Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Synthesis of the glycan moiety of ganglioside HPG-7 with an unusual trimer of sialic acid as the inner sugar residue†

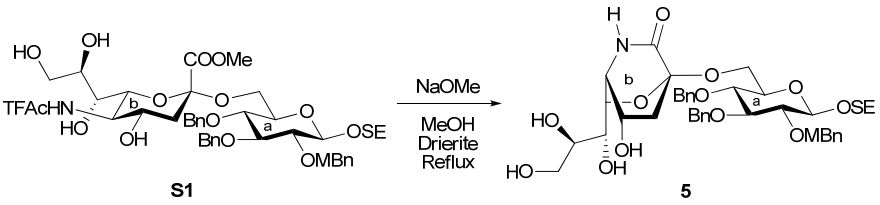
Yuki Iwayama,[a,b] Hiromune Ando,*[a,b] Hide-Nori Tanaka,[a,b] Hideharu Ishida[a] and Makoto Kiso*[a,b]

[a]*Department of Applied Bioorganic Chemistry, Gifu University, 1-1 Yanagido, Gifu-shi, Gifu 501-1193, Japan*
E-mail: hando@ gifu-u.ac.jp; Fax: +81-58-293-3452; Tel.: +81-58-293-3452

[b]*Institute for Integrated Cell-Material Sciences (WPI program), Kyoto University, Yoshida Ushinomiya-cho, Sakyo-ku, Kyoto 606-8501, Japan*

Experimental

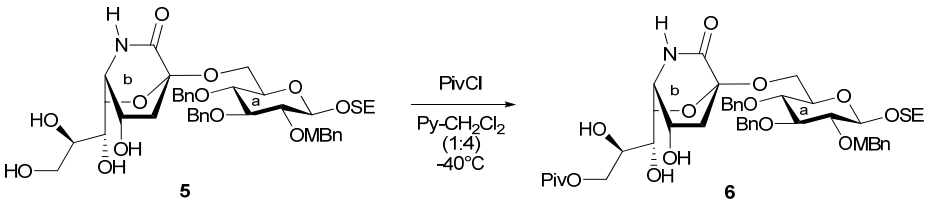
General procedures: ^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-ECX400P, JNM-ECA500, JMN-ECA600, and Bruker Avance III 500 spectrometers. Chemical shifts are expressed in ppm (δ) relative to the signal of Me_4Si as an internal standard. High-resolution mass spectrometry (HRMS) was performed with a Bruker Daltonics micrOTOF (ESI-TOF) mass spectrometer. Specific rotations were determined with a Horiba SEPA-300 high-sensitivity polarimeter. Molecular sieves were purchased from Wako Chemicals Inc. and dried at 300 °C for 2 h in a muffle furnace prior to use. Drierite was powdered and dried at 300 °C for 6 h in a muffle furnace prior to use. Solvents as reaction media were dried over molecular sieves and used without further purification. TLC analysis was performed on Merck TLC plates (silica gel $60F_{254}$ on glass). Compounds were visualized either by exposure to UV light (254 nm) or by spraying 10 % H_2SO_4 solution in EtOH, 20 % phosphomolybdic acid solution in EtOH, or ninhydrin reagent, followed by heating. Flash column chromatography on silica gel (Fuji Silysia Co., 80 mesh and 300 mesh) or Sephadex (Pharmacia LH-20) was performed with the solvent system (v/v) specified. Evaporation and concentration were conducted in vacuo.



S1 **5**

Drierite (2.00 g) was added to a solution of 2-(Trimethylsilyl)ethyl (methyl 3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→6)-3,4-di-*O*-benzyl-2-*O*-*p*-methoxybenzyl-β-D-glucopyranoside **S1** (1.00 g, 1.06 mmol) in MeOH (111 mL) and the suspension was stirred for 1 h at room temperature. A 28 % solution of sodium methoxide in MeOH (602 µL) was added and the resulting mixture was stirred for 45 h under reflux. The suspension was stirred under a hydrogen stream for 5 h at room temperature. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 10:1), whereupon the reaction mixture was neutralized with Dowex-50 (H^+) and filtered through Celite. The combined filtrate and washings were concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 15:1) to give compound **5** (777 mg, 90 %).

$[\alpha]_D$ = +28.5 ° (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD): δ 7.26-7.19 (m, 12 H, Ar), 6.79 (d, 2 H, J = 8.7 Hz, Ar), 4.82-4.59 (m, 6 H, ArCH_2), 4.40 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1^a), 4.35 (dd, 1 H, $J_{5,6}$ = 1.9 Hz, $J_{6,7}$ = 3.4 Hz, H-6^b), 4.28 (dd, 1 H, $J_{5,6a}$ = 2.0 Hz, J_{gem} = 10.5 Hz, H-6a^a), 4.06 (m, 1 H, H-4^b), 3.99 (m, 1 H, TMSCH$_2$CH_2), 3.88 (dd, 1 H, $J_{5,6b}$ = 6.1 Hz, H-6b^a), 3.78 (dd, 1 H, $J_{8,9a}$ = 2.3 Hz, J_{gem} = 7.7 Hz, H-9b^a), 3.71-3.57 (m, 9 H, H-3^a, H-5^a, H-7^b, H-8^b, H-9b^b, OMe, TMSCH$_2$CH_2), 3.50 (dd, 1 H, $J_{4,5}$ = 3.0 Hz, H-5^b), 3.43 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4^a), 3.30 (dd, 1 H, $J_{2,3}$ = 9.1 Hz, H-2^a), 2.26 (dd, 1 H, J_{gem} = 13.7 Hz, $J_{3eq,4}$ = 10.4 Hz, H-3eq^b), 1.99 (dd, 1 H, $J_{3ax,4}$ = 4.9 Hz, H-3ax^b), 0.99 ppm (m, 2 H, TMSCH_2CH$_2$); ^{13}C NMR (125 MHz, CD_3OD): δ 172.2, 160.7, 140.0, 139.7, 132.0, 130.7, 129.3, 129.2, 129.0, 128.8, 128.8, 128.6, 128.5, 114.6, 104.2, 97.2, 85.7, 83.2, 79.4, 79.4, 76.4, 75.6, 75.2, 72.2, 71.8, 68.4, 68.3, 64.6, 64.4, 55.7, 55.0, 40.3, 19.4, -1.3 ppm; HRMS: *m/z*: found $[M+Na]^+$ 834.3492, $C_{42}H_{57}NO_{13}Si$ calcd for $[M+Na]^+$ 834.3491.

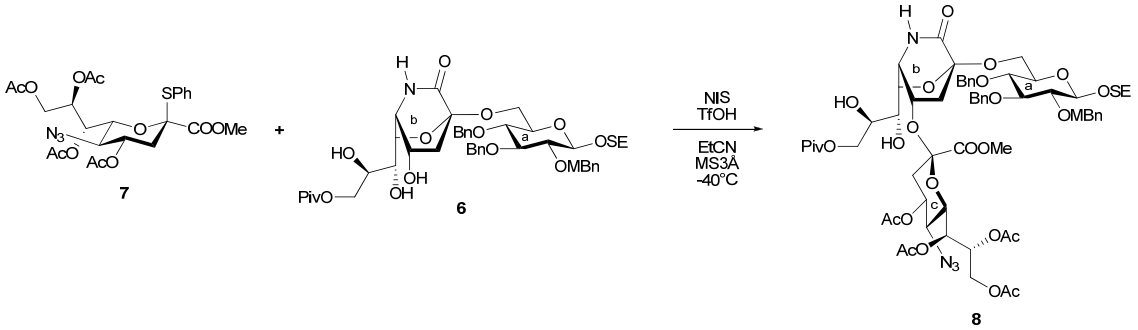


5 **6**

Pivaloyl chloride (159 µL, 1.29 mmol) was added to a solution of compound **5** (522 mg, 643 µmol) in pyridine (2.6 mL)/CH_2Cl_2 (10.4 mL) at -40 °C. The resulting mixture was stirred for 30 min at -40 °C. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 10:1). After quenching by water, the reaction mixture was diluted with $CHCl_3$ and the organic layer was washed

with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 45:1→30:1) to give compound **6** (575 mg, quant.).

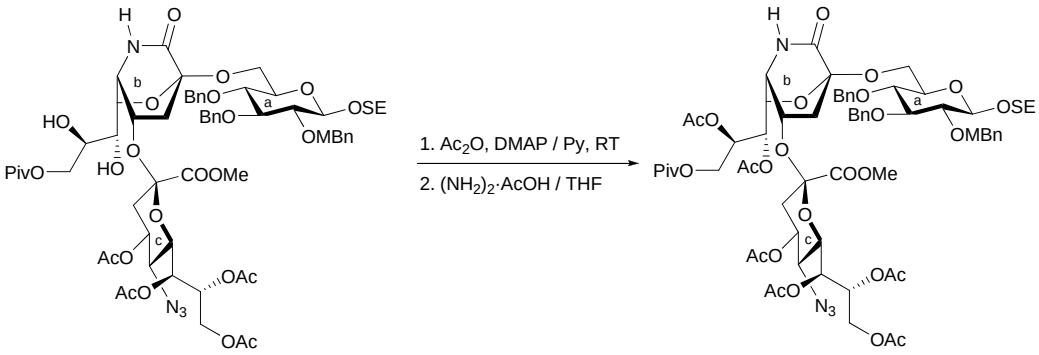
$[\alpha]_D$ = +3.7 ° (c 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 12 H, Ar), 6.83 (d, 2 H, J = 8.7 Hz, Ar), 6.49 (d, 1 H, $J_{NH,5}$ = 6.4 Hz, NH), 4.92-4.63 (m, 6 H, ArCH_2), 4.42 (m, 1 H, H-6^b), 4.40 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1^a), 4.35 (dd, 1 H, $J_{8.9a}$ = 2.3 Hz, J_{gem} = 11.9 Hz, H-9a^b), 4.32 (m, 1 H, H-6a^a), 4.24 (dd, 1 H, $J_{8,9b}$ = 5.1 Hz, H-9b^b), 4.11 (m, 1 H, H-4^b), 4.05-3.95 (m, 2 H, H-6b^a, $TMSCH_2CH_2$), 3.86 (m, 1 H, H-7^b), 3.79 (s, 3 H, OMe), 3.75 (m, 1 H, H-8^b), 3.66-3.59 (m, 3 H, H-3^a, H-4^a, $TMSCH_2CH_2$), 3.56 (m, 2 H, H-5^a, H-5^b), 3.36 (dd, 1 H, $J_{2,3}$ = 8.7 Hz, H-2^a), 2.92 (d, 1 H, $J_{OH,8}$ = 3.7 Hz, OH-8^b), 2.44 (dd, 1 H, J_{gem} = 14.2 Hz, $J_{3eq,4}$ = 10.5 Hz, H-3eq^b), 1.98 (dd, 1 H, $J_{3ax,4}$ = 5.0 Hz, H-3ax^b), 1.22 (s, 9 H, $(CH_3)_3C$), 1.07 ppm (m, 2 H, $TMSCH_2CH_2$); ^{13}C NMR (150MHz, $CDCl_3$): δ 179.3, 170.0, 159.2, 138.4, 130.3, 128.4, 128.3, 127.7, 127.6, 127.6, 113.7, 113.6, 103.6, 95.6, 84.5, 82.0, 75.6, 74.9, 74.6, 74.3, 70.5, 69.5, 69.1, 67.4, 66.3, 62.3, 55.2, 38.9, 29.6, 27.1, 18.4, -1.5 ppm; HRMS: *m/z*: found $[M+Na]^+$ 918.4067, $C_{47}H_{65}NO_{14}Si$ calcd for $[M+Na]^+$ 918.4067.



3Å molecular sieves (122 mg) were added to a solution of compounds **7** (230 mg, 405 µmol) and **6** (182 mg, 203 µmol) in EtCN (3.7 mL). The suspension was stirred for 1 h at room temperature, and then cooled to -40 °C. NIS (182 mg, 810 µmol) and TfOH (7.2 µL, 81.0 µmol) were added to the solution and stirring was continued for 1 h, when completion of the reaction was confirmed by TLC (PhMe/EtOAc 1:1). The reaction mixture was made alkaline to pH 8 with saturated aqueous $NaHCO_3$ solution at 0 °C, filtered through Celite, and the filter bed was washed with EtOAc. The combined filtrate and washings were extracted with EtOAc, and the organic layer was washed with saturated aqueous $Na_2S_2O_3$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on Sephadex LH-20 (MeOH) and silica gel (PhMe/EtOAc 2:1→1:1) to give compound **8** (137 mg, 50 %).

$[\alpha]_D$ = -5.1 ° (c 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.25 (m, 12 H, Ar), 6.86 (d, 1 H, $J_{NH,5}$ = 6.0 Hz, NH), 6.83 (d, 2 H, J = 8.7 Hz, Ar), 5.48 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 9.5 Hz, H-7^c), 5.35 (m, 1 H, H-8^c), 4.92-4.64 (m, 7 H, H-4^c, ArCH_2), 4.39 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1^a), 4.35 (dd, 1 H, $J_{5,6a}$ = 1.9 Hz, J_{gem} = 10.5 Hz, H-6a^a), 4.30 (dd, 1 H, $J_{8.9a}$ = 4.8 Hz, J_{gem} = 11.7 Hz, H-9a^b),

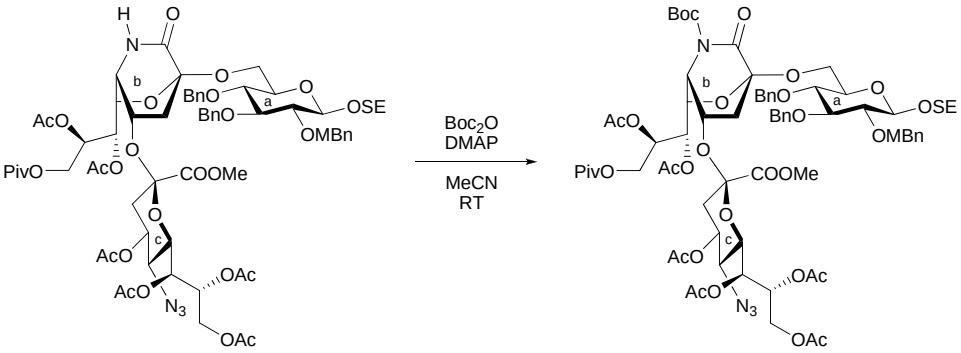
4.25-4.20 (m, 3 H, H-6^{b}, H-9b^{b}, H-9a^{c}), 4.11 (m, 1 H, H-7^{b}), 4.07-4.00 (m, 3 H, H-6^{c}, H-9b^{c}, TMSCH$_2$CH_2), 3.97 (m, 1 H, H-5^{b}), 3.93-3.86 (m, 2 H, H-6b^{a}, H-8^{b}), 3.85-3.79 (m, 7 H, H-4^{b}, COOMe, OMe), 3.62 (m, 2 H, H-3^{a}, TMSCH$_2$CH_2), 3.56 (m, 1 H, H-5^{a}), 3.49 (dd, 1 H, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.0 Hz, H-4^{a}), 3.39 (dd, 1 H, $J_{2,3}$ = 9.1 Hz, H-2^{a}), 3.27 (t, 1 H, $J_{4,5}$ = $J_{5,6}$ = 10.2 Hz, H-5^{c}), 3.08 (br s, 1 H, OH-7^{b}), 2.69 (dd, 1 H, J_{gem} = 12.6 Hz, $J_{3eq,4}$ = 4.5 Hz, H-3eq^{c}), 2.52 (d, 1 H, $J_{OH,8}$ = 8.7 Hz, OH-8^{b}), 2.26 (dd, 1 H, J_{gem} = 14.2 Hz, $J_{3eq,4}$ = 10.7 Hz, H-3eq^{b}), 2.22-2.07 (4 s, 12 H, 4 Ac), 1.99 (dd, 1 H, $J_{3ax,4}$ = 5.5 Hz, H-3ax^{b}), 1.79 (t, 1 H, $J_{3ax,4}$ = 12.6 Hz, H-3ax^{c}), 1.22 (s, 9 H, (CH$_3$)$_3$C), 1.05 ppm (m, 2 H, TMSCH_2CH$_2$); ^{13}C NMR (125 MHz, CDCl$_3$): δ 179.1, 171.2, 170.3, 169.6, 169.5, 169.3, 167.9, 159.2, 138.7, 138.3, 130.8, 129.8, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 113.7, 103.1, 99.9, 95.8, 84.7, 82.0, 79.1, 78.1, 75.6, 74.7, 74.3, 74.2, 72.7, 72.4, 71.7, 70.3, 67.8, 67.5, 66.9, 66.0, 63.8, 62.8, 60.3, 59.4, 55.2, 53.3, 52.3, 38.8, 37.8, 37.5, 29.7, 27.2, 21.0, 20.9, 20.8, 20.6, 18.6, 14.2, -1.4 ppm; HRMS: *m/z*: found [M+Na]$^{+}$ 1375.5398, $C_{65}H_{88}N_4O_{25}Si$ calcd for [M+Na]$^{+}$ 1375.5399.



8 **S2**

Acetic anhydride (1.0 mL) and DMAP (1.0 mg) were added to a solution of compound **8** (243 mg, 180 μmol) in pyridine (2.0 mL). The reaction mixture was stirred for 2 h at room temperature. Completion of the reaction was confirmed by TLC (hexane/EtOAc 1:1). After quenching with MeOH, the residual mixture was diluted with EtOAc and washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was exposed to high vacuum for 2 h. The crude material was redissolved in THF (4.5 mL), and hydrazine acetate (33.0 mg, 359 μmol) was added to the solution. The reaction mixture was stirred for 12 h at room temperature. Completion of the reaction was confirmed by TLC (hexane/EtOAc 1:1). The mixture was then diluted with EtOAc, washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to give compound **S2** (256 mg, 99 %). $[\alpha]_D$ = -59.0 ° (c 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.23 (m, 12 H, Ar), 6.93 (d, 1 H, $J_{NH,5}$ = 5.7 Hz, NH), 6.82 (d, 2 H, J = 8.6 Hz, Ar), 5.83 (dd, 1 H, $J_{6,7}$ = 1.6 Hz, $J_{7,8}$ = 9.6 Hz, H-7^{b}), 5.48 (dd, 1 H, $J_{6,7}$ = 1.6 Hz, $J_{7,8}$ = 9.6 Hz, H-7^{c}), 5.40 (m, 2 H, H-8^{b}, H-8^{c}), 4.89-4.64 (m, 7 H, H-4^{c},

ArCH_2), 4.39 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1^a), 4.37 (dd, 1 H, $J_{8.9a}$ = 4.4 Hz, J_{gem} = 11.6 Hz, H-9a^b), 4.33 (d, 1 H, $J_{5,6}$ = 9.4 Hz, H-6^b), 4.22 (dd, 1 H, $J_{8,9a}$ = 2.2 Hz, J_{gem} = 12.1 Hz, H-9a^c), 4.19 (dd, 1 H, $J_{5,6a}$ = 1.5 Hz, J_{gem} = 10.2 Hz, H-6a^a), 4.09 (dd, 1 H, $J_{8,9b}$ = 4.9 Hz, H-9b^b), 4.06-3.99 (m, 3 H, H-6^c, H-9b^c, TMSCH$_2$CH_2), 3.84-3.72 (m, 9 H, H-6b^a, H-4^b, H-5^b, COOMe, OMe), 3.63-3.49 (m, 5 H, H-3^a, H-4^a, H-5^a, H-5^c, TMSCH$_2$CH_2), 3.40 (dd, 1 H, $J_{2,3}$ = 9.0 Hz, H-2^a), 2.58 (dd, 1 H, J_{gem} = 12.6 Hz, $J_{3eq,4}$ = 4.7 Hz, H-3eq^c), 2.26 (dd, 1 H, J_{gem} = 14.0 Hz, $J_{3eq,4}$ = 5.9 Hz, H-3eq^b), 2.19-1.93 (m, 19 H, H-3ax^b, 6 Ac), 1.58 (t, 1 H, $J_{3ax,4}$ = 12.6 Hz, H-3ax^c), 1.21 (s, 9 H, (CH$_3$)$_3$C), 1.05 ppm (m, 2 H, TMSCH_2CH$_2$); ^{13}C NMR (125 MHz, CDCl$_3$): δ 177.6, 171.2, 170.4, 169.9, 169.9, 169.6, 169.5, 169.3, 169.2, 168.2, 159.1, 138.7, 138.6, 130.8, 129.7, 129.6, 129.0, 128.2, 128.2, 127.8, 127.6, 127.4, 125.2, 113.7, 113.5, 103.0, 100.0, 95.5, 84.6, 81.8, 78.0, 75.6, 75.5, 74.4, 74.3, 73.9, 72.9, 72.5, 71.8, 70.4, 69.0, 67.8, 67.4, 66.8, 63.5, 62.9, 60.8, 58.6, 55.2, 53.1, 51.8, 38.7, 36.7, 35.9, 29.6, 27.1, 20.9, 20.8, 20.8, 20.7, 20.5, 18.5, -1.5 ppm; HRMS: *m/z*: found [M+Na]$^+$ 1459.5610, C$_{69}$H$_{92}$N$_4$O$_{27}$Si calcd for [M+Na]$^+$ 1459.5610.

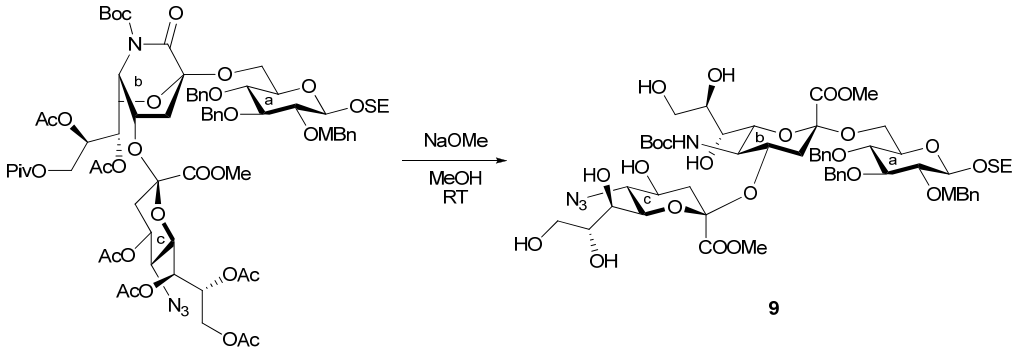


S2 **S3**

Di-*t*-butyl dicarbonate (20.7 µL, 94.8 µmol) and DMAP (0.4 mg, 3.16 µmol) were added to a solution of compound **S2** (90.8 mg, 63.2 µmol) in MeCN (1.3 mL). The reaction mixture was stirred for 20 min at room temperature. Completion of the reaction was confirmed by TLC (hexane/EtOAc 2:1). The mixture was diluted with $CHCl_3$, and washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 5:2→2:1) to give compound **S3** (95.9 mg, 99 %).

$[\alpha]_D$ = -45.2 ° (c 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.25 (m, 12 H, Ar), 6.82 (d, 2 H, J = 8.7 Hz, Ar), 5.97 (dd, 1 H, $J_{6,7}$ = 2.0 Hz, $J_{7,8}$ = 9.6 Hz, H-7^b), 5.62 (m, 1 H, H-8^c), 5.53 (dd, 1 H, $J_{6,7}$ = 0.7 Hz, $J_{7,8}$ = 10.3 Hz, H-7^c), 5.36 (m, 1 H, H-8^b), 4.90-4.64 (m, 8 H, H-5^b, H-4^c, ArCH_2), 4.41 (dd, 1 H, $J_{8,9a}$ = 2.6 Hz, J_{gem} = 12.9 Hz, H-9a^c), 4.38 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1^a), 4.29 (m, 2 H, H-6^b, H-9a^b), 4.16-4.09 (m, 4 H, H-6a^a, H-4^b, H-9b^b, H-9b^c), 4.03 (m, 1 H, TMSCH$_2$CH_2), 3.98 (d, 1 H, $J_{5,6}$ = 10.7 Hz, H-6^c), 3.78-3.72 (m, 7 H, H-6b^a, COOMe, OMe), 3.63-3.56 (m, 3 H, H-3^a, H-4^a, TMSCH$_2$CH_2), 3.53-3.47 (m, 2 H, H-5^a, H-5^c), 3.40 (dd, 1 H, $J_{2,3}$ = 8.3 Hz, H-2^a), 2.57 (dd, 1 H, J_{gem}

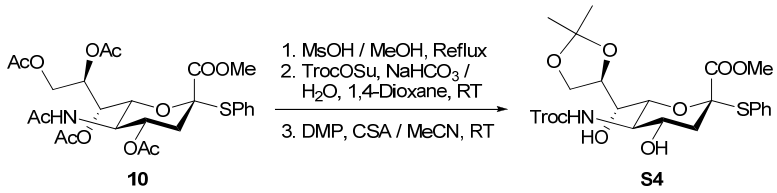
= 12.9 Hz, $J_{3eq,4}$ = 5.0 Hz, H-3eq^{c}), 2.30 (dd, 1 H, J_{gem} = 14.3 Hz, $J_{3eq,4}$ = 5.8 Hz, H-3eq^{b}), 2.20 (dd, 1 H, $J_{3ax,4}$ = 10.7 Hz, H-3ax^{b}), 2.16-1.95 (6 s, 18 H, 6 Ac), 1.54 (s, 9 H, $(CH_3)_3C$), 1.47 (dd, 1 H, $J_{3ax,4}$ = 12.6 Hz, H-3ax^{c}), 1.19 (s, 9 H, $(CH_3)_3C$), 1.06 ppm (m, 2 H, TMSCH_2CH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.8, 170.8, 170.0, 169.8, 169.7, 169.4, 169.1, 168.3, 164.2, 159.1, 149.9, 138.7, 138.5, 130.7, 129.8, 128.3, 128.2, 128.2, 127.7, 127.7, 127.6, 127.4, 113.7, 103.0, 98.7, 95.6, 84.5, 84.4, 81.8, 77.9, 75.5, 75.1, 74.4, 74.2, 73.7, 72.1, 71.8, 70.7, 70.0, 69.0, 67.3, 67.0, 66.9, 63.3, 62.0, 60.6, 58.9, 55.2, 52.9, 52.4, 38.6, 36.9, 35.8, 28.1, 27.1, 20.9, 20.8, 20.8, 20.7, 20.6, 18.5, -1.5 ppm; HRMS: *m/z*: found [M+Na]$^{+}$ 1559.6137, $C_{74}H_{100}N_4O_{29}Si$ calcd for [M+Na]$^{+}$ 1559.6135.



S3 **9**

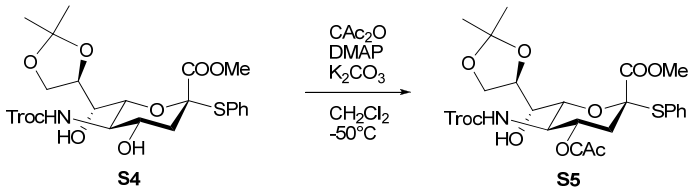
A 28 % solution of sodium methoxide in MeOH (397 µL) was added to a solution of compound **S3** (95.9 mg, 62.4 µmol) and the resulting mixture was stirred for 2.5 h with the monitoring the reaction by TLC ($CHCl_3$/MeOH 6:1). The reaction mixture was then neutralized with Dowex-50 (H^{+}), filtered, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 30:1→25:1→20:1) to give compound **9** (64.2 mg, 83 %).

$[\alpha]_D$ = -23.3 ° (c 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD): δ 7.18-7.10 (m, 12 H, Ar), 6.70 (d, 2 H, *J* = 8.6 Hz, Ar), 6.58 (d, 1 H, $J_{NH,5}$ = 8.6 Hz, NH), 4.75-4.48 (m, 6 H, ArCH_2), 4.26 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1^{a}), 3.96 (m, 1 H, H-4^{b}), 3.73, 3.70, 3.63 (3 s, 9 H, 2 COOMe, OMe), 3.25 (m, 1 H, H-5^{b}), 3.18 (dd, 1 H, $J_{2,3}$ = 8.6 Hz, H-2^{a}), 2.57 (dd, 1 H, J_{gem} = 13.2 Hz, $J_{3eq,4}$ = 4.6 Hz, H-3eq^{c}), 2.35 (dd, 1 H, J_{gem} = 12.6 Hz, $J_{3eq,4}$ = 4.0 Hz, H-3eq^{b}), 1.64 (t, 1 H, $J_{3ax,4}$ = 12.6 Hz, H-3ax^{b}), 1.53 (dd, 1 H, J_{gem} = $J_{3ax,4}$ = 12.6 Hz, H-3ax^{c}), 1.38 (s, 9 H, $(CH_3)_3C$), 0.90 ppm (m, 2 H, TMSCH_2CH$_2$); ^{13}C NMR (125 MHz, CD_3OD): δ 170.3, 160.6, 159.1, 140.0, 139.6, 132.0, 130.7, 129.3, 129.3, 129.1, 128.8, 128.7, 128.5, 114.6, 111.7, 104.2, 100.0, 98.8, 85.8, 83.1, 81.4, 78.6, 76.5, 75.7, 75.7, 75.2, 75.0, 73.3, 72.4, 70.9, 70.3, 70.1, 68.3, 64.6, 64.5, 64.1, 56.8, 55.7, 53.5, 52.7, 52.6, 41.7, 39.9, 28.8, 19.3, -1.3 ppm; HRMS: *m/z*: found [M+Na]$^{+}$ 1255.5188, $C_{58}H_{84}N_4O_{23}Si$ calcd for [M+Na]$^{+}$ 1255.5188.



10 **S4**

MsOH (4.00 mL, 61.7 mmol) was added to a solution of compound **10** (9.00 g, 15.4 mmol) and the mixture was stirred for 36 h under reflux. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH/AcOH 5:1:0.1). The mixture was then neutralized with triethylamine and the volatiles were co-evaporated with toluene. The residue was exposed to high vacuum for 3 h. The crude material was redissolved in 1 M aqueous $NaHCO_3$ solution (15.4 mL) and then 1 M TrocOSu solution in 1,4-dioxane (16.9 mL) was added to the solution. The mixture was stirred for 1 h at room temperature with the monitoring of the reaction by TLC ($CHCl_3$/MeOH 5:1). The reaction mixture was then diluted with EtOAc, washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was exposed to high vacuum for 30 h. The curde material was redissolved in MeCN (102 mL)/THF (52 mL) and DMP (2.83 mL, 23.1 mmol) and CSA (358 mg, 1.54 mmol) were added to the solution. The reaction mixture was strirred for 15 min at room temperature, and the progress of the reaction was monitored by TLC (hexane/EtOAc 1:1). After quenching the reaction by triethylamine, the reaction mixture was concentrated and the residual volatile was co-evaporated with toluene. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 100:1→80:1→70:1) to give compound **S4** (5.92 g, 65 %).
$[\alpha]_D$ = -6.1 ° (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.33 (m, 5 H, Ph), 5.25 (d, 1 H, $J_{NH,5}$ = 7.7 Hz, NH), 4.85 (d, 1 H, J_{gem} = 12.1 Hz, Cl_3CCH_2), 4.61 (d, 1 H, Cl_3CCH_2), 4.15 (dd, 1 H, $J_{7,8}$ = 7.2 Hz, $J_{8,9a}$ = 6.3 Hz, $J_{8,9b}$ = 6.5 Hz, H-8), 4.06 (dd, 1 H, J_{gem} = 8.5 Hz, H-9a), 3.94 (dd, 1 H, H-9b), 3.70 (m, 2 H, H-4, H-5), 3.61 (t, 1 H, $J_{7,OH}$ = 7.3 Hz, H-7), 3.51 (s, 3 H, COOMe), 3.43 (d, 1 H, $J_{5,6}$ = 9.4 Hz, H-6), 3.28 (d, 1 H, OH-7), 2.94 (dd, 1 H, J_{gem} = 12.9 Hz, $J_{3eq,4}$ = 4.1 Hz, H-3eq), 2.80 (d, 1 H, $J_{4,OH}$ = 3.6 Hz, OH-4), 1.90 (dd, 1 H, $J_{3ax,4}$ = 11.0 Hz, H-3ax), 1.33, 1.25 ppm (2 s, 6 H, $(CH_3)_2C$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1,155.9, 136.7, 130.0, 128.9, 128.6, 108.8, 95.2, 87.3, 76.1, 74.9, 74.7, 70.1, 68.2, 67.2, 54.0, 52.3, 40.7, 26.7, 25.4 ppm; HRMS: *m/z*: found $[M+Na]^+$ 610.0443, $C_{22}H_{28}Cl_3NO_9S$ calcd for $[M+Na]^+$ 610.0443.

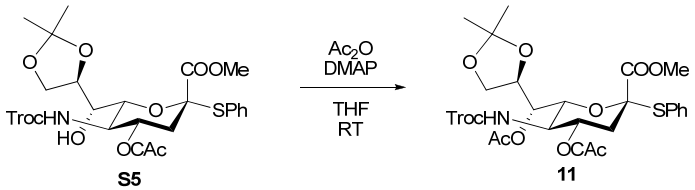


S4 **S5**

DMAP (2.1 mg, 17.0 μmol) and K_2CO_3 (235 mg, 1.70 mmol) were added to a solution of compound **S4** (200 mg, 340 μmol) in CH_2Cl_2 (6.8 mL). The mixture was then cooled to -50 °C, and chloroacetic anhydride (67.0 mg, 374 μmol) was added to the solution. The reaction mixture was

stirred for 3 h at -50 °C with monitoring of the reaction by TLC (PhMe/EtOAc 5:2). After quenching the reaction with water, the resulting mixture was extracted with $CHCl_3$, and combined extracts were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (PhMe/EtOAc 5:2) to give compound **S5** (217 mg, 96 %).

$[\alpha]_D$ = -67.0 ° (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55-7.33 (m, 5 H, Ph), 5.48 (d, 1 H, $J_{NH,5}$ = 9.0 Hz, NH), 5.11 (td, 1 H, $J_{3ax,4}$ = $J_{4,5}$ = 11.7 Hz, $J_{3eq,4}$ = 5.1 Hz, H-4), 4.78 (d, 1 H, J_{gem} = 12.1 Hz, Cl_3CCH_2), 4.67 (d, 1 H, Cl_3CCH_2), 4.17 (dd, 1 H, $J_{7,8}$ = 7.2 Hz, $J_{8,9a}$ = 6.3 Hz, $J_{8,9b}$ = 6.1 Hz, H-8), 4.06 (m, 3 H, H-9a, $ClCH_2$), 3.95 (dd, 1 H, H-9b), 3.88 (dd, 1 H, $J_{5,6}$ = 10.6 Hz, H-5), 3.60 (dd, 1 H, $J_{7,OH}$ = 6.9 Hz, H-7), 3.53 (s, 3 H, COOMe), 3.49 (d, 1 H, H-6), 3.18 (d, 1 H, OH-7), 2.91 (dd, 1 H, J_{gem} = 12.7 Hz, H-3eq), 1.99 (dd, 1 H, H-3ax), 1.34, 1.26 ppm (2 s, 6 H, $(CH_3)_2C$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5, 167.5, 155.4, 36.7, 130.0, 128.7, 128.6, 108.8, 95.2, 86.9, 77.2, 76.0, 74.7, 74.5, 70.8, 69.9, 67.0, 52.4, 51.9, 40.6, 37.3, 26.8, 25.3 ppm; HRMS: *m/z*: found $[M+Na]^+$ 686.0155, $C_{24}H_{29}Cl_4NO_{10}S$ calcd for $[M+Na]^+$ 686.0158.



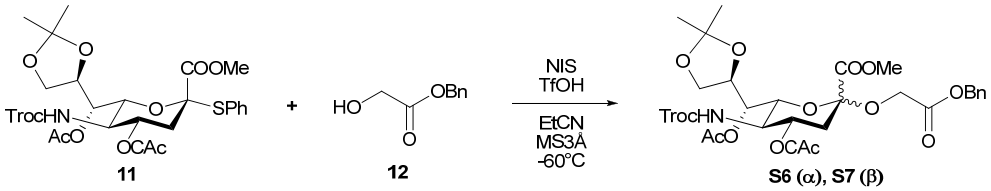
S5 **11**

Acetic anhydride (655 µL, 6.94 mmol) and DMAP (42.0 mg, 347 µmol) were added to a solution of compound **S5** (2.31 g, 3.47 mmol) in THF (34.7 mL)[1]. The reaction mixture was stirred for 3.5 h at room temperature. Completion of the reaction was confirmed by TLC (hexane/EtOAc 2:1). After quenching with EtOH, the residual mixture was diluted with EtOAc and washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1→3:2) to give compound **11** (2.43 g, 99 %).

$[\alpha]_D$ = +19.4 ° (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.35 (m, 5 H, Ph), 5.31 (dd, 1 H, $J_{6,7}$ = 1.4 Hz, $J_{7,8}$ = 5.5 Hz, H-7), 5.12 (ddd, 1 H, $J_{3ax,4}$ = 11.9 Hz, $J_{3eq,4}$ = 5.0 Hz, $J_{4,5}$ = 10.5 Hz, H-4), 4.87 (d, 1 H, $J_{NH,5}$ = 9.6 Hz, NH), 4.79 (d, 1 H, J_{gem} = 11.9 Hz, Cl_3CCH_2), 4.51 (d, 1 H, Cl_3CCH_2), 4.27 (dd, 1 H, $J_{8,9a}$ = 6.0 Hz, $J_{8,9b}$ = 6.4 Hz, H-8), 4.03-3.91 (m, 4 H, H-9a, H-9b, $ClCH_2$), 3.79 (dd, 1 H, $J_{5,6}$ = 10.5 Hz, H-6), 3.64 (s, 3 H, COOMe), 3.59 (dd, 1 H, H-5), 2.91 (dd, 1 H, J_{gem} = 12.8 Hz, H-3eq), 2.17 (s, 3 H, Ac), 1.94 (dd, 1 H, H-3ax), 1.34, 1.29 ppm (2 s, 6 H, $(CH_3)_2C$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.0, 166.7, 154.2, 135.1, 129.1, 128.8, 128.8, 109.3, 97.8, 95.2, 74.6, 73.1, 71.1, 70.8, 69.5, 67.2, 66.9, 61.1, 52.9, 50.9, 40.5, 36.8, 26.6, 25.3, 20.9 ppm; HRMS:

[1] A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi, K. Ishihara, *J. Am.Chem. Soc.* 2007, **129**, 14775-14779.

m/z: found $[M+Na]^+$ 728.0264, $C_{26}H_{31}Cl_4NO_{11}S$ calcd for $[M+Na]^+$ 728.0264.

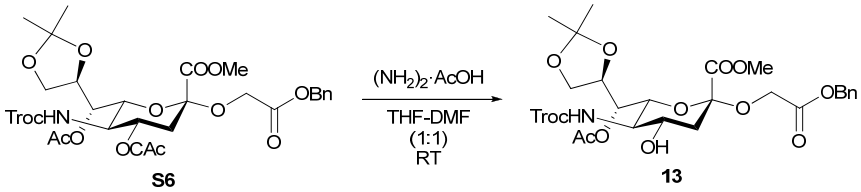


3Å molecular sieves (1.0 g) were added to a solution of compounds **11** (400 mg, 565 µmol) and **12** (96.4 µL, 679 µL) in EtCN (11.3 mL). The suspension was stirred for 1 h at room temperature, then cooled to -60 °C. NIS (161 mg, 679 µmol) and TfOH (18.1 µL, 204 µmol) were added to the solution and stirring was continued for 2 h, after which TLC analysis ($CHCl_3$/acetone 25:1) indicated completion of the reaction. The reaction mixture was made alkaline to pH 8 with saturated aqueous $NaHCO_3$ solution at 0 °C, filtered through Celite, and the filter bed was washed with EtOAc. The combined filtrate and washings were extracted with EtOAc, and the organic layer was washed with saturated aqueous $Na_2S_2O_3$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/acetone 33:1→30:1) to give compounds **S6** (249 mg, 58 %) and **S7** (151 mg, 35 %).

Compound **S6**: $[\alpha]_D$ = +3.1 ° (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.33 (m, 5 H, Ph), 5.33 (dd, 1 H, $J_{6,7}$ = 1.4 Hz, $J_{7,8}$ = 4.8 Hz, H-7), 5.26 (ddd, 1 H, $J_{3ax,4}$ = 11.0 Hz, $J_{3eq,4}$ = 4.9 Hz, $J_{4,5}$ = 10.4 Hz, H-4), 5.19 (d, 1 H, J_{gem} = 15.9 Hz, PhCH_2), 5.17 (d, 1 H, PhCH_2), 5.00 (d, 1 H, $J_{NH,5}$ = 9.8 Hz, NH), 4.78 (d, 1 H, J_{gem} = 12.1 Hz, Cl_3CCH_2), 4.54 (d, 1 H, Cl_3CCH_2), 4.36 (s, 2 H, OCH_2CO), 4.30 (dd, 1 H, $J_{8,9a}$ = 6.9 Hz, $J_{8,9b}$ = 6.2 Hz, H-8), 4.02 (m, 3 H, H-9a, $ClCH_2$), 3.93 (dd, 1 H, J_{gem} = 8.3 Hz, H-9b), 3.90 (dd, 1 H, $J_{5,6}$ = 11.0 Hz, H-6), 3.76 (s, 3 H, COOMe), 3.67 (dd, 1 H, H-5), 2.85 (dd, 1 H, J_{gem} = 12.4 Hz, H-3eq), 2.13 (s, 3 H, Ac), 1.99 (t, 1 H, H-3ax), 1.35, 1.34 ppm (2 s, 6 H, $(CH_3)_2C$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 168.9, 167.2, 166.9, 154.0, 135.1, 128.6, 128.6, 108.8, 98.3, 95.1, 75.0, 74.6, 72.8, 70.4, 69.0, 66.9, 65.8, 61.7, 53.0, 51.6, 40.5, 37.1, 26.5, 25.3, 20.8 ppm; HRMS: *m/z*: found $[M+Na]^+$ 784.0705, $C_{29}H_{35}Cl_4NO_{14}$ calcd for $[M+Na]^+$ 784.0704.

Compound **S7**: $[\alpha]_D$ = -12.2 ° (c 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.35 (m, 5 H, Ph), 5.31 (m, 1 H, H-4), 5.28 (d, 1 H, J_{gem} = 11.9 Hz, PhCH_2), 5.03 (dd, 1 H, $J_{6,7}$ = 1.9 Hz, $J_{7,8}$ = 8.4 Hz, H-7), 4.84 (d, 1 H, J_{gem} = 12.1 Hz, Cl_3CCH_2), 4.67 (d, 1 H, $J_{NH,5}$ = 10.4 Hz, NH), 4.50 (d, 1 H, Cl_3CCH_2), 4.47 (d, 1 H, J_{gem} = 16.3 Hz, OCH_2CO), 4.28 (d, 1 H, OCH_2CO), 4.27 (m, 1 H, H-8), 4.04 (dd, 1 H, $J_{5,6}$ = 10.8 Hz, H-6), 4.02-3.95 (m, 3 H, H-9a, $ClCH_2$), 3.89-3.81 (m, 2 H, H-5, H-9b), 3.76 (s, 3 H, COOMe), 2.57 (dd, 1 H, J_{gem} = 13.1 Hz, H-3eq), 2.10 (s, 3 H, Ac), 2.03 (t, 1 H, H-3ax), 1.34, 1.28 ppm (2 s, 6 H, $(CH_3)_2C$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.0, 166.7, 166.6, 154.2, 135.0, 129.0, 128.8, 128.7, 109.2, 97.7, 95.2, 74.6, 73.1, 71.1, 70.8, 69.5, 67.1, 66.9, 61.0, 52.8, 50.9, 40.5, 36.7, 26.5, 25.2, 20.8 ppm; HRMS: *m/z*: found $[M+Na]^+$ 784.0804, $C_{29}H_{35}Cl_4NO_{14}$ calcd for

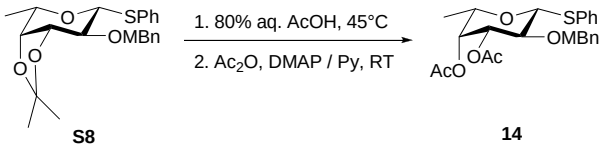
$[M+Na]^+$ 784.0704.



S6 **13**

Hydrazine acetate (90.0 mg, 972 µmol) was added to the solution of compound **S6** (296 mg, 389 µmol) in THF (3.9 mL)/DMF (3.9 mL). The mixture was stirred for 3.5 h at room temperature with monitoring of the reaction by TLC (hexane/EtOAc 1:1). The mixture was diluted with EtOAc, and this solution was washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 3:4) to give compound **13** (244 mg, 92 %).

$[\alpha]_D$ = +8.7 ° (c 1.2, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.33 (m, 5 H, Ph), 5.48 (d, 1 H, $J_{NH,5}$ = 8.9 Hz, NH), 5.33 (d, 1 H, $J_{6,7}$ = 4.1 Hz, H-7), 5.20 (d, 1 H, J_{gem} = 11.7 Hz, PhCH_2), 5.17 (d, 1 H, PhCH_2), 4.71 (d, 1 H, J_{gem} = 12.3 Hz, Cl_3CCH_2), 4.64 (d, 1 H, Cl_3CCH_2), 4.39 (d, 1 H, J_{gem} = 16.5 Hz, OCH_2CO), 4.31 (m, 2 H, H-8, OCH_2CO), 4.05 (m, 2 H, H-4, H-9a), 3.94 (m, 2 H, H-6, H-9b), 3.74 (s, 3 H, COOMe), 3.32 (dd, 1 H, $J_{4,5}$ = 8.3 Hz, $J_{5,6}$ = 10.3 Hz, H-5), 3.14 (d, 1 H, $J_{OH,7}$ = 4.8 Hz, OH-7), 2.78 (dd, 1 H, J_{gem} = 13.7 Hz, $J_{3eq,4}$ = 5.2 Hz, H-3eq), 2.09 (s, 3 H, Ac), 1.96 (dd, 1 H, $J_{3ax,4}$ = 9.6 Hz, H-3ax), 1.34, 1.26 ppm (2 s, 6 H, $(CH_3)_2C$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6, 169.5, 167.8, 154.4, 135.1, 128.6, 128.6, 128.5, 108.8, 98.7, 95.2, 75.2, 74.6, 72.3, 69.5, 67.5, 66.9, 65.7, 61.4, 55.0, 52.8, 39.0, 29.7, 26.4, 25.4, 20.7 ppm; HRMS: *m/z*: found $[M+Na]^+$ 708.0986, $C_{27}H_{34}Cl_3NO_{13}$ calcd for $[M+Na]^+$ 708.0988.

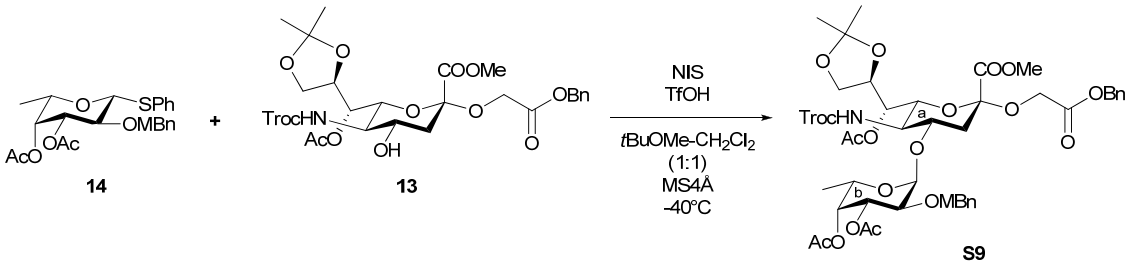


S8 **14**

80 % aqueous AcOH (180 mL) was added to a flask containing compound **S8** (3.75 g, 9.00 mmol). The mixture was stirred for 3 h at 45 °C, as the progress of the reaction was monitored by TLC (hexane/EtOAc 1:1). The reaction mixture was then concentrated, the remaining volatiles were co-evaporated with toluene, and the residue was exposed to high vacuum for 20 h. The crude material was redissolved in pyridine (90.0 mL) and then acetic anhydride (3.40 mL, 36.0 mmol) and DMAP (110 mg, 0.900 mmol) were added to the solution at 0 °C. The mixture was stirred for 45 min at room temperature, when completion of the reaction was confirmed by TLC (hexane/EtOAc 2:1). After quenching with EtOH, the mixture was concentrated and the residual volatiles were co-evaporated with toluene. The residue was redissolved in EtOAc, and this solution was washed

with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1) to give compound **14** (3.51 g, 85 %).

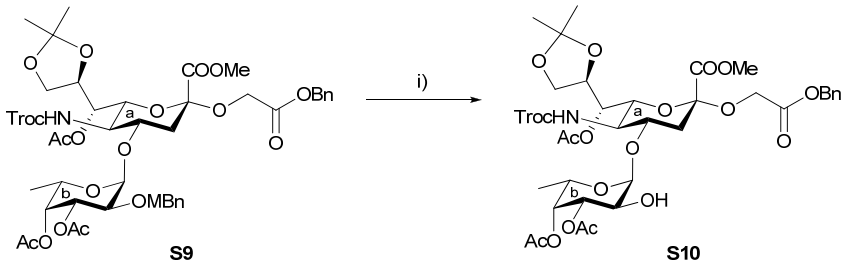
$[\alpha]_D$ = +15.0 ° (c 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-6.84 (m, 9 H, Ar), 5.24 (d, 1 H, $J_{3,4}$ = 3.2 Hz, H-4), 5.00 (dd, 1 H, $J_{2,3}$ = 9.6 Hz, H-3), 4.75 (d, 1 H, J_{gem} = 10.5 Hz, ArCH_2), 4.69 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 4.51 (d, 1 H, ArCH_2), 3.78 (s, 3 H, OMe), 3.75 (m, 1 H, H-5), 3.71 (dd, 1 H, H-2), 2.15 (2 s, 6 H, 2 Ac), 1.21 ppm (d, 3 H, $J_{5,6}$ = 6.8 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 169.8, 159.3, 133.5, 131.8, 130.0, 129.5, 128.8, 127.5, 113.7, 87.5, 74.9, 74.6, 72.7, 70.8, 55.2, 20.7, 20.6, 16.5 ppm; HRMS: *m/z*: found $[M+Na]^+$ 483.1448, $C_{24}H_{28}O_7S$ calcd for $[M+Na]^+$ 483.1448.



4Å molecular sieves (605 mg) were added to a solution of compounds **14** (331 mg, 718 µmol) and **13** (274 mg, 399 µmol) in *t*BuOMe (14.4 mL)/CH_2Cl_2 (14.4 mL). The suspension was stirred for 1 h at room temperature, then cooled to -40 °C. NIS (204 mg, 862 µmol) and TfOH (7.6 µL, 86.2 µmol) were added to the solution and stirring was continued for 2 h, after which TLC analysis (PhMe/EtOAc 2:1) indicated completion of the reaction. The reaction mixture was made alkaline to pH 8 with saturated aqueous $NaHCO_3$ solution at 0 °C, filtered through Celite, and the filter bed was washed with EtOAc. The combined filtrate and washings were extracted with EtOAc, and the organic layer was washed with saturated aqueous $Na_2S_2O_3$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (PhMe/EtOAc 2:1) to give compound **S9** (313 mg, 76 %).

$[\alpha]_D$ = +50.0 ° (c 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.32 (m, 5 H, Ph), 7.24, 6.89 (2 d, 4 H, *J* = 8.6 Hz, Ar), 5.30 (dd, 1 H, $J_{6,7}$ = 1.2 Hz, $J_{7,8}$ = 5.1 Hz, H-7^a), 5.21-5.14 (m, 5 H, H-3^b, H-4^b, NH, PhCH_2), 4.88 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1^b), 4.84, 4.45 (2 d, 2 H, J_{gem} = 12.1 Hz, Cl_3CCH_2), 4.59, 4.52 (2 d, 2 H, J_{gem} = 11.4 Hz, ArCH_2), 4.39, 4.32 (2 d, 2 H, J_{gem} = 16.1 Hz, OCH_2CO), 4.29 (m, 1 H, H-8^a), 4.21-4.13 (m, 2 H, H-4^a, H-5^b), 4.06 (dd, 1 H, J_{gem} = 8.6 Hz, $J_{8,9a}$ = 6.9 Hz, H-9a^a), 4.00 (d, 1 H, $J_{5,6}$ = 10.9 Hz, H-6^a), 3.94 (dd, 1 H, H-9b^a), 3.82-3.72 (m, 7 H, H-2^b, COOMe, ArO*Me*), 3.30 (dd, 1 H, $J_{4,5}$ = 10.3 Hz, $J_{NH,5}$ = 8.6 Hz, H-5^a), 2.84 (dd, 1 H, J_{gem} = 12.6 Hz, $J_{3eq,4}$ = 4.6 Hz, H-3eq^a), 2.15, 2.12, 1.98 (3 s, 9 H, 3 Ac), 1.77 (dd, 1 H, $J_{3ax,4}$ = 11.5 Hz, H-3ax^a), 1.34 (s, 6 H, $(CH_3)_2C$), 1.06 ppm (d, 3 H, $J_{5,6}$ = 6.3 Hz, H-6^b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 170.3, 169.8, 169.1, 167.4,

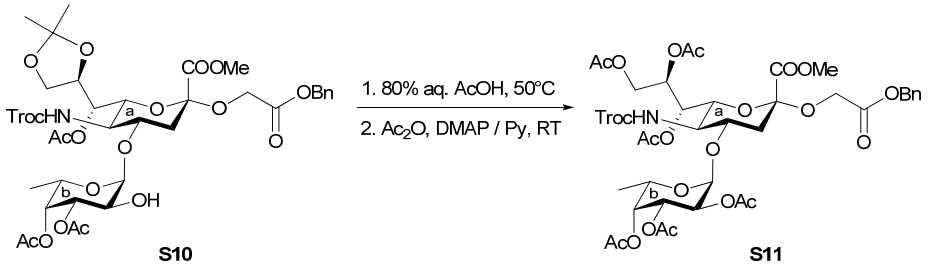
159.4, 153.4, 135.2, 129.8, 129.5, 128.6, 128.5, 128.4, 113.9, 108.7, 98.5, 95.2, 95.0, 75.2, 74.6, 72.9, 72.4, 72.0, 71.4, 71.0, 69.8, 69.5, 66.7, 65.8, 64.9, 61.5, 55.2, 52.7, 52.4, 37.0, 29.6, 26.4, 25.4, 20.9, 20.7, 20.6, 16.0 ppm; HRMS: *m/z*: found $[M+Na]^+$ 1058.2354, $C_{45}H_{56}Cl_3NO_{20}$ calcd for $[M+Na]^+$ 1058.2353.



S9 **S10**

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (80.2 mg, 335 µmol) was added to a solution of compound **S9** (232 mg, 224 µmol) in CH_2Cl_2 (4.5 mL)/H_2O (450 µL). The suspension was stirred for 4 h at room temperature. Completion of the reaction was confirmed by TLC (hexane/EtOAc 1:1). The mixture was diluted with $CHCl_3$, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to give compound **S10** (195 mg, 95 %).

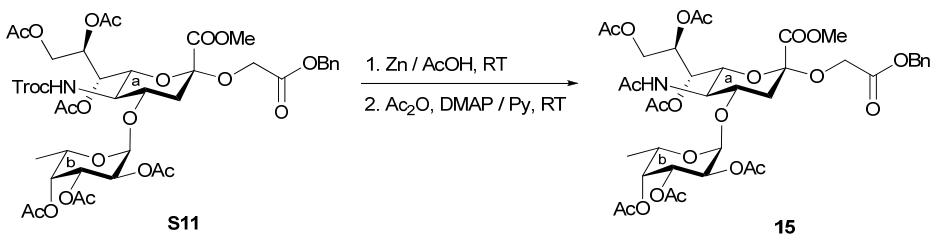
$[\alpha]_D$ = +81.0 ° (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.33 (m, 5 H, Ph), 5.35 (dd, 1 H, $J_{6,7}$ = 1.2 Hz, $J_{7,8}$ = 5.2 Hz, H-7^a), 5.27 (d, 1 H, $J_{NH,5}$ = 9.2 Hz, NH), 5.22 (d, 1 H, $J_{3,4}$ = 2.9 Hz, H-4^b), 5.20, 5.17 (2 d, 2 H, J_{gem} = 12.6 Hz, PhCH_2), 5.05 (dd, 1 H, $J_{2,3}$ = 10.0 Hz, H-3^b), 5.00 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1^b), 4.70, 4.62 (2 d, 2 H, J_{gem} = 12.1 Hz, Cl_3CCH_2), 4.38, 4.34 (2 d, 2 H, J_{gem} = 16.6 Hz, OCH_2CO), 4.31 (m, 1 H, H-8^a), 4.13 (m, 1 H, H-5^b), 4.07-3.99 (m, 2 H, H-4^a, H-9a^a), 3.93 (dd, 1 H, J_{gem} = 8.1 Hz, $J_{8,9b}$ = 6.9 Hz, H-9b^a), 3.88-3.77 (m, 2 H, H-6^a, H-2^b), 3.74 (s, 3 H, COOMe), 3.47 (dd 1 H, $J_{4,5}$ = 10.3 Hz, $J_{5,6}$ = 9.7 Hz, H-5^a), 2.85 (dd, 1 H, J_{gem} = 13.2 Hz, $J_{3eq,4}$ = 5.1 Hz, H-3eq^a), 2.14, 2.14, 2.07 (3 s, 9 H, 3 Ac), 1.94 (dd, 1 H, $J_{3ax,4}$ = 11.5 Hz, H-3ax^a), 1.34 (s, 6 H, $(CH_3)_2C$), 1.13 ppm (d, 3 H, $J_{5,6}$ = 6.9 Hz, H-6^b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 170.5, 170.4, 169.1, 167.5, 154.5, 135.1, 128.6, 128.5,108.8, 100.9, 98.3, 95.0, 75.6, 75.0, 74.8, 72.3, 71.1, 70.9, 69.1, 66.8, 66.7, 65.7, 65.4, 61.6, 60.4, 52.8, 52.6, 39.0, 26.4, 25.3, 21.0, 20.8, 20.8, 20.6, 15.9, 14.1 ppm; HRMS: *m/z*: found $[M+Na]^+$ 938.1778, $C_{37}H_{48}Cl_3NO_{19}$ calcd for $[M+Na]^+$ 938.1778.



S10 S11

80 % aqueous AcOH (25.0 mL) was added to a flask containing compound **S10** (912 mg, 994 µmol). The mixture was stirred for 16 h at 50 °C. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 15:1). The mixture was then concentrated and remaining volatiles were co-evaporated with toluene, and the residue was exposed to high vacuum for 1 h. The crude material was redissolved in pyridine (20.0 mL) and then acetic anhydride (1.0 mL) and DMAP (12.1 mg, 99.4 µmol) was added to the solution at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature, when completion of the reaction was confirmed by TLC (hexane/EtOAc 1:2). After quenching with EtOH, the mixture was concentrated and the residual volatiles were co-evaporated with toluene. The residue was redissolved in EtOAc, and this solution was washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:3) to give compound **S11** (971 mg, 97 %).

$[\alpha]_D$ = +38.3 ° (c 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38-7.31 (m, 5 H, Ph), 5.34-5.31 (m, 3 H, NH, H-8^a, H-4^b), 5.25 (m, 2 H, H-7^a, H-3^b), 5.19, 5.14 (2 d, 2 H, J_{gem} = 12.3 Hz, PhCH_2), 5.13 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1^b), 5.10 (m, 1 H, H-2^b), 5.07, 4.36 (2 d, 2 H, J_{gem} = 12.4 Hz, Cl_3CCH_2), 4.33, 4.29 (2 d, 2 H, J_{gem} = 16.5 Hz, OCH_2CO), 4.24-4.15 (m, 5 H, H-4^a, H-6^a, H-9a^a, H-9b^a, H-5^b), 3.72 (s, 3 H, COOMe), 3.18 (dd 1 H, $J_{4,5}$ = $J_{5,6}$ = 10.3 Hz, H-5^a), 2.74 (dd, 1 H, J_{gem} = 13.0 Hz, $J_{3eq,4}$ = 4.8 Hz, H-3eq^a), 2.18-1.98 (6 s, 18 H, 6 Ac), 1.69 (dd, 1 H, $J_{3ax,4}$ = 11.7 Hz, H-3ax^a), 1.08 ppm (d, 3 H, $J_{5,6}$ = 6.2 Hz, H-6^b); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.6, 170.4, 170.3, 169.9, 169.8, 169.2, 167.1, 153.6, 135.3, 128.5, 128.3, 128.3, 97.9, 95.4, 94.2, 74.2, 71.2, 70.9, 70.3, 67.9, 67.7, 67.7, 67.4, 66.6, 65.0, 61.8, 61.7, 52.9, 52.3, 37.5, 20.9, 20.9, 20.7, 20.6, 20.6, 15.8 ppm; HRMS: *m/z*: found $[M+Na]^+$ 1024.1783, $C_{40}H_{50}Cl_3NO_{22}$ calcd for $[M+Na]^+$ 1024.1782.

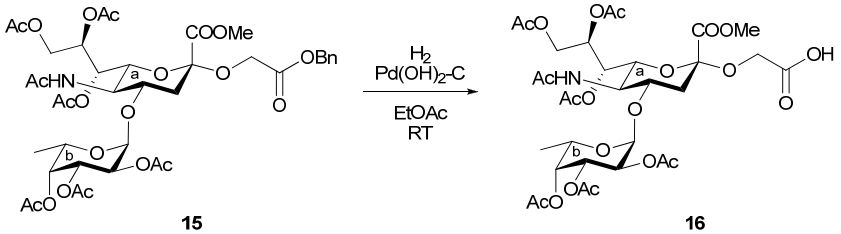


S11 15

Activated zinc powder (4.84 g) was added to a solution of compound **S11** (971 mg, 968 µmol) in AcOH (32.3 mL). The suspension was stirred for 4.5 h at room temperature with monitoring the

reaction by TLC ($CHCl_3$/MeOH 10:1). The mixture was filtered through Celite, and the filter bed was washed with $CHCl_3$. The combined filtrate and washings were washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4) and concentrated. The residue was exposed to high vacuum for 1 h, and was then redissolved in pyridine (20.0 mL) and then acetic anhydride (1.0 mL) and DMAP (12.1 mg, 99.4 μmol) were added to the solution at 0 °C. The reaction mixture was stirred for 2.5 h at room temperature until the completion of the reaction was indicated by TLC ($CHCl_3$/acetone 4:1). The reaction mixture was then concentrated and the residual volatiles were co-evaporated with toluene. The residue was redissolved in EtOAc, and this solution was washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/acetone 2:1) to give compound **15** (681 mg, 81 %).

$[\alpha]_D$ = +68.5 ° (c 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.31 (m, 5 H, Ph), 5.36 (m, 1 H, H-8^a), 5.30 (m, 3 H, NH, H-3^b, H-4^b), 5.25 (dd, 1 H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 8.6 Hz, H-7^a), 5.20, 5.14 (2 d, 2 H, J_{gem} = 12.6 Hz, PhCH_2), 5.17 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1^b), 5.02 (dd, 1 H, $J_{2,3}$ = 10.9 Hz, H-2^b), 4.32 (s, 2 H, OCH_2CO), 4.26 (dd, 1 H , $J_{8,9a}$ = 2.9 Hz, J_{gem} = 12.6 Hz, H-9a^a), 4.18-4.09 (m, 3 H, H-4^a, H-9b^a, H-5^b), 4.04 (dd, 1 H, $J_{5,6}$ = 10.3 Hz, H-6^a), 3.73 (s, 3 H, COOMe), 3.48 (m 1 H, H-5^a), 2.77 (dd, 1 H, J_{gem} = 12.6 Hz, $J_{3eq,4}$ = 4.6 Hz, H-3eq^a), 2.15-1.91 (7 s, 21 H, 7 Ac), 1.90 (m, 1 H, H-3ax^a), 1.12 ppm (d, 3 H, $J_{5,6}$ = 6.9 Hz, H-6^b); ^{13}C NMR (--- MHz, $CDCl_3$): δ --- ppm; HRMS: *m/z*: found $[M+Na]^+$ 892.2845, $C_{39}H_{51}NO_{21}$ calcd for $[M+Na]^+$ 892.2846.

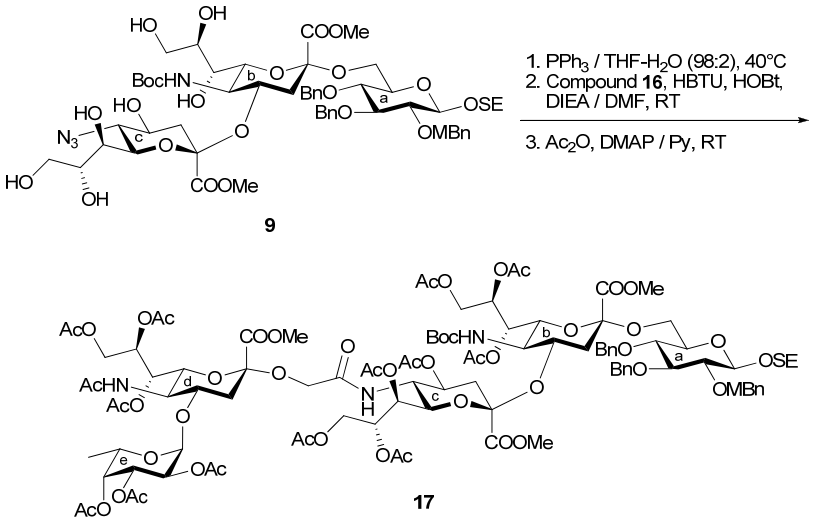


15 **16**

20 % $Pd(OH)_2$ on activated carbon (82 mg) was added to a solution of compound **15** (164 mg, 189 μmol) in EtOAc (9.4 mL). The suspension was stirred under a hydrogen stream for 5 h at room temperature. After the completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 10:1), the mixture was filtered through Celite, and the filtrate was concentrated to give compound **16** (146 mg, 99 %).

$[\alpha]_D$ = +91.5 ° (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.77 (d, 1 H, $J_{NH,5}$ = 7.9 Hz, NH), 5.36 (m, 1 H, H-8^a), 5.26 (m, 3 H, H-7^a, H-1^b, H-4^b), 5.10 (m, 2 H, H-2^b, H-3^b), 4.36, 4.26 (2 d, 2 H, J_{gem} = 16.8 Hz, OCH_2CO), 4.31 (m, 3 H, H-4^a, H-6^a, H-9a^a), 4.15 (m, 2 H, H-9b^a, H-5^b), 3.80 (s, 3 H, COOMe), 3.26 (dd 1 H, $J_{4,5}$ = $J_{5,6}$ = 8.7 Hz, H-5^a), 2.69 (dd, 1 H, J_{gem} = 13.5 Hz, $J_{3eq,4}$ = 4.8 Hz, H-3eq^a), 2.20-1.99 (7 s, 21 H, 7 Ac), 1.78 (dd, 1 H, $J_{3ax,4}$ = 9.6 Hz, H-3ax^a), 1.10 ppm (d, 3 H, $J_{5,6}$ = 6.6 Hz, H-6^b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 171.1, 170.7, 170.5, 170.4, 170.2, 170.1, 167.4,

98.2, 94.7, 77.6, 72.1, 70.9, 70.2, 68.4, 67.9, 67.8, 67.8, 65.1, 62.2, 61.6, 53.1, 52.3, 36.3, 23.5, 21.0, 20.9, 20.8, 20.7, 20.7, 20.6, 15.9 ppm; HRMS: *m/z*: found $[M+Na]^+$ 802.2375, $C_{32}H_{45}NO_{21}$ calcd for $[M+Na]^+$ 802.2376.

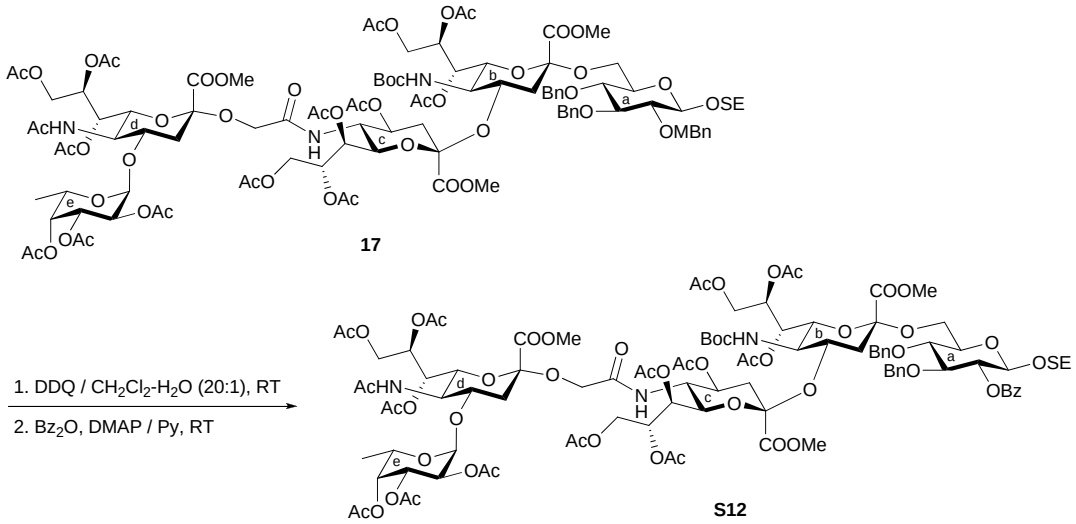


9

17

PPh_3 (26.6 mg, 101 μmol) was added to a solution of compound **9** (41.7 mg, 33.8 μmol) in THF (1.1 mL)/H_2O (30 μL). The mixture was stirred for 6 h at 40 °C with the monitoring the reaction by TLC ($CHCl_3$/MeOH 5:1). The reaction mixture was then concentrated and remaining volatiles were co-evaporated with toluene. The residue wase exposed to high vacuum for 12 h. Then the crude material and compound **16** (26.3 mg, 33.8 μmol) were dissolved in DMF (1.0 mL) and then HBTU (15.4 mg, 40.6 μmol) and HOBt (5.5 mg, 4.06 μmol) were added to the solution. The mixture was stirred for 9 h at room temperature. DIEA (14.1 μL, 81.8 μmol) was added to the solution, and then stirring was continued for 45 min at room temperature. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 6:1). The mixture was diluted with EtOAc, and this solution was washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was subjected to column chromatography on silica gel ($CHCl_3$/MeOH 25:1→15:1) and Sephadex LH-20 (MeOH) to give crude pentasaccharide (57.0 mg). The crude material was dissolved in pyridine (1.0 mL), and acetic anhydride (500 μL) and DMAP (1.0 mg) were added to the solution. The reaction mixture was stirred for 4 h at room temperature. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 15:1). After quenching with MeOH, the mixture was diluted with EtOAc, and this solution washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 55:1→45:1) to give compound **17** (65.0 mg, 85 %). $[\alpha]_D$ = -37.2 ° (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.25 (m, 12 H, Ar), 6.83 (d, 2 H, J = 8.7 Hz, Ar), 5.98 (d, 1 H, $J_{NH,5}$ = 10.3 Hz, NH^c), 5.48 (d, 1 H, $J_{NH,5}$ = 8.2 Hz, NH^d), 5.45-5.40 (m,

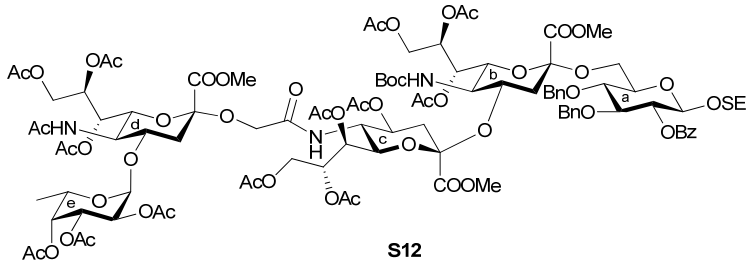
3 H, H-7[b], H-8[b], H-8[d]), 5.37-5.26 (m, 6 H, NH[b], H-7[c], H-8[c], H-7[d], H-1[e], H-3[e]), 5.15 (d, 1 H, $J_{3,4}$ = 3.8 Hz, H-4[e]), 5.07 (dd, 1 H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.6 Hz, H-2[e]), 4.87-4.64 (m, 7 H, H-4[c], ArCH_2), 4.35 (d, 1 H, $J_{5,6}$ = 10.9 Hz, H-6[b]), 4.32 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1[a]), 4.28 (m, 2 H, H-9a[d], OCH_2CO), 4.23-3.94 (m, 11 H, H-6a[a], H-9a[b], H-5[c], H-9a[c], H-9b[c], H-4[d], H-6[d], H-9b[d], H-5[e], OCH_2CO, $TMSCH_2CH_2$), 3.91-3.79 (m, 14 H, H-9b[b], H-6[c], 3 COOMe, OMe), 3.72-3.48 (m, 6 H, H-3[a], H-4[a], H-6b[a], H-4[b], H-5[b], $TMSCH_2CH_2$), 3.36 (m, 3 H, H-2[a], H-5[a], H-5[d]), 2.67 (m, 2 H, H-3eq[c], H-3eq[d]), 2.27 (dd, 1 H, J_{gem} = 12.6 Hz, $J_{3eq,4}$ = 3.9 Hz, H-3eq[b]), 2.19-1.97 (14 s, 42 H, 14 Ac), 1.86-1.68 (m, 3 H, H-3ax[b], H-3ax[c], H-3ax[d]), 1.45 (s, 9 H, $(CH_3)_3C$), 1.11 (d, 3 H, $J_{5,6}$ = 6.5 Hz, H-6[e]) 1.02 ppm (m, 2 H, $TMSCH_2CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 170.5, 170.5, 170.4, 170.2, 170.1, 170.0, 169.9, 169.9, 169.8, 169.8, 169.7, 167.8, 167.5, 167.2, 159.1, 155.7, 138.7, 138.4, 130.7, 129.7, 128.3, 128.2, 128.2, 127.8, 127.7, 127.4, 113.7, 103.1, 98.6, 98.5, 98.4, 94.9, 84.5, 81.8, 79.2, 77.6, 77.4, 75.6, 74.9, 74.3, 73.7, 72.7, 72.5, 72.3, 71.2, 70.9, 70.8, 68.7, 68.3, 68.2, 68.1, 67.9, 67.7, 67.5, 67.3, 67.0, 65.1, 63.5, 63.4, 62.5, 62.3, 62.1, 55.2, 53.1, 53.0, 51.9, 51.7, 50.5, 48.5, 39.6, 38.4, 37.4, 29.6, 28.4, 28.3, 23.6, 21.3, 21.3, 21.1, 21.0, 20.8, 20.8, 20.7, 20.7, 20.6, 20.5, 20.5, 18.4, 15.9, -1.5 ppm; HRMS: *m/z*: found $[M+Na]^+$ 2284.8403, $C_{104}H_{143}N_3O_{50}Si$ calcd for $[M+Na]^+$ 2284.8401.

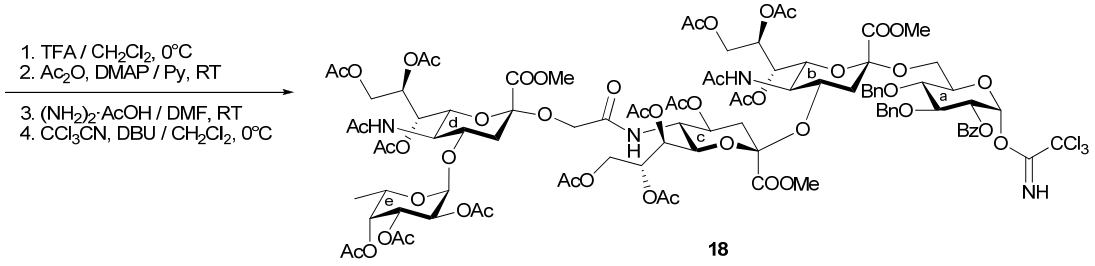


DDQ (4.5 mg, 19.8 μmol) was added to a solution of compound **17** (37.3 mg, 16.5 μmol) in CH_2Cl_2 (830 μL)/H_2O (40 μL). The reaction mixture was stirred for 3.5 h at room temperature with monitoring of the reaction by TLC (PhMe/acetone 3:2). The mixture was diluted with $CHCl_3$, and the organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried (Na_2SO_4), and concentrated. The crude material was exposed to high vacuum for 24 h, and redissolved in pyridine (1.0 mL). Benzoic anhydride (8.4 mg, 37.1 μmol) and DMAP (200 μg, 1.24 μmol) were added to the solution, and the reaction mixture was stirred for h at room temperature. Completion of the reaction was confirmed by TLC (PhMe/acetone 3:2). After quenching with water, the mixture was diluted with EtOAc, and the organic layer was washed with 2 M aqueous HCl, water,

saturated aqueous $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 50:1→40:1) to give compound **S12** (24.8 mg, 67 %).

$[\alpha]_D$ = -45.3 ° (c 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00-7.09 (m, 15 H, Ph), 6.00 (d, 1 H, $J_{NH,5}$ = 10.3 Hz, NH^c), 5.49 (d, 1 H, $J_{NH,5}$ = 8.0 Hz, NH^d), 5.47-5.41 (m, 3 H, H-7^b, H-8^b, H-8^c), 5.38-5.27 (m, 6 H, NH^b, H-7^c, H-7^d, H-8^d H-1^e, H-3^e), 5.19 (dd, 1 H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 10.6 Hz, H-2^a), 5.16 (d, 1 H, $J_{3,4}$ = 3.8 Hz, H-4^e), 5.07 (dd, 1 H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 10.6 Hz, H-2^e), 4.87-4.59 (m, 5 H, H-4^c, PhCH_2), 4.42 (d, 1 H, H-1^a), 4.36 (d, 1 H, J5,6 = 10.8 Hz, H-6^d), 4.31-4.25 (m, 2 H, H-9a^b, H-9a^c), 4.23-4.08 (m, 6 H, H-6a^a, H-9b^b, H-5^c, H-4^d, H-5^e, OCH_2CO), 4.06-3.98 (m, 3 H, H-6^b, H-9b^c, H-9a^d), 3.92-3.80 (m, 10 H, H-6^c, H-9b^d, OCH_2CO, 2 COOMe, $TMSCH_2CH_2$), 3.74-3.57 (m, 7 H, H-3^a, H-4^a, H-6b^a, H-5^b, COOMe), 3.46 (m, 2 H, H-5^a, $TMSCH_2CH_2$), 3.34 (m, 1 H, H-5^d), 2.68 (m, 2 H, H-3eq^c, H-3eq^d), 2.30 (dd, 1 H, J_{gem} = 12.9 Hz, $J_{3eq,4}$ = 4.0 Hz, H-3eq^b), 2.19-1.88 (14 s, 42 H, 14 Ac), 1.84-1.75 (m, 2 H, H-3ax^b, H-3ax^d), 1.70 (t, 1 H, J_{gem} = $J_{3ax,4}$ = 12.3 Hz, H-3ax^c), 1.46 (s, 9 H, $(CH_3)_3C$), 1.11 (d, 3 H, $J_{5,6}$ = 6.6 Hz, H-6^e) 0.82 ppm (m, 2 H, $TMSCH_2CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.6, 170.5, 170.3, 170.2, 170.0, 169.9, 169.8, 168.8, 167.6, 167.5, 167.2, 165.2, 155.7, 138.3, 137.8, 132.9, 130.1, 129.7, 129.0, 128.5, 128.4, 128.2, 128.2, 128.0, 127.8, 127.5, 125.3, 100.5, 98.7, 98.5, 98.4, 94.8, 82.5, 79.3, 77.7, 77.2, 75.0, 74.9, 74.0, 73.7, 72.7, 72.6, 72.5, 72.2, 71.3, 70.9, 70.8, 68.7, 68.3, 68.2, 68.1, 68.0, 67.7, 67.6, 67.0, 65.2, 63.6, 63.0, 62.6, 62.3, 62.1, 53.1, 53.1, 52.0, 51.8, 50.5, 48.5, 39.7, 38.5, 37.4, 29.7, 28.5, 28.3, 23.6, 21.4, 21.3, 21.2, 21.0, 20.9, 20.8, 20.7, 20.7, 20.6, 17.8, 15.9, -1.5 ppm; HRMS: *m/z*: found $[M+Na]^+$ 2268.8087, $C_{103}H_{139}N_3O_{50}Si$ calcd for $[M+Na]^+$ 2268.8088.

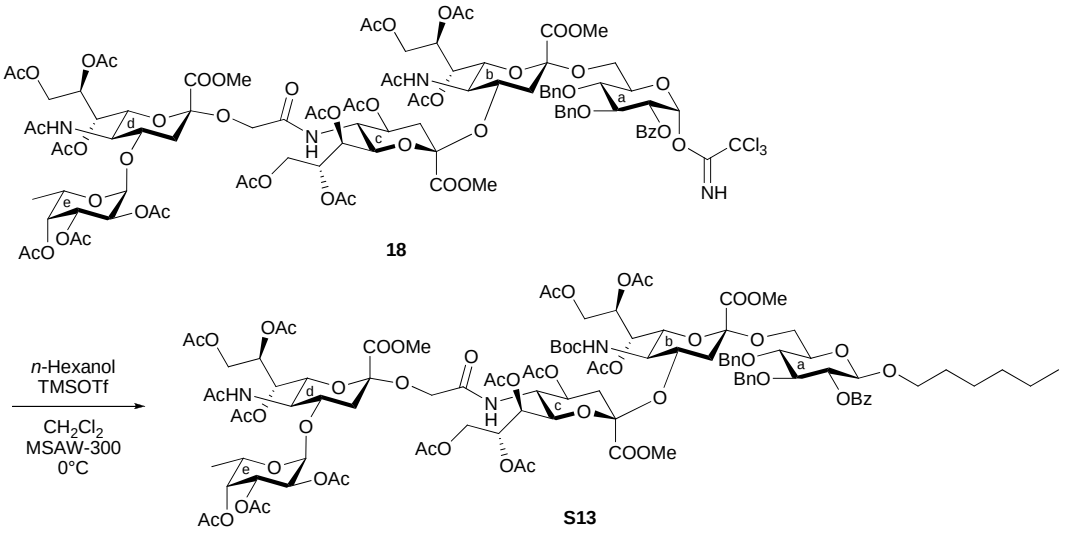




TFA (250 µL) was added to a solution of compound **S12** (17.3 mg, 7.70 µmol) in CH_2Cl_2 (750 µL). The reaction mixture was stirred for 3 h at 0 °C until TLC analysis ($CHCl_3$/MeOH 15:1) indicated

completion of the reaction. After quenching by saturated aqueous $NaHCO_3$ solution, the mixture was extracted with $CHCl_3$, dried (Na_2SO_4), and concentrated. The residue was exposed to high vacuum for 18 h and redissolved in pyridine (1.0 mL). Acetic anhydride (500 µL) and DMAP (1.0 mg) were added to the solution, and the mixture was stirred for 1 h at room temperature. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 10:1). The mixture was then diluted with EtOAc, and this solution washed with 2 M aqueous HCl, water, saturated aqueous $NaHCO_3$ solution, and brine, dried (Na_2SO_4), and concentrated. The residue was exposed to high vacuum for 18 h, and redissolved in DMF (770 µL). Hydrazine acetate (1.0 mg, 11.2 µmol) was added to the solution, and the mixture was stirred for 1 h at room temperature. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 15:1). The mixture was then diluted with EtOAc and washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was exposed to high vacuum for 18 h, and redissolved in CH_2Cl_2 (500 µL). CCl_3CN (7.5 µL, 74.6 µmol) and DBU (0.6 µL, 3.73 µmol) were added to the solution, and the reaction mixture was stirred for 45 min at 0 °C. After the completion of the reaction was indicated by TLC ($CHCl_3$/MeOH 15:1), the reaction mixture was concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 40:1→35:1) to give compound **18** (7.9 mg, 46 %).

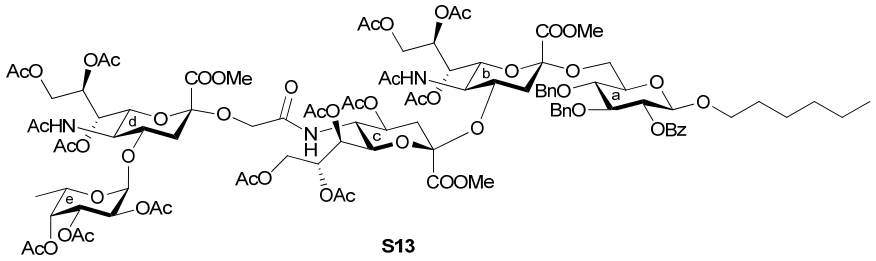
$[\alpha]_D$ = -33.2 ° (c 1.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.41 (s, 1 H, Cl_3CC=NH), 7.94-7.01 (m, 15 H, Ph), 6.57 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1^a), 6.07 (d, 2 H, $J_{NH,5}$ = 10.4 Hz, NH^b, NH^c), 5.63 (m, 1 H, H-8^c), 5.52 (d, 1 H, $J_{NH,5}$ = 7.6 Hz, NH^d), 5.43-5.38 (m, 2 H, H-7^b, H-8^d), 5.34-5.26 (m, 5 H, H-2^a, H-8^b, H-7^d, H-3^e, H-4^e), 5.16 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1^e), 5.13 (dd, 1 H, $J_{6,7}$ = 2.4 Hz, $J_{7,8}$ = 9.3 Hz, H-7^c), 5.06 (dd, 1 H, $J_{2,3}$ = 10.7 Hz, H-2^e), 4.97-4.72 (4 d, 4 H, PhCH_2), 4.83 (m, 1 H, H-4^c), 4.38 (dd, 1 H, $J_{8,9a}$ = 2.4 Hz, J_{gem} = 12.1 Hz, H-9a^c), 4.35 (d, 1 H, $J_{5,6}$ = 10.3 Hz, H-6^d), 4.29 (m, 2 H, H-6a^a, H-9a^b), 4.22-4.08 (m, 7 H, H-3^a, H-9b^b, H-5^c, H-4^d, H-9a^d, H-5^e, OCH_2CO), 4.04-3.93 (m, 3 H, H-4^a, H-5^b, H-6^b), 3.91-3.79 (m, 13 H, H-5^a, H-6^c, H-9b^c, H-9b^d, 3 COOMe), 3.71 (m, 1 H, H-4^b), 3.44 (d, 1 H, J_{gem} = 9.7 Hz, H-6b^a), 3.32 (br m, 1 H, H-5^d), 2.69-2.64 (m, 2 H, H-3eq^c, H-3eq^d), 2.32 (dd, 1 H, J_{gem} = 12.8 Hz, $J_{3eq,4}$ = 4.5 Hz, H-3eq^b), 2.12-1.75 (15 s, 45 H, 15 Ac), 1.90-1.85 (m, 2 H, H-3ax^b, H-3ax^c), 1.69 (m, 1 H, H-3ax^d), 1.11 ppm (d, 3 H, $J_{5,6}$ = 6.2 Hz, H-6^e); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 170.6, 170.5, 170.4, 170.2, 170.0, 169.9, 169.9, 168.8, 167.6, 167.2, 167.1, 165.6, 160.8, 138.1, 137.9, 133.3, 129.8, 129.3, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.6, 98.6, 98.3, 97.9, 94.8, 94.1, 91.0, 78.7, 77.9, 77.6, 77.2, 75.4, 75.3, 72.7, 72.5, 72.3, 72.0, 71.1, 70.9, 70.7, 68.3, 68.2, 68.0, 67.7, 67.6, 67.2, 66.9, 65.2, 64.3, 63.4, 62.2, 62.1, 53.2, 53.0, 52.6, 51.8, 49.0, 48.6, 39.5, 38.1, 37.3, 37.1, 32.7, 31.9, 30.0, 29.7, 29.5, 29.3, 27.1, 23.6, 23.3, 22.7, 21.2, 21.0, 21.0, 20.9, 20.8, 20.7, 20.6, 20.4, 19.7, 15.9, 14.1 ppm; HRMS: *m/z*: found $[M+Na]^+$ 2253.6057, $C_{97}H_{121}Cl_3N_4O_{49}$ calcd for $[M+Na]^+$ 2253.6057.



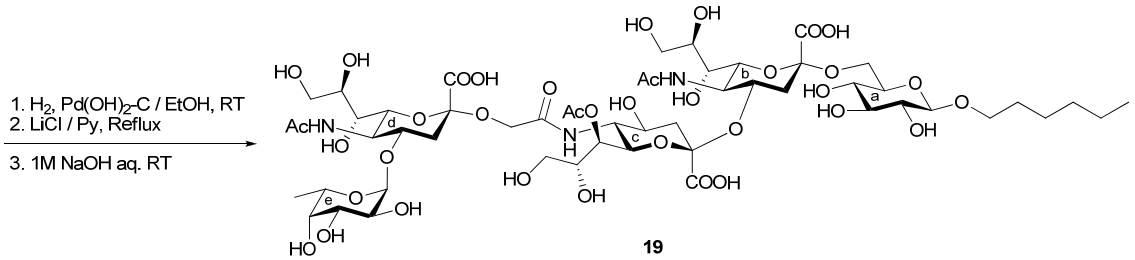
4Å molecular sieves AW-300 (150 mg) were added to a solution of compound **18** (16.4 mg, 7.34 μmol) and n-hexanol (4.1 μL, 36.7 μmol) in CH_2Cl_2 (730 μL). The suspension was stirred for 1 h at room temperature, then cooled to 0 °C. TMSOTf (0.27 μL, 1.47 μmol) was added to the solution and stirring was continued for 1 h, after which TLC analysis ($CHCl_3$/MeOH 15:1) indicated completion of the reaction. The reaction mixture was made alkaline to pH 8 with triethylamine at 0 °C, filtered through Celite, and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 40:1→35:1) and preparative TLC ($CHCl_3$/MeOH 15:1) to give compound **S13** (313 mg, 76 %).

$[\alpha]_D$ = +12.3 ° (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00-7.11 (m, 15 H, Ph), 6.09 (d, 1 H, $J_{NH,5}$ = 9.9 Hz, NH^b), 6.06 (d, 1 H, $J_{NH,5}$ = 10.4 Hz, NH^c), 5.63 (td, 1 H, $J_{7,8}$ = 9.3 Hz, $J_{8,9a}$ = 2.2 Hz, $J_{8,9b}$ = 8.8 Hz, H-8^c), 5.50 (d, 1 H, $J_{NH,5}$ = 7.7 Hz, NH^d), 5.45 (m, 2 H, H-7^b, H-8^b), 5.34-5.27 (m, 4 H, H-7^d, H-8^d, H-3^e, H-4^e), 5.18 (dd, 1H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 9.4 Hz, H-2^a), 5.16 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1^e), 5.13 (dd, 1 H, $J_{6,7}$ = 2.8 Hz, H-7^c), 5.06 (dd, 1 H, $J_{2,3}$ = 10.5 Hz, H-2^e), 4.87-4.62 (4 d, 4 H, PhCH_2), 4.82 (m, 1 H, H-4^c), 4.38 (m, 2 H, H-1^a, H-9a^c), 4.36 (d, 1 H, $J_{5,6}$ = 11.0 Hz, H-6^d), 4.28 (d, 2 H, J_{gem} = 12.1 Hz, H-9a^b, H-9a^d), 4.20-4.08 (m, 6 H, H-6a^a, H-5^c, H-4^d, H-9b^d, H-5^e, OCH_2CO), 4.04-3.96 (m, 3 H, H-5^b, H-6^b, H-9b^b), 3.89-3.78 (m, 14 H, H-4^a, H-5^a, H-6^c, H-9b^c, 3 COOMe, OCH_2CH_2), 3.74 (dd, 1 H, $J_{3,4}$ = 8.7 Hz, H-3^a), 3.69 (m, 1 H, H-4^b), 3.59 (d, 1 H, J_{gem} = 10.4 Hz, OCH_2CO), 3.43 (m, 1 H, H-6b^a), 3.37 (m, 1 H, OCH_2CH_2), 3.31 (br m, 1 H, H-5^d), 2.66 (m, 2 H, H-3eq^c, H-3eq^d), 2.30 (dd, 1 H, J_{gem} = 12.7 Hz, $J_{3eq,4}$ = 4.4 Hz, H-3eq^b), 2.23-1.89 (15 s, 45 H, 15 Ac), 1.86-1.78 (m, 2 H, H-3ax^b, H-3ax^c), 1.69 (t, 1 H, J_{gem} = $J_{3ax,4}$ = 12.1 Hz, H-3ax^d), 1.48-1.01 (m, 8 H, -$(CH_2)_4$-), 1.11 (d, 3 H, $J_{5,6}$ = 6.6 Hz, H-6^e), 0.71 ppm (t, 3 H, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.0, 170.7, 170.6, 170.5, 170.4, 170.3, 170.2, 170.0, 169.9, 168.8, 167.6, 167.2, 167.1, 165.3, 138.3, 137.9, 132.9, 130.1, 129.7, 128.4, 128.3, 128.2, 128.2, 128.0, 127.8, 127.6, 101.1, 98.7, 98.3, 97.9, 94.8, 82.4, 75.0, 74.0, 73.7, 72.3, 72.0, 71.2, 70.9, 70.7, 69.8, 68.3,

68.2, 67.7, 67.6, 67.4, 66.9, 65.2, 64.3, 63.4, 62.9, 62.5, 62.1, 53.2, 52.2, 51.9, 49.0, 48.7, 39.4, 38.2, 37.3, 31.4, 29.7, 29.3, 25.5, 23.6, 23.3, 22.7, 22.4, 21.3, 21.2, 21.0, 21.0, 20.9, 20.8, 20.7, 20.6, 15.9, 13.9 ppm; HRMS: *m/z*: found $[M+Na]^+$ 2194.7901, $C_{101}H_{133}N_3O_{49}$ calcd for $[M+Na]^+$ 2194.7900.



S13

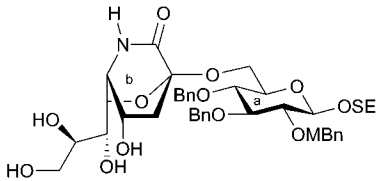


19

20 % $Pd(OH)_2$ on activated carbon (10.1 mg) was added to a solution of compound **15** (10.1 mg, 4.65 μmol) in EtOH (1.0 mL). The suspension was stirred under a hydrogen stream for 3.5 h at room temperature. After the completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH 10:1), the mixture was filtered through Celite, and the filtrate was concentrated. The residue was subjected to column chromatography on silica gel ($CHCl_3$/MeOH 30/1→25/1) to give debenzylated compound. This was redissolved in pyridine (1.5 mL) and lithium chloride (5.9 mg, 140 μmol) was added. The mixture was stirred for 14 h under reflux. The progress of the reaction was monitored by TLC ($CHCl_3$/MeOH/AcOH 5/1/0.1). The resulting mixture was then concentrated and the residual volatiles were co-evaporated with toluene. The residue was subjected to column chromatography on Sephadex LH-20 (MeOH) to give crude tricarboxylic acid. The crude material was dissolved in 0.1 M aqueous NaOH solution (1.0 mL) and the mixture was stirred for 4 h at room temperature. Completion of the reaction was confirmed by TLC ($CHCl_3$/MeOH/0.1 % aq. $CaCl_2$ 5/6/2). After neutralization with Dowex-50 (H^+), the mixture was concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 5/4→2/3) to give **19** (6.0 mg, 95 %).

$[\alpha]_D$ = -14.2 ° (c 0.6, $CHCl_3$/MeOH 1/1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.40 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H-1^e), 4.05 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1^a), 3.95 (d, 1 H, J_{gem} = 16.6 Hz, OCH_2CO), 3.84 (br dd, 1 H, $J_{5,6}$ = 6.3 Hz, H-5^e), 2.90-2.64 (br dd, 3 H, 3 H-3eq), 2.00 (s, 3 H, Ac), 1.81 (s, 3 H, Ac), 1.63-0.84 (m, 14 H, 3 H-3ax, -$(CH_2)_4$-, CH_2CH_3), 1.08 ppm (d, 3 H, H-6^e); ^{13}C NMR (125 MHz, DMSO-d_6): HRMS: *m/z*: found $[M-3H+2Na]^-$ 1342.4531, $C_{51}H_{85}N_3O_{35}$ calcd for $[M-3H+2Na]^-$ 1342.4350.

2010.9.27
Lactam tetraol



5

2010.9.27
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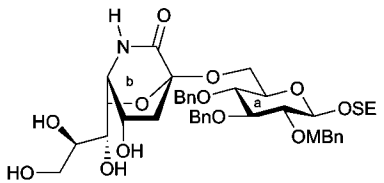

5

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SFO1	125.7703643 MHz
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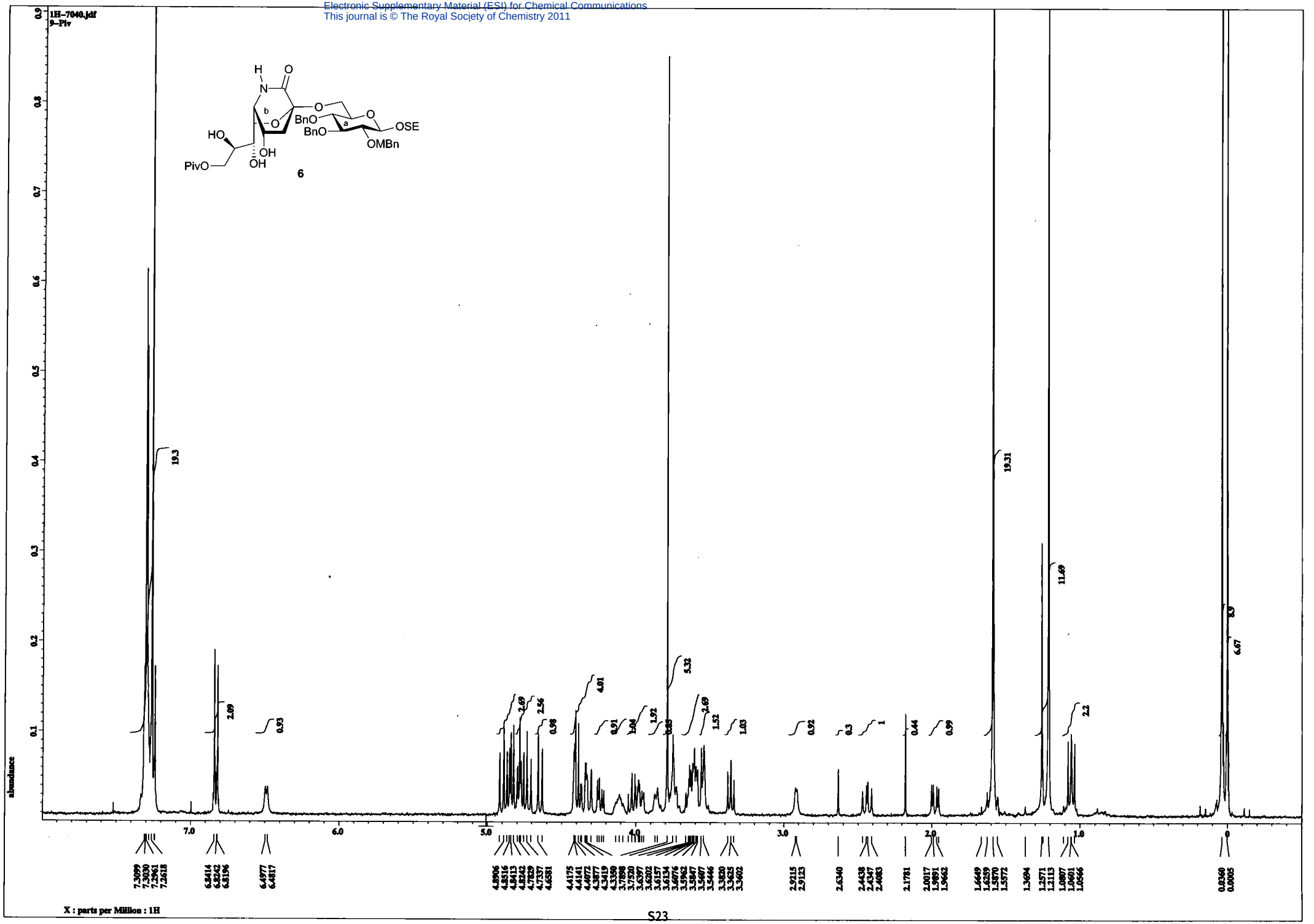

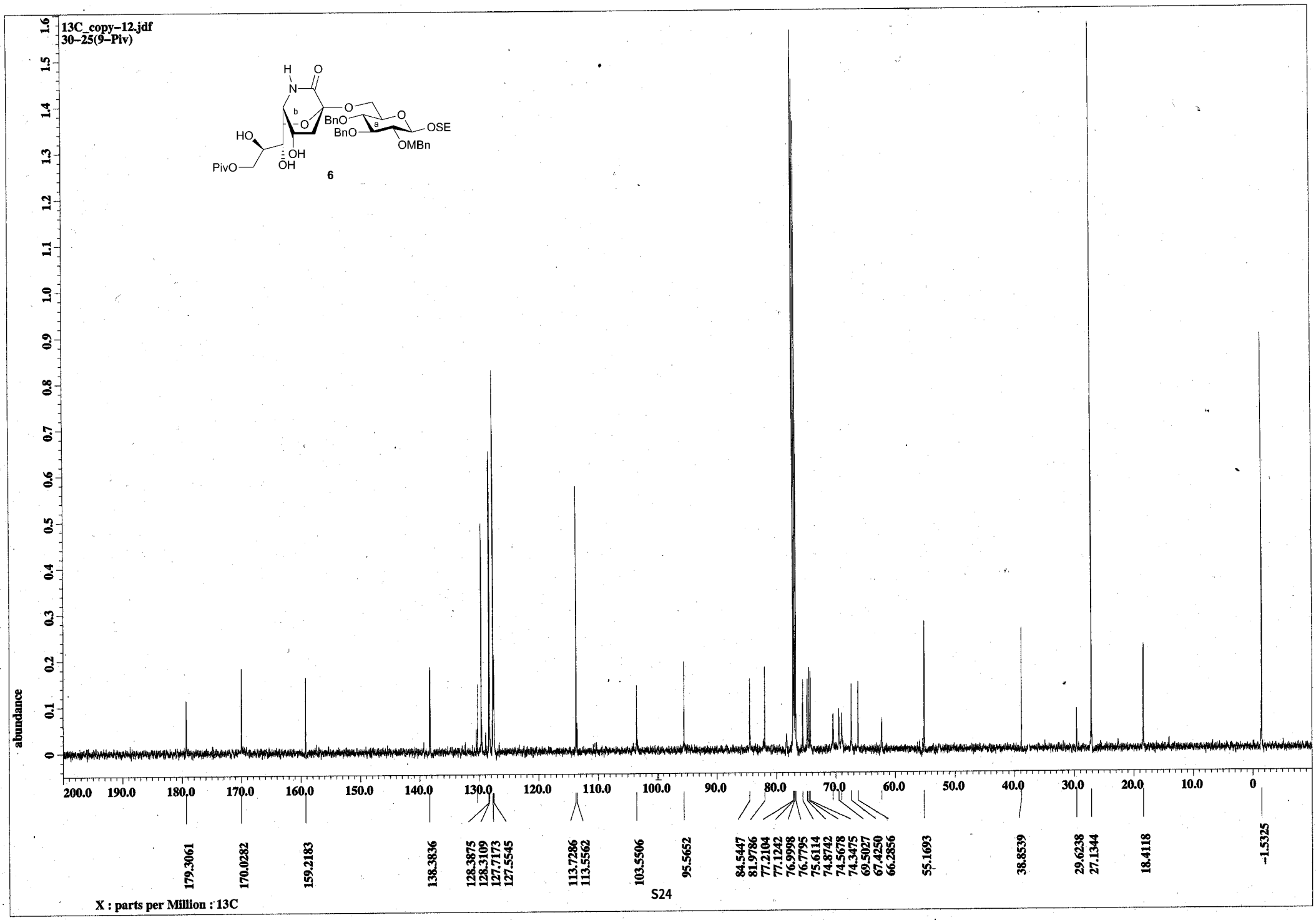
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X : parts per Million : 13C
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113.5562
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29.6238
27.1344
18.4118
-1.5325

6

2010.12.03
Trisaccharide(Neu5N3+Lactam)

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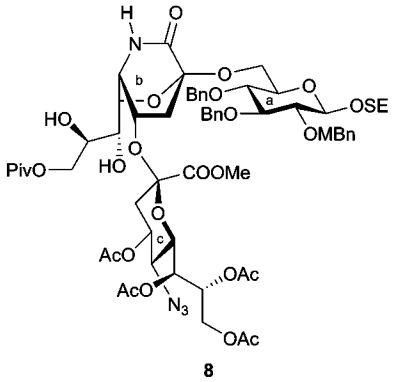
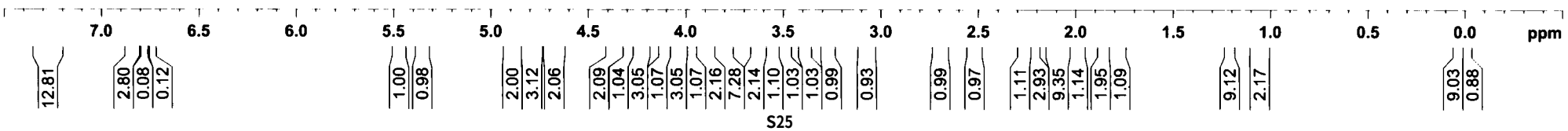


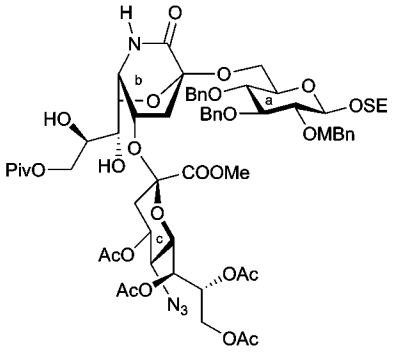
8



2010.10.27
Neu5N3-Lactam

179.05 171.20 170.28 169.61 169.52 169.32 167.86 159.15 138.72 138.25 130.78 129.75 128.37 128.28 127.98 127.81 127.69 127.48 113.71 103.06 99.89 95.82 84.70 81.96 79.14 78.10 77.25 77.00 76.75 75.58 74.72 74.31 74.21 72.71 72.45 71.69 70.29 67.92 67.48 66.93 65.97 63.83 62.84 60.34 59.44 55.21 53.27 52.25 38.80 37.80 37.49 29.65 27.20 21.00 20.93 20.76 20.58 18.56 14.16 -1.39 -1.42

NAME	28-2(Neu5N3-Lactam)
EXPNO	3
PROCNO	1
Date_	20101027
Time	11.01
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1000
DS	2
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	203
DW	16.800 usec
DE	6.50 usec
TE	299.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-0.10 dB
PL1W	106.67142487 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.70 dB
PL12	18.50 dB
PL13	18.50 dB
PL2W	17.32208443 W
PL12W	0.36190966 W
PL13W	0.36190966 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577950 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

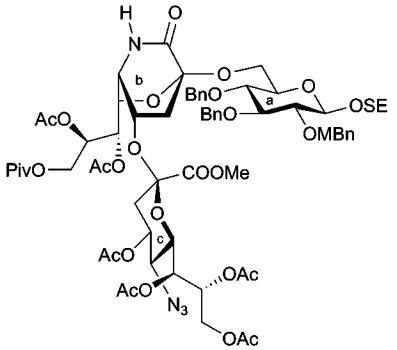


8

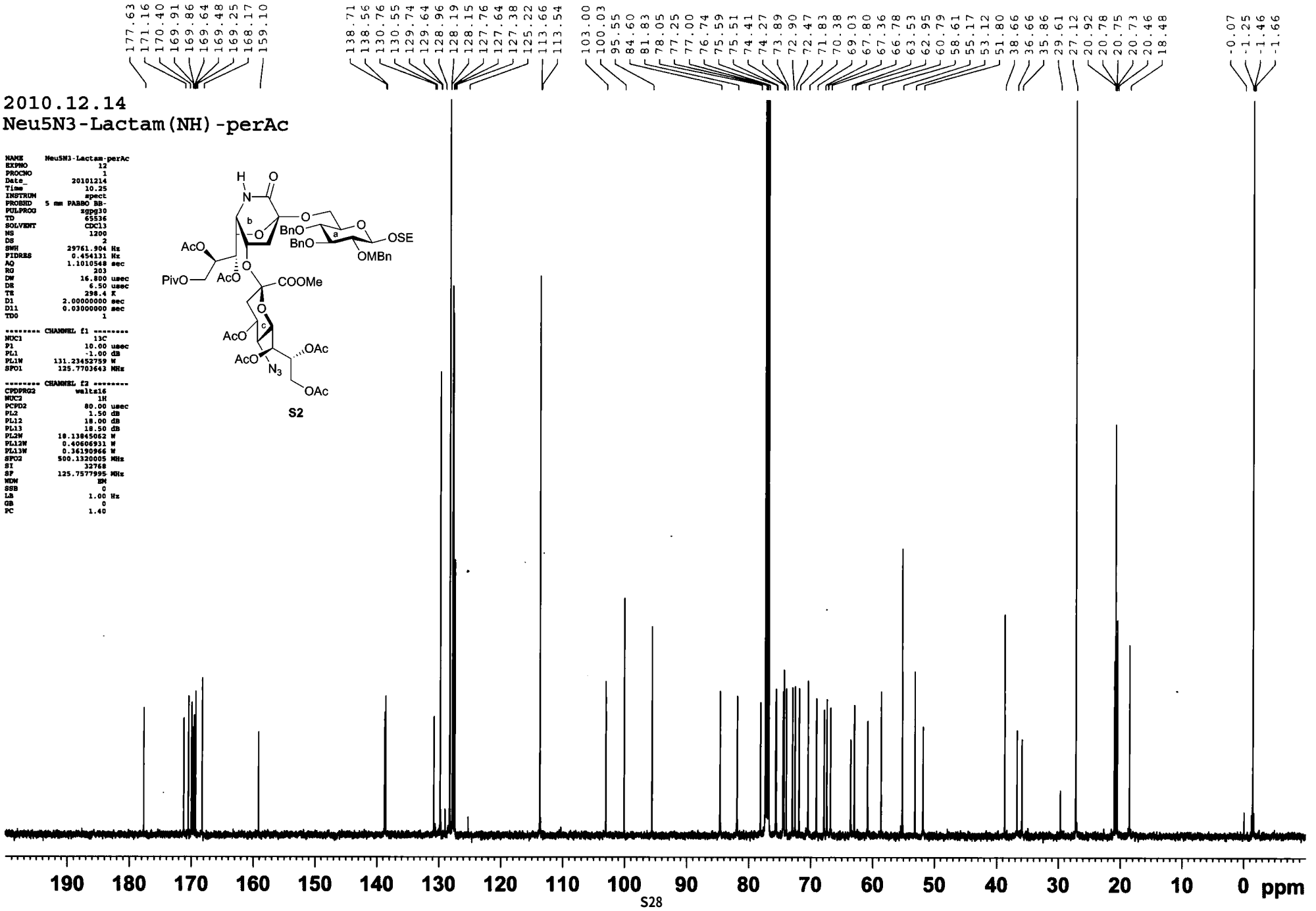
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

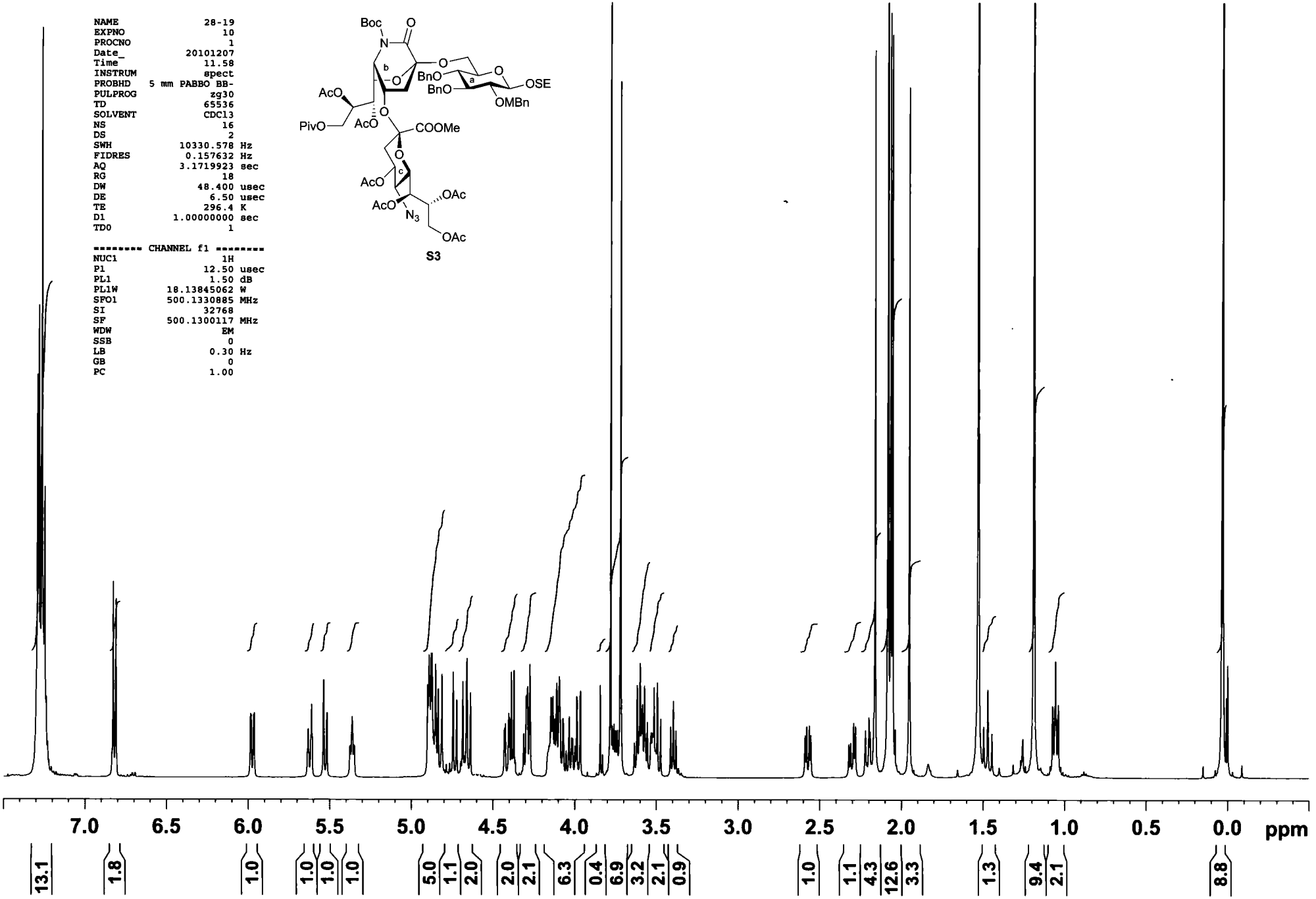
2010.12.14
Neu5N3-Lactam(NH)-perAc

NAME	Neu5N3-Lactam-perAc
EXPNO	10
PROCNO	1
Date_	20101214
Time	9.11
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	20.2
DW	48.400 usec
DE	6.50 usec
TE	295.9 K
D1	1.00000000 sec
TD0	1
******** CHANNEL f1 ********	
NUC1	1H
P1	12.50 usec
PL1	1.50 dB
PL1W	18.13845062 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1300117 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



S2




NAME 28-19
EXPNO 10
PROCNO 1
Date_ 20101207
Time 11.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 18
DW 48.400 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.50 usec
PL1 1.50 dB
PL1W 18.13845062 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Boc
N
O
b
O
BnO
BnO
a
O
OSE
OMBn
AcO
PivO
AcO
O
COOMe
O
c
AcO
AcO
OAc
N3
OAc
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
ppm
13.1
1.8
1.0
1.0
1.0
1.0
5.0
1.1
2.0
2.0
2.1
6.3
0.4
6.9
3.2
2.1
0.9
1.0
1.1
4.3
12.6
3.3
1.3
9.4
2.1
8.8

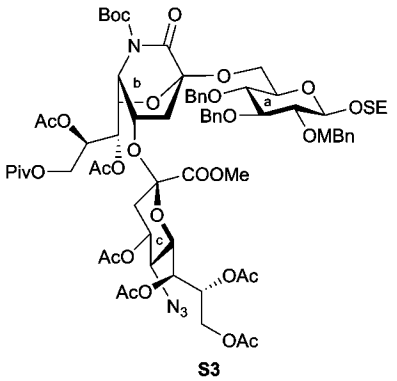
S3

2010.12.07

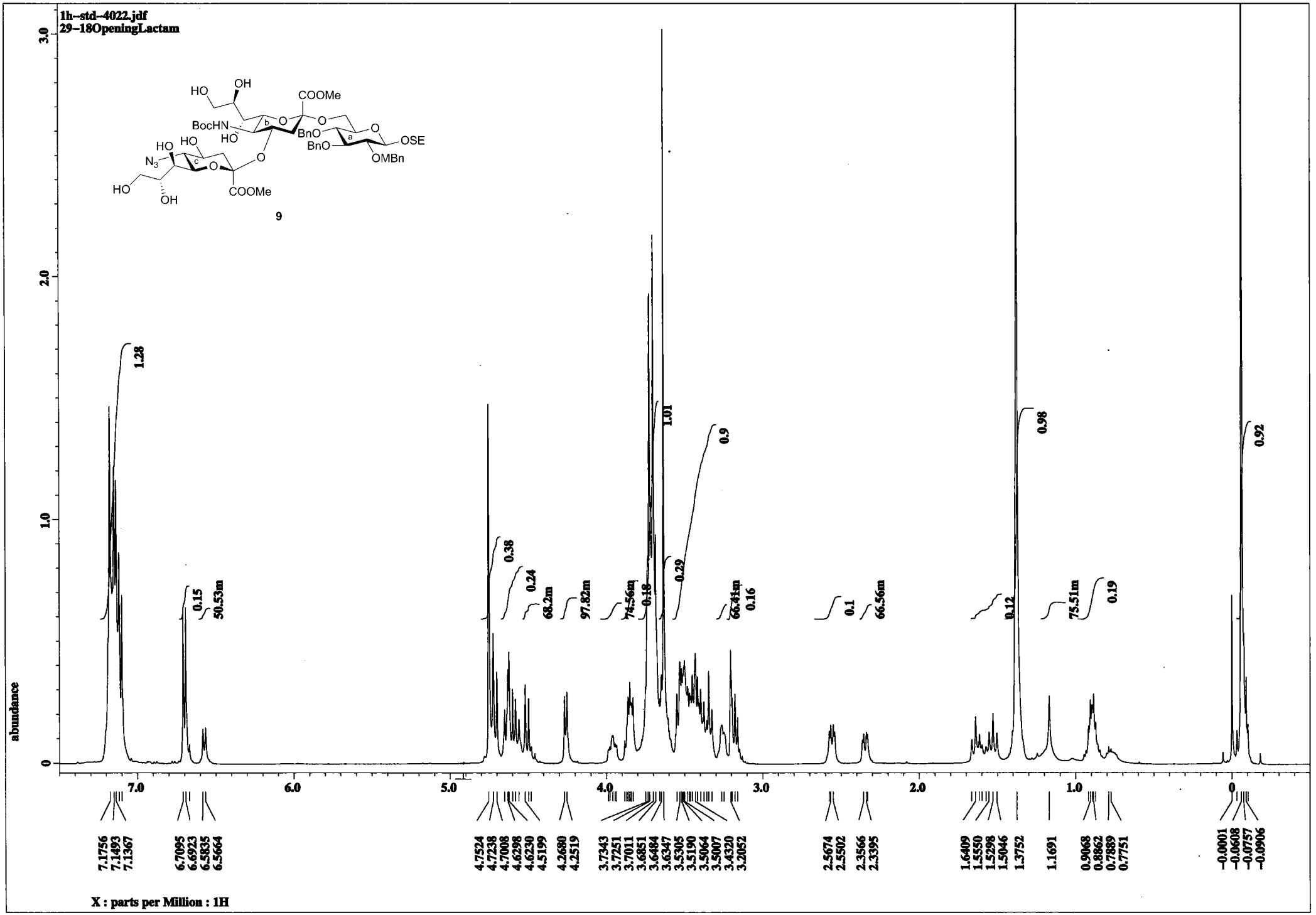
N3-N-BocLactam

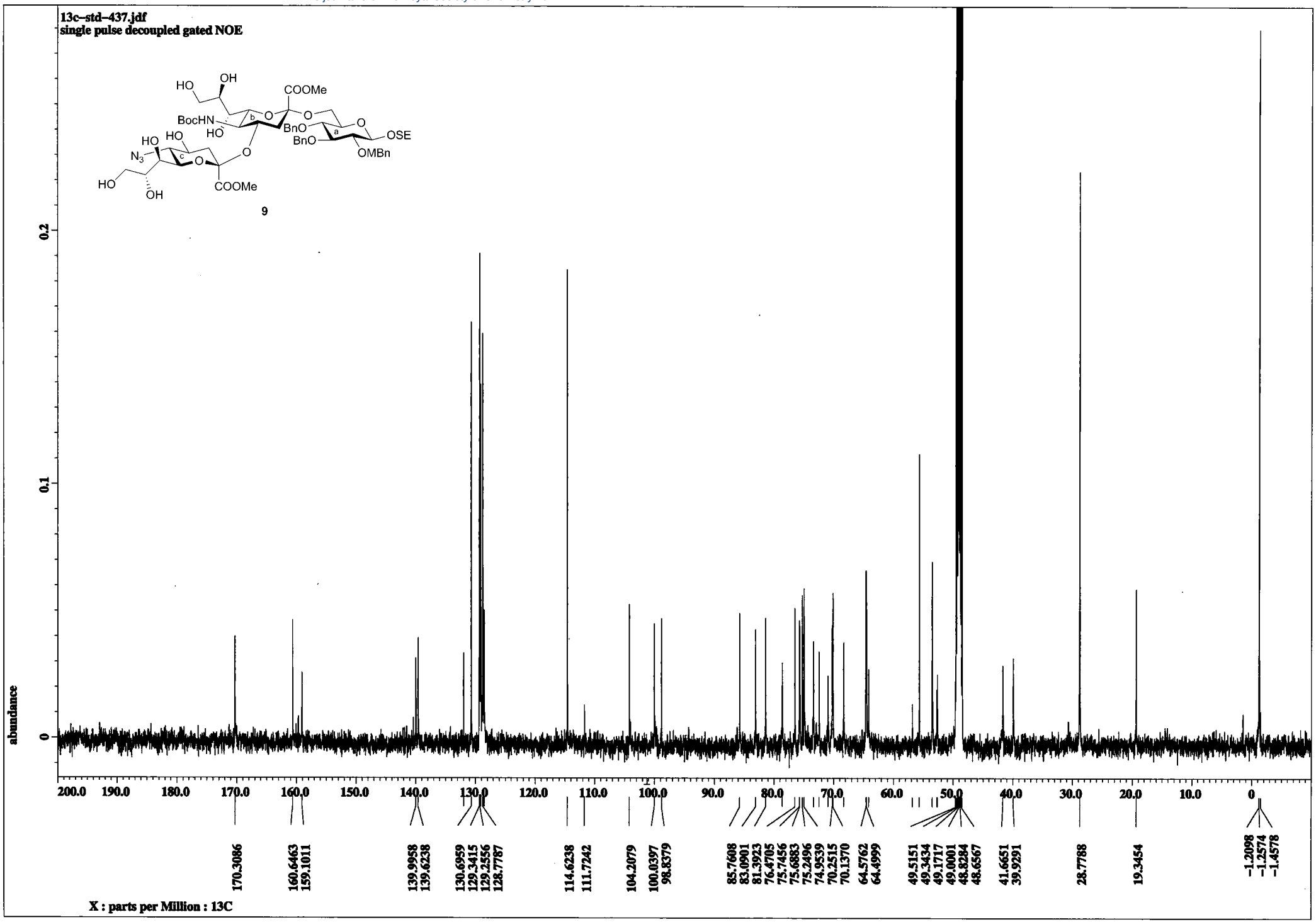
177.71 170.49 169.70 169.43 169.12 168.29 164.21 159.10 149.88 138.70 138.55 130.71 129.76 128.26 128.19 128.17 127.72 127.69 127.59 127.37 113.65 103.03 98.67 95.65 84.55 84.42 81.75 77.89 77.26 77.20 77.00 76.75 75.48 75.13 74.39 74.23 73.75 72.10 71.76 70.66 69.97 69.01 67.29 66.97 66.86 63.29 62.05 60.64 58.85 55.16 52.93 52.44 38.64 36.91 35.83 28.05 27.06 20.89 20.80 20.76 20.72 20.60 18.46 -1.44 -1.47

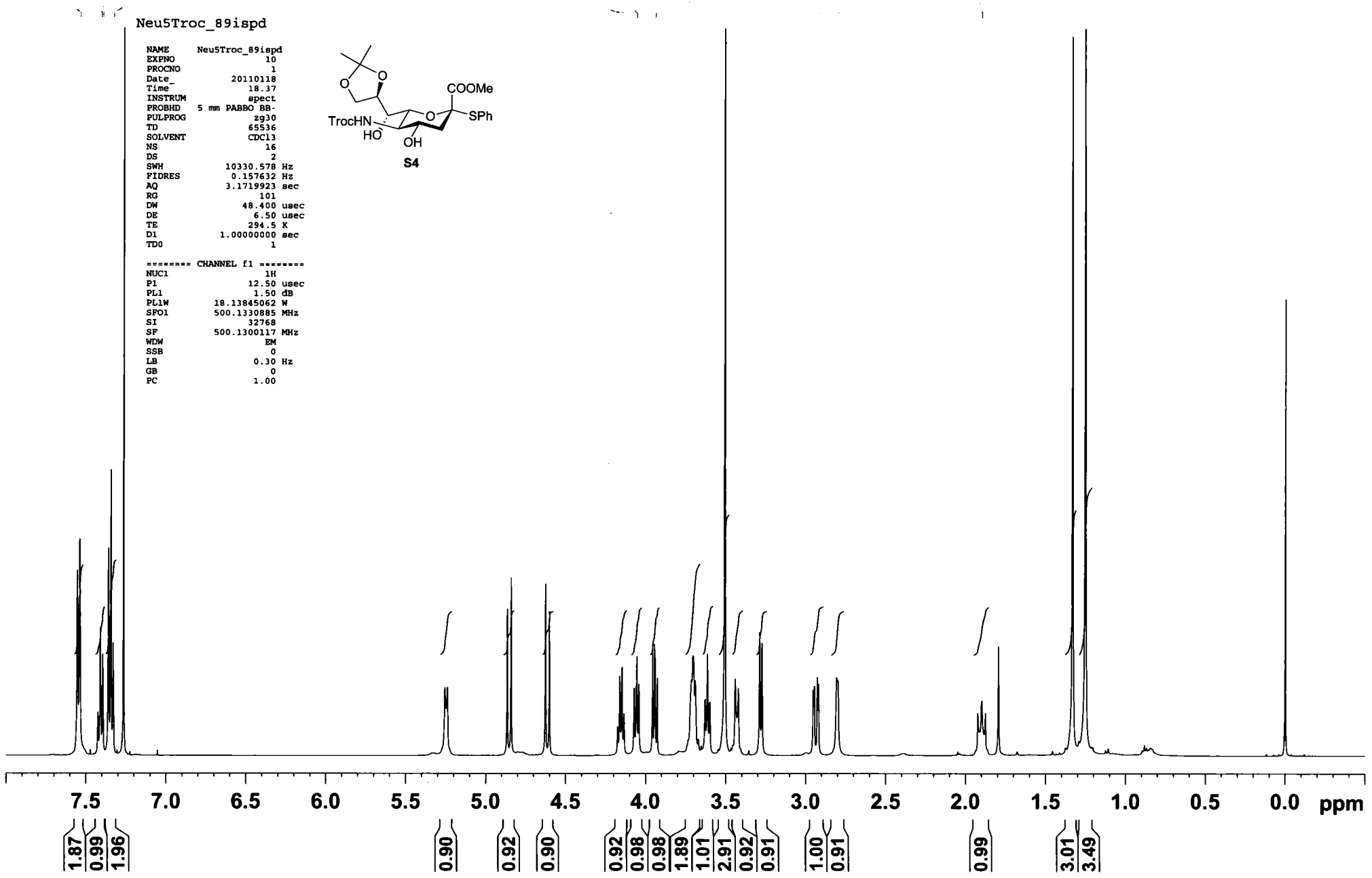
NAME	28-19
EXPNO	12
PROCNO	1
Date_	20101207
Time	13.09
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1152
DS	2
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	203
DW	16.800 usec
DE	6.50 usec
TE	298.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.00 dB
PL1W	131.23452759 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.50 dB
PL12	18.00 dB
PL13	18.50 dB
PL2W	18.13845062 W
PL12W	0.40606931 W
PL13W	0.36190966 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7578004 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

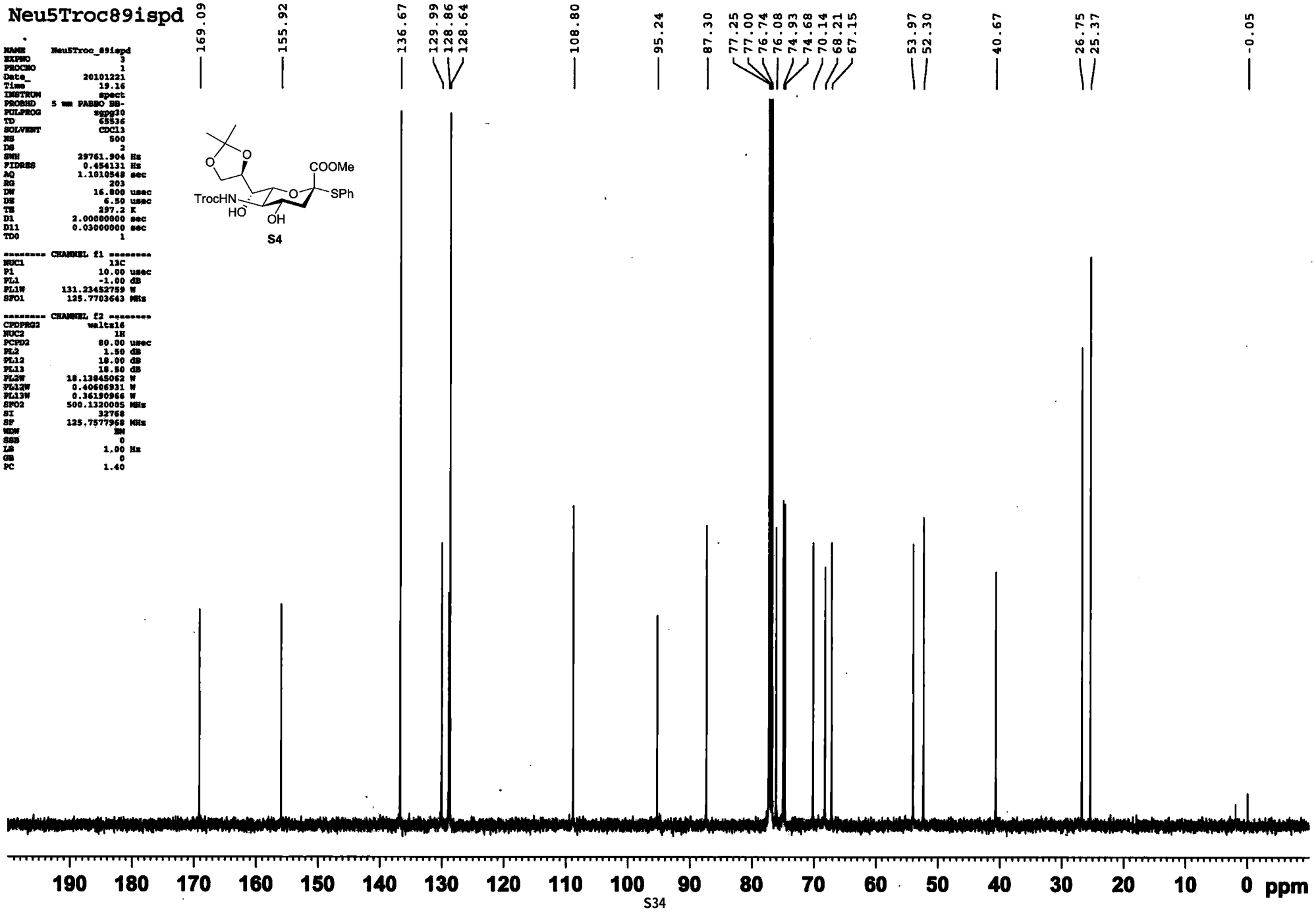


S3


1h-std-4022.jdf
29-18OpeningLactam
HO
OH
COOMe
BocHN
HO
BnO
O
OSE
HO
HO
BnO
N3
OMBn
HO
OH
COOMe
9
abundance
1.28
0.15
50.53m
0.38
0.24
68.2m
97.82m
74.56m
0.18
1.01
0.29
0.9
66.41m
0.16
0.1
66.56m
0.12
0.98
75.51m
0.19
0.92
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.1756
7.1493
7.1367
6.7095
6.6923
6.5835
6.5664
4.7524
4.7238
4.7008
4.6298
4.6230
4.5199
4.2680
4.2519
3.7343
3.7251
3.7011
3.6851
3.6484
3.6347
3.5305
3.5190
3.5064
3.5007
3.4320
3.2052
2.5674
2.5502
2.3566
2.3395
1.6409
1.5550
1.5298
1.5046
1.3752
1.1691
0.9068
0.8862
0.7889
0.7751
-0.0001
-0.0608
-0.0757
-0.0906
X : parts per Million : 1H

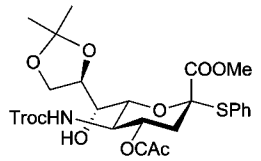

13c-std-437.jdf
single pulse decoupled gated NOE
HO
OH
COOMe
BocHN
HO
BnO
OSE
HO
HO
BnO
N3
OMBn
HO
OH
COOMe
9
abundance
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.3086
160.6463
159.1011
139.9958
139.6238
130.6959
129.3415
129.2556
128.7787
114.6238
111.7242
104.2079
100.0397
98.8379
85.7608
83.0901
81.3923
76.4705
75.7456
75.6883
75.2496
74.9539
70.2515
70.1370
64.5762
64.4999
49.5151
49.3434
49.1717
49.0001
48.8284
48.6567
41.6651
39.9291
28.7788
19.3454
-1.2098
-1.2574
-1.4578
X : parts per Million : 13C


Neu5Troc_89ispd
NAME Neu5Troc_89ispd
EXPNO 10
PROCNO 1
Date_ 20110118
Time 18.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 101
DW 48.400 usec
DE 6.50 usec
TE 294.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.50 usec
PL1 1.50 dB
PL1W 18.13845062 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
COOMe
SPh
TrocHN
HO
OH
S4
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
ppm
1.87
0.99
1.96
0.90
0.92
0.90
0.92
0.98
0.98
1.89
1.01
2.91
0.92
0.91
1.00
0.91
0.99
3.01
3.49

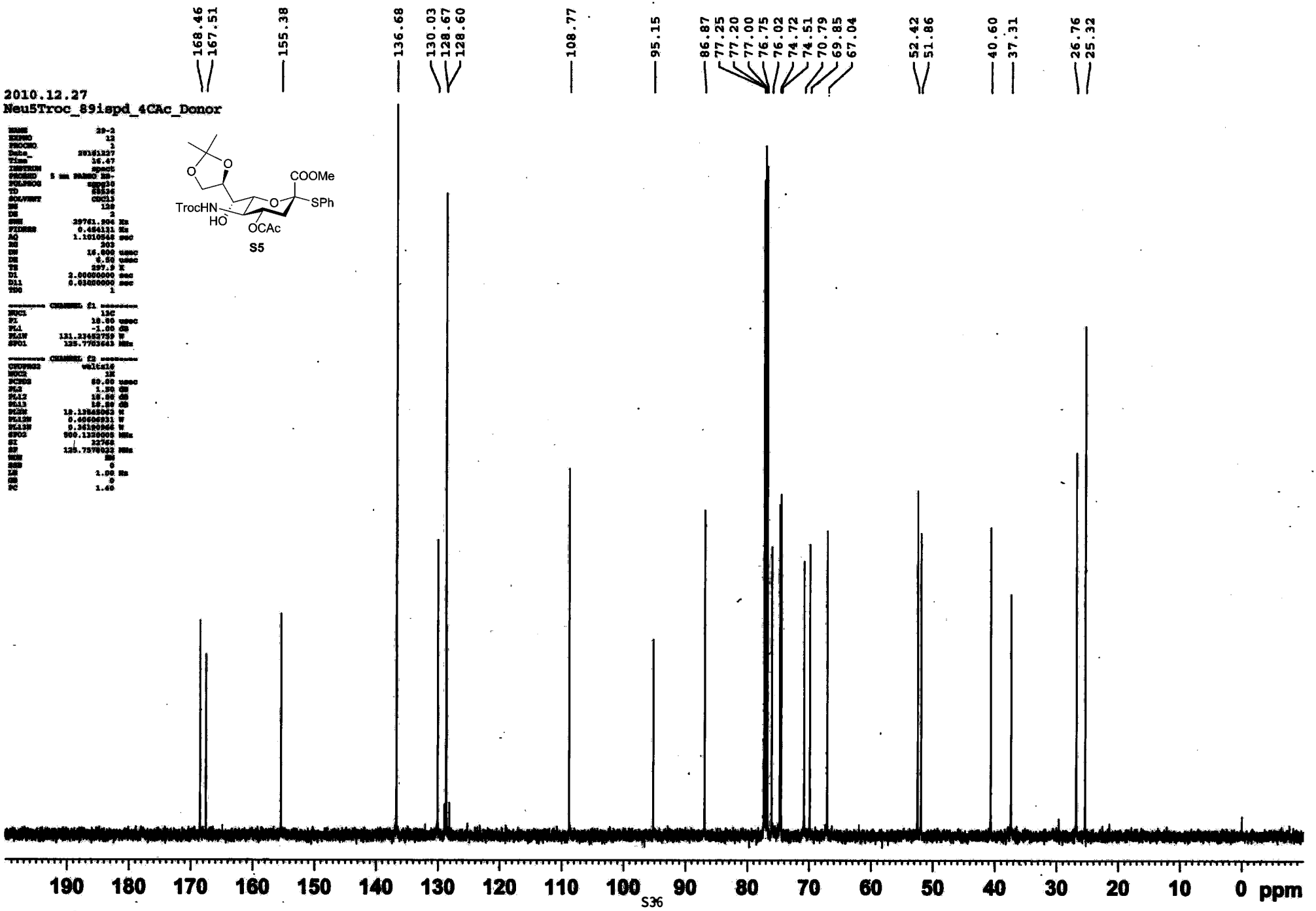

Neu5Troc89ispd
169.09
155.92
136.67
129.99
128.86
128.64
108.80
95.24
87.30
77.25
77.00
76.74
76.08
74.93
74.68
70.14
68.21
67.15
53.97
52.30
40.67
26.75
25.37
-0.05
NAME Neu5Troc_89ispd
EXPNO 3
PROCNO 1
Date_ 20101221
Time 19.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 2
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 -1.00 dB
PL1W 131.23452759 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.50 dB
PL12 18.00 dB
PL13 18.50 dB
PL2W 18.13845062 W
PL12W 0.40606931 W
PL13W 0.36190966 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577968 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
COOMe
SPh
TrocHN
HO
OH
O
S4
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

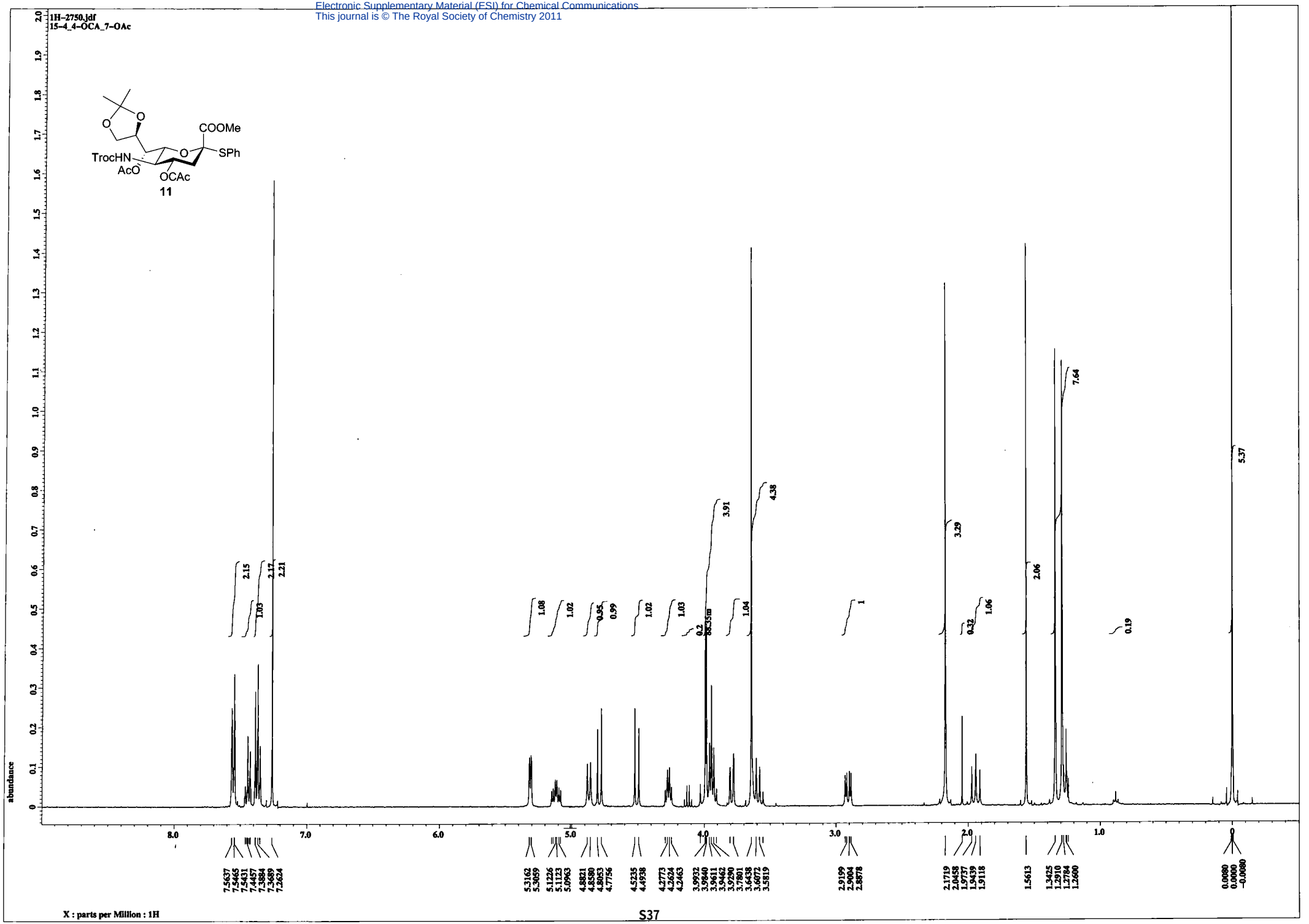
2010.12.27
Neu5Troc_89ispd_4CAc_Donor

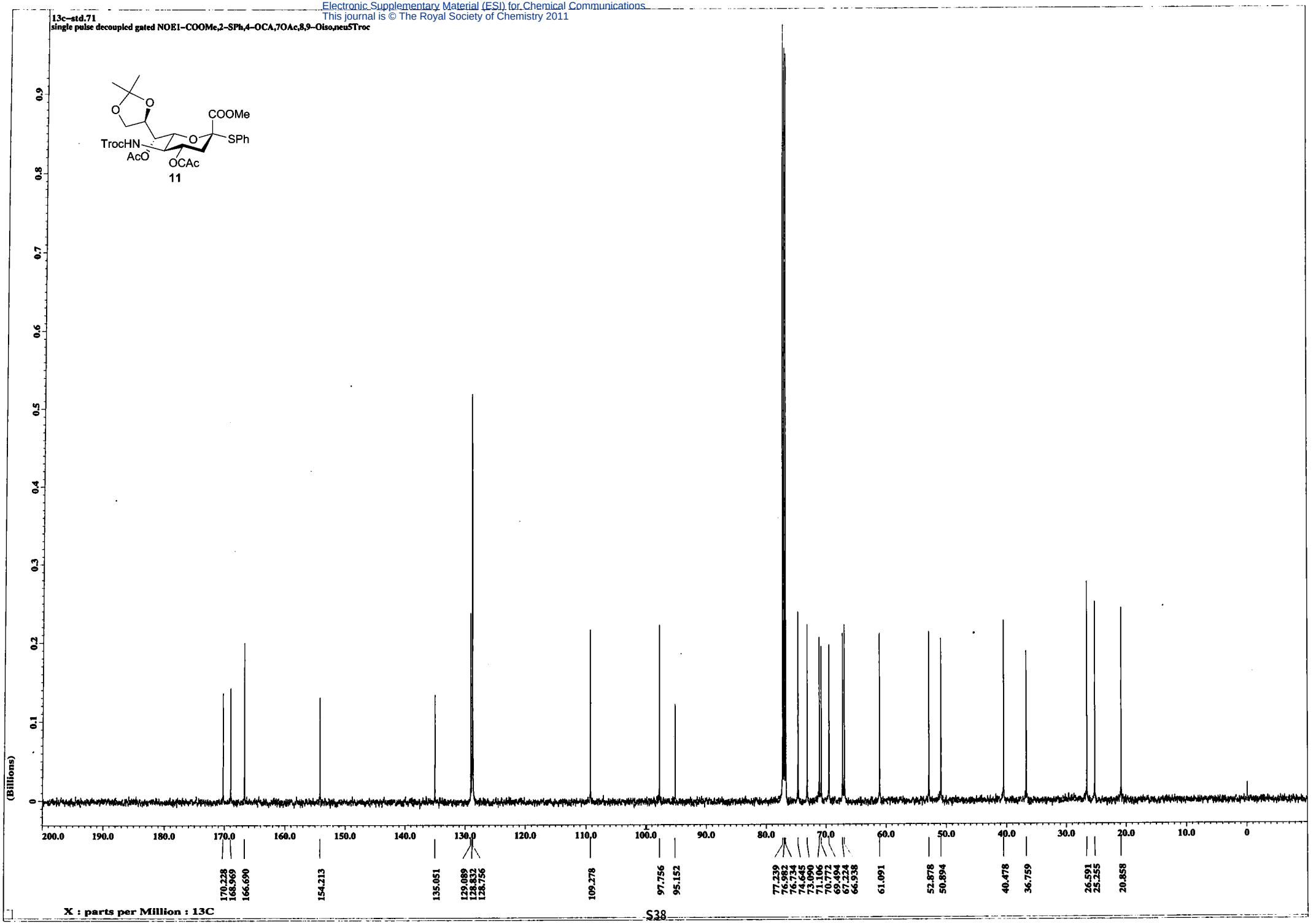
NAME	29-2
EXPNO	10
PROCNO	1
Date_	20101227
Time	16.34
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	20.2
DW	48.400 usec
DE	6.50 usec
TE	296.8 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.50 usec
PL1	1.50 dB
PL1W	18.13845062 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1300032 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

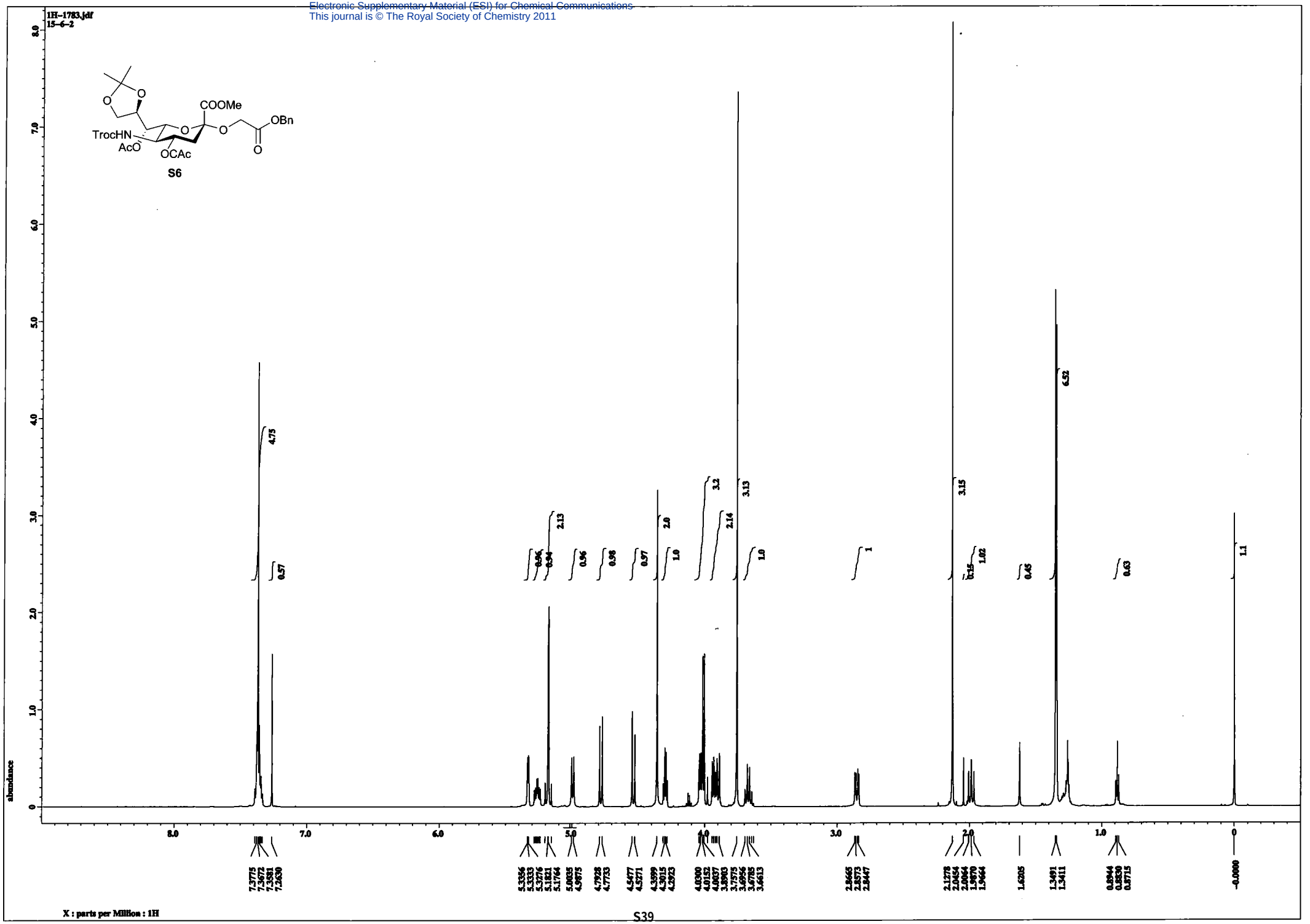


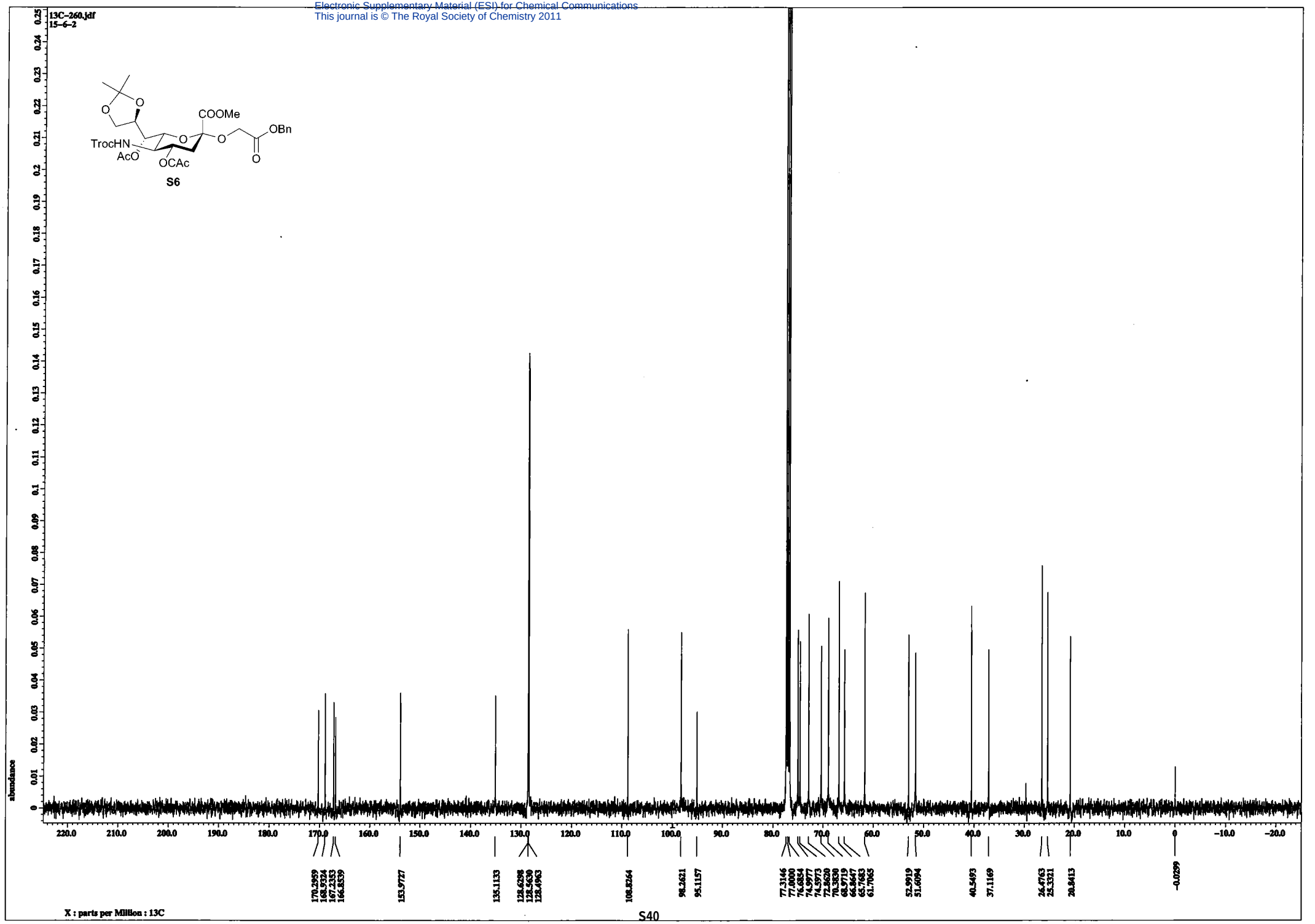
S5

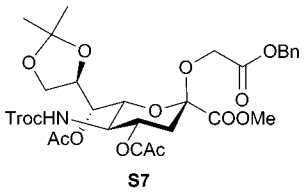






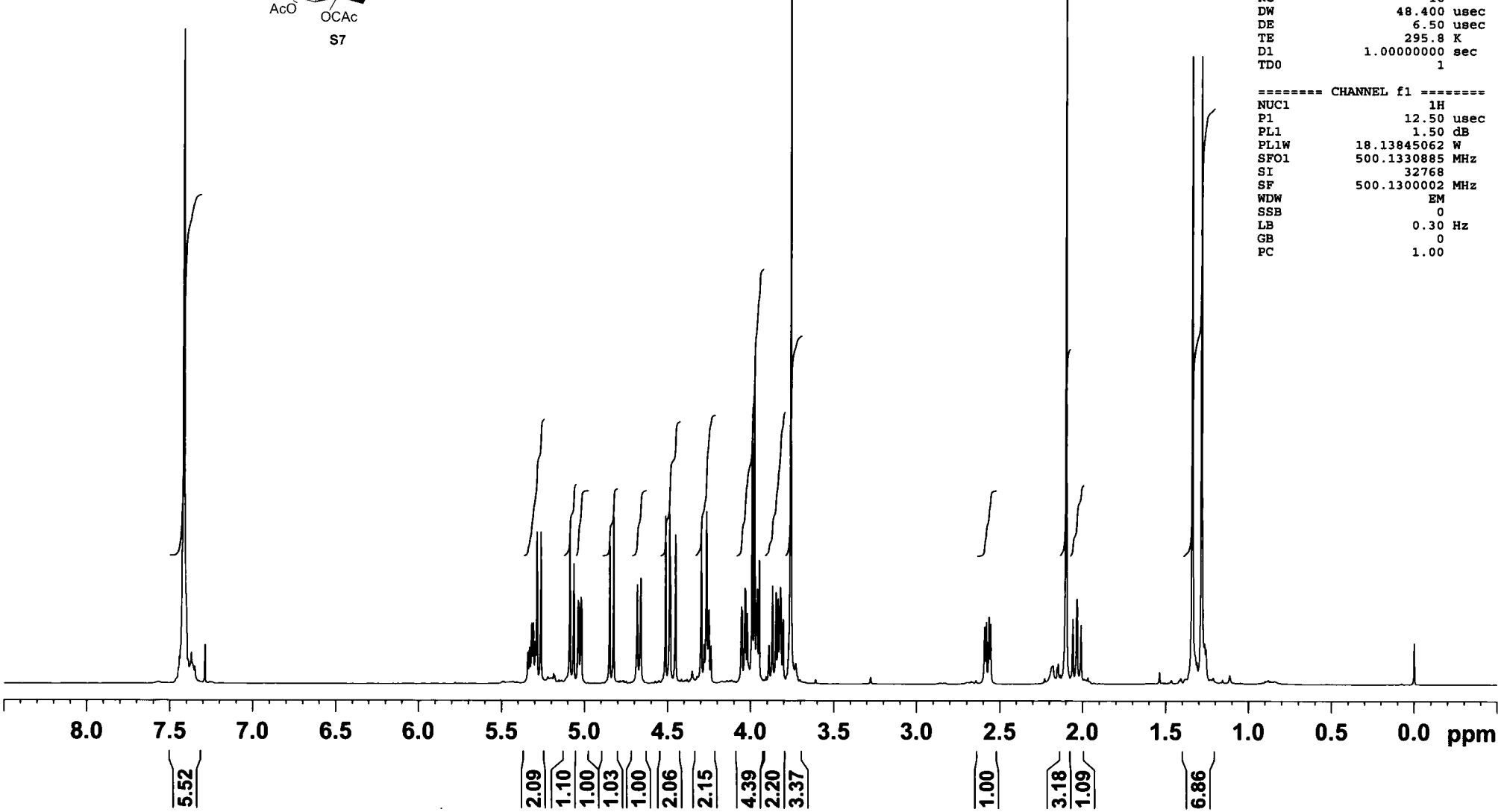


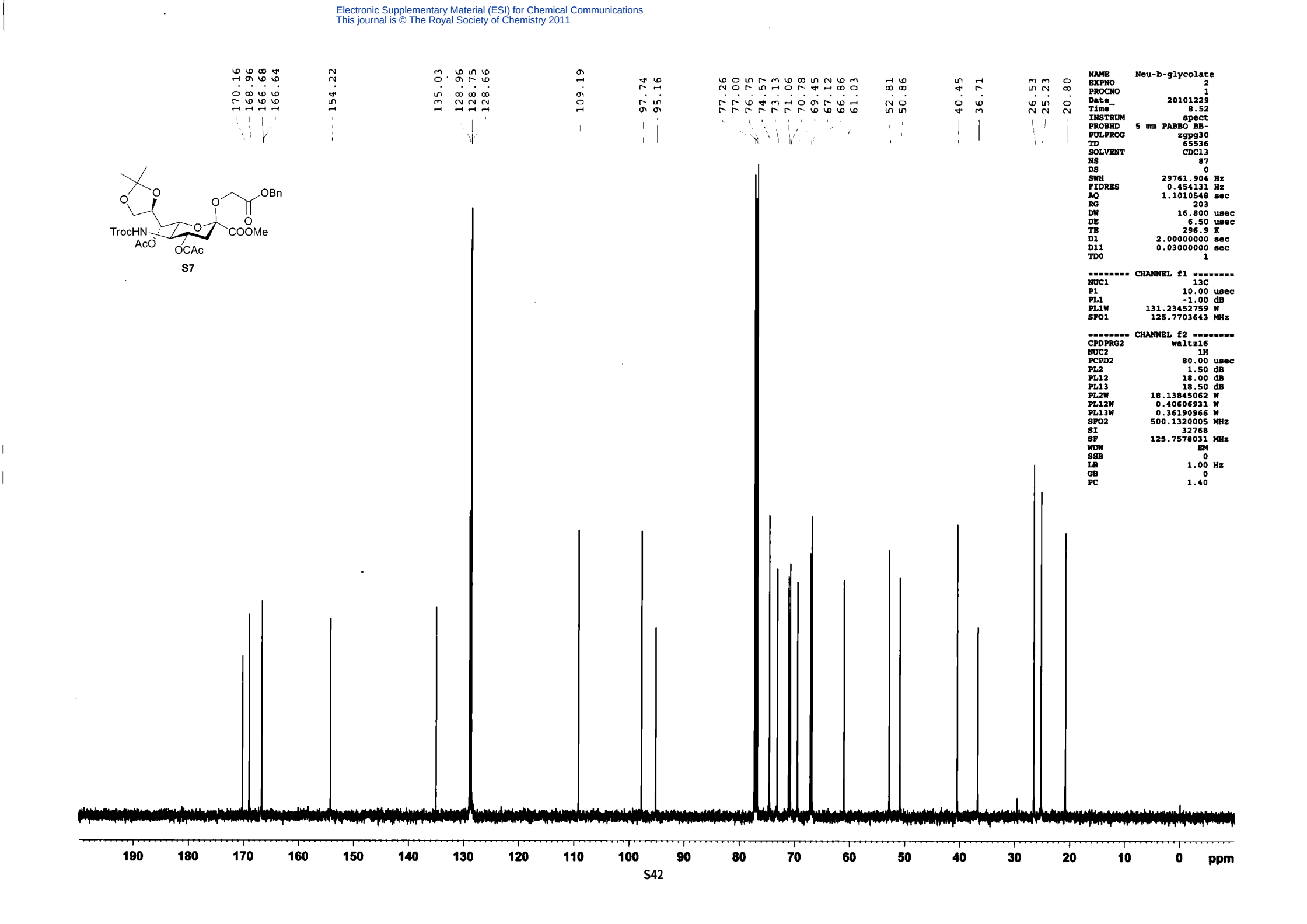


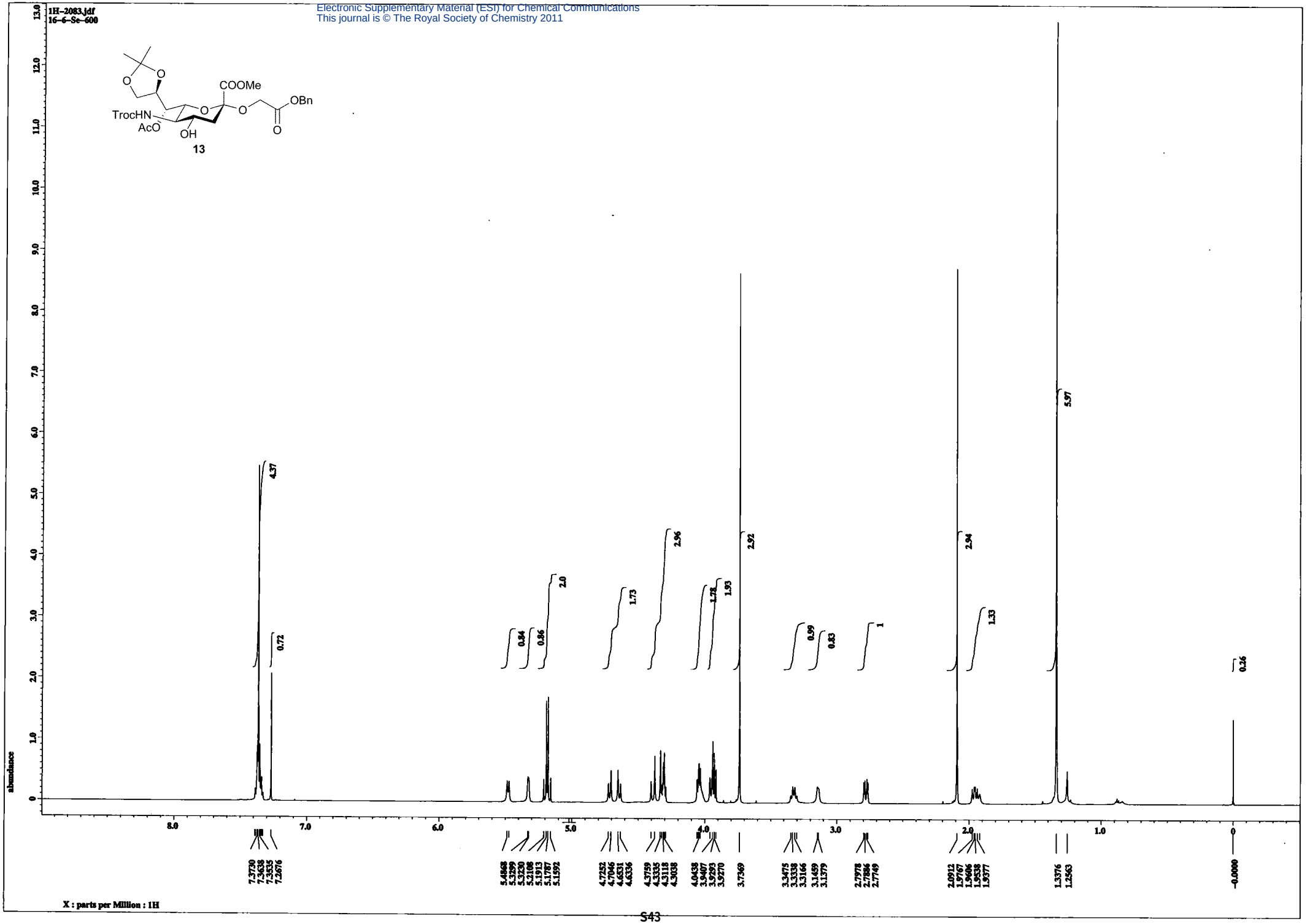


S7

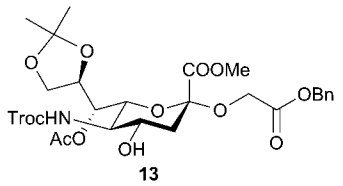
```
NAME          Neu-b-glycolate
EXPNO                       1
PROCNO                      1
Date_                20101229
Time                     8.43
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                          4
DS                          0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719923 sec
RG                         16
DW                   48.400 usec
DE                    6.50 usec
TE                   295.8 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                   12.50 usec
PL1                   1.50 dB
PL1W            18.13845062 W
SFO1            500.1330885 MHz
SI                      32768
SF              500.1300002 MHz
WDW                        EM
SSB                         0
LB                    0.30 Hz
GB                          0
PC                    1.00
```



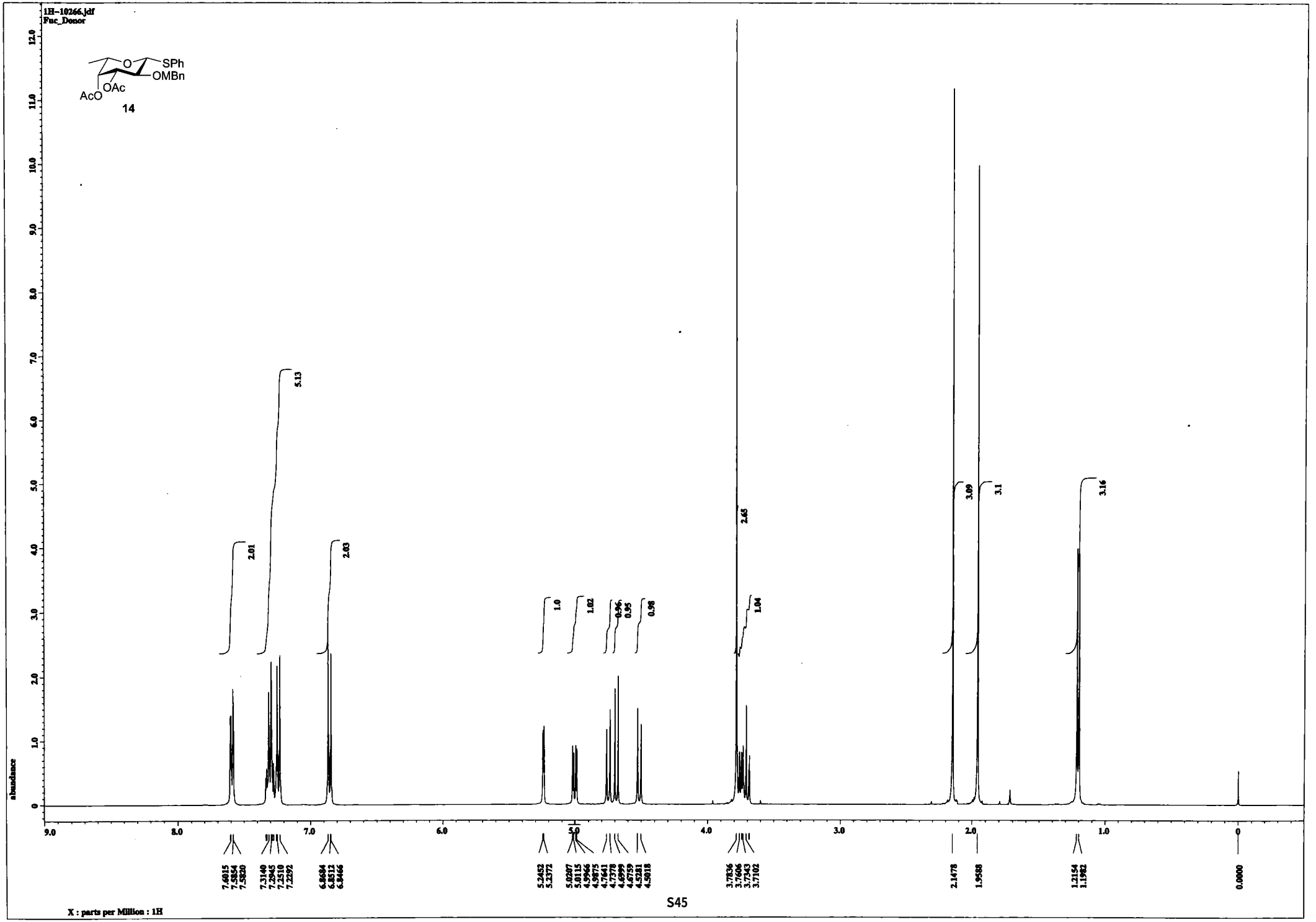


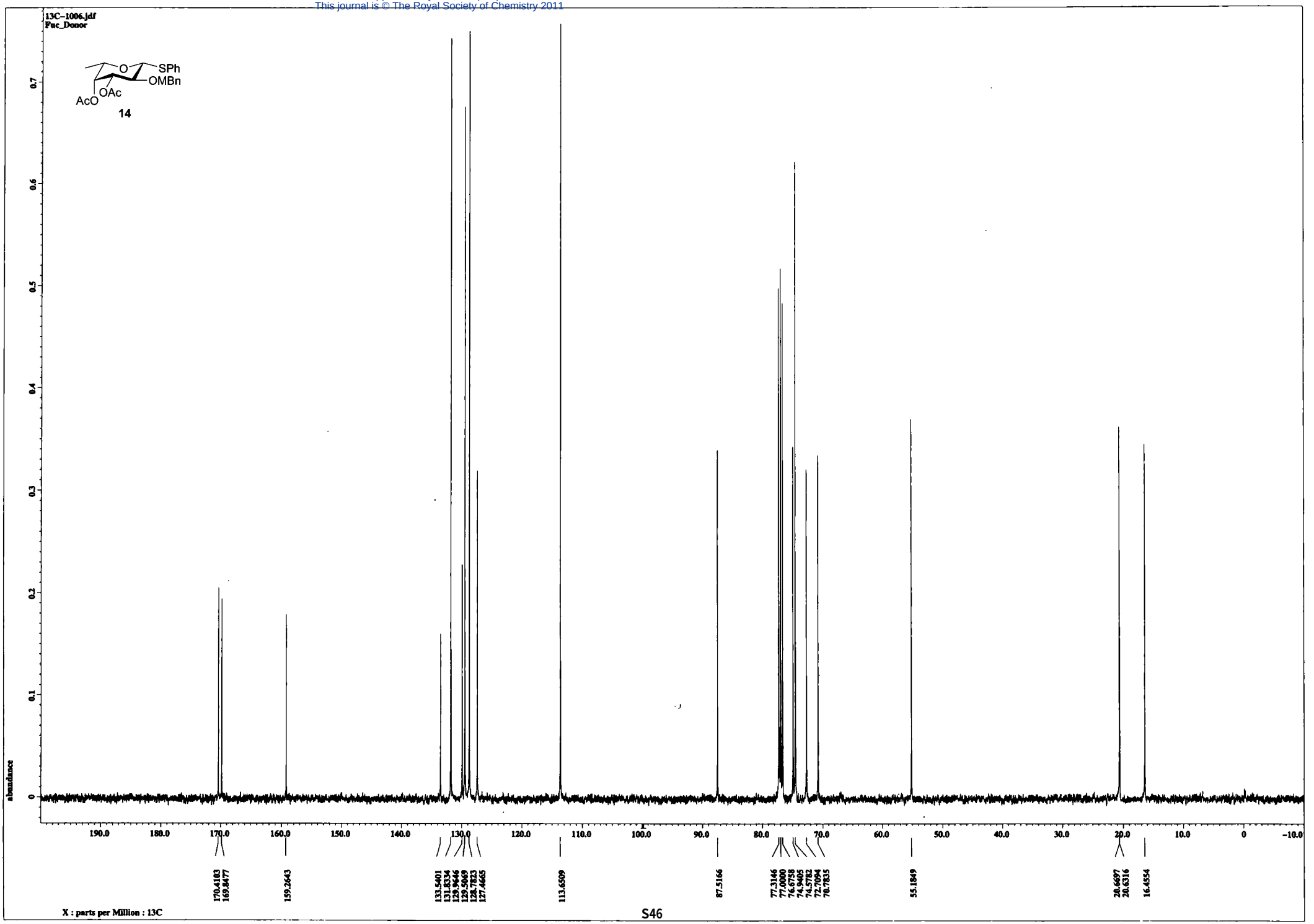


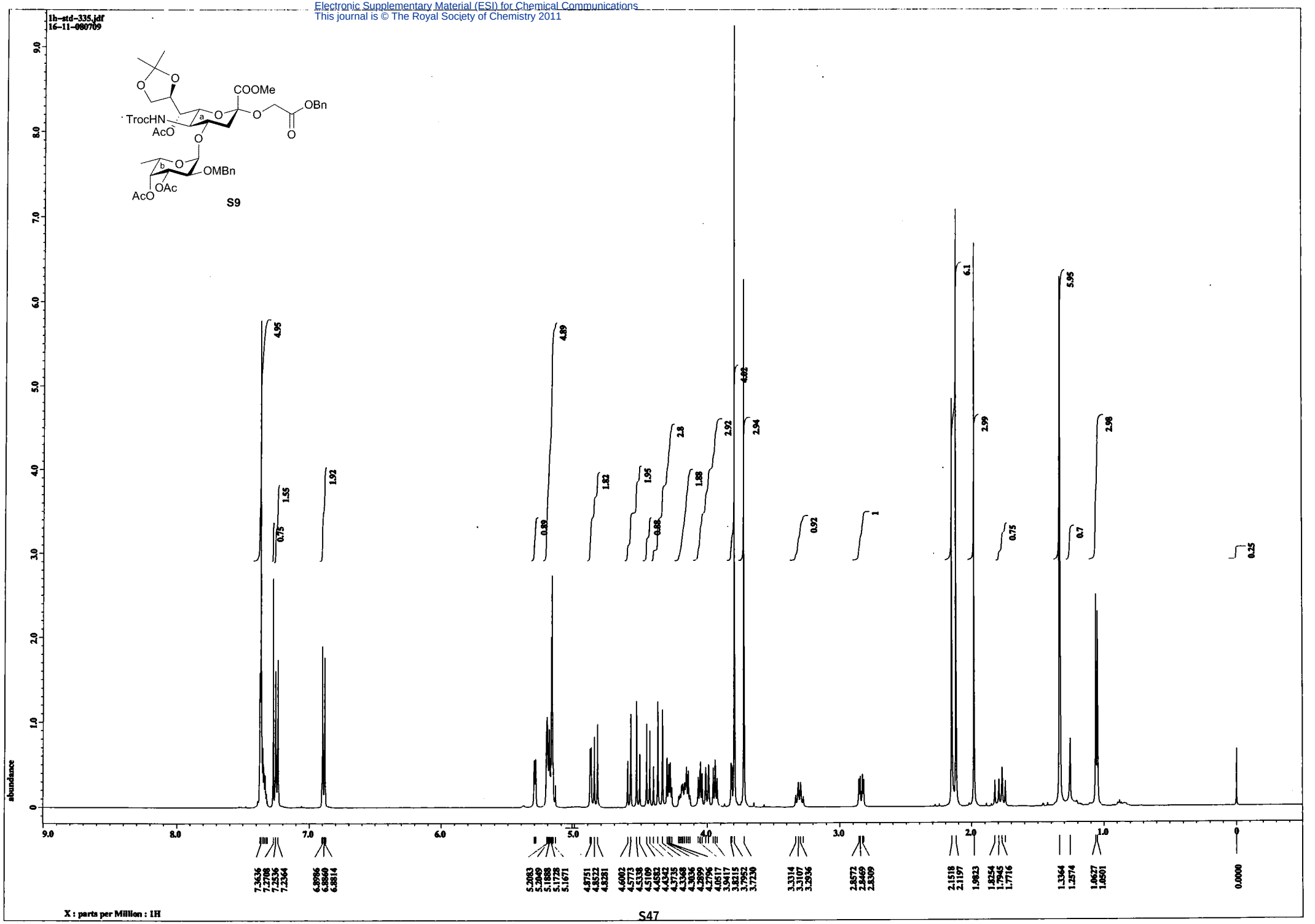
13C-261.jdf
15-24_600

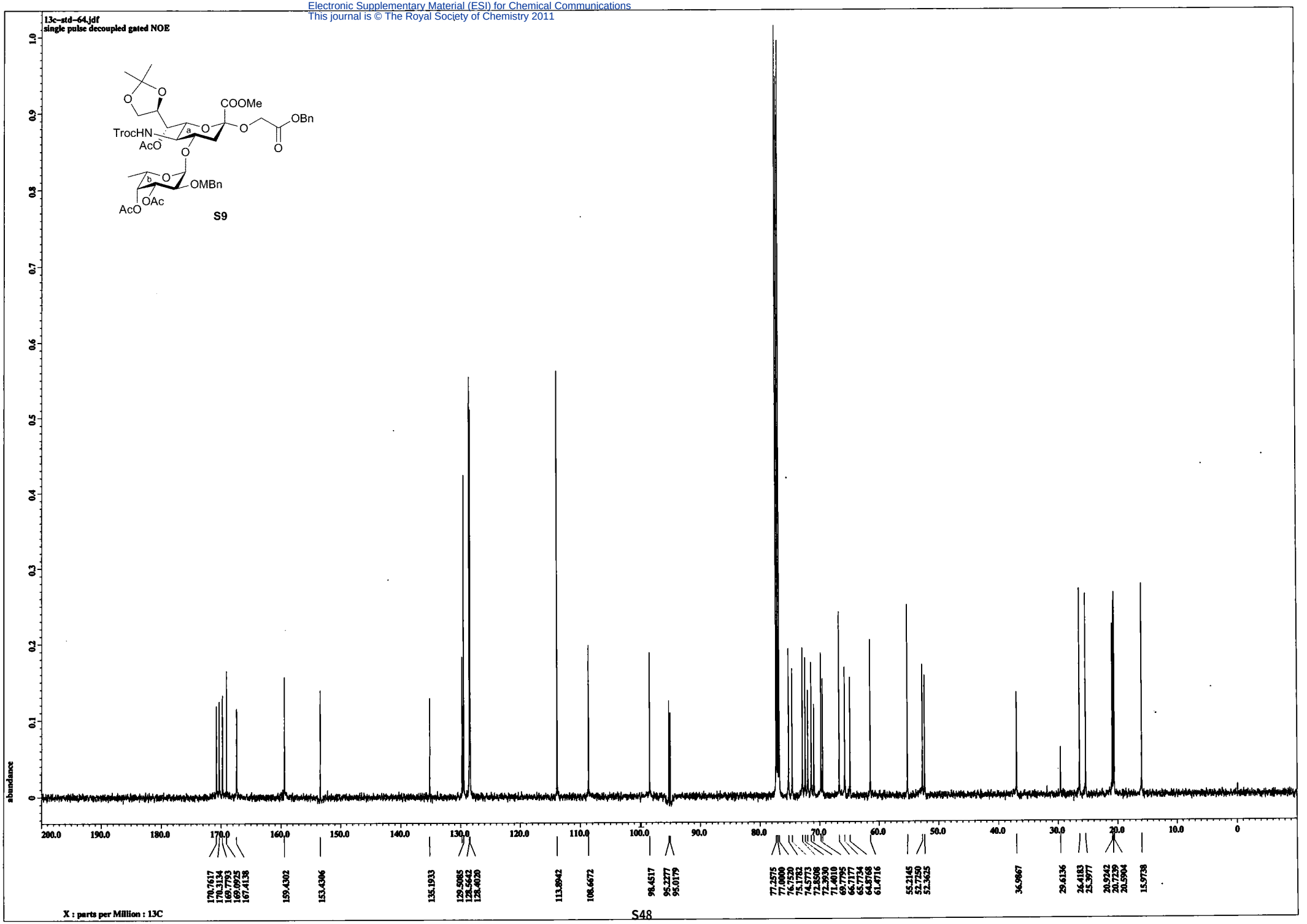


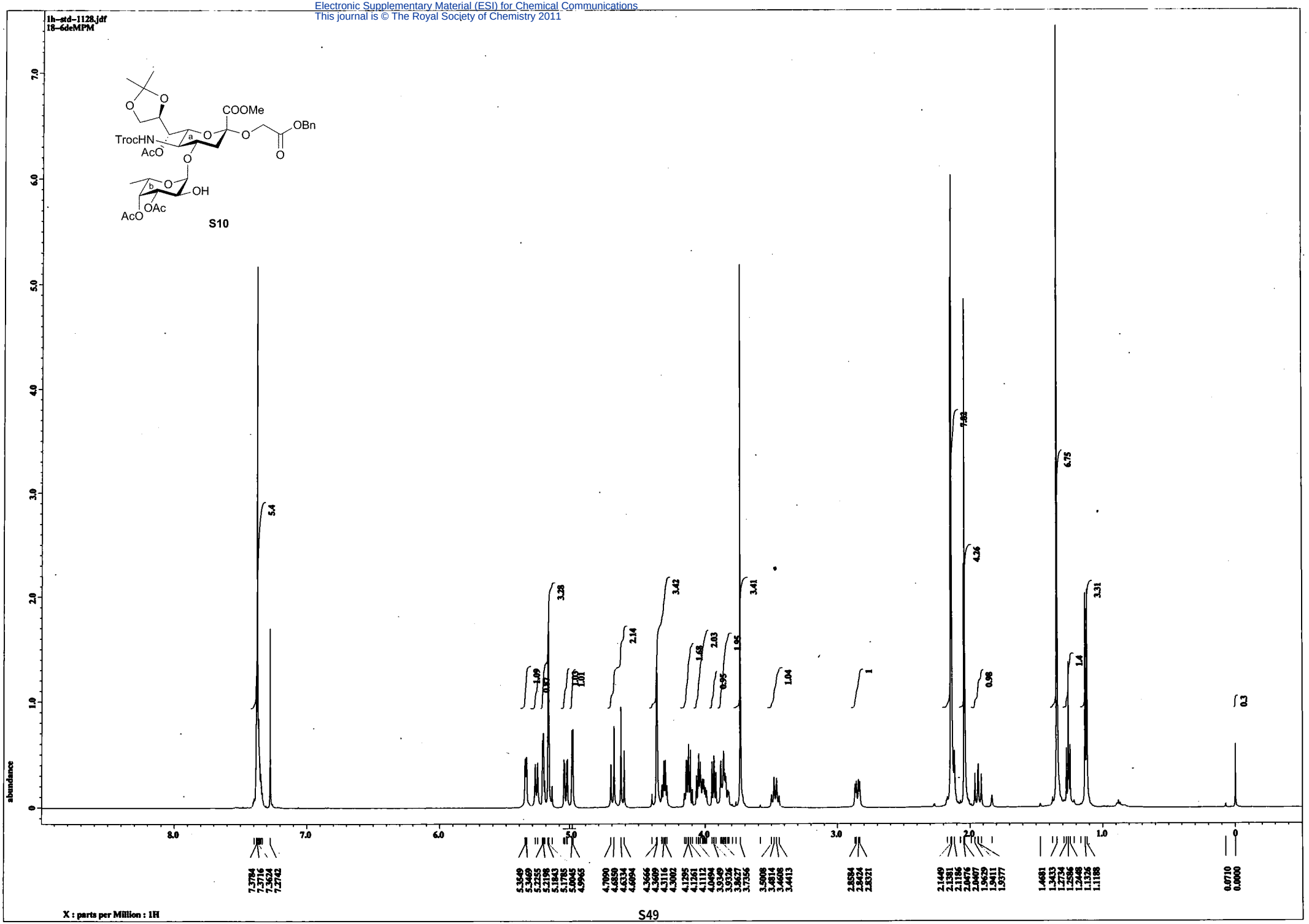
13

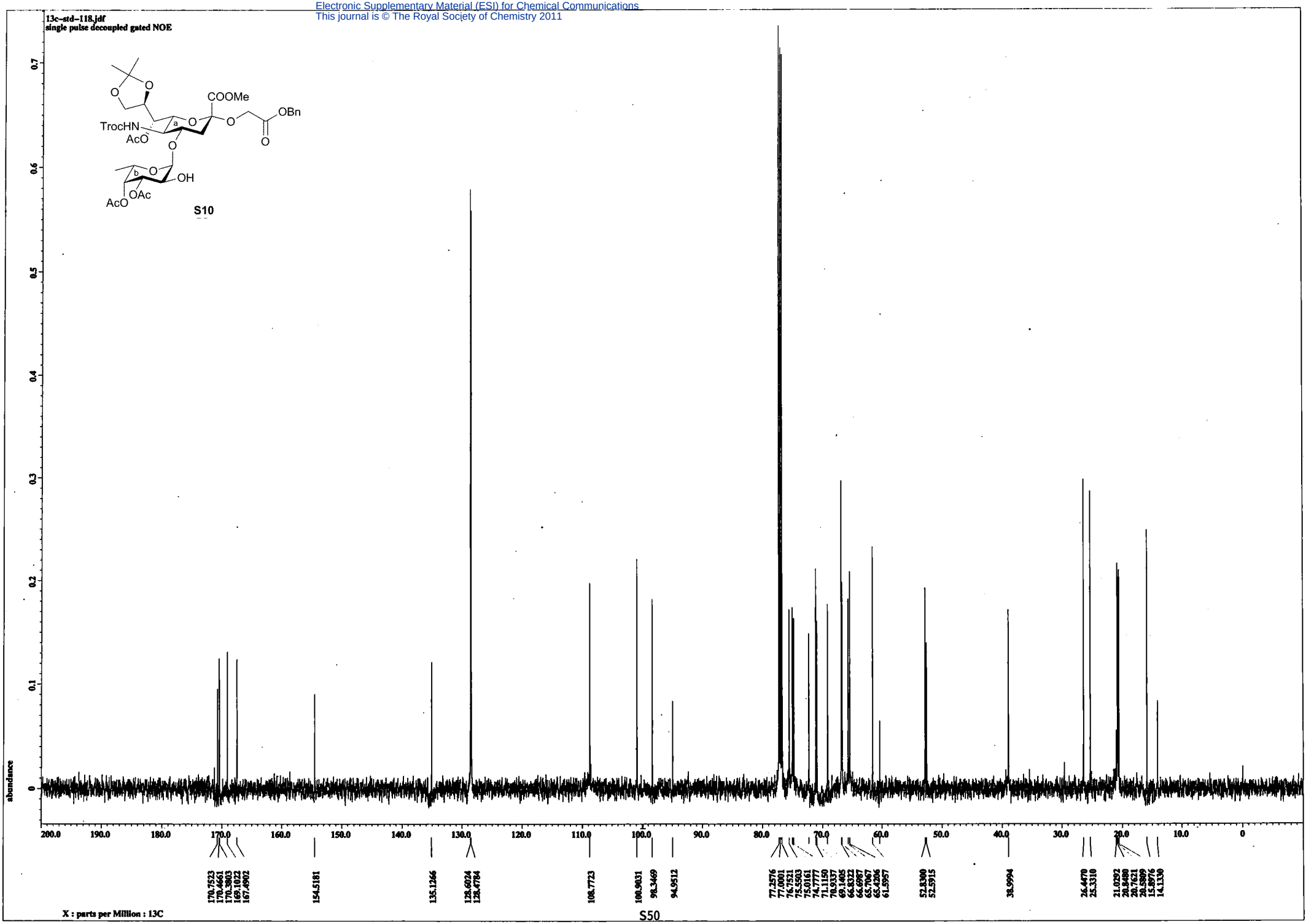

1H-10266.jdf
Fuc_Donor
O
SPh
OMBn
OAc
AcO
14
abundance
2.01
5.13
2.03
1.0
1.02
0.96
0.95
0.98
2.65
1.04
3.09
3.1
3.16
X : parts per Million : 1H

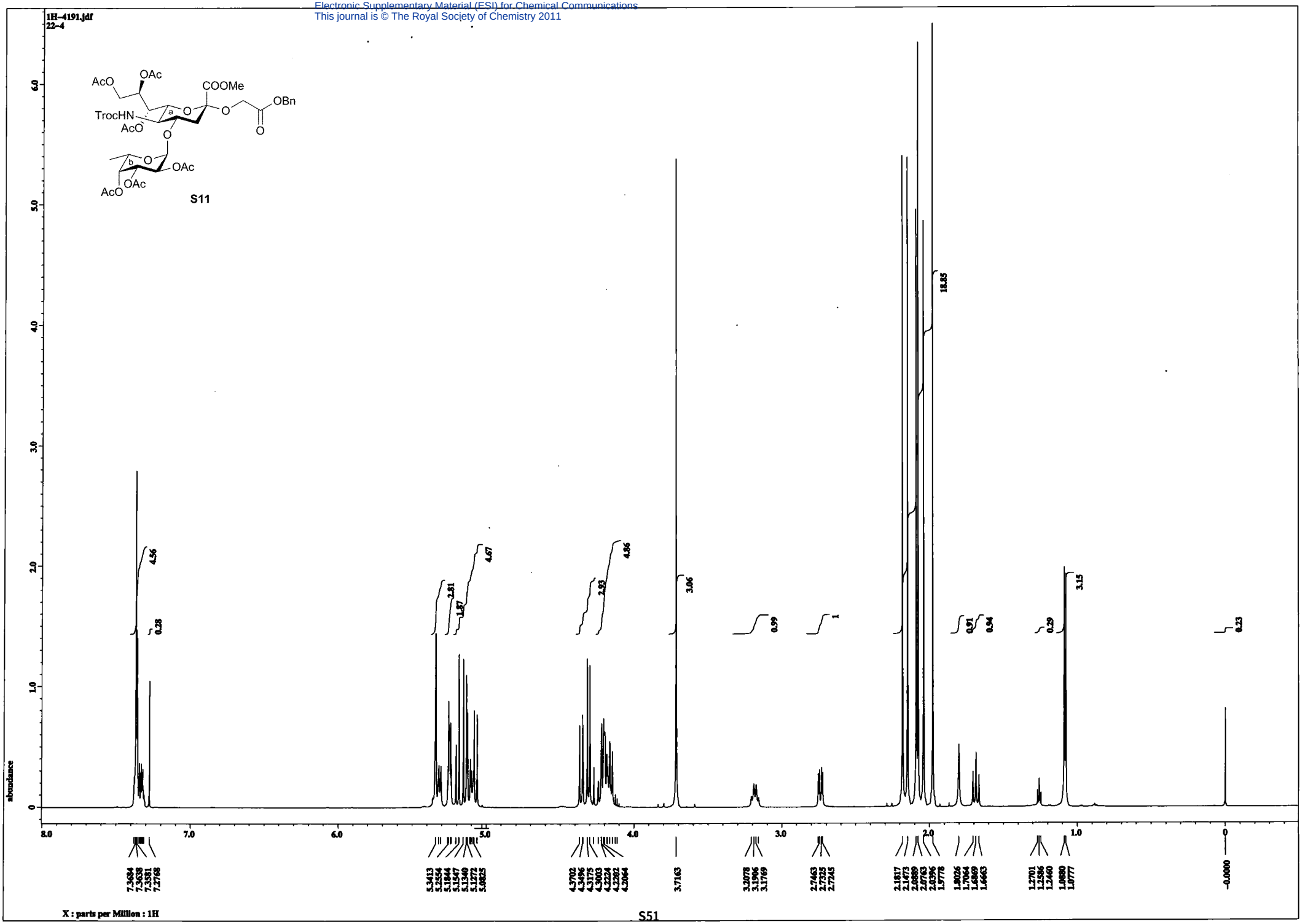


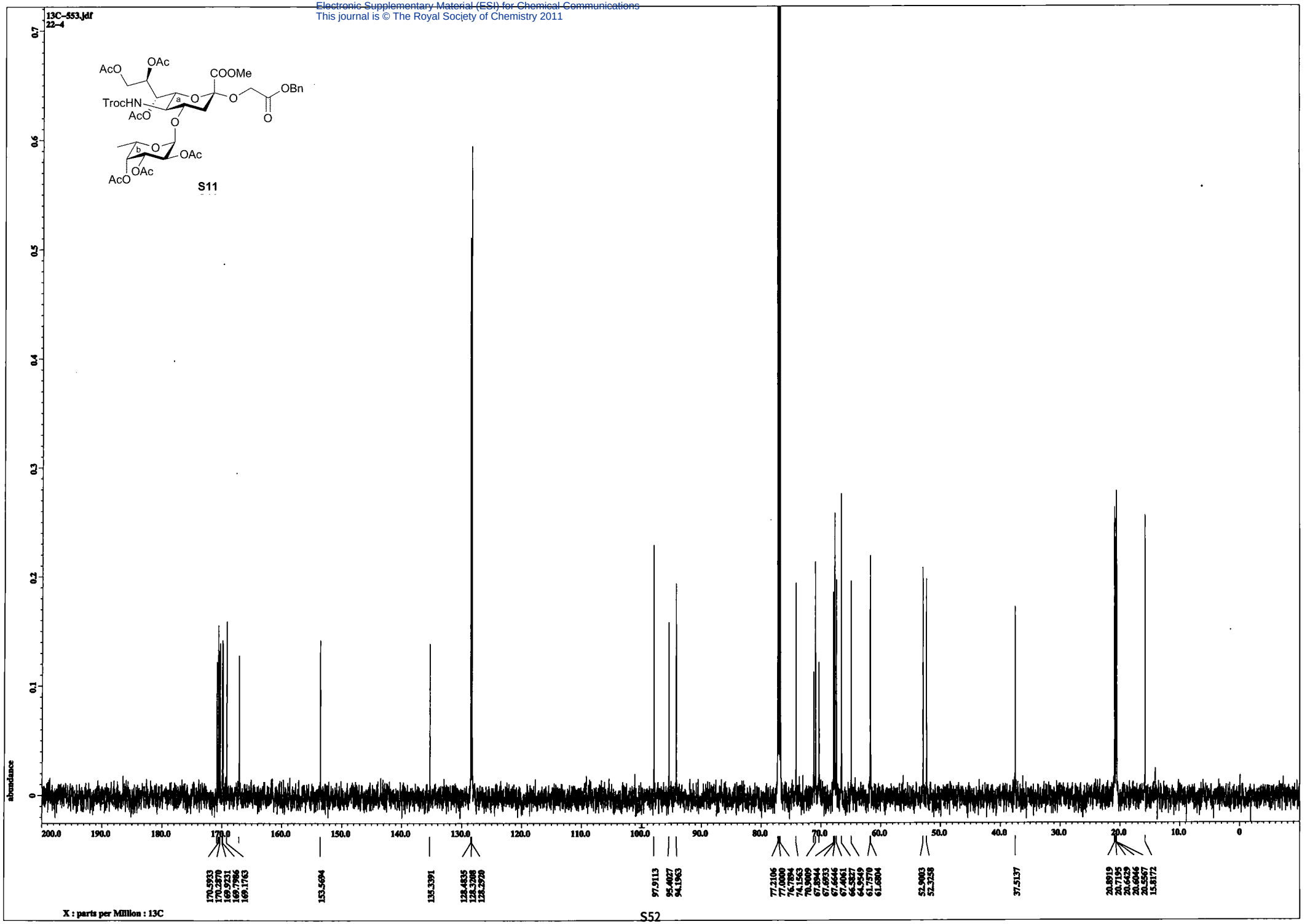


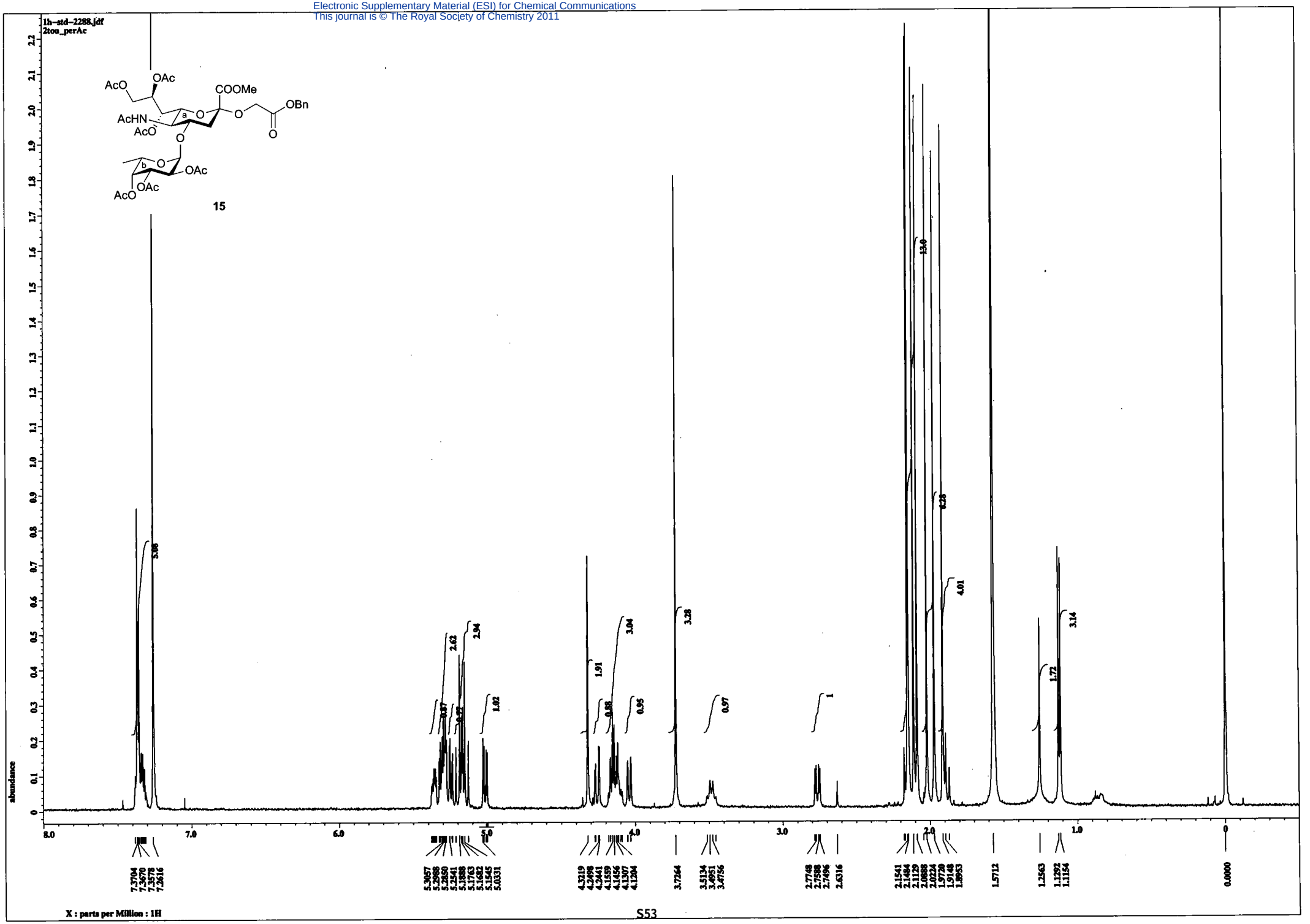


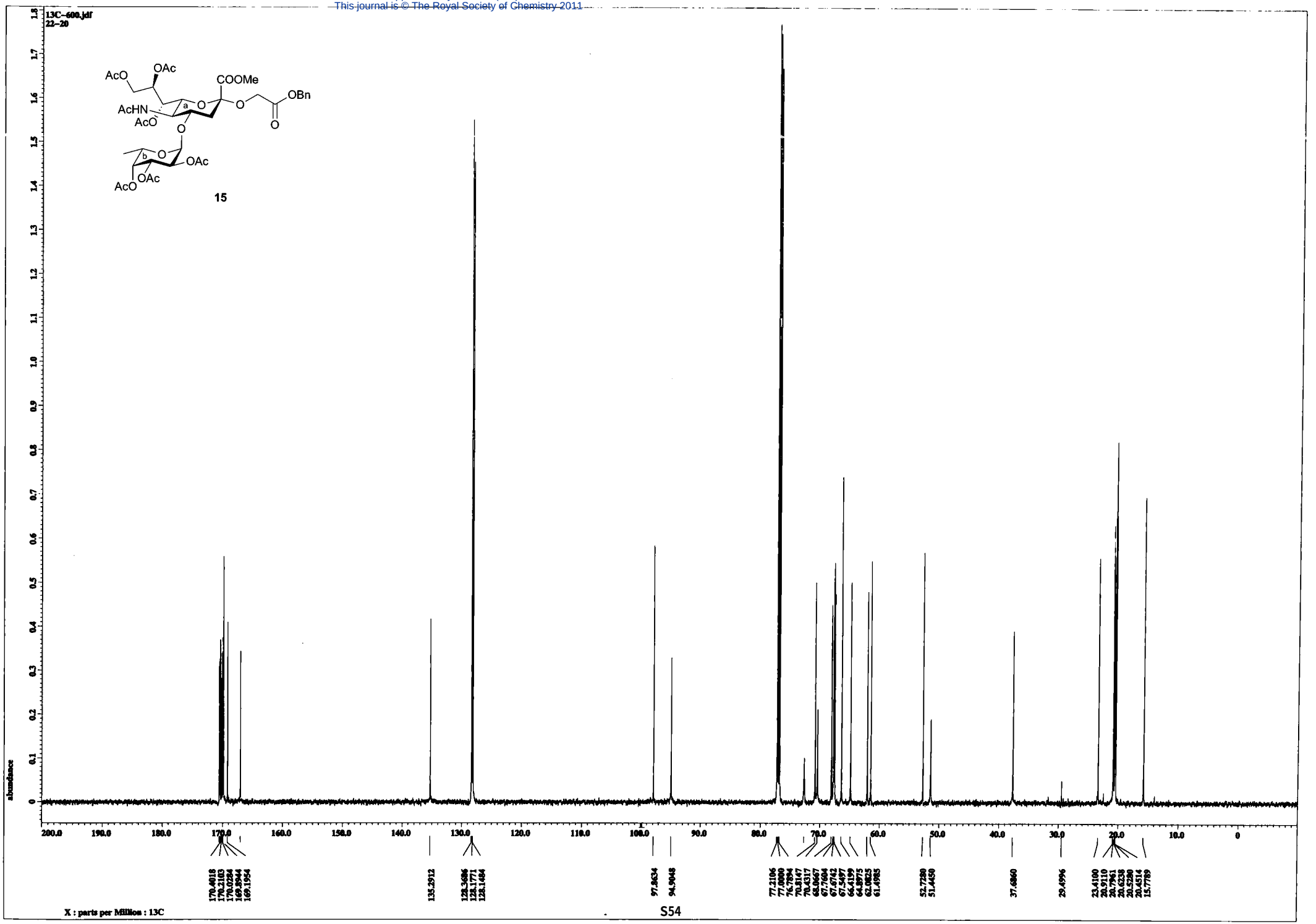


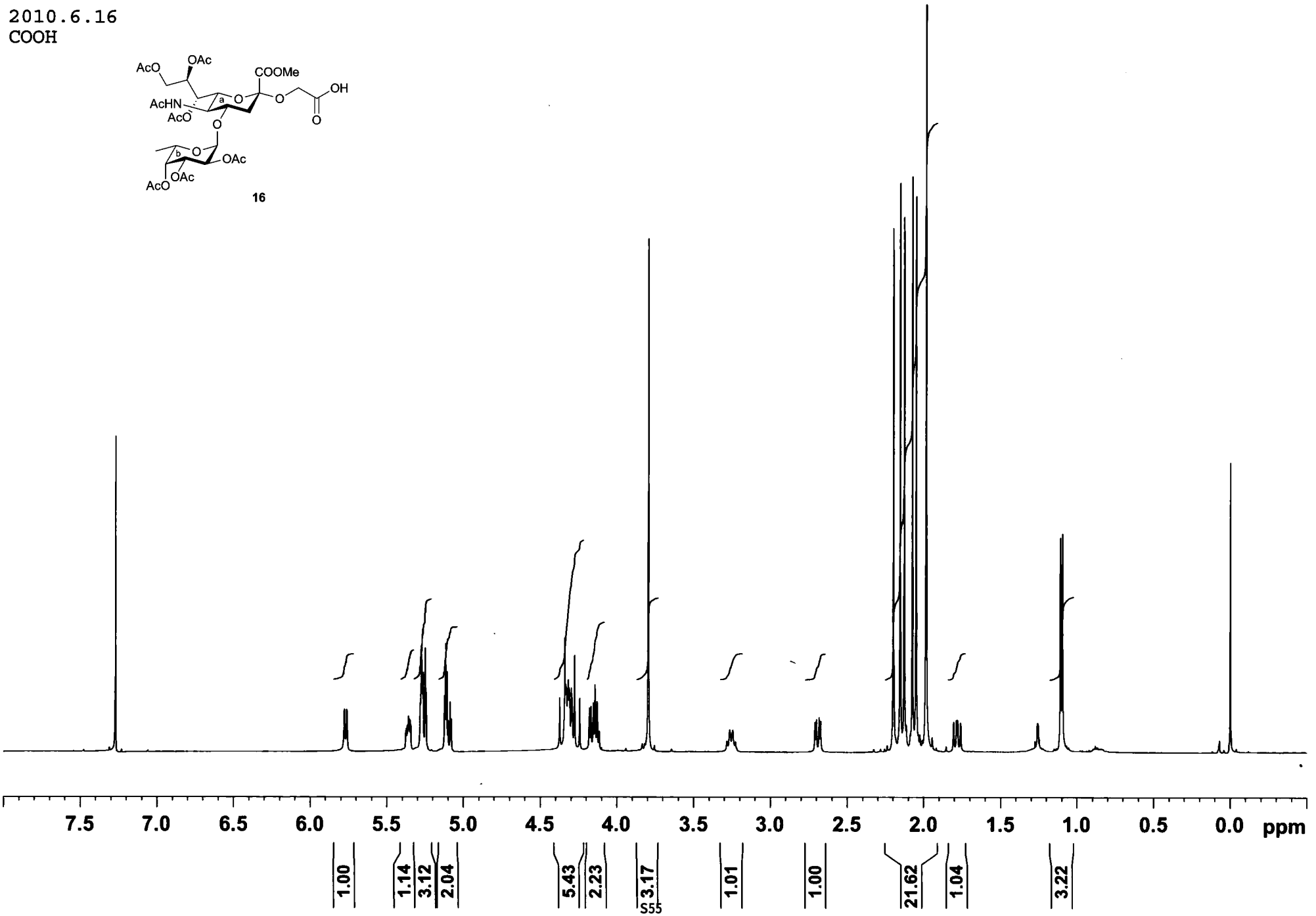


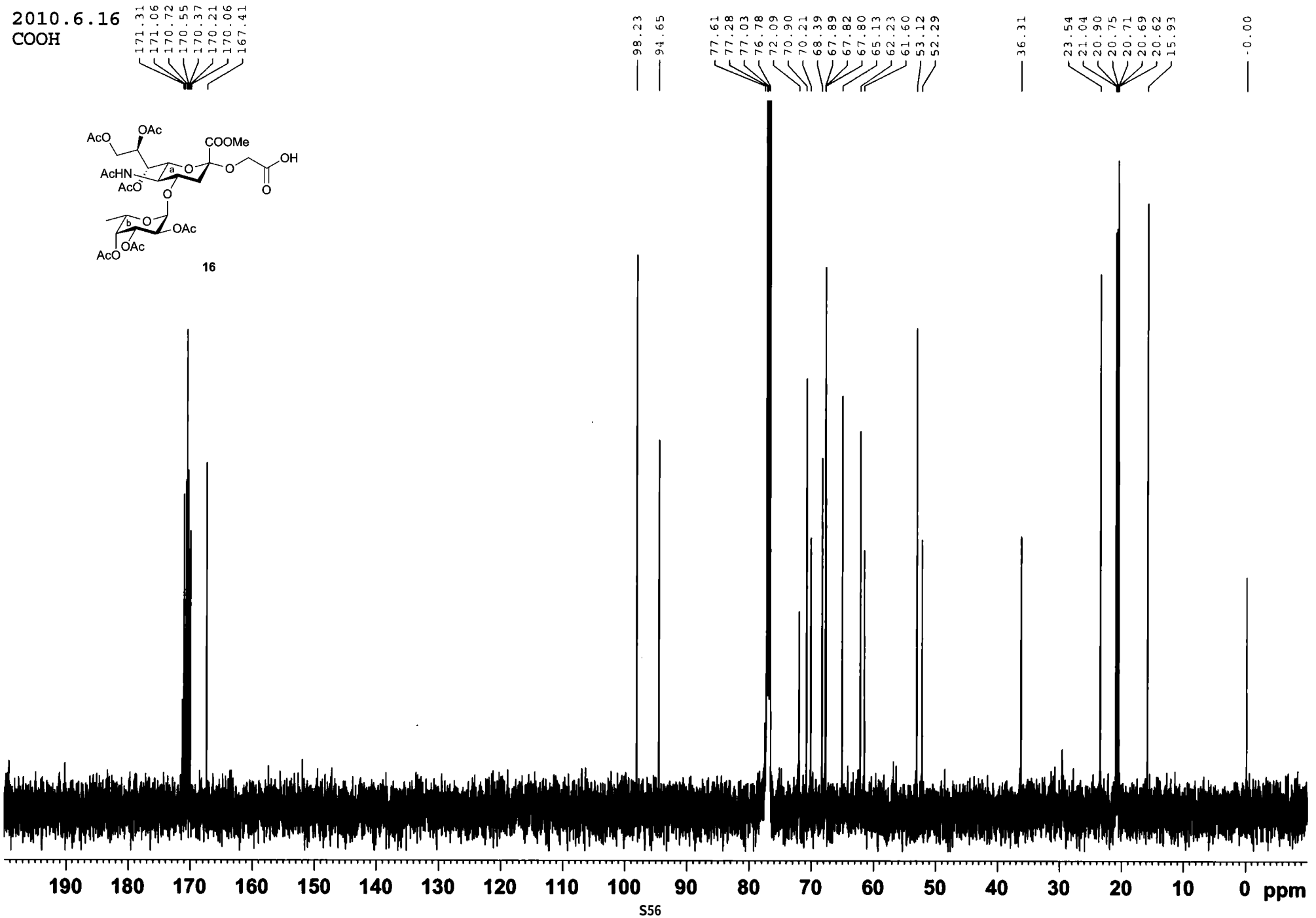


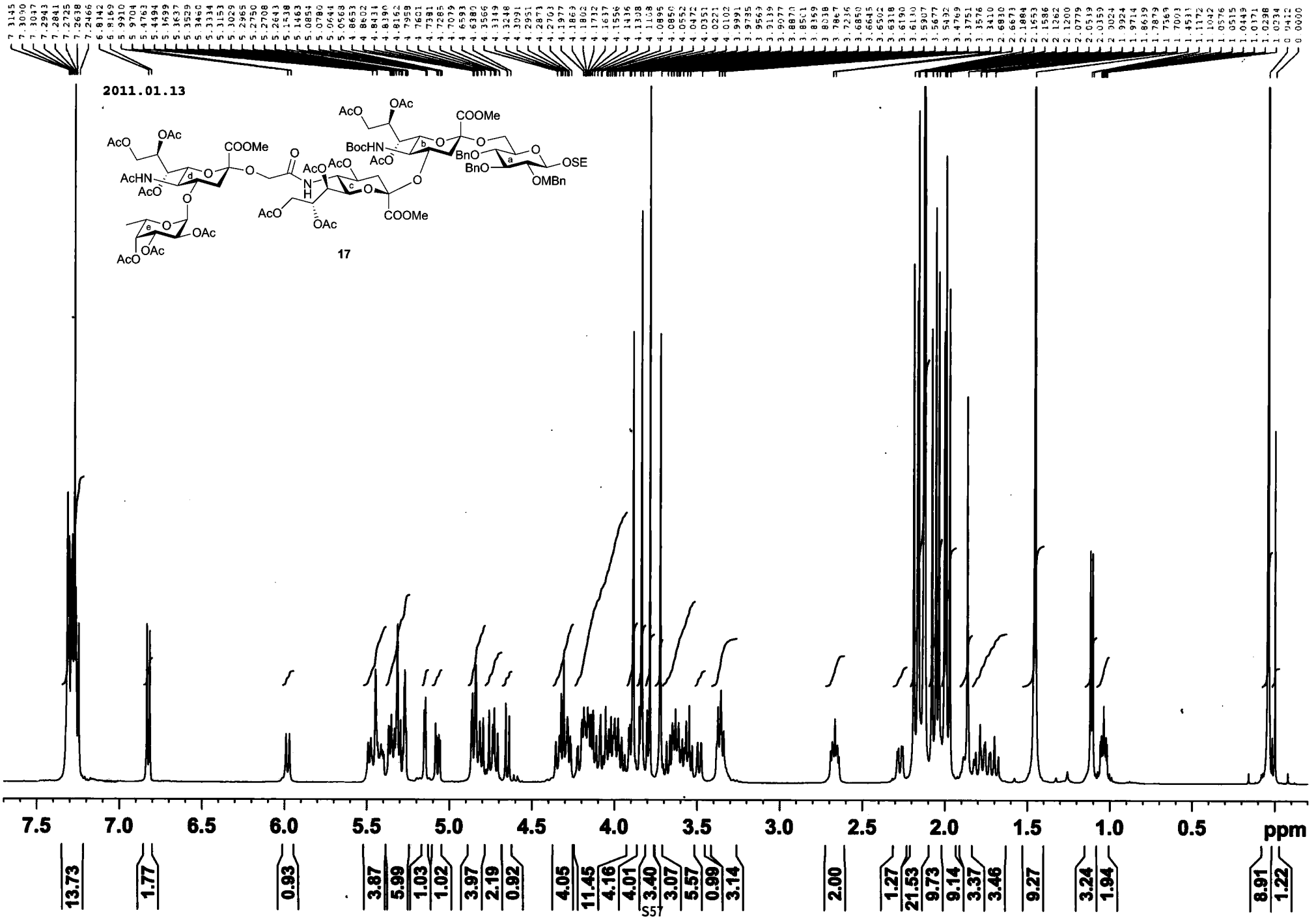






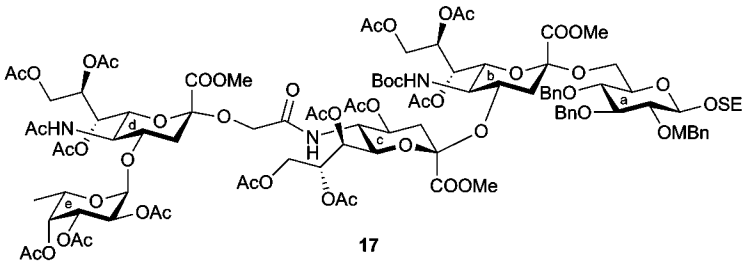

2010.6.16
COOH
AcO
OAc
COOMe
OH
AcHN
AcO
a
O
O
O
O
b
O
OAc
AcO
OAc
16
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.14
3.12
2.04
5.43
2.23
3.17
1.01
1.00
21.62
1.04
3.22



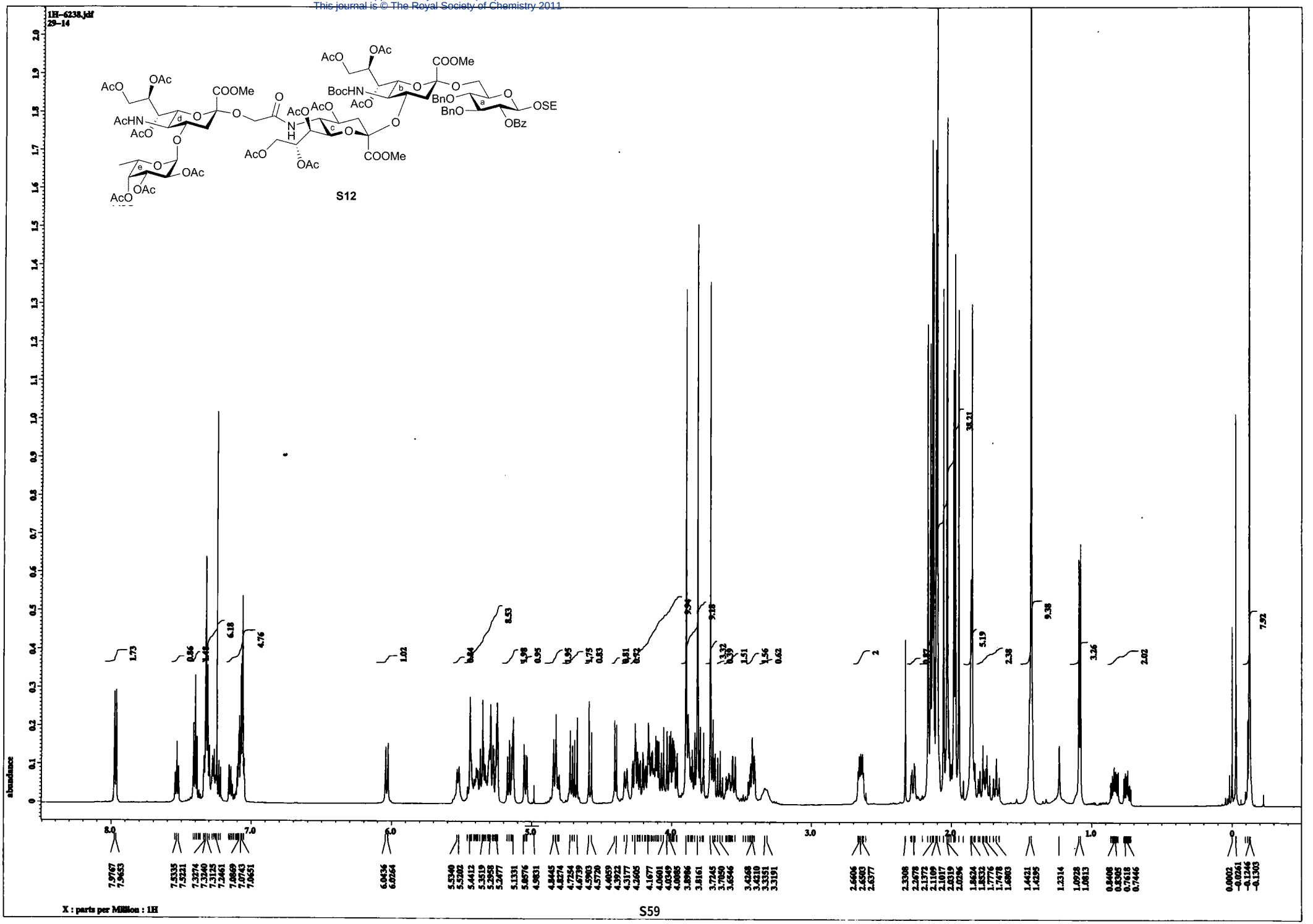

2011.01.13
17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
13.73
1.77
0.93
3.87
5.99
1.03
1.02
3.97
2.19
0.92
4.05
11.45
4.16
4.01
3.40
3.07
5.57
0.99
3.14
2.00
1.27
21.53
9.73
9.14
3.37
3.46
9.27
3.24
1.94
8.91
1.22

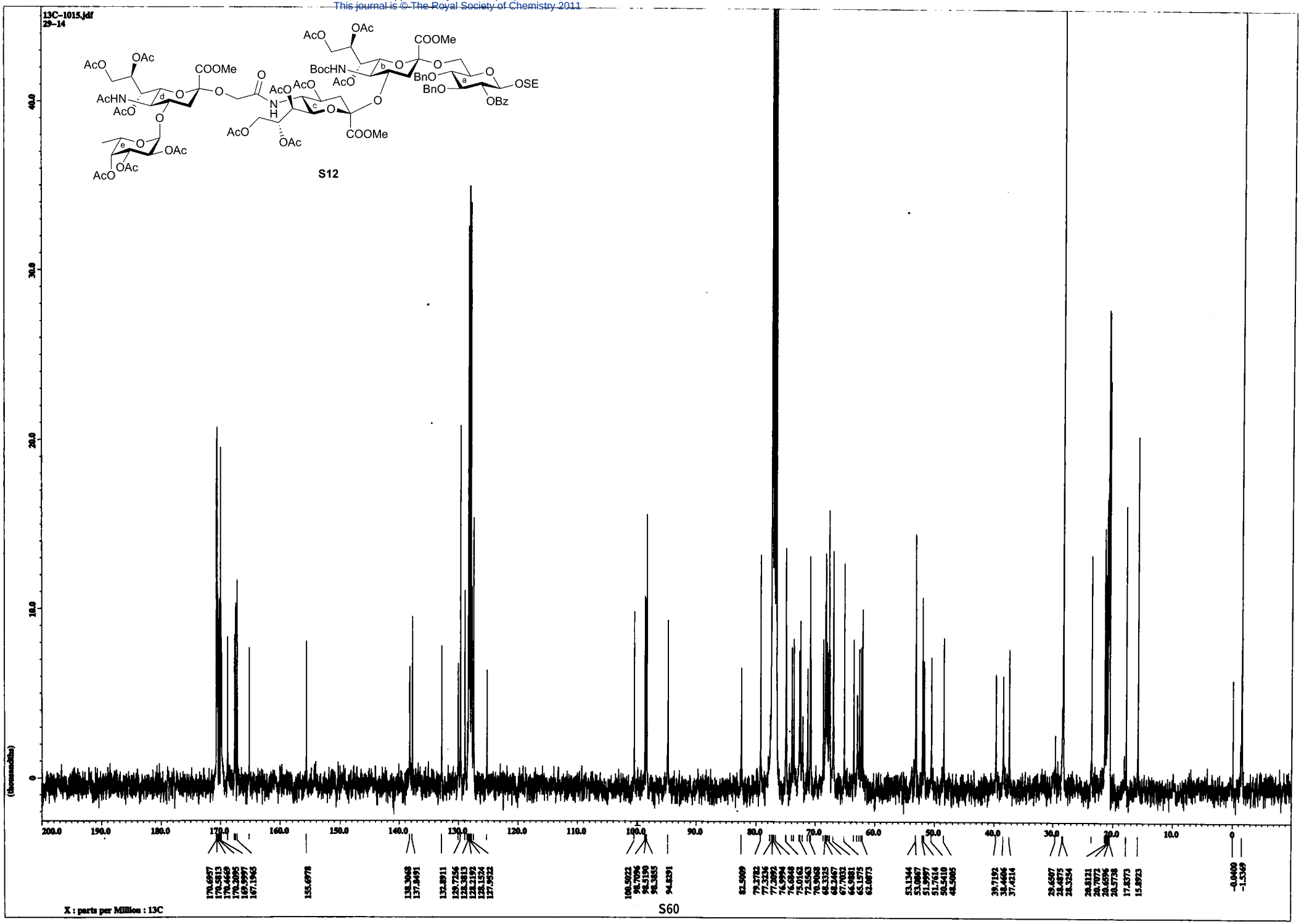
2011-01-24
Pentasaccharide

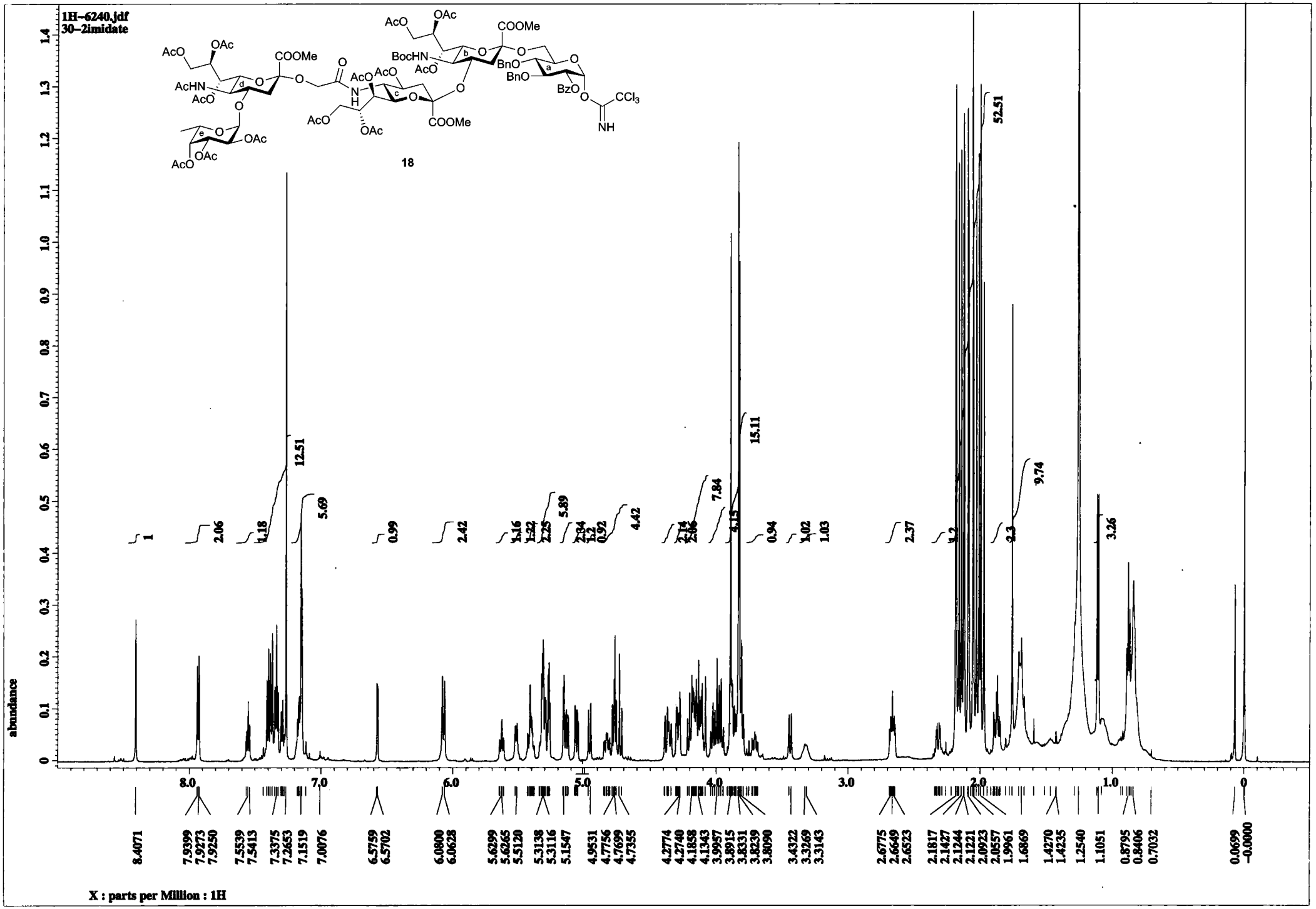
NAME	29-8
EXPNO	40
PROCNO	1
Date_	20110124
Time	11.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2000
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	203
DW	16.800 usec
DE	6.50 usec
TE	298.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.00 dB
PL1W	131.23452759 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.50 dB
PL12	18.00 dB
PL13	18.50 dB
PL2W	18.13845062 W
PL12W	0.40606931 W
PL13W	0.36190966 W
SFO2	500.1320005 MHz
SI	32768
SF	125.7577977 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

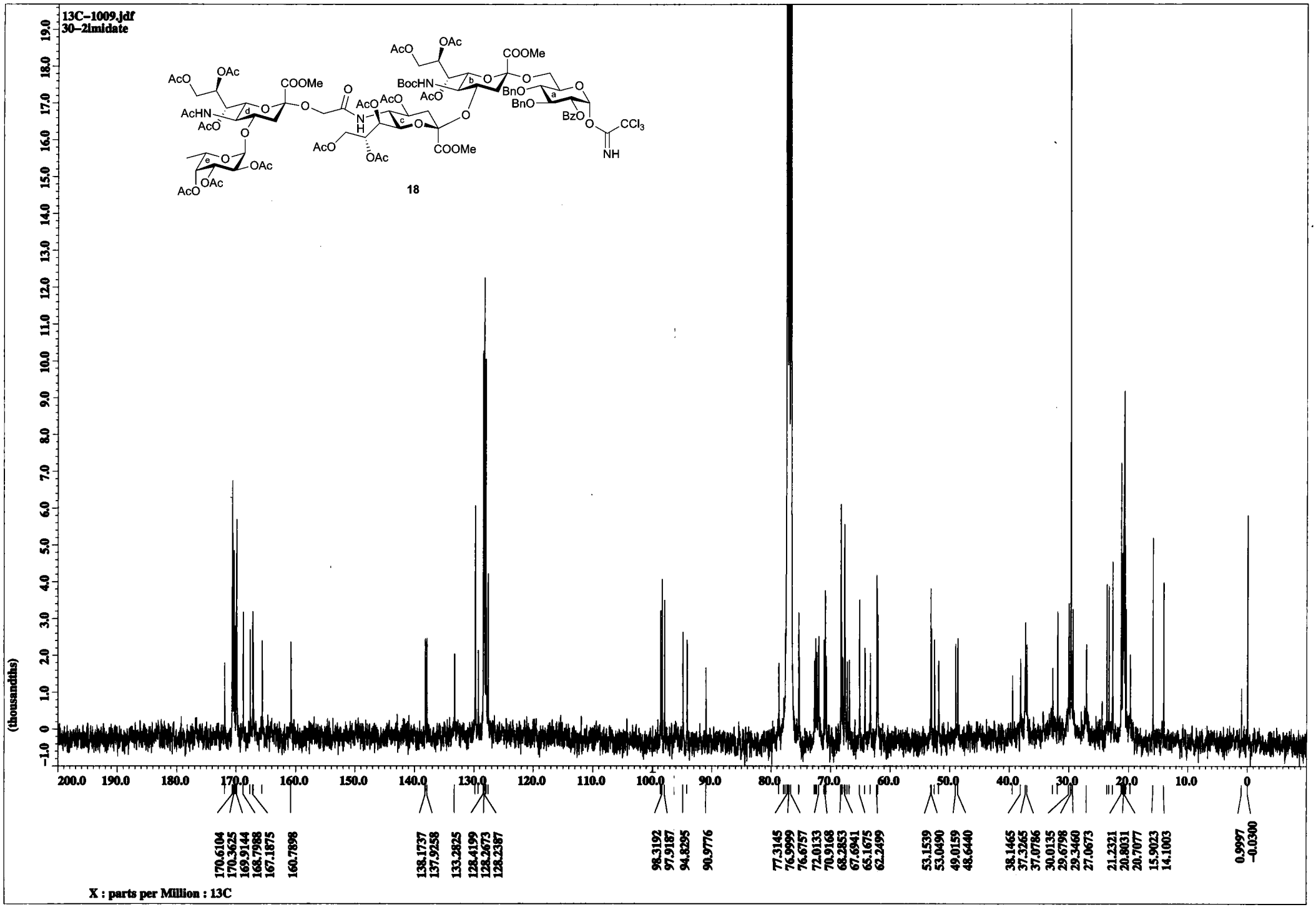


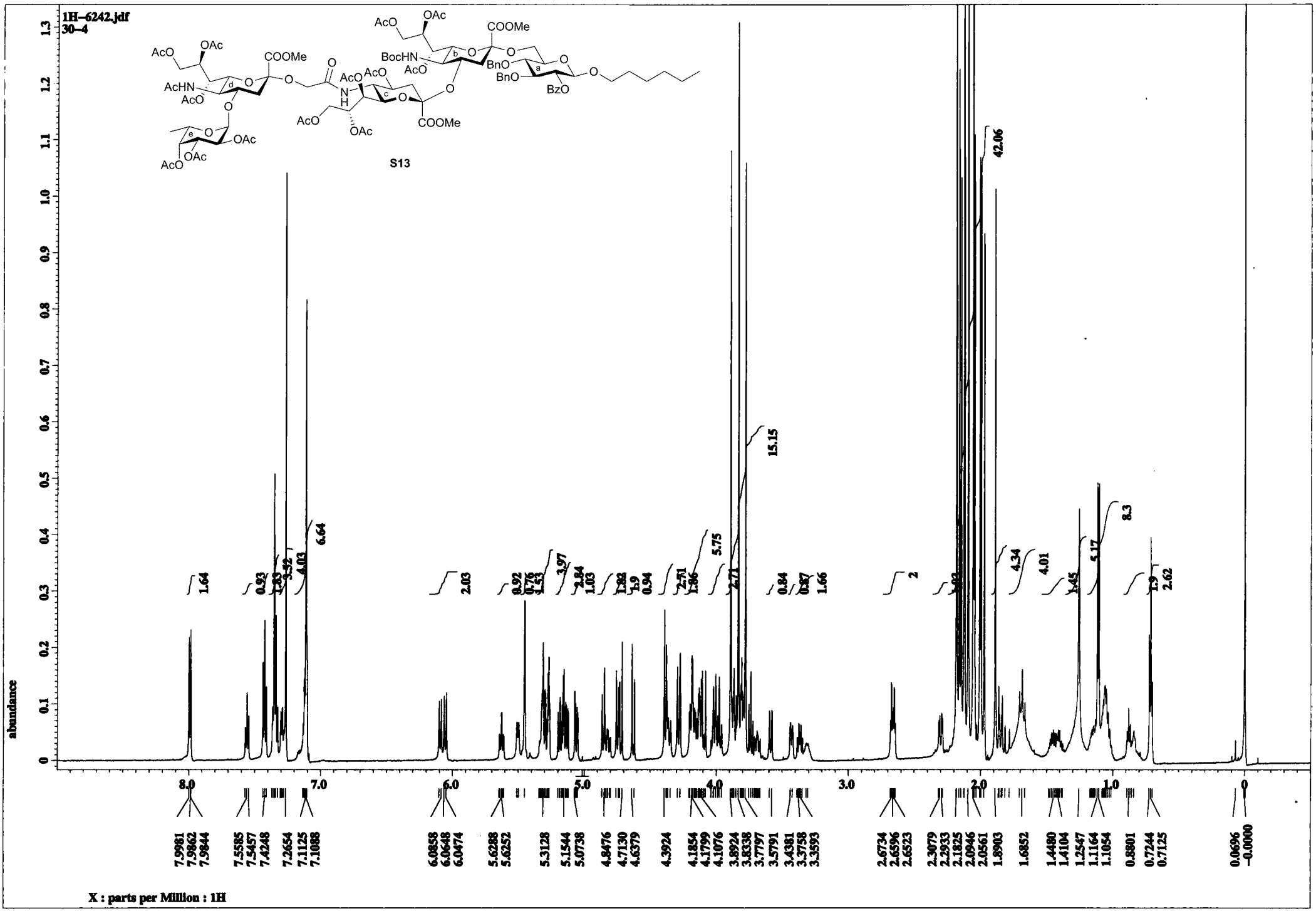
17

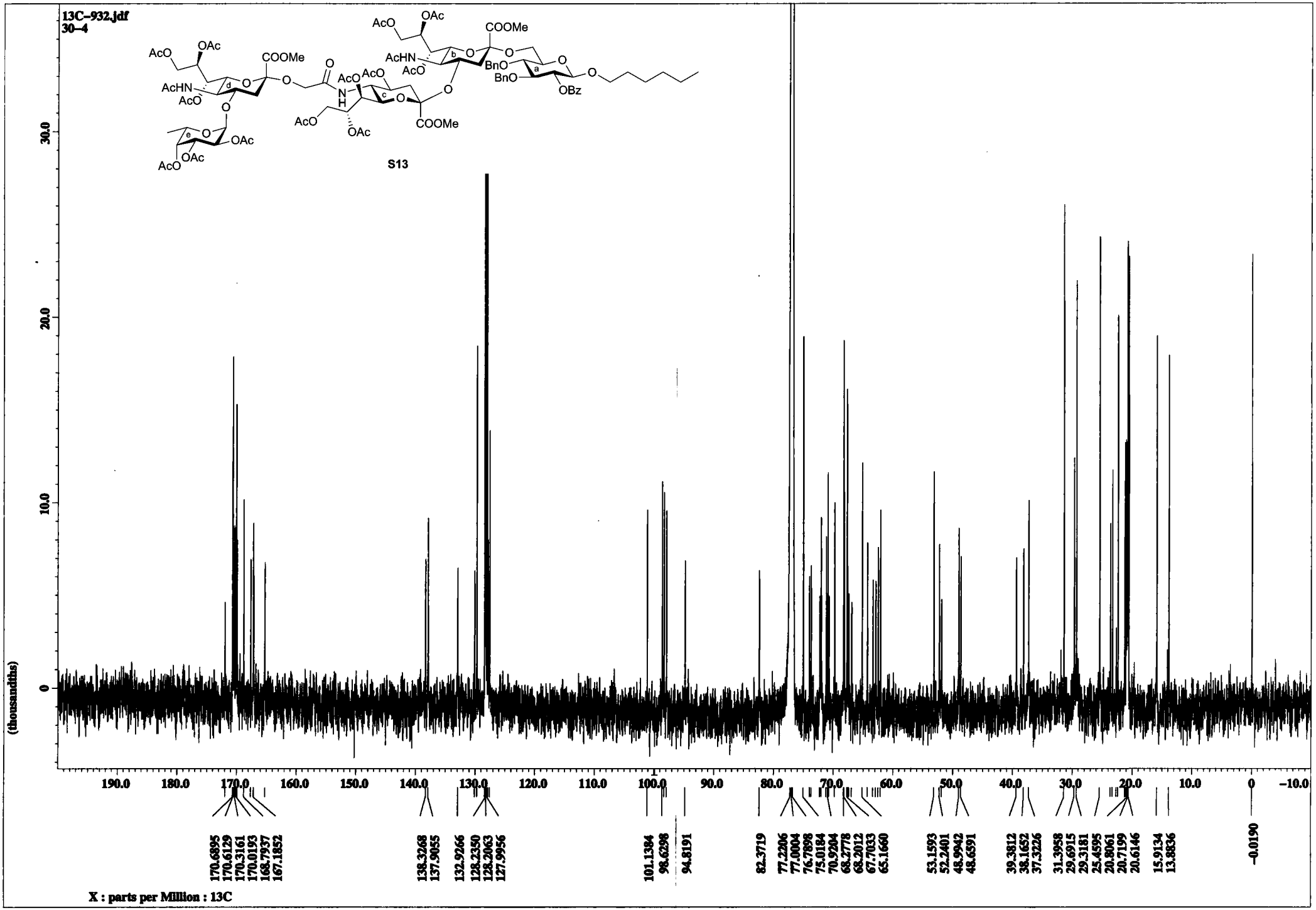


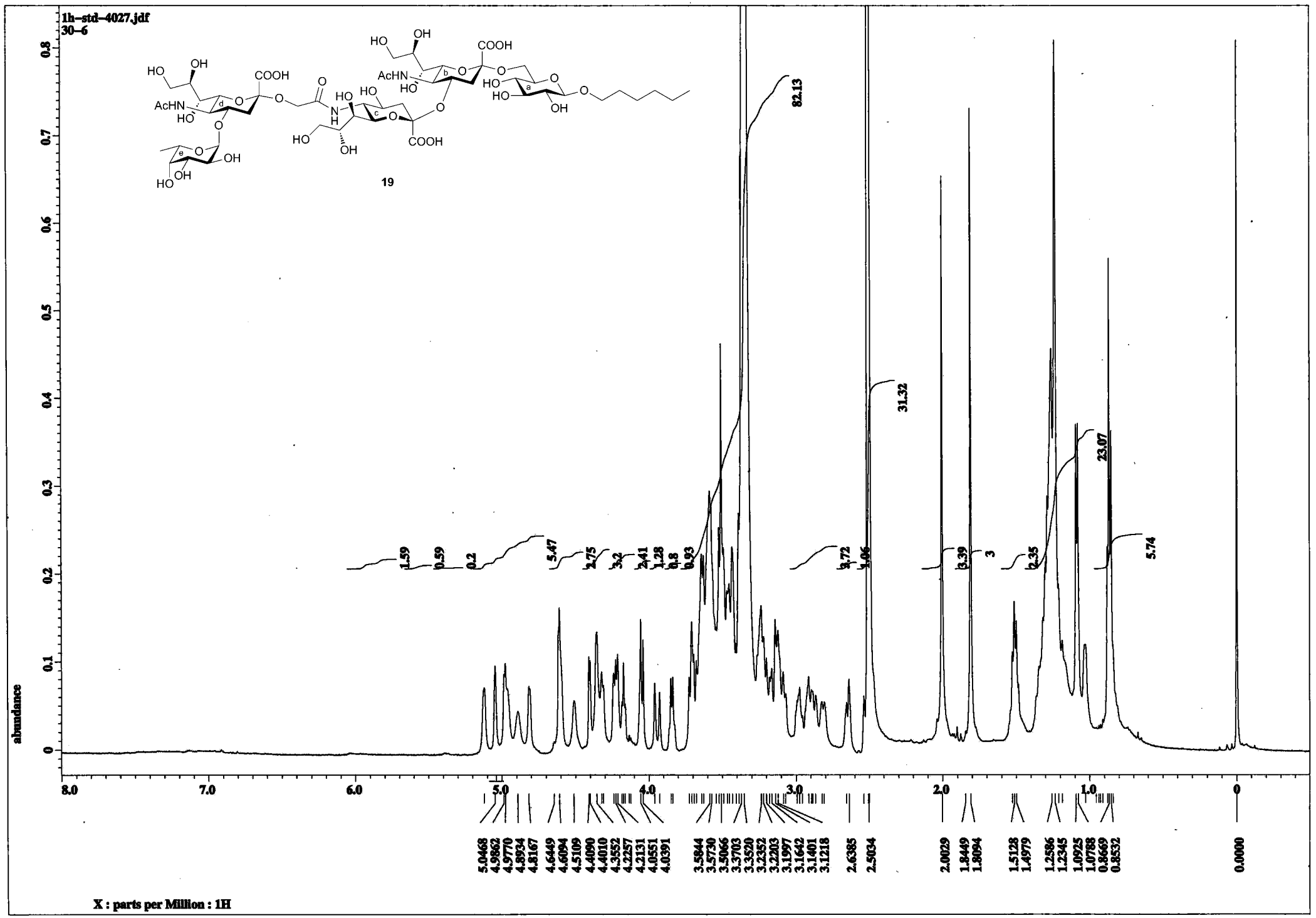

13C-1015.jdf
29-14
S12
(thousands)
X : parts per Million : 13C


1H-6240.jdf
30-2imidate
18
abundance
X : parts per Million : 1H


13C-1009.jdf
30-2imidate
18
(thousandths)
X : parts per Million : 13C
170.6104
170.3625
169.9144
168.7988
167.1875
160.7898
138.1737
137.9258
133.2825
128.4199
128.2673
128.2387
98.3192
97.9187
94.8295
90.9776
77.3145
76.9999
76.6757
72.0133
70.9168
68.2853
67.6941
65.1675
62.2499
53.1539
53.0490
49.0159
48.6440
38.1465
37.3265
37.0786
30.0135
29.6798
29.3460
27.0673
21.2321
20.8031
20.7077
15.9023
14.1003
0.9997
-0.0300




13C-932.jdf
30-4
S13
(thousandths)
30.0
20.0
10.0
0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
170.6895
170.6129
170.3161
170.0193
168.7937
167.1852
138.3268
137.9055
132.9266
128.2350
128.2063
127.9956
101.1384
98.6298
94.8191
82.3719
77.2206
77.0004
76.7898
75.0184
70.9204
68.2778
68.2012
67.7033
65.1660
53.1593
52.2401
48.9942
48.6591
39.3812
38.1652
37.3226
31.3958
29.6915
29.3181
25.4595
20.8061
20.7199
20.6146
15.9134
13.8836
-0.0190
X : parts per Million : 13C


1h-std-4027.jdf
30-6
19
abundance
X : parts per Million : 1H
82.13
31.32
23.07
5.74
1.59
0.59
0.2
5.47
2.75
3.2
2.41
1.28
0.8
0.93
2.72
1.06
3.39
3
2.35
5.0468
4.9862
4.9770
4.8934
4.8167
4.6449
4.6094
4.5109
4.4090
4.4010
4.3552
4.2257
4.2131
4.0551
4.0391
3.5844
3.5730
3.5066
3.3703
3.3520
3.2352
3.2203
3.1997
3.1642
3.1401
3.1218
2.6385
2.5034
2.0029
1.8449
1.8094
1.5128
1.4979
1.2586
1.2345
1.0925
1.0788
0.8669
0.8532
0.0000