Supporting Information

for

$SnCl_4$-catalyzed Solvent-free Acetolysis of 2,7-Anhydrosialic Acid Derivatives

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Experimental section and NMR spectra

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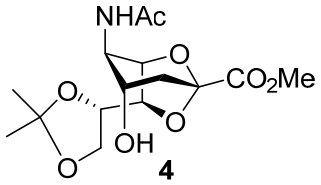
Experimental Section

General information. All dry solvents and chemicals were purchased from commercial sources, and were used without further purification unless otherwise mentioned. All moisture-sensitive reactions were conducted in flame-dried glasswares under dry nitrogen atmosphere. Flash column chromatography was carried out as recommended with Silica Gel 60 (230-400 mesh, E. Merck). TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by UV (254 nm) or spraying with a solution of $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6M_7O_{24}$, as well as H_2SO_4 in water and subsequent heating on a hot plate. Specific rotations were measured on Jasco P-2000 digital polarimeter using a 100 mm cell at 589 nm and at ambient temperature conditions and reported in $10^{-1}\cdot deg\cdot cm^2\cdot g^{-1}$; the sample concentrations are in $g\cdot dL^{-1}$. ^1H and ^{13}C NMR spectra were recorded with Bruker AVIII-400, AV500 or N600 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the $CDCl_3$ lock signals at δ 7.24 for ^1H spectra and 77.16 for ^{13}C spectra, respectively. Multiplicities are reported by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; *J* = coupling constant values in Hertz. Proton peaks were assigned based on 2D NMR spectra (COSY, HSQC, HMBC and NOESY). Mass spectra were obtained with a JEOL JMS-700 mass spectrometer in FAB mode or Waters Premier XE mass spectrometer in ESI mode. IR spectra were taken with a Perkin-Elmer Paragon 1000 FT-IR spectrometer.

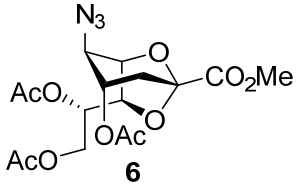


4

Methyl 5-acetamido-2,7-anhydro-8, 9-*O*-acetonide-3, 5-dideoxy-*α*-D-*glycero*-D-*galacto*-2-nonulopyranosidonate (4)

To the solution of **2** in CH_3CN, 2, 2-dimethoxypropane (625 µL, 5.1 mmol, 3 equiv.) and camphorsulfonic acid (80 mg, 0.33 mmol, 0.2 equiv.) were added at room temperature and stirred for 8 h. When reaction was completed, the mixture neutralized with trimethylamine (Et_3N) and concentrated in rota. The crude product was purified by column chromatography (60% EtOAc in hexane) to afford the desired product as pale yellow solid crystalized compound **4** (366.2 mg, 63% yield). $[\alpha]^{28}_D$ +6 (c = 1.1, $CHCl_3$); mp 150.6-152 °C; IR ($CHCl_3$) *v* 3312, 2987, 1752, 1655, 1540, 1440, 1373, 1265, 1206, 1157, 1088, 1073, 1051, 840,742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ =

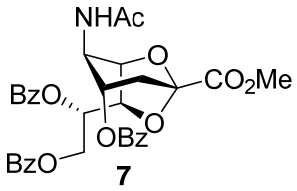
6.15 (d, J = 8.51 Hz, 1H, NH), 4.55 (s, 1H, H-6), 4.50 (d, J = 8.81 Hz, 1H, H-7), 4.10-4.05 (overlap, 2H, H-5, H-9a), 3.96-3.89 (overlap, 3H, H-4, H-8, H-9b), 3.81 (s, 3H, OCH_3), 3.41 (d, J = 4.85 Hz, 1H, 4-OH), 2.14 (d, J = 3.35 Hz, 2H, H-3eq, H-3ax), 1.99 (s, 3H, NAc), 1.38, 1.29 (each s, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.97 (CO), 167.31 (CO), 109.96 (C), 104.21 (C-2), 79.09 (CH), 78.32 (CH), 75.34 (CH), 67.34 (CH_2), 67.11 (CH), 53.27 (OCH_3), 52.03 (CH), 35.82 (CH_2), 27.09 (CH_3), 25.39 (CH_3), 23.38 (CH_3); HRMS (ESI): *m/z* calcd for $C_{15}H_{23}NO_8$ ($[M+Na]^+$): 368.1321, found: 368.1317.



6

Methyl 5-azido-2,7-anhydro-4, 8, 9-*tri*-*O*-acetyl-3, 5-dideoxy-D-*glycero*-D-*galacto*-2-nonulpyranosonate (6)

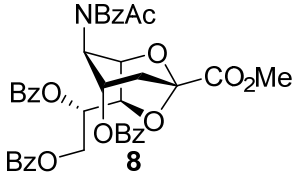
Compound **3** (235.8 mg, 0.815 mmol, 1 equiv) and DMAP (20 mg, 0.163 mmol, 0.2 equiv) were dissolved in dry pyridine (4 mL). To this solution, acetic anhydride (1.5 mL) was added drop wise and stirred overnight at room temperature. After the reaction completed, the solvent was evaporated through the addition of Toluene. Then, the crude product was dissolved in 1N HCl aqueous solution and extracted three times with EtOAc. The extract was dried over anhydrous $MgSO_4$, filtered and evaporated to dryness in vacuo. The crude product was purified in a column of silica gel with 80% EtOAc in hexane to give **6** (261.6 mg, 77%) as a colorless syrup product. $[\alpha]^{25}_D$ +78 (c = 0.24, $CHCl_3$); IR ($CHCl_3$) *v* 2105, 1744, 1439, 1371, 1224, 1162, 1099, 1050, 1017, 798, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.05 (d, J = 5.63 Hz, 1H, H-4), 4.95 (m, 1H, H-8), 4.54 (s, 1H, H-6), 4.51 (dd, J = 2.76, 12.41 Hz, 1H, H-9a), 4.45 (d, J = 7.71 Hz, 1H, H-7), 4.14 (dd, J = 4.65, 12.47 Hz, 1H, H-9b), 3.80 (s, 3H, OCH_3), 3.44 (s, 1H, H-5), 2.35 (dd, J = 5.91, 15.70 Hz, 1H, H-3eq), 2.16 (d, J = 15.54 Hz, 1H, H-3ax), 2.08, 2.07, 2.04 ppm (each s, 9H, OAc); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.55 (CO), 169.91 (CO), 169.66 (CO), 166.36 (CO), 103.66 (C-2), 77.85 (CH), 75.40 (CH), 71.08 (CH), 67.89 (CH), 62.00 (CH_2), 59.02 (CH), 53.32 (OCH_3), 33.39 (CH_2), 21.19, 21.04, 20.82 (each CH_3) ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}N_3O_{10}$ ($[M+Na]^+$): 438.1125, found: 438.1133.



7

Methyl 5-Acetamido-2,7-anhydro-4, 8, 9-*tri-O*-benzoyl-3, 5-dideoxy-D-*glycero*-D-*galacto-2*-nonulpyranosonate (**7**)

Compound **8** (26.5 mg, 0.037 mmol, 1 equiv.) was dissolved in dry Ac_2O (104 µL, 1.1 mmol, 30 equiv.). $Cu(OTf)_2$ (2.6 mg, 0.008 mmol, 0.2 equiv.) was added to the reaction mixture and stirred for 2 h at 70 °C. The degree of the reaction was monitored by TLC. Upon completion, the mixture was azeotroped with toluene at 35 °C and directly purified by flash column chromatography (40% EtOAc in hexane) and afforded **7** (12 mg, 47%) as colorless syrup products. $[\alpha]^{25}_D$ +62 (c = 1.35, $CHCl_3$); IR ($CHCl_3$) *v* 2924, 1751, 1720, 1657, 1602, 1584, 1451, 1274, 1095, 1070, 710 cm^{-1} ;^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03-7.91 (6H, Ar), 7.55-7.33 (7H, Ar), 7.15-7.11 (2H, Ar), 6.23 (d, *J* = 8.85 Hz, 1H, NH), 5.43-5.42 (m, 1H, H-8), 5.20 (d, *J* = 3.94 Hz, 1H, H-4), 5.06 (d, *J* = 7.67 Hz, 1H, H-7), 4.83 (br d, *J* = 12.36 Hz, 1H, H-9a), 4.64 (br s, 1H, H-6), 4.62 (d, *J* = 4.16 Hz, 1H, H-9b), 4.41 (d, *J* = 8.74 Hz, 1H, H-5), 3.77 (s, 3H, OCH_3), 2.36 (dd, *J* = 5.12, 16.00 Hz, 1H, H-3eq), 2.32 (s, 1H, H-3ax), 2.01 ppm (s, 3H, NAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.27 (CO), 166.79 (CO), 166.27 (CO), 165.73 (CO), 165.31 (CO), 133.67 (C), 133.31 (C), 130.06 (C), 129.81 (CH), 129.70 (CH), 129.47 (CH), 128.68 (CH), 128.60 (CH), 104.21 (C-2), 78.77 (CH), 75.95 (CH), 71.63 (CH), 68.98 (CH), 62.61 (CH_2), 53.31 (OCH_3), 49.13 (CH), 33.71 (CH_2), 23.29 (CH_3) ppm; HRMS (ESI): *m/z* calcd for $C_{33}H_{31}NO_{11}$ ($[M+Na]^+$): 640.1795, found: 640.1802.

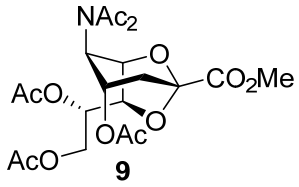


8

Methyl 5-(*N*-benzoylacetamido)-2,7-anhydro-4,8,9-*tri-O*-benzoyl-3, 5-dideoxy-D-*glycero*-D-*galacto-2*-nonulpyranosonate (**8**)

Compound **2** (176 mg, 0.58 mmol, 1 equiv) and DMAP (250 mg, 2.41 mmol, 0.2 equiv) were dissolved in dry pyridine (3.5 mL). To this solution, benzoic anhydride (1.17 mL) was added drop wise and kept for 15 h at room temperature. After the reaction completed, the solvent was evaporated through the addition of Toluene. Then, the crude product was dissolved in saturated $CuSO_4.5H_2O$ aqueous solution and extracted three times with EtOAc. The extract was dried over

anhydrous $MgSO_4$, filtered and evaporated to dryness in vacuo. The crude product was purified in a column of silica gel with 40% EtOAc in hexane to give **8** (201.5 mg, 57% NBzAc) as colorless syrup products. $[\alpha]^{25}_D$ +78 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05-7.26 (m, 20H, Ar), 5.80-5.79 (m, 1H, H-4), 5.37-5.35 (m, 1H, H-8), 4.89 (br d, *J* = 2.22 Hz, 1H, H-9a), 4.87 (br s, 1H, H-6), 4.77 (d, *J* = 8.10 Hz, 1H, H-7), 4.72 (s, 1H, H-5), 4.63 (dd, *J* = 4.07, 12.40 Hz, 1H, H-9b), 3.74 (s, 3H, OCH_3), 2.95 (dd, *J* = 7.03, 15.15 Hz, 1H, H-3eq), 2.12 (dd, *J* = 2.57, 15.36 Hz, 1H, H-3ax), 1.86 ppm (s, 3H, NAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.15 (CO), 172.20 (CO), 166.84 (CO), 166.18 (CO), 165.63 (CO), 165.55 (CO), 135.79 (C) , 133.86 (C), 133.45 (C) , 133.37 (C), 133.15 (CH), 130.01 (CH), 129.92 (CH), 129.77 (CH), 129.52 (CH), 129.30 (CH), 128.58 (CH), 103.94 (C-2), 79.37 (CH), 77.55 (CH), 71.79 (CH), 68.26 (CH), 62.54 (CH_2), 59.31 (CH), 53.13 (OCH_3), 34.72 (CH_2), 26.85 (CH_3) ppm; HRMS (ESI): *m/z* calcd for $C_{40}H_{35}NO_{12}$ ($[M+Na]^+$): 744.2057, found: 744.2060.

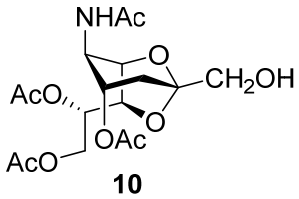


9

Methyl 5-(*N*-acetylacetamido)-2,7-anhydro-4, 8, 9-*tri-O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulpyranosonate (9)

Compound **5** (60 mg, 0.14 mmol, 1 equiv) and *p*-TsOH.H_2O (3 mg, 0.014 mmol. 0.2 equiv) were dissolved in isopropenyl acetate (0.6 mL, 40 equiv) and stirred overnight at 80 ^oC for 16 h. Upon completion, the reaction was neutralized with in Et_3N (0.3 mL). The solution was evaporated in vacuo. The crude product was purified by silica gel column chromatography (80% gradient EtOAc in hexane) to afford as a white foam **9** (44.4 mg, 67%). $[\alpha]^{25}_D$ +88(c = 0.6, $CHCl_3$); IR ($CHCl_3$) *v* 1742, 1660, 1537, 1372, 1224, 1052, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.39-5.34 (m, 1H, H-4), 4.93-4.89 (m, 1H, H-8), 4.52 (dd, *J* = 2.66, 12.40 Hz, 1H, H-9a), 4.46 (d, *J* = 1.64 Hz, 1H, H-6), 4.23 (br s, 1H, H-5), 4.22 (br d, *J* = 3.33, 1H, H-7), 4.11 (dd, *J* = 4.29, 12.49 Hz, 1H, H-9b), 3.80 (s, 3H, OCH_3), 2.97 (dd, *J* = 7.93, 14.77 Hz, 1H, H-3eq), 2.4 (s, 6H, NAc), 2.06 (s, 6H, OAc), 2.00 (s, 3H, OAc), 1.85 ppm (dd, *J* = 5.9, 14.78 Hz, 1H, H-3ax); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.55 (CO), 170.66 (CO), 169.98 (CO), 169.90 (CO), 166.73 (CO), 103.19 (C-2), 79.11 (CH), 78.79 (CH), 70.85 (CH), 67.09 (CH), 61.97 (CH_2), 60.18 (CH), 53.35

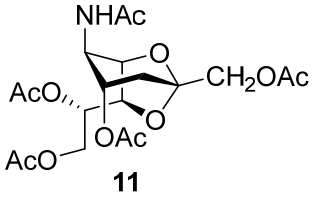
(OCH_3), 35.80 (CH_2), 27.07, 21.07, 21.03, 20.86 (each CH_3) ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{27}NO_{12}$ ($[M+Na]^+$): 496.1431, found: 496.1432.



10

Hydroxymethyl 5-acetamido-2,7-anhydro-4, 8, 9-*tri*-*O*-acetyl-3, 5-dideoxy-*α*-D-*glycero*-D-*galacto*-*2*-nonulopyranosonate (10)

Compound **5** (111.9 mg, 0.276 mmol, 1 equiv.) was dissolved in tetrahydrofuran (THF) and heated to 100 °C. Then $LiBH_4$ (10.13 µL, 0.414 mmol, 1.5 equiv.) and MeOH (16.75 µL, 0.414 mmol) were added to the solution at the same temperature and refluxed for 30 minutes. After the reaction get completed, the solution was neutralized by a drop of 1N HCl and concentrated in rotary vapor. The crude product was purified using column chromatography with 2% MeOH in $CHCl_3$ elution system to afford a colorless syrup in 50% yield (51.8 mg) for compound **10**. $[\alpha]^{28}_D$ +75 (c = 0.28, $CHCl_3$); IR ($CHCl_3$) *v* 3338, 1740, 1658, 1541, 1434, 1373, 1228, 1144, 1057 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.29 (d, *J* = 8.80 Hz, 1H, NH), 4.92-4.88 (m, 1H, H-8), 4.83 (d, *J* = 5.02 Hz, 1H, H-4), 4.53-4.48 (overlap, 2H, H-7, H-9a), 4.23 (s, 1H, H-6), 4.15-4.08 (overlap, 2H, H-5, H-9b), 3.62 (s, 2H, CH_2), 2.51 (broad s, OH), 2.07 (s, 6H, 2Ac), 2.05 (s, 3H, 1Ac), 2.04-1.97 (overlap, 4H, H-3eq, 1Ac), 1.86 ppm (t, *J* = 8.91 Hz, 1H, H-3ax); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.89 (CO), 170.37 (CO), 169.66 (CO), 169.49 (CO), 107.77 (C-2), 78.14 (CH), 74.94 (CH), 71.41 (CH), 68.97 (CH), 64.86 (CH_2), 62.91 (CH_2), 49.49 (CH), 32.51 (CH_2), 23.26, 21.36, 21.10, 20.82 ppm (each CH_3). HRMS (ESI): *m/z* calcd for $C_{17}H_{25}NO_{10}$ ($[M+Na]^+$): 426.1376, found: 426.1375.

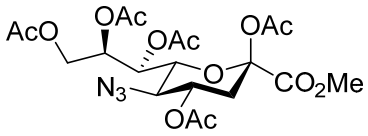


11

Methylene 5-acetamido-2,7-anhydro-1,4,8,9-*tetra*-*O*-acetyl-3, 5-dideoxy-*α*-D-*glycero*-D-*galacto*-*2*-nonulopyranosonate (11)

Compound **10** (59.2 mg, 0.147 mmol) was dissolved in dry pyridine (1.5 mL) and 4-Dimethylaminopyridine (DMAP) (3.6 mg, 0.029 mmol, 0.2 equiv) and acetic anhydride (55 µL,

40 equiv.) were and stirred overnight at room temperature. After the reaction completed, the solvent was evaporated through the addition of Toluene. The crude product was purified in a column of silica gel with 90% EtOAc in hexane to give **11** in 82% (53.7 mg) yield. $[\alpha]^{28}_{D}$ +76 (c = 0.97, $CHCl_3$); IR ($CHCl_3$) *v* 1741, 1660, 1537, 1372, 1223, 1054 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.06 (d, *J* = 8.90 Hz, 1H, NH), 4.87-4.82 (overlap, 2H, H-8, H-4), 4.52 (d, *J* = 8.60 Hz, 1H, H-7), 4.49 (dd, *J* = 2.51, 12.36 Hz, 1H, H-9a), 4.27 (d, *J* = 12.33 Hz, 1H, H-1), 4.23 (broad s, 1H, H-6), 4.18-4.13 (overlap, 2H, H-5, H-9b), 4.06 (d, *J* = 12.33 Hz, 1H, H-1), 2.11, 2.08, 2.07, 2.06, 2.01 (each s, 15H, 5Ac), 1.99-1.89 (overlap, 2H, H-3eq, H-3ax) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.63 (CO), 170.40 (CO), 170.20 (CO), 169.60 (CO), 169.33 (CO), 106.45 (C-2), 78.28 (CH), 74.81 (CH), 71.23 (CH), 68.74 (CH), 64.49 (CH_2), 62.32 (CH_2), 49.29 (CH), 32.79 (CH_2), 23.34, 21.35, 21.10, 20.81 (each CH_3) ppm. HRMS (ESI): *m/z* calcd for $C_{19}H_{27}NO_{11}$ ($[M+Na]^+$): 468.1476, found: 468.1474.

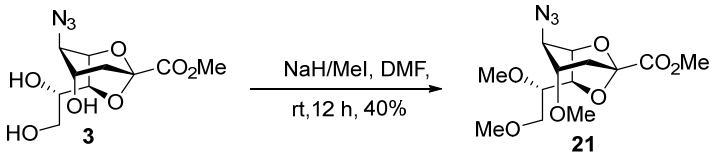


12

Methyl 5-azido-2, 4, 7, 8, 9-*penta*-*O*-acetyl-3, 5-dideoxy-D-*glycero*-D-*galacto*-2-nonulpyranosonate (12)

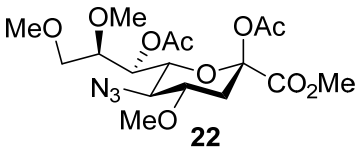
Compound **6** (36 mg, 0.09 mmol, 1 equiv.) was dissolved in dry Ac_2O (250 µL, 2.66 mmol, 30 equiv.). $SnCl_4$ (5.2 µL, 0.044 mmol, 0.5 equiv.) was added to the reaction mixture and stirred for 19 h at room temperature. The degree of the reaction was monitored by TLC. Upon completion, the mixture was azeotroped with toluene at 35 °C and directly purified by flash column chromatography (40% EtOAc in hexane) and afforded **12** (24.84 mg, 54%) and **13** (15.87 mg, 34%) as colorless syrup products. $[\alpha]^{25}_{D}$ -56 (c = 0.87, $CHCl_3$); IR ($CHCl_3$) *v* 2116, 1746, 1438, 1372, 1222, 1199, 1166, 1085 cm^{-1}; β-isomer: ^1H NMR (500 MHz, $CDCl_3$): δ = 5.49 (dd, *J* = 1.72, 6.95 Hz, 1H, H-7), 5.17-5.15 (overlap, 2H, H-4, H-8), 4.39 (dd, *J* = 2.42, 12.54 Hz, 1H, H-9a), 4.16 (dd, *J* = 5.37, 12.63 Hz, 1H, H-9b), 3.74 (dd, *J* = 1.75, 10.61 Hz, 1H, H-6), 3.74 (s, 3H, OCH_3), 3.33 (t, *J* = 10.10 Hz, 1H, H-5), 2.63 (dd, *J* = 5.17, 13.38 Hz, 1H, H-3eq), 2,17, 2,10, 2.08, 2.03, 2.02 (each s, 15H, 5OAc), 1.88 ppm (dd, *J* = 1.8, 13.40 Hz, 1H, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$): δ =170.77 (CO), 170.03 (CO), 169.80 (CO), 169.66 (CO), 168.28 (CO), 166.31 (CO), 97.16 (C-2), 71.67 (CH), 70.37 (CH), 70.02 (CH), 68.38 (CH), 61.92

(CH_2), 59.89 (CH), 53.31 (OCH_3), 35.49 (CH_2), 20.99, 20.92, 20.88, 20.83, 20.82 (each CH_3) ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{27}N_3O_{13}$ ($[M+Na]^+$): 540.1442, found: 540.1434.



Methyl 5-azido-2,7-anhydro-4, 8, 9-*tri-O*-methyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulpyranosonate (21)

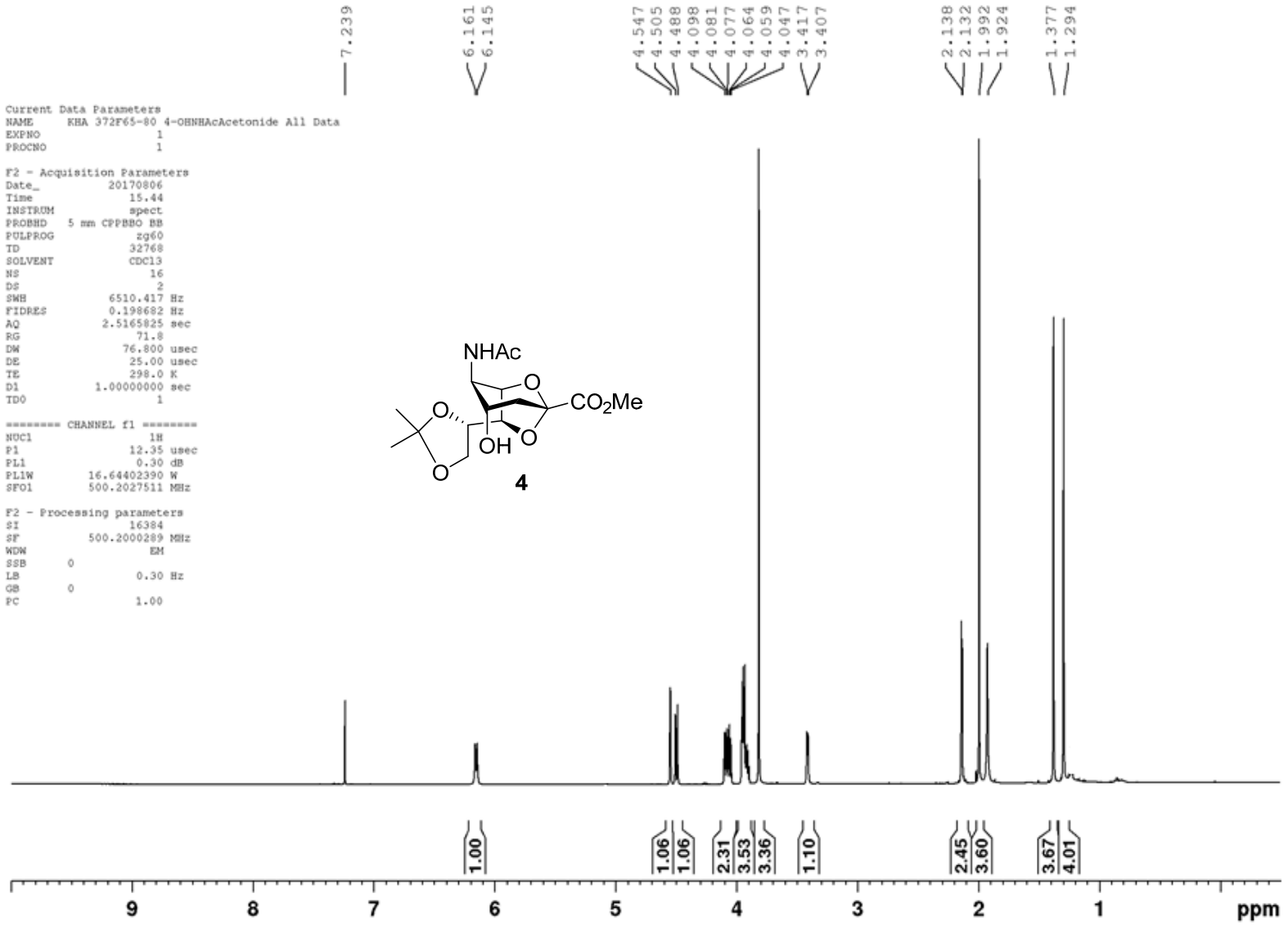
Compound **3** (38.1 mg, 0.132 mmol, 1 equiv.) was dissolved in dry DMF (2 mL), and cooled to 0 ºC. Then NaH (60%) (26.3 mg, 0.659 mmol, 5 equiv.) was added slowly and stirred for 30 min until hydrogen gas released completely. Methyl iodide (49.2 µL, 0.79 mmol, 6 equiv.) was added drop wise over 15 minutes. The reaction mixture was stirred overnight at room temperature. Upon completion of the reaction, the mixture was quenched with ice water and diluted with EtOAc (5 mL). The desired product was extracted with EtOAc (three times) from the aqueous phase and separated. Then the combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated. Silica gel column chromatography (1:1 hexane-EtOAc) afforded compound **21** as a colorless syrup (17 mg, 40%). $[\alpha]^{25}_D$ +57 (c = 1.85, $CHCl_3$); IR ($CHCl_3$) *v* 2933, 2101, 1752, 1441, 1309, 1262, 1193, 1091, 1048, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.69 (s, 1H, H-6), 4.36 (d, *J* = 9.05 Hz, 1H, H-7), 3.79 (s, 3H, OCH_3), 3.66 (dd, *J* = 2.38, 10.74 Hz, 1H, H-9a), 3.52 (br dd, *J* = 1.34, 5.89 Hz, 1H, H-4), 3.48 (dd, *J* = 3.84, 10.74 Hz, 1H, H-9b), 3.44 (br s, 1H, H-5), 3.42, 3.36, 3.34 (each s, 9H, OMe), 3.18-3.15 (m, 1H, H-8), 2.24 (d, *J* = 15.14 Hz, 1H, H-3eq), 2.15 (dd, *J* = 5.71, 15.18 Hz, 1H, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.25 (CO), 103.64 (C-2), 79.83 (CH), 78.32 (CH), 76.13 (CH), 75.77 (CH), 69.86 (CH_2), 59.54 (CH), 58.46 (OCH_3), 57.96 (OCH_3)), 57.71 (OCH_3), 57.07 (OCH_3), 33.64 (CH_2) ppm; HRMS (ESI): *m/z* calcd for $C_{13}H_{21}N_3O_7$ ($[M+Na]^+$): 354.1277, found: 354.1268.



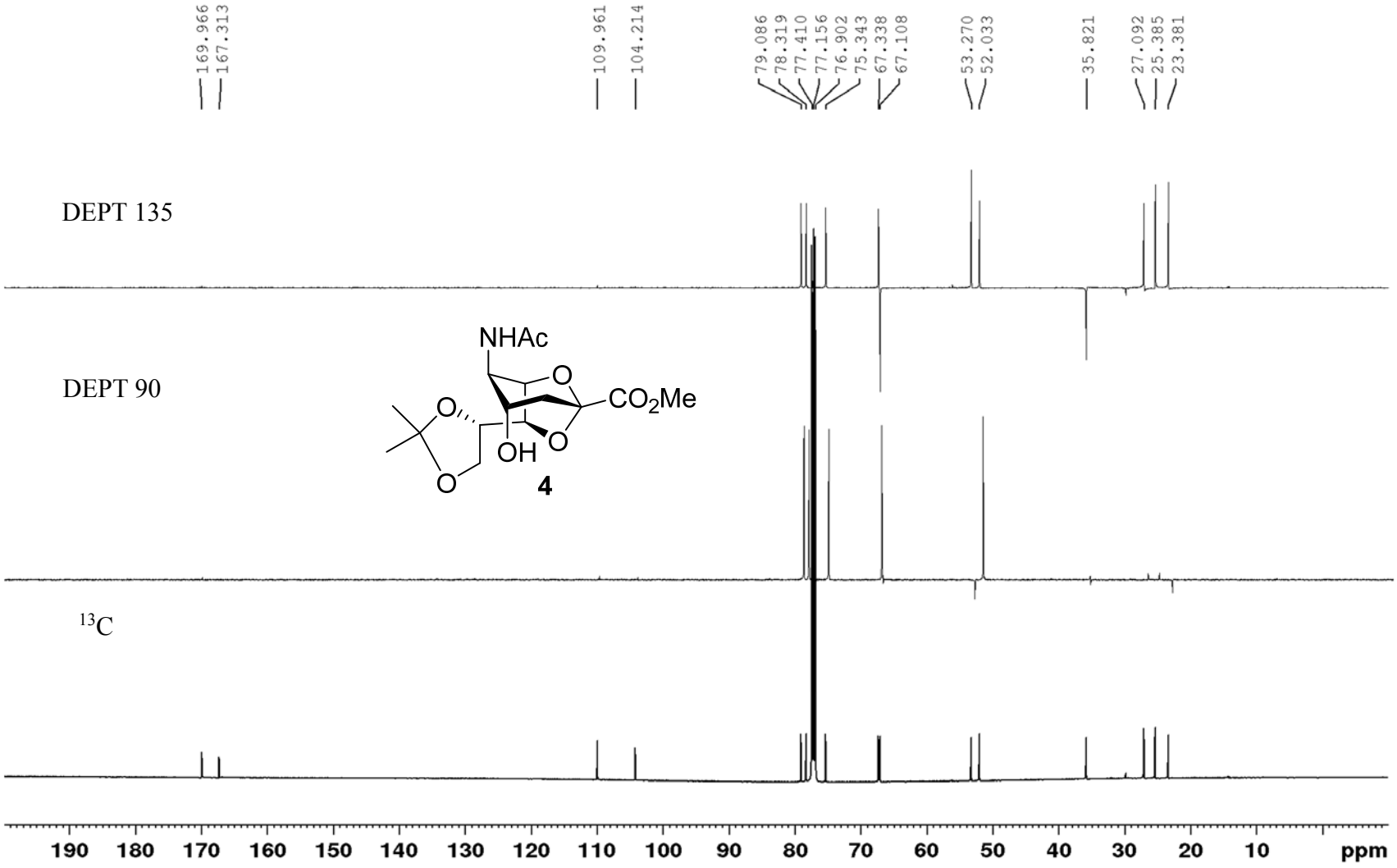
Methyl 5-azido-2,7-*di-O*-acetyl-4, 8, 9-*tri-O*-methyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulpyranosonate (22)

Compound **21** (16.3 mg, 0.0.05 mmol, 1 equiv.) was dissolved in dry Ac_2O (150 µL, 1.48 mmol, 30 equiv.). $SnCl_4$ (2.9 µL, 0.025 mmol, 0.6 equiv.) was added to the reaction mixture and stirred

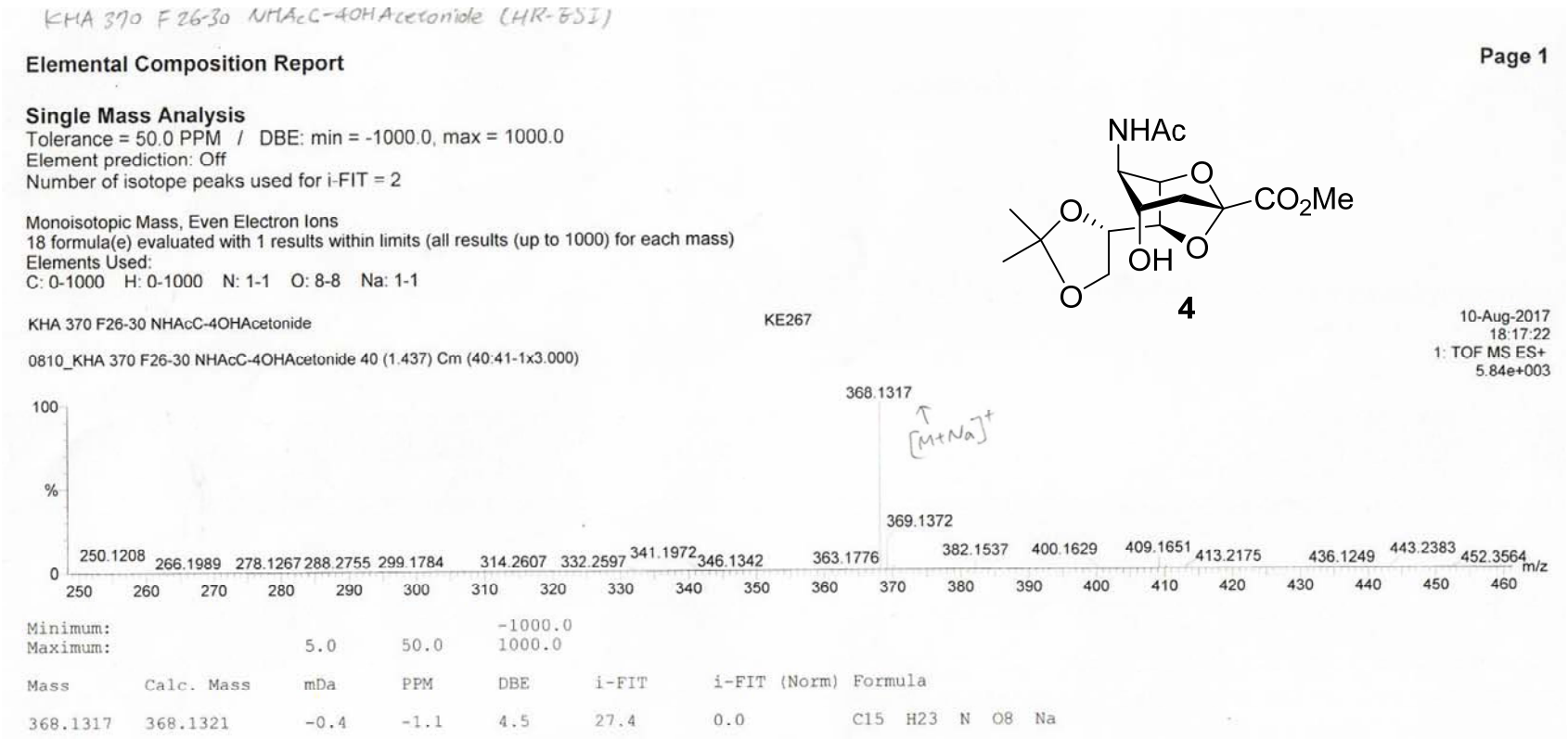
for 2 h at room temperature. The degree of the reaction was monitored by TLC. Upon completion, the mixture was azeotroped with toluene at 35 ^{o}C and directly purified by flash column chromatography (50% EtOAc in hexane) to give **22** (14.14 mg, 66%) and glycal **23** (6 mg, 27%) as colorless syrup products. $[\alpha]^{25}_{D}$ -133 (c = 0.29, $CHCl_3$); IR ($CHCl_3$) *v* 2929, 2115, 1750, 1556, 1441, 1271, 1232, 1205, 1163, 1101, 929 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.34 (dd, *J* = 1.48, 9.19 Hz, 1H, H-7), 3.81 (dd, *J* = 1.53, 10.92 Hz, 1H, H-6), 3.77 (s, 3H, OCH_3), 3.65-3.60 (m, 1H, H-4), 3.57 (dd, *J* = 2.91, 10.70 Hz, 1H, H-9a), 3.54-3.50 (m, 1H, H-8), 3.45, 3.32, 3.30 (each s, 9H, OMe), 3.27 (dd, *J* = 3.82, 10.76 Hz, 1H, H-9b), 3.13 (dd, *J* = 1.41, 10.75 Hz, 1H, H-5), 2.59 (dd, *J* = 5.03, 13.51 Hz, 1H, H-3eq), 2.11, 2.08 (each s, 6H, 2OAc), 1.66 (dd, *J* = 2.16, 13.41 Hz, 1H, H-3ax); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.98 (CO), 168.36 (CO), 167.37 (CO), 97.39 (C-2), 77.91 (CH), 76.59 (CH), 71.11 (CH), 70.31 (CH_2), 69.05 (CH), 61.36 (CH), 59.49 (OCH_3), 57.59 (OCH_3), 57.43 (OCH_3), 53.18 (OCH_3), 35.69 (CH_2), 20.96, 20.76 (each CH_3) ppm; HRMS (ESI): *m/z* calcd for $C_{17}H_{27}N_3O_{10}$ ($[M+Na]^+$): 456.1594, found: 456.1594.



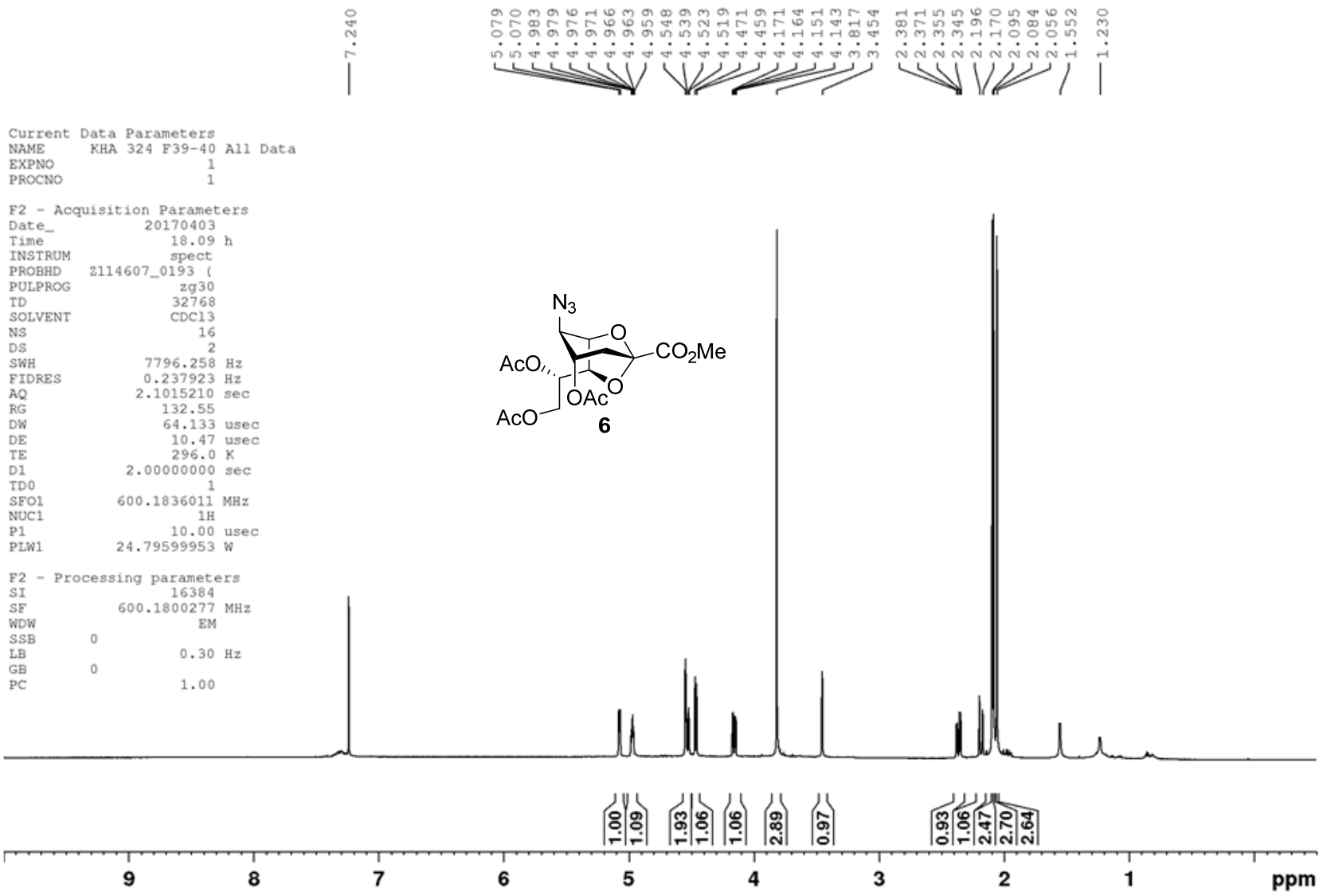
The ^{1}H Spectrum of Compound **4**



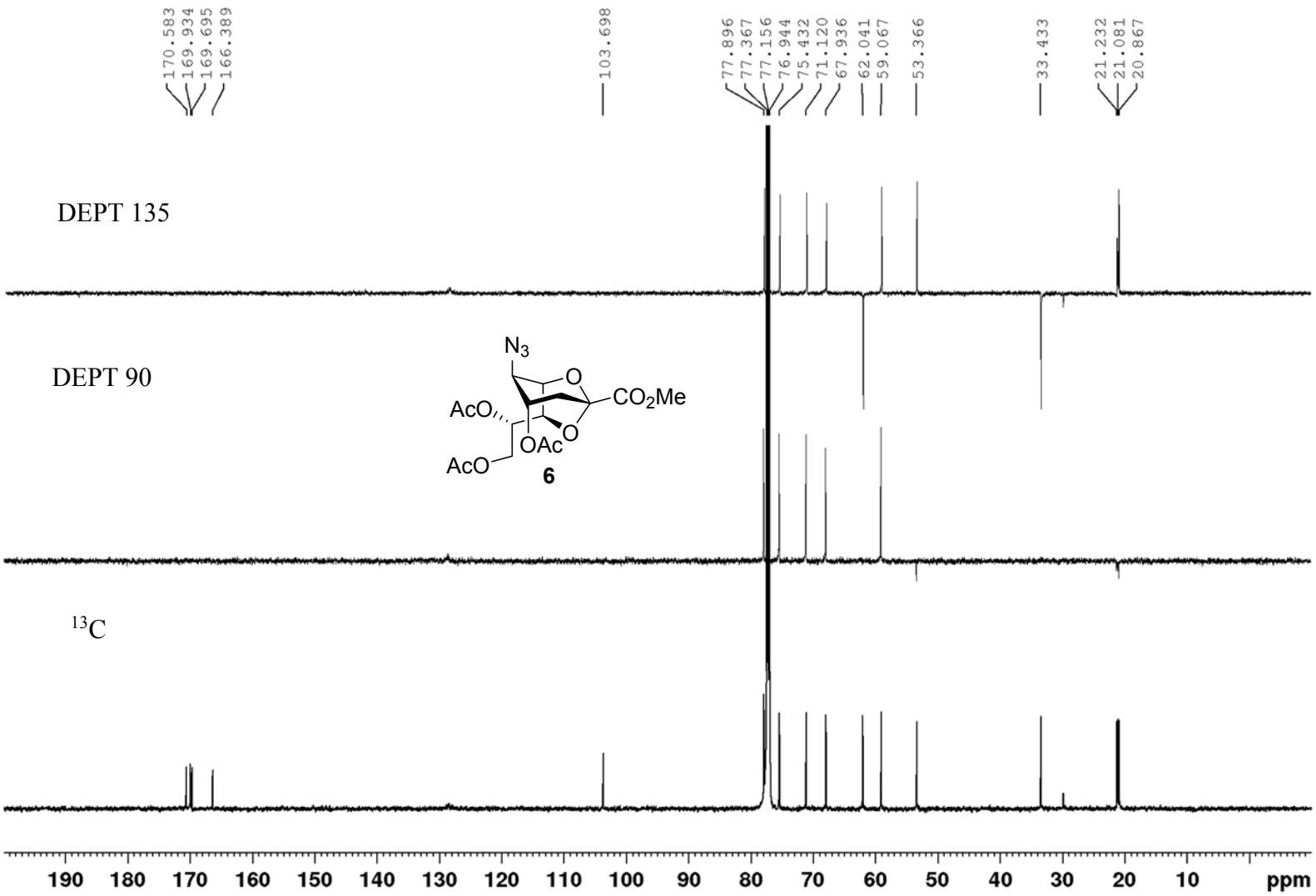
The ^{13}C Spectrum of Compound **4**



The High-resolution Mass Spectrometry of Compound **4**



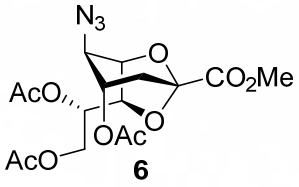
The ^{1}H Spectrum of Compound **6**



The ^{13}C Spectrum of Compound **6**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

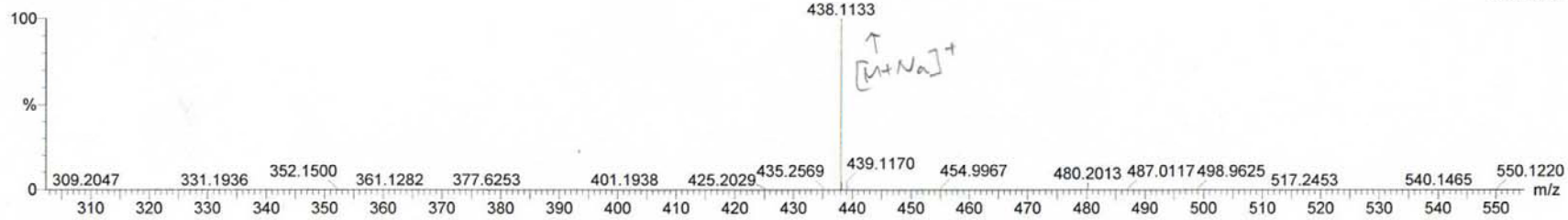


6

Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-2000 H: 0-2000 N: 3-3 O: 10-11 Na: 1-1

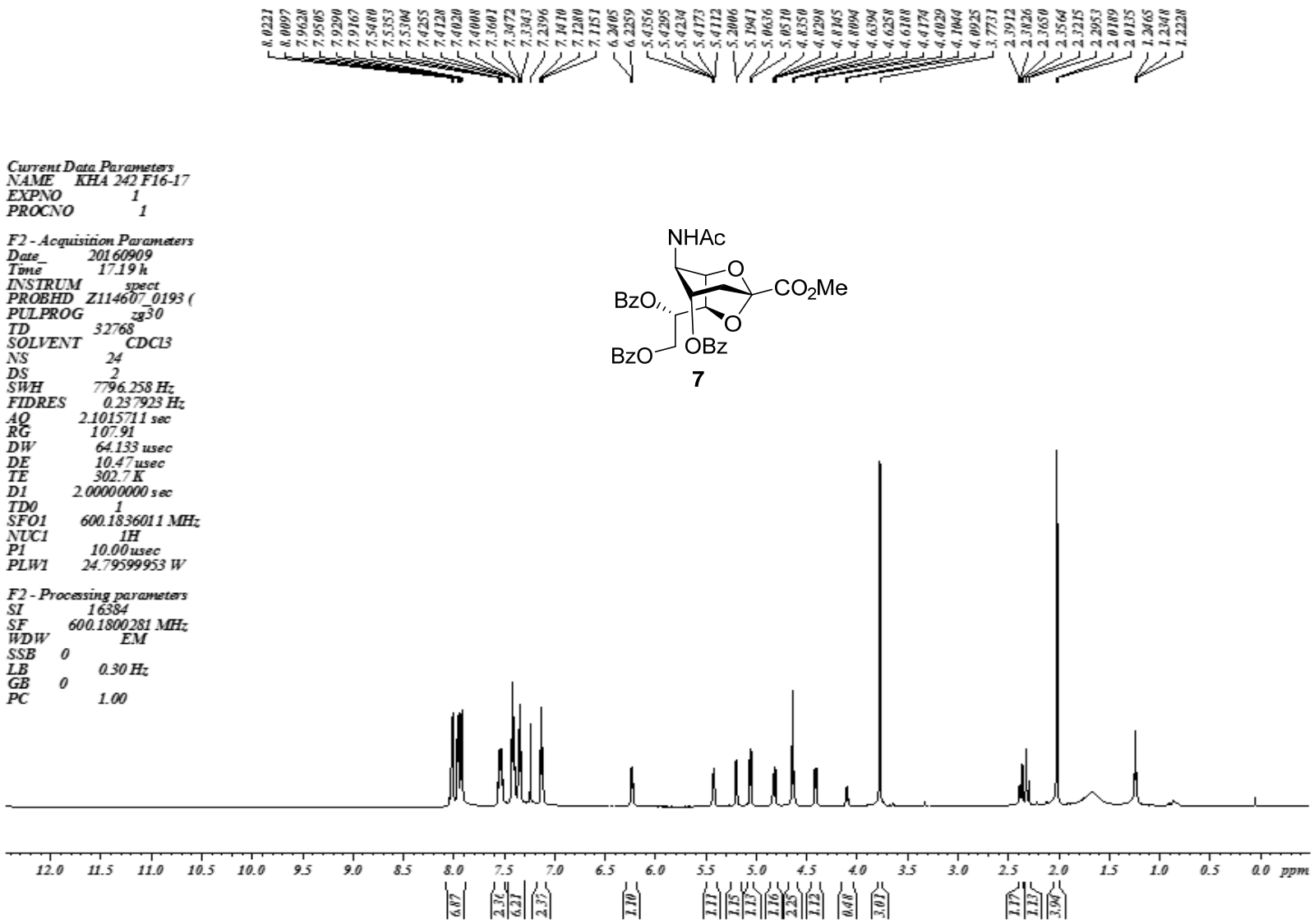
KHA 249B F15-16 3OAc N3 KE267 05-Oct-2016 17:47:45

1005_KHA 249B F15-16 3OAc N3 39 (3.134) Cm (39-1x10.000) 1: TOF MS ES+ 2.47e+003

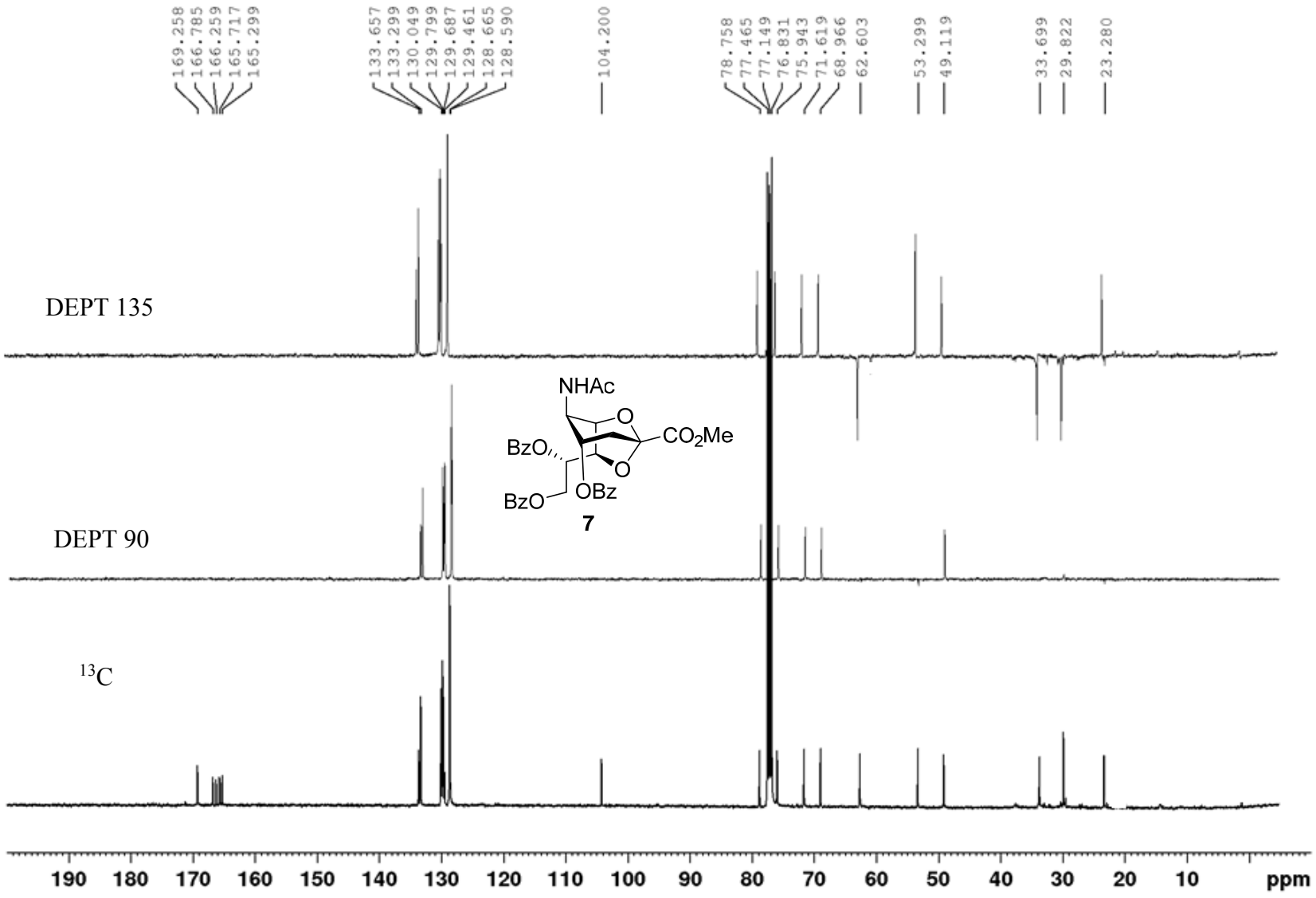


Minimum:				-1000.0			
Maximum:		5.0	30.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
438.1133	438.1125	0.8	1.8	7.5	27.5	0.0	C16 H21 N3 O10 Na

The High-resolution Mass Spectrometry of Compound **6**

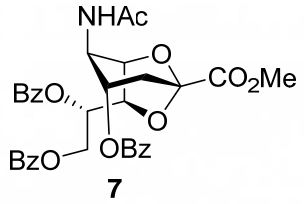


The ^{1}H Spectrum of Compound **7**



The ^{13}C Spectrum of Compound **7**

Elemental Composition Report

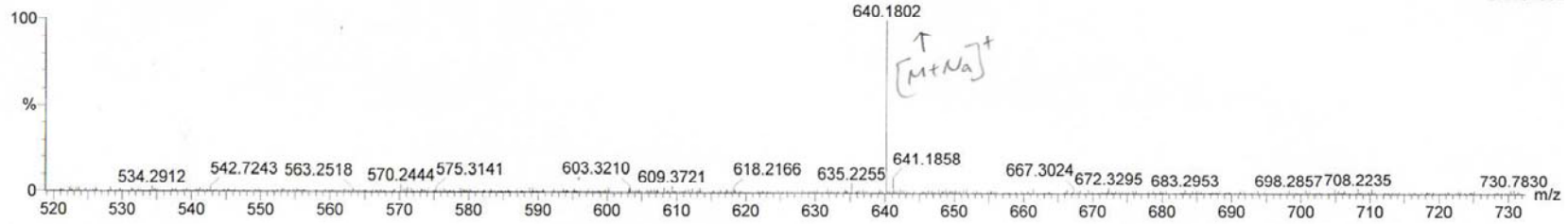


7

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

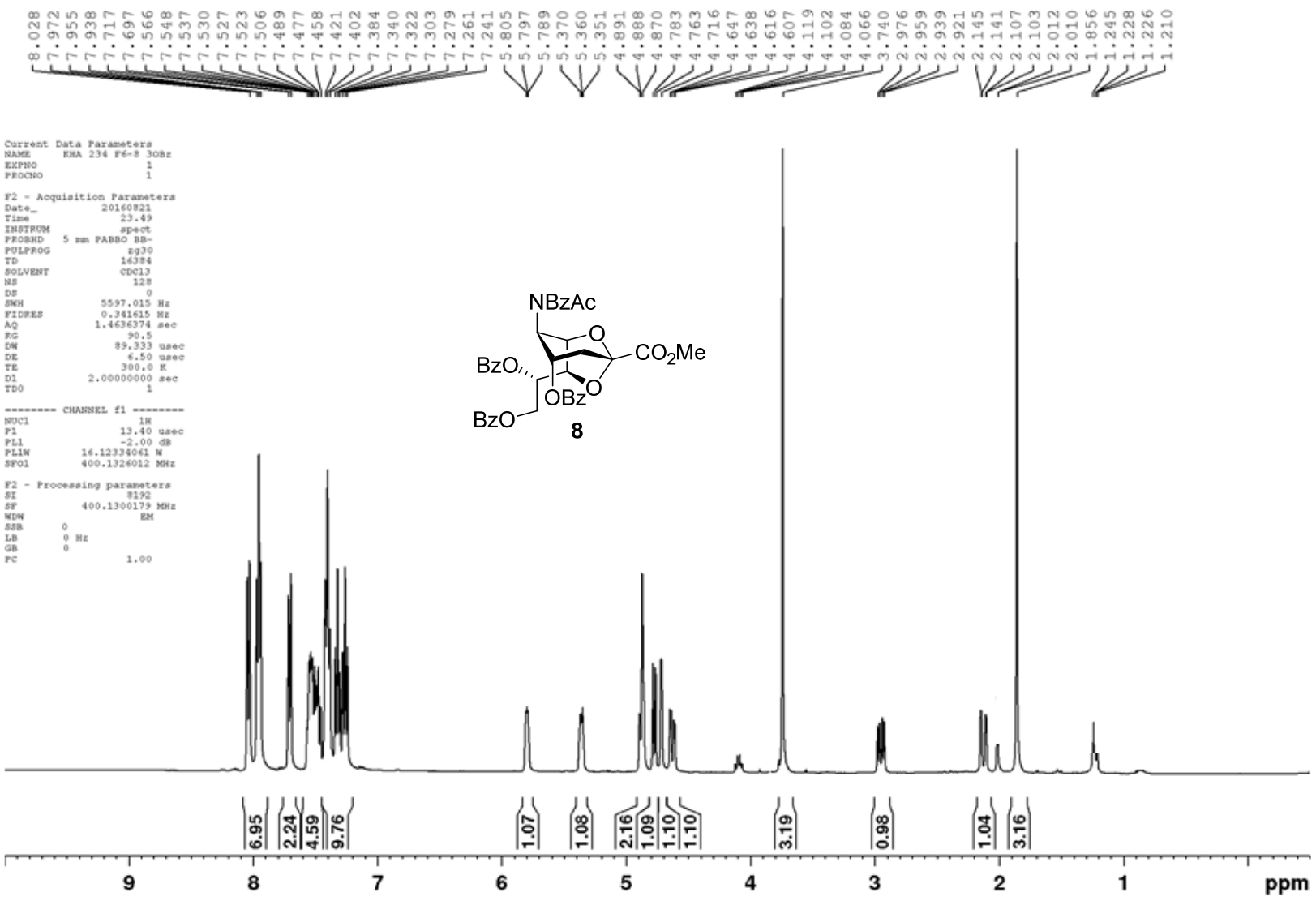
Monoisotopic Mass, Even Electron Ions
35 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-1000 H: 0-4000 N: 1-1 O: 11-11 Na: 1-1

KHA 238 F14-16 3OBzNHAc KE267 09-Sep-2016
17:05:05
0909_KHA 238 F14-16 3OBzNHAc 17 (1.387) Cm (17-26x2.000) 1: TOF MS ES+
2.11e+002

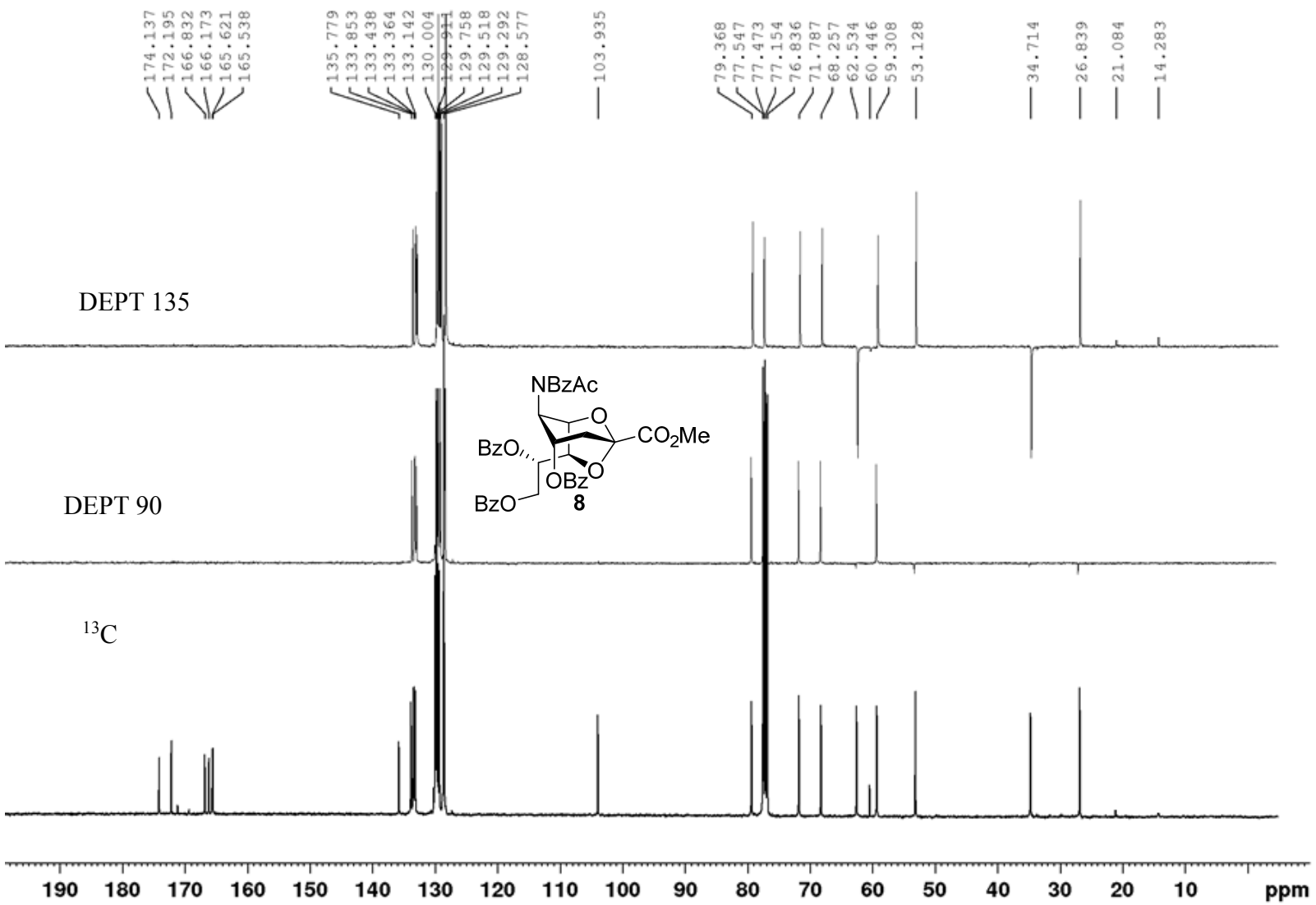


Minimum:				-1000.0			
Maximum:		5.0	50.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
640.1802	640.1795	0.7	1.1	18.5	25.5	0.0	C33 H31 N O11 Na

The High-resolution Mass Spectrometry of Compound **7**



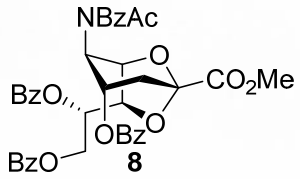
The ^{1}H Spectrum of Compound **8**



The ^{13}C Spectrum of Compound **8**

KHA 234 F6-8 3OBzNBzAc (HR-ESI)

Elemental Composition Report Page 1



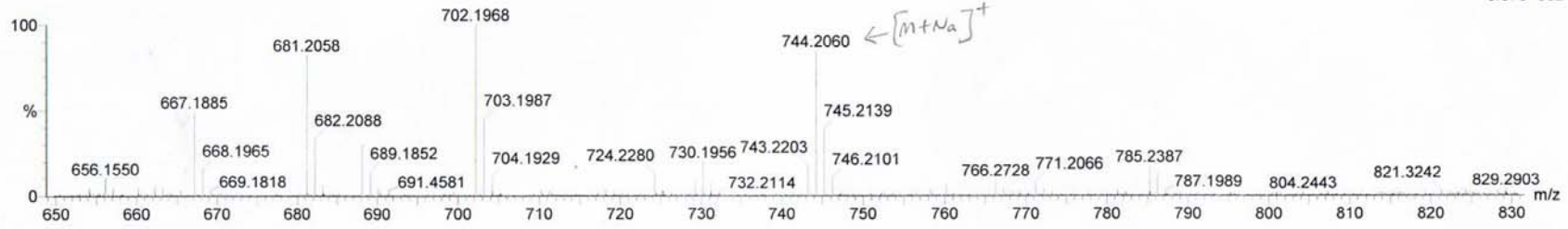
8

Single Mass Analysis
Tolerance = 4.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
44 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-10000 H: 0-10000 N: 1-1 O: 12-12 Na: 1-1

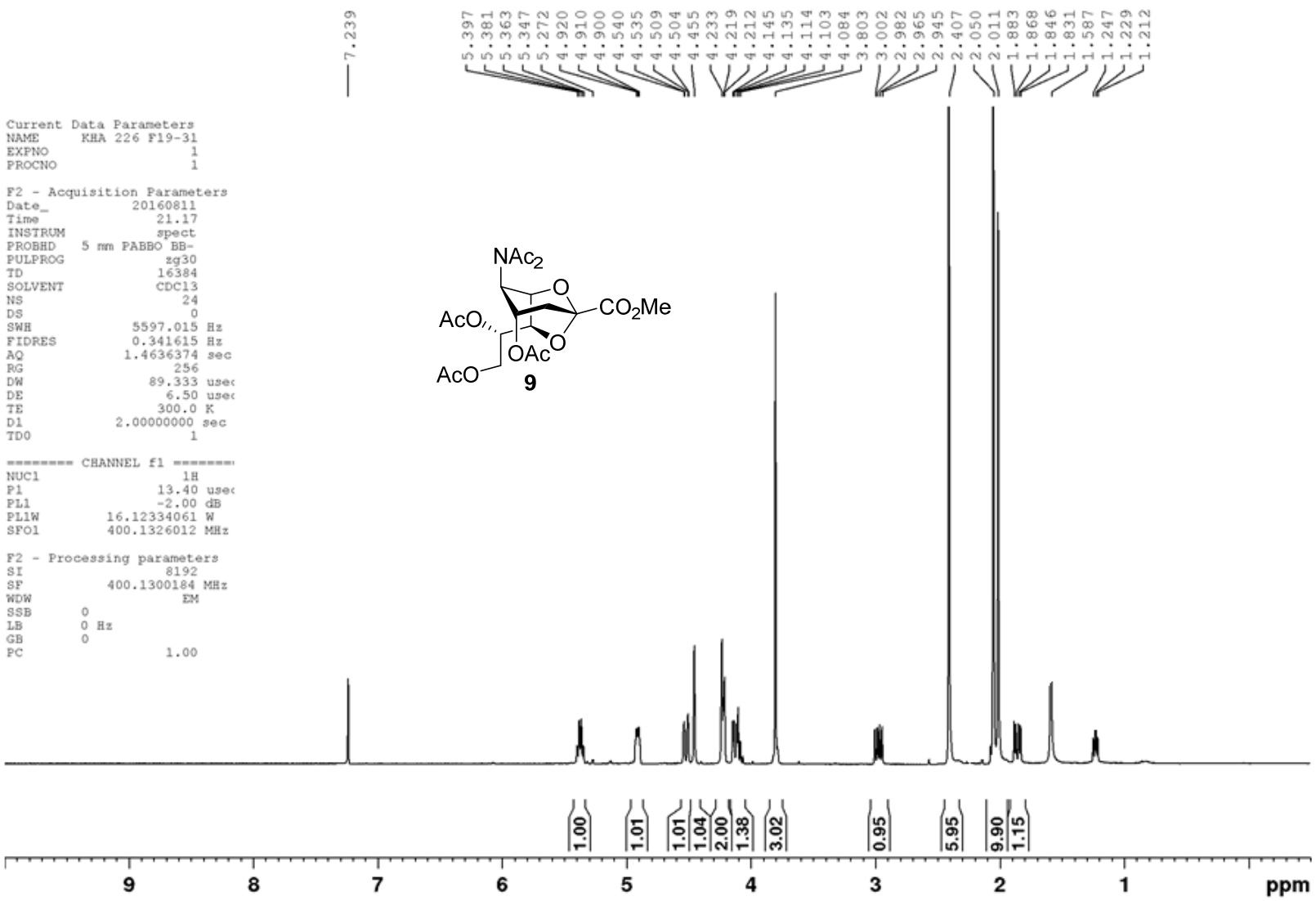
KHA 234 F6-8 3OBzNBzAc KE267 11-May-2017 14:22:53

0511_KHA 234 F6-8 3OBzNBzAc 28 (0.999) Cm (25:28) 1: TOF MS ES+ 6.67e+002

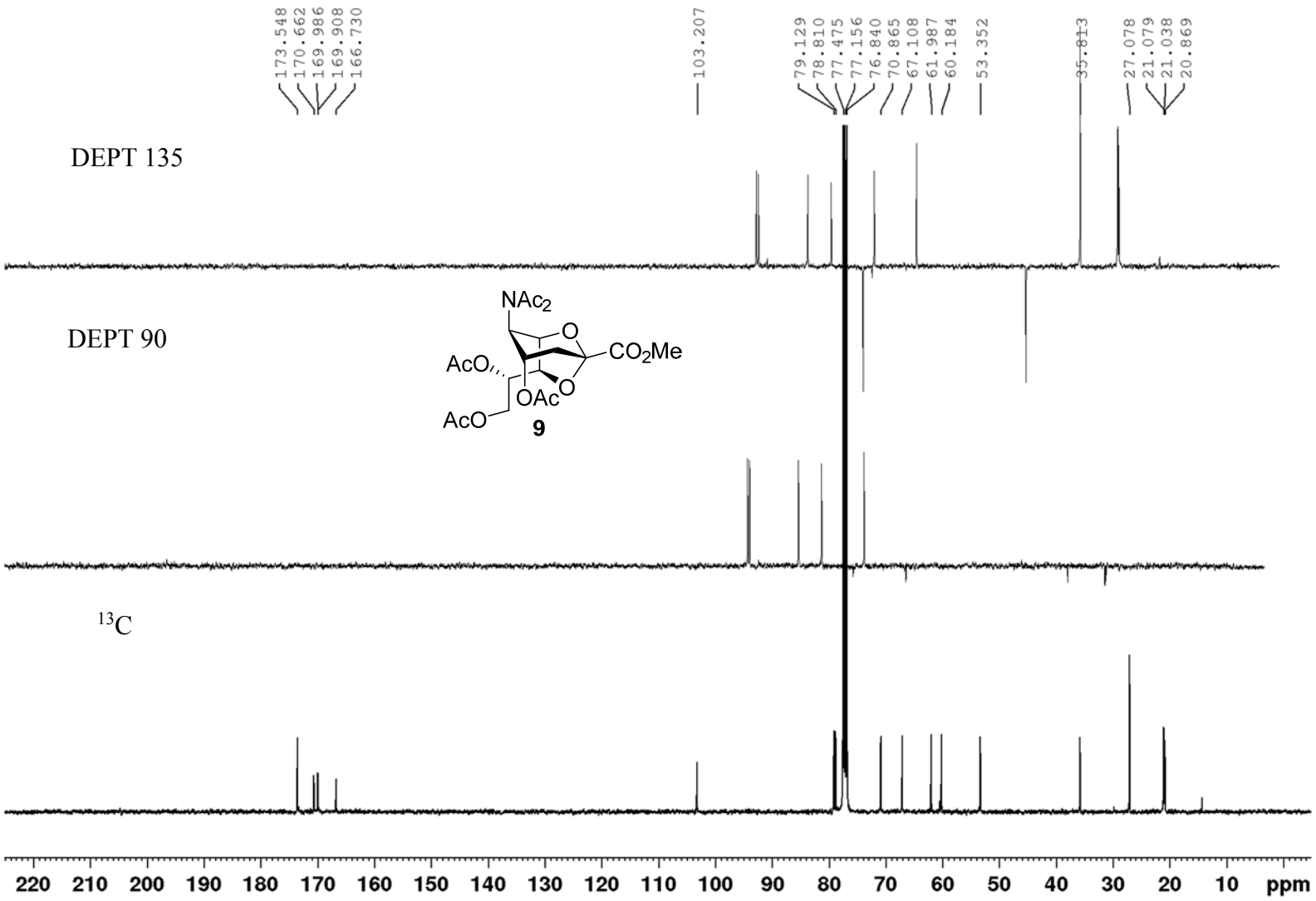


Minimum:				-1000.0			
Maximum:		5.0	4.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
744.2060	744.2057	0.3	0.4	23.5	55.5	0.0	C40 H35 N O12 Na

The High-resolution Mass Spectrometry of Compound **8**



The ^{1}H Spectrum of Compound **9**

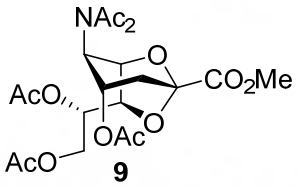


The ^{13}C Spectrum of Compound **9**

Elemental Composition Report **Page 1**

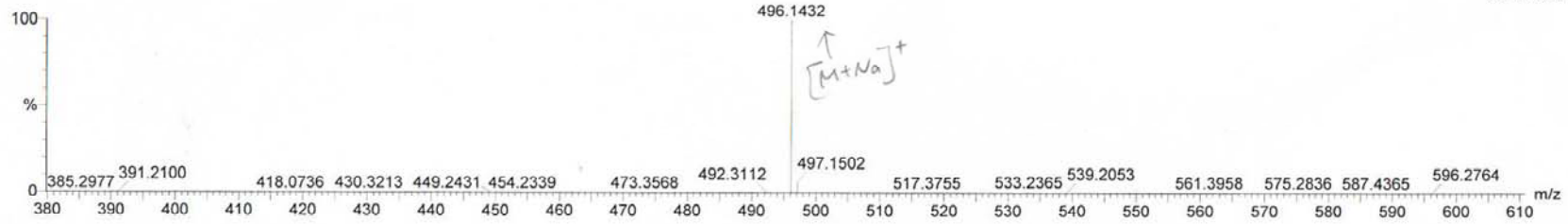
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
22 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 1-1000 H: 0-4000 N: 1-1 O: 12-12 Na: 1-1



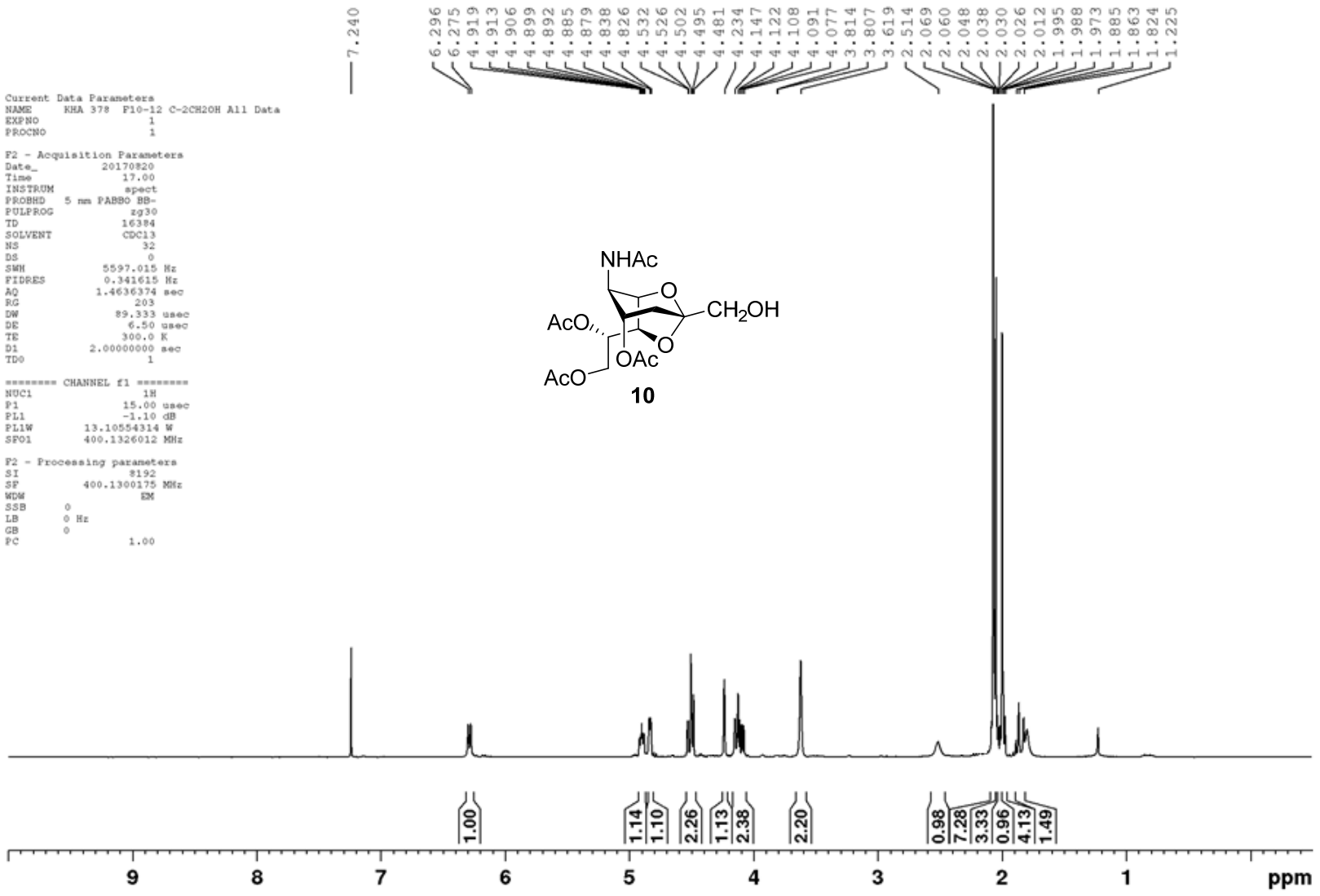
9

KHA 224 F13-16 NAc2 KE267 09-Sep-2016
17:09:02
0909_KHA 224 F13-16 NAc2 6 (0.479) Cm (6-7) 1: TOF MS ES+
5.74e+003

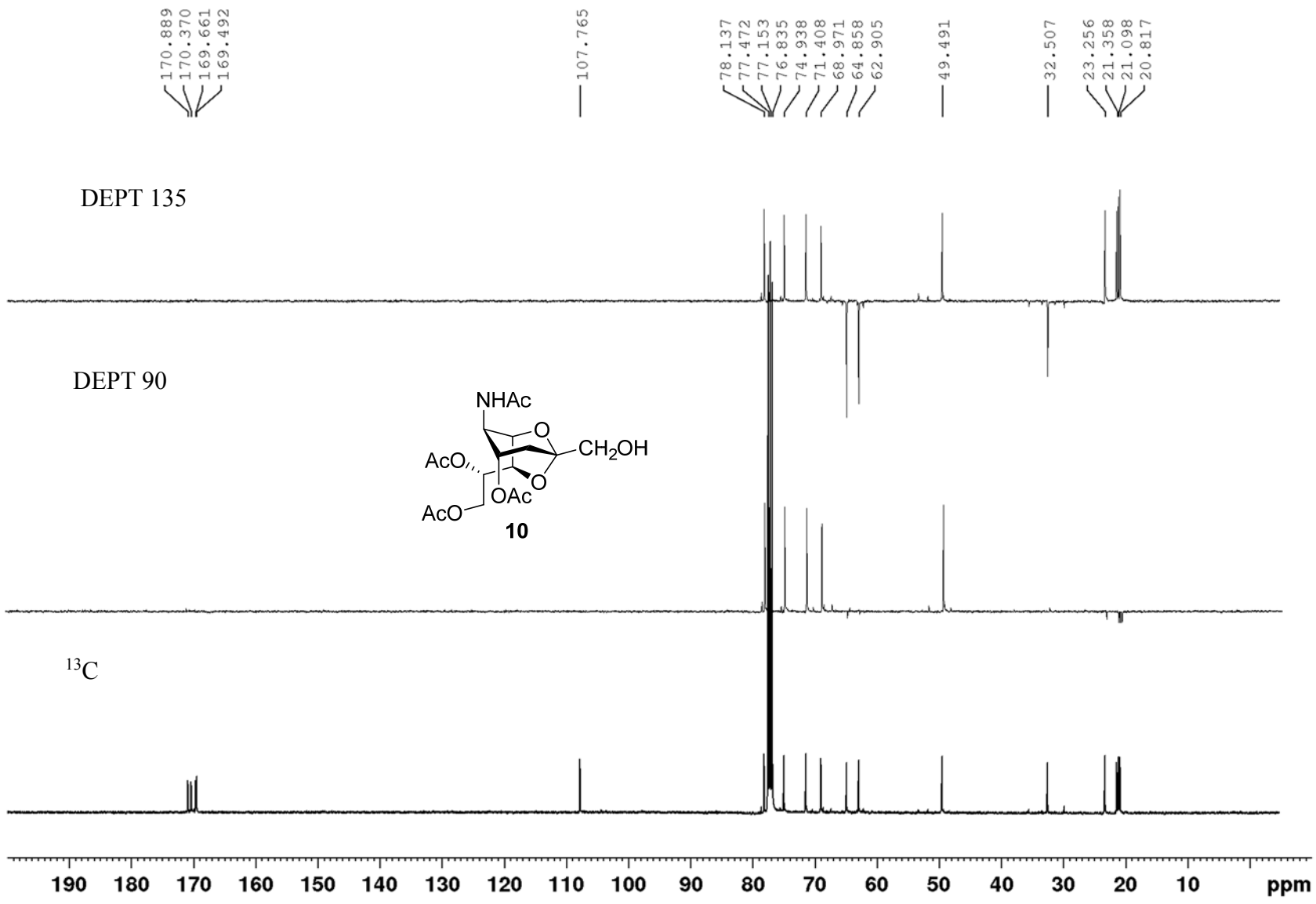


Minimum:				-1000.0			
Maximum:		5.0	50.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
496.1432	496.1431	0.1	0.2	7.5	25.6	0.0	C20 H27 N O12 Na

The High-resolution Mass Spectrometry of Compound **9**



The ^{1}H Spectrum of Compound **10**



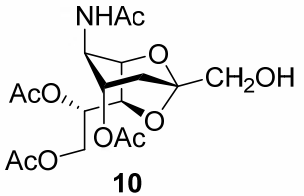
The ^{13}C Spectrum of Compound **10**

KHA 378 F10-12C-2CH2OH (HR-ESI)

Elemental Composition Report

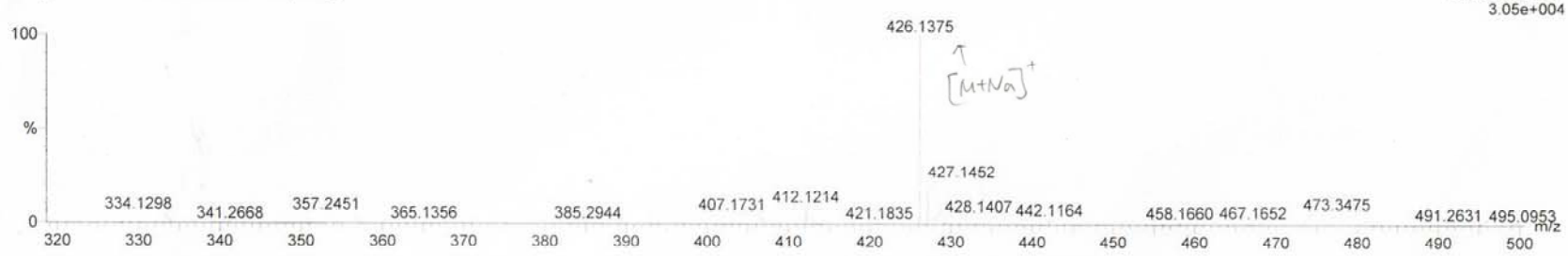
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-500 H: 0-1000 N: 1-1 O: 10-10 Na: 0-1
KHA 378 F10-11 C-2CH2OH
0828_KHA 378 F10-11 C-2CH2OH 49 (1.786)



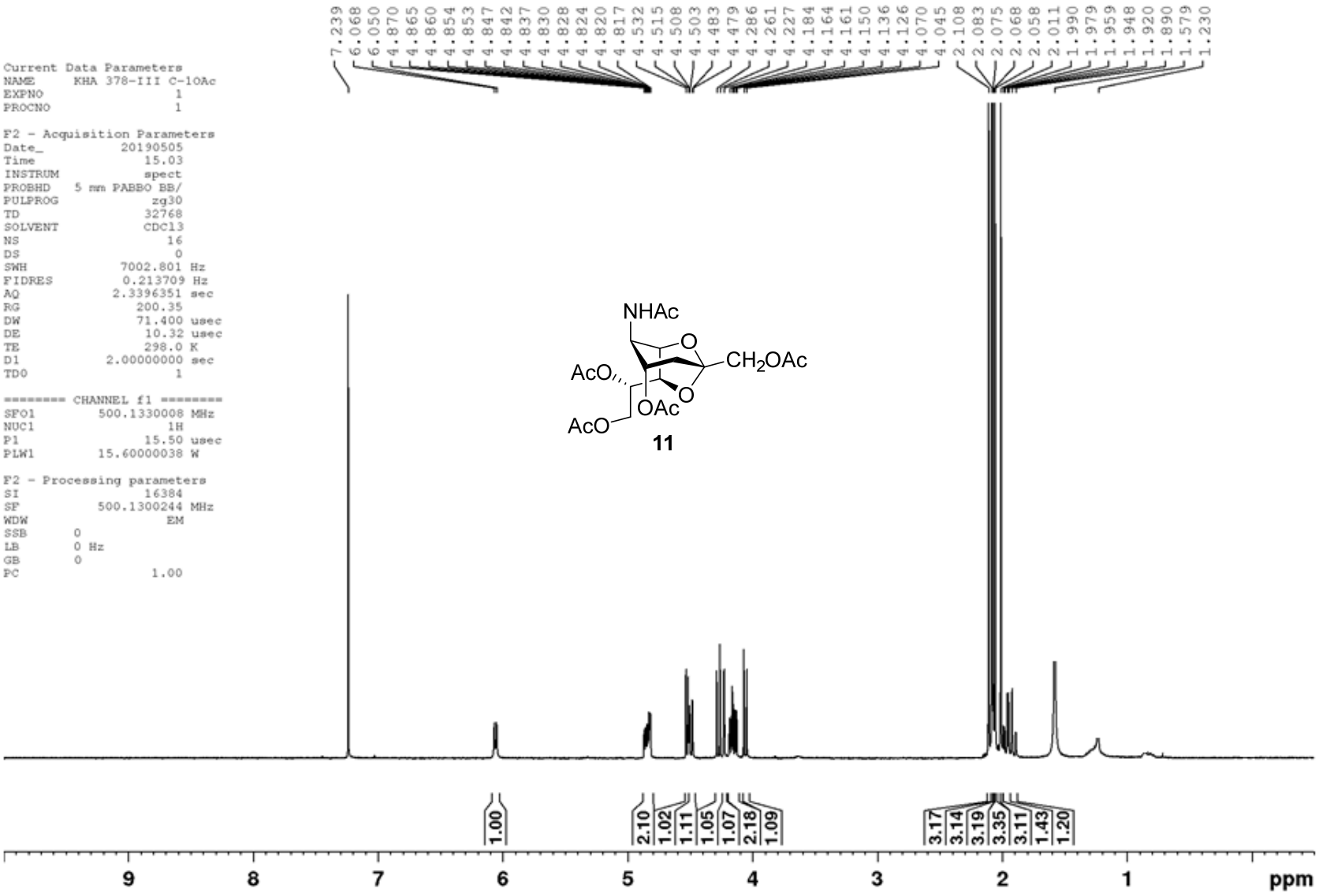
10

1: TOF MS ES+
3.05e+004

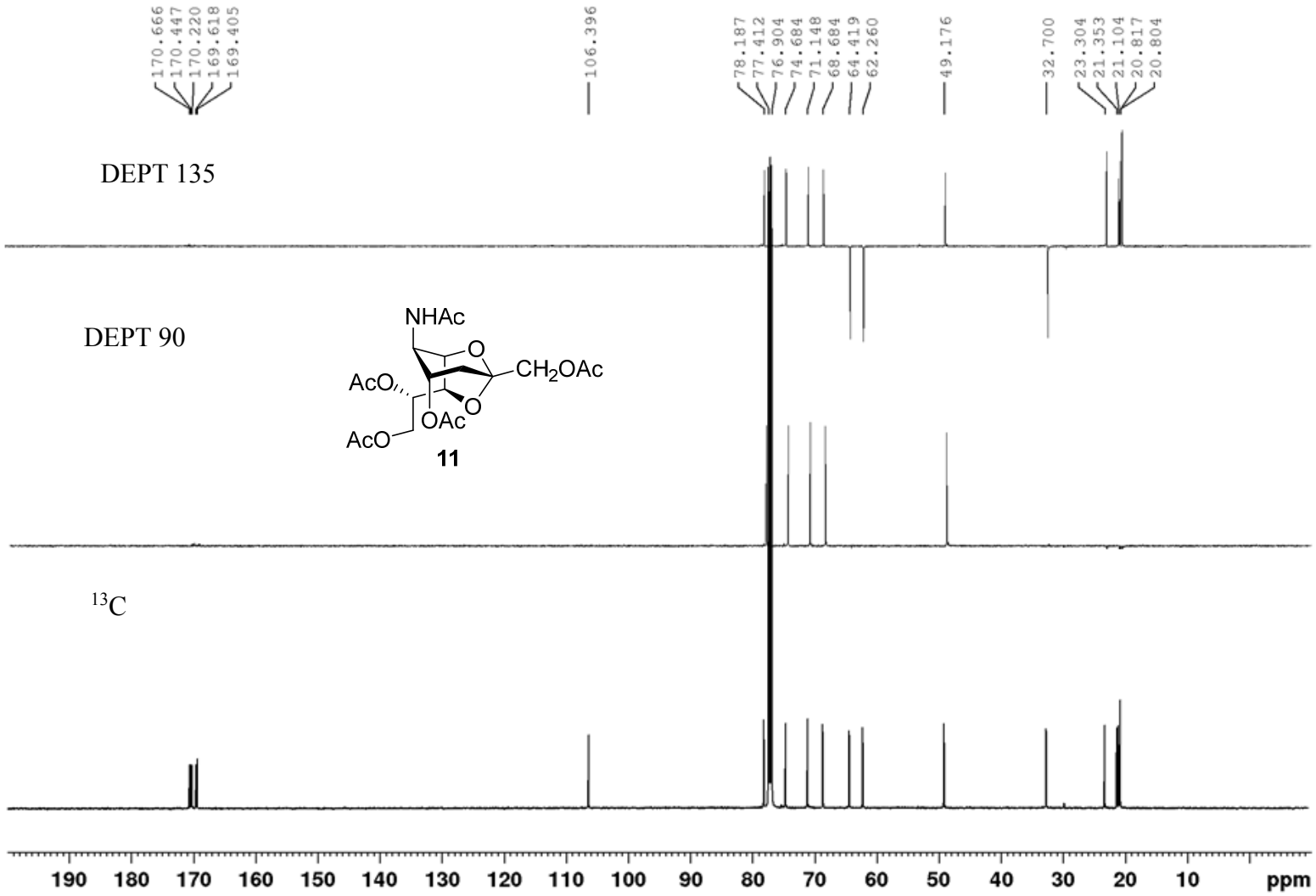


Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
426.1375	426.1376	-0.1	-0.2	5.5	84.5	0.0	C17 H25 N O10 Na	

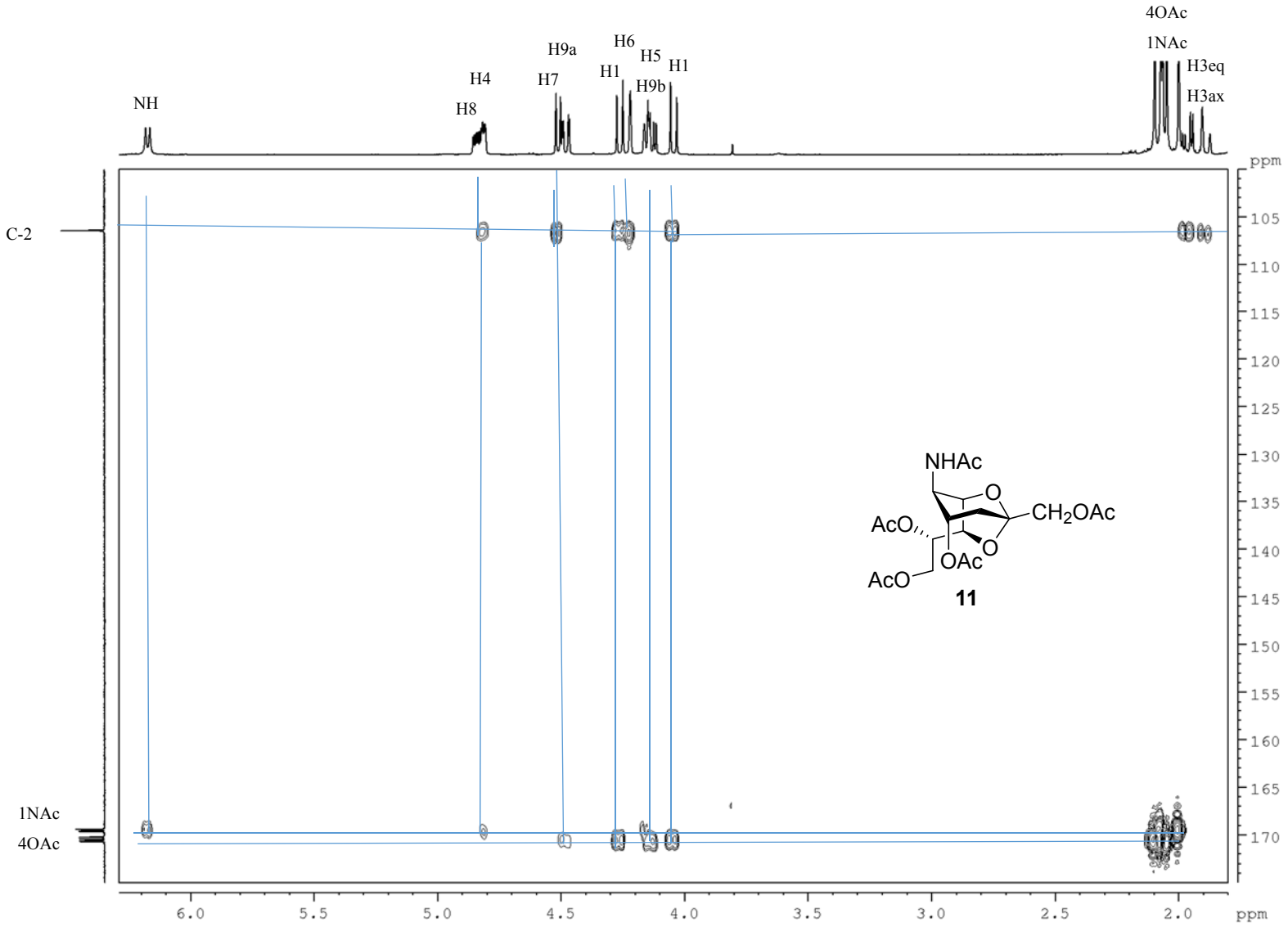
The High-resolution Mass Spectrometry of Compound **10**



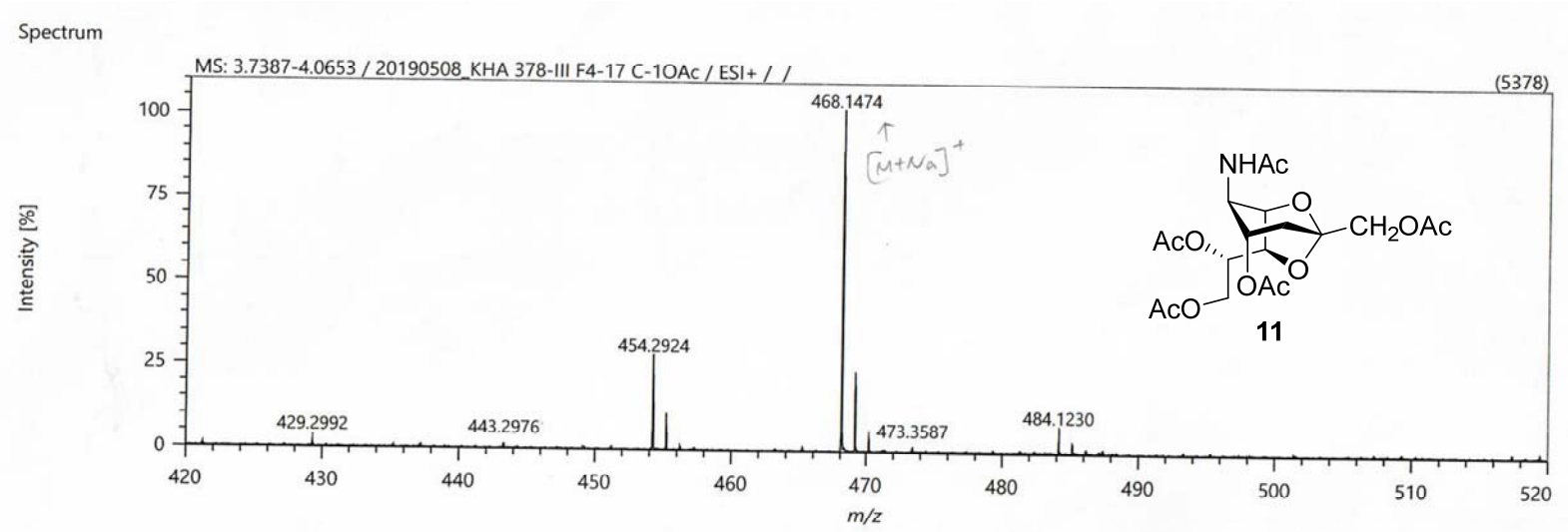
The ^{1}H Spectrum of Compound **11**



The ^{13}C Spectrum of Compound **11**



The HMBC Spectrum of Compound **11**



Elemental Composition

Parameters	
Tolerance:	±20.00 ppm
Electron:	Odd/Even
Charge:	+1
DBE:	-1.5 - 999.0

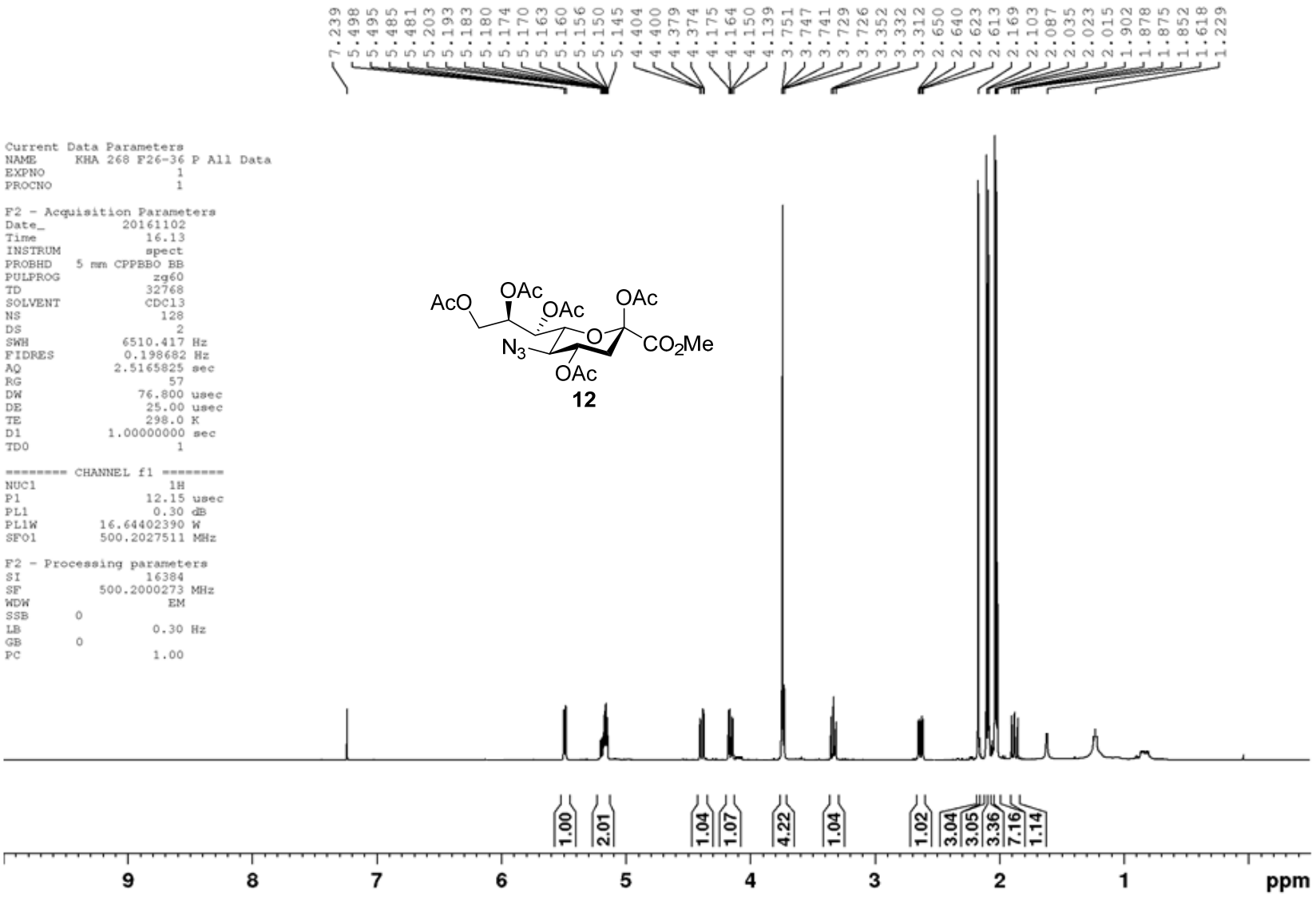
Elements Set 1:

Symbol	C	H	O	Na	Cl	F	N	S
Min	0	0	11	1	0	0	1	0
Max	400	1000	11	1	0	0	1	0

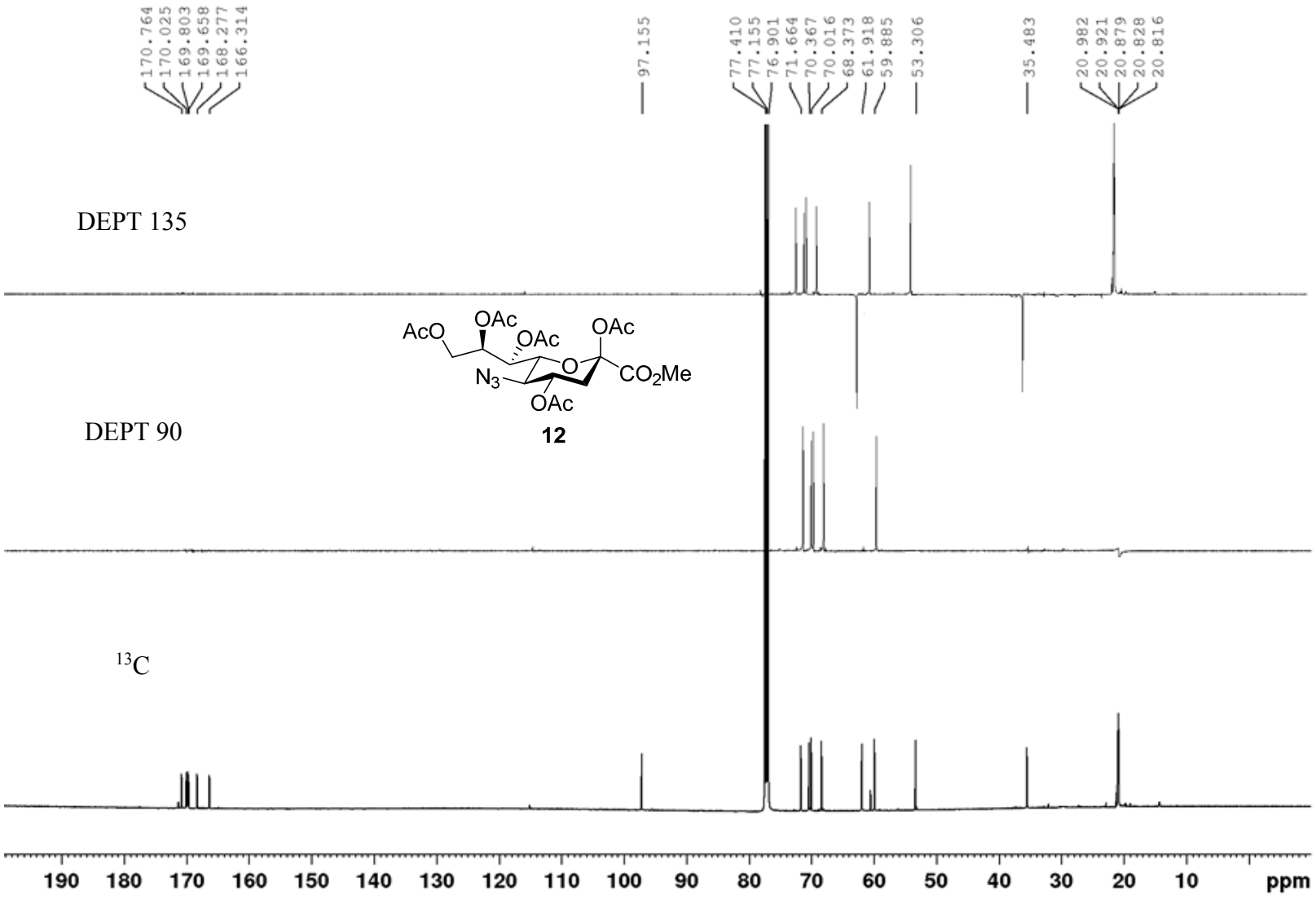
Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
468.14741	C19 H27 N O11 Na	468.14763	-0.22	-0.47	6.5

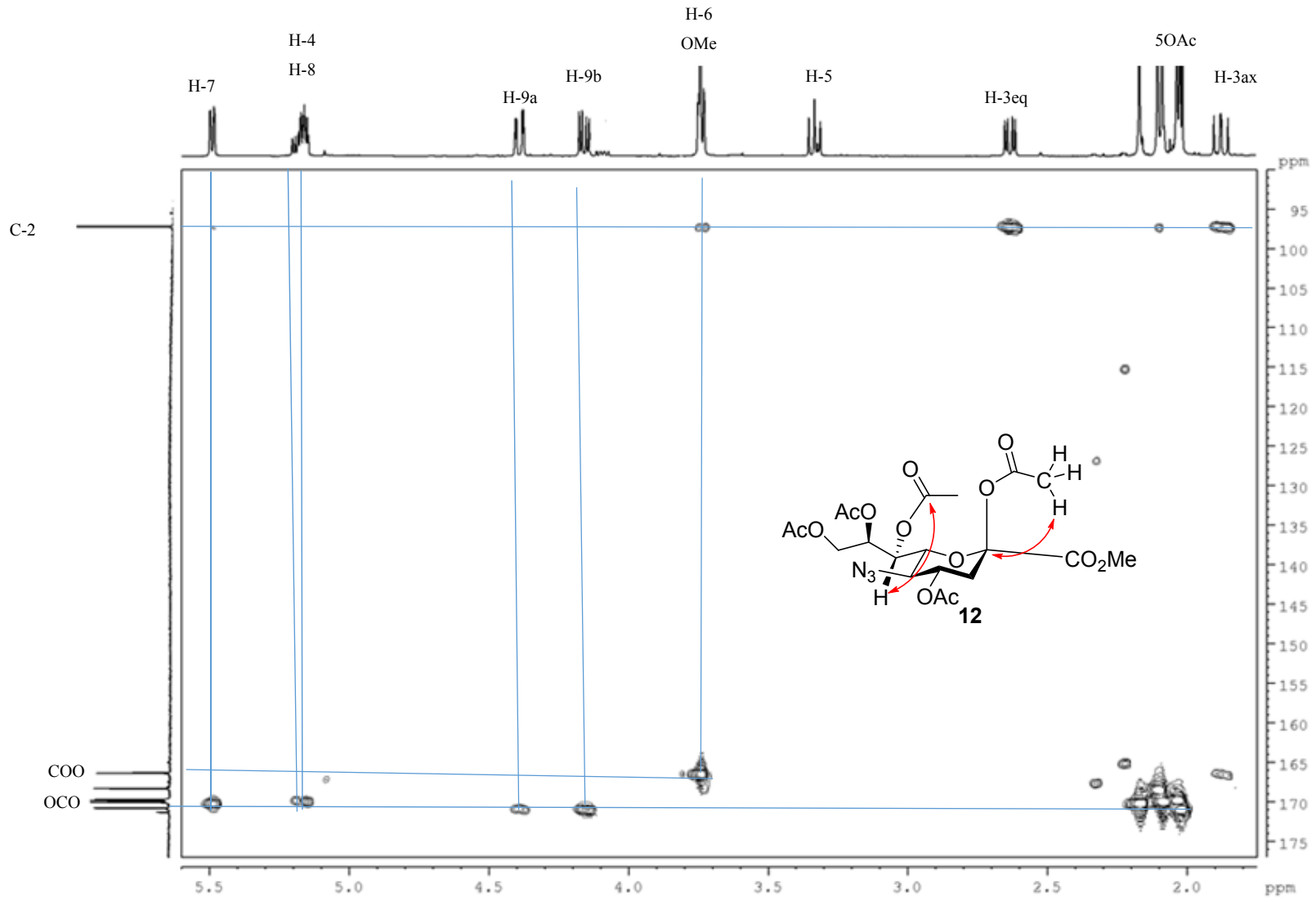
The High-resolution Mass Spectrometry of Compound **11**



The ^{1}H Spectrum of Compound **12**



The ^{13}C Spectrum of Compound **12**

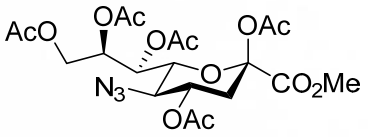


The HMBC Spectrum of Compound 1**2**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

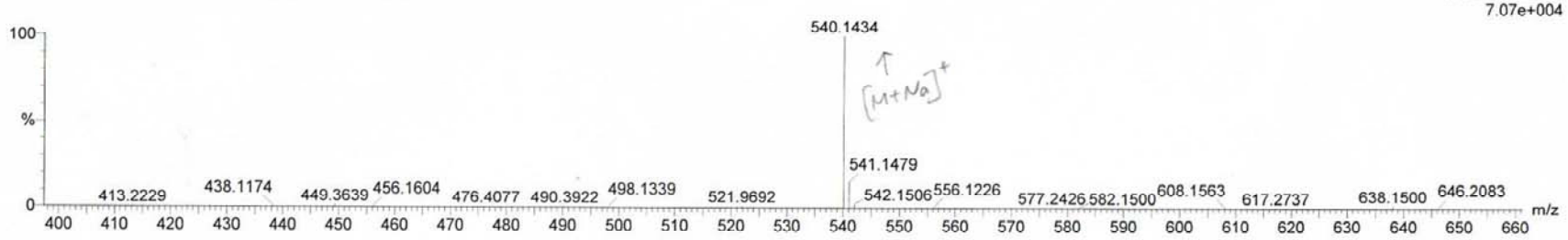
Monoisotopic Mass, Even Electron Ions
23 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-1000 H: 0-1000 N: 3-3 O: 13-13 Na: 1-1



12

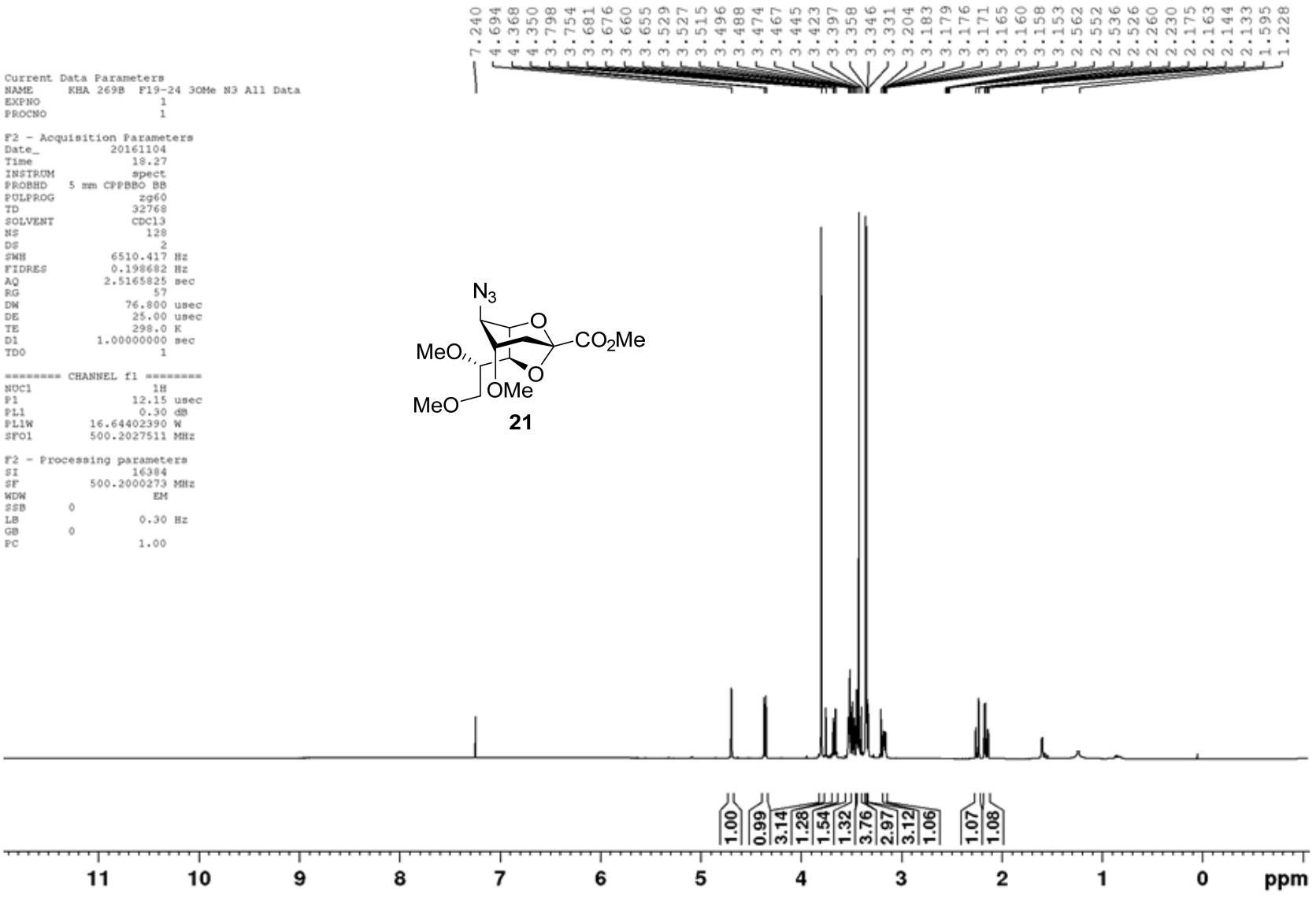
KHA 268 F26-36 5OAc N3 KE267 08-Nov-2016 16:02:21

1108_KHA 268 F26-36 5OAc N3 39 (3.135) Cm (39:41) 1: TOF MS ES+ 7.07e+004

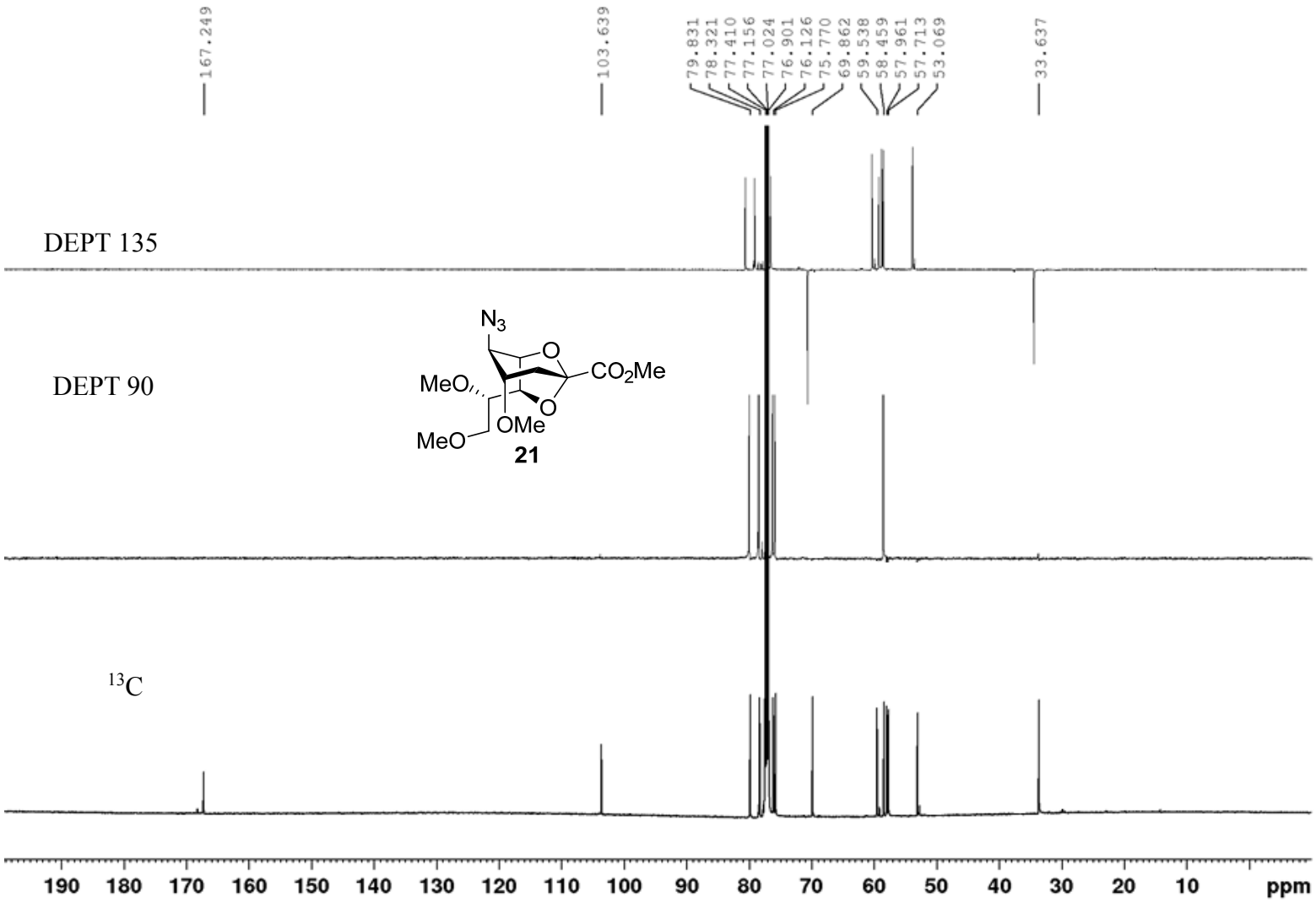


Minimum:				-1000.0			
Maximum:		5.0	100.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
540.1434	540.1442	-0.8	-1.5	8.5	27.4	0.0	C20 H27 N3 O13 Na

The High-resolution Mass Spectrometry of Compound **12**



The ^{1}H Spectrum of Compound **21**

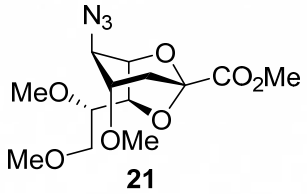


The ^{13}C Spectrum of Compound **21**

Elemental Composition Report Page 1

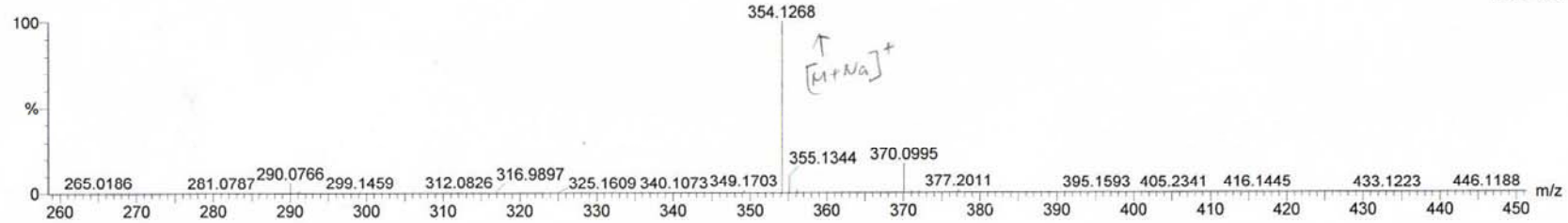
Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
15 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-1000 H: 0-1000 N: 3-3 O: 7-7 Na: 1-1



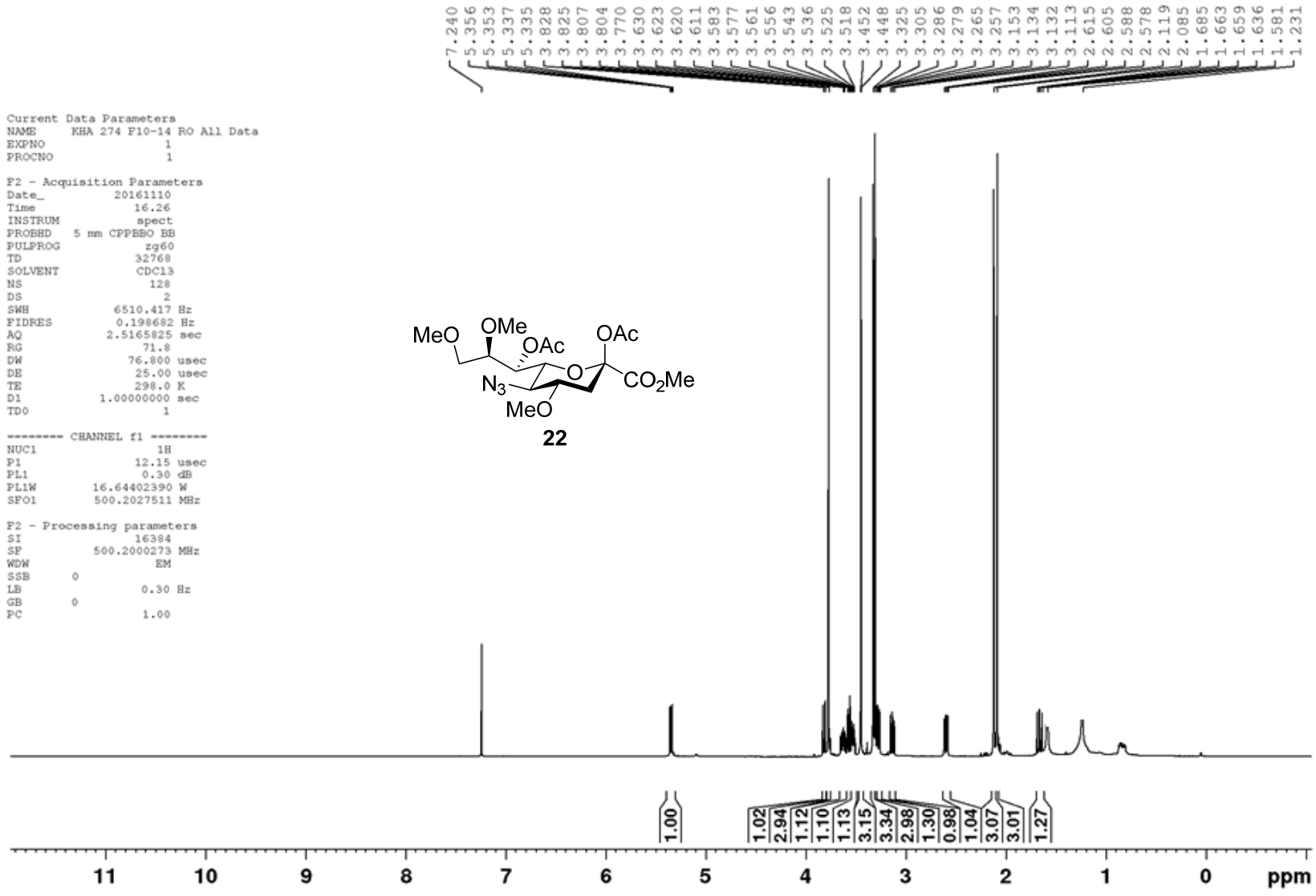
21

KHA 269B F19-243OMe N3 KE267 08-Nov-2016
16:57:10
1108_KHA 269B F19-243OMe N3 42 (3.395) Cm (42-5) 1: TOF MS ES+
1.31e+004

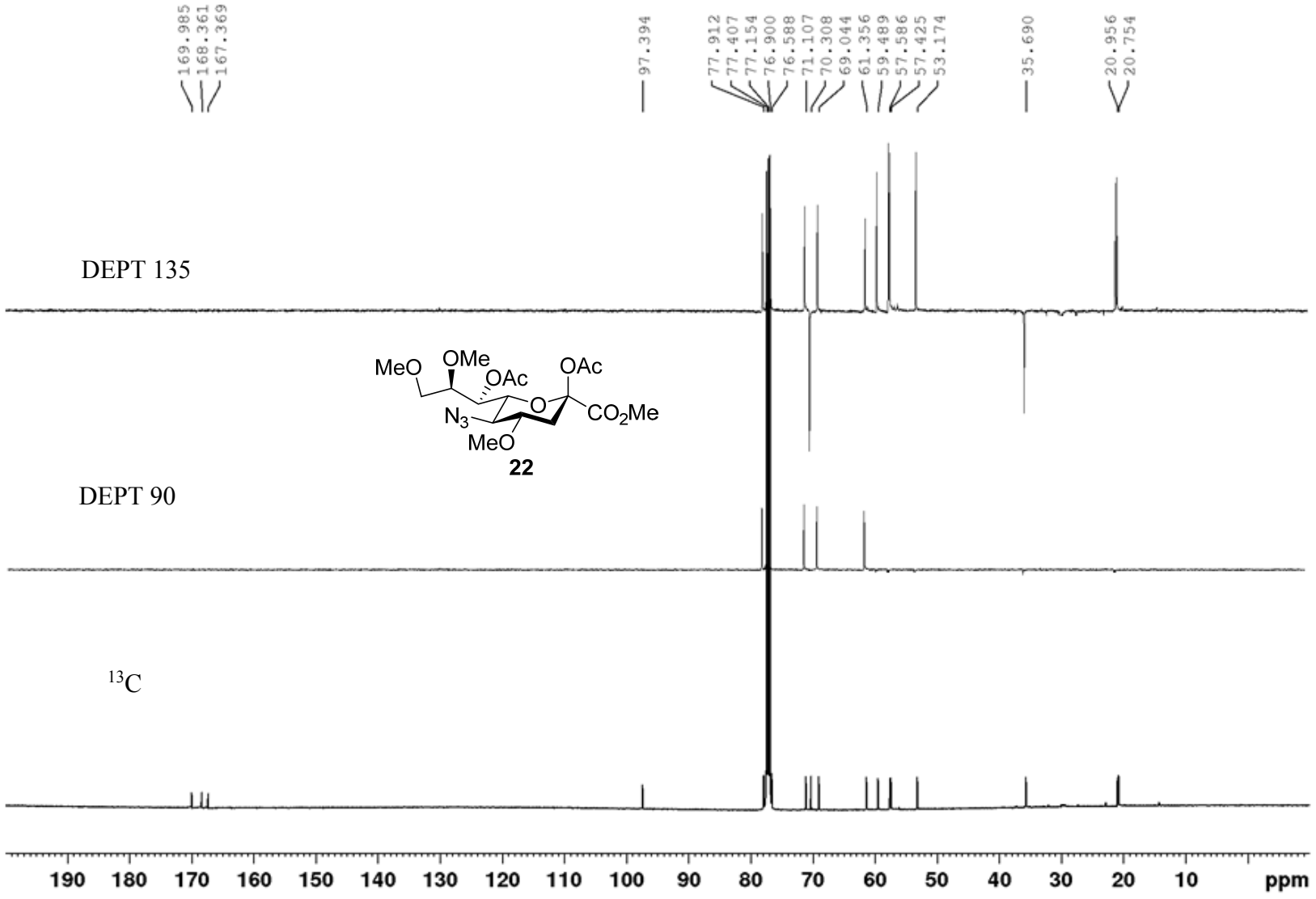


Minimum:				-1000.0			
Maximum:		5.0	50.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
354.1268	354.1277	-0.9	-2.5	4.5	19.2	0.0	C13 H21 N3 O7 Na

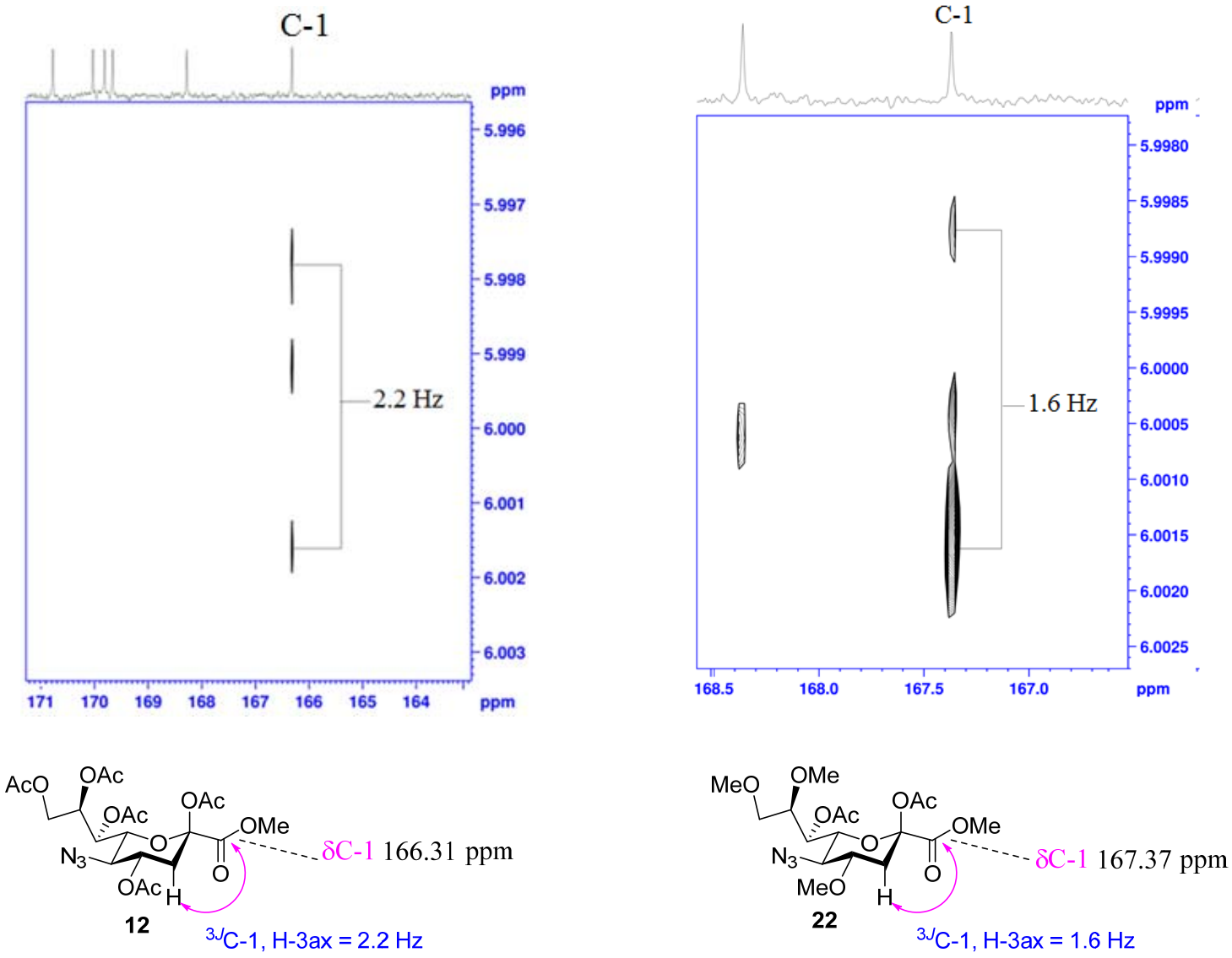
The High-resolution Mass Spectrometry of Compound **21**



The ^{1}H Spectrum of Compound **22**



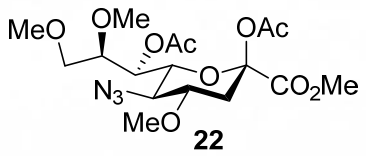
The ^{13}C Spectrum of Compound **22**



The 2D Selective Heteronuclear *J*-Resolved Spectrum of Compounds **12** and **22**

Elemental Composition Report **Page 1**

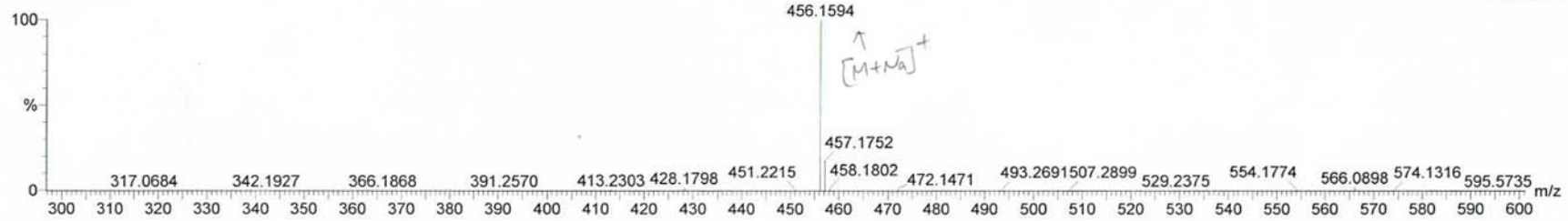
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2



22

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-1000 H: 0-1000 N: 3-3 O: 10-10 Na: 1-1

KHA 274 F10-14RO KE267 17-Nov-2016 17:33:59
1117_KHA 274 F10-14RO 56 (4.495) Cm (56-1x20.000) 1: TOF MS ES+ 2.05e+004



Minimum:				-1000.0			
Maximum:		5.0	20.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
456.1594	456.1594	0.0	0.0	5.5	24.5	0.0	C17 H27 N3 O10 Na

The High-resolution Mass Spectrometry of Compound **22**