

Use of Olefin-Cross Metathesis to Release Azide-containing Sugars From Solid Support

Takuya Kanemitsu and Peter H. Seeberger*

*Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

Supplementary Material

Supporting Information Available: Experimental procedures for the preparation of compounds **3**, **4**, **5**, **10**, **11**, **12**, **13**, **14**, **16**, and **17** including spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental Section

General Methods. All chemicals used were reagent grade and used as supplied except where noted. Dichloromethane and tetrahydrofuran were purified by a JT Baker Cycle-Tainer Solvent Delivery System. Solutions were evaporated under reduced pressure at a bath temperature not exceeding 40°C. Analytical thin layer chromatography (TLC) was performed on Merck Art. 5715, Kieselgel 60 F₂₅₄/0.25 mm thickness plates. Visualization was accomplished with UV light and cerium sulfate-ammonium molybdate solution followed by heating. Column chromatography was performed using forced flow of the indicated solvent on Sigma H-type silica (10-40 m). ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were recorded with a Varian Unity 300 spectrometer in deuterated solvents using CHCl₃ as an internal standard.

8-*O*-Benzyl-4- (Z) - o c t e n y l 6 -*O*-acetyl-2,3,4-tri-*O*-benzyl- α,β -D-glucopyranoside (3). A mixture of 8-*O*-Benzyl-4-(Z)-octenol (**1**, 80 mg, 0.341 mmol), 6-*O*-acetyl-2,3,4-tri-*O*-benzyl- α,β -D-glucopyranosyl trichloroacetimidate (**2**, 110 mg, 0.173 mmol), and 4Å molecular sieves (400 mg) in dry CH₂Cl₂ (5 mL) was stirred at room temperature for 5 h. To the stirred mixture, a solution of 0.5M

trimethylsilyltrifluoromethanesulfonic acid in CH₂Cl₂ (0.035 ml 0.0175 mmol) were added at -20 °C. The mixture was stirred under nitrogen atmosphere at -20 °C for 30 min. The reaction mixture was then filtered and the filtrate was purified on a silica gel column using hexane/ethyl acetate (80:20) as an eluent to provide **3α** (59 mg, 48%) and **3β** (44 mg 36%).

3α; ¹H NMR (CDCl₃) δ 7.39-7.26 (m, 20 H), 5.42 (t, 2 H, *J* = 4.6 Hz), 4.99 (d, 2 H, *J* = 10.9 Hz), 4.90-4.73 (m, 4 H), 4.59 (d, 1 H, *J* = 10.9 Hz), 4.50 (s, 2 H), 4.42 (d, 1 H, *J* = 7.8 Hz), 4.38-4.23 (m, 2 H), 3.99-3.92 (m, 1 H), 3.72-3.45 (m, 7 H), 2.19-2.07 (m, 4 H), 2.06 (s, 3 H), 1.79-1.64 (m, 4 H); ¹³C NMR (CDCl₃) δ 171.0, 138.9, 138.7, 138.6, 138.0, 130.1, 129.6, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 104.0, 84.9, 82.4, 76.0, 75.3, 75.1, 73.2, 73.1, 70.1, 70.0, 63.5, 33.0, 30.5, 30.1, 30.0, 24.1, 24.0, 21.2; IR (thin film): 3350, 3031, 2937, 1743, 1496, 1453, 1365, 1237, 1070; [α]_D +24.0° (*c* 1.3, CH₂Cl₂); HR-ESI MS: Calcd for C₄₄H₅₂O₈: [M+Na]⁺ *m/z*: 731.3560; Found: *m/z*: 731.3590.

3β; ¹H NMR (CDCl₃) δ 7.43-7.26 (m, 20 H), 5.44 (t, 2 H, *J* = 5.3 Hz), 5.07 (d, 1 H, *J* = 10.8 Hz), 4.96-4.60 (m, 6 H), 4.52 (s, 2 H), 4.33-4.31 (m, 2 H), 4.08 (t, 1 H, *J* = 9.2 Hz), 3.93-3.90 (m, 1 H), 3.70-3.46 (m, 6 H), 2.19-2.07 (m, 4 H), 2.06 (s, 3 H), 1.78-1.70 (m, 4 H); ¹³C NMR (CDCl₃) δ 171.0, 139.0, 138.9, 138.5, 138.2, 130.2, 129.6, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 97.1, 82.3, 80.4, 77.7, 76.0, 75.3, 73.4, 73.2, 70.1, 69.0, 68.1, 63.4, 38.4, 30.0, 29.7, 24.2, 24.0, 21.1; IR (thin film): 3352, 3031, 2920, 1739, 1496, 1454, 1363, 1237, 1070; [α]_D +4.0° (*c* 1.1, CH₂Cl₂); HR-ESI MS: Calcd for C₄₄H₅₂O₈: [M+Na]⁺ *m/z*: 731.3560; Found: *m/z*: 731.3599.

8-*O*-Benzyl-4-(*Z*)-octenyl 6-*O*-acetyl-2-azide -3,4-di-*O*-benzyl-2-deoxy-α,β-D-glucopyranoside (10). A mixture of 8-*O*-benzyl-4-(*Z*)-octenol (**1**, 205 mg, 0.875 mmol), 6-*O*-acetyl-2-azide-2-deoxy-3,4-di-*O*-benzyl-α,β-D-glucopyranosyl trichloroacetimidate (**9**, 250 mg, 0.437 mmol), and 4 Å molecular sieves (800 mg) in dry CH₂Cl₂ (10 mL) was stirred at room temperature for 5 h. To the stirred mixture, a solution of 0.5M trimethylsilyltrifluoromethanesulfonic acid in CH₂Cl₂ (0.09 ml 0.045 mmol) were added at -20 °C. The mixture was stirred under nitrogen atmosphere at -20 °C for 30 min. The

reaction mixture was then filtered and the filtrate was purified on a silica gel column using hexane/ethyl acetate (80:20) as an eluent to provide **10** (241 mg 86%).

10 α ; ^1H NMR (CDCl_3) δ 7.40-7.24 (m, 15 H), 5.45-5.33 (m, 2 H), 4.92 (d, 1 H, J = 10.8 Hz), 4.85 (d, 1 H, J = 10.8 Hz), 4.79 (d, 1 H, J = 10.8 Hz), 4.57 (d, 1 H, J = 10.9 Hz), 4.50 (s, 2 H), 4.33 (dd, 1 H, J = 2.1, 12.0 Hz), 4.27-4.18 (m, 2 H), 3.94-3.87 (m, 1 H), 3.56-3.40 (m, 7 H), 2.19-2.04 (m, 4 H), 2.03 (s, 3 H), 1.75-1.63 (m, 4 H); ^{13}C NMR (CDCl_3) δ 170.9, 138.9, 138.1, 137.7, 130.2, 129.5, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 127.7, 102.4, 83.3, 75.8, 75.3, 73.2, 73.1, 70.1, 70.0, 66.6, 63.1, 58.7, 44.2, 33.0, 29.9, 29.8, 24.0, 23.8, 21.1; IR (thin film): 2866, 2110, 1742, 1496, 1454, 1363, 1235, 1074; $[\alpha]_{\text{D}} +13.5^\circ$ (c 1.7, CH_2Cl_2); HR-ESI MS: Calcd for $\text{C}_{37}\text{H}_{44}\text{N}_3\text{O}_7$: $[\text{M}+\text{Na}]^+$ m/z : 665.3077; Found: m/z : 665.3089.

10 β ; ^1H NMR (CDCl_3) δ 7.41-7.23 (m, 15 H), 5.45-5.33 (m, 2 H), 4.94-4.85 (m, 4 H), 4.58 (d, 1 H, J = 10.8 Hz), 4.49 (s, 2 H), 4.32-4.22 (m, 2 H), 4.03 (dd, 1 H, J = 8.7, 10.3 Hz), 3.91-3.85 (m, 1 H), 3.72-3.64 (m, 1 H), 3.58-3.43 (m, 4 H), 3.32 (dd, 1 H, J = 3.6, 10.3 Hz), 2.18-2.11 (m, 4 H), 2.04 (s, 3 H), 1.74-1.63 (m, 4 H); ^{13}C NMR (CDCl_3) δ 170.8, 138.9, 138.0, 137.7, 130.3, 129.3, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 127.7, 98.0, 80.5, 78.2, 75.6, 75.4, 73.1, 70.0, 69.3, 68.1, 63.6, 63.0, 45.4, 44.6, 33.0, 29.9, 29.6, 24.1, 23.9, 21.1; IR (thin film): 2917, 2109, 1734, 1230, 1037; $[\alpha]_{\text{D}} -1.2^\circ$ (c 0.5, CH_2Cl_2); HR-ESI MS: Calcd for $\text{C}_{37}\text{H}_{44}\text{N}_3\text{O}_7$: $[\text{M}+\text{Na}]^+$ m/z : 665.3077; Found: m/z : 665.3043.

8-*O*-Benzyl-4-(*Z*)-octenyl 2-*N*-acetyl-6-*O*-acetyl-3,4-di-*O*-benzyl-2-deoxy- α,β -D-glucopyranoside (13**).** A solution of compound **10** (22 mg, 0.0342 mmol) in pyridine-AcSH (1:1, v/v, 4 mL) was stirred at room temperature for 24 h. The reaction mixture was diluted with CH_2Cl_2 , washed with aqueous NaHCO_3 and water, and then dried over Na_2SO_4 , filtered, and concentrated. The residue was purified on a silica gel column using hexane/ethyl acetate (80:20) as an eluent to provide **13** (19 mg, 82%); ^1H NMR (CDCl_3) δ 7.34-7.20 (m, 15 H), 5.83-5.26 (m, 2 H), 5.05-4.49 (m, 7 H), 4.38-4.12 (m, 3 H), 3.85-3.31 (m, 8 H), 2.80-2.16 (m, 7 H), 1.85 (s, 3 H), 1.69-1.56 (m, 4 H); IR (thin film): 3278, 2919, 1741, 1652, 1558, 1454, 1367, 1251, 1116.

8-*O*-Benzyl-4-(*Z*)-octenyl 3-*O*-acetyl-2,4-diazide-6-*O*-benzyl-2,4-dideoxy- α,β -D-galactopyranoside (16**).** A mixture of 8-*O*-benzyl-4-(*Z*)-octenol (**1**, 28 mg, 0.119 mmol), 3-*O*-acetyl-2,4-diazide-2,4-dideoxy-6-*O*-benzyl- α,β -D-galactopyranosyl trichloroacetimidate (**15**, 30 mg, 0.0592 mmol), and 4Å molecular sieves (300 mg) in dry CH₂Cl₂ (4 mL) was stirred at room temperature for 5 h. To the stirred mixture, a solution of 0.5M trimethylsilyltrifluoromethanesulfonic acid in CH₂Cl₂ (0.012 ml 0.006 mmol) were added at -20 °C. The mixture was stirred under nitrogen atmosphere at -20 °C for 30 min. The reaction mixture was then filtered and the filtrate was purified on a silica gel column using hexane/ethyl acetate (80:20) as an eluent to provide **16** (33 mg, 97%).

16 α ; ¹H NMR (CDCl₃) δ 7.39-7.25 (m, 10 H), 5.41-5.35 (m, 2 H), 4.81 (dd, 1 H, *J* = 3.7, 10.7 Hz), 4.55 (s, 2 H), 4.50 (s, 2 H), 4.25 (d, 1 H, *J* = 7.9 Hz), 4.07-4.06 (m, 1 H), 3.92-3.85 (m, 1 H), 3.72-3.60 (m, 4 H), 3.54-3.45 (m, 3 H), 2.19 (s, 3 H), 2.18-2.09 (m, 4 H), 1.71-1.62 (m, 4 H); ¹³CNMR (CDCl₃) δ 170.2, 138.9, 137.7, 130.2, 129.5, 128.8, 128.6, 128.2, 128.1, 127.8, 127.7, 102.5, 73.9, 73.1, 71.8, 70.1, 70.0, 68.2, 61.4, 59.9, 44.6, 38.4, 29.9, 29.7, 24.0, 23.8, 20.8; IR (thin film): 2866, 2109, 1751, 1453, 1366, 1223, 1076; [α]_D +22.3° (c 1.0, CH₂Cl₂); HR-ESI MS: Calcd for C₃₀H₃₈N₆O₆: [M+Na]⁺ *m/z*: 601.2751; Found: *m/z*: 601.2729.

16 β ; ¹H NMR (CDCl₃) δ 7.37-7.26 (m, 10 H), 5.42-5.34 (m, 2 H), 5.03-4.96 (m, 2 H), 4.66 (d, 1 H, *J* = 12.3 Hz), 4.53-4.15 (m, 6 H), 3.79-3.68 (m, 1 H), 3.62-3.44 (m 5 H), 3.24 (t, 1 H, *J* = 4.0 Hz), 2.21-1.97 (m, 4 H), 1.98 (s, 3 H), 1.95-1.63 (m, 4 H); ¹³CNMR (CDCl₃) δ 169.8, 138.9, 137.9, 130.2, 129.5, 128.7, 128.6, 128.2, 128.1, 127.8, 127.7, 97.6, 73.6, 73.1, 70.1, 68.8, 68.3, 67.6, 64.8, 61.3, 57.1, 45.4, 38.4, 30.0, 29.7, 24.0, 20.7; IR (thin film): 2918, 2110, 1744, 1455, 1229, 1043; [α]_D +14.0° (c 0.9, CH₂Cl₂); HR-ESI MS: Calcd for C₃₀H₃₈N₆O₆: [M+Na]⁺ *m/z*: 601.2751; Found: *m/z*: 601.2744.

Olefin Metathesis Cleavage Reaction in Solution Phase General Procedure. A mixture of *O*-benzyl octenediol linked carbohydrate (1 equiv.), the indicated Grubbs' catalyst (0.1 equiv.) and 1-pentene (10 equiv.) or ethylen in dry CH₂Cl₂ or ClCH₂CH₂Cl was stirred at the indicated temperature for the indicated time. After the reaction was complete, the reaction mixture was filtered through a short silica gel column to remove the catalyst and the filtrate was washed with hexane/ethyl acetate (70:30). The filtrate

was concentrated and the residue was purified on a silica gel column using hexane/ethyl acetate (80:20) as an eluent to provide pentenyl or octenyl glycoside.

4 α ; ^1H NMR (CDCl_3) δ 7.33-7.24 (m, 15 H), 5.88-5.75 (m, 1 H), 5.05-4.93 (m, 4 H), 4.82 (dd, 2 H, $J = 10.7, 19.1$ Hz), 4.72 (d, 1H, $J = 11.0$ Hz), 4.55 (d, 1H, $J = 10.8$ Hz), 4.39 (d, 1H, $J = 7.8$ Hz), 4.34-4.20 (m, 2 H), 3.97-3.89 (m, 1 H), 3.69-3.41 (m, 5 H), 2.17-2.05 (m, 2 H), 2.04 (s, 3 H), 1.80-1.71 (m, 2 H); ^{13}C NMR (CDCl_3) δ 171.0, 138.7, 138.6, 138.0, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 115.2, 103.9, 84.9, 82.4, 76.0, 75.3, 75.1, 73.0, 69.8, 63.4, 58.7, 45.4, 33.0, 30.5, 30.4, 29.3, 21.1; IR (thin film): 2918, 1238, 1026; $[\alpha]_{\text{D}} +28.8^\circ$ (c 0.2, CH_2Cl_2).

4 β ; ^1H NMR (CDCl_3) δ 7.38-7.25 (m, 15 H), 5.88-5.74 (m, 1 H), 5.07-4.93 (m, 4 H), 4.90-4.54 (m, 5 H), 4.30-4.19 (m, 2 H), 4.01 (t, 1 H, $J = 9.1$ Hz), 3.87-3.81 (m, 1 H), 3.67-3.38 (m, 4 H), 2.17-2.04 (m, 2 H), 2.02 (s, 3 H), 1.79-1.69 (m, 2 H); ^{13}C NMR (CDCl_3) δ 176.2, 138.9, 138.4, 138.1, 128.7, 128.4, 128.2, 127.9, 115.2, 97.1, 82.2, 80.3, 76.0, 75.3, 73.4, 68.8, 67.9, 63.3, 58.7, 47.1, 45.4, 44.6, 38.3, 33.0, 30.5, 28.7, 21.1; IR (thin film): 2918, 1733, 1037; $[\alpha]_{\text{D}} +0.9^\circ$ (c 0.5, CH_2Cl_2).

5; ^1H NMR (CDCl_3) δ 7.33-7.23 (m, 15 H), 5.42-5.30 (m, 2 H), 4.96 (dd, 2 H, $J = 1.5, 11.0$ Hz), 4.82 (dd, 2 H, $J = 10.9, 19.7$ Hz), 4.72 (d, 1 H, $J = 11.0$ Hz), 4.55 (d, 1 H, $J = 10.8$ Hz), 4.38 (d, 1 H, $J = 2.0, 7.9$ Hz), 4.32 (dd, 1 H, $J = 2.0, 12.1$ Hz), 4.23 (dd, 1 H, $J = 4.2, 11.7$ Hz), 3.96-3.88 (m, 1 H), 3.67 (t, 1 H, $J = 8.4$ Hz), 3.58-3.41 (m, 4 H), 2.13-2.06 (m, 2 H), 2.04 (s, 3 H), 1.98-1.92 (m, 2 H), 1.74-1.69 (m, 2 H), 1.39-1.32 (m, 2 H), 0.88 (t, 3 H, $J = 7.3$ Hz); IR (thin film): 2924, 1743, 1455, 1363, 1235, 1069, 1029.

11; ^1H NMR (CDCl_3) δ 7.42-7.25 (m, 10 H), 5.90-5.77 (m, 1 H), 5.10-4.80 (m, 6 H), 4.62-4.57 (m, 1 H), 4.37-4.19 (m, 3 H), 3.96-3.89 (m, 1 H), 3.73-2.22 (m, 4 H), 2.22-2.07 (m, 2 H), 2.06, 2.05 (each s, 3 H), 1.81-1.68 (m, 2 H); ^{13}C NMR (CDCl_3) δ 170.9, 138.1, 138.0, 137.7, 128.8, 128.7, 128.3, 128.2, 115.5, 115.3, 98.1, 83.4, 80.5, 78.3, 77.6, 75.8, 75.7, 75.3, 73.2, 69.8, 69.4, 68.0, 66.7, 63.6, 63.1, 58.7, 44.6, 38.4, 33.0, 30.4, 30.2, 29.0, 28.8, 21.1, 18.9; IR (thin film): 2917, 2109, 1740, 1641, 1497, 1455, 1362, 1235, 1073.

12; ^1H NMR (CDCl_3) δ 7.40-7.23 (m, 10 H), 5.49-5.34 (m, 2 H), 4.92 (d, 1 H, $J = 10.8$ Hz), 4.85 (d, 1 H, $J = 10.8$ Hz), 4.79 (d, 1 H, $J = 10.8$ Hz), 4.56 (d, 1 H, $J = 10.9$ Hz), 4.33 (dd, 1 H, $J = 2.0, 12.0$ Hz), 4.27-4.18 (m, 2 H), 3.93-3.86 (m, 1 H), 3.58-3.37 (m, 5

H), 2.16-2.05 (m, 2 H), 2.03 (s, 3 H), 2.00-1.93 (m, 2 H), 1.78-1.65 (m, 2 H), 1.43-1.31 (m, 2 H), 0.88 (t, 3 H, $J = 7.3$ Hz); ^{13}C NMR (CDCl_3) δ 170.9, 138.1, 137.7, 131.3, 129.5, 128.8, 128.7, 128.3, 128.2, 102.4, 83.4, 75.8, 75.3, 73.2, 70.0, 66.6, 63.1, 58.7, 34.9, 33.0, 30.5, 29.6, 29.0, 22.9, 21.1, 13.9; IR (thin film): 2927, 2111, 1744, 1455, 1363, 1235, 1071.

14; ^1H NMR (CDCl_3) δ 7.39-7.21 (m, 10 H), 5.83-5.25 (m, 2 H), 5.02-4.49 (m, 7 H), 4.38-4.13 (m, 3 H), 3.87-3.31 (m, 8 H), 2.09-2.06 (m, 2 H), 2.04 (s, 3 H), 1.85 (s, 3 H), 1.71-1.60 (m, 2 H); IR (thin film): 2920, 1741, 1652, 1558, 1244, 1036.

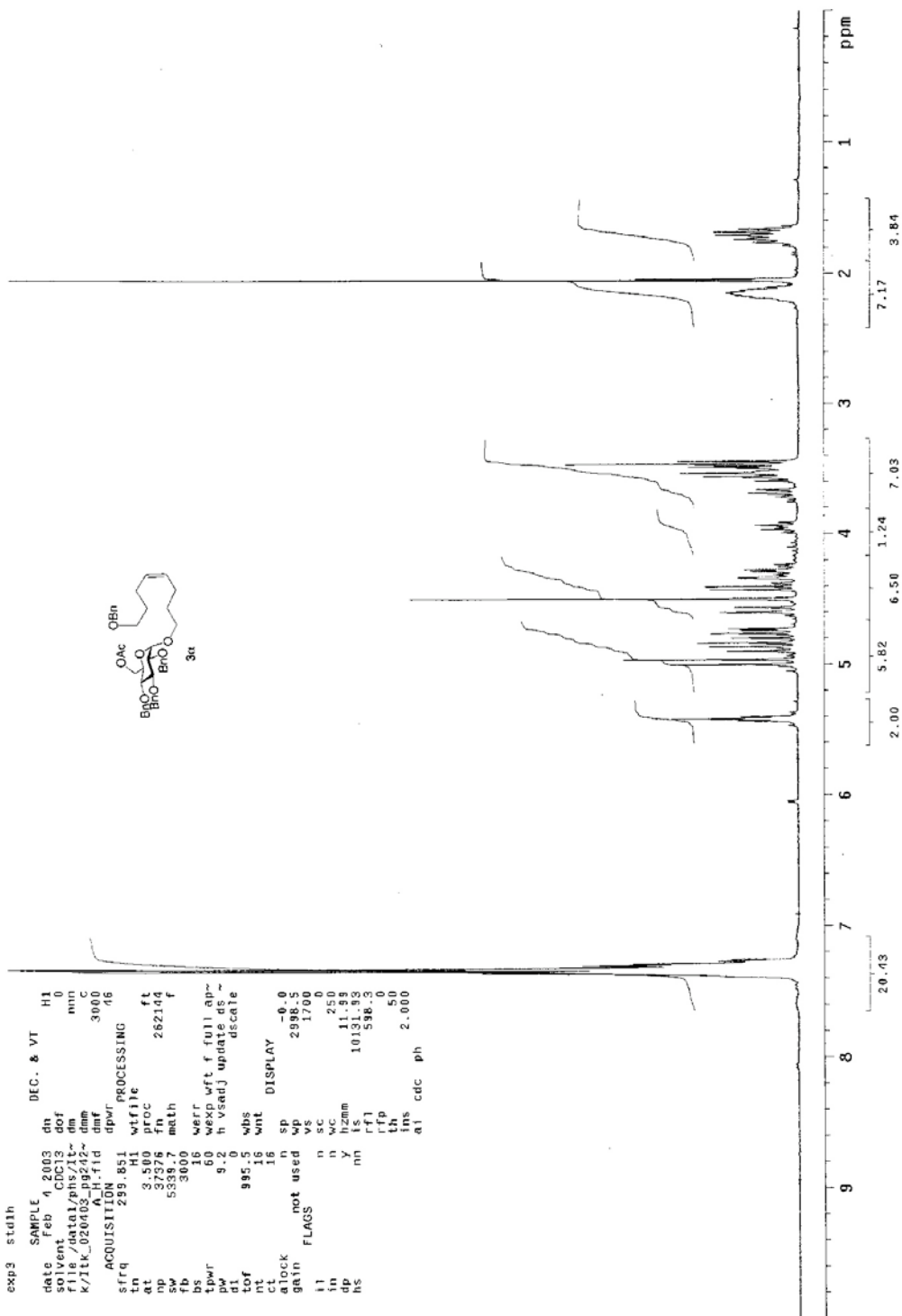
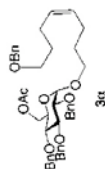
17; ^1H NMR (CDCl_3) δ ^1H NMR (CDCl_3) δ 7.60-7.27 (m, 5 H), 5.47-5.31 (m, 2 H), 5.07-4.91 (m, 1 H), 4.82 (dd, 1 H, $J = 3.7, 10.7$ Hz), 4.67-4.42 (m, 3 H), 4.27-4.21 (m, 1 H), 4.07 (dd, 1 H, $J = 1.1, 3.7$ Hz), 3.98-3.84 (m, 1 H), 3.71-3.43 (m, 6 H), 2.40-1.91 (m, 7 H), 1.77-1.61 (m, 2 H), 1.42-1.25 (m, 2 H), 0.92-0.85 (m, 3 H); ^{13}C NMR (CDCl_3) δ 165.8, 137.7, 131.3, 129.4, 128.7, 128.2, 128.1, 102.6, 98.8, 73.9, 73.1, 71.8, 69.9, 68.2, 61.4, 59.9, 57.7, 47.1, 45.4, 42.3, 34.9, 33.0, 30.5, 29.6, 29.0, 20.8; IR (thin film): 2926, 2110, 1744, 1455, 1363, 1234, 1071.

Glycosylation Reaction on Solid Phase General Procedure. A mixture of octenediol linker bound resin (300 mg, 1 equiv.) and glycosylating agent (2 equiv.) in anhydrous CH_2Cl_2 (10 mL) was shaken at room temperature for 15 min and the suspension was cooled down to -20°C . To the mixture, a solution of 0.5M trimethylsilyltrifluoromethane sulfonic acid in CH_2Cl_2 (0.2 equiv.) was added. The suspension was then shaken under nitrogen atmosphere at -20°C for 1 h. The resin was then washed with CH_2Cl_2 , THF and CH_2Cl_2 . This procedure was repeated twice.

Olefin Metathesis Cleavage Reaction on Solid Phase General Procedure. A mixture of carbohydrate bound resin (120 mg, 1 equiv.), Grubbs' catalyst **8** (0.1 equiv.) and 1-pentene (10 equiv.) in dry CH_2Cl_2 (5 mL) was shaken at 0°C for 10h. The resin was then washed with CH_2Cl_2 . This procedure was repeated twice. The combined CH_2Cl_2 solution was filtered through a short silica gel column to remove the catalyst and washed with hexane/ethyl acetate (70:30). The filtrate was concentrated and then the residue was purified on a silica gel column using hexane/ethyl acetate (80:20) as an eluent to provide octenyl glycoside (82-88% in 2 steps).

STANDARD 1H OBSERVE

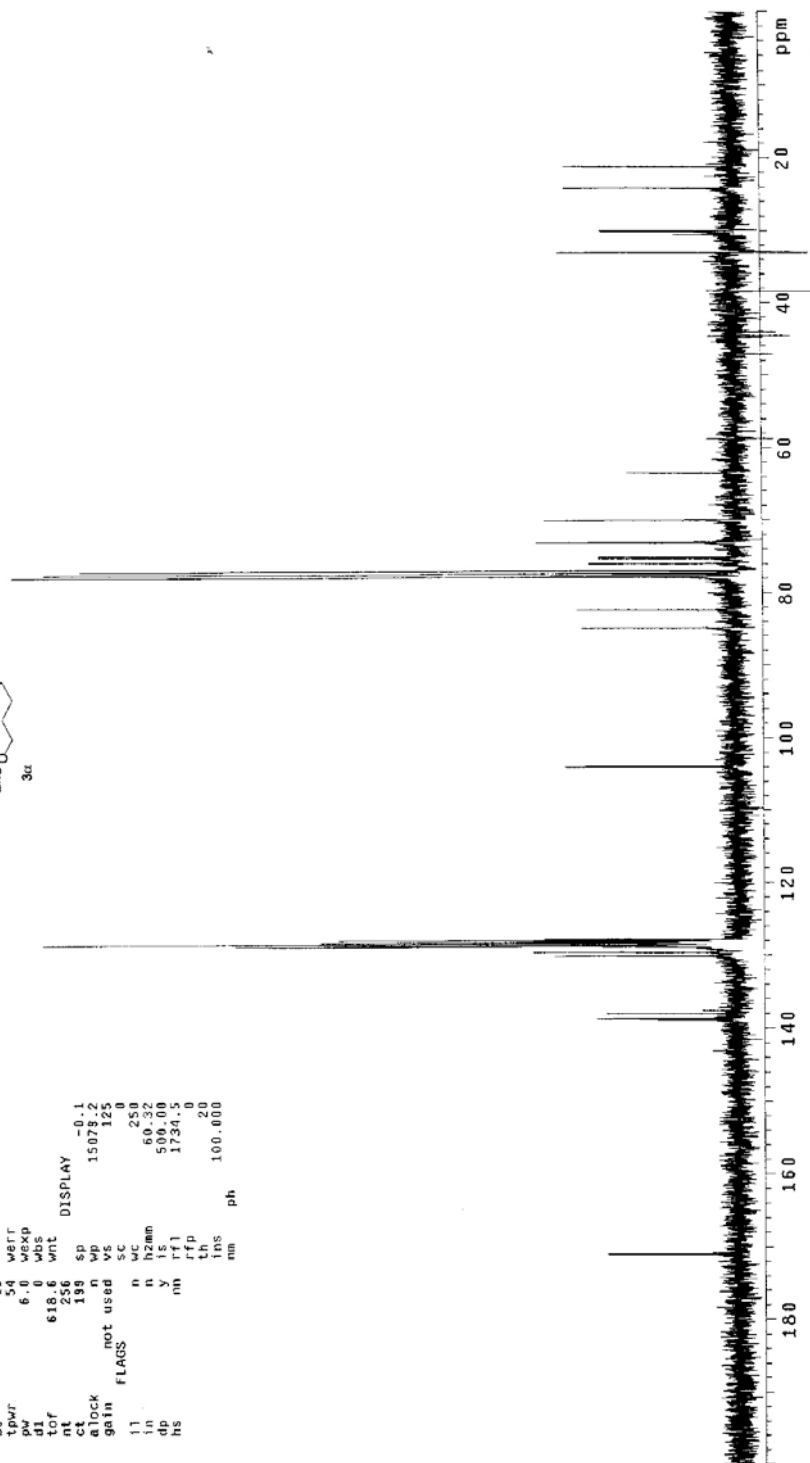
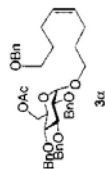
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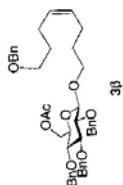
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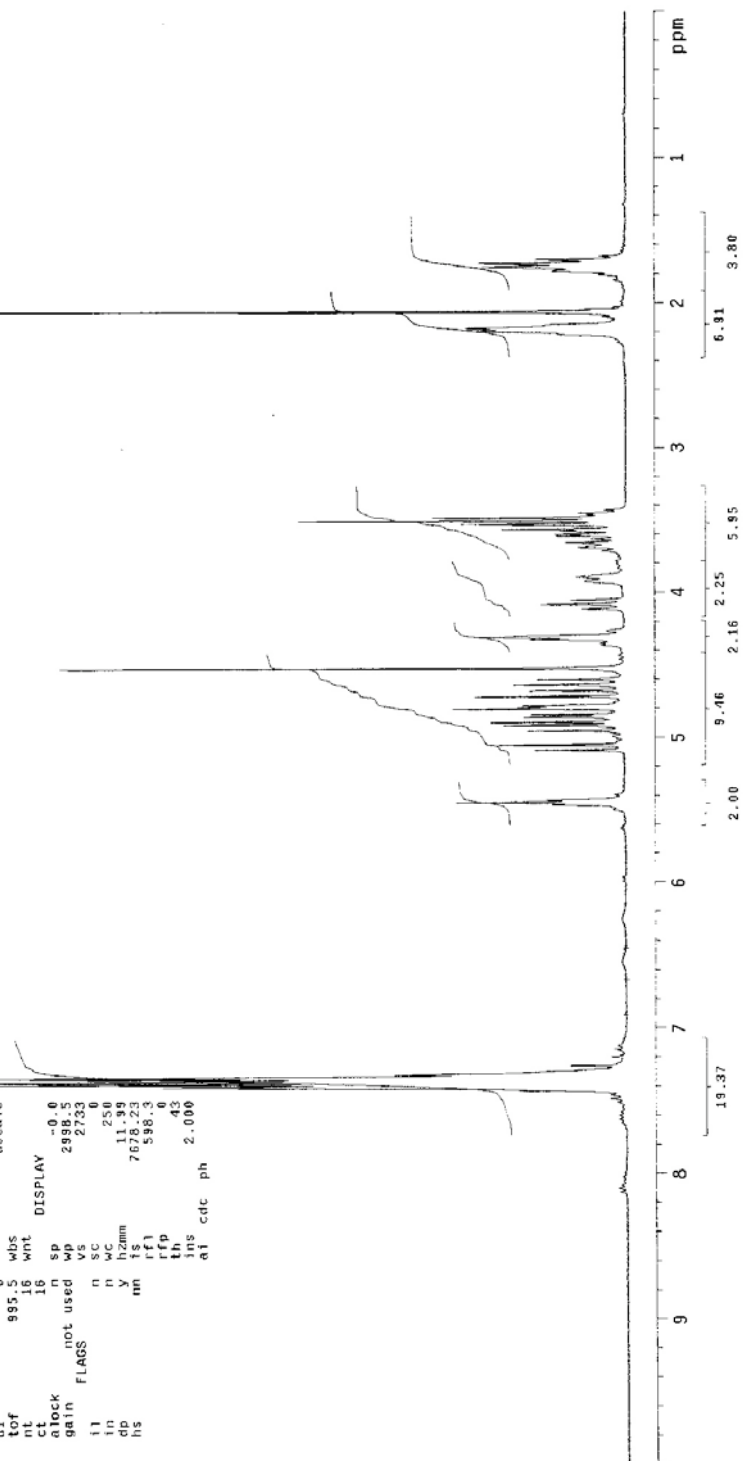
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 ins 43
 at cdc ph 2.000



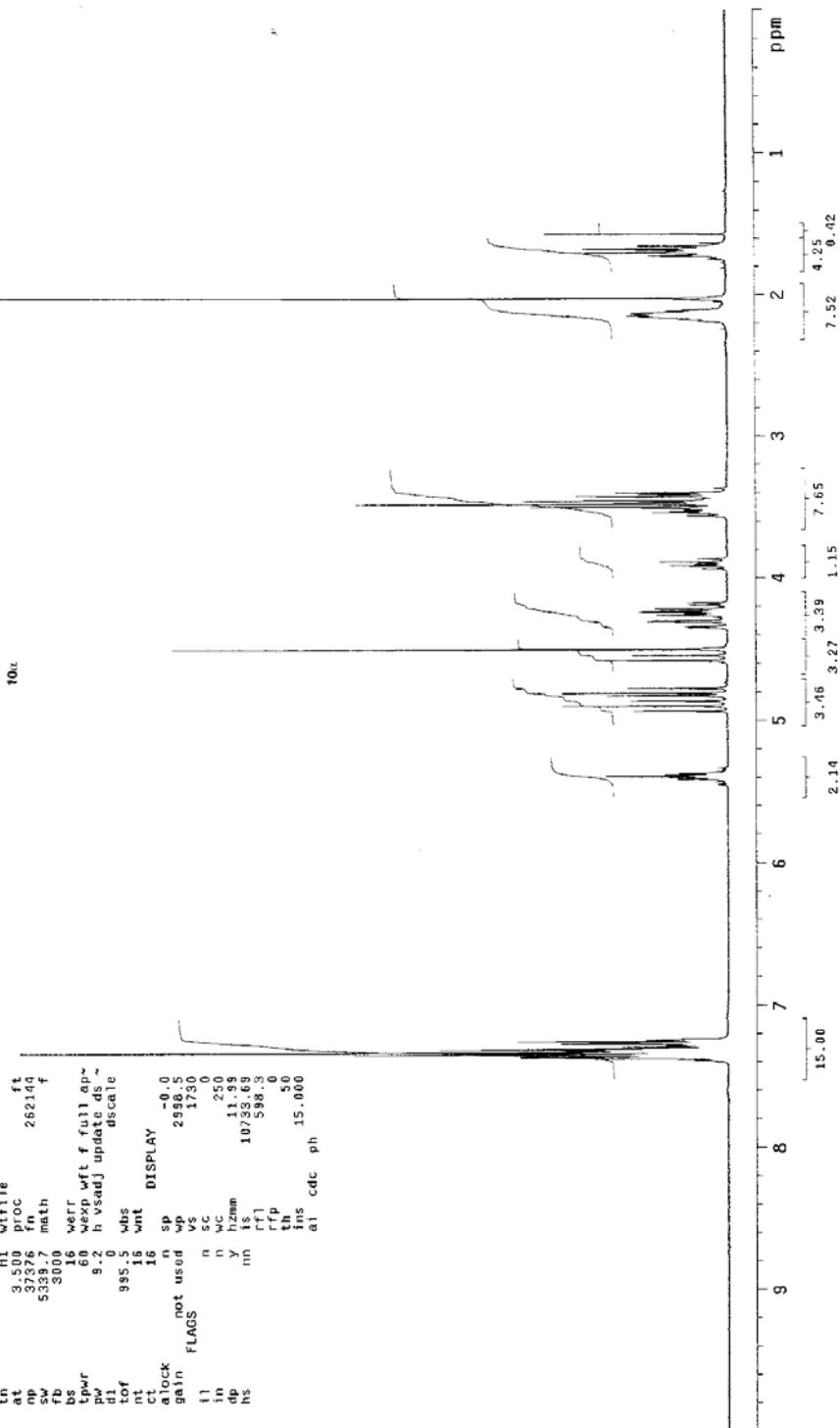
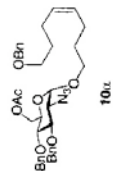
3b



STANDARD 1H OBSERVE

```

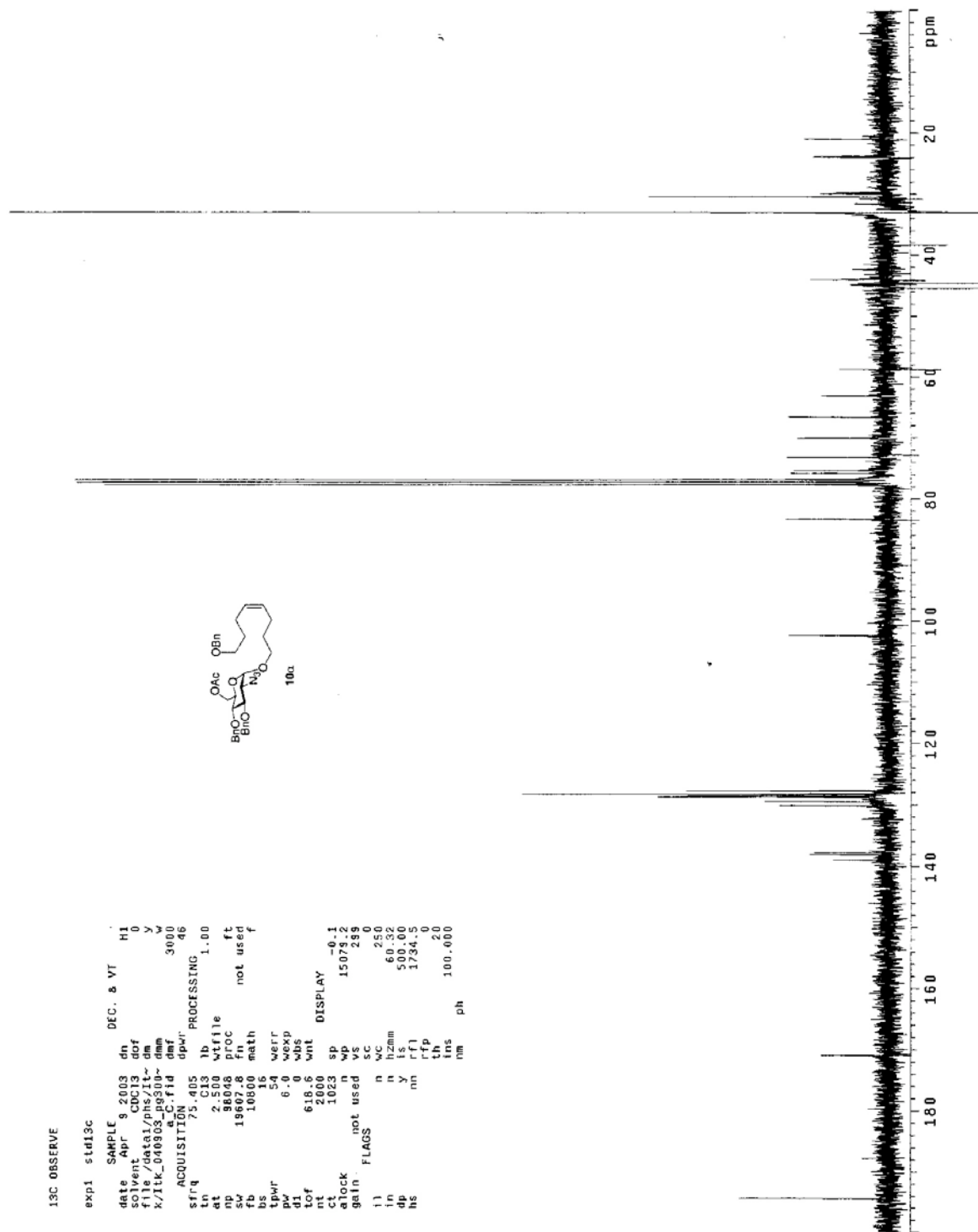
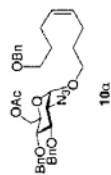
exp1 std1h
SAMPLE
date 2003 dn H1
solvent CDC13 dof 0
file /data1/pns/It- dm
k/Itk_040903-pg300- dnm
a-h.fid dar 3000
ACQUISITION
sfrq 299.851 wifile 46
in 3.500 proc ft
at 37376 fn 262144
np 5339.7 math f
fb 3000
bs 16 werr 16
tpr 60 wexp vft f full ap-
di 9.0 h vstdj update ds-
tof 985.5 wbs
nt 16 wnt
ct 16 DISPLAY
alock n sp -0.0
gain not used wp 299.5
il 173.0
in n sc 250
dp y hznm 11.99
hs nm is 10733.69
rfi 598.3
rfp 0
tms 0
ins 50
at cdc ph 15.000
  
```



13C OBSERVE

exp1 std13c

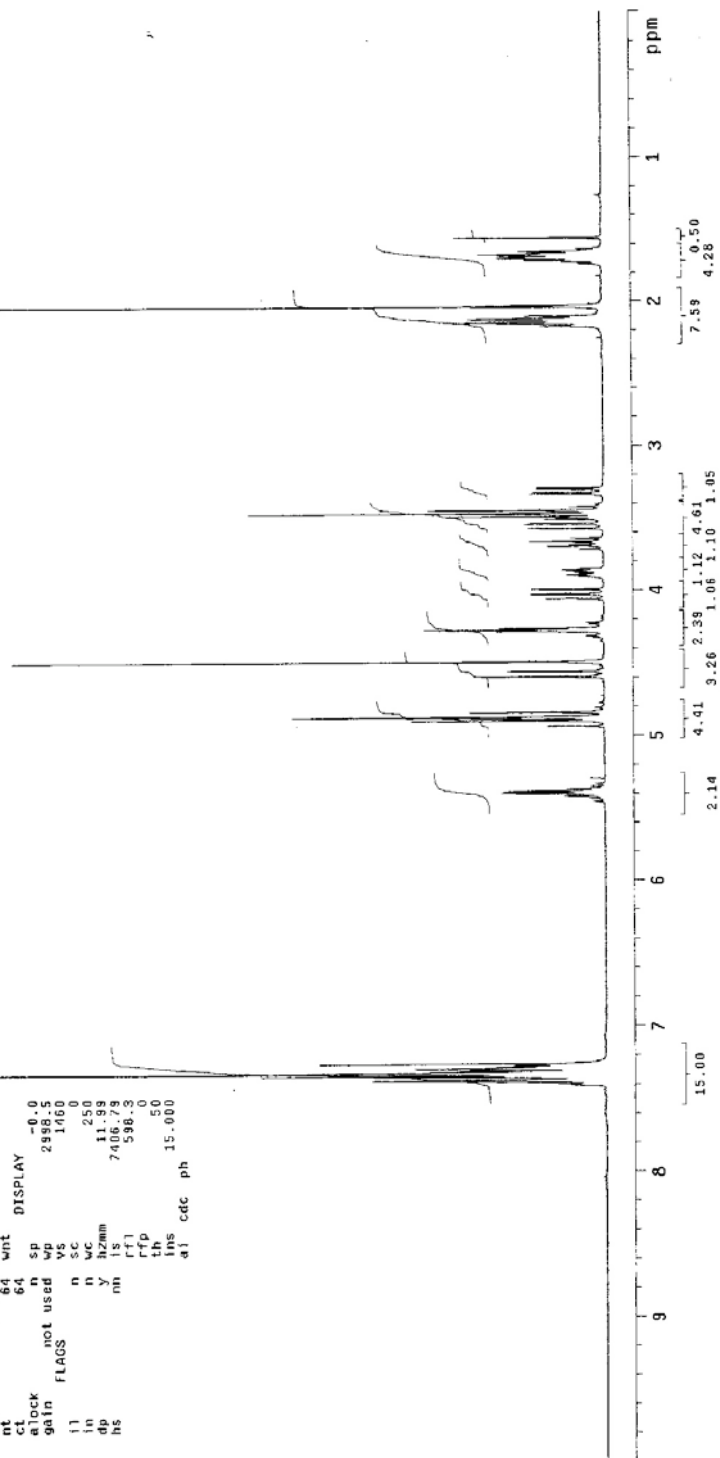
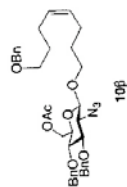
date	Apr 9 2003	dn	H1
solvent	CDCl3	dof	0
file	/data1/pns/it-dm	y	
x/itk_040903	03500-dm	w	
dmr	03500-dm	3000	
acq	03500-dm	46	
ACQUISITION	75.405	PROCESSING	46
tn	C13	lb	1.00
at	2.500	wtfile	
np	98048	proc	ft
sw	19607.8	fn	not used
bs	10600	math	f
bp	15	weir	
tpwr	54	wexp	
pw	6.0	wbs	
d1	0	wnt	
tof	618.6	wt	
nt	2000	sp	0.1
clock	1023	vs	15078.2
gain	not used	sc	289
il	n	wc	0
in	n	hzm	250
dp	y	ts	60.32
hs	nm	rfl	500.00
		tp	1734.5
		trp	0
		trn	20
		ins	100.000
		nm	ph



STANDARD 1H OBSERVE

exp1 std1h

SAMPLE g 2003 dn H1
 date Apr 0
 solvent CDCl3 dof
 file /data1/phs/1t- dm nm
 k/ltk_040903-89300- dm C
 CN1.fid dm 3000
 CN1.fid dm 3000
 ACQUISITION 46
 PROCESSING
 sfrq 298.851
 tn H1 wfile
 at 3.500 proc ft
 np 37276 fn 262144
 sw 5388.7 math f
 fb 3000
 ls 16
 ts 16
 twr 60
 pw 9.2 h vsad) update ds-
 d1 995.5 wbs
 nt 64 wnt
 ct 64
 alock n
 gain not used vs
 flags n sc
 il n sc 0
 in n wc 250
 dp y hzmm 11.99
 hs nm 7406.79
 rll 598.3
 rfp 50
 th 50
 lns 15.000
 al cdc ph

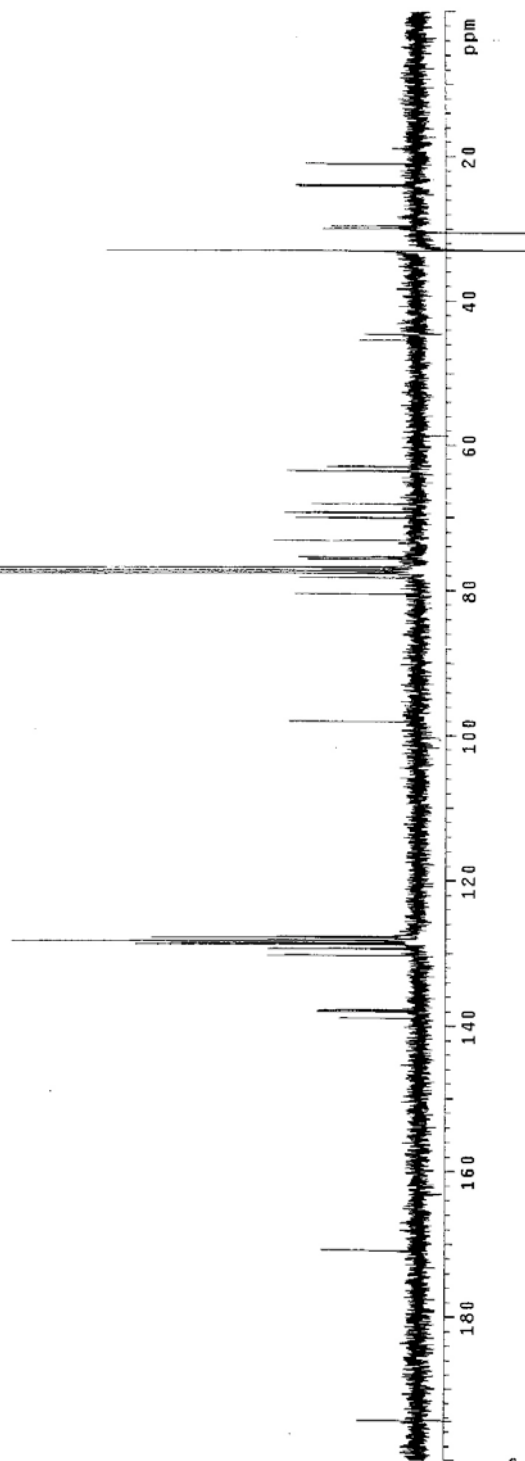
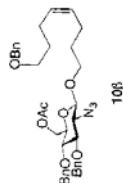


S13

13C OBSERVE

exp1 std13c

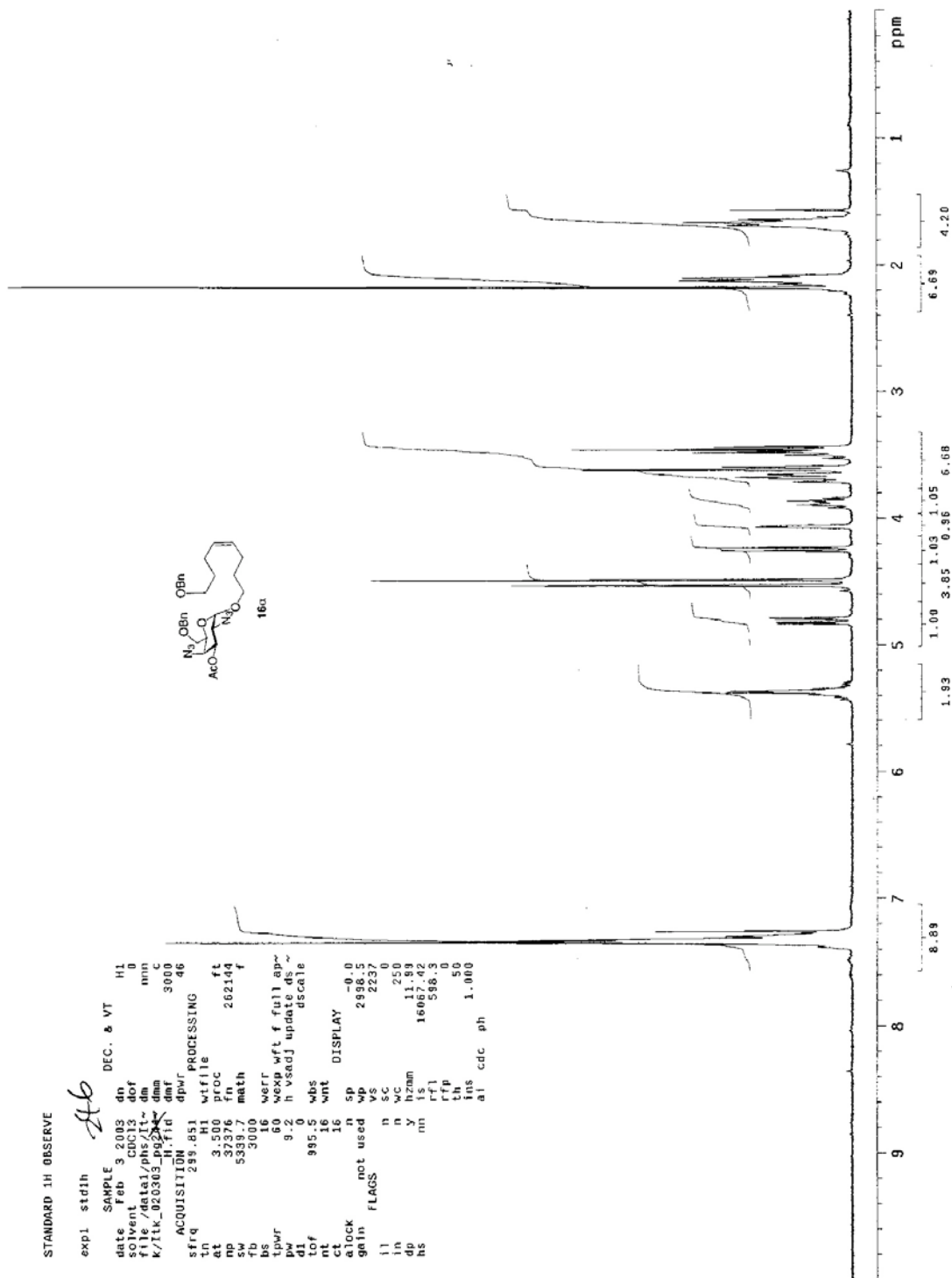
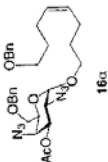
SAMPLE		DEC. & VT		H1
date	Apr 11 2003	dn		0
solvent	CDC13	dof		Y
file	/data1/pts/it~dm	dm		W
k/itk_041103~C9300~dm		dm		3000
ACQUISITION	75.405	dpwr	PROCESSING	46
tn	C13	lb		1.00
at	2.500	wtfile		
np	98048	proc	ft	
sw	19807.8	fn	not used	f
tb	10600	math		
td	54	werr		
tpwr	6.0	wexp		
d1	0	wbs		
tof	618.6	wnt		
nt	2000	sp	DISPLAY	-0.0
clock	859	wp		150792
gain	not used	sc		3650
il		sc		250
in		n	h2mm	60.32
dp		y	ls	500.00
hs		nm	rfp	7558.3
			rfp	5622.9
			lms	100.000
			al	ph



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STANDARD 1H OBSERVE

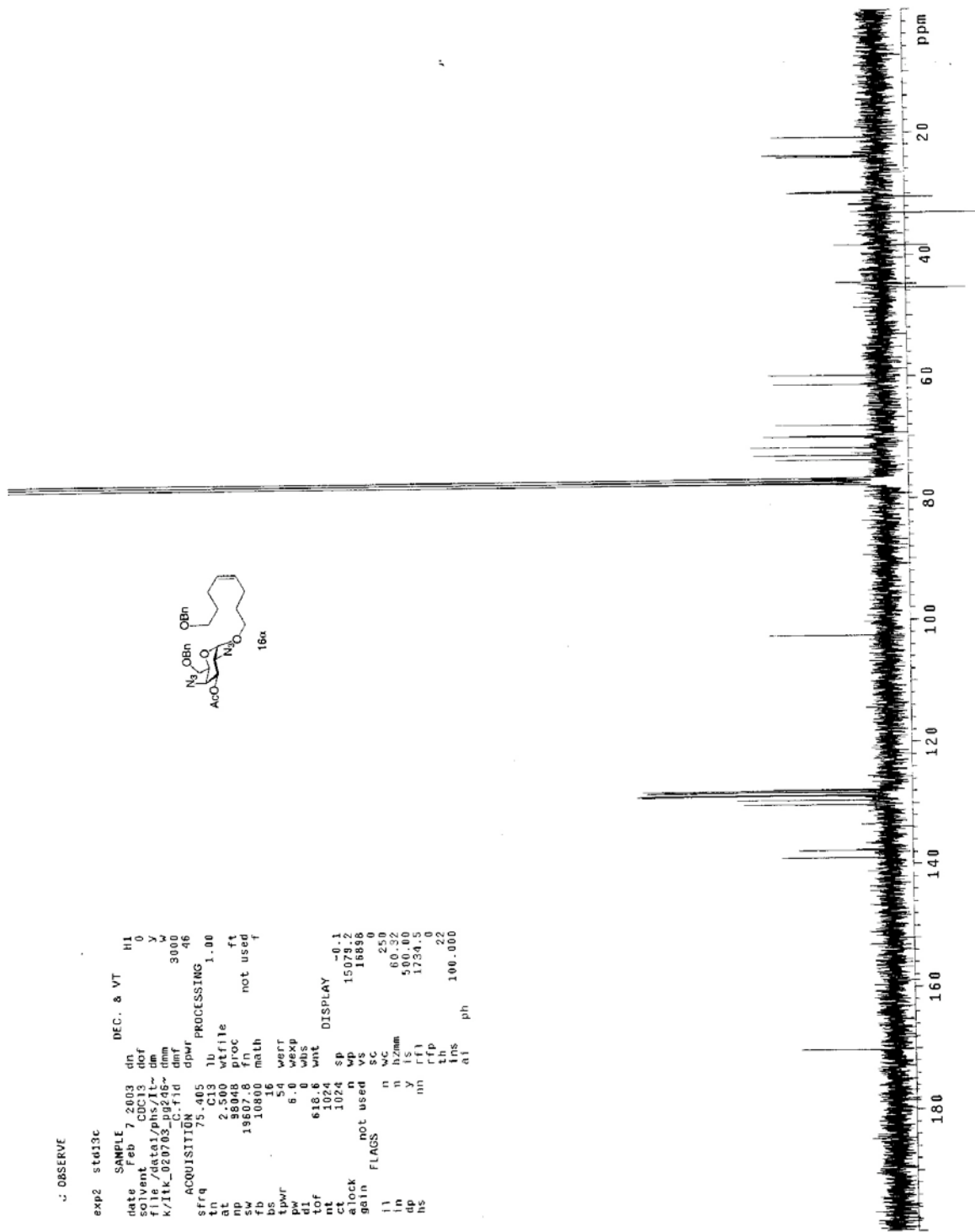
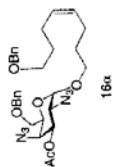
expl stdlh *46* DEC. & VT
 date Feb 3 2003 dn
 solvent Feb 3 2003 dn
 file /data1/pbs/11~ dn
 k/tlk_020303_p024~ dnm
 _n_fid dmf 3000
 ACQUISITION
 sfrq 299.851 wfile
 tn 3.500 roc ft
 at 32376 f16 262144
 sw 5339.7 math
 fb 3000
 bs 16 werr
 tpwr 60 wep wft f full ap~
 pw 9.2 n vsadj update ds~
 dt 0 wbs
 tcf 995.5
 nt 16 wnt
 ct 16
 alock n sp
 gain not used wp 2998.5
 flags vs 2237
 ll n sc 0
 ln n sc 250
 ds y hznm 11.89
 bs nm ls 16067.42
 rfl 588.3
 rfp 0
 th 50
 al cdc ph 1.000



S15

exp2 std13c

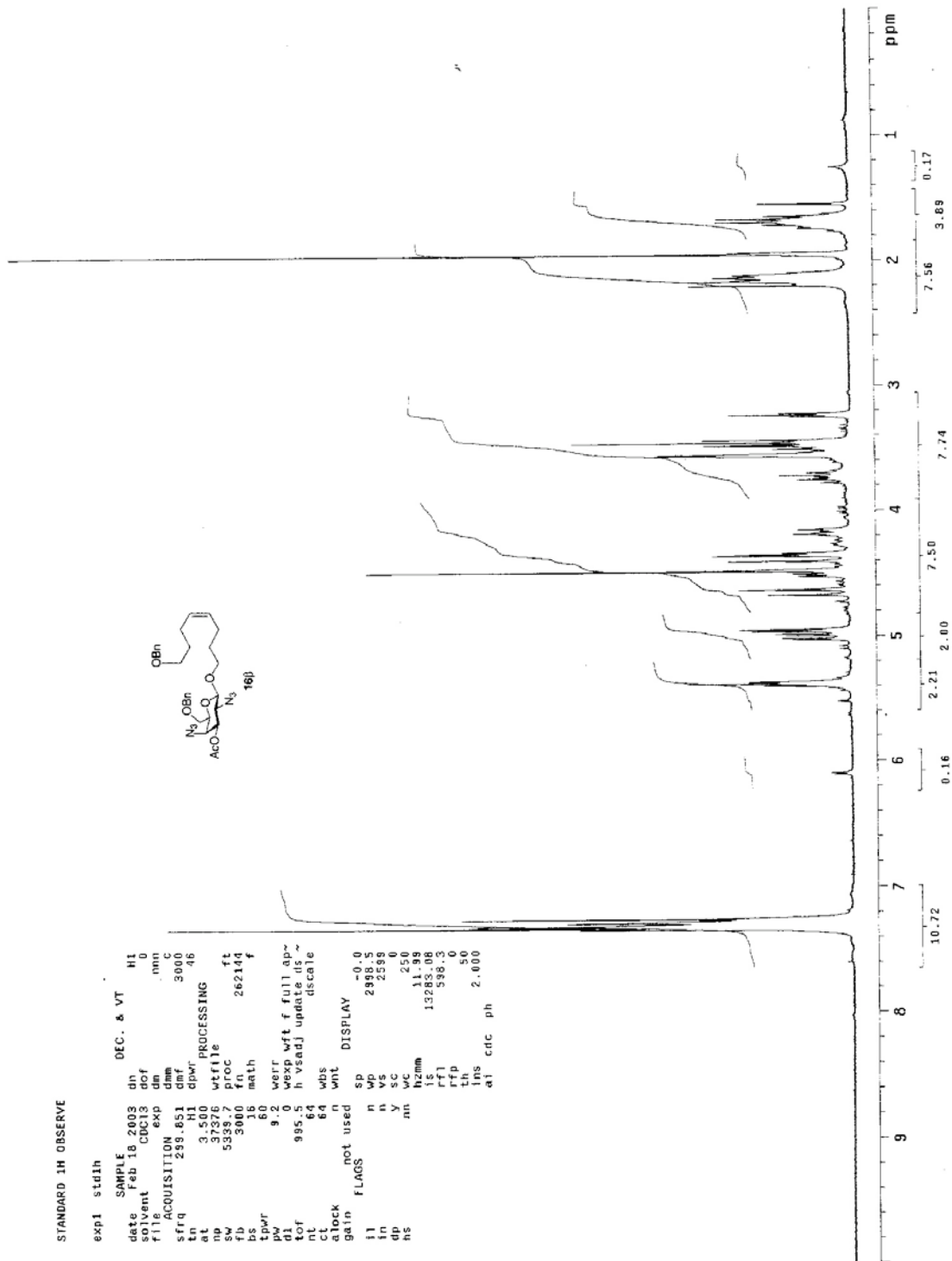
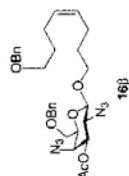
SAMPLE DEC. & VT
 date Feb 7 2003 dn H1
 solvent CDCl3 dof 0
 file /data1/phs/1t~ dm y
 k/1tk_020703_09246~ dmm x
 C.fid dmf 3000
 ACQUISITION 46
 75 C13 1u
 tn 2.500 vtfile 1.00
 at 88048 proc ft
 sw 19607.8 fn not used
 fb 10490 math f
 bs 54
 tpwr 54 wext
 pw 6.0 wexp
 d1 0 wbs
 nt 618.6 wnt
 ct 1024
 alock n
 gain not used sp
 15079.2
 18856
 0
 250
 60.32
 500.00
 1734.5
 0
 22
 100.000
 al ph



STANDARD 1H OBSERVE

```

exp1 std1h
SAMPLE
date Feb 18 2003 dn DEC. & VT H1
solvent CDCl3 dof 0
file exp dm nnn
ACQUISITION 851
sfrq 299.851 dnm 3000 c
nucl 13C dpr 48
at 3.500 wtfile
nb 37376 proc ft
sw 5335.7 fn 262144
bs 3000 math f
tpwr 60 werr
dpr 9.0 wexp wft f full ap~
nt 995.5 h vsadj update ds~
ct 64 wbs
alock n wnt
gain not used sp DISPLAY -0.0
il n sp 2998.5
in n vs 2559
dp y sc 0
hs nn
hzmm 250
ls 11.99
f1 13283.08
rf1 536.3
th 50
ins 2.000
ai cdc ph
  
```

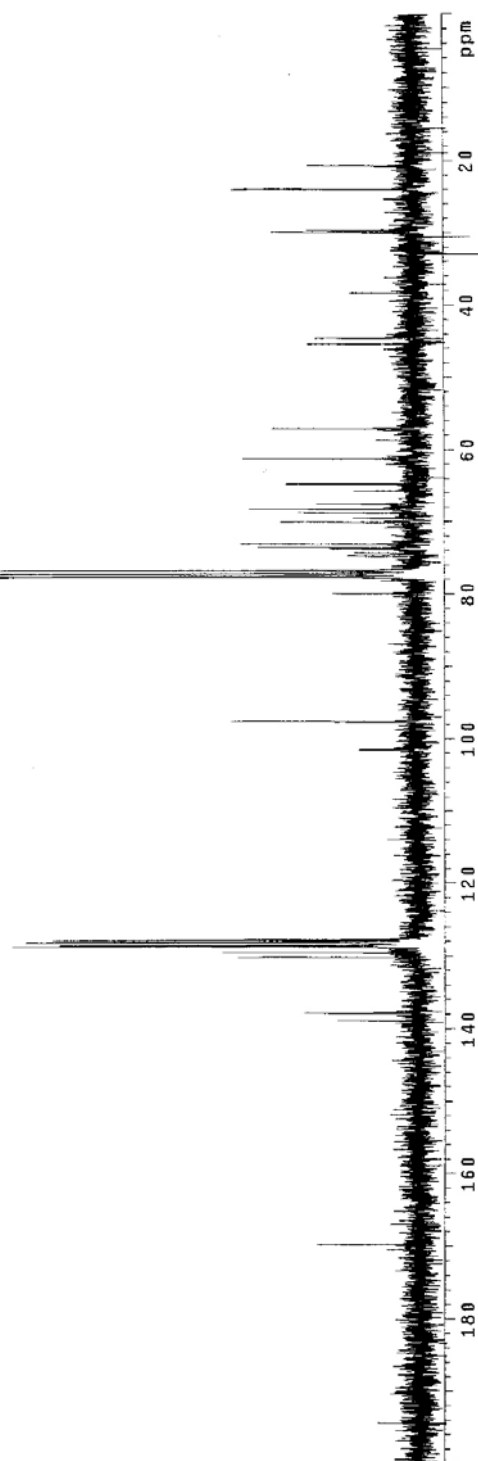
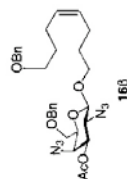


S17

13C OBSERVE

exp2 std13c

SAMPLE		DEC. & VT		H1	
date	May 10 2003	dn			0
solvent	CDC13	dof			Y
file		dm			W
ACQUISITION		exp			3000
sfrq	75.405	dnt			46
tn	2.130	lb			1.00
at	96098	proc			not used
sw	19607.8	ft			f
fb	10800	math			
bs	16	werr			
tpwr	54	exp			
pw	6.0	whs			
dt	619.6	wnt			
nt	4000	DISPLAY			
ct	1284	sp			-0.1
alock	not used	wp			15079.2
gain		vs			332
l1		vc			0
l2		h2mm			250
ds		ls			60.32
hs		rfl			500.00
		th			1734.5
		ins			0
		nm			100.000
		ph			

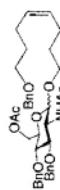


518

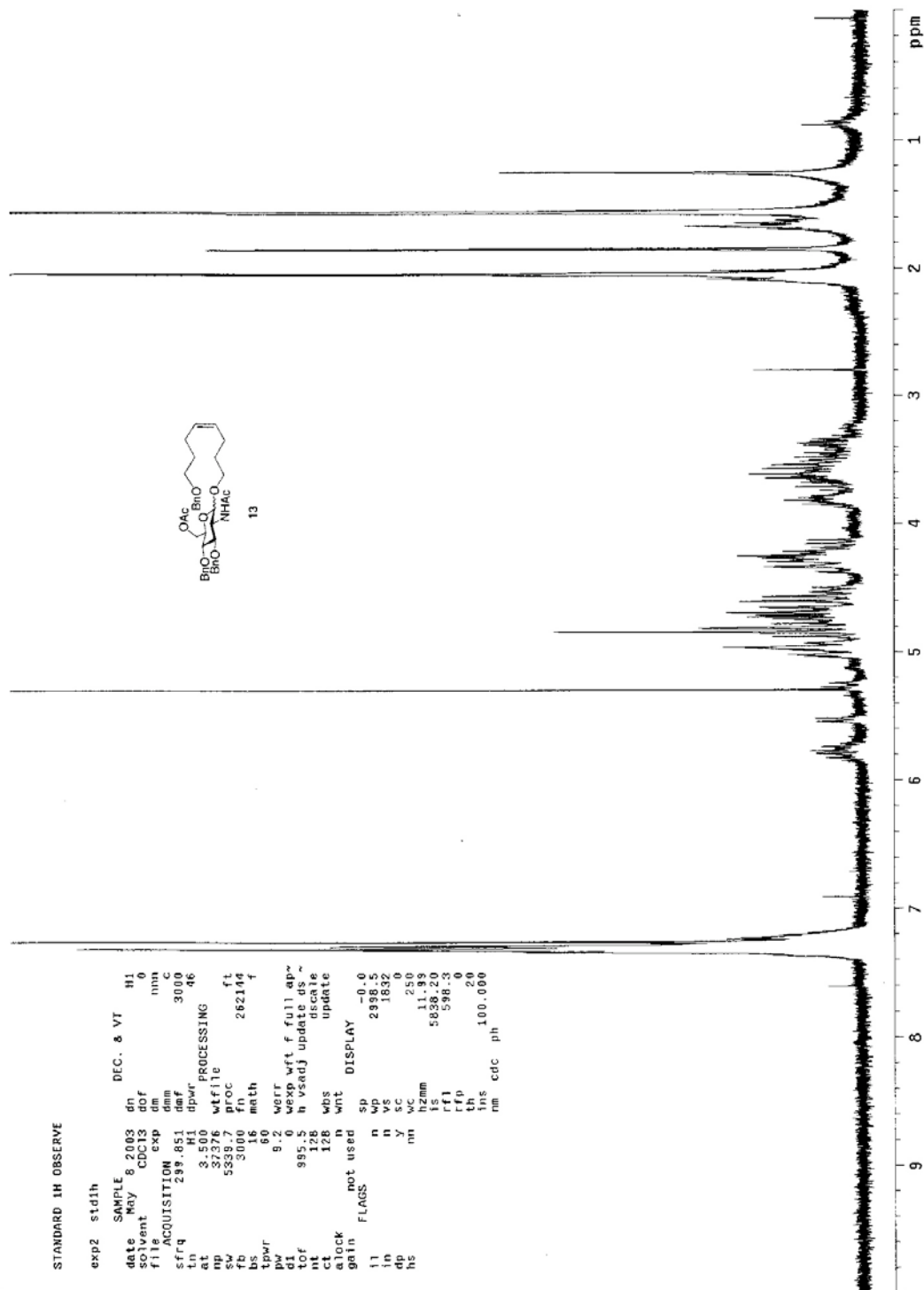
STANDARD 1H OBSERVE

exp2 std1h

SAMPLE
 date May 8 2003 dn DEC. & VT H1
 solvent CDC13 dof 0
 file exp dm nm
 ACQUISITION exp dm C
 sfrq 299.851 def 3000
 in H1 dpr PROCESSING 46
 at 3.576
 sw 32376 wfile
 sb 5339.7 proc fl
 fb 3000 fn 262144
 bs 16 math f
 tpwr 60
 pw 9.2 verr
 di 0 wexp wft f full ap~
 acf 995.5 n vsadj update
 ct 128 wbs
 ct 128 wbs update
 alock n wnt
 gain not used
 flags
 il sp -0.0
 in n 2998.5
 de n 1632
 bs y 0
 nm
 hzmm 250
 is 11.99
 rf1 5038.20
 rf2 598.3
 rfp 0
 rfs 20
 rms 100.000
 nm cdc ph



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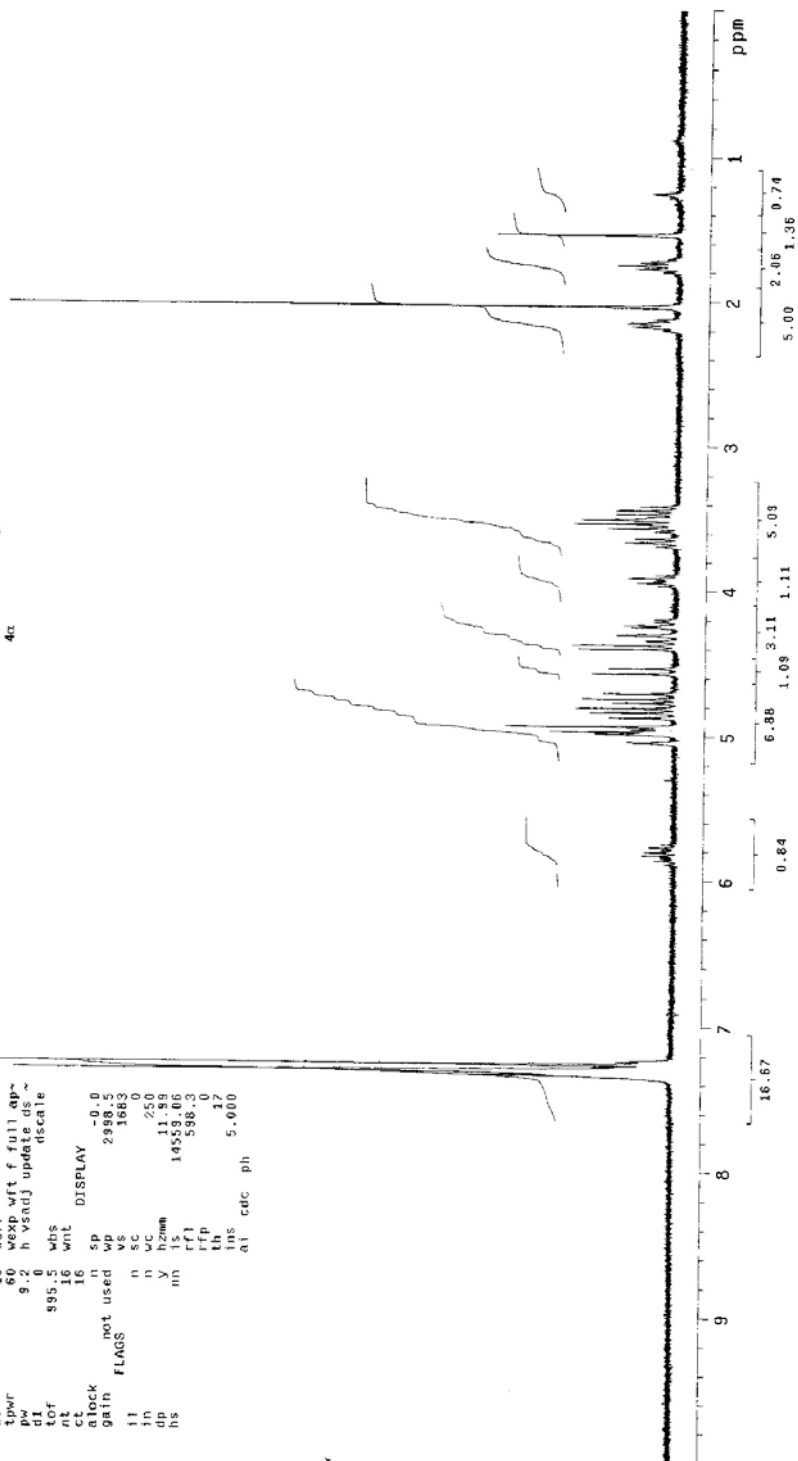
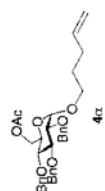


S19

STANDARD 1H OBSERVE

exp1 std1h

SAMPLE
 date Jan 27 2003 dn H1
 solvent CDCl3 dof 0
 file /data1/pbs/1t~ dm nm
 k/ltk_012703_pg143~ dm C
 dm 3000
 dprc 46
 ACQUISITION
 sfrq 299.851
 tn H1 wfile
 at 3.500 proc ft
 np 37376 fn 262144
 sw 5338.7 math f
 lb 3000
 bprc 16
 twrr 60
 pw 9.2 h vsadj update ds~
 dt 895.5 whs
 nt 16 wnt
 ct 16
 check n
 gain not used sp
 flags VS 299853
 it n SC 1683
 in n WC 0
 dp n Y hzmm 250
 hs nm 11.99
 rf 14559.06
 th 596.3
 ti 0
 tr 1
 ins 1
 al cdc ph 5.000



STANDARD 1H OBSERVE

exp1 stdih

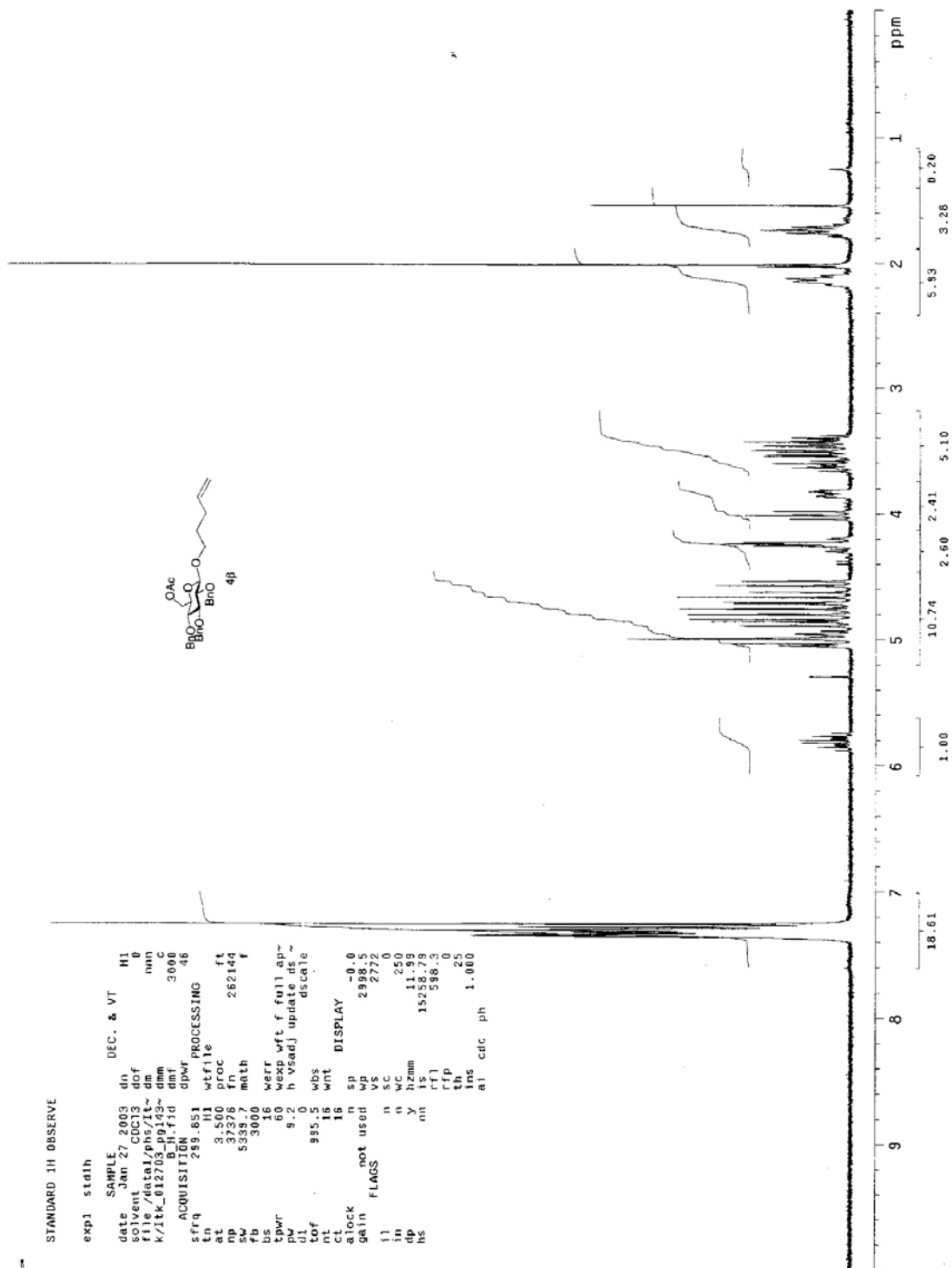
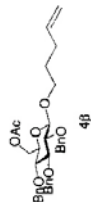
SAMPLE DEC. & VT H1
 date Jan 27 2003 dn
 solvent CDCl3 dof
 file /data1/pbs/it~dm
 k/itk_012703_dp143~dm
 dm 3000 C
 dnm 4000
 dpr PROCESSING 46

ACQUISITION
 sfrq 289.851
 tn H1 wtfile
 at 3.500 proc ft
 np 37376 fn 282144
 pw 538.7 math f
 pr 3000
 bs 16 weir
 tovr 60 wexp wft f full ap~
 dl 9.2 h vsadJ update ds~
 dscale

nt 995.5 wbs
 nt 16 wnt
 nt 16 wnt

clock
 gain not used vs
 flags
 il n sc 0
 in n wc 250
 dp y hzmm 11.99
 hs nt 15258.79
 rfi 538.0
 rfp
 th 25
 lns
 al cdc ph 1.000

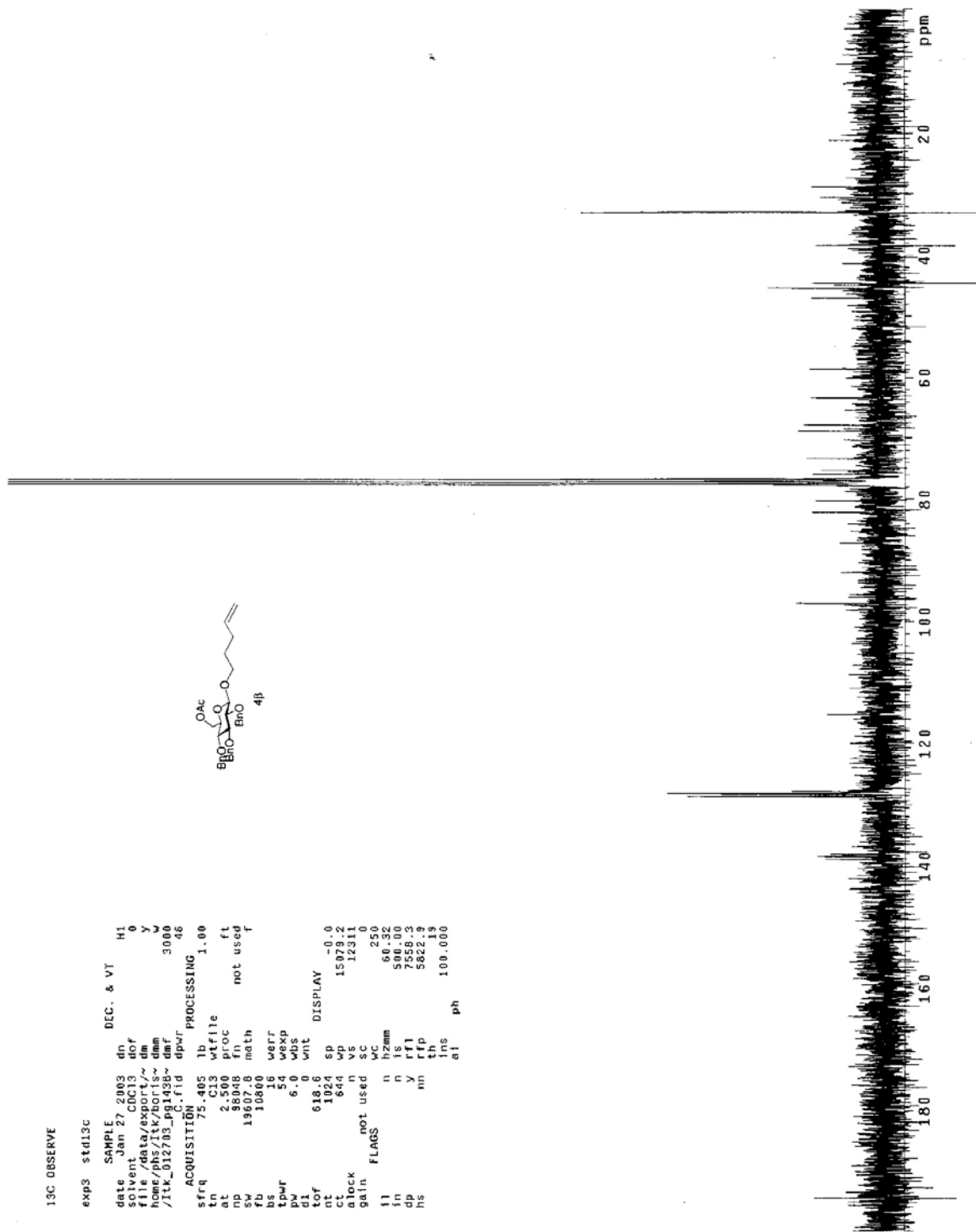
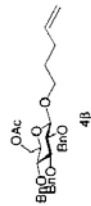
DISPLAY -0.0
 2998.5
 2772



13C OBSERVE

exp3 std13c

SAMPLE		DEC. & VT	
date	Jan 27 2003	dp	H1
solvent	CDCl3	do	0
file	/data/export/~	dm	y
home/pbs/ltk/borisw	dam	dm	y
/ltk_012703_pg1438w	dam	dm	y
C.fid	dpwr	dm	3000
ACQUISITION	405	lb	PROCESSING
sfreq	75.405	lb	1.00
at	2.500	proc	ft
np	88048	fn	not used
sw	19607.8	meth	f
fb	10800	verr	
bs	16	exp	
tpwr	54	wt	
el	6.0	wt	
nt	618.6	sp	-0.0
ct	1024	vp	15079.2
alock	644	ve	12311
gain	not used	sc	0
fl	FLAGS	h2mm	250
in	n	is	60.32
dp	y	rfl	500.00
hs	nn	rfl	7558.3
	th	ins	5822.9
	al	ins	100.000
		ph	

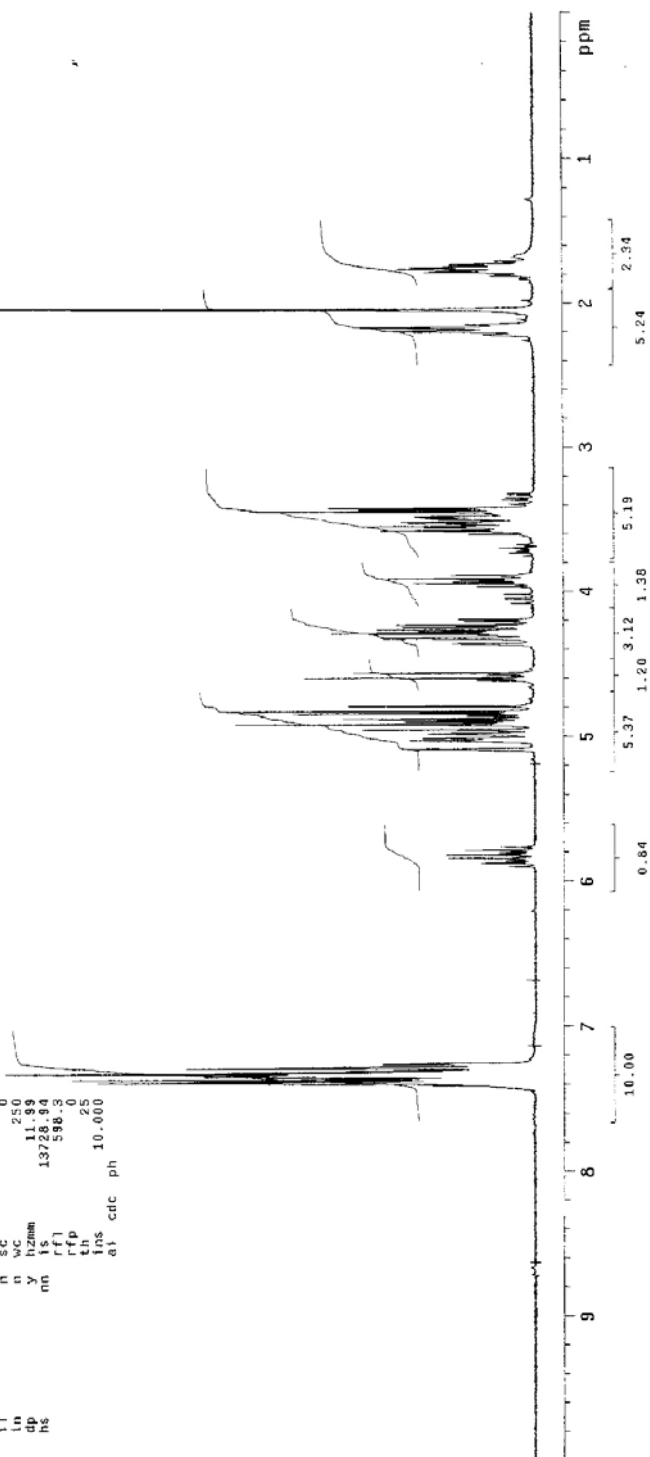
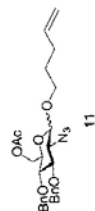


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STANDARD 1H OBSERVE

```

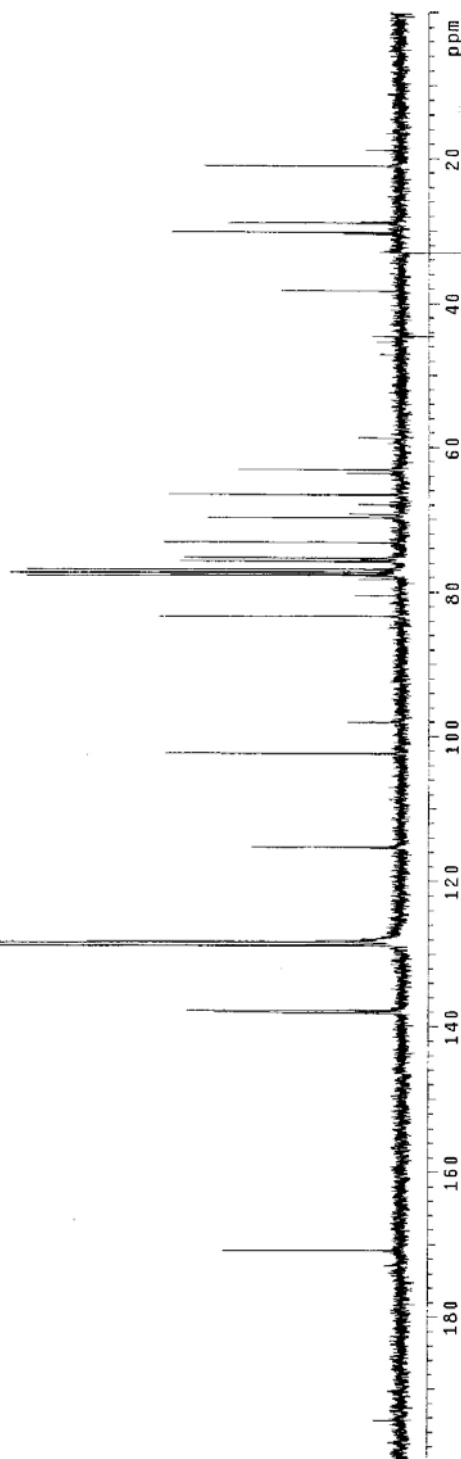
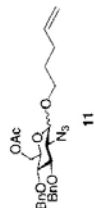
exp1 std1h
SAMPLE      2003      .H1
date       May 05013
solvent    CDCl3
file       /data1/pbs/11~
k/ltk_050803_pp204~
             dmh      C
             N.fid     3000
             dmf       46
ACQUISITION
sfrq      299.851
tn         3.501
nt         37376
sw         5339.7
fb         3000
bs         16
tpwr       60
pw         9.2
de         995.5
tf         16
nt         16
ci         16
alock      not used
gain       2996.5
l1         0
l2         0
dp         250
hs         11.89
nm         13728.94
rfl        596.3
rfp         0
th         25
lms        10.000
at cdc ph
  
```



13C OBSERVE

expl std13c

SAMPLE		DEC. & VT		H1
date	May 6 2003	dn		0
solvent	CDCl3	dof		Y
file	/data1/phs/It~	dm		W
k/itk_050805_09204~	dmf	dmf		3000
C.fid				
ACQUISITION 405				
sfreq	75.405	lb	PROCESSING	46
at	2.500	wtfile		1.00
np	38048	proc		ft
sw	19507.8	fn	not used	f
fb	10880	math		
bs	16	verr		
tpwr	55	wdw		
gm	6.0	gbs		
d1	618.6	wnt		
nt	256		DISPLAY	-0.1
ct	256	sp		15079.2
alock	not used	vc		3137
gain		sc		0
fl		h2mm		250
in		y	ls	60.32
dp		nn	rfl	500.00
hs			rfd	1734.5
			th	0
			ins	6
			at	100.000
			ph	

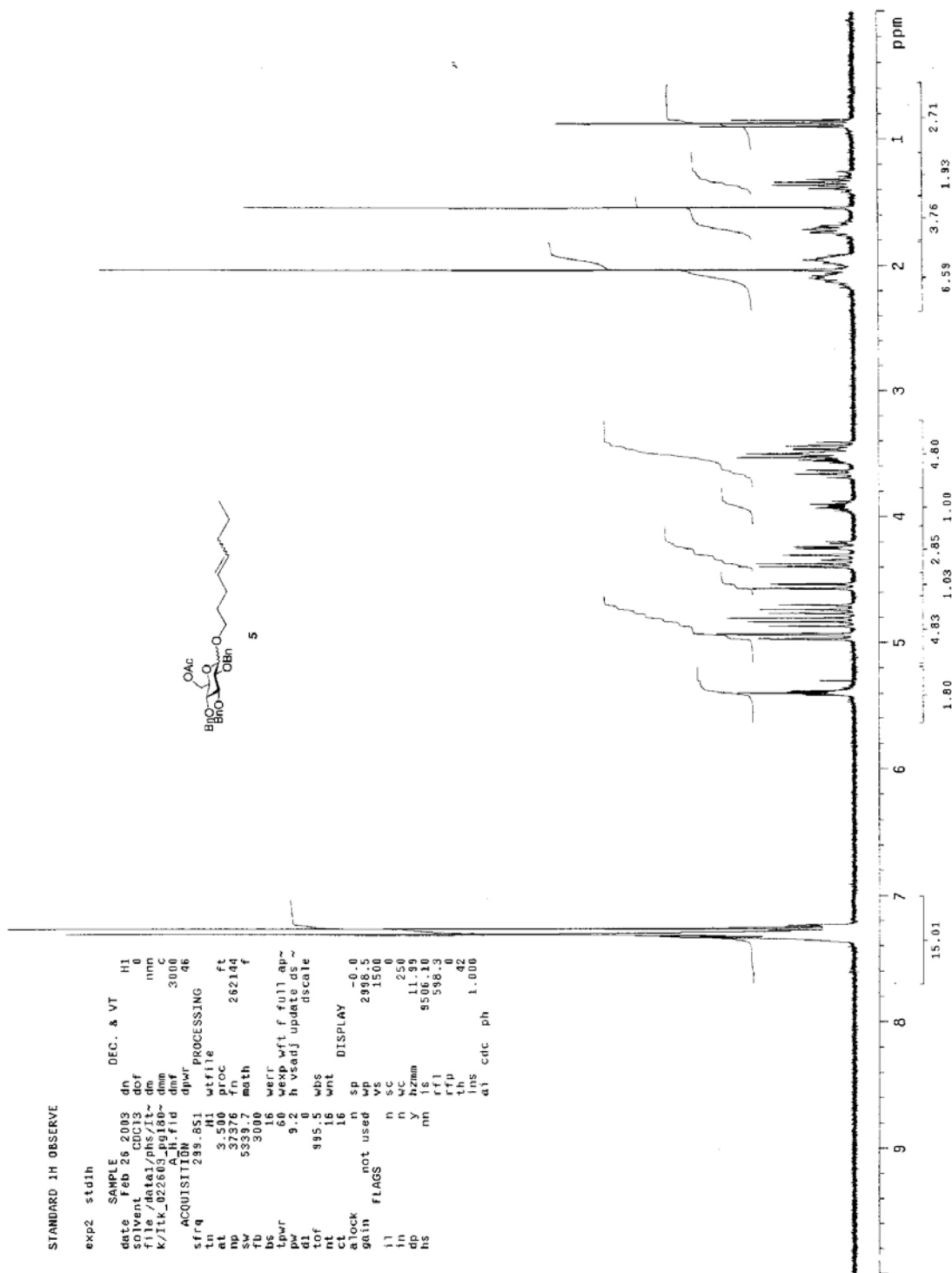
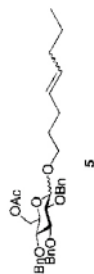


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STANDARD 1H OBSERVE

exp2 std1h

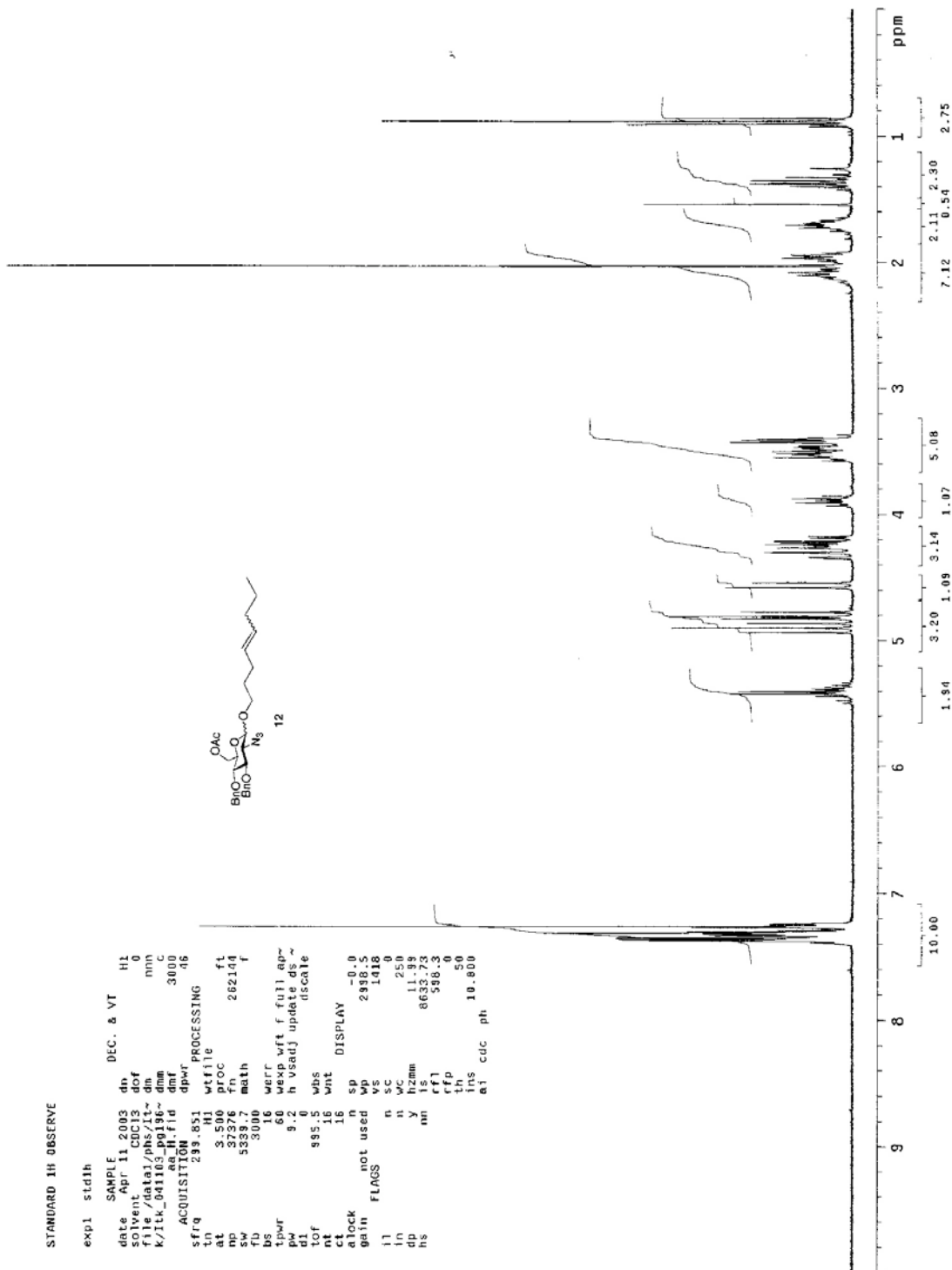
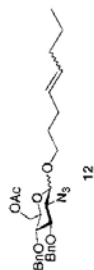
SAMPLE
date Feb 26 2003 dn DEC. & VT H1
solvent CDCl3 def 0
file /data1/pbs/it~ nnn
K/1tk_022603_p0180~ c
nmr 3000
ACQUISITION: f1d dmr 46
PROC. PROCESSING
sfrq 299.851 wfile
at 3.500 proc ft
np 37376 fn 262144
sw 5339.7 math f
td 3000
f2 3000
t1 3000
t2 3000
pw 9.2 hvsadj update ds~
nt 895.5 wbs
nt 16 wnt
ct 16 wnt
atlock n
gain not used
flags n sc 0
il n sc 0
in n wc 250
dp y hzmm 11.89
hs nn ls 9506.10
rfi 586.3
t1p 0
t2p 0
t3p 42
ins 1.000
d1 cdc ph



STANDARD 1H OBSERVE

```

exp1 stdh
SAMPLE
date      11.2003   dp
solvent    CDCl3    dof
file      /data1/pbs/11~ dm
k/ltk_041103_pg196~ dmm
aa_h_fid   3000    c
dmf        46
ACQUISITION
sfrq      299.851  ft
nu1       3500    ft
at        37376   fn
np        3339.7  math
sw        3000    f
fb        16      werr
bs        60      wexp wft f full ap~
tpwr      9.2    n vsadj update ds~
pw        885.5   wbs
tof       16      wnt
nt        16      DISPLAY
ct        16      alock
gain      not used
il        n      wp
in        n      vs
dp        n      vc
hs        n      hzmm
nn        15     11.99
rf1       8632.73
rfp       598.3
th        0
ins       50
at1       10.800 cdc ph
  
```



13C OBSERVE

exp4 std13c

SAMPLE DEC. & VT N1
date Apr 11 2003 dn
solvent CDCl3 dof
file /data/export/~dm
home/pbs/ltk/poris~dm
/ltk_041103_pg136a~dmf 3000 W
a_c.fid dpwr 46
ACQUISITION 405 1b
sfreq 75.205 1b
at 2.503 wfile
nt 2.500 proc ft
np 58048 fn not used
sw 19607.8 math f
fb 10800
bs 16 werr
tpwr 54
pw 6.0 wds
cl 6.0 wnt
nt 618.6 sp
ct 1000 sp
ct 564 wp
galt not used
f1 flags
in n bnm
dp y rfi
hs nm rfp
tms th 14
al ph 100.000

DISPLAY

-0.0

15079.2

6422

250

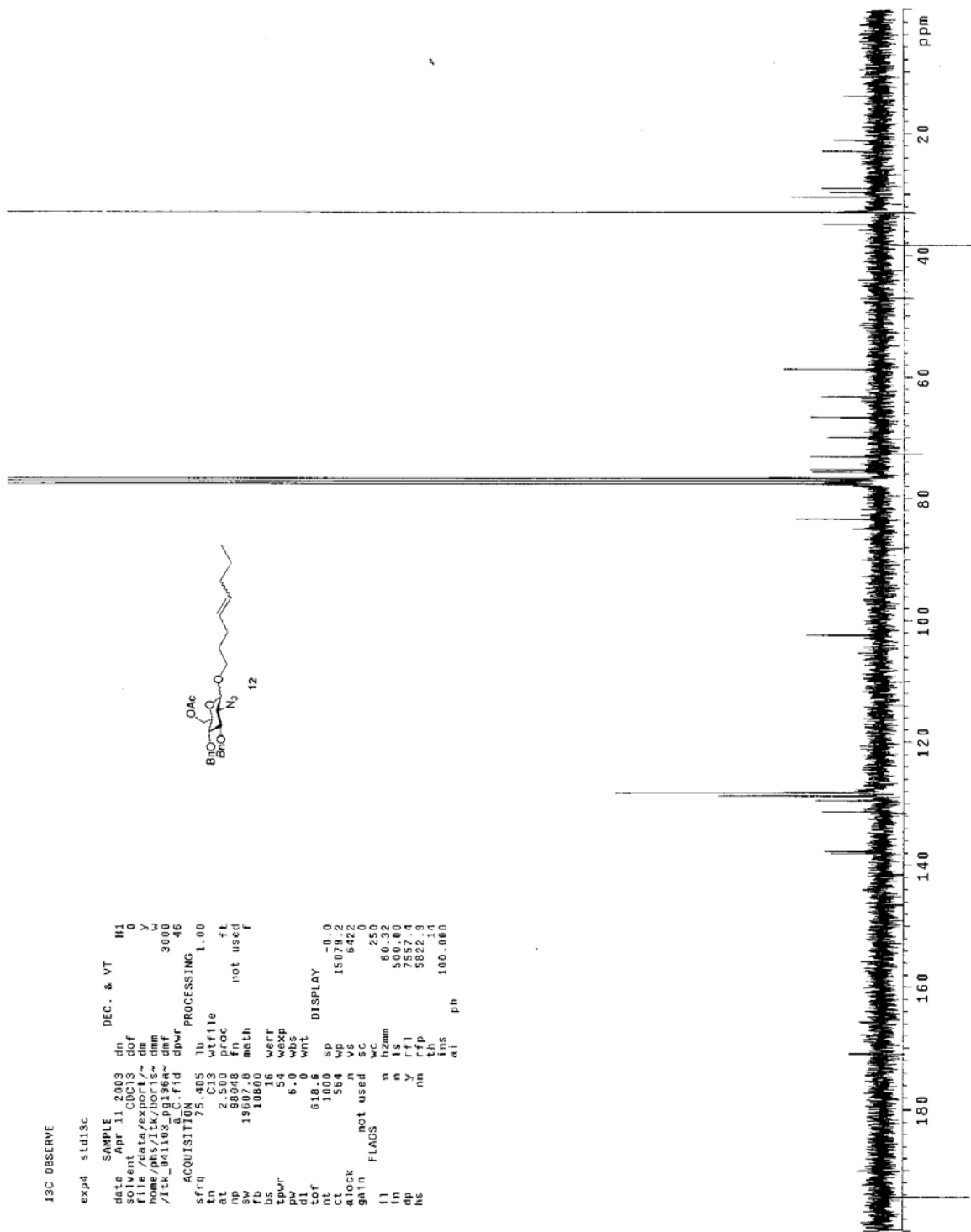
500.00

7552.4

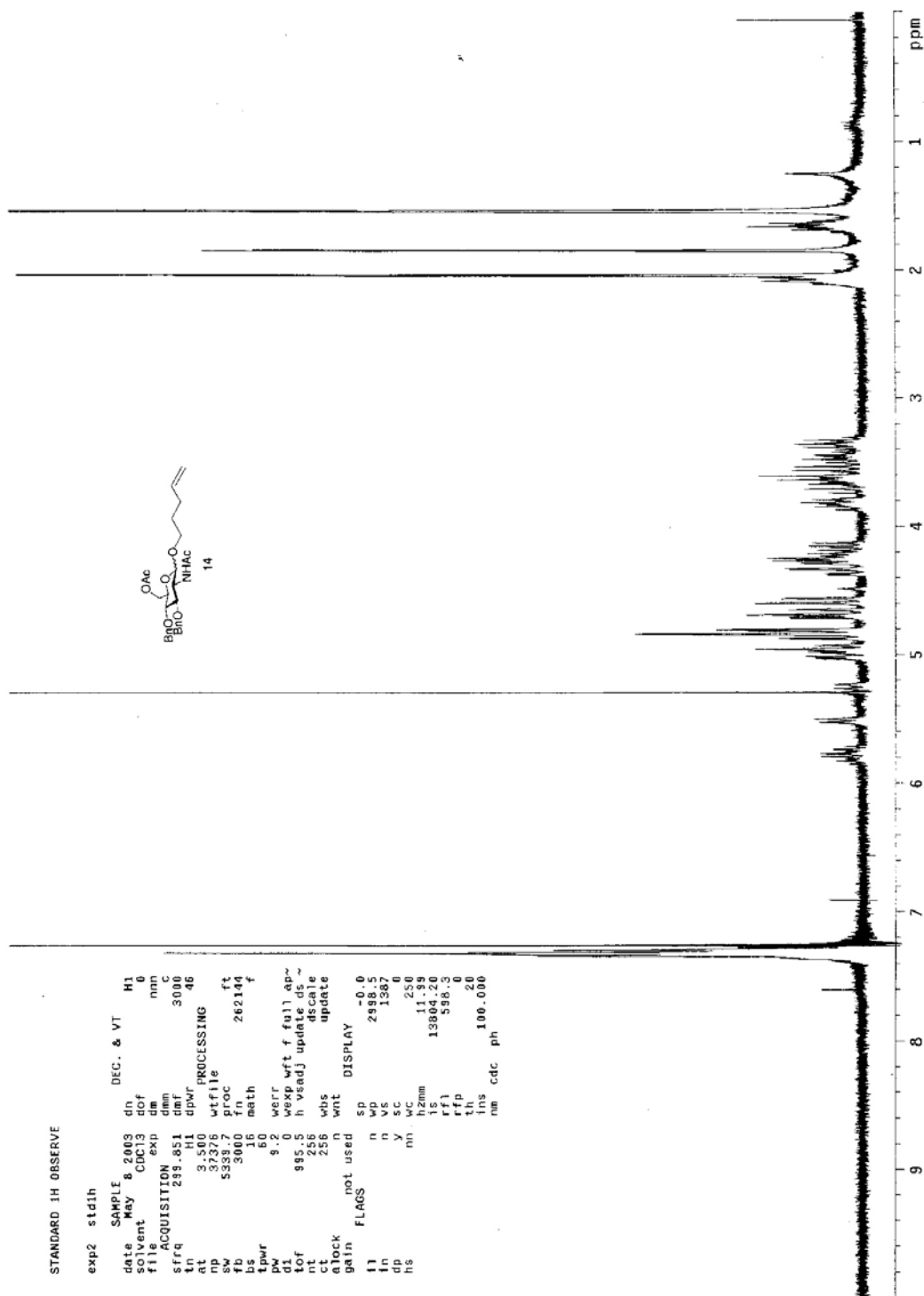
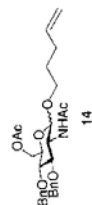
5822.9

14

100.000



exp2	stdih	SAMPLE	B.2003	DEC.	& VT	H1
		date	May	din		0
		solvnt	CDC13	dof		nmm
		solvent		dmm		c
		freq	295.851	dpr		3000
		ACQUISITION	exp	nmr		40
		time	3.500	PROC		ft
		ap	37376	wfile		f
		mp	5393.7	proc		262144
		fb	3000	fn		
		bus	16	math		
		tpwr	\$2	verr		
		id	0	expw	wf f full ap	
		tof	995.5	h veadj	update ds ~	
		nt	256	whs	update	
		ctt	256	discale	update	
		block	n	wnt	DISPLAY	
		not used	n	sp	-0.0	
		FLAGS	n	wp	2998.5	
		magin	n	wv	1387	
		his	y	wc	250	
		dpd	nc	hzmm	11.99	
		his	16	ns	13804.20	
			ff1	ff1	596.3	
			th	th	20	
			ins	cdc	100.000	
			nm	ph		

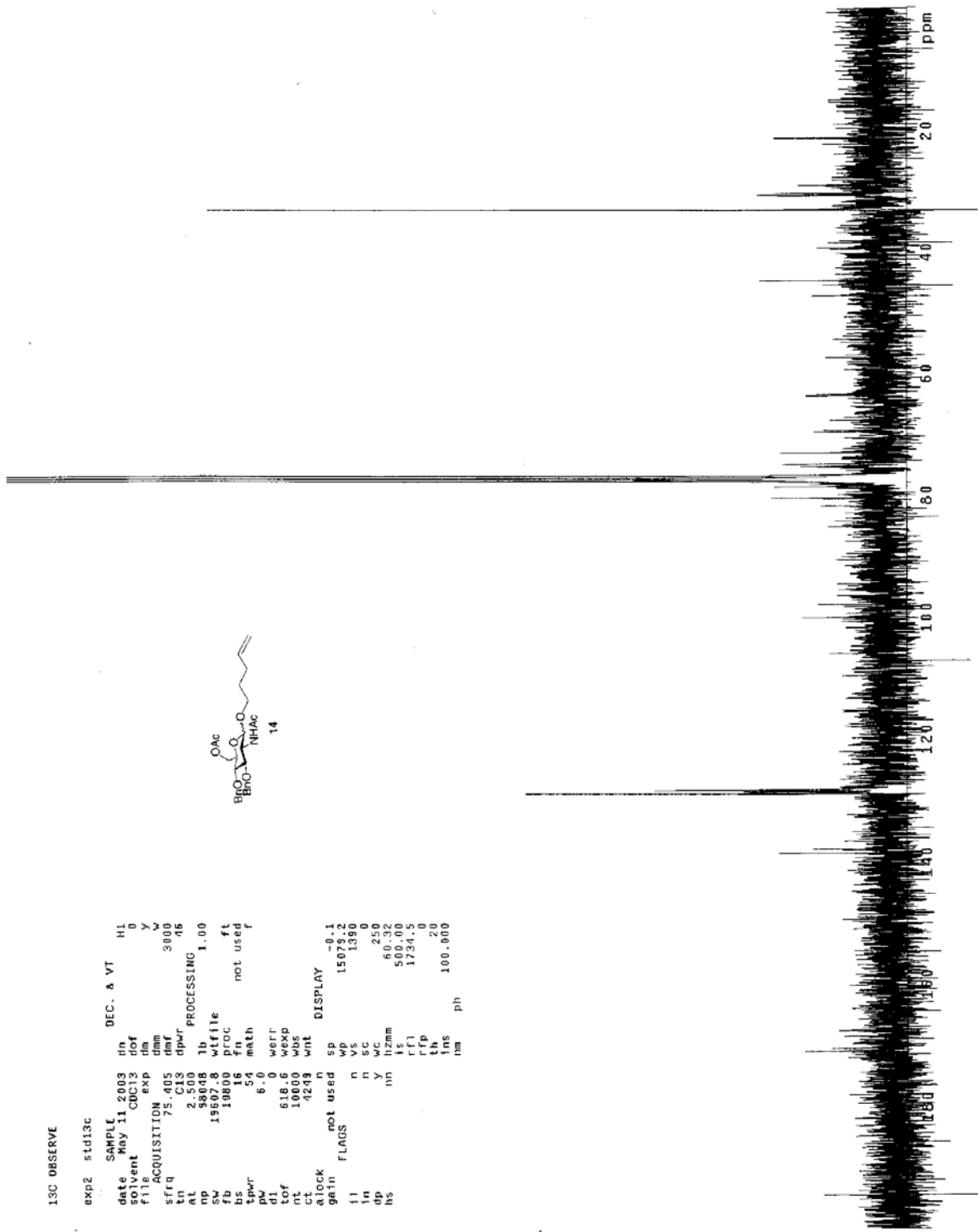
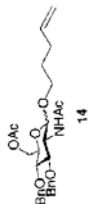


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13C OBSERVE

exp2 std13c

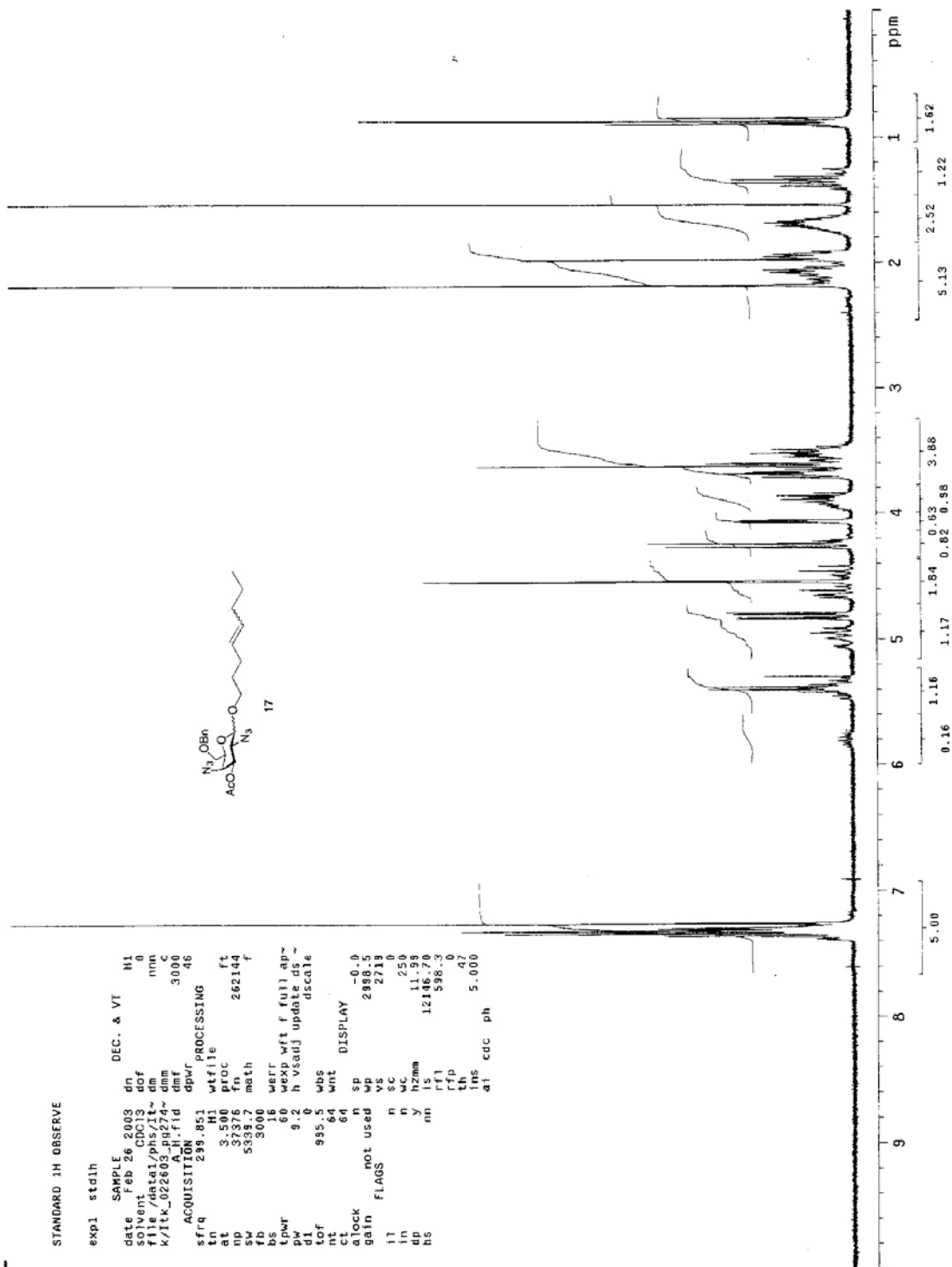
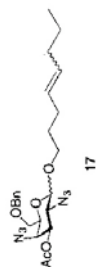
SAMPLE		DEC. & VT		H1
date	May 11 2003	in		0
solvent	CDCl3	dof		Y
file	ACQUISITION	exp	dm	Y
sfreq	75.405	nmr		3000
in	2.500	opwr	PROCESSING	46
np	38048	lb		1.00
sw	19507.8	wfile		ft
fb	10800	proc		not used
bs	16	fn		f
spwr	50	math		
del	6.0	werr		
nt	618.6	wexp		
ct	10000	wbs		
alock	4249	wnt		
gain	not used	sp	DISPLAY	-0.1
fl	FLAGS	wp		15079.2
in		vt		1380
dp		n	sc	0
hs		nn	yc	250
			hzmm	60.32
			ts	500.00
			rfl	1734.5
			thp	20
			th	100.000
			nm	ph



S3c

STANDARD 1H OBSERVE

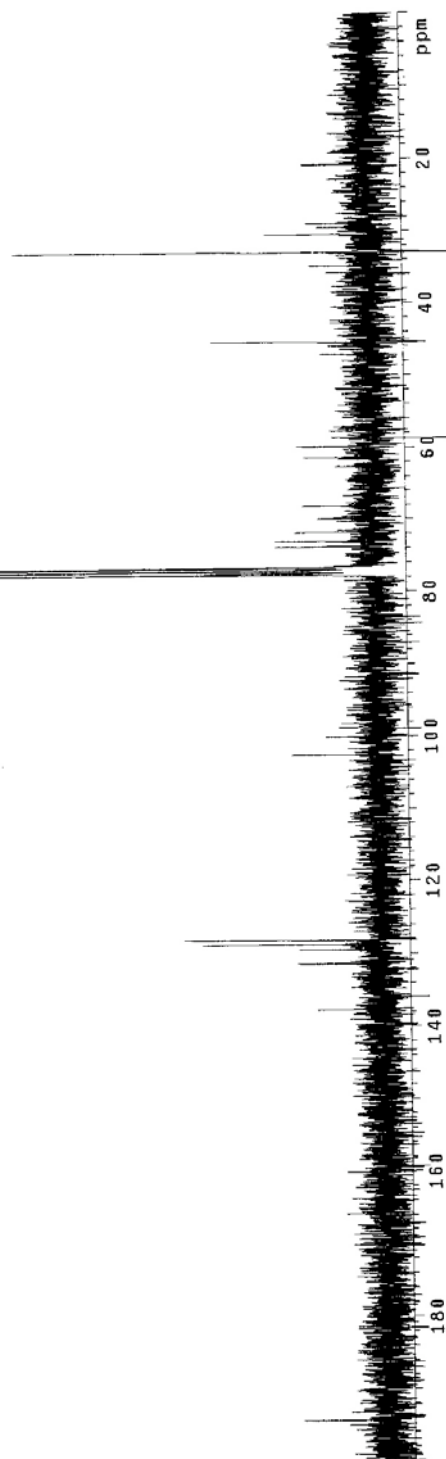
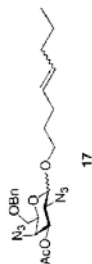
exp1 std1h
 SAMPLE DEC. & VT H1
 date Feb 26 2003 dn
 solvent CDCl3 dof
 file /data1/pbs/lt~ dm nna
 k/ltk_022603_pg274~ dmm C
 A_H.fid dmf 3000
 ACQUISITION
 sffrq 299.951
 at 60
 in 3.500
 up 37376
 sw 5339.7
 fb 3000
 bs 16
 tpwr 60
 pw 9.6
 dt 1.0
 tof 995.5
 nt 64
 ct 64
 alock not used
 gain 2989.5
 il 271.8
 in 250
 dp 11.99
 bs nn
 ls 12146.70
 rfl 598.3
 rfp 0
 th 47
 lms 5.000
 dt cdc ph



13C OBSERVE

exp2 std13c

SAMPLE		DEC. & VT	
date	8.2003	dn	H1
solvent	CDCl3	dof	0
file	exp	dm	y
ACQUISITION		dmr	3000
sfreq	75.405	dmr	46
at	2.000	dmr	1.00
pw	38008	dmr	1.00
fb	19607.8	dmr	1.00
bs	16	dmr	not used
tpwr	54	dmr	f
di	6.0	dmr	
cof	618.6	dmr	
ct	4000	dmr	
alock	1924	dmr	
gain	not used	dmr	
FLAGS		dmr	
l1	n	dmr	
l2	n	dmr	
l3	n	dmr	
l4	n	dmr	
l5	n	dmr	
l6	n	dmr	
l7	n	dmr	
l8	n	dmr	
l9	n	dmr	
l10	n	dmr	
l11	n	dmr	
l12	n	dmr	
l13	n	dmr	
l14	n	dmr	
l15	n	dmr	
l16	n	dmr	
l17	n	dmr	
l18	n	dmr	
l19	n	dmr	
l20	n	dmr	
l21	n	dmr	
l22	n	dmr	
l23	n	dmr	
l24	n	dmr	
l25	n	dmr	
l26	n	dmr	
l27	n	dmr	
l28	n	dmr	
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l30	n	dmr	
l31	n	dmr	
l32	n	dmr	
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l40	n	dmr	
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l42	n	dmr	
l43	n	dmr	
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l47	n	dmr	
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l78	n	dmr	
l79	n	dmr	
l80	n	dmr	
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l92	n	dmr	
l93	n	dmr	
l94	n	dmr	
l95	n	dmr	
l96	n	dmr	
l97	n	dmr	
l98	n	dmr	
l99	n	dmr	
l100	n	dmr	



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