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Supporting Information

Microwave-assisted Simultaneous *O*,*N*-Sulfonation for the Synthesis of Heparin-like Oligosaccharides

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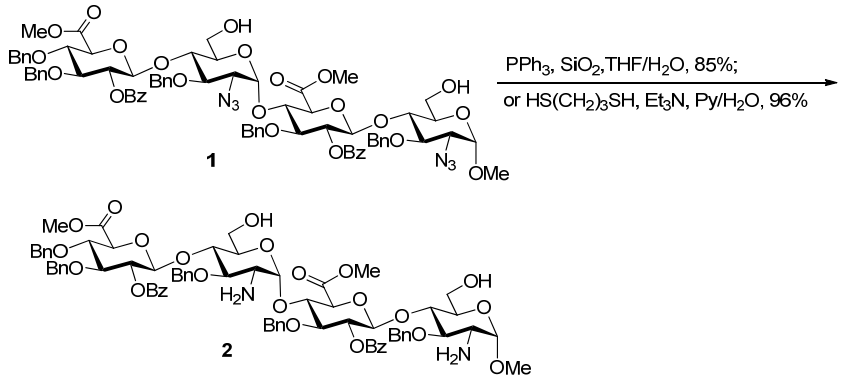
General experimental procedures. All reactions were carried out under nitrogen or argon with anhydrous solvents in flame-dried glassware, unless otherwise noted. All glycosylation reactions were performed in the presence of 4Å or 5Å molecular sieves, which were flame-dried immediately before use in the reaction under high vacuum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. The chemicals used were reagent grade as supplied, except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) or by heating with a solution with 10% H_2SO_4 in ethanol. Flash column chromatography was performed on silica gel H. NMR spectra were referenced using Me_4Si (0 ppm), residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.16 ppm), CD_3OD (^{1}H NMR δ = 3.31 ppm, ^{13}C NMR δ = 49.00 ppm), D_2O (^{1}H NMR δ = 4.79 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C HMQC experiments. All optical rotations were measured at room temperature using the sodium D line. Splitting patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), and brs (broad singlet) for ^{1}H NMR data. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument using HP5989A or VG Quattro MS. Optical rotations were measured using a Perkin-Elmer 241 polarimeter. Microwave-based sulfonation reactions were performed using a CEM Initiator synthesizer in sealed reaction vessels.

Methyl (methyl 3,4-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-amino-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-amino-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (2)

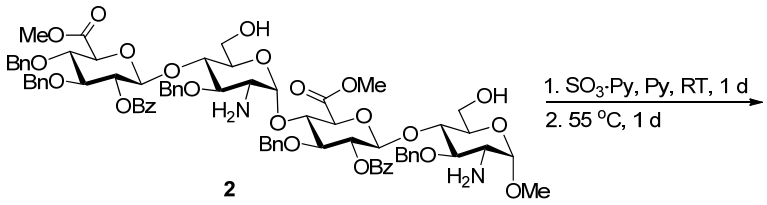


Tetrasaccharide **1** (44 mg, 0.030 mmol) was dissolved in THF (1 mL) containing H_2O (0.1 mL). Silica gel (88 mg) and PPh_3 (40 mg, 0.15 mmol) were added at room temperature. Stirring was continued until TLC indicated disappearance of the raw material (~ 1 d). The mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by Sephadex LH-20 chromatography column (CH_2Cl_2/MeOH, 1/1) to give **2** (36 mg, 85%) as a white solid.

An alternative method. Tetrasaccharide **1** (125 mg, 0.085 mmol) was dissolved in pyridine (3 mL) and H_2O (0.75 mL), protected from light and stirred with propane-1,3-dithiol (0.68 mL) and trimethylamine (0.34 mL) overnight. The mixture was concentrated in vacuum, and then co-evaporated with toluene and ethanol (4 mL, 5/1 v/v) for three times. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1 + 1% Et_3N) to give **2** (114 mg, 96%) as a white solid: $[\alpha]_D^{25} = 67.4$ (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.4 Hz, 2H), 8.01 (d, J = 7.4 Hz, 2H), 7.62–7.00 (m, 31H), 5.38–5.28 (m, 3H), 5.20 (d, J = 11.2 Hz, 1H), 5.08 (d, J = 11.4 Hz, 1H), 4.94–4.69 (m, 4H), 4.62 (dd, J = 11.0, 8.5 Hz, 2H), 4.53 (t, J = 10.6 Hz, 2H), 4.46 (d, J = 11.4 Hz, 1H), 4.14 (t, J = 8.6 Hz, 1H), 4.01 (d, J = 6.1 Hz, 2H), 3.90 (d, J = 8.9 Hz, 1H), 3.88–3.74 (m, 3H), 3.74–3.50 (m, 6H), 3.33 (ddd, J = 18.9, 16.0, 9.5 Hz, 3H), 3.17 (s, 2H), 3.13 (d, J = 10.0 Hz, 1H), 3.00 (s, 3H), 2.66–2.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.77, 168.26,

166.01, 165.57, 164.87, 138.22, 138.09, 137.83, 137.75, 137.35, 133.44, 133.31, 132.91, 130.15, 129.98, 129.90, 129.85, 129.68, 129.33, 129.27, 128.64, 128.57, 128.52, 128.45, 128.42, 128.31, 128.30, 128.23, 128.11, 128.02, 127.98, 127.79, 127.71, 127.68, 127.34, 102.06, 101.46, 98.56, 98.06, 81.10, 79.49, 79.45, 78.26, 78.17, 77.41, 77.16, 76.91, 75.73, 75.54, 75.39, 75.27, 74.70, 74.61, 74.57, 73.52, 73.21, 73.15, 72.89, 70.86, 70.66, 68.89, 66.72, 63.17, 62.64, 62.50, 55.53, 52.88, 51.77; ESI-MS *m/z* calcd for $C_{76}H_{84}N_2O_{23}Na$ $[M+Na]^+$ 1415.5357, found 1415.5371.

Methyl (methyl 3,4-di-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (4)



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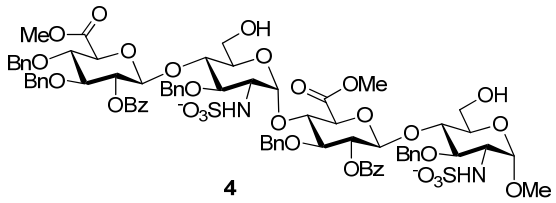
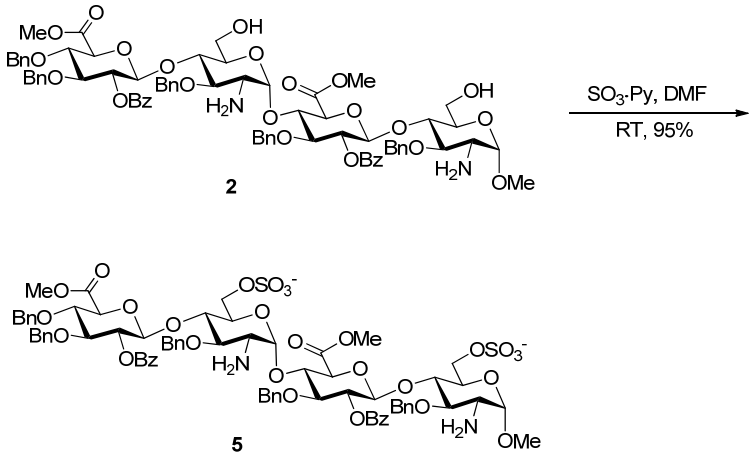


4

SO_3·Py (23 mg, 0.145 mmol) was added to a solution of tetrasaccharide **2** (10 mg, 0.0073 mmol) in pyridine (1.0 mL). The mixture was protected from light, stirred for 24 h at room temperature and then heated for 24 h at 55 °C. MeOH (0.4 mL) was added to quench the reaction. The mixture was concentrated in vacuum, and successively purified by a small RP-18 silica gel column (H_2O/CH_3OH, 1/0 to 1/3). The fractions containing product were concentrated in vacuum, and the residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using CH_3OH as eluent. The fractions containing product were concentrated in vacuum to provide **4** (7.4 mg, 66%) as a white solid: $[\alpha]_D^{28}$ = 16.1 (*c* 0.3, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 8.24 (d, *J* = 7.4 Hz, 2H), 8.15 (d, *J* = 7.5 Hz, 2H), 7.72–7.01 (m, 31H), 5.37 (d, *J* = 3.4 Hz, 1H), 5.32–5.18 (m, 6H), 4.83–4.69 (m, 4H), 4.69–4.54 (m, 4H),

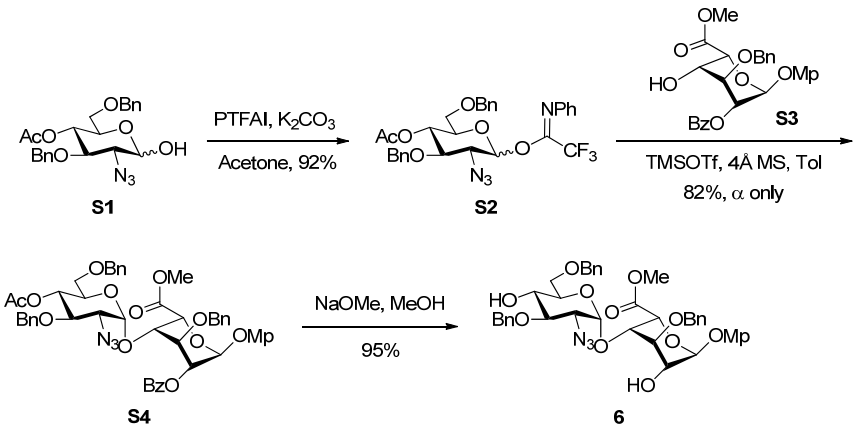
4.53–4.37 (m, 3H), 4.32–3.84 (m, 10H), 3.81–3.63 (m, 2H), 3.60 (s, 3H), 3.51–3.40 (m, 2H), 3.27 (s, 3H), 3.21 (s, 3H), 3.17 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.03 (d, *J* = 10.2 Hz, 1H); ESI-MS *m/z* calcd for $C_{76}H_{82}N_2O_{29}S_2$ $[M\text{-}2H]^{2-}$ 775.2, found 775.1.

Methyl (methyl 3,4-di-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-amino-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-amino-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (5)



SO_3·Py (10.0 mg, 0.063 mmol) was added to a solution of tetrasaccharide **2** (4.4 mg, 0.00316 mmol) in DMF (0.8 mL). The mixture was stirred for 24 h at room temperature. MeOH (0.4 mL) was added to quench the reaction. The mixture was concentrated in vacuum, and successively purified by a small RP-18 silica gel column (H_2O/CH_3OH, 1/0 to 1/4). The fractions containing product were concentrated in vacuum, and the residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using CH_3OH as eluent. The fractions containing product were concentrated in vacuum to provide tetrasaccharide **5** (4.7 mg, 95%): $[\alpha]_D^{26}$ = 28.4 (*c* 0.4, MeOH); ^{1}H NMR (400 MHz, CD_3OD) *δ* 8.26 (d, *J* = 7.5 Hz, 2H), 8.17 (d, *J* = 7.5 Hz, 2H), 7.80–6.95 (m, 31H), 5.33–5.09 (m, 7H), 4.76 (dd, *J* = 14.5, 6.6 Hz, 3H), 4.68 (d, *J* = 3.4 Hz, 1H), 4.65–4.52 (m, 4H), 4.51–4.34 (m, 3H), 4.24 (d, *J* = 9.7 Hz, 1H), 4.21–3.98 (m, 5H), 3.97–3.84 (m, 4H), 3.67–3.53 (m, 4H), 3.52–3.37 (m, 4H), 3.25 (s, 3H), 3.23 (s, 3H), 2.91 (dd, 1H), 2.71 (d, *J* = 10.2 Hz, 1H); ESI-MS *m/z* calcd for $C_{76}H_{82}N_2O_{29}S_2$ $[M\text{-}2H]^{2-}$ 775.2, found 775.5.

4-Methoxyphenyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 2-*O*-benzoyl-*α*-L-iduropyranosiduronate) (6)



To hemiacetal **S1** (1.10 g, 2.09 mmol) in acetone (10 mL), *N*-phenyl-trifluoroacetimidoyl chloride (350 μL, 3.13 mmol) and K_2CO_3 (720 mg, 5.23 mmol) were added. Stirring was continued until TLC indicated disappearance of the starting material (~ 2 h). The mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1, containing 1% Et_3N) to give **S2** (1.25 g, 99%) as a white solid.

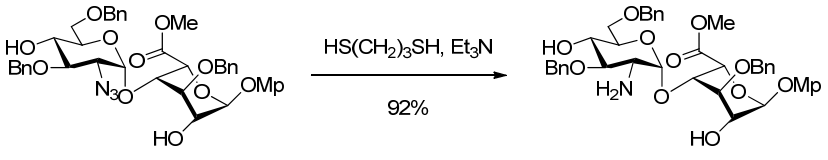
Compound **S2** (778 mg, 1.3 mmol) and monosaccharide **S3** (507 mg, 1.0 mmol) were combined in a flask and co-evaporated with toluene (3 × 3 mL), and were then dissolved in toluene (20 mL). Powdered freshly activated 5Å molecular sieves (1.3 g) were added, and the mixture was stirred for 1 hour at ambient temperature and then cooled to -30 ^{o}C. TMSOTf (20 μL, 0.1 mmol) was added, and stirring was continued until TLC indicated the disappearance of the donor (2 hour). The reaction was quenched by the addition of Et_3N (0.5 mL). The mixture was filtered, and the filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to give **S4** (851 mg, 93%) as a white solid: $[\alpha]_D^{28}$ = -20.9 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.4 Hz, 2H), 7.56–7.20 (m, 16H), 7.13–7.05 (m, 4H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.81 (s, 1H), 5.35 (s, 1H), 5.12 (t, *J* = 9.8 Hz, 1H), 5.00 (d, *J* = 12.1 Hz, 2H), 4.87–4.76 (m, 2H), 4.47 (dd, *J* = 24.6, 11.8 Hz, 2H), 4.27 (s, 1H), 4.08 (dd, *J* = 23.2, 14.5 Hz, 3H), 3.88 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.64–3.49 (m, 2H), 3.41 (dd, *J* = 11.1, 3.7 Hz, 1H), 3.33 (dd, *J* = 10.0, 3.1 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.43,

169.33, 165.70, 155.41, 150.67, 137.84, 137.66, 137.60, 133.51, 130.15, 129.82, 128.70, 128.56, 128.47, 128.43, 128.12, 127.88, 127.80, 118.10, 114.80, 99.03, 98.36, 78.33, 75.32, 74.57, 73.78, 72.94, 72.72, 70.78, 70.00, 68.49, 63.37, 55.79, 52.39, 20.91; ESI-MS *m/z* calcd for $C_{50}H_{51}N_3O_{14}Na$ $[M+Na]^+$ 940.3263, found 940.3264.

General Procedure for the Deprotection of the Esters. The starting material was stirred with MeONa (1.0 equiv) in MeOH (0.2 M) until TLC indicated disappearance of the material (~ 1 h). The mixture was then neutralized with acidic resin, filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 4:1) to give the product.

Compound **6** (500 mg, 95%) was thus obtained as a white solid: $[\alpha]_D^{28}$ = -23.4 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.27 (m, 15H), 7.13–7.02 (m, 2H), 6.91–6.79 (m, 2H), 5.69 (s, 1H), 5.05 (dd, *J* = 5.7, 2.5 Hz, 2H), 4.93–4.79 (m, 3H), 4.71–4.58 (m, 2H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.27 (s, 1H), 4.12–3.96 (m, 2H), 3.83–3.69 (m, 9H), 3.67–3.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.77, 155.11, 150.71, 138.04, 137.64, 137.58, 128.70, 128.63, 128.28, 128.15, 128.10, 128.04, 127.85, 127.77, 117.70, 114.78, 100.14, 94.99, 80.87, 75.67, 73.88, 72.12, 72.03, 71.59, 70.88, 69.47, 67.66, 66.06, 63.26, 55.77, 52.52; ESI-MS *m/z* calcd for $C_{41}H_{45}N_3O_{12}Na$ $[M+Na]^+$ 794.2896, found 794.2920.

4-Methoxyphenyl 2-amino-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-α-L-iduropyranosiduronate) (7)

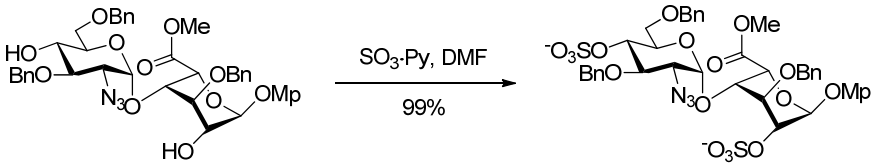


6 **7**

General Procedure for the Reduction of the Azide group. A portion of the starting material was dissolved in pyridine and H_2O (0.1 M, 4/1), protected from light and stirred with propane-1,3-dithiol (10 equiv) and trimethylamine (20 equiv) for overnight. The mixture was concentrated in vacuum, and then concentrated with toluene and ethanol (4 mL, 5/1) for three times. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1 + 1% Et_3N) to give the product.

Compound **7** (130 mg, 92%) was thus prepared as a light yellow solid: $[\alpha]_D^{25}$ = -3.0 (*c* 0.8, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.27 (m, 15H), 7.06 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 5.64 (s, 1H), 5.07–4.89 (m, 3H), 4.83 (d, *J* = 11.5 Hz, 1H), 4.73–4.48 (m, 4H), 4.28 (s, 1H), 4.02 (s, 2H), 3.79–3.60 (m, 9H), 3.55 (dd, *J* = 9.4, 4.5 Hz, 1H), 3.50–3.40 (m, 1H), 2.90 (dd, *J* = 10.1, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 155.09, 150.88, 138.69, 137.79, 137.71, 128.76, 128.66, 128.62, 128.08, 128.07, 128.04, 128.02, 127.94, 127.76, 117.83, 114.79, 100.45, 97.02, 82.44, 75.58, 73.94, 73.25, 71.94, 71.82, 71.16, 70.76, 70.29, 67.95, 66.28, 55.82, 54.52, 52.41; ESI-MS *m/z* $C_{41}H_{47}NO_{12}Na$ $[M+Na]^+$ 768.2991, found 768.3005.

4-Methoxyphenyl 2-azido-3,6-di-*O*-benzyl-4-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfo-*α*-L-iduropyranosiduronate) (8)

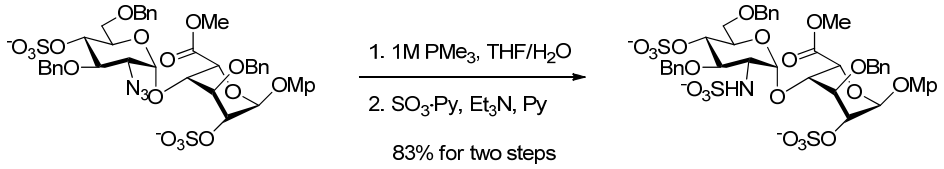


6 **8**

SO_3·Py (82 mg, 0.52 mmol) was added to a solution of disaccharide **6** (20 mg, 0.026 mmol) in DMF (1.0 mL). The mixture was stirred at ambient temperature for 4 h until TLC indicated completion of the reaction. After addition of CH_3OH (0.5 mL), stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 15:1 + 5% Et_3N) to give **8** (24 mg, 99%) as a white solid: $[\alpha]_D^{27}$= 24.8 (*c* 0.2, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.27 (m, 6H), 7.24–7.01 (m, 9H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.02 (s, 1H), 4.93–4.61 (m, 6H), 4.56 (d, *J* = 8.8 Hz, 1H), 4.47 (d, *J* = 20.0 Hz, 3H), 4.28 (s, 2H), 4.01 (s, 2H), 3.83 (s, 1H), 3.72 (d, *J* = 9.2 Hz, 1H), 3.54 (s, 3H), 3.43 (s, 3H), 3.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 155.09, 150.88, 138.69, 137.79, 137.71, 128.76, 128.66, 128.62, 128.08, 128.07, 128.04, 128.02, 127.94, 127.76, 117.83, 114.79, 100.45, 97.02, 82.44, 77.48, 77.16, 76.84, 75.58, 73.94, 73.25, 71.94, 71.82, 71.16, 70.76, 70.29, 67.95, 66.28, 55.82,

54.52, 52.41; ESI-MS *m/z* calcd for $C_{41}H_{43}N_3O_{18}S_2$ $[M\text{-}2H]^{2-}$ 464.6, found 465.0.

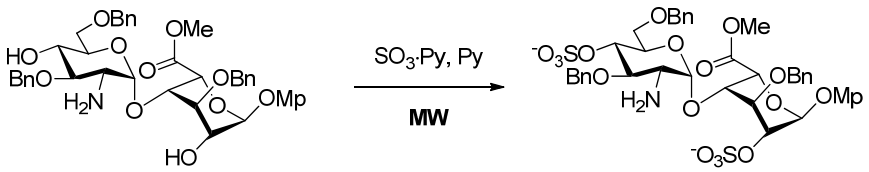
4-Methoxyphenyl
2-*N*-sulfo-3,6-di-*O*-benzyl-4-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfo-*α*-L-iduropyranosiduronate) (9)



8 **9**

A solution of PMe_3 in THF (1 M, 0.016 mL, 0.016 mmol) was added to a solution of disaccharide **8** (3.0 mg, 0.0032 mmol) in THF (1.0 mL) and H_2O (0.1 mL). The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, 1/3). The mixture was concentrated in vacuum and co-evaporated with toluene (3 × 3 mL). The residue was dissolved in pyridine (1.0 mL) and trimethylamine (0.1 mL). SO_3·Py (2.5 mg, 0.16 mmol) was added. The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, 1/3). MeOH (0.4 mL) was then added to quench the reaction. The mixture was concentrated in vacuum. The residue was purified by a small RP-18 silica gel column (H_2O/CH_3OH, 1/0 to 1/9 to 1/2). The fractions containing product were concentrated in vacuum, and the residue was immediately passed through a column of Dowex 50WX4 Na^+ resin (CH_3OH/H_2O, 9/1). The fractions containing product were concentrated in vacuum to provide **9** (2.6 mg, 83%) as a white solid: $[\alpha]_D^{28} = 5.7$ (*c* 0.1, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.65 (d, J = 7.2 Hz, 2H), 7.53–7.15 (m, 12H), 7.05 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 5.88 (s, 1H), 5.43 (d, J = 3.2 Hz, 1H), 5.05–4.93 (m, 3H), 4.80–4.71 (m, 2H), 4.66 (d, J = 11.8 Hz, 1H), 4.53 (d, J = 10.6 Hz, 3H), 4.28 (s, 1H), 3.98–3.70 (m, 8H), 3.65 (s, 3H), 3.54 (dd, J = 10.7, 3.2 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 171.28, 156.64, 151.87, 139.92, 139.66, 130.46, 129.26, 129.21, 129.18, 128.98, 128.78, 128.55, 128.43, 128.32, 119.09, 115.63, 99.66, 99.45, 79.02, 77.49, 75.50, 74.39, 74.33, 74.27, 73.20, 72.48, 72.29, 69.90, 68.59, 58.76, 56.03, 53.06; ESI-MS *m/z* calcd for $C_{41}H_{45}NO_{21}S_3$ $[M\text{-}2H]^{2-}$ 491.6, found 492.2.

4-Methoxyphenyl
2-amino-3,6-di-*O*-benzyl-4-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfo-*α*-L-iduropyranosiduronate) (10)



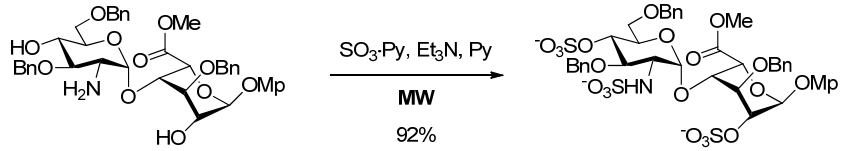
7 **10**

SO_3·Py (32 mg, 0.201 mmol) was added to a solution of disaccharide **7** (10 mg, 0.013 mmol) in pyridine (1.0 mL). The mixture was stirred at room temperature for 5 min, then subjected to microwave radiation for 15 min at a fix temperature of 55 ^oC (average power of 18 W). The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/3). The mixture was subjected to microwave radiation for 15 min at 55 ^oC (fix temperature) twice. After the addition of CH_3OH (0.5 mL) stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was applied to a small RP-18 silica gel column (H_2O/CH_3OH, 1/0 to 1/9 to 1/4). The fractions containing the product were concentrated in vacuum. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin (CH_3OH). The fractions containing the product were concentrated in vacuum to provide **10** (8.0 mg, 66%) as a white solid: $[\alpha]_D^{28}$ = 26.4 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.31 (m, 13H), 7.03 (d, *J* = 9.1 Hz, 2H), 6.87 (d, *J* = 9.1 Hz, 2H), 5.79 (s, 1H), 5.36 (t, *J* = 6.6 Hz, 2H), 5.08 (s, 1H), 4.72–4.52 (m, 5H), 4.43 (t, *J* = 9.4 Hz, 1H), 4.34 (d, *J* = 19.4 Hz, 2H), 4.10 (d, *J* = 9.6 Hz, 1H), 3.93–3.63 (m, 9H); ^{13}C NMR (100 MHz, MeOD) δ 171.13, 156.92, 151.68, 139.85, 139.34, 138.82, 130.24, 129.47, 129.29, 129.12, 129.01, 128.94, 128.91, 128.75, 128.53, 119.15, 115.81, 99.53, 92.45, 77.98, 77.80, 76.38, 74.43, 73.09, 72.87, 70.41, 69.86, 69.26, 68.14, 56.09, 54.83, 53.32; ESI-MS *m/z* calcd for $C_{41}H_{46}NO_{18}S_2$ $[M-H]^-$ 904.2, found 904.8.

The reaction temperature was elevated to 100 ^oC. SO_3·Py (19.0 mg, 0.120 mmol) was added to a solution of disaccharide **7** (6.0 mg, 0.008 mmol) in pyridine (1.0 mL). The mixture was stirred at room temperature for 5 min, then subjected to microwave

radiation for 15 min at a fix temperature of 100 °C (average power of 18 W). The progress of the reaction was monitored by TLC (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/3). After the addition of CH_3OH (0.5 mL), stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0, to 1/9, to 1/4). The fractions containing the product were concentrated in vacuum. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using CH_3OH as eluent. The fractions containing the product were concentrated in vacuum to provide **10** (7.0 mg, 96%) as a white solid.

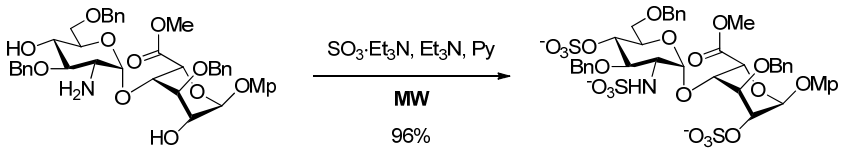
4-Methoxyphenyl
2-*N*-sulfo-3,6-di-*O*-benzyl-4-*O*-sulfo-2-deoxy-α-D-glucopyranosyl-(1→4)-(methyl
3-*O*-benzyl-2-*O*-sulfo-α-L-iduropyranosiduronate) (9)



7 **9**

General Procedure for the Microwave-assisted Simultaneous O,N-Sulfonation with SO_3·Py. SO_3·Py (5 equiv per OH/NH_2) was added to a solution of the starting material in pyridine (1.0 mL for 20 - 30 mg starting material). Then trimethylamine (0.1 mL) was added. The mixture was stirred at room temperature for 5 min, then subjected to microwave radiation for 15 min at a fix temperature of 100 °C (average power of 18 W). The color changed from light yellow to dark red. After the addition of CH_3OH (0.5 mL) stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0, to 1/9, to 1/2). The fractions containing the product were concentrated in vacuum. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using a mixture of CH_3OH and H_2O (v/v = 9/1) as eluent. The fractions containing the product were concentrated in vacuum to provide the product as sodium salt.

Compound **9** (30.4 mg, 92%) was thus obtained as a white solid.

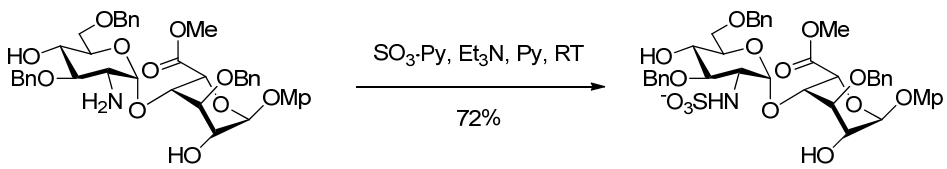


7 **9**

General Procedure for the Microwave-assisted Simultaneous O,N-Sulfonation with SO_3·NEt_3. SO_3·NEt_3 (5 equiv per OH/NH_2) was added to a solution of the starting material in pyridine (1.0 mL for 20-30 mg starting material). Then trimethylamine (0.1 mL) was added. The mixture was stirred at room temperature for 5 min, then subjected to microwave radiation for 15 min at a fix temperature of 100 ^oC (average power of 18 W). The color was changed from light yellow to dark red. After the addition of CH_3OH (0.5 mL), stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0, to 1/9, to 1/2). The fractions containing the product were concentrated in vacuum. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using a mixture of CH_3OH and H_2O (v/v = 9/1) as eluent. The fractions containing the product were concentrated in vacuum to provide the product as sodium salt.

Compound **9** (31.7 mg, 96%) was thus obtained as a white solid.

4-Methoxyphenyl
2-*N*-sulfo-3,6-di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl
3-*O*-benzyl-*β*-D-glucopyranosiduronate) (11)

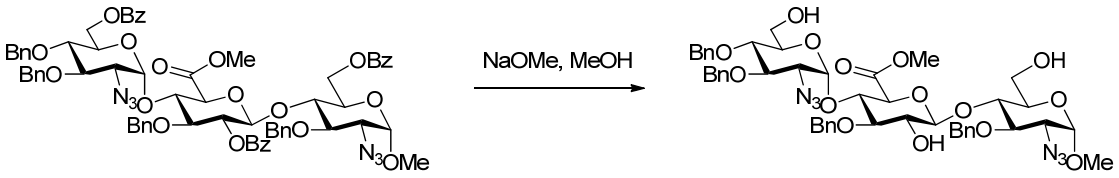


7 **11**

SO_3·Py (38.0 mg, 0.24 mmol) was added to a solution of disaccharide **7** (12.0 mg, 0.016 mmol) in pyridine (1.0 mL). The mixture was stirred at room temperature for overnight. TLC monitor (RP-18 silica gel, H_2O/CH_3OH, v/v = 1/3) indicated the completion of the reaction. After the addition of CH_3OH (0.5 mL) and trimethylamine

(1.0 mL), stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0, to 1/9, to 1/3). The fractions containing the product were concentrated in vacuum. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using a mixture of CH_3OH and H_2O (v/v = 9/1) as eluent. The fractions containing the product were concentrated in vacuum to provide the product **11** (9.6 mg, 72%) as a white solid: $[\alpha]_D^{28} = 7.7$ (*c* 0.3, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.55–7.15 (m, 15H), 7.03 (d, *J* = 9.1 Hz, 2H), 6.85 (d, *J* = 9.1 Hz, 2H), 5.51 (s, 1H), 5.44 (d, *J* = 3.2 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 4.93 (s, 1H), 4.82–4.67 (m, 3H), 4.58 (s, 2H), 4.30 (s, 1H), 4.20 (s, 1H), 4.05 (s, 1H), 3.81–3.63 (m, 8H), 3.61–3.41 (m, 4H); ^{13}C NMR (100 MHz, MeOD) δ 171.54, 156.54, 152.06, 140.54, 139.72, 129.35, 129.32, 129.07, 128.88, 128.66, 128.58, 128.29, 118.92, 115.64, 101.56, 97.99, 80.95, 75.53, 74.66, 73.68, 73.33, 73.27, 71.42, 70.75, 68.87, 67.69, 59.11, 56.03, 53.04; ESI-MS *m/z* calcd for $C_{41}H_{46}NO_{15}S$ $[M-H]^-$ 824.3, found 824.7.

Methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-*β*-D-glucopyranosiduronate)-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (S6)

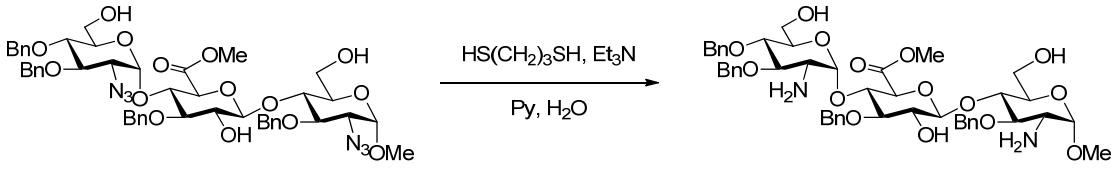


S5 **S6**

The general procedure for the deprotection of the esters was applied to provide compound **S6** (151 mg, 90%) as a white solid: $[\alpha]_D^{22} = 76.3$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–6.91 (m, 20H), 5.48 (d, *J* = 3.7 Hz, 1H), 4.94 (t, *J* = 11.2 Hz, 2H), 4.90–4.80 (m, 4H), 4.78 (dd, *J* = 7.1, 3.5 Hz, 2H), 4.67 (dd, *J* = 15.5, 9.3 Hz, 2H), 4.10–3.59 (m, 14H), 3.53 (t, *J* = 9.4 Hz, 1H), 3.45–3.18 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.76, 138.26, 137.92, 137.84, 137.77, 128.65, 128.64, 128.61,

128.54, 128.20, 128.08, 128.06, 127.96, 127.90, 127.84, 103.06, 98.85, 97.70, 83.87, 79.93, 79.10, 77.75, 77.36, 76.06, 75.57, 75.34, 75.15, 75.10, 74.98, 74.84, 74.67, 72.14, 70.99, 63.72, 63.50, 61.32, 60.94, 55.49, 52.91; ESI-MS *m/z* calcd for $C_{48}H_{56}N_6O_{15}Na$ $[M+Na]^+$ 979.3696, found 979.3693.

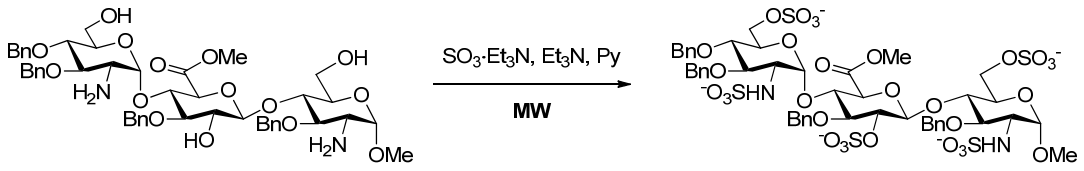
Methyl 2-amino-3,4-di-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-*β*-D-glucopyranosiduronate)-(1→4)-2-amino-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (12)



S6 **12**

The general procedure for the reduction of the azide was applied to provide compound **12** (135 mg, 95%) as a light yellow solid: $[\alpha]_D^{22} = 94.6$ (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, CD_3OD) δ 7.55–7.14 (m, 20H), 5.23 (d, J = 3.4 Hz, 1H), 5.14 (t, J = 10.6 Hz, 2H), 4.85–4.61 (m, 6H), 4.55 (d, J = 11.0 Hz, 1H), 4.12–3.97 (m, 3H), 3.93–3.82 (m, 2H), 3.80–3.64 (m, 7H), 3.64–3.45 (m, 6H), 3.40 (s, 3H), 3.37–3.27 (m, 2H), 2.67 (dd, J = 10.0, 3.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 170.45, 140.35, 139.99, 139.96, 139.86, 129.67, 129.45, 129.40, 129.38, 129.36, 129.00, 128.78, 128.70, 128.63, 104.69, 101.13, 100.84, 84.88, 83.67, 82.94, 79.27, 78.98, 77.30, 76.35, 76.27, 76.19, 75.60, 75.55, 74.26, 73.03, 61.25, 56.93, 56.43, 55.50, 53.08; ESI-MS *m/z* calcd for $C_{48}H_{60}N_2O_{15}Na$ 927.3886 $[M+Na]^+$, found 927.3886.

Methyl 2-*N*-sulfo-3,4-di-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyranosiduronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (13)

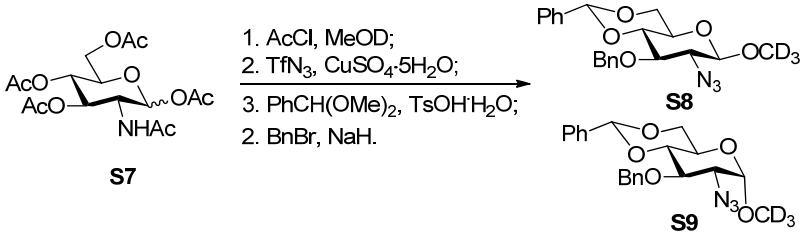


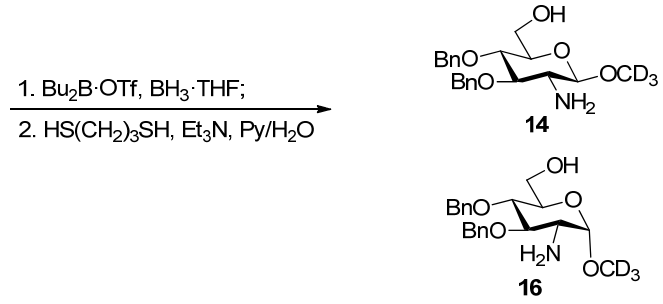
12 **13**

The general procedure for the microwave-assisted simultaneous O,N-sulfonation

with $SO_3{\cdot}NEt_3$ was applied to provide compound **13** (30 mg, 95%) as a white solid: $[\alpha]_D^{25}$ = 38.1 (*c* 0.2, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.81–6.96 (m, 20H), 5.38 (brs, *J* = 3.4 Hz, 1H), 5.15–5.05 (m, 3H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.82–4.73 (m, 1H), 4.70 (d, *J* = 11.0 Hz, 2H), 4.54 (t, 1H), 4.32 (d, *J* = 8.4 Hz, 1H), 4.27–4.19 (m, 2H), 4.18–4.07 (m, 3H), 3.96 (d, *J* = 6.1 Hz, 2H), 3.76–3.52 (m, 11H), 3.51–3.37 (m, 4H); ^{13}C NMR (100 MHz, CD_3OD) δ 170.78, 140.62, 140.28, 140.07, 139.00, 130.33, 129.40, 129.32, 129.16, 129.14, 129.09, 129.05, 128.73, 128.38, 128.24, 128.19, 102.20, 99.97, 99.83, 81.66, 80.51, 80.17, 79.44, 78.65, 78.50, 77.13, 76.41, 75.90, 74.94, 74.46, 71.43, 70.22, 67.18, 66.95, 59.67, 58.42, 58.29, 55.78, 53.25; ESI-MS *m/z* calcd for $C_{48}H_{58}N_2O_{30}S_5$ $[M\text{-}2H]^{2-}$ 651.1, found 651.5; $C_{48}H_{57}N_2O_{30}S_5$ $[M\text{-}3H]^{3-}$ 433.7, found 434.1.

d3-Methyl 2-amino-2-deoxy-3,4-di-*O*-benzyl-*β/a*-D-glucopyranosides (14 and 16)





To a solution of pentaacetyl glucosamine **S7** (500 mg, 1.28 mol) in CD_3OD (10 mL) was slowly added acetyl chloride (1 mL) at 0 ^{o}C. Stirring was continued for another 15 min. The reaction mixture was heated to reflux for 8 h. TLC analysis showed complete consumption of the starting material. The mixture was cooled to room temperature and concentrated in vacuum.

The residue was dissolved in methanol (4 mL), $CuSO_4{\cdot}H_2O$ (2 mg) and NEt_3 (0.36 mL) were added. The mixture was cooled to 0 ^{o}C, then fresh TfN_3 in CH_3CN

was added dropwise. The mixture was slowly warmed to room temperature. After 24 h, TLC analysis showed completed disappearance of the starting material. The reaction mixture was concentrated and the residue was co-evaporated twice with toluene and dissolved in acetonitrile (5 mL). Benzaldehyde dimethyl acetal (224 μL, 1.48 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg) were added to adjust pH = ~3, stirring was continued until TLC indicated disappearance of the raw material. Triethylamine was added and the solvent was evaporated.

The residue was dissolved in DMF (6 mL). The mixture was cooled to 0 ^{o}C, then NaH (60%) was added in batches. After 30 min, BnBr (224 μL, 1.84 mmol) was added, After 2 h, TLC analysis showed disappearance of the starting material. MeOH (2 mL) was then added to quench the reaction. The mixture was poured into CH_2Cl_2, and washed with brine twice. The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuum. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 8:1) to give the β-product **S8** (123 mg, 12%) and α-product **S9** (368 mg, 36%) as white solids.

S9: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.26 (m, 10 H), 5.56 (s, 1 H), 4.95 (d, 1 H, J = 10.8 Hz), 4.80–4.75 (m, 2 H), 4.27 (dd, 1 H, J = 10.0 Hz, 4.4 Hz), 4.05 (t, 1 H, J = 9.2 Hz), 3.86–3.66 (m, 3 H), 3.42 (dd, 1 H, J = 10.0 Hz, 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.92, 137.32, 129.11, 128.48, 128.35, 128.29, 127.94, 127.84, 126.09, 101.50, 99.40, 82.83, 76.40, 75.07, 68.98, 63.22, 62.64; ESI-MS 423.3 $[M+Na]^+$.

Compound **S8** (72 mg, 0.18 mmol) was dissolved in BH_3·THF (1 M, 1.8 mL, 1.8 mmol) under nitrogen and cooled to 0 ^{o}C. After 15 min, Bu_2B·OTf (1 M, 0.18 mL, 0.18 mmol) was added dropwise and stirring was continued at 0 ^{o}C for 2 h. The reaction mixture was quenched by the addition of Et_3N and the excess BH_3·THF was consumed by slowly adding methanol. The solvent was removed in vacuum, and was then co-evaporated with methanol twice to give a residue: ESI-MS *m/z* 425.2 $[M+Na^+]$.

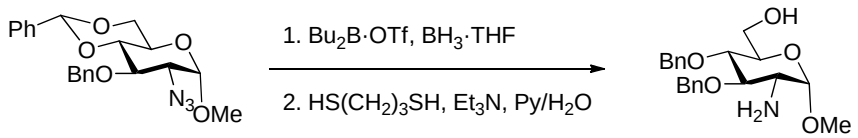
The residue was dissolved in pyridine (1 mL) and water (0.25 mL), trimethylamine (0.04 mL) and propane-1,3-dithiol (0.08 mL) were added. TLC

analysis showed complete disappearance of the starting material. The mixture was concentrated in vacuum, and was then co-evaporated with toluene/ethanol (5 mL, v/v = 5/1) twice. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20: 1 + 1% Et_3N) to give compound **14** (56 mg, 85%) as a light yellow solid: $[\alpha]_D^{24} = 3.8$ (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.18 (m, 10H), 4.97 (d, *J* = 11.3 Hz, 1H), 4.84 (d, *J* = 10.9 Hz, 1H), 4.71 (dd, *J* = 11.1, 6.1 Hz, 2H), 4.15 (d, *J* = 7.9 Hz, 1H), 3.88 (dd, *J* = 12.0, 2.1 Hz, 1H), 3.76 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.66 (t, *J* = 9.3 Hz, 1H), 3.47 (t, *J* = 9.4 Hz, 1H), 3.42–3.33 (m, 1H), 2.80 (dd, *J* = 9.7, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.26, 137.89, 128.53, 128.49, 127.92, 127.89, 127.86, 127.82, 104.75, 84.57, 78.21, 75.60, 75.30, 74.82, 61.37, 56.94; ESI-MS *m/z* calcd for $C_{21}H_{24}D_3NO_5Na$ $[M+Na]^+$ 399.1970, found 399.1962.

Compound **S9** (72 mg, 0.18 mmol) was dissolved in BH_3·THF (1 M, 1.8 mL, 1.8 mmol) under nitrogen and cooled to 0 °C. After 15 min, Bu_2B·OTf (1 M, 0.18 mL, 0.18 mmol) was added dropwise and the stirring was continued at 0 °C for 2 h. The reaction mixture was quenched by the addition of Et_3N and the excess BH_3·THF was consumed by slowly adding methanol. The solvent was removed in vacuum with co-evaporation with methanol twice. ESI-MS *m/z* 425.2 $[M+Na^+]$.

The residue was dissolved in pyridine (1 mL) and water (0.25 mL), trimethylamine (0.04 mL) and propane-1,3-dithiol (0.08 mL) were added. TLC showed complete disappearance of the starting material. The mixture was concentrated in vacuum, and co-evaporated with toluene/ethanol (5 mL, v/v = 5/1) twice. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1 + 1% Et_3N) to give compound **16** (60 mg, 89%) as a white solid: $[\alpha]_D^{25} = 122.2$ (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–6.91 (m, 20H), 5.48 (d, *J* = 3.7 Hz, 1H), 4.94 (t, *J* = 11.2 Hz, 2H), 4.90–4.80 (m, 4H), 4.78 (dd, *J* = 7.1, 3.5 Hz, 2H), 4.67 (dd, *J* = 15.5, 9.3 Hz, 2H), 4.10–3.59 (m, 14H), 3.53 (t, *J* = 9.4 Hz, 1H), 3.45–3.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.57, 138.15, 128.66, 128.62, 128.01, 127.96, 100.50, 83.70, 78.72, 77.48, 77.16, 76.84, 75.69, 74.89, 71.61, 61.78, 56.07; ESI-MS *m/z* calcd for $C_{21}H_{24}D_3NO_5Na$ $[M+Na]^+$ 399.1970, found 399.1964.

Methyl 2-amino-2-deoxy-3,4-di-*O*-benzyl-α-D-glucopyranose (18)

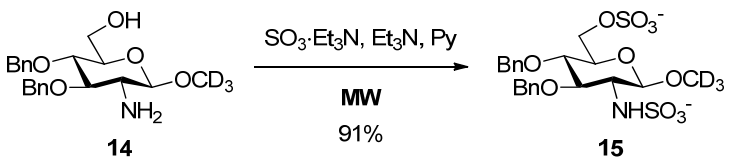


S10 **18**

Compound **S10** (200 mg, 0.50 mmol) was dissolved in BH_3·THF (1 M, 5.0 mL, 5.0 mmol) under nitrogen and cooled to 0 ^oC. After 15 min, Bu_2B·OTf (1 M, 0.50 mL, 0.50 mmol) was added dropwise and the stirring was continued at 0 ^oC for 2 h. The reaction mixture was quenched by addition of Et_3N and the excess BH_3·THF was consumed by slowly adding methanol. The solvent was removed in vacuum, and then co-evaporated with methanol twice. ESI-MS *m/z* 422.3 [M+Na^+].

The residue was dissolved in pyridine (2 mL) and water (0.5 mL), trimethylamine (0.08 mL) and propane-1,3-dithiol (0.16 mL) were added. TLC analysis showed complete disappearance of the starting material. The mixture was concentrated in vacuum, and then co-evaporated with toluene/ethanol (5 mL, v/v = 5/1) twice. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 20:1 + 1% Et_3N) to give compound **18** (150 mg, 93%) as a white solid: $[\alpha]_D^{22}$ = 110.8 (*c* 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.13 (m, 10H), 4.97 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.78–4.58 (m, 3H), 3.88–3.48 (m, 5H), 3.35 (s, 3H), 2.75 (dd, *J* = 9.4, 3.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.60, 138.17, 128.66, 128.00, 100.67, 83.89, 78.73, 77.48, 77.16, 76.84, 75.71, 74.88, 71.63, 61.78, 56.14, 55.22; ESI-MS *m/z* calcd for $C_{21}H_{27}NO_5Na$ $[M+Na]^+$ 396.1782, found 396.1790.

d3-Methyl 2-*N*-sulfo-2-deoxy-3,4-di-*O*-benzyl-6-*O*-sulfo-β-D-glucopyranoside (15)

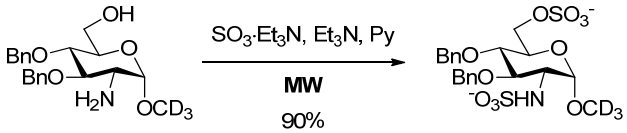


14 **15**

The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **15** (26 mg, 91%) as a white solid:

$[\alpha]_D^{25}$ = -26.9 (*c* 0.2, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 7.57–7.13 (m, 10H), 5.17 (d, *J* = 10.7 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 3H), 4.69 (d, *J* = 6.2 Hz, 1H), 4.36 (s, 2H), 4.00 (s, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 140.21, 139.66, 129.37, 129.21, 129.21, 129.18, 128.58, 128.43, 104.19, 82.82, 78.68, 75.31, 75.25, 74.64, 67.86, 60.56; ESI-MS *m/z* calcd for $C_{21}H_{22}D_3NO_{11}S_2$ $[M-2H]^{2-}$ 267.1, found 267.0.

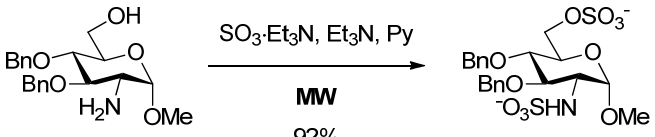
d3-Methyl 2-*N*-sulfo-2-deoxy-3,4-di-*O*-benzyl-6-*O*-sulfo-α-D-glucopyranoside (17)



16 **17**

The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **17** (35 mg, 90%) as a white solid: $[\alpha]_D^{25}$ = 37.8 (*c* 0.2, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.42 (d, *J* = 6.6 Hz, 2H), 7.37–7.16 (m, 7H), 5.08 (dd, *J* = 7.1, 3.4 Hz, 2H), 4.80–4.66 (m, 3H), 4.27 (d, *J* = 3.1 Hz, 2H), 3.80 (dt, *J* = 9.8, 3.0 Hz, 1H), 3.71–3.52 (m, 2H), 3.47 (dd, *J* = 10.1, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 140.20, 139.70, 129.36, 129.21, 129.18, 129.14, 128.56, 128.42, 100.14, 81.93, 78.99, 76.20, 75.94, 70.55, 67.66, 59.50; ESI-MS *m/z* calcd for $C_{21}H_{23}D_3NO_{11}S_2$ $[M-H]^-$ 535.1, found 535.3; $C_{21}H_{22}D_3NO_{11}S_2$ $[M-2H]^{2-}$ 267.1, found 267.2.

Methyl 2-*N*-sulfo-2-deoxy-3,4-di-*O*-benzyl-6-*O*-sulfo-α-D-glucopyranose (19)

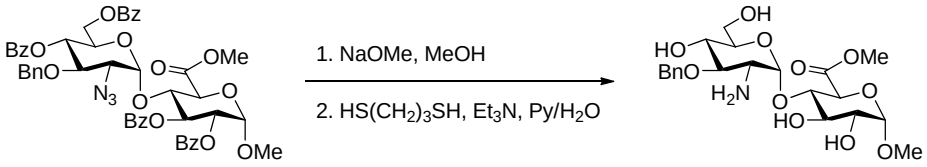


18 **19**

The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **19** (39 mg, 92%) as a white solid: ^{1}H NMR (400 MHz, CD_3OD) δ 7.46–7.38 (m, 2H), 7.34–7.18 (m, 8H), 5.12 – 4.99 (m, 2H), 4.81 – 4.67 (m, 3H), 4.27 (d, *J* = 3.2 Hz, 2H), 3.80 (dt, *J* = 9.8, 3.1 Hz, 1H), 3.61 (dt, *J* = 18.7, 9.0 Hz, 2H), 3.47 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR

(100 MHz, CD_3OD) δ 140.22, 139.71, 129.37, 129.23, 129.18, 129.14, 128.57, 128.42, 100.22, 81.95, 78.99, 76.22, 75.95, 70.56, 67.66, 59.51, 55.82; ESI-MS *m/z* calcd for $C_{21}H_{26}NO_{11}S_2$ $[M-H]^-$ 532.1, found 532.3; $C_{21}H_{24}NO_{11}S_2$ $[M-2H]^{2-}$ 265.6, found 265.7.

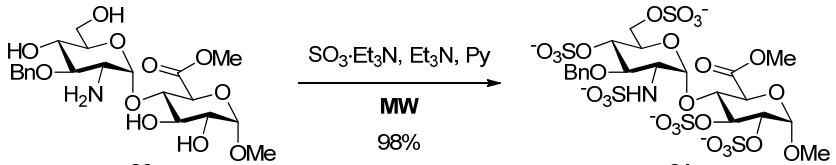
Methyl 2-amino-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl *α*-D-glucopyranosiduronate) (20)



S11 **20**

The general procedures for the deprotection of the ester and the reduction of the azide were applied to provide compound **20** (35 mg, 66%) as a light yellow solid: $[\alpha]_D^{22}$ = 169.9 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.43–7.28 (m, 5H), 5.28 (d, *J* = 3.6 Hz, 1H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.74–4.71 (m, 2H), 4.2 (d, *J* = 11.2 Hz, 1H), 3.81–3.48 (m, 8H), 3.48–3.43 (m, 7H), 2.71 (dd, *J* = 4.0, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 171.32, 140.29, 129.37, 129.19, 128.70, 101.68, 83.58, 80.31, 76.05, 74.59, 74.48, 72.67, 71.80, 71.75, 61.85, 56.27, 56.10, 53.21; ESI-MS *m/z* calcd for $C_{21}H_{31}NO_{11}Na$ $[M+Na]^+$ 496.1789, found 496.4791.

Methyl 2-*N*-sulfo-3-*O*-benzyl-4,6-di-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 2,3-di-*O*-sulfo-*α*-D-glucopyranosiduronate) (21)

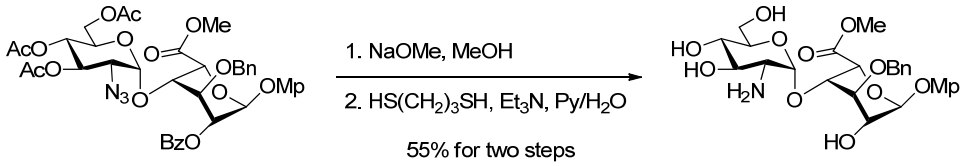


20 **21**

The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **21** (20 mg, 98%) as a white solid: $[\alpha]_D^{28}$ = 12.3 (*c* 0.6 H_2O); ^{1}H NMR (400 MHz, D_2O) δ 7.68–7.27 (m, 5H), 5.42 (d, *J* = 3.5 Hz, 1H), 5.22 (d, *J* = 3.1 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.46 (dd, *J* = 8.7, 3.2 Hz, 1H), 4.40–4.28 (m, 3H), 4.23 (dd, *J* = 10.9, 4.7 Hz, 1H), 4.19–4.11 (m, 1H), 3.89–3.80 (m, 5H), 3.55 (d, *J* = 4.7 Hz, 3H), 3.40 (dd, *J* = 10.7, 3.5 Hz, 1H); ^{13}C

NMR (125 MHz, D_2O) δ 170.33, 137.77, 129.13, 128.38, 128.03, 98.90, 97.17, 77.41, 77.15, 76.14, 75.15, 74.97, 73.79, 71.68, 69.49, 66.58, 57.44, 56.12, 55.46, 53.50; ESI-MS *m/z* calcd for $C_{21}H_{29}NO_{26}S_5$ $[M-2H]^{2-}$ 435.5, found 435.8.

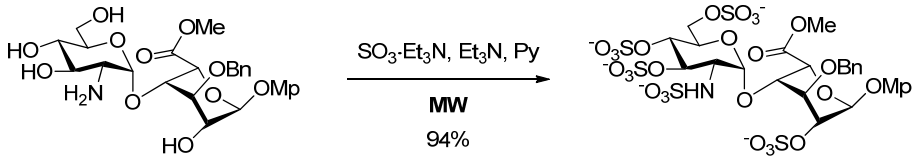
4-Methoxyphenyl 2-amino-2-deoxy-α-D-glucopyranosyl-(1→4)-(methyl α-L-iduropyranosiduronate) (22)



S12 **22**

The general procedures for the deprotection of ester and the reduction of azide were applied to provide compound **22** (68 mg, 55%) as a light yellow solid: $[\alpha]_D^{24}$ = +5.8 (*c* 0.4, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.56–7.17 (m, 5H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 5.47 (d, *J* = 2.3 Hz, 1H), 5.02 (d, *J* = 3.4 Hz, 1H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.22 (brs, 1H), 4.10–3.90 (m, 2H), 3.90–3.62 (m, 8H), 3.49–3.37 (m, 2H), 2.60 (dd, *J* = 10.0, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 171.48, 156.59, 152.23, 139.58, 129.43, 128.87, 128.80, 118.95, 115.59, 101.76, 99.13, 75.77, 75.15, 74.64, 73.39, 73.34, 71.53, 69.95, 69.03, 62.41, 57.04, 56.02, 52.93; ESI-MS *m/z* calcd for $C_{27}H_{35}NO_{12}Na$ $[M+Na]^+$ 588.2052, found 588.2047.

4-Methoxyphenyl 2-*N*-sulfo-3,4,6-tri-*O*-sulfo-2-deoxy-α-D-glucopyranosyl-(1→4)-(methyl 2-*O*-sulfo-α-L-iduropyranosiduronate) (23)

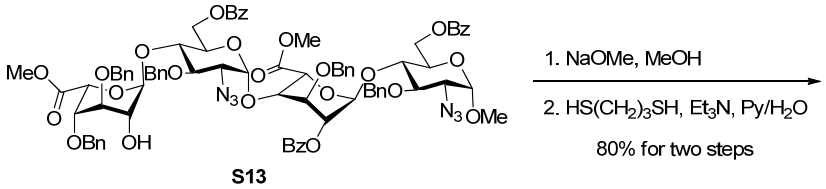


22 **23**

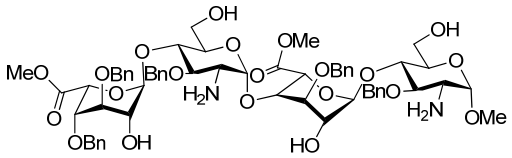
The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **23** (20 mg, 94%) as a white solid: $[\alpha]_D^{28}$ = 21.4 (*c* 0.2 H_2O); ^{1}H NMR (400 MHz, D_2O) δ 7.49–7.26 (m, 5H), 7.07–6.99 (m, 2H), 6.93–6.85 (m, 2H), 5.67 (d, *J* = 2.4 Hz, 1H), 5.30 (d, *J* = 3.2 Hz, 1H), 5.01 (d, *J* = 2.6 Hz, 1H), 4.80 (dd, *J* = 26.5, 11.2 Hz, 2H), 4.54 (dd, *J* = 4.5, 2.6 Hz, 1H), 4.32–4.23 (m, 5H), 4.16 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.96–3.84 (m, 1H), 3.74 (d, *J* = 17.0 Hz, 6H), 3.42 (dd, *J* = 10.6, 3.2 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 173.08,

157.52, 152.50, 139.80, 131.37, 131.00, 121.78, 117.75, 101.48, 99.79, 77.87, 77.69, 77.00, 76.64, 75.56, 75.48, 72.41, 71.31, 69.50, 59.30, 58.48, 55.87; ESI-MS *m/z* calcd for $C_{27}H_{33}NO_{27}S_5$ $[M-2H]^{2-}$ 481.5, found 481.7; $C_{27}H_{32}NO_{27}S_5Na$ $[M+Na-2H]^{2-}$ 492.5, found 492.7.

Methyl (methyl 3,4-di-*O*-benzyl-*α*-L-iduropyranosyluronate)-(1→4)-(2-amino-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-(methyl 3-*O*-benzyl-*α*-L-iduropyranosyluronate)-(1→4)-2-amino-3-*O*-benzyl-2-deoxy-*α*-D-glucopyranoside (24)



S13

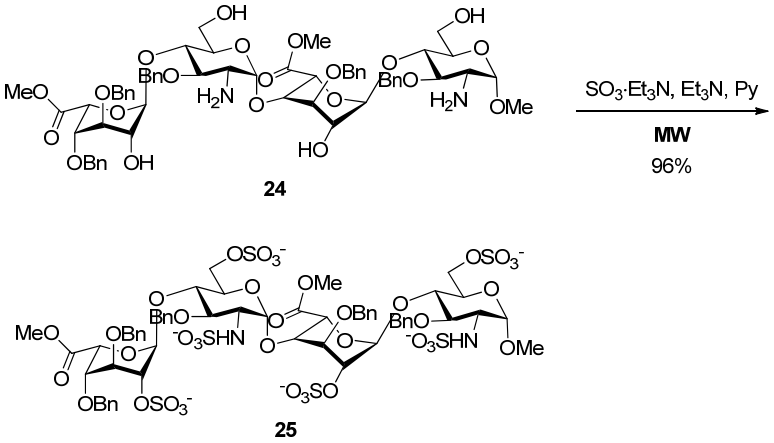


24

The general procedures for the deprotection of ester and the reduction of azide were applied to provide compound **24** (109 mg, 80%) as a light yellow solid: $[\alpha]_D^{22}$ = 37.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.00 (m, 25H), 5.27 (d, *J* = 6.1 Hz, 2H), 4.99–4.80 (m, 4H), 4.74 (d, *J* = 9.6 Hz, 1H), 4.72–4.66 (m, 2H), 4.66–4.35 (m, 7H), 4.18 (s, 1H), 3.99 (t, *J* = 9.5 Hz, 1H), 3.93 (s, 1H), 3.89–3.71 (m, 7H), 3.71–3.59 (m, 3H), 3.53–3.28 (m, 10H), 2.87–2.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 169.83, 138.69, 138.53, 137.58, 136.77, 128.61, 128.47, 128.45, 128.28, 128.18, 128.05, 128.02, 127.93, 127.85, 127.77, 127.41, 127.30, 127.04, 101.34, 100.98, 100.44, 96.97, 82.00, 81.76, 775.74, 75.32, 74.79, 74.74, 74.69, 74.08, 72.91, 72.78, 72.59, 72.13, 71.88, 71.25, 69.79, 69.23, 68.66, 68.22, 61.14, 61.04, 55.89, 55.22, 55.13, 51.85; ESI-MS *m/z* calcd for $C_{62}H_{76}N_2O_{21}Na$ $[M+Na]^+$ 1207.4833, found 1207.4867.

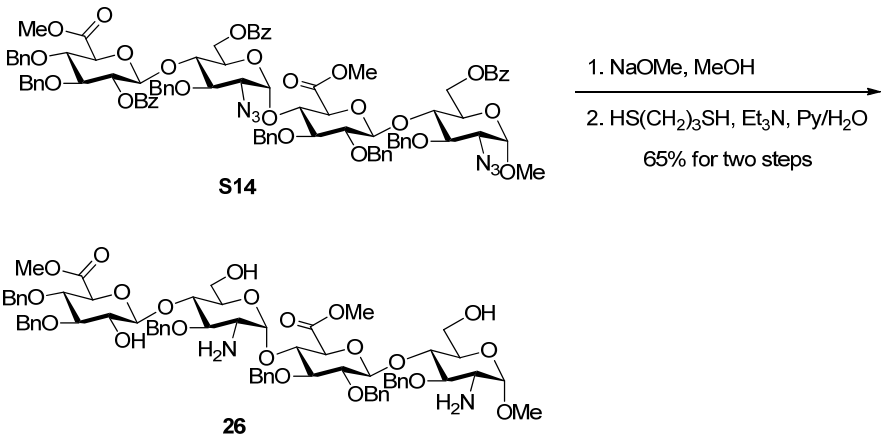
Methyl (methyl 3,4-di-*O*-benzyl-2-*O*-sulfo-*α*-L-iduropyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-

_O_-sulfo-2-deoxy-_α_-D-glucopyranosyl-(1→4)-(methyl 3-_O_-benzyl-2-_O_-sulfo-_α_-L-iduropyranosyluronate)-(1→4)-2-_N_-sulfo-3-_O_-benzyl-6-_O_-sulfo-2-deoxy-_α_-D-glucopyranoside (25)



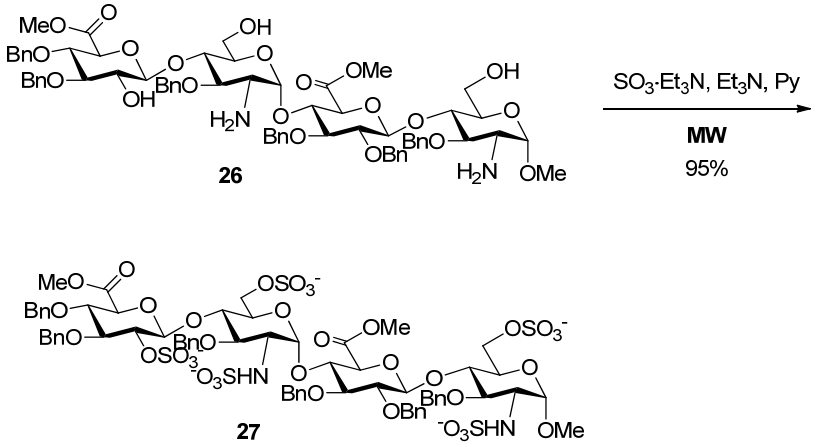
The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **25** (43 mg, 96%) as a white solid: $[\alpha]_D^{25}$ = 10.1 (*c* 0.8, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.79–6.94 (m, 25H), 5.46 (s, 1H), 5.40 (s, 1H), 5.33 (brs, *J* = 8.4 Hz, 1H), 5.14–5.05 (m, 2H), 5.02 (s, 1H), 4.93 (d, *J* = 9.8 Hz, 2H), 4.84–4.75 (m, 2H), 4.67 (t, *J* = 4.7 Hz, 2H), 4.63–4.45 (m, 5H), 4.39–4.11 (m, 7H), 4.05 (s, 1H), 3.94 (t, *J* = 9.2 Hz, 2H), 3.83 (dd, *J* = 22.2, 9.8 Hz, 2H), 3.56–3.36 (m, 11H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 172.49, 172.06, 139.91, 139.51, 139.49, 138.86, 138.20, 130.15, 130.07, 129.97, 129.90, 129.72, 129.67, 129.32, 129.26, 129.04, 128.89, 128.84, 128.71, 128.24, 128.01, 100.79, 100.08, 99.17, 98.43, 79.92, 79.06, 76.88, 76.58, 76.08, 73.83, 73.64, 72.95, 72.34, 72.10, 71.48, 71.37, 71.12, 70.76, 70.63, 68.33, 68.23, 67.59, 67.43, 59.95, 59.87, 55.91, 53.02, 52.41, 49.85; ESI-MS *m/z* calcd for $C_{62}H_{73}N_2O_{39}S_6$ $[M-3H]^{3-}$ 553.7, found 554.1.

Methyl (methyl 3,4-di-_O_-benzyl-_β_-D-glucopyranosyluronate)-(1→4)-2-amino-3-_O_-benzyl-2-deoxy-_α_-D-glucopyranosyl-(1→4)-(methyl 2,3-di-_O_-benzyl-_β_-D-glucopyranosyluronate)-(1→4)-2-amino-3-_O_-benzyl-2-deoxy-_α_-D-glucopyranoside (26)



The general procedures for the deprotection of the ester and the reduction of the azide were applied to provide compound **26** (6 mg, 65%) as a light yellow solid: $[\alpha]_D^{27} = 9.3$ (*c* 0.4, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.12 (m, 30H), 5.26 (d, J = 3.7 Hz, 1H), 5.14 (d, J = 11.2 Hz, 1H), 5.02 (d, J = 11.1 Hz, 1H), 4.96–4.67 (m, 7H), 4.56 (ddd, J = 25.6, 17.3, 9.3 Hz, 4H), 4.13 (t, J = 8.7 Hz, 1H), 4.04–3.64 (m, 9H), 3.64–3.39 (m, 13H), 3.35 (s, 3H), 2.78 (d, J = 6.2 Hz, 4H), 2.69 (td, J = 10.4, 3.8 Hz, 2H); ESI-MS *m/z* calcd for $C_{69}H_{82}N_2O_{21}Na$ $[M+Na]^+$ 1297.5302, found 1297.5306.

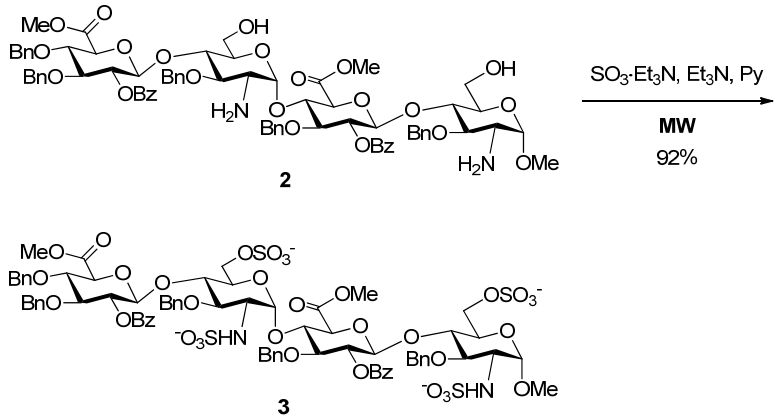
Methyl (methyl 3,4-di-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 2,3-di-*O*-benzyl-*β*-D-glucopyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (27)



The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **27** (6 mg, 95%) as a white solid: $[\alpha]_D^{25} = 26.4$ (*c* 19.8, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 7.56–7.02 (m, 30H),

5.43 (d, J = 3.3 Hz, 1H), 5.20 (d, J = 10.6 Hz, 1H), 5.11–5.00 (m, 4H), 4.84–4.59 (m, 10H), 4.49 (t, J = 8.4 Hz, 2H), 4.40 (d, J = 8.4 Hz, 1H), 4.23–4.00 (m, 6H), 3.98–3.79 (m, 7H), 3.68 (s, 3H), 3.64–3.44 (m, 8H), 3.42–3.37 (m, 5H); ^{13}C NMR (100 MHz, CD_3OD) δ 171.15, 170.70, 140.34, 140.10, 140.04, 139.93, 139.73, 139.53, 130.02, 129.99, 129.88, 129.79, 129.24, 129.20, 129.14, 129.10, 128.98, 128.69, 128.47, 128.44, 128.35, 128.07, 103.36, 102.31, 100.78, 99.92, 84.07, 82.45, 80.90, 80.37, 80.22, 79.00, 78.71, 77.89, 77.19, 76.38, 76.06, 75.85, 75.57, 75.38, 75.19, 75.11, 71.79, 70.46, 66.82, 59.17, 58.50, 55.87, 53.81, 52.75; ESI-MS *m/z* calcd for $C_{69}H_{79}N_2O_{36}S_5$ $[M-3H]^{3-}$ 557.1, found 557.6.

Methyl (methyl 3,4-di-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-*β*-D-glucopyranosyluronate)-(1→4)-2-*N*-sulfo-3-*O*-benzyl-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (3)

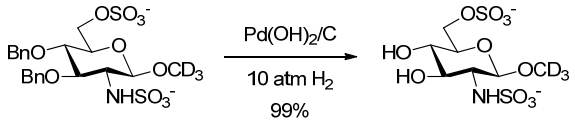


The general procedure for the microwave-assisted simultaneous O,N-sulfonation with SO_3·NEt_3 was applied to provide compound **3** (50 mg, 92%) as a white solid: $[\alpha]_D^{25}$ = 23.9 (*c* 2.4, MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 8.29–8.20 (m, 2H), 8.17–8.06 (m, 2H), 7.71–6.96 (m, 30H), 5.55 (d, J = 3.3 Hz, 1H), 5.29–5.22 (m, 2H), 5.21–5.15 (m, 1H), 5.07 (d, J = 8.1 Hz, 1H), 4.97 (d, J = 3.5 Hz, 1H), 4.94 (dd, J = 11.2, 2.3 Hz, 2H), 4.86 (d, J = 10.6 Hz, 1H), 4.80–4.70 (m, 4H), 4.61 (dd, J = 13.6, 11.0 Hz, 3H), 4.50–4.39 (m, 2H), 4.33 (dd, J = 10.9, 2.3 Hz, 1H), 4.22 (d, J = 9.8 Hz, 1H), 4.10 (tt, J = 9.8, 6.5 Hz, 4H), 4.01 (d, J = 9.6 Hz, 1H), 3.98–3.93 (m, 1H), 3.93–3.80 (m, 3H), 3.56 (s, 3H), 3.50–3.41 (m, 3H), 3.39 (dd, J = 10.6, 3.4 Hz, 1H),

3.31 (d, J = 1.8 Hz, 3H), 3.22 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 170.59, 170.11, 166.75, 166.63, 139.88, 139.84, 139.42, 139.14, 139.08, 134.76, 134.57, 131.16, 131.10, 130.71, 130.58, 130.00, 129.95, 129.84, 129.75, 129.55, 129.25, 129.14, 129.12, 128.94, 128.90, 128.73, 128.67, 128.60, 128.37, 128.33, 128.29, 101.63, 101.55, 99.88, 99.23, 83.73, 82.54, 81.22, 78.81, 77.93, 77.58, 77.48, 76.70, 76.01, 75.77, 75.69, 75.53, 75.47, 75.27, 74.98, 71.38, 70.29, 66.16, 65.75, 58.66, 58.27, 55.75, 53.14, 52.91; ESI-MS *m/z* calcd for $C_{76}H_{81}N_2O_{35}S_4$ $[M\text{-}3H]^{3-}$ 569.8, found 570.3; *m/z* calcd for $C_{76}H_{82}N_2O_{35}S_4$ $[M\text{-}2H]^{2-}$ 855.2, found 855.7.

General procedure for full deprotection of the corresponding per-O,N-sulfonated substrates. **Method A** (**28-30**). Palladium hydroxide on carbon (Degussa type, 20%, 1.5~2.0 times the weight of the starting material) was added to a solution of the starting material in CH_3OH and H_2O (1 mL for 10~20 mg, v/v = 1/1). The mixture was placed under 10 atm atmosphere of hydrogen for 3 d at 30 ^{o}C. The mixture was filtered and concentrated. The residue was diluted with H_2O and immediately passed through a column of Dowex 50WX4 Na^+ resin using H_2O as eluent. The appropriate fraction was freeze dried to provide the final product as a white solid.

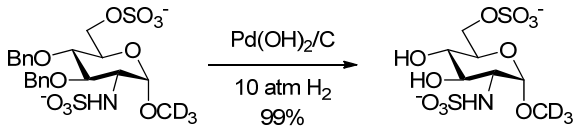
d3-Methyl 2-deoxy-2-*N*-sulfo-6-*O*-sulfo-*β*-D-glucopyranoside (28)



15 **28**

Method A was applied to provide compound **28** (15 mg, 99%) as a white solid: ^{1}H NMR (400 MHz, D_2O) δ 8.45 (s, 1H), 4.48 (d, J = 8.4 Hz, 1H), 4.35 (dd, J = 11.1, 2.0 Hz, 1H), 4.23 (dd, J = 11.2, 5.2 Hz, 1H), 3.73–3.59 (m, 2H), 3.57–3.44 (m, 1H), 3.02 (dd, J = 10.0, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 102.43, 74.45, 73.36, 69.46, 66.95, 59.77; ESI-MS *m/z* calcd for $C_7H_{10}D_3NO_{11}S_2$ $[M\text{-}2H]^{2-}$ 177.0, found 176.8.

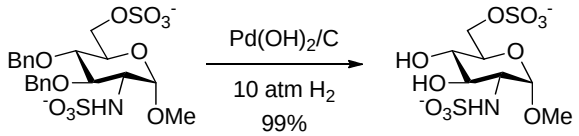
d3-Methyl 2-deoxy-2-*N*-sulfo-6-*O*-sulfo-*α*-D-glucopyranoside (29)



17 **29**

Method A was applied to provide compound **29** (21 mg, 99%) as a white solid: ^{1}H NMR (400 MHz, D_2O) δ 4.98 (d, J = 3.5 Hz, 1H), 4.28 (dd, J = 11.2, 2.0 Hz, 1H), 4.21 (dd, J = 11.2, 5.0 Hz, 1H), 3.88–3.78 (m, 1H), 3.52 (dt, J = 18.9, 9.2 Hz, 2H), 3.22 (dd, J = 10.1, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 98.35, 71.12, 69.54, 69.33, 67.00, 57.43; ESI-MS *m/z* calcd for $C_7H_{10}D_3NO_{11}S_2$ $[M\text{-}2H]^{2-}$ 177.0, found 176.8.

Methyl 2-deoxy-2-*N*-sulfo-6-*O*-sulfo-*α*-D-glucopyranose (30)



19 **30**

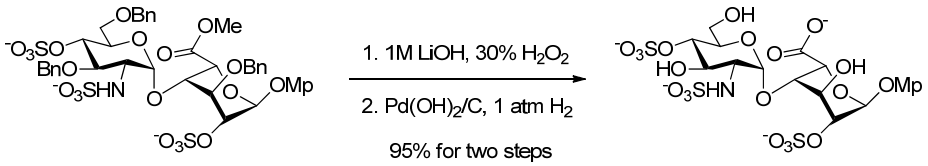
Method A was applied to provide compound **30** (23 mg, 99%) as a white solid: ^{1}H NMR (400 MHz, D_2O) δ 5.03 (d, J = 3.6 Hz, 1H), 4.33 (dd, J = 11.2, 2.1 Hz, 1H), 4.26 (dd, J = 11.2, 5.1 Hz, 1H), 3.88 (ddd, J = 9.7, 4.9, 2.0 Hz, 1H), 3.64–3.48 (m, 2H), 3.43 (s, 3H), 3.28 (dd, J = 10.1, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 98.50, 71.26, 69.62, 69.45, 67.09, 57.56, 55.42; ESI-MS *m/z* calcd for $C_7H_{13}NO_{11}S_2$ $[M\text{-}H]^-$ 352.0, found 351.9; $[M\text{-}2H]^{2-}$ 175.5, found 175.3.

General procedure for full deprotection of the corresponding per-O,N-sulfonated substrates. **Method B** (**31-34**). A premixed solution of 30% solution of H_2O_2 in water (100 equiv per CO_2Me) and 1 M LiOH (50 equiv per CO_2Me) was added to a solution of the starting material in THF (0.02 M) at 0 ^oC. The mixture was stirred at 0 ^oC for 24 h. The mixture was then brought to pH = 8~8.5 by addition of acidic resin, and was then filtered. The filtrate was concentrated *in vacuum* (bath temperature 20~30 °C). The residue was dissolved in CH_2Cl_2/MeOH (v/v = 1/1). The resulting solution was layered on the top of a Sephadex LH-20 chromatography column and was then eluted

with CH_2Cl_2/MeOH (v/v = 1/1). The appropriate fraction was concentrated *in vacuum* to provide the product.

Palladium hydroxide on carbon (Degussa type, 20%, 1.5~2.0 times the weight of the starting material) was added to a solution of the starting material in CH_3OH and pH = 7 Buffer H_2O (1 mL for 10~20 mg, v/v = 1/1). The mixture was placed under an atmosphere of hydrogen for 24 h. The mixture was filtered and concentrated. The residue was diluted with H_2O. The solution was layered on the top of a Sephadex G-10 column that was eluted with H_2O. The fractions containing product were concentrated *in vacuum*. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using H_2O as eluent. The appropriate fraction was freeze dried to provide the final product as a white solid.

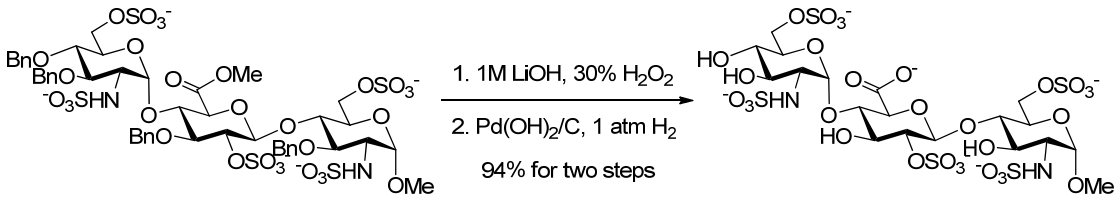
4-Methoxyphenyl 2-*N*-sulfo-4-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-2-*O*-sulfo-*α*-L-iduropyranosiduronate (31)



9 **31**

Method B was applied to provide compound **31** (7 mg, 95%) as a white solid: ^{1}H NMR (400 MHz, D_2O) δ 7.63–6.91 (m, 20H), 5.48 (d, J = 3.7 Hz, 1H), 4.94 (t, J = 11.2 Hz, 2H), 4.90–4.80 (m, 4H), 4.78 (dd, J = 7.1, 3.5 Hz, 2H), 4.67 (dd, J = 15.5, 9.3 Hz, 2H), 4.10–3.59 (m, 14H), 3.53 (t, J = 9.4 Hz, 1H), 3.45–3.18 (m, 6H); ^{13}C NMR (100 MHz, D_2O) δ 174.53, 154.90, 150.37, 129.27, 125.44, 119.68, 115.18, 99.21, 97.03, 77.18, 76.10, 75.61, 70.26, 69.62, 69.07, 68.51, 60.22, 57.96, 55.92; ESI-MS *m/z* calcd for $C_{19}H_{25}NO_{21}S_3$ $[M-2H]^{2-}$ 349.5, found 349.6.

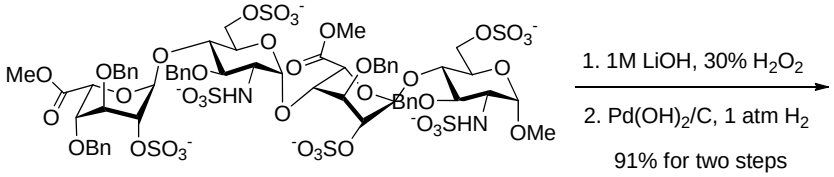
Methyl 2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-2-*O*-sulfo-*β*-D-glucopyanosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (32)



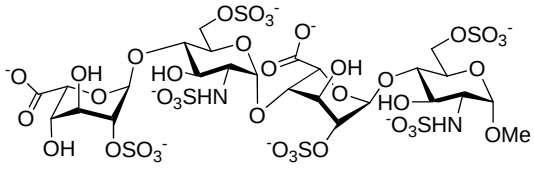
13 **32**

Method B was applied to provide compound **32** (11 mg, 94%) as a white solid: $[\alpha]_D^{28}$ = 23.9 (*c* 0.3, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.69 (d, 1 H, *J* = 2.4 Hz), 5.07 (d, 1 H, *J* = 2.8 Hz), 4.62 (d, 1 H, *J* = 10.0 Hz), 4.40 (d, 1 H, *J* = 10.4 Hz), 4.29 (d, 1 H, *J* = 11.2 Hz), 4.23–4.15 (m, 2 H), 4.04–3.60 (m, 9 H), 3.46 (s, 3 H), 3.33-3.27 (m, 2 H); ^{13}C NMR (100 MHz, D_2O) δ 100.07, 98.31, 97.82, 79.93, 77.91, 76.47, 75.05, 71.30, 69.95, 69.48, 69.08, 68.10, 66.39, 65.97, 57.94, 57.26, 55.51; ESI-MS *m/z* calcd for $C_{19}H_{31}N_2O_{30}S_5$ $[M-3H]^{3-}$ 309.0, found 309.2; *m/z* calcd for $C_{19}H_{32}N_2O_{30}S_5$ $[M-2H]^{2-}$ 464.0, found 464.2.

Methyl 2-*O*-sulfo-*α*-L-iduropyanosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-2-*O*-sulfo-*α*-L-iduropyanosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (33)



25

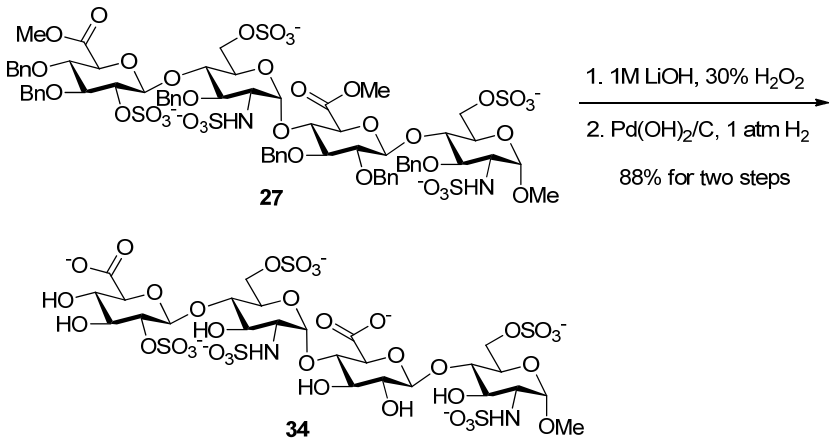


33

Method B was applied to provide compound **33** (20 mg, 91%) as a white solid: $[\alpha]_D^{28}$ = 13.8 (*c* 0.8, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.44 (d, *J* = 3.5 Hz, 1H), 5.23 (d, *J* = 3.2 Hz, 1H), 5.19 (s, 1H), 5.04 (d, *J* = 3.6 Hz, 1H), 4.87 (d, *J* = 2.3 Hz, 1H), 4.41–4.24 (m, 7H), 4.20 (dd, *J* = 6.3, 3.8 Hz, 1H), 4.13 (d, *J* = 3.7 Hz, 2H), 4.07 (d, *J* = 9.7 Hz, 1H), 4.03–3.95 (m, 2H), 3.83–3.62 (m, 4H), 3.44 (s, 3H), 3.29 (dt, *J* = 10.2,

3.7 Hz, 2H); ^{13}C NMR (100 MHz, D_2O) δ 176.38, 174.53, 99.47, 99.19, 98.32, 96.51, 77.09, 76.48, 76.04, 74.16, 69.98, 69.72, 69.21, 68.98, 68.62, 67.00, 58.08, 57.80, 55.50; ESI-MS *m/z* calcd for $C_{25}H_{42}N_2O_{39}S_6$ $[M-3H]^{3-}$ 394.3, found 394.6.

Methyl 2-*O*-sulfo-*β*-D-glucopyranosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-*β*-D-glucopyanosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (34)



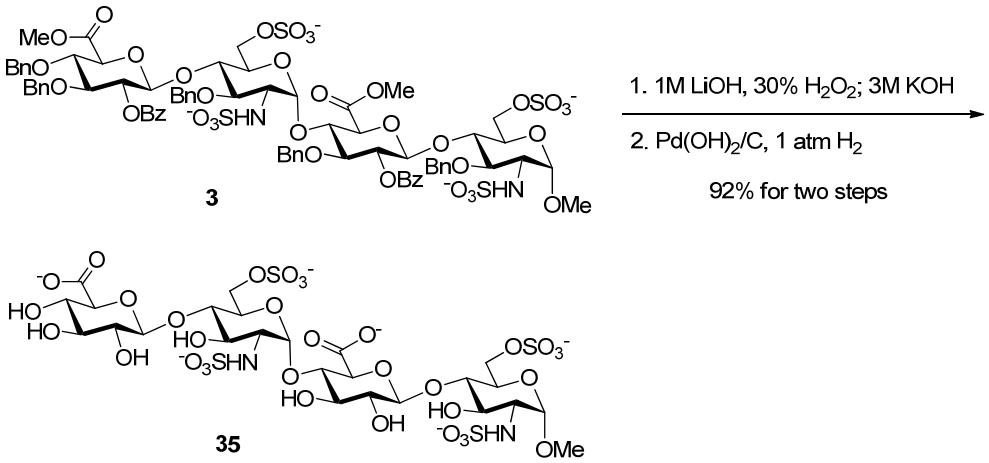
Method B was applied to provide compound **34** (16 mg, 88%) as a white solid: $[\alpha]_D^{28}$ = 21.4 (*c* 0.2, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.52 (d, 1 H, *J* = 3.6 Hz), 5.05 (d, 1 H, *J* = 3.2 Hz), 4.79 (d, 1 H), 4.60 (d, 1 H, *J* = 8.0 Hz), 4.56 (d, 1 H, *J* = 10.8 Hz), 4.42 (d, 1 H, *J* = 10.8 Hz), 4.33 (dd, 1 H, *J* = 11.2 Hz, 3.6 Hz) , 4.20 (d, 1 H, *J* = 10.8 Hz), 4.12 (t, 1 H, *J* = 8.8 Hz), 4.03–4.01 (m, 2 H), 3.88–3.68 (m, 9 H), 3.60 (t, 1 H, *J* = 9.6 Hz), 3.44 (s, 3 H), 3.42–3.31 (m, 3 H); ^{13}C NMR (100 MHz, D_2O) δ 181.53, 175.60, 102.23, 100.81, 99.84, 98.21, 79.70, 78.81, 78.67, 77.58, 76.63, 75.74, 75.68, 74.48, 72.96, 71.74, 69.70, 69.36, 69.01, 68.25, 66.62, 65.87, 57.86, 57.24, 55.50; ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{36}S_5$ $[M-3H^+]^{3-}$ 367.7, found 367.5.

General procedure for full deprotection of the corresponding per-O,N-sulfonated substrates. **Method C (35).** A premixed solution of 30% solution of H_2O_2 in water (100 equiv per CO_2Me) and 1 M LiOH (50 equiv per CO_2Me) were added to a solution of the starting material in THF (0.02 M). The mixture was stirred at rt for 24 h. A solution of KOH (3 M) was added until pH = ~14. The mixture was left stirring for 24 h at room temperature. The mixture was then brought to pH = 8~8.5 by

addition of acidic resin, and was then filtered. The filtrate was concentrated *in vacuum* (bath temperature 20~30 °C). The residue was dissolved in CH_2Cl_2/MeOH (v/v = 1/1). The resulting solution was layered on the top of a Sephadex LH-20 chromatography column and was then eluted with CH_2Cl_2/MeOH (v/v = 1/1). The appropriate fraction was concentrated *in vacuum* to provide the pure product.

Palladium hydroxide on carbon (Degussa type, 20%, 1.5~2.0 times the weight of the starting material) was added to a solution of the starting material in CH_3OH and pH = 7 Buffer H_2O (1 mL for 10~20 mg, v/v = 1/1). The mixture was placed under an atmosphere of hydrogen for 24 h. The mixture was filtered and concentrated. The residue was diluted with H_2O. The solution was layered on the top of a Sephadex G-10 column that was eluted with H_2O. The fractions containing product were concentrated *in vacuum*. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using H_2O as eluent. The appropriate fraction was freeze dried to provide the final product as a white solid.

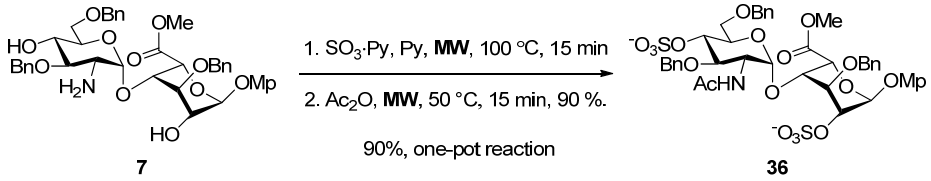
Methyl *β*-D-glucopyranosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-*β*-D-glucopyanosyluronate-(1→4)-2-*N*-sulfo-6-*O*-sulfo-2-deoxy-*α*-D-glucopyranoside (35)



Method B was applied to provide compound **35** (36 mg, 92%) as a white solid: $[\alpha]_D^{28}$ = 21.0 (*c* 0.1, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.66 (d, *J* = 3.5 Hz, 1H), 5.05 (d, *J* = 3.5 Hz, 2H), 4.60 (d, *J* = 7.8 Hz, 3H), 4.48 (d, *J* = 10.0 Hz, 1H), 4.41 (d, *J* = 10.0 Hz, 1H), 4.33 (dd, *J* = 11.1, 4.9 Hz, 1H), 4.19 (d, *J* = 10.8 Hz, 1H), 4.03 (d, *J* = 9.7 Hz, 2H), 3.91–3.63 (m, 9H), 3.60–3.25 (m, 10H); ^{13}C NMR (100 MHz, D_2O) δ

175.73, 174.87, 101.90, 101.71, 98.14, 97.03, 78.14, 76.86, 76.25, 76.19, 75.99, 75.65, 74.98, 72.86, 72.80, 71.79, 69.53, 69.34, 68.55, 68.08, 66.30, 65.70, 57.45, 57.13, 55.45; ESI-MS *m/z* calcd for $C_{25}H_{39}N_2O_{33}S_4Na$ $[M+Na-3H]^{2-}$ 523.1, found 523.6.

4-Methoxyphenyl 2-*N*-acetyl-3,6-di-*O*-benzyl-4-*O*-sulfo-2-deoxy-*α*-D-glucopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-sulfo-*β*-D-glucopyranosiduronate) (36)

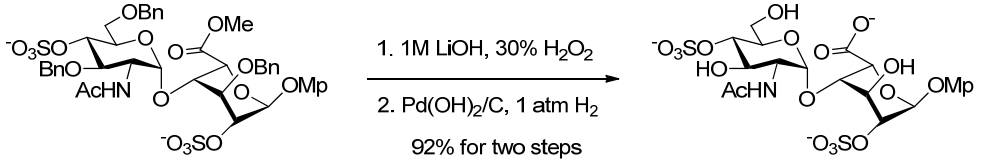


General Procedure for the microwave-assisted simultaneous O-sulfonation and N-acetylation. Sulfur trioxide pyridine complex (3 equiv per OH) was added to a solution of the starting material in pyridine (1.0 mL for 30 mg starting material). The mixture was stirred at room temperature for 5 min, then subjected to microwave radiation for 15 min at a fix temperature of 100 ^oC (average power of 18 W). Acetic anhydride (2 equiv per NH_2) was added, the mixture was then subjected to microwave radiation for another 15 min at a fix temperature of 50 ^oC. After the addition of CH_3OH (0.5 mL) and trimethylamine (1 mL), stirring was continued for 15 min. The mixture was concentrated in vacuum. The residue was applied to a small RP-18 silica gel column, which was eluted with a stepwise gradient of H_2O and CH_3OH (from v/v = 1/0, to 1/9, to 1/2). The fractions containing the product were concentrated in vacuum. The residue was immediately passed through a column of Dowex 50WX4 Na^+ resin using CH_3OH as eluent. The fractions containing the product were concentrated in vacuum to provide the product as sodium salt.

The general procedure for the microwave-assisted simultaneous O-sulfonation and N-acetylation was applied to provide compound **36** (7 mg, 90%) as a white solid: $[\alpha]_D^{27}$ = 14.4 (*c* 0.7, MeOH); ^1H NMR (400 MHz, CD_3OD) δ 7.55 (d, *J* = 9.6 Hz, 1H), 7.43–7.14 (m, 14H), 7.04 (d, *J* = 9.1 Hz, 2H), 6.86 (d, *J* = 9.1 Hz, 2H), 5.82 (s, 1H), 5.12 (d, *J* = 10.7 Hz, 1H), 5.00 (s, 2H), 4.81 (d, *J* = 11.9 Hz, 2H), 4.72–4.51 (m, 5H), 4.39 (t, *J* = 9.3 Hz, 1H), 4.26 (s, 2H), 4.21–4.12 (m, 1H), 4.05 (d, *J* = 9.2 Hz, 1H),

3.77 (d, J = 10.0 Hz, 7H), 3.71–3.62 (m, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 174.01, 171.27, 156.72, 151.79, 140.20, 139.90, 139.07, 129.62, 129.38, 129.24, 129.06, 128.92, 128.77, 128.43, 128.37, 119.11, 115.68, 99.76, 96.03, 80.55, 78.38, 76.49, 74.35, 72.88, 72.42, 71.45, 71.00, 70.87, 70.55, 68.43, 56.04, 53.62, 53.14, 23.36; ESI-MS *m/z* calcd for $C_{43}H_{47}NO_{19}S_2$ $[M-2H]^{2-}$ 472.6, found 473.6.

4-Methoxyphenyl 2-*N*-acetyl-4-*O*-sulfo-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-sulfo-α-L-iduropyranosiduronate (37)



36 **37**

Method B was applied to provide compound **37** (5 mg, 92%) as a white solid: ^{1}H NMR (400 MHz, D_2O) δ 7.17 (d, J = 9.1 Hz, 2H), 7.00 (d, J = 9.1 Hz, 2H), 5.70 (s, 1H), 5.18 (d, J = 3.5 Hz, 1H), 4.49 (s, 1H), 4.39 (s, 1H), 4.26 (t, J = 9.3 Hz, 1H), 4.16–4.04 (m, 2H), 3.97–3.77 (m, 7H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, D_2O) δ 174.66, 154.74, 149.96, 119.49, 114.96, 98.72, 93.32, 76.73, 73.43, 70.68, 70.17, 69.71, 67.50, 63.63, 59.99, 55.66, 52.98, 22.11; ESI-MS *m/z* calcd for $C_{21}H_{27}NO_{19}S_2$ $[M-2H]^{2-}$ 330.5, found 330.8.

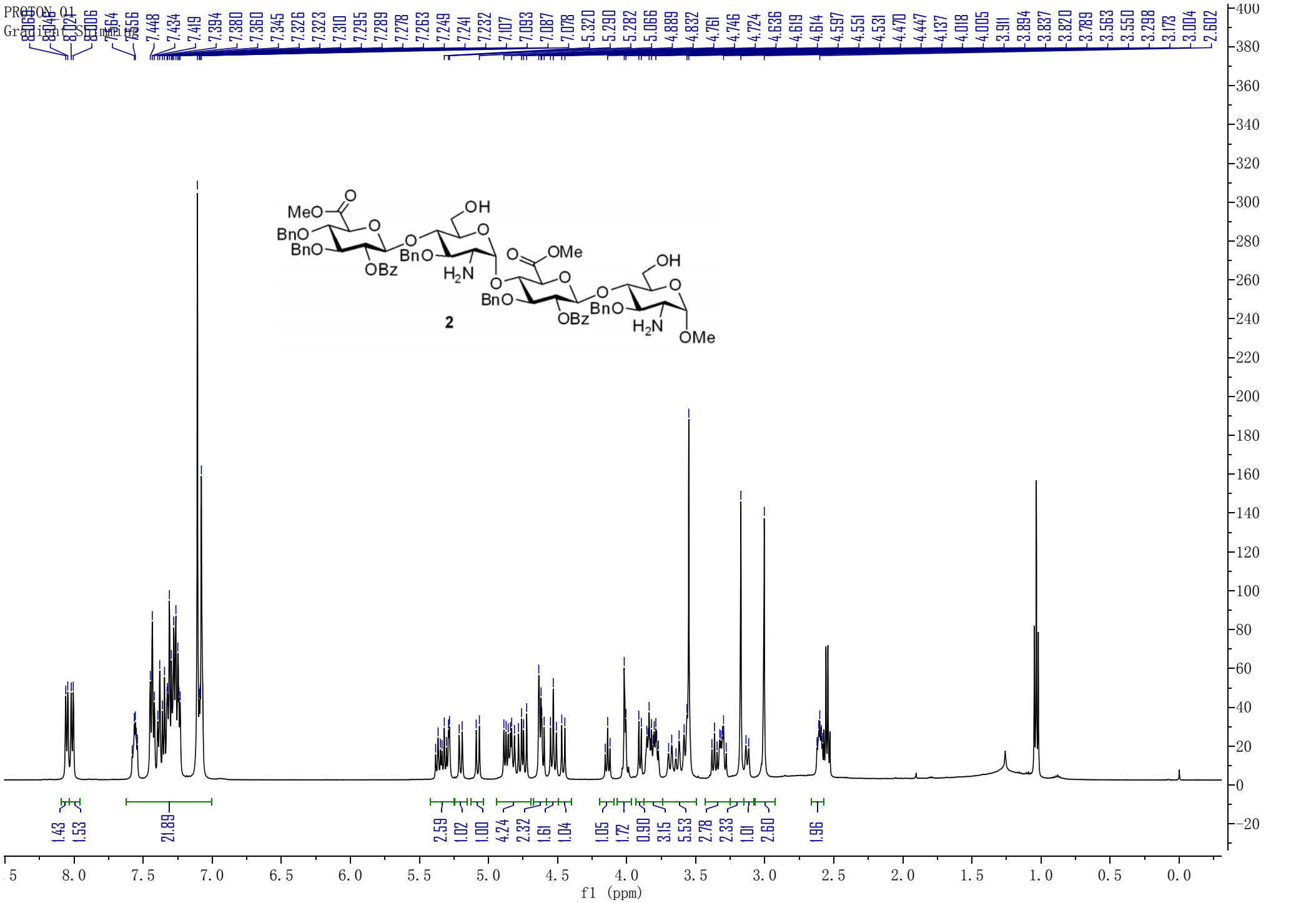
References for known compounds:

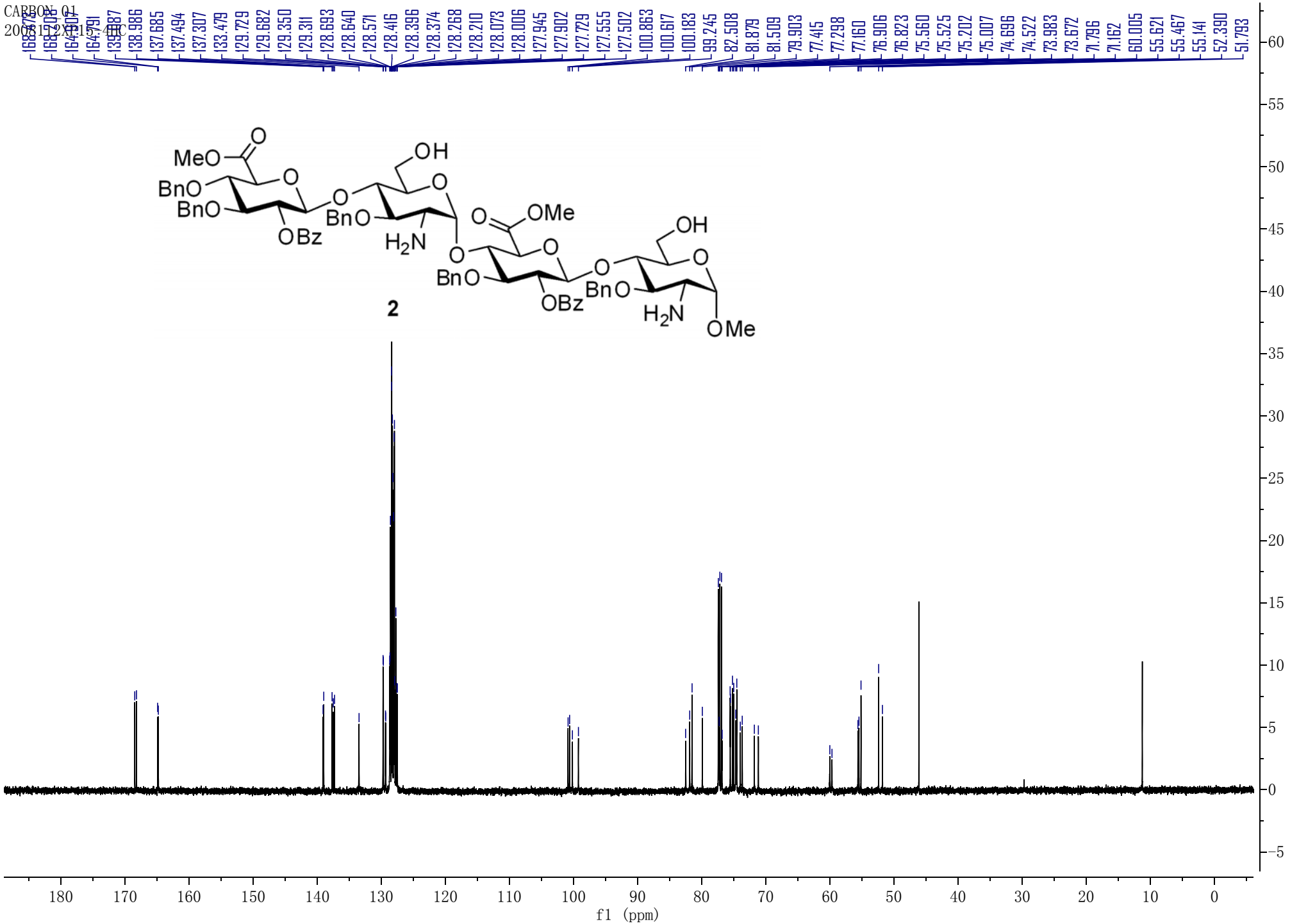
Compounds **1, S5, S10, S13, S14:** P. Xu, W. Xu, Y. Dai, Y. Yang and B. Yu, *Org. Chem. Front.*, **2014**, *1*, 405-414.

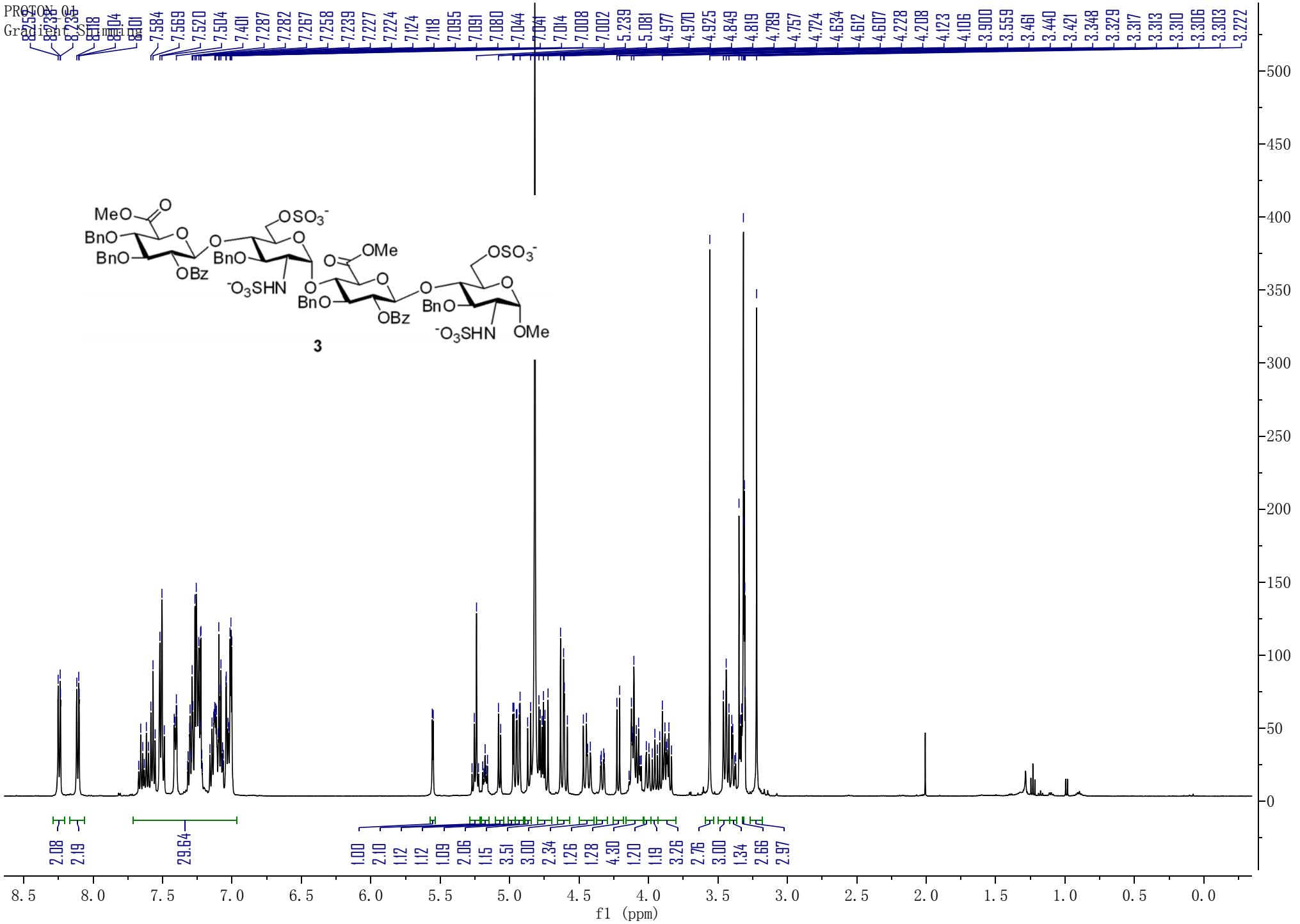
Compounds **S11, S12**: J. Li, Y. Dai, W. Li, S. Laval, P. Xu, and B. Yu, *Asian J. Org. Chem.,* **2015**, 4, 756-762.

Compound **S1**: M. Martin-Lomas, N. Khiar, S. Garcia, J. Koessler, P. M. Nieto, T. W. Rademacher, *Chem. Eur. J.,* **2000**, 6, 3608-3621.

Compound **S7**: P. Traar, F. Belaj, K. A. Francesconi, *Aust. J. Chem.,* **2004**, 57, 1051-1053.


PROTON-01
Gradient, 32 scans
MeO
BnO
BnO
OBz
OH
BnO
H_2N
OMe
OBz
BnO
H_2N
OMe
2
f1 (ppm)


CARBON-01
MeO
BnO
BnO
OBz
O
OH
BnO
H2N
OMe
OBz
BnO
H2N
OMe
2
f1 (ppm)


PROTON-01
Gradient Shimmed
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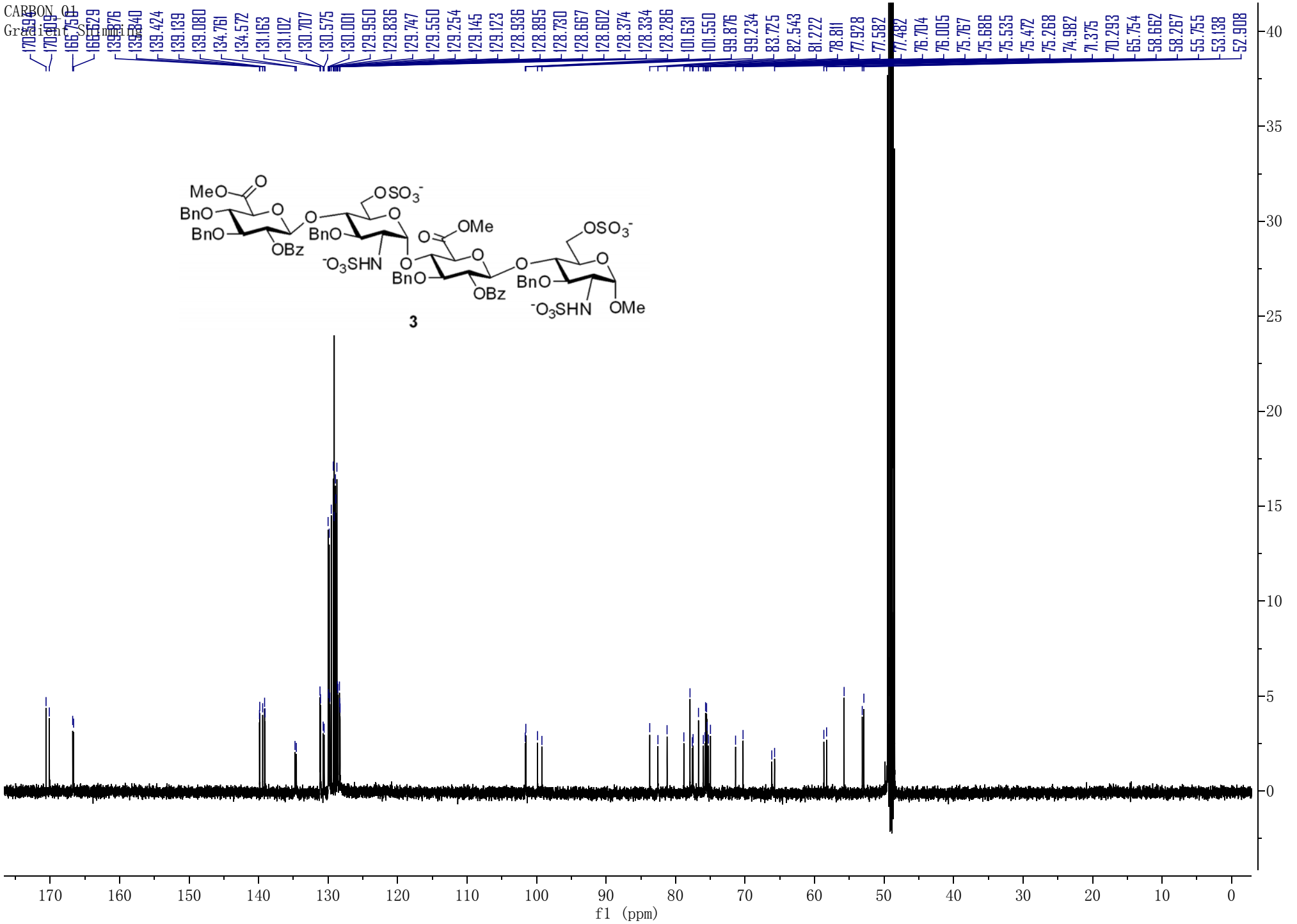
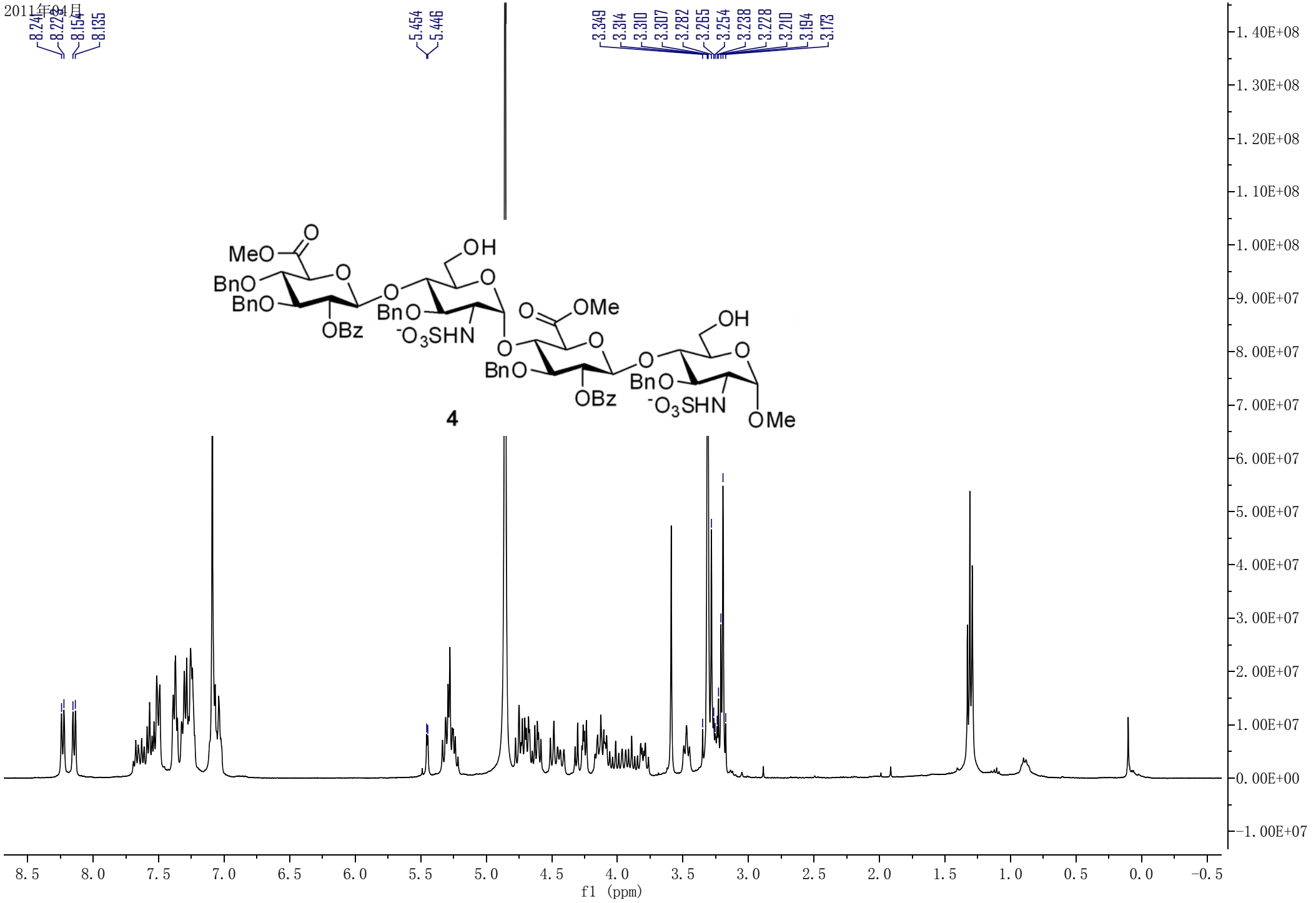
8.233
8.118
8.104
8.101
7.584
7.569
7.520
7.504
7.401
7.287
7.282
7.267
7.258
7.239
7.227
7.224
7.124
7.118
7.095
7.091
7.080
7.044
7.041
7.014
7.008
7.002
5.239
5.081
4.977
4.970
4.925
4.849
4.819
4.789
4.757
4.724
4.634
4.612
4.607
4.228
4.208
4.123
4.106
3.900
3.559
3.461
3.440
3.421
3.348
3.329
3.317
3.313
3.310
3.306
3.303
3.222
MeO
BnO
BnO
OBz
O
OSO3-
BnO
-O3SHN
OMe
BnO
OBz
OSO3-
BnO
-O3SHN
OMe
3
2.08
2.19
29.64
1.00
2.10
1.12
1.12
1.09
2.06
1.15
3.51
3.00
2.34
1.26
1.28
4.30
1.20
1.19
3.26
2.76
3.00
1.34
2.66
2.97
f1 (ppm)


CARBON_01
Gradient_Shimmed
MeO
BnO
BnO
OBz
O
OSO3-
BnO
-O3SHN
OMe
BnO
OBz
OSO3-
BnO
-O3SHN
OMe
3
f1 (ppm)

2011年04月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8.229
8.154
8.135
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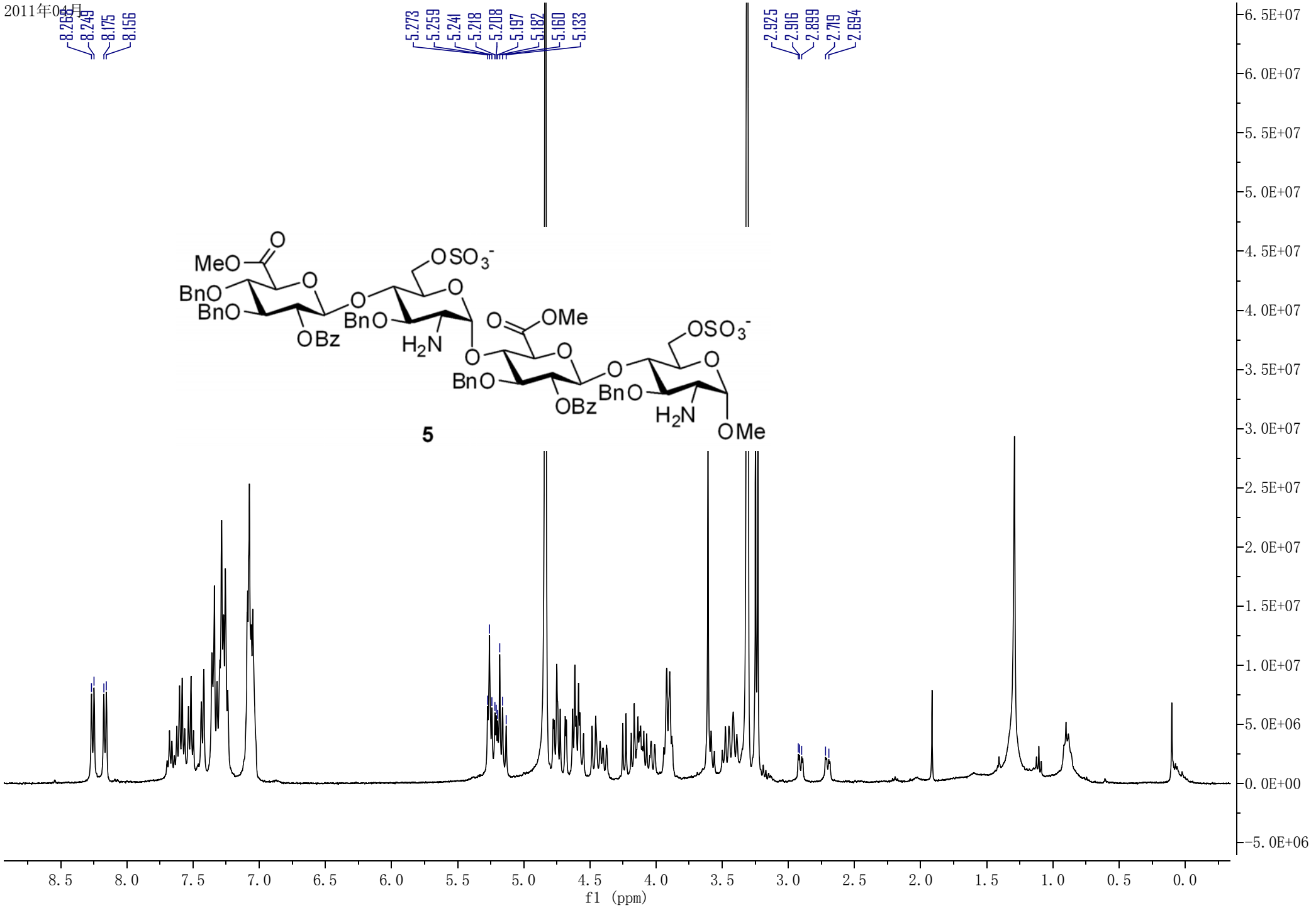
5.446
3.349
3.314
3.310
3.307
3.282
3.265
3.254
3.238
3.228
3.210
3.194
3.173
MeO
BnO
BnO
OBz
OH
BnO
$^{-}O_3SHN$
OMe
BnO
OBz
OH
BnO
$^{-}O_3SHN$
OMe
4
1.40E+08
1.30E+08
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


2011年04月
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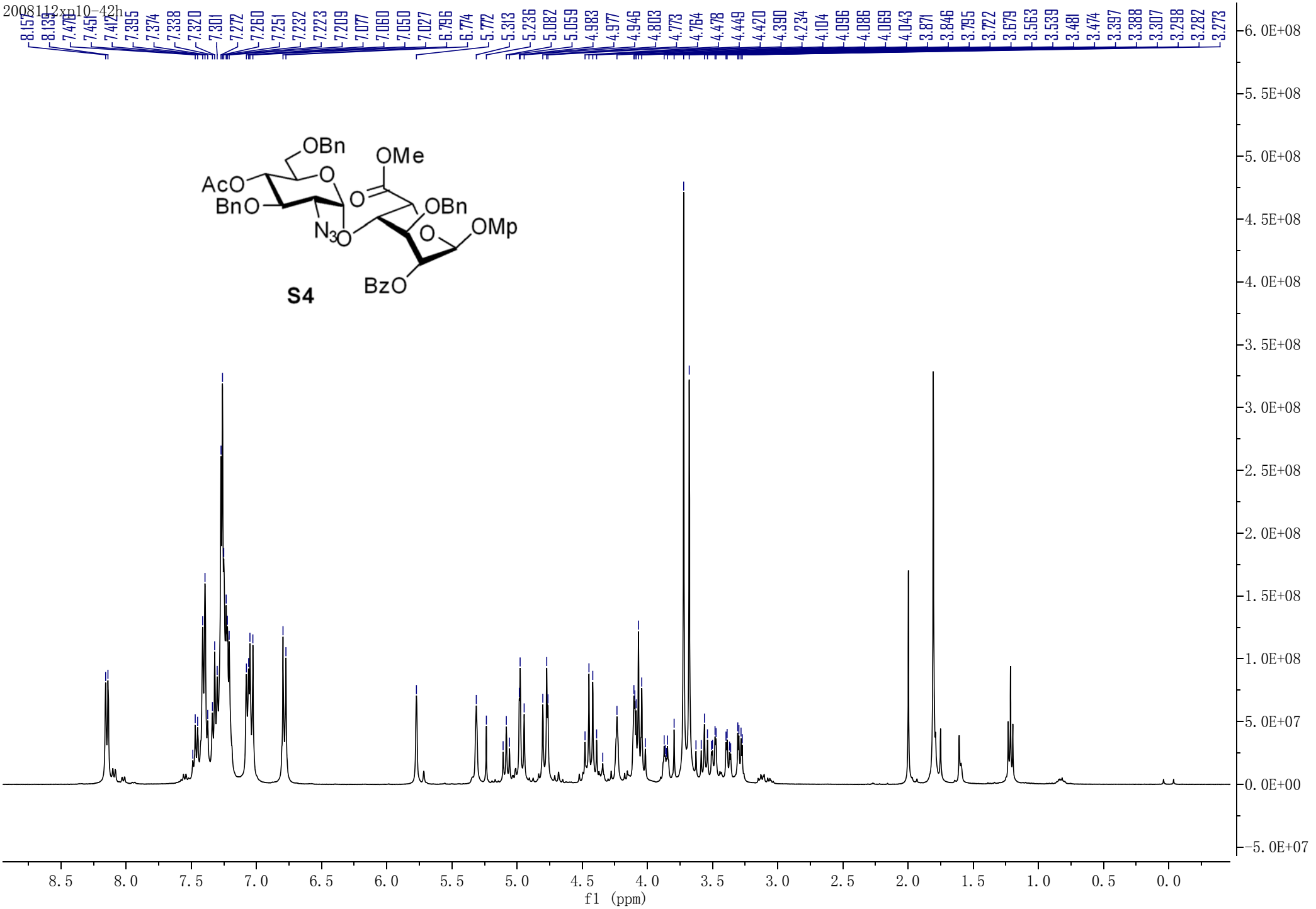
8.175
8.156
5.273
5.259
5.241
5.218
5.208
5.197
5.182
5.160
5.133
2.925
2.916
2.899
2.719
2.694
MeO
BnO
BnO
OBz
BnO
H2N
OSO3-
O
OMe
BnO
OBz
BnO
H2N
OSO3-
OMe
5
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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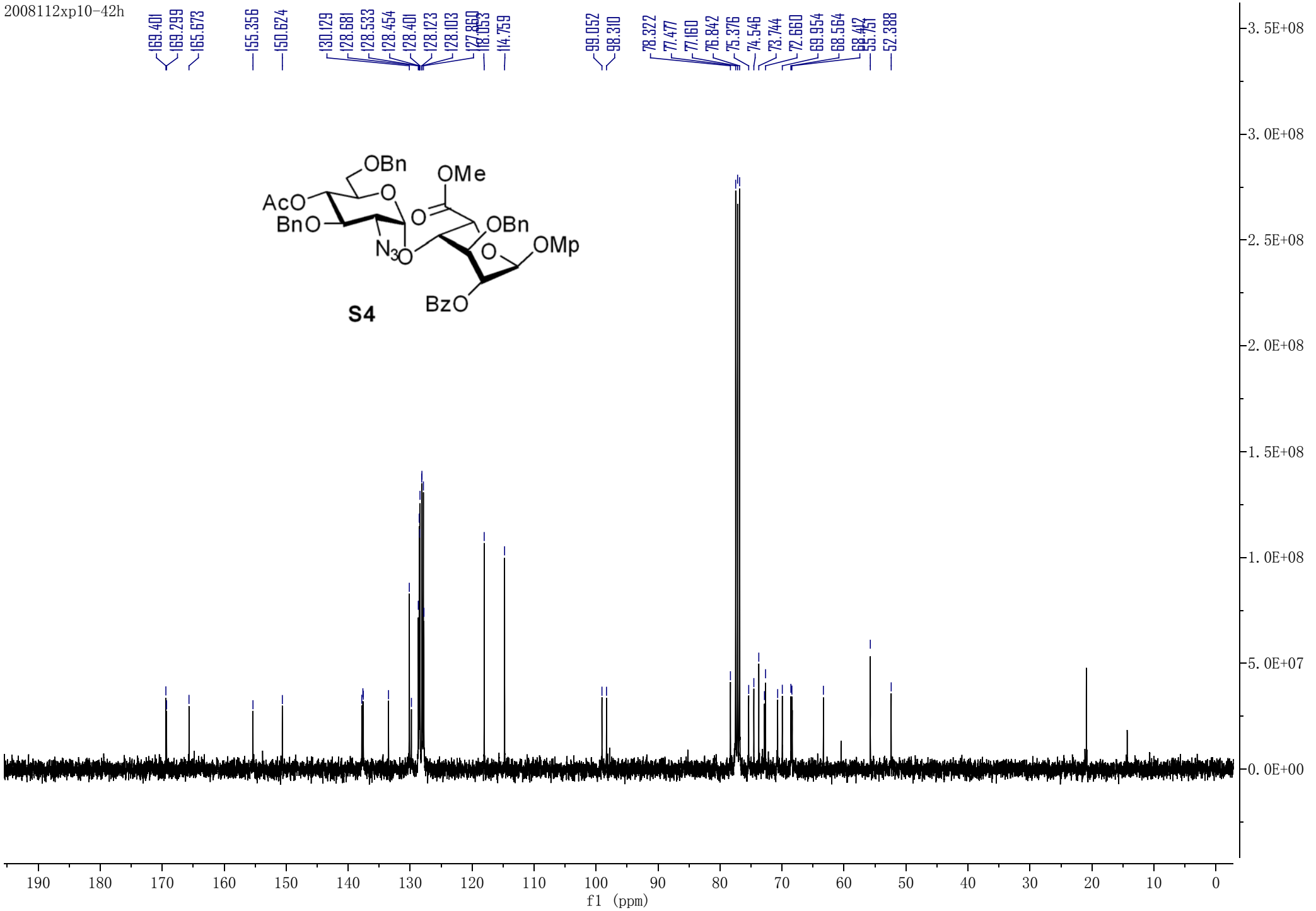
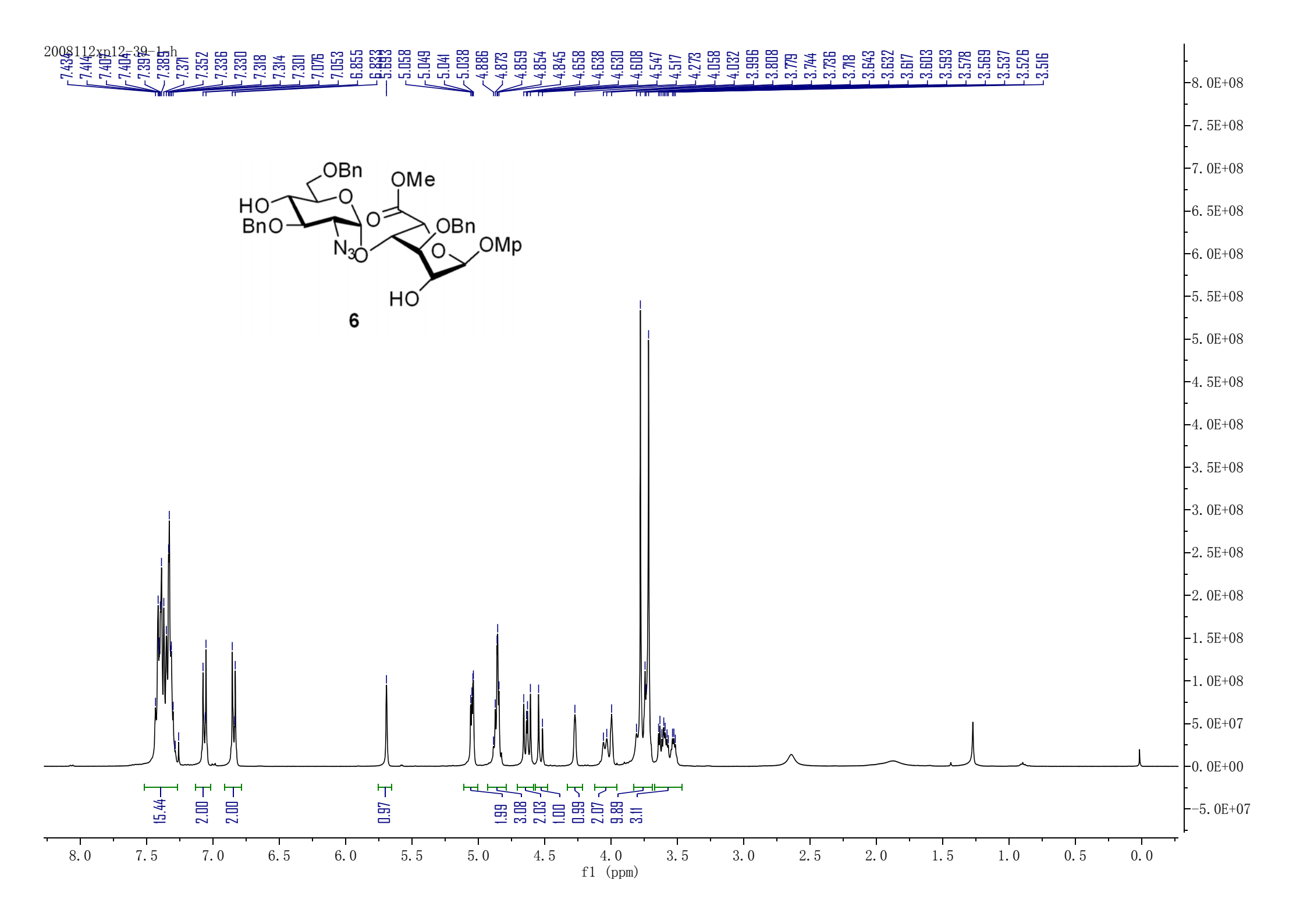
7.478
7.451
7.412
7.395
7.374
7.338
7.320
7.301
7.272
7.260
7.251
7.232
7.223
7.209
7.077
7.060
7.050
7.027
6.796
6.774
5.772
5.313
5.236
5.082
5.059
4.983
4.977
4.946
4.803
4.773
4.764
4.478
4.449
4.420
4.390
4.234
4.104
4.096
4.086
4.069
4.043
3.871
3.846
3.795
3.722
3.679
3.563
3.539
3.481
3.474
3.397
3.388
3.307
3.298
3.282
3.273
OBn
OMe
AcO
O
O
BnO
OBn
N3
O
OMp
BzO
S4
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2008112xp10-42h

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7.407
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7.352
7.336
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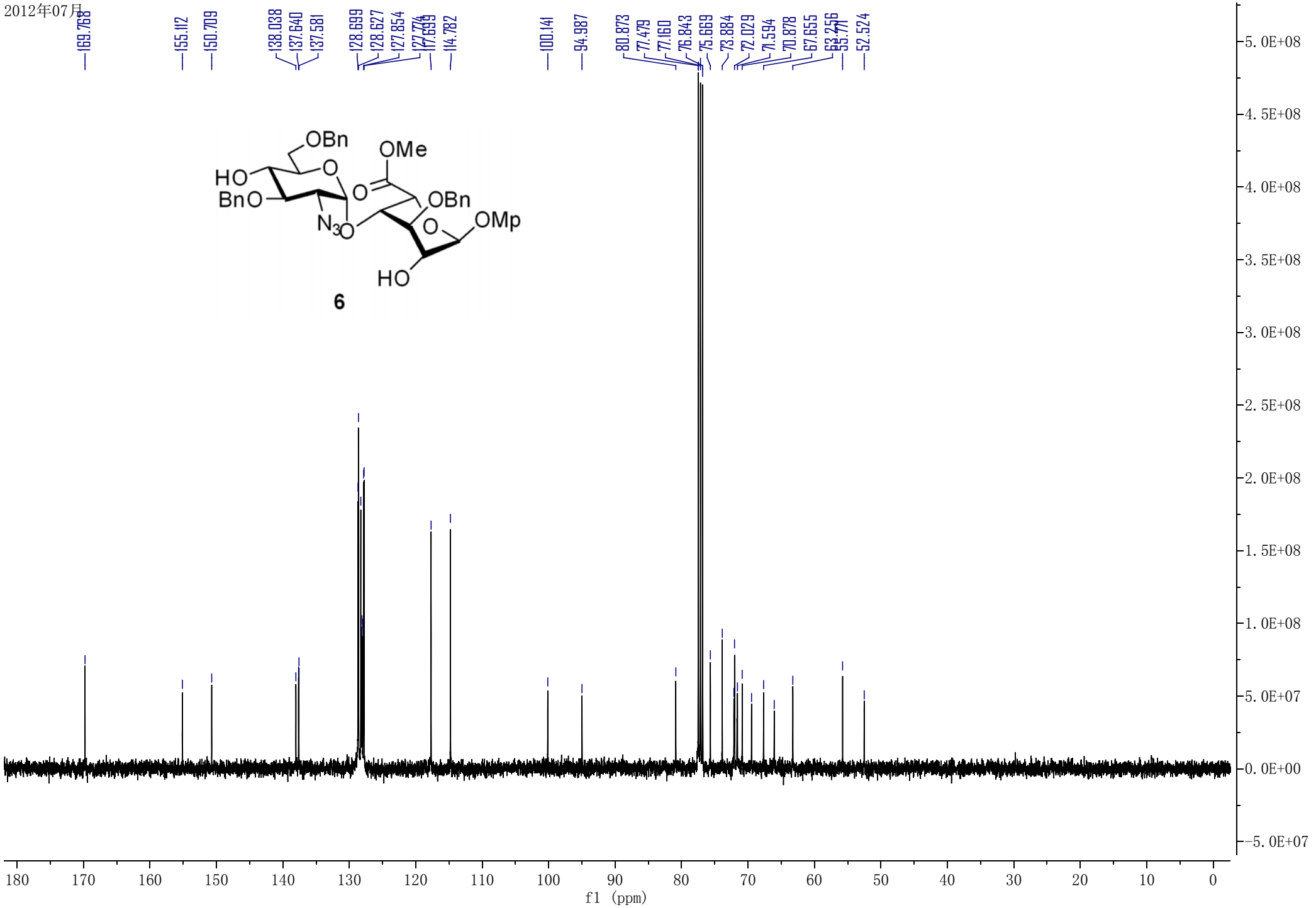
7.318
7.314
7.301
7.076
7.053
6.855
6.833
6.693
5.058
5.049
5.041
5.038
4.886
4.873
4.859
4.854
4.845
4.658
4.638
4.630
4.608
4.547
4.517
4.273
4.058
4.032
3.996
3.808
3.779
3.744
3.736
3.718
3.643
3.632
3.617
3.603
3.593
3.578
3.569
3.537
3.526
3.516
OBn
OMe
HO
O
BnO
O
OBn
N3
O
O
OMp
HO
6
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
15.44
2.00
2.00
0.97
1.99
3.08
2.03
1.00
0.99
2.07
9.89
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2012年07月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155.112
150.709
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137.640
137.581
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128.627
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127.699
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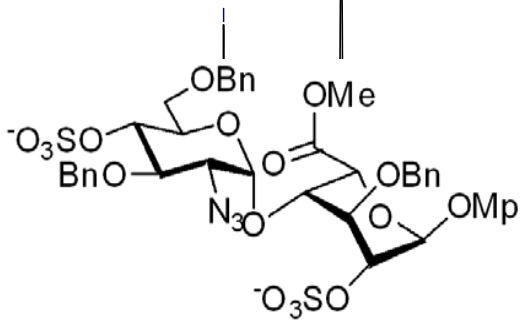
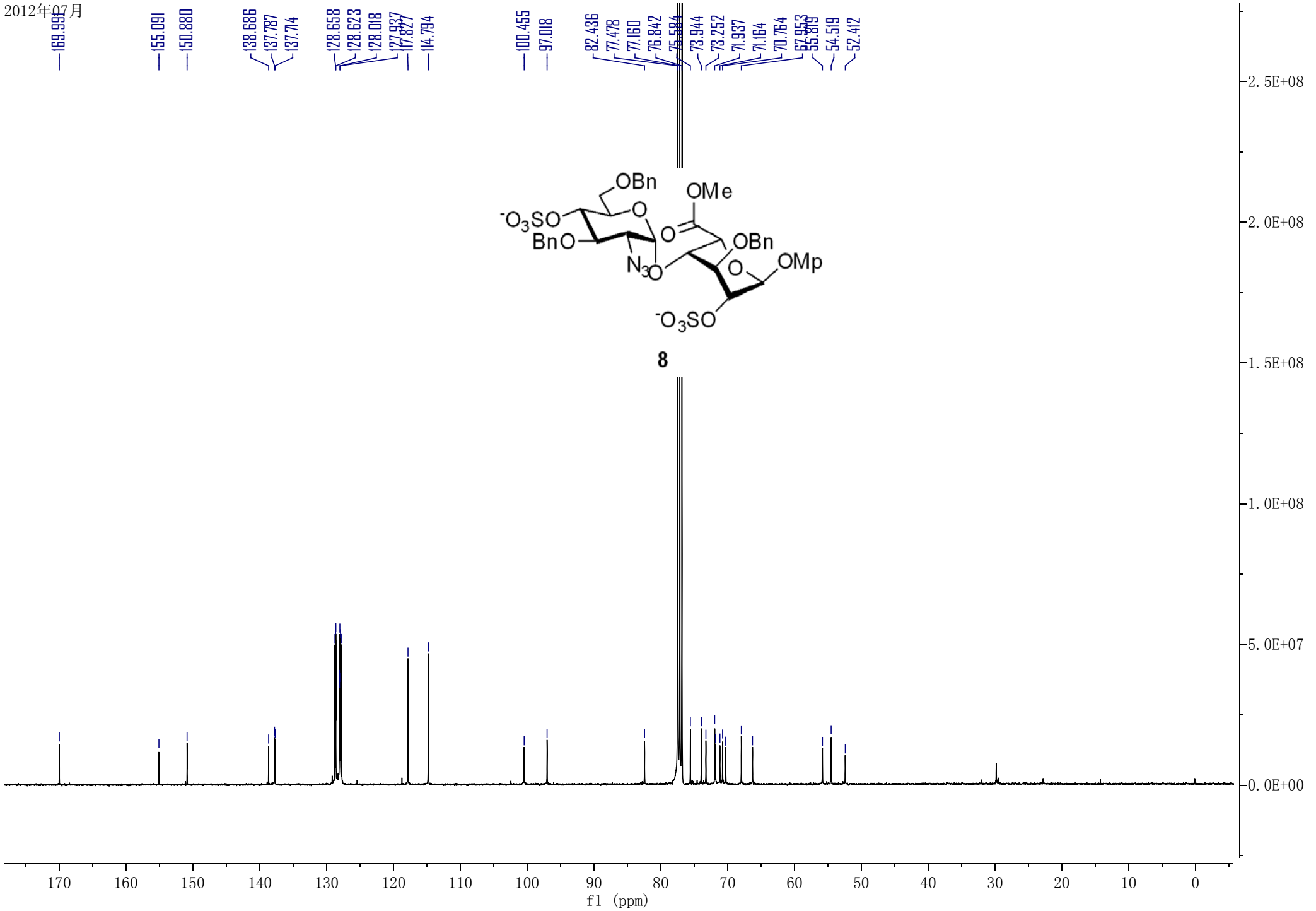
100.141
94.987
80.873
77.479
77.160
76.843
75.669
73.884
72.029
71.594
70.878
67.655
63.256
55.771
52.524
OBn
OMe
HO
O
BnO
OBn
N3
O
OMp
HO
6
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2008112xp12-44--h



8

2012年07月


169.999
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137.787
137.714
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127.937
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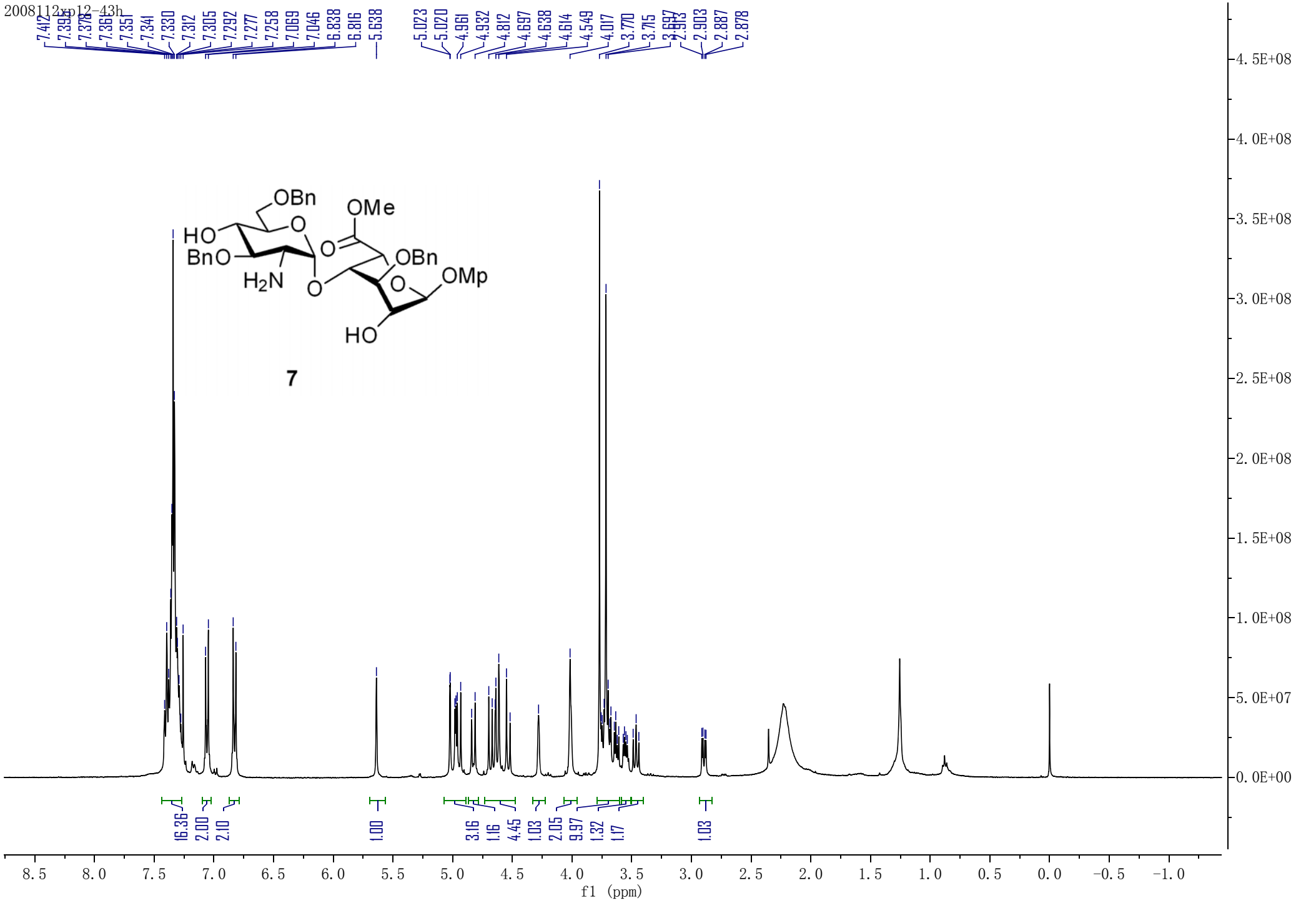
114.794
100.455
97.018
82.436
77.478
77.160
76.842
75.584
73.944
73.252
71.937
71.164
70.764
67.953
55.819
54.519
52.412
OBn
OMe
$^{-}O_3SO$
BnO
O
N3
OBn
OMp
$^{-}O_3SO$
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8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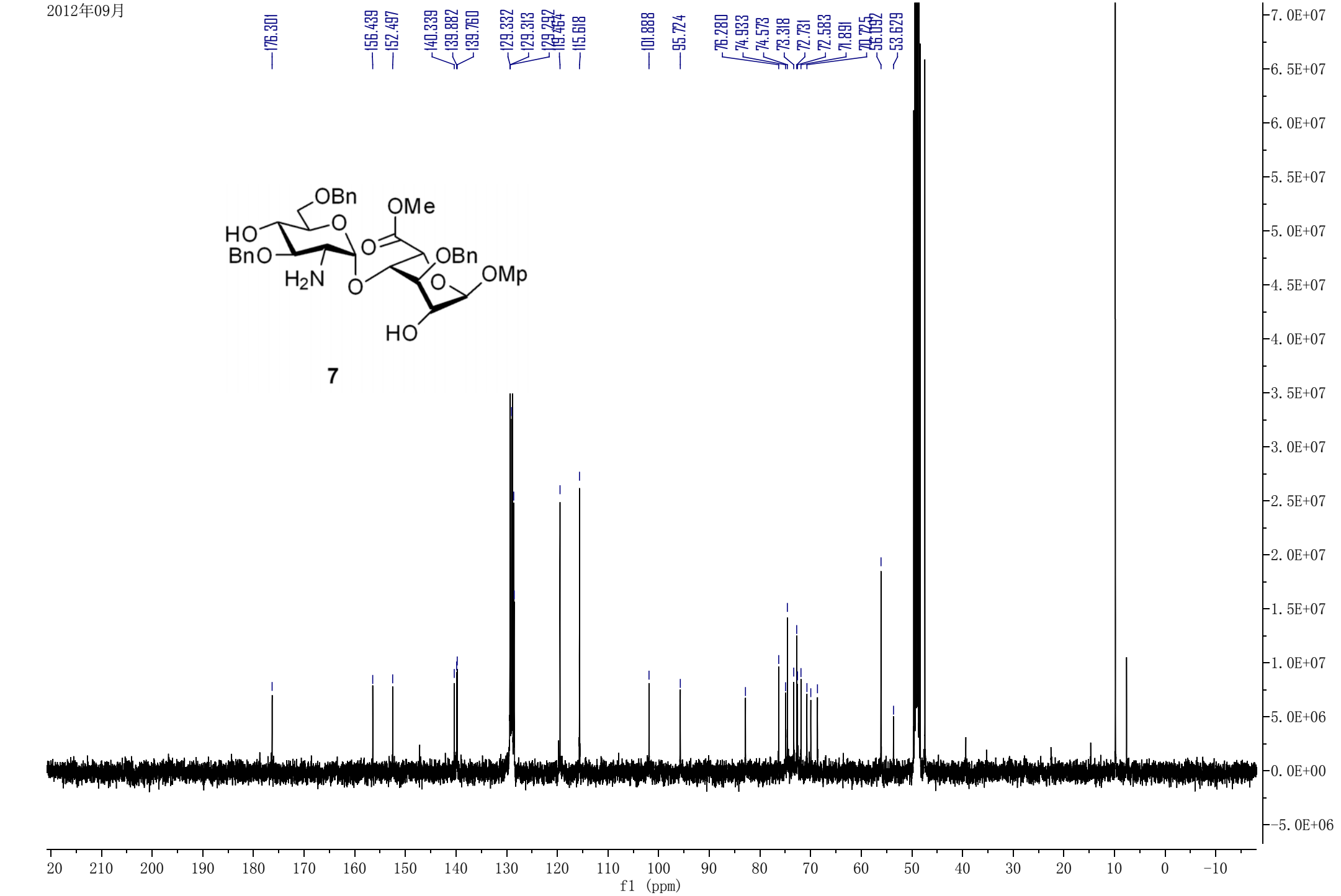
7.277
7.258
7.069
7.046
6.838
6.816
5.638
5.023
5.020
4.961
4.932
4.812
4.697
4.638
4.614
4.549
4.017
3.770
3.715
2.913
2.903
2.887
2.878
OBn
OMe
HO
BnO
H2N
O
OBn
OMp
HO
7
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
16.36
2.00
2.10
1.00
3.16
1.16
4.45
1.03
2.05
9.97
1.32
1.17
1.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2012年09月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156.439
152.497
140.339
139.882
139.760
129.332
129.313
129.292
119.464
115.618
101.888
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76.280
74.933
74.573
73.318
72.731
72.583
71.891
70.725
56.1092
53.629
OBn
OMe
HO
BnO
H2N
O
OBn
OMp
HO
7
7.0E+07
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
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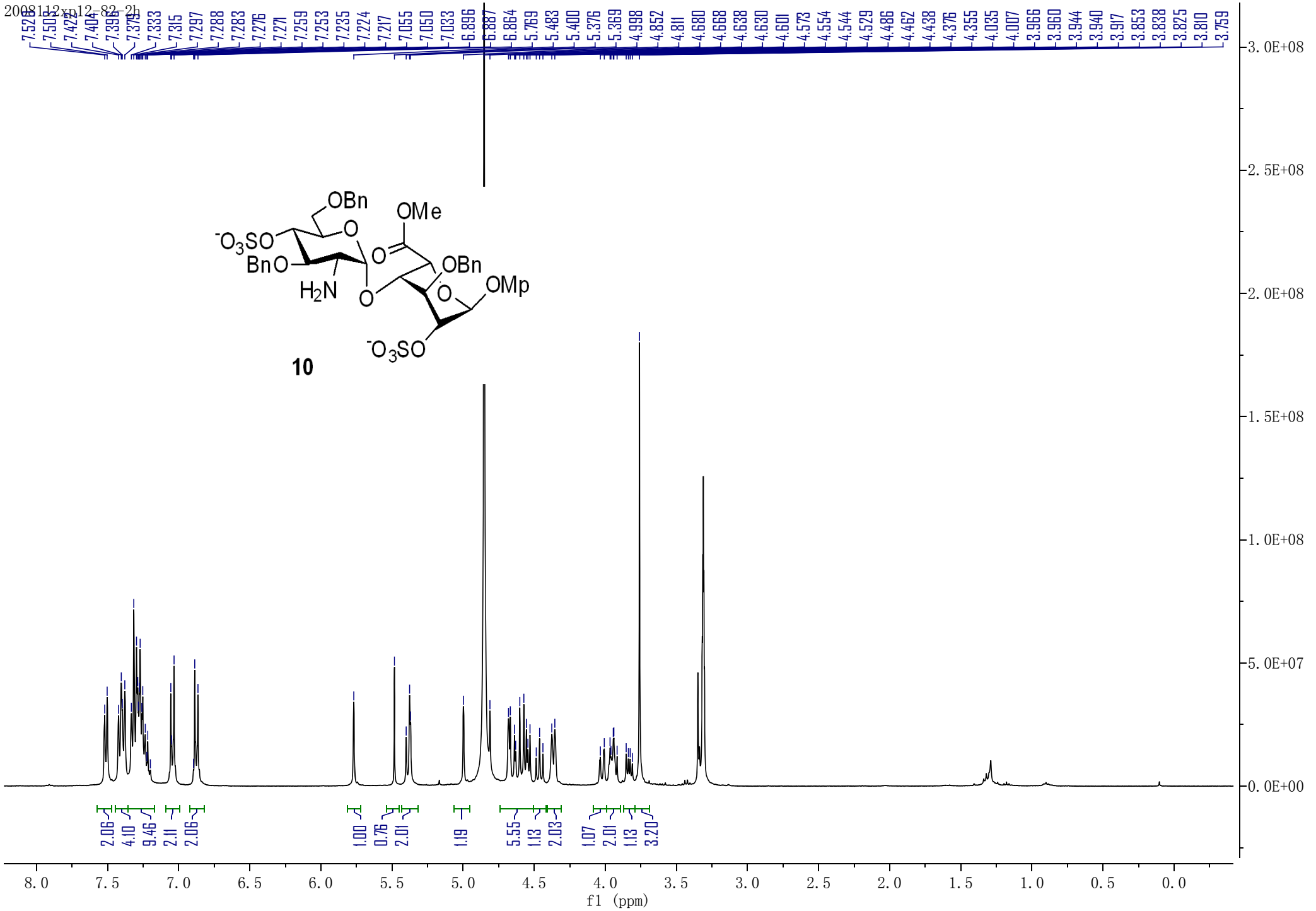
f1 (ppm)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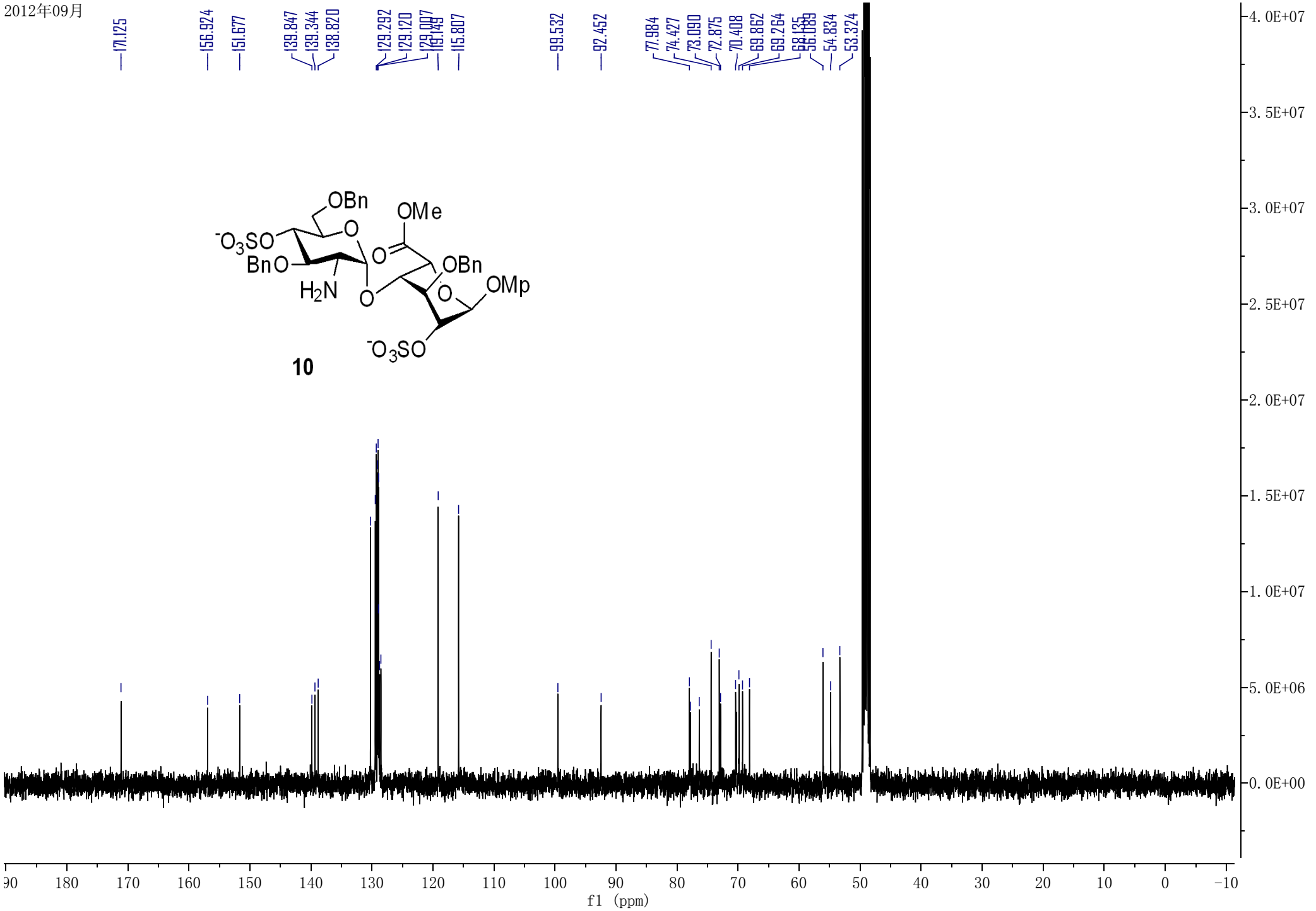
OBn
OMe
$^{-}O_3SO$
O
O
BnO
OBn
H_2N
O
O
OMp
$^{-}O_3SO$
10
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
2.06 4.10 9.46 2.11 2.06 1.00 0.76 2.01 1.19 5.55 1.13 2.03 1.07 2.01 1.13 3.20
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2012年09月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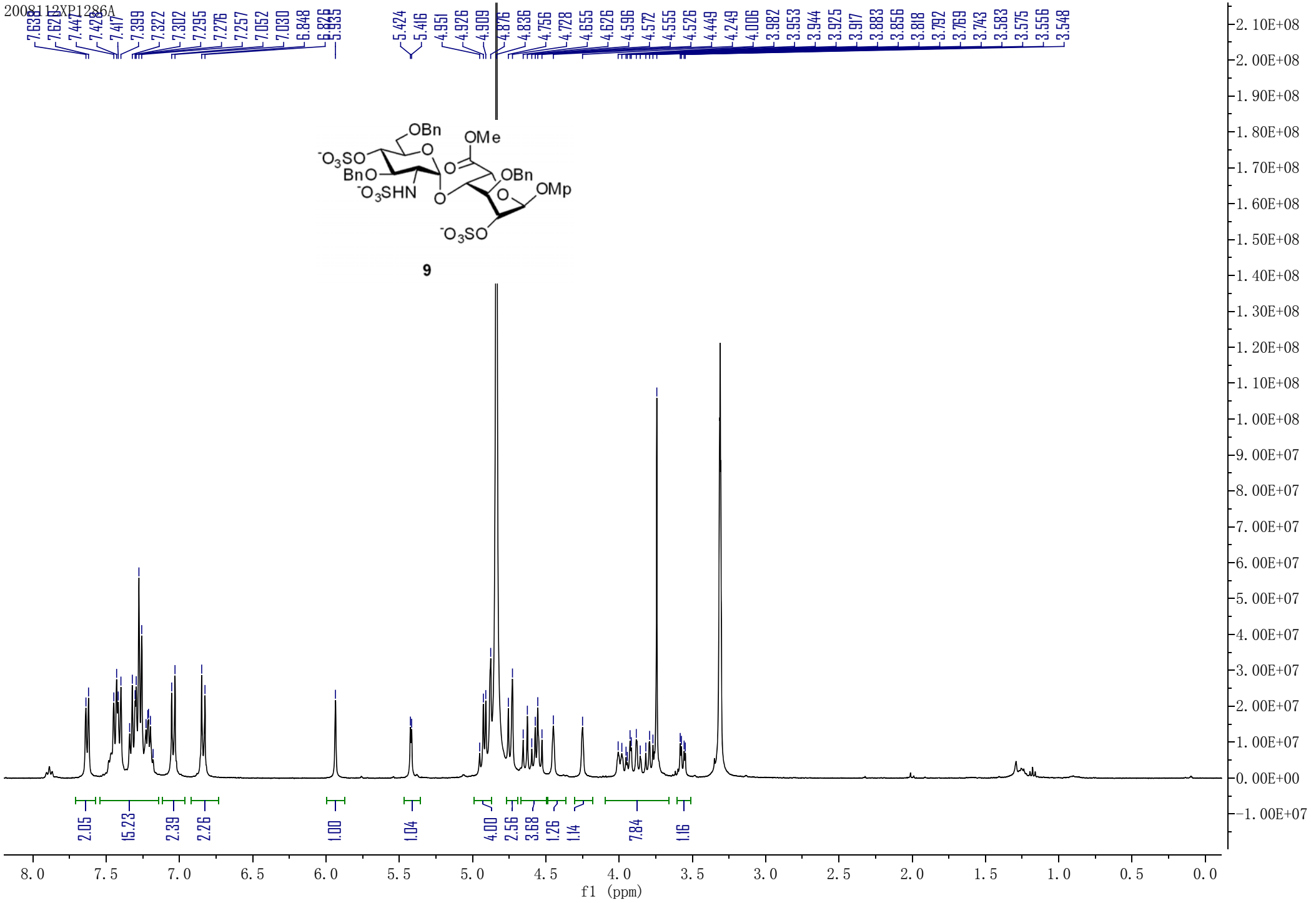
139.344
138.820
129.292
129.120
128.007
119.149
115.807
99.532
92.452
77.984
74.427
73.090
72.875
70.408
69.862
69.264
68.135
66.089
54.834
53.324
OBn
OMe
$^{-}O_3SO$
BnO
H_2N
O
OBn
OMp
$^{-}O_3SO$
10
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
f1 (ppm)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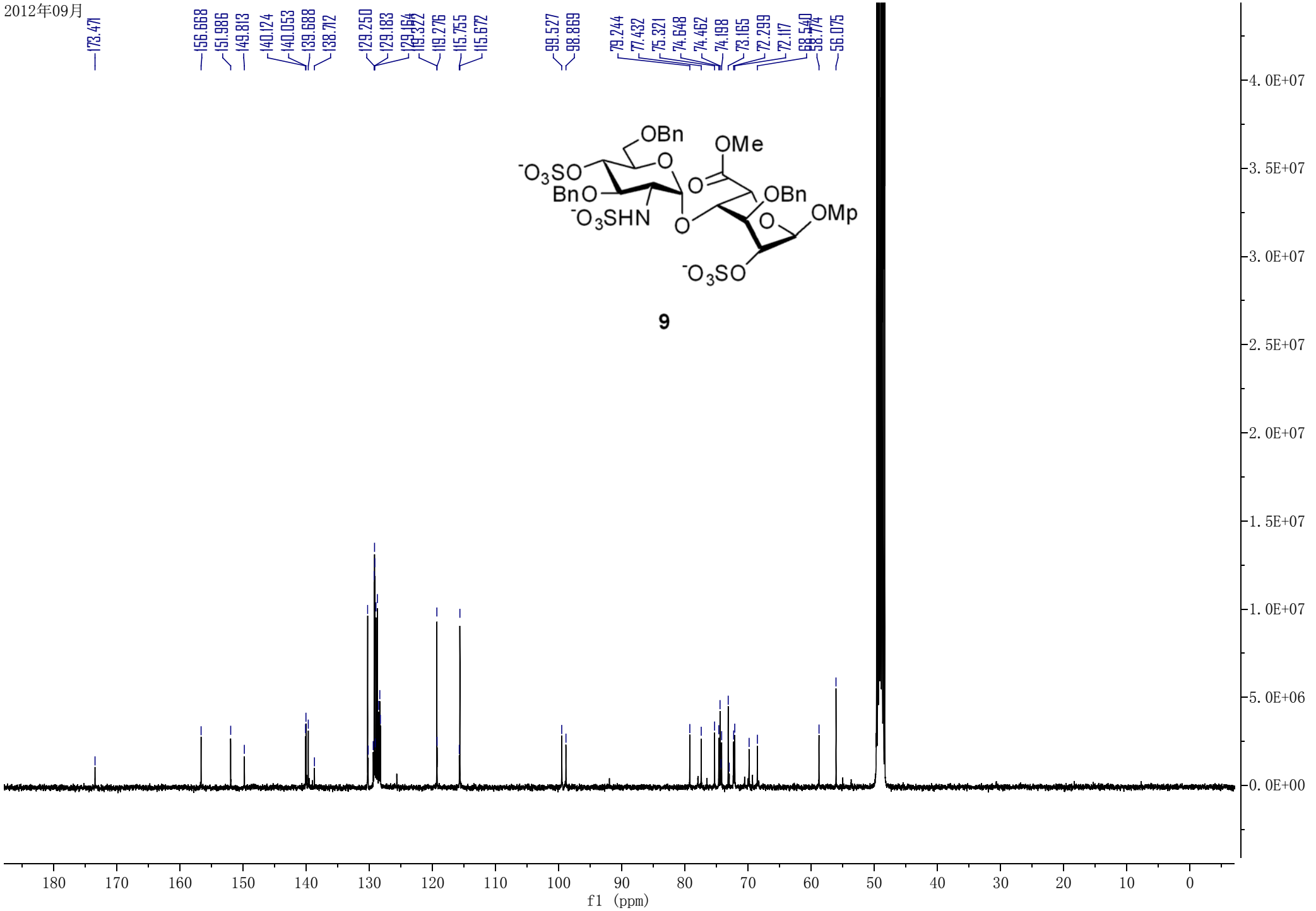
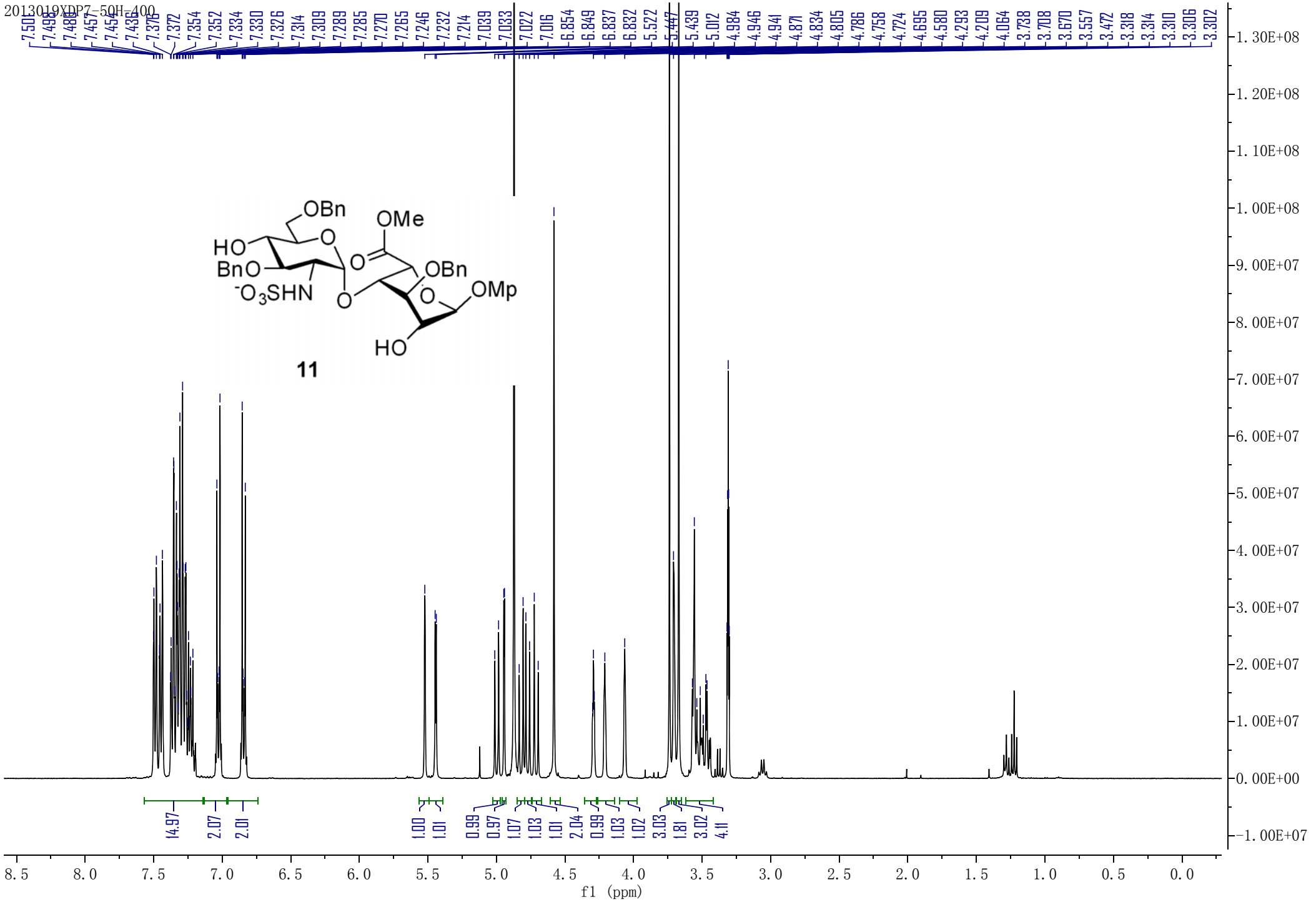
5.424 5.416 4.951 4.926 4.909 4.876 4.836 4.756 4.728 4.655 4.626 4.596 4.572 4.555 4.526 4.449 4.249 4.006 3.982 3.953 3.944 3.925 3.917 3.883 3.856 3.818 3.792 3.769 3.743 3.583 3.575 3.556 3.548
OBn
OMe
$^{-}O_3SO$
BnO
$^{-}O_3SHN$
OBn
OMp
$^{-}O_3SO$
9
2.05 15.23 2.39 2.26 1.00 1.04 4.00 2.56 3.68 1.26 1.14 7.84 1.16
f1 (ppm)

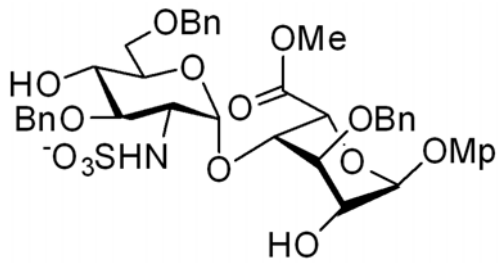
2012年09月


173.471
156.668
151.986
149.813
140.124
140.053
139.688
138.712
129.250
129.183
129.164
129.322
119.276
115.755
115.672
99.527
98.869
79.244
77.432
75.321
74.648
74.462
74.198
73.165
72.299
72.117
68.540
68.774
56.075
OBn
OMe
$^{-}O_3SO$
BnO
$^{-}O_3SHN$
OBn
OMp
$^{-}O_3SO$
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

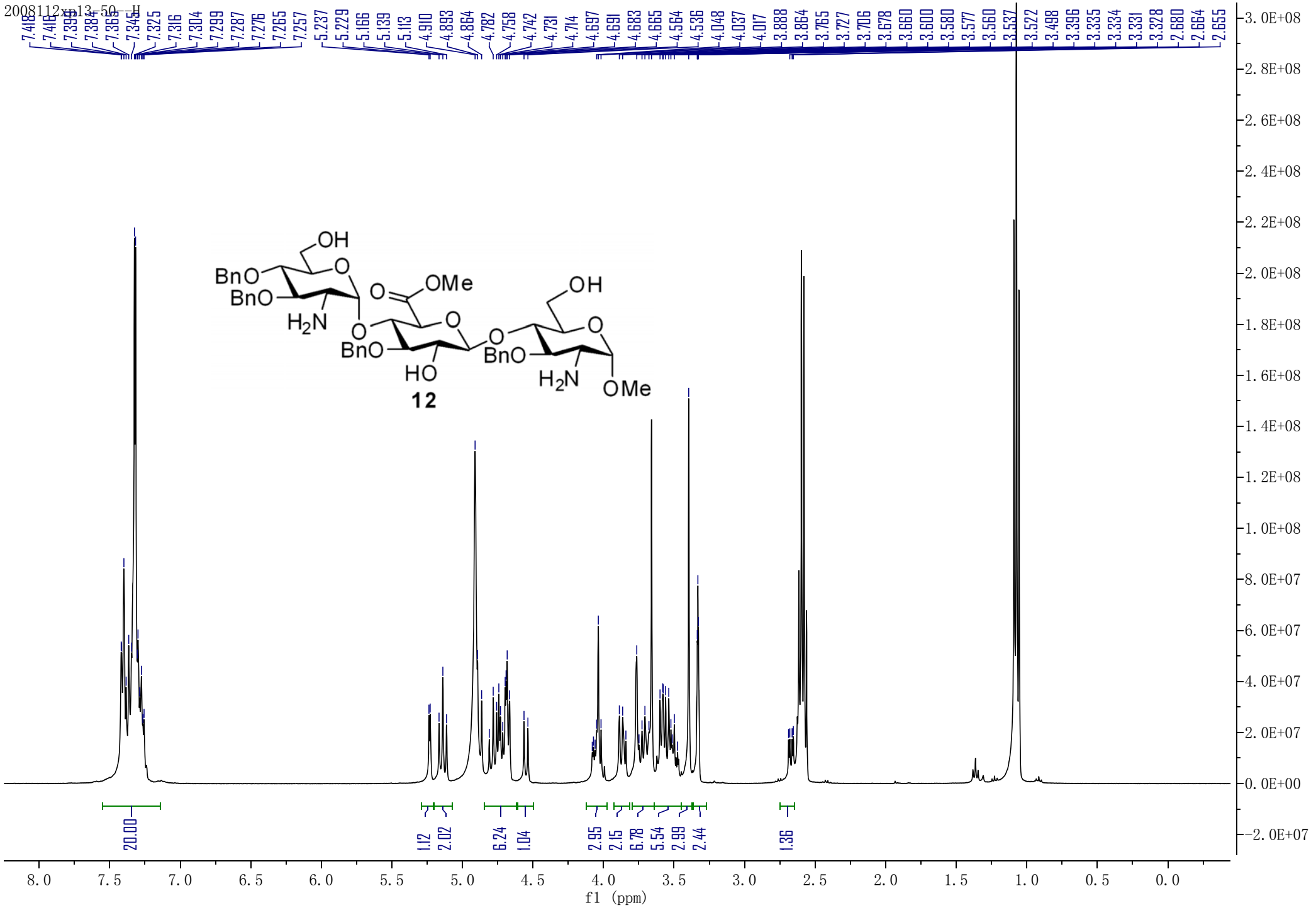
9

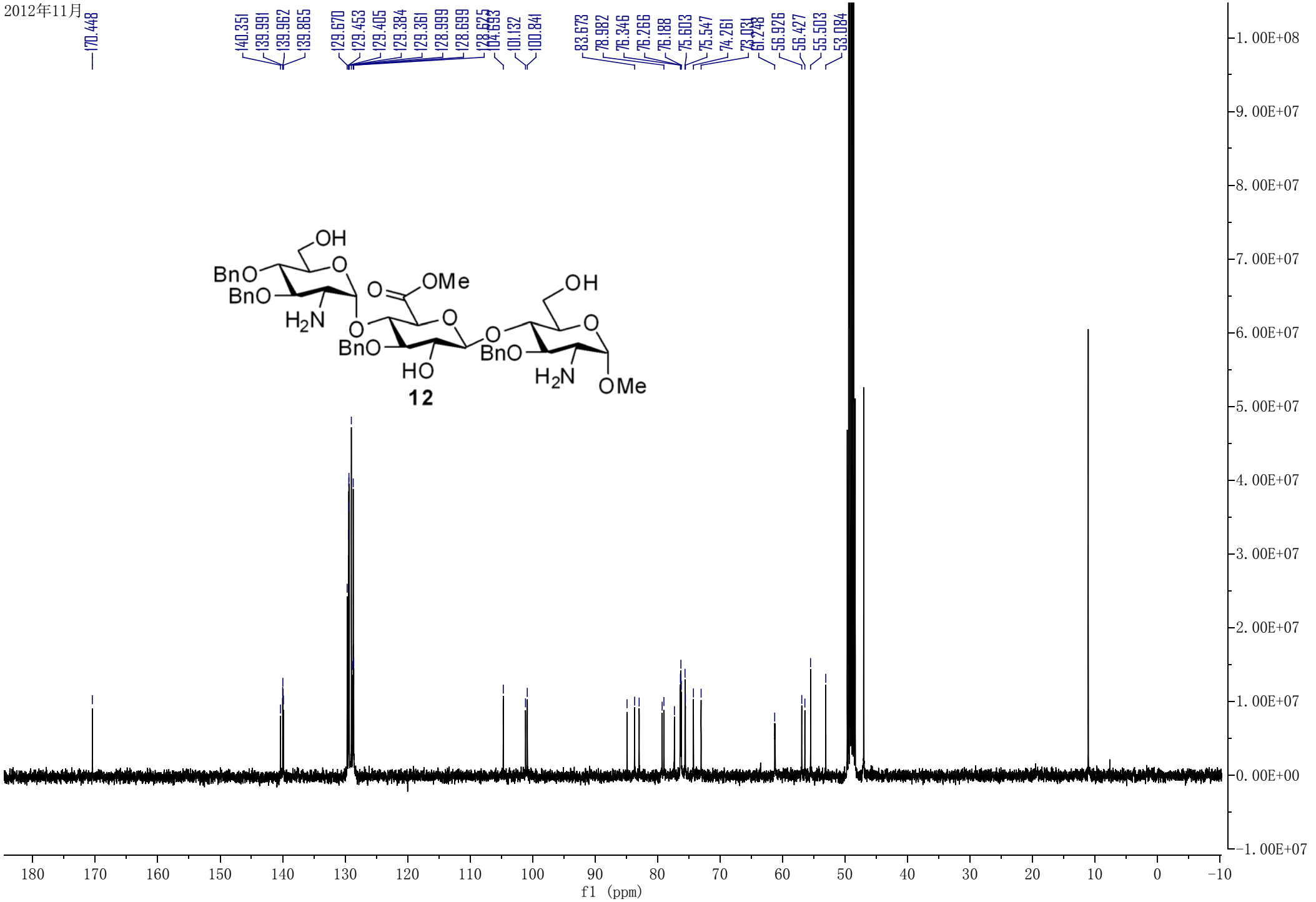

2013019XDP7-50H-400
OBn
OMe
HO
O
BnO
O
OBn
$^{-}O_3SHN$
O
O
OMp
HO
11
f1 (ppm)

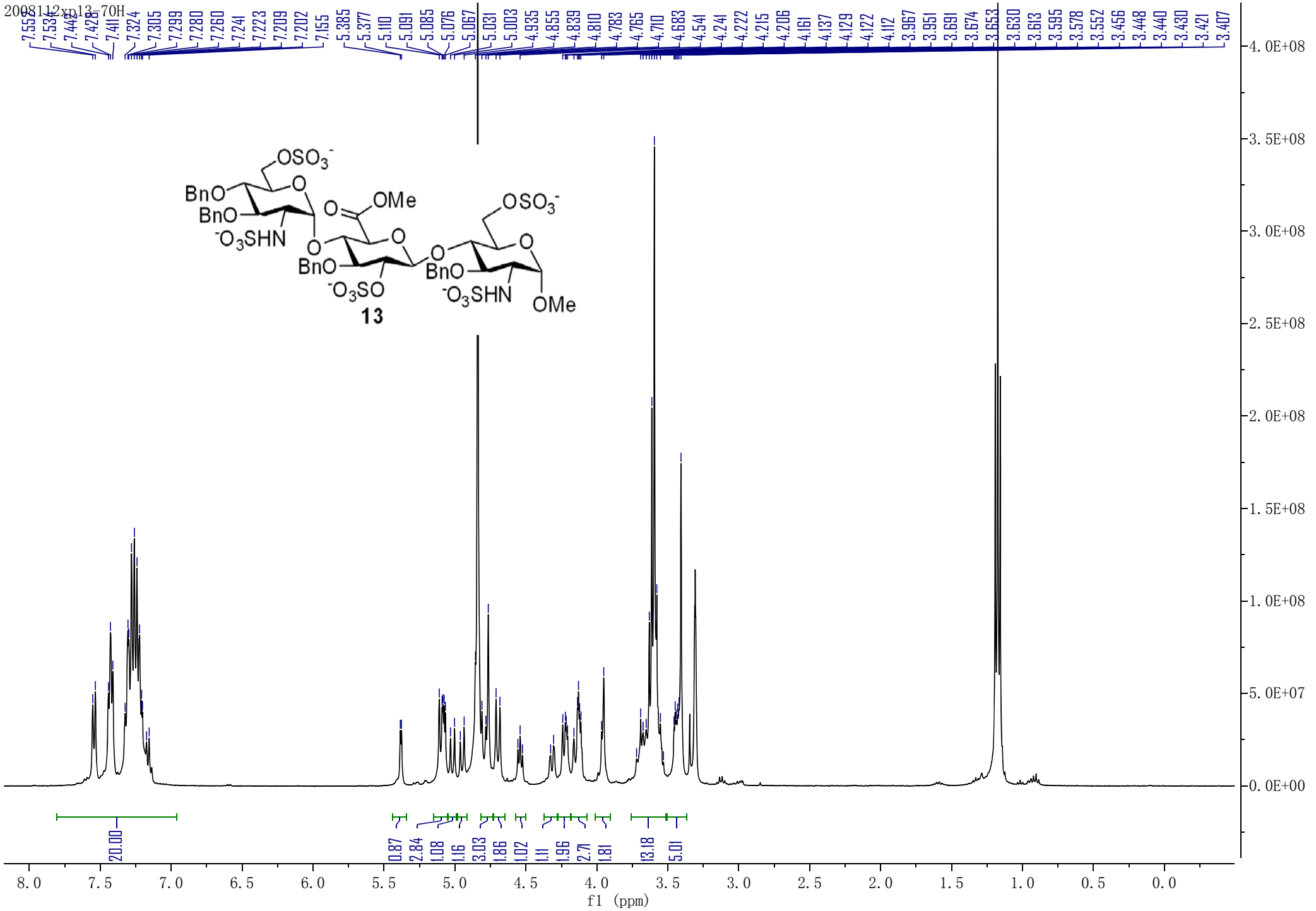
2013019XDP7-50H-400



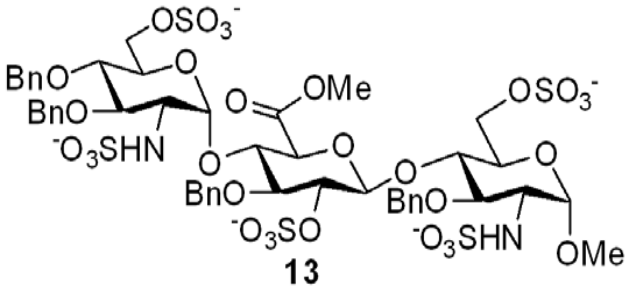
11


2008112xm13-50-H
7.418 7.410 7.399 7.384 7.365 7.345 7.325 7.316 7.304 7.299 7.287 7.276 7.265 7.257
5.237 5.229 5.166 5.139 5.113 4.910 4.893 4.864 4.782 4.758 4.742 4.731 4.714 4.697 4.691 4.683 4.665 4.564 4.536 4.048 4.037 4.017 3.888 3.864 3.765 3.727 3.706 3.678 3.660 3.600 3.580 3.577 3.560 3.537 3.522 3.498 3.396 3.335 3.334 3.331 3.328 2.680 2.664 2.655
OH
BnO
BnO
O
O
OMe
O
O
H2N
BnO
HO
O
BnO
OH
O
H2N
OMe
12
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
20.00
1.12
2.02
6.24
1.04
2.95
2.15
6.78
5.54
2.99
2.44
1.36
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2012年11月
170.448
140.351
139.991
139.962
139.865
129.670
129.453
129.405
129.384
129.361
128.999
128.699
128.625
104.693
101.132
100.841
83.673
78.982
76.346
76.266
76.188
75.603
75.547
74.261
73.031
61.248
56.926
56.427
55.503
53.084
OH
O
BnO
BnO
H2N
O
OMe
O
O
BnO
HO
O
OH
O
BnO
H2N
OMe
12
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


20081124xp13-70H
7.555 7.534 7.442 7.428 7.411 7.324 7.305 7.299 7.280 7.260 7.241 7.223 7.209 7.202 7.155 5.385 5.377 5.110 5.091 5.085 5.076 5.067 5.031 5.003 4.935 4.855 4.839 4.810 4.783 4.765 4.710 4.683 4.541 4.241 4.222 4.215 4.206 4.161 4.137 4.129 4.122 4.112 3.967 3.951 3.691 3.674 3.653 3.630 3.613 3.595 3.578 3.552 3.456 3.448 3.440 3.430 3.421 3.407
OSO3-
BnO
BnO
-O3SHN
O
OMe
BnO
-O3SO
13
OSO3-
BnO
-O3SHN
OMe
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
20.00
0.87
2.84
1.08
1.16
3.03
1.86
1.02
1.11
1.96
2.71
1.81
13.18
5.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

xp13-70C

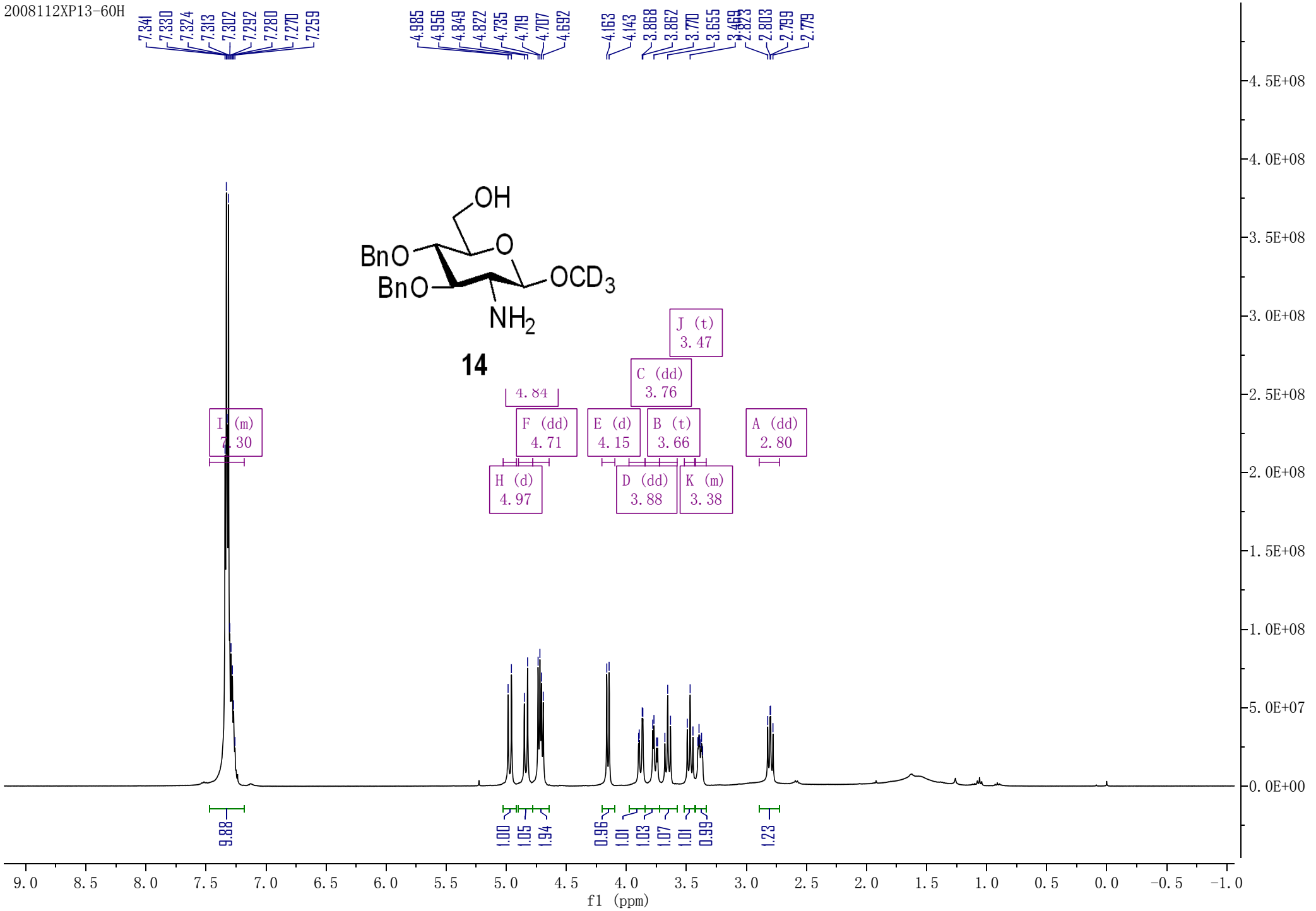


13

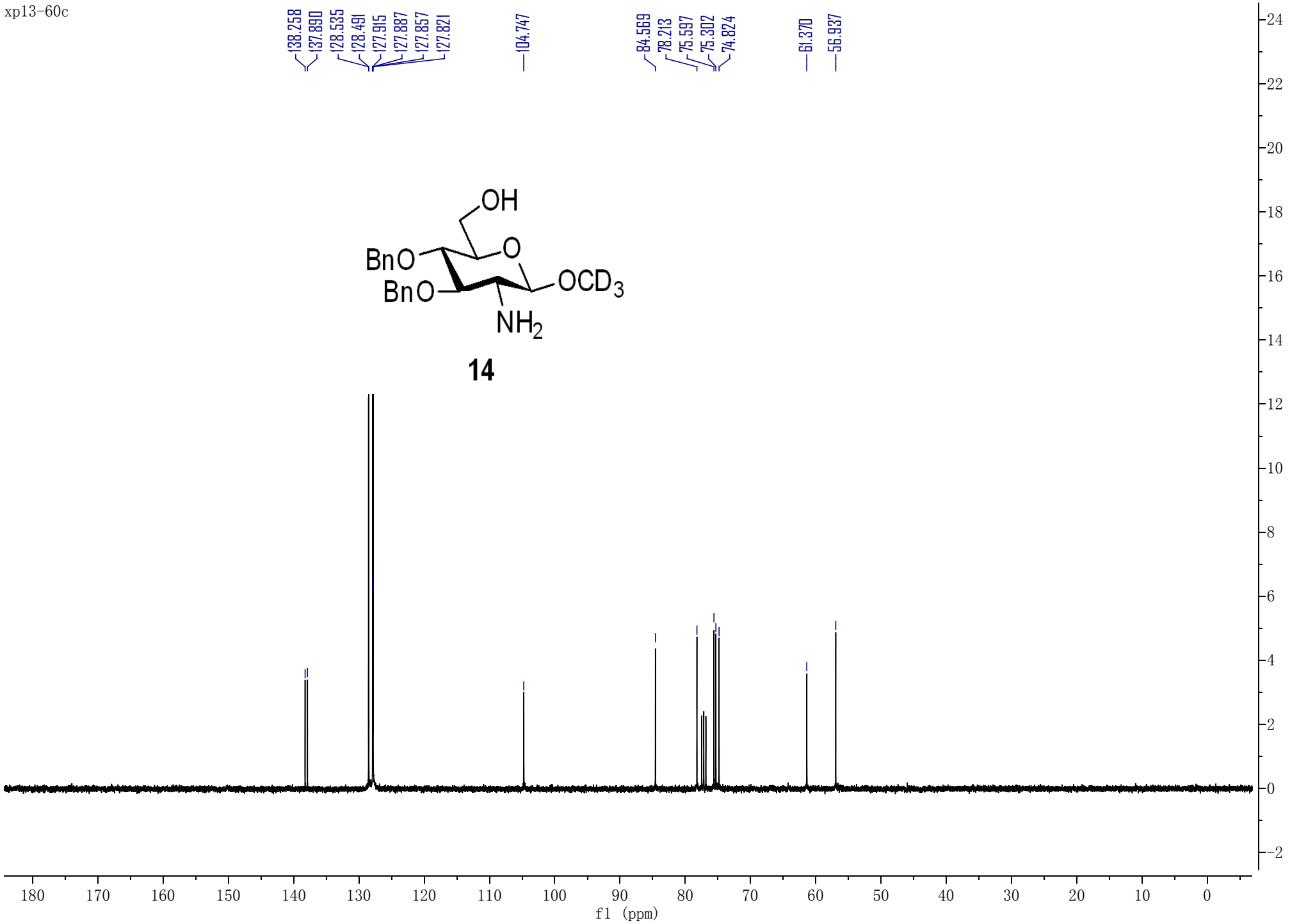
170.781
140.621
140.276
140.065
139.004
130.328
129.397
129.322
129.156
129.139
129.091
129.049
102.197
99.970
99.828
81.657
79.441
78.654
77.132
76.413
75.896
74.937
74.456
59.674
58.418
58.294
55.777
53.254

f1 (ppm)

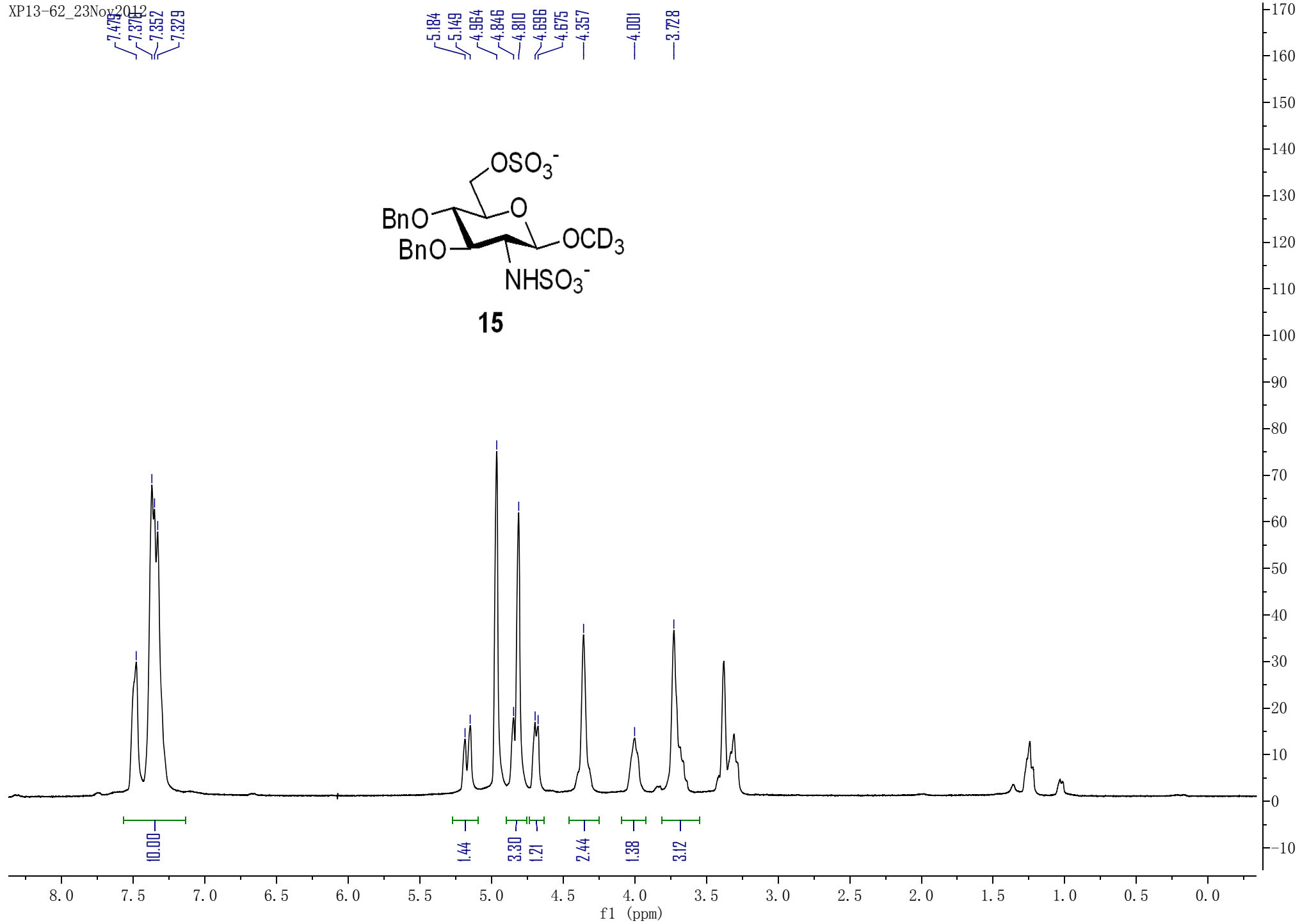
2008112XP13-60H



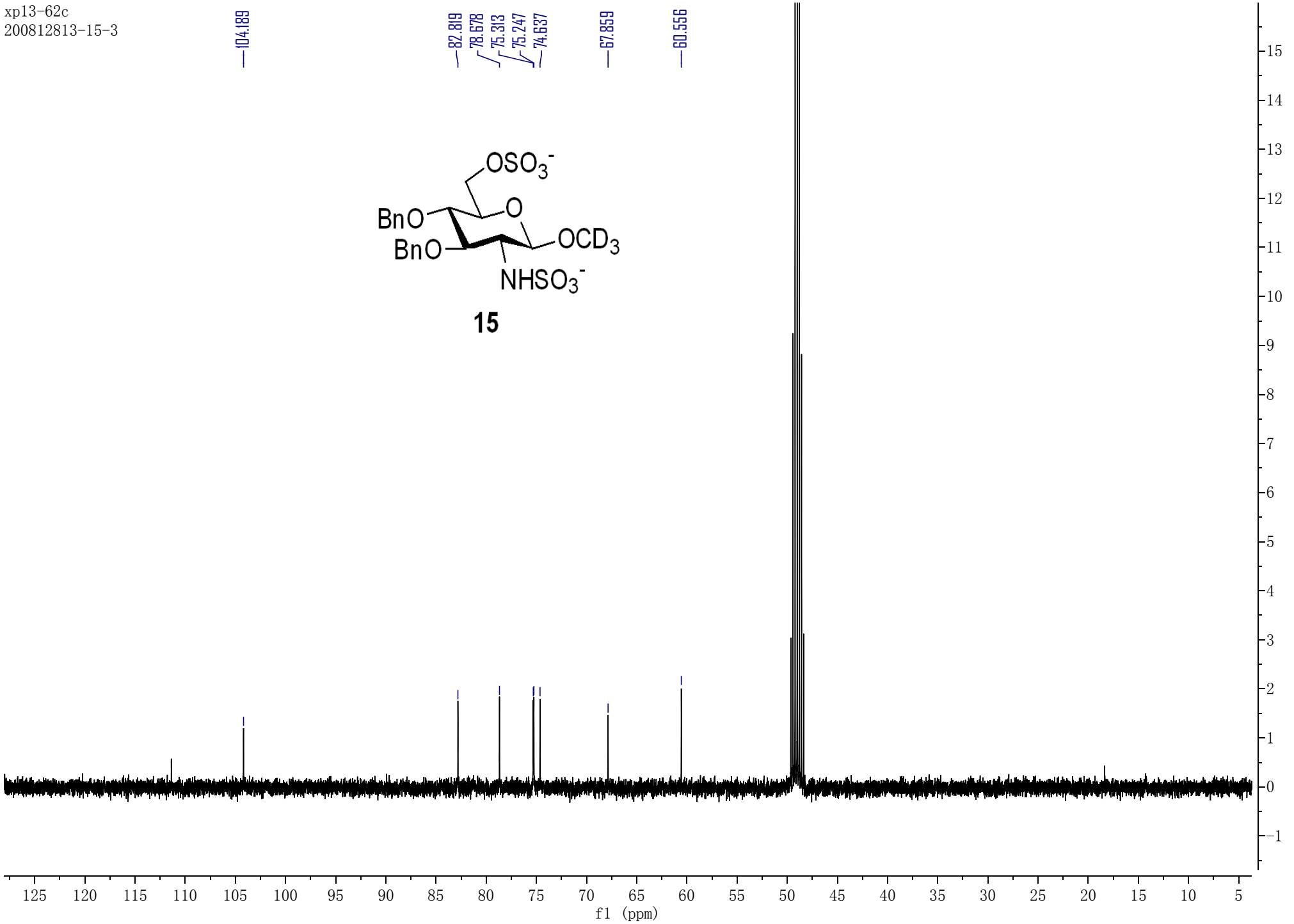
xp13-60c


138.258
137.890
128.535
128.491
127.915
127.887
127.857
127.821
104.747
84.569
78.213
75.597
75.302
74.824
61.370
56.937
OH
O
BnO
BnO
OCD3
NH2
14
f1 (ppm)

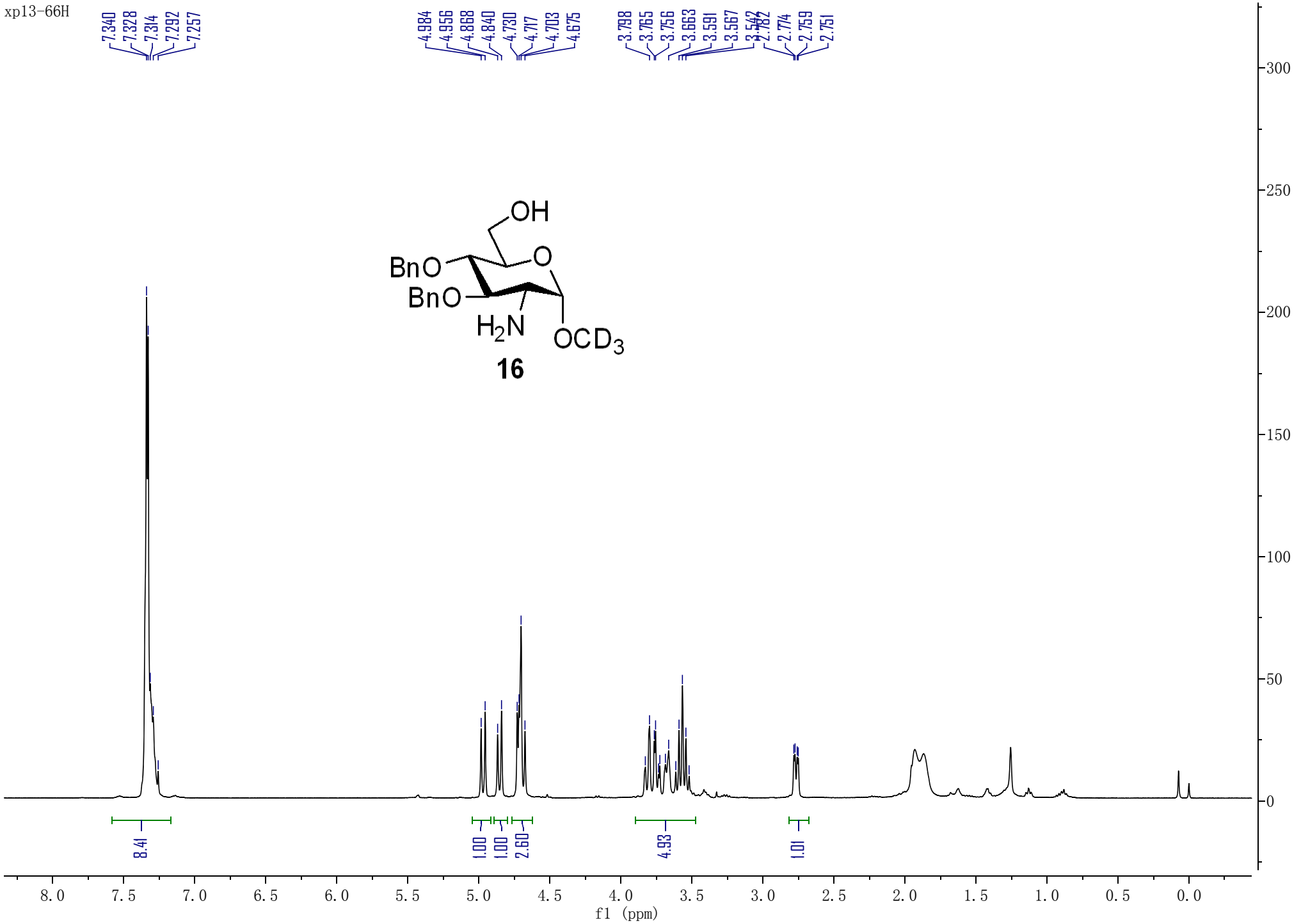
XP13-62_23Nov2012



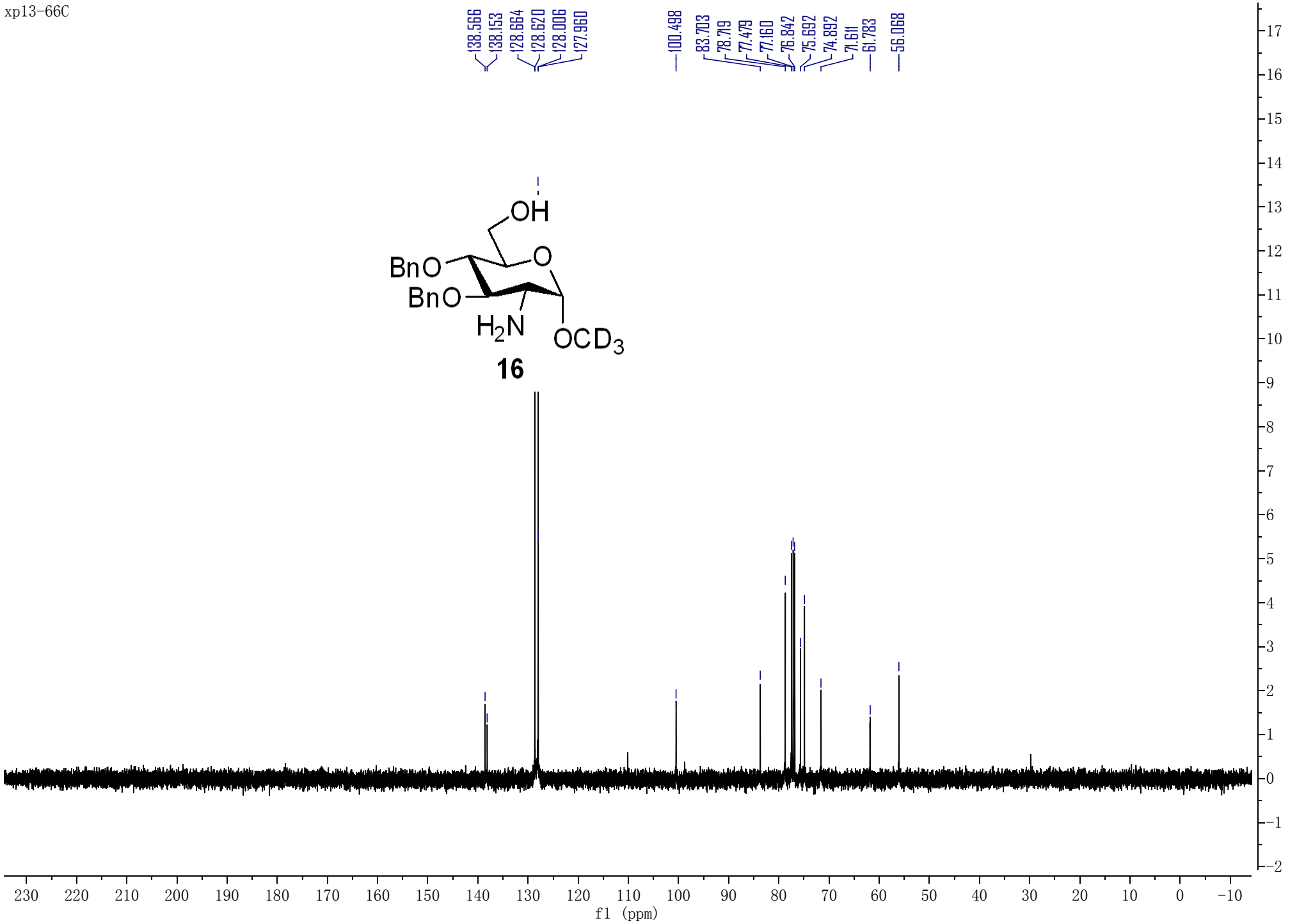
xp13-62c
200812813-15-3

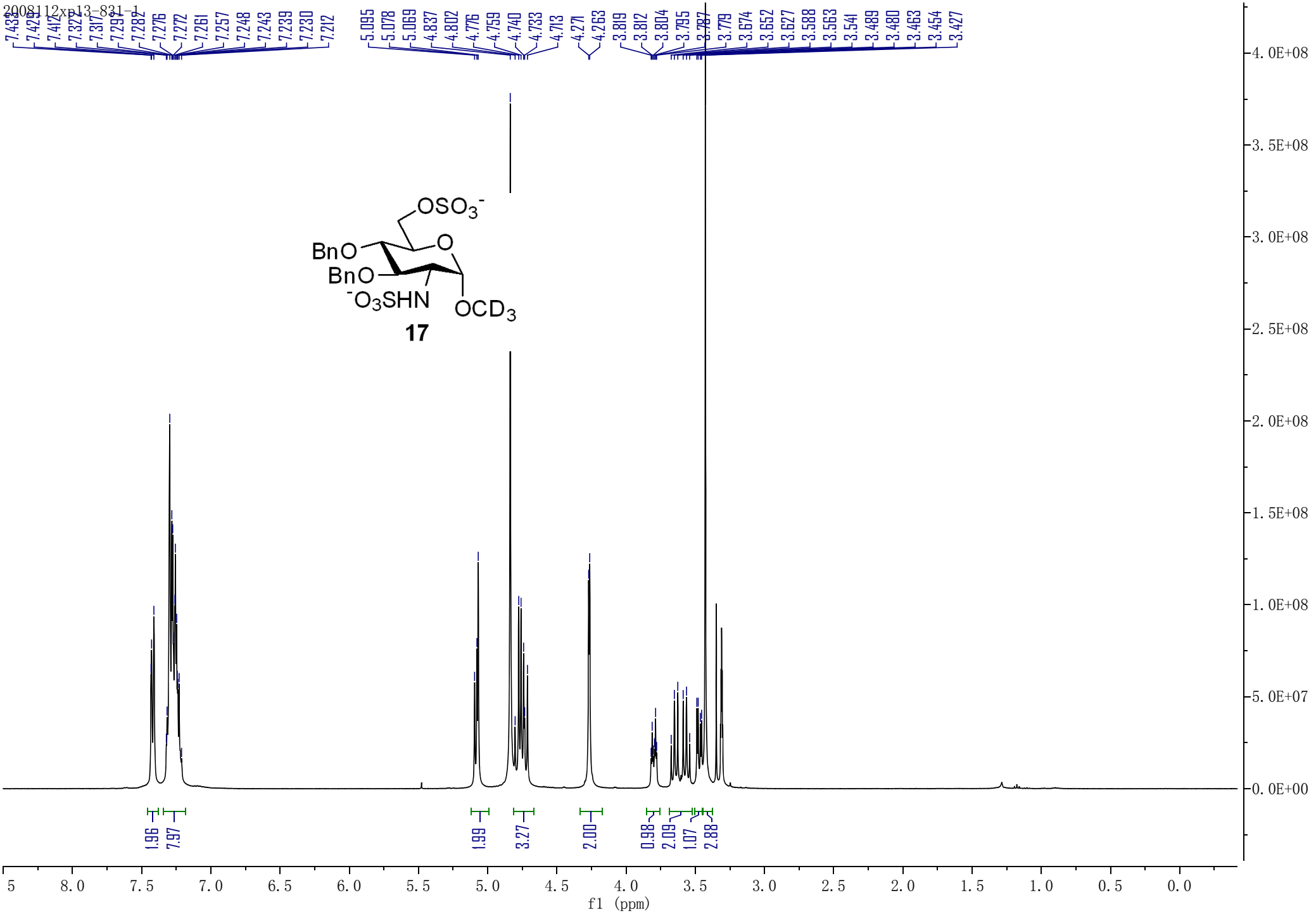


xp13-66H

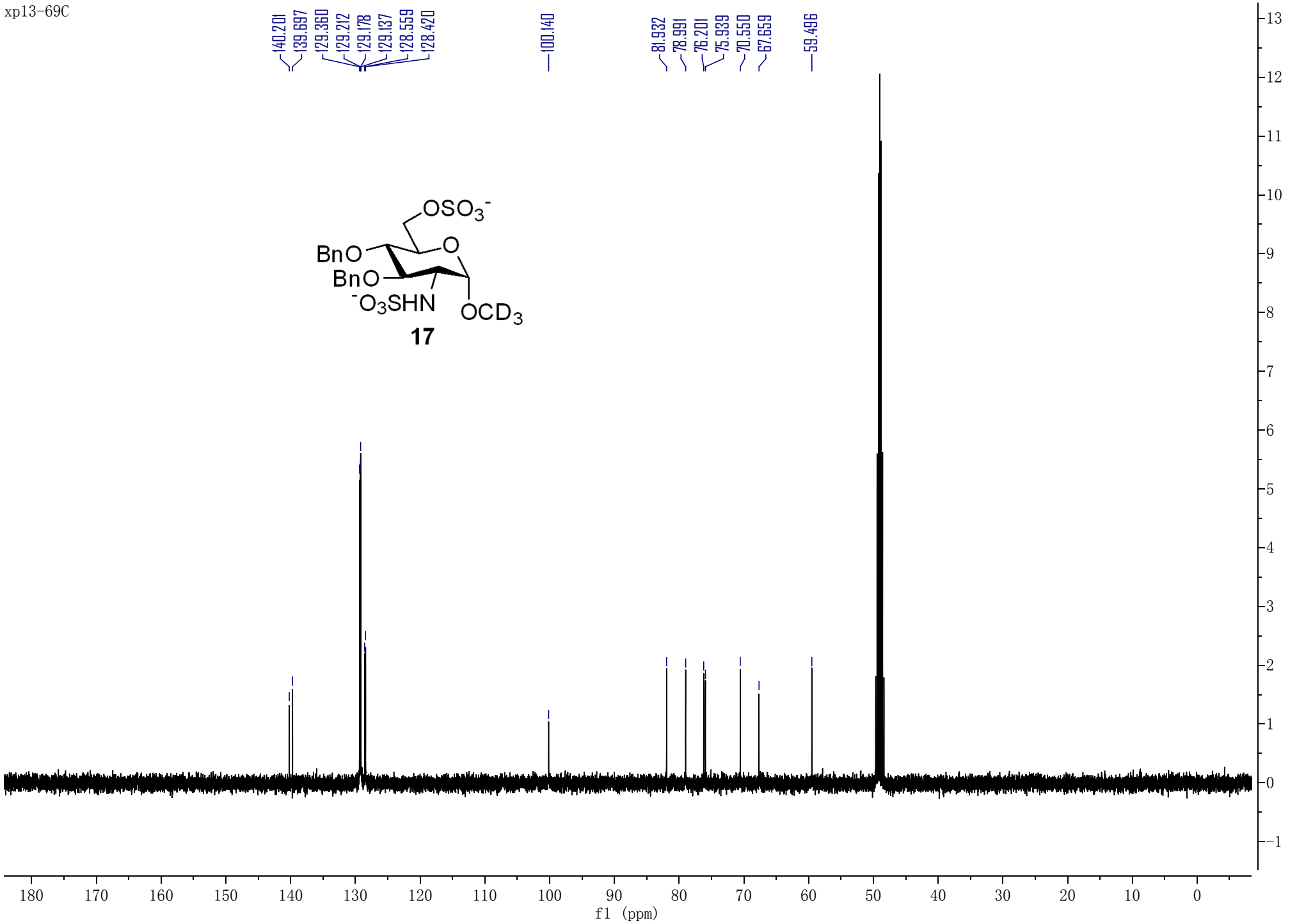

7.340
7.328
7.314
7.292
7.257
4.984
4.956
4.868
4.840
4.730
4.717
4.703
4.675
3.798
3.765
3.756
3.663
3.591
3.567
2.774
2.759
2.751
OH
O
BnO
BnO
H2N
OCD3
16
8.41
1.00
1.00
2.60
4.93
1.01
f1 (ppm)

xp13-66C

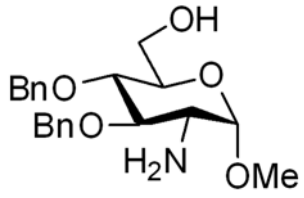

138.566
138.153
128.664
128.620
128.006
127.960
100.498
83.703
78.719
77.479
77.160
76.842
75.692
74.892
71.611
61.783
56.068
OH
O
BnO
BnO
H2N
OCD3
16
f1 (ppm)


2008112xp13-831-1
7.438
7.428
7.417
7.329
7.317
7.297
7.282
7.276
7.272
7.261
7.257
7.248
7.243
7.239
7.230
7.212
5.095
5.078
5.069
4.837
4.802
4.776
4.759
4.740
4.733
4.713
4.271
4.263
3.819
3.812
3.804
3.795
3.787
3.779
3.674
3.652
3.627
3.588
3.563
3.541
3.489
3.480
3.463
3.454
3.427
OSO3-
O
BnO
BnO
-O3SHN
OCD3
17
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
1.96
7.97
1.99
3.27
2.00
0.98
2.09
1.07
2.88
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

xp13-69C

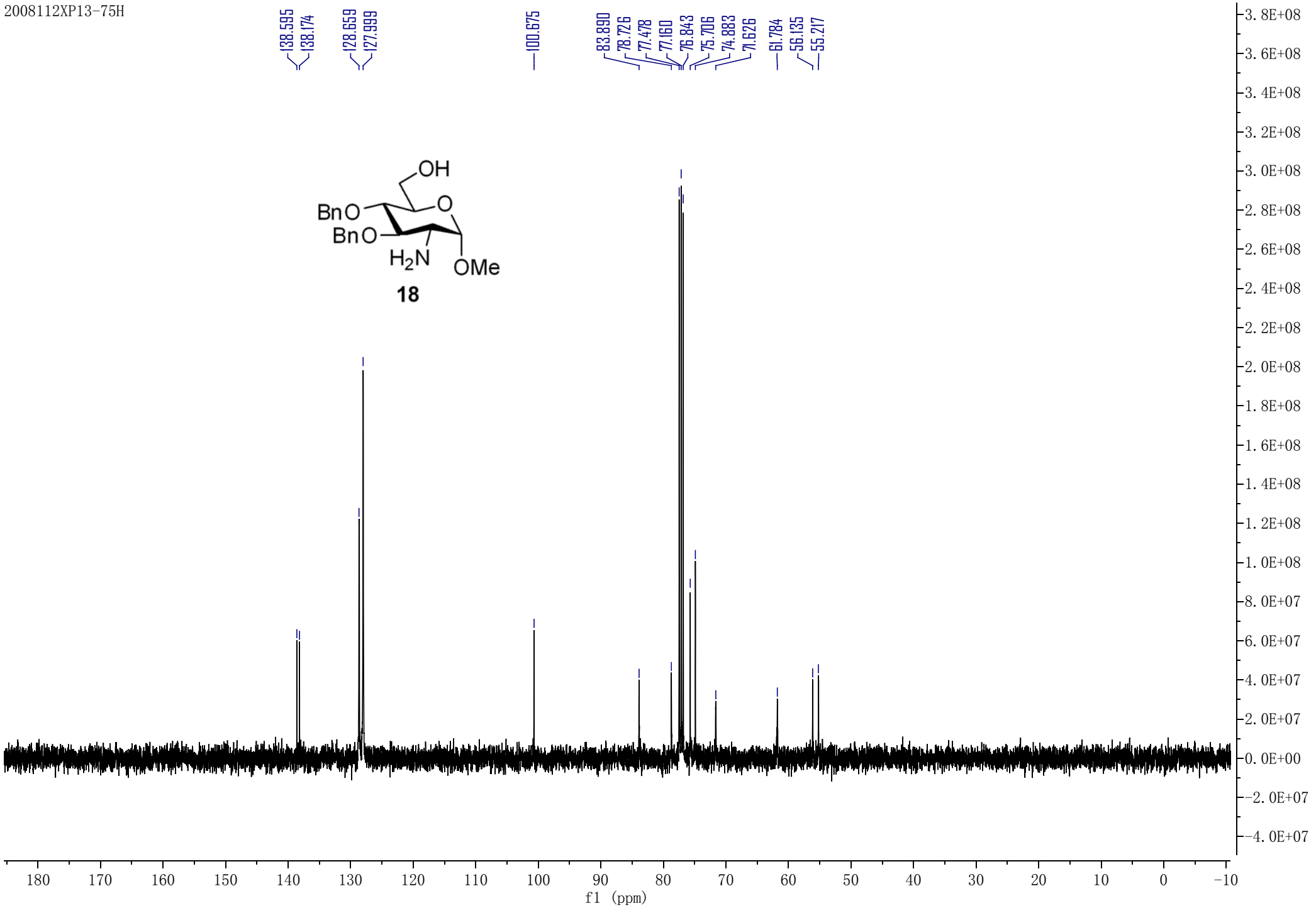

140.201
139.697
129.360
129.212
129.178
129.137
128.559
128.420
100.140
81.932
78.991
76.201
75.939
70.550
67.659
59.496
OSO3-
BnO
O
BnO
-O3SHN
OCD3
17
f1 (ppm)

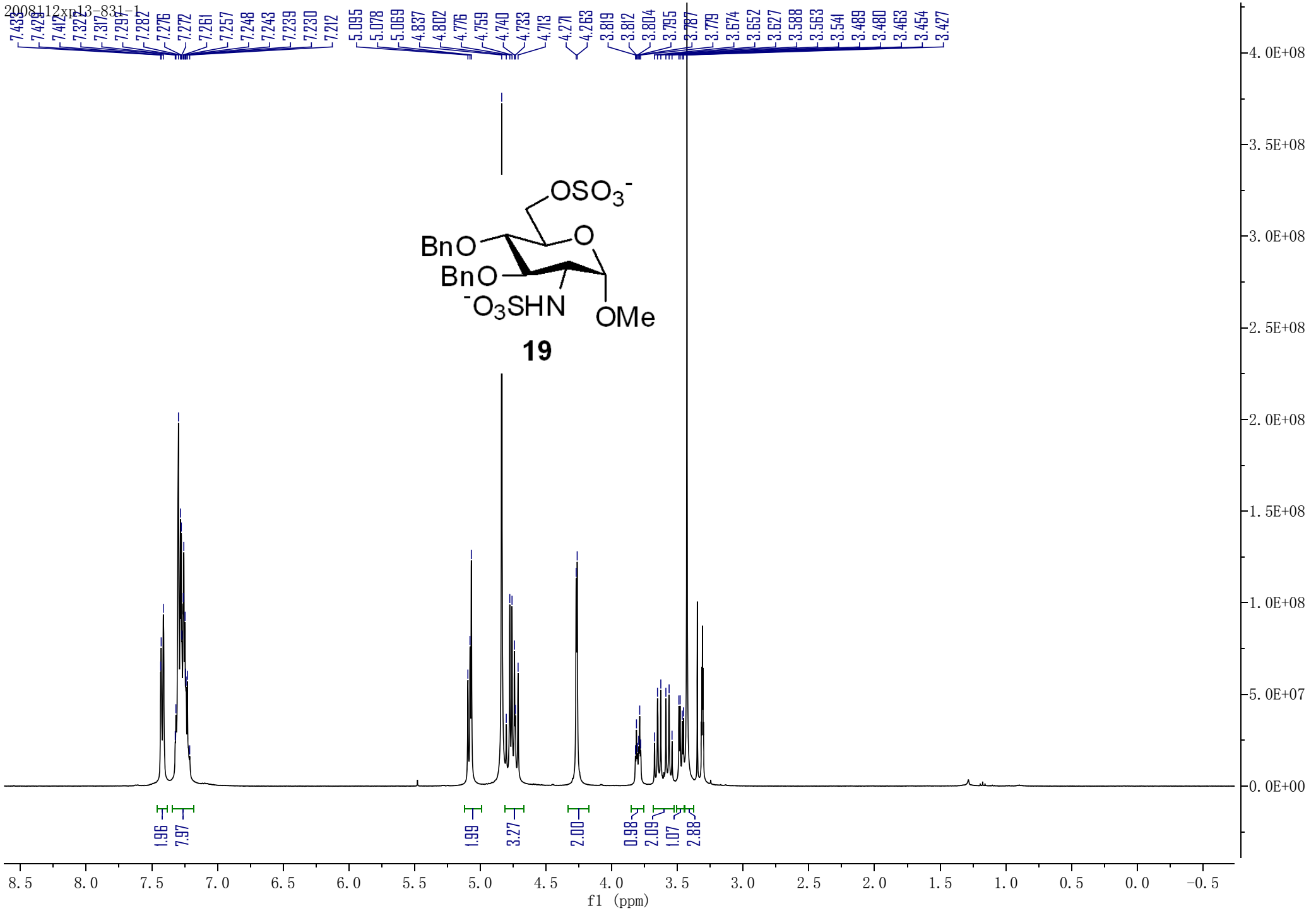
2008112XP13-75H



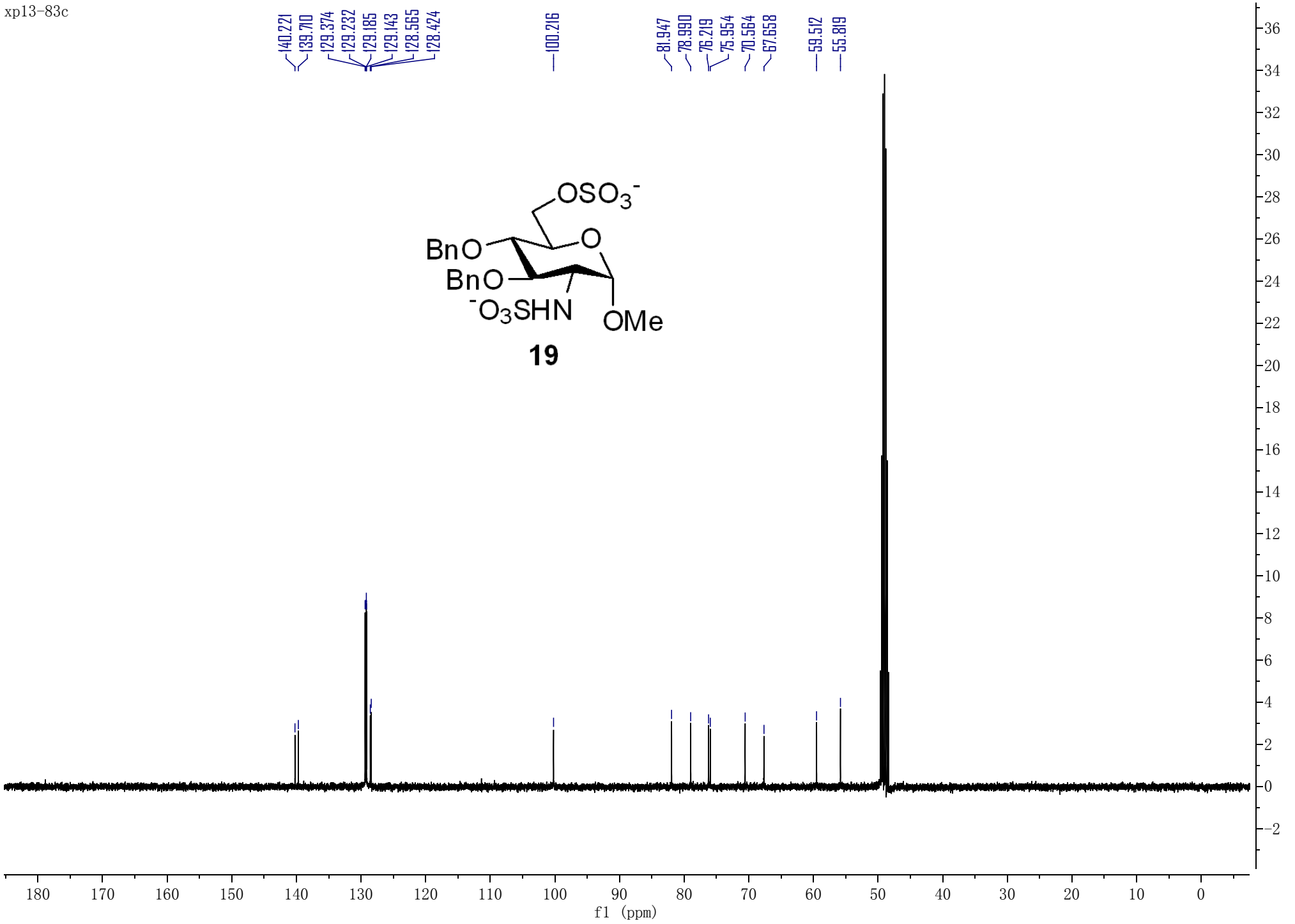
18

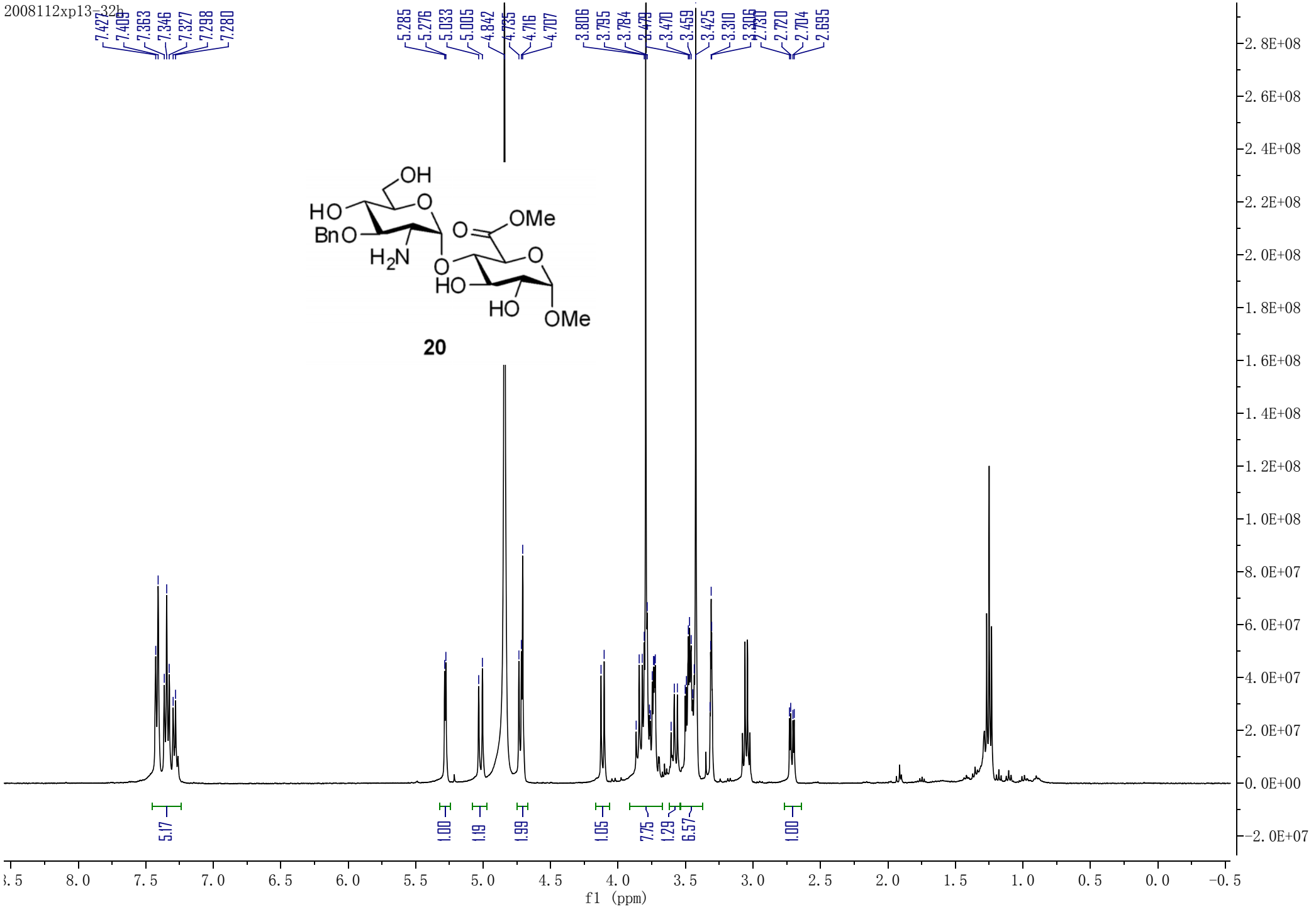
2008112XP13-75H



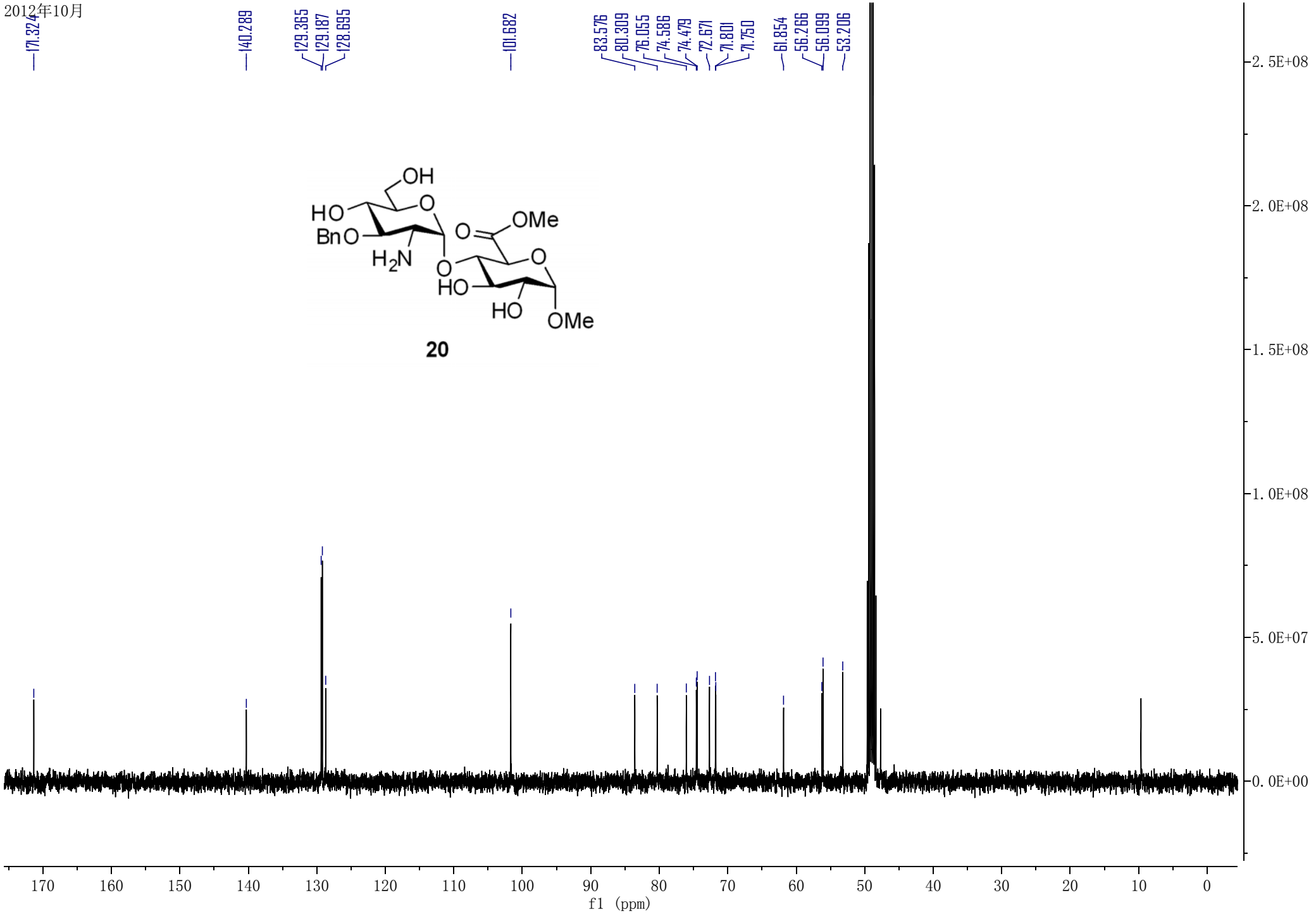

20081112xp13-831-1
7.435 7.429 7.412 7.327 7.317 7.297 7.282 7.276 7.272 7.261 7.257 7.248 7.243 7.239 7.230 7.212
5.095 5.078 5.069 4.837 4.802 4.776 4.759 4.740 4.733 4.713 4.271 4.263
3.819 3.812 3.804 3.795 3.787 3.779 3.674 3.652 3.627 3.588 3.563 3.541 3.489 3.480 3.463 3.454 3.427
OSO3-
O
BnO
BnO
-O3SHN
OMe
19
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
1.96 7.97 1.99 3.27 2.00 0.98 2.09 1.07 2.88
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

xp13-83c

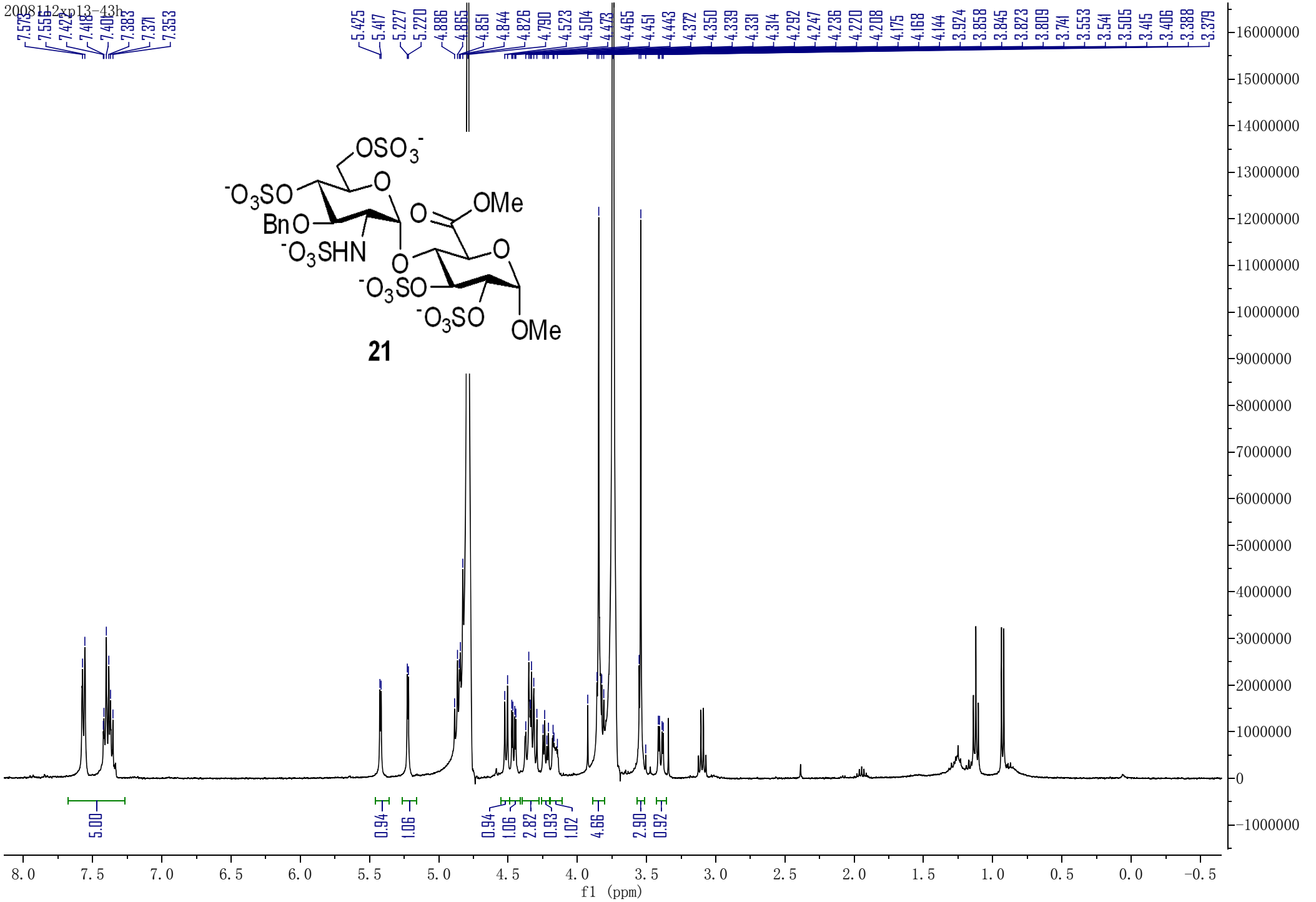

140.221
139.710
129.374
129.232
129.185
129.143
128.565
128.424
100.216
81.947
78.990
76.219
75.954
70.564
67.658
59.512
55.819
OSO3-
O
BnO
BnO
-O3SHN
OMe
19
f1 (ppm)


2008112xp13-32b
7.427
7.408
7.363
7.346
7.327
7.298
7.280
5.285
5.276
5.033
5.005
4.842
4.735
4.716
4.707
3.806
3.795
3.784
3.478
3.470
3.459
3.425
3.310
3.306
2.730
2.720
2.704
2.695
OH
HO
O
BnO
H2N
O
OMe
O
O
HO
HO
OMe
20
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
5.17
1.00
1.19
1.99
1.05
7.75
1.29
6.57
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

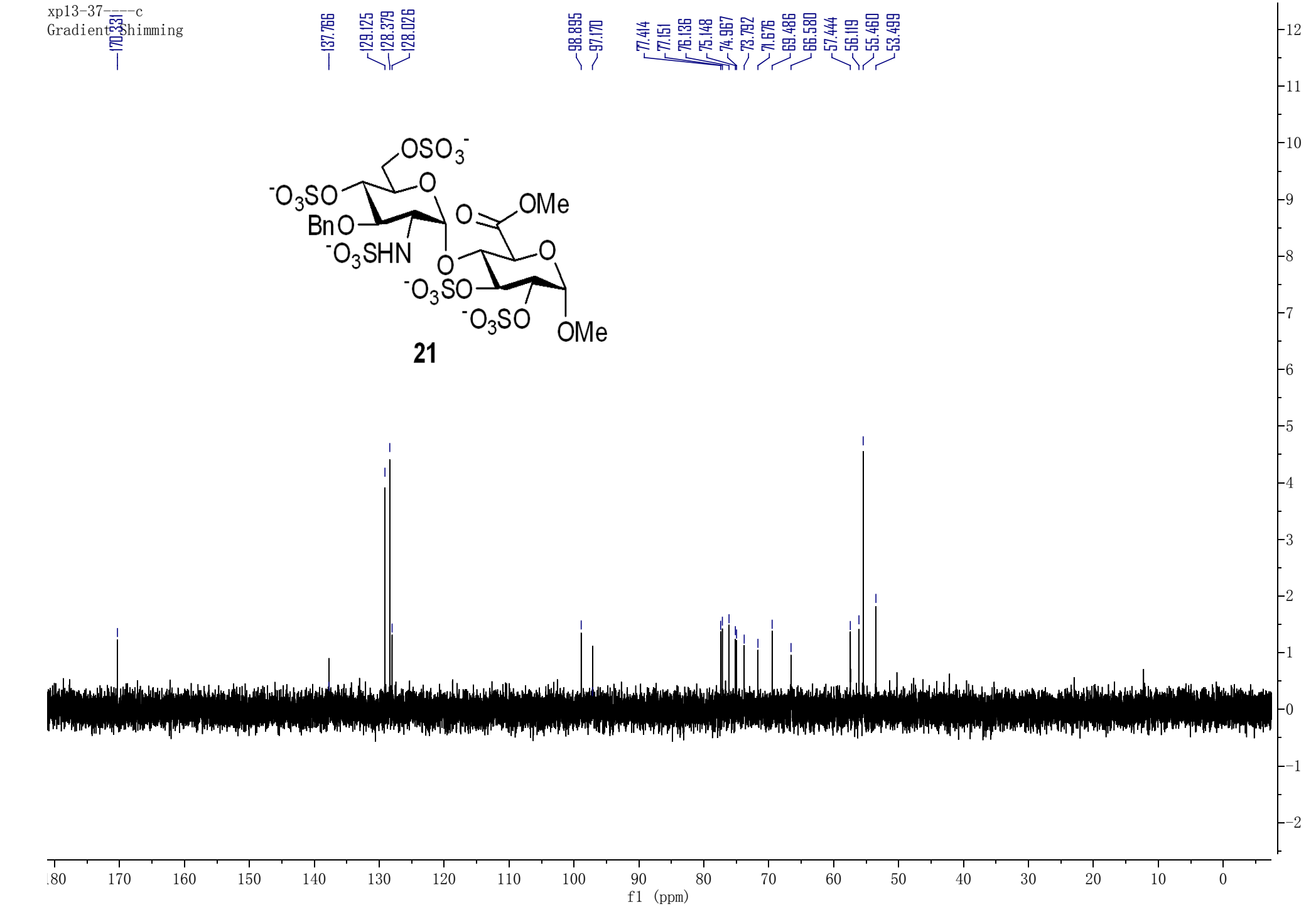
2012年10月


171.824
140.289
129.365
129.187
128.695
101.682
83.576
80.309
76.055
74.586
74.479
72.671
71.801
71.750
61.854
56.266
56.099
53.206
OH
HO
BnO
O
H2N
O
OMe
O
O
HO
HO
OMe
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

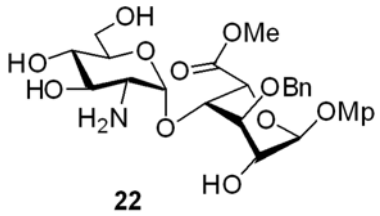
20


2008112xp13-43h
7.575
7.556
7.422
7.418
7.404
7.383
7.371
7.353
5.425
5.417
5.227
5.220
4.886
4.865
4.851
4.844
4.826
4.790
4.523
4.504
4.473
4.465
4.451
4.443
4.372
4.350
4.339
4.331
4.314
4.292
4.247
4.236
4.220
4.208
4.175
4.168
4.144
3.924
3.858
3.845
3.823
3.809
3.741
3.553
3.541
3.505
3.415
3.406
3.388
3.379
OSO3-
-O3SO
BnO
-O3SHN
OMe
-O3SO
-O3SO
OMe
21
5.00
0.94
1.06
0.94
1.06
2.82
0.93
1.02
4.66
2.90
0.92
f1 (ppm)

xp13-37----c
Gradient Shimming



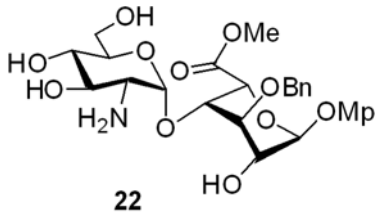
2008112xp13-48-4H



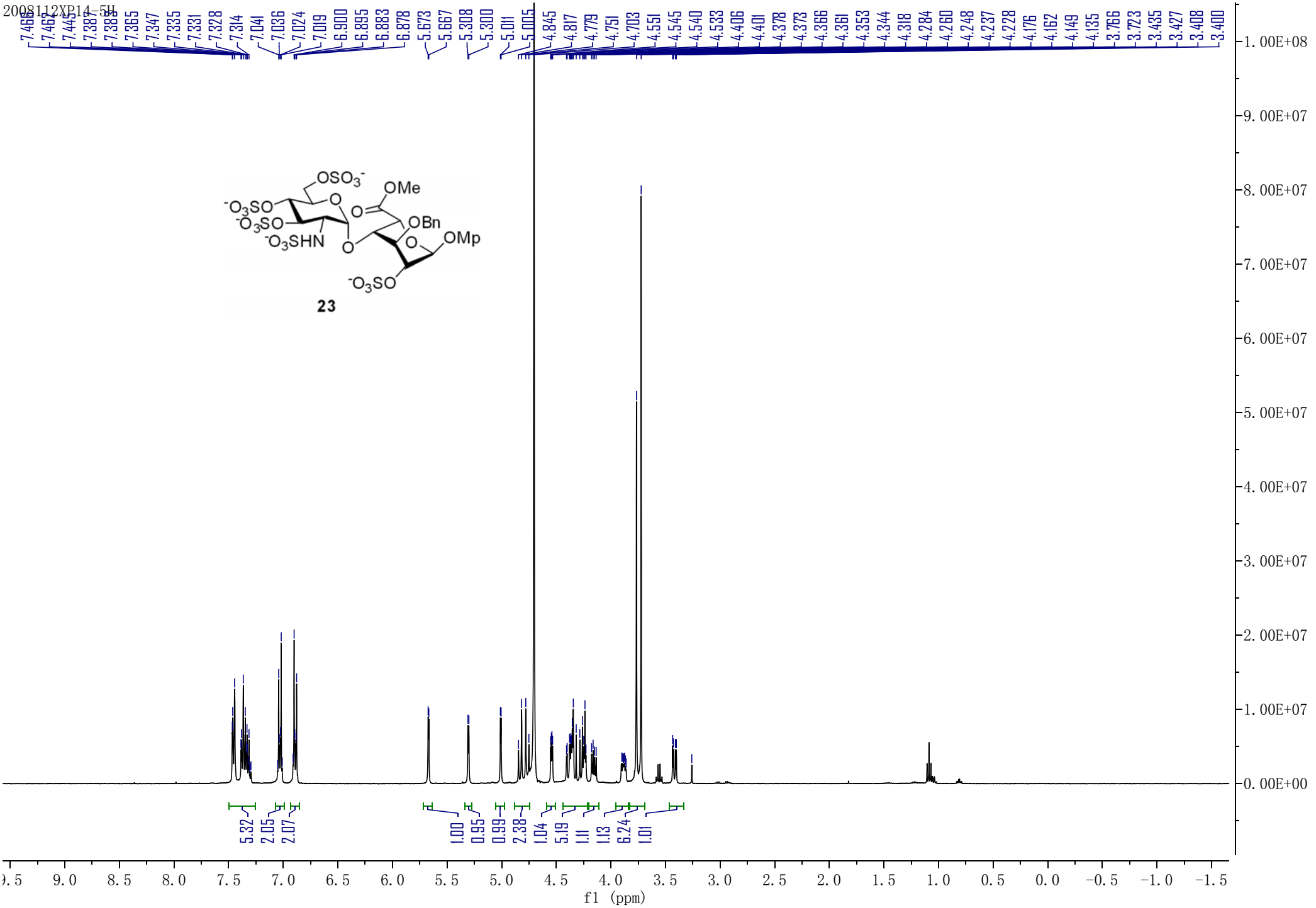
22

f1 (ppm)

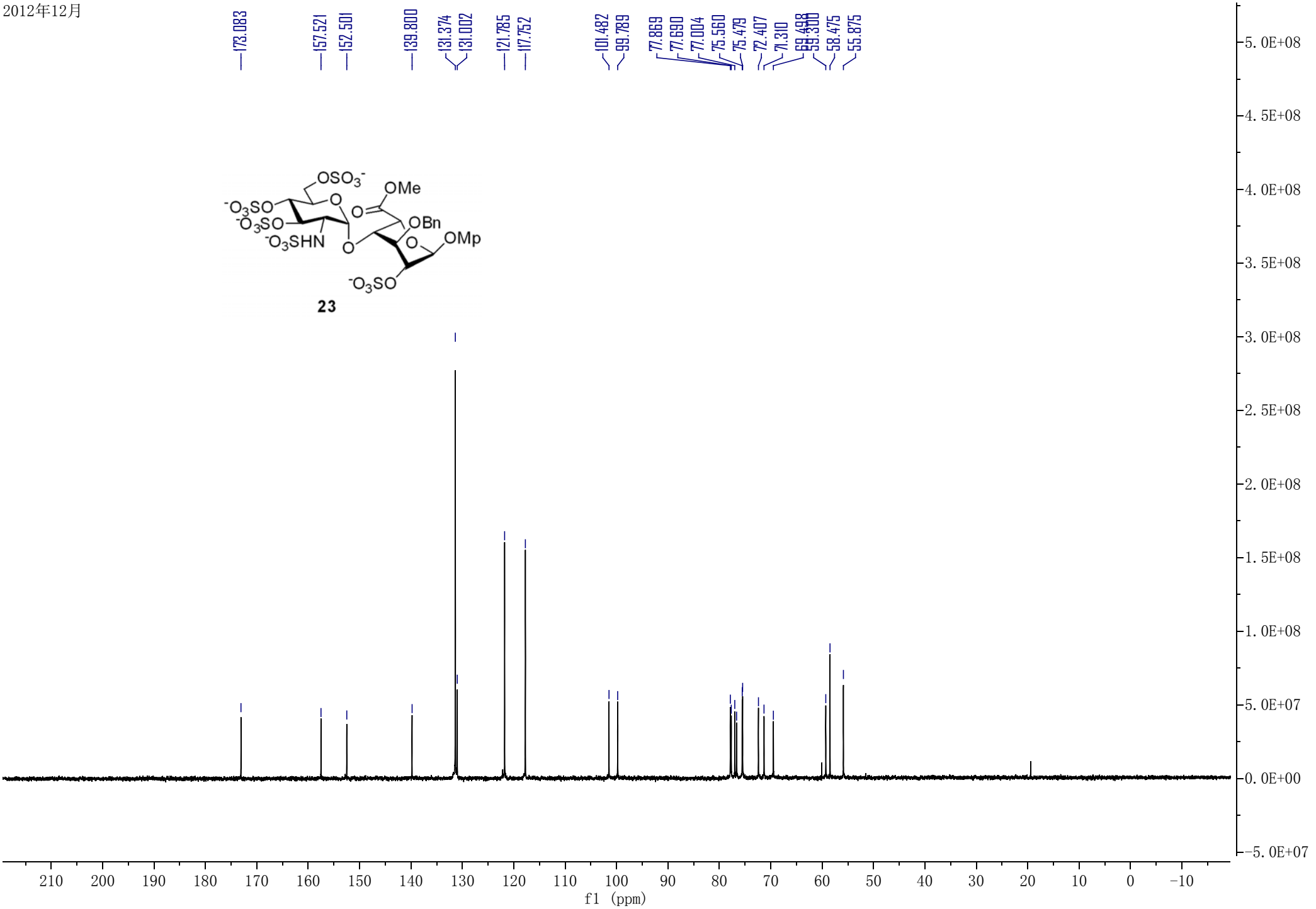
xp13-48c
Ethylindanone standard test sample
Recorded on 400-MR with OneNMR probe and PFG running



22

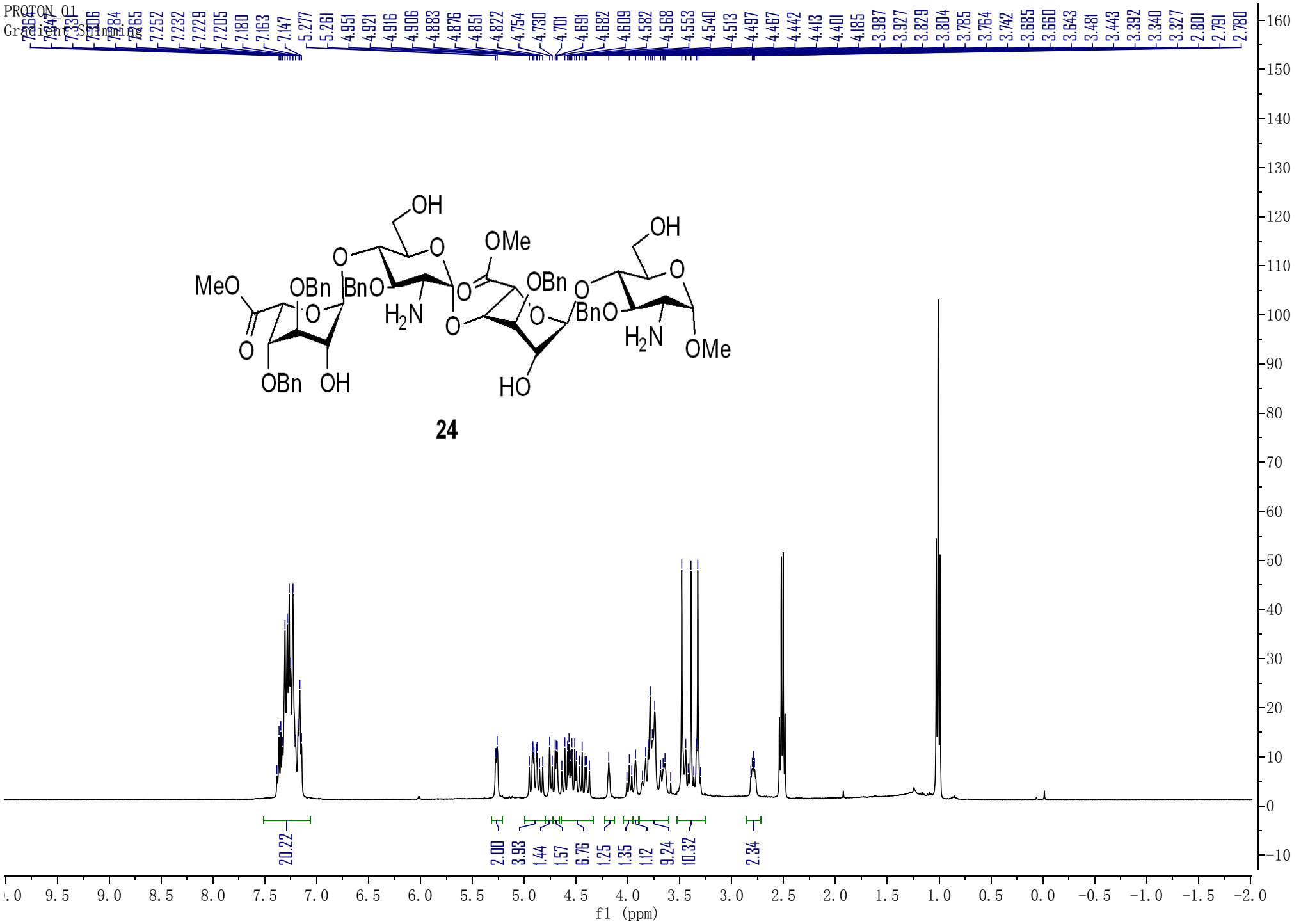

20081112XP14-5H
7.466
7.462
7.445
7.387
7.383
7.365
7.347
7.335
7.331
7.328
7.314
7.041
7.036
7.024
7.019
6.900
6.895
6.883
6.878
5.673
5.667
5.308
5.300
5.011
5.005
4.845
4.817
4.779
4.751
4.703
4.551
4.545
4.540
4.533
4.406
4.401
4.378
4.373
4.366
4.361
4.353
4.344
4.318
4.284
4.260
4.248
4.237
4.228
4.176
4.162
4.149
4.135
3.766
3.723
3.435
3.427
3.408
3.400
OSO3-
OMe
-O3SO
-O3SO
-O3SHN
OBn
OMp
-O3SO
23
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
5.32
2.05
2.07
1.00
0.95
0.99
2.38
1.04
5.19
1.11
1.13
6.24
1.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

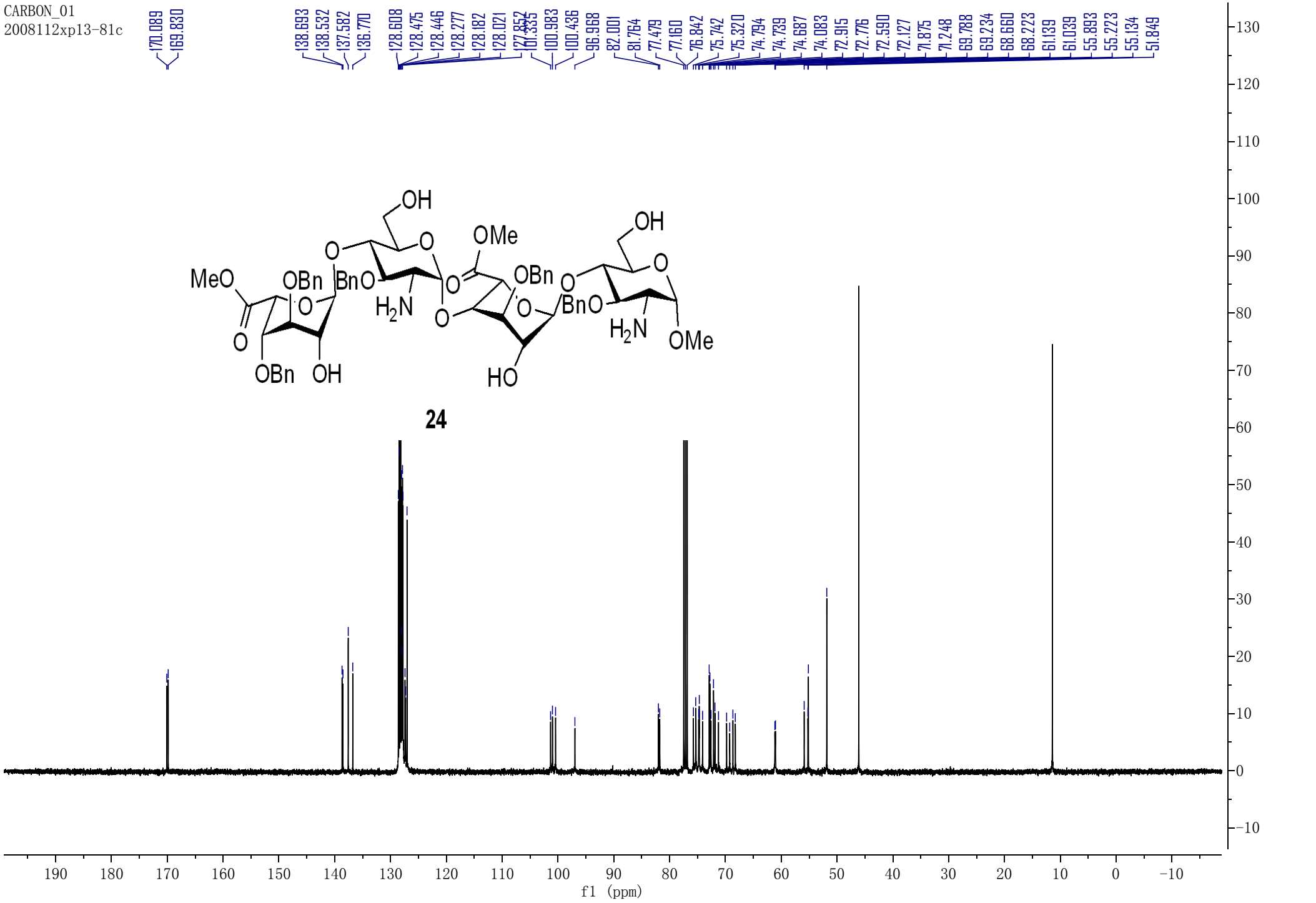
2012年12月

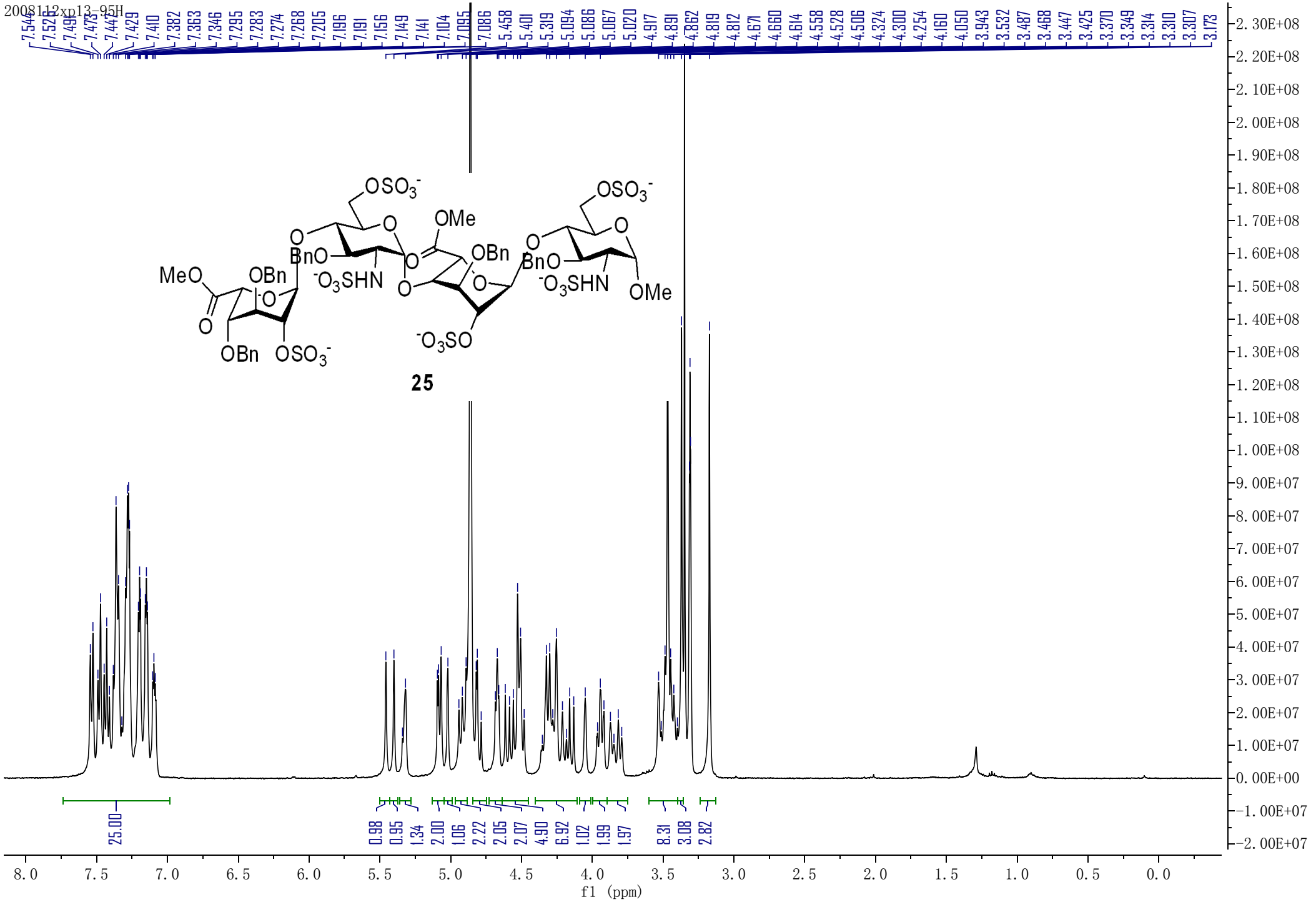

173.083
157.521
152.501
139.800
131.374
131.002
121.785
117.752
101.482
99.789
77.869
77.690
77.004
75.560
75.479
72.407
71.310
69.498
59.300
58.475
55.875
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

OSO3-
OMe
-O3SO
-O3SO
-O3SHN
OBn
OMp
-O3SO

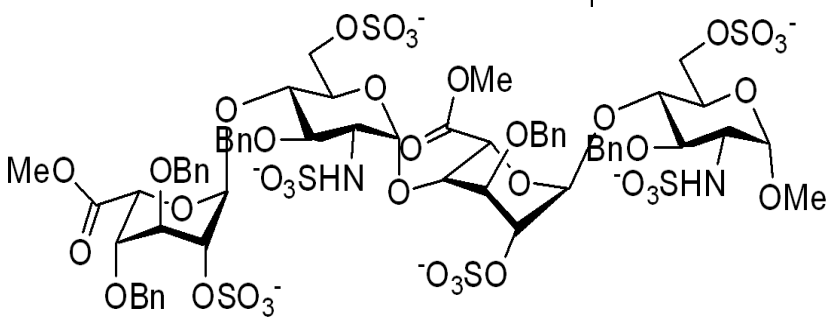
23


PROTON_01
Gradient Standard
7.264
7.247
7.231
7.206
7.184
7.165
7.252
7.232
7.229
7.205
7.180
7.163
7.147
5.277
5.261
4.951
4.921
4.916
4.906
4.883
4.876
4.851
4.822
4.754
4.730
4.701
4.691
4.682
4.609
4.582
4.568
4.553
4.540
4.513
4.497
4.467
4.442
4.413
4.401
4.185
3.987
3.927
3.829
3.804
3.785
3.764
3.742
3.685
3.660
3.643
3.481
3.443
3.392
3.340
3.327
2.801
2.791
2.780
MeO
OBn
BnO
OMe
OBn
BnO
OMe
OBn
OH
HO
OH
OH
H2N
H2N
24
20.22
2.00
3.93
1.44
1.57
6.76
1.25
1.35
1.12
9.24
10.32
2.34
f1 (ppm)


CARBON_01
2008112xp13-81c
170.089
169.830
138.693
138.532
137.582
136.770
128.608
128.475
128.446
128.277
128.182
128.021
127.852
101.333
100.983
100.436
96.968
82.001
81.764
77.479
77.160
76.842
75.742
75.320
74.794
74.739
74.687
74.083
72.915
72.776
72.590
72.127
71.875
71.248
69.788
69.234
68.660
68.223
61.139
61.039
55.893
55.223
55.134
51.849
OH
O
OMe
MeO
OBn
BnO
O
O
H2N
O
OBn
O
OBn
O
BnO
O
H2N
OMe
O
OBn
OH
HO
24
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

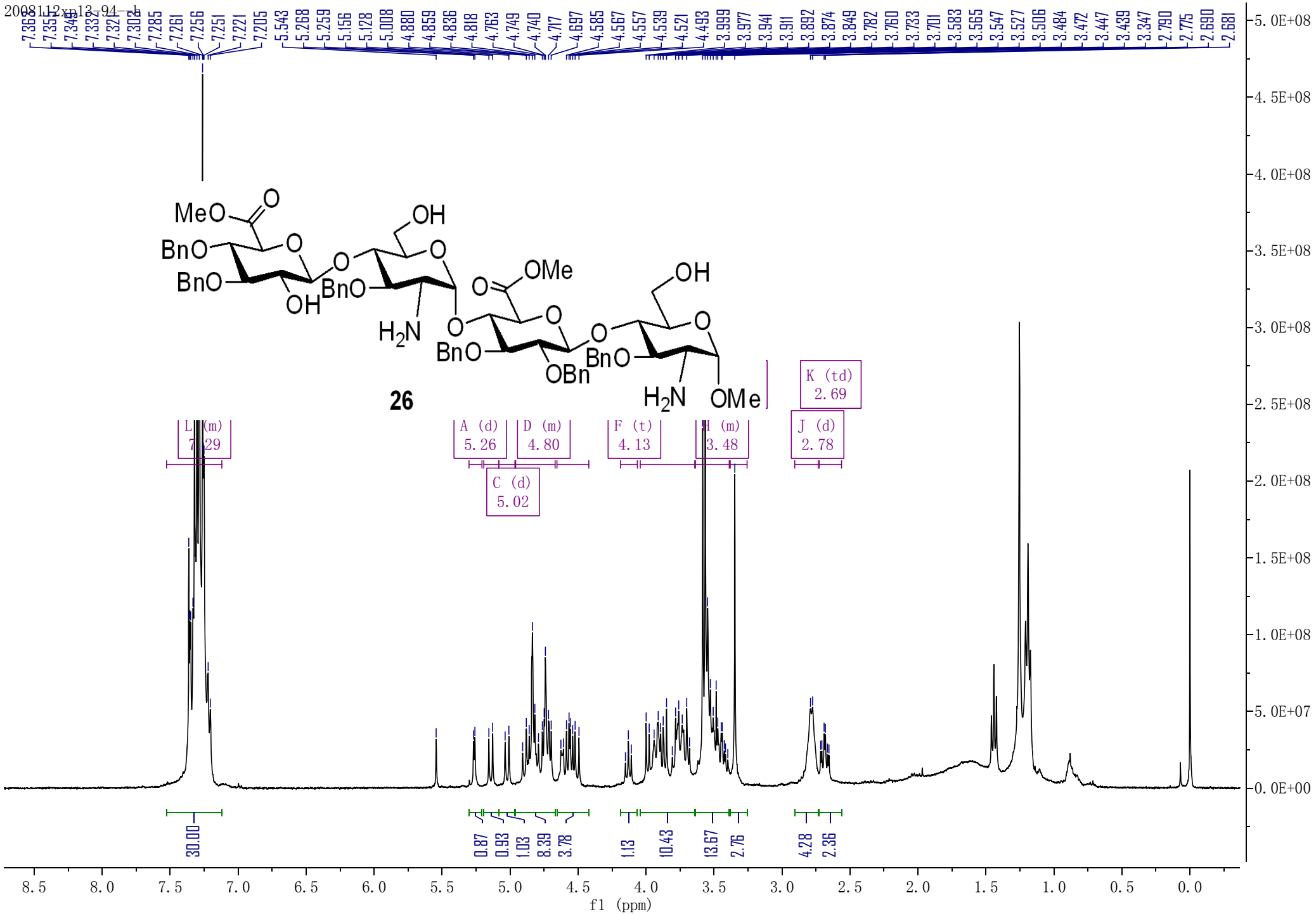

20081122xp13-95H
f1 (ppm)
25

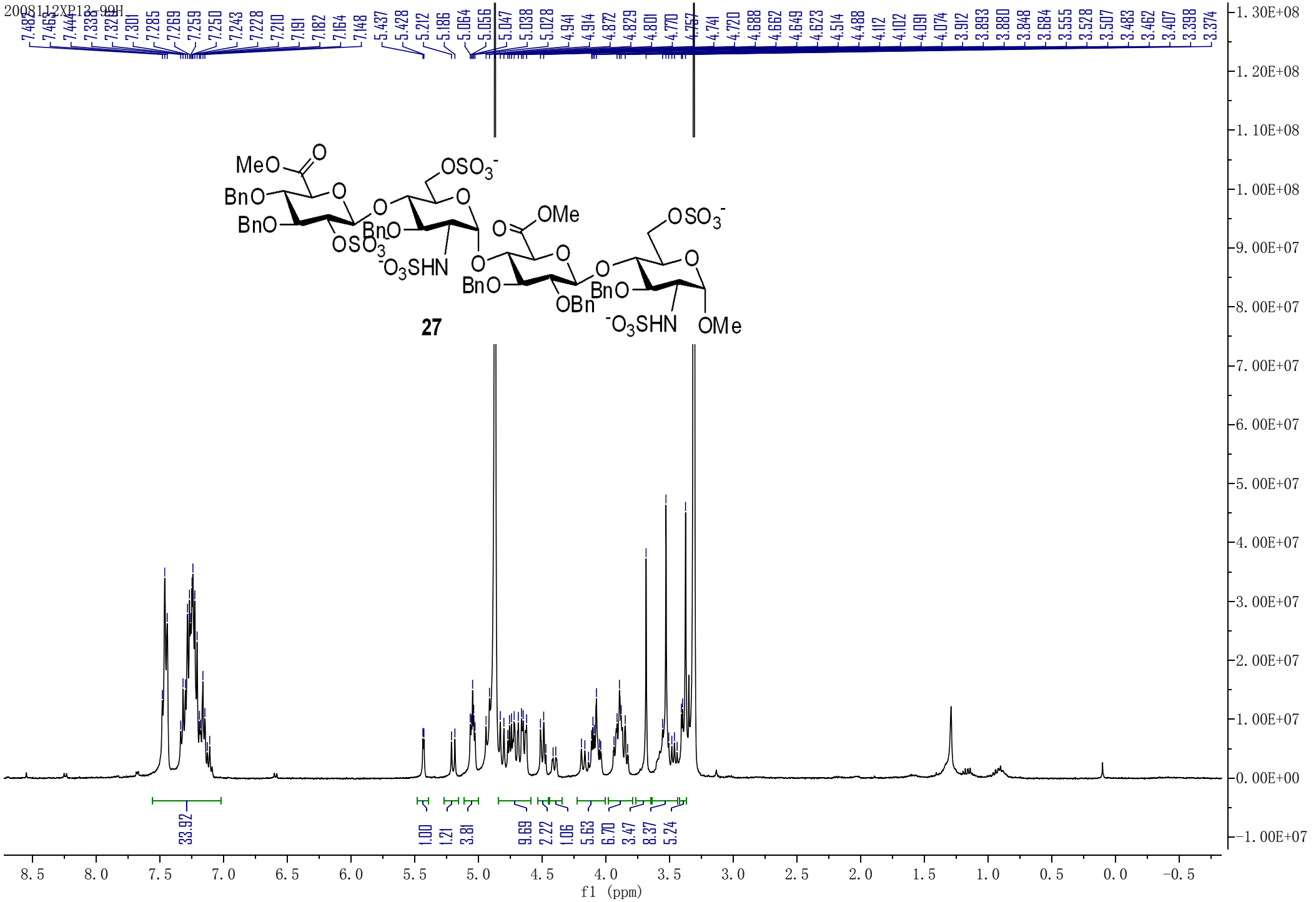
xp13-95c


OSO3-
OMe
BnO
OBn
MeO
-O3SHN
O
OBn
OSO3-
-O3SO
OSO3-
BnO
-O3SHN
OMe

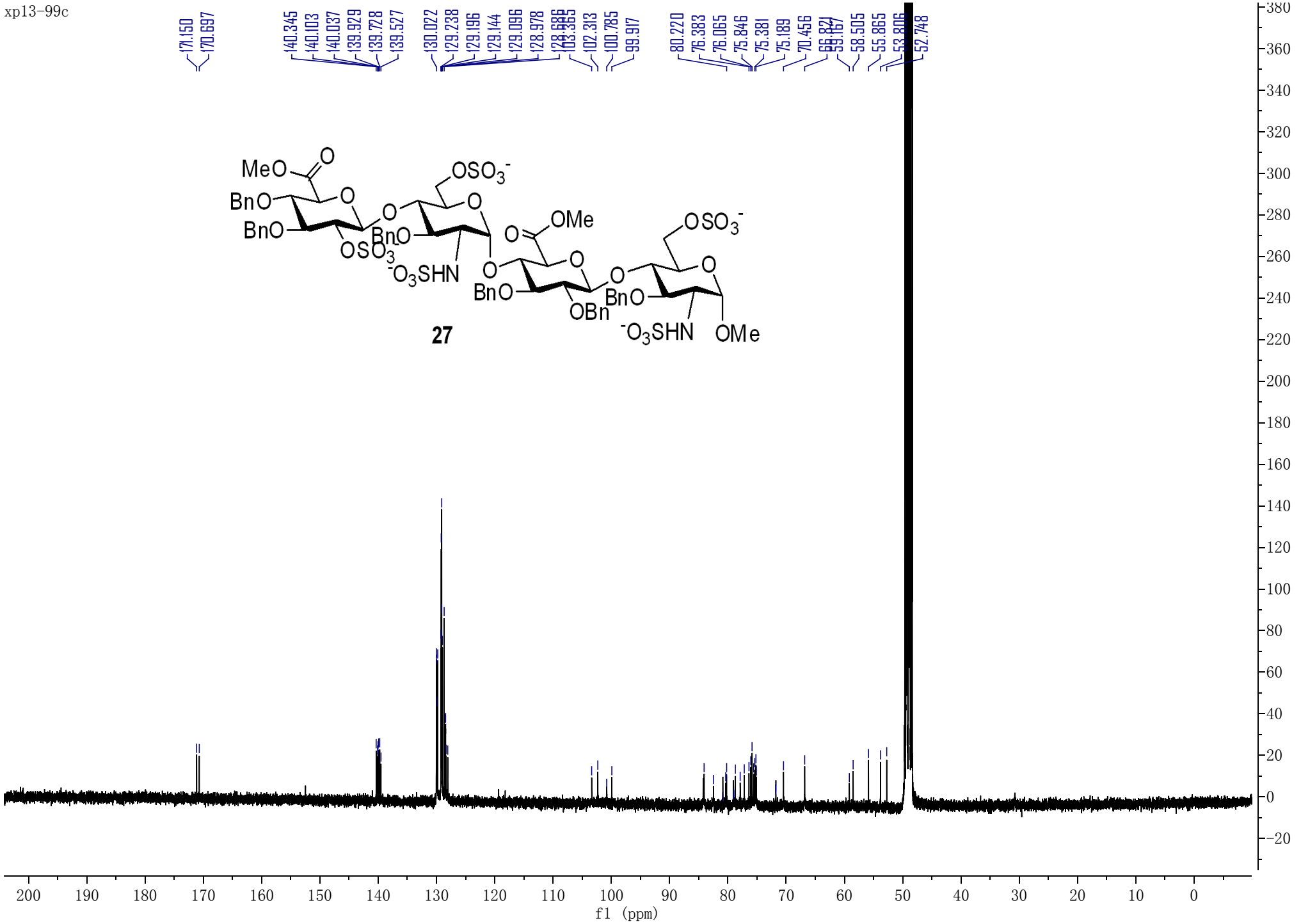
25

172.487
172.056
139.486
138.860
138.198
130.147
130.070
129.965
129.901
129.717
129.675
129.322
129.260
129.039
128.843
100.080
99.169
98.427
79.920
79.061
76.876
76.580
76.082
73.830
73.637
72.951
72.104
71.479
71.372
71.124
70.756
70.633
68.329
68.233
67.587
59.950
59.872
55.911
53.022
52.415
49.849
f1 (ppm)

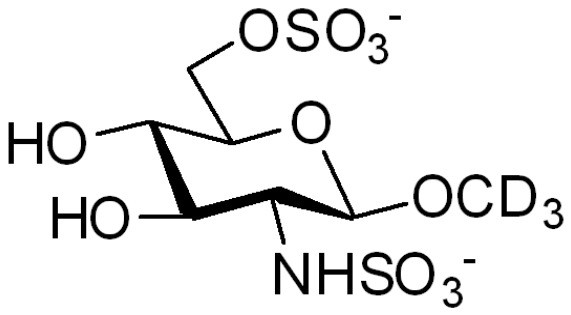

20081112xp13-94-h
7.365 7.355 7.348 7.332 7.327 7.305 7.285 7.261 7.256 7.251 7.221 7.205
5.543 5.268 5.259 5.156 5.128 5.008 4.880 4.859 4.836 4.818 4.763 4.749 4.740 4.717 4.697 4.585 4.567 4.557 4.539 4.521 4.493
3.999 3.977 3.941 3.911 3.892 3.874 3.849 3.782 3.760 3.733 3.701 3.583 3.565 3.547 3.527 3.506 3.484 3.472 3.447 3.439 3.347 2.790 2.775 2.690 2.681
MeO
BnO
BnO
OH
BnO
OMe
OH
H2N
BnO
OBn
BnO
H2N
OMe
26
L (m) 7.29
A (d) 5.26
D (m) 4.80
C (d) 5.02
F (t) 4.13
H (m) 3.48
K (td) 2.69
J (d) 2.78
30.00
0.87
0.93
1.03
8.39
3.78
1.13
10.43
13.67
2.76
4.28
2.36
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


20081112XP13-99H
MeO
BnO
BnO
OSO3
O3SHN
OSO3-
OMe
BnO
OBn
BnO
O3SHN
OSO3-
OMe
27
33.92
1.00
1.21
3.81
9.69
2.22
1.06
5.63
6.70
3.47
8.37
5.24
f1 (ppm)

xp13-99c

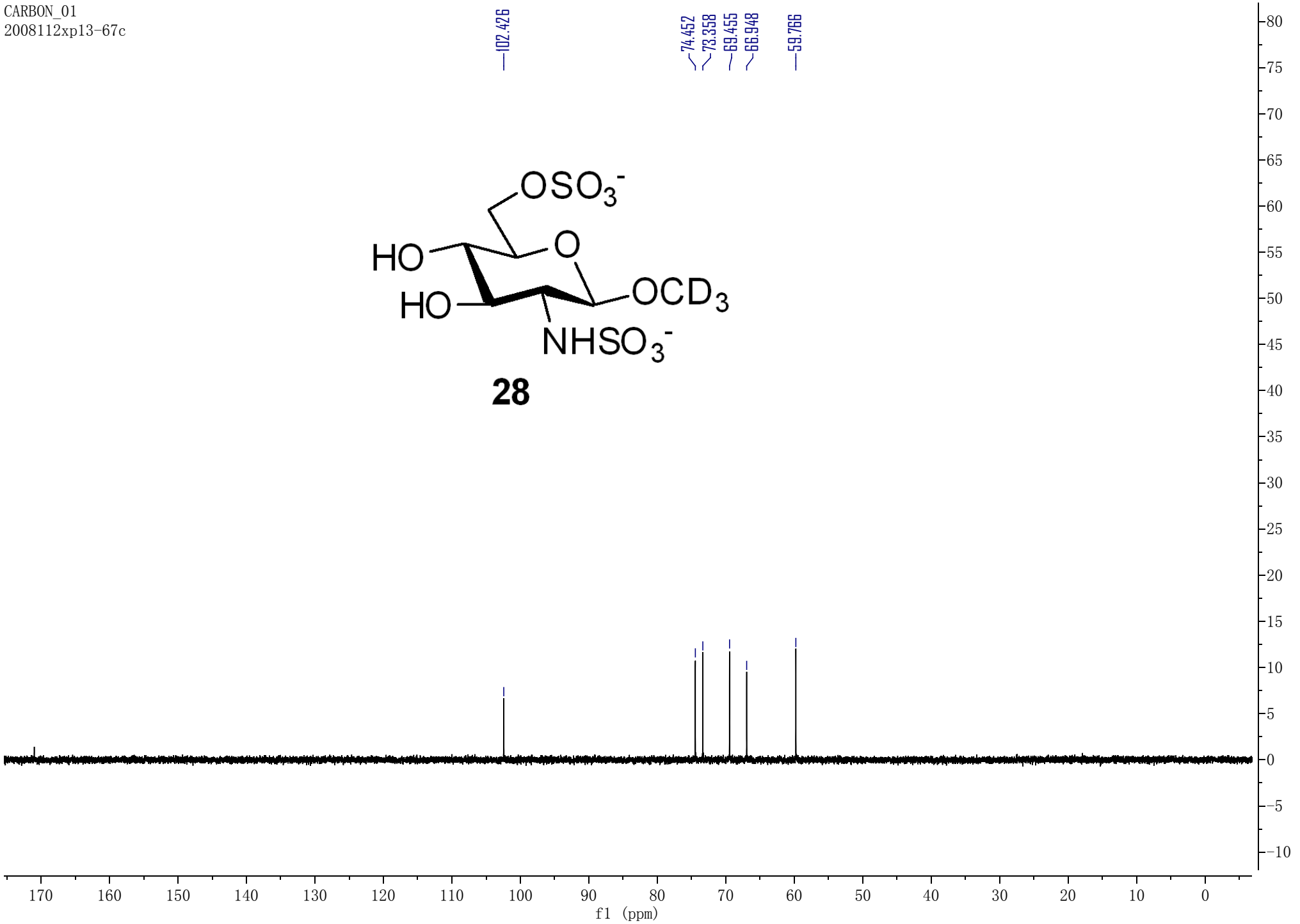

171.150
170.697
140.345
140.103
140.037
139.929
139.728
139.527
130.022
129.238
129.196
129.144
129.096
128.978
103.365
102.313
100.785
99.917
80.220
76.383
76.065
75.846
75.381
75.189
70.456
58.505
55.865
52.748
MeO
BnO
BnO
OSO3-
-O3SHN
BnO
OMe
OBn
BnO
OSO3-
-O3SHN
OMe
27
f1 (ppm)

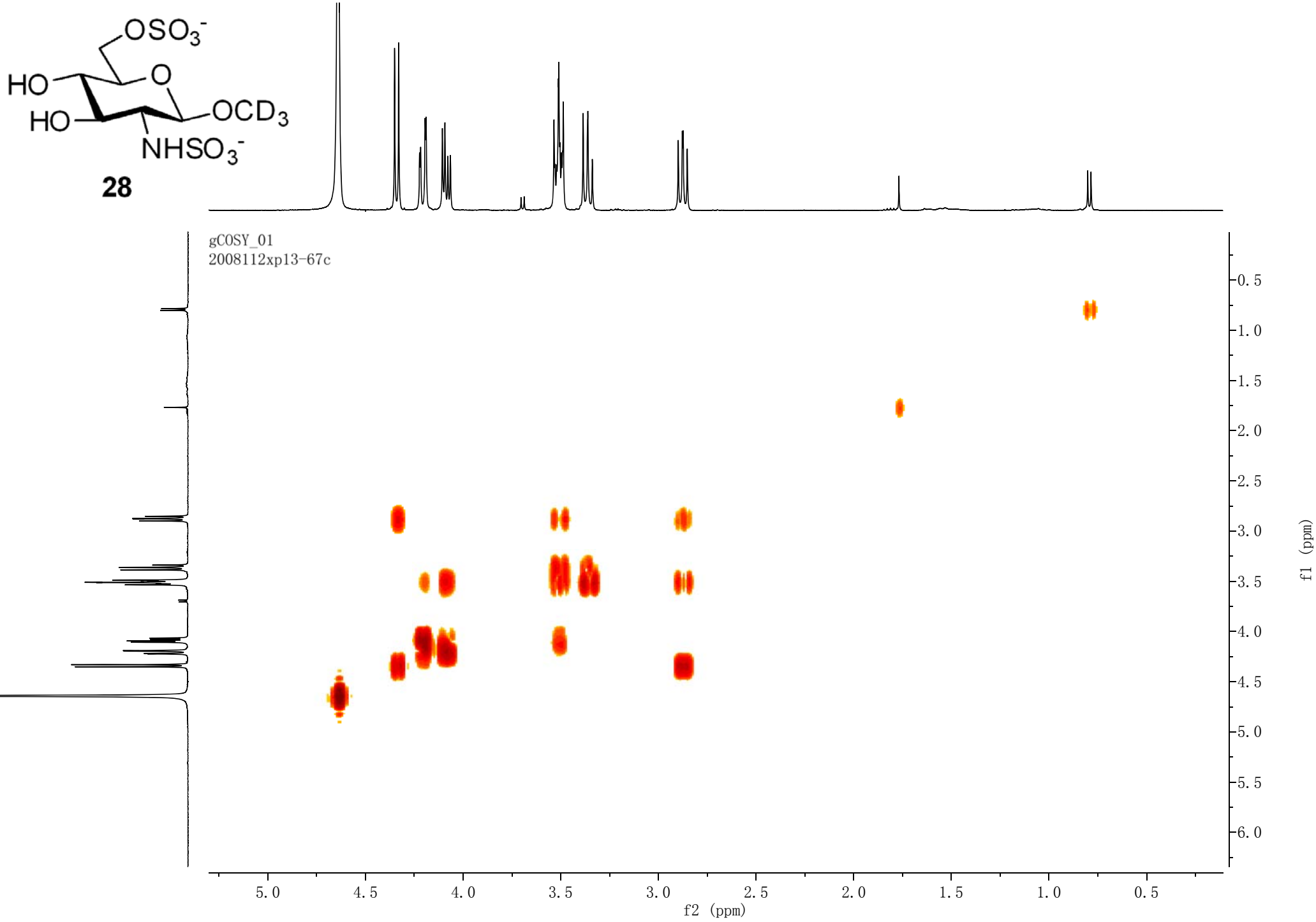
2008112xp13-67c



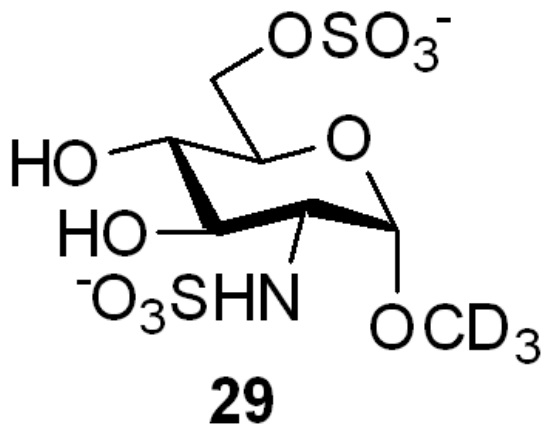
28

CARBON_01
2008112xp13-67c




OSO3-
HO
O
HO
OCD3
NHSO3-
28
gCOSY_01
2008112xp13-67c
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)

2008112xp13-92H



29

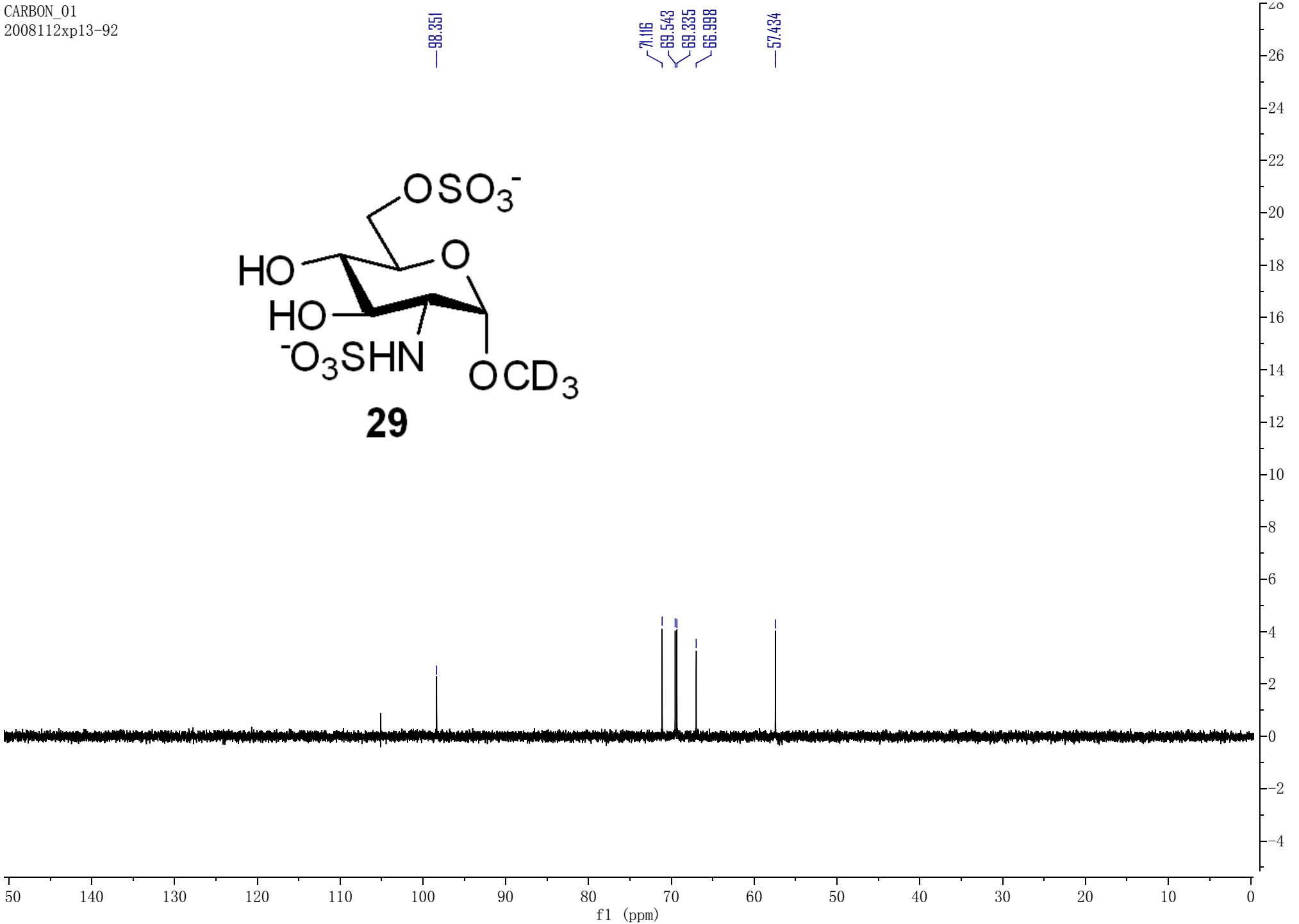
4.985 4.977 4.790 4.736 4.297 4.292 4.269 4.265 4.234 4.221 4.206 4.193 3.850 3.845 3.838 3.833 3.825 3.821 3.813 3.584 3.561 3.536 3.508 3.484 3.461 3.241 3.233 3.216 3.207

(d) 98 | B (dd) 4.28 | C (dd) 4.21 | D (m) 3.83 | E (dt) 3.52 | F (dd) 3.22

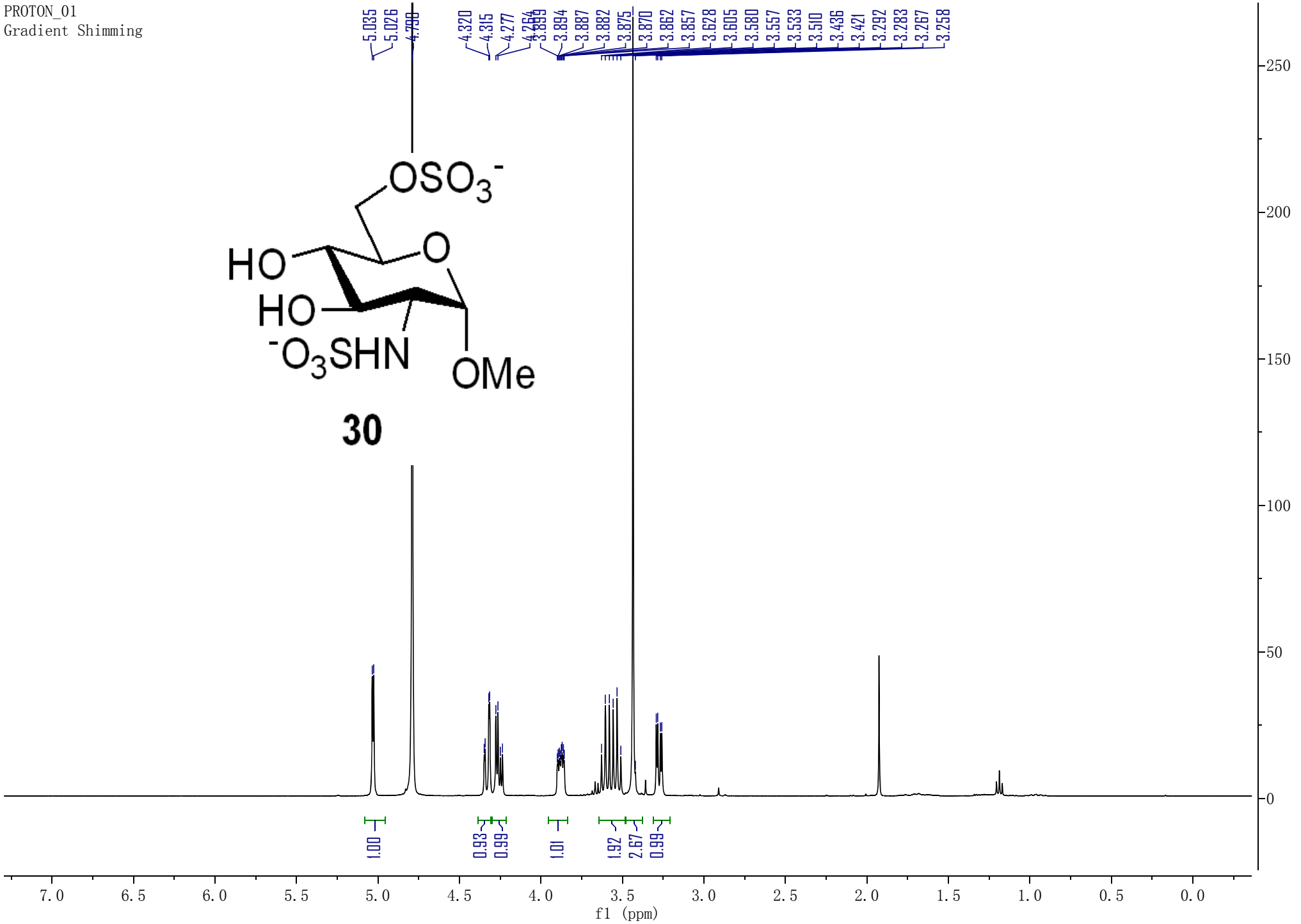
1.00 0.85 0.86 0.82 1.71 0.81

f1 (ppm)

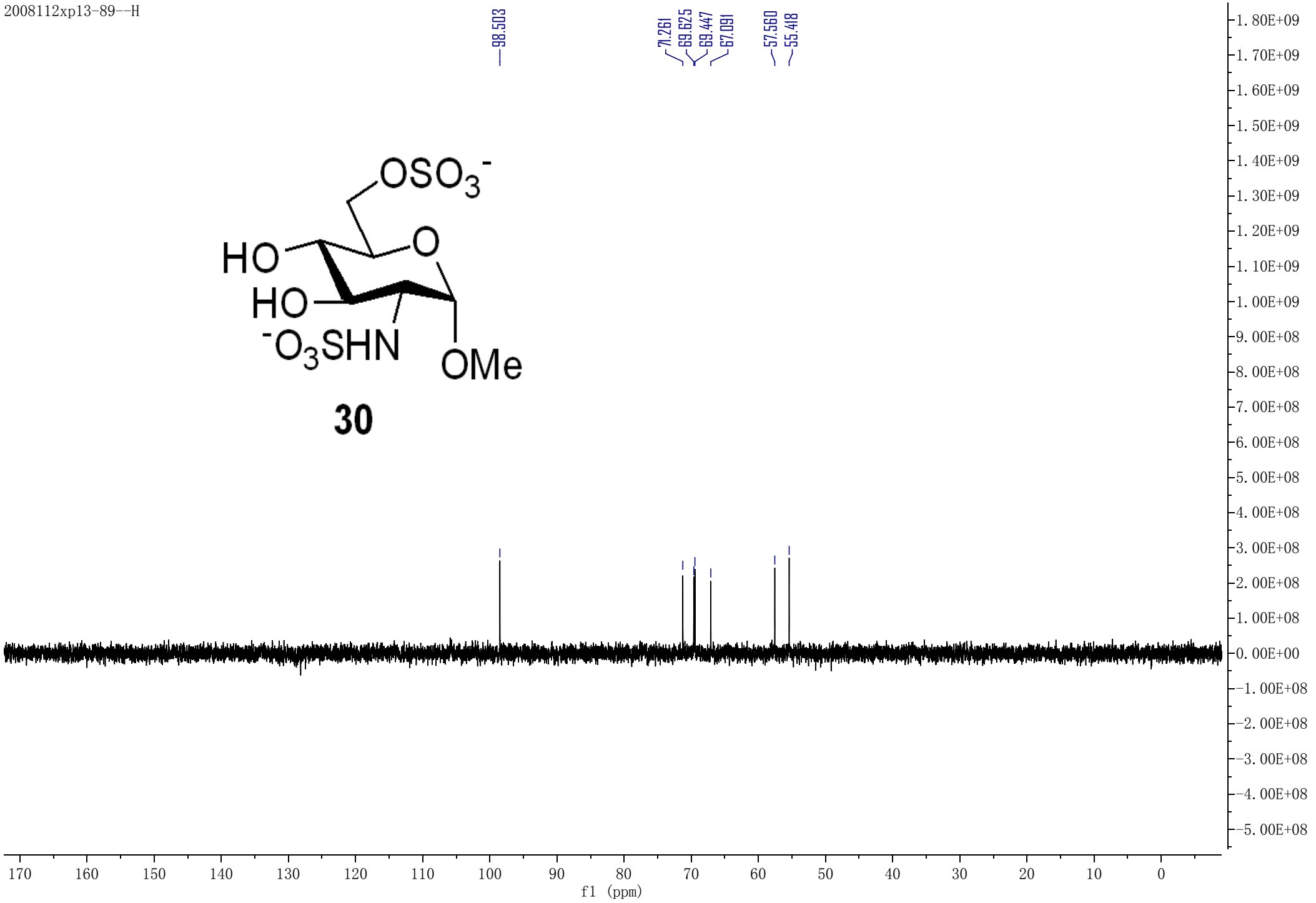
CARBON_01
2008112xp13-92

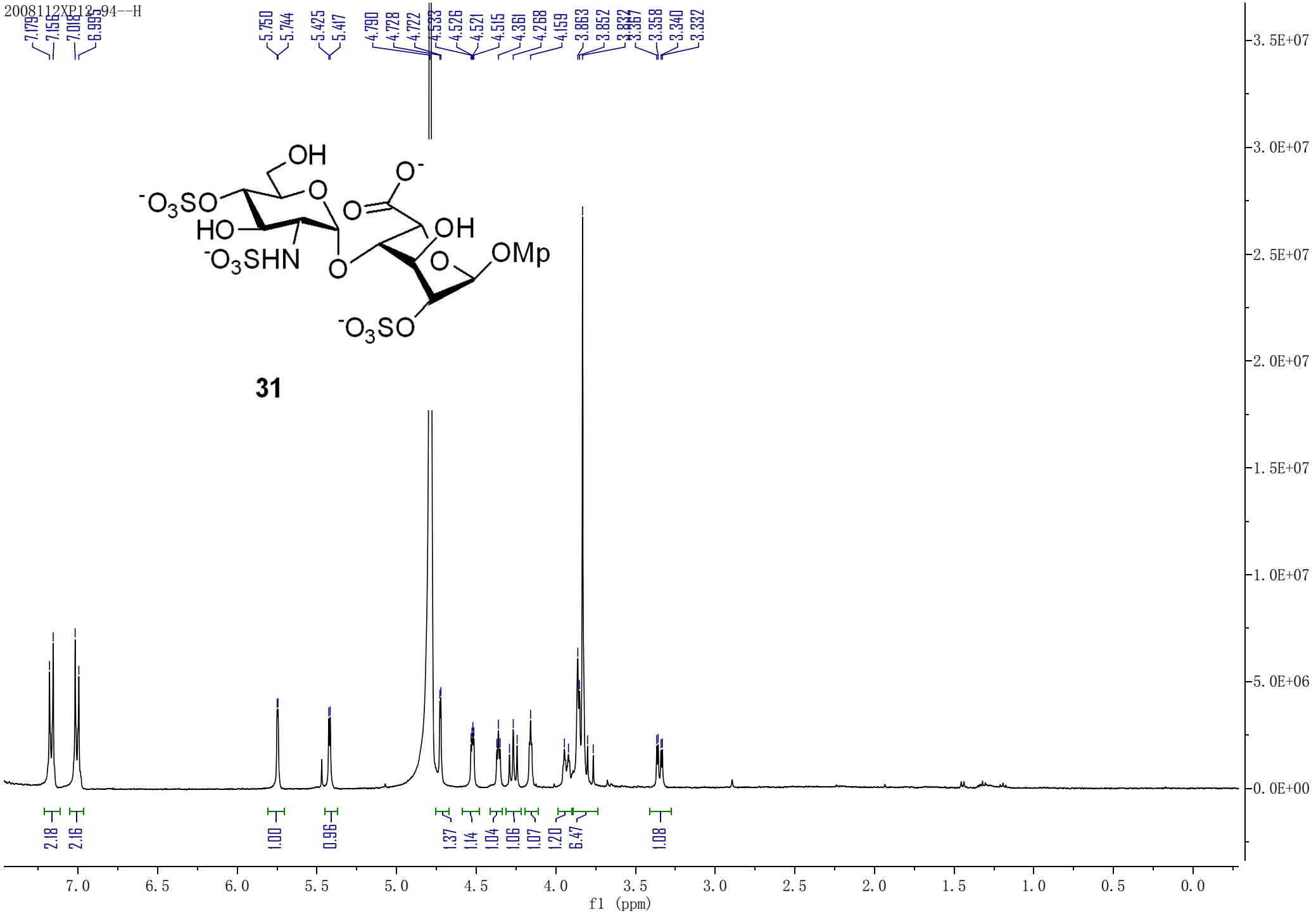


PROTON_01
Gradient Shimming

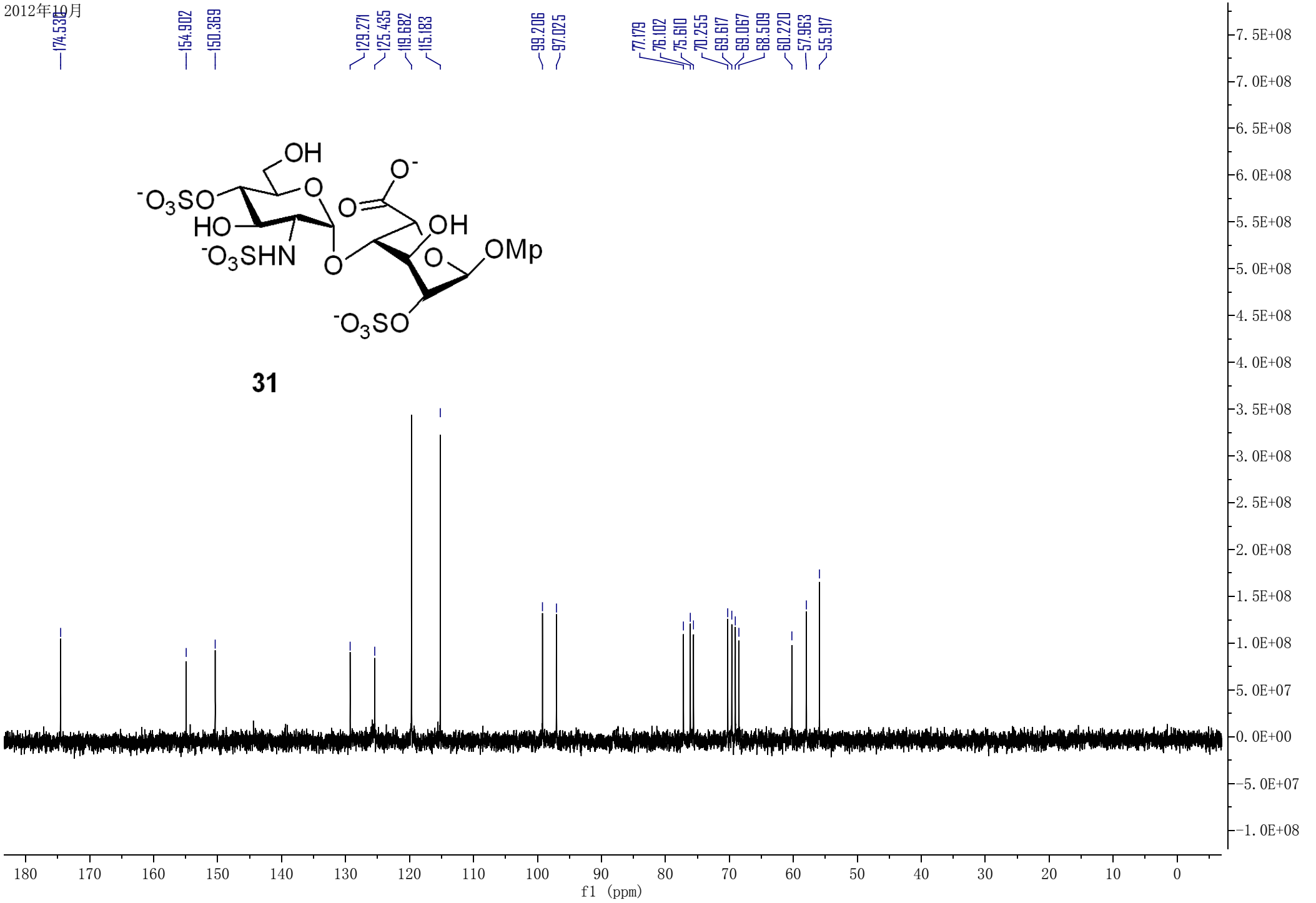


2008112xp13-89--H




2008112XP12-94--H
7.179
7.156
7.018
6.995
5.750
5.744
5.425
5.417
4.790
4.728
4.722
4.533
4.526
4.521
4.515
4.361
4.268
4.159
3.863
3.852
3.832
3.667
3.358
3.340
3.332
OH
O
O-
-O3SO
HO
-O3SHN
O
O
OH
O
OMp
-O3SO
31
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
2.18
2.16
1.00
0.96
1.37
1.14
1.04
1.06
1.07
1.20
6.47
1.08
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

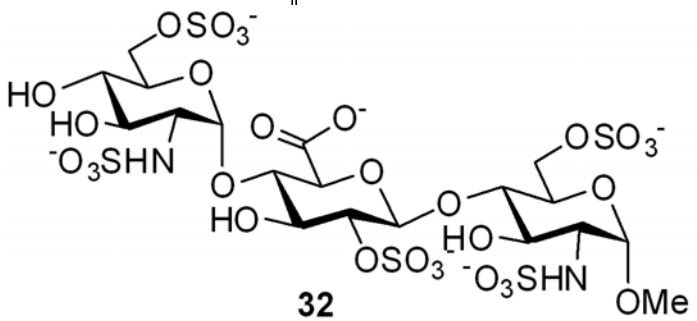
2012年10月


174.538
154.902
150.369
129.271
125.435
119.682
115.183
99.206
97.025
77.179
76.102
75.610
70.255
69.617
69.067
68.509
60.220
57.963
55.917
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
-1.0E+08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OH
O
O-
-O3SO
O
OH
HO
-O3SHN
O
O
OMp
-O3SO

31

2008112xp13-80cH



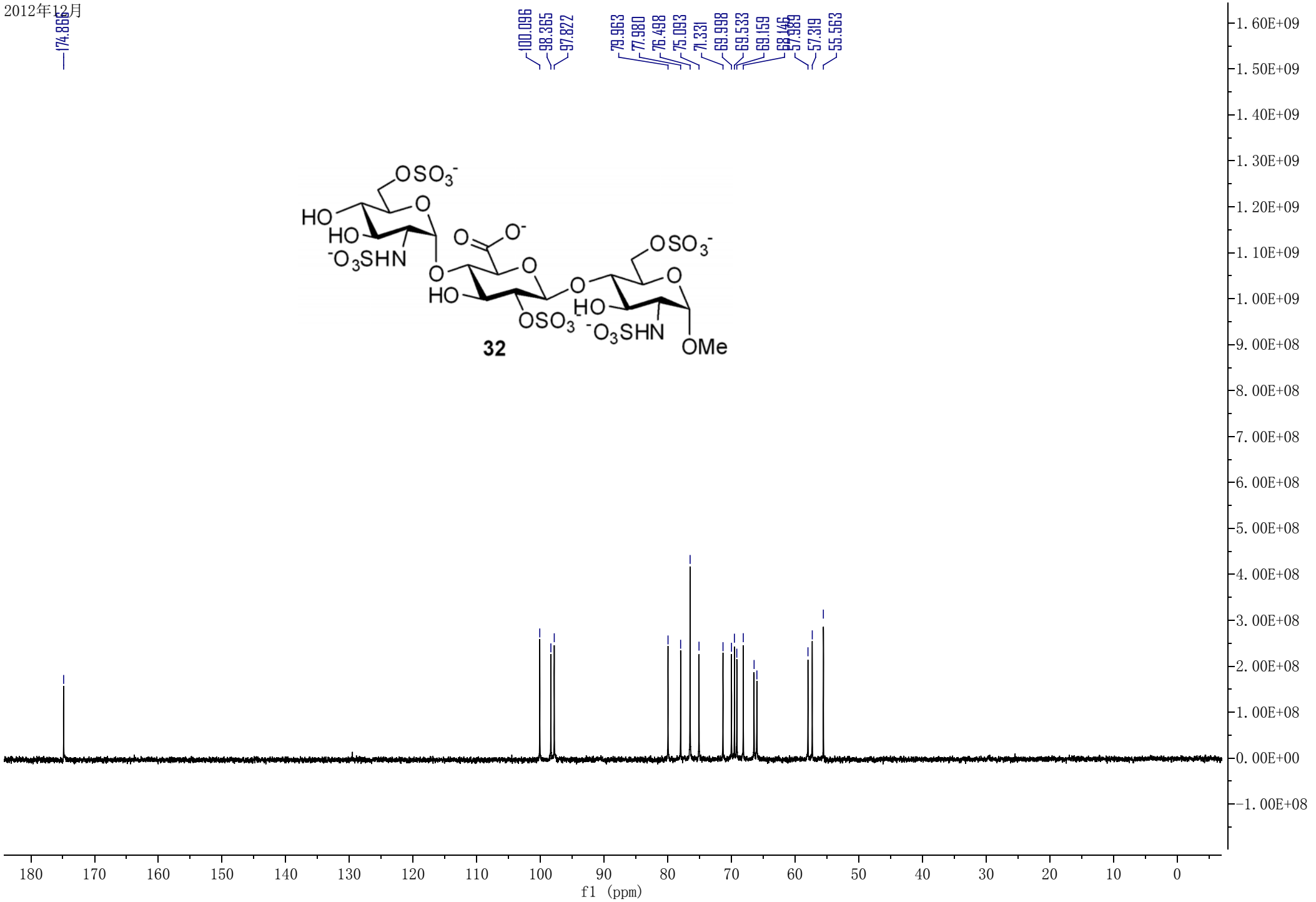
32

5.738 5.113 4.833 4.790 4.678 4.651 4.454 4.427 4.347 4.319 4.278 4.249 4.221 4.077 4.053 4.030 3.979 3.954 3.932 3.838 3.818 3.798 3.719 3.690 3.659 3.501 3.383 3.348 3.318

1.00 1.04 0.86 0.95 2.73 8.39 2.73 2.02

f1 (ppm)

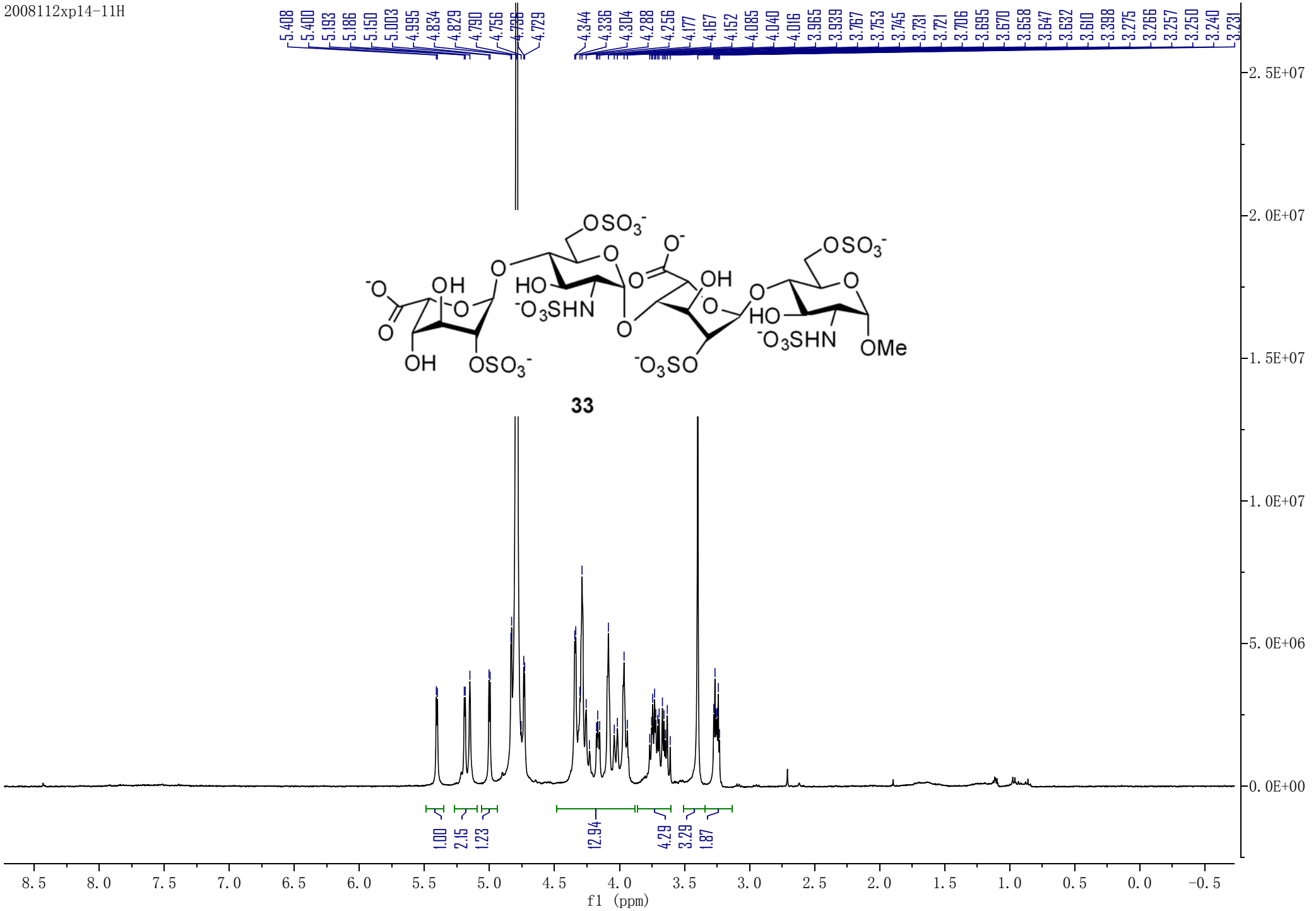
2012年12月


174.866
100.096
98.365
97.822
79.963
77.980
76.498
75.093
71.331
69.998
69.533
69.159
68.146
57.319
55.563
1.60E+09
1.50E+09
1.40E+09
1.30E+09
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OSO3-
HO
HO
-O3SHN
O
O-
O
O
HO
OSO3-
OSO3-
HO
-O3SHN
OMe

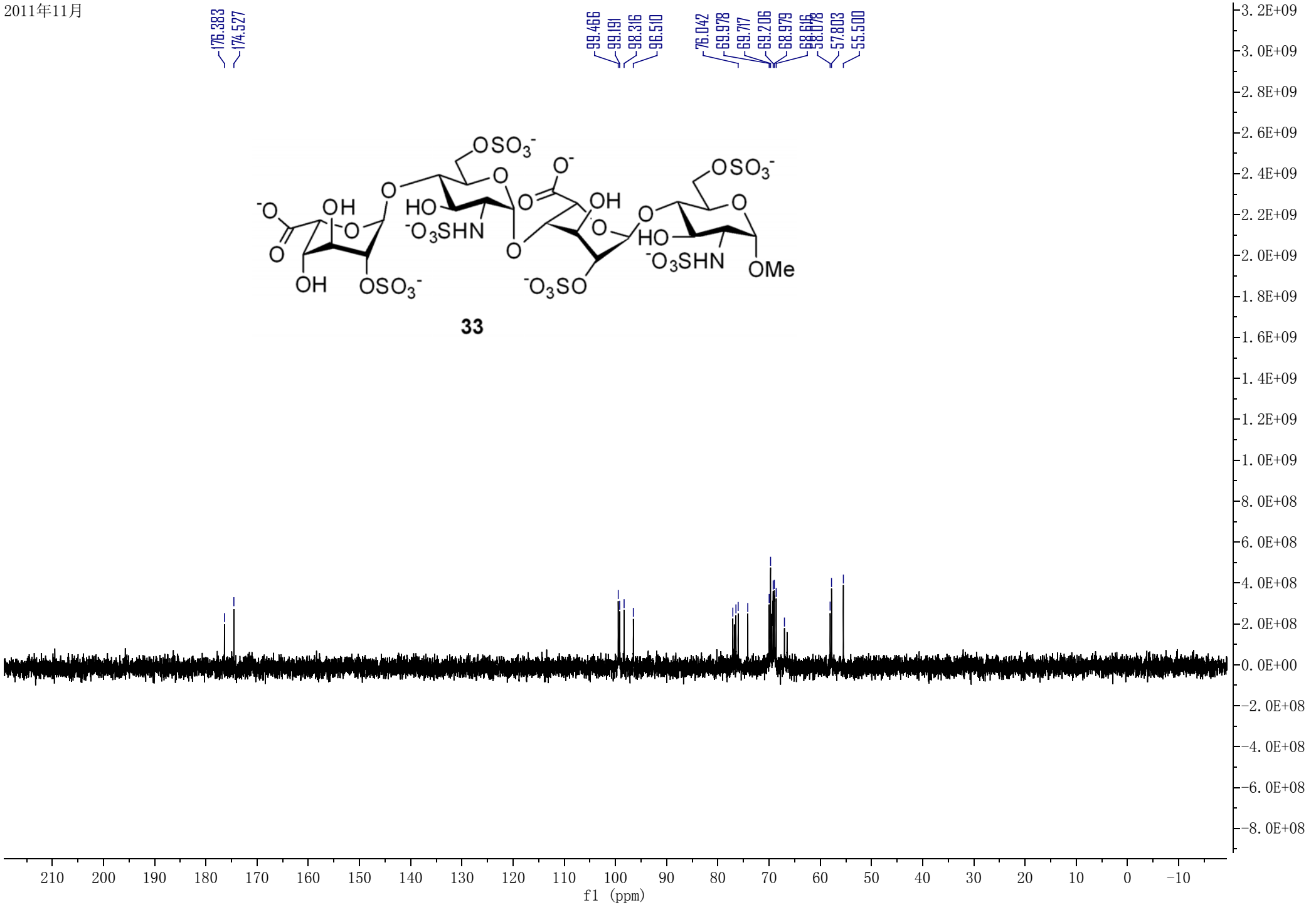
32

2008112xp14-11H



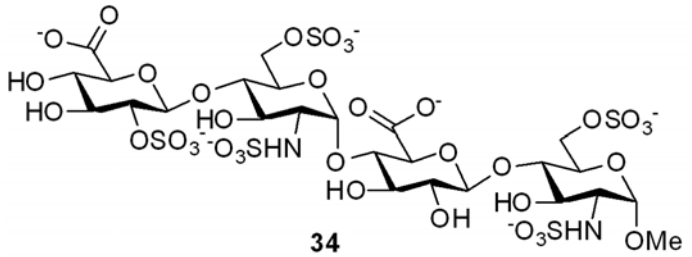
33

2011年11月


176.383
174.527
99.466
99.191
98.316
96.510
76.042
69.978
69.717
69.206
68.979
57.803
55.500
3.2E+09
3.0E+09
2.8E+09
2.6E+09
2.4E+09
2.2E+09
2.0E+09
1.8E+09
1.6E+09
1.4E+09
1.2E+09
1.0E+09
8.0E+08
6.0E+08
4.0E+08
2.0E+08
0.0E+00
-2.0E+08
-4.0E+08
-6.0E+08
-8.0E+08
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

33

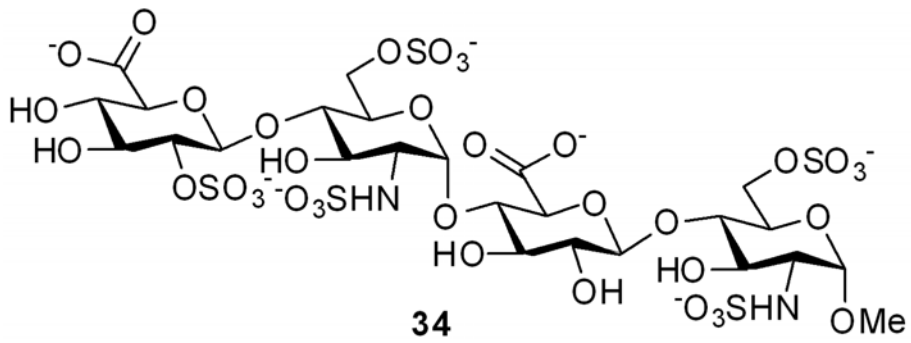
2006118-9-02



34

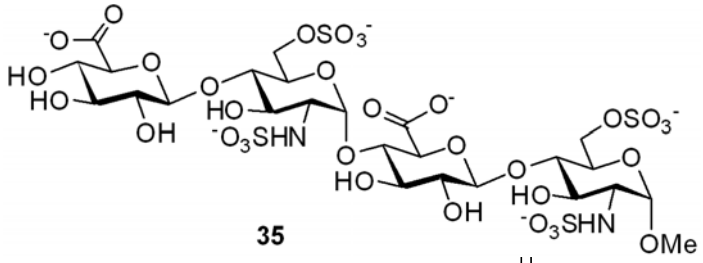
f1 (ppm)

2006118-9-02C



34

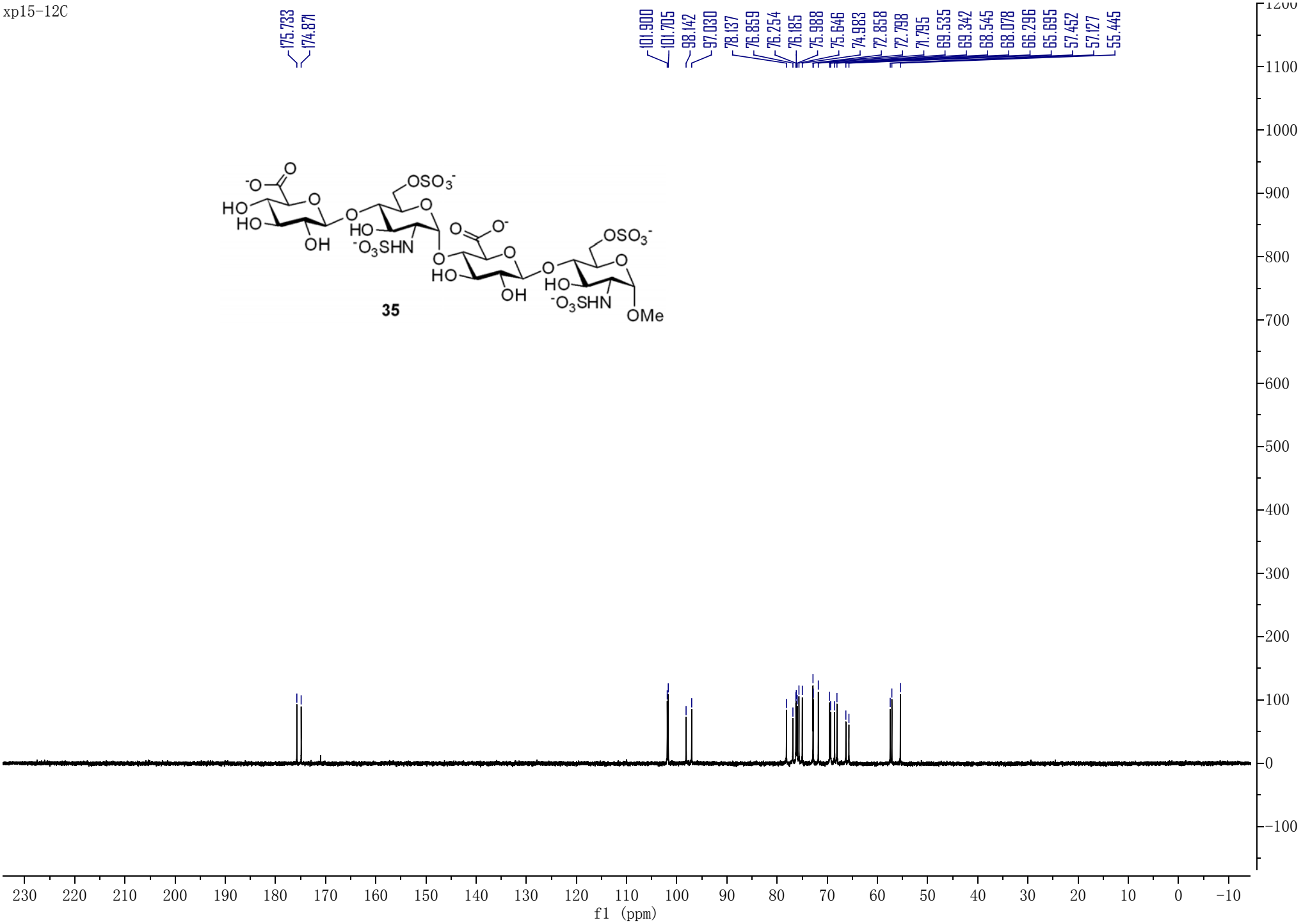
2008112xp15-12_20130513_01
2008132-17-41-bn

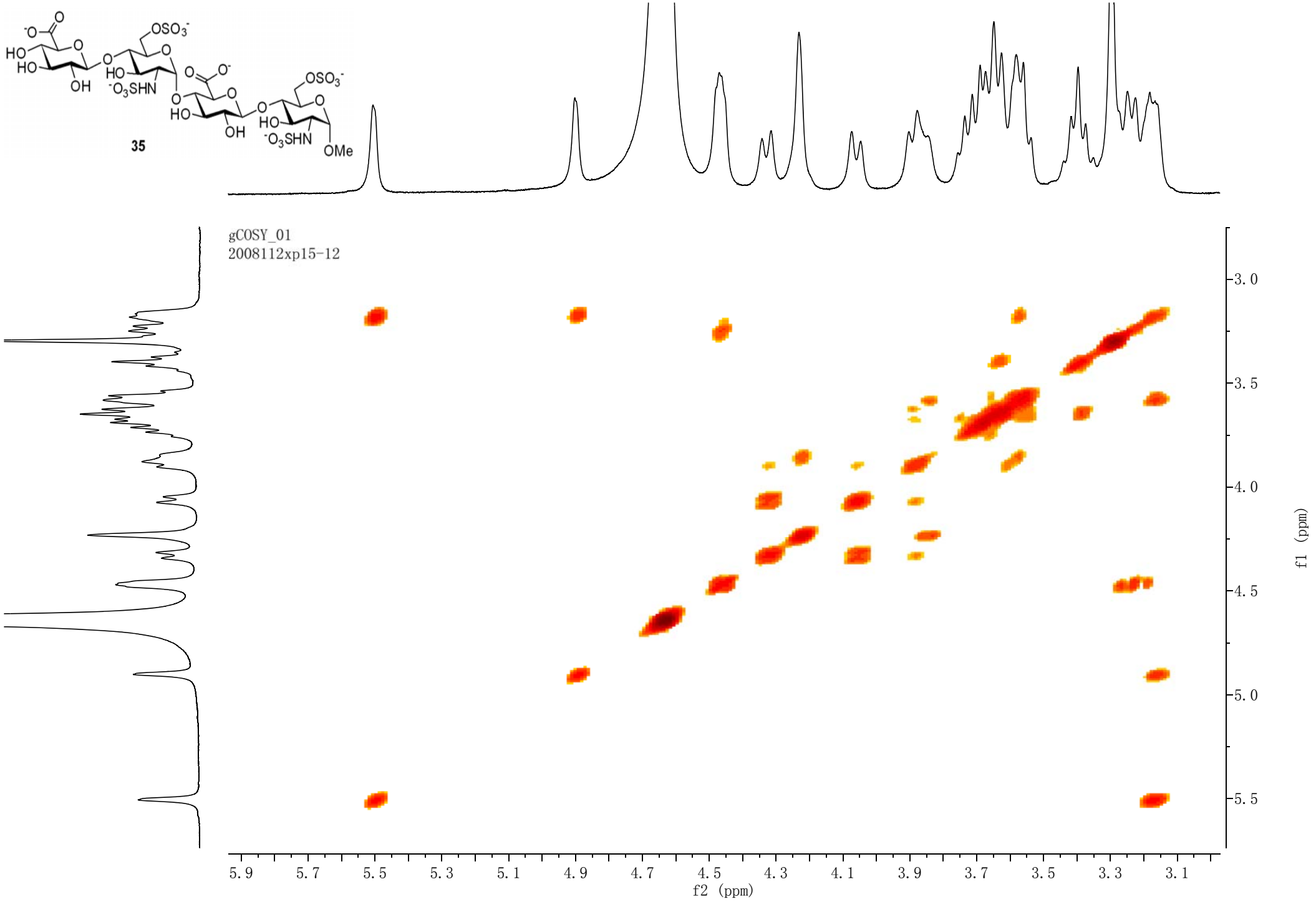


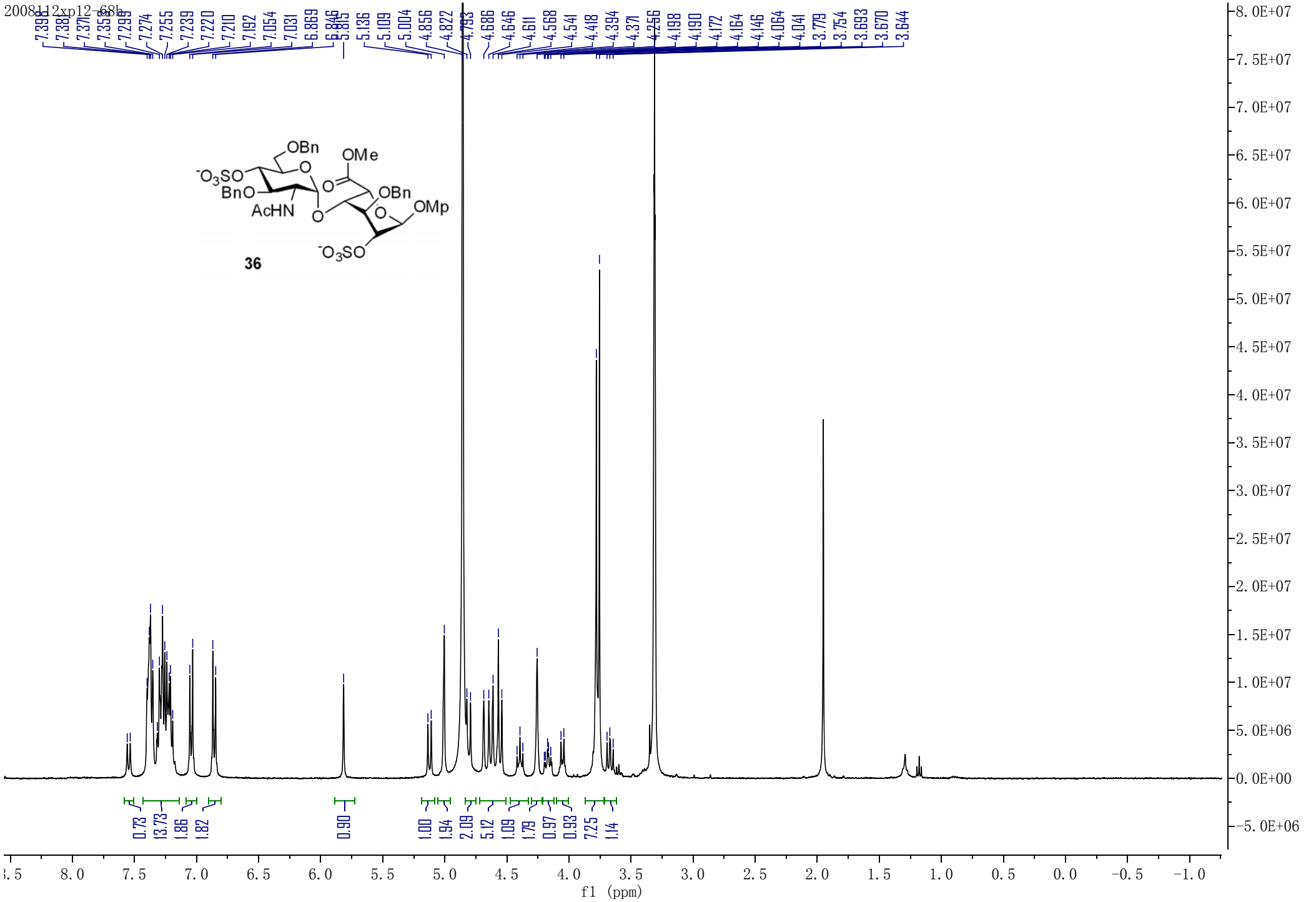
35

f1 (ppm)

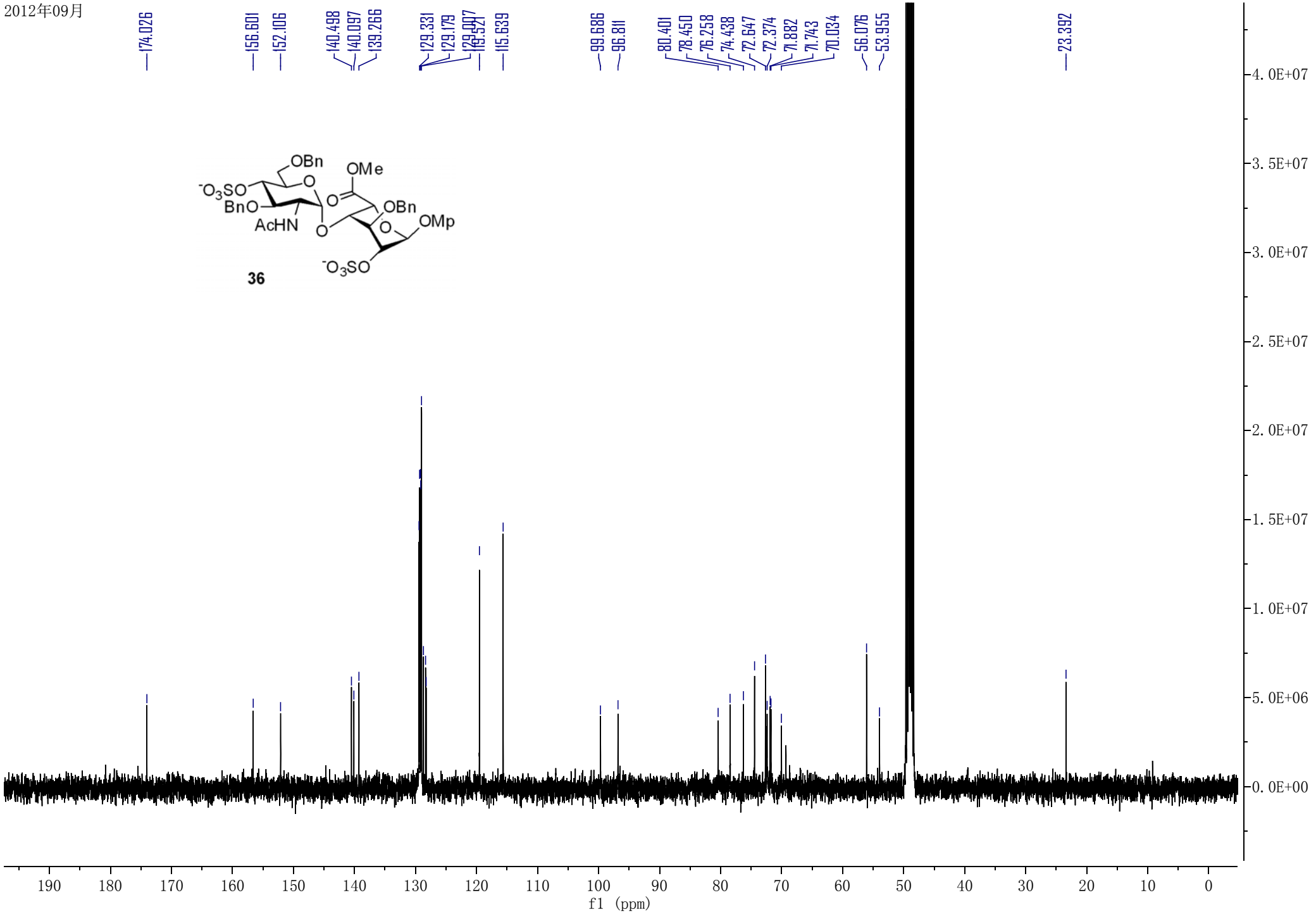
xp15-12C


175.733
174.871
101.900
101.705
98.142
97.030
78.137
76.859
76.254
76.185
75.988
75.646
74.983
72.858
72.798
71.795
69.535
69.342
68.545
68.078
66.296
65.695
57.452
57.127
55.445
35
f1 (ppm)

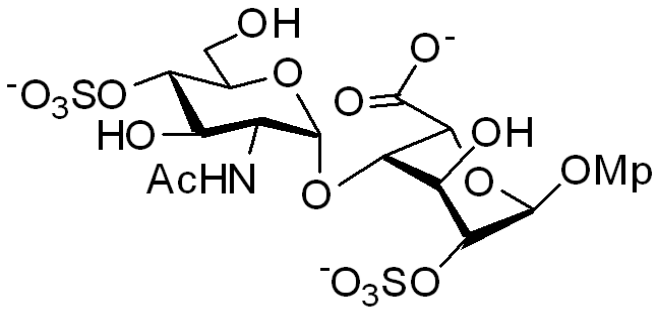

35
gCOSY_01
2008112xp15-12
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
f2 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)


2008112xp12-68h
7.391
7.382
7.371
7.358
7.299
7.274
7.255
7.239
7.220
7.210
7.192
7.054
7.031
6.869
6.846
5.815
5.136
5.109
5.004
4.856
4.822
4.793
4.686
4.646
4.611
4.568
4.541
4.418
4.394
4.371
4.256
4.198
4.190
4.172
4.164
4.146
4.064
4.041
3.779
3.754
3.693
3.670
3.644
OBn
OMe
$^{-}O_3SO$
BnO
AcHN
OBn
OMp
$^{-}O_3SO$
36
0.73
13.73
1.86
1.82
0.90
1.00
1.94
2.09
5.12
1.09
1.79
0.97
0.93
7.25
1.14
8.0E+07
7.5E+07
7.0E+07
6.5E+07
6.0E+07
5.5E+07
5.0E+07
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
-5.0E+06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

2012年09月


174.026
156.601
152.106
140.498
140.097
139.266
129.331
129.179
128.007
119.521
115.639
99.686
96.811
80.401
78.450
76.258
74.438
72.647
72.374
71.882
71.743
70.034
56.076
53.955
23.392
OBn
OMe
$^{-}O_3SO$
BnO
AcHN
OBn
OMp
$^{-}O_3SO$
36
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

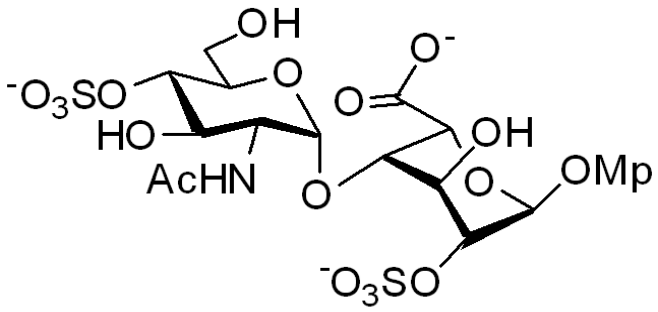
2008112xp12-100h



37

xp12-100c
Gradient Shimming

174.663
154.736
149.960
119.490
114.963
98.723
93.324
76.733
73.427
70.683
70.175
69.707
67.499
63.628
59.992
55.659
52.981
22.108



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