

Supporting Information

General Procedures. All chemicals were reagent grade and were used as supplied. Technical grade or reagent grade solvents for extraction and chromatography were used without further purification. Silica gel 60 F₂₅₄ plates (E. Merck) were used for analytical and preparative thin-layer chromatography. Silica gel 60N (spherical, neutral, Kanto Chemical Co., Inc, Tokyo) was used for flash column chromatography (40-100 mm) and open column (100-200 mm) chromatography. ¹H and ¹³C NMR spectra were recorded at ambient temperature (23~24 °C) in CDCl₃ using JEOL EX 400 MHz spectrometer. ¹³C-NMR spectra were taken in CDCl₃ unless otherwise mentioned, and CHCl₃ (δ 77.0 ppm) was used as an internal standard. Chemical shifts are reported in ppm relative to internal tetramethylsilane (δ = 0.00 ppm or CHCl₃ as 7.26 ppm) for ¹H and internal CDCl₃ (δ = 77.00 ppm) for ¹³C NMR spectra. Optical rotations were measured with a JASCO DIP-310 polarimeter. MALDI-TOF MS spectra were measured by Shimadzu AXIMA-CFR using DHBA and CHCA as matrix.

General procedure for preparation of glycosyl bromide from thioglycoside

To a solution of thioglycoside (1 equiv.) in CH₂Cl₂, Br₂ solution (1 M in CH₂Cl₂, 1.2 equiv.) was dropped at 4 °C. The mixture was stirred at 4 °C-room temperature under N₂ atmosphere (normally 30 min ~ 2 h). After consuming the thioglycoside, the reaction was quenched with 10% Na₂S₂O₃ aq. and the aqueous layer was extracted with EtOAc. The combined layers were washed with sat. NaHCO₃ and brine. After drying the mixture over Na₂SO₄. The mixture was filtered and concentrated. The residue was purified by silica gel column chromatography.

Yields **1a** (94%), **1b** (93%), **1c** (44%), **6a** (46%), **6b** (95%), **6c** (94%), **9** (94%).

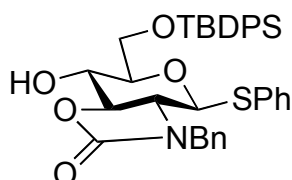
General Procedure for Keck reaction;

A mixture of bromide (1 equiv.), allyl-*n*-tributylstannane (12 equiv.) and AIBN (15.5 mg/substrate mmol) in PhH (0.2 M solution) was refluxed under N₂ atmosphere for 12 h. The mixture was purified by silica gel column chromatography. The α/β ratio is based on integration of ¹H-NMR.

General Procedure for chain reaction:

To a solution of bromide (1 equiv.), Bu₃SnH (2 equiv) and olefin (15 equiv) in PhH

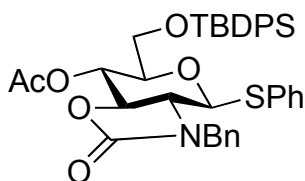
(substrate concentration 0.2 M), AIBN (16.8 mg/substrate mmol) was added. The mixture was refluxed under N₂ atmosphere for 12 h. After cooling the mixture to room temperature, the mixture was purified by silica gel column chromatography. The α/β ratio is based on integration of ¹H-NMR.



Phenyl

N-benzyl-2-amino-4,6-*O*-benzylidene-2,3-*N,O*-carbonyl-2-deoxy-1-thio- α -D-glucopyranoside¹ (3.00g, 6.31 mmol) in AcOH (16 mL) and H₂O (4 mL) was stirred at 100 °C for 2 h. After concentration, the residue was filtered and washed with ether. The precipitate was dissolved in DMF (10 mL) and imidazole (858 mg, 12.62 mmol) was added. To a solution, TBDPSCl (1.93mL, 7.57 mmol) was dropped. The mixture was stirred at room temperature under N₂ atmosphere overnight. The solution was diluted with EtOAc and washed with sat. NH₄Cl, sat. NaHCO₃ and brine. After concentration, the residue was purified by silica gel column chromatography (hexane:EtOAc 7:3-1:1) to give product (3.08 g, 78%).

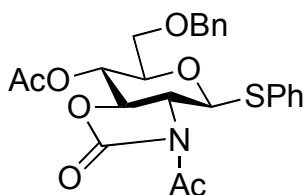
¹H-NMR δ 7.67-7.65 (m, 4H), 7.42-7.18 (m, 16H), 4.78-4.68 (m, 3H), 4.11-4.06 (m, 2H), 3.93 (s, 1H), 3.91 (s, 1H), 3.51 (m, 1H), 3.41-3.36 (m, 1H), 1.04 (s, 9H); ¹³C-NMR δ 150.9, 136.3, 135.6, 135.5, 132.4, 132.0, 129.9, 129.0, 128.6, 128.2, 128.1, 127.8, 127.8, 127.5, 86.8, 82.4, 80.5, 69.0, 64.0, 60.2, 47.7, 26.8, 19.3; $[\alpha]$ -54.5 (*c* 0.73, CHCl₃); calcd for [C₃₆H₃₉NO₅SSi+Na]⁺ 648.2210, found 648.2217.



To a solution of alcohol (2.00 g, 3.20 mmol) in pyridine (5 mL), Ac₂O (3 mL) was added. After 2 h, the reaction was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane:EtOAc 7:3) to give product (2.00 g, 94%).

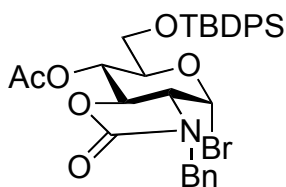
¹H-NMR δ 7.66-7.63 (m, 4H), 7.40-7.18 (m, 16H), 5.30 (t, *J* = 8.8 Hz, 1H), 4.79-4.72 (m,

3H), 4.13 (t, $J = 10.4$ Hz, 1H), 3.75-3.73 (m, 2H), 3.57 (m, 1H), 3.53 (t, $J = 10.0$ Hz, 1H), 1.95 (s, 3H), 1.02 (s, 9H); ^{13}C -NMR δ 168.9, 158.6, 136.1, 135.6, 135.5, 132.8, 132.8, 132.3, 132.3, 129.7, 129.1, 128.6, 128.3, 128.1, 127.7, 127.6, 86.8, 80.3, 67.2, 62.6, 60.4, 47.7, 26.7, 20.6, 19.3; $[\alpha] -37.1$ (c 0.56, CHCl_3); calcd for $[\text{C}_{38}\text{H}_{41}\text{NO}_6\text{SSi}+\text{Na}]^+$ 690.2316, found 690.2326.

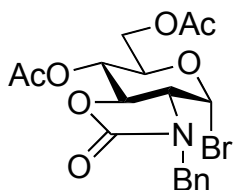


To a solution of phenyl 2-amino-6-*O*-benzyl-2,3-*N,O*-carbonyl-2-deoxy-1-thio- α -D-glucopyranoside (1.00 g, 2.60 mmol)^{2,3} in pyridine (3 mL), Ac_2O (2 mL) and DMAP (50 mg, 0.41 mmol) was added. After stirring at room temperature overnight, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (hexane: EtOAc 7:3) to give the product (1.20 g, 95%).

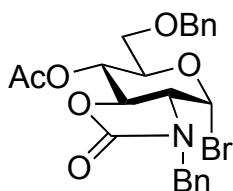
^1H -NMR δ 7.52-7.50 (m, 2H), 7.32-7.19 (m, 8H), 5.33 (t, $J = 8.4$ Hz, 1H), 4.95 (d, $J = 7.6$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.46 (d, $J = 12.0$ Hz, 1H), 4.24 (d, $J = 10.8$ Hz, 1H), 4.22 (d, $J = 10.8$ Hz, 1H), 3.72 (m, 1H), 3.65 (s, 1H), 3.63 (s, 1H), 2.55 (s, 3H), 2.02 (s, 3H); ^{13}C NMR δ 172.5, 169.1, 153.2, 137.5, 134.1, 132.0, 128.8, 128.3, 127.8, 127.7, 87.4, 79.3, 79.1, 76.7, 73.6, 68.9, 68.4, 59.8, 24.8, 20.7; $[\alpha] -55.2$ (c 1.4, CHCl_3); calcd for $[\text{C}_{24}\text{H}_{25}\text{NO}_7\text{SNa}]^+$ 494.1244, found 494.1243.



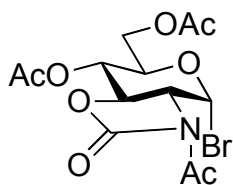
^1H -NMR δ 7.56-7.54 (m, 4H), 7.40-7.15 (m, 11H), 6.24 (d, $J = 3.2$ Hz, 1H) 5.44 (t, $J = 10.0$ Hz, 1H), 4.78 (d, $J = 14.8$ Hz, 1H), 4.63 (t, $J = 11.6$ Hz, 1H), 4.09 (d, $J = 14.8$ Hz, 1H), 3.80 (m, 1H), 3.70 (m, 2H), 3.27 (dd, $J = 11.2, 2.8$ Hz, 1H), 1.98 (s, 3H), 1.01 (s, 9H); ^{13}C -NMR δ 168.7, 159.6, 135.5, 133.7, 132.7, 132.6, 129.8, 129.7, 129.1, 129.0, 128.9, 128.7, 128.1, 127.7, 127.6, 83.9, 75.8, 66.8, 61.2, 61.0, 47.8, 26.8, 20.6, 19.3; calcd for $[\text{C}_{33}\text{H}_{37}\text{NO}_7\text{SSi}+\text{Na}]^+$ 642.1952, found 642.1950.



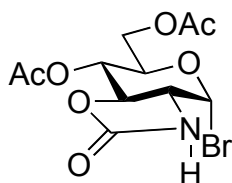
$^1\text{H-NMR}$ δ 7.38-7.36 (m, 3H), 7.28-7.26 (m, 2H), 6.21 (d, $J = 3.2$ Hz, 1H), 5.30 (t, $J = 10.0$ Hz, 1H), 4.80 (d, $J = 14.4$ Hz, 1H), 4.65 (t, $J = 10.0$ Hz, 1H), 4.27 (dd, $J = 12.8, 4.4$ Hz, 1H), 4.09-4.04 (m, 2H), 4.01 (m, 1H), 3.31 (dd, $J = 11.2, 2.8$ Hz, 1H), 2.10 (s, 3H), 2.03 (s, 3H); $^{13}\text{C-NMR}$ δ 170.1, 168.8, 157.3, 133.5, 129.1, 128.8, 128.7, 83.0, 75.3, 74.1, 66.8, 60.8, 47.8, 20.8; $[\alpha]$ 194.0 (c 1.1, CHCl_3); calcd for $[\text{C}_{18}\text{H}_{20}\text{BrNO}_7+\text{Na}]^+$ 464.0315, found 464.0314.



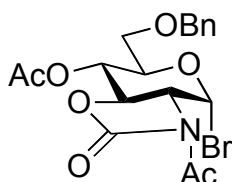
$^1\text{H-NMR}$ δ 7.36-7.17 (m, 10H), 6.24 (d, $J = 3.2$ Hz, 1H), 5.43 (t, $J = 9.6$ Hz, 1H), 4.80 (d, $J = 14.8$ Hz, 1H), 4.62 (t, $J = 10.4$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.39 (d, $J = 12.0$ Hz, 1H), 3.90 (d, $J = 14.8$ Hz, 1H), 3.89 (m, 1H), 3.54-3.47 (m, 2H), 3.33 (d, $J = 11.6, 3.2$ Hz, 1H), 1.97 (t, 3H); $^{13}\text{C-NMR}$ δ 168.7, 157.5, 136.9, 133.7, 129.2, 129.0, 128.8, 128.7, 128.4, 128.1, 128.0, 127.9, 83.7, 75.7, 75.2, 73.6, 67.0, 66.4, 60.7, 47.7, 20.6; $[\alpha]$ 121.2 (c 1.85, CHCl_3); calcd for $[\text{C}_{29}\text{H}_{29}\text{NO}_5\text{S}+\text{Na}]^+$ 526.1659, found 526.1653.



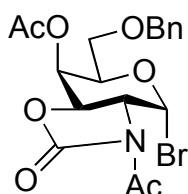
$^1\text{H-NMR}$ δ 7.06 (d, $J = 3.2$ Hz, 1H), 5.41 (t, $J = 10.0$ Hz, 1H), 4.76 (t, $J = 11.6$ Hz, 1H), 4.31 (dd, $J = 12.8$ Hz, 4.0 Hz, 1H), 4.17 (dd, $J = 12.8$ Hz, 2.0 Hz, 1H), 4.16 (m, 1H), 3.95 (dd, $J = 11.6$ Hz, 3.2 Hz, 1H); $^{13}\text{C-NMR}$ δ 170.8, 170.2, 168.7, 152.5, 83.7, 75.4, 73.8, 66.6, 61.0, 60.7, 23.7, 20.8, 20.7; $[\alpha]$ 159.0 (c 2.56, CHCl_3); calcd for $[\text{C}_{13}\text{H}_{16}\text{BrNO}_8+\text{Na}]^+$ 415.9952, found 415.9953.



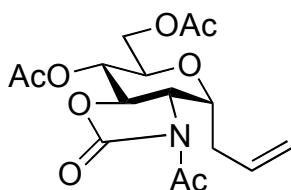
$^1\text{H-NMR}$ δ 6.52 (d, J = 3.2 Hz, 1H), 5.50 (bs, 1H), 5.43 (t, J = 10.0 Hz, 1H), 4.75 (t, J = 11.2 Hz, 1H), 4.30 (dd, J = 12.4 Hz, 4.4 Hz, 1H), 4.16 (dd, J = 12.8, 2.0 Hz, 1H), 4.16 (dd, J = 12.8 Hz, 2.0 Hz, 1H), 4.06 (m, 1H), 3.76 (m, 1H), 2.12 (s, 3H), 2.08 (s, 3H); $^{13}\text{C-NMR}$ δ 170.2, 168.8, 157.6, 83.6, 77.6, 73.9, 66.9, 60.9, 59.6, 20.8; $[\alpha]$ 149.1 (c 1.50, CHCl_3).



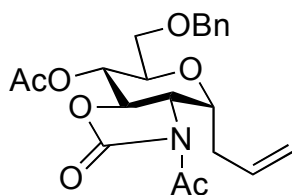
$^1\text{H-NMR}$ δ 7.33-7.15 (m, 5H), 7.08 (d, J = 2.8 Hz, 1H), 5.54 (t, J = 10.0 Hz, 1H), 4.74 (t, J = 10.8 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 12.0 Hz, 1H), 3.97-3.91 (m, 2H), 3.60-3.57 (m, 2H), 2.49 (s, 3H), 2.01 (s, 3H); $^{13}\text{C-NMR}$ δ 170.8, 168.6, 151.9, 137.0, 128.8, 128.4, 128.1, 127.9, 125.2, 84.4, 75.8, 75.1, 73.6, 66.9, 66.5, 60.9, 23.7, 20.9; $[\alpha]$ 242.8 (c 2.25, CHCl_3); calcd for $[\text{C}_{18}\text{H}_{20}\text{BrNO}_7+\text{Na}]^+$ 464.0315, found 464.0307.



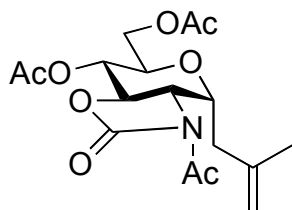
$^1\text{H-NMR}$ δ 7.34-7.27 (m, 4H), 7.10 (d, J = 2.8 Hz, 1H), 5.72 (s, 1H), 4.80 (dd, J = 2.4 Hz, 1H), 4.53 (d, J = 11.6 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 4.25 (dd, J = 12.0, 2.8 Hz, 1H), 4.21 (t, J = 6.4 Hz, 1H), 3.54 (m, 2H), 2.50 (s, 3H), 2.05 (s, 3H); $^{13}\text{C-NMR}$ δ 171.4, 168.8, 152.0, 137.0, 128.5, 128.0, 127.9, 85.8, 76.1, 74.0, 73.7, 73.3, 66.7, 65.1, 56.9, 23.8, 20.6; $[\alpha]$ 162.0 (c 0.80, CHCl_3); calcd for $[\text{C}_{18}\text{H}_{20}\text{BrNO}_7+\text{Na}]^+$ 426.1523, found 426.1527.



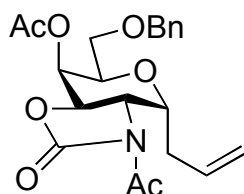
$^1\text{H-NMR}$ δ 5.74 (m, 1H), 5.19 (t, $J=9.6$ Hz, 1H), 5.13-5.09 (m, 2H), 4.92 (m, 1H), 4.37 (t, $J=12.4$ Hz, 1H), 4.20-4.11 (m, 2H), 4.05 (dd, $J=12.0, 5.2$ Hz, 1H), 3.75 (m, 1H), 2.46 (s, 3H), 2.46 (m, 1H), 2.17 (m, 1H), 2.10 (s, 3H), 2.05 (s, 3H); $^{13}\text{C-NMR}$ δ 171.4, 170.5, 169.0, 152.7, 132.3, 118.0, 75.3, 73.4, 70.7, 68.6, 62.1, 59.5, 29.5, 23.9, 20.7; $[\alpha]$ 89.9 (c 1.2, CHCl_3); calcd for $[\text{C}_{16}\text{H}_{21}\text{NO}_8+\text{Na}]^+$ 378.1159, found 378.1157.



$^1\text{H-NMR}$ δ 7.29-7.19 (m, 5H), 5.76 (m, 1H), 5.25 (t, $J=9.0$ Hz, 1H), 5.09-5.03 (m, 2H), 4.87 (m, 1H), 4.52 (d, $J=12.0$ Hz, 1H), 4.42 (d, $J=12.0$ Hz, 1H), 4.31 (t, $J=12.2$ Hz, 1H), 4.03 (dd, $J=12.4$ Hz, 4.8 Hz, 1H), 3.67 (m, 1H), 3.51-3.47 (m, 2H), 2.41 (s, 3H), 2.13 (m, 1H), 1.92 (s, 3H); $^{13}\text{C-NMR}$ δ 171.3, 168.9, 152.8, 137.4, 132.6, 128.2, 127.8, 127.6, 117.8, 75.6, 73.6, 73.4, 72.4, 69.2, 68.4, 59.3, 29.9, 24.0, 20.8; $[\alpha]$ 126.8 (c 1.86, CHCl_3); calcd for $[\text{C}_{21}\text{H}_{25}\text{NO}_7+\text{Na}]^+$ 426.1523; found 426.1527.

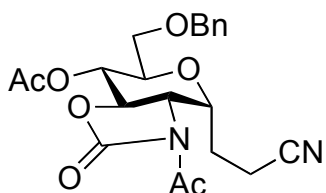


$^1\text{H-NMR}$ δ 5.22 (t, $J=9.6$ Hz, 1H), 5.04 (m, 1H), 4.84 (s, 1H), 4.76 (s, 1H), 4.38 (t, $J=10.0$ Hz, 1H), 4.18 (dd, $J=12.0, 5.2$ Hz, 1H), 4.09 (dd, $J=12.0, 2.4$ Hz, 1H), 4.05 (dd, $J=12.4, 5.2$ Hz, 1H), 3.78 (m, 1H), 2.44 (s, 3H), 2.44-2.42 (m, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 2.05-2.00 (m, 1H); $^{13}\text{C-NMR}$ δ 171.3, 170.5, 169.0, 152.8, 140.4, 113.8, 75.4, 72.4, 70.6, 68.6, 62.2, 59.7, 32.9, 23.9, 21.9, 20.7, 20.7; $[\alpha]$ 105.1 (c 0.84, CHCl_3); calcd for $[\text{C}_{17}\text{H}_{23}\text{NO}_8+\text{Na}]^+$ 392.1316, found 392.1315.

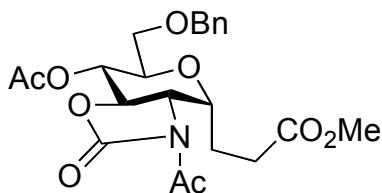


$^1\text{H-NMR}$ δ 7.34-7.24 (m, 5H), 5.73 (m, 1H), 5.08 (s, 1H), 4.96-4.54 (m, 2H), 4.41 (m,

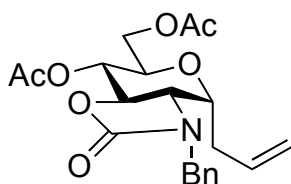
1H), 4.52 (d, $J = 11.6$ Hz, 1H), 4.43-4.34 (m, 3H), 3.91 (t, $J = 6.0$ Hz, 1H), 3.48-3.46 (m, 2H), 2.46 (s, 3H), 2.05 (m, 1H), 205 (s, 3H); $^{13}\text{C-NMR}$ δ 171.6, 169.0, 152.8, 137.3, 132.7, 128.3, 127.8, 127.8, 117.9, 77.2, 74.4, 73.8, 73.6, 69.8, 67.8, 65.9, 55.7, 29.1, 24.2, 20.8; $[\alpha]$ 51.7 (c 1.00, CHCl_3); calcd for $[\text{C}_{21}\text{H}_{25}\text{NO}_7+\text{Na}]^+$ 426.1523, found 426.1520.



$^1\text{H-NMR}$ δ 7.29-7.19 (m, 5H), 5.26 (t, $J = 8.4$ Hz, 1H), 4.77 (m, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.22 (t, $J = 12.4$ Hz, 1H), 4.07 (m, 1H), 3.64 (m, 1H), 3.58-3.50 (m, 2H), 2.43 (s, 3H), 2.39-2.29 (m, 2H), 1.97 (m, 1H), 1.94 (s, 3H), 1.67 (m, 1H); $^{13}\text{C-NMR}$ δ 171.4, 168.9, 152.5, 137.2, 128.3, 127.8, 118.7, 75.3, 73.7, 73.3, 73.2, 69.1, 68.2, 58.8, 23.4, 21.8, 20.7, 14.2; $[\alpha]$ 87.7 (c 0.90, CHCl_3); calcd for $[\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_7+\text{Na}]^+$ 439.1476, found 439.1463.

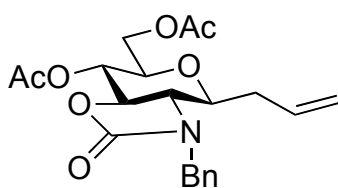


$^1\text{H-NMR}$ δ 7.28-7.19 (m, 5H), 5.25 (t, $J = 9.2$ Hz, 1H), 4.75 (m, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 12.0$ Hz, 1H), 4.30 (t, $J = 10.0$ Hz, 1H), 4.00 (dd, $J = 12.4, 5.6$ Hz, 1H), 3.63 (m, 1H), 3.59 (s, 3H), 3.45 (m, 2H), 2.45-2.28 (m, 2H), 2.42 (s, 3H), 2.03 (m, 1H), 1.93 (s, 3H), 1.55 (m, 1H); $^{13}\text{C-NMR}$ δ 173.0, 171.3, 168.9, 152.8, 137.3, 128.3, 127.8, 127.7, 75.6, 74.0, 73.6, 72.1, 69.0, 68.2, 59.4, 51.9, 30.5, 25.0, 20.8, 20.3; $[\alpha]$ 88.6 (c 1.25, CHCl_3); calcd for $[\text{C}_{22}\text{H}_{27}\text{NO}_9+\text{Na}]^+$ 472.1578, found 472.1572.

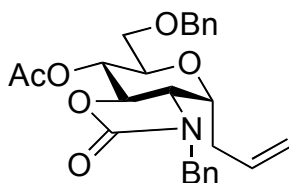


Detectable peak; $^1\text{H-NMR}$ δ 7.36 (m, 2H), 7.35 (m, 1H), 7.29 (dd, $J = 8.0, 1.0$ Hz, 2H),

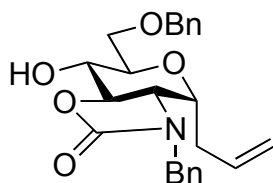
5.60 (dddd, $J = 17.1, 10.0, 7.0, 6.6$ Hz, 1H), 5.14 (dd, $J = 10.1$ Hz, 9.6 Hz, 1H), 4.48 (d, $J = 14.6$ Hz, 1H), 4.28 (d, $J = 14.6$ Hz, 1H), 4.17 (dd, $J = 12.6, 5.0$ Hz, 1H), 4.29 (dd, $J = 12.1$ Hz, 10.1 Hz, 1H), 4.06 (dd, $J = 12.6, 2.0$ Hz, 1H), 4.06 (ddd, $J = 11.1, 5.1, 3.1$ Hz, 1H), 3.71 (ddd, $J = 9.6, 5.0, 2.0$ Hz, 1H), 3.50 (dd, $J = 12.1, 5.1$ Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H); $^{13}\text{C-NMR}$ δ 170.6, 169.2, 158.8, 134.8, 132.6, 129.1, 129.0, 128.6, 118.2, 74.8, 73.7, 70.9, 68.9, 62.2, 60.4, 49.2, 29.3, 20.7, 20.7; calcd for $[\text{C}_{21}\text{H}_{25}\text{NO}_7 + \text{Na}]^+$ 426.1523, found 426.1524.



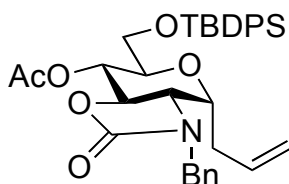
Detectable peak; $^1\text{H-NMR}$ δ 7.36-7.29 (m, 5H), 5.71 (dddd, $J = 17.1, 10.1, 6.5, 6.5$ Hz, 1H), 5.23 (dd, $J = 10.6, 9.1$ Hz, 1H), 5.01 (br, $J = 10.1$ Hz, 1H), 4.88 (dddd, $J = 17.1, 1.5, 1.5, 1.5$ Hz, 1H), 4.67 (d, $J = 16.1$ Hz, 1H), 4.45 (d, $J = 17.1$ Hz, 1H), 4.21 (dd, $J = 12.1, 5.1$ Hz, 1H), 4.17 (dd, $J = 11.6, 10.6$ Hz, 1H), 4.12 (dd, $J = 12.1, 2.5$ Hz), 3.50 (m, 1H), 3.29 (ss, $J = 11.6, 9.1$ Hz, 1H), 2.30 (m, 1H), 2.11 (s, 3H), 2.04 (m, 1H), 2.05 (s, 3H), $^{13}\text{C-NMR}$ δ 159.3, 132.7, 126.9, 118.1, 79.9, 76.7, 67.8, 62.2, 62.1, 48.4, 36.5 20.7, 20.7.



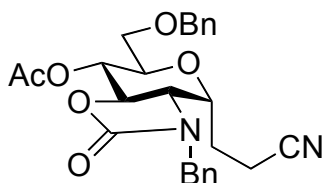
Detectable peak; $^1\text{H-NMR}$ δ 7.19-7.41 (m, 10H), 5.56-5.70 (m, 1H), 5.24 (t, $J = 9.6$ Hz, 1H), 5.07 (d, $J = 10.0$ Hz, 1H), 5.01 (d, $J = 17.2$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 14.8$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.26 (t, $J = 11.2$ Hz, 1H), 4.25 (d, $J = 14.8$ Hz, 1H), 4.07 (ddd, $J = 11.2, 4.8, 4.0$ Hz, 1H), 3.64 (ddd, $J = 8.8, 3.6, 2.8$ Hz, 1H), 3.41-3.58 (m, 3H), 2.35-2.48 (m, 1H), 1.95 (s, 3H), 1.83-2.03 (m, 1H); $^{13}\text{C-NMR}$ δ 168.8, 158.7, 137.3, 134.6, 132.7, 128.9, 128.8, 128.4, 128.2, 127.8, 127.6, 118.0, 75.2, 73.7, 73.5, 72.0, 69.2, 68.0, 60.2, 49.1, 29.4, 20.8; MALDI-TOFMS: calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_6\text{Na}$:474.19 $[\text{M} + \text{Na}]^+$; found 474.52.



Detectable peak; $^1\text{H-NMR}$ δ 7.33 (m, 6H), 7.29 (m, 4H), 5.61 (ddd, $J = 17.2, 10.3, 6.9$ Hz, 1H), 5.05 (br.d. $J = 10.3$ Hz, 1H), 4.98 (br.d. $J = 17.2$ Hz, 1H), 4.44 (d, $J = 14.9$ Hz, 1H), 4.29 (d, $J = 14.9$ Hz, 1H), 4.20 (dd, $J = 12.0, 9.8$ Hz, 1H), 4.00 (ddd, $J = 10.3, 5.2, 3.5$ Hz, 1H), 3.95 (ddd, $J = 9.8, 8.6, 2.9$ Hz, 1H), 3.70 (dd, $J = 10.3, 4.0$ Hz, 1H), 3.62 (dd, $J = 10.3, 4.6$ Hz, 1H), 3.53 (ddd, $J = 8.6, 4.6, 4.0$ Hz, 1H), 3.39 (dd, $J = 12.0, 5.2$ Hz, 1H), 2.97 (d, $J = 2.9$ Hz, 1H), 3.95 (ddd, $J = 9.8, 8.6, 2.9$ Hz, 1H), 2.40 (br.ddd, $J = 15.4, 10.3, 6.9$ Hz, 1H), 1.85 (ddd, $J = 15.4, 6.9, 3.5$ Hz, 1H); $^{13}\text{C-NMR}$ δ 159.4, 137.3, 135.0, 133.0, 128.9, 128.9, 128.4, 128.3, 127.8, 127.7, 117.8, 77.3, 73.7, 73.6, 72.8, 70.6, 69.6, 60.1, 49.0, 29.3; MALDI-TOFMS: calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_5$ 409.1, found 410.24.

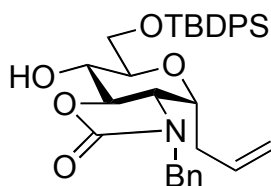


Detectable peak; $^1\text{H-NMR}$ δ 7.58-7.63 (m, 4H), 7.25-7.45 (m, 11H), 5.60-5.70 (m, 1H), 5.13 (t, $J = 10.0$ Hz, 1H), 5.05 (dd, $J = 11.6, 1.2$ Hz, 1H), 4.99 (dd, $J = 17.2, 1.2$ Hz, 1H), 4.45 (d, $J = 14.4$ Hz, 1H), 4.31 (d, $J = 14.4$ Hz, 1H), 4.26 (t, $J = 10.4$ Hz, 1H), 4.00-4.08 (m, 1H), 3.63-3.68 (m, 2H), 3.54-3.59 (m, 1H), 3.46 (dd, $J = 12.0, 5.2$ Hz, 1H), 2.35-2.47 (m, 1H), 1.93 (s, 3H), 1.80-1.90 (m, 1H), 1.01 (s, 9H); $^{13}\text{C-NMR}$ δ 168.8, 158.8, 135.5, 135.4, 134.8, 133.0, 132.9, 132.8, 129.6, 129.5, 128.9, 128.8, 128.3, 127.5, 127.4, 117.9, 75.2, 73.7, 73.5, 69.1, 62.9, 60.6, 49.2, 29.4, 26.8, 20.8, 19.3; MALDI-TOFMS: calcd for $\text{C}_{35}\text{H}_{41}\text{NO}_6\text{SiNa}$: 622.26 $[\text{M}+\text{Na}]^+$; found 622.69.

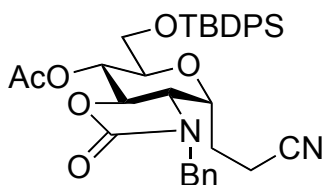


Detectable peak; $^1\text{H-NMR}$ δ 7.15-7.45 (m, 10H), 5.25 (t, $J = 9.6$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 14.4$ Hz, 1H), 4.35 (d, $J = 14.4$ Hz, 1H),

4.15 (t, $J = 10.8$ Hz, 1H), 3.95-4.05 (m, 1H), 3.45-3.63 (m, 3H), 3.45 (dd, $J = 10.8, 4.4$ Hz, 1H), 2.20-2.32 (m, 1H), 2.06-2.20 (m, 1H), 2.35-2.48 (m, 1H), 1.96 (s, 3H), 1.83-2.03 (m, 1H), 1.22-1.35 (ddd, $J = 13.6, 7.6, 5.2$ Hz, 1H); $^{13}\text{C-NMR}$ δ 168.8, 158.5, 137.1, 134.6, 128.9, 128.6, 128.3, 128.1, 127.8, 127.7, 118.4, 74.9, 73.6, 72.8, 72.6, 68.9, 67.8, 60.2, 49.5, 21.1, 20.7, 14.1; MALDI-TOFMS: calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_6\text{Na}$: 487.18 $[\text{M}+\text{Na}]^+$; found 487.40.

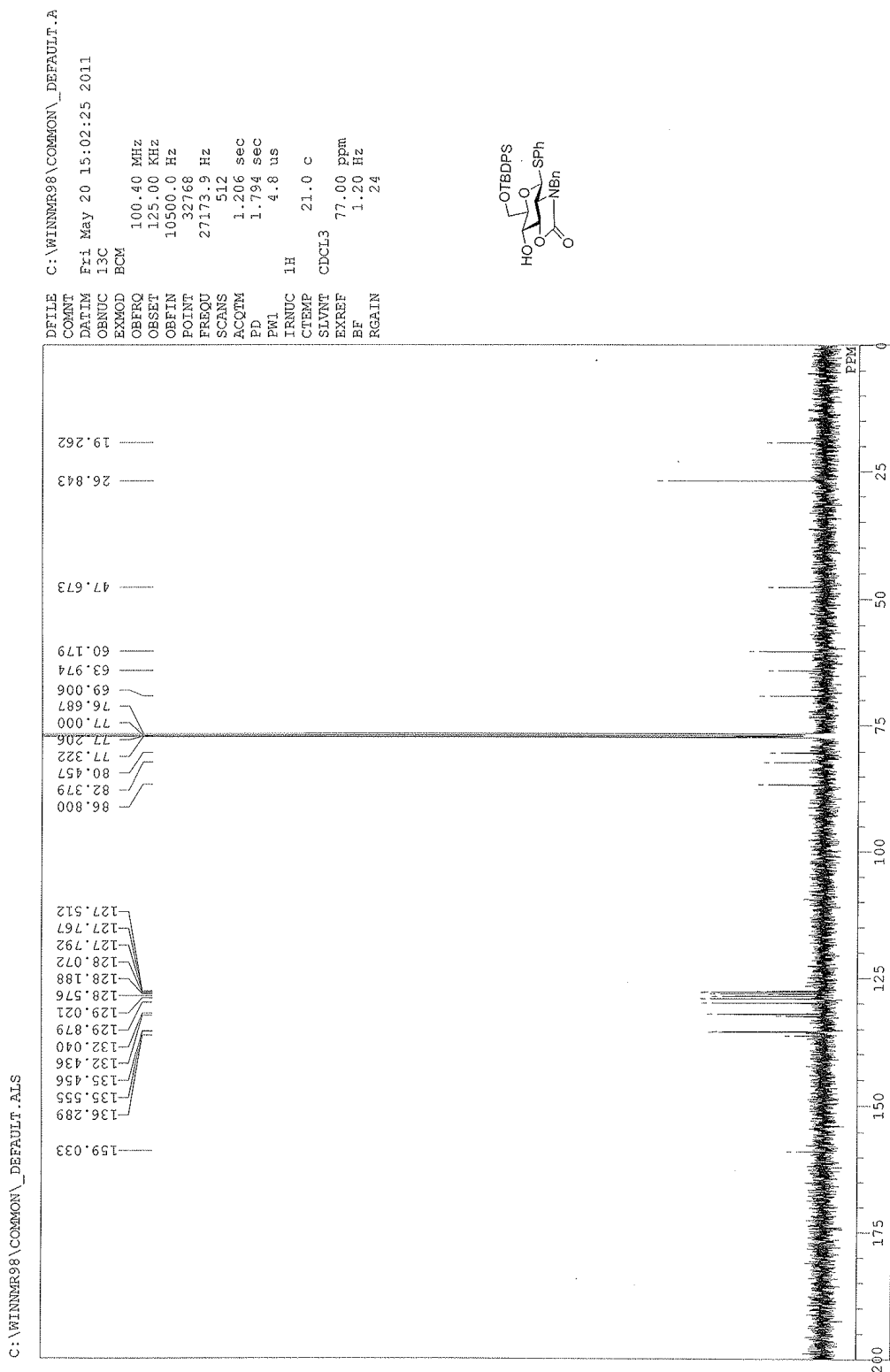


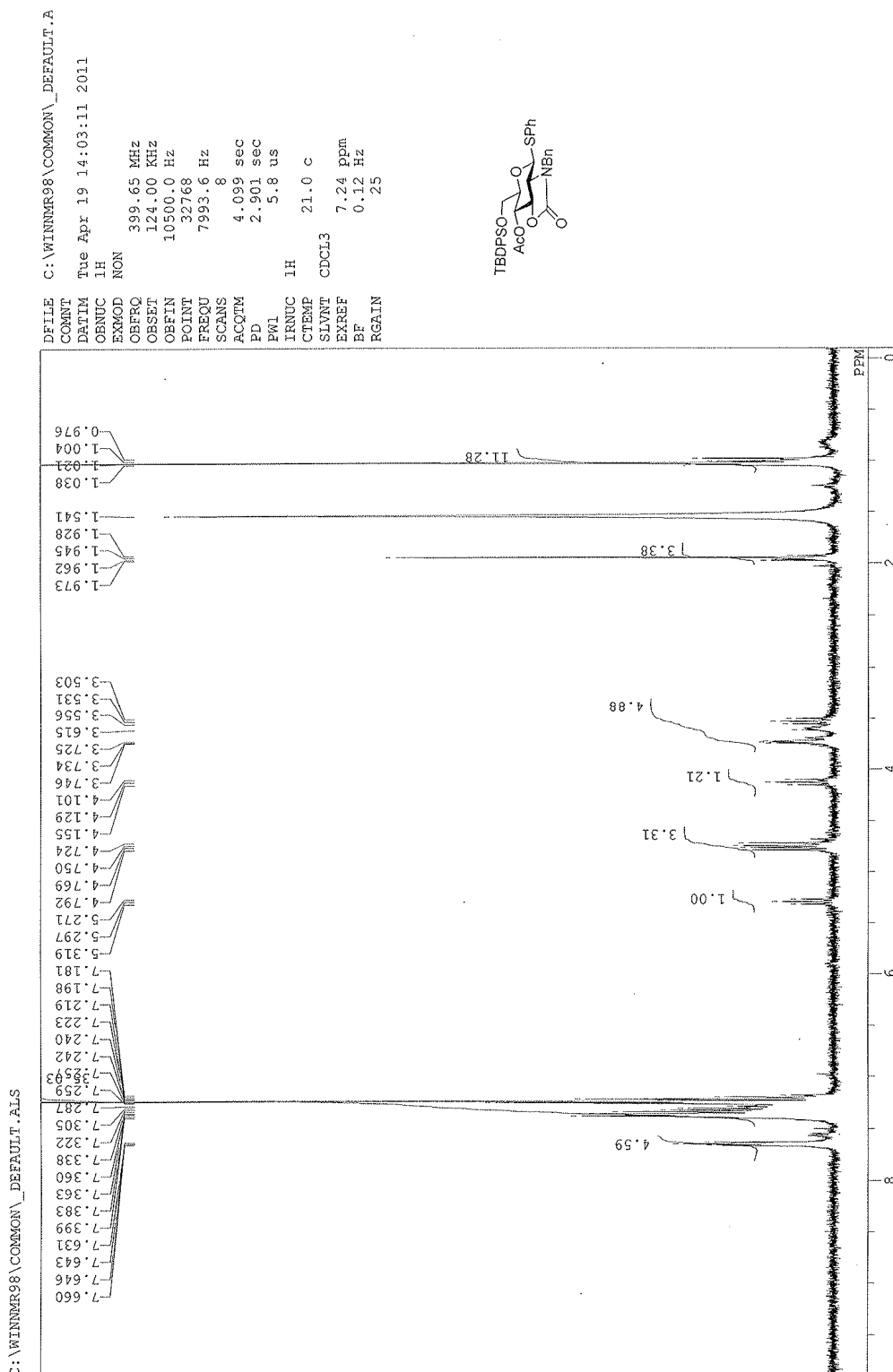
Detectable peak; $^1\text{H-NMR}$ δ 7.63 (m, 2H), 7.62 (m, 2H), 7.37 (m, 4H), 7.43 (m, 4H), 7.33 (m, 2H), 7.29 (m, 1H), 7.29 (m, 2H), 5.56 (ddt, $J = 17.2, 10.3, 6.9$ Hz, 1H), 5.00 (br.d, $J = 10.3$ Hz, 1H), 4.92 (br.d, $J = 17.2$ Hz, 1H), 4.41 (d, $J = 14.6$ Hz, 1H), 4.32 (d, $J = 14.6$ Hz, 1H), 4.20 (dd, $J = 12.1, 9.8$ Hz, 1H), 3.94 (m, 1H), 3.94 (m, 1H), 3.85 (dd, $J = 10.6, 4.6$ Hz, 1H), 3.81 (dd, $J = 10.6, 4.8$ Hz, 1H), 3.45 (ddd, $J = 9.1, 4.8, 4.6$ Hz, 1H), 3.33 (dd, $J = 12.1, 5.1$ Hz, 1H), 3.01 (d, $J = 2.9$ Hz, 1H); $^{13}\text{C-NMR}$ δ 159.6, 135.2, 132.7, 132.6, 135.6, 135.5, 133.1, 130.0, 129.9, 129.0, 129.0, 128.4, 127.8, 127.8, 117.8, 77.1, 73.7, 73.7, 71.2, 64.7, 60.2, 49.1, 29.4, 26.8, 19.4; calcd for $\text{C}_{33}\text{H}_{39}\text{NO}_5\text{Si}+\text{Na}$ 580.88, found 557.26.

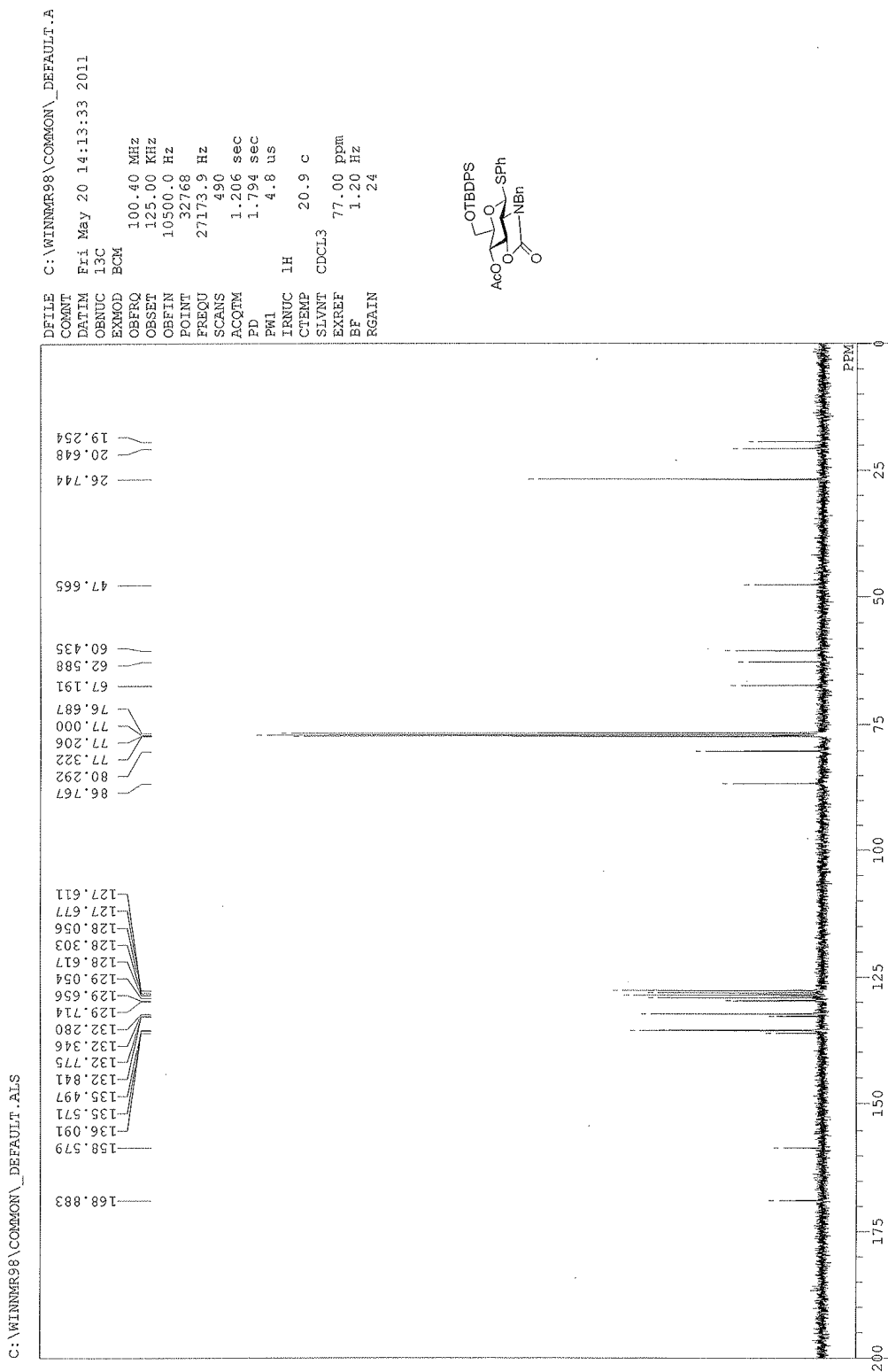


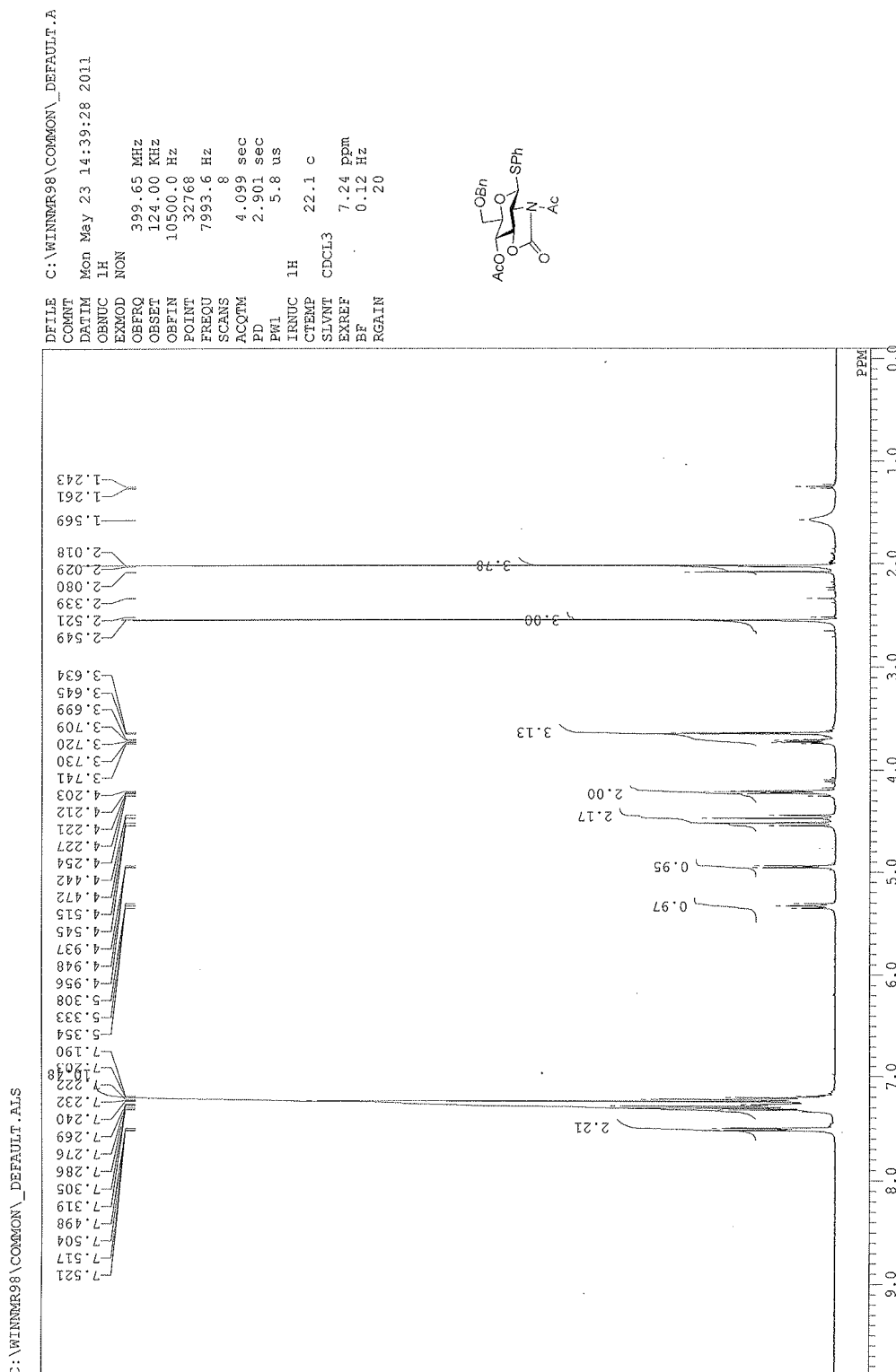
Detectable peak; $^1\text{H-NMR}$ δ 7.58-7.63 (m, 4H), 7.25-7.45 (m, 11H), 5.17 (t, $J = 9.2$ Hz, 1H), 4.45 (d, $J = 14.8$ Hz, 1H), 4.33 (d, $J = 14.8$ Hz, 1H), 4.14 (t, $J = 10.0$ Hz, 1H), 3.92-4.01 (m, 1H), 3.67 (d, $J = 3.6$ Hz, 2H), 3.50 (dd, $J = 12.4, 5.6$ Hz, 1H), 3.40-3.47 (m, 1H), 2.24-2.32 (m, 1H), 2.05-2.12 (m, 1H), 1.95 (s, 3H), 1.83-1.92 (m, 1H), 1.22-1.35 (m, 1H), 1.02 (s, 9H); $^{13}\text{C-NMR}$ δ 168.7, 158.5, 135.4, 135.4, 134.8, 132.8, 132.6, 129.7, 129.1, 128.9, 128.6, 127.6, 127.5, 118.2, 75.0, 74.0, 72.3, 68.7, 62.6, 60.5, 49.6, 26.8, 21.2, 20.7, 19.3, 13.8; MALDI-TOFMS: calcd for $\text{C}_{35}\text{H}_{41}\text{N}_2\text{O}_6\text{Si}$: 613.27 $[\text{M}+\text{H}]^+$; found 613.81.

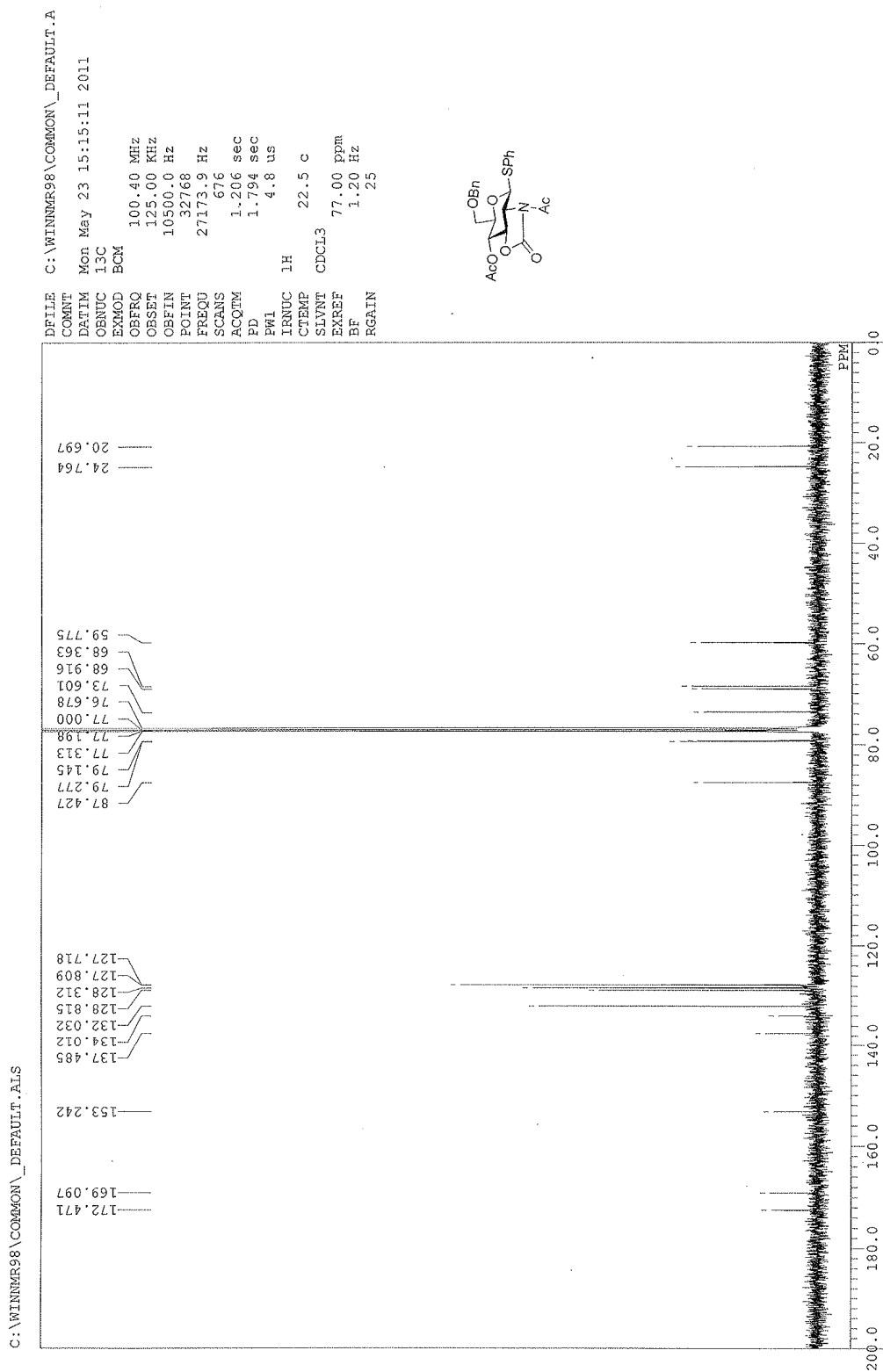
1. S. Manabe, K. Ishii, Y. Ito, *J. Am. Chem. Soc.*, 2006, **128**, 10666.
2. K. Benakli, C. Zha, R. J. Kerns, *J. Am. Chem. Soc.*, 2001, **123**, 9461.
3. H. Satoh, S. Manabe, Y. Ito, H. P. Lüthi, T. Laino, J., Hutter, *J. Am. Chem. Soc.* **2011**, *133*, 5610-5619.





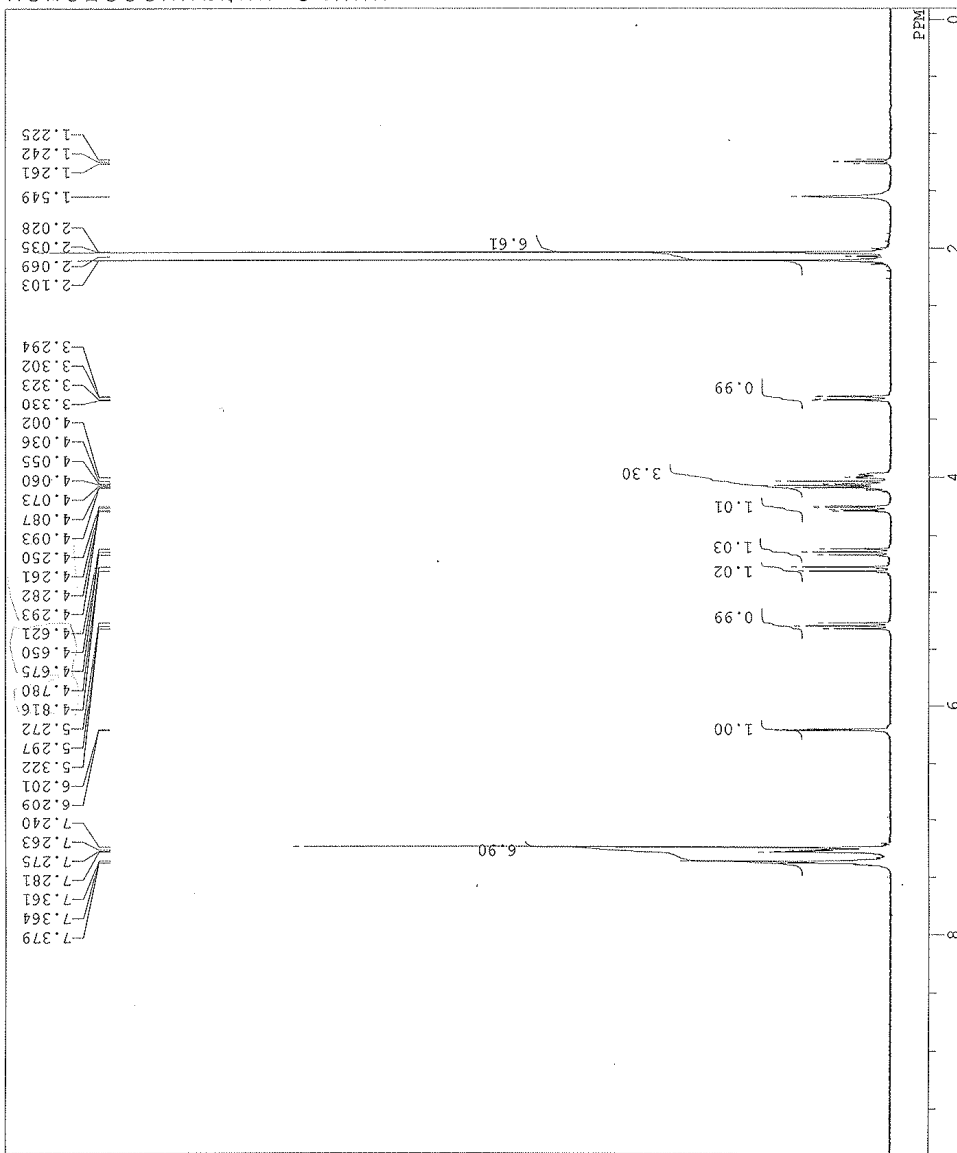
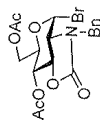


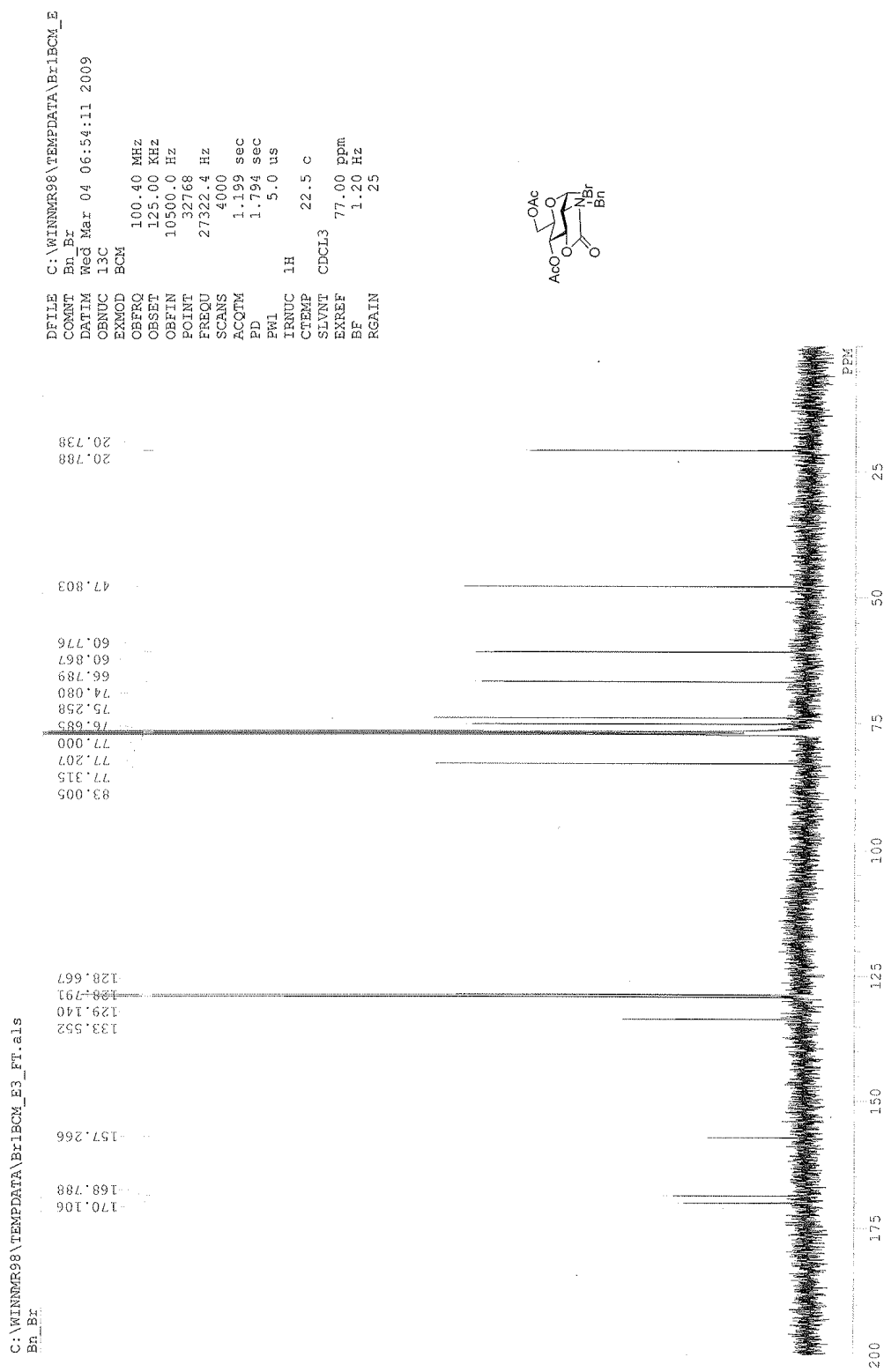


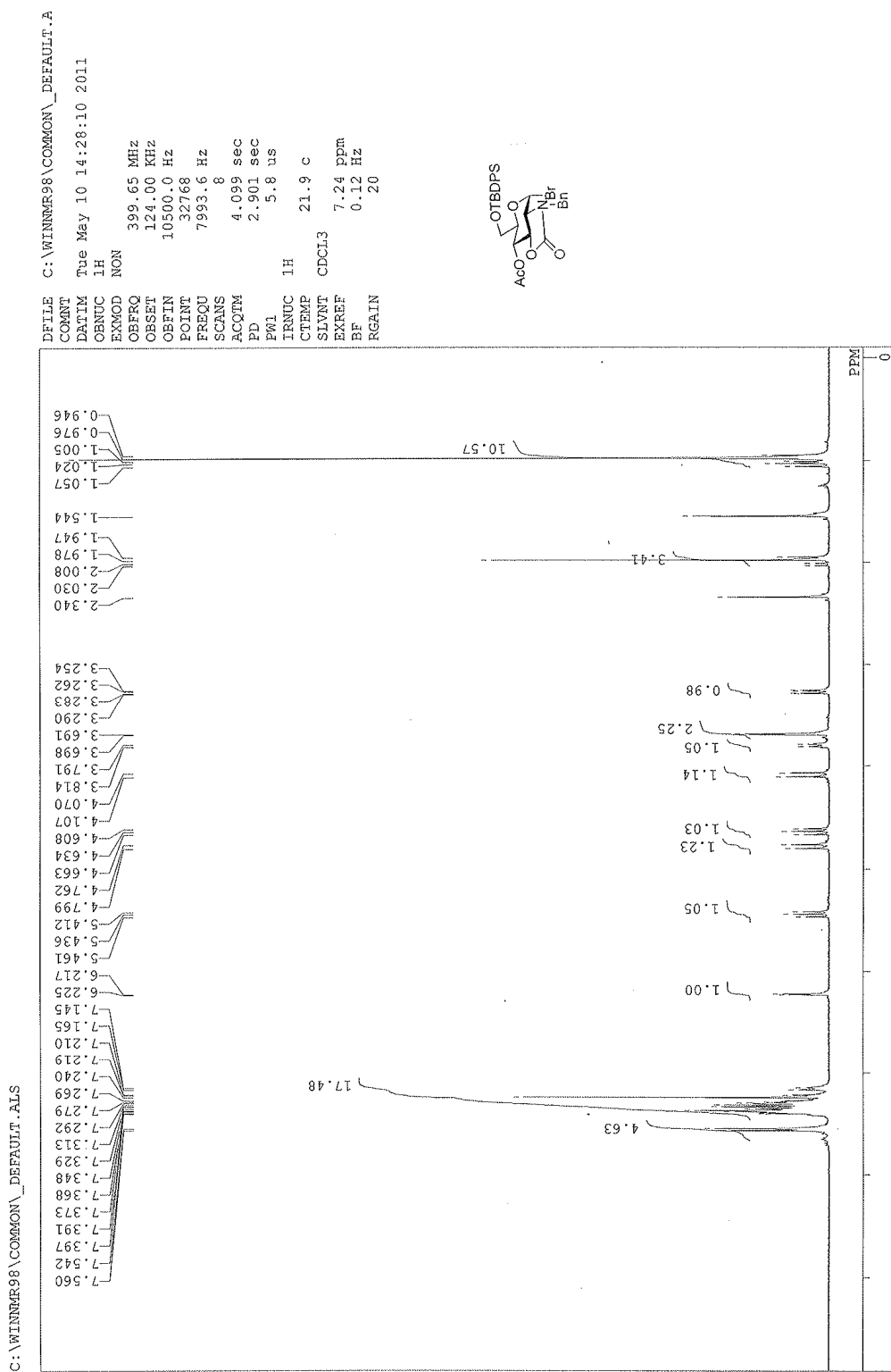


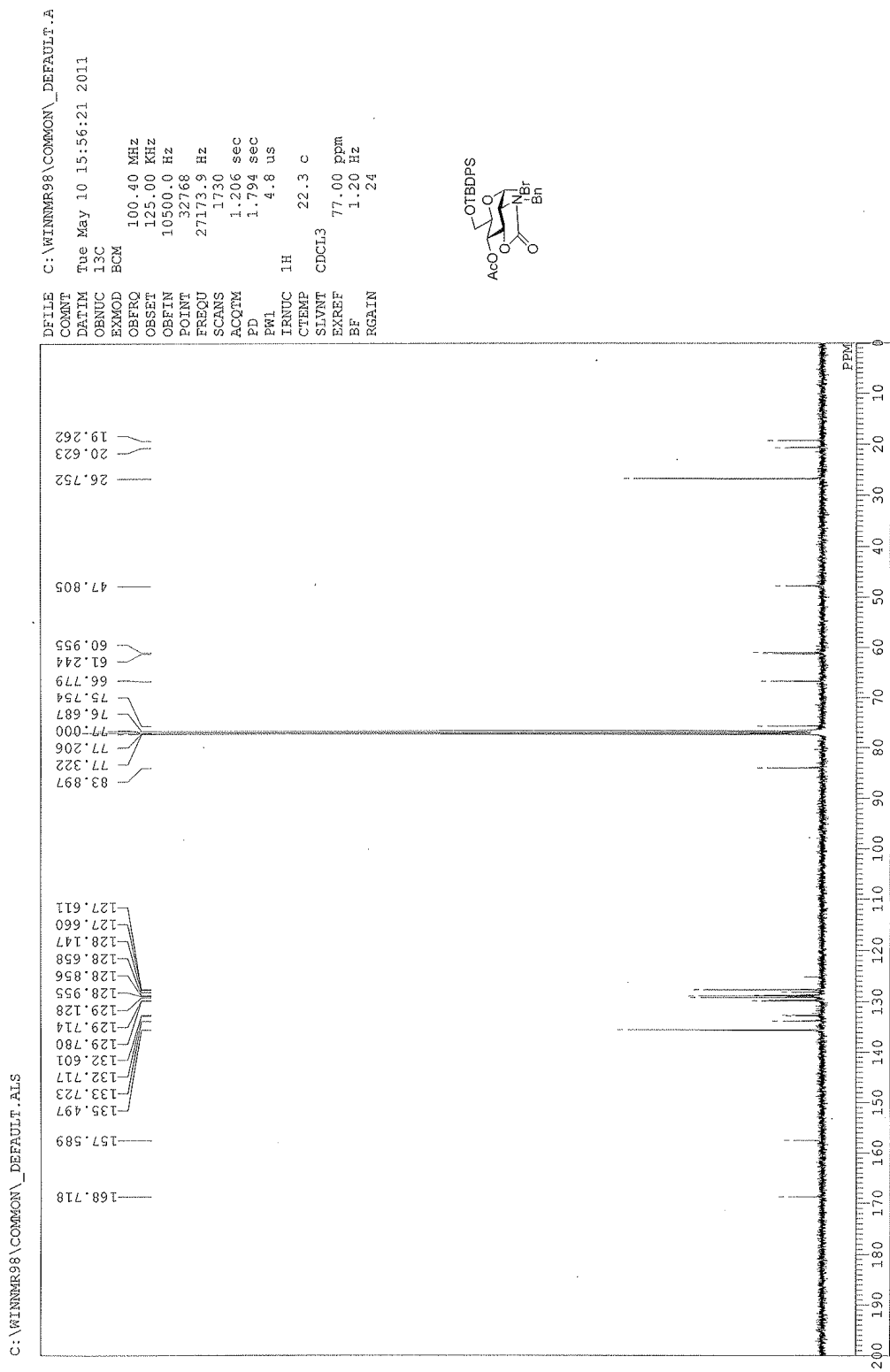
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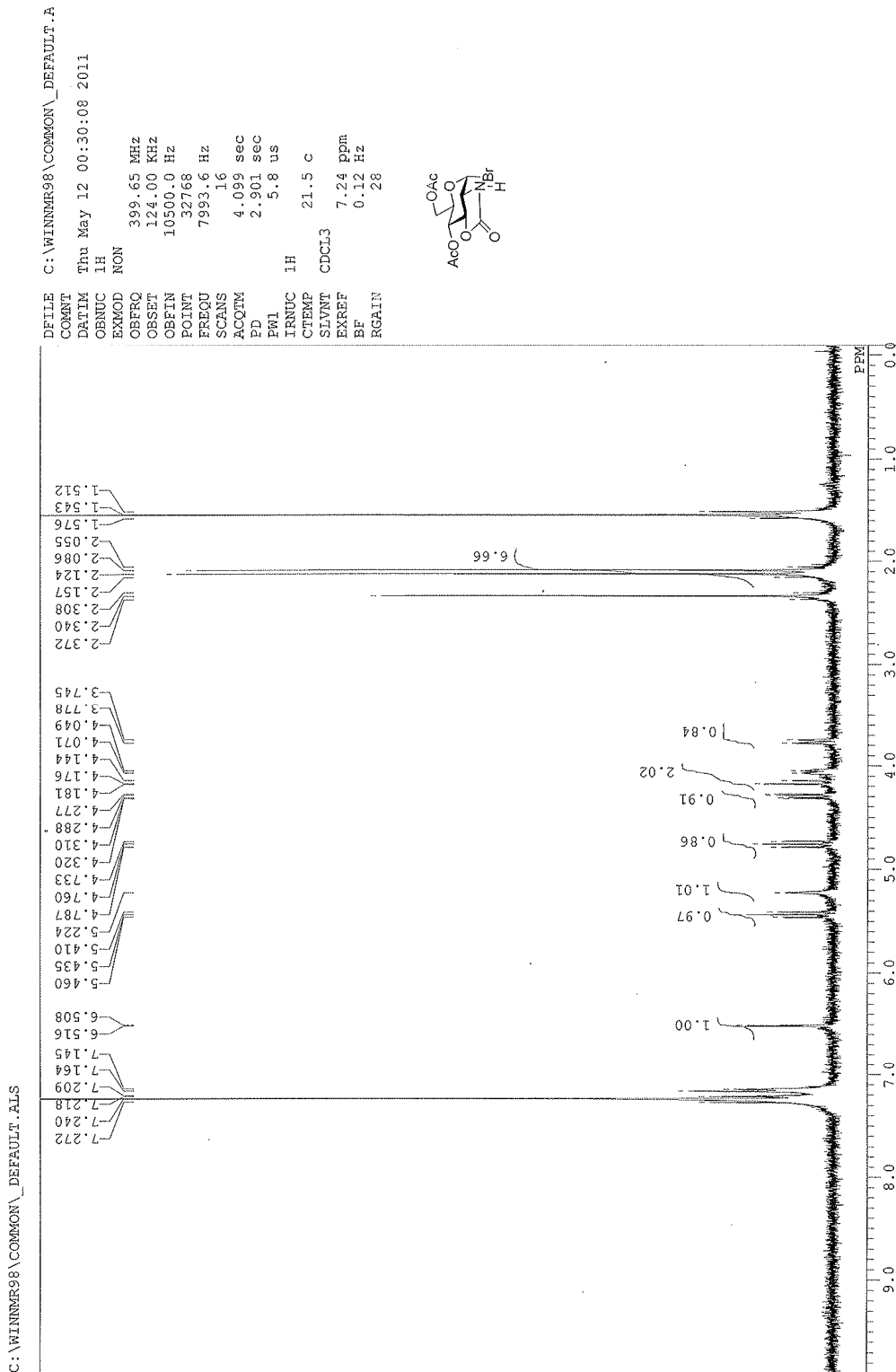
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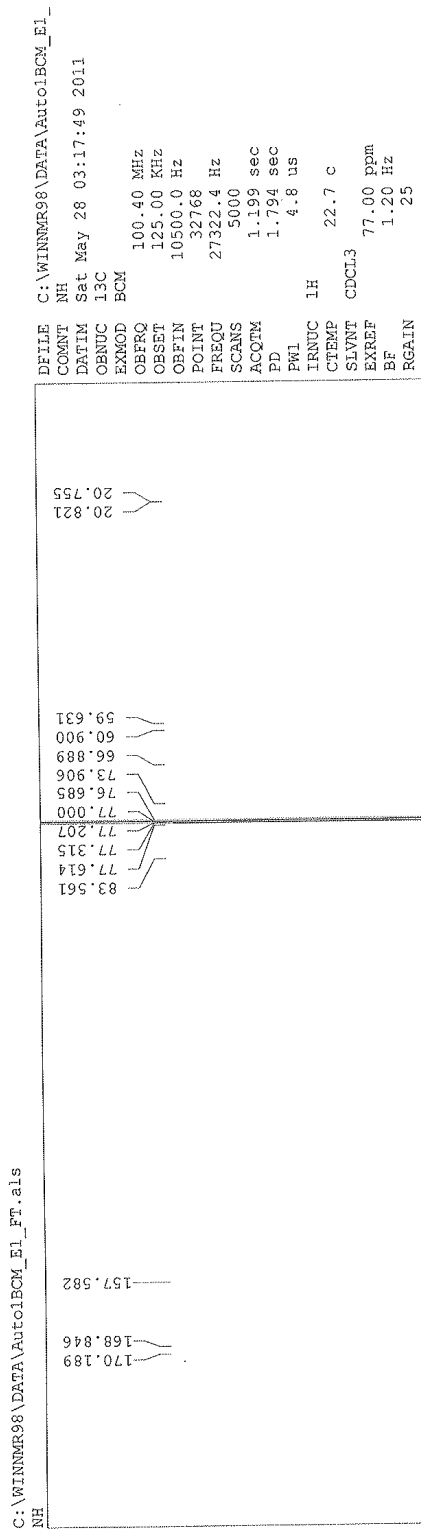


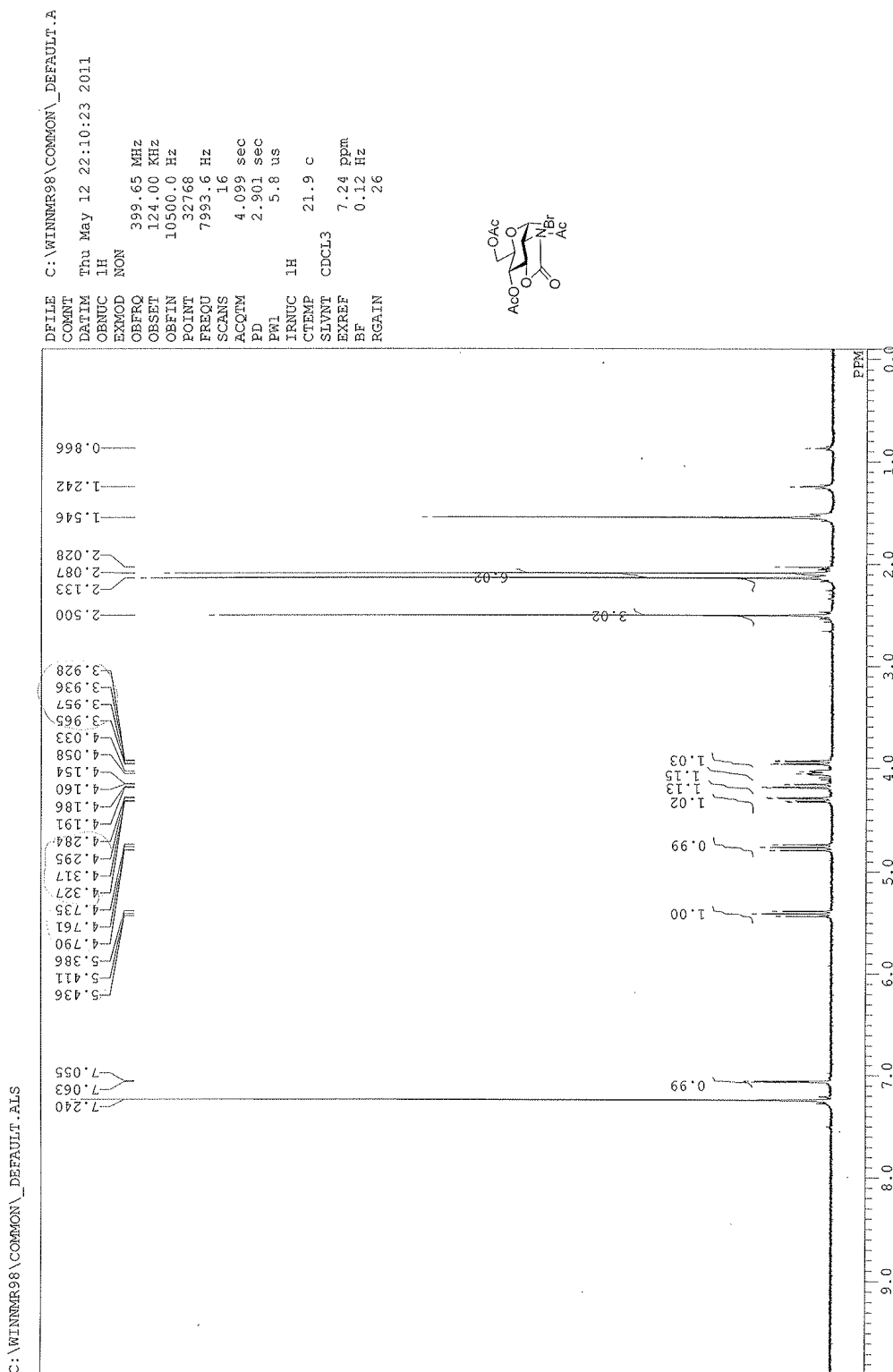


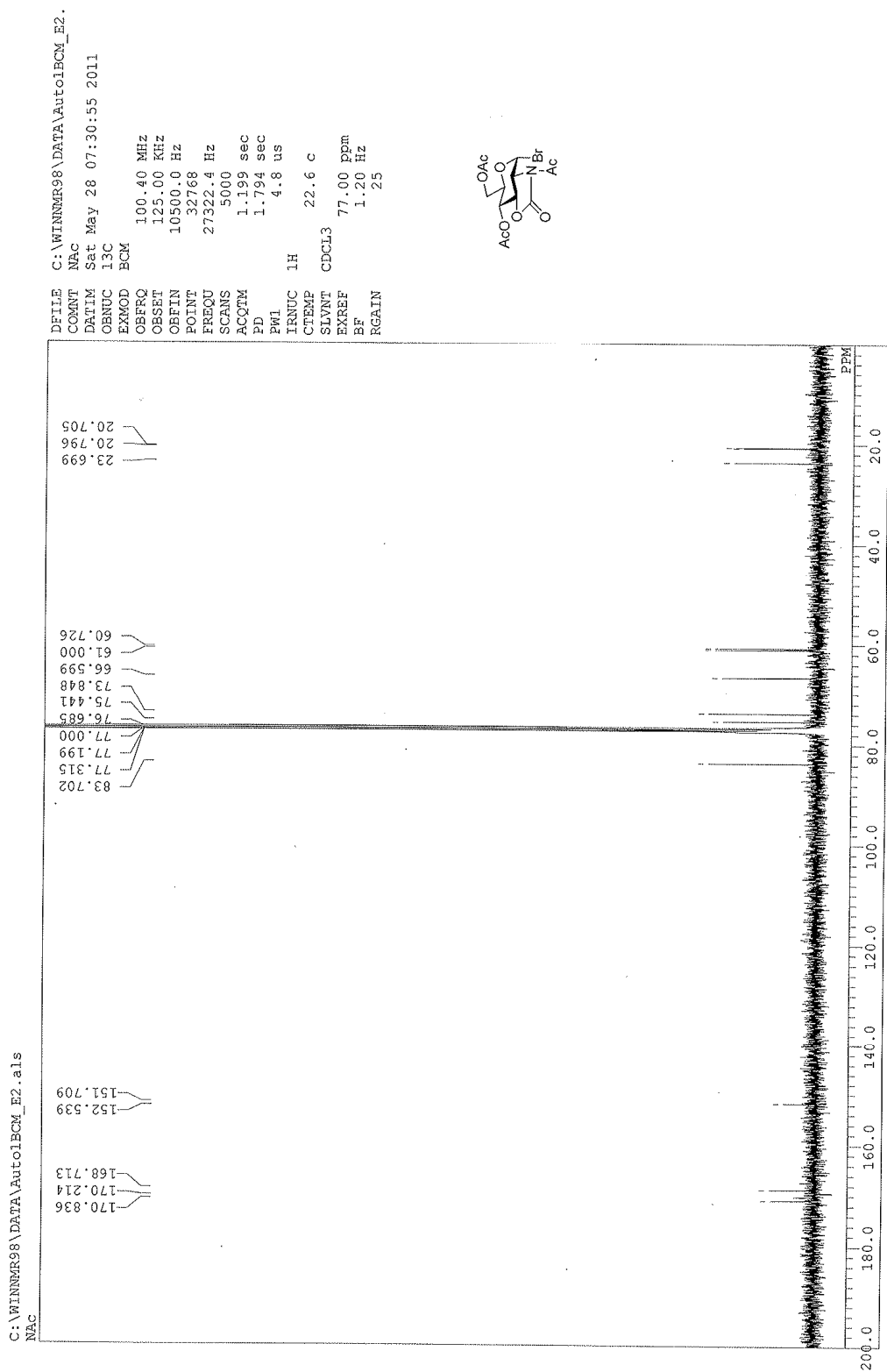


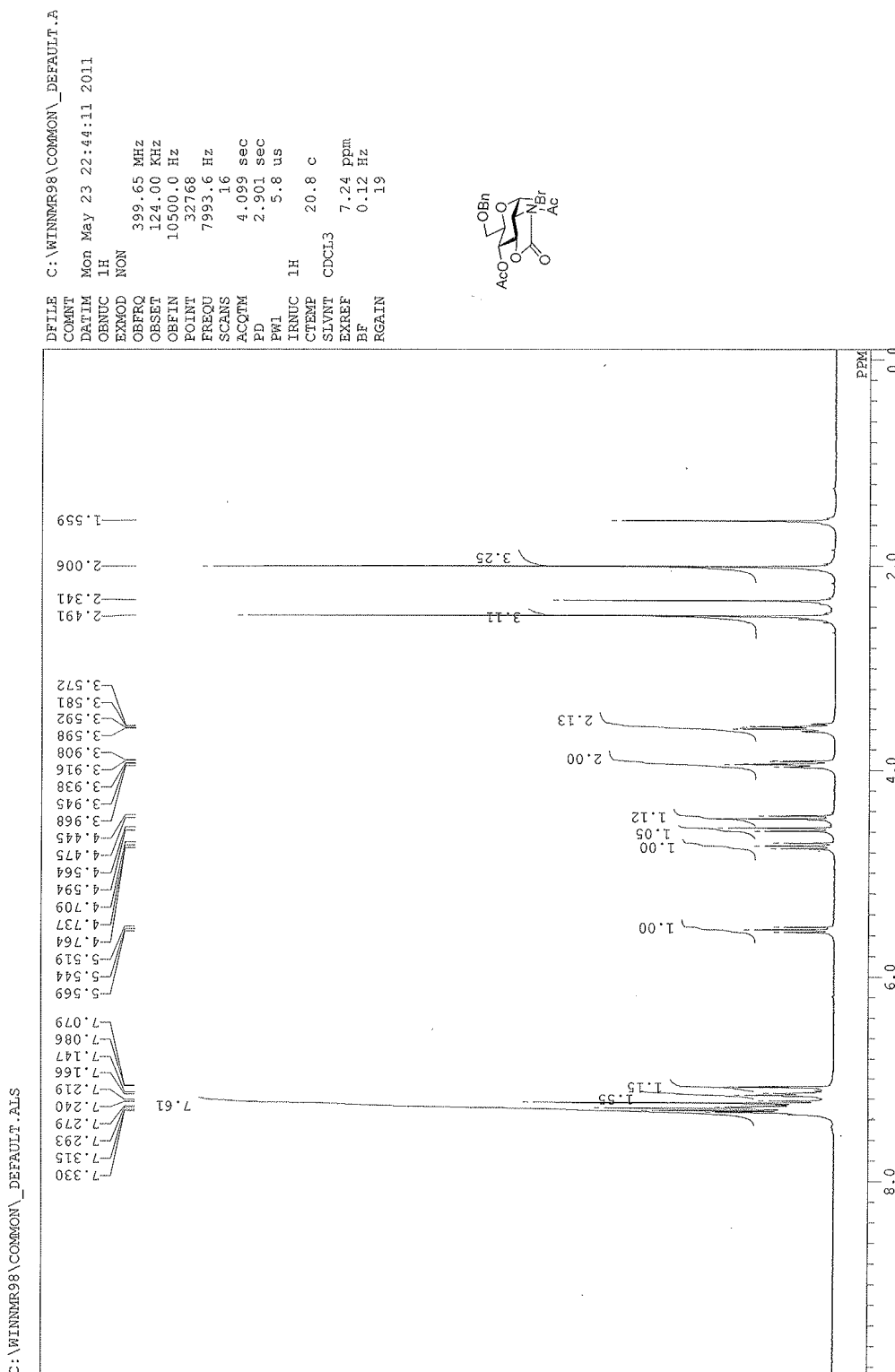


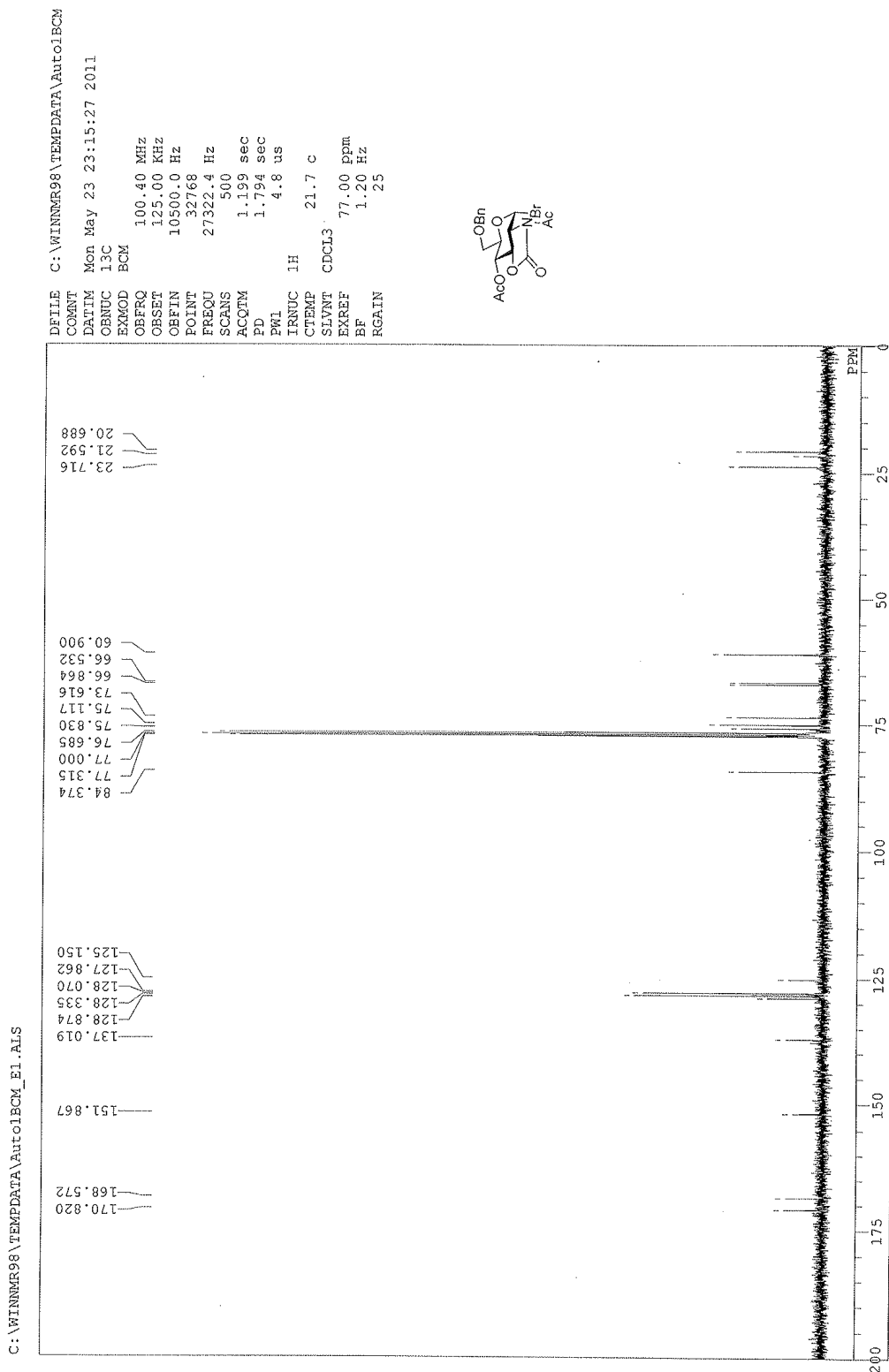


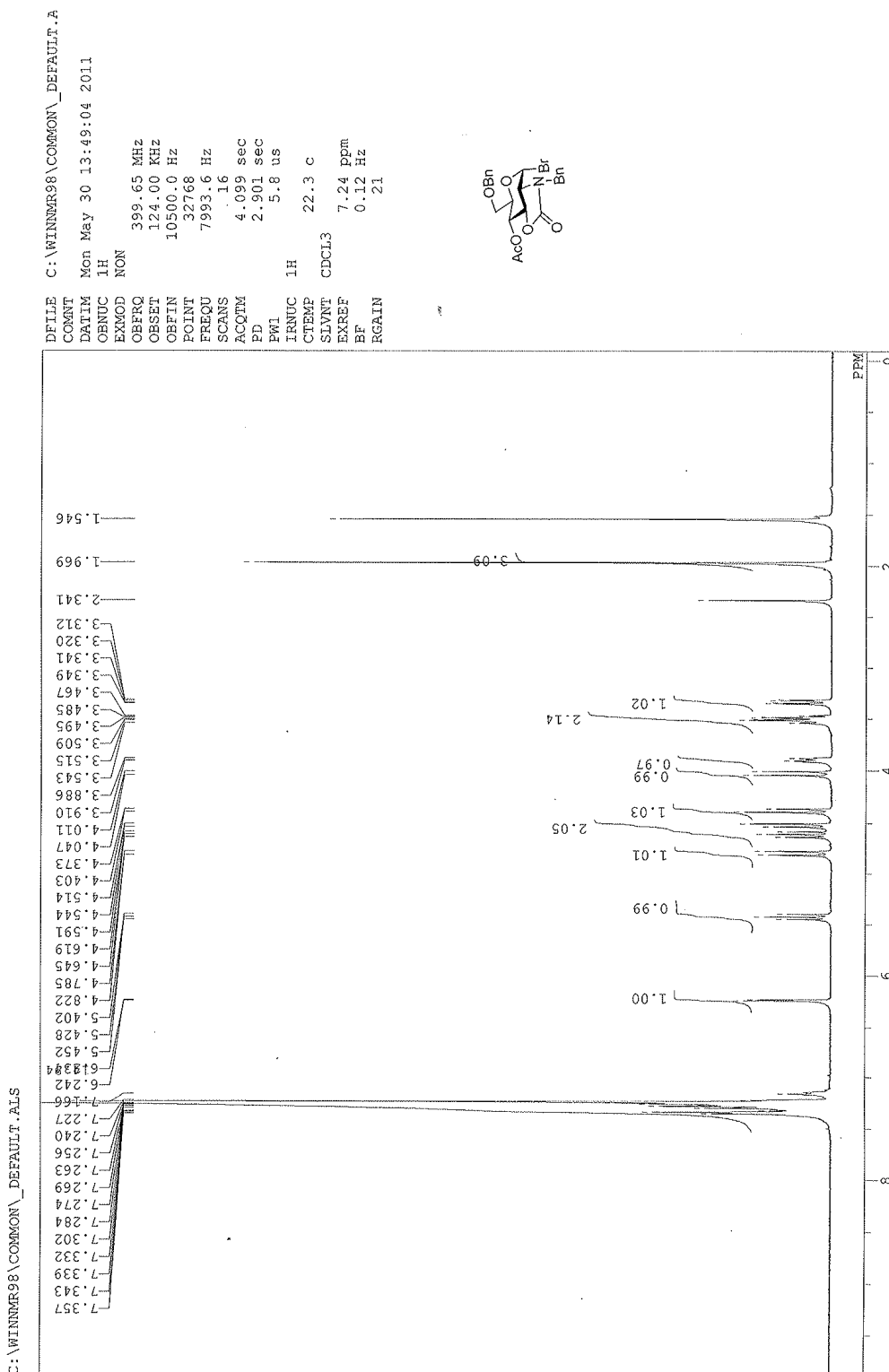


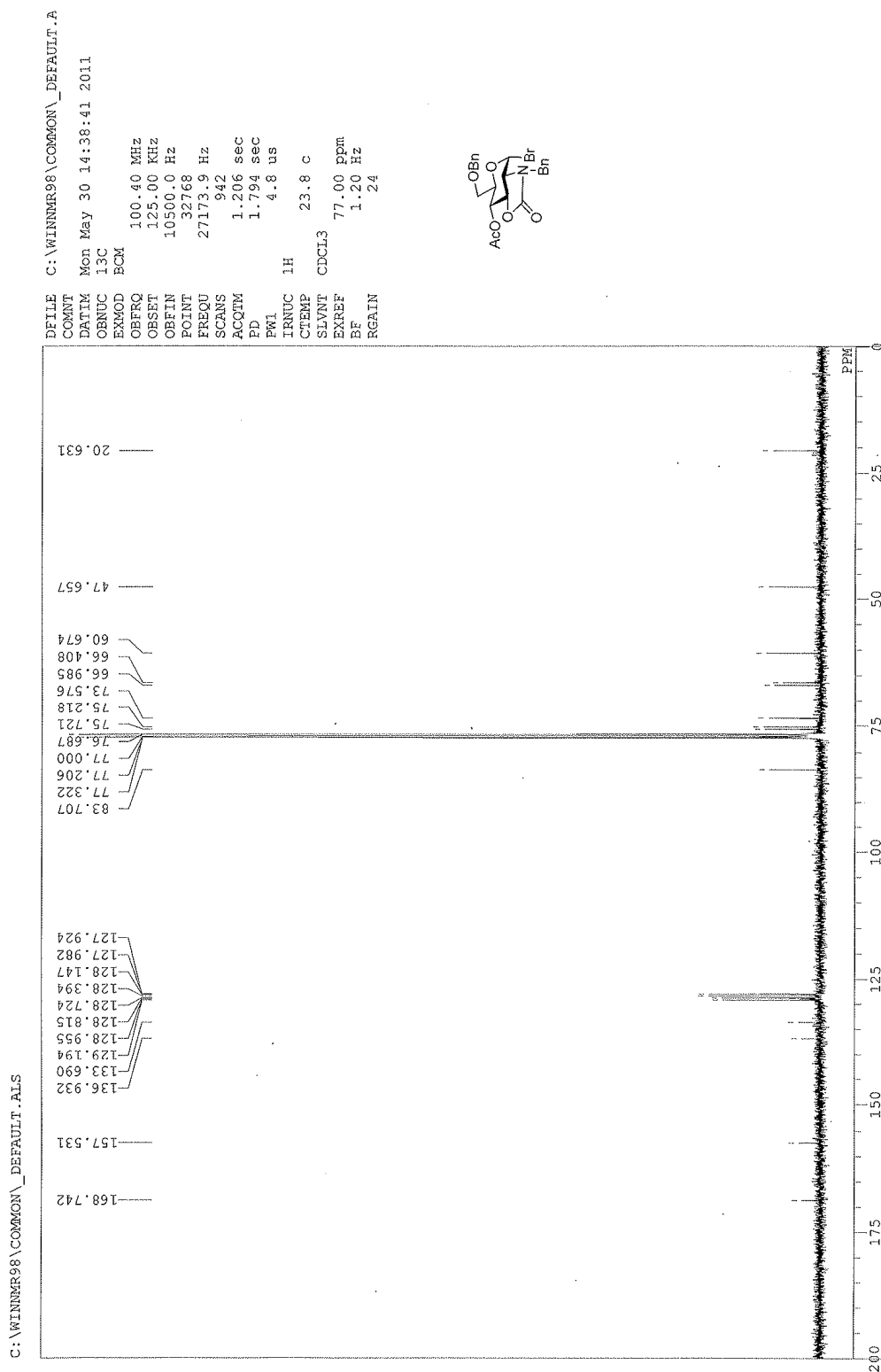


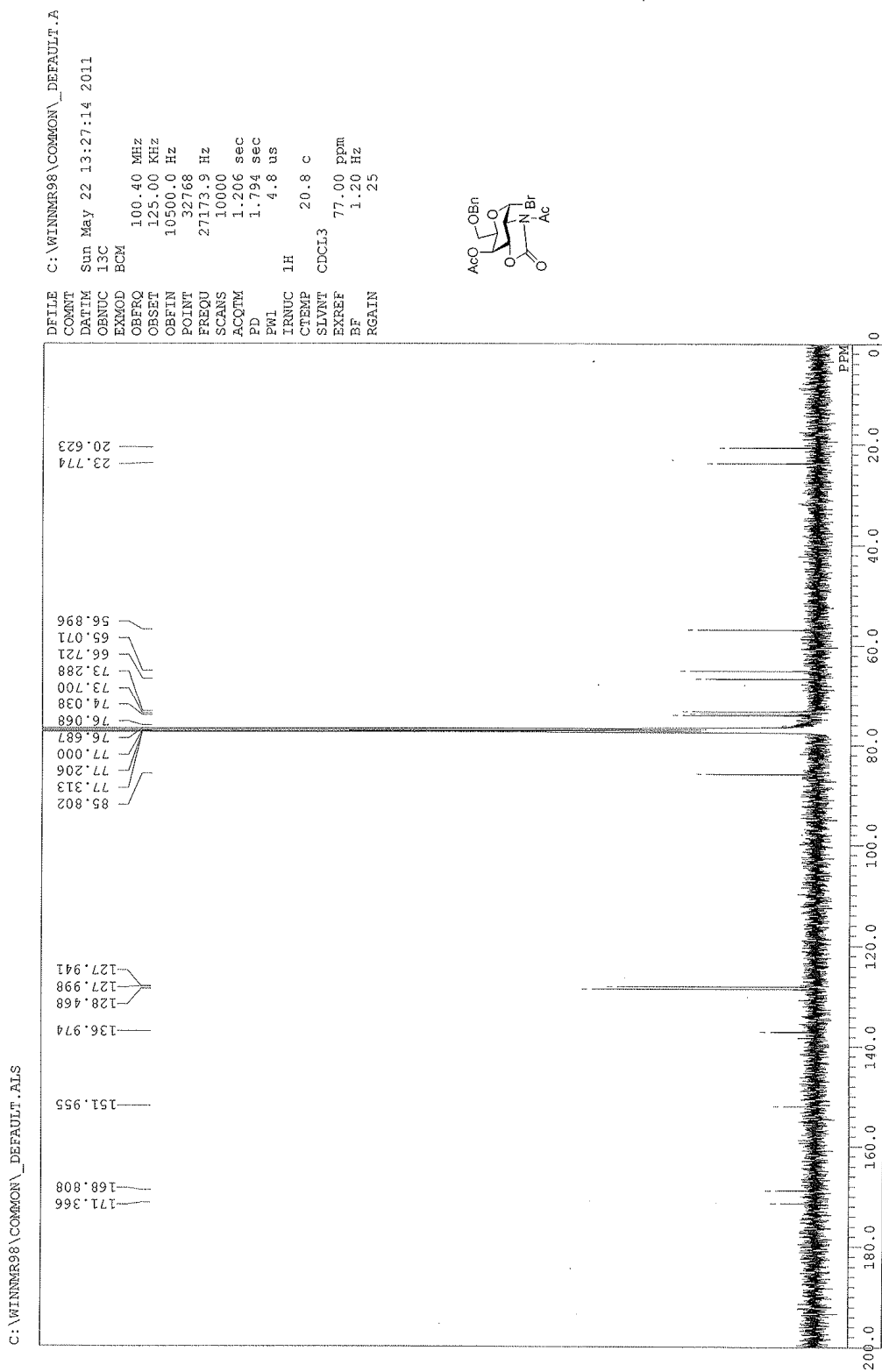


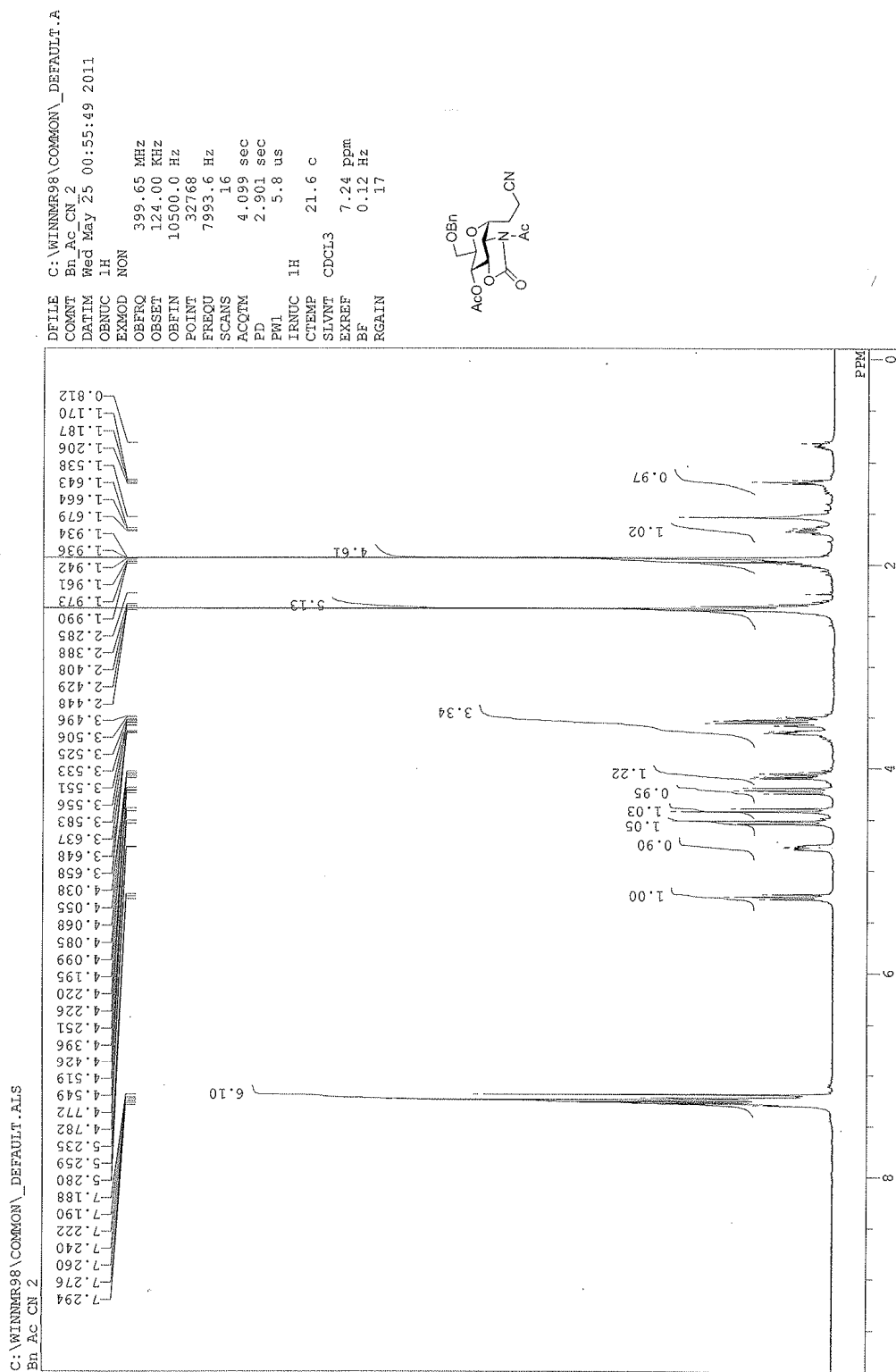


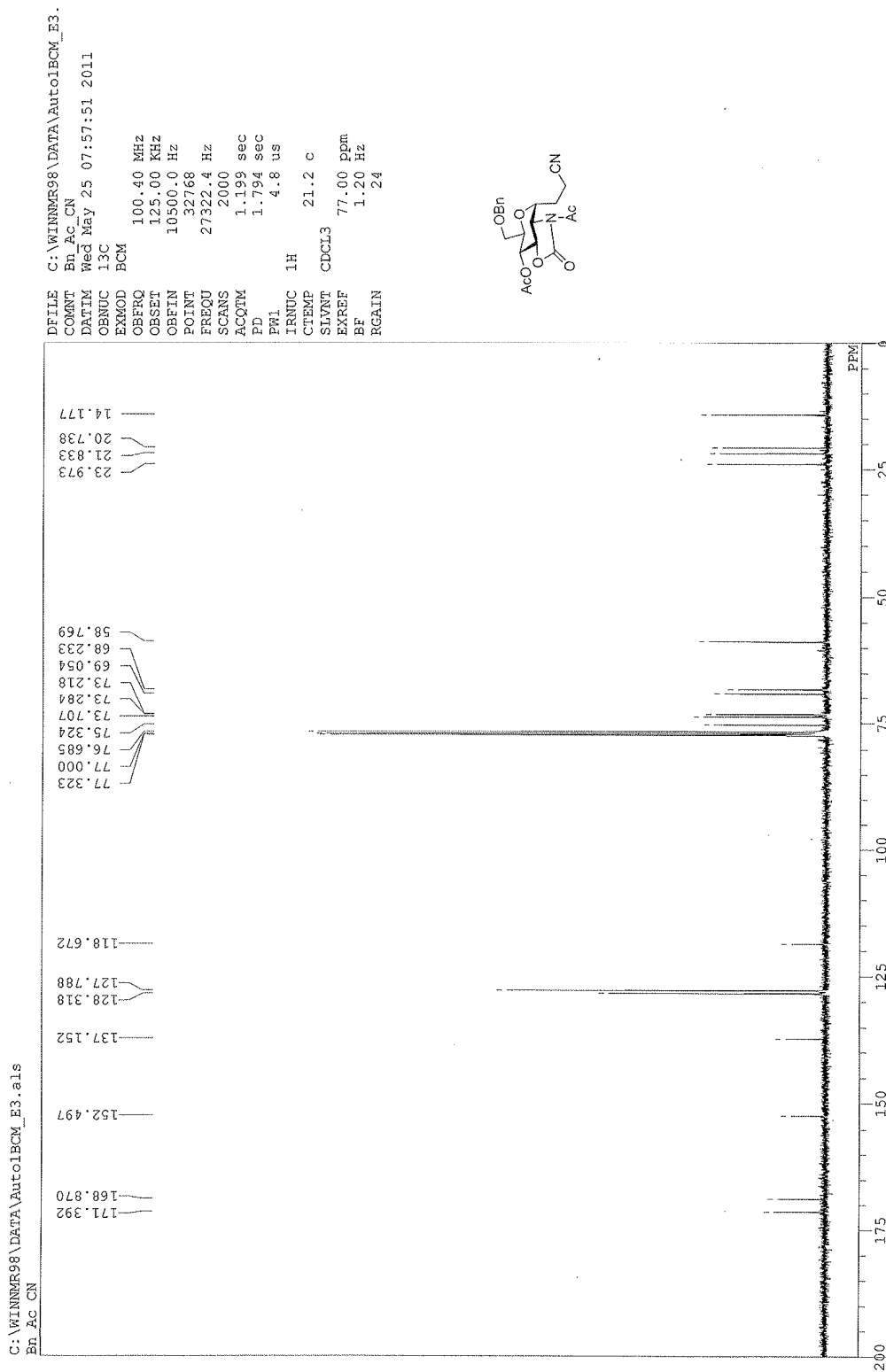


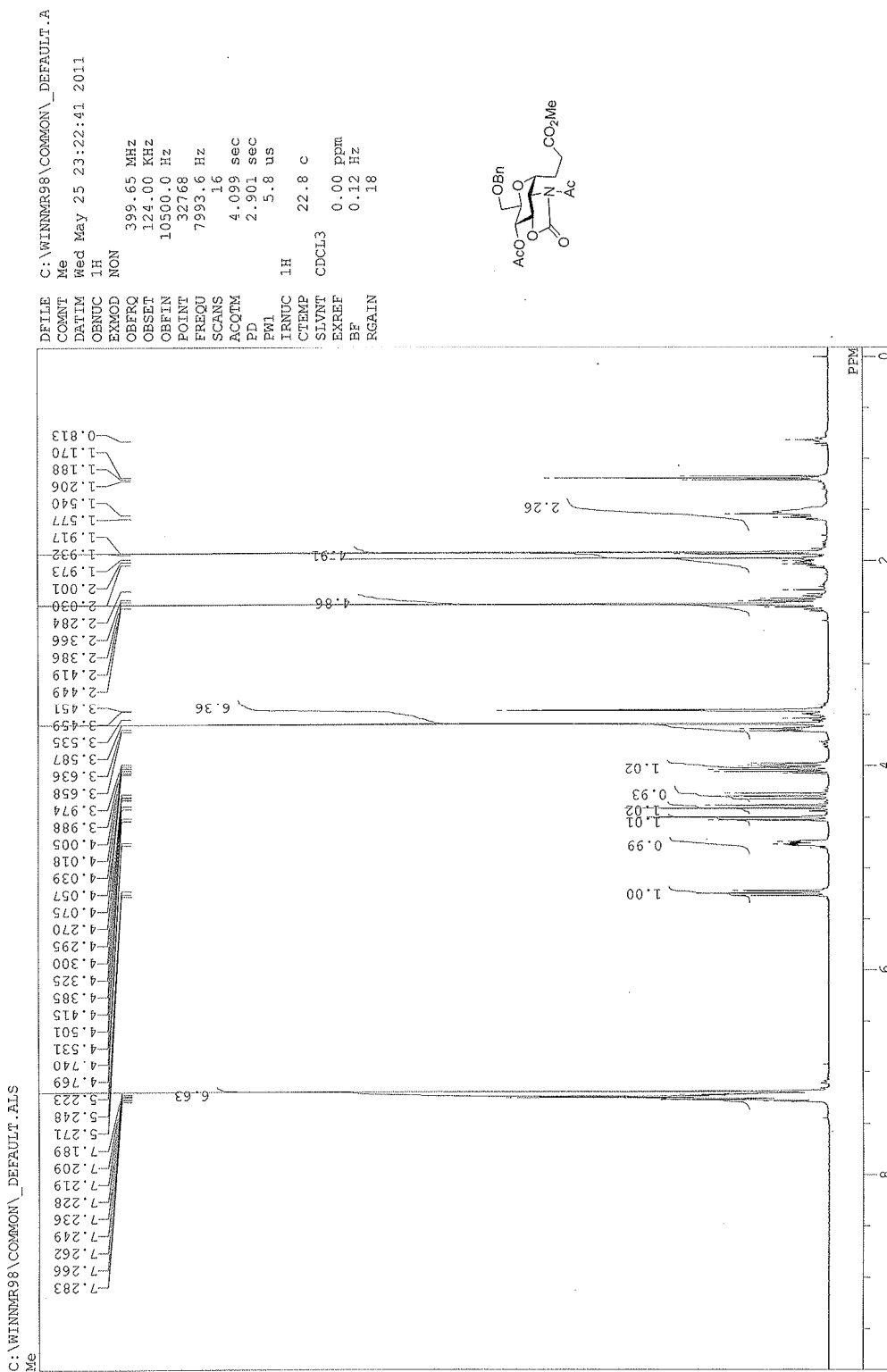


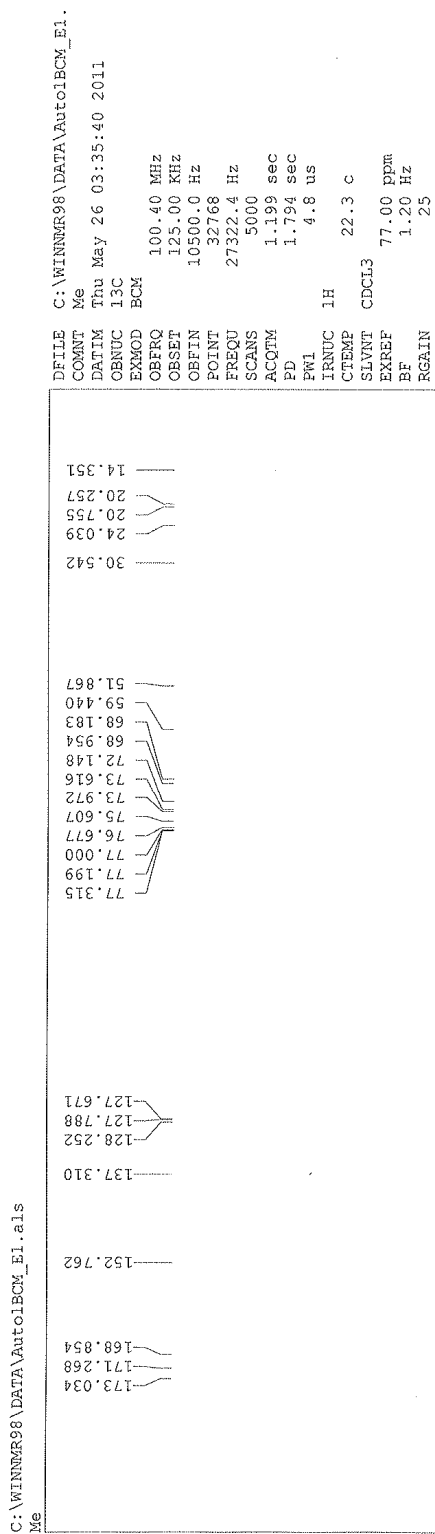


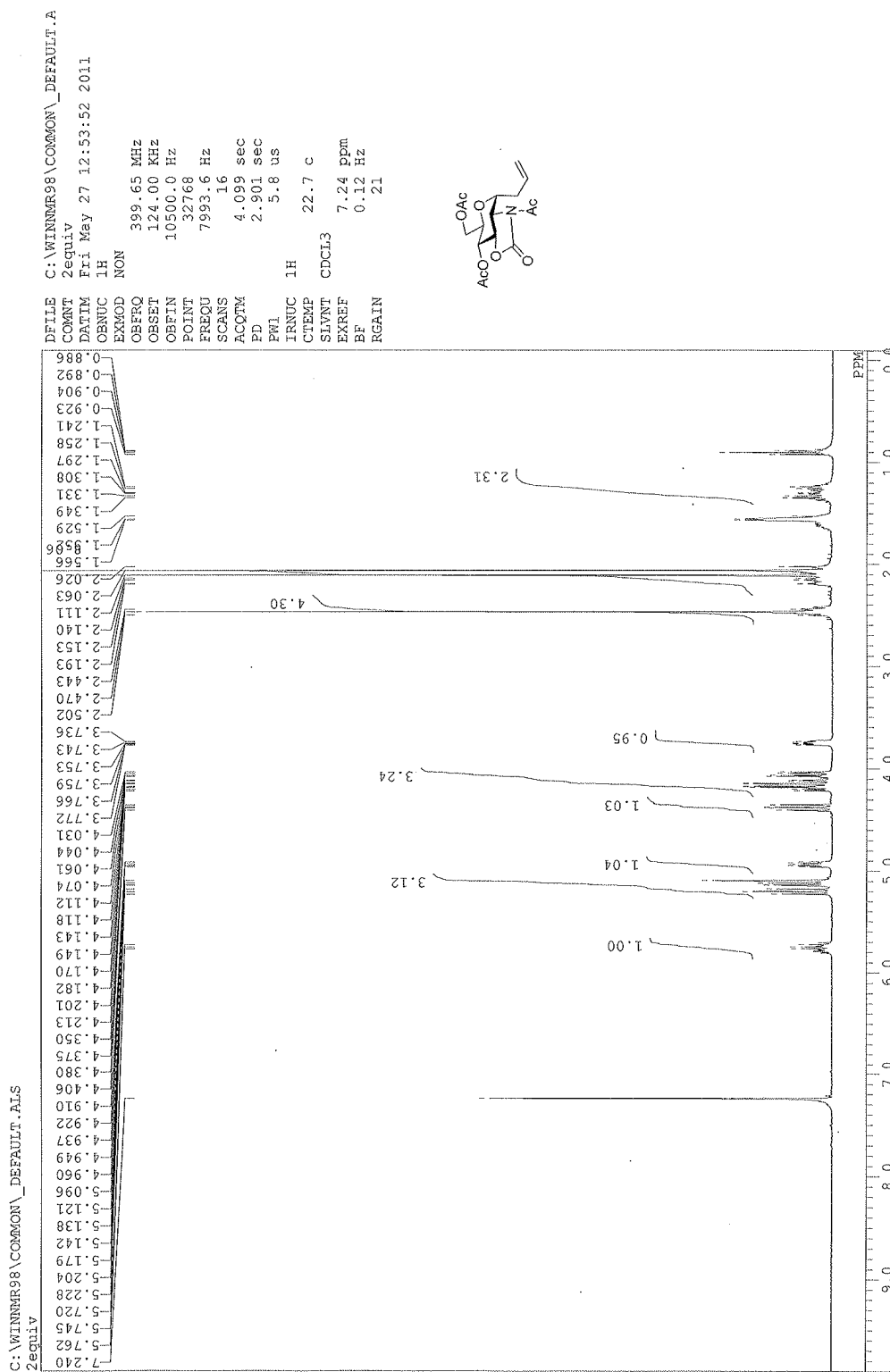


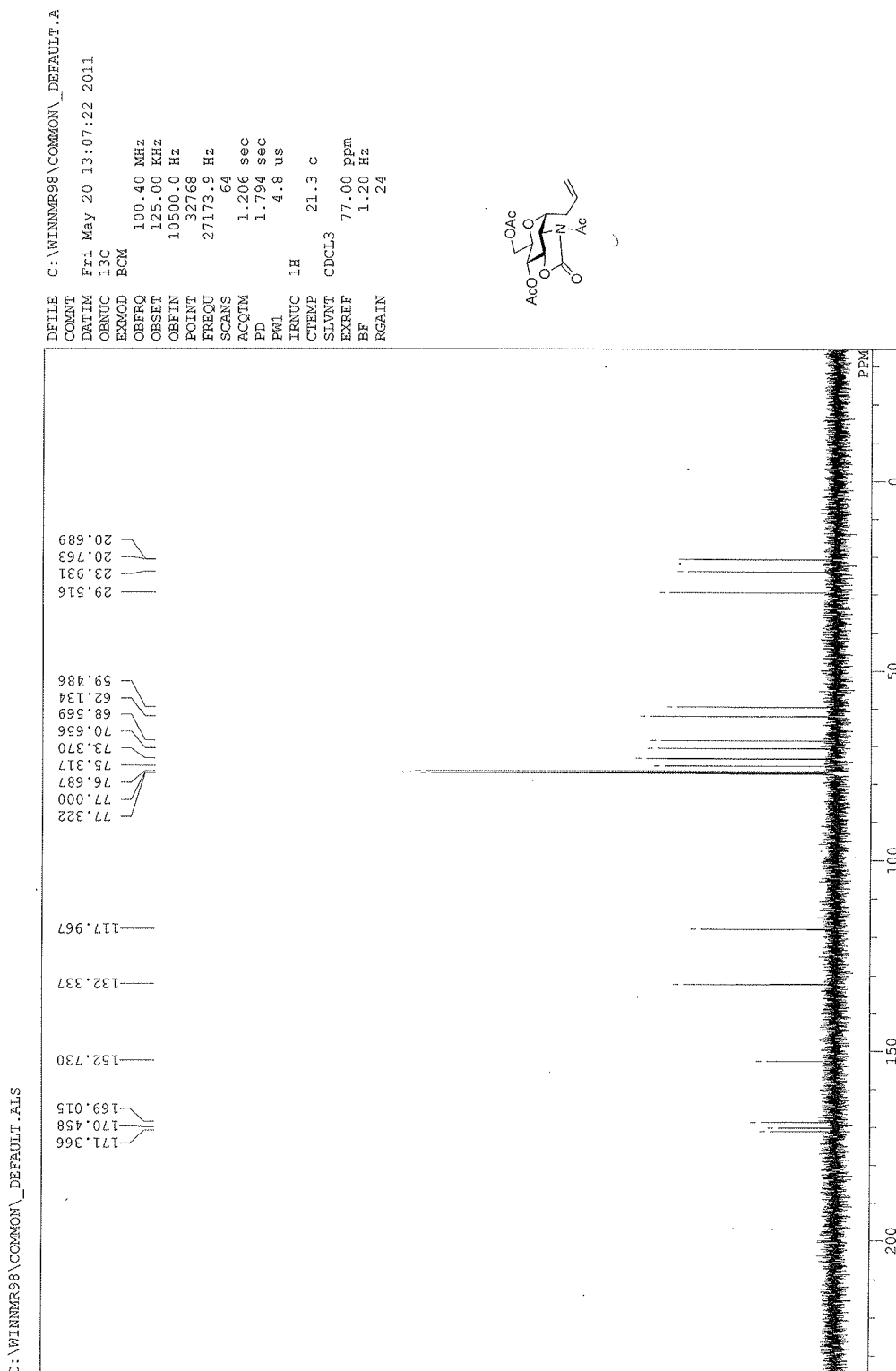


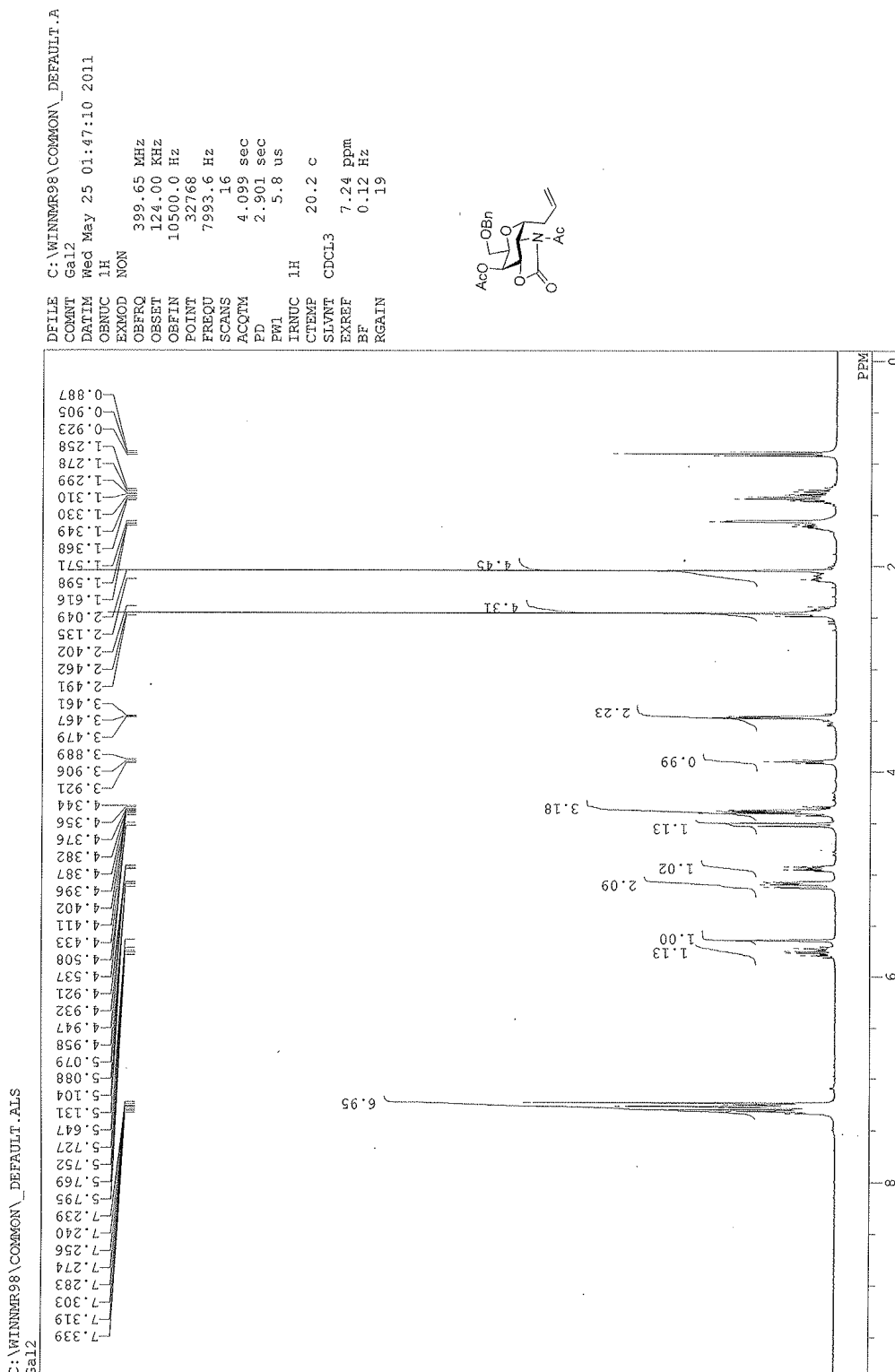


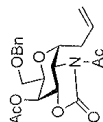
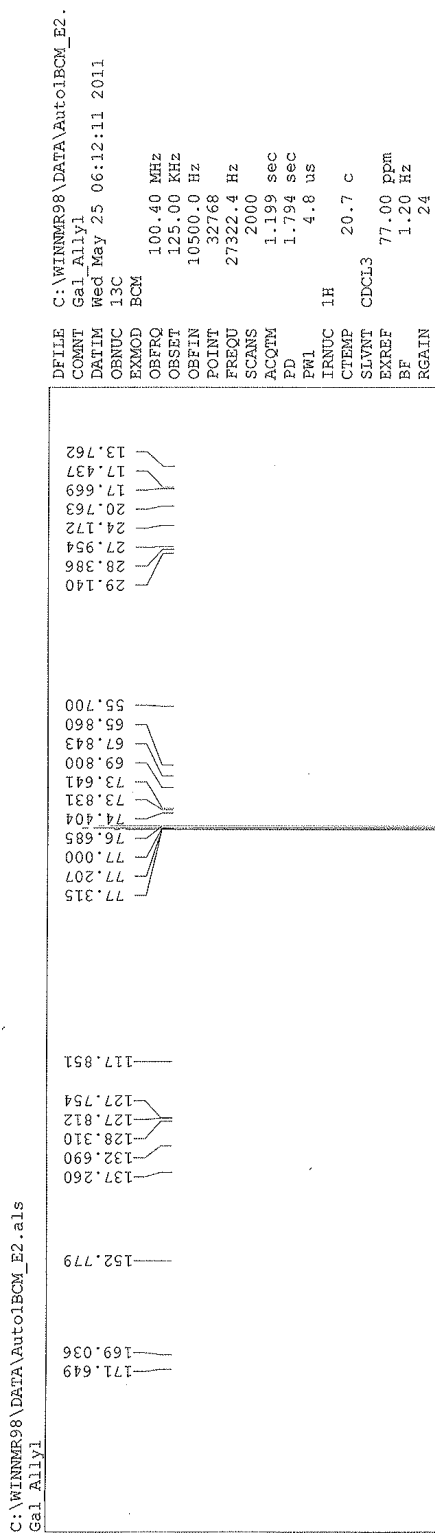






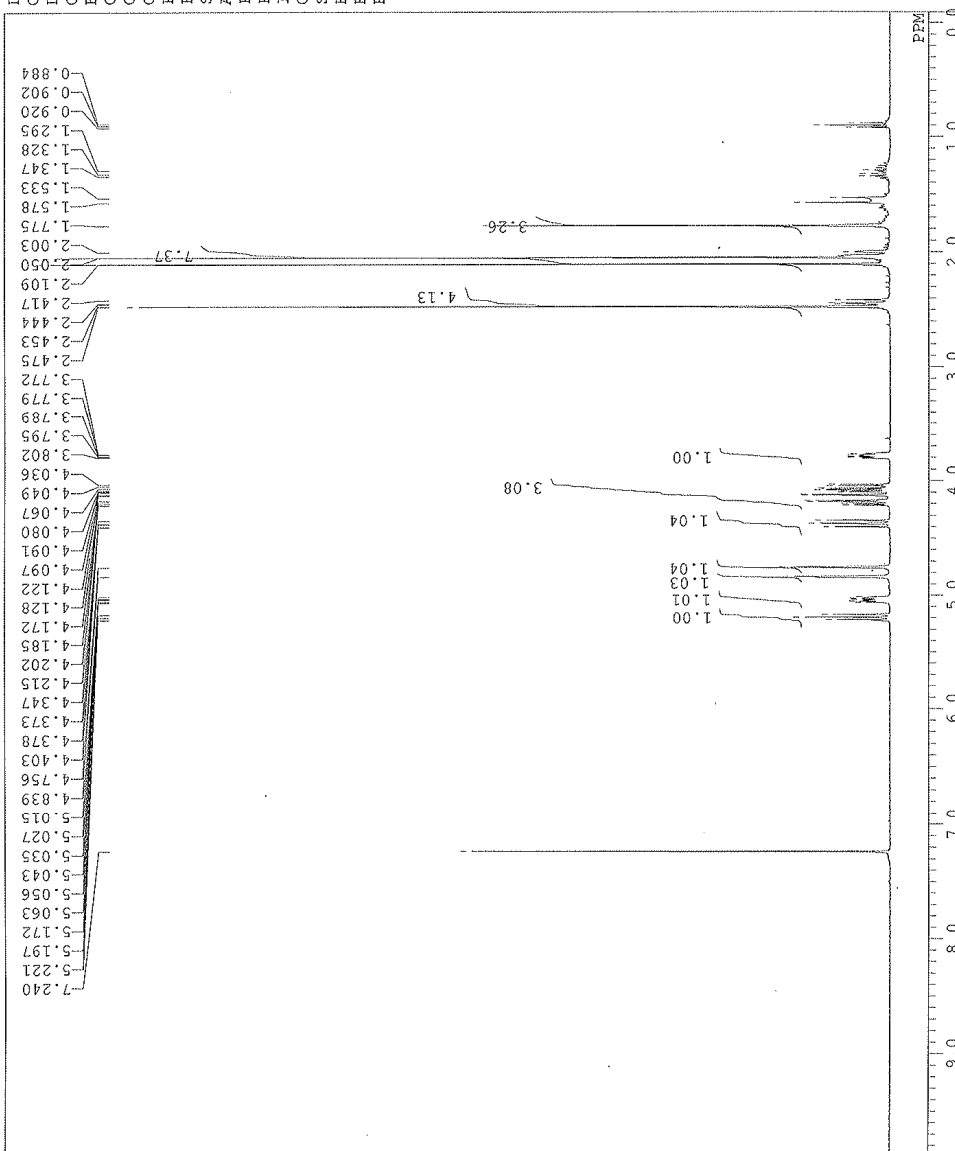
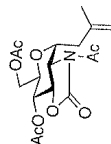


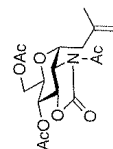
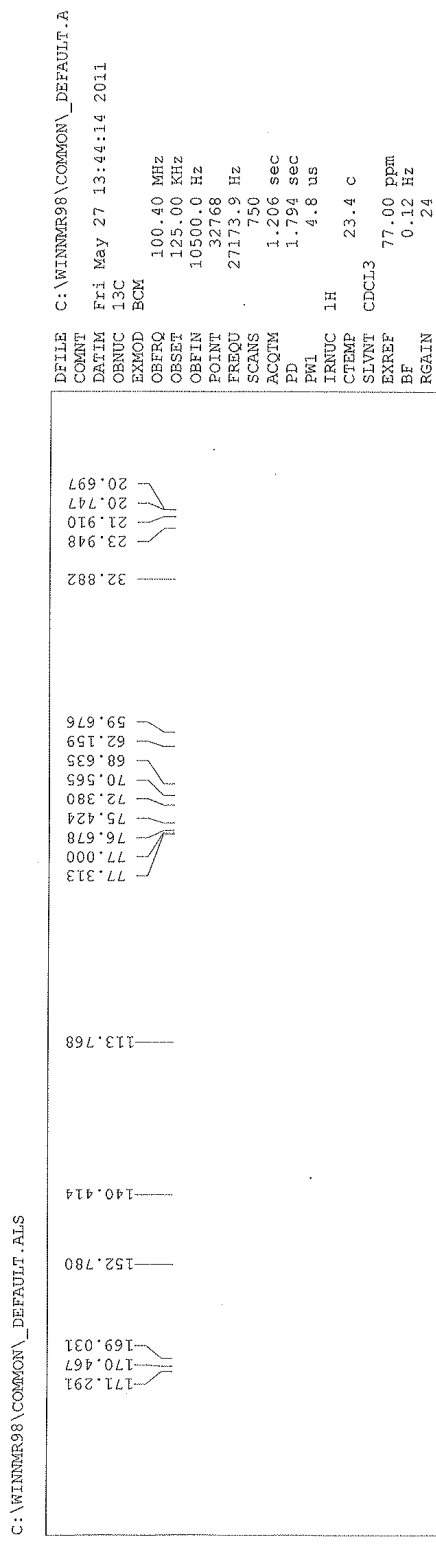




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 EXREF 7.24 ppm
 EF 0.12 Hz
 RGAIN 19





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Bn_Ac_Allyl

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RGAIN 25

