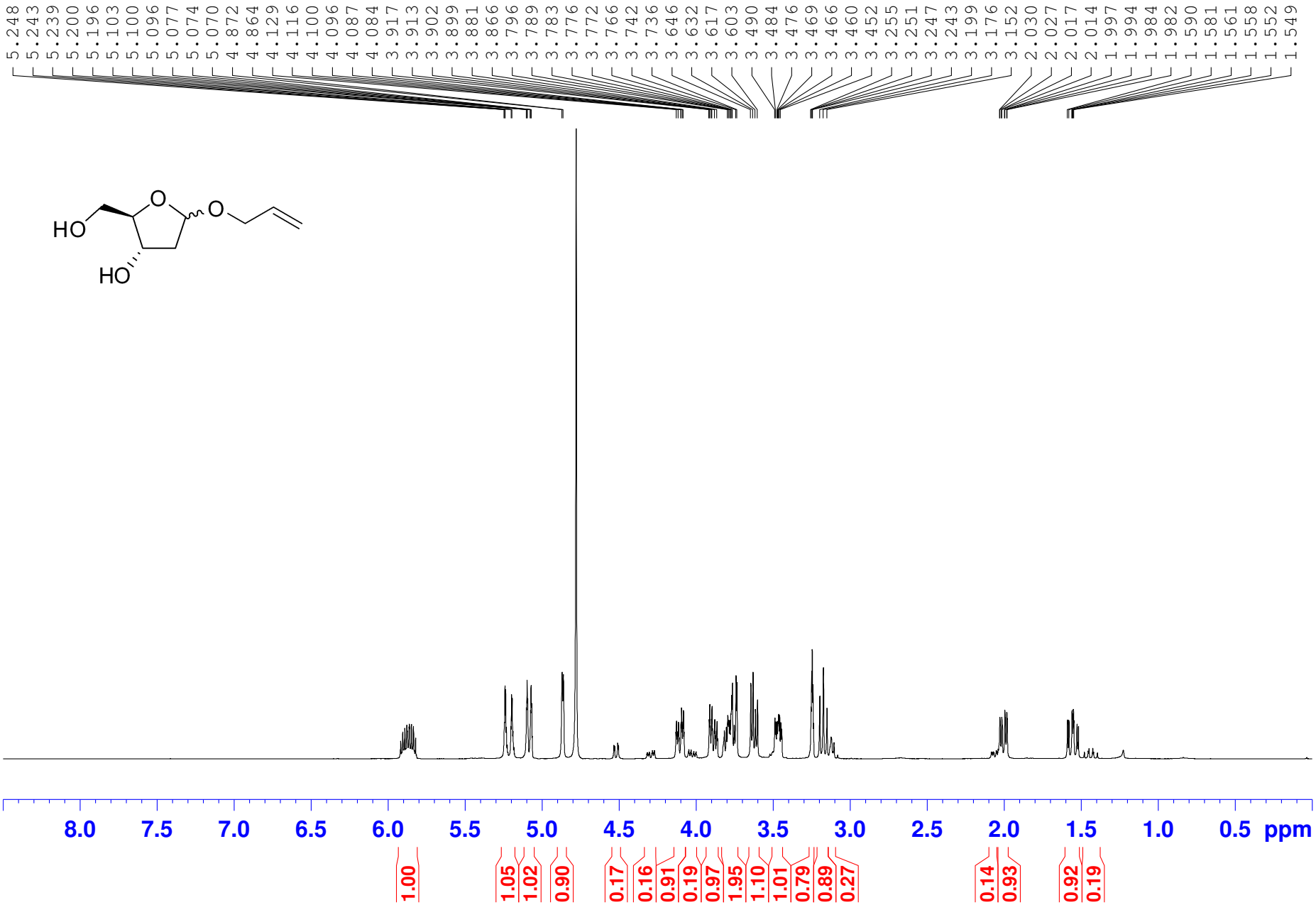
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

1.59 1.37 1.38 0.13 0.33 1.00 0.15 0.06 1.54 3.40 1.19 0.51 1.97 1.86 1.19 0.55 0.18 0.81

GBK-552, 13C NMR, 400NMR MEOD



GBK-553-deoxyribose, Av400 MeOD, 01-Dec-10



GBK-553 3 1 D:\spms\cbc\DrLiu\Dec10 GBK

GBK-553-deoxyribose, 13C Av400 MeOD, 01-Dec-10