Supporting Information for the Paper entitled

Efficient Synthesis of β(1,3) Oligosaccharides Exhibiting Dectin-1 Agonist Activity.

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General Techniques

NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane for solutions in $CDCl_3$. ^{1}H NMR spectrum data is reported as follows: $CDCl_3$ (7.26 ppm) or D_2O (HOD (4.7015 ppm at 303 K, 4.5025 ppm at 323 K, 4.3168 ppm at 343 K). ^{13}C NMR spectrum data is reported as follow: $CDCl_3$ (77.1 ppm) or acetone-d_6 (30.3 ppm) as internal standard for D_2O. Multiplicities are reported by using the following abbreviations: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, br; broad, *J*; coupling constants in Hertz.

Optical rotations were measured on a JASCO model P-1020 polarimeter.

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Only the strongest and/or structurally important peaks are reported as the IR data given in cm^{-1}.

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by *p*-anisaldehyde H_2SO_4 ethanol solution.

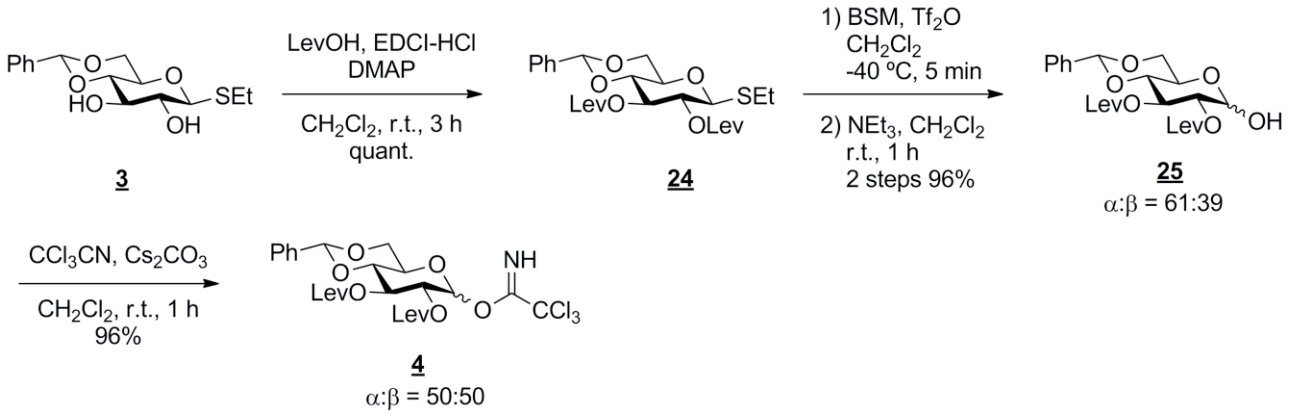
Merck silica gel was used for column chromatography.

Gel permeation chromatography (GPC) for qualitative analysis were performed on Japan Analytical Industry Model LC908 (recycling preparative HPLC), on a Japan Analytical Industry Model RI-5 refractive index detector and on a Japan Analytical Industry Model 310 ultra violet detector with a polystylene gel column (JAIGEL-1H, 20mm x 600 mm), using chloroform as solvent (3.5 mL / min).

ESI-TOF Mass spectra were measured with Waters LCT Premier™ XE.

Dry dichloromethane, dry THF, and dry toluene were obtained from solvent purification columns. *N*-iodosuccinimide was recrystallized from CCl_4-1,4 dioxane. Pulverized MS-4A was activated by heating at 350 ˚C for 8 h.

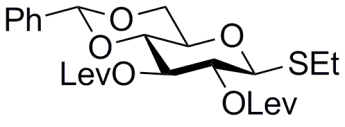
Preparation of the monosaccharide donor 4



Ethylthio 4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranoside (24)

To a stirred solution of ethylthio 4,6-*O*-benzylidene-β-D-glucopyranoside[1] (3) (9.50 g, 30.4 mmol, 1.00 eq.) in CH_2Cl_2 (60.8 mL) was added EDCI-HCl (12.8 g, 66.9 mmol, 2.20 eq.), levulinic acid (6.85 mL, 66.9 mmol, 2.20 eq.) and a catalytic amount of DMAP (371 mg, 3.04 mmol, 0.100 eq.) at 0 ˚C. After being stirred at room temperature for 3 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 80:20 toluene:ethyl acetate to give ethylthio 4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranoside (24) (15.4 g, 30.3 mmol, quant.).

$[\alpha]_D^{24}$ = -74.7 (c = 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.45 (m, 2H, aromatic), 7.33-7.36 (m, 3H, aromatic), 5.50 (s, 1H, benzylidene), 5.36 (dd, 1H, H-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.7 Hz), 5.06 (dd, 1H, H-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.56 (d, 1H, H-1, $J_{1,2}$ = 9.7 Hz), 4.36 (dd, 1H, H-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 3.77 (dd, 1H, H-6b, $J_{5,6b}$ = 9.7 Hz, J_{gem} = 10.6 Hz), 3.68 (dd, 1H, H-4, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 9.2 Hz), 3.55 (ddd, 1H, H-5, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.7 Hz), 2.52-2.87 (m, 10H, Lev, SC*H*$_2$CH$_3$), 2.17 (s, 3H, Lev), 2.13 (s, 3H, Lev), 1.26 (t, 3H, SCH$_2$C*H*$_3$, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 206.2, 171.8, 171.5, 136.8, 129.0, 128.2, 126.2, 101.4, 84.2, 78.4, 72.6, 70.8, 70.5, 68.5, 37.8 x 2, 29.7 x 2, 27.9, 24.3, 23.5, 14.9; IR (solid): 2971, 2873, 1746, 1718, 1369, 1208, 1152, 1080, 1026, 918, 753, 701, 544 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{36}NO_9S$ $[M+NH_4]^+$ *m/z* = 526.2111, found: 526.2112.

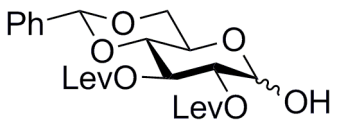


4,6-*O*-Benzylidene-2,3-di-*O*-levulinoyl-D-glucopyranose (25)

To a stirred solution of ethylthio 4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranoside (24) (102 mg, 0.201 mmol, 1.00 eq.) in CH_2Cl_2 (2.01 mL) was added benzenesulfinyl morpholine[2] (46.7 mg, 0.221 mmol, 1.10 eq.) and Tf_2O (40.6 μl, 0.241 mmol, 1.20 eq.) at -40 ˚C. After being stirred at the same temperature for 5 min, the reaction mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in CH_2Cl_2 (2.00 mL) was added triethylamine (0.500 mL) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was concentrated *in vacuo*. The residue was chromatographed on silica gel with 40:60 hexane:ethyl acetate to give 4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-D-glucopyranose (25) (89.9 mg, 0.194 mmol, 2 steps 96%, α:β = 61:39). The α:β ratio was determined by ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.46 (m, 10H, aromaticαβ), 5.63 (dd, 1H, H-3α, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.7 Hz), 5.50 (s, 2H, benzylideneαβ), 5.40 (br-d, 1H, H-1α, $J_{1,2}$ = 2.4 Hz), 5.37 (dd, 1H, H-3β, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz), 4.89-4.93 (m, 2H, H-2α, H-2β), 4.82 (br-d, 1H, H-1β, $J_{1,2}$ = 8.2 Hz), 4.37 (dd, 1H, H-6aβ, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.30 (dd, 1H, H-6aα, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.18 (ddd, 1H, H-5α, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz), 3.95 (br-s, 1H, OHβ), 3.52-3.83 (m, 6H, H-4α, H-4β, H-5β, H-6bα, H-6bβ, OHα), 2.50-2.84 (m, 16H, Levαβ), 2.14-2.19 (m, 12H, Levαβ); IR (solid): 3457, 2920, 2871, 1758, 1391, 974, 919, 769, 648, 509 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{32}NO_{10}$ $[M+NH_4]^+$ *m/z* = 482.2026, found: 482.2027.



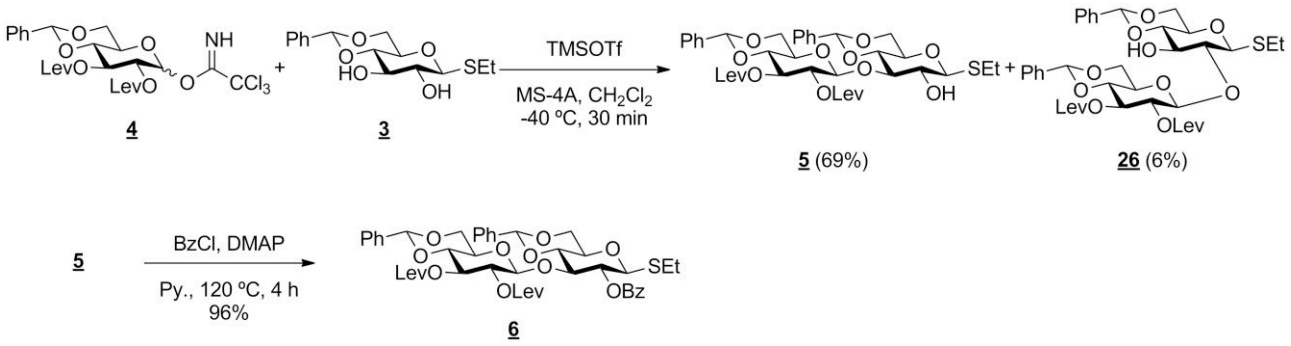
O-(4,6-*O*-Benzylidene-2,3-di-*O*-levulinoyl-D-glucopyranosyl)trichloroacetimidate (4)

To a stirred solution of 4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-D-glucopyranose (25) (31.7 g, 68.3 mmol, 1.00 eq.) in CH_2Cl_2 (68.3 mL) was added trichloroacetonitrile (20.5 mL, 205 mmol, 3.00 eq.) and a catalytic amount of Cs_2CO_3 (222 mg, 0.683 mmol, 0.0100 eq.) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 60:40 hexane:ethyl acetate to give

O-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-D-glucopyranosyl)trichloroacetimidate (4) (39.7 g, 65.2 mmol, 96%, α:β = 50:50). The α:β ratio was determined by ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, NHβ), 8.67 (s, 1H, NHα), 7.35-7.47 (m, 10H, aromaticαβ), 6.50 (d, 1H, H-1α, $J_{1,2}$ = 3.9 Hz), 5.96 (d, 1H, H-1β, $J_{1,2}$ = 7.7 Hz), 5.69 (dd, 1H, H-3α, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.2 Hz), 5.54 (s, 1H, benzylideneα), 5.52 (s, 1H, benzylideneβ), 5.42 (dd, 1H, H-3β, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.7 Hz), 5.32 (dd, 1H, H-2β, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.2 Hz), 5.19 (dd, 1H, H-2α, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 9.7 Hz), 4.43 (dd, 1H, H-6aβ, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.35 (dd, 1H, H-6aα, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.12 (ddd, 1H, H-5α, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz), 3.70-3.85 (m, 5H, H-4α, H-4β, H-5β, H-6bα, H-6bβ), 2.49-2.84 (m, 16H, Levαβ), 2.14-2.16 (m, 12H, Levαβ); IR (solid): 3316, 2920, 1751, 1718, 1677, 1364, 1146, 921, 797, 648 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{32}N_2O_{10}$ $[M+NH_4]^+$ *m/z* = 625.1123, found: 625.1124.

Preparation of the disaccharide donor 6



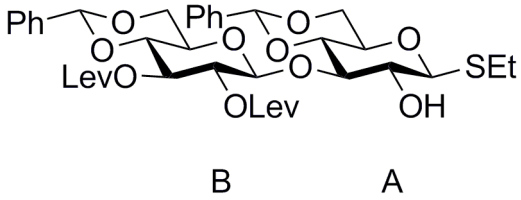
Ethylthio 4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (5)

A mixture of ethylthio 4,6-*O*-benzylidene-β-D-glucopyranoside (3) (6.99 g, 22.4 mmol, 1.10 eq.), *O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-D-glucopyranosyl)trichloroacetimidate (4) (12.4 g, 20.4 mmol, 1.00 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (20.0 g) in dry CH_2Cl_2 (407 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -40 ˚C. A catalytic amount of trimethylsilyltrifluoromethanesulfonate (0.369 mL, 2.04 mmol, 0.100 eq.) was added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine, filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 48:52 hexane:ethyl acetate to give ethylthio 4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (5) (10.6 g, 14.0 mmol, 69%) and ethylthio 4,6-*O*-benzylidene-2-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (26) (0.994 g, 1.31 mmol, 6%).

β(1,3) isomer (5)

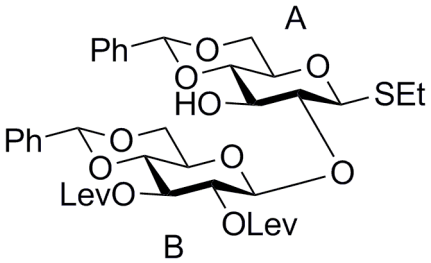
$[\alpha]_D^{24}$ = -54.0 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.51 (m, 10H, aromatic), 5.55 (s, 1H, benzylidene), 5.44 (s, 1H, benzylidene), 5.33 (dd, 1H, B-3, $J_{2,3}$ = 9.7 Hz, $J_{3,4}$ = 9.7 Hz), 5.10 (dd, 1H, B-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.7 Hz), 4.85 (d, 1H, B-1, $J_{1,2}$ = 7.7 Hz), 4.47 (d, 1H, A-1, $J_{1,2}$ = 9.7 Hz), 4.36 (dd, 1H, A-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.28 (d, 1H, OH, $J_{A\text{-}2,OH}$ = 4.8 Hz), 4.20 (dd, 1H, B-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 3.73-3.79 (m, 3H, A-3, A-6b, B-6b), 3.68 (dd, 1H, B-4, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 9.7 Hz), 3.59-3.64 (m, 2H, A-2, A-4), 3.41-3.49 (m, 2H, A-5, B-5), 2.44-3.01 (m, 10H, Lev, SCH_2CH_3), 2.22 (s, 3H, Lev), 2.13 (s, 3H, Lev), 1.32 (t, 3H, SCH_2CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 206.3,

171.7 x 2, 137.4, 136.9, 129.1 x 2, 128.3, 128.2, 126.3, 126.1, 103.1, 101.5, 101.0, 87.0, 84.7, 79.2, 78.3, 72.8, 72.4, 71.9, 70.9, 68.7, 66.3, 37.8, 30.1, 29.8, 27.9, 27.7, 24.3, 15.1; IR (solid): 3488, 2868, 2457, 2272, 1719, 1387, 1147, 1106, 917, 693, 524 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{38}H_{50}NO_{14}S$ $[M+NH_4]^+$ *m/z* = 776.2952, found: 776.2944.



β(1,2) isomer (26)

$[\alpha]_D^{26}$ = -65.8 (c = 1.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.52 (m, 10H, aromatic), 5.53 (s, 1H, benzylidene), 5.49 (s, 1H, benzylidene), 5.35 (dd, 1H, B-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz), 5.04-5.11 (m, 2H, B-1, B-2), 4.52 (d, 1H, A-1, $J_{1,2}$ = 9.7 Hz), 4.31-4.38 (m, 2H, A-6a, B-6a), 3.93 (ddd, 1H, A-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 8.7 Hz, $J_{3,OH}$ = 3.9 Hz), 3.81-3.87 (m, 2H, B-6b, OH), 3.71-3.76 (m, 2H, B-4, A-6b), 3.65 (dd, 1H, A-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.7 Hz), 3.48-3.54 (m, 2H, A-4, B-5), 3.44 (ddd, 1H, A-5, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.7 Hz), 2.46-2.84 (m, 10H, Lev, SCH_2CH_3), 2.19 (s, 3H, Lev), 2.13 (s, 3H, Lev), 1.28 (t, 3H, SCH_2CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 206.3, 171.8, 171.5, 137.2, 136.9, 129.2, 129.1, 128.3, 128.2, 126.4, 126.2, 101.8, 101.7, 101.5, 84.1, 80.4, 80.3, 78.2, 75.2, 72.7, 71.9, 70.3, 68.7, 68.5, 66.3, 37.8 x 2, 29.9, 29.8, 27.9, 24.4, 14.7; IR (solid): 3425, 2856, 2351, 1742, 1706, 1368, 1307, 1154, 1097, 971, 749, 698, 547 cm^{-1}.

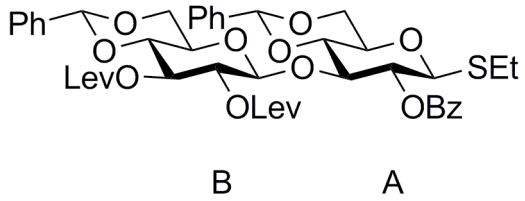


Ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (6)

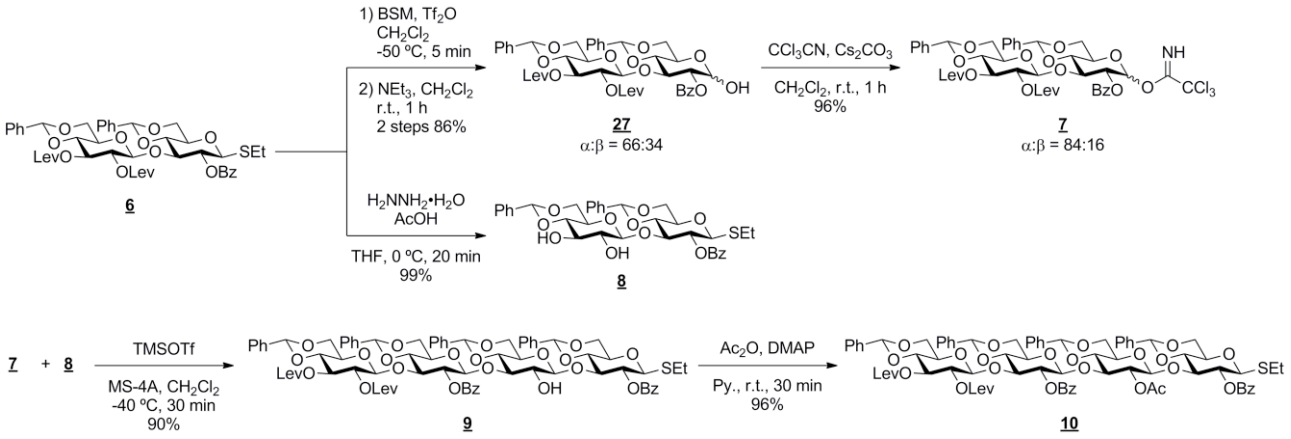
To a stirred solution of ethylthio 4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (5) (1.02 g, 1.34 mmol, 1.00 eq.) in pyridine (6.70 mL) was added

benzoyl chloride (0.471 mL, 4.02 mmol, 3.00 eq.) and a catalytic amount of DMAP (16.4 mg, 0.134 mmol, 0.100 eq.) at room temperature. After being stirred at 120 ˚C for 4 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 97:3 toluene:acetone to give ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl) -β-D-glucopyranoside (**6**) (1.11 g, 1.28 mmol, 96%).

$[\alpha]_D^{24}$ = -42.7 (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 2H, aromatic, J = 7.7 Hz), 7.32-7.65 (m, 13H, aromatic), 5.57 (s, 1H, benzylidene), 5.38 (s, 1H, benzylidene), 5.31 (dd, 1H, A-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.2 Hz), 5.08 (dd, 1H, B-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 5.01 (dd, 1H, B-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 8.7 Hz), 4.70 (d, 1H, B-1, $J_{1,2}$ = 7.7 Hz), 4.60 (d, 1H, A-1, $J_{1,2}$ = 9.7 Hz), 4.38 (dd, 1H, A-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.24 (dd, 1H, B-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.18 (dd, 1H, A-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 8.7 Hz), 3.81 (dd, 1H, A-6b, $J_{5,6b}$ = 10.1 Hz, J_{gem} = 10.6 Hz), 3.75 (dd, 1H, A-4, $J_{3,4}$ = 8.7 Hz, $J_{4,5}$ = 9.7 Hz), 3.68 (dd, 1H, B-6b, $J_{5,6b}$ = 10.1 Hz, J_{gem} = 10.1 Hz), 3.63 (dd, 1H, B-4, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.7 Hz), 3.56 (ddd, 1H, A-5, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz), 3.37 (ddd, 1H, B-5, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz), 2.33-2.76 (m, 10H, Lev, SC*H*$_2$CH$_3$), 2.08 (s, 6H, Lev), 1.20 (t, 3H, SCH$_2$C*H*$_3$, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4 x 2, 171.8, 171.5, 165.1, 137.3, 136.9, 133.6, 129.9, 129.6, 129.2, 129.1, 128.8, 128.3, 128.2, 126.2, 126.1, 101.4, 101.2, 101.1, 84.4, 79.6, 78.9, 78.4, 72.2, 71.9, 71.8, 71.2, 68.6, 66.3, 37.9, 37.8, 29.7 x 2, 28.0, 27.5, 24.1, 14.8; IR (solid): 2972, 1753, 1717, 1401, 1364, 1149, 1095, 1015, 917, 751, 698, 540 cm^{-1}.



Preparation of the tetrasaccharide donor 10



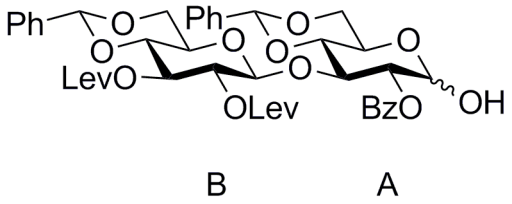
2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranose (27)

To a stirred solution of ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (6) (103 mg, 0.119 mmol, 1.00 eq.) in CH_2Cl_2 (1.19 mL) was added benzenesulfinyl morpholine (27.8 mg, 0.131 mmol, 1.10 eq.) and Tf_2O (24.0 μl, 0.143 mmol, 1.20 eq.) at -50 ˚C. After being stirred at the same temperature for 5 min, the reaction mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in CH_2Cl_2 (2.00 mL) was added triethylamine (0.500 mL) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was concentrated *in vacuo*. The residue was chromatographed on silica gel with 91:9 toluene:acetone to give 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranose (27) (84.2 mg, 0.103 mmol, 2 steps 86%, α:β = 66:34). The α:β ratio was determined by ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.07 (m, 4H, aromaticαβ), 7.31-7.64 (m, 26H, aromaticαβ), 5.55 (s, 1H, benzylideneα), 5.53 (s, 1H, benzylideneβ), 5.46 (br-s, 1H, A-1α), 5.37 (s, 1H, benzylideneα), 5.35 (s, 1H, benzylideneβ), 5.06-5.17 (m, 4H, A-2α, A-2β, B-3α, B-3β), 4.98-5.03 (m, 2H, B-2α, B-2β), 4.85 (d, 1H, B-1α, $J_{1,2}$ = 7.7 Hz), 4.78 (dd, 1H, A-1β, $J_{1,2}$ = 8.2 Hz, $J_{1,OH}$ = 8.7 Hz), 4.75 (d, 1H, B-1β, $J_{1,2}$ = 7.7 Hz), 4.44 (dd, 1H, A-3α, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.7 Hz), 4.34 (dd, 1H, A-6aβ, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.11-4.30 (m,

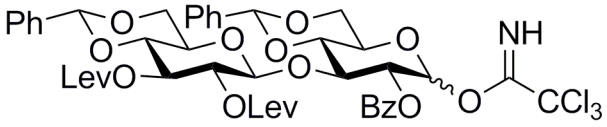
6H, A-3β, A-5α, A-6aα, B-6aα, B-6aβ, OHβ), 3.89 (d, 1H, OHα, $J_{1,OH}$ = 2.4 Hz), 3.59-3.81 (m, 8H, A-4α, A-4β, B-4α, B-4β, A-6bα, A-6bβ, B-6bα, B-6bβ), 3.38-3.54 (m, 3H, A-5β, B-5α, B-5β), 2.01-2.71 (m, 28H, Levαβ); IR (solid): 3493, 2921, 2862, 2056, 1895, 1709, 1601, 1413, 1265, 975, 772, 672, 534 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{43}H_{50}NO_{16}$ $[M+NH_4]^+$ *m/z* = 836.3130, found: 836.3127.



O-(2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranosyl)trichloroacetimidate (7)

To a stirred solution of 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranose (27) (4.34 mg, 5.30 mmol, 1.00 eq.) in CH_2Cl_2 (26.5 mL) was added trichloroacetonitrile (2.66 mL, 26.5 mmol, 5.00 eq.) and a catalytic amount of Cs_2CO_3 (173 mg, 0.530 mmol, 0.100 eq.) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 94:6 toluene:acetone to give *O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranosyl)trichloroacetimidate (7) (4.86 g, 5.06 mmol, 96%, α:β = 84:16). The α:β ratio was determined by ^{1}H NMR analysis.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H, NHβ), 8.57 (s, 1H, NHα), 7.99-8.03 (m, 4H, aromaticαβ), 7.33-7.64 (m, 26H, aromaticαβ), 6.61 (d, 1H, A-1α, $J_{1,2}$ = 4.3 Hz), 6.05 (d, 1H, A-1β, $J_{1,2}$ = 7.2 Hz), 5.62 (s, 1H, benzylideneα), 5.60 (s, 1H, benzylideneβ), 5.56 (dd, 1H, A-2β, $J_{1,2}$ = 7.2 Hz, $J_{2,3}$ = 7.7 Hz), 5.37-5.40 (m, 3H, A-2α, benzylideneαβ), 5.13-5.18 (m, 2H, B-3α, B-3β), 5.02-5.08 (m, 2H, B-2α, B-2β), 4.84 (d, 1H, B-1α, $J_{1,2}$ = 7.7 Hz), 4.77 (d, 1H, B-1β, $J_{1,2}$ = 7.7 Hz), 4.44-4.48 (m, 2H, A-3α, A-6aβ), 4.37 (dd, 1H, A-6aα, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.33 (dd, 1H, B-6aα, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.22-4.26 (m, 2H, A-3β, B-6aβ), 4.11 (ddd, 1H, A-5α, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz), 3.96 (dd, 1H, A-4β, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz), 3.63-3.88 (m, 8H, A-4α, B-4α, B-4β, A-5β, A-6bα, A-6bβ, B-6bα, B-6bβ), 3.51 (ddd, 1H, B-5α, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.7 Hz), 3.42 (ddd, 1H, B-5β, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.6 Hz), 2.06-2.75 (m, 28H, Levαβ); IR (solid): 2886, 1720, 1368, 1142, 959, 793, 664, 530 cm^{-1}.

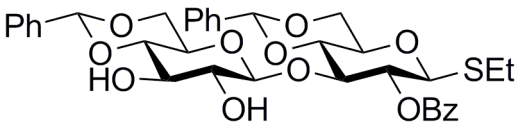


B A

Ethylthio
2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranoside (8)

To a stirred solution of ethylthio 4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (6) (4.03 g, 4.67 mmol, 1.00 eq.) in THF (50.0 mL) was added acetic acid (5.00 mL) and hydrazine monohydrate (2.00 mL) at 0 ˚C. After being stirred at the same temperature for 20 min, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 89:11 toluene:acetone to give ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranoside (8) (3.09 g, 4.63 mmol, 99%).

$[\alpha]_D^{24}$ = -49.6 (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, 2H, aromatic, J = 7.7 Hz), 7.31-7.61 (m, 13H, aromatic), 5.61 (s, 1H, benzylidene), 5.41 (s, 1H, benzylidene), 5.35 (dd, 1H, A-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.72 (d, 1H, A-1, $J_{1,2}$ = 9.7 Hz), 4.46 (d, 1H, B-1, $J_{1,2}$ = 7.7 Hz), 4.42 (dd, 1H, A-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.20 (dd, 1H, A-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 8.7 Hz), 3.77-3.86 (m, 3H, A-4, B-6a, A-6b), 3.57-3.63 (m, 2H, B-3, A-5), 3.42-3.47 (m, 3H, B-2, B-4, B-6b), 3.28 (ddd, 1H, B-5, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.7 Hz), 2.92 (d, 1H, OH, $J_{B\text{-}2,OH}$ = 2.4 Hz), 2.66-2.80 (m, 2H, SCH_2CH$_3$), 2.54 (d, 1H, OH, $J_{B\text{-}3,OH}$ = 1.0 Hz), 1.25 (t, 3H, SCH$_2$CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 137.0, 136.7, 133.6, 130.0, 129.7, 129.5, 129.3, 128.6, 128.4, 128.3, 126.4, 126.2, 103.1, 101.9, 101.7, 84.4, 80.3, 79.4, 79.1, 73.5, 72.8, 72.0, 71.0, 68.6, 68.4, 66.7, 24.2, 14.9; IR (solid): 3488, 2980, 2868, 1721, 1452, 1388, 1287, 1183, 1071, 971, 922, 751, 710, 572 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{35}H_{42}NO_{11}S$ $[M+NH_4]^+$ *m/z* = 684.2479, found: 684.2487.

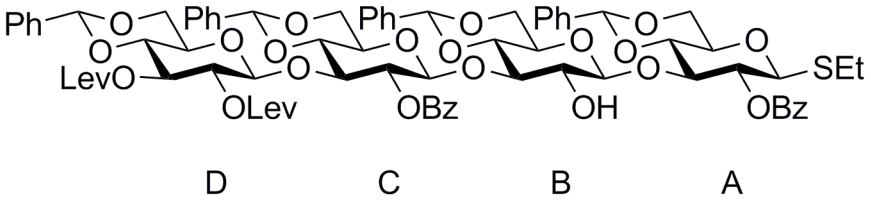


B A

Ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (9)

A mixture of ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranoside (8) (46.8 mg, 0.0702 mmol, 1.17 eq.), *O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranosyl)trichloroacetimidate (7) (56.1 mg, 0.0600 mmol, 1.00 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (120 mg) in dry CH_2Cl_2 (2.40 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -50 ˚C. A catalytic amount of trimethylsilyltrifluoromethanesulfonate (1.09 μL, 6.00 μmol, 0.100 eq.) was added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine, filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 94:6 toluene:acetone to give ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (9) (79.2 mg, 0.0540 mmol, 90%).

$[\alpha]_D^{24}$ = -32.8 (c = 1.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-8.02 (m, 4H, aromatic), 7.20-7.64 (m, 26H, aromatic), 5.56 (s, 1H, benzylidene), 5.44 (s, 1H, benzylidene), 5.42 (s, 1H, benzylidene), 5.23-5.29 (m, 2H, A-2, D-3), 5.11 (dd, 1H, C-2, $J_{1,2}$ = 4.8 Hz, $J_{2,3}$ = 4.3 Hz), 5.06 (dd, 1H, D-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.2 Hz), 5.01 (d, 1H, C-1, $J_{1,2}$ = 4.8 Hz), 4.88 (d, 1H, D-1, $J_{1,2}$ = 7.7 Hz), 4.85 (s, 1H, benzylidene), 4.66 (d, 1H, A-1, $J_{1,2}$ = 9.7 Hz), 4.39-4.41 (m, 2H, B-1, A-6a), 4.23 (dd, 1H, D-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz), 4.18 (dd, 1H, A-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 8.7 Hz), 4.03-4.08 (m, 2H, C-4, C-6a), 3.93 (dd, 1H, C-3, $J_{2,3}$ = 4.3 Hz, $J_{3,4}$ = 8.2 Hz), 3.39-3.86 (m, 13H, B-2, B-3, A-4, B-4, D-4, A-5, C-5, D-5, A-6b, B-6a, B-6b, C-6b, D-6b), 3.25 (ddd, 1H, B-5, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 10.1 Hz), 3.07 (d, 1H, OH, $J_{B\text{-}2,OH}$ = 3.4 Hz), 2.49-2.80 (m, 10H, Lev, SCH_2CH_3), 2.14 (s, 3H, Lev), 2.12 (s, 3H, Lev), 1.23 (t, 3H, SCH_2CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 206.4, 171.9, 171.3, 165.7, 165.2, 137.5, 137.3, 137.0, 136.7, 133.6, 133.4, 129.9, 129.8, 129.6, 129.4, 129.1, 128.9, 128.7, 128.5, 128.3 x 3, 128.0, 126.4, 126.2, 126.1, 126.0, 103.1, 101.9, 101.6, 101.5, 100.5 x 2, 99.2, 84.4, 79.1, 78.9, 78.4, 77.7, 77.2, 74.2, 73.9, 72.0, 70.8, 68.8, 68.6 x 2, 68.5, 66.9, 66.3, 65.5, 37.9 x 2, 29.8 x 3, 29.7, 28.1, 27.8, 24.3, 14.9; IR (solid): 3523, 2923, 2853, 2362, 1720, 1380, 1069, 917, 734, 672, 507 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{78}H_{86}NO_{26}S$ $[M+NH_4]^+$ *m/z* = 1484.5159, found: 1484.5149.

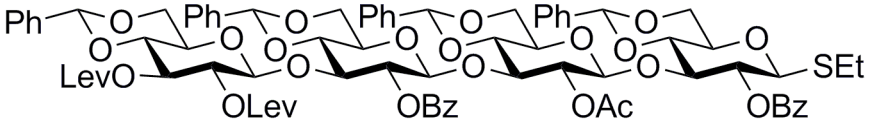


Ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (10)

To a stirred solution of ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (9) (3.53 g, 2.40 mmol, 1.00 eq.) in pyridine (12.0 mL) was added acetic anhydride (2.25 mL, 24.0 mmol, 10.0 eq.) and a catalytic amount of DMAP (29.3 mg, 0.240 mmol, 0.100 eq.) at room temperature. After being stirred at the same temperature for 30 min, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 95:5 toluene:acetone to give ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (10) (3.48 g, 2.30 mmol, 96%).

$[\alpha]_D^{24}$ = -33.5 (c = 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, 2H, aromatic, J = 7.2 Hz), 7.98 (d, 2H, aromatic, J = 7.2 Hz), 7.29-7.68 (m, 25H, aromatic), 7.21 (t, 1H, aromatic, J = 7.2 Hz), 5.53 (s, 1H, benzylidene), 5.38 (s, 1H, benzylidene), 5.17-5.21 (m, 2H, H-2', benzylidene), 5.11 (dd, 1H, D-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 4.99 (dd, 1H, D-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 8.7 Hz), 4.93 (dd, 1H, A-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.90 (s, 1H, benzylidene), 4.88 (d, 1H, H-1', $J_{1,2}$ = 6.8 Hz), 4.83 (dd, 1H, H-2, $J_{1,2}$ = 5.3 Hz, $J_{2,3}$ = 5.8 Hz), 4.70 (d, 1H, D-1, $J_{1,2}$ = 7.7 Hz), 4.64 (d, 1H, H-1, $J_{1,2}$ = 5.3 Hz), 4.50 (d, 1H, A-1, $J_{1,2}$ = 9.7 Hz), 4.34 (dd, 1H, A-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.22 (dd, 1H, D-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.09-4.18 (m, 3H, A-3, H-6a, H-6a'), 4.05 (dd, 1H, H-3', $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 3.90 (dd, 1H, H-4, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz), 3.84 (dd, 1H, H-4', $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz), 3.54-3.77 (m, 6H, H-3, D-4, A-6b, D-6b, H-6b, H-6b'), 3.32-3.50 (m, 5H, A-4, A-5, D-5, H-5, H-5'), 2.34-2.72 (m, 10H, Lev, SCH_2CH_3), 2.09 (s, 3H, Lev), 2.05 (s, 3H, Lev), 1.73 (s, 3H, Ac), 1.20 (t, 3H, SCH_2CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 206.4, 171.8, 171.4, 169.2, 164.9, 164.8, 137.4, 137.3, 137.2, 136.9, 133.8, 133.4, 129.9, 129.8, 129.7, 129.3, 129.1, 129.0, 128.9, 128.6, 128.3, 128.2 x 2, 126.3 x 2, 126.2, 126.1, 101.6, 101.4, 101.1, 100.9, 100.7, 99.0,

98.4, 84.4, 78.6, 78.4 x 2, 78.1, 76.7, 76.2, 73.9, 72.8, 72.5, 71.8 x 2, 71.2, 68.8, 68.6 x 2, 66.2, 66.1, 65.7, 37.9, 37.8, 29.7 x 2, 28.0, 27.6, 24.3, 20.5, 14.8; IR (solid): 2983, 2884, 1753 1719, 1374, 1267, 1095, 1006, 746, 696, 515 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{80}H_{88}NO_{27}S$ $[M+NH_4]^+$ *m/z* = 1526.5264, found: 1526.5272.



D C B A

H-, H-' = B- or C-

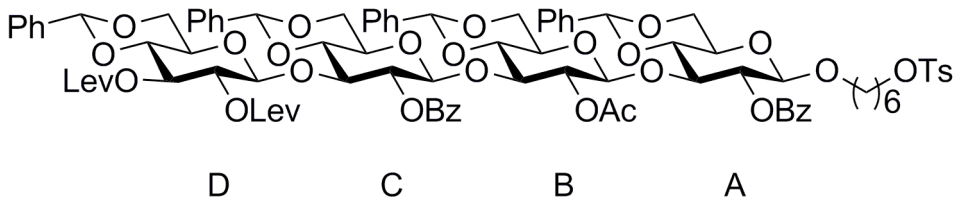
Preparation of the tetrasaccharide acceptor 11

6-(((4-Methylphenyl)sulfonyl)oxy)hexyl
2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (28)

A mixture of 1,6-hexanediol mono-*p*-toluenesulfonate (21.7 mg, 79.5 μmol, 1.20 eq.), ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (10) (100 mg, 66.2 μmol, 1.00 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (265 mg) in dry CH_2Cl_2 (2.65 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (17.9 mg, 79.5 μmol, 1.20 eq.) and a catalytic amount of trifluoromethanesulfonic acid (2.93 μL, 33.1 μmol, 0.500 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 92:8 toluene:acetone to give 6-(((4-methylphenyl)sulfonyl)oxy)hexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (28) (35.2 mg, 20.5 μmol, 31%).

$[\alpha]_D^{24}$ = -31.9 (c = 0.290, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 2H, aromatic, J = 8.2 Hz), 7.97 (d, 2H, aromatic, J = 7.7 Hz), 7.76 (d, 2H, aromatic, J = 7.7 Hz), 7.24-7.64 (m, 28H, aromatic), 5.51 (s, 1H, benzylidene), 5.38 (s, 1H, benzylidene), 5.09-5.18 (m, 3H, H-2', D-3, benzylidene), 4.94-5.01 (m, 3H, A-2, D-2, benzylidene), 4.87 (d, 1H, H-1', $J_{1,2}$ = 6.3 Hz), 4.84 (dd, 1H, H-2, $J_{1,2}$ = 6.3 Hz, $J_{2,3}$ = 6.3 Hz), 4.70 (d, 1H, D-1, $J_{1,2}$ = 7.7 Hz), 4.62 (d, 1H, H-1, $J_{1,2}$ = 6.3 Hz), 4.47 (d, 1H, A-1, $J_{1,2}$ = 7.7 Hz), 4.32 (dd, 1H, A-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.22 (dd, 1H, D-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.17 (dd, 1H, H-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.01-4.14 (m, 3H, A-3, H-3', H-6a'), 3.57-3.87 (m, 11H, H-3, D-4, H-4, H-4', A-6b, D-6b, H-6b, H-6b', CH_2OTs, OCHaHbCH$_2$), 3.32-3.47 (m, 6H, A-4, A-5, D-5, H-5, H-5', OCHaHbCH$_2$), 2.38-2.76 (m, 11H, Lev, SO_2PhCH_3), 2.09 (s, 3H, Lev), 2.05 (s, 3H, Lev), 1.70 (s, 3H, Ac), 1.07-1.56 (m, 8H, aliphatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 206.4, 171.9, 171.5, 169.1, 164.8, 144.7, 137.4, 137.3, 133.7, 133.5, 133.4, 129.9, 129.8, 129.7, 129.6, 129.3, 129.2, 129.1, 128.9, 128.7, 128.3, 128.2 x 2, 127.9, 126.3, 126.2, 126.1, 101.7, 101.5, 101.4, 101.3, 100.8, 100.7, 99.4, 98.6, 78.7 x 2, 78.4 x 2, 77.7, 76.3, 76.1,

74.3, 73.9, 72.6, 71.8 x 2, 70.5, 69.8, 68.8, 68.7 x 2, 68.6, 66.7, 66.3, 66.1, 65.9, 38.0, 37.8, 29.8, 29.7, 29.2, 28.7, 28.0, 27.6, 25.3, 25.0, 21.7, 20.5; IR (solid): 2873, 2350, 2111, 1720, 1450, 1366, 1266, 1084, 916, 752, 634, 494 cm^{-1}.



H-, H-' = B- or C-

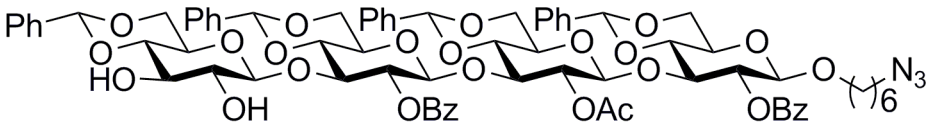
6-Azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (11)

To a stirred solution of 6-(((4-methylphenyl)sulfonyl)oxy)hexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (28) (52.2 mg, 30.4 μmol, 1.00 eq.) in DMF (1.52 mL) was added sodium azido (3.95 mg, 60.7 μmol, 2.00 eq.) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was poured into water. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in THF (1.00 mL) was added acetic acid (0.300 mL) and hydrazine monohydrate (0.100 mL) at 0 ˚C. After being stirred at the same temperature for 20 min, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 88:12 toluene:acetone to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (11) (31.0 mg, 22.2 μmol, 2 steps 73%).

$[\alpha]_D^{24}$ = -34.6 (c = 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, 2H, aromatic, J = 8.2 Hz), 8.00 (d, 2H, aromatic, J = 8.2 Hz), 7.25-7.62 (m, 26H, aromatic), 5.51 (s, 1H, benzylidene), 5.42 (s, 1H, benzylidene), 5.27 (s, 1H, benzylidene), 5.23 (dd, 1H, H-2', $J_{1,2}$ = 6.3 Hz, $J_{2,3}$ = 6.3 Hz), 5.06 (dd, 1H, A-2, $J_{1,2}$ = 8.2 Hz,

$J_{2,3}$ = 8.7 Hz), 5.02 (d, 1H, H-1', $J_{1,2}$ = 6.3 Hz), 4.96 (s, 1H, benzylidene), 4.90 (dd, 1H, H-2, $J_{1,2}$ = 5.3 Hz, $J_{2,3}$ = 5.8 Hz), 4.69 (d, 1H, H-1, $J_{1,2}$ = 5.3 Hz), 4.53 (d, 1H, D-1, $J_{1,2}$ = 8.2 Hz), 4.50 (d, 1H, A-1, $J_{1,2}$ = 8.2 Hz), 4.32 (dd, 1H, A-6a, $J_{5,6a}$ = 3.4 Hz, J_{gem} = 9.7 Hz), 4.05-4.17 (m, 4H, A-3, H-3', H-6a, H-6a'), 3.35-3.92 (m, 17H, D-2, D-3, H-3, A-4, D-4, H-4, H-4', A-5, H-5, H-5', D-6a, A-6b, D-6b, H-6b, H-6b', OCH_2CH$_2$), 3.31 (ddd, 1H, D-5, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.7 Hz), 3.03-3.06 (m, 3H, OH, CH_2N$_3$), 2.60 (br-s, 1H, OH), 1.74 (s, 3H, Ac), 1.14-1.50 (m, 8H, aliphatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 169.5, 165.5, 164.8, 137.3, 137.2, 137.1, 136.9, 133.7, 133.4, 130.0, 129.8, 129.7, 129.6, 129.3 x 2, 128.8, 128.7, 128.3 x 2, 126.4 x 2, 126.3, 126.1, 102.5, 101.9, 101.6, 101.4 x 2, 101.3, 99.1, 98.4, 80.3, 78.8, 78.7, 78.6, 78.5, 78.2, 76.1, 74.4, 73.7, 73.5, 72.9, 72.3, 69.9, 68.8, 68.7 x 2, 68.5, 66.7, 65.8, 65.6, 51.3, 29.3, 28.6, 26.3, 25.4, 20.5; IR (solid): 3625, 2974, 2884, 2831, 2089, 1760, 1719, 1380, 1275, 1220, 1095, 765, 697, 515 cm^{-1}.



D C B A

H-, H-' = B- or C-

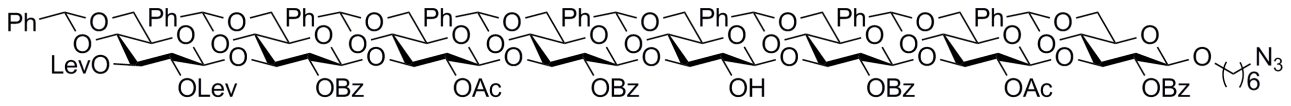
Preparation of the octasaccharide acceptor 13

6-Azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (12)

A mixture of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (11) (631 mg, 0.453 mmol, 1.00 eq.), ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (10) (752 mg, 0.498 mmol, 1.10 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (906 mg) in dry CH_2Cl_2 (18.1 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (135 mg, 0.598 mmol, 1.32 eq.) and a catalytic amount of trifluoromethanesulfonic acid (20.0 μL, 0.227 mmol, 0.500 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 92:8 toluene:acetone and further purified by gel permeation chromatography (GPC) to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (12) (1.25 g, 0.441 mmol, 97%).

$[\alpha]_D^{24}$ = -28.3 (c = 0.840, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-8.03 (m, 8H), 7.18-7.63 (m, 52H), 5.50 (s, 1H), 5.47 (s, 1H), 5.39 (s, 1H), 4.85-5.21 (m, 16H), 4.71-4.74 (m, 2H), 4.67 (d, 1H, *J* = 6.3 Hz), 4.52 (d, 1H, *J* = 7.7 Hz), 4.32-4.37 (m, 2H), 3.22-4.24 (m, 41H), 3.05 (t, 2H, *J* = 7.2 Hz), 2.35-2.74 (m, 9H, Lev, OH), 2.09 (s, 3H), 2.01 (s, 3H), 1.80 (s, 3H), 1.77 (s, 3H), 1.10-1.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5 x 2, 171.9, 171.4, 169.6, 169.0, 165.5, 165.2, 164.8 x 3, 137.4 x 3, 137.3 x 2, 137.1, 137.0, 136.9,

133.9, 133.8, 133.6, 133.5, 130.0, 129.9, 129.8 x 2, 129.7 x 2, 129.6, 129.5, 129.4, 129.3, 129.2 x 2, 129.1, 129.0, 128.9, 128.7 x 2, 128.3 x 2, 128.2 x 2, 126.4, 126.3 x 2, 126.2, 126.1, 126.0, 102.9, 101.7, 101.6 x 2, 101.5, 101.4, 101.3, 101.1, 101.0, 100.8, 100.6, 99.8, 99.6, 98.9, 98.7, 98.6, 78.8, 78.7, 78.6 x 2, 78.5, 78.4, 78.3, 78.0, 77.8, 77.7, 77.6, 76.6, 76.5, 76.4, 76.2, 74.5, 74.4, 74.3 x 2, 73.9, 73.8, 72.6, 72.4, 71.8 x 2, 69.9, 68.8 x 2, 68.7 x 2, 68.6 x 2, 68.5 x 2, 66.8, 66.7, 66.2, 66.1, 65.9 x 2, 65.8, 65.7 x 2, 51.3, 38.0, 37.8, 29.8, 29.7, 29.3, 28.6, 28.0, 27.6, 26.3, 25.4, 20.8, 20.5; IR (solid): 2989, 2883, 2822, 2267, 1725, 1386, 1262, 1091, 675, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{152}H_{161}N_4O_{51}$ $[M+NH_4]^+$ *m/z* = 2858.0128, found: 2858.0181.



6-Azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (13)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (12) (57.9 mg, 20.4 μmol, 1.00 eq.) in pyridine (0.408 mL) was added acetic anhydride (19.1 μL, 0.204 mmol, 10.0 eq.) and a catalytic amount of DMAP (1.25 mg, 10.2 μmol, 0.500 eq.) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in THF (1.00 mL) was added acetic acid (0.300 mL) and hydrazine monohydrate (0.100 mL) at 0 ˚C. After being stirred at the same temperature for 20 min, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 88:12

toluene:acetone to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (13) (50.8 mg, 18.9 μmol, 2 steps 93%).

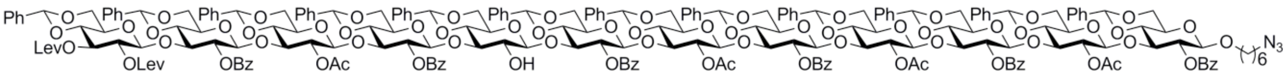
$[\alpha]_D^{23}$ = -23.8 (c = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-8.06 (m, 8H), 7.17-7.63 (m, 52H), 5.52 (s, 1H), 5.42 (s, 1H), 5.32 (s, 1H), 5.26 (dd, 1H, *J* = 6.8 Hz, 6.8 Hz), 5.12 (s, 2H), 5.06 (d, 1H, *J* = 6.8 Hz), 4.94-5.00 (m, 3H), 4.76-4.88 (m, 8H), 4.70 (d, 1H, *J* = 5.3 Hz), 4.63 (br-d, 2H, *J* = 5.3 Hz), 4.48-4.52 (m, 2H), 4.33 (dd, 1H, *J* = 4.3 Hz, 10.1 Hz), 3.25-4.19 (m, 42H), 3.06 (br-s, 1H), 3.05 (t, 2H, *J* = 7.2 Hz), 2.71 (br-s, 1H), 1.79 (s, 3H), 1.77 (s, 3H), 1.71 (s, 3H), 1.14-1.48 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 169.0, 168.9, 165.5, 164.8, 164.6 x 2, 137.8, 137.2, 137.0, 136.8, 133.9, 133.8, 133.5, 133.3, 129.8, 129.7 x 2, 129.6, 129.5 x 2, 129.4, 129.3, 129.2 x 2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4 x 2, 128.2 x 2, 128.1 x 2, 128.0 x 2, 127.8, 126.3, 126.2, 126.1, 126.0, 125.3, 102.5, 101.7, 101.6, 101.5, 101.4 x 2, 101.3 x 2, 101.0, 100.9, 100.8, 99.1, 98.2 x 2, 98.0, 97.8, 80.2, 78.7, 78.5, 78.2 x 2, 78.0, 77.9, 75.9, 75.7 x 2, 75.4, 75.2, 74.2, 74.1, 73.4, 73.3, 72.7, 72.2, 72.0 x 2, 71.9 x 2, 69.7, 68.6, 68.5, 68.4 x 2, 68.3, 66.5, 65.9, 65.7, 65.5, 65.3, 51.1, 29.1, 28.5, 26.1, 25.3, 21.4, 20.5 x 2, 20.3; IR (solid): 3046, 2883, 2320, 1732, 1373, 1266, 1097, 997, 700, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{144}H_{151}N_4O_{48}$ $[M+NH_4]^+$ *m/z* = 2703.9498, found: 2703.9475.

Preparation of the dodecasaccharide acceptor 15

6-Azidohexyl
2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (14)

A mixture of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (13) (125 mg, 46.6 μmol, 1.00 eq.), ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (10) (84.3 mg, 55.9 μmol, 1.20 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (279 mg) in dry CH_2Cl_2 (2.79 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (15.1 mg, 67.0 μmol, 1.44 eq.) and a catalytic amount of trifluoromethanesulfonic acid (2.10 μL, 23.3 μmol, 0.500 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 91:9 toluene:acetone and further purified by gel permeation chromatography (GPC) to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (14) (170 mg, 41.1 μmol, 88%).

$[\alpha]_D^{16}$ = -24.6 (c = 0.950, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-8.03 (m, 12H), 7.16-7.62 (m, 78H), 5.51 (s, 1H), 5.47 (s, 1H), 5.38 (s, 1H), 5.10-5.21 (m, 6H), 4.91-5.04 (m, 11H), 4.78-4.88 (m, 9H), 4.68-4.72 (m, 3H), 4.63 (br-d, 2H, *J* = 6.3 Hz), 4.48 (d, 1H, *J* = 7.7 Hz), 4.31-4.37 (m, 2H), 3.22-4.24 (m, 61H), 3.05 (t, 2H, *J* = 7.2 Hz), 2.35-2.75 (m, 9H, Lev, OH), 2.09 (s, 3H), 2.01 (s, 3H), 1.85 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H), 1.72 (s, 3H), 1.10-1.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 206.4, 171.8, 171.4, 169.6, 169.1, 169.0 x 2, 165.5, 165.1, 164.9, 164.8 x 2, 164.7, 137.4, 137.3, 137.2, 137.0, 136.9, 134.0, 133.9, 133.7, 133.6, 133.4, 129.9, 129.8 x 3, 129.7 x 2, 129.6, 129.5 x 2, 129.4, 129.3 x 2, 129.2 x 2, 129.1, 129.0, 128.9, 128.8 x 2, 128.7, 128.6, 128.3, 128.2 x 3, 128.1, 126.3 x 2, 126.2, 126.1, 126.0, 102.9, 101.7, 101.6, 101.5, 101.4 x 2, 101.3, 101.2, 101.1, 100.9, 100.8, 100.6, 99.9, 99.2, 98.8, 98.5, 98.4, 98.2, 97.9, 78.7, 78.6 x 2, 78.5, 78.4, 78.2, 78.1, 78.0, 76.3, 76.1, 75.9 x 2, 75.7, 75.5, 74.5, 74.4 x 2, 74.2, 74.1, 73.8 x 2, 72.5, 72.4, 72.2, 71.8, 71.7, 69.9, 68.8, 68.7, 68.6, 68.5, 66.8, 66.7, 66.2, 66.0 x 2, 65.8, 65.7, 51.2, 37.9, 37.7, 29.7 x 2, 29.3, 28.6, 28.0, 27.6, 26.3, 25.4, 20.7 x 3, 20.5; IR (solid): 3492, 2971, 2877, 2417, 2097, 1732, 1602, 1452, 1373, 1262, 1222, 1096, 996, 765, 697, 508 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{222}H_{229}N_4O_{75}$ $[M+NH_4]^+$ *m/z* = 4150.4228, found: 4150.4053.



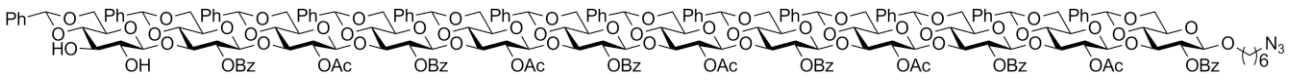
6-Azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (15)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (14) (72.6 mg, 17.6 μmol, 1.00 eq.) in pyridine (1.76 mL) was added acetic anhydride (16.4 μL, 0.176 mmol,

10.0 eq.) and a catalytic amount of DMAP (1.07 mg, 8.80 μmol, 0.500 eq.) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used for the next reaction without further purification.

To a stirred solution of the residue in THF (1.00 mL) was added acetic acid (0.300 mL) and hydrazine monohydrate (0.100 mL) at 0 ˚C. After being stirred at the same temperature for 20 min, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 88:12 toluene:acetone to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (**15**) (65.2 mg, 16.4 μmol, 2 steps 93%).

$[\alpha]_D^{16}$ = -24.2 (c = 1.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-8.06 (m, 12H), 7.17-7.62 (m, 78H), 5.52 (s, 1H), 5.42 (s, 1H), 5.32 (s, 1H), 5.26 (dd, 1H, *J* = 6.8 Hz, 7.2 Hz), 5.16 (s, 2H), 5.13 (s, 1H), 5.12 (s, 1H), 5.06 (d, 1H, *J* = 6.3 Hz), 4.94-4.98 (m, 3H), 4.77-4.88 (m, 16H), 4.71 (d, 1H, *J* = 5.3 Hz), 4.63-4.64 (m, 4H), 4.47-4.52 (m, 2H), 4.33 (dd, 1H, *J* = 4.3 Hz, 10.1 Hz), 3.18-4.19 (m, 62H), 3.03-3.08 (m, 3H), 2.65 (br-s, 1H), 1.79 (s, 3H), 1.77 (s, 3H), 1.76 (br-s, 6H), 1.72 (s, 3H), 1.14-1.46 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 169.1 x 3, 165.6, 164.9 x 2, 164.8 x 2, 137.4 x 3, 137.3 x 2, 137.1, 136.9, 134.0 x 2, 133.6, 129.9, 129.8 x 2, 129.7, 129.6, 129.5, 129.3 x 4, 129.2 x 2, 129.1 x 5, 129.0 x 3, 128.9, 128.8 x 2, 128.6 x 2, 128.4, 128.3 x 3, 128.2 x 4, 128.1 x 2, 126.4 x 2, 126.3, 126.2, 102.7, 101.9, 101.7, 101.6 x 3, 101.5, 101.4, 101.2, 101.1, 101.0 x 2, 98.5, 98.4, 98.3 x 3, 97.9, 78.9, 78.7, 78.4, 78.3 x 3, 78.2 x 3, 78.1, 76.6, 75.9, 75.8, 75.7, 74.4, 74.3 x 2, 74.2 x 3, 73.6, 72.8, 72.1 x 3, 69.9, 68.8, 68.7, 68.6 x 4, 68.4, 66.7, 66.1, 66.0 x 2, 65.8, 65.6, 51.3, 29.8, 29.3, 28.6, 26.3, 25.4, 20.7, 20.6 x 2, 20.5; IR (solid): 2971, 2877, 2825, 1733, 1374, 1262, 1222, 1091, 695, 505 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{214}H_{219}N_4O_{72}$ $[M+NH_4]^+$ *m/z* = 3996.3598, found: 3996.3635.



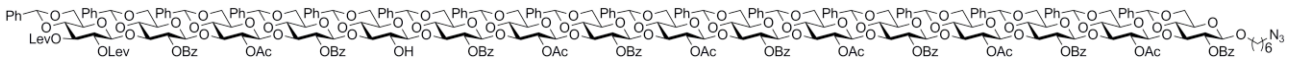
Preparation of the hexadecasaccharide 18

6-Azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (18)

A mixture of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (15) (20.4 mg, 5.12 μmol, 1.00 eq.), ethylthio 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (10) (9.30 mg, 6.15 μmol, 1.20 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (51.2 mg) in dry CH_2Cl_2 (0.512 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (1.70 mg, 7.37 μmol, 1.44 eq.) and a catalytic amount of trifluoromethanesulfonic acid (0.317 μL, 3.58 μmol, 0.700 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 91:9 toluene:acetone and further purified by gel permeation chromatography (GPC) to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzyl

idene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (**18**) (22.8 mg, 4.20 μmol, 82%).

$[\alpha]_D^{24}$ = -17.6 (c = 2.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-8.03 (m, 16H), 7.14-7.62 (m, 104H), 5.51 (s, 1H), 5.47 (s, 1H), 5.38 (s, 1H), 4.63-5.21 (m, 43H), 4.48 (d, 1H, *J* = 7.7 Hz), 4.31-4.37 (m, 2H), 3.17-4.24 (m, 81H), 3.05 (t, 2H, *J* = 7.2 Hz), 2.35-2.70 (m, 9H, Lev, OH), 2.08 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H), 1.78 (s, 3H), 1.76 (s, 9H), 1.71 (s, 3H), 1.08-1.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5 x 2, 171.8, 171.4, 169.6, 169.1 x 3, 169.0, 165.6 165.2, 164.9 x 2, 164.8 x 3, 137.4, 137.3, 137.2, 137.1, 137.0, 136.9, 134.1 x 2, 134.0 x 3, 133.9 x 3, 133.7, 133.6, 133.4, 129.9, 129.8 x 2, 129.7 x 2, 129.6, 129.5 x 2, 129.4, 129.3 x 2, 129.2, 129.1, 129.0, 128.9, 128.8 x 2, 128.7, 128.6, 128.3 x 2, 128.2 x 3, 128.1, 128.0, 126.4, 126.3 x 3, 126.2, 126.1, 126.0, 125.4, 102.9, 102.8, 101.7, 101.6, 101.5 x 2, 101.4, 101.3 x 2, 101.2 x 2, 101.1 x 3, 101.0, 100.9, 100.8, 100.6, 99.9, 99.2, 98.8, 98.4 x 2, 98.2, 98.0 x 2, 97.8 x 2, 78.7 x 3, 78.6, 78.5 x 2, 78.4, 78.2 x 2, 78.1, 78.0 x 3, 77.9, 77.8, 77.7, 76.6 x 2, 76.4, 76.3 x 2, 76.0, 75.9, 75.8, 75.7 x 2, 75.6 x 3, 75.4, 75.3, 74.5 x 2, 74.4 x 2, 74.3 x 2, 74.2 x 2, 74.1, 73.9, 73.8, 72.5, 72.3, 72.2 x 2, 72.1 x 2, 71.8 x 2, 71.7, 69.9, 68.9 x 3, 68.8, 68.7, 68.6, 68.5, 68.4 x 2, 68.2, 66.8, 66.7, 66.2, 66.1, 66.0 x 2, 65.9, 65.8, 65.7, 65.6, 51.2, 38.8, 37.9, 37.7, 32.0, 29.8, 29.7, 29.6 x 3, 29.5 x 2, 29.4, 29.3, 29.0, 28.6, 28.0, 27.6, 26.3, 25.4, 23.0, 22.7, 21.5, 20.7 x 2, 20.6, 20.5; IR (solid): 3536, 2926, 2093, 1720, 1369, 1256, 1093, 909, 647, 496 cm^{-1}.

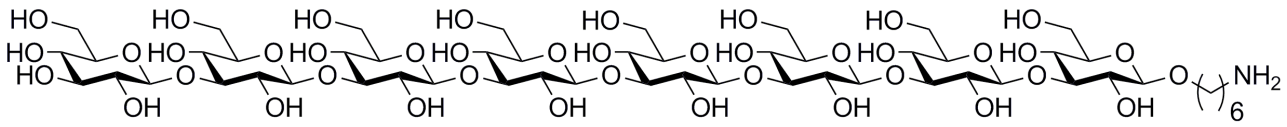


Deprotection of the octa-, dodeca- and hexadecasaccharide 12, 14 and 18

6-Aminohexyl
3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (22)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (12) (28.5 mg, 10.6 μmol, 1.00 eq.) in NH_3/THF/EtOH (8.50 mL/1.00 mL/0.500 mL) was added a large amount of lithium (100 mg) at -78 ˚C. After being stirred under reflux for 1.5 h, the reaction mixture was added methanol (1.00 mL). After being stirred at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water and further purified by revese-phase column chromatography (Bond Elut-C18) with 90:10 water:methanol to give 6-aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (22) (7.00 mg, 4.58 μmol, 43%).

$[\alpha]_D^{24}$ = -33.7 (c = 0.255, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.70-4.76 (m, 7H, anomericH x 7), 4.44 (d, 1H, anomericH, *J* = 7.7 Hz), 3.88-3.91 (m, 9H), 3.70-3.85 (m, 16H), 3.33-3.56 (m, 27H), 2.99 (t, 2H, *J* = 7.2 Hz), 1.59-1.68 (m, 4H), 1.37-1.40 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ 103.7, 103.6, 103.5, 103.4, 102.8, 85.5 x 2, 85.4, 85.3, 85.2 x 2, 85.0, 76.8, 76.6, 76.5, 76.4, 74.3, 74.2, 74.1, 74.0, 73.7, 71.2, 70.4, 69.0, 68.9, 61.5, 40.5, 29.3, 28.7, 26.2, 25.4; IR (solid): 3307, 2897, 2341, 1591, 1438, 1307, 1154, 1042, 669, 525 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{54}H_{96}NO_{41}$ $[M+H]^+$ *m/z* = 1414.5458, found: 1414.5460.

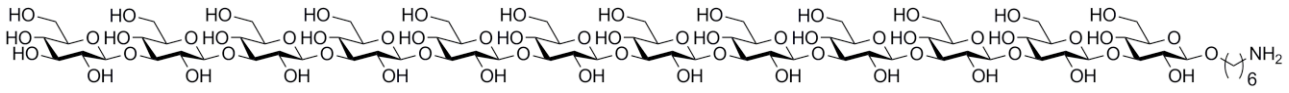


6-Aminohexyl
3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyran

oside (20)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (14) (30.8 mg, 7.45 μmol, 1.00 eq.) in NH_3/THF/EtOH (8.50 mL/1.00 mL/0.500 mL) was added a large amount of lithium (100 mg) at -78 ˚C. After being stirred under reflux for 1.5 h, the reaction mixture was added methanol (1.00 mL). After being stirred at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water and further purified by revese-phase column chromatography (Bond Elut-C18) with 90:10 water:methanol to give 6-aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (20) (13.8 mg, 6.69 μmol, 90%).

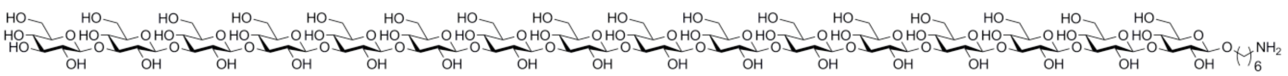
$[\alpha]_D^{24}$ = -13.9 (c = 0.315, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.70-4.76 (m, 11H, anomericH x 11), 4.44 (d, 1H, anomericH, *J* = 8.2 Hz), 3.88-3.91 (m, 13H), 3.63-3.81 (m, 24H), 3.32-3.56 (m, 37H), 2.77 (t, 2H, *J* = 7.2 Hz), 1.49-1.63 (m, 4H), 1.28-1.36 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ 103.6, 103.4, 102.8, 85.5, 85.2, 85.0, 76.8, 76.5, 76.4, 74.3, 74.1, 73.7, 71.2, 70.4, 69.0, 68.9, 61.5, 40.4, 30.9, 30.7, 30.5, 30.3, 30.1, 29.9, 29.7, 29.3, 28.1, 26.1, 25.4; IR (solid): 3341, 2912, 2352, 2014, 1836, 1592, 1439, 1309, 1154, 1077, 1044, 911, 671, 526 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{78}H_{136}NO_{61}$ $[M+H]^+$ *m/z* = 2062.7571, found: 2062.7598.



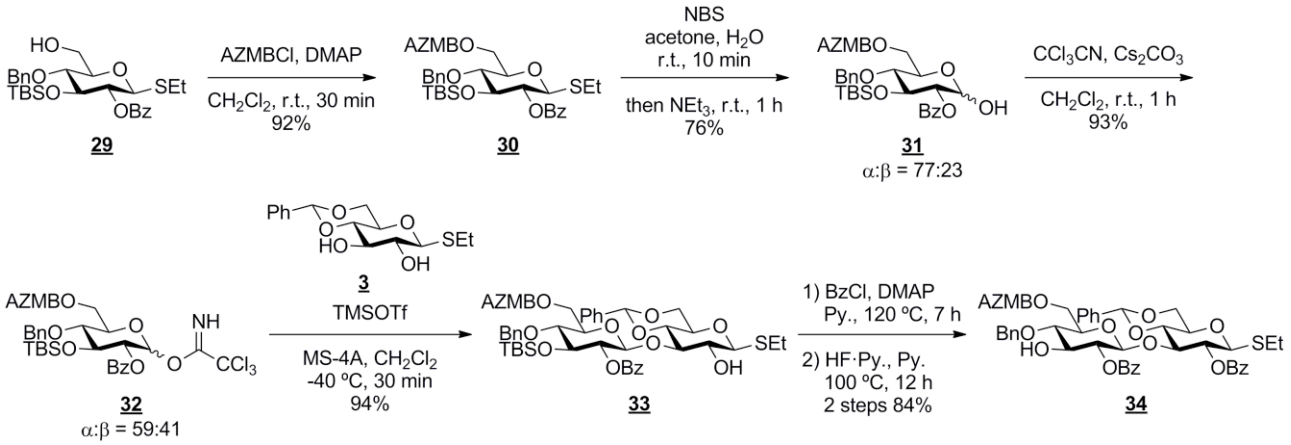
6-Aminohexyl
3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (2)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (**18**) (50.7 mg, 9.34 μmol, 1.00 eq.) in NH_3/THF/EtOH (8.50 mL/1.00 mL/0.500 mL) was added a large amount of lithium (100 mg) at -78 ˚C. After being stirred under reflux for 1.5 h, the reaction mixture was added methanol (1.00 mL). After being stirred at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water and further purified by revese-phase column chromatography (Bond Elut-C18) with 80:20 water:methanol to give 6-aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (**2**) (20.2 mg, 7.45 μmol, 80%).

$[\alpha]_D^{23}$ = -22.5 (c = 0.130, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.71-4.77 (m, 14H, anomericH x 14), 4.58 (d, 1H, anomericH, *J* = 7.7 Hz), 4.45 (d, 1H, anomericH, *J* = 7.7 Hz), 3.88-3.92 (m, 17H), 3.67-3.78 (m, 32H), 3.32-3.56 (m, 49H), 2.96 (t, 2H, *J* = 7.7 Hz), 1.57-1.63 (m, 4H), 1.38 (br-s, 4H); ^{13}C NMR (100 MHz, D_2O) δ 103.4, 85.1, 76.5, 74.1, 70.4, 69.0, 61.5; IR (solid): 3341, 2898, 2327, 2155, 1597, 1458, 1313, 1154, 1072, 1042, 806, 670, 526 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{102}H_{176}NO_{81}$ $[M+H]^+$ *m/z* = 2710.9684, found: 2710.9724.



Preparation of the disaccharide acceptor 34

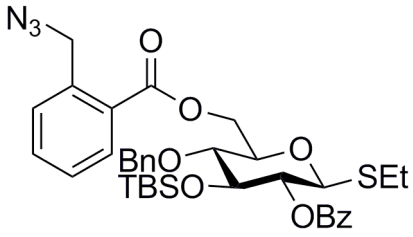


Ethylthio 6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (30)

To a stirred solution of ethylthio 2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside[3] (29) (778 mg, 1.46 mmol, 1.00 eq.) in CH_2Cl_2 (7.26 mL) was added 2-(azidomethyl)benzoyl chloride[4] (4.84 mmol, 3.32 eq.) and DMAP (1.48 g, 12.1 mmol, 8.29 eq.) at room temperature. After being stirred at the same temperature for 30 min, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 90:10 hexane:ethyl acetate to give ethylthio 6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (30) (927 mg, 1.34 mmol, 92%).

$[\alpha]_D^{20}$ = +24.6 (c = 0.855, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-8.06 (m, 3H, aromatic), 7.30-7.61 (m, 11H, aromatic), 5.25 (dd, 1H, H-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.89 (d, 1H, PhC*H*$_2$, J_{gem} = 11.1 Hz), 4.80 (s, 2H, N_3CH_2), 4.63 (dd, 1H, H-6a, $J_{5,6a}$ = 2.4 Hz, J_{gem} = 12.1 Hz), 4.58 (d, 1H, PhC*H*$_2$, J_{gem} = 11.1 Hz), 4.56 (d, 1H, H-1, $J_{1,2}$ = 9.7 Hz), 4.35 (dd, 1H, H-6b, $J_{5,6b}$ = 4.8 Hz, J_{gem} = 12.1 Hz), 4.01 (dd, 1H, H-4, $J_{3,4}$ = 8.7 Hz, $J_{4,5}$ = 9.2 Hz), 3.74 (ddd, 1H, H-5, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 4.8 Hz), 3.63 (dd, 1H, H-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 8.7 Hz), 2.60-2.78 (m, 2H, SC*H*$_2$CH$_3$), 1.18 (t, 3H, SCH_2CH_3, J = 7.2 Hz), 0.80 (s, 9H, TBS), 0.04 (s, 3H, TBS), -0.13 (s, 3H, TBS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.6, 137.6, 137.5, 133.2, 133.0, 121.4, 130.3, 130.0, 129.8, 128.5, 128.4, 128.2, 128.0, 127.8, 83.7, 78.8, 77.0, 75.4, 72.9, 63.9, 53.1, 25.9, 25.7, 23.9, 17.9, 14.9, -3.9, -4.1; IR (solid): 2959, 2928, 2856, 2104, 1724, 1452, 1262, 1070, 838, 711, 519

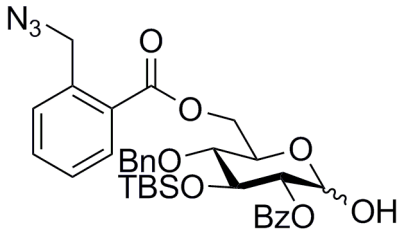
cm^{-1}; HRMS (ESI-TOF) calcd for $C_{36}H_{49}N_4O_7SiS$ $[M+NH_4]^+$ *m/z* = 709.3091, found: 709.3082.



6-*O*-(2-(Azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-D-glucopyranose (31)

To a stirred solution of ethylthio 6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranoside (30) (682 mg, 0.986 mmol, 1.00 eq.) in acetone (4.93 mL) and water (49.3 μL) was added *N*-bromosuccinimide (211 mg, 1.18 mmol, 1.20 eq.) at 0 ˚C. After being stirred at the same temperature for 10 min, the reaction mixture was added triethylamine (1.00 mL). After being stirred at room temperature for 1 h, the reaction mixture was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 85:15 hexane:ethyl acetate to give 6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-D-glucopyranose (31) (488 mg, 0.753 mmol, 76%, α:β = 77:23). The α:β ratio was determined by ^{1}H NMR analysis.

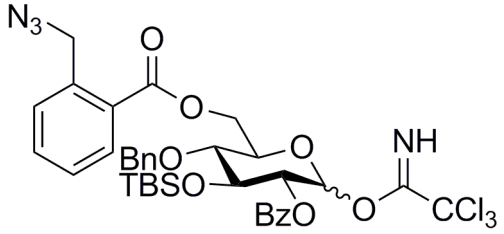
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-8.10 (m, 6H, aromaticαβ), 7.22-7.66 (m, 22H, aromaticαβ), 5.41 (br-s, 1H, H-1α), 5.14 (dd, 1H, H-2α, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 9.2 Hz), 5.10 (dd, 1H, H-2β, $J_{1,2}$ = 8.7 Hz, $J_{2,3}$ = 8.7 Hz), 4.88-4.93 (m, 2H, PhC*H*$_2$), 4.73-4.83 (m, 5H, H-1β, N_3CH_2αβ), 4.57-4.65 (m, 4H, H-6aα, H-6aβ, PhC*H*$_2$), 4.37-4.42 (m, 3H, H-3α, H-6bα, H-6bβ), 4.30 (ddd, 1H, H-5α, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 1.9 Hz, $J_{5,6b}$ = 4.3 Hz), 4.06 (dd, 1H, H-3β, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 8.7 Hz), 3.77 (ddd, 1H, H-5β, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 4.3 Hz), 3.58-3.67 (m, 2H, H-4α, H-4β), 3.34 (d, 1H, OHβ, $J_{1,OH}$ = 9.7 Hz), 2.97 (br-s, 1H, OHα), 0.79 (s, 18H, TBSαβ), -0.05-0.08 (m, 12H, TBSαβ); IR (solid): 3427, 2928, 2856, 2411, 2101, 1724, 1453, 1264, 1097, 838, 713, 520 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{45}N_4O_8Si$ $[M+NH_4]^+$ *m/z* = 665.3007, found: 665.3002.



O-(6-*O*-(2-(Azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-D-glucopyranosyl)trichloroacetimidate (32)

To a stirred solution of 6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-D-glucopyranose (31) (960 mg, 1.48 mmol, 1.00 eq.) in CH_2Cl_2 (2.96 mL) was added trichloroacetonitrile (0.742 mL, 7.40 mmol, 5.00 eq.) and a catalytic amount of Cs_2CO_3 (48.0 mg, 0.148 mmol, 0.100 eq.) at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 90:10 hexane:ethyl acetate to give *O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-D-glucopyranosyl)trichloroacetimidate (32) (1.09 g, 1.38 mmol, 93%, α:β = 59:41). The α:β ratio was determined by ^{1}H NMR analysis.

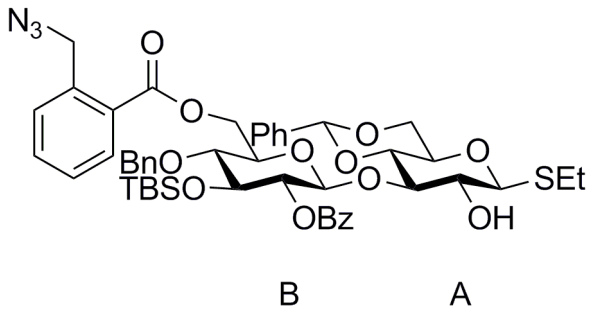
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H, NHβ), 8.51 (s, 1H, NHα), 8.00-8.05 (m, 6H, aromaticαβ), 7.22-7.61 (m, 22H, aromaticαβ), 6.55 (d, 1H, H-1α, $J_{1,2}$ = 3.4 Hz), 5.97 (d, 1H, H-1β, $J_{1,2}$ = 7.2 Hz), 5.51 (dd, 1H, H-2β, $J_{1,2}$ = 7.2 Hz, $J_{2,3}$ = 8.2 Hz), 5.40 (dd, 1H, H-2α, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 9.7 Hz), 4.93 (d, 1H, PhC*H*$_2$, J_{gem} = 11.1 Hz), 4.89 (d, 1H, PhC*H*$_2$, J_{gem} = 11.6 Hz), 4.74-4.83 (m, 4H, N_3CH_2αβ), 4.56-4.65 (m, 4H, H-6aα, H-6aβ, PhC*H*$_2$), 4.38-4.49 (m, 3H, H-3α, H-6bα, H-6bβ), 4.25 (ddd, 1H, H-5α, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 1.9 Hz, $J_{5,6b}$ = 3.4 Hz), 4.12 (dd, 1H, H-3β, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 8.7 Hz), 3.96 (ddd, 1H, H-5β, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 2.4 Hz, $J_{5,6b}$ = 4.8 Hz), 3.72-3.79 (m, 2H, H-4α, H-4β), 0.80-0.83 (m, 18H, TBSαβ), -0.08-0.11 (m, 12H, TBSαβ); IR (solid): 2959, 2855, 2105, 1725, 1672, 1452, 1255, 1070, 712, 519 cm^{-1}.



Ethylthio
3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (33)

A mixture of ethylthio 4,6-*O*-benzylidene-β-D-glucopyranoside (3) (5.64 g, 18.1 mmol, 1.20 eq.), *O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-D-glucopyranosyl) trichloroacetimidate (32) (11.9 g, 15.1 mmol, 1.00 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (15.1 g) in dry CH_2Cl_2 (151 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -15 ˚C. A catalytic amount of trimethylsilyltrifluoromethanesulfonate (0.544 mL, 3.01 mmol, 0.200 eq.) was added to the reaction mixture. After being stirred at the same temperature for 1 h, the reaction mixture was neutralized with triethylamine, filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 90:10 hexane:ethyl acetate to give ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (33) (13.3 g, 14.2 mmol, 94%).

$[\alpha]_D^{19}$ = -3.94 (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 2H, aromatic, J = 7.2 Hz), 7.97 (d, 1H, aromatic, J = 7.7 Hz), 7.15-7.60 (m, 16H, aromatic), 5.48 (s, 1H, benzylidene), 5.23 (dd, 1H, B-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 8.7 Hz), 4.93 (d, 1H, B-1, $J_{1,2}$ = 7.7 Hz), 4.83 (d, 1H, PhCH_2, J_{gem} = 11.1 Hz), 4.74 (d, 1H, N_3CH_2, J_{gem} = 14.5 Hz), 4.67 (d, 1H, N_3CH_2, J_{gem} = 14.5 Hz), 4.50 (d, 1H, PhCH_2, J_{gem} = 11.1 Hz), 4.46 (dd, 1H, B-6a, $J_{5,6a}$ = 1.9 Hz, J_{gem} = 11.6 Hz), 4.25-4.31 (m, 3H, A-1, A-6a, B-6b), 4.00 (dd, 1H, B-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 3.79 (dd, 1H, A-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 8.7 Hz), 3.54-3.72 (m, 4H, A-4, B-4, B-5, A-6b), 3.31-3.42 (m, 2H, A-2, A-5), 2.48-2.64 (m, 2H, SCH_2CH$_3$), 2.42 (d, 1H, OH, $J_{A\text{-}2,OH}$ = 1.9 Hz), 1.18 (t, 3H, SCH_2CH_3, J = 7.2 Hz), 0.79 (s, 9H, TBS), 0.03 (s, 3H, TBS), -0.11 (s, 3H, TBS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.9, 137.5, 137.3, 137.1, 133.3, 132.8, 131.6, 130.2, 129.9, 129.7, 129.0, 128.6, 128.5 x 2, 128.2 x 2, 127.9, 127.8, 126.0, 101.4, 101.3, 86.2, 81.8, 79.2, 78.7, 75.4, 75.3, 72.9, 72.8, 71.0, 68.6, 63.7, 53.1, 25.7, 24.0, 17.9, 15.2, -4.0, -4.2; IR (solid): 3478, 2928, 2855, 2102, 1724, 1600, 1452, 1264, 1071, 985, 837, 700, 518 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{49}H_{63}N_4O_{12}S$ $[M+NH_4]^+$ *m/z* = 959.3932, found: 959.3979.



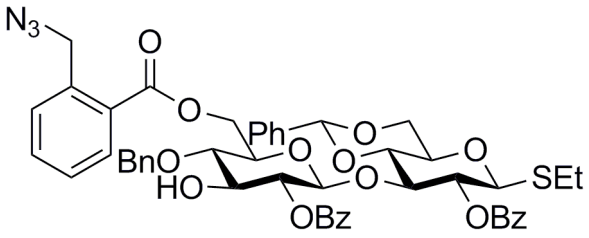
Ethylthio

3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (34)

To a stirred solution of ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (33) (3.05 g, 3.23 mmol, 1.00 eq.) in pyridine (16.2 mL) was added benzoyl chloride (1.14 mL, 9.69 mmol, 3.00 eq.) and a catalytic amount of DMAP (39.5 mg, 0.323 mmol, 0.100 eq.) at room temperature. After being stirred at 120 ˚C for 7 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was used for the next reaction without further purification.

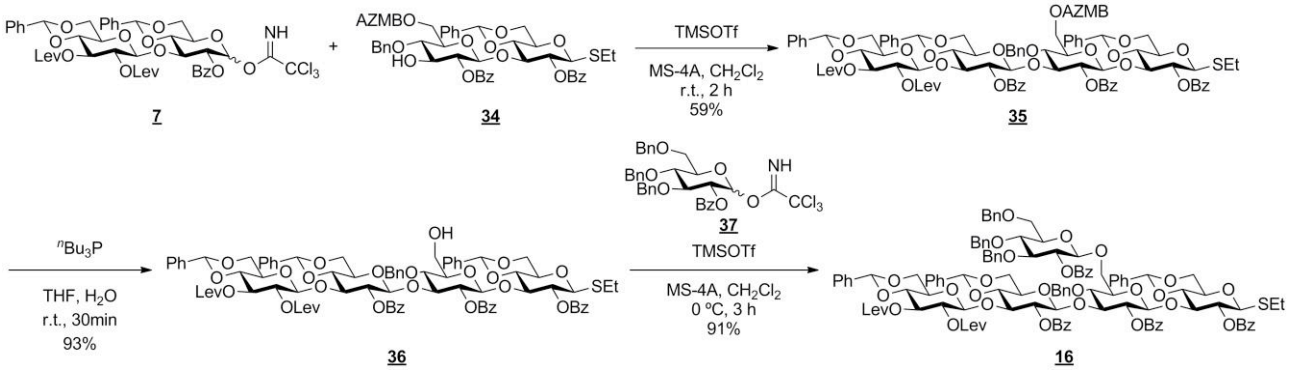
To a stirred solution of the residue in pyridine (16.2 mL) was added HF/ pyridine (1.62 mL) at room temperature. After being stirred at 100 ˚C for 12 h, the reaction mixture was poured into 1 M HCl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 78:22 hexane:ethyl acetate to give ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (34) (2.53 g, 2.72 mmol, 2 steps 84%).

$[\alpha]_D^{18}$ = -8.44 (c = 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, 1H, aromatic, J = 7.7 Hz), 7.83 (d, 2H, aromatic, J = 8.2 Hz), 7.73 (d, 2H, aromatic, J = 8.2 Hz), 7.21-7.59 (m, 19H, aromatic), 5.55 (s, 1H, benzylidene), 5.30 (dd, 1H, A-2, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 8.7 Hz), 5.01 (dd, 1H, B-2, $J_{1,2}$ = 7.2 Hz, $J_{2,3}$ = 8.2 Hz), 4.86 (d, 1H, B-1, $J_{1,2}$ = 7.2 Hz), 4.65-4.78 (m, 3H, PhCH_2, N_3CH_2), 4.50-4.60 (m, 3H, A-1, B-6a, PhCH_2), 4.32-4.37 (m, 2H, A-6a, B-6b), 4.27 (dd, 1H, A-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 3.71-3.83 (m, 3H, B-3, A-4, A-6b), 3.62 (dd, 1H, B-4, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 8.7 Hz), 3.49-3.55 (m, 2H, A-5, B-5), 2.61-2.68 (m, 2H, SCH_2CH$_3$), 2.57 (d, 1H, OH, $J_{B\text{-}3,OH}$ = 4.8 Hz), 1.16 (t, 3H, SCH_2CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 164.8, 137.6, 137.2, 137.1, 133.2, 132.9, 131.6, 130.1, 130.0, 129.8, 129.5, 129.2 x 2, 128.7, 128.6 x 2, 128.5, 128.3 x 3, 128.1, 126.1, 101.6, 99.9, 84.3, 79.4, 78.7, 77.8, 76.5, 75.3, 74.9, 72.8, 72.2, 71.1, 68.7, 63.7, 53.1, 24.1, 14.8; IR (solid): 3499, 2967, 2875, 2105, 1732, 1602, 1452, 1273, 1096, 913, 712, 542 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{50}H_{53}N_4O_{13}S$ $[M+NH_4]^+$ m/z = 949.3330, found: 949.3322.



B A

Preparation of the pentasaccharide donor 16

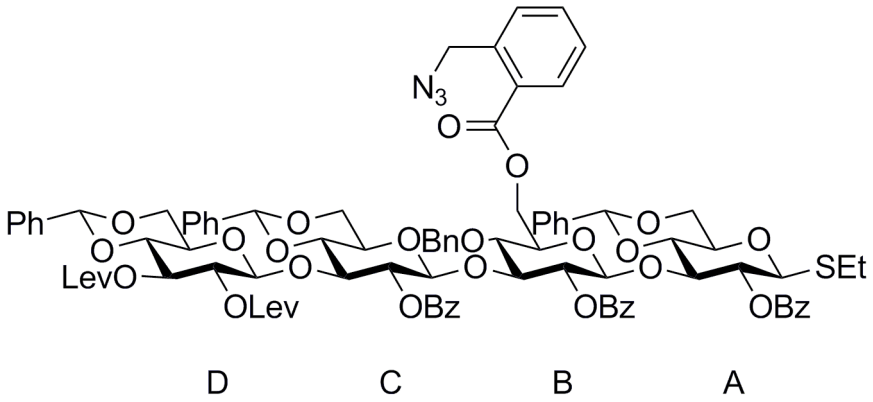


Ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (35)

A mixture of ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (34) (521 mg, 0.559 mmol, 1.00 eq.), *O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-D-glucopyranosyl)trichloroacetimidate (7) (592 mg, 0.615 mmol, 1.10 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (280 mg) in dry CH_2Cl_2 (2.80 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -50 ˚C. A catalytic amount of trimethylsilyltrifluoromethanesulfonate (10.1 μL, 55.9 μmol, 0.100 eq.) was added to the reaction mixture. After being stirred at room temperature for 2 h, the reaction mixture was neutralized with triethylamine, filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 85:15 toluene:ethyl acetate and further purified by gel permeation chromatography (GPC) to give ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (35) (573 mg, 0.330 mmol, 59%).

$[\alpha]_D^{18}$ = -17.0 (c = 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 1H, aromatic, *J* = 7.7 Hz), 7.92 (d, 2H, aromatic, *J* = 7.7 Hz), 7.81 (d, 2H, aromatic, *J* = 7.7 Hz), 7.14-7.72 (m, 34H, aromatic), 5.52 (s, 1H, benzylidene), 5.49 (s, 1H, benzylidene), 5.37 (s, 1H, benzylidene), 5.25 (dd, 1H, C-2, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 8.7 Hz), 4.93-5.06 (m, 4H, C-1, B-2, D-2, D-3), 4.69-4.81 (m, 4H, B-1, A-2, N_3CH_2), 4.63 (d, 1H, PhC*H*$_2$, J_{gem} = 10.6 Hz), 4.55 (d, 1H, D-1, $J_{1,2}$ = 7.7 Hz), 4.37-4.44 (m, 3H, A-1, B-6a, B-6b), 4.16-4.32 (m, 4H, A-3, A-6a,

C-6a, D-6a), 4.02 (dd, 1H, B-3, $J_{2,3}$ = 5.8 Hz, $J_{3,4}$ = 7.2 Hz), 3.93-3.98 (m, 2H, C-3, PhC*H*$_2$), 3.77 (dd, 1H, B-4, $J_{3,4}$ = 7.2 Hz, $J_{4,5}$ = 10.1 Hz), 3.62-3.70 (m, 5H, C-4, B-5, A-6b, C-6b, D-6b), 3.58 (dd, 1H, D-4, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.7 Hz), 3.36-3.44 (m, 2H, A-5, C-5), 3.25-3.32 (m, 2H, A-4, D-5), 2.14-2.71 (m, 10H, Lev, SC*H*$_2$CH$_3$), 2.08 (s, 3H, Lev), 2.03 (s, 3H, Lev), 1.14 (t, 3H, SCH$_2$C*H*$_3$, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 206.3, 171.8, 171.4, 166.5, 165.0, 164.8, 164.5, 138.0, 137.3, 137.2, 137.1, 136.9, 133.8, 133.3, 133.2, 132.8, 131.7, 130.0, 129.9, 129.8, 129.6 x 2, 129.3, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 128.2, 127.8, 126.5, 126.2, 126.0, 102.0, 101.3, 101.2, 101.0, 99.5, 98.0, 84.3, 79.9, 79.2, 78.8, 78.4 x 2, 76.0, 75.4, 74.3, 73.5, 73.3, 72.9, 72.0, 71.8, 71.6, 70.9, 68.7, 68.6, 66.6, 66.2, 64.6, 53.1, 37.9, 37.7, 29.8, 29.7, 27.9, 27.4, 24.4, 14.8; IR (solid): 2881, 2101, 1716, 1367, 1261, 1096, 994, 879, 702, 517 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{93}H_{97}N_4O_{28}S$ $[M+NH_4]^+$ *m/z* = 1749.6010, found: 1749.6022.

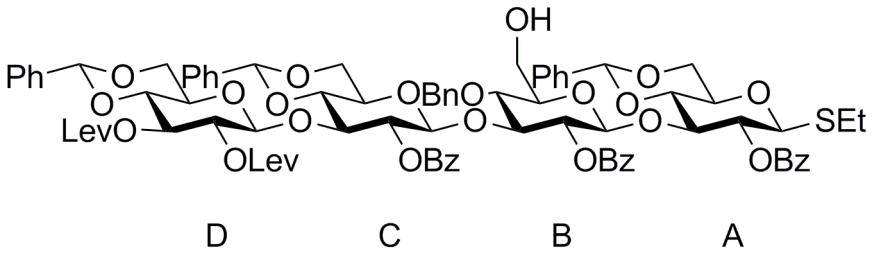


Ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (36)

To a stirred solution of ethylthio 3-*O*-(6-*O*-(2-(azidomethyl)benzoyl)-2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (35) (251 mg, 0.145 mmol, 1.00 eq.) in THF (1.45 mL) was added water (13.1 μL, 0.725 mmol, 5.00 eq.) and ^{n}Bu$_3$P (0.109 mL, 0.435 mmol, 3.00 eq.) at 0 ˚C. After being stirred at room temperature for 30 min, the reaction mixture was poured into saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel with 91:9 toluene:acetone to give ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopy

ranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (36) (212 mg, 0.134 mmol, 93%).

$[\alpha]_D^{17}$ = -13.1 (c = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, 2H, aromatic, J = 7.2 Hz), 7.73 (d, 2H, aromatic, J = 7.2 Hz), 7.22-7.69 (m, 31H, aromatic), 5.47 (s, 2H, benzylidene), 5.37 (s, 1H, benzylidene), 5.21 (dd, 1H, C-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 8.7 Hz), 5.01 (dd, 1H, D-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.7 Hz), 4.88-4.96 (m, 3H, A-2, B-2, D-2), 4.86 (d, 1H, C-1, $J_{1,2}$ = 7.7 Hz), 4.67-4.71 (m, 2H, B-1, PhCH_2), 4.52 (d, 1H, D-1, $J_{1,2}$ = 7.7 Hz), 4.46 (d, 1H, A-1, $J_{1,2}$ = 10.1 Hz), 4.32 (dd, 1H, A-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.24 (dd, 1H, C-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.18 (dd, 1H, D-6a, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.6 Hz), 4.12 (d, 1H, PhCH_2, J_{gem} = 10.6 Hz), 4.09 (dd, 1H, A-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz), 4.01 (dd, 1H, B-3, $J_{2,3}$ = 6.8 Hz, $J_{3,4}$ = 7.7 Hz), 3.88 (dd, 1H, C-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 3.54-3.70 (m, 7H, B-4, C-4, D-4, B-6a, A-6b, C-6b, D-6b), 3.33-3.51 (m, 5H, A-4, A-5, B-5, C-5, B-6b), 3.26 (ddd, 1H, D-5, $J_{4,5}$ = 9.7 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.7 Hz), 2.17-2.67 (m, 10H, Lev, SCH_2CH$_3$), 2.07 (s, 3H, Lev), 2.03 (s, 3H, Lev), 1.93 (br-s, 1H, OH), 1.14 (t, 3H, SCH$_2$CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 206.3, 171.8, 171.7, 171.4, 165.0, 164.6, 164.2, 143.7, 138.2, 137.1, 136.8, 133.6, 133.2, 133.1, 132.1, 131.8, 129.9, 129.8, 129.7, 129.5, 129.4, 129.2 x 2, 129.0, 128.8, 128.4, 128.3, 128.2 x 3, 128.0, 127.8, 126.3, 126.1, 126.0, 123.8, 123.2, 102.0, 101.3, 101.0, 100.9, 99.7, 98.8, 84.4, 79.5, 79.0, 78.8, 78.4, 78.3, 75.6, 74.5, 74.2, 73.6, 73.4, 72.4, 71.6 x 2, 71.0, 68.6, 68.5, 66.5, 66.1, 63.7, 62.3, 45.6, 37.8, 37.6, 29.7, 29.6, 28.1, 27.9, 27.3, 27.2, 24.3, 24.1 x 2, 24.0 x 2, 18.9, 14.7, 13.7, 13.6; IR (solid): 3531, 2875, 1737, 1602, 1452, 1376, 1264, 984, 750, 703, 484 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{85}H_{89}O_{27}S$ $[M+H]^+$ m/z = 1573.5312, found: 1573.5287.

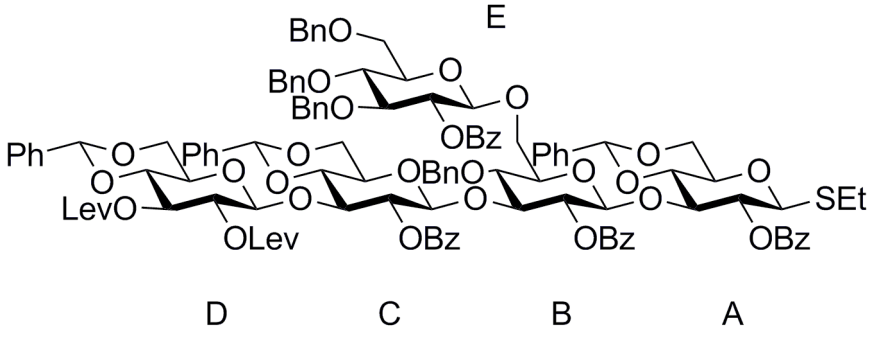


Ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (16)

A mixture of ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (36) (212 mg, 0.134 mmol, 1.00 eq.), *O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-D-glucopyranosyl)trichloroacetimidate[5] (37) (188 mg, 0.269 mmol, 2.00 eq.) (azeotroped

twice with dry toluene) and pulverized activated MS-4A (134 mg) in dry CH_2Cl_2 (1.34 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -10 ˚C. A catalytic amount of trimethylsilyltrifluoromethanesulfonate (2.43 μL, 13.4 μmol, 0.100 eq.) was added to the reaction mixture. After being stirred at 0 ˚C for 3 h, the reaction mixture was neutralized with triethylamine, filtered through a pad of Celite and concentrated *in vacuo*. The residue was chromatographed on silica gel with 94:6 toluene:acetone to give ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyrano syl)-4,6-*O*-benzylidene-β-D-glucopyranoside (16) (259 mg, 0.123 mmol, 91%).

$[\alpha]_D^{17}$ = -10.4 (c = 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, aromatic, J = 7.2 Hz), 7.84 (d, 2H, aromatic, J = 7.7 Hz), 7.69 (d, 2H, aromatic, J = 7.2 Hz), 7.10-7.67 (m, 49H, aromatic), 5.47 (s, 1H, benzylidene), 5.41 (s, 1H, benzylidene), 5.36 (s, 1H, benzylidene), 5.26 (dd, 1H, B-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 8.7 Hz), 5.15 (dd, 1H, C-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 8.7 Hz), 5.00 (dd, 1H, D-3, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz), 4.93 (dd, 1H, D-2, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.88 (dd, 1H, E-2, $J_{1,2}$ = 6.3 Hz, $J_{2,3}$ = 6.3 Hz), 4.73-4.80 (m, 4H, C-1, A-2, PhCH_2), 4.54-4.66 (m, 6H, B-1, E-1, PhCH_2), 4.51 (d, 1H, D-1, $J_{1,2}$ = 7.7 Hz), 4.46 (d, 1H, PhCH_2, J_{gem} = 12.1 Hz), 4.13-4.26 (m, 4H, A-1, A-6a, C-6a, D-6a), 4.05 (d, 1H, PhCH_2, J_{gem} = 12.1 Hz), 3.85-3.96 (m, 4H, A-3, C-3, E-3, B-6a), 3.78 (dd, 1H, B-3, $J_{2,3}$ = 8.7 Hz, $J_{3,4}$ = 9.2 Hz), 3.69 (dd, 1H, A-6b, $J_{5,6a}$ = 10.1 Hz, J_{gem} = 10.1 Hz), 3.45-3.65 (m, 9H, C-4, D-4, B-5, E-5, E-6a, B-6b, C-6b, D-6b, E-6b), 3.40 (dd, 1H, E-4, $J_{3,4}$ = 7.7 Hz, $J_{4,5}$ = 9.2 Hz), 3.15-3.32 (m, 5H, A-4, B-4, A-5, C-5, D-5), 2.22-2.68 (m, 10H, Lev, SCH_2CH$_3$), 2.07 (s, 3H, Lev), 2.02 (s, 3H, Lev), 1.15 (t, 3H, SCH_2CH_3, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4 x 2, 171.8, 171.4, 165.4, 165.0, 164.7, 164.2, 138.3, 138.2, 137.9, 137.4, 137.1, 136.8, 133.5, 133.1, 133.0, 130.2, 129.9 x 2, 129.8, 129.6 x 2, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6 x 2, 128.4, 128.3 x 2, 128.2 x 3, 128.0 x 2, 127.9, 127.8 x 2, 127.7, 127.6 x 2, 126.6, 126.1, 126.0, 125.4, 101.6, 101.3, 101.0, 100.9, 100.8, 99.4, 98.2, 84.0, 82.7, 79.3 x 2, 79.0, 78.9, 78.4, 78.3, 78.1, 75.7, 75.1, 75.0, 74.8, 74.3, 74.0, 73.8, 73.6, 73.5, 73.4, 72.3, 71.7, 71.6, 71.0, 68.6, 68.5 x 2, 68.4, 66.4, 66.1, 37.9, 37.7, 29.7, 29.6, 27.9, 27.4, 24.1, 14.8; IR (solid): 2967, 2318, 1955, 1730, 1602, 1451, 1265, 1096, 772, 702, 527 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{119}H_{124}NO_{33}S$ $[M+NH_4]^+$ m/z = 2126.7776, found: 2126.7778.



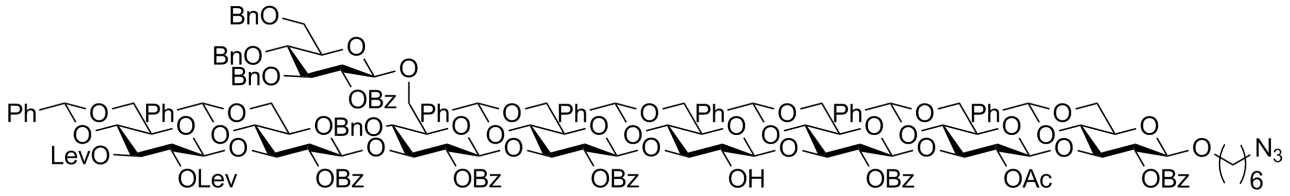
Preparation of the nonasaccharide 38

6-Azidohexyl
2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (38)

A mixture of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (11) (87.0 mg, 62.4 μmol, 1.00 eq.), ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (16) (158 mg, 74.9 mmol, 1.20 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (374 mg) in dry CH_2Cl_2 (3.74 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (20.2 mg, 89.9 μmol, 1.44 eq.) and a catalytic amount of trifluoromethanesulfonic acid (1.66 μL, 18.7 μmol, 0.300 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 91:9 toluene:acetone and further purified by gel permeation chromatography (GPC) to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (38) (191 mg, 55.5 μmol, 89%).

$[\alpha]_D^{21}$ = -5.37 (c = 0.980, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-8.01 (m, 4H), 7.91 (d, 2H, *J* = 7.2 Hz), 7.81 (d, 2H, *J* = 7.2 Hz), 7.76 (d, 2H, *J* = 7.7 Hz), 7.63 (d, 2H, *J* = 7.2 Hz), 7.03-7.61 (m, 73H), 5.48 (s, 1H), 5.41 (s, 1H), 5.37 (s, 1H), 5.30 (s, 1H), 5.28 (s, 1H), 5.25 (dd, 1H, *J* = 8.7 Hz, 8.7 Hz), 5.09-5.17 (m, 2H), 4.88-5.05 (m, 8H), 4.76-4.84 (m, 5H), 4.64-4.69 (m, 3H), 4.54-4.61 (m, 3H), 4.50 (br-d, 2H, *J* = 7.7 Hz),

4.40-4.46 (m, 2H), 4.29-4.34 (m, 2H), 4.05-4.23 (m, 7H), 3.98 (dd, 1H, J = 4.8 Hz, 10.1 Hz), 3.20-3.94 (m, 36H), 3.14 (ddd, 1H, J = 4.8 Hz, 9.7 Hz, 10.1 Hz), 3.01-3.06 (m, 3H), 2.25-2.72 (m, 10H, Lev, H-2, OH), 2.07 (s, 3H), 2.01 (s, 3H), 1.72 (s, 3H), 1.10-1.48 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3 x 2, 171.7, 171.3, 169.3, 165.4, 165.2, 165.1, 164.8, 164.7, 163.9, 138.7, 138.4, 138.3, 138.0, 137.6, 137.2 x 2, 136.9, 136.8, 133.7, 133.4, 133.3, 133.2 x 2, 133.0 x 2, 129.8 x 2, 129.7, 129.6, 129.5 x 2, 129.2 x 3, 129.1 x 2, 129.0, 128.9, 128.8 x 2, 128.7, 128.6, 128.5 x 2, 128.4, 128.3, 128.2 x 2, 128.1 x 2, 128.0, 127.9, 127.8, 127.6, 127.5 x 2, 127.4, 126.4, 126.3, 126.2 x 2, 126.1, 126.0 x 2, 102.6, 101.6 x 2, 101.5, 101.4, 101.3, 101.2, 101.0, 100.9, 100.8, 100.6, 99.9, 99.2, 98.7, 98.5, 97.7, 82.8, 79.5, 78.8, 78.6, 78.5, 78.4, 78.3, 78.0, 77.8, 76.3, 76.0, 75.9, 75.7, 75.2, 74.8, 74.3 x 2, 74.1 x 2, 74.0, 73.9, 73.8, 73.4, 73.3, 72.1, 71.6, 69.8, 69.2, 68.7 x 3, 68.6 x 2, 68.5 x 2, 68.4 x 3, 68.3, 66.6 x 2, 66.3, 66.1, 65.9, 65.6, 65.2, 51.2, 37.8, 37.6, 29.6 x 2, 29.2, 28.5, 27.9, 27.3, 26.2, 25.3, 20.4; IR (solid): 3513, 2869, 2092, 1734, 1451, 1374, 1264, 1069, 752, 696, 654, 501 cm^{-1}.



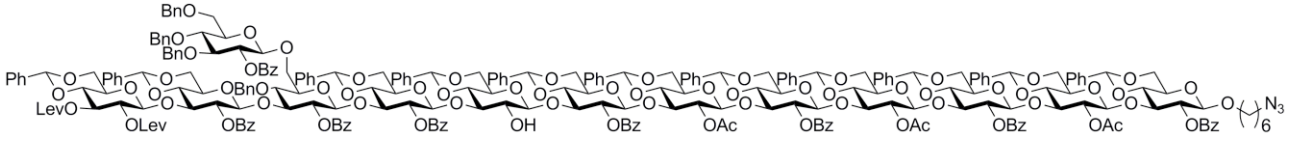
Preparation of the tridecasaccharide 39

6-Azidohexyl
2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (39)

A mixture of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (13) (73.0 mg, 27.2 μmol, 1.00 eq.), ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (16) (86.0 mg, 40.8 μmol, 1.50 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (163 mg) in dry CH_2Cl_2 (1.63 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (11.0 mg, 48.9 μmol, 1.80 eq.) and a catalytic amount of trifluoromethanesulfonic acid (1.20 μL, 13.6 mmol, 0.500 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 91:9 toluene:acetone and further purified by gel permeation chromatography (GPC) to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopy

ranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopy ranoside (39) (102 mg, 21.5 μmol, 79%).

$[\alpha]_D^{21}$ = -9.17 (c = 0.960, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-8.00 (m, 8H), 7.90 (d, 2H, *J* = 7.2 Hz), 7.81 (d, 2H, *J* = 7.2 Hz), 7.75 (d, 2H, *J* = 7.2 Hz), 6.99-7.63 (m, 101H), 5.51 (s, 1H), 5.40 (s, 1H), 5.36 (s, 1H), 5.33 (s, 1H), 5.30 (s, 1H), 5.24 (dd, 1H, *J* = 8.2 Hz, 8.7 Hz), 5.11-5.16 (m, 4H), 4.76-5.02 (m, 21H), 4.54-4.70 (m, 8H), 4.49 (d, 1H, *J* = 6.8 Hz), 4.48 (d, 1H, *J* = 7.7 Hz), 4.40-4.45 (m, 2H), 4.31-4.34 (m, 2H), 3.22-4.22 (m, 64H), 3.14 (ddd, 1H, *J* = 4.8 Hz, 8.7 Hz, 9.2 Hz), 3.00-3.07 (m, 3H), 2.22-2.67 (m, 10H, Lev, H-2, OH), 2.07 (s, 3H), 2.04 (s, 3H), 1.76 (s, 3H), 1.75 (s, 3H), 1.71 (s, 3H), 1.10-1.48 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 206.4, 171.8, 171.4, 169.3, 169.1, 169.0, 165.3, 165.1, 164.9, 164.8 x 2, 138.7, 138.4, 138.3, 138.0, 137.7, 137.4, 137.3 x 3, 137.0, 136.9, 133.4 x 2, 133.3 x 2, 133.2, 133.1, 130.0 x 2, 129.8 x 2, 129.7 x 2, 129.6 x 2, 129.5 x 2, 129.4, 129.3 x 2, 129.2 x 3, 129.1 x 2, 129.0 x 2, 128.9 x 2, 128.8, 128.7, 128.6 x 2, 128.5 x 2, 128.3, 128.2 x 2, 128.1 x 2, 128.0, 127.9 x 2, 127.8, 127.7, 127.6, 127.5, 127.4, 126.5, 126.4, 126.3, 126.2, 126.1 x 3, 102.7, 101.8, 101.7, 101.6 x 2, 101.5 x 2, 101.4, 101.3, 101.2 x 2, 101.1 x 2, 101.0, 100.8, 100.6, 100.0, 99.2, 98.6 x 2, 98.5 x 2, 98.2, 98.0, 97.8, 82.9, 78.8, 78.7, 78.5 x 2, 78.4, 78.3, 78.2 x 2, 78.0, 77.9, 76.5, 76.1, 76.0, 75.9 x 2, 75.7, 75.2, 74.9, 74.4, 74.3, 74.2 x 2, 74.1, 73.9 x 2, 73.8, 73.5, 73.4, 72.4, 72.1, 71.6, 69.9, 68.8, 68.7 x 3, 68.6 x 3, 68.5, 68.4 x 2, 66.7, 66.6, 66.4, 66.1 x 2, 66.0 x 2, 65.8, 65.6 x 2, 65.2, 53.5, 51.2, 37.9, 37.7, 29.7, 29.6, 29.3, 28.6, 28.0, 27.4, 26.3, 25.4, 20.6 x 2, 20.5; IR (solid): 3631, 2964, 2093, 1734, 1412, 1258, 1089, 773, 696, 500 cm^{-1}.



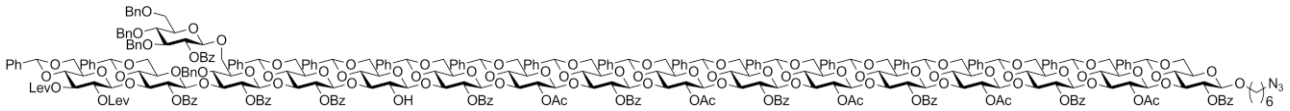
Preparation of the heptadecasaccharide 17

6-Azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (17)

A mixture of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (15) (70.0 mg, 17.6 μmol, 1.00 eq.), ethylthio 2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (16) (55.7 mg, 26.4 mol, 1.50 eq.) (azeotroped twice with dry toluene) and pulverized activated MS-4A (176 mg) in dry CH_2Cl_2 (1.76 mL) was stirred at room temperature for 30 min under argon to remove a trace amount of water. Then the reaction mixture was cooled to -35 ˚C. *N*-iodosuccinimide (7.13 mg, 31.7 μmol, 1.80 eq.) and a catalytic amount of trifluoromethanesulfonic acid (0.467 μL, 5.28 μmol, 0.300 eq.) were added to the reaction mixture. After being stirred at the same temperature for 30 min, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate was poured into a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with a mixture of saturated aq. $NaHCO_3$ and 10% aq. $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was chromatographed on silica gel with 85:15 toluene:ethyl acetate and further purified by gel permeation chromatography (GPC) to give 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-ben

zoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (17) (87.0 mg, 14.4 μmol, 82%).

$[\alpha]_D^{21}$ = -10.6 (c = 2.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-8.01 (m, 14H), 7.90 (d, 2H, *J* = 7.7 Hz), 7.81 (d, 2H, *J* = 7.7 Hz), 7.74 (d, 2H, *J* = 7.7 Hz), 6.99-7.63 (m, 125H), 5.52 (s, 1H), 5.41 (s, 1H), 5.36 (s, 1H), 5.33 (s, 1H), 5.30 (s, 1H), 5.25 (dd, 1H, *J* = 8.7 Hz, 8.7 Hz), 5.09-5.17 (m, 6H), 4.76-5.03 (m, 29H), 4.54-4.70 (m, 10H), 4.48 (br-d, 2H, *J* = 7.7 Hz), 4.40-4.45 (m, 2H), 4.31-4.35 (m, 2H), 3.12-4.22 (m, 85H), 3.00-3.07 (m, 3H), 2.17-2.67 (m, 10H, Lev, H-2, OH), 2.07 (s, 3H), 2.00 (s, 3H), 1.76 (s, 12H), 1.72 (s, 3H), 1.10-1.48 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4 x 2, 171.8, 171.4, 169.3, 169.1 x 2, 165.7 x 3, 165.3, 165.1, 165.0, 164.9 x 2, 164.8, 164.0, 138.7, 138.5, 138.4, 138.1, 137.7, 137.5 x 2, 137.4, 137.3 x 2, 137.1, 136.9, 134.1, 134.0 x 3, 133.7, 133.6, 133.4 x 2, 133.3 x 3, 133.2, 133.1 x 2, 130.3, 130.2 x 2, 130.1, 129.8 x 2, 129.7, 129.6, 129.5 x 2, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6 x 2, 128.5, 128.4, 128.3, 128.2 x 2, 128.1, 128.0, 127.9, 127.7, 127.6 x 2, 127.4, 126.6 x 3, 126.4 x 2, 126.3, 126.2, 126.1, 102.7 x 2, 102.5, 101.8 x 3, 101.7 x 2, 101.6 x 2, 101.5 x 3, 101.4 x 3, 101.3 x 2, 101.2 x 2, 101.1 x 3, 101.0, 100.9, 100.7 x 2, 100.1, 100.0, 99.2, 98.7, 98.6, 98.5, 98.4 x 3, 98.3 x 2, 98.2, 98.1, 98.0 x 3, 97.9 x 2, 82.9, 79.6, 79.5, 79.0, 78.9, 78.8, 78.7, 78.5, 78.4, 78.3, 78.2, 78.1, 77.9, 77.8 x 2, 77.7 x 3, 76.5 x 2, 76.4, 76.0 x 3, 75.9, 75.8, 75.7, 75.6 x 2, 75.5 x 2, 75.3 x 2, 75.2 x 2, 74.9, 74.4 x 2, 74.2 x 3, 73.9 x 2, 73.8, 73.5, 73.4, 72.4, 72.1, 71.7, 70.6, 69.9, 68.9, 68.7, 68.6 x 2, 68.4, 66.7, 66.6, 66.4, 66.1 x 2, 66.0, 65.8, 65.7, 65.6, 51.3, 37.9, 37.7, 29.7, 29.6, 29.3, 28.6, 28.0, 27.4, 26.3, 25.4, 20.7, 20.6, 20.5; IR (solid): 3729, 2863, 2344, 2138, 1968, 1734, 1496, 1368, 1218, 1023, 876, 770, 654, 508 cm^{-1}.

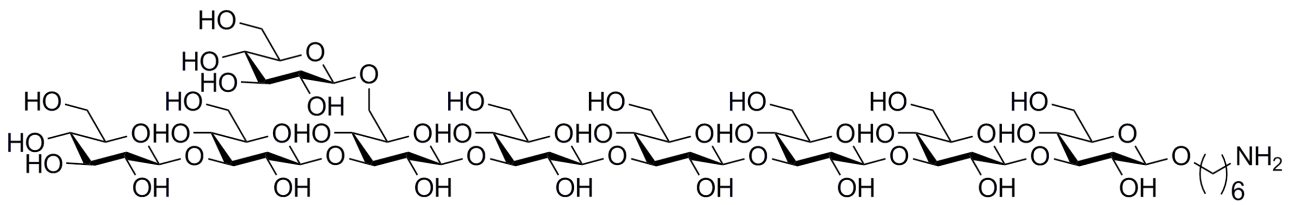


Deprotection of the nona-, trideca- and heptadecasaccharide 38, 39, and 17

6-Aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(6-*O*-(β-D-glucopyranosyl)-3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (21)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (38) (33.9 mg, 9.85 μmol, 1.00 eq.) in NH_3/THF/EtOH (8.50 mL/1.00 mL/0.500 mL) was added a large amount of lithium (100 mg) at -78 ˚C. After being stirred under reflux for 1.5 h, the reaction mixture was added methanol (1.00 mL). After being stirred at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water and further purified by revese-phase column chromatography (Bond Elut-C18) with 90:10 water:methanol to give 6-aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(6-*O*-(β-D-glucopyranosyl)-3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (21) (15.5 mg, 9.83 μmol, quant.).

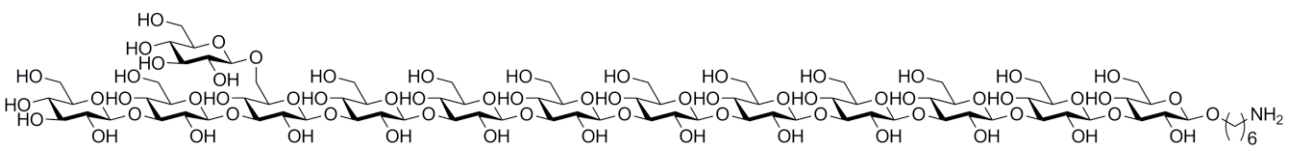
$[\alpha]_D^{24}$ = -24.2 (c = 0.335, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.70-4.80 (m, 7H, anomericH x 7), 4.49 (d, 1H, anomericH, *J* = 7.7 Hz), 4.44 (d, 1H, anomericH, *J* = 7.7 Hz), 4.18 (br-d, 1H, *J* = 10.6 Hz), 3.27-3.91 (m, 55H), 2.80 (t, 2H, *J* = 7.2 Hz), 1.51-1.63 (m, 4H), 1.35-1.36 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ 103.6 x 2, 103.4 x 2, 102.7, 85.7, 85.5, 85.2, 85.1, 84.8, 76.8, 76.7, 76.5, 76.4, 75.4, 74.3, 74.1, 74.0 x 2, 73.9, 73.8, 73.7, 71.2, 70.4, 69.6, 69.0 x 2, 68.9, 61.5, 40.5, 29.3, 28.5, 26.2, 25.4; IR (solid): 3481, 2884, 1846, 1669, 1438, 1314, 1153, 1032, 855, 664, 526 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{60}H_{106}NO_{46}$ $[M+H]^+$ *m/z* = 1576.5986, found: 1576.5981.



6-Aminohexyl
3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(6-*O*-(β-D-glucopyranosyl)-3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (19)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (39) (16.1 mg, 3.40 μmol, 1.00 eq.) in NH_3/THF/EtOH (8.50 mL/1.00 mL/0.500 mL) was added a large amount of lithium (100 mg) at -78 ˚C. After being stirred under reflux for 1.5 h, the reaction mixture was added methanol (1.00 mL). After being stirred at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water and further purified by revese-phase column chromatography (Bond Elut-C18) with 80:20 water:methanol to give 6-aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(6-*O*-(β-D-glucopyranosyl)-3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (19) (6.10 mg, 2.74 μmol, 81%).

$[\alpha]_D^{24}$ = -22.9 (c = 0.135, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.70-4.76 (m, 11H, anomericH x 11), 4.49 (d, 1H, anomericH, *J* = 7.7 Hz), 4.45 (d, 1H, anomericH, *J* = 8.7 Hz), 4.18 (br-d, 1H, *J* = 11.1 Hz), 3.27-3.91 (m, 79H), 2.79 (t, 2H, *J* = 7.2 Hz), 1.52-1.63 (m, 4H), 1.35-1.37 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ 103.6, 103.4 x 2, 102.5, 85.1, 76.5, 76.4, 74.1, 74.0, 70.4, 69.0, 68.9, 61.5, 40.6, 29.3, 29.0, 26.2, 25.4; IR (solid): 3413, 2885, 1821, 1648, 1591, 1368, 1154, 1077, 1042, 652, 519 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{84}H_{146}NO_{66}$ $[M+H]^+$ *m/z* = 2224.8099, found: 2224.8054.

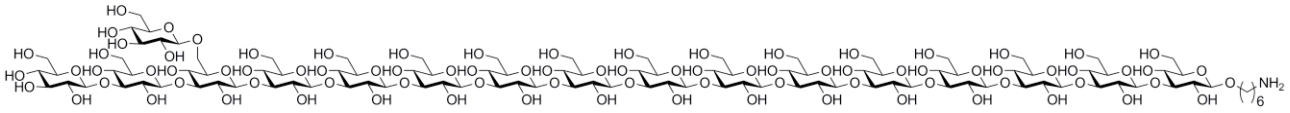


6-Aminohexyl

3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(6-*O*-(**β**-D-glucopyranosyl)-3-*O*-(3-*O*-(**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranosyl)-**β**-D-glucopyranoside (1)

To a stirred solution of 6-azidohexyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(3-*O*-(2-*O*-benzoyl-3-*O*-(2-*O*-benzoyl-6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-3-*O*-(2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-4-*O*-benzyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (17) (40.7 mg, 6.75 μmol, 1.00 eq.) in NH_3/THF/EtOH (8.50 mL/1.00 mL/0.500 mL) was added a large amount of lithium (100 mg) at -78 ˚C. After being stirred under reflux for 1.5 h, the reaction mixture was added methanol (1.00 mL). After being stirred at room temperature for 12 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water and further purified by revese-phase column chromatography (Bond Elut-C18) with 70:30 water:methanol to give 6-aminohexyl 3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(6-*O*-(β-D-glucopyranosyl)-3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (1) (9.80 mg, 3.41 μmol, 51%).

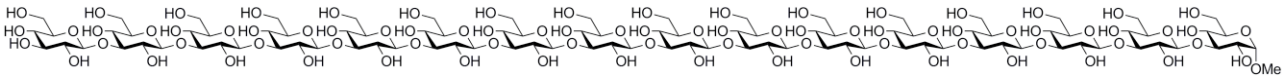
$[\alpha]_D^{24}$ = -31.9 (c = 0.125, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.70-4.76 (m, 15H, anomericH x 15), 4.49 (d, 1H, anomericH, *J* = 7.7 Hz), 4.44 (d, 1H, anomericH, *J* = 7.7 Hz), 4.18 (br-d, 1H, *J* = 11.1 Hz), 3.26-3.95 (m, 103H), 2.82 (br-s, 1H), 2.50 (br-s, 1H), 1.55-1.64 (m, 4H), 1.36 (br-s, 4H); ^{13}C NMR (100 MHz, D_2O) δ 103.6, 103.3, 85.1, 85.0 x 2, 76.5, 74.2, 74.1, 74.0 x 2, 70.4, 69.3, 68.9, 61.6, 61.5, 20.9; IR (solid): 3308, 2897, 1982, 1811, 1656, 1373, 1043, 891, 649, 526 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{108}H_{186}NO_{86}$ $[M+H]^+$ *m/z* = 2873.0212, found: 2873.0244.



Methyl hexadecasaccharide 23

Methyl
3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(3-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranosyl)-α-D-glucopyranoside (23)

$[\alpha]_D^{24}$ = -2.36 (c = 0.0800, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.79 (d, 1H, anomericHα, *J* = 3.9 Hz), 4.75-4.77 (m, 13H, anomericH x 13), 4.72 (d, 1H, anomericH, *J* = 7.2 Hz), 4.70 (d, 1H, anomericH, *J* = 7.2 Hz), 3.83-3.91 (m, 17H), 3.63-3.78 (m, 31H), 3.44-3.55 (m, 46H), 3.31-3.41 (m, 5H); ^{13}C NMR (100 MHz, D_2O) δ 103.3, 85.0, 76.4, 74.1, 68.9, 61.5; IR (solid): 3637, 3022, 2716, 2573, 2012, 1465, 1198, 1077, 797, 663, 524 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{97}H_{165}O_{81}$ $[M+H]^+$ *m/z* = 2625.8792, found: 2625.8809.



References

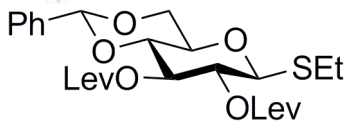
(1) S. C. Ennis, J. J. Gridley, H. M. I. Osborn, D. G. Spackman *Synlett* 2000, 1593-1596.

(2) C. Wang, H. Wang, X. Huang, L.-H. Zhang, X.-S. Ye *Synlett* 2006, 2846-2850.

(3) T. Takahashi, A. Okano, T. Amaya, H. Tanaka, T. Doi *Synlett* 2002, 911-914.

(4) T. Wada, A. Ohkubo, A. Mochizuki, M. Sekine *Tetrahedron Lett.* 2001, 42, 1069-1072.

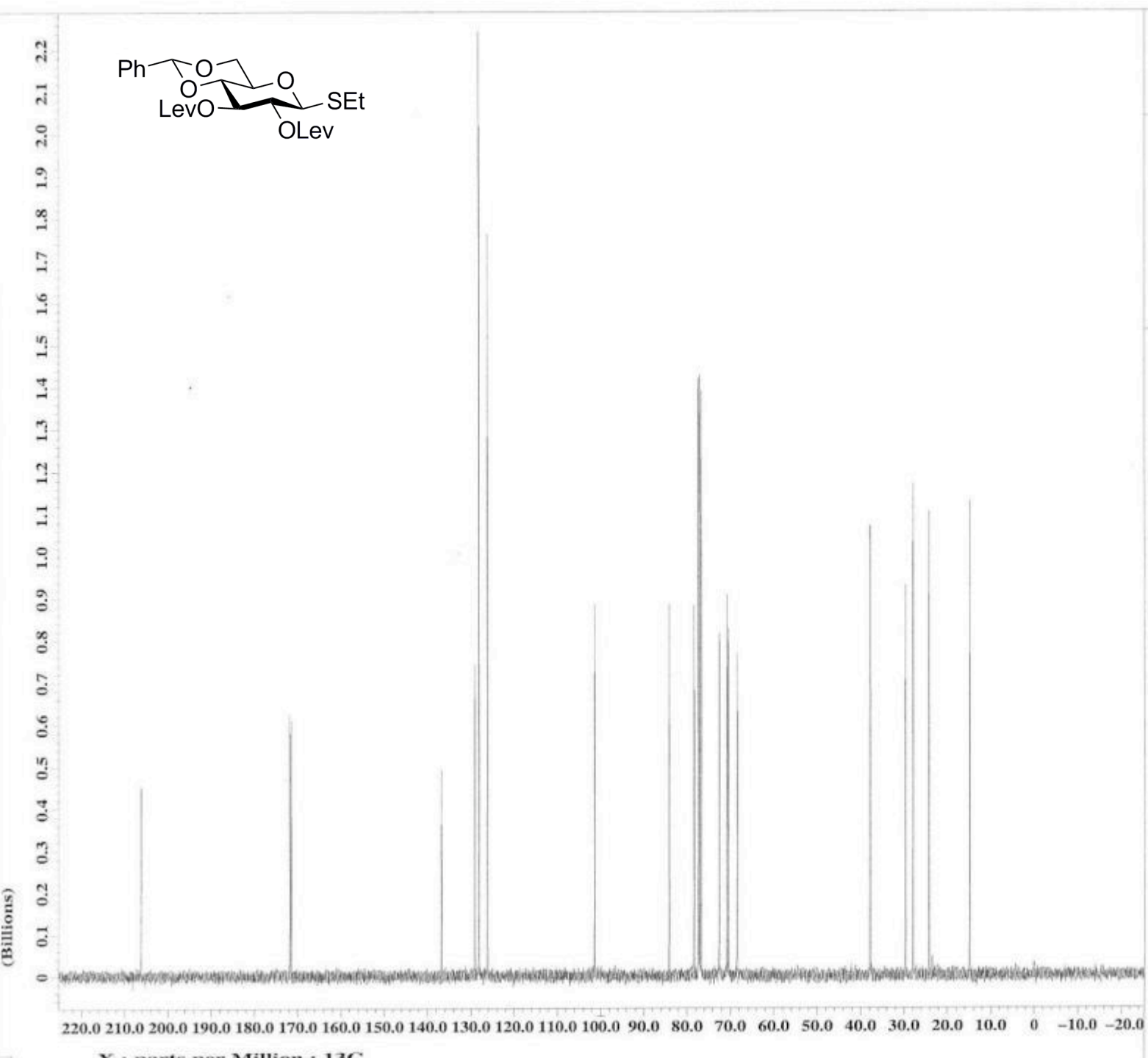
(5) Y. Okada, O. Nagata, M. Taira, H. Yamada *Org. Lett.* 2007, 9, 2755-2758.



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

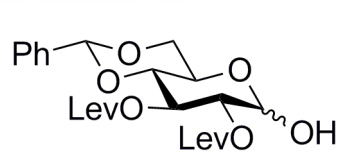
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091214No478.9
Author              = JEOL LTD.
Sample ID           = S#785770
Content             = Single Pulse Experim
Creation Date       = 14-DEC-2009 20:52:34

Revision Date       = 18-MAR-2010 13:29:01
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 14-DEC-2009 20:50:45
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 14-DEC-2009 20:52:32
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 14-DEC-2009 20:52:33
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 11
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

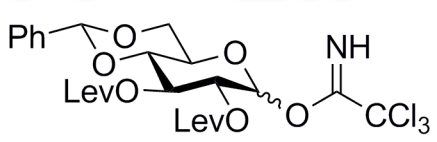
File Name	= tetsu091214No478_13c
Author	= JEOL LTD.
Sample ID	= 13C
Content	= Single Pulse with Br
Creation Date	= 14-DEC-2009 21:13:45
Revision Date	= 18-MAR-2010 13:34:23
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Actual_start_time	= 14-DEC-2009 20:54:17
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 14-DEC-2009 21:33:07
Experiment	= single_pulse_dec
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 12.46882793[kHz]
Irr_code	= 146
Irr_domain	= 1H
Irr_freq	= 395.88252601[MHz]
Irr_noise	= WALTZ
Irr_offset	= 5[ppm]
Irr_pwidth	= 40[us]
Iterations	= 1
Local_time	= 14-DEC-2009 21:13:44
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 30
Relaxation_delay	= 1[s]
Scans	= 497
Solvent	= CHLOROFORM-D
Spin_get	= 17[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 27.9[dC]
X90	= 10[us]
X_acq_duration	= 1.3139968[s]
X_angle	= 30[deg]
X_domain	= 13C
X_freq	= 99.54473003[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_pulse	= 3.33333333[us]
X_resolution	= 0.76103686[Hz]



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

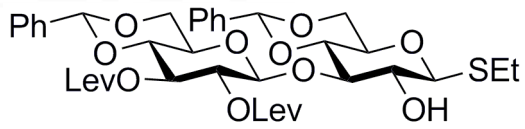
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091214No598.3
Author              = JEOL LTD.
Sample ID           = S#639481
Content             = Single Pulse Experim
Creation Date       = 14-DEC-2009 16:48:13

Revision Date       = 18-MAR-2010 13:40:48
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 14-DEC-2009 16:46:24
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 14-DEC-2009 16:48:11
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 14-DEC-2009 16:48:12
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.8[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

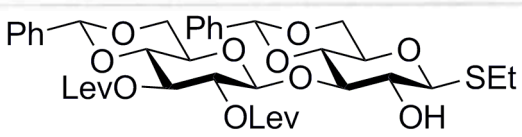
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091214No563.3
Author              = JEOL LTD.
Sample ID           = S#527830
Content             = Single Pulse Experim
Creation Date       = 14-DEC-2009 13:42:06

Revision Date       = 18-MAR-2010 13:44:37
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 14-DEC-2009 13:40:16
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 14-DEC-2009 13:42:03
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 14-DEC-2009 13:42:05
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.9[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu080624No251.4
Author              = JEOL LTD.
Sample ID           = S#645338
Content             = Single Pulse Experim
Creation Date       = 24-JUN-2008 17:19:55

Revision Date       = 18-MAR-2010 13:56:58
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 24-JUN-2008 17:18:05
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 24-JUN-2008 17:19:52
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 50[us]
Iterations          = 0
Local_time          = 24-JUN-2008 17:19:54
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.1[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



(Millions)

240.0 220.0 200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0

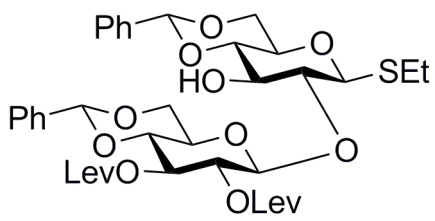
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

X : parts per Million : 13C

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

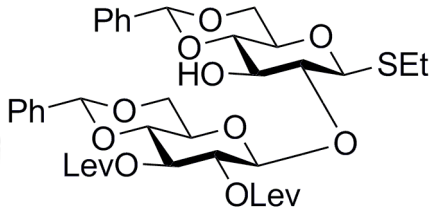
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091215No499-2OH
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 15-DEC-2009 23:12:41

Revision Date       = 18-MAR-2010 14:00:16
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 15-DEC-2009 22:59:33
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 15-DEC-2009 23:38:23
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 15-DEC-2009 23:12:41
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 333
Solvent             = CHLOROFORM-D
Spin_get            = 14[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.6[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

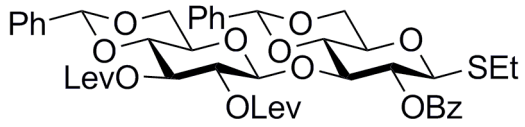
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100217No603bypr
Author              = JEOL LTD.
Sample ID           = S#605630
Content             = Single Pulse Experim
Creation Date       = 17-FEB-2010 15:50:21

Revision Date       = 18-MAR-2010 14:04:07
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 17-FEB-2010 15:48:32
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-FEB-2010 15:50:19
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 17-FEB-2010 15:50:21
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 12
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 23.9[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

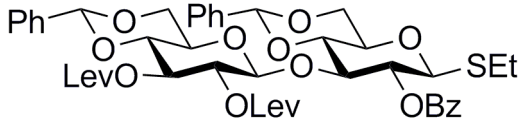
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100217No603bypr
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 17-FEB-2010 16:29:19

Revision Date       = 18-MAR-2010 14:03:27
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 17-FEB-2010 16:07:32
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-FEB-2010 16:46:22
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 17-FEB-2010 16:29:18
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 557
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.6[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091215No303-2Bz
Author              = JEOL LTD.
Sample ID           = S#774330
Content             = Single Pulse Experim
Creation Date       = 15-DEC-2009 20:33:19

Revision Date       = 18-MAR-2010 20:17:22
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 15-DEC-2009 20:31:31
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 15-DEC-2009 20:33:18
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 15-DEC-2009 20:33:18
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.9[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

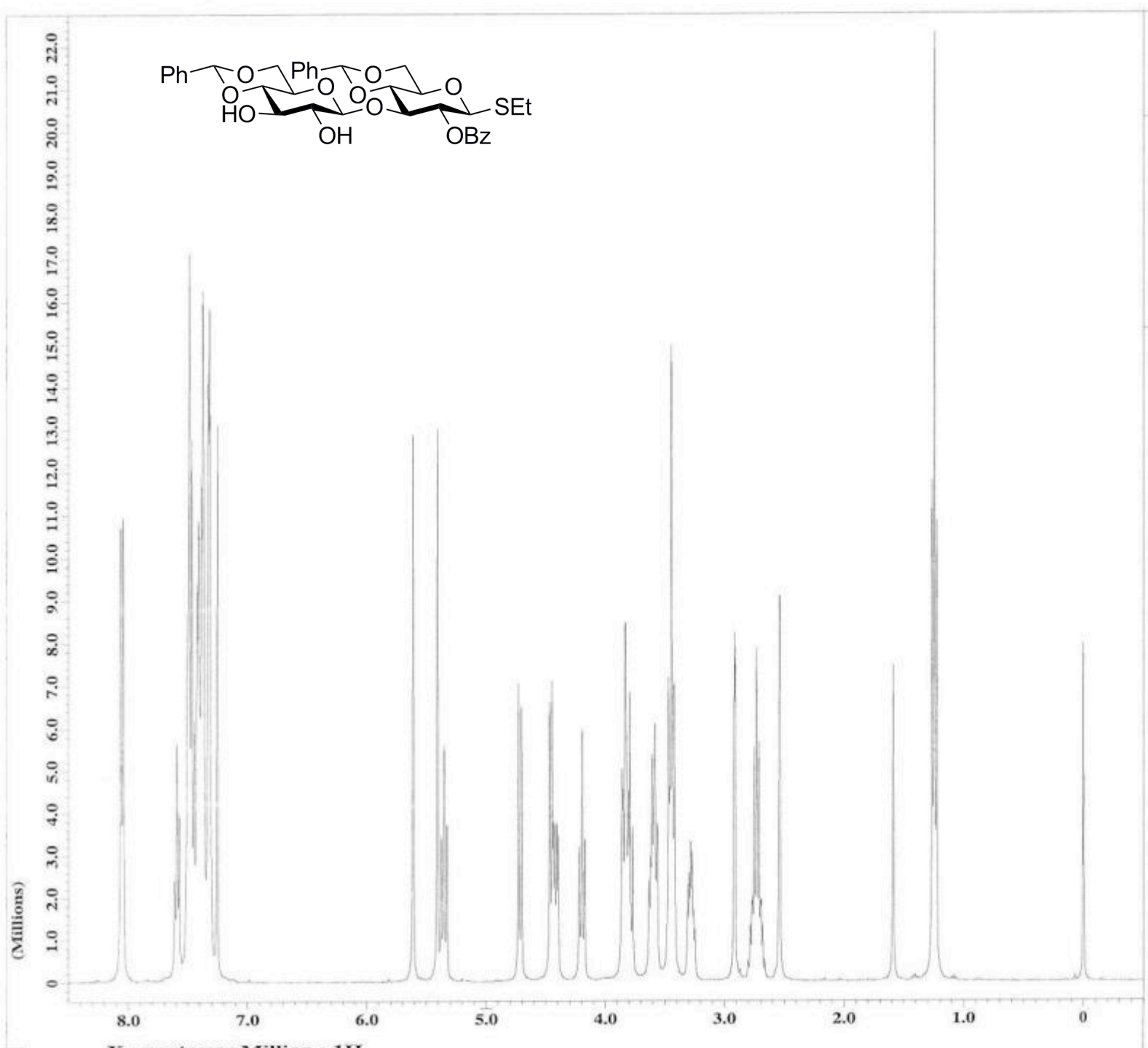
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091215No303-2Bz
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 15-DEC-2009 20:53:30

Revision Date       = 18-MAR-2010 20:18:48
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 15-DEC-2009 20:43:59
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 15-DEC-2009 21:22:49
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 15-DEC-2009 20:53:28
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 239
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.7[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```

400.0
300.0
200.0
100.0
0
(Millions)

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

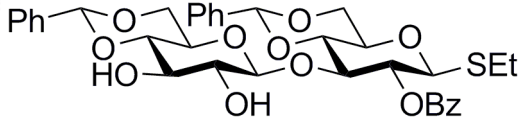
X : parts per Million : 13C

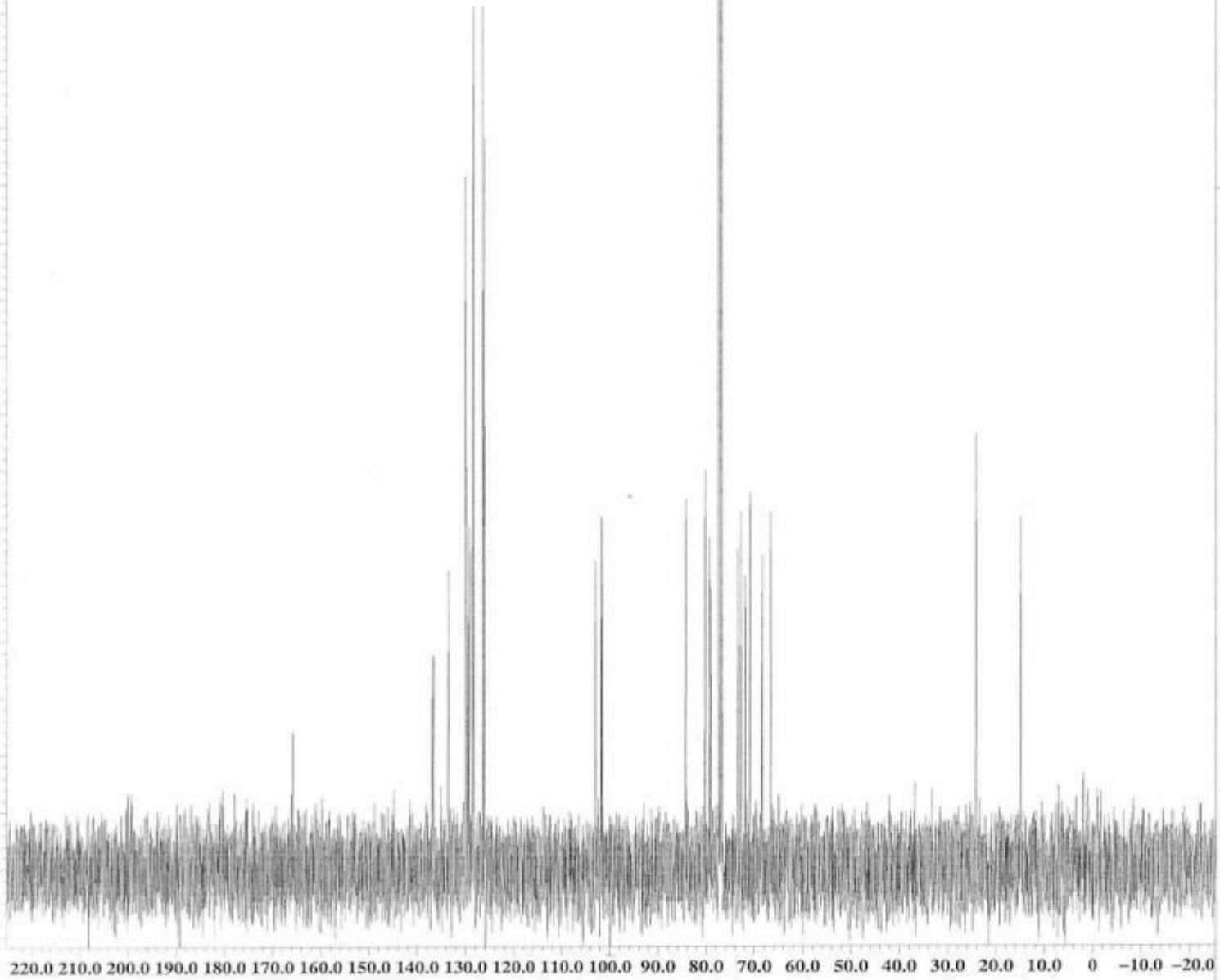


JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091215No306-2Di
Author              = JEOL LTD.
Sample ID           = S#790447
Content             = Single Pulse Experim
Creation Date       = 15-DEC-2009 20:59:55

Revision Date       = 18-MAR-2010 20:24:17
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 15-DEC-2009 20:58:05
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 15-DEC-2009 20:59:52
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 15-DEC-2009 20:59:54
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 18[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26.1[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

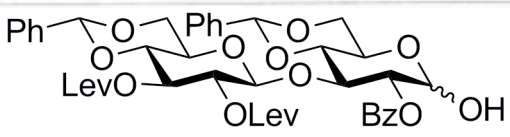




JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091215No306-2Di
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 15-DEC-2009 21:15:08

Revision Date       = 18-MAR-2010 20:26:50
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 15-DEC-2009 21:09:03
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 15-DEC-2009 21:47:53
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 15-DEC-2009 21:15:08
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 150
Solvent             = CHLOROFORM-D
Spin_get            = 13[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.8[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```

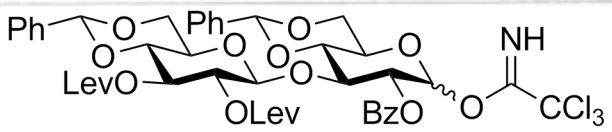


(Millions)

X : parts per Million : 1H

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

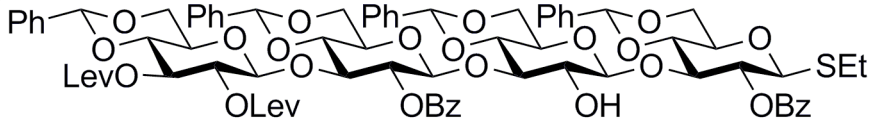
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100107No599.5
Author              = JEOL LTD.
Sample ID           = S#448222
Content             = Single Pulse Experim
Creation Date       =  7-JAN-2010 11:29:19

Revision Date       = 18-MAR-2010 20:32:13
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   =  7-JAN-2010 11:27:29
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  7-JAN-2010 11:29:16
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          =  7-JAN-2010 11:29:18
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 10
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.8[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

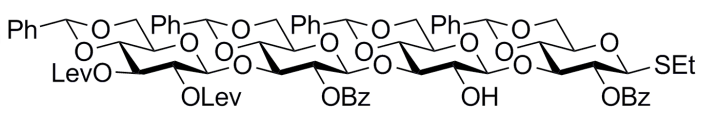
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090623No514.3
Author              = JEOL LTD.
Sample ID           = S#774168
Content             = Single Pulse Experim
Creation Date       = 23-JUN-2009 20:44:26

Revision Date       = 18-MAR-2010 20:34:21
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 23-JUN-2009 20:42:38
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 23-JUN-2009 20:44:25
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 23-JUN-2009 20:44:26
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 17
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 21.9[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

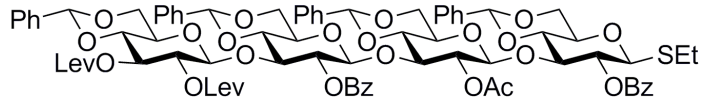
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091217No305-4OH
Author              = JEOL LTD.
Sample ID           = S#620601
Content             = Single Pulse Experim
Creation Date       = 17-DEC-2009 16:16:56

Revision Date       = 18-MAR-2010 20:36:52
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 17-DEC-2009 16:15:07
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-DEC-2009 16:16:54
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 17-DEC-2009 16:16:55
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 14[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.9[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091217No305-4OH
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 17-DEC-2009 14:19:02

Revision Date       = 18-MAR-2010 20:40:46
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 17-DEC-2009 13:34:47
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-DEC-2009 14:52:14
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 17-DEC-2009 14:19:01
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 1140
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.7[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



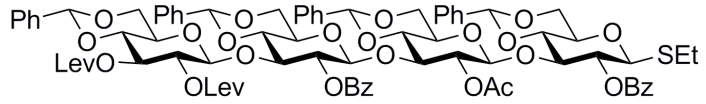
(Millions)

X : parts per Million : 1H

---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

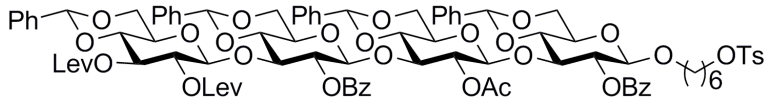
File Name	= tetsu090817No307.5
Author	= JEOL LTD.
Sample ID	= S#815159
Content	= Single Pulse Experim
Creation Date	= 17-AUG-2009 21:43:47
Revision Date	= 18-MAR-2010 20:44:29
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 17-AUG-2009 21:41:58
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 17-AUG-2009 21:43:45
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 17-AUG-2009 21:43:46
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 16
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= CHLOROFORM-D
Spin_get	= 15[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 26.4[dC]
X90	= 11.8[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.9[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090817No307_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 17-AUG-2009 22:27:22

Revision Date       = 18-MAR-2010 20:45:44
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 17-AUG-2009 22:07:24
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-AUG-2009 22:46:14
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 17-AUG-2009 22:27:20
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 510.0
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.8[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



(Millions)

13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

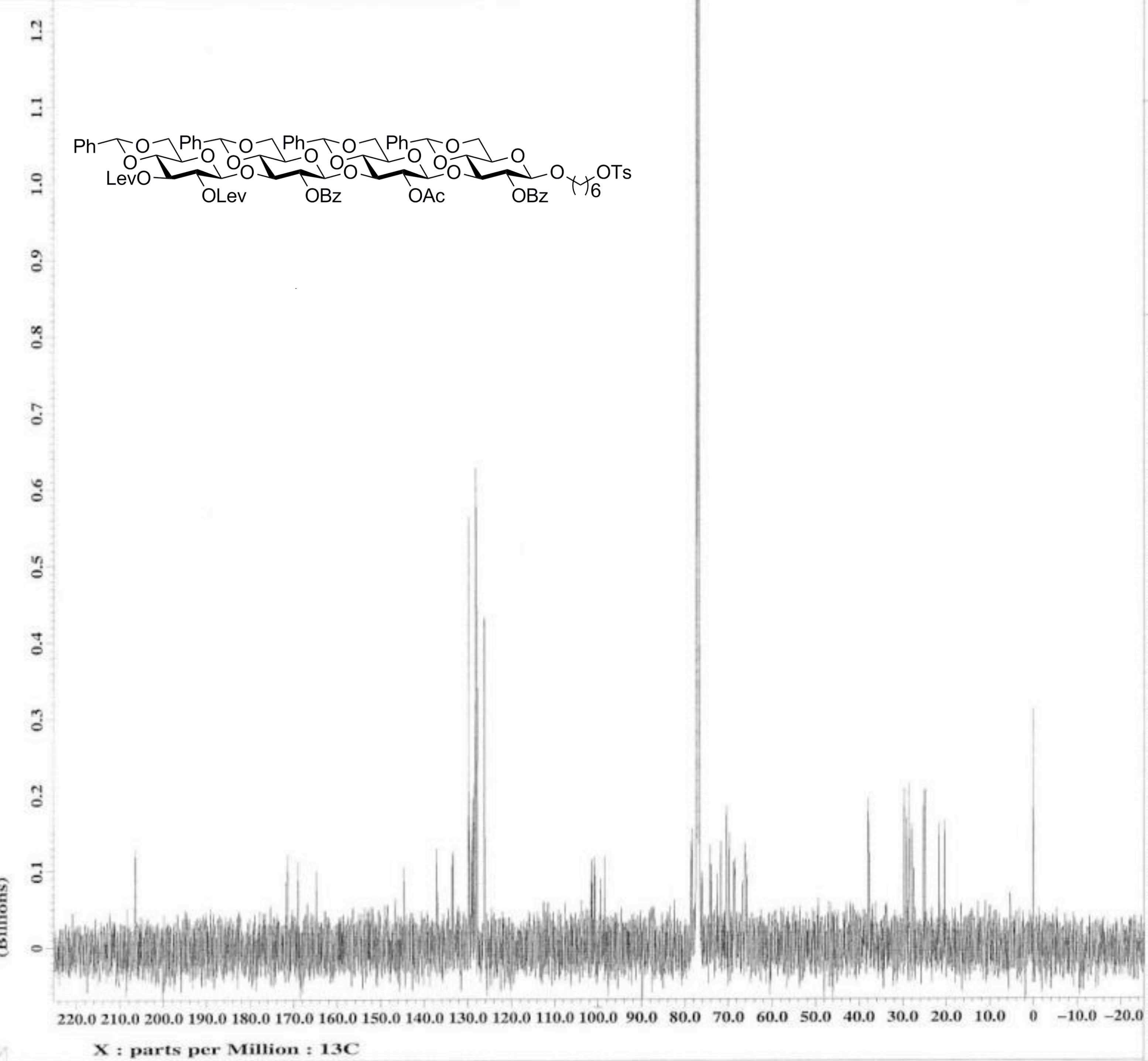
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

X : parts per Million : 1H

JEOL

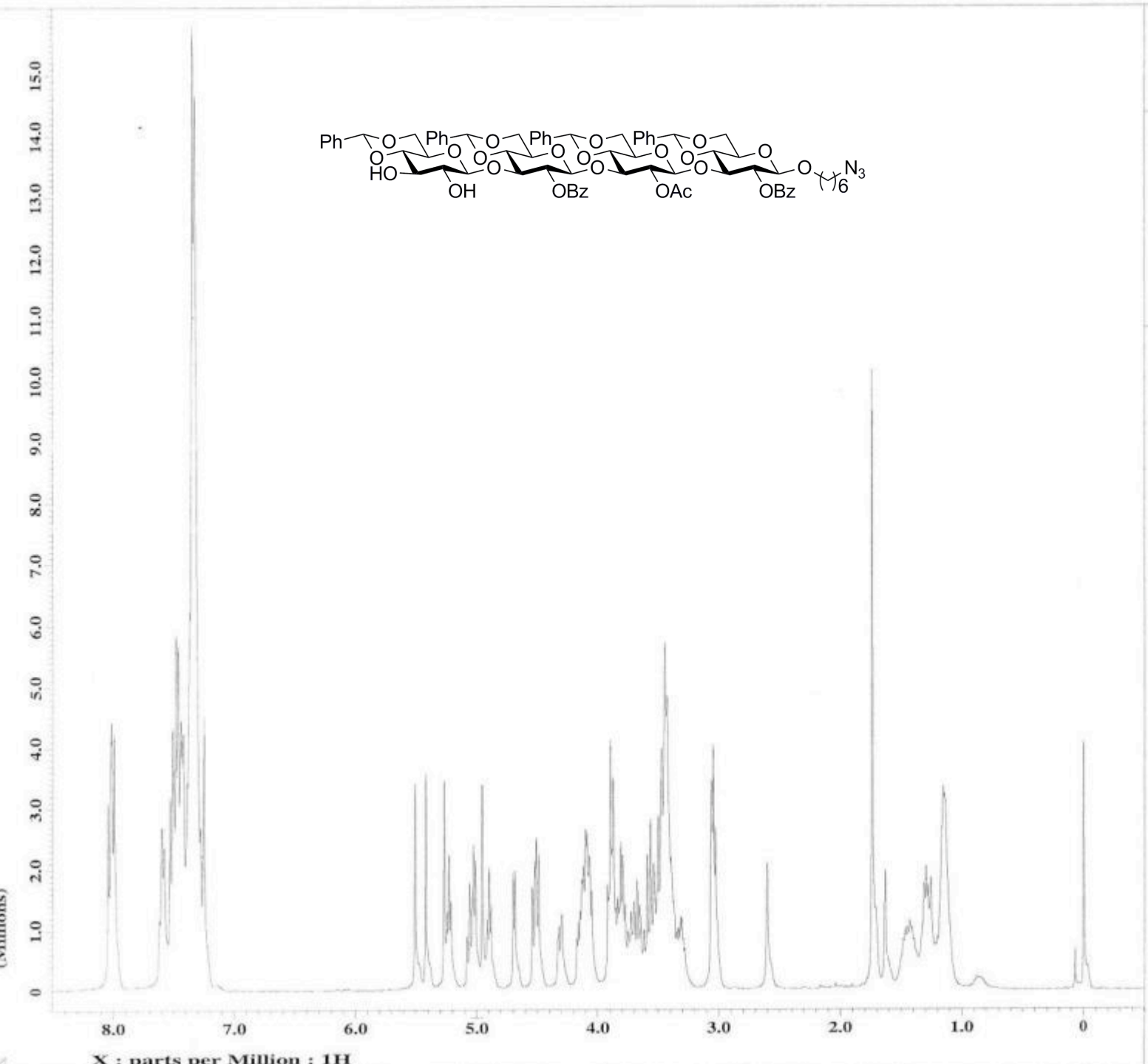
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091217No498-4Ts
Author              = JEOL LTD.
Sample ID           = S#608165
Content             = Single Pulse Experim
Creation Date       = 17-DEC-2009 15:56:13

Revision Date       = 18-MAR-2010 20:56:02
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 17-DEC-2009 15:54:24
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-DEC-2009 15:56:11
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 17-DEC-2009 15:56:12
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 18
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.9[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

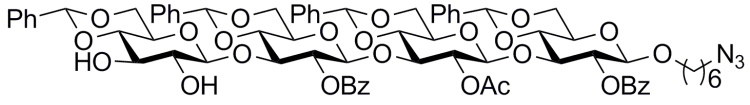
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----
File Name          = tetsu091215No498-4Ts
Author             = JEOL LTD.
Sample ID          = 13C
Content            = Single Pulse with Br
Creation Date      = 16-DEC-2009 01:35:13

Revision Date      = 18-MAR-2010 20:55:22
Spec Site          = ECP400SL

Spec Type          = DELTA_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Actual_start_time  = 15-DEC-2009 23:18:30
Delay_of_start     = 1[s]
Digital_filter     = FALSE
End_time           = 16-DEC-2009 05:44:50
Experiment         = single_pulse_dec
Field_strength     = 9.2981736[T]
Filter_mode        = BUTTERWORTH
Filter_width       = 12.46882793[kHz]
Irr_code           = 146
Irr_domain         = 1H
Irr_freq           = 395.88252601[MHz]
Irr_noise          = WALTZ
Irr_offset         = 5[ppm]
Irr_pwidth         = 40[us]
Iterations         = 1
Local_time         = 16-DEC-2009 01:35:11
Obs_noise          = WAUGH
Obs_pwidth         = 1[us]
Probe_id           = 2692
Recvr_gain         = 30
Relaxation_delay   = 1[s]
Scans              = 3538
Solvent            = CHLOROFORM-D
Spin_get           = 14[Hz]
Spin_lock_90       = 1[us]
Spin_lock_attn     = 29[dB]
Temp_get           = 27.6[dC]
X90                = 10[us]
X_acq_duration     = 1.3139968[s]
X_angle            = 30[deg]
X_domain           = 13C
X_freq             = 99.54473003[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_pulse            = 3.33333333[us]
X_resolution       = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

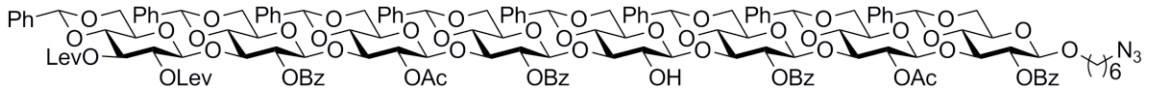
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091217No334-4N3
Author              = JEOL LTD.
Sample ID           = S#567035
Content             = Single Pulse Experim
Creation Date       = 17-DEC-2009 14:47:37

Revision Date       = 18-MAR-2010 21:45:38
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 17-DEC-2009 14:45:48
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-DEC-2009 14:47:35
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 17-DEC-2009 14:47:37
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.8[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

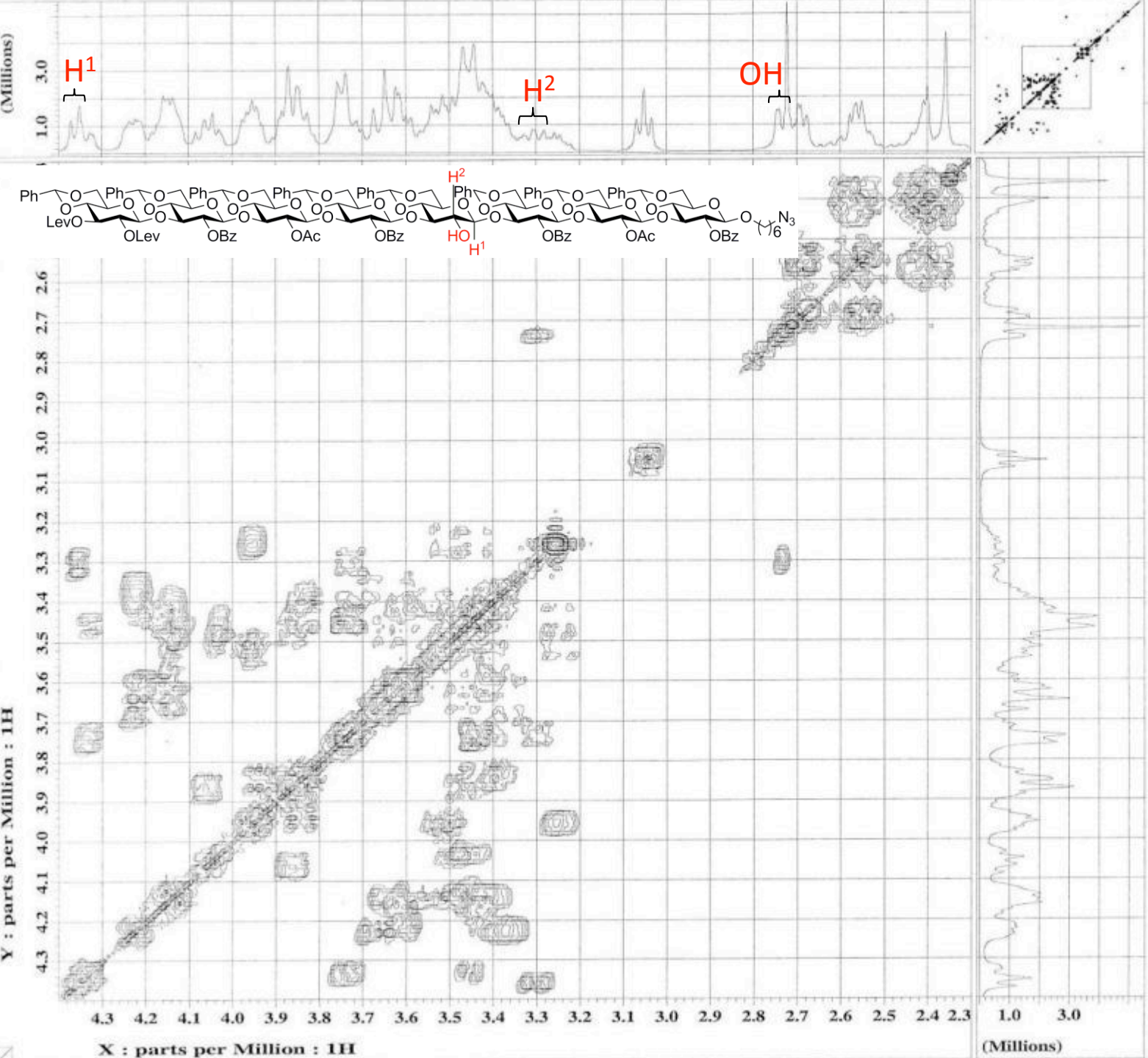
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091217No334-4N3
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 17-DEC-2009 15:29:09

Revision Date       = 18-MAR-2010 21:41:17
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 17-DEC-2009 14:56:53
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-DEC-2009 15:35:43
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 17-DEC-2009 15:29:09
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 829.0
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.8[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu081011No310.5
Author              = JEOL LTD.
Sample ID           = S#775765
Content             = Single Pulse Experim
Creation Date       = 11-OCT-2008 20:54:01

Revision Date       = 18-MAR-2010 21:55:23
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 11-OCT-2008 20:52:12
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 11-OCT-2008 20:53:59
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 11-OCT-2008 20:54:00
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.7[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

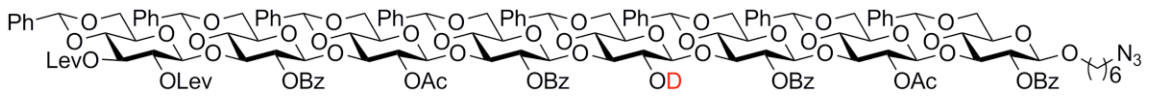


---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
thresh : 1 : 1
symmetrize : Cosy : 24
[transpose]

---- ACQUISITION PARAMETERS ----

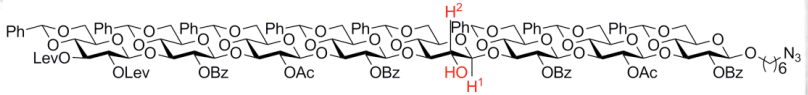
File Name	= tetsu081011No310_cos
Author	= JEOL LTD.
Sample ID	= S#778452
Content	= gradient absolute va
Creation Date	= 11-OCT-2008 21:07:16
Revision Date	= 18-MAR-2010 21:49:50
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 2D REAL REAL
Dimensions	= X Y
Dim Title	= 1H 1H
Dim Size	= 512, 1024
Dim Units	= [ppm][ppm]
Actual_start_time	= 11-OCT-2008 20:55:50
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 11-OCT-2008 21:07:13
Experiment	= cosy_pfg_m.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 1.03241792[kHz]
Grad_1	= 1[ms]
Grad_1_amp	= 50[%]
Grad_2	= 1[ms]
Grad_2_amp	= 50[%]
Grad_recover	= 1[ms]
Grad_shape	= square
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 11-OCT-2008 21:07:15
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 15
Relaxation_delay	= 1[s]
Scans	= 2
Solvent	= CHLOROFORM-D
Spin_get	= 0[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 26.3[dC]
X90	= 12.4[us]
X_acq_duration	= 0.2479616[s]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 3.25611[ppm]
X_points	= 512
X_prescans	= 4

deuteration of the OH group

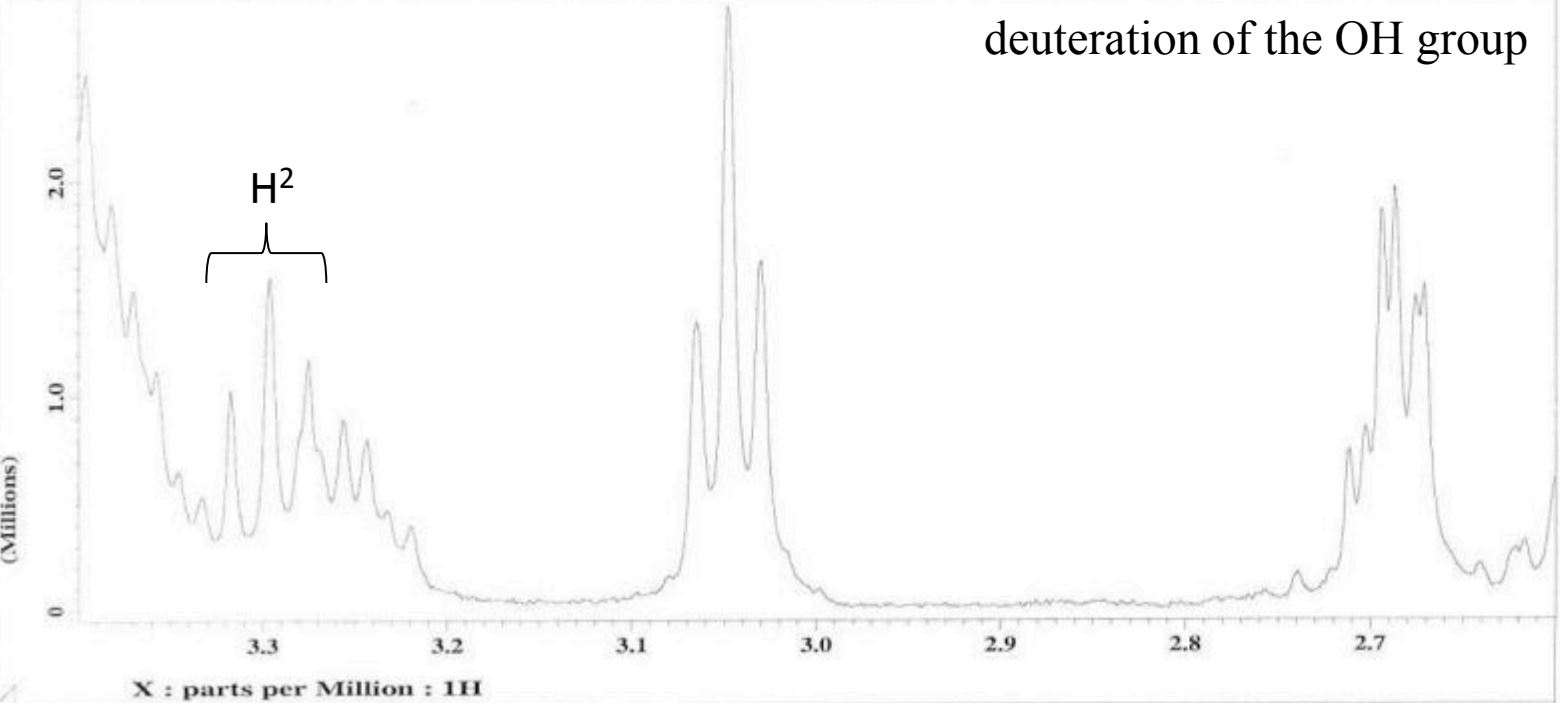



```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
reference : 0[ppm] : 0[ppm]
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100222No417_D2O
Author              = JEOL LTD.
Sample ID           = S#467165
Content             = Single Pulse Experim
Creation Date       = 22-FEB-2010 11:59:37

Revision Date       = 10-MAR-2010 23:08:23
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 22-FEB-2010 11:57:48
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 22-FEB-2010 11:59:35
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 22-FEB-2010 11:59:36
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.4[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

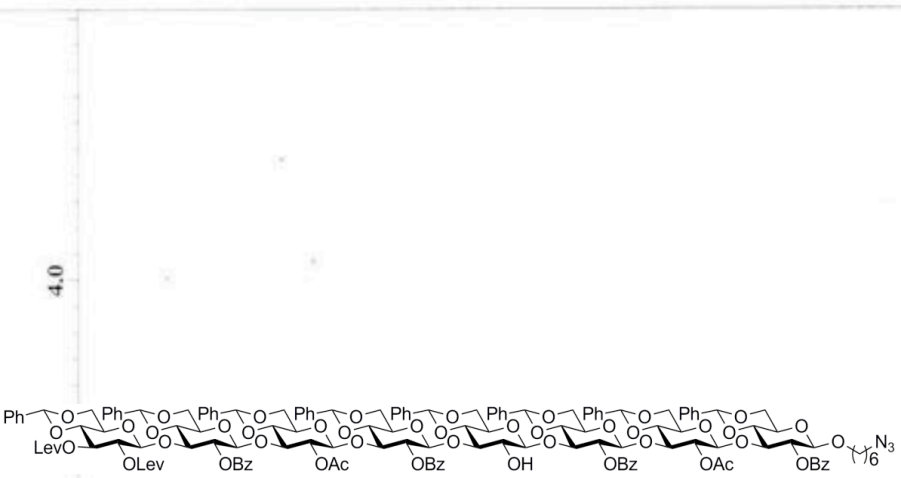


deuteration of the OH group




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
reference : 0[ppm] : 0[ppm]
```

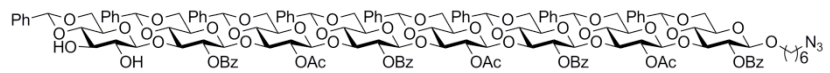
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100222No417_D2O
Author              = JEOL LTD.
Sample ID           = S#467165
Content             = Single Pulse Experim
Creation Date       = 22-FEB-2010 11:59:37

Revision Date       = 10-MAR-2010 23:19:55
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 22-FEB-2010 11:57:48
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 22-FEB-2010 11:59:35
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 22-FEB-2010 11:59:36
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.4[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

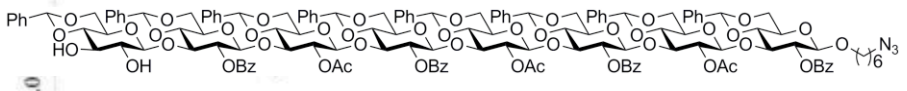
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100217No417_8N3
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 17-FEB-2010 22:23:16

Revision Date       = 18-MAR-2010 21:59:43
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 17-FEB-2010 17:07:02
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 20-FEB-2010 09:28:27
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 17-FEB-2010 22:23:15
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 8193
Solvent             = CHLOROFORM-D
Spin_get            = 14[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26.4[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

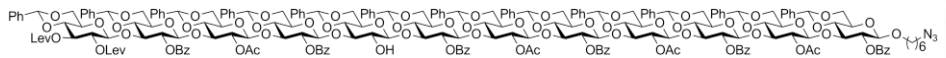
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090218No436.3
Author              = JEOL LTD.
Sample ID           = S#495340
Content             = Single Pulse Experim
Creation Date       = 18-FEB-2009 13:02:46

Revision Date       = 18-MAR-2010 22:30:33
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-FEB-2009 13:00:57
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-FEB-2009 13:02:44
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 18-FEB-2009 13:02:46
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 7
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.5[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

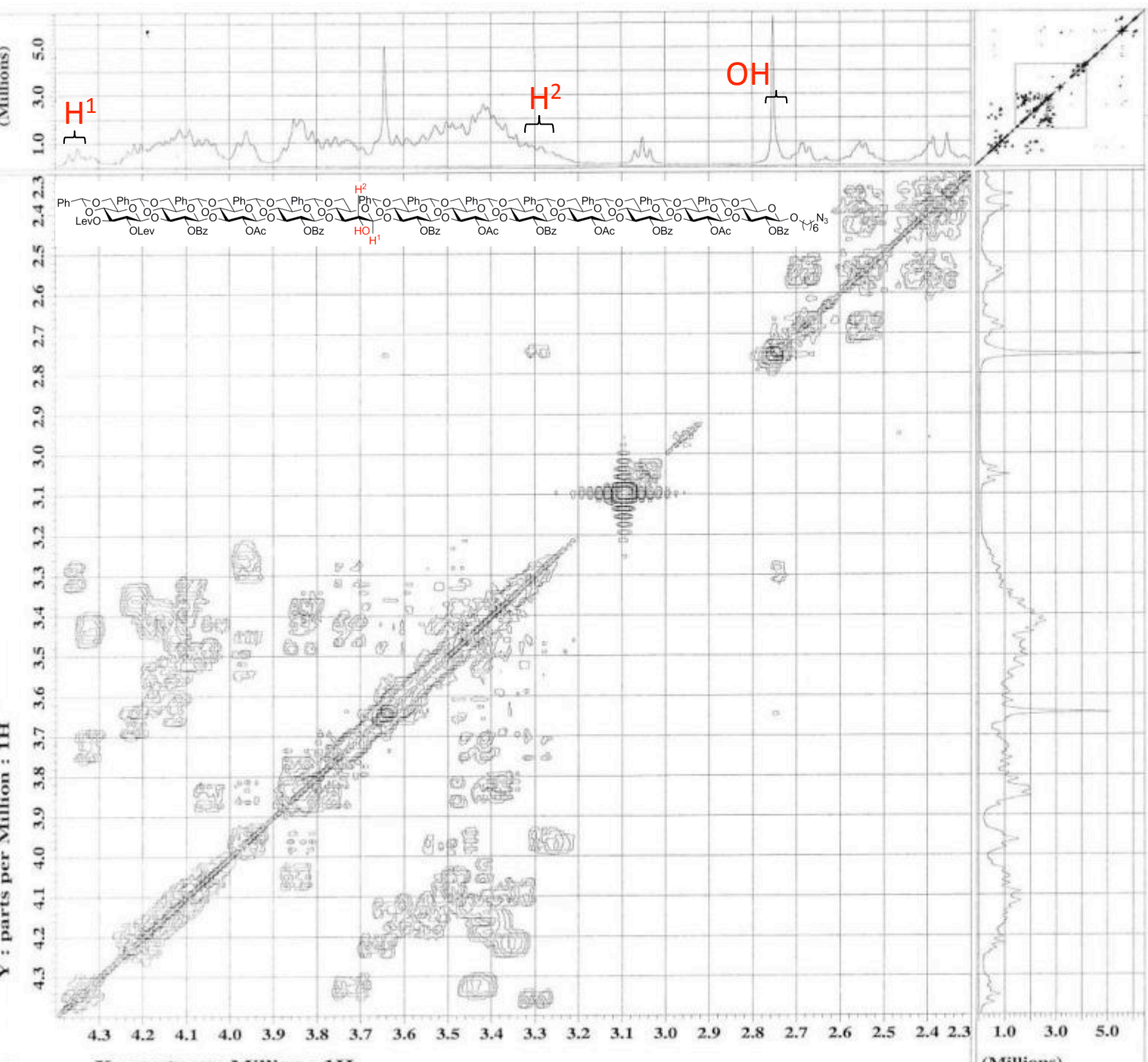
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090218No436_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 18-FEB-2009 13:49:04

Revision Date       = 18-MAR-2010 22:31:48
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 18-FEB-2009 13:30:19
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-FEB-2009 14:09:09
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 18-FEB-2009 13:49:02
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 478
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.5[dC]
X90                 = 11.75[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.91666667[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu081017No312.3
Author              = JEOL LTD.
Sample ID           = S#782442
Content             = Single Pulse Experim
Creation Date       = 17-OCT-2008 21:05:08

Revision Date       = 18-MAR-2010 22:35:02
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 17-OCT-2008 21:03:19
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-OCT-2008 21:05:06
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 17-OCT-2008 21:05:08
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 17
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 13[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.7[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

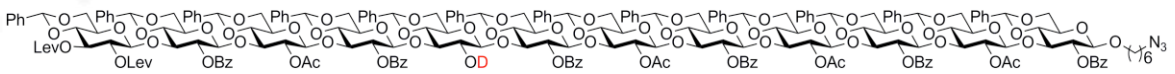


JEOL

```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
thresh : 1 : 1
symmetrize : Cosy : 24
[transpose]
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu081017No312_cos
Author              = JEOL LTD.
Sample ID           = S#785527
Content             = gradient absolute va
Creation Date       = 17-OCT-2008 21:18:51

Revision Date       = 18-MAR-2010 22:34:01
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 1H 1H
Dim Size            = 512, 1024
Dim Units           = [ppm] [ppm]
Actual_start_time   = 17-OCT-2008 21:07:20
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 17-OCT-2008 21:18:48
Experiment          = cosy_pfg_m.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 996.61152083[Hz]
Grad_1              = 1[ms]
Grad_1_amp          = 50[%]
Grad_2              = 1[ms]
Grad_2_amp          = 50[%]
Grad_recover        = 1[ms]
Grad_shape          = square
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 17-OCT-2008 21:18:50
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 15
Relaxation_delay    = 1[s]
Scans               = 2
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.5[dC]
X90                 = 12.4[us]
X_acq_duration      = 0.2568704[s]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 3.09373[ppm]
X_points            = 512
X_prescans          = 4
```

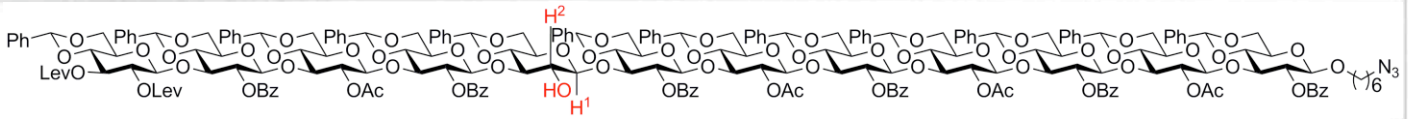
deuteration of the OH group



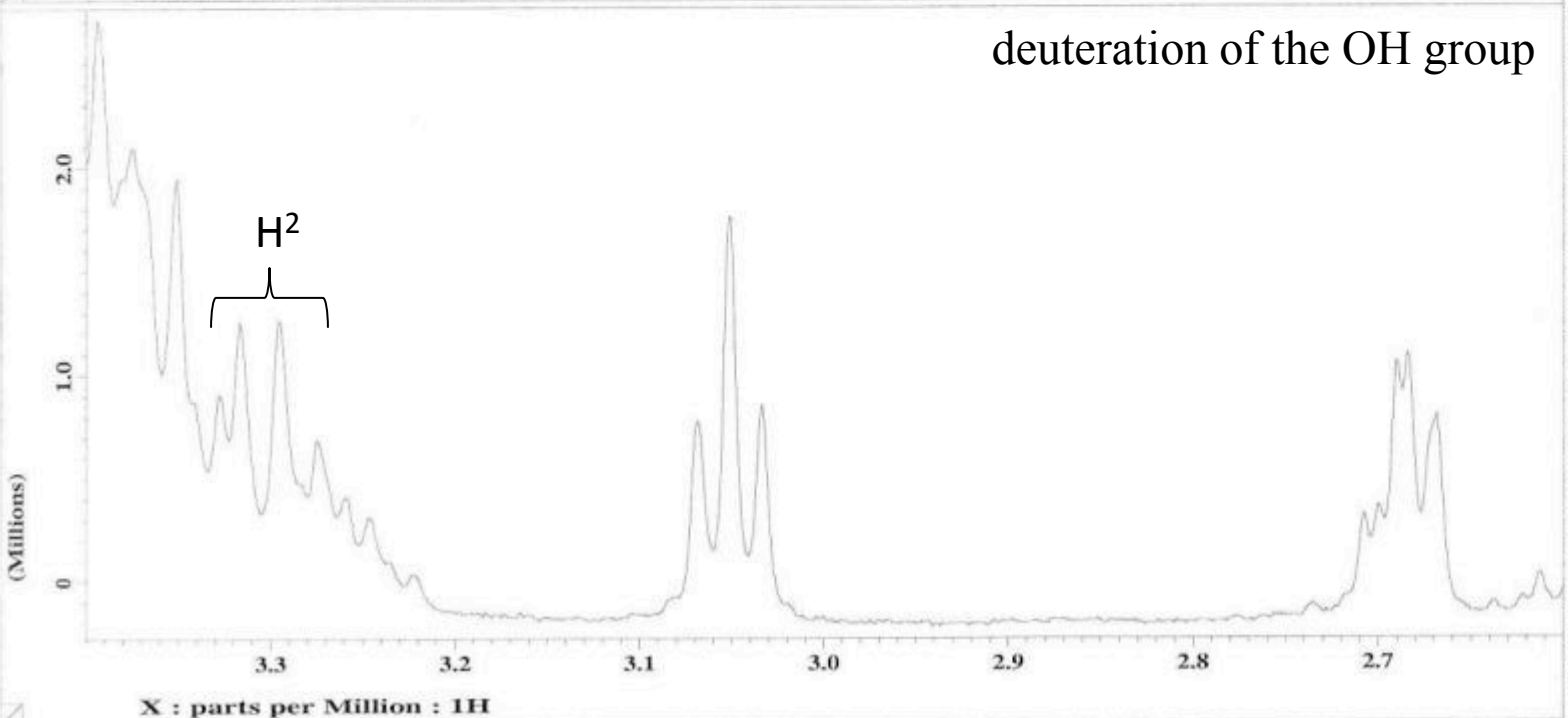
JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No548-12N
Author              = JEOL LTD.
Sample ID           = S#751978
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 19:53:38

Revision Date       = 18-MAR-2010 21:26:03
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 19:51:49
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 19:53:36
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 19:53:37
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.3[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

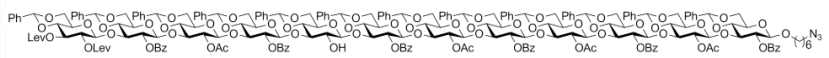


deuteration of the OH group




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No540-12N
Author              = JEOL LTD.
Sample ID           = S#751978
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 19:53:38

Revision Date       = 18-MAR-2010 21:21:11
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 19:51:49
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 19:53:36
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 19:53:37
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.3[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



(Billions)

17.0 16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

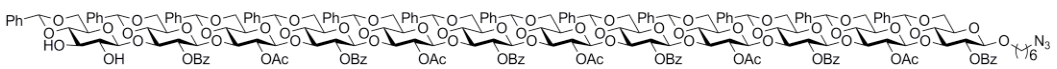
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

X : parts per Million : 13C

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100217No548_12N
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 18-FEB-2010 09:23:17

Revision Date       = 18-MAR-2010 22:41:52
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 17-FEB-2010 22:28:58
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 20-FEB-2010 14:50:23
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 18-FEB-2010 09:23:15
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 16958
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26.4[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



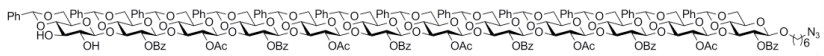
(Millions)

X : parts per Million : 1H

---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm

---- ACQUISITION PARAMETERS ----

File Name	= tetsu100318No488-12N
Author	= JEOL LTD.
Sample ID	= S#487020
Content	= Single Pulse Experim
Creation Date	= 18-MAR-2010 12:32:04
Revision Date	= 18-MAR-2010 13:37:16
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 18-MAR-2010 12:30:15
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 18-MAR-2010 12:32:02
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 1[us]
Iterations	= 0
Local_time	= 18-MAR-2010 12:32:04
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 16
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= CHLOROFORM-D
Spin_get	= 16[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 24.2[dC]
X90	= 11[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.5[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ



(Millions)
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0

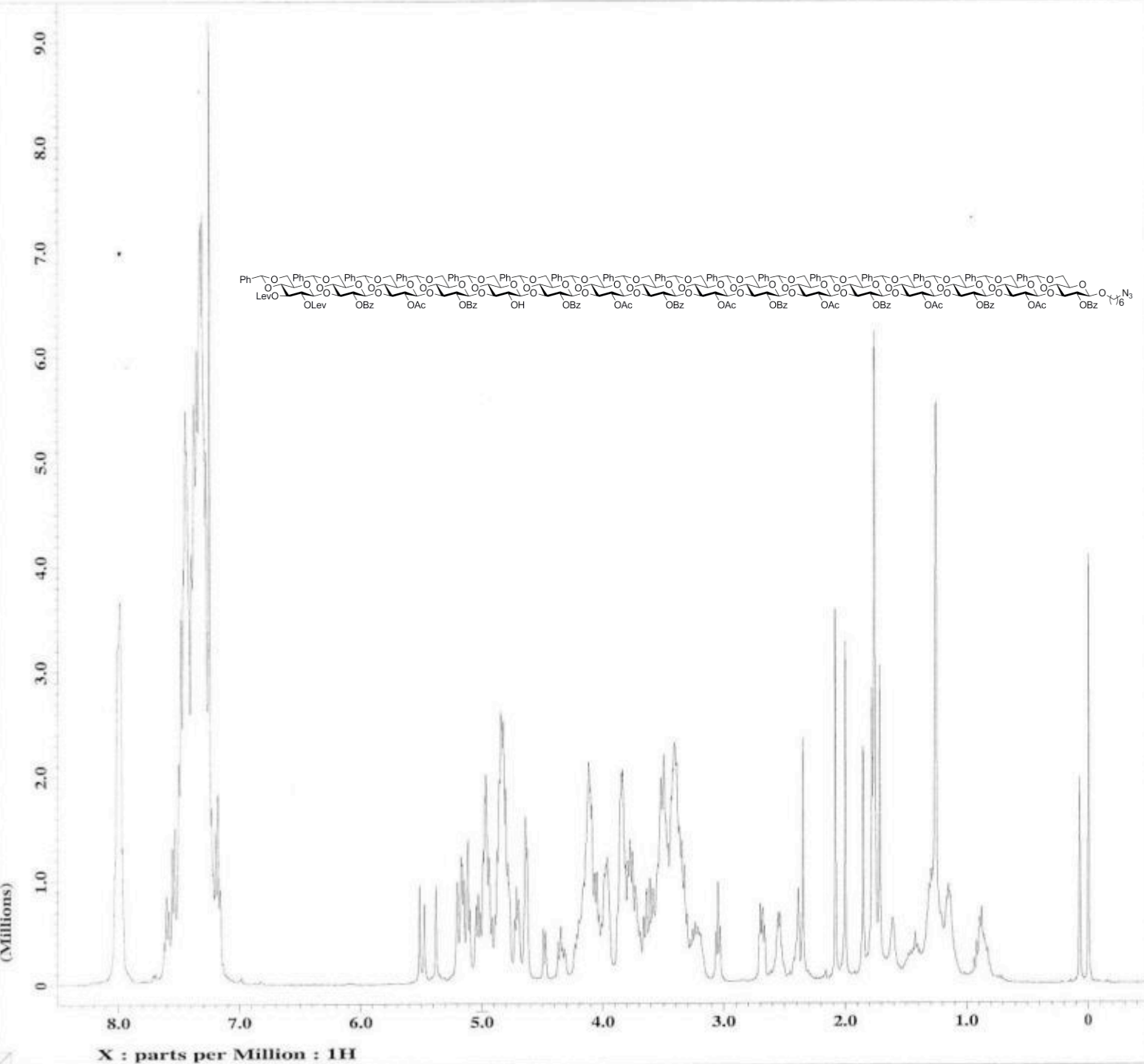
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

X : parts per Million : 13C

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

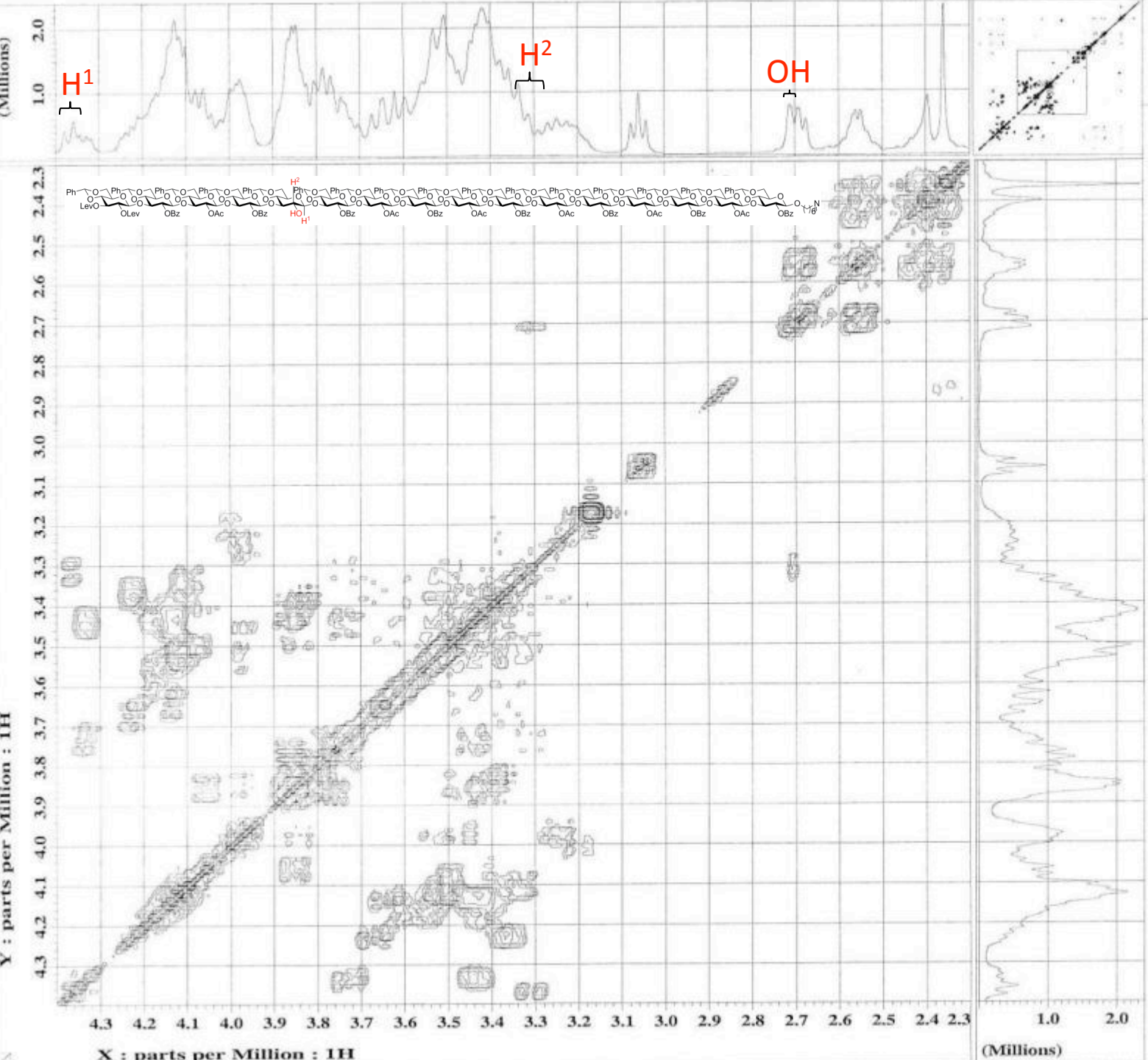
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090713No488_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 13-JUL-2009 18:32:18

Revision Date       = 18-MAR-2010 22:44:25
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 13-JUL-2009 18:02:42
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 13-JUL-2009 19:20:09
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 13-JUL-2009 18:32:17
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 760
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.8[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

File Name	= tetsu091228No600.4
Author	= JEOL LTD.
Sample ID	= S#838343
Content	= Single Pulse Experim
Creation Date	= 28-DEC-2009 22:18:57
Revision Date	= 18-MAR-2010 22:51:00
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 28-DEC-2009 22:17:08
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 28-DEC-2009 22:18:55
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 28-DEC-2009 22:18:56
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 12
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= CHLOROFORM-D
Spin_get	= 14[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 25.4[dC]
X90	= 11[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.5[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ

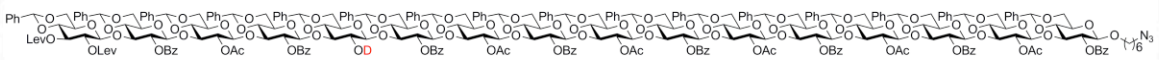


JEOL

```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
thresh : 1 : 1
symmetrize : Cosy : 24
[transpose]
```

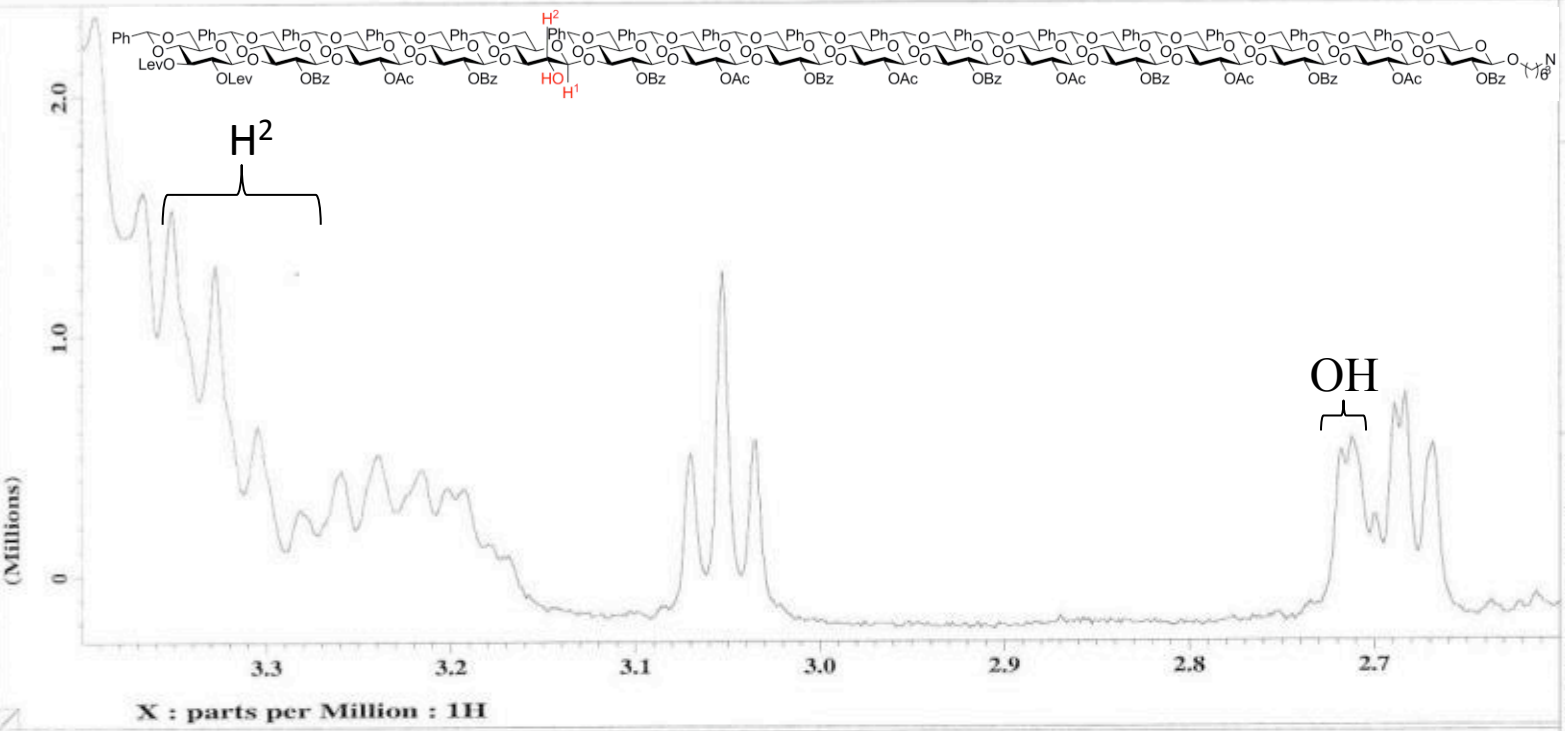
```
---- ACQUISITION PARAMETERS ----
File Name            = tetsu091228No600_cos
Author               = JEOL LTD.
Sample ID            = S#840489
Content              = gradient absolute va
Creation Date        = 28-DEC-2009 22:31:55

Revision Date        = 18-MAR-2010 22:46:29
Spec Site            = ECP400SL

Spec Type            = DELTA_NMR
Data Format          = 2D REAL REAL
Dimensions           = X Y
Dim Title            = 1H 1H
Dim Size             = 512, 1024
Dim Units            = [ppm][ppm]
Actual_start_time    = 28-DEC-2009 22:20:26
Delay_of_start       = 1[s]
Digital_filter       = FALSE
End_time             = 28-DEC-2009 22:31:51
Experiment           = cosy_pfg_m.exp
Field_strength       = 9.2981736[T]
Filter_mode          = BUTTERWORTH
Filter_width         = 1.01461039[kHz]
Grad_1               = 1[ms]
Grad_1_amp           = 50[%]
Grad_2               = 1[ms]
Grad_2_amp           = 50[%]
Grad_recover         = 1[ms]
Grad_shape           = square
Irr_code             = 146
Irr_noise            = WALTZ
Irr_pwidth           = 40[us]
Iterations           = 0
Local_time           = 28-DEC-2009 22:31:54
Obs_noise            = WAUGH
Obs_pwidth           = 1[us]
Probe_id             = 2692
Recvr_gain           = 15
Relaxation_delay     = 1[s]
Scans                = 2
Solvent              = CHLOROFORM-D
Spin_get             = 0[Hz]
Spin_lock_90         = 1[us]
Spin_lock_attn       = 29[dB]
Temp_get             = 25.5[dC]
X90                  = 11[us]
X_acq_duration       = 0.2523136[s]
X_domain             = 1H
X_freq               = 395.88252601[MHz]
X_offset             = 3.16994[ppm]
X_points             = 512
X_prescans           = 4
```

deuteration of the OH group

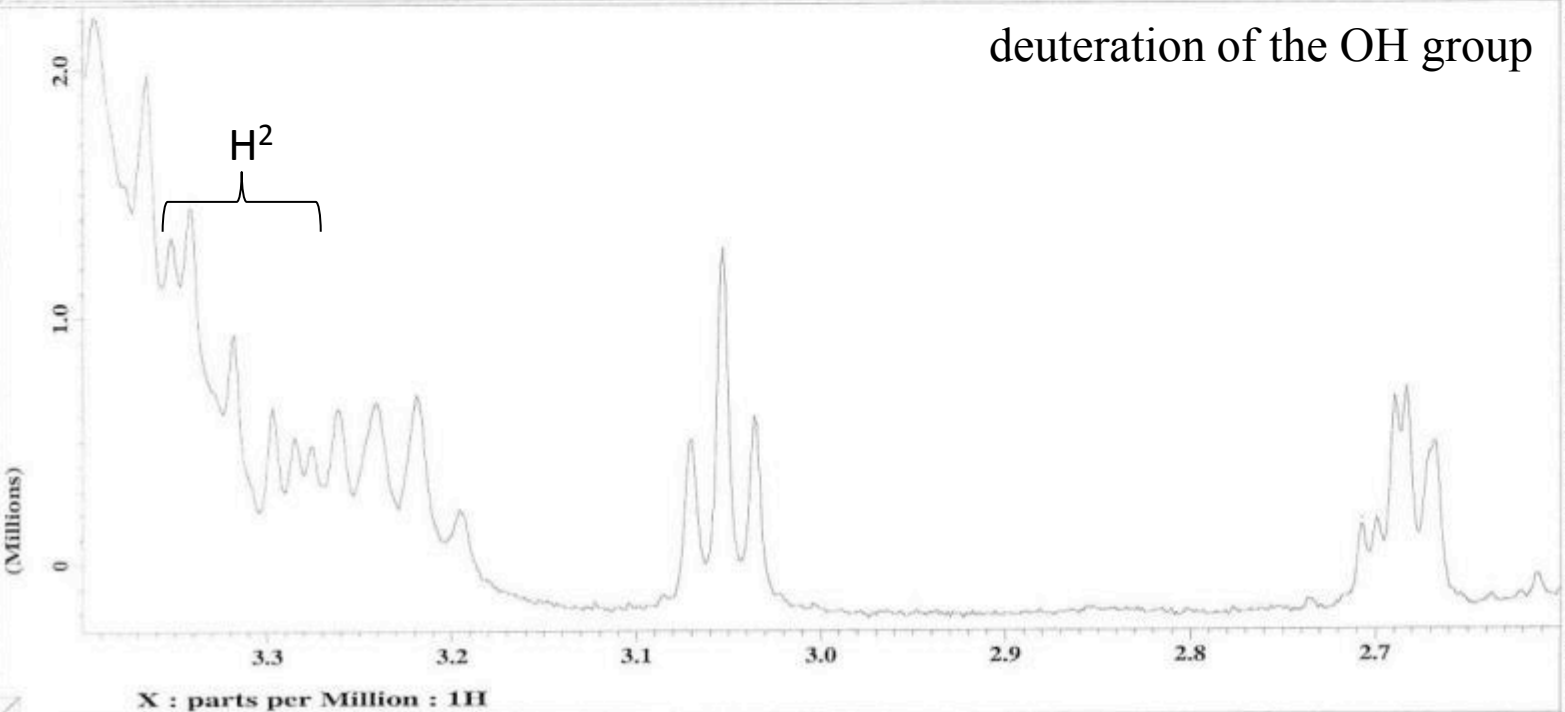



```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No600-16N
Author              = JEOL LTD.
Sample ID           = S#770101
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:23:51

Revision Date       = 18-MAR-2010 21:27:53
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:22:02
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:23:49
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:23:50
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

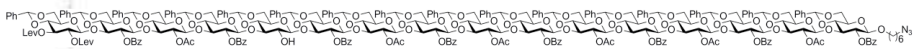


deuteration of the OH group




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
ppm
```

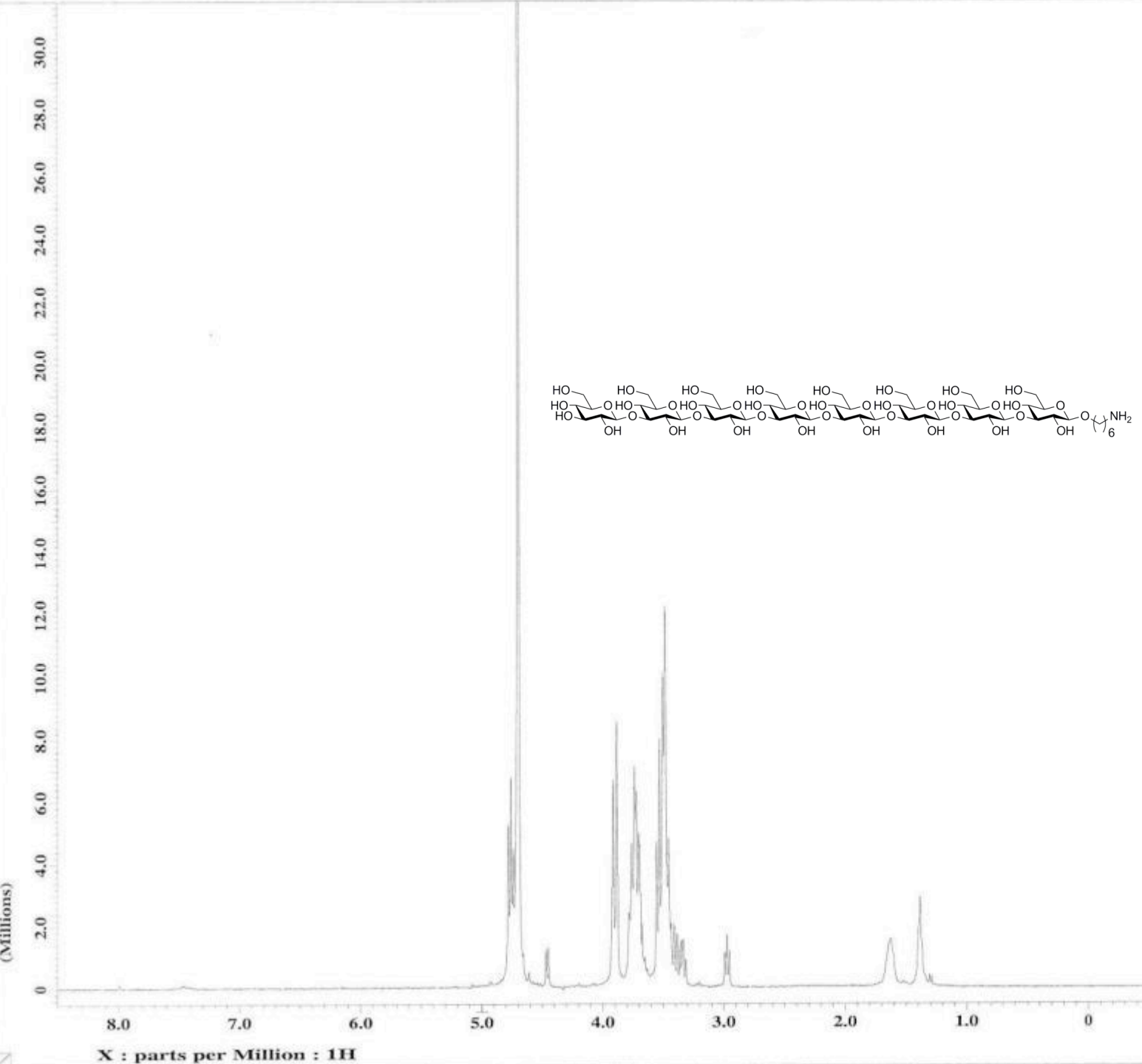
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No600-16N
Author              = JEOL LTD.
Sample ID           = S#770101
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:23:51

Revision Date       = 18-MAR-2010 21:27:53
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:22:02
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:23:49
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:23:50
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

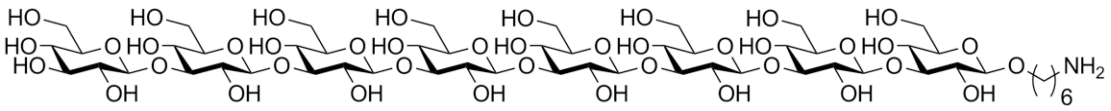
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100105No600_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       =  5-JAN-2010 17:40:18

Revision Date       = 18-MAR-2010 22:49:41
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   =  5-JAN-2010 13:58:29
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  5-JAN-2010 20:24:49
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          =  5-JAN-2010 17:40:17
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 5744
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 25.8[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090224No385_30.
Author              = JEOL LTD.
Sample ID           = 30
Content             = Single Pulse Experim
Creation Date       = 24-FEB-2009 14:03:51

Revision Date       = 18-MAR-2010 22:55:08
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 24-FEB-2009 14:02:02
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 24-FEB-2009 14:03:49
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 45[us]
Iterations          = 0
Local_time          = 24-FEB-2009 14:03:50
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 21
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = D2O
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



5.0
4.0
3.0
2.0
1.0
0
(Billions)

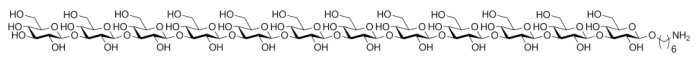
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

X : parts per Million : 13C

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

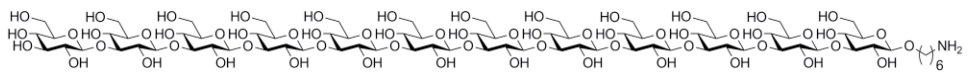
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090930No449_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       =  1-OCT-2009 08:27:54

Revision Date       = 18-MAR-2010 22:57:21
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 30-SEP-2009 22:53:00
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  3-OCT-2009 15:14:25
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          =  1-OCT-2009 08:27:53
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 14900
Solvent             = D2O
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091003No549-70.
Author              = JEOL LTD.
Sample ID           = 70
Content             = Single Pulse Experim
Creation Date       =  3-OCT-2009 16:14:38

Revision Date       = 18-MAR-2010 23:01:44
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   =  3-OCT-2009 16:12:49
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  3-OCT-2009 16:14:36
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          =  3-OCT-2009 16:14:37
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 18
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = D2O
Spin_get            = 18[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 70[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



(Billions)

5.0
4.0
3.0
2.0
1.0
0

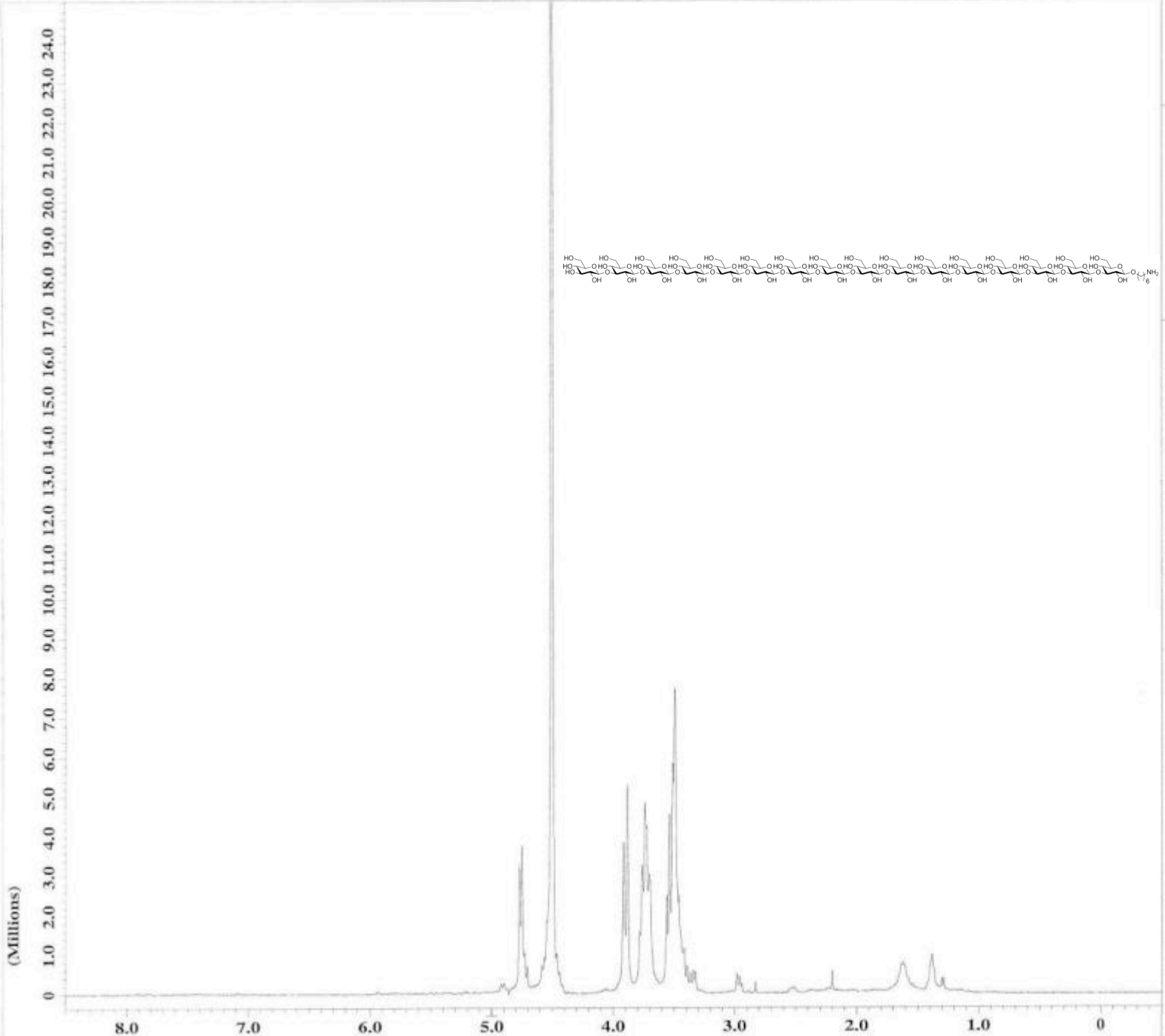
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

X : parts per Million : 13C

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

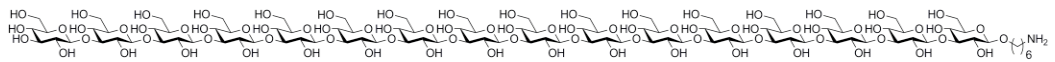
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091124No549-30_
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 25-NOV-2009 08:35:36

Revision Date       = 18-MAR-2010 23:01:16
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 24-NOV-2009 22:39:42
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 27-NOV-2009 15:01:07
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 25-NOV-2009 08:35:34
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 15443
Solvent             = D2O
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090319No450_50.
Author              = JEOL LTD.
Sample ID           = 50
Content             = Single Pulse Experim
Creation Date       = 19-MAR-2009 11:04:15

Revision Date       = 18-MAR-2010 23:04:36
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 19-MAR-2009 11:02:25
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 19-MAR-2009 11:04:12
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 19-MAR-2009 11:04:14
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 19
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = D2O
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 50[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



(Billions)

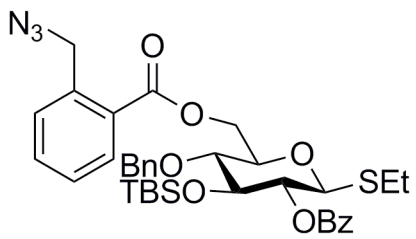
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

X : parts per Million : 13C

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

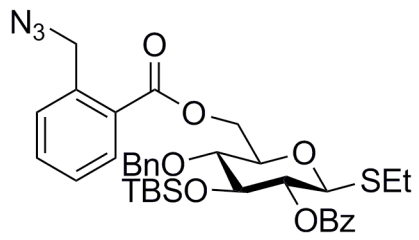
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091109No473-16t
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 10-NOV-2009 07:25:13

Revision Date       = 18-MAR-2010 23:06:55
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   =  9-NOV-2009 22:03:27
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 12-NOV-2009 14:24:52
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 10-NOV-2009 07:25:12
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 14558
Solvent             = D2O
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

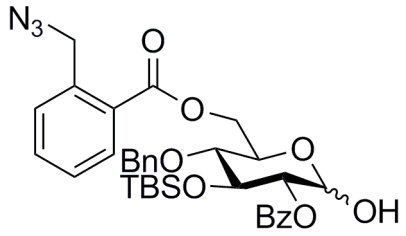
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090619No500.3
Author              = JEOL LTD.
Sample ID           = S#795492
Content             = Single Pulse Experim
Creation Date       = 19-JUN-2009 21:20:13

Revision Date       = 18-MAR-2010 23:08:53
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 19-JUN-2009 21:18:24
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 19-JUN-2009 21:20:11
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 19-JUN-2009 21:20:12
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 15
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 12[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 21.9[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

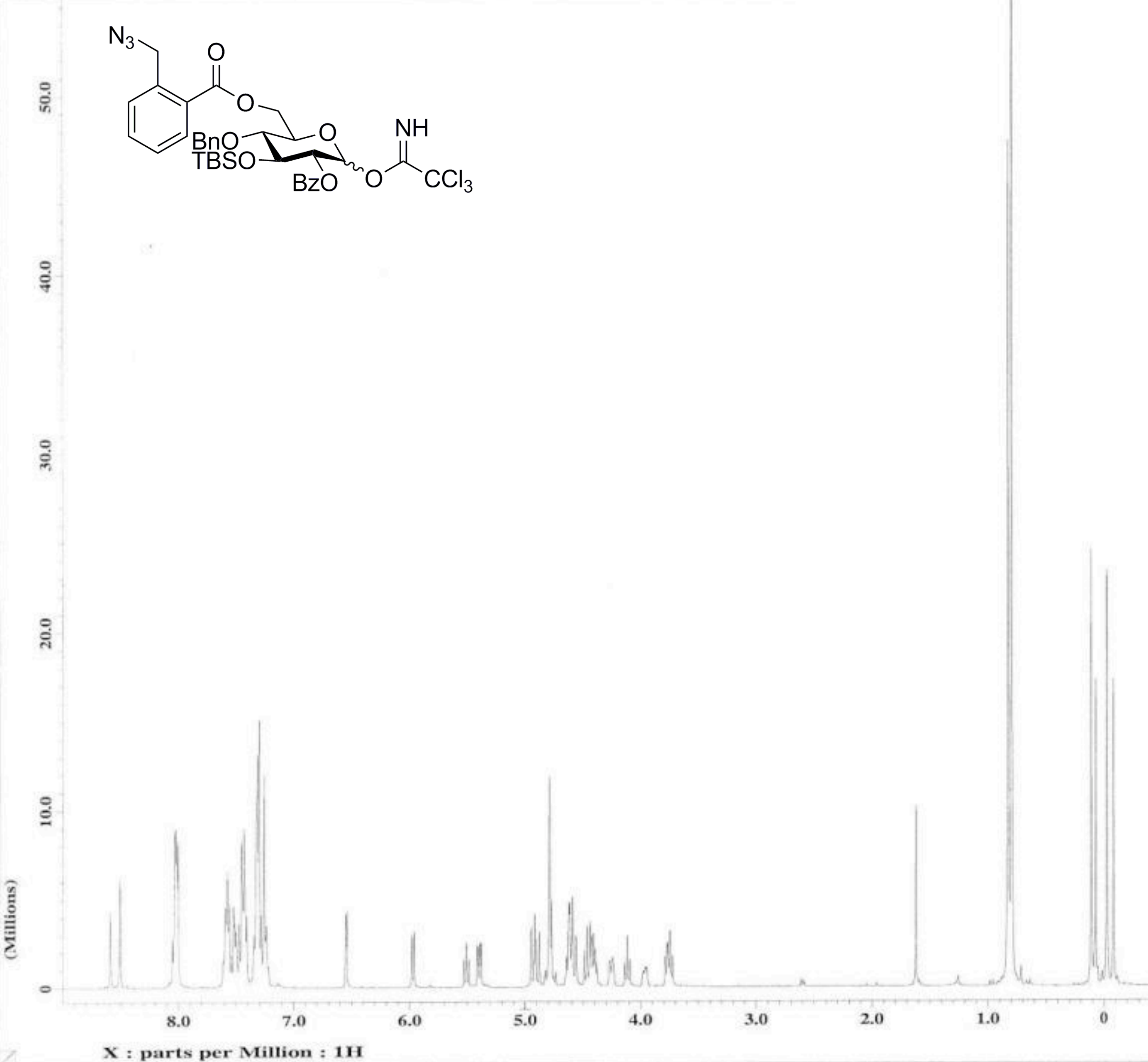
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090619No500_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 19-JUN-2009 21:39:14

Revision Date       = 18-MAR-2010 23:10:15
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 19-JUN-2009 21:21:29
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 19-JUN-2009 22:00:19
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 19-JUN-2009 21:39:14
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 453
Solvent             = CHLOROFORM-D
Spin_get            = 10[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.4[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

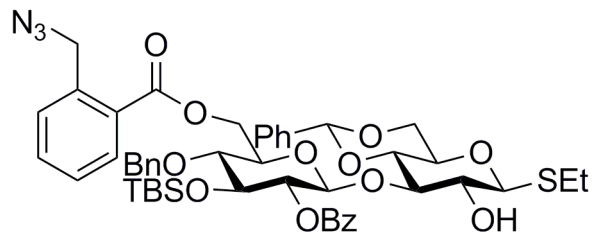
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090610No495.3
Author              = JEOL LTD.
Sample ID           = S#415422
Content             = Single Pulse Experim
Creation Date       = 10-JUN-2009 10:47:10

Revision Date       = 18-MAR-2010 23:12:32
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 10-JUN-2009 10:45:21
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 10-JUN-2009 10:47:08
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 10-JUN-2009 10:47:09
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 17
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.6[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

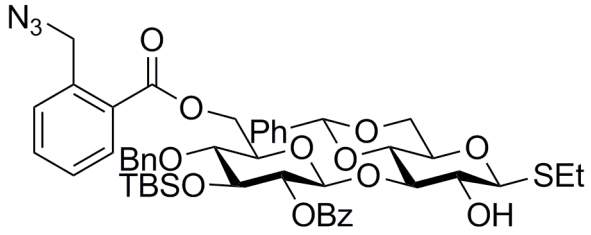
File Name	= tetsu090616No505.3
Author	= JEOL LTD.
Sample ID	= S#419057
Content	= Single Pulse Experim
Creation Date	= 16-JUN-2009 10:53:04
Revision Date	= 18-MAR-2010 23:14:18
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 16-JUN-2009 10:51:15
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 16-JUN-2009 10:53:02
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 16-JUN-2009 10:53:03
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 13
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= CHLOROFORM-D
Spin_get	= 17[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 20.6[dC]
X90	= 11.8[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.9[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090618No507.3
Author              = JEOL LTD.
Sample ID           = S#747163
Content             = Single Pulse Experim
Creation Date       = 18-JUN-2009 19:59:32

Revision Date       = 18-MAR-2010 23:16:03
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-JUN-2009 19:57:43
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-JUN-2009 19:59:30
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-JUN-2009 19:59:31
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 21.6[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

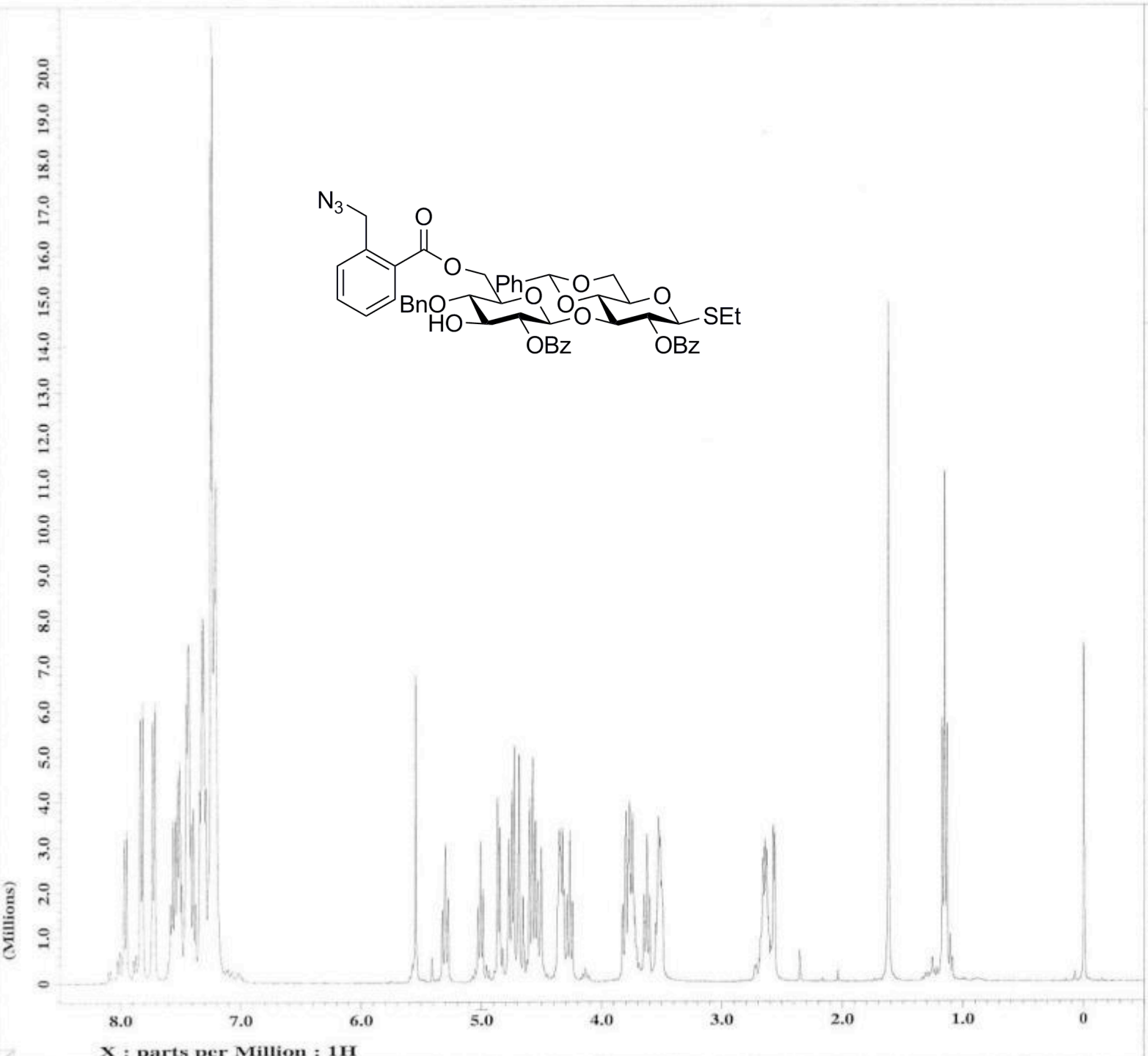
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090618No507_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 18-JUN-2009 20:32:00

Revision Date       = 18-MAR-2010 23:17:05
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 18-JUN-2009 20:16:50
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-JUN-2009 20:55:40
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 18-JUN-2009 20:32:00
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 386
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.5[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```

600.0 500.0 400.0 300.0 200.0 100.0 0 (Millions)

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

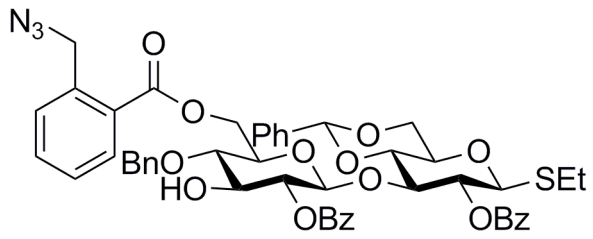
X : parts per Million : 13C



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

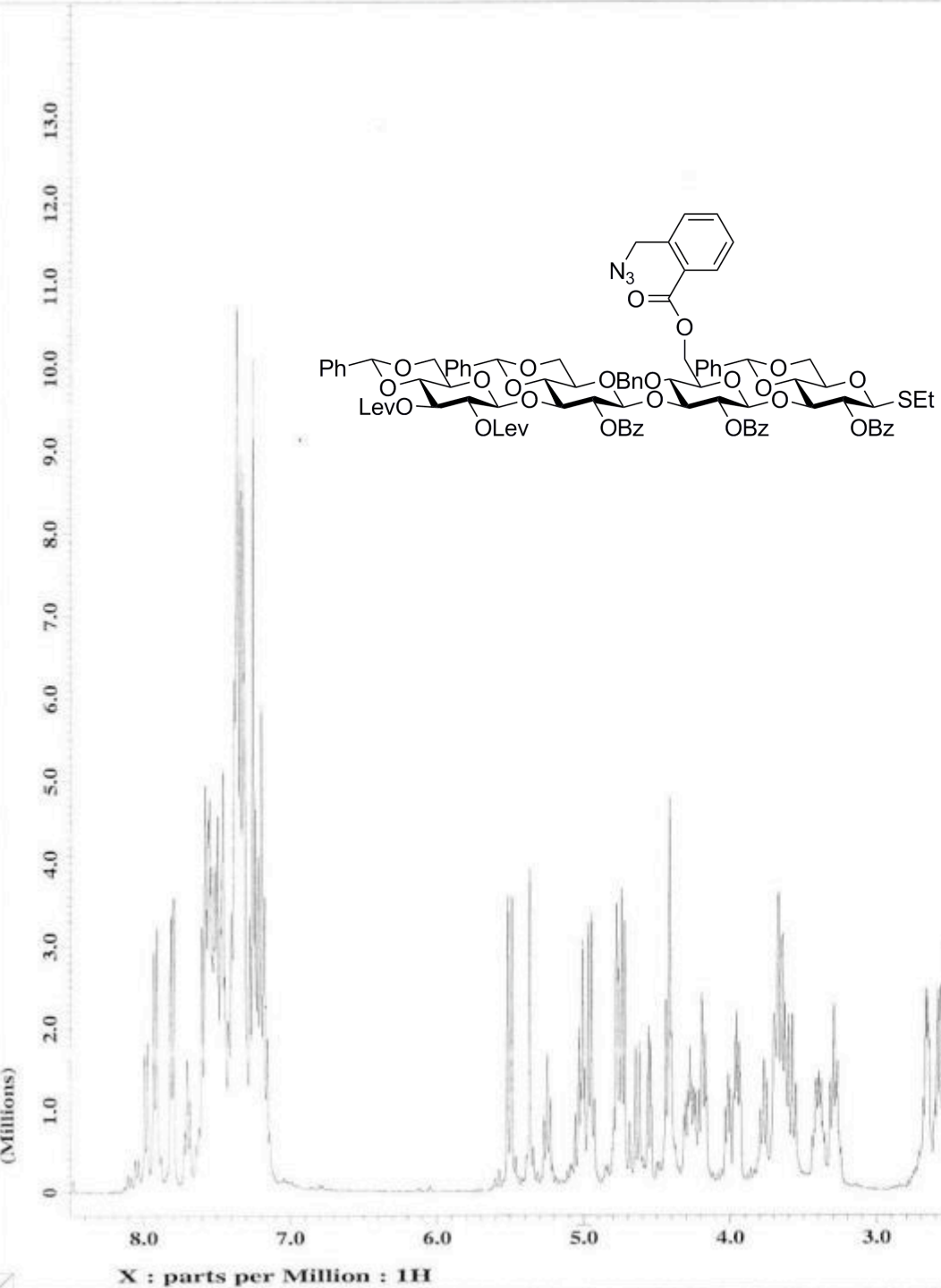
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090623No510.3
Author              = JEOL LTD.
Sample ID           = S#585246
Content             = Single Pulse Experim
Creation Date       = 23-JUN-2009 15:29:25

Revision Date       = 18-MAR-2010 23:19:41
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 23-JUN-2009 15:27:36
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 23-JUN-2009 15:29:23
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 23-JUN-2009 15:29:24
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 21.6[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

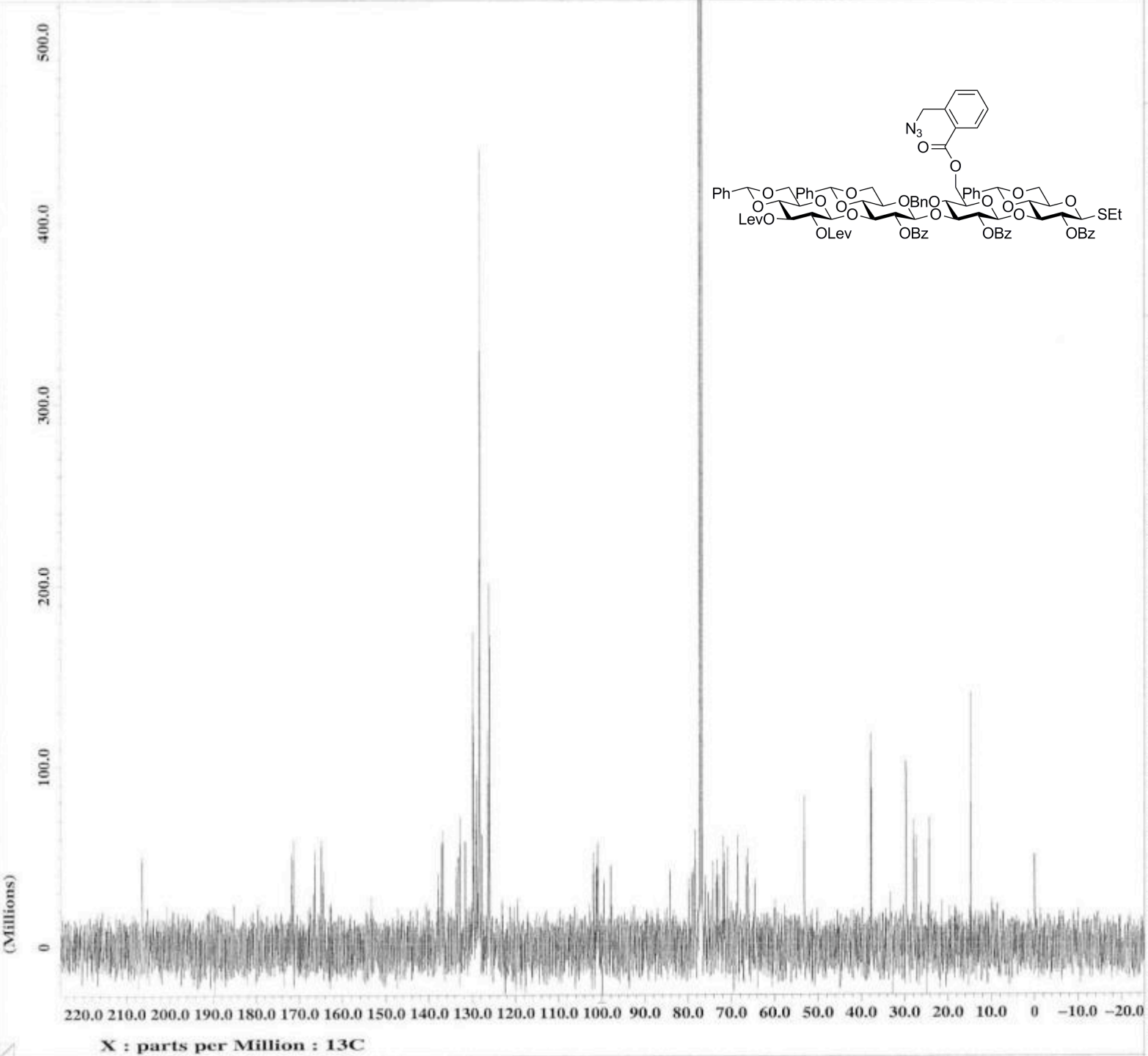
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090623No510_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 23-JUN-2009 16:05:49

Revision Date       = 18-MAR-2010 23:18:44
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 23-JUN-2009 15:44:26
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 23-JUN-2009 16:23:16
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 23-JUN-2009 16:05:48
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 548
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.8[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

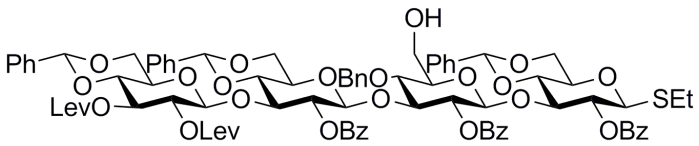
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090626No515.3
Author              = JEOL LTD.
Sample ID           = S#570810
Content             = Single Pulse Experim
Creation Date       = 26-JUN-2009 15:05:24

Revision Date       = 18-MAR-2010 23:21:38
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 26-JUN-2009 15:03:34
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 26-JUN-2009 15:05:21
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 26-JUN-2009 15:05:23
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 14
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 21.4[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090626No515_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Nr
Creation Date       = 26-JUN-2009 15:46:34

Revision Date       = 18-MAR-2010 23:22:49
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 26-JUN-2009 15:20:36
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 26-JUN-2009 15:59:26
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 26-JUN-2009 15:46:34
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 666
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.2[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



(Millions)

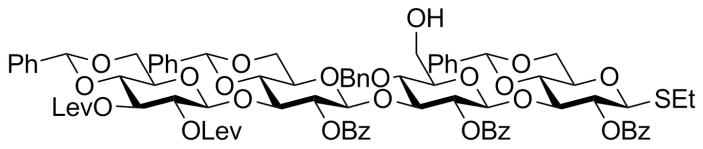
18.0 17.0 16.0 15.0 14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

X : parts per Million : 1H

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090713No518.3
Author              = JEOL LTD.
Sample ID           = S#596202
Content             = Single Pulse Experim
Creation Date       = 13-JUL-2009 15:46:54

Revision Date       = 19-MAR-2010 13:02:35
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 13-JUL-2009 15:45:05
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 13-JUL-2009 15:46:52
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          = 13-JUL-2009 15:46:53
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 16
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26.2[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



(Billions)

1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

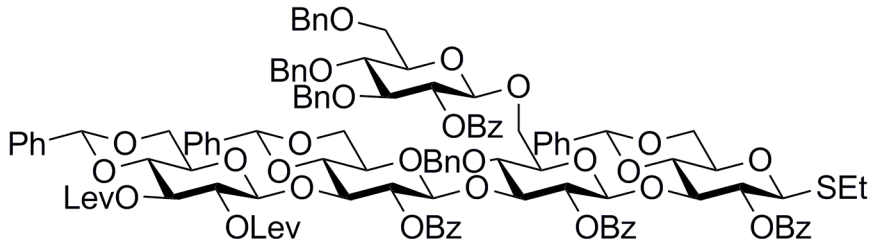
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

X : parts per Million : 13C

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

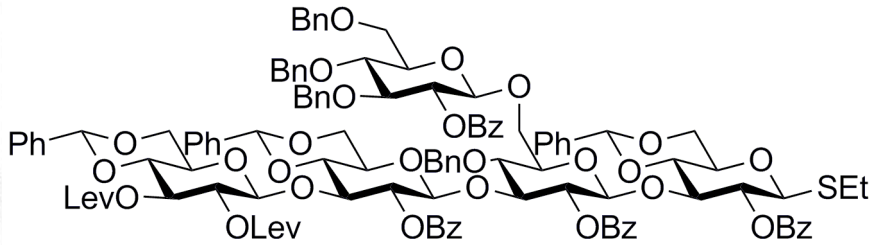
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090626No518_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 26-JUN-2009 19:05:48

Revision Date       = 19-MAR-2010 13:06:21
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 26-JUN-2009 18:43:22
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 26-JUN-2009 19:22:12
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 26-JUN-2009 19:05:47
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 574
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.4[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

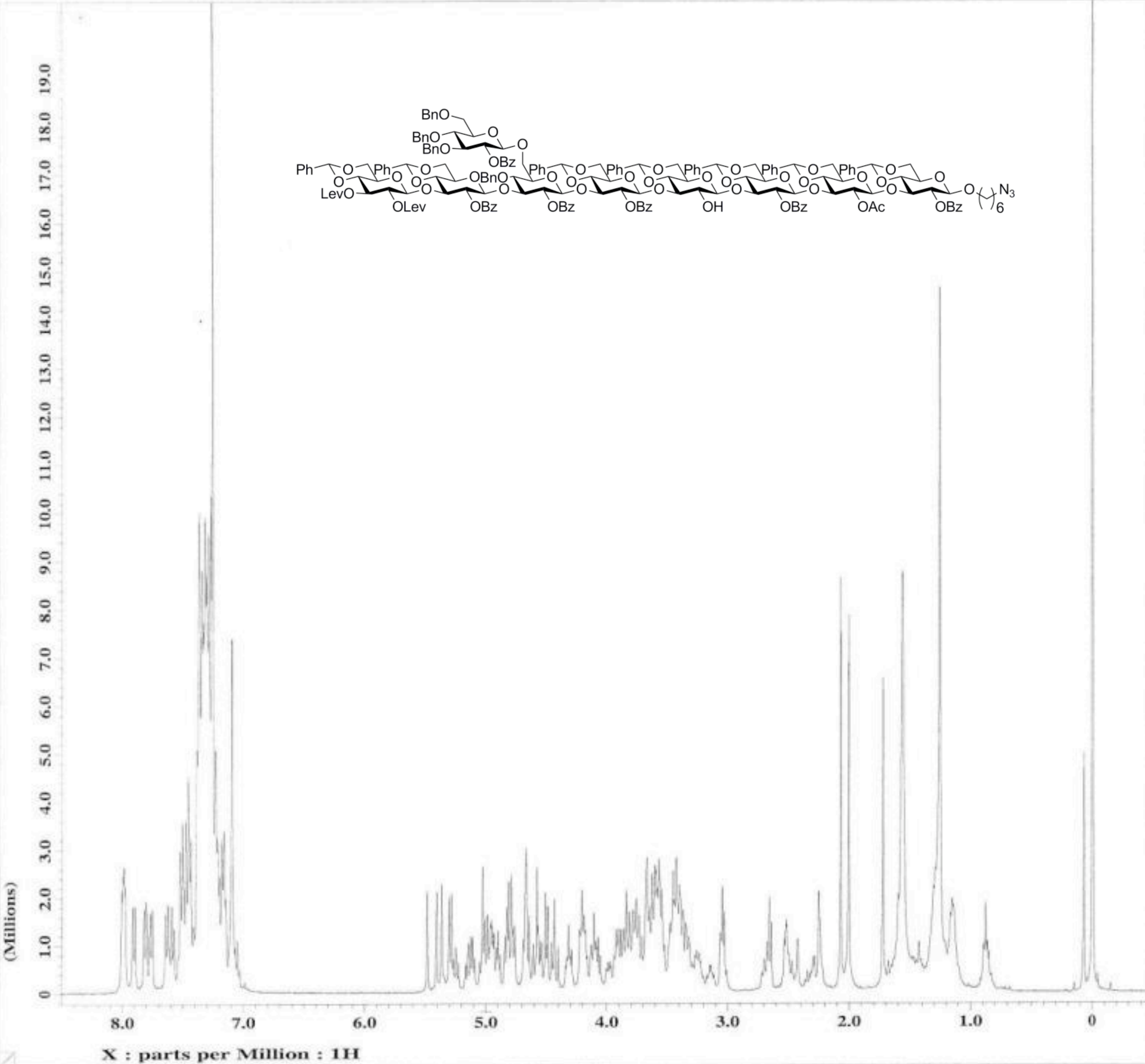
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090630No520.3
Author              = JEOL LTD.
Sample ID           = S#473016
Content             = Single Pulse Experim
Creation Date       = 30-JUN-2009 12:27:30

Revision Date       = 19-MAR-2010 13:12:04
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 30-JUN-2009 12:20:49
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 30-JUN-2009 12:27:28
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 30-JUN-2009 12:27:29
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 20
Relaxation_delay    = 4[s]
Scans               = 64
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 21.6[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

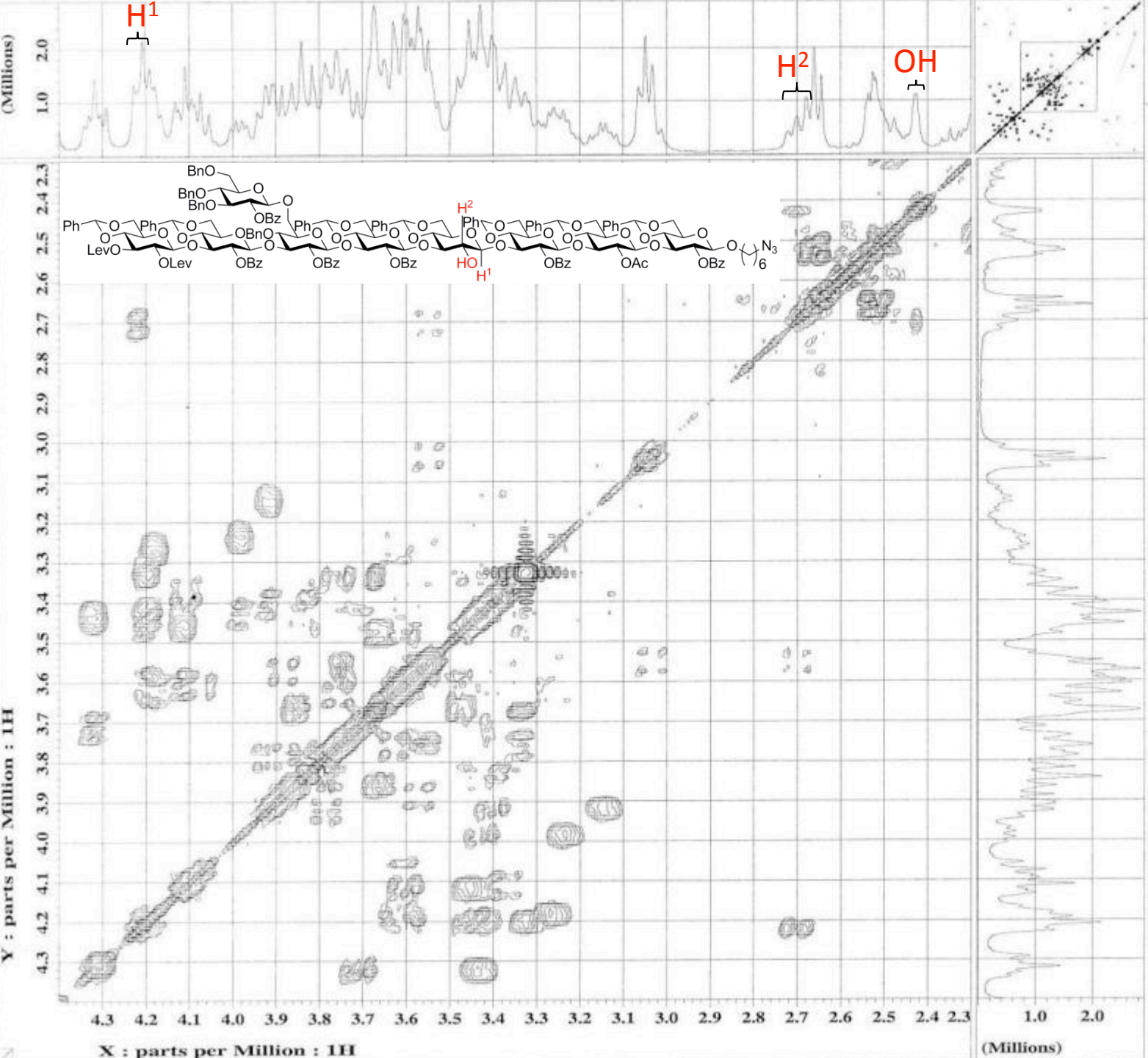
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090629No520_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 29-JUN-2009 22:05:59

Revision Date       = 19-MAR-2010 13:13:42
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 29-JUN-2009 21:50:23
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 29-JUN-2009 22:29:13
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 29-JUN-2009 22:05:59
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 29
Relaxation_delay    = 1[s]
Scans               = 397
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.4[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

File Name	= tetsu090819No545.3
Author	= JEOL LTD.
Sample ID	= S#436163
Content	= Single Pulse Experim
Creation Date	= 19-AUG-2009 11:12:30
Revision Date	= 19-MAR-2010 13:17:54
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 19-AUG-2009 11:10:41
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 19-AUG-2009 11:12:28
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 19-AUG-2009 11:12:29
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 19
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= CHLOROFORM-D
Spin_get	= 16[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 26.1[dC]
X90	= 11.8[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.9[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ

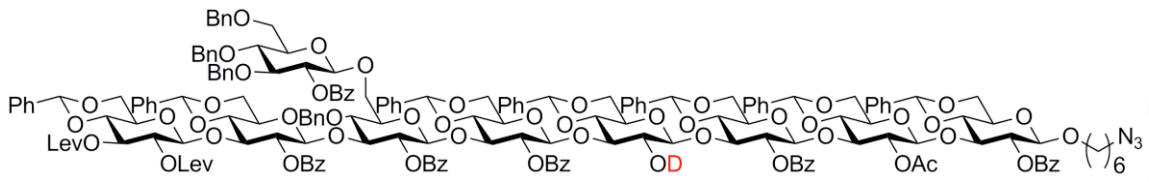


JEOL

```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
thresh : 1 : 1
symmetrize : Cosy : 24
[transpose]
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090819No545_cos
Author              = JEOL LTD.
Sample ID           = S#439293
Content             = gradient absolute va
Creation Date       = 19-AUG-2009 11:26:37

Revision Date       = 19-MAR-2010 13:16:06
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 1H 1H
Dim Size            = 512, 1024
Dim Units           = [ppm][ppm]
Actual_start_time   = 19-AUG-2009 11:14:53
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 19-AUG-2009 11:26:34
Experiment          = cosy_pfg_m.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 927.81592132[Hz]
Grad_1              = 1[ms]
Grad_1_amp          = 50[%]
Grad_2              = 1[ms]
Grad_2_amp          = 50[%]
Grad_recover        = 1[ms]
Grad_shape          = square
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 19-AUG-2009 11:26:37
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 15
Relaxation_delay    = 1[s]
Scans               = 2
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26.3[dC]
X90                 = 11.8[us]
X_acq_duration      = 0.2759168[s]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 3.32506[ppm]
X_points            = 512
X_prescans          = 4
```

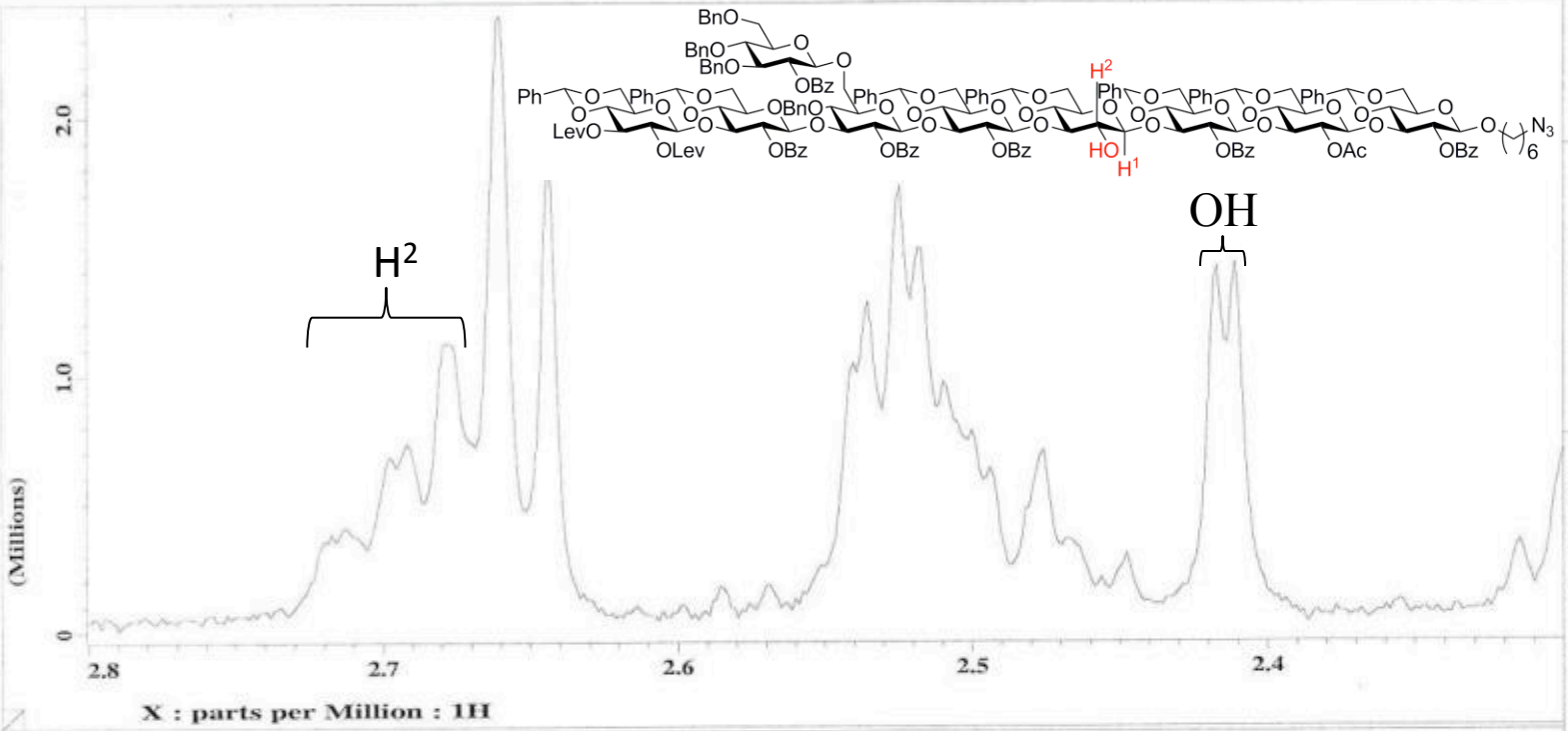
deuteration of the OH group



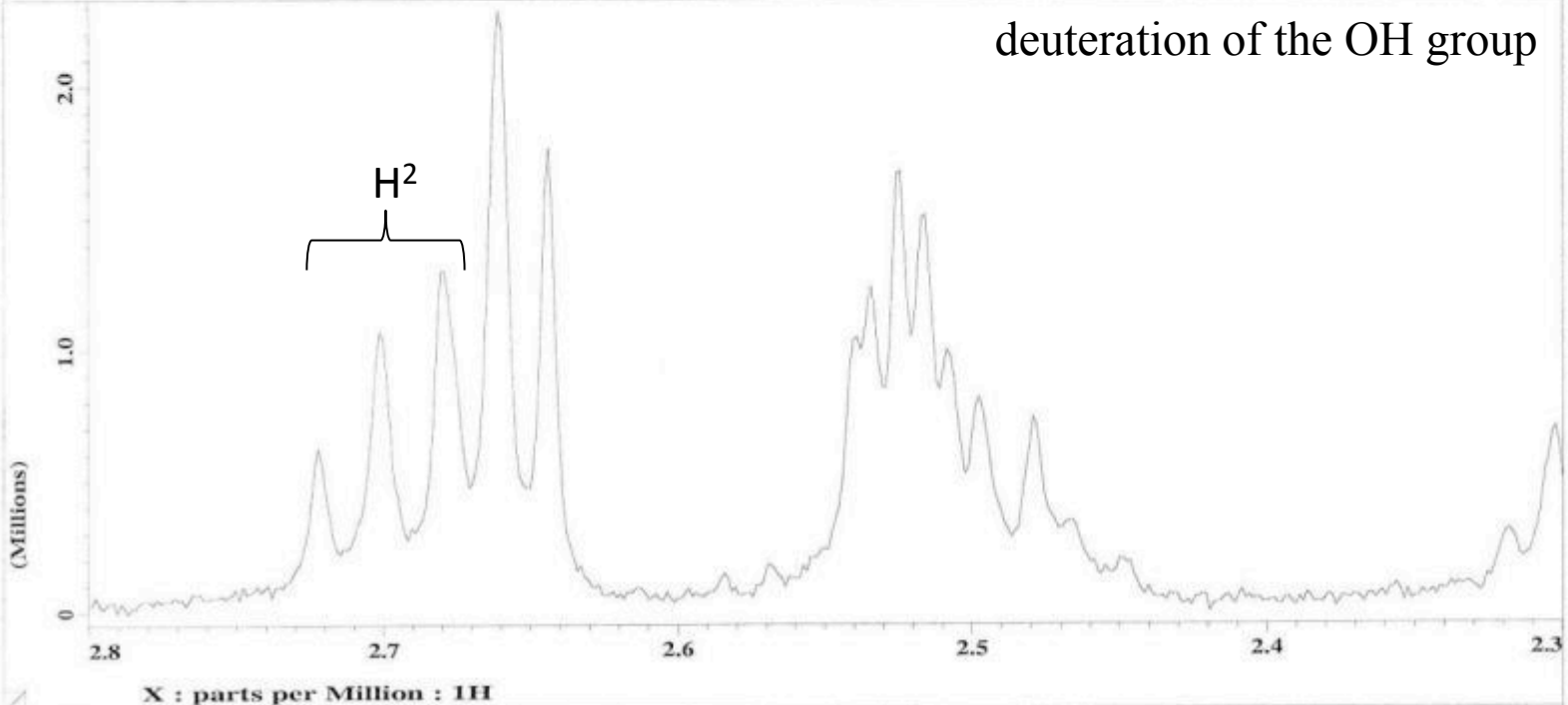
JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu10318No545-9N3
Author              = JEOL LTD.
Sample ID           = S#777010
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:35:34

Revision Date       = 18-MAR-2010 22:06:00
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:33:45
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:35:32
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:35:33
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 18
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.1[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

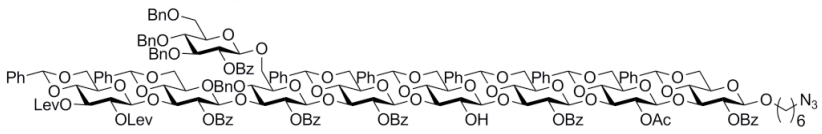


deuteration of the OH group



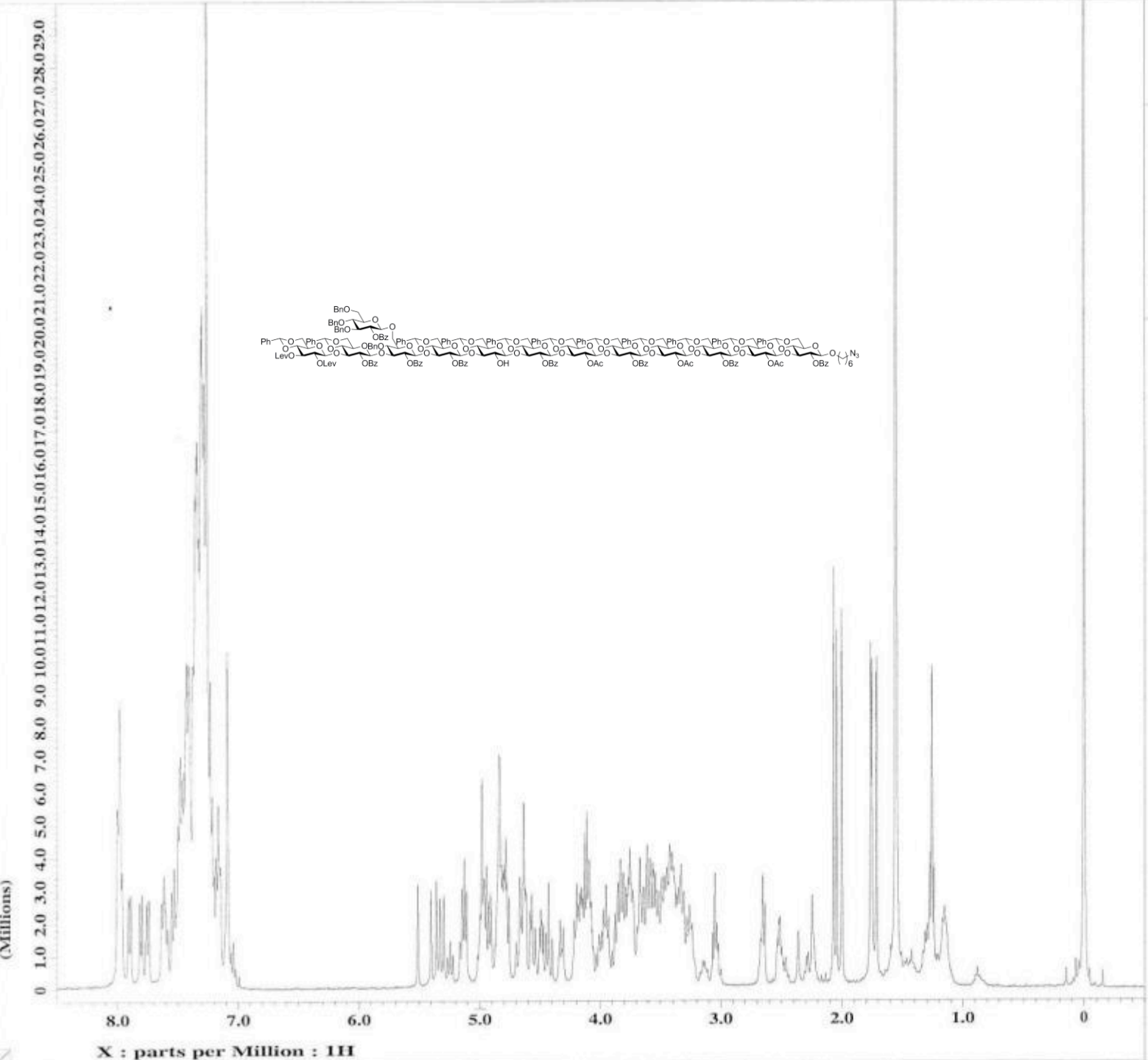

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No545-9N3
Author              = JEOL LTD.
Sample ID           = S#777010
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:35:34

Revision Date       = 18-MAR-2010 22:06:00
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:33:45
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:35:32
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:35:33
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 18
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.1[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

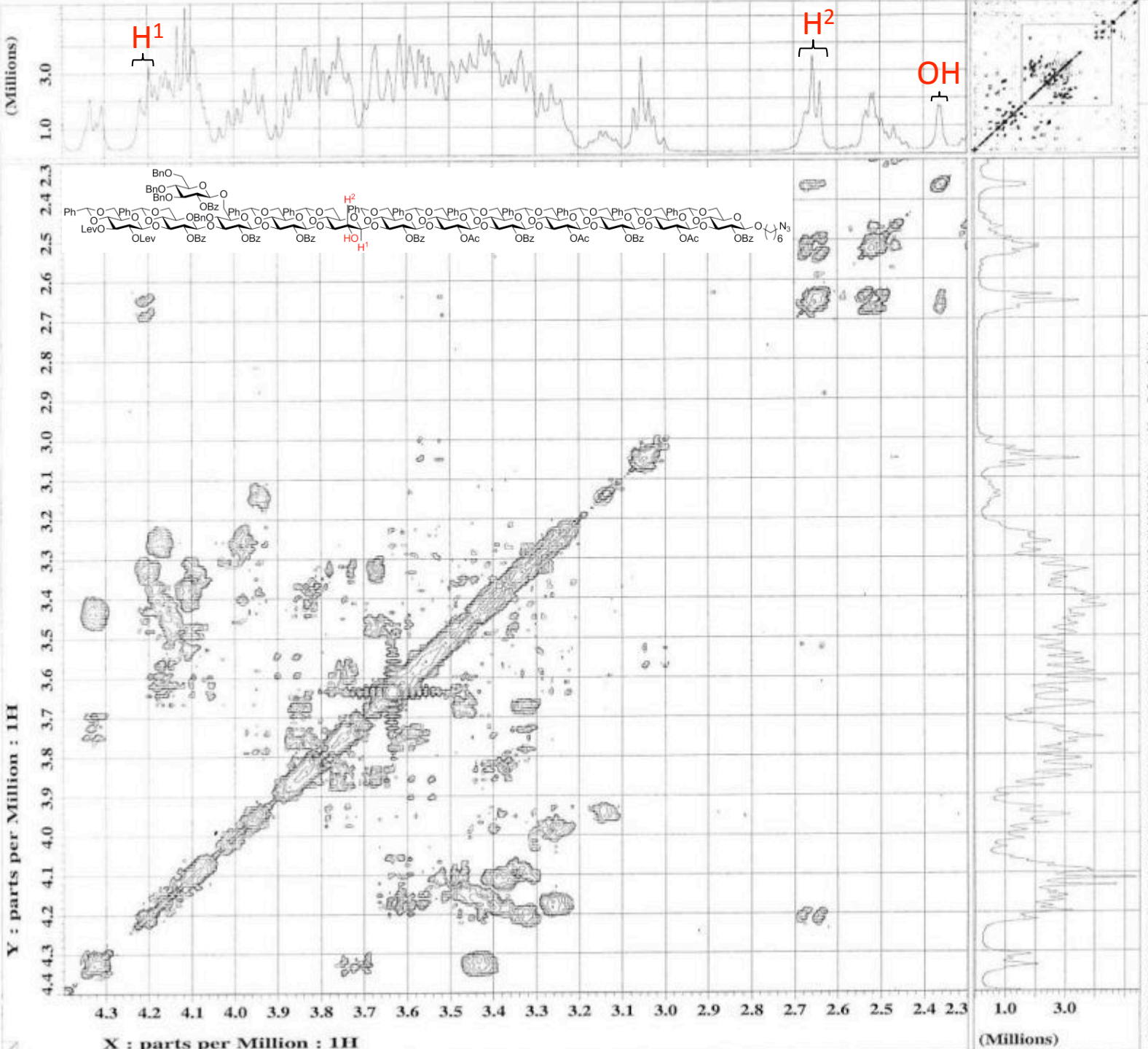
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090819No545_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 19-AUG-2009 11:57:54

Revision Date       = 19-MAR-2010 13:17:11
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 19-AUG-2009 11:32:21
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 19-AUG-2009 12:11:11
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 19-AUG-2009 11:57:54
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 655
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 28.1[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

File Name	= tetsu090805No534.3
Author	= JEOL LTD.
Sample ID	= S#623755
Content	= Single Pulse Experim
Creation Date	= 5-AUG-2009 16:26:25
Revision Date	= 19-MAR-2010 13:27:11
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 5-AUG-2009 16:22:59
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 5-AUG-2009 16:26:23
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 5-AUG-2009 16:26:24
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 21
Relaxation_delay	= 4[s]
Scans	= 32
Solvent	= CHLOROFORM-D
Spin_get	= 17[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 26.3[dC]
X90	= 11.8[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.9[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ

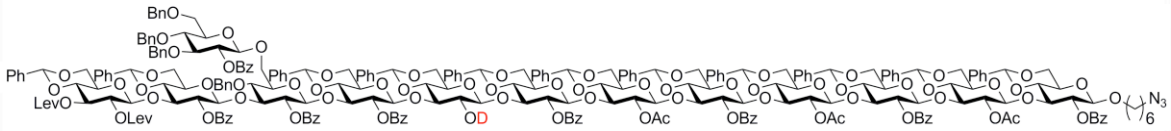


JEOL

```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
thresh : 1 : 1
symmetrize : Cosy : 24
[transpose]
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090805No534_cos
Author              = JEOL LTD.
Sample ID           = S#627121
Content             = gradient absolute va
Creation Date       =  5-AUG-2009 16:40:27

Revision Date       = 19-MAR-2010 13:26:27
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 1H 1H
Dim Size            = 512, 1024
Dim Units           = [ppm] [ppm]
Actual_start_time   =  5-AUG-2009 16:28:11
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  5-AUG-2009 16:40:24
Experiment          = cosy_pfg_m.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 782.10542781[Hz]
Grad_1              = 1[ms]
Grad_1_amp          = 50[%]
Grad_2              = 1[ms]
Grad_2_amp          = 50[%]
Grad_recover        = 1[ms]
Grad_shape          = square
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          =  5-AUG-2009 16:40:26
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 15
Relaxation_delay    = 1[s]
Scans               = 2
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 26.7[dC]
X90                 = 11.8[us]
X_acq_duration      = 0.3273216[s]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 3.63346[ppm]
X_points            = 512
X_prescans          = 4
```

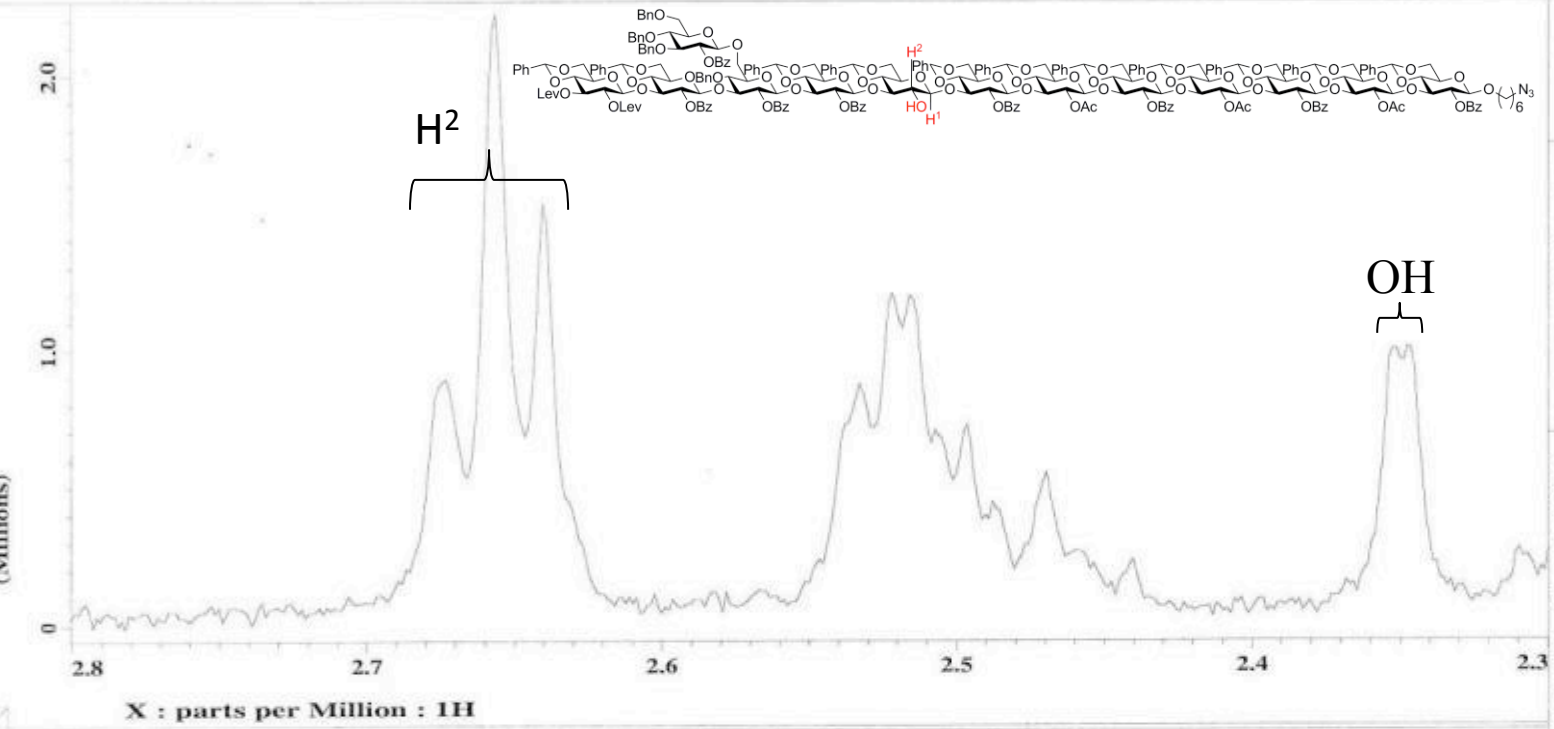
deuteration of the OH group

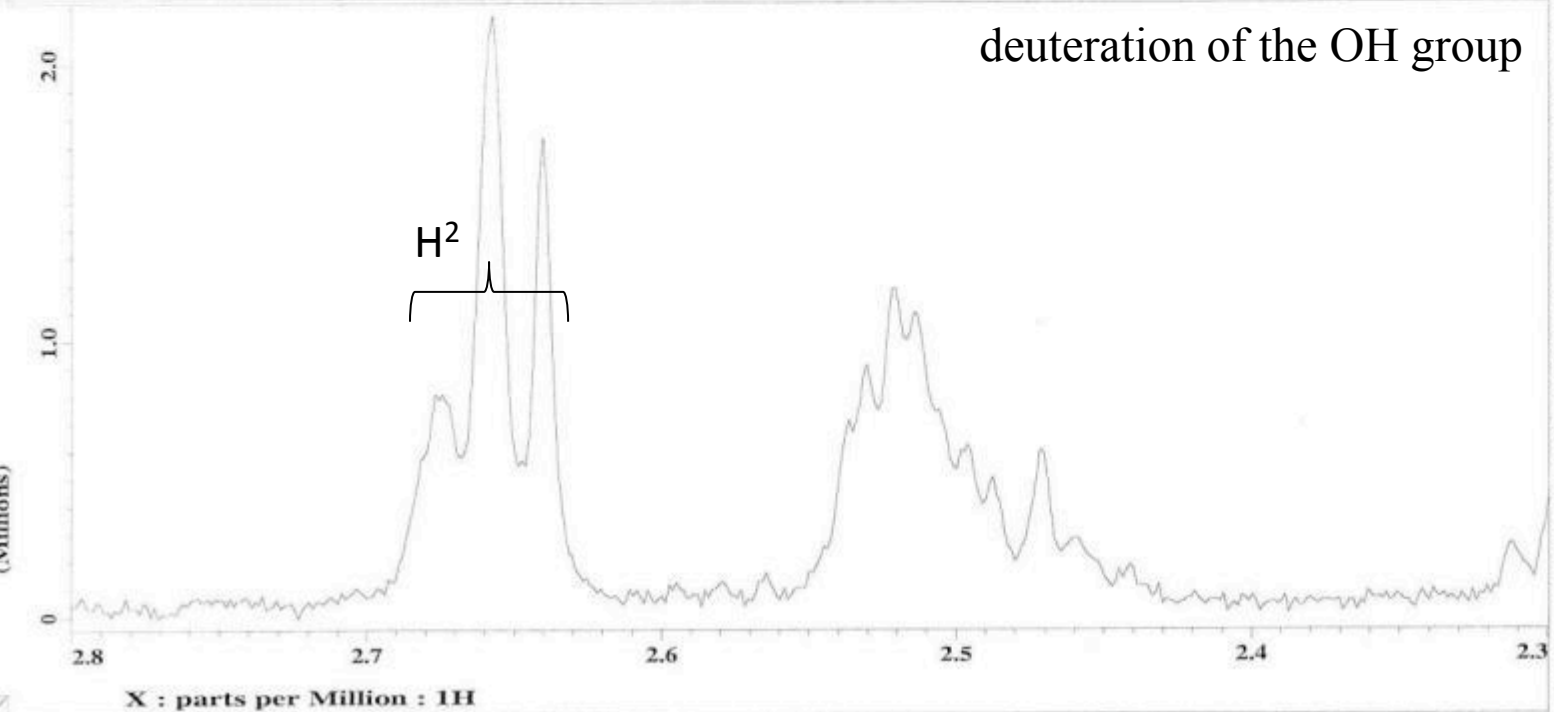


JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
reference : -1[mppm] : 0[ppm]
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No534-13N
Author              = JEOL LTD.
Sample ID           = S#781935
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:43:57

Revision Date       = 18-MAR-2010 22:14:38
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:42:08
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:43:55
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:43:56
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 19
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.1[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

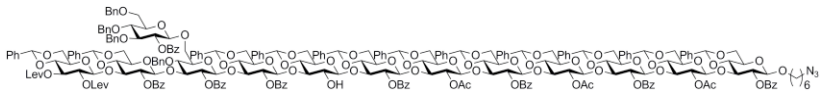




deuteration of the OH group

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
reference : -1[mppm] : 0[ppm]
```

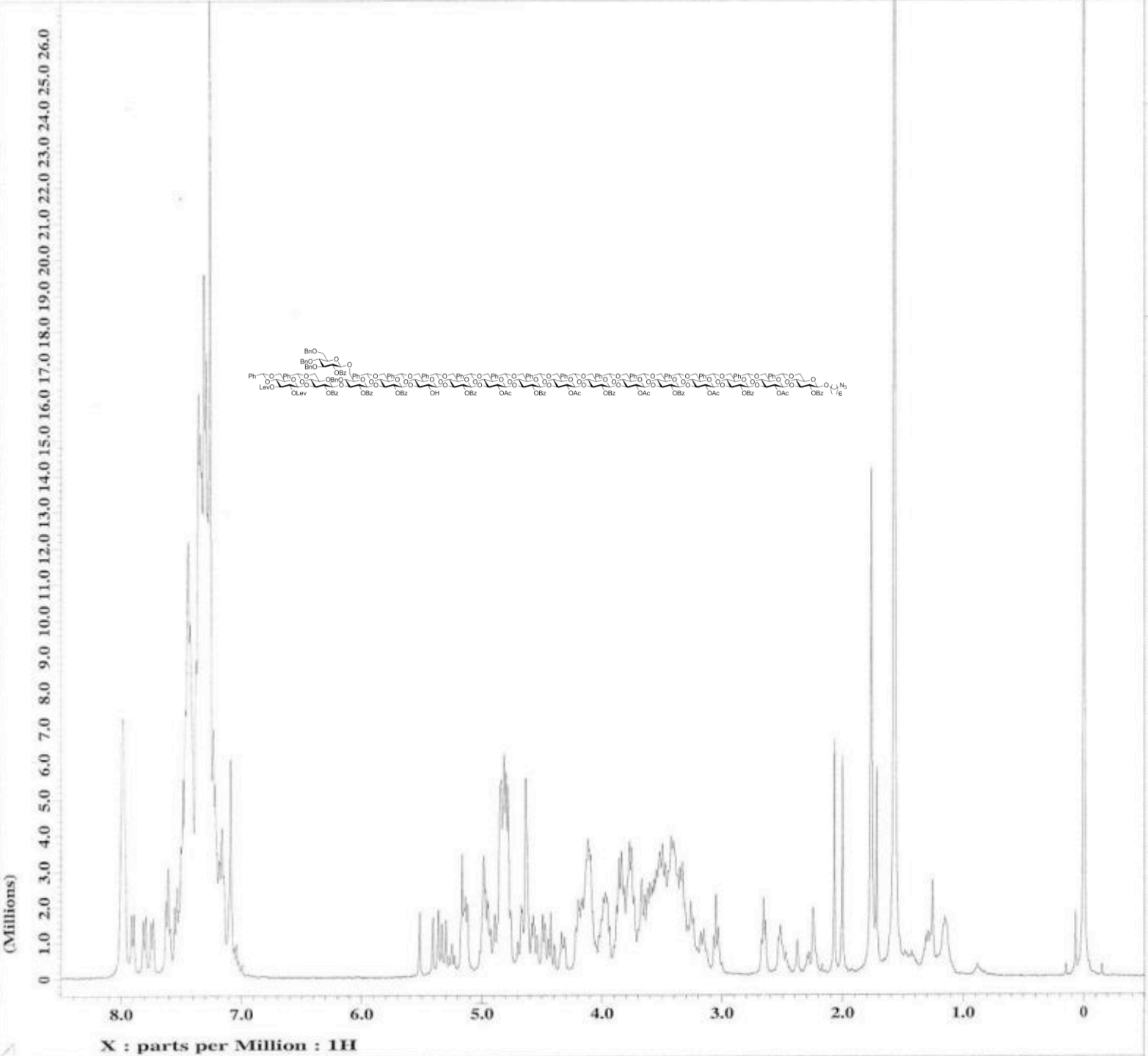
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No534-13N
Author              = JEOL LTD.
Sample ID           = S#781935
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:43:57

Revision Date       = 18-MAR-2010 22:15:35
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:42:08
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:43:55
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:43:56
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 19
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.1[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

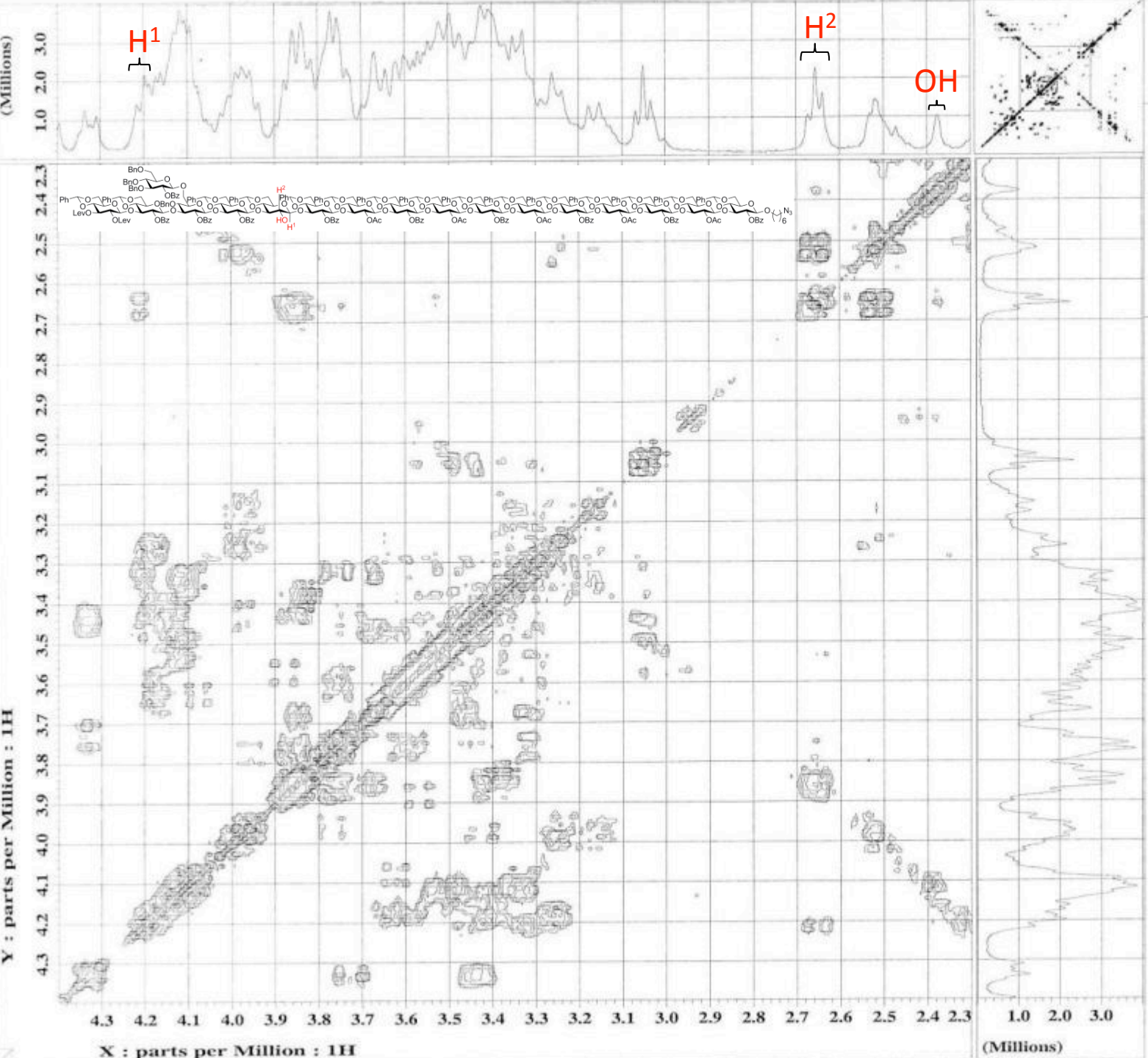
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090805No534_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       =  5-AUG-2009 17:47:41

Revision Date       = 19-MAR-2010 13:34:48
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   =  5-AUG-2009 17:06:50
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  5-AUG-2009 18:24:17
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          =  5-AUG-2009 17:47:40
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 1052
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 28.2[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090701No521.5
Author              = JEOL LTD.
Sample ID           = S#597077
Content             = Single Pulse Experim
Creation Date       =  2-JUL-2009 15:50:54

Revision Date       = 19-MAR-2010 13:40:03
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   =  2-JUL-2009 15:47:28
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  2-JUL-2009 15:50:52
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          =  2-JUL-2009 15:50:54
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 19
Relaxation_delay    = 4[s]
Scans               = 32
Solvent             = CHLOROFORM-D
Spin_get            = 17[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 22.4[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

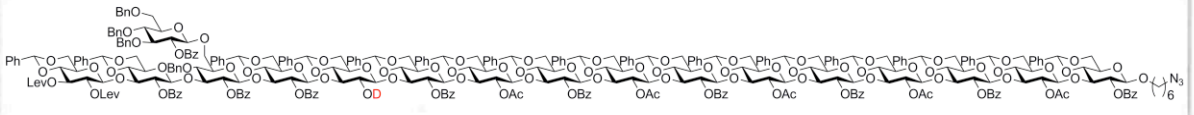


JEOL

```
---- PROCESSING PARAMETERS ----
sinbell_auto
fft : 1 : TRUE
ppm
[transpose]
zerofill : 4
sinbell_auto
fft : 1 : TRUE
ppm
abs
thresh : 1 : 1
symmetrize : Cosy : 24
[transpose]
```

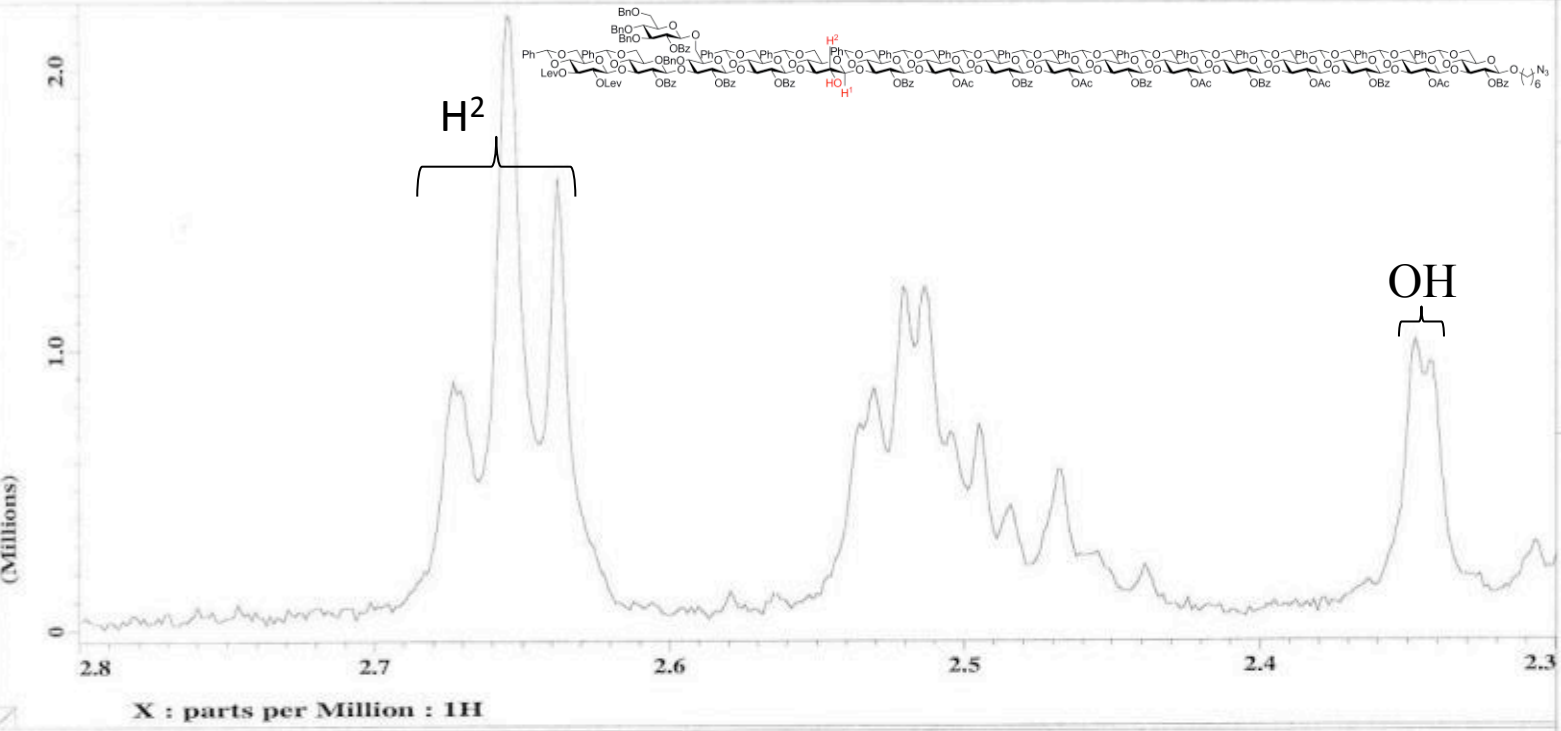
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090701No521_cos
Author              = JEOL LTD.
Sample ID           = S#600673
Content             = gradient absolute va
Creation Date       =  2-JUL-2009 16:15:04

Revision Date       = 19-MAR-2010 13:38:16
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 2D REAL REAL
Dimensions          = X Y
Dim Title           = 1H 1H
Dim Size            = 512, 1024
Dim Units           = [ppm][ppm]
Actual_start_time   =  2-JUL-2009 15:52:13
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  2-JUL-2009 16:15:01
Experiment          = cosy_pfg_m.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 998.20323418[Hz]
Grad_1              = 1[ms]
Grad_1_amp          = 50[%]
Grad_2              = 1[ms]
Grad_2_amp          = 50[%]
Grad_recover        = 1[ms]
Grad_shape          = square
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          =  2-JUL-2009 16:15:03
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 15
Relaxation_delay    = 1[s]
Scans               = 4
Solvent             = CHLOROFORM-D
Spin_get            = 0[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 22.6[dC]
X90                 = 11.8[us]
X_acq_duration      = 0.2564608[s]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 3.25503[ppm]
X_points            = 512
X_prescans          = 4
```

deuteration of the OH group

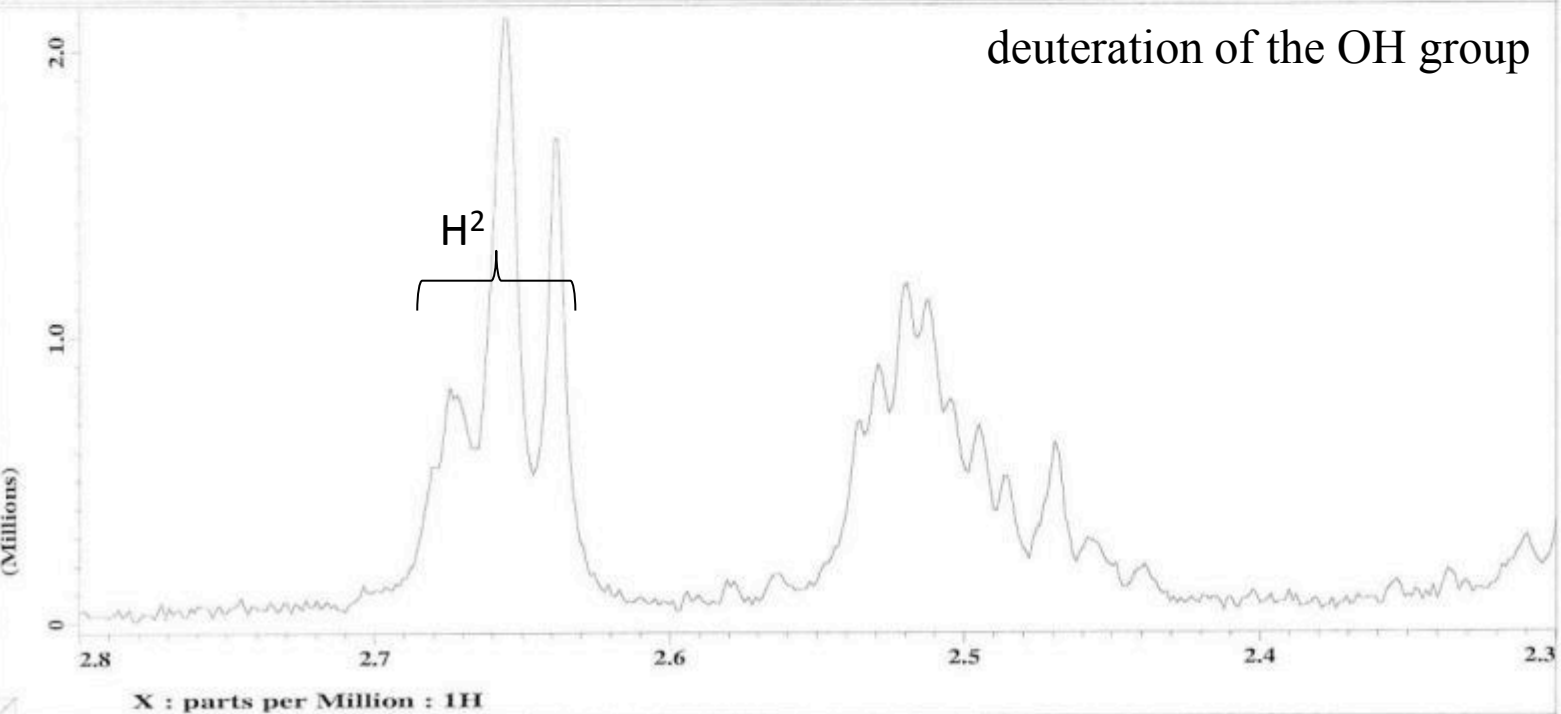



```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No521-17N
Author              = JEOL LTD.
Sample ID           = S#788433
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:54:35

Revision Date       = 18-MAR-2010 22:19:10
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:52:46
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:54:33
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:54:34
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 18
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.3[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```

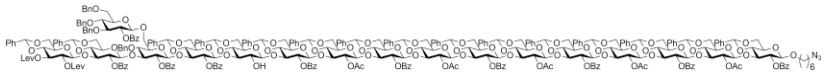


deuteration of the OH group




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 0.2[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

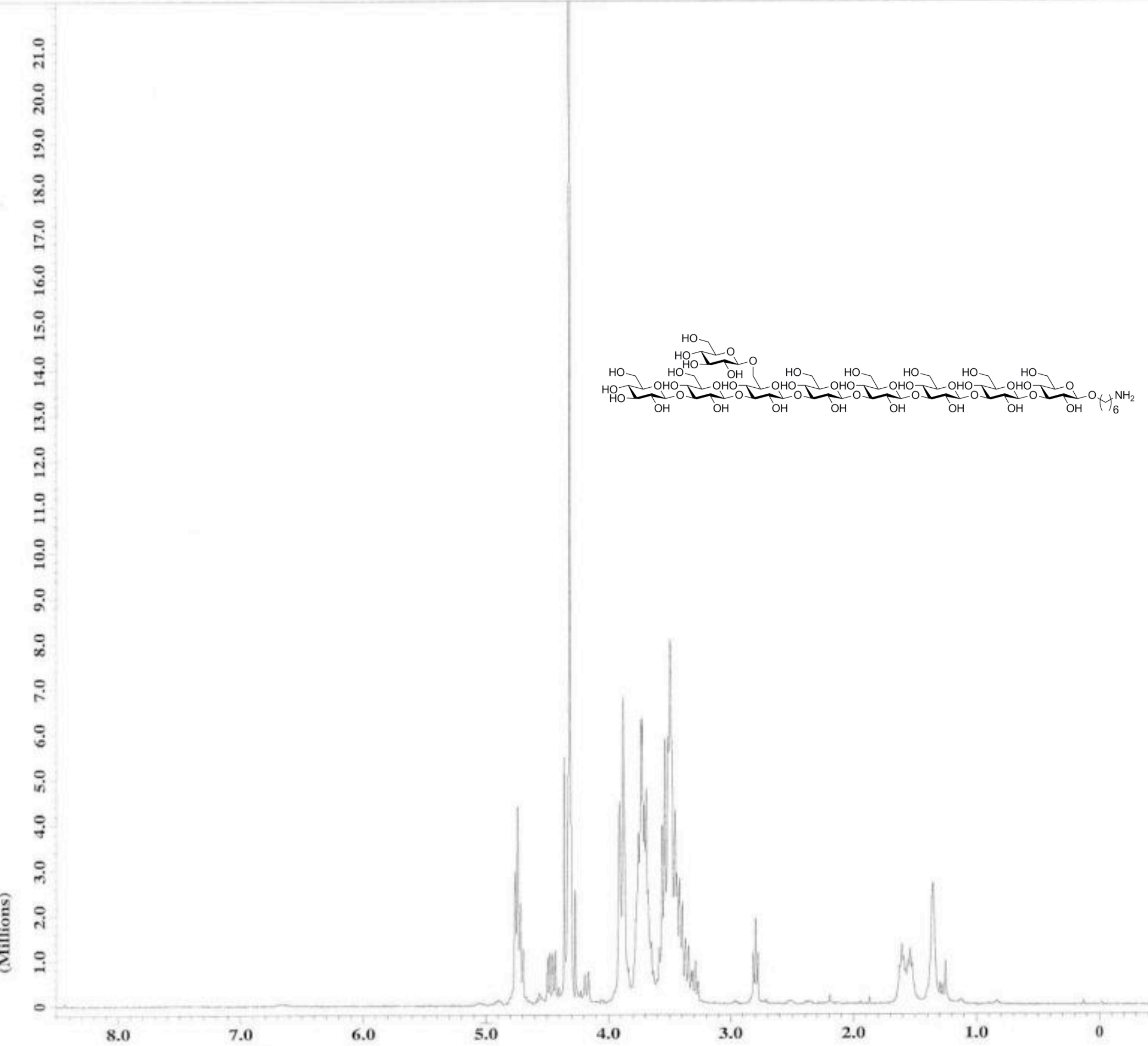
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu100318No521-17N
Author              = JEOL LTD.
Sample ID           = S#788433
Content             = Single Pulse Experim
Creation Date       = 18-MAR-2010 20:54:35

Revision Date       = 18-MAR-2010 22:19:10
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   = 18-MAR-2010 20:52:46
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-MAR-2010 20:54:33
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 40[us]
Iterations          = 0
Local_time          = 18-MAR-2010 20:54:34
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 18
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 24.3[dC]
X90                 = 11[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.5[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090714No521_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 14-JUL-2009 22:54:30

Revision Date       = 19-MAR-2010 13:37:16
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 14-JUL-2009 22:54:30
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 14-JUL-2009 23:23:13
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 14-JUL-2009 22:54:29
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 9265
Solvent             = CHLOROFORM-D
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 27.7[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



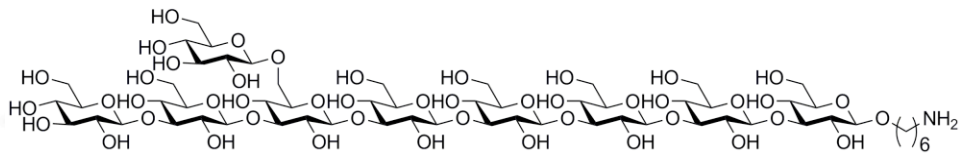
X : parts per Million : 1H

JEOL

---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

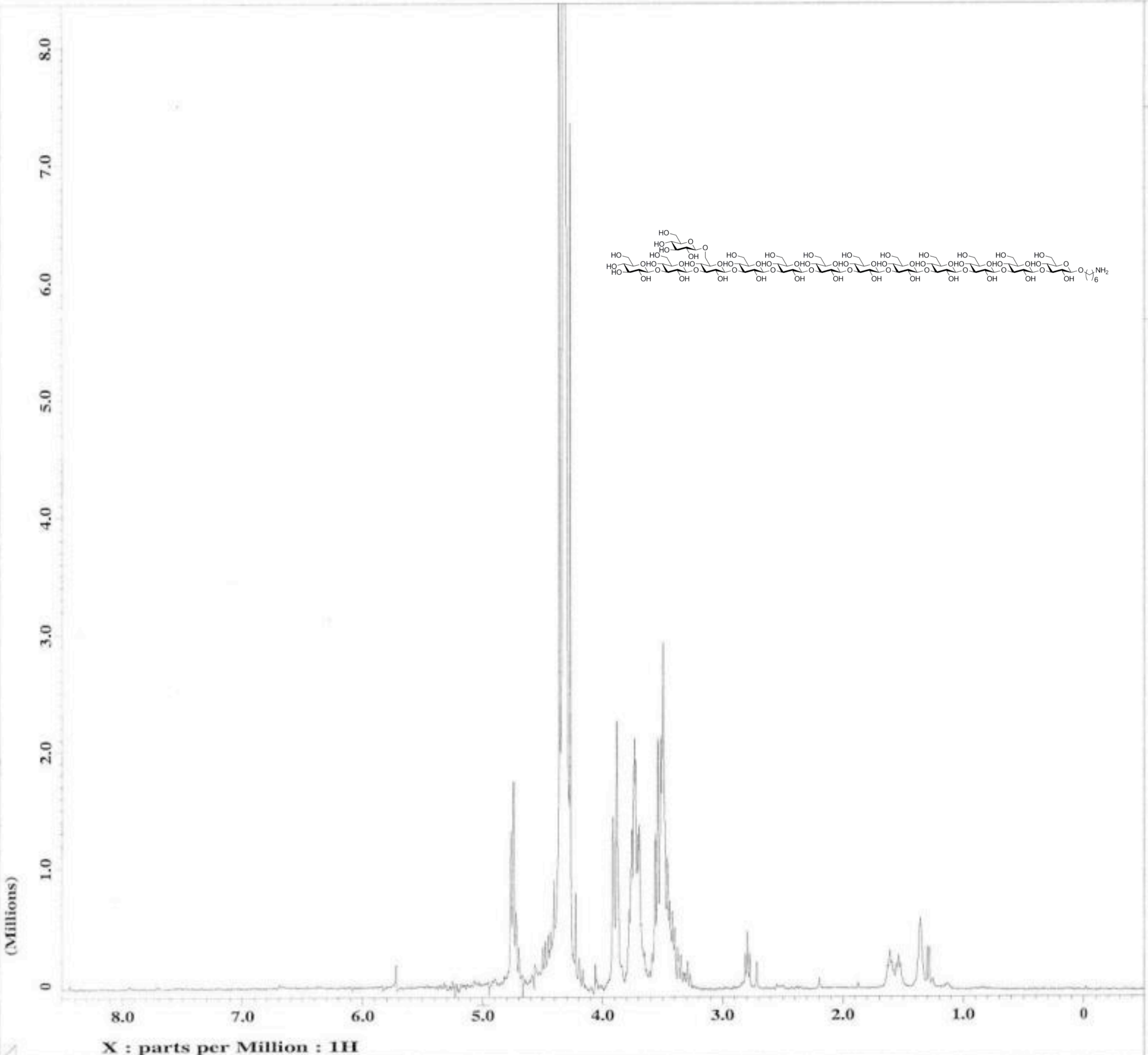
File Name	= tetsu091002No550-70.
Author	= JEOL LTD.
Sample ID	= 70
Content	= Single Pulse Experim
Creation Date	= 2-OCT-2009 15:50:33
Revision Date	= 19-MAR-2010 13:52:35
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 2-OCT-2009 15:48:43
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 2-OCT-2009 15:50:30
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 2-OCT-2009 15:50:32
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 18
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= D2O
Spin_get	= 16[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 70[dC]
X90	= 11.8[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.9[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ



JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Kz] : Both
```

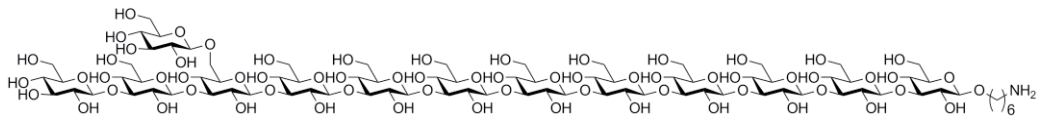
```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091006No550_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       =  7-OCT-2009 08:28:22

Revision Date       = 19-MAR-2010 13:53:10
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   =  6-OCT-2009 22:50:16
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  9-OCT-2009 15:11:41
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          =  7-OCT-2009 08:28:20
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 14982
Solvent             = D2O
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

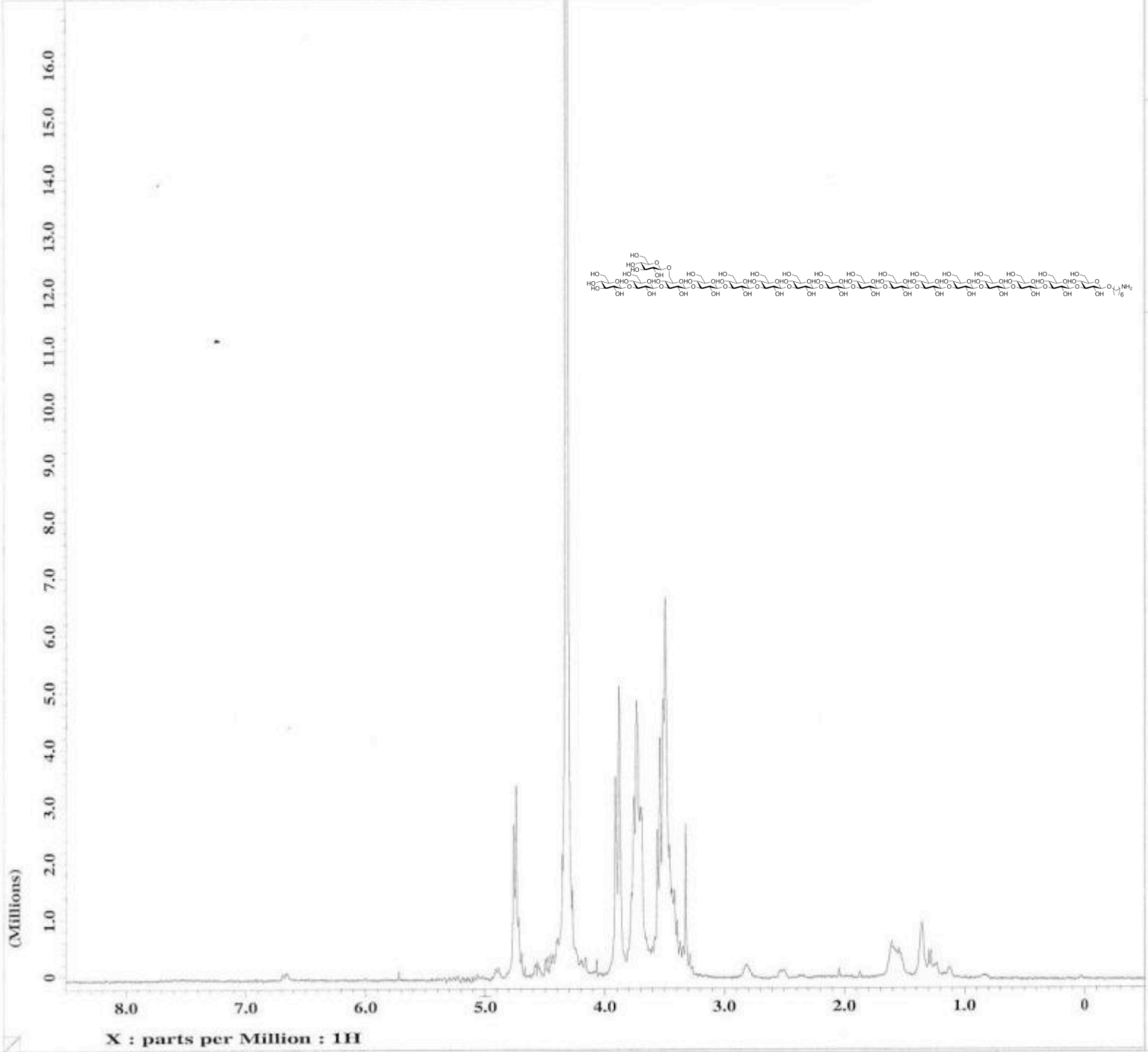
File Name	= tetsu090924No552-13t
Author	= JEOL LTD.
Sample ID	= 70
Content	= Single Pulse Experim
Creation Date	= 24-SEP-2009 17:25:30
Revision Date	= 19-MAR-2010 14:03:26
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 1H
Dim Size	= 16384
Dim Units	= [ppm]
Actual_start_time	= 24-SEP-2009 17:23:41
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 24-SEP-2009 17:25:28
Experiment	= single_pulse.exp
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 3.95882819[kHz]
Irr_code	= 146
Irr_noise	= WALTZ
Irr_pwidth	= 40[us]
Iterations	= 0
Local_time	= 24-SEP-2009 17:25:29
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 17
Relaxation_delay	= 4[s]
Scans	= 16
Solvent	= D2O
Spin_get	= 17[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 70[dC]
X90	= 11.8[us]
X_acq_duration	= 2.0692992[s]
X_angle	= 45[deg]
X_domain	= 1H
X_freq	= 395.88252601[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_pulse	= 5.9[us]
X_resolution	= 0.48325539[Hz]
X_sweep	= 7.91765637[kHz]
Tri90	= 10[us]
Tri_noise	= WALTZ



JEOL

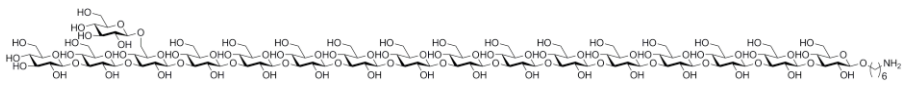
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091125No552_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 26-NOV-2009 08:35:05

Revision Date       = 19-MAR-2010 13:58:10
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 25-NOV-2009 23:05:40
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 28-NOV-2009 15:27:05
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 26-NOV-2009 08:35:05
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 14757
Solvent             = D2O
Spin_get            = 16[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu090709No522_70.
Author              = JEOL LTD.
Sample ID           = 70
Content             = Single Pulse Experim
Creation Date       =  9-JUL-2009 13:49:53

Revision Date       = 19-MAR-2010 14:05:40
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   =  9-JUL-2009 13:48:03
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  9-JUL-2009 13:49:50
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 1[us]
Iterations          = 0
Local_time          =  9-JUL-2009 13:49:51
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 21
Relaxation_delay    = 4[s]
Scans               = 16
Solvent             = D2O
Spin_get            = 15[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 70[dC]
X90                 = 11.8[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 5.9[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



(Billions)

1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

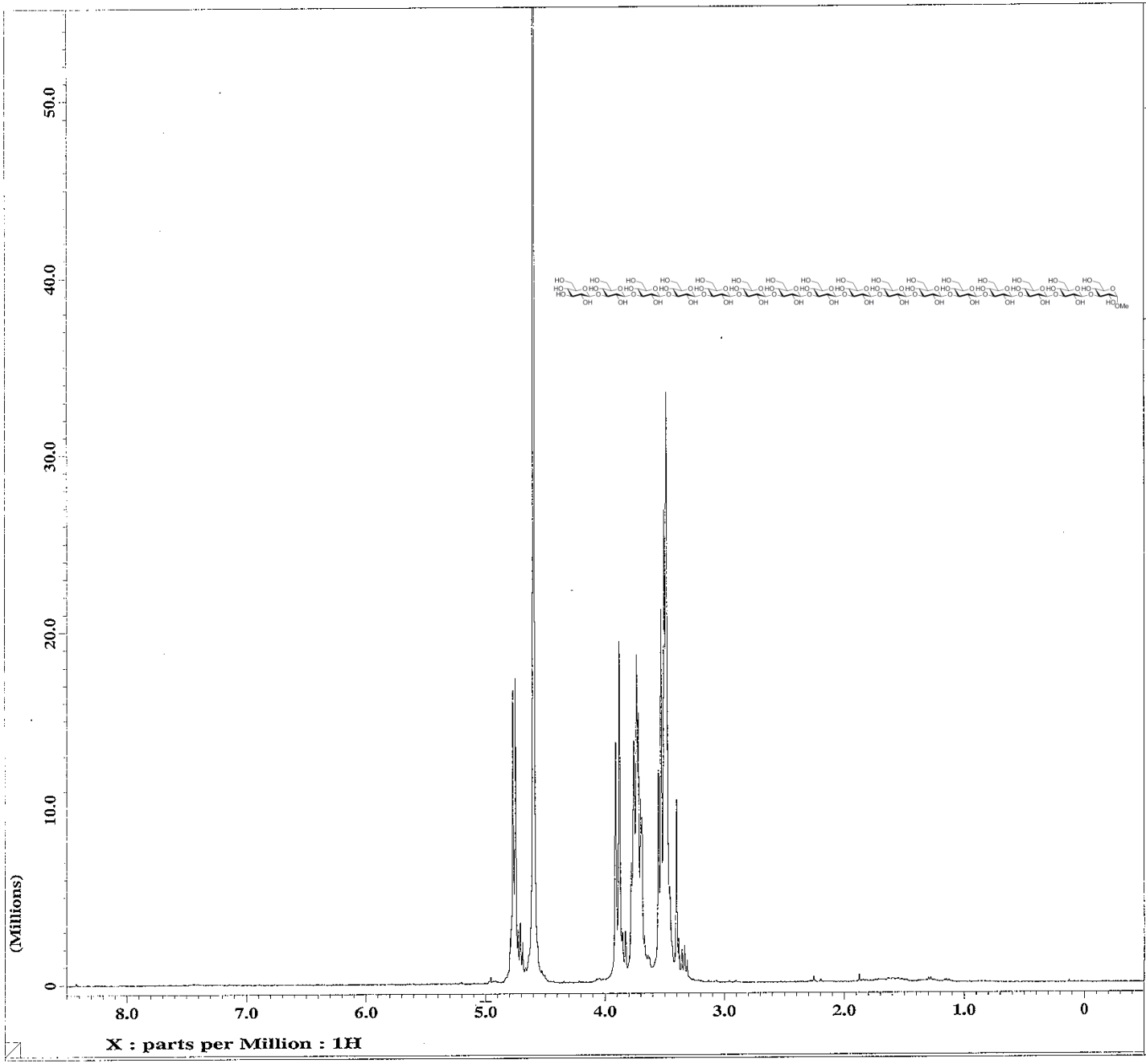
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0

X : parts per Million : 13C

JEOL

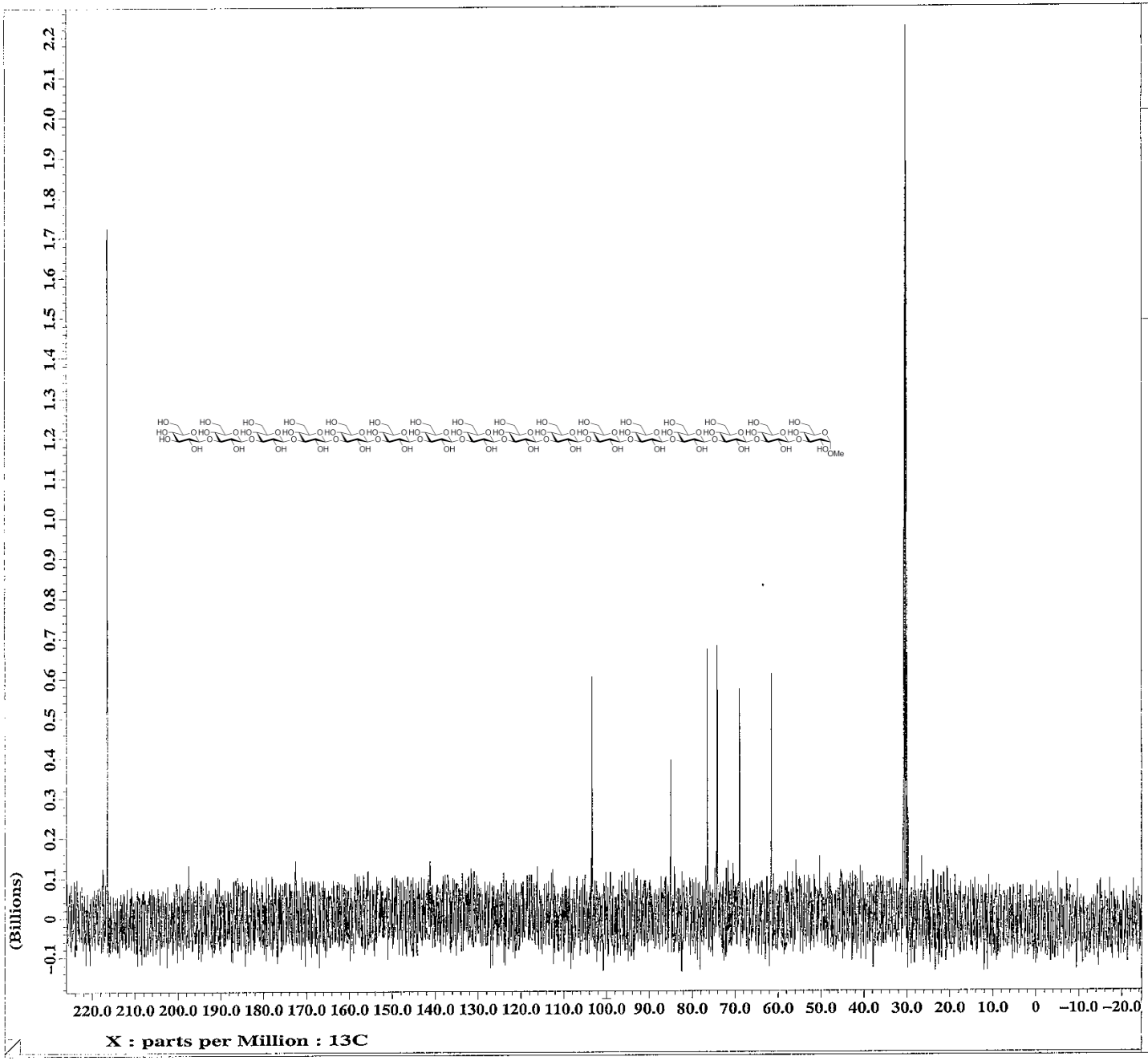
```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu091215No522_13c
Author              = JEOL LTD.
Sample ID           = 13C
Content             = Single Pulse with Br
Creation Date       = 16-DEC-2009 08:17:22

Revision Date       = 19-MAR-2010 14:06:11
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Actual_start_time   = 16-DEC-2009 01:41:50
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            = 18-DEC-2009 18:03:15
Experiment          = single_pulse_dec
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 12.46882793[kHz]
Irr_code            = 146
Irr_domain          = 1H
Irr_freq            = 395.88252601[MHz]
Irr_noise           = WALTZ
Irr_offset          = 5[ppm]
Irr_pwidth          = 40[us]
Iterations          = 1
Local_time          = 16-DEC-2009 08:17:21
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 30
Relaxation_delay    = 1[s]
Scans               = 10248
Solvent             = D2O
Spin_get            = 14[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 30.1[dC]
X90                 = 10[us]
X_acq_duration      = 1.3139968[s]
X_angle             = 30[deg]
X_domain            = 13C
X_freq              = 99.54473003[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_pulse             = 3.33333333[us]
X_resolution        = 0.76103686[Hz]
```




```
---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both
```

```
---- ACQUISITION PARAMETERS ----
File Name           = tetsu080604No245_40.
Author              = JEOL LTD.
Sample ID           = S#604230
Content             = Single Pulse Experim
Creation Date       =  4-JUN-2008 16:13:08

Revision Date       = 22-JUL-2010 14:40:10
Spec Site           = ECP400SL

Spec Type           = DELTA_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Actual_start_time   =  4-JUN-2008 16:09:42
Delay_of_start      = 1[s]
Digital_filter      = FALSE
End_time            =  4-JUN-2008 16:13:06
Experiment          = single_pulse.exp
Field_strength      = 9.2981736[T]
Filter_mode         = BUTTERWORTH
Filter_width        = 3.95882819[kHz]
Irr_code            = 146
Irr_noise           = WALTZ
Irr_pwidth          = 50[us]
Iterations          = 0
Local_time          =  4-JUN-2008 16:13:07
Obs_noise           = WAUGH
Obs_pwidth          = 1[us]
Probe_id            = 2692
Recvr_gain          = 21
Relaxation_delay    = 4[s]
Scans               = 32
Solvent             = D2O
Spin_get            = 14[Hz]
Spin_lock_90        = 1[us]
Spin_lock_attn      = 29[dB]
Temp_get            = 40[dC]
X90                 = 12.4[us]
X_acq_duration      = 2.0692992[s]
X_angle             = 45[deg]
X_domain            = 1H
X_freq              = 395.88252601[MHz]
X_offset            = 5[ppm]
X_points            = 16384
X_prescans          = 1
X_pulse             = 6.2[us]
X_resolution        = 0.48325539[Hz]
X_sweep             = 7.91765637[kHz]
Tri90               = 10[us]
Tri_noise           = WALTZ
```



---- PROCESSING PARAMETERS ----
dc_balance
sexp : 1[Hz]
fft : 1 : TRUE
machinephase
dc_correct
ppm
peak_pick : 0[Hz] : 50[Hz] : Both

---- ACQUISITION PARAMETERS ----

File Name	= tetsu080609No245_13c
Author	= JEOL LTD.
Sample ID	= 13C
Content	= Single Pulse with Br
Creation Date	= 10-JUN-2008 08:52:47
Revision Date	= 22-JUL-2010 14:43:47
Spec Site	= ECP400SL
Spec Type	= DELTA_NMR
Data Format	= 1D COMPLEX
Dimensions	= X
Dim Title	= 13C
Dim Size	= 32768
Dim Units	= [ppm]
Actual_start_time	= 9-JUN-2008 21:55:29
Delay_of_start	= 1[s]
Digital_filter	= FALSE
End_time	= 12-JUN-2008 14:16:54
Experiment	= single_pulse_dec
Field_strength	= 9.2981736[T]
Filter_mode	= BUTTERWORTH
Filter_width	= 12.46882793[kHz]
Irr_code	= 146
Irr_domain	= 1H
Irr_freq	= 395.88252601[MHz]
Irr_noise	= WALTZ
Irr_offset	= 5[ppm]
Irr_pwidth	= 50[us]
Iterations	= 1
Local_time	= 10-JUN-2008 08:52:45
Obs_noise	= WAUGH
Obs_pwidth	= 1[us]
Probe_id	= 2692
Recvr_gain	= 30
Relaxation_delay	= 1[s]
Scans	= 17035
Solvent	= D2O
Spin_get	= 15[Hz]
Spin_lock_90	= 1[us]
Spin_lock_attn	= 29[dB]
Temp_get	= 26.8[dC]
X90	= 11.75[us]
X_acq_duration	= 1.3139968[s]
X_angle	= 30[deg]
X_domain	= 13C
X_freq	= 99.54473003[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 4
X_pulse	= 3.91666667[us]
X_resolution	= 0.76103686[Hz]

References

Review

- Adachi, Y. *Trends Glycosci. Glycotechnol.* **2007**, *19*, 195-207.

Soluble dectin-1

- Tada R, Adachi Y, Ishibashi K, Tsubaki K, Ohno N. *J. Agric. Food Chem*. **2008**, 56, 1442-1450.

dectin-1 b-glucan binding ability.

- Adachi, Y., Ishii, T., Ikeda, Y., Hoshino, A., Tamura, H., Aketagawa, J., Tanaka,S., Ohno, N. *Infect. Immun.* **2004**,*72*, 4159-4171.

Preparation of soluble dectin-1 molecule.

Mouse cDNA of dectin-1 was isolated from RAW264 macrophage cell line by reverse transcriptase-assisted polymerase chain reaction. The carbohydrate recognition domain (CRD) was linked with human IgG1 heavy chain constant region including hinge, CH2, and CH3 domain. The cDNA construct was inserted in multiple cloning site of pDisplay vector which has signal sequence of immunoglobulin kappa chain followed by hemaggulutinin A (HA) epitope gene. The nucleotide sequence of the cDNA constructs was confirmed by BigDye terminator Sequencing Kit (Applied Biosystems) and ABI PRISM 3730 Genetic Analyzer (Applied Biosystems).

Recombinant dectin-1 molecule was prepared as Fc fusion proteins conjugated with C-type lectin carbohydrate recognition domain of mouse dectin-1. The chimeric proteins of dectin-1 CRD and Fc portion of human IgG1 were expressed by 293T cells which were transfected with pDisplay-based expression vectors. The recombinant Fc molecules produced in the culture supernatant was isolated with Hi-trap Protein A column (GE Healthcare and Biotechnology).

Binding assay to soluble dectin-1

Binding ability of various oligosaccharides to dectin-1 was assessed by competitive enzyme linked immunosorbent assay (ELISA). Briefly, (1, 6)-monoglucosyl branched (1, 3)-β-D-glucan from *Schizophyllum commune*, SPG (1 μg/ml), dissolved in phosphate buffer pH 6.9, was coated on ELISA plate (NUNC) by overnight incubation at 4 °C. The unbound SPG was washed with phosphate-buffered saline (PBS) containing 0.05% Tween20 (PBST), and the plate was blocked with PBS containing 0.5% BSA (BPBS) by 2 h incubation at room temperature. Various oligosaccharides or SPG samples were diluted with BPBS to prepare 0 to 500 μg/ml and mixed with soluble dectin-1-Fc (1 μg/ml) for 30 min before adding to the SPG-coated ELISA plate. The plate containing soluble dectin-1-Fc (sDectin-1) was incubated for 1 h at room temperature, washed with PBST, and further incubated with 2000-fold diluted peroxidase-conjugated anti-HA IgG (SantaCruz). The binding of sDectin-1 to solid-phase SPG was monitored by reaction of peroxidase substrate TMB (KPL Inc., MD) and color development was stopped with 1M phosphoric acid. The absorbance at 450 nm was measured by microplate reader, MTP450 (Corona electric, Japan) The data are presented as means for duplicate samples.

	ug/ml	0.016	0.08	0.4	2	10	50
SPG	mean(OD450)	0.85	0.6	0.26	0.05	0.03	0.01
	SD	0.02	0.01	0.01	0.03	0	0
2	mean	0.93	0.87	0.62	0.32	0.24	0.17
	SD	0.07	0	0.02	0	0	0.01
1	mean	0.97	0.89	0.71	0.4	0.26	0.2
	SD	0.04	0.01	0.01	0.01	0.01	0

	ug/ml	0.16	0.8	4	20	100	500
vehicle	mean	0.88	0.91	0.93	0.95	0.94	0.94
	SD	0.01	0.02	0	0.02	0.01	0.01
23	mean	0.98	0.94	0.92	0.9	0.89	0.89
	SD	0.021	0.019	0.001	0.007	0.007	0.015
22	mean	0.95	0.94	0.93	0.9	0.9	0.77
	SD	0.02	0.01	0.01	0.04	0.01	0.02
21	mean	0.93	0.92	0.91	0.89	0.88	0.65
	SD	0	0.01	0	0.04	0.01	0.02
20	mean	0.91	0.9	0.88	0.85	0.83	0.62
	SD	0.03	0.02	0.04	0.02	0.02	0.01
19	mean	0.94	0.87	0.88	0.79	0.73	0.4
	SD	0.03	0.01	0.01	0.06	0.05	0.03

Luciferase-assisted NF-κB assay

On the day prior to transfection, 293T cells were plated (1×10^4 cells/well) in 96-well plates cultured in DMEM containing 10% FBS. The cells incubated for 20 hr at 37 °C under 5% CO_2 atmospheres. Then, transfection was performed in the 96-well plates using Lipofectamine LTX (Invitrogen) and PLUS Reagent (Invitrogen) with 95 ng of Plasmid DNA mixture (p3x-FLAG-CMV 14/dectin-1A, p3x-FLAG-CMV 14/CARD9, pBud-CE.1/Bcl10, pGL4.32[luc2P/NF-κB-RE/Hygro] Vector, and pGL4.74[hRluc/TK]). The transfection mixture was added dropwise to the cells and incubated for 18 hr in DMEM containing 10% FBS. At 18 hr after transfection, the cells were stimulated with the oligosaccharides or SPG for 6 hr. The cells were then lysed with Passive Lysis Buffer (Promega). Luciferase activity was measured using the Dual-Luciferase Reporter Assay System (Promega). The luciferase assay reagents were added to 20 μL of the lysate with an infector, and the results were read immediately with Microplate Luminometer (Berthold Technologies GmbH, KG, Bad Wildbad, Germany). Luciferase activity was expressed as the ratio of the NF-κB luciferase (firefly) activity to the RL-TK (renilla) activity. The data are presented as means ± standard deviation for triplicate samples.

	ug/ml	0	0.005	0.05	0.5	5
SPG	mean (relative activity)		1.47	3	5.04	4.94
	Standard Deviation		0.3	0.1	0.2	0.37

		1.5	6	25	100
22	mean	1.08	0.82	0.87	0.81
	SD	0.23	0.09	0.1	0.08
21		0.96	1.12	0.88	1.33
		0.14	0.74	0.16	0.15
20		1.09	0.89	1.01	1.09
		0.15	0.24	0.16	0.36
19		1.21	0.95	1.05	1.23
		0.24	0.12	0.16	0.26
2		1.25	1.58	2.3	2.57
		0.13	0.29	0.48	0.58
1		0.85	1.19	1.78	2.12
		0.14	0.13	0.11	0.29