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Supporting Information

Automated Solid-Phase Synthesis of Protected Oligosaccharides Containing β-Mannosidic Linkages

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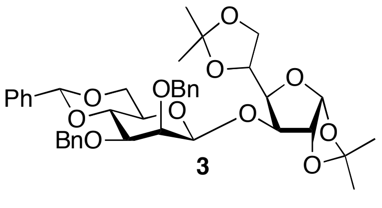
Supporting Information

General procedures:

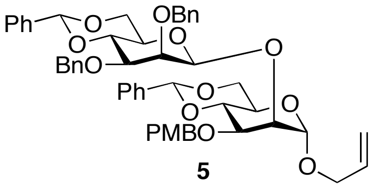
All chemicals used were reagent grade and used as supplied. Tf_2O was purified by drying over P_2O_5 for 4 hours, followed by distillation. All reactions were performed in oven-dried glassware under an inert argon atmosphere unless noted otherwise. Reagent grade dichloromethane (DCM), was passed through activated neutral alumina column prior to use. Triethylamine was distilled over CaH_2 and stored over KOH. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25mm). Compounds were visualized by UV irradiation or dipping the plate in a cerium sulfate-ammonium molybdate solution. Flash column chromatography was carried out using forced flow of the indicated solvent on Fluka Kieselgel 60 (230-400 mesh). LCMS analysis was performed on an Agilent 1100 Series LC/MSD instrument on a Waters Symmetry® C18 5μm column (3.9 x 150 mm), using solvent systems A (20% isopropanol and 0.1% TFA in H_2O) and B (20% isopropanol and 0.1% TFA in acetonitrile), at a flowrate of 1 mL/min.^1H and ^{13}C and NMR spectra were recorded on a Varian Mercury 300 (300 MHz and 75 MHz respectively), spectrometer in $CDCl_3$ unless specified otherwise, with chemical shifts referenced to internal standards $CDCl_3$ (7.26 ppm ^1H, 77.0 ppm ^{13}C). High-resolution mass spectral (HRMS) analyses were performed by the MS-service at the Laboratory for Organic Chemistry at ETH Zurich. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument. The automated synthesis was performed on an ABI 431A peptide synthesizer with a custom-made jacketed glass reaction vessel. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. Optical rotations were measured at room temperature using a Perkin Elmer 241 polarimeter. Recycling HPLC system (GPC: LC-9101 Japan Analytical Industry Co. Ltd., JAIGEL-2H and 2.5H, mobile phase: $CHCl_3$) was used for size exclusion chromatography. Preparative HPLC was performed using a Waters 1525 pump and Waters 2487 detector on a Waters Sunfire prep C_8 reversed-phase column (10 × 150 mm).

General procedure A. Condensations Using *S*-Phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-thia-α-D-mannopyranoside sulfoxide (1). A mixture of **1** (1.25 equiv.), acceptor (**2**, **4**, **6** or **9**; 1.0 equiv., ~0.15 mmol, 0.04 M) and di-*tert*-butylmethylpyridine (DTBMP, 2.5 equiv.) in DCM was stirred over freshly activated powdered molecular sieves for 30 min and cooled to -78°C. Trifluoromethanesulfonic anhydride (Tf_2O, 0.65 equiv.) was added and the reaction mixture was allowed to very slowly warm to room temperature overnight. The reaction was quenched by the addition of triethylamine (~5 equiv.), filtered over celite in a mixture of aqueous $Na_2S_2O_3$ (1M) and saturated aqueous NaHCO$_3$. The layers were separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with saturated aqueous NaCl, dried (NaSO$_4$) and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc in hexanes or toluene) to provide the title compound.



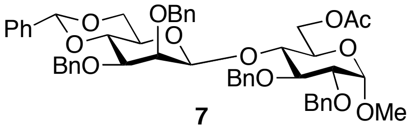
3

3-*O*-[2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]- 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (3). Using general procedure **A**, **3** was prepared on a 0.157 mmol (acceptor glycoside) scale. Flash silica gel column chromatography (0%→25% EtOAc in hexanes) to provide the title compound in 58% yield. Spectral data were in full accord with those reported previously.[1]



5

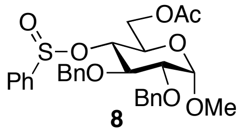
Allyl 4,6-*O*-benzylidene-2-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl-α-D-mannopyranoside (5). Using general procedure **A**, **5** was prepared on a 0.145 mmol (acceptor glycoside) scale. Flash silica gel column chromatography (0%→5% EtOAc in toluene) to provide the title compound in 63% yield. Spectral data were in full accord with those reported previously.[1]



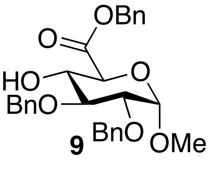
7

Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-α-D-glucopyranoside (7). Using general procedure **A**, **7** was prepared on a 0.127 mmol (acceptor glycoside) scale. LCMS-analysis (20% B in A: 2 min; linear gradient to 100% B in A in 30 min) of the crude mixture showed the presence of several new products. Selected data: t_R 14.43 min, ESI-MS = 563.2 [M+Na]$^+$, 1102.8 [2M+Na]$^+$: **8 (*R* or *S*)**; t_R 15.04 min, ESI-MS = 563.2 [M+Na]$^+$, 1102.8 [2M+Na]$^+$: **8 (*R* or *S*)**; t_R 22.36 min, ESI-MS =

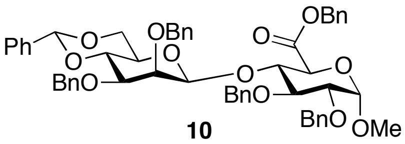
540.8 [M+H]$^+$: *S*-phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-thia-α-D-mannopyranoside; t_R 23.20 min, ESI-MS = 864.8 [M+NH$_4$]$^+$, 870.0 [M+Na]$^+$: **7β**; t_R 24.10 min, ESI-MS = 870.0 [M+Na]$^+$: **7α.** Flash silica gel column chromatography (0%→15% EtOAc in toluene) provided a mixture of **7** and **8**, that was separated by Recycling HPLC. Pure **7** was obtained in 50% yield. R$_f$ 0.55 (3/2 hexanes/EtOAc); ^{1}H-NMR, δ 2.06 (s, 3H), 3.18 (m, 1H), 3.42 (s, 3H), 3.49 (dd, 1H, *J* = 5.7, 9.3 Hz), 3.56-3.63 (m, 2H), 3.69-3.71 (m, 2H), 3.88-3.94 (m, 2H), 4.05 (dd, 1H, *J* = 4.8, 10.2 Hz), 4.13-4.18 (m, 3H), 4.45 (s, 1H), 4.59 (d, 1H, *J* = 3.9 Hz), 4.65 (d, 1H, *J* = 12.0 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 4.79-4.90 (m, 3H), 4.92 (d, 1H, *J* = 12.0 Hz), 5.05 (d, 1H, *J* = 10.8 Hz), 5.55 (s, 1H), 7.26-7.50 (m, 25H); ^{13}C-NMR, δ 21.0, 55.5, 62.6, 67.7, 68.3, 68.5, 72.7, 73.7, 75.2, 75.4, 76.9, 78.2, 78.4, 78.6, 79.1, 79.9, 98.1, 101.3, 101.9, 126.0, 127.3, 127.5, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.8, 137.4, 138.0, 138.3, 138.4, 139.1, 170.4; [α]$_D$ -18.7 (*c* = 1.0); IR, ν = 1740, 1453, 1094, 1047 cm^{-1}; HR-MS *m/z*: 869.3502 (calculated for $C_{50}H_{54}O_{12}Na^+$ 869.3513).


8

Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-(*S*-phenylsulfinyl)-α-D-glucopyranoside (8). The title compound was obtained as a side-product in the condensation of **1** and **6** as described above. The compound was obtained as a 3:2 diastereomeric mixture of phenylsulfinyl esters in 31% yield. R$_f$ 0.55 (3/2 hexanes/EtOAc); ^{1}H-NMR, δ 2.09 (s, 3H), 2.12 (s, 2H), 3.57 (dd, 1H, *J* = 3.3, 9.3 Hz), 3.62 (dd, 0.67H, *J* = 3.6, 9.6 Hz), 3.86-3.90 (m, 1.66H), 3.98 (t, 0.67H, *J* = 9.0 Hz), 4.03 (t, 1H, *J* = 9.3 Hz), 4.20 (m, 1.67H), 4.29-4.40 (m, 3.33H), 4.56 (d, 1H, *J* = 3.9 Hz), 4.62-4.69 (m, 2.33H), 4.74-4.87 (m, 3.33H), 5.04-5.08 (m, 1.67H), 7.26-7.77 (m, 25H); IR, ν = 1741, 9094, 1028, 908 cm^{-1}; HR-MS *m/z*: 563.1712 (calculated for $C_{29}H_{32}O_8SNa^+$ 563.1716).

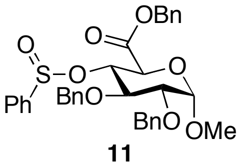

9

Benzyl (methyl 2,3-di-*O*-benzyl-α-D-glucopyranosyl-uronate) (9). ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.37-7.29 (m, 15H), 5.23 (s, 2H), 4.91 (d, *J*= 11.3 Hz, 1H), 4.81-4.77 (m, 2H), 4.70-4.64 (m, 2H), 4.23-4.20 (m, 1H), 3.85-3.82 (m, 2H), 3.57-3.53 (m, 1H), 3.43 (s, 3H), 2.84 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.9, 138.5, 137.9, 135.1, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 98.6, 80.3, 78.4, 75.3, 73.6, 71.7, 70.9, 67.2, 55.9; $[\alpha]_D$ 14.3(c = 1.0); IR, ν = 3494, 3088, 3063, 32032, 2932, 1747, 1497, 1454 cm^{-1}; HR-MS *m/z*: 501.1891 (calculated for $C_{28}H_{30}O_7Na^+$ 501.1884).



10

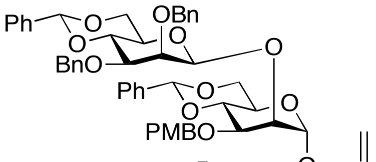
Benzyl (methyl 2,3-di-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-α-D-glucopyranosyl-uronate) (10). Using the general procedure **A**, **10** was prepared on a 0.171 mmol (acceptor glycoside) scale. Flash silica gel column chromatography (0%→25% EtOAc in hexanes) provided a mixture of **10** and **11**, that was separated by Recycling HPLC. Pure **10** was obtained in 50% yield. R_f 0.65 (4/1 toluene/EtOAc); ^{1}H-NMR, : 2.83 (m, 1H), 3.24 (dd, 1H, J = 3.3, 9.9 Hz), 3.48 (s, 3H), 3.52-3,57 (m, 2H), 3.70 (d, 1H, J = 3.0 Hz), 3.86-3.90 (m, 2H), 4.00-4.06 (m, 3H), 4.14 (m, 1H), 4.57-4.73 (m, 5H), 4.81 (s, 2H), 4.84 (d, 1H, J = 12 Hz), 5.02 (d, 1H, J = 12 Hz), 5.06 (d, 1H, J = 12 Hz), 5.28 (d, 1H, J = 12 Hz), 5.51 (s, 1H), 7.26-7.55 (m, 30H); ^{13}C-NMR, δ 56.1, 67.3, 67.4, 68.7, 70.5, 72.3, 74.1, 75.5, 75.8, 76.9, 77.8, 78.4, 78.7, 79.6, 80.0, 99.0, 101.5, 101.9, 126.3, 127.5, 127.6, 127.7, 128.0, 128.1, 128.3, 128.4, 128.6, 128.7, 129.0, 129.1, 129.2, 135.2, 137.9, 138.3, 138.8, 138.9, 139.2, 169.3; $[\alpha]_D$ -38.1 (c = 1.0); IR, ν = 1724, 1454, 1994, 1049 cm^{-1}; HR-MS *m/z*: 931.3663 (calculated for $C_{55}H_{56}O_{12}Na^+$ 931.3664)



11

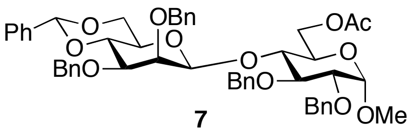
Benzyl (methyl 2,3-di-*O*-benzyl-4-*O*-(*S*-phenylsulfinyl)-α-D-gluco-pyranosyluronate) (11). The title compound was obtained as a side-product in the condensation of **1** and **9** as described above. The compound was obtained as a 1:2 diastereomeric mixture of phenylsulfinyl esters in 30% yield. R_f 0.65 (4/1 toluene/EtOAc); ^{1}H-NMR, δ 3.38 (s, 1.5H), 3.40 (s, 3H), 3.59 (dd, 1H, J = 3,6, 9.6 Hz), 3.68 (dd, 0.5H, J = 3.6, 9.6 Hz), 3.96 (t, 0.5H, J = 9.3 Hz), 3.98 (t, 1H, J = 9.3 Hz), 4.27 (d, 1H, J = 10.2 Hz), 2.31 (d, 0.5H, J = 9.9 Hz), 4.51-4.64 (m, 5H), 4,74-4.84 (m, 2.5H), 4.98-5.03 (m, 1.5H), 5.08 (d, 1H, J = 12.0 Hz), 5.21 (d, 1H, *J* = 12.0 Hz), 5.29 (s, 1H), 7.23-7.68 (m, 30H); IR, ν = 1754, 1139, 1092, 909 cm^{-1}; HR-MS *m/z*: 625.1857 (calculated for $C_{34}H_{34}O_8SNa^+$ 625.1872).

General procedure B: Condensations Using Carboxybenzyl Donors. A mixture of **12**[2] (1.25 equiv.), acceptor (**4**, **6** or **13**; 1.0 equiv., ~0.12 mmol, 0.04 M) and di-*tert*-butylmethylpyridine (DTBMP, 3.0 equiv.) in DCM was stirred over freshly activated powdered molecular sieves for 30 min and cooled to -60°C. Trifluoromethanesulfonic anhydride (Tf_2O, 1.25 equiv.) was added and the reaction mixture was allowed to very slowly warm to room temperature overnight. The reaction was quenched by the addition of triethylamine (~5 equiv.), filtered over celite and concentrated. The crude product was purified by flash silica gel column chromatography (EtOAc in hexanes or toluene) to provide the title compound.



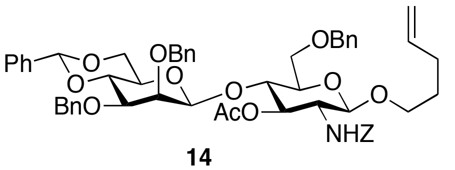
5

Allyl 4,6-*O*-benzylidene-2-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl-α-D-mannopyranoside (5). Using general procedure **B**, **5** was prepared on a 0.132 mmol (acceptor glycoside) scale. Flash silica gel column chromatography (0%→5% EtOAc in toluene) to provide the title compound in 81% yield.



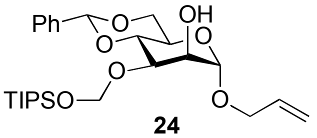
7

Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α/β-D-mannopyranosyl]-α-D-glucopyranoside (7). In three separate experiments, **7** was prepared on ~0.10 mmol (acceptor glycoside) scale following general procedure **B**, with the following variations: *Experiment 1:* the general procedure was exactly followed. *Experiment 2:* the reaction was conducted at -30°C and quenched at this temperature after 2 h. *Experiment 3:* the reaction was conducted at -30°C in toluene and quenched at this temperature after 2 h. The crude product from experiment 1 was purified by flash silica gel column chromatography (0%→30% EtOAc in hexanes) to provide the title compound in 85% yield. LCMS-analysis (20% B in A: 2 min.; linear gradient to 100% B in A in 30 min) of the crude mixtures showed the presence of several new products. Selected data: t_R 22.30 min, ESI-MS = 864.0 $[M+NH_4]^+$, 869.2 $[M+Na]^+$: **7β**; t_R 23.70 min, ESI-MS = 864.0 $[M+NH_4]^+$, 869.2 $[M+Na]^+$: **7α**; t_R 25.90 min, ESI-MS = 1030.0 $[M+NH_4]^+$, 1034.8 $[M+Na]^+$: self condensed ester of **12**; t_R 26.50 min, ESI-MS = 1030.0 $[M+NH_4]^+$, 1034.8 $[M+Na]^+$: self condensed ester of **12**. In Experiment 3 remaining acceptor (t_R 6.80 min) was also found. Ratio **7β/7α :** Experiment 1: 10:1; Experiment 2: 10:1; Experiment 3: 11:1.



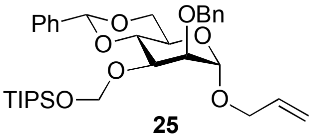
14

***n*-Pentenyl 3-*O*-Acetyl-6-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α/β-D-mannopyranosyl]-2-benzyloxy-carbonylamino-2-deoxy-β-D-glucopyranoside (14).** Using general procedure **B**, **20** was prepared on a 0.126 mmol (acceptor glycoside) scale. Flash silica gel column chromatography (0%→15% EtOAc in toluene) to provide the title compound in 82% yield. Spectral data were in full accord with those reported previously.[1]



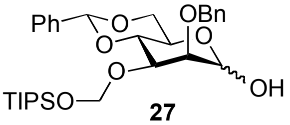
24

Allyl 4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside (24). Allyl mannoside **23** (3.08 g, 10.0 mmol) in 1,2-dichloroethane (40 mL), was treated with dibutyltindichloride (3.04 g, 10.0 mmol) and D*i*PEA (6.3 mL, 36 mmol), until all starting material was dissolved, and the resulting solution was stirred for an additional 1.5 h, after which the mixture was brought to 80°C. Tri-*iso*-propylsilyloxymethylchloride[3] (2.9 g, 13 mmol) was added and the reaction mixture was stirred for 15 min, after which it was cooled to RT. The mixture was diluted with DCM (150 mL) and washed with saturated aqueous $NaHCO_3$ (100 mL). The water layer was extracted three times with DCM, after which the organic layers were combined, filtered over Celite®, dried ($MgSO_4$) and concentrated. The crude product was purified by flash silicagel column chromatography (2:1 cyclohexane/EtOAc) to give the pure title compound as a yellow oil (34.51 g, 9.1 mmol, 91%). R_f 0.60 (hexanes/EtOAc 2:1); ^{1}H-NMR, δ 1.15 (m, 21H), 2.97 (d, 1H, J = 1.5 Hz), 3.81-4.29 (m, 8H), 4.94 (d, 1H, J = 1.2 Hz), 5.05 (d, 1H, J = 5.1 Hz), 5.17 (d, 1H, J = 4.8 Hz), 5.19-5.36 (m, 2H) 5.57 (s, 1H), 5.84-5.98 (m, 1H), 7.34-7.59 (m, 5H); ^{13}C-NMR, δ 12.0, 17.9, 64.3, 67.9, 68.8, 73.3, 73.8, 78.2, 78.8, 90.1, 98.7, 101.6, 116.9, 126.1, 127.6, 127.8, 128.0, 128.3, 128.8, 133.5, 137.6, 138.3; [α]$_D$ +74.1 (*c* = 1.0); IR, ν = 2944, 1464, 1044 cm^{-1}; HR-MS *m/z*: 517.2583 (calculated for $C_{26}H_{42}O_7Si + Na^+$: 517.2598).



25

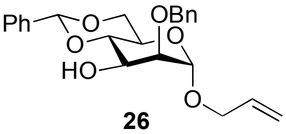
Allyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside (25). Allyl mannoside **24** (3.42 g, 6.90 mmol) and benzylbromide (1.07 mL, 8.97 mmol) were dissolved in DMF (30 mL) and cooled to 0°C. Sodium hydride (317 mg, 7.94 mmol, 60% in mineral oil) was added in small portions. The mixture was allowed to reach room temperature and stirred for 1 h. Methanol (0.5 mL) was added to quench the reaction, after which the mixture was diluted with diethyl ether and washed with water. The aqueous phase was extracted three times with diethyl ether and the combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification by flash silica gel chromatography (0% to 10% EtOAc in hexanes) yielded **24** as a colorless oil (4.03 g, 6.90 mmol, 100%). R$_f$ 0.65 (hexanes/EtOAc 3:1); ^{1}H-NMR, δ 1.15 (m, 21H), 3.92 (m, 4H), 4.21 (m, 1H), 4.24-4.32 (m, 2H), 4.41 (dd, 1H, *J* = 3.3, 10.2 Hz), 4.78 (d, 1H, *J* = 12.0 Hz), 4.91 (d, 1H, *J* = 1.2 Hz), 4.98 (d, 1H, *J* = 12.0 Hz), 5.17-5.35 (m, 4H), 5.66 (s, 1H), 5.84-5.98 (m, 1H), 7.34-7.59 (m, 10H); ^{13}C-NMR (75 MHz, $CDCl_3$), δ=138.6, 137.9, 133.8, 129.1, 128.6, 128.4, 128.1, 127.9, 126.4, 117.2, 101.9, 99.0, 90.4, 79.0, 78.5, 74.1, 73.6, 69.1, 68.2, 64.6, 18.2, 12.3; [α]$_D$ + 54.3 (*c* = 1.0); IR, ν = 2943, 1463, 1044 cm^{-1}; HR-MS *m/z*: 607.3049 (calculated for $C_{33}H_{48}O_7Si + Na^+$ 607.3067).



27

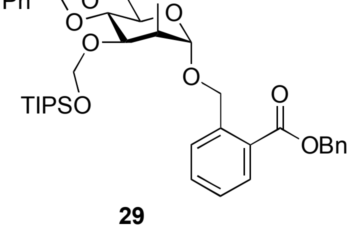
2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside (27) Allyl mannoside **25** (507 mg, 0.969 mmol) was dissolved in EtOAc (6 mL). Aqueous acetic acid (90%, 20 mL) was added, followed by NaOAc (476 mg, 5.80 mmol) and $PdCl_2$ (258 mg, 1.46 mmol) and the mixture was stirred overnight. After filtration over Celite, the mixture was diluted with EtOAc and washed with water. The aqueous phase was extracted once with EtOAc and the combined organic layers were washed with saturated aqueous

$NaHCO_3$ until they reached neutral pH. The aqueous phase was extracted three times with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification by flash column chromatography (0 to 17.5% EtOAc in hexanes) gave the title compound as a colorless oil (389 mg, 0.714 mmol, 74%). R_f 0.45 (hexanes/EtOAc 3:1); Major isomer: ^{1}H-NMR, δ 1.10 (m, 21H), 3.46 (bs, 1H), 3.82-3.92 (m, 2H), 4.02-4.62 (m, 4H), 4.35 (1H, m), 4.69 (d, 1H, J = 12.0 Hz), 4.89 (d, 1H, J = 12.0 Hz), 5.12 (m, 3H), 5.61 (s, 1H), 7.30-7.5.53 (m, 10H); ^{13}C-NMR, δ 11.9, 17.8, 64.1, 68.8, 72.9, 73.7, 78.3, 78.8, 90.1, 94.0, 101.6, 126.1, 126.1, 127.5, 127.8, 128.0, 128.2, 128.3, 128.7, 137.5, 138.3; IR, ν = 2944, 1464, 1095 cm^{-1}; HR-MS *m/z*: 567.2737 (calculated for $C_{30}H_{44}O_7Si + Na^+$ 567.2754).



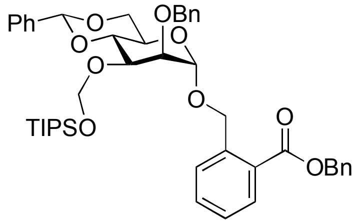
26

Allyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (26). Allyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxy-methyl)-α-D-mannopyranoside **25** (100 mg, 0.171 mmol) was dissolved in THF (1.7 mL) and treated with TBAF (1 M in THF), and the reaction progress was monitored by TLC analysis. Within 5 min all starting material had been consumed. The solution was diluted with EtOAc, washed with water and saturated aqueous NaCl, dried ($MgSO_4$) and concentrated. Purification by flash column chromatography (0 to 25% EtOAc in hexanes) gave the title compound as a white solid (64 mg, 0.161 mmol, 94%). R_f 0.45 (hexanes/EtOAc 3:1); ^{1}H-NMR, δ 2.44 (d, 1H, J = 7.8 Hz), 3.82-4.00 (m, 5H), 4.11-4.27 (m, 3H), 4.70 (d, 1H, J = 11.7 Hz), 4.75 (d, 1H, J = 11.7 Hz), 4.90 (s, 1H), 5.20-5.32 (m, 2H), 5.58 (s, 1H), 5.87 (m, 1H), 7.26-7.52 (m, 10H); ^{13}C-NMR, δ 63.6, 68.1, 68.77, 68.81, 73.8, 78.6, 79.5, 97.5, 102.1, 117.6, 126.2, 127.9, 128.0, 128.2, 128.5, 129.0, 133.3, 137.2, 137.5; $[\alpha]_D$ + 85.2 (c = 1.0); IR, ν = 3564, 3007, 2918, 1455, 1383 cm^{-1}; HR-MS *m/z*: 421.1625 (calculated for $C_{23}H_{26}O_6 + Na^+$ 421.1627).



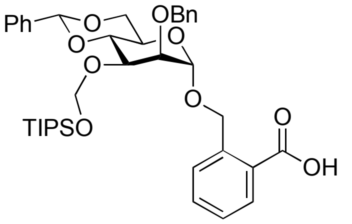
29

Benzyloxycarbonylbenzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside (29). Benzyloxycarbonylbenzyl-4,6-*O*-benzylidene-α-D-mannopyranoside **28**[4] (2.10 g, 4.27 mmol) in 1,2-dichloroethane (22 mL), was treated with dibutyltindichloride (1.43 g, 4.70 mmol) and D*i*PEA (2.97 mL, 17.1 mmol), until all starting material was dissolved, and the resulting solution was stirred for an additional 2 h. Tri-*iso*-propylsilyloxymethylchloride[3] (1.05 mL, ~ 4.7 mmol) was added and the reaction mixture was stirred overnight. The mixture was diluted with DCM (150 mL) and washed with saturated aqueous $NaHCO_3$ (100 mL). The water layer was extracted three times with DCM, after which the organic layers were combined, washed with aqueous saturated NaCl, dried over $MgSO_4$ and concentrated. The crude product was purified by flash silica gel column chromatography (0%→15% EtOAc in hexanes) to give the pure title compound as a colorless oil (2.27 g, 3.34 mmol, 79%). R_f 0.45 (3/1 hexanes/EtOAc); ^{1}H-NMR, δ. 1.11 (m, 21H), 2.99 (bs, 1H), 3.88 (t, 1H, J = 9.9 Hz), 3.98 (m, 1H), 4.13 (t, 1H, J = 9.0 Hz), 4.23-4.31 (m, 3H), 5.01 (d, 1H, J = 14.4 Hz), 5.08-5.13 (m, 2H), 5.21-5.25 (m, 2H), 5.37 (s, 2H), 5.61 (s, 1H), 7.36-7.59 (m, 12H), 7.68 (m, 1H), 8.07 (m, 1H); ^{13}C-NMR, δ. 11.9, 17.9, 63.7, 66.7, 67.4, 68.8, 70.9, 74.6, 77.8, 89.9, 99.8, 101.8, 126.0, 127.0, 127.2, 127.7, 127.9, 128.0, 128.1, 128.4, 128.7, 130.5, 135.6, 137.3, 139.6, 166.2; IR, ν = 2934, 1713, 1256, 1046 cm^{-1}; $[\alpha]_D$ + 70.9 (c = 1.0); HR-MS *m/z*: 701.3102 (calculated for $C_{30}H_{50}O_9SiNa^+$ 701.3116).



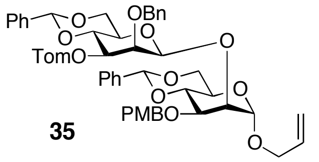
30

Benzyloxycarbonylbenzyl-2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside (30). Benzyloxycarbonylbenzyl 4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside **29** (4.55 g, 6.70 mmol) and benzylbromide (1.03 mL, 8.66 mmol) were dissolved in DMF (35 mL) and cooled to 0°C. Sodium hydride (308 mg, 7.70 mmol, 60% in mineral oil) was added in small portions. The mixture was allowed to reach room temperature and stirred for 1.25 h. Saturated aqueous NH_4Cl was added to quench the reaction, after which the mixture was diluted with diethyl ether and washed with water. The aqueous phase was extracted three times with diethyl ether and the combined organic layers were dried ($MgSO_4$), filtered and concentrated. Purification by flash silica gel chromatography (0% to 10% EtOAc in hexanes) yielded **30** (4.97 g) in 96% yield. R$_f$ 0.45 (3/1 hexanes/EtOAc); ^{1}H-NMR, δ 1.13 (m, 21H), 3.88 (m, 2H), 4.00 (m, 1H), 4.22 (d, 2H), 4.38 (dd, 1H, *J* = 3.3, 9.9 Hz), 4.72 (d, 1H, *J* = 11.7 Hz), 5.87-4.95 (m, 3H), 5.09-5.16 (m, 3H), 5.31 (s, 2H), 5.59 (s, 1H), 7.36-7.59 (m, 19), 8.03 (d, 1H, *J* = 8.1 Hz); ^{13}C-NMR, δ 12.2, 18.1, 64.8, 66.9, 67.6, 69.0, 73.5, 73.9, 78.3, 79.0, 90.3, 99.5, 101.8, 126.4, 127.2, 127.3, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 128.9, 129.0, 130.9, 132.7, 136.0, 137.9, 138.5, 140.3, 177.7; IR, ν = 2933, 1713, 1256, 1041 cm^{-1}; [α]$_D$ + 68.8 (*c* = 1.0); HR-MS *m/z*: 791.3586 (calculated for $C_{45}H_{56}O_9SiNa^+$ 791.3591).



31

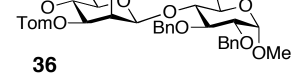
Carbonylbenzyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside (31). Benzyloxycarbonylbenzyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside **30** (1.0 g, 1.30 mmol) and NH_4OAc (300 mg, 3.9 mmol) were dissolved in a mixture of EtOAc and methanol (1:4, 50 mL). The mixture was degassed three times and then Pd/C (94 mg) was added. The suspension was degassed once more. H_2 was bubbled through the mixture for 1 min, after which the solution was stirred for 2 h under a H_2-atmosphere. The catalyst was filtered off and the solvents were evaporated *in vacuo*. The crude product was purified by flash silica gel column chromatography (30%→80% EtOAc in hexanes, containing 1% AcOH) to provide 869 mg (1.28 mmol, 98%) of the title compound as a white foam. R$_f$ 0.50 (1/1 hexanes/EtOAc, 5% AcOH); ^{1}H-NMR, δ 1.12 (m, 21H), 3.91 (m, 2H), 4.05 (m, 1H), 4.27 (d, 2H), 4.43 (dd, 1H, *J* = 3.0, 10.2 Hz), 4.74 (d, 1H, *J* = 12.0 Hz), 4.89-5.02 (m, 3H), 5.13-5.22 (m, 3H), 5.61 (s, 1H), 7.36-7.59 (m, 14), 8.12 (d, 1H, *J* = 7.5 Hz), 10.6 (bs, 1H); ^{13}C-NMR, δ 12.2, 18.1, 64.9, 67.7, 69.0, 73.4, 74.0, 78.4, 79.0, 90.3, 99.5, 101.8, 126.4, 127.3, 127.4, 127.9, 128.0, 128.3, 128.6, 129.0, 131.8, 133.5, 137.8, 138.5, 140.9, 172.7; IR, ν = 2944, 1713, 1046 cm^{-1}; [α]$_D$ + 66.1 (*c* = 1.0); HR-MS *m/z*: 701.3104 (calculated for $C_{38}H_{50}O_9SiNa^+$ 701.3116).



35

Allyl 4,6-*O*-benzylidene-2-*O*-[4,6-*O*-benzylidene-2-*O*-benzyl-3-*O*-tri-*iso*-propylsilyloxymethyl-β-D-mannopyranosyl]-3-*O*-*p*-methoxybenzyl-α-D-mannopyranoside (35). A mixture of 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(tri-*iso*-propylsilyloxymethyl)-α-D-mannopyranoside **27** (109 mg, 0.200 mmol), diphenylsulfoxide (81 mg, 0.40 mmol) and tri-*tert*-butylpirimidine (124 mg, 0.500 mmol) in dichloromethane (5 mL) was stirred over activated molecular sieves for 30 min, after which the mixture was cooled to -40°C. Triflic anhydride (35 μL, 0.21 mmol) was added and the reaction mixture was allowed to reach -25°C over a period of 1.5 h, after which a solution of allyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-α-D-mannopyranoside **4** (57 mg, 0.133 mmol) in dichloromethane (1 mL) was added. The mixture was stirred overnight, while warming to room temperature. Triethylamine (0.2 mL) was added and the mixture was filtered through Celite and concentrated. Purification by flash column chromatography (0 to 10% EtOAc in toluene) gave the title compound (114 mg, 0.120 mmol, 90%). R$_f$ 0.55 (toluene/EtOAc 4:1); ^{1}H-NMR, δ 1.05 (m, 21H), 3.35 (m, 1H), 3.71-3.92 (m, 6H), 3.96-4.09 (m, 5H), 4.13-4.31 (m, 5H), 4.64-4.75 (m, 3H), 4.89-5.08 (m, 5H), 5.22, 5.33 (m, 2H), 5.49 (s, 1H), 5.56 (s, 1H), 5.88 (m, 1H), 6.83 (m, 2H), 7.24-7.52 (m, 17H); ^{13}C-NMR, δ 11.8, 17.8, 18.0, 55.2, 64.2 67.8, 68.1, 68.5, 68.8, 70.9, 73.7, 74.5, 74.9, 77.8, 78.5, 88.8, 97.5, 100.7, 101.5, 113.4, 117.7, 126.0, 126.1, 127.3, 128.0, 128.1, 128.2, 128.8, 129.1, 129.3, 130.9, 133.3, 137.4, 137.5, 138.6, 158.9; [α]$_D$ -29.5 (*c* = 1.0); IR, ν = 2943, 1512, 1087 cm^{-1}; HR-MS *m/z*: 977.4461 (calculated for $C_{54}H_{70}O_{13}Si + Na^+$ 977.4484).

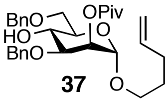
Using general procedure **B**, **35** was prepared on a 0.057 mmol (acceptor glycoside) scale in 81% yield.



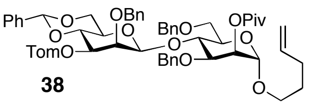
36

Benzyl (methyl 2,3-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-tri-*iso*-propylsilyloxymethyl-β-D-mannopyranosyl]-α-D-glucopyranosyluronate) (36). Using general procedure **B**, **36** was prepared on a 0.102 mmol (acceptor glycoside) scale in 73%

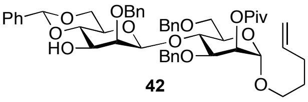
yield. R$_f$ (hexanes/EtOAc 1:1); ^{1}H-NMR δ 1.07 (s, 21H), 2.85 (m, 1H), 3.45 (s, 3H), 3.45 (s, 3H), 3.45-3.55 (m, 2H), 3.67 (dd, 1H, *J* = 3.0, 12.0 Hz), 3.82-4.03 (m, 5H), 4.13 (d, 1H, *J* = 9.3 Hz), 4.20 (s, 1H), 4.62-4.69 (m, 2H), 4.72-4.85 (m, 3H), 4.99-5.06 (m, 4H), 5.38 (d, 1H, *J* = 11.7 Hz), 5.44 (s, 1H), 7.25-7.50 (m, 25H); ^{13}C-NMR, δ. 11.9, 17.8, 55.8, 67.0, 68.4, 70.2, 73.8, 74.9, 75.3, 75.5, 78.1, 79.2, 79.7, 89.4, 98.7, 101.5, 101.6, 126.1, 127.2, 127.7, 127.8, 127.9, 128.0, 128.4, 128.8, 128.9, 135.0, 137.6, 138.0, 138.8, 139.0, 168.9; $[\alpha]_D$ -54.1 (*c* = 1.0); IR, ν = 2943, 2866, 1764, 1453, 1052 cm^{-1}; HR-MS *m/z*: 1027.457 (calculated for $C_{58}H_{72}O_{13}Si + Na^+$ 1027.464).


37

***n*-Pentenyl 3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-mannopyranoside (37).** ^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.36.7.26 (m, 10H), 5.87-5.74 (m, 1H) 5.34-5.32 (m, 1H), 5.06-4.95 (m, 2H), 4.81 (d, *J*= 1.8 Hz, 1H), 4.71 (d, *J*= 11.1 Hz, 1H), 4.65 (d, *J*= 12.0 Hz, 1H), 4.58 (d, *J*= 12.0 Hz, 1H), 4.44 (d, *J*= 11.1 Hz, 1H), 3.98-3.88 (m, 1H), 3.81-3.78 (m, 4H), 3.78-3.68 (m, 1H), 3.48-3.40 (m, 1H), 2.46 (s, 1H), 2.16-2.03 (m, 2H), 1.74-1.65 (m, 2H), 1.20 (s, 9H); ^{13}C-NMR (CDCl$_3$, 75 MHz) δ 177.8, 138.3, 138.0, 137.8, 128.4, 128.3, 128.1, 127.9, 127.5, 127.4, 115.0, 98.0, 77.8, 77.2, 73.5, 71.3, 71.2, 70.1, 67.5, 67.3, 39.0, 30.3, 28.6, 27.2; $[\alpha]_D$ 1.5° (*c* = 0.5); IR, ν = 3494, 3065, 3031, 2920, 1732, 1640, 1497, 1479, 1454, 1396, 1364, 1280 cm^{-1}; HR-MS *m/z*: 535.2675 (calculated for $C_{30}H_{40}O_7Na^+$ 535.2666).

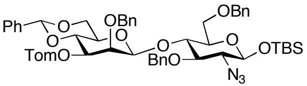

38

***n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-tri-*iso*-propylsilyloxymethyl-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (38).** Using general procedure **B**, **38** was prepared on a 0.096 mmol (acceptor glycoside) scale in 94% yield (α/β 1:9). R$_f$ (hexanes/EtOAc 1:1); ^{1}H-NMR δ. 1.08 (s, 21H), 1.20 (s, 9H), 1.72 (m, 2H), 2.15 (m, 2H), 3.03 (m, 1H), 3.46 (m, 1H), 3.57 (t, 1H, *J* = 9.9 Hz), 3.68-4.03 (m, 9H), 4.22 (t, 1H, *J* = 9.6 Hz), 4.48 (d, 1H, *J* = 11.7 Hz), 4.63-4.73 (m, 4H), 4.78-4.88 (m, 3H), 4.98-5.10 (m, 4H), 5.36 (m, 1H), 5.44 (s, 1H), 5.83 (m, 1H), 7.27-7.43 (m, 20H); ^{13}C-NMR, δ 12.1, 12.2, 27.2, 28.7, 30.4, 39.0, 67.3, 68.5, 68.9, 69.0, 71.1, 71.5, 73.3, 75.2, 75.6, 78.1, 78.4, 78.5, 89.5, 97.7, 101.3, 101.5, 115.0, 126.1, 127.1, 127.3, 127.4, 128.0, 128.2, 128.7, 137.5, 137.8, 138.2, 138.6, 138.7, 177.4; [α]$_D$ -1.5 (*c* = 0.5); IR, ν = 2943, 2871, 1730, 1456, 1093 cm^{-1}; HR-MS *m/z*: 1061.542 (calculated for $C_{60}H_{82}O_{13}Si + Na^+$ 1061.542).



42

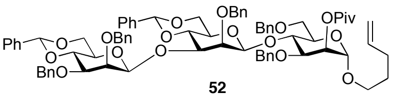
***n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (42).** *n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-tri-*iso*-propylsilyloxymethyl-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (**38**, 85 mg, 0.085 mmol) was dissolved in THF (1 mL), after which TBAF (1M in THF, 0.1 mL) was added. The mixture was stirred for 10 min after which the mixture was diluted with EtOAc and washed with water and a saturated aqueous solution of NaCl. The organic phase was dried over $MgSO_4$, and concentrated. Flash silica gel column chromatograhy (5 to 20% EtOAc in hexanes) gave the title compound (55 mg, 0.064 mmol, 79%). R$_f$ 0.50 (hexanes/EtOAc 2:1); ^{1}H-NMR δ 1.22 (s, 9H), 1.73 (m, 2H), 2.14 (m, 2H), 2.34 (bs, 1H), 2.95 (m, 1H), 3.42-3.59 (m, 3H), 3.65-3.87 (m, 6H), 4.23 (t, 1H, *J* = 9.6 Hz), 4.48 (d, 1H, *J* = 12.07 Hz), 4.55-4.61 (m, 3H), 4.67 (s, 2H), 4.75 (d, 1H, *J* = 12.0 Hz), 4.84 (d, 1H, *J* = 2.1 Hz), 4.93 (d, 1H, *J* = 11.7 Hz), 4.97-5.10 (m, 2H), 5.37 (m, 1H), 5.41 (s, 1H), 5.83 (m, 1H), 7.27-7.43 (m, 20H); ^{13}C-NMR, δ: 27.2, 28.6, 30.3, 39.0, 66.7, 67.3, 68.3, 68.6, 68.7, 70.8, 70.9, 71.3, 73.3, 74.9, 75.4, 75.6, 78.9, 79.1, 97.7, 101.3, 101.8, 115.0, 126.1, 126.8, 127.2, 127.4, 127.7, 127.8, 128.0, 128.1, 128.3, 128.9, 137.1, 137.7, 138.0, 138.0, 138.4, 177.3; [α]$_D$ -11.1 (*c* = 0.5); IR, ν = 3054, 1729, 1421, 695 cm^{-1}; HR-MS *m/z*: 875.3988 (calculated for $C_{50}H_{60}O_{12} + Na^+$ 875.3983).



40

***tert*-Butyldimethylsilyl 2-azido-3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-tri-*iso*-propylsilyloxy-methyl-β-D-mannopyranosyl]-2-deoxy-β-D-glucopyranoside (40).** The title compound was synthesized according to general procedure **B**. The product was isolated as an α/β-mixture (85%, α/β 1:7), that could not be completely separated by column chromatoghraphy. A pure fraction of the major isomer (β) was collected: ^{1}H-NMR δ 0.18 (s, 3H), 0.19 (s, 3H), 0.96 (s, 9H), 1.12 (m, 21H), 3.18 (m, 1H), 3.27-3.37 (m, 2H), 3.54 (t, 1H, *J* = 10.2 Hz), 3.59-3.68 (m, 2H), 3.83 (dd, 1H, *J* = 2.7, 9.9 Hz), 3.93 (m, 1H), 3.98-4.11 (m, 2H), 4.47-4.55 (m, 2H), 4.62-4.69 (m, 3H), 4.81 (d, 1H, *J* = 11.4 Hz), 4.90 (d, 1H, *J* = 12.0

Hz), 5.00-5.09 (m, 3H), 5.49 (s, 1H), 7.24-7.51 (m, 20H); ^{13}C-NMR, δ -4.91, -4.06; 12.1, 18.1, 18.2, 25.8, 67.5, 68.2, 68.4, 68.6, 69.7, 73.5, 75.0, 75.1, 75.4, 75.8, 77.3, 78.3, 78.8, 81.2, 89.9, 97.1, 101.4, 101.6, 126.1, 127.3, 127.4, 127.7, 127.9, 128.0, 128.4, 129.0, 137.5, 137.7, 138.6, 138.7; $[\alpha]_D$ -26.5 (*c* = 0.5); IR, ν = 2944, 2866, 2112, 1463, 1058 cm^{-1}; HR-MS *m/z*: 1048.513 (calculated for $C_{56}H_{79}O_{11}N_3Si$ + Na$^+$ 1048.515). LCMS-analysis (85% B in A: 2 min; linear gradient to 100% B in A in 10 min) of the α/β-mixture revealed the α/β-ratio to be 1:7; **40-β** t_R 8.43 min; **40-α** t_R 9.47 min.



52

***n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (52):** Using general procedure **B**, **52** was prepared on a 0.053 mmol (acceptor glycoside) scale. LCMS-analysis (85% B in A: 2 min; linear gradient to 95% B in A in 30 min) of the reaction mixture revealed the α/β-ratio to be 12:1; **52-β** t_R 4.83 min; **52-α** t_R 5.85 min. Flash silica gel column chromatograhy (0 to 25% EtOAc in hexanes) gave the title compound (50 mg, 0.039 mmol, 74%). R_f 0.60 (hexanes/EtOAc 2:1); ^{1}H-NMR δ 1.20 (s, 9H), 1.70 (m, 2H), 2.13 (m, 2H), 3.10 (m, 2H), 3.27 (dd, 1H, *J* = 3.0, 9.6 Hz), 3.46 (m, 1H), 3.61-3.90 (m, 9H), 3.95-4.18 (m, 5H), 4.25 (t, 1H, *J* = 9.6 Hz), 4.48 (d, 1H, *J* = 12.0 Hz), 4.54-4.67 (m, 7H), 4.70 (s, 1H), 4.74 (s, 1H), 4.80-4.84 (m, 2H), 4.88 (d, 1H, *J* = 11.7 Hz), 4.97-5.07 (m, 2H), 5.37 (dd, 1H, *J* = 1.8, 3.0 Hz), 5.49 (s, 1H), 5.51 (s, 1H), 5.81 (m, 1H), 7.115-7.36 (m, 35H); $[\alpha]_D$ -44.0 (*c* = 1.0) ; IR, ν = 2672, 1730, 1453, 1091 cm^{-1}; HR-MS *m/z*: 1305.576 (calculated for $C_{77}H_{87}O_{17}$ + Na$^+$ 1305.576).

General Procedure for the Automated Solid-Phase Synthesis of β-Mannoside-Containing Oligosaccharides:

Automated Modules:

Module A: The resin is washed with DCM for 15 s followed by hexanes for 10 s Repeated six times.

Module B: The resin is washed six times with DCM for 15 s each.

Module C: The building block (5 eq., 0.125 mmol) and DTBMP (15 eq., 0.375 mmol) in DCM (2.5 mL) is delivered to the reaction vessel containing the resin. The mixture is allowed to cool for 3 min (with vortex for 30 s followed by standing for 30 s). Tf_2O (5 eq., 0.125 mmol, in 0.5 mL DCM) is added to the reaction vessel with vortex. The reaction mixture is then left for 120 min (with vortex for 30 s followed by standing for 30 s). After that time, the solution is drained and the resin is washed once with DCM.

Module D: The resin is washed six times with THF for 15 s each.

Module E: The resin is washed six times with MeOH:DCM (1:9) for 15 s each.

Module F: The resin is washed is treated with TBAF (5 eq., 0.125 mmol) in 1.6 mL THF for 15 min (with vortex for 30 s followed by standing for 30 s). After that time, the solution is drained and the resin is washed once with THF. Repeated once.

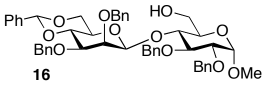
Module G: The resin is treated with 1.5 mL 20% piperidine/DMF for 35 s, then washed once with DCM.

Module H: The resin is washed with DCM for 15 sec. followed by MeOH for 15 s Repeated six times.

Module I: The resin is washed six times with acetic acid (0.2 M in THF) for 15 s each.

Module J: The resin is washed six times with DMF for 15 s each.

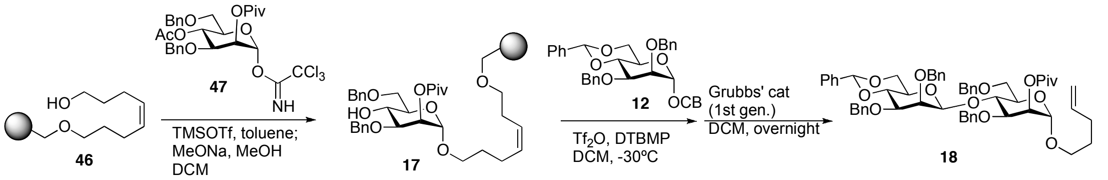
Module K: The resin is submitted to piperidine (20% v/v in DMF, 2 mL) for 5 min (with vortex for 30 s, followed by standing for 30 s). After that time, the solution is drained and the resin is submitted to the same conditions twice.


16

Methyl 2,3-di-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-α-D-glucopyranoside (16). Resin **15** was subjected to modules D, A and . The reaction vessel was then cooled to -30ºC. Module C was then performed with building block **12**, followed by module B, D, B, B. Module C was then performed again with building block **12**. The resin was then subjected twice to module B. The reaction vessel was warmed to room temperature, and module D, A and B were then performed to afford the resin-bound disaccharide.

The resin was then manually washed several times with DCM, then treated with 0.1 mmol MeONa in 0.2 mL MeOH and 2 mL DCM and agitated for two hours. The resin was washed several times with DCM, and the cleavage step was repeated once. The combined washing solutions were concentrated and purified by silica gel chromatography to afford compound **(16):** ^{1}H-NMR, δ 3.21 (m, 1H), 3.38 (s, 3H), 3.45 (dd, 1H, *J* = 3.9 Hz, *J* = 9.6 Hz), 3.47-3.62

(m, 4H), 3.65-3.70 (m, 1H), 3.78 (t, 1H, $J = 9.6$ Hz), 3.87-3.93 (m, 2H), 4.04 (dd, 1H, $J = 4.8$, 10.5 Hz), 4.11-4.17 (m, 1H), 4.54 (d, 1H, $J = 3.6$ Hz), 4.62 (s, 2H), 4.65 (s, 2H), 4.77-4.82 (m, 3H), 4.90 (d, 1H, $J = 11.7$ Hz), 5.05 (d, 1H, $J = 10.5$ Hz), 5.53 (s, 1H), 7.24-7.50 (m, 25H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 30.0, 55.7, 61.9, 67.7, 68.9, 70.6, 73.1, 74.0, 75.3, 75.6, 77.6, 78.7, 79.1, 79.6, 80.4, 98.7, 101.7, 102.1, 126.4, 127.6, 127.9, 127.9, 127.9, 128.2, 128.4, 128.5, 128.5, 128.7, 128.8, 129.2, 137.9, 138.6, 138.8, 139.7; $[\alpha]_D$ -8.0 ($c = 0.5$); IR, ν = 2927, 1095, 1049 cm^{-1}; HR-MS *m/z*: 827.3408 (calculated for $C_{48}H_{52}O_{11} + Na^+$ 827.3402).

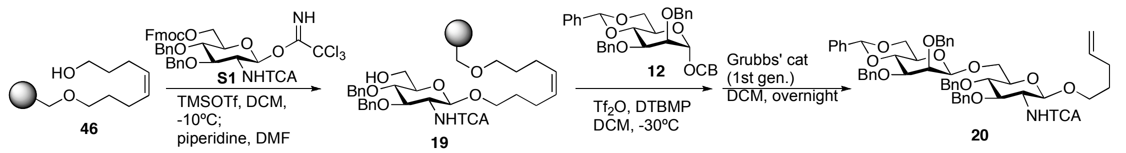


***n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (18).** Resin **46** (0.26 mmol/g, 95 mg, 0.025 mmol) was loaded in the reaction vessel of the synthesizer. Modules D, A, B were performed. Then, the resin was glycosylated twice with building block **47** (5 eq., 0.125 mmol) in toluene (2 mL) for 15 min with a module B in between. Then, modules B, D, B, were performed. The acetate protecting group was removed by treating the resin twice with MeONa (10 eq., 0.25 mmol) in MeOH (0.4 mL) and DCM (3.5 mL) for 30 min. Module E, D, I, D, A and B were performed to afford resin-bound mannose **17**.

An aliquot of resin **17** was then subjected to modules A, B, B. The reaction vessel was then cooled to -30ºC. Module C was then performed twice with building block **12** with four module B in between glaycosylations. The resin was then subjected twice to module B. The reaction vessel was warmed to room temperature, and module D, A, E, B were then performed to afford the resin-bound disaccharide.

The resin was charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphere of argon. Grubbs' catalyst (1st generation, 2 mg) was then added and the flask was put under ethylene atmosphere and stirred overnight. The resin was washed eight times with DCM. The resulting solution was filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. The crude residue was purified by column chromatography to afford the title compound (**18**). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.46-7.20 (m, 25H), 5.89-5.75 (m, 1H),5.49 (s, 1H), 5.34-5.31 (m, 1H), 5.08-4.97 (m, 2H), 4.84-4.74 (m, 3H), 4.7-4.58 (m, 5H), 4.53 (d, J=14.3 Hz, 1H), 4.40 (d, J=12.6 Hz, 1H), 4.15 (t, J= 9.6 Hz, 1H), 4.06 (t, J= 9.6 Hz, 1H), 3.96 (dd, J= 3.4 Hz, 9.4 Hz, 1H), 3.89

(dd, J= 4.9 Hz, 10.4 Hz, 1H), 3.83-3.77 (m, 1H), 3.74-3.65 (m, 4H), 3.58 (t, J= 10.4 Hz, 1H), 3.48-3.38 (m, 2H), 3.01-2.91 (m, 1H), 2.18-2.09 (m, 2H), 1.7 (quintet, J= 7.6 Hz, 2H), 1.19 (s, 9H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 177.8, 138.9, 138.8, 138.8, 138.6, 138.1, 137.9, 129.0, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.8, 127.7, 127.7, 127.6, 127.6, 127.4, 127.3, 115.3, 101.6, 101.6, 98.0, 78.9, 78.5, 77.3, 75.8, 75.2, 75.1, 73.5, 72.7, 71.5, 71.1, 69.1, 68.9, 68.7, 67.5, 67.4, 39.2, 30.5, 28.8, 27.3; $[\alpha]_D$ -13.8 (*c* = 0.145) ; IR, ν = 3031, 2923, 1732, 1454, 1366, 1277 cm^{-1}; HR-MS *m/z*: 965.4434 (calculated for $C_{57}H_{66}O_{12}$ + Na$^+$ 965.4447).

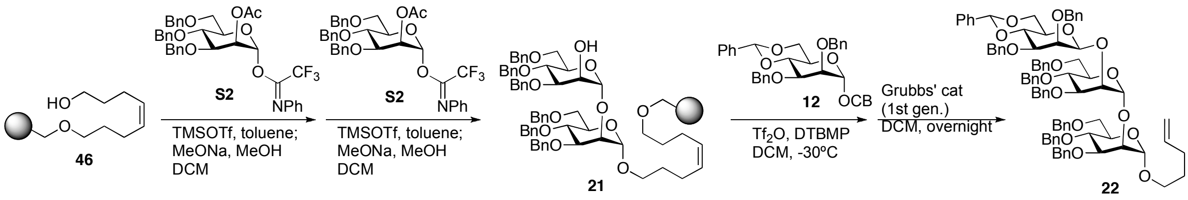


***n*-Pentenyl 3,4-di-*O*-benzyl-6-*O*-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-2-deoxy-2-*N*-trichloroacetyl-β-D-glucopyranoside (20):** Resin **46** (0.22 mmol/g, 120 mg, 0.026 mmol) was loaded in the reaction vessel of the synthesizer. Modules D, A, B were performed. Then, the reaction vessel was cooled to -10ºC and the resin was glycosylated twice with building block **S1** (0.125 mmol) in DCM (1 mL) for 30 min with a module B in between glycosylation. The resin was washed with module B, and warmed to room temperature. Then, module D, J, K, J, I, D, A and B were performed to afford resin-bound glucosamine **19**.

Resin **17** was subjected to modules A, B, B. The reaction vessel was cooled to -30ºC. Module C was then performed twice with building block **12** with two module B in between. The resin was subjected to module B and G. The reaction vessel was warmed to room temperature, and modules B, H and B were performed to afford the resin-bound disaccharide.

The resin was charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphere of argon. Grubbs' catalyst (1st generation, 2 mg) was added and the flask was put under ethylene atmosphere and stirred overnight. The resin was washed eight times with DCM. The resulting solution is filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. The crude residue was purified by column chromatography to afford the title compound **20** (11.7 mg, 11.6 μmol, 44% yield from resin **46**) as a mixture of anomers. Pure **β-20** was obtained by preparative HPLC: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.52-7.44 (m, 4H), 7.42-7.20 (m, 21H), 7.03 (d, J= 7.7 Hz, 1H), 5.81-5.67 (m, 1H), 5.61 (s, 1H), 5.01-4.68 (m, 9H), 4.59 (d, J= 12.4 Hz, 1H), 4.52

(d, *J*= 11.4 Hz, 1H), 4.31-4.13 (m, 5H), 3.92 (t, *J*= 10.3 Hz, 1H), 3.84-3.76 (m, 2H), 3.73-3.66 (m, 1H), 3.61-3.36 (m, 5H), 3.30-3.21 (m, 1H) 2.10-2.00 (m, 2H), 1.67-1.55 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 161.8, 138.3, 138.3, 137.8, 137.7, 137.7, 137.6, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.6, 126.1, 115.0, 102.5, 101.4, 99.1, 92.5, 79.5, 78.7, 78.4, 77.9, 77.2, 75.6, 74.9, 74.7, 74.6, 74.5, 72.6, 69.1, 68.6, 67.6, 58.1, 30.0, 28.7; $[\alpha]_D$ -13.8 (*c* = 0.39) ; IR, ν = 3294, 2923, 1688, 1537, 1453, 1362 cm^{-1}; HR-MS *m/z*: 1024.298 (calculated for $C_{54}H_{58}Cl_3NNaO_{11}^+$ 1024.2968).

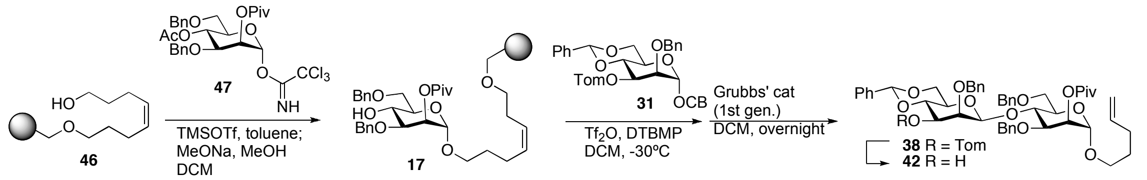


***n*-Pentenyl 3,4,6-tri-*O*-benzyl-2-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (22):** Resin **46** (0.22 mmol/g, 220 mg, 0.048 mmol) was loaded in the reaction vessel of the synthesizer. Modules D, A, B were performed. Then, the resin was glycosylated twice with building block **S2** (2 eq., 0.100 mmol) in toluene (3 mL) for 15 min, performing a module B in between glycosylations. Then modules B, D, B, were carried out. The acetate protecting group was removed by treating the resin four times with MeONa (10 eq., 0.5 mmol) in MeOH (0.8 mL) and DCM (5 mL) for 30 min. Module E, D, I, D, A and B were performed and the resin dried under vacuum to afford resin-bound disaccharide **21**.

Half of the dried resin was loaded in the reaction vessel of the synthesizer. Modules A, B, B were performed. The reaction vessel was cooled to -30ºC. Module C was performed twice with building block **12** with four modules B in between. The resin was subjected twice to module B. The reaction vessel was warmed to room temperature, and module D, A, E, D were performed to afford resin-bound trisaccharide.

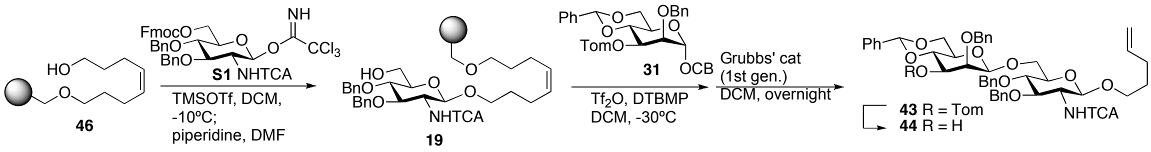
The resin was then charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphereof argon. Grubbs' catalyst (1st generation, 2 mg) was added and the flask was put under ethylene atmosphere and stirred overnight. The resin was washed eight times with DCM. The resulting solution is filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. The crude residue was then purified by column chromatography followed by recycling size-exclusion HPLC to afford the title compound **22** (12.7 mg, 9.2 μmol, 38% yield from resin **46**) as a pure anomer.

^{1}H-NMR (CDCl$_3$, 300 MHz) δ 7.50-7.46 (m, 4H), 7.42-7.17 (m, 37H), 7.10-7.03 (m, 4H), 5.83-5.69 (m, 1H), 5.54 (s, 1H), 5.10-4.91 (m, 4H), 4.88-4.75 (m, 4H), 4.71-4.34 (m, 12H), 4.26-4.06 (m, 5H), 3.97-3.87 (m, 3H), 3.82’3.55 (m, 10H), 3.32-3.22 (m, 2H), 3.03, 2.92 (m, 1H) 2.07-2.00 (m, 2H), 1.64-1.55 (m, 2H); ^{13}C-NMR (CDCl$_3$, 75 MHz) δ 138.6, 138.4, 138.3, 138.1, 138.0, 137.9, 137.6, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.7, 127.5, 127.3, 127.3, 127.1, 126.0, 114.8, 101.3, 99.9, 98.9, 80.2, 78.4, 77.7, 77.2, 76.2, 75.2, 75.0, 74.7, 74.2, 73.4, 73.2, 72.8, 71.7, 71.6, 71.5, 71.3, 70.1, 69.3, 69.1, 68.5, 67.1, 66.9, 30.3, 28.7; $[\alpha]_D$ -39.2 (*c* = 0.48) ; IR, ν = 3062, 3030, 2924, 2860, 2354, 1723, 1453, 1364, 1266 cm^{-1}; HR-MS *m/z*: 1403.631 (calculated for $C_{86}H_{92}NaO_{16}^+$ 1403.6278).



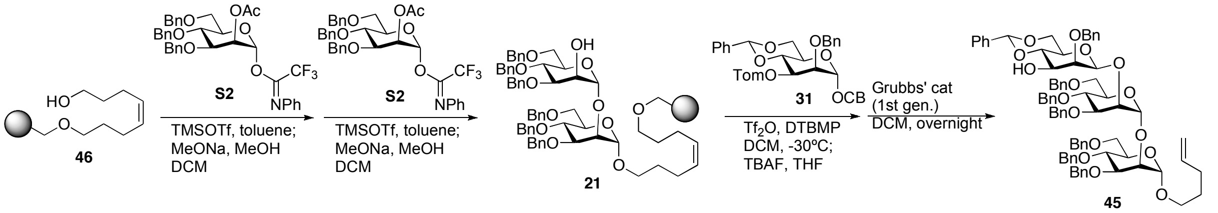
***n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (42):** Resin **17** was prepared as described before on a 20 μmol scale. Modules D, A and B were executed before the reaction vessel was cooled to -30ºC. Module C was performed with building block **31**, followed by module B, D, B, B. Module C was performed again with building block **31** before the resin was subjected twice to module B. The reaction vessel was warmed to room temperature, and module D, A and B were performed to afford the resin-bound disaccharide.

The resin was then charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphere of argon. Grubbs’ catalyst (1st generation, 2 mg) was then added and the flask was put under ethylene atmosphere and stirred overnight. The resin was then washed eight times with DCM. The resulting solution is filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. LCMS-analysis (60% B in A: 2 min; linear gradient to 100% B in A in 10 min; 100% B for 3 min) of the crude cleavage product showed a major product peak for **38** (t_R 14.34 min). The crude product was taken up in THF (2 mL) and treated with TBAF (~ 1 M in THF, 0.2 mL) for 10 min. The reaction mixture was diluted with EtOAc, washed with an aqueous solution of NaCl, dried over Na_2SO_4 and concentrated. LCMS analysis (60% B in A: 2 min; linear gradient to 100% B in A in 10 min) of the crude reaction mixture showed the major product peak for **42-β** (t_R 9.88 min) and a peak for **42-α** (t_R 10.32 min) in a 6.5:1 ratio. Flash silica gel column chromatography (0 to 25% EtOAc in hexanes) gave the pure title compound, the spectroscopic data of which were identical to the data obtained for the same compound, synthesized in solution (*vide supra*).



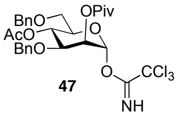
***n*-Pentenyl 3,4-di-*O*-benzyl-6-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-2-deoxy-2-*N*-trichloroacetyl-β-D-glucopyranoside (44):** Resin **19** was prepared as described before on a 25 μmol scale. Resin **19** was subjected to modules A, B, B. The reaction vessel was cooled to -30ºC. Module C was performed twice with building block **31** with two modules B in between. The resin was subjected to module B and G. The reaction vessel was warmed to room temperature, and modules B, H and B were performed to afford resin-bound disaccharide.

The resin was charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphere of argon. Grubbs' catalyst (1st generation, 2 mg) was added and the flask was put under ethylene atmosphere and stirred overnight. The resin was washed eight times with DCM. The resulting solution was filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. The crude residue was then purified by column chromatography to afford compound **43** (16.1 mg, 14.6 μmol, 58% yield from resin **46**) as a mixture of anomers. The mixture was treated with TBAF (1.5 eq. 0.022 mmol, 22 μL, 1.0 M in THF) in THF (0.5 mL) for 15 min. The mixture was washed with saturated $NaHCO_3$, extracted with EtOAc. The solution was dried with Na_2CO_3, filtered and concentrated to afford the title compound **44** after column chromatography using 20-30% EtOAc/hexanes.: ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.50-7.46 (m, 4H), 7.42-7.27 (m, 16H), 7.03 (d, *J*= 7.8, 1H), 5.81-5.67 (m, 1H), 5.53 (s, 1H), 5.06 (d, *J*= 5.8 Hz, 1H), 5.01-4.91 (m, 2H), 4.89-4.64 (m, 5H), 4.58 (d, *J*= 11.5 Hz, 1H), 4.48 (s, 1H) 4.29 (dd, *J*= 4.7 Hz, 10.2 Hz, 1H), 4.24-4.16 (m, 2H), 3.90-3.78 (m, 4H), 3.77-3.62 (m, 3H), 3.59-3.39 (m, 3H), 3.33-3.24 (m, 1H), 2.37 (d, *J*= 8.7 Hz, 1H), 2.10-201 (m, 2H), 1.69-1.58 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 161.8, 138.0, 137.8, 137.7, 137.6, 137.2, 129.1, 128.6, 128.3, 128.3, 128.1, 128.1, 127.9, 126.3, 115.1, 102.6, 102.0, 99.1, 92.5, 79.4, 79.3, 78.6, 78.1, 77.2, 75.6, 75.0, 74.7, 74.6, 70.8, 69.2, 68.5, 67.1, 58.2, 30.0, 28.7; $[\alpha]_D$ -20.0 (*c* = 0.20) ; IR, ν = 3307, 2923, 1688, 1527, 1453, 1361 cm^{-1}; HR-MS *m/z*: 934.2494 (calculated for $C_{47}H_{52}Cl_3NNaO_{11}^+$ 934.2498).

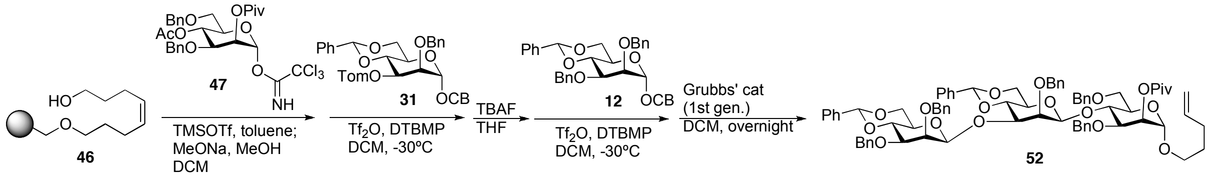


***n*-Pentenyl 3,4,6-tri-*O*-benzyl-2-*O*-[3,4,6-tri-*O*-benzyl-2-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (45):** Resin **21** was prepared as described before on a 24 μmol scale. Resin **21** was subjected to modules A, B, B. The reaction vessel was cooled to -30ºC. Module C was performed twice with building block **31** with four modules B in between. The resin was subjected twice to module B. The reaction vessel was warmed to room temperature, and module D, A, E, D, F, D, I, D, A, B and B were performed to afford resin-bound trisaccharide.

The resin was charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphere of argon. Grubbs' catalyst (1st generation, 2 mg) was added and the flask was put under ethylene atmosphere and stirred overnight. The resin was washed eight times with DCM. The resulting solution is filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. The crude residue was purified by column chromatography to afford compound **45** (12.7 mg, 9.8 μmol, 40% yield from resin **46**) as a pure anomer. ^{1}H-NMR δ 1.69 (m, 2H), 2.04 (m, 2H), 2.30 (d, 1H, J = 9.6 Hz), 3.01 (m, 1H), 3.29 (m, 1H), 3.43 (m, 1H), 3.57-3.95 (m, 13H), 4.13-4.24 (m, 4H), 4.37-4.77 (m, 13H), 4.86-5.13 (m, 6H), 5.46 (s, 1H), 5.77 (m, 1H), 7.06-7.44 (m, 40H); ^{13}C-NMR, (CDCl$_3$, 75 MHz) δ 138.6, 138.3, 138.2, 138.1, 137.9, 137.2, 128.9, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 126.2, 114.8, 102.0, 100.1, 99.8, 98.9, 80.3, 79.2, 78.4, 77.8, 77.2, 75.6, 75.2, 75.0, 74.7, 74.5, 74.4, 73.8, 73.5, 73.2, 72.9, 71.7, 71.6, 71.3, 70.3, 69.2, 68.5, 67.0, 66.7, 30.3, 28.7; $[\alpha]_D$ -11.4 (c = 0.5); IR, ν = 2929, 1454, 1093 cm^{-1}; HR-MS *m/z*: 1313.585 (calculated for $C_{79}H_{86}O_{16}$ + Na$^+$ 1313.581).


47

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-*O*-pivaloyl-α-D-mannopyranosyl trichloroacetimidate (47). ^{1}H-NMR δ 1.23 (s, 9H), 1.95 (s, 3H), 3.60 (d, 2H, J = 3.9 Hz), 3.93 (dd, 1H, J = 3.3 Hz, J = 9.9 Hz), 4.06 (m, 1H), 4.43 (d, 1H, J = 12.0 Hz), 4.52 (m, 2H), 4.65 (d, 1H, J = 12.0 Hz), 5.41 (t, 1H, J = 10.2 Hz), 5.49 (m, 1H), 6.27 (d, 1H, J = 1.8 Hz), 7.24-7.33 (m, 10H), 8.72 (s, 1H); ^{13}C-NMR δ 21.0, 27.3, 39.2, 66.51, 67.6, 69.3, 71.5, 73.0, 90.9, 95.3, 127.7, 127.9, 128.0, 128.4, 128.5, 137.6, 138.1, 160.0, 169.8, 177.7; IR, ν = 2974, 1735, 1676, 1147 cm^{-1}; $[\alpha]_D$ +26.0 (c = 1.0); HR-MS (calculated for $C_{29}H_{34}Cl_3NO_8$ + Na^+ 652.1248).



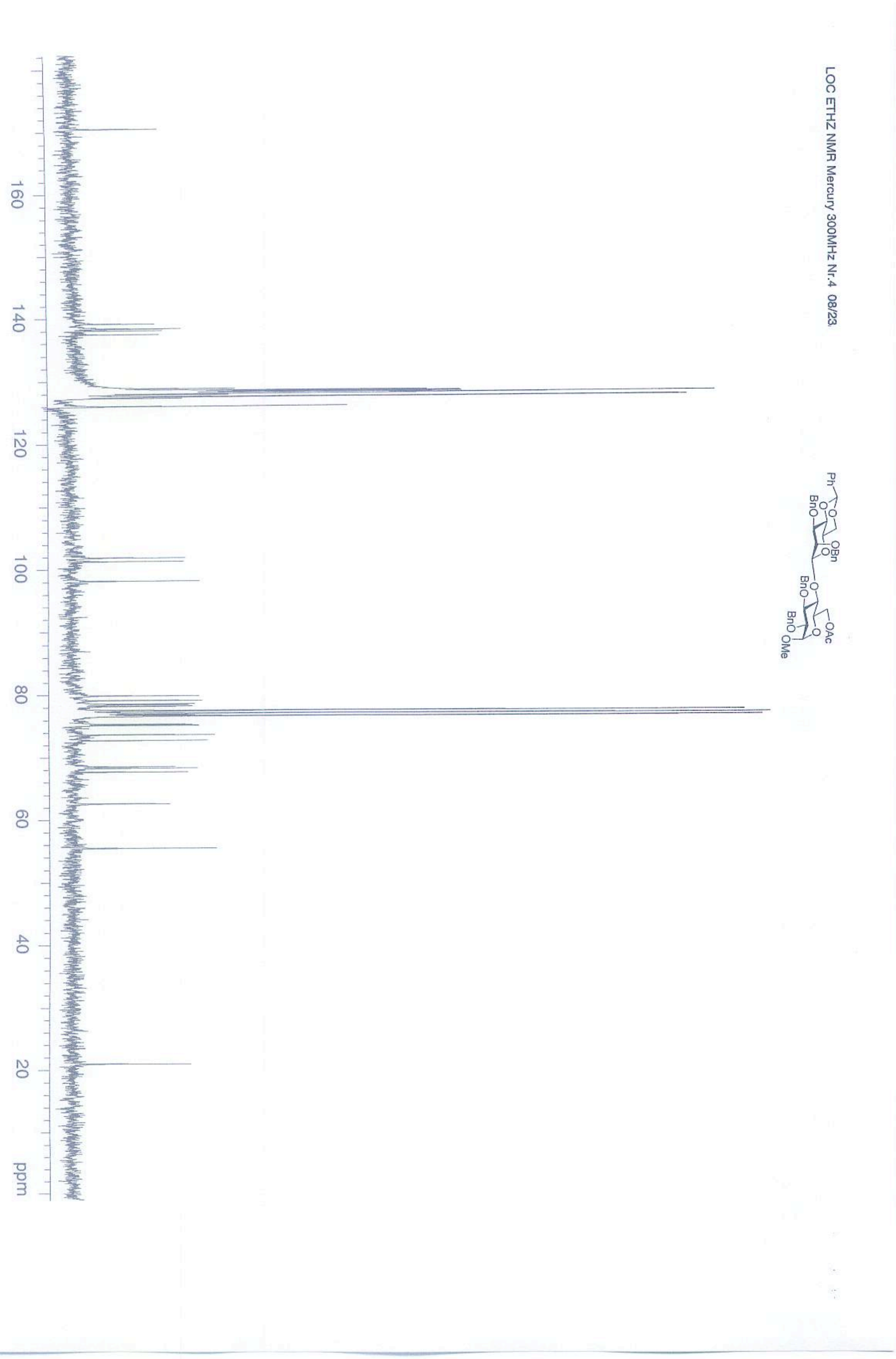
***n*-Pentenyl 3,6-di-*O*-benzyl-4-*O*-[2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-β-D-mannopyranosyl]-2-*O*-pivaloyl-α-D-mannopyranoside (52):** Resin **46** (0.22 mmol/g, 113 mg, 0.025 mmol) was loaded in the reaction vessel of the synthesizer. Modules D, A, B were performed. Then, the resin was glycosylated twice with building block **47** (4.5 eq., 0.112 mmol) in toluene (2 mL) and TMSOTf (0.5 eq., 0.012 mmol in 0.5 mL DCM) for 15 min with one module B in between. Modules B, D, B, were performed. The acetate protecting group was removed by treating the resin twice with MeONa (10 eq., 0.25 mmol) in MeOH (0.4 mL) and DCM (3.5 mL) for 30 min. Modules E, D, I, D, A, B, D, A and B were executed. The reaction vessel was cooled to -30ºC. Module C was then performed twice with building block **31** with 2 modules B in between. The resin was subjected to module B and G. The reaction vessel was warmed to room temperature, and modules B, H, and B were performed. The resin was then treated twice manually with TBAF (5 eq., 0.125 mmol) in 1.5 mL THF for 20 min each, before washing with THF and DCM several times.

The resin was charged in the synthesizer reaction vessel. Module D, A and B were performed. The reaction vessel was then cooled to -30ºC. Module C was performed twice with building block **12** with two modules B in between. The resin was subjected to module B and G. The reaction vessel was warmed to room temperature, and modules B, H, and B were performed.

The resin was charged in a 10 mL round-bottom flask and swelled with 2 mL DCM under an atmosphere of argon. Grubbs' catalyst (1st generation, 2 mg) was added and the flask was put under ethylene atmosphere and stirred overnight. The resin was washed eight times with DCM. The resulting solution was filtered through a pipet column with 3 cm silica, eluting with ethyl acetate. The eluted solution was concentrated under vacuum. The crude residue was purified by column chromatography to afford the title compound **52** (16 mg, 12.5 μmol, 50% yield from resin **46**) as a mixture of anomers. Anomerically pure **52** was obtained by preparative HPLC. The spectroscopic data of this compound was in perfect agreements with the compound prepared in solution.

References

1. Codée, J. D. C.; Hossain, L. H. Seeberger, P. H. *Org. Lett.* **2005**, *7*, 3251.
2. Kim, K. S.; Kim, J. H.; Lee, Y. J.; Lee, Y. J.; Park, J. *J. Am. Chem. Soc.* **2001**, *123*, 8477.
3. Pitsch, S.; Weiss, P. A.; Jenny, L.; Stutz, A.; Wu, X. *Helv. Chim. Acta* **2001**, *84*, 3773.
4. Kim, K. S.; Kim, J. H.; Lee, Y. J.; Lee, Y. J.; Park, J. *J. Am. Chem. Soc.* **2001**, *123*, 8477.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OBn
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BnO
O
OAc
BnO
OMe
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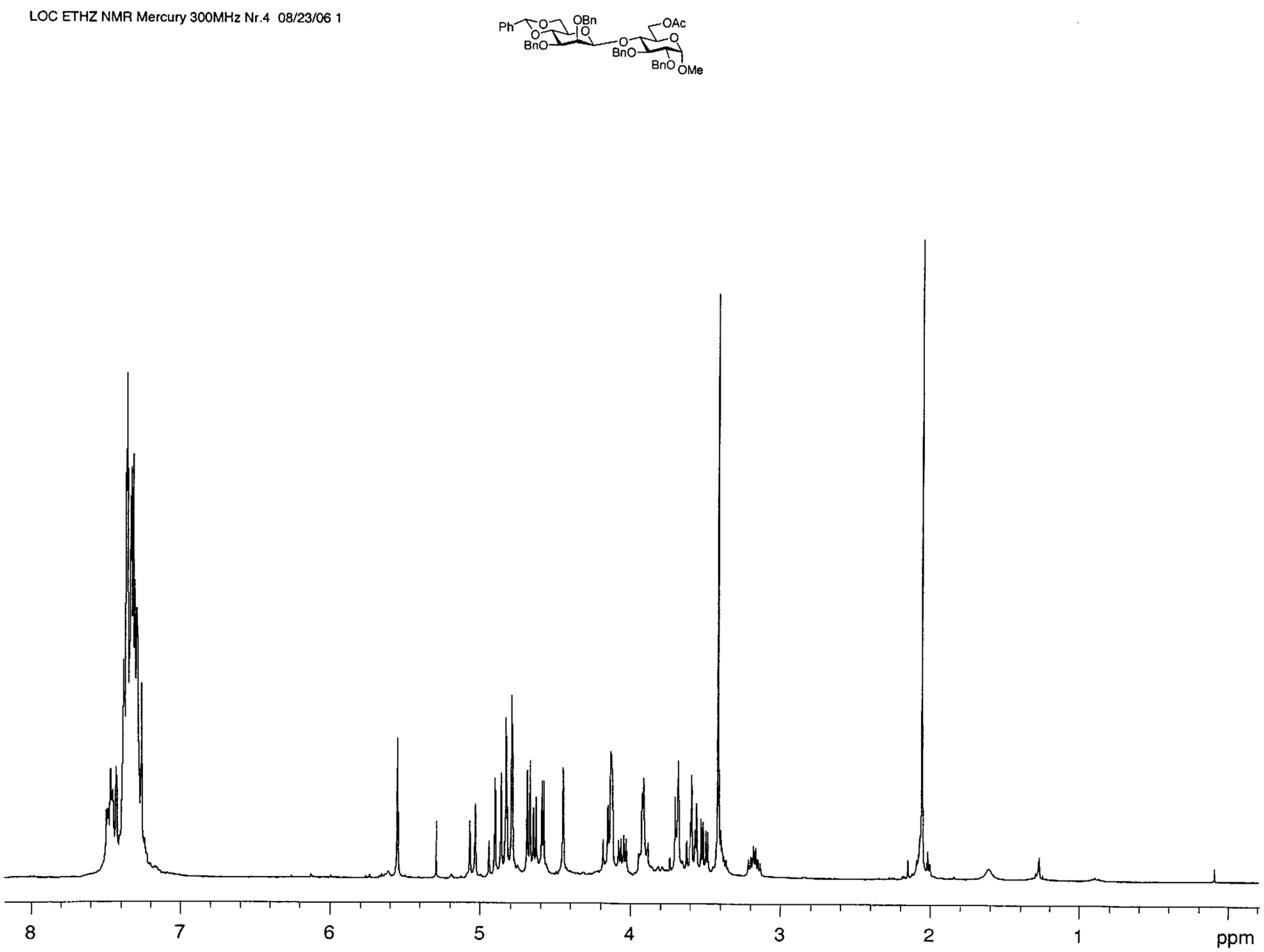
80
60
40
20
ppm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OBn
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BnO
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OAc
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BnO
OMe
8
7
6
5
4
3
2
1
ppm

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EXPNO                 1
PROCNO                1

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SOLVENT           CDCl3
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FIDRES         0.100003 Hz
AQ            4.9999123 sec
RG                  114
DW               62.400 usec
DE                30.00 usec
TE                298.0 K
D1           0.03000000 sec

============ CHANNEL f1 =============
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PL1               -1.00 dB
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F2 - Processing parameters
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SSB                   0
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GB                    0
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1D NMR plot parameters
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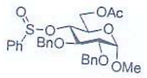

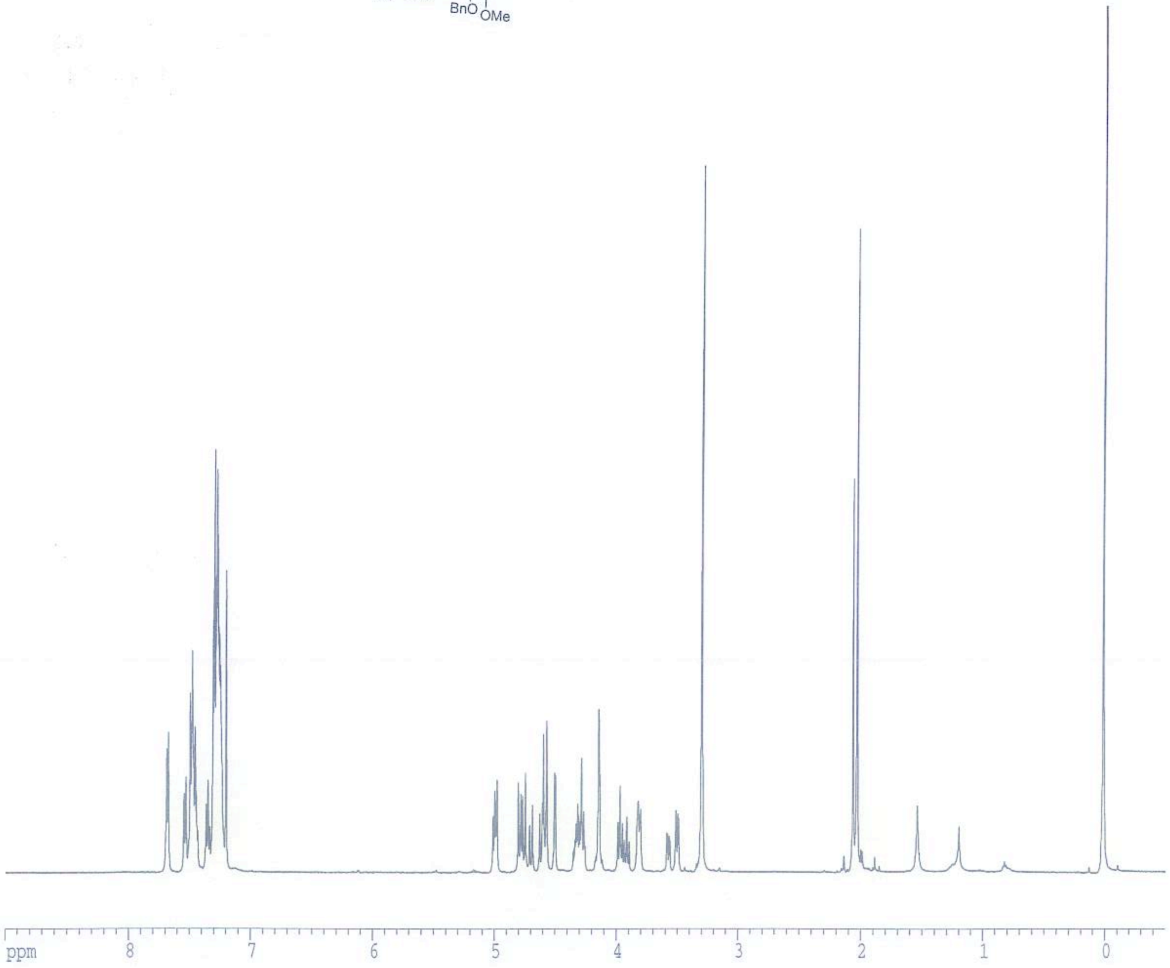

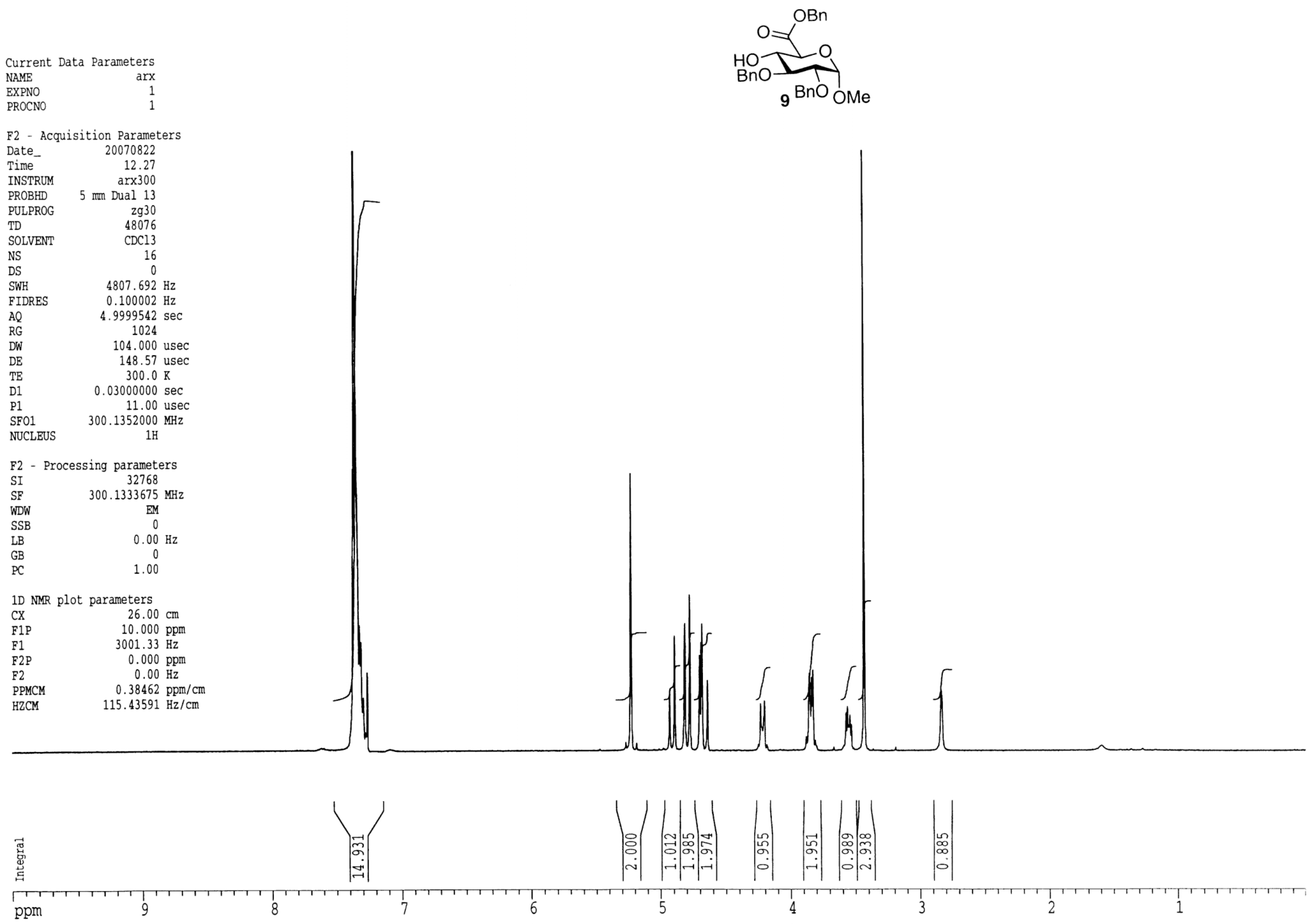

9

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PROCNO 1

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NS 16
DS 0
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FIDRES 0.100002 Hz
AQ 4.9999542 sec
RG 1024
DW 104.000 usec
DE 148.57 usec
TE 300.0 K
D1 0.03000000 sec
P1 11.00 usec
SFO1 300.1352000 MHz
NUCLEUS 1H

F2 - Processing parameters
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WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
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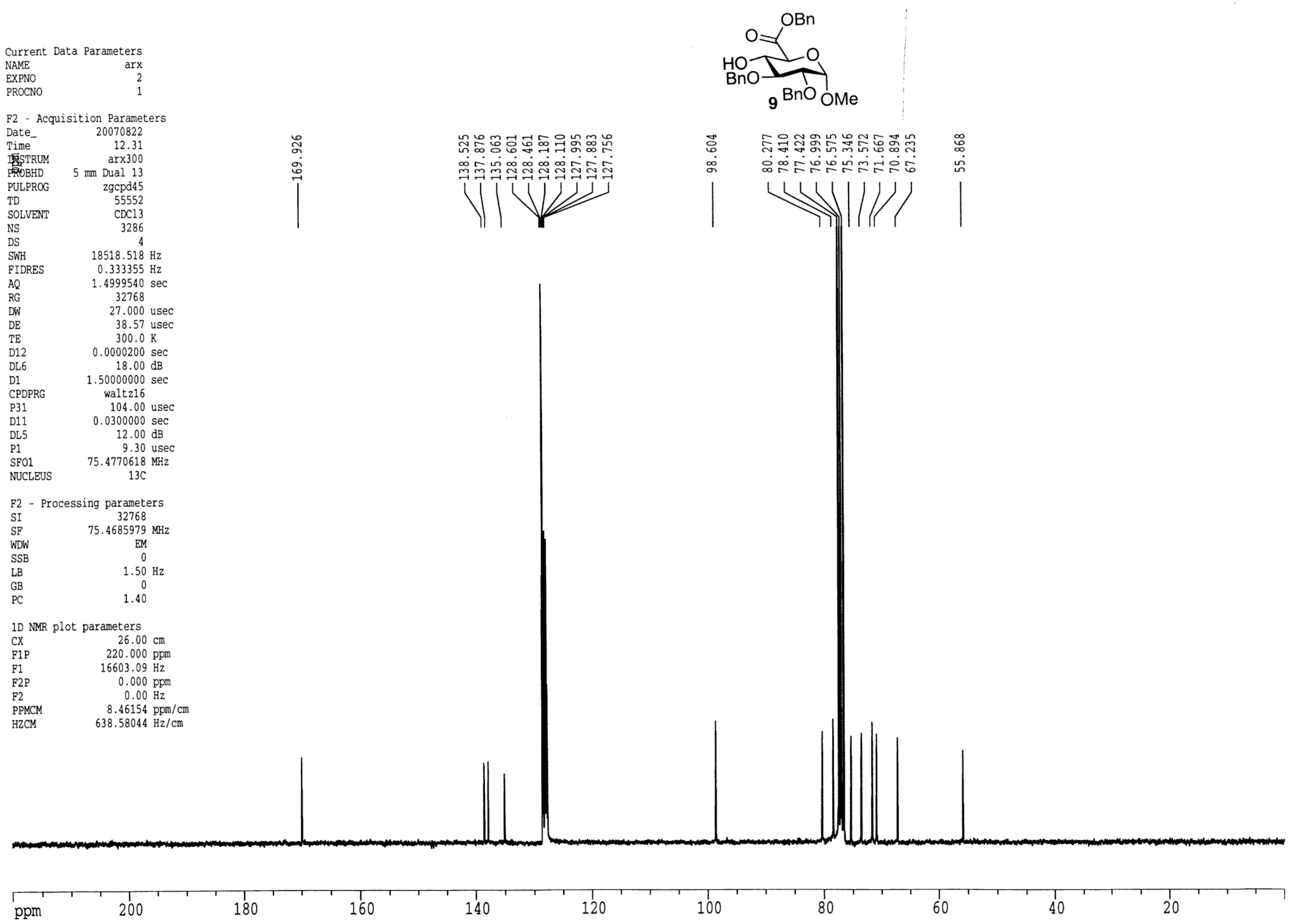

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PROCNO                1

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RG                32768
DW               27.000 usec
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TE                300.0 K
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DL6               18.00 dB
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CPDPRG          waltz16
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NUCLEUS             13C

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1D NMR plot parameters
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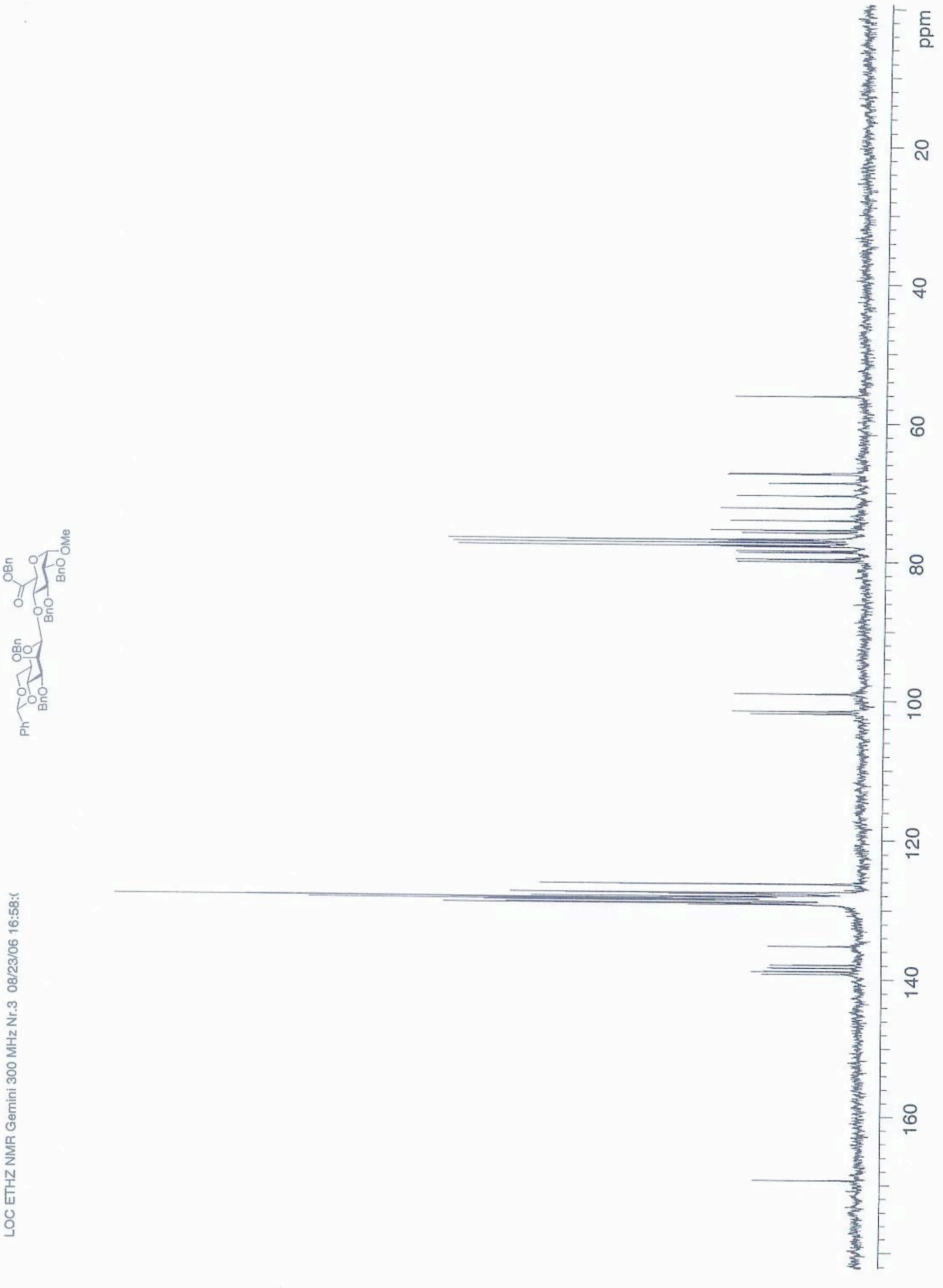

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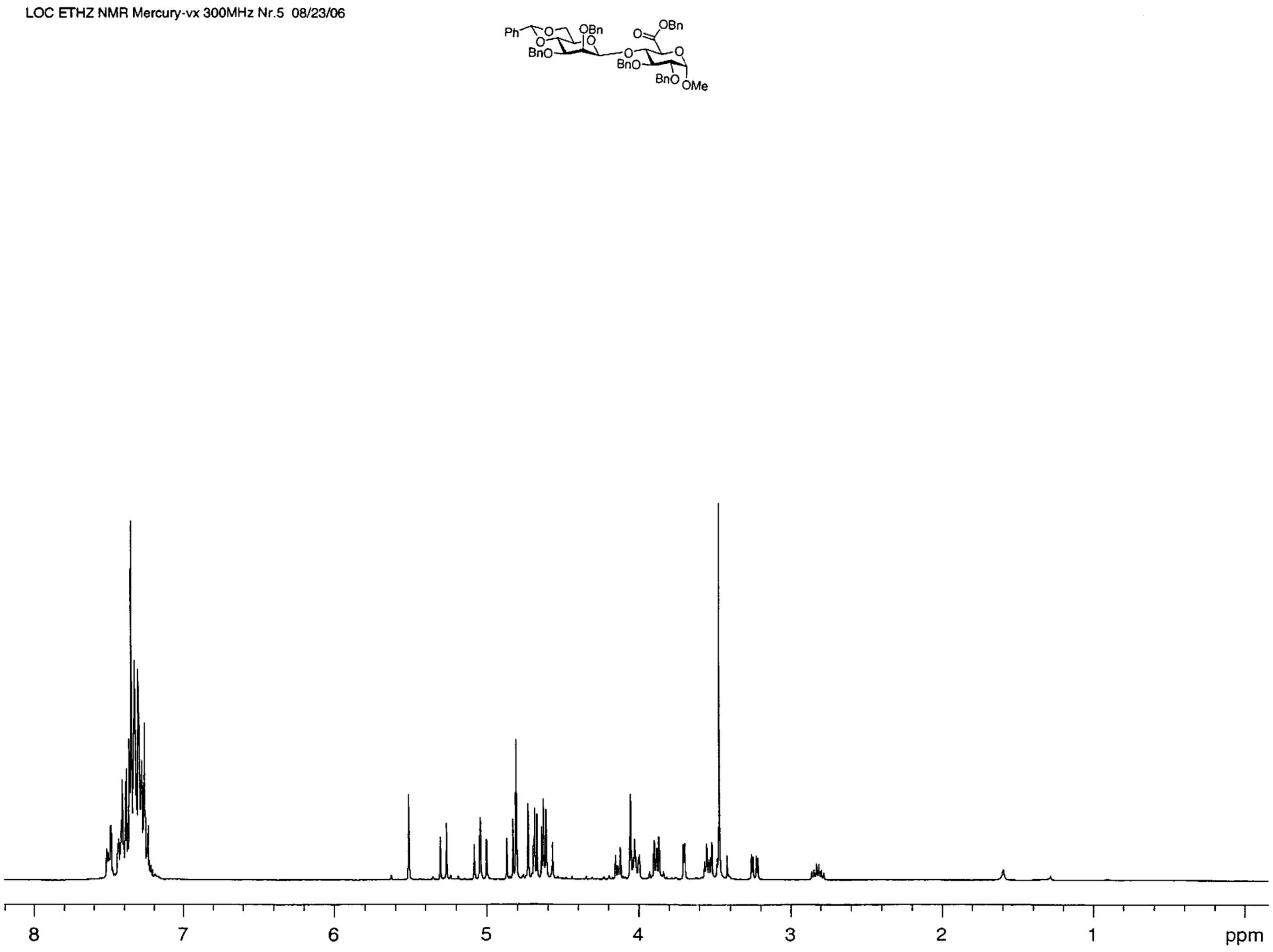
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BnO
BnO
OBn
OMe
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7
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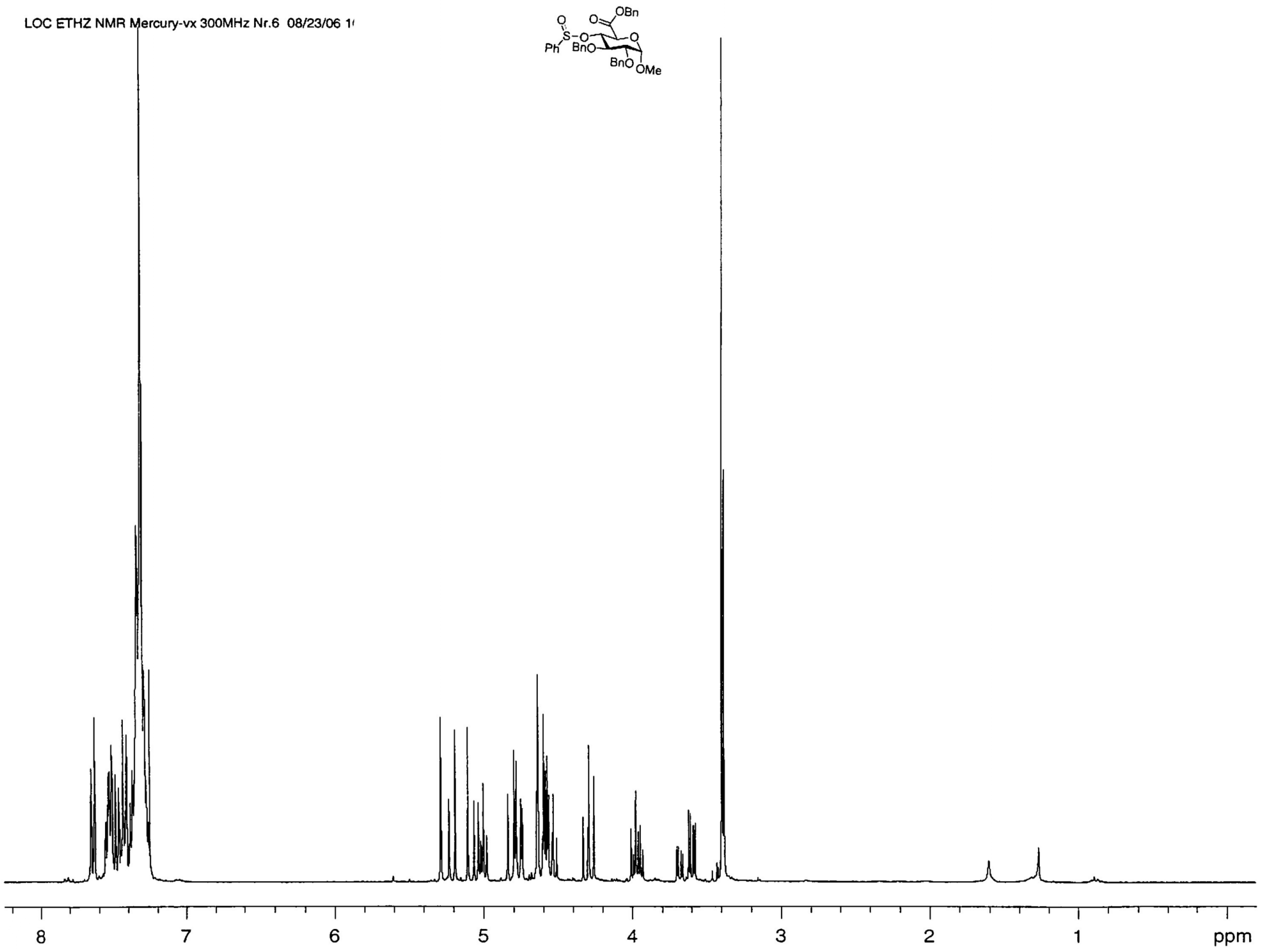
5
4
3
2
1
ppm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S
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Ph
BnO
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BnO
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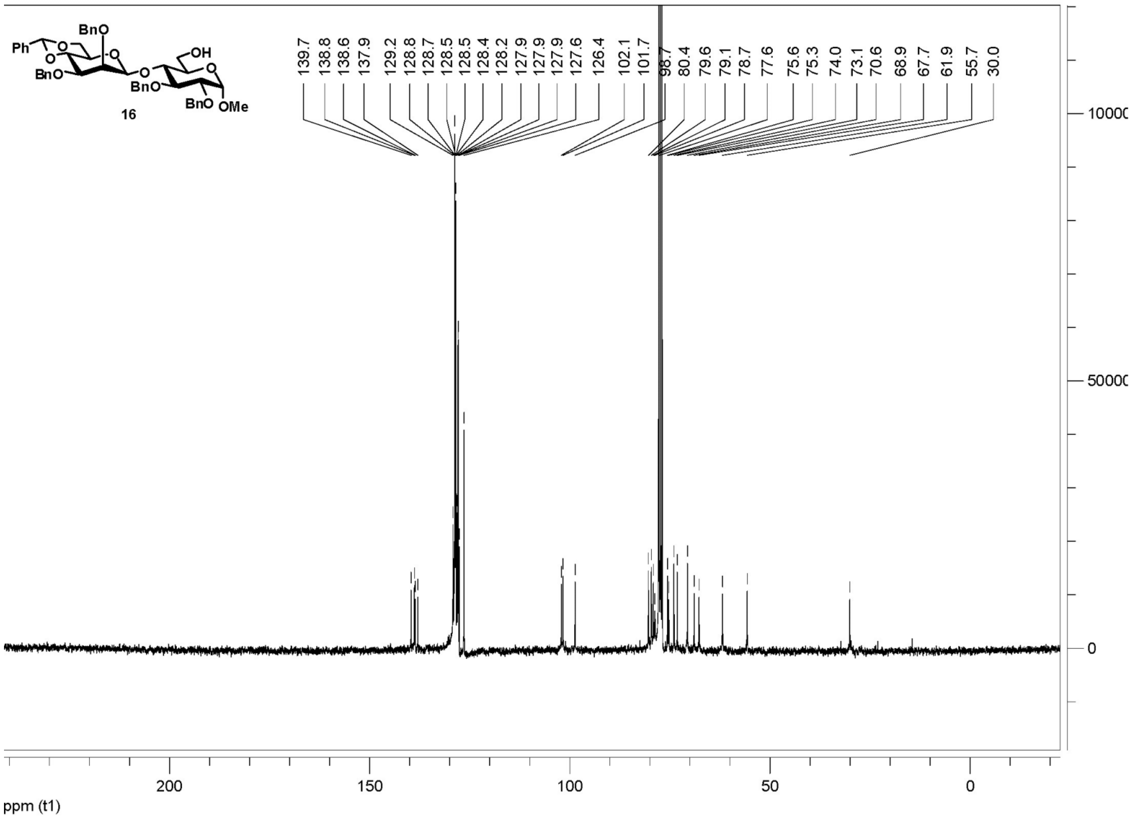
ppm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77.6
75.6
75.3
74.0
73.1
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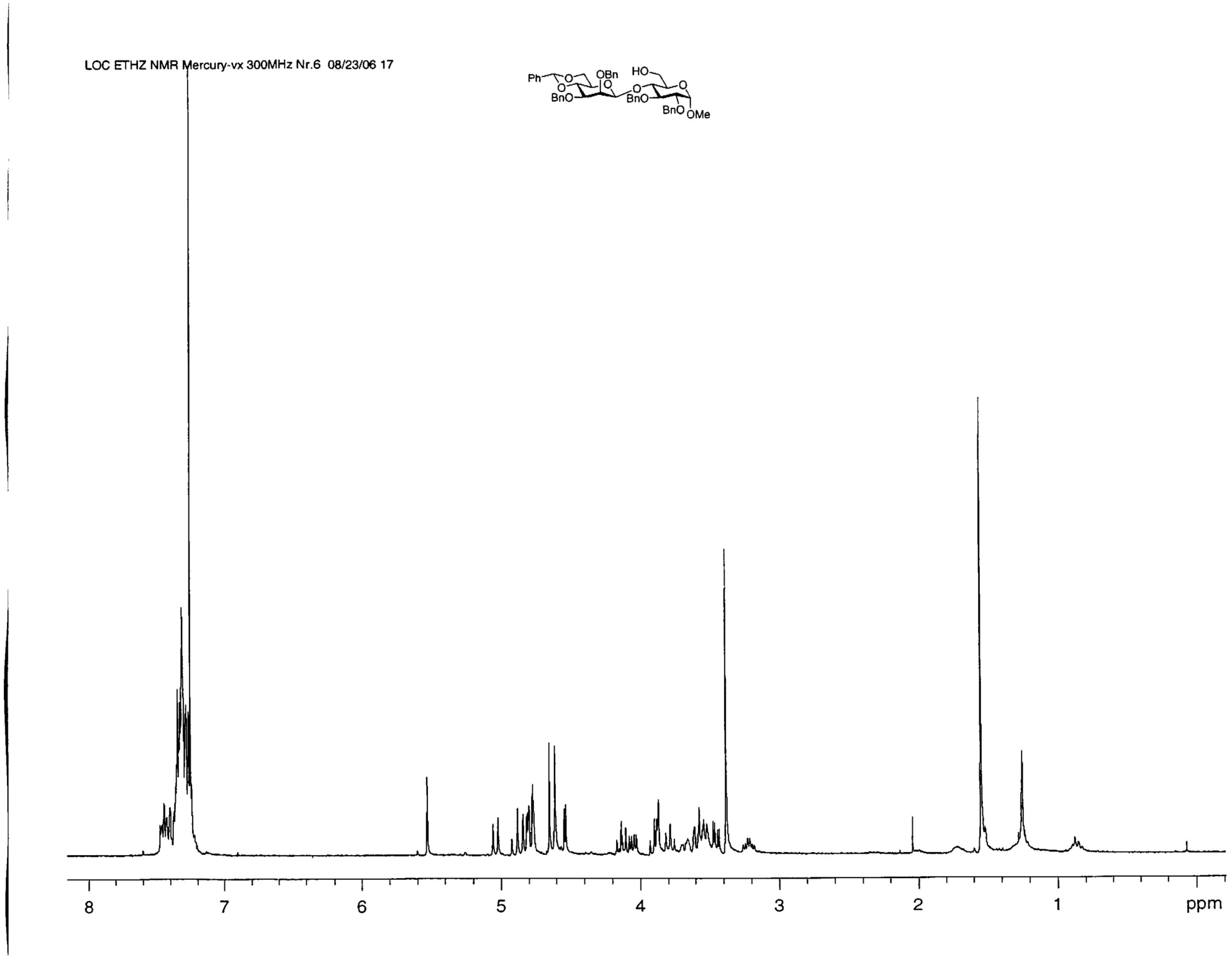
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OMe
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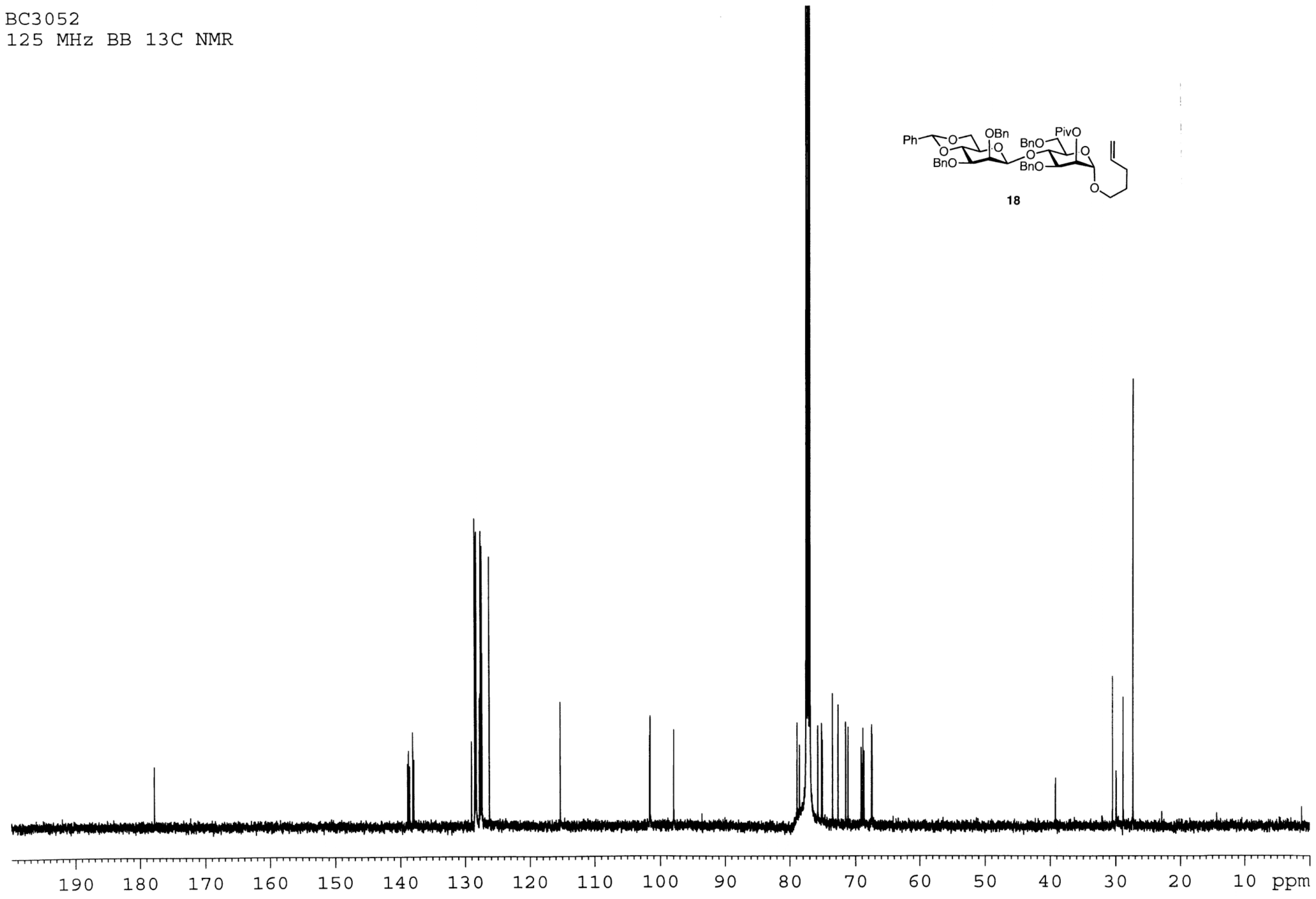
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PivO
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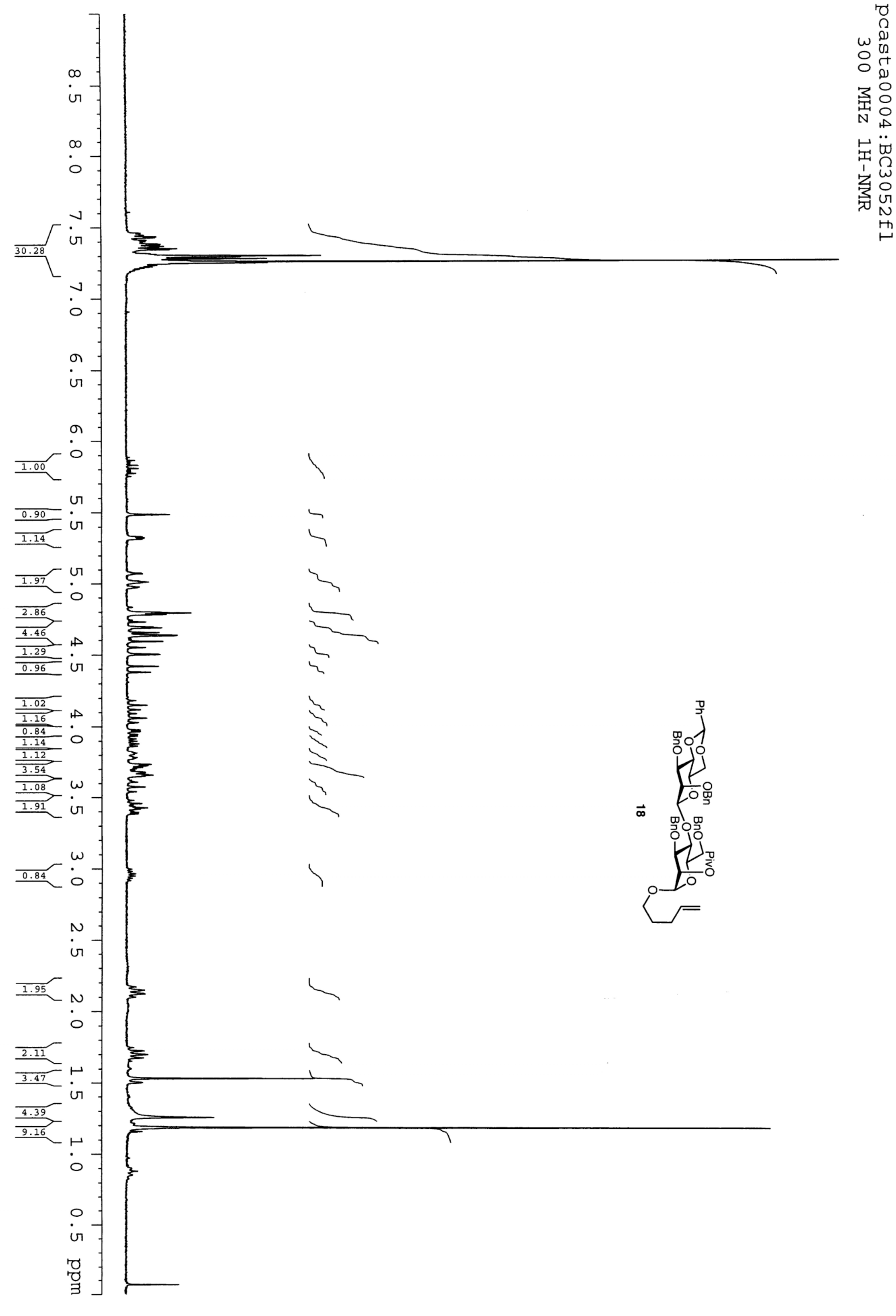
ppm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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.00
0.90
1.14
1.97
2.86
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1.29
0.96
1.02
1.16
0.84
1.14
1.12
3.54
1.08
1.91
0.84
1.95
2.11
3.47
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BnO
BnO
OBn
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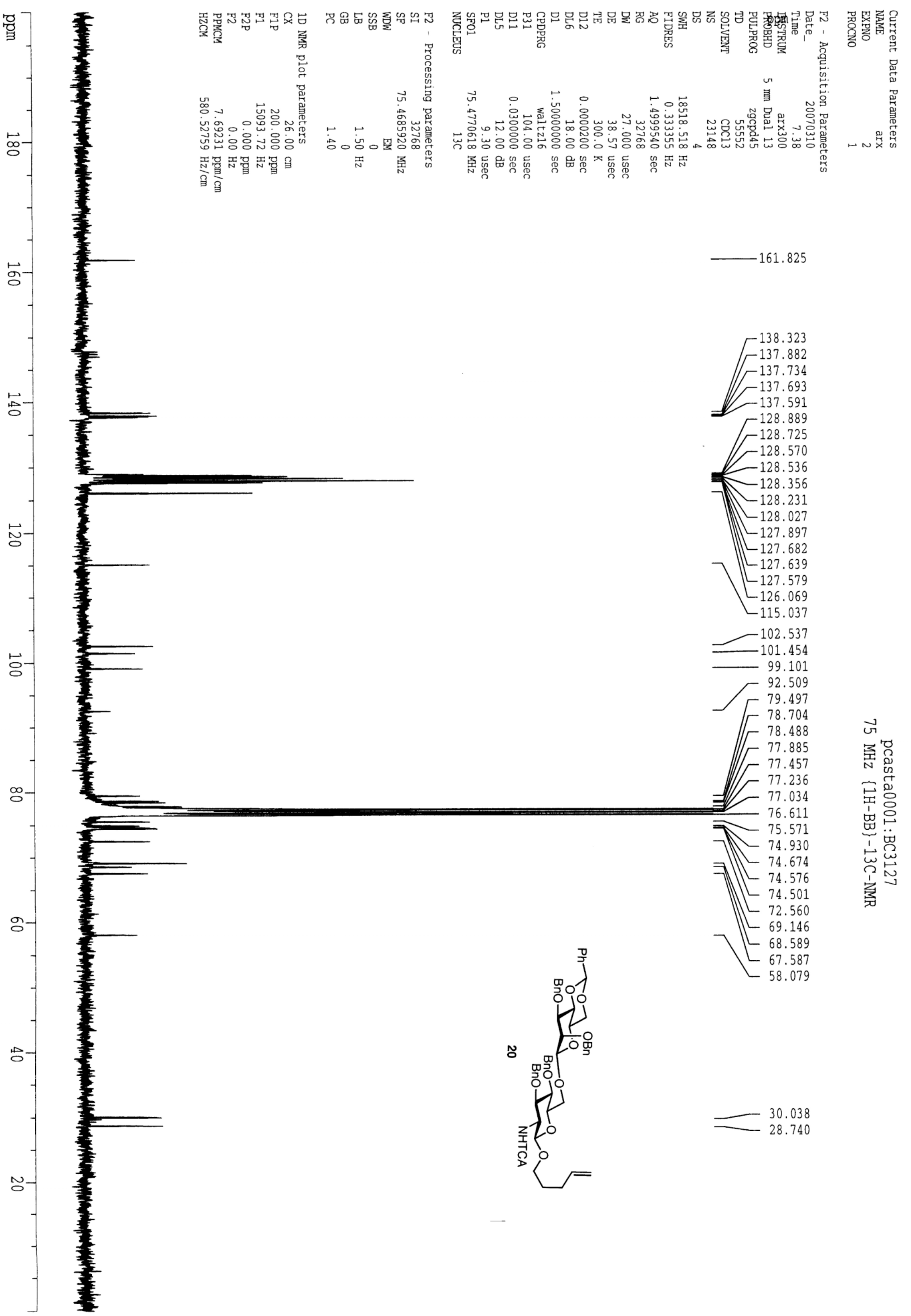
BnO
BnO
O
PivO
O
O
18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CPDPRG waltz16
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58.079
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28.740
Ph
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BnO
OBn
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BnO
BnO
O
O
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ppm
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40
20

pcasta0001:BC3127
300 MHz 1H-NMR

20

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PROCNO                 1

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RG                  5700
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NUCLEUS               1H

F2 - Processing parameters
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WDW                   EM
SSB                    0
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GB                     0
PC                  1.00

1D NMR plot parameters
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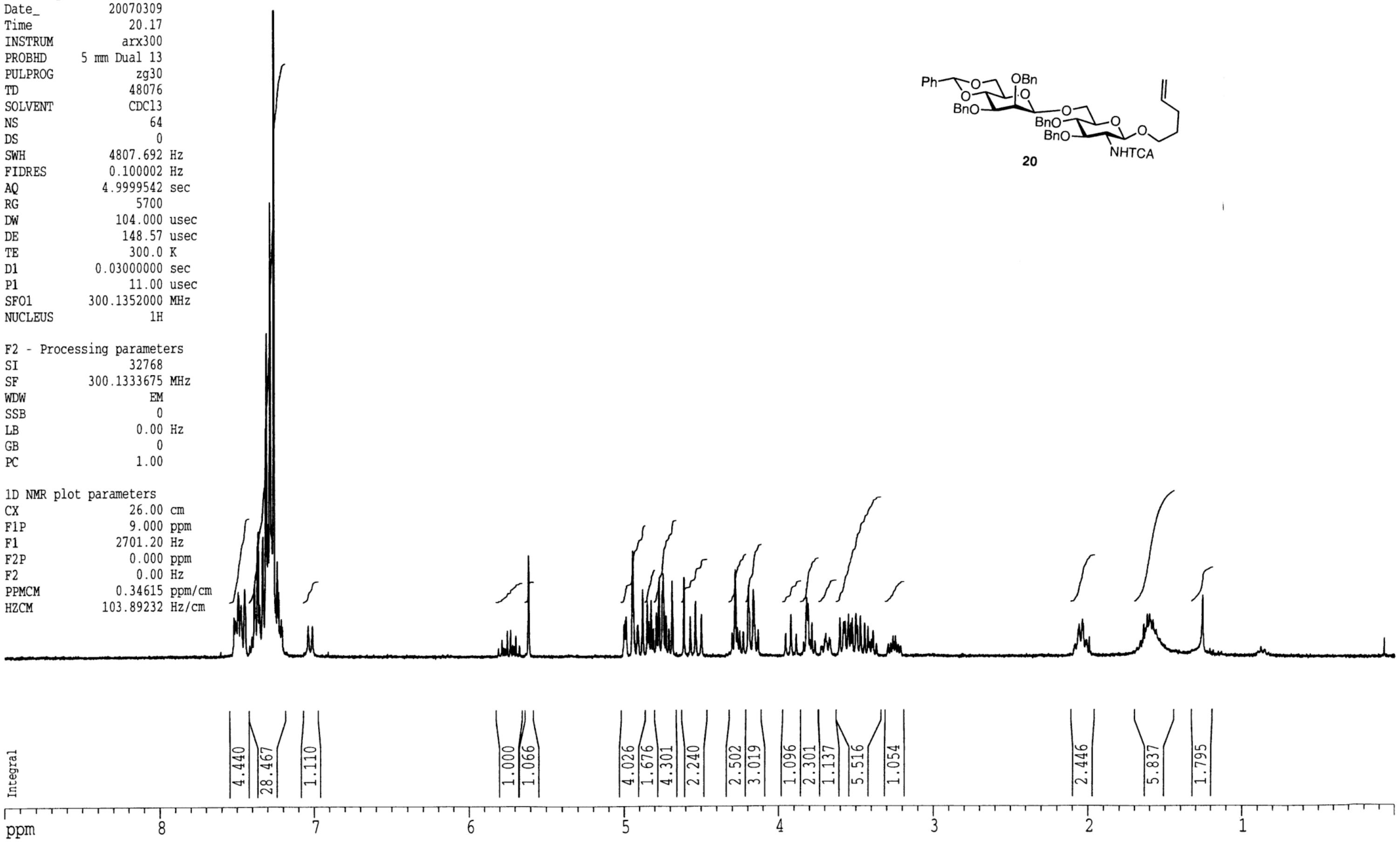

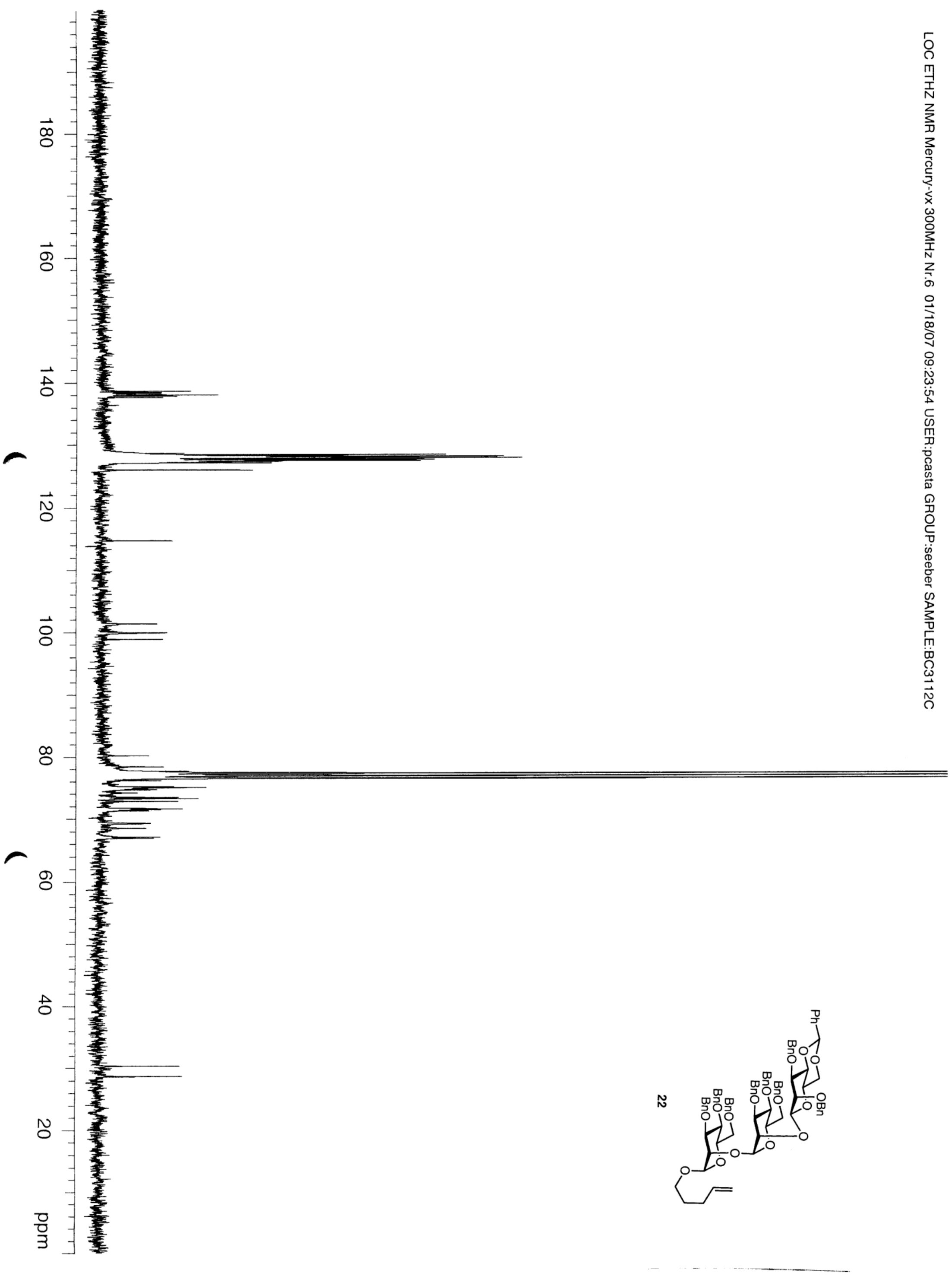
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ppm
Ph
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BnO
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BnO
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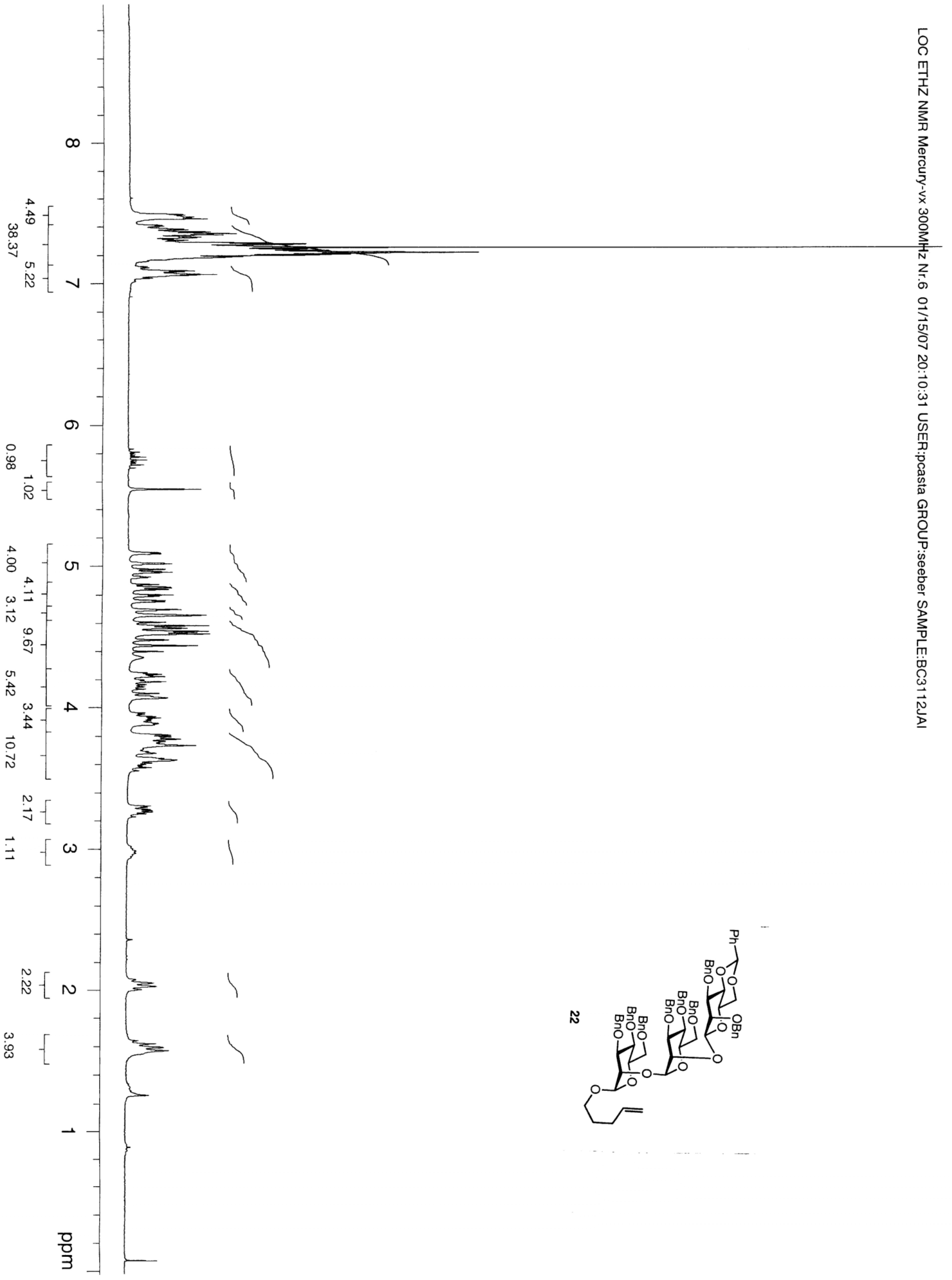
BnO
O
O

22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22
Ph
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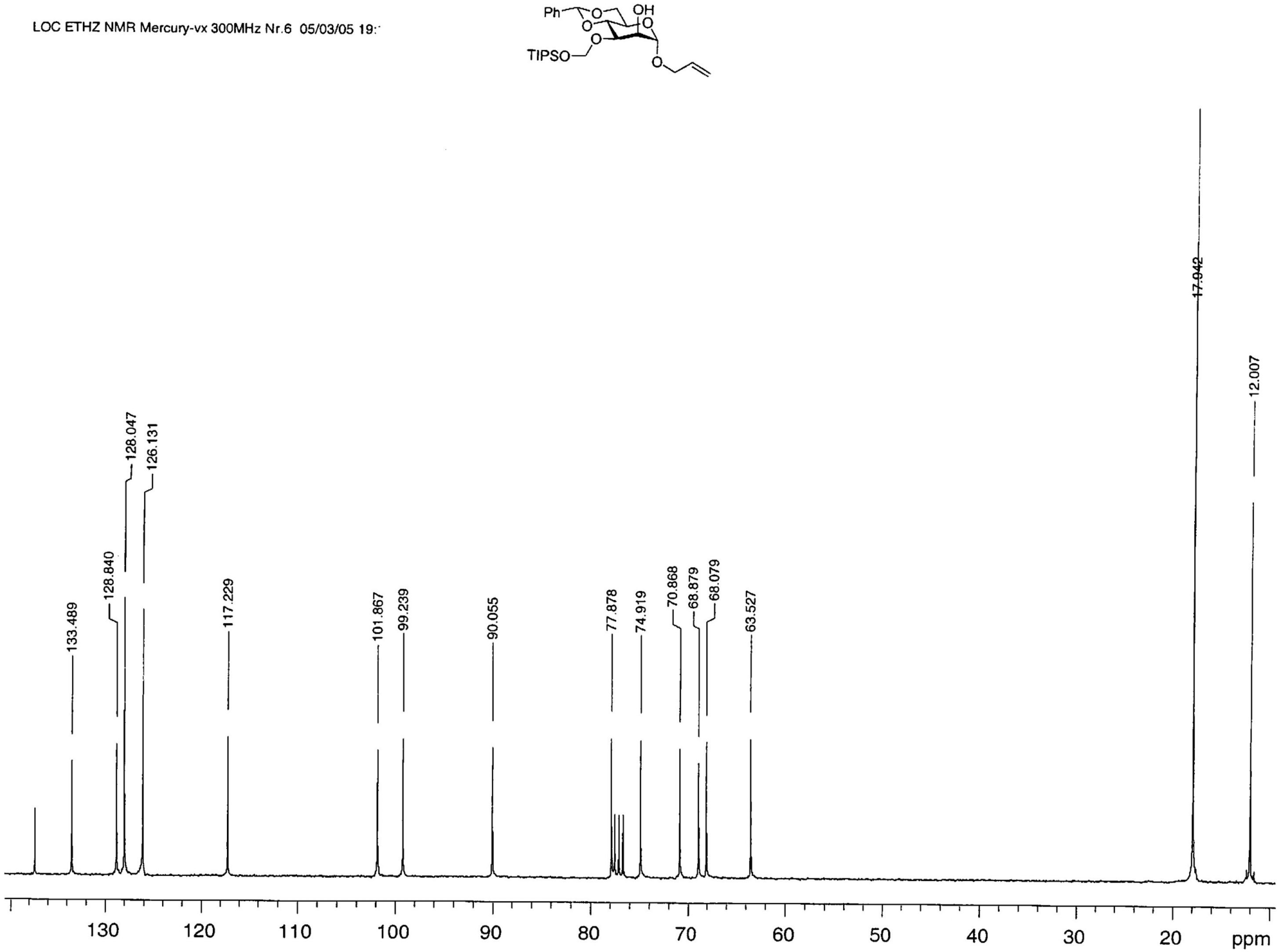
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74.919
70.868
68.879
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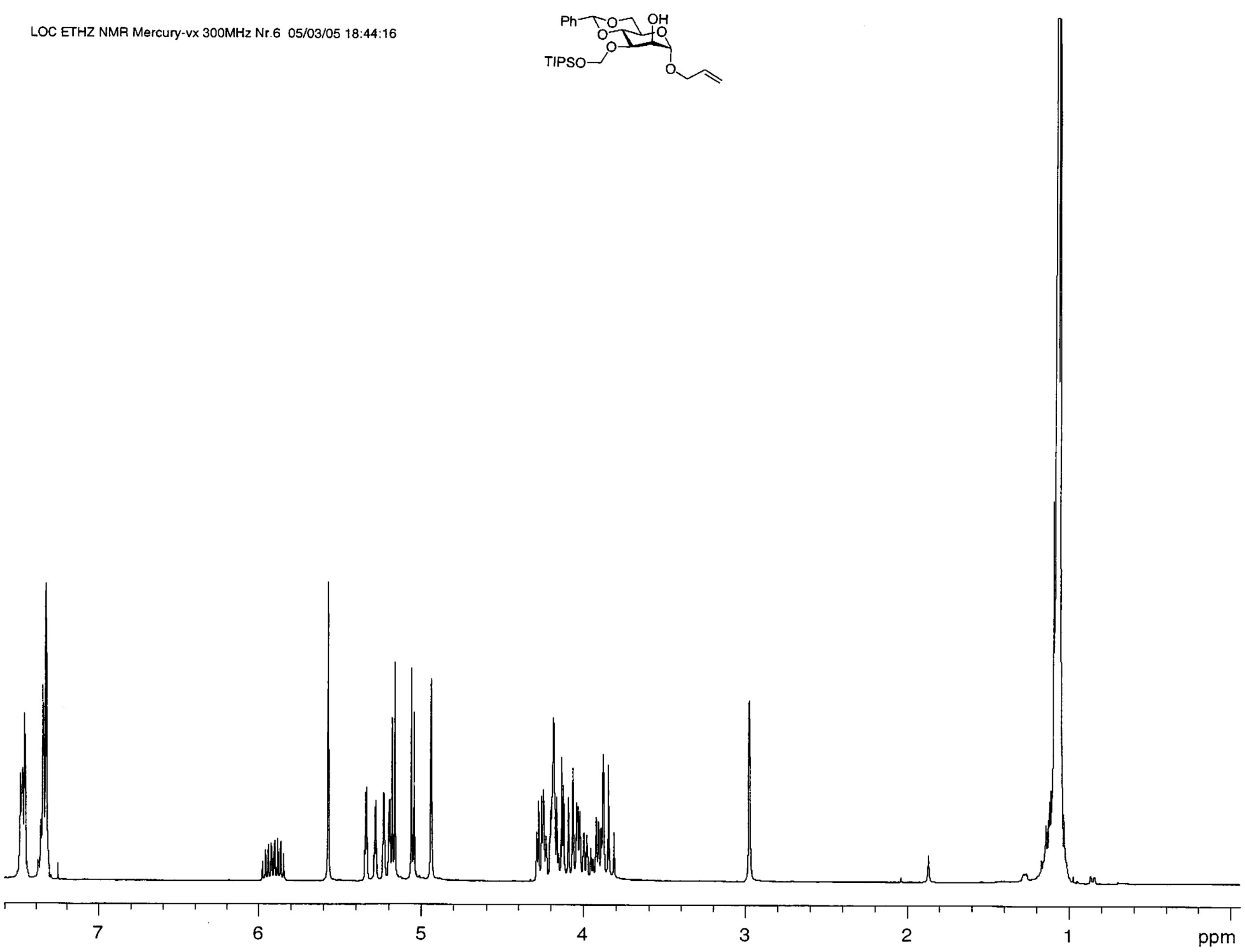
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4
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2
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ppm

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 05/04/05 18:38:33 L

STANDARD 1H OBSERVE

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Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
User: pcodee
Mercury-300BB "gem5oc"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 299.7729185 MHz
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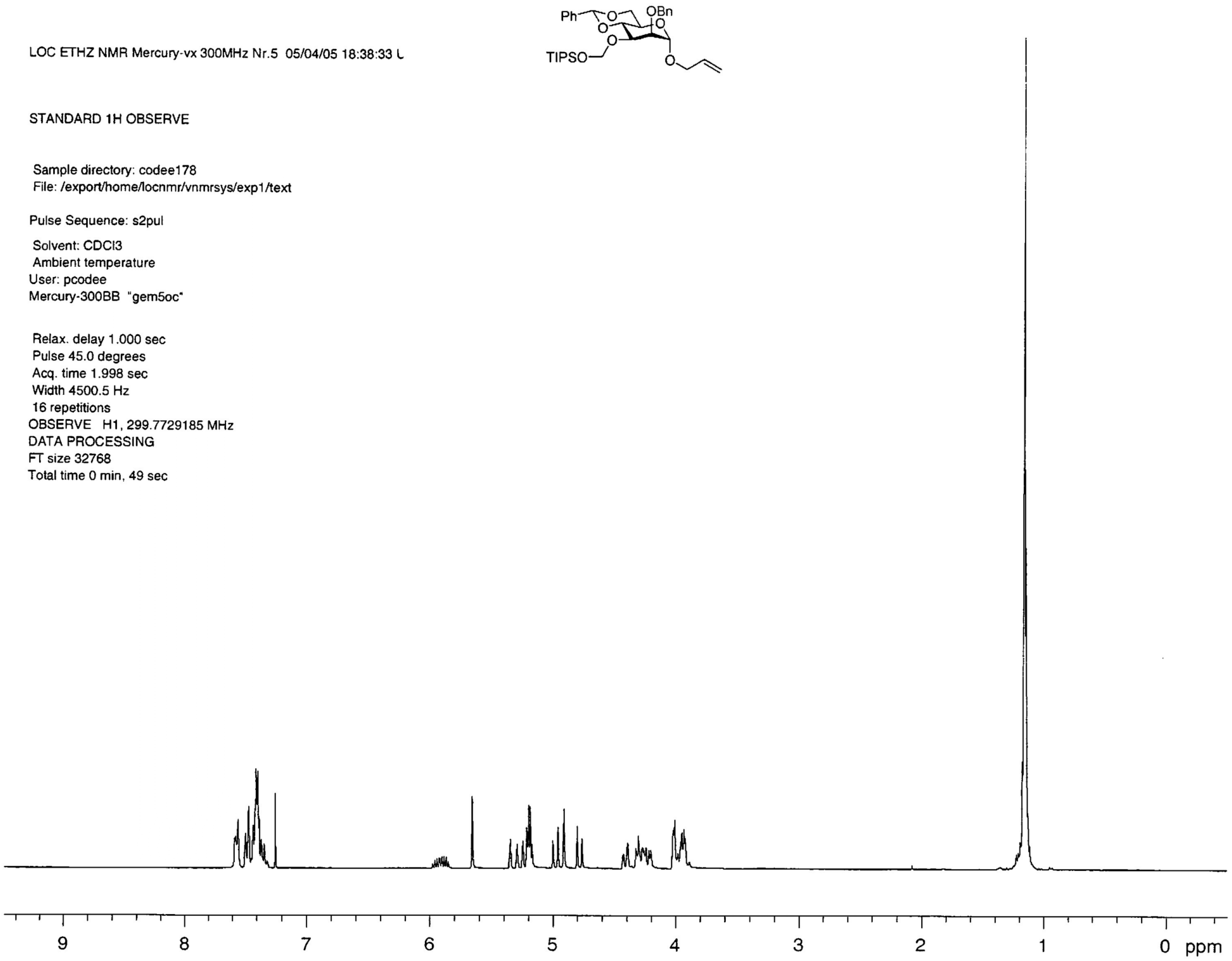
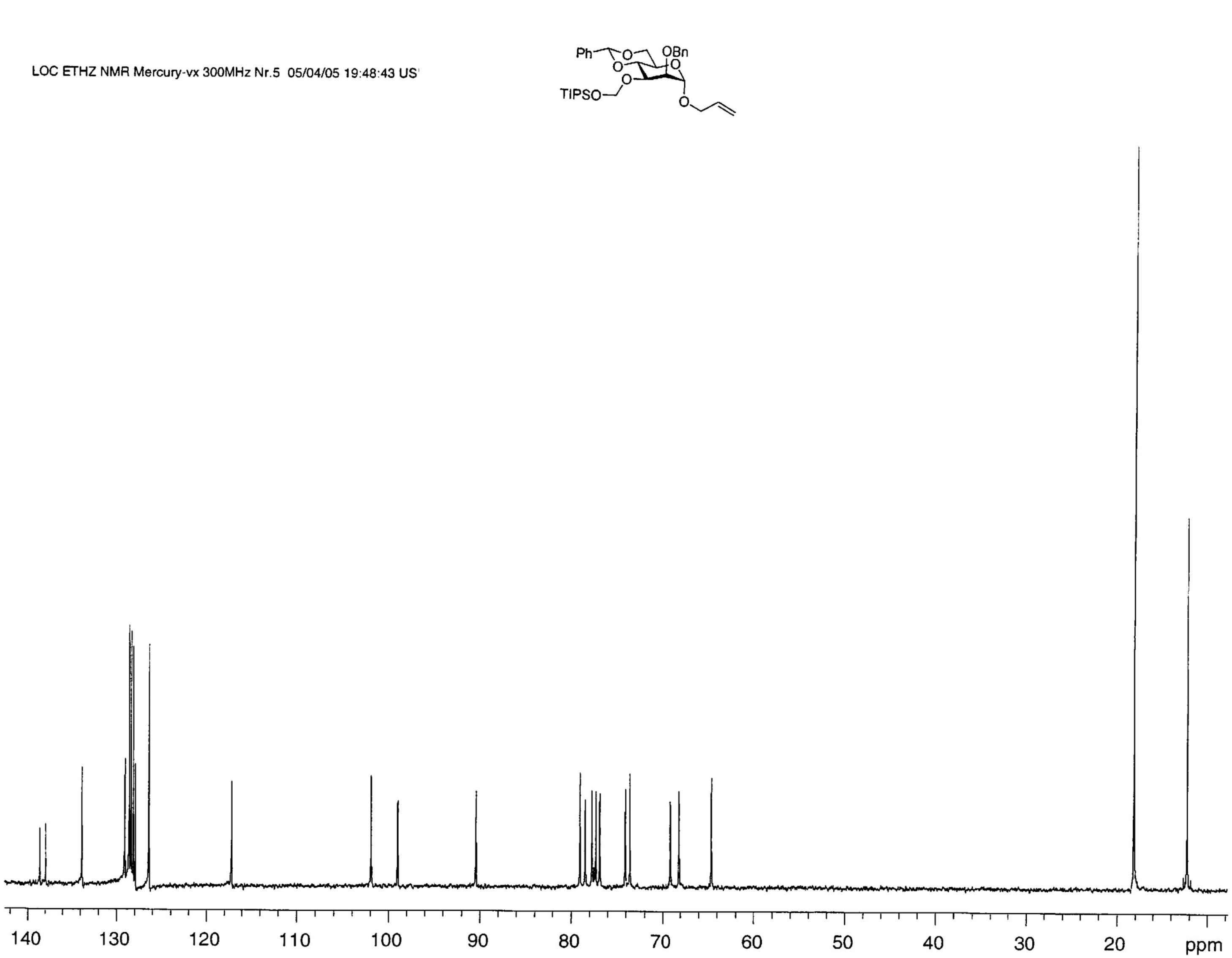
FT size 32768
Total time 0 min, 49 sec

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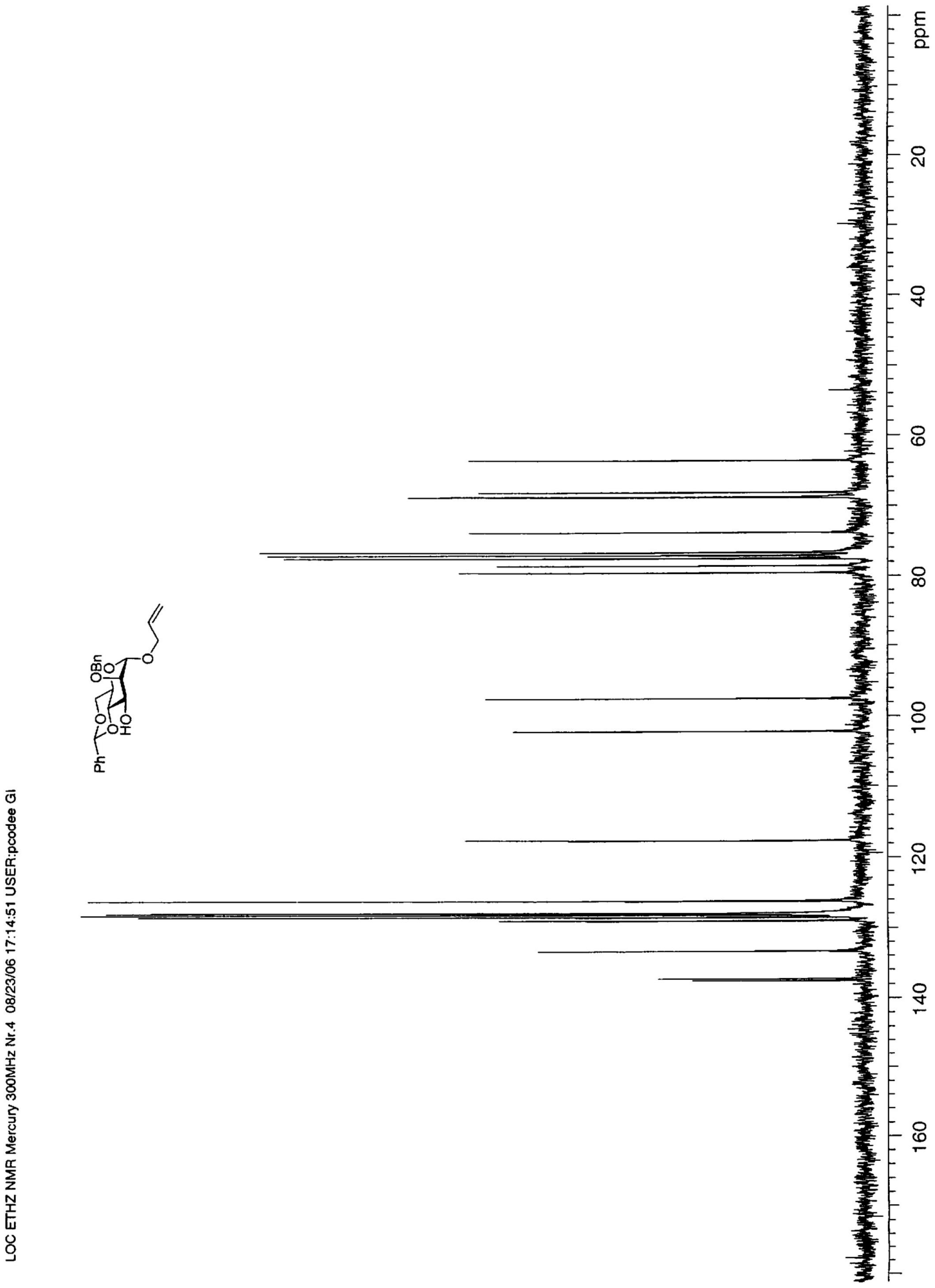
ppm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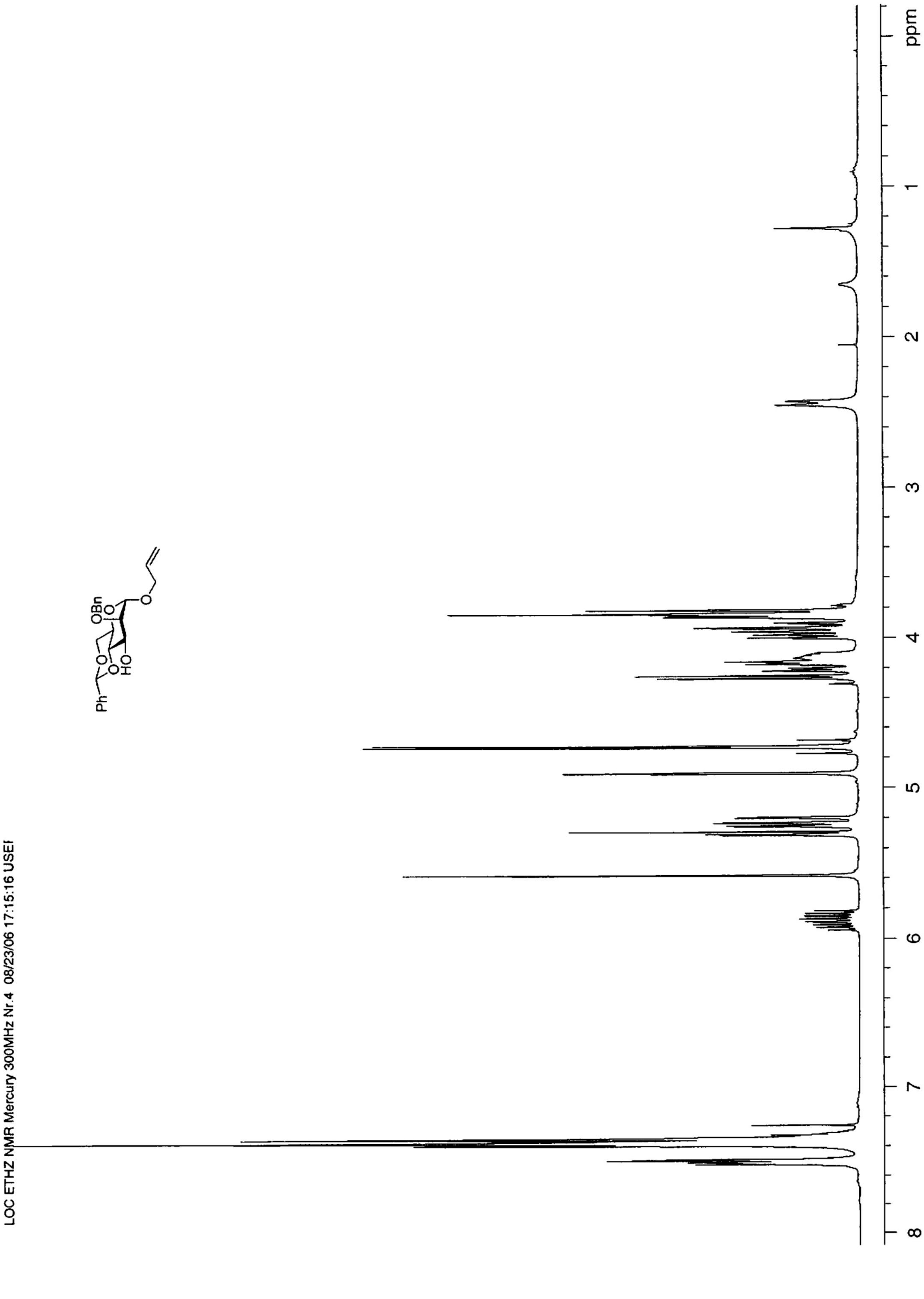
20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Ph
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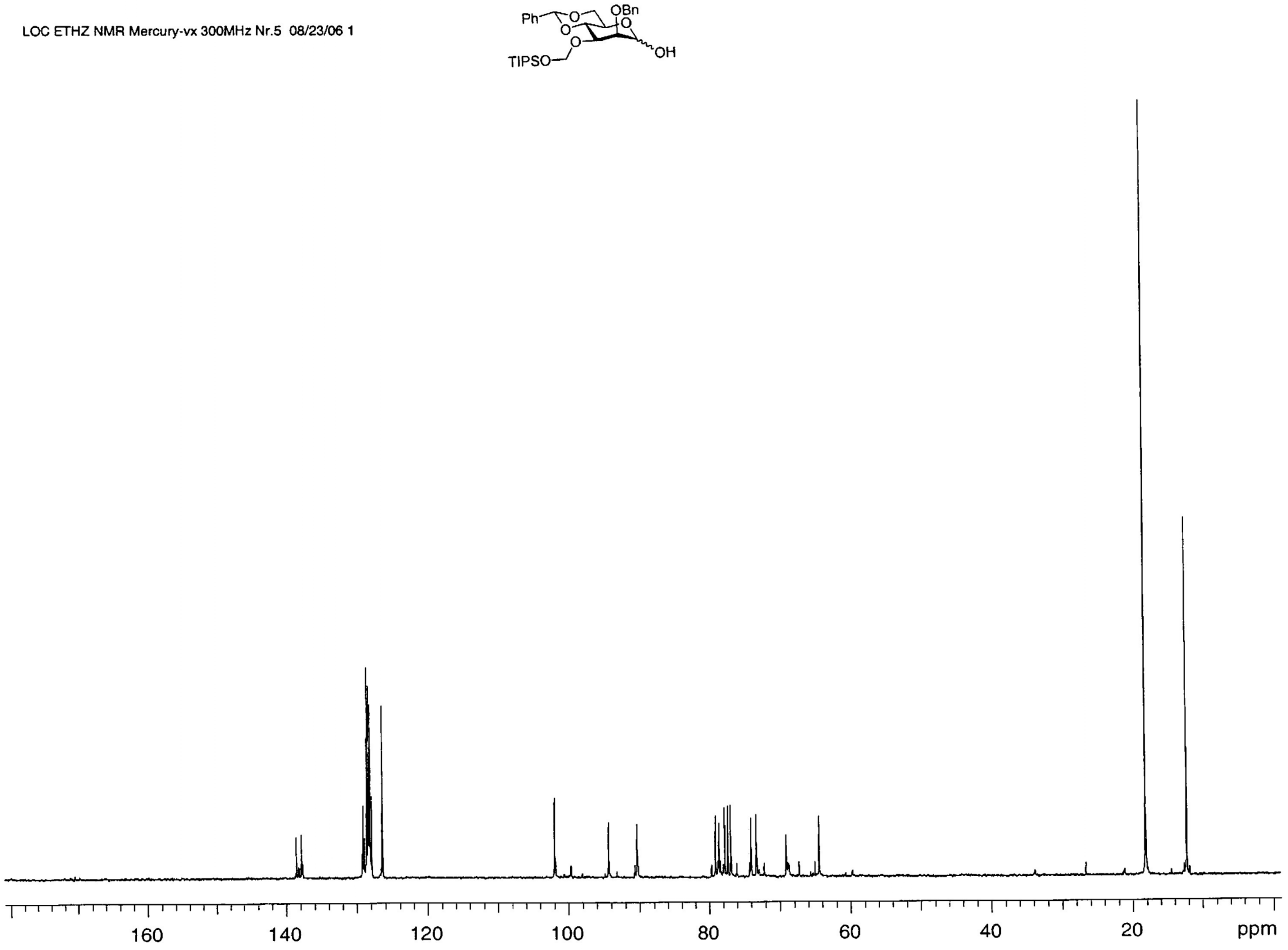
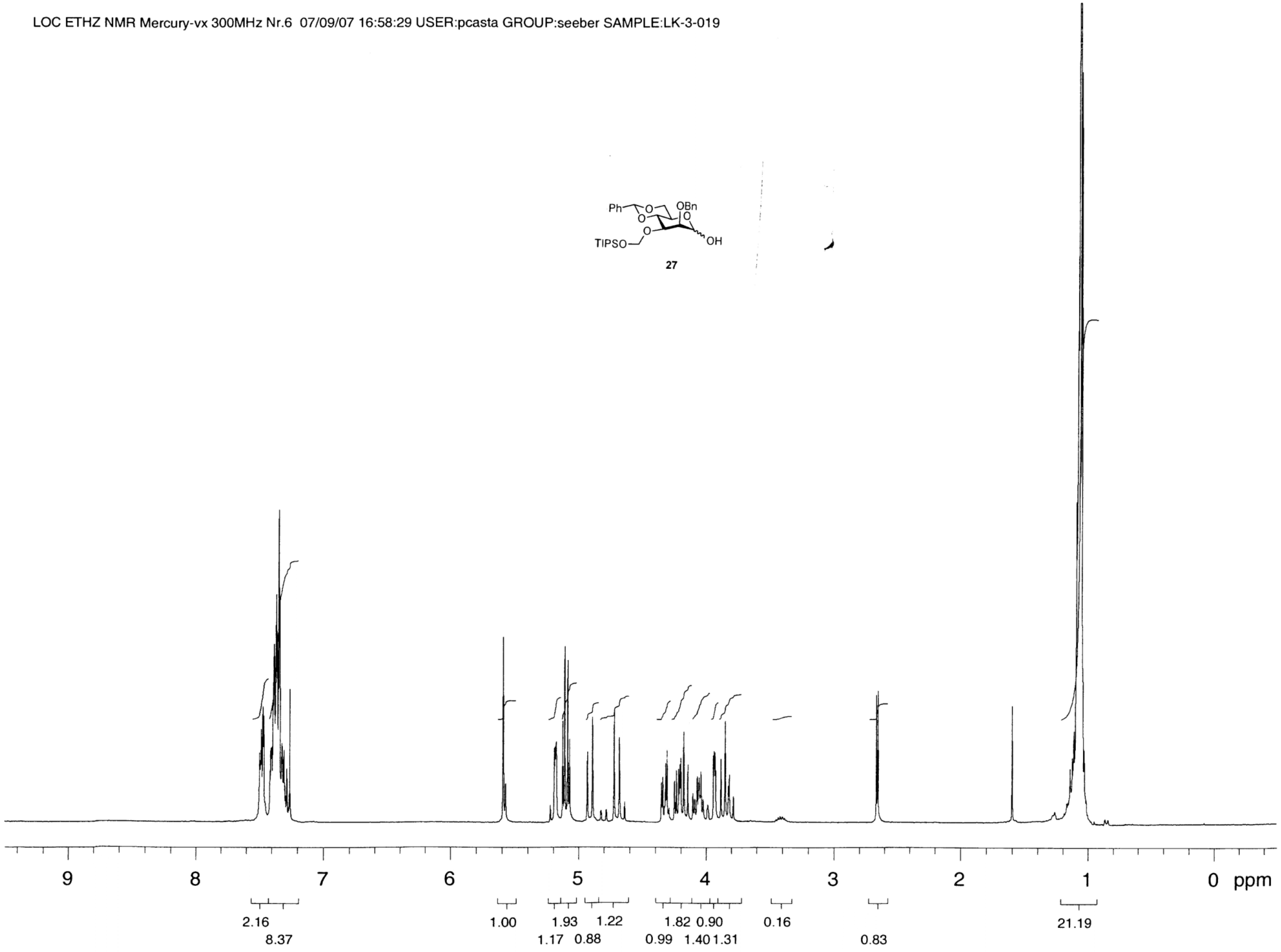
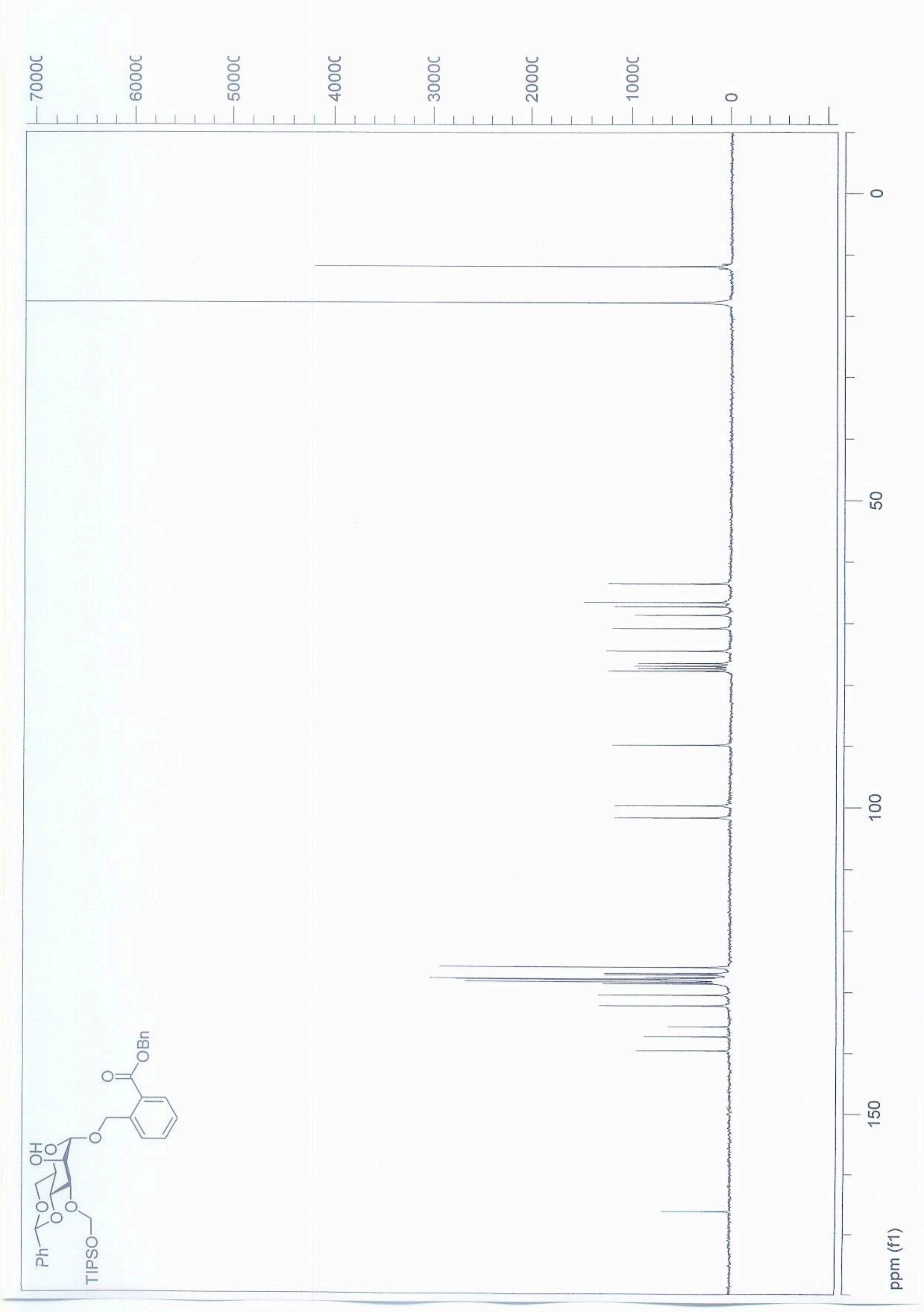
4
3
2
1
ppm

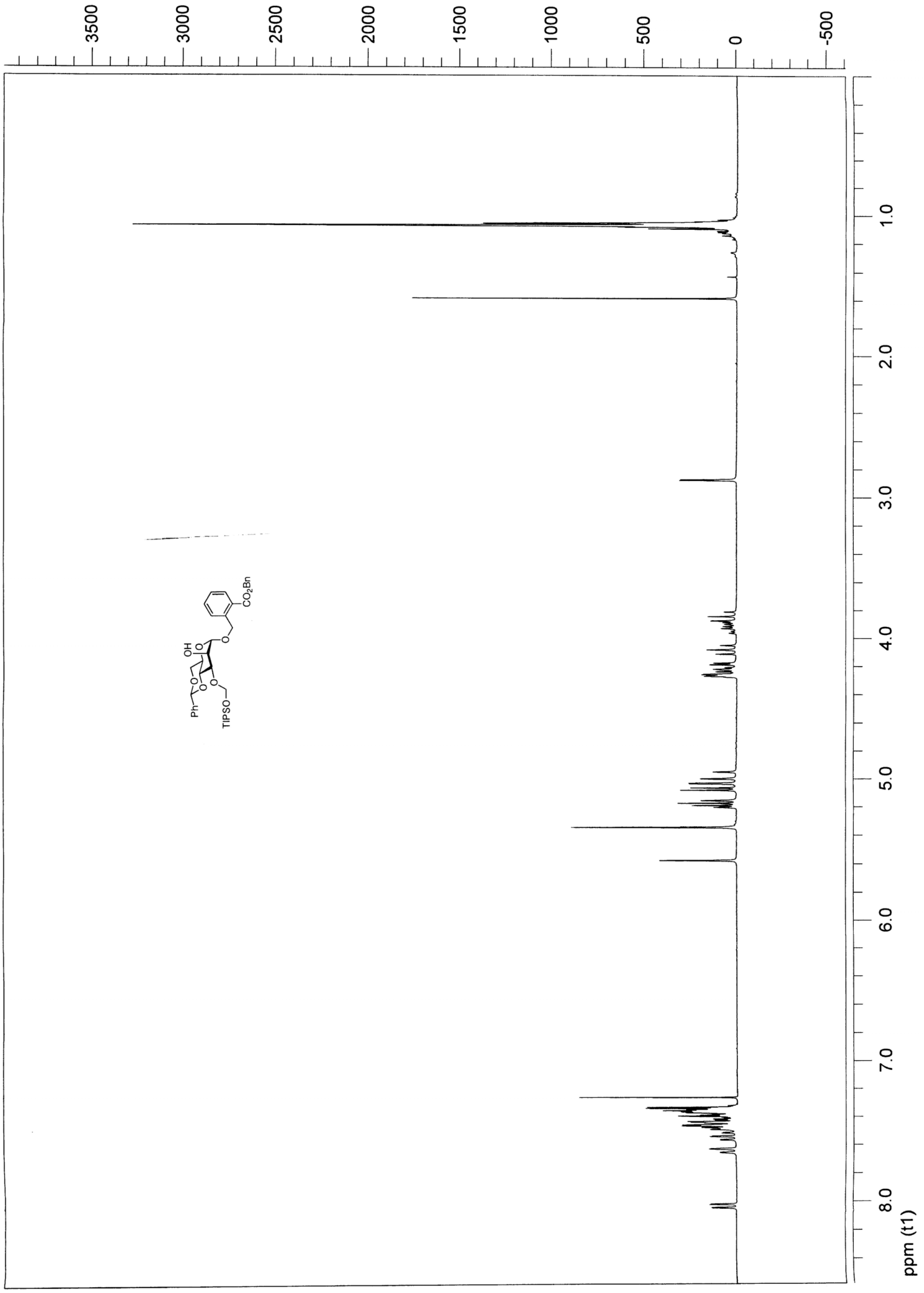

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 08/23/06 1
Ph
O
O
OBn
O
O
OH
TIPSO
160
140
120
100
80
60
40
20
ppm


LOC ETHZ NMR Mercury-vx 300MHz Nr.6 07/09/07 16:58:29 USER:pcasta GROUP:seeber SAMPLE:LK-3-019
Ph
O
O
OBn
O
OH
TIPSO
O
9
8
7
6
5
4
3
2
1
0 ppm
2.16
8.37
1.00
1.93
1.17
0.88
1.22
1.82
0.99
0.90
1.40
1.31
0.16
0.83
21.19

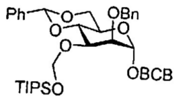
27

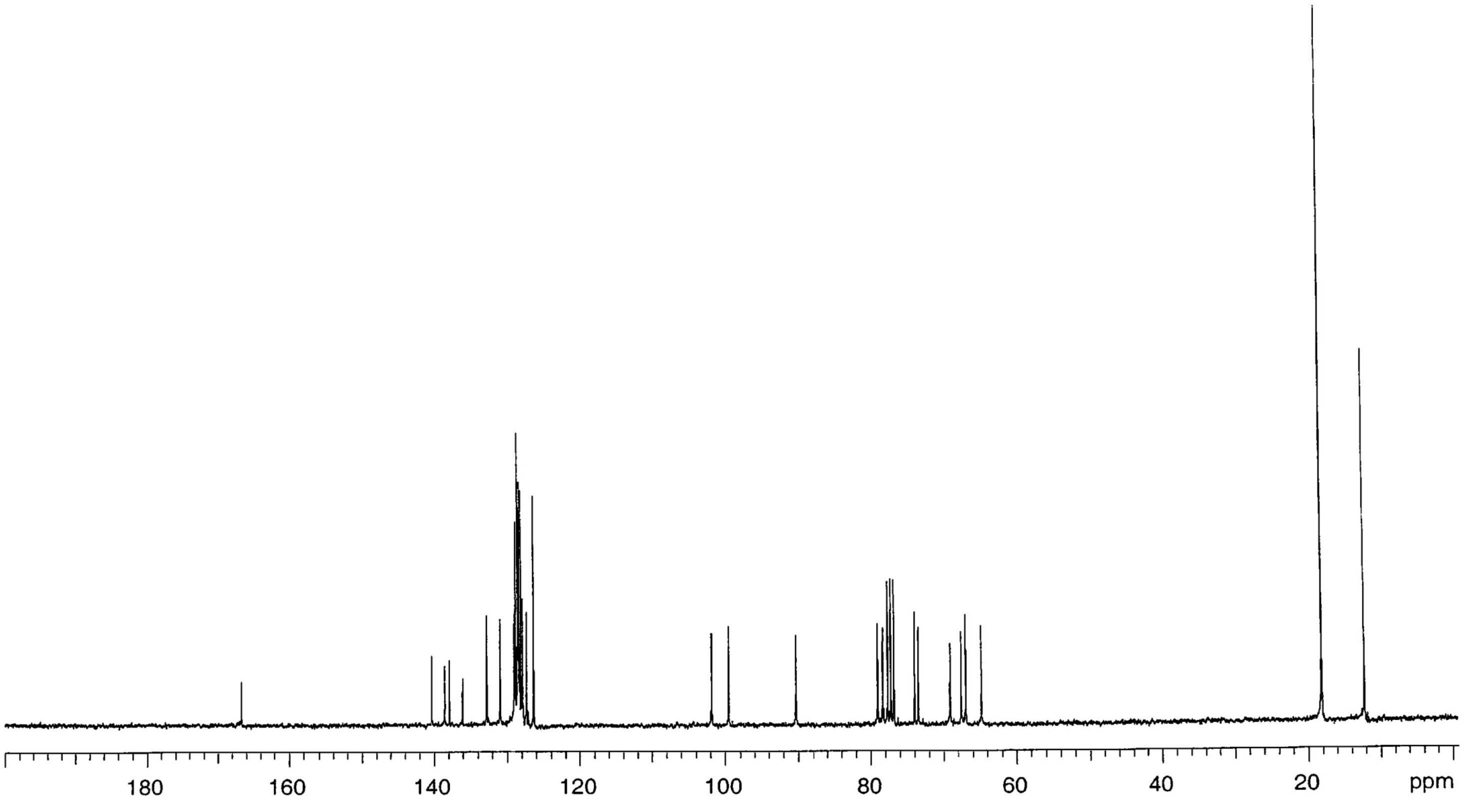


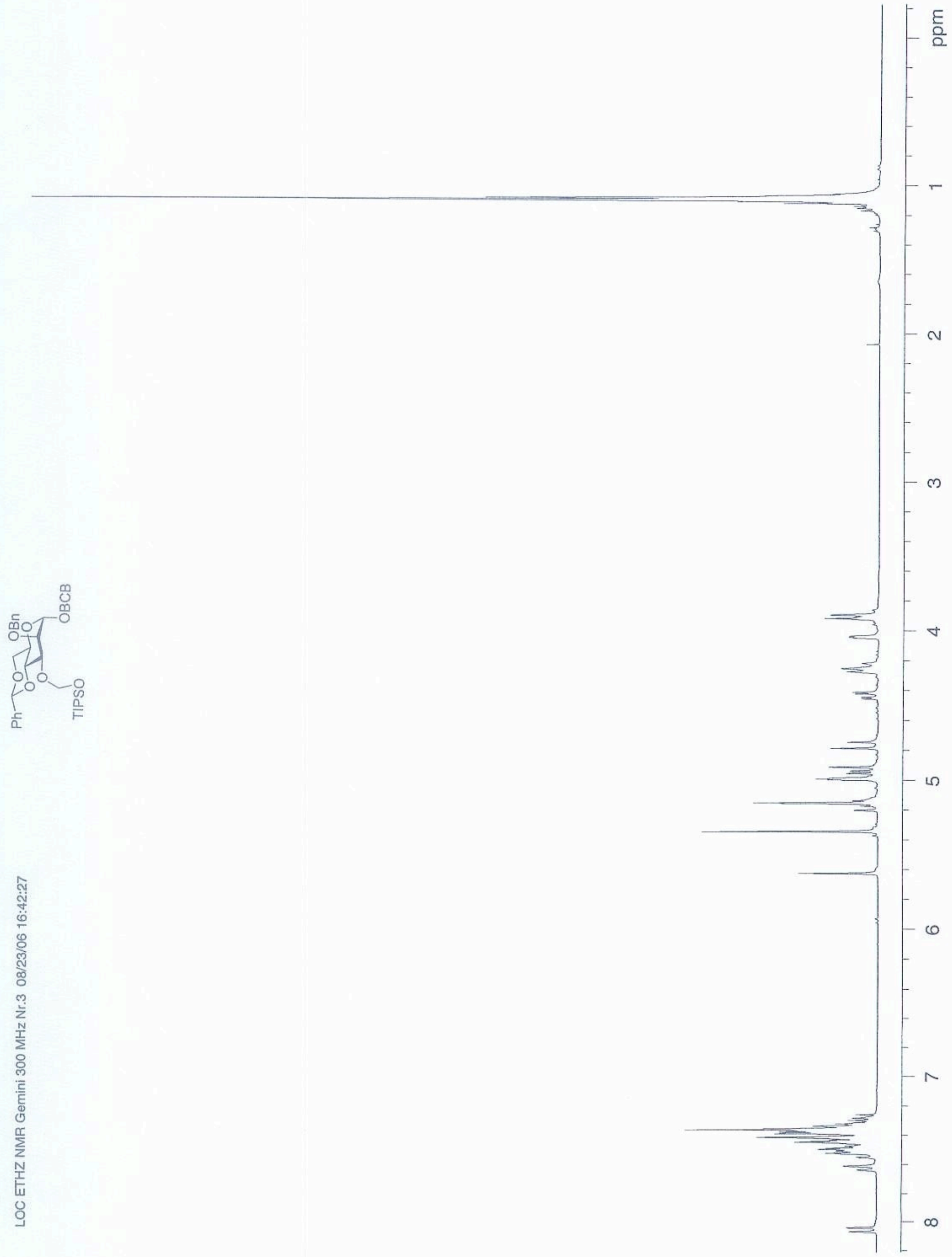
TIPSO
Ph
O
O
OH
O
O
OBn
O
7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
ppm (f1)


3500
3000
2500
2000
1500
1000
500
0
-500
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)
Ph
O
O
OH
O
O
TIPSO
O
CO_2Bn

LOC ETHZ NMR Gemini 300 MHz Nr.3 08



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Ph
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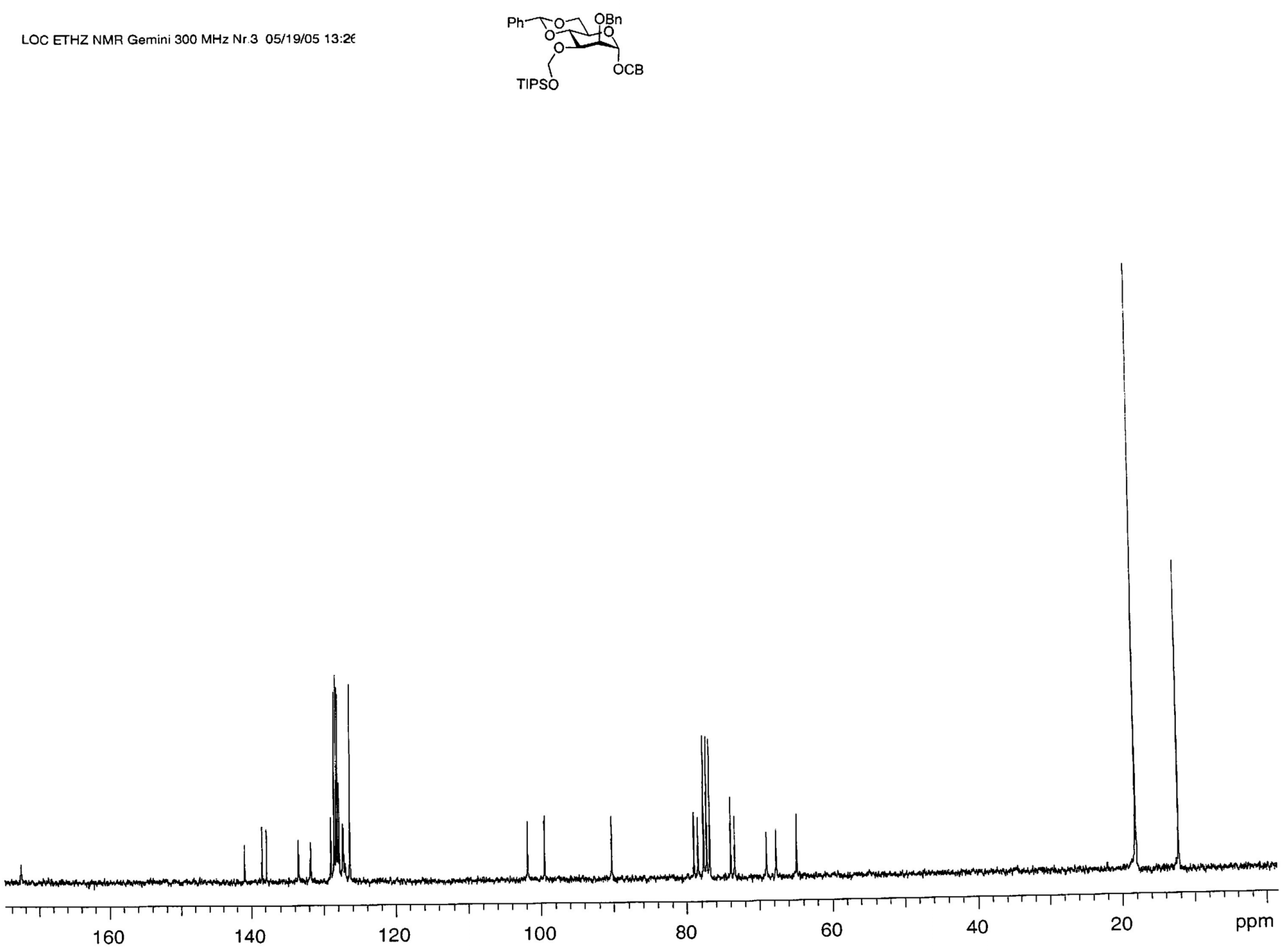
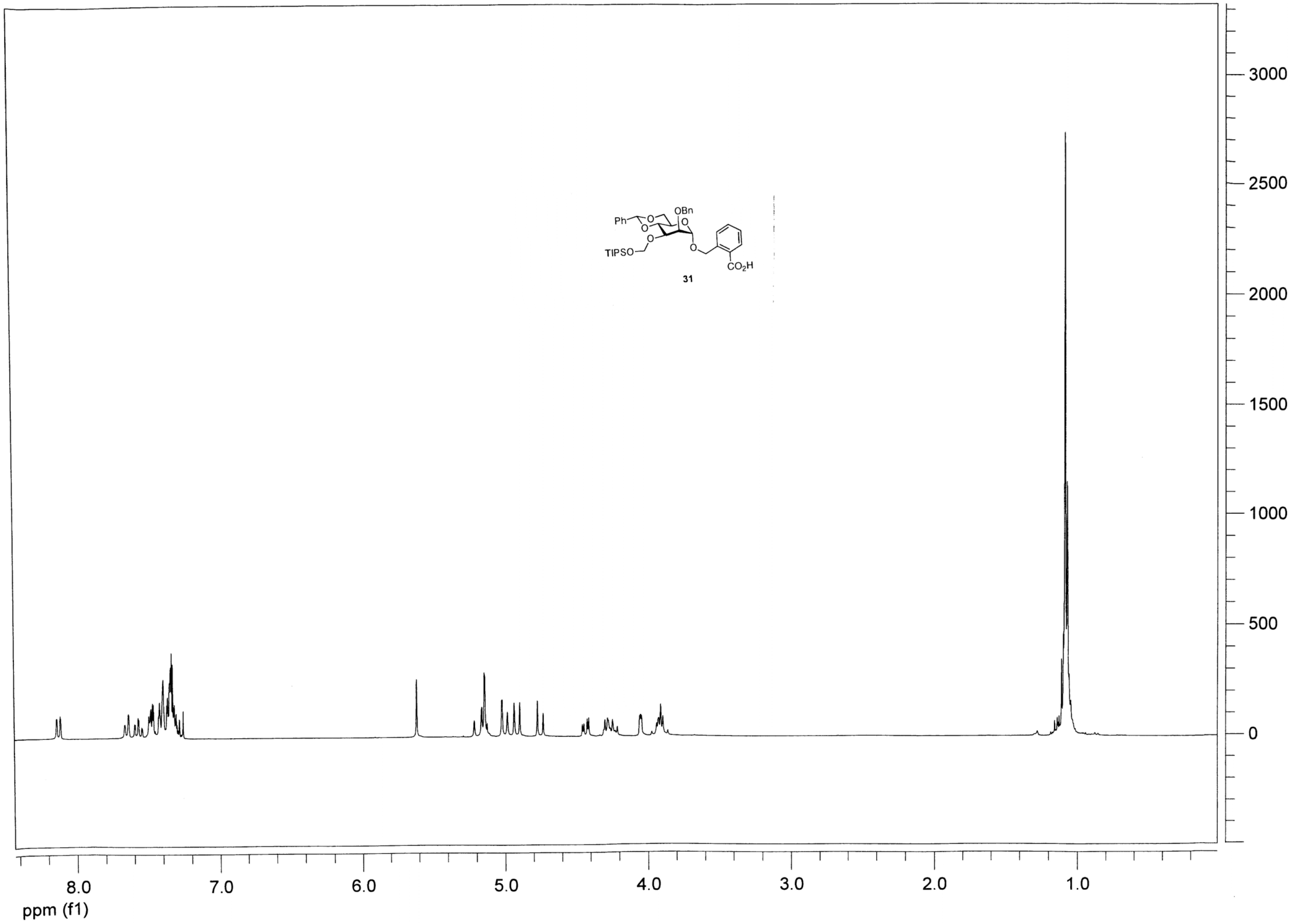
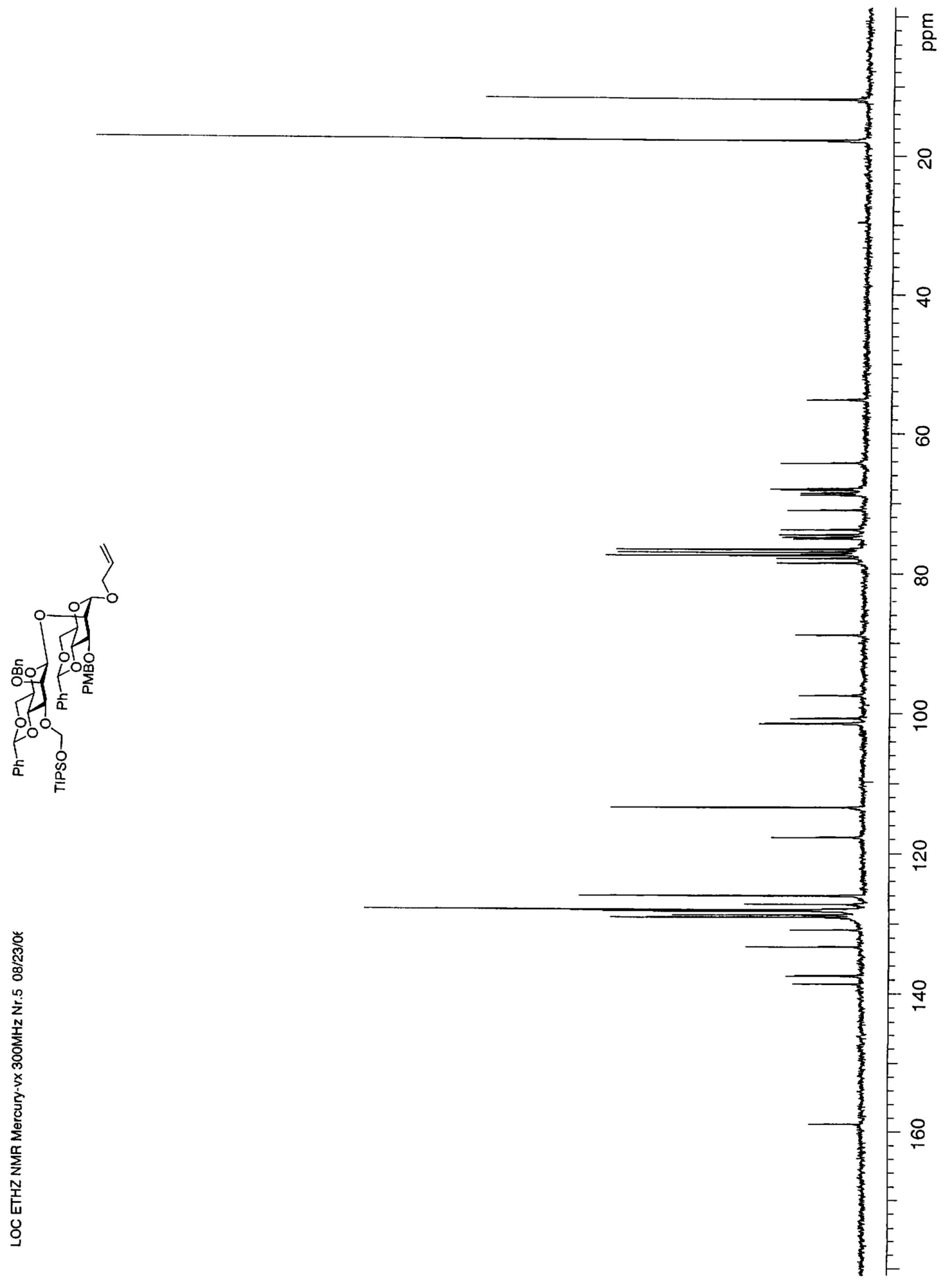
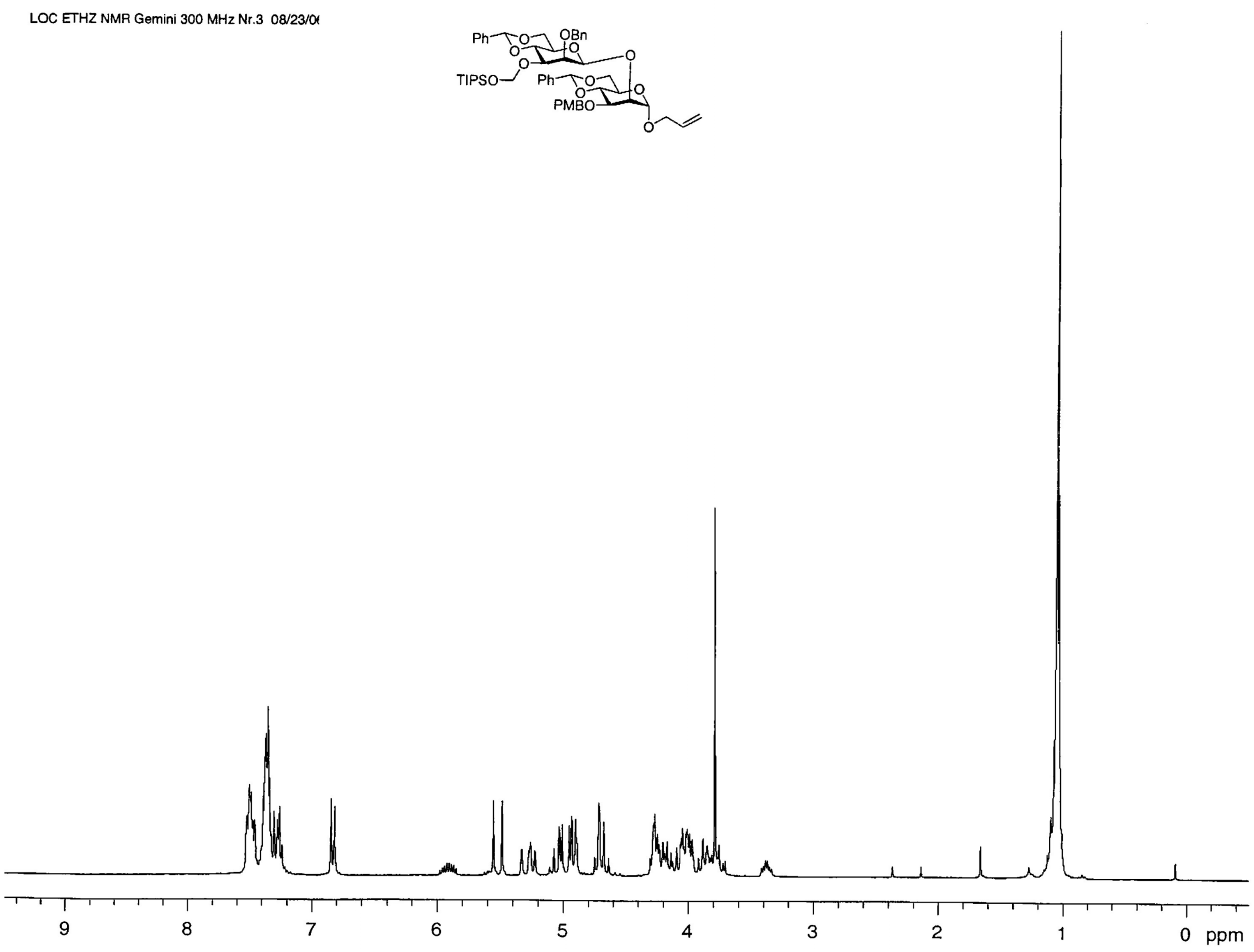
O
OBn
O
O
OBCB
TIPSO
8
7
6
5
4
3
2
1
ppm

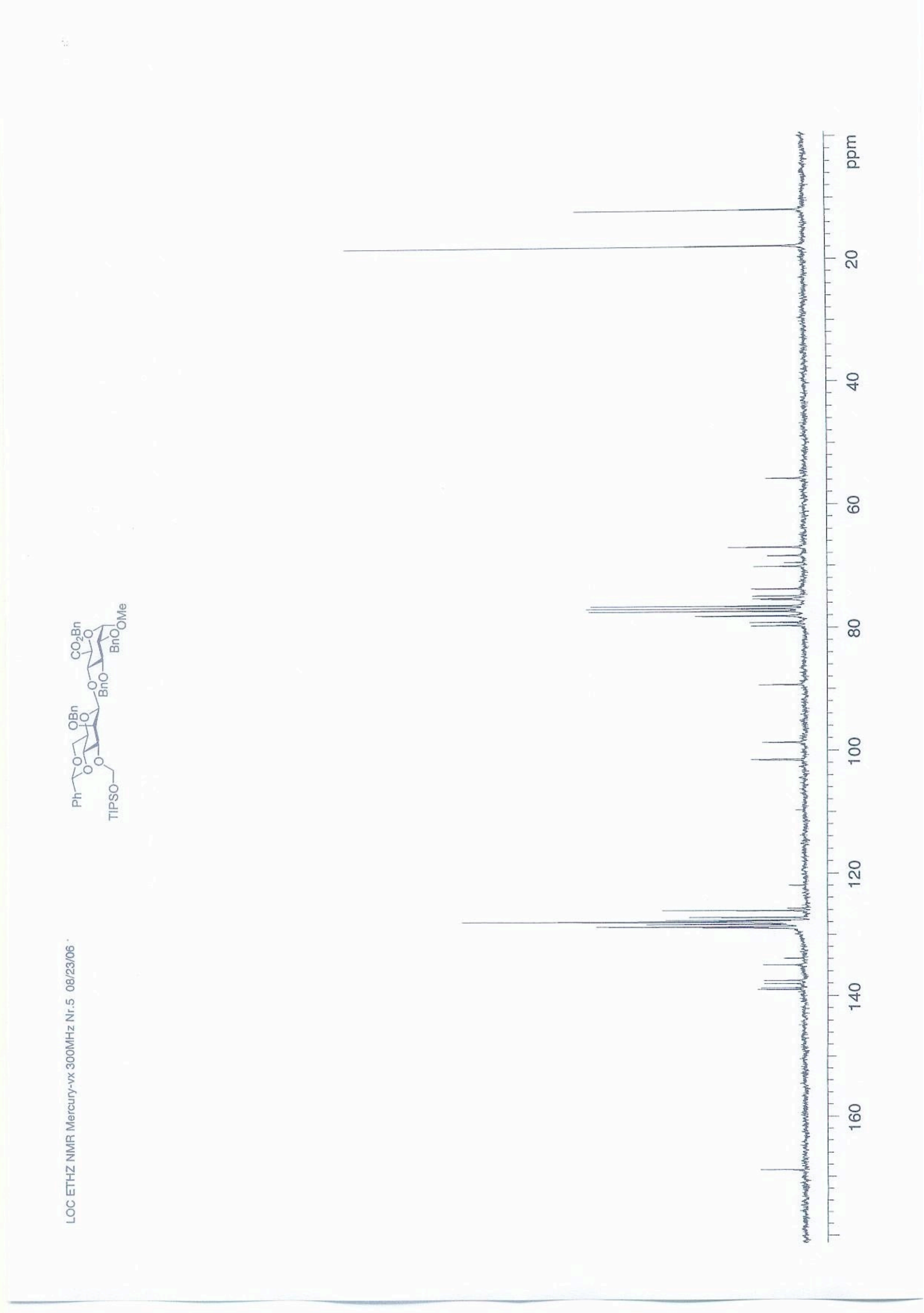

LOC ETHZ NMR Gemini 300 MHz Nr.3 05/19/05 13:26
Ph
O
O
O
OBn
O
OCB
TIPSO
160
140
120
100
80
60
40
20
ppm

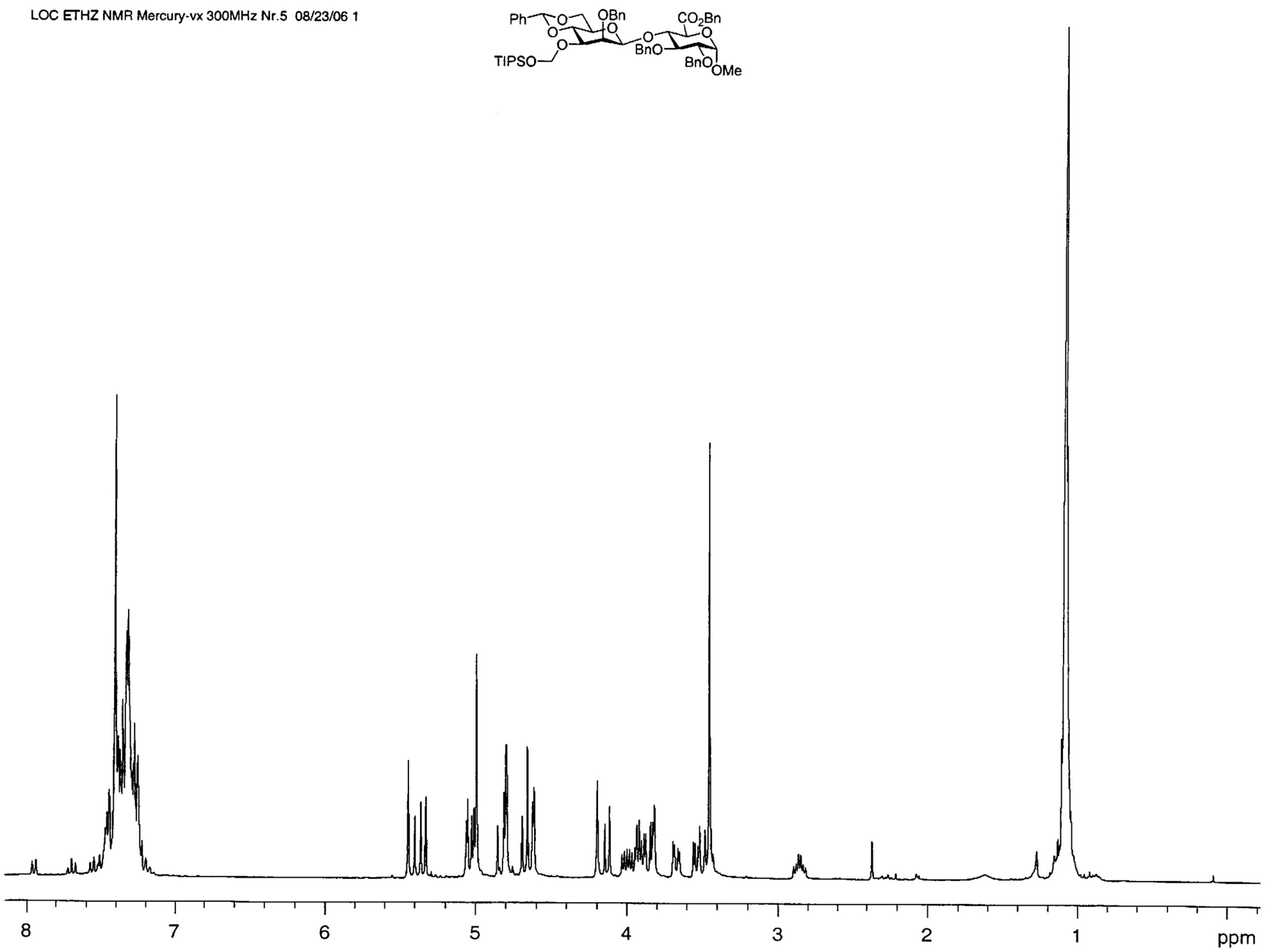


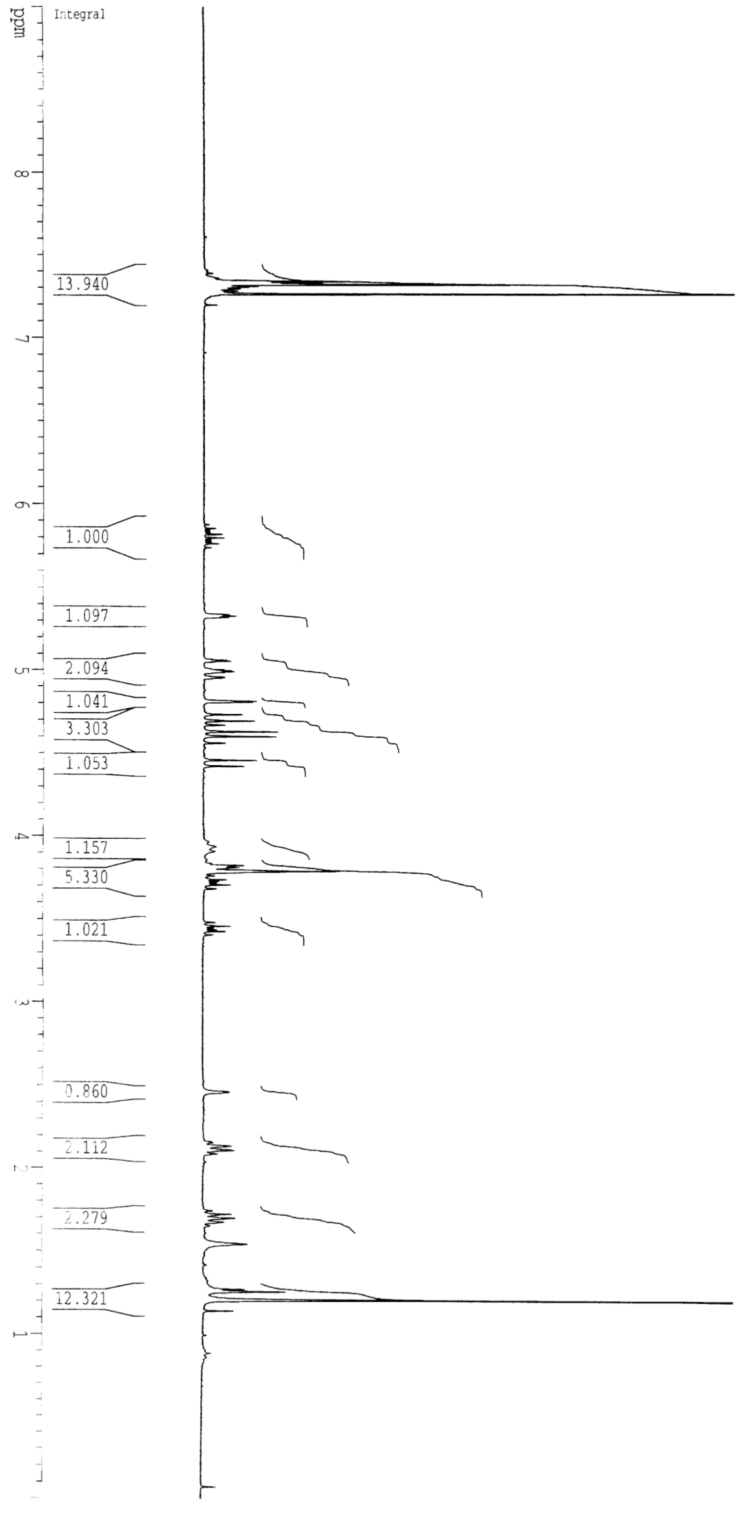
Ph
O
O
OBn
O
TIPSO
O
CO2H
31
3000
2500
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

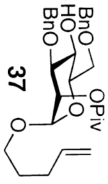

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 08/23/0
OBn
Ph
TIPSO
Ph
PMBO
ppm
20
40
60
80
100
120
140
160


LOC ETHZ NMR Gemini 300 MHz Nr.3 08/23/0(
Ph
O
O
OBn
O
O
TIPSO
Ph
O
O
O
PMBO
O
O
9
8
7
6
5
4
3
2
1
0 ppm

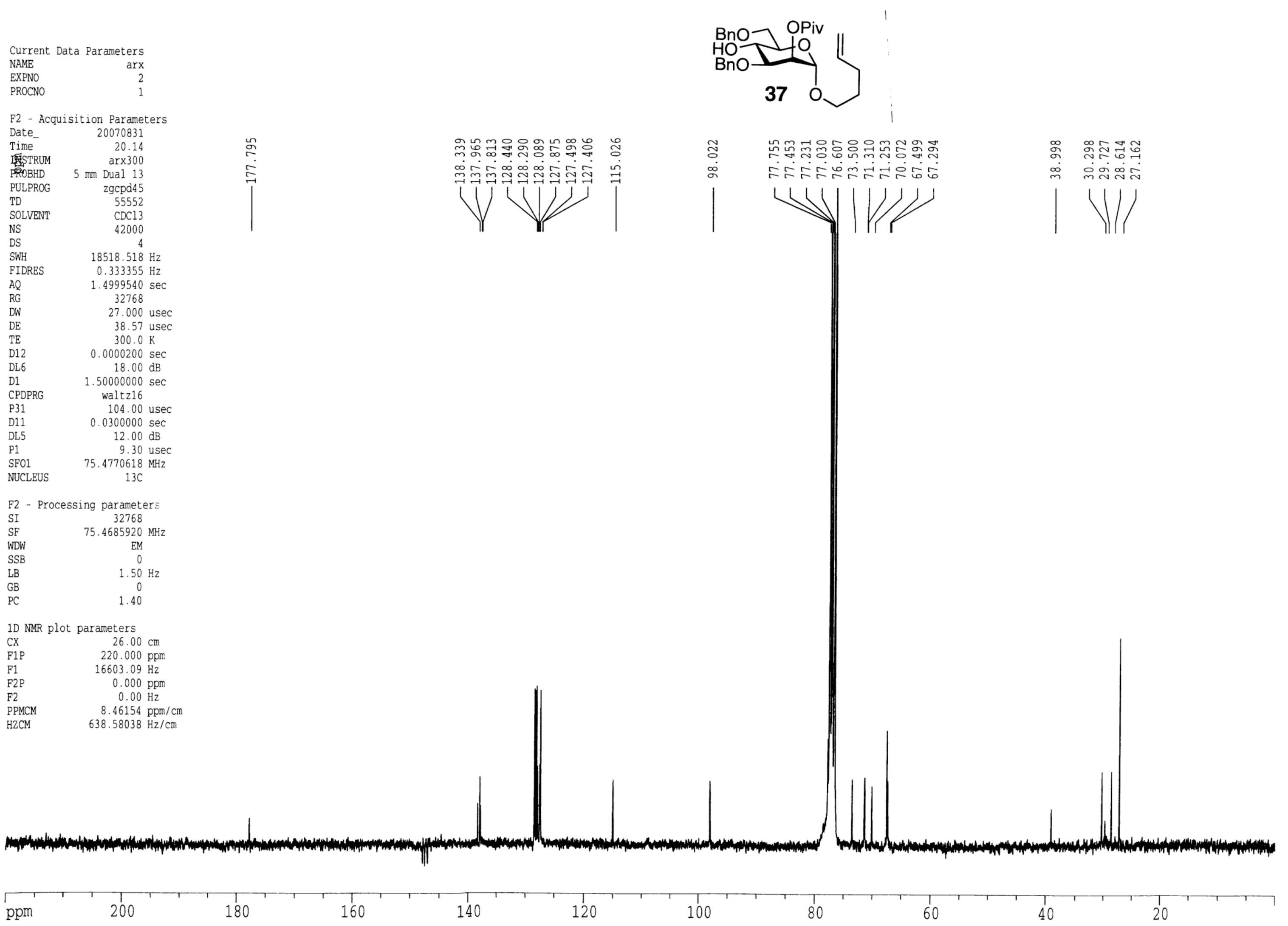

LOC ETHZ NMR Mercury-vx 300MHz Nr.5 08/23/06
Ph
O
OBn
TIPSO
BnO
CO_2Bn
BnO
OMe
160
140
120
100
80
60
40
20
ppm


LOC ETHZ NMR Mercury-vx 300MHz Nr.5 08/23/06 1
Ph
OBn
CO2Bn
TIPSO
BnO
BnO
OMe
8
7
6
5
4
3
2
1
ppm


ppm
Integral
8
7
6
5
4
3
2
1
13.940
1.000
1.097
2.094
1.041
3.303
1.053
1.157
5.330
1.021
0.860
2.112
2.279
12.321

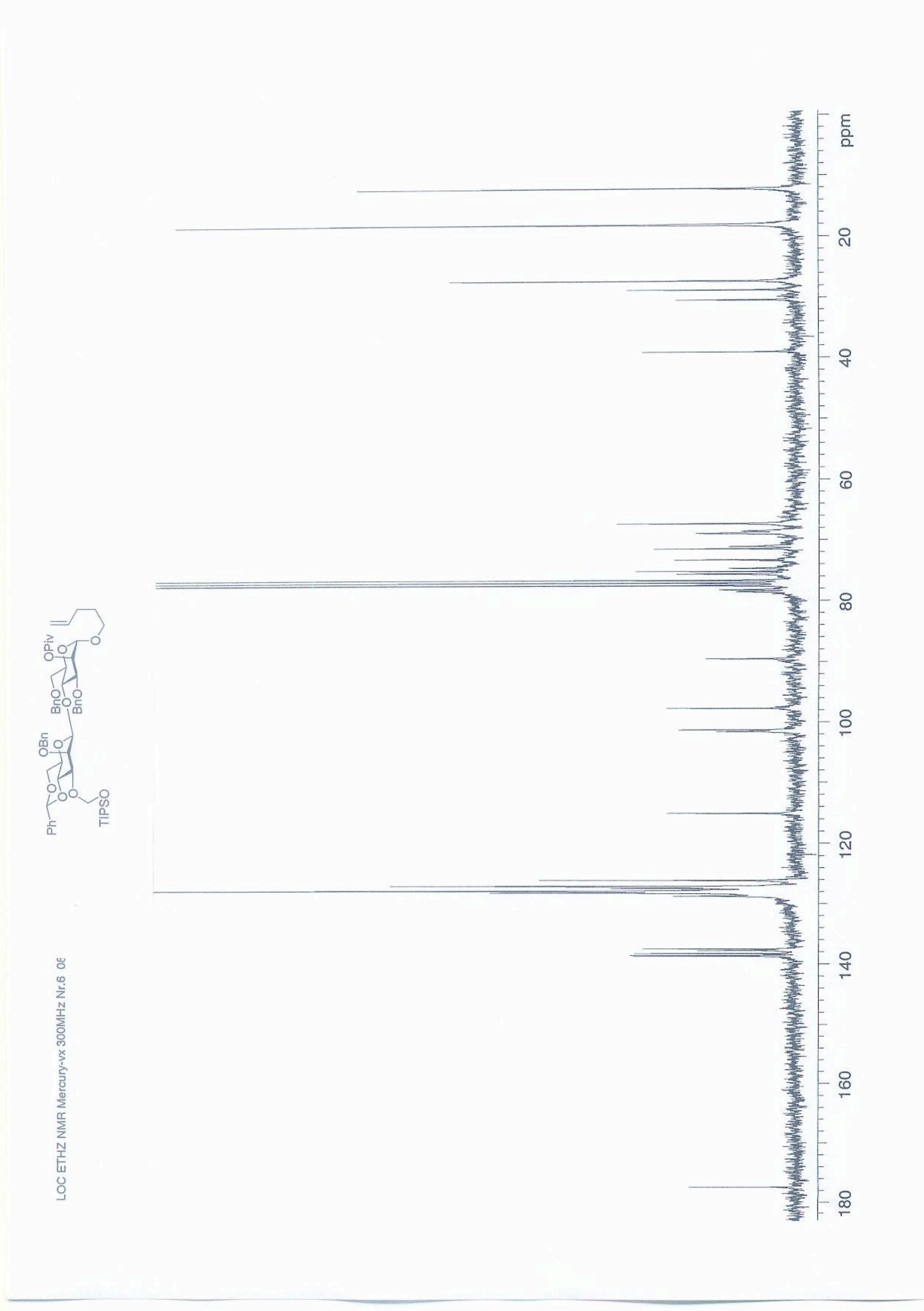

BnO
HO
BnO
OPiv
O
O

37

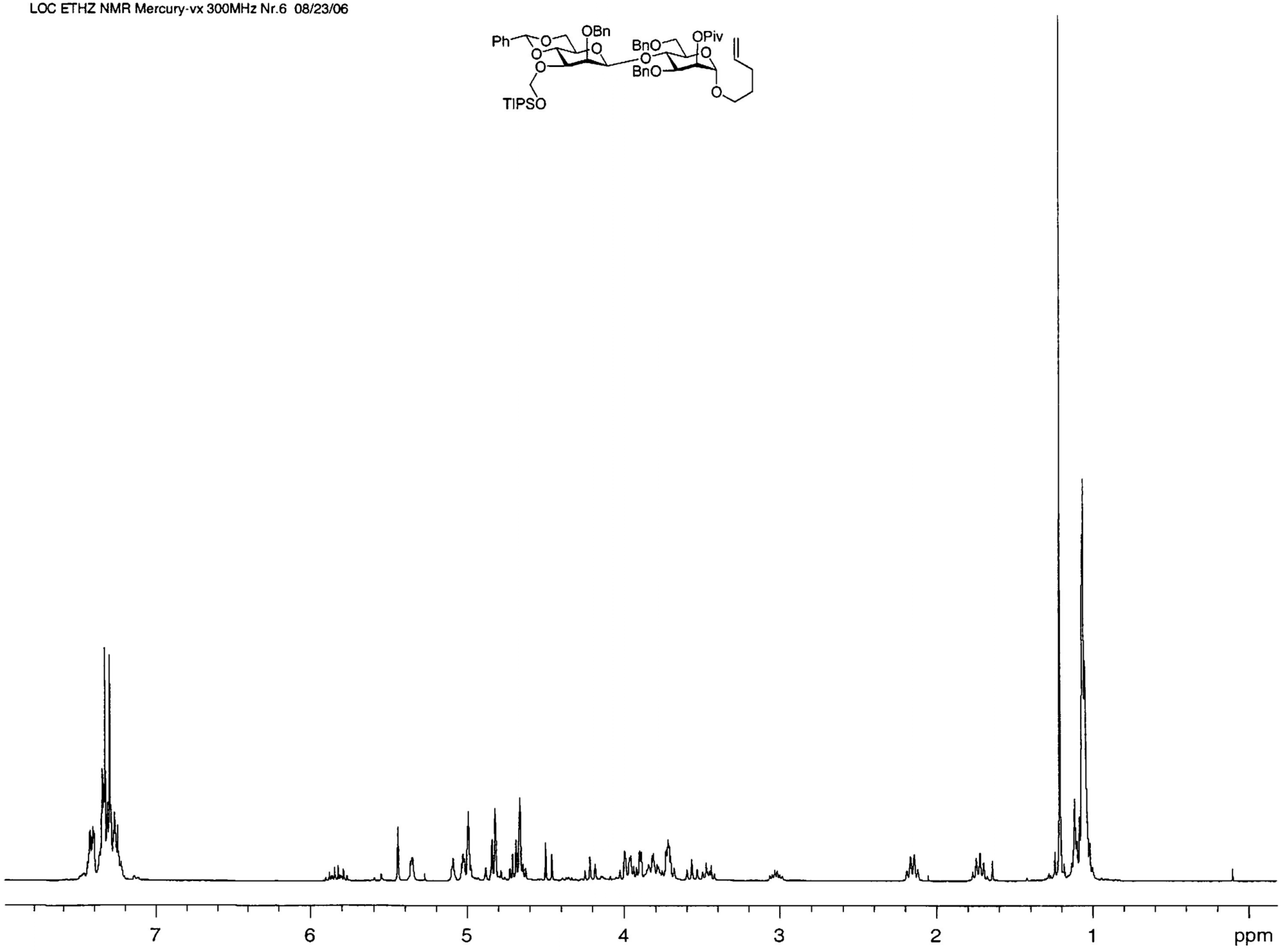


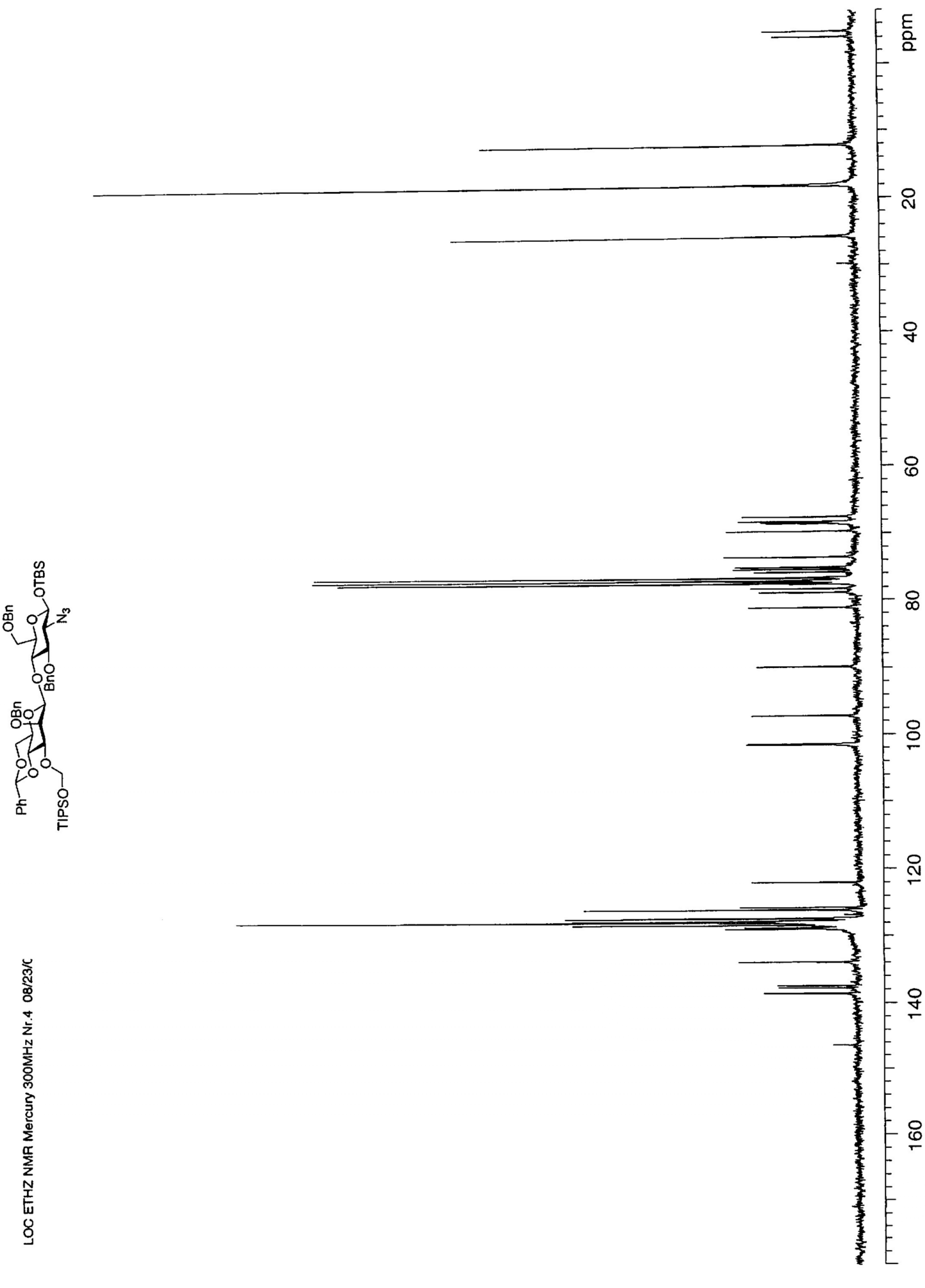
37

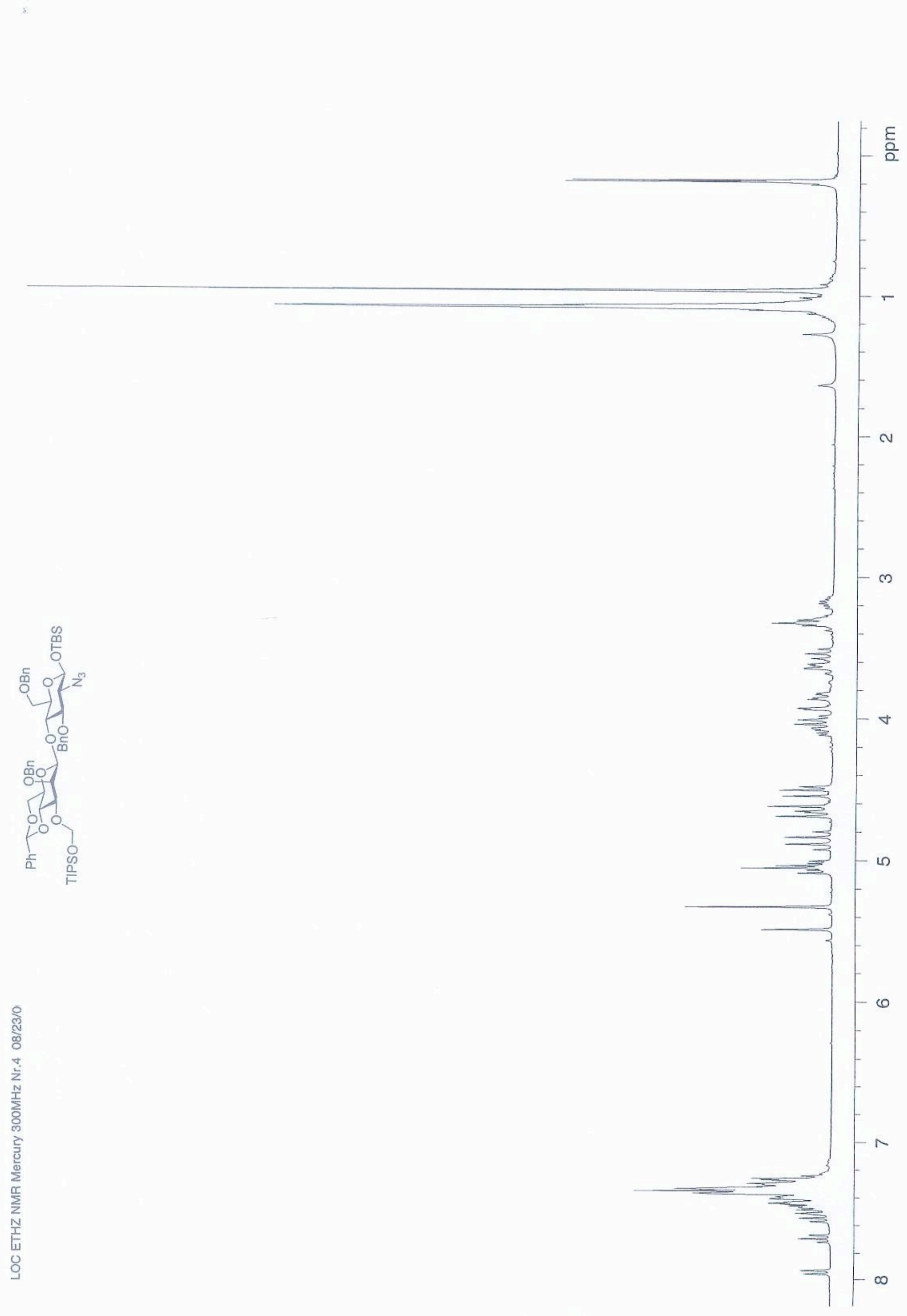
```
Current Data Parameters
NAME                arx
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20070831
Time              20.14
INSTRUM          arx300
PROBHD     5 mm Dual 13
PULPROG        zgcpd45
TD                55552
SOLVENT           CDCl3
NS                42000
DS                    4
SWH           18518.518 Hz
FIDRES         0.333355 Hz
AQ            1.4999540 sec
RG                32768
DW               27.000 usec
DE                38.57 usec
TE                300.0 K
D12          0.0000200 sec
DL6               18.00 dB
D1          1.50000000 sec
CPDPRG          waltz16
P31              104.00 usec
D11          0.0300000 sec
DL5               12.00 dB
P1                 9.30 usec
SFO1         75.4770618 MHz
NUCLEUS             13C

F2 - Processing parameters
SI                32768
SF           75.4685920 MHz
WDW                  EM
SSB                   0
LB                 1.50 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                26.00 cm
F1P             220.000 ppm
F1             16603.09 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           8.46154 ppm/cm
HZCM          638.58038 Hz/cm
```

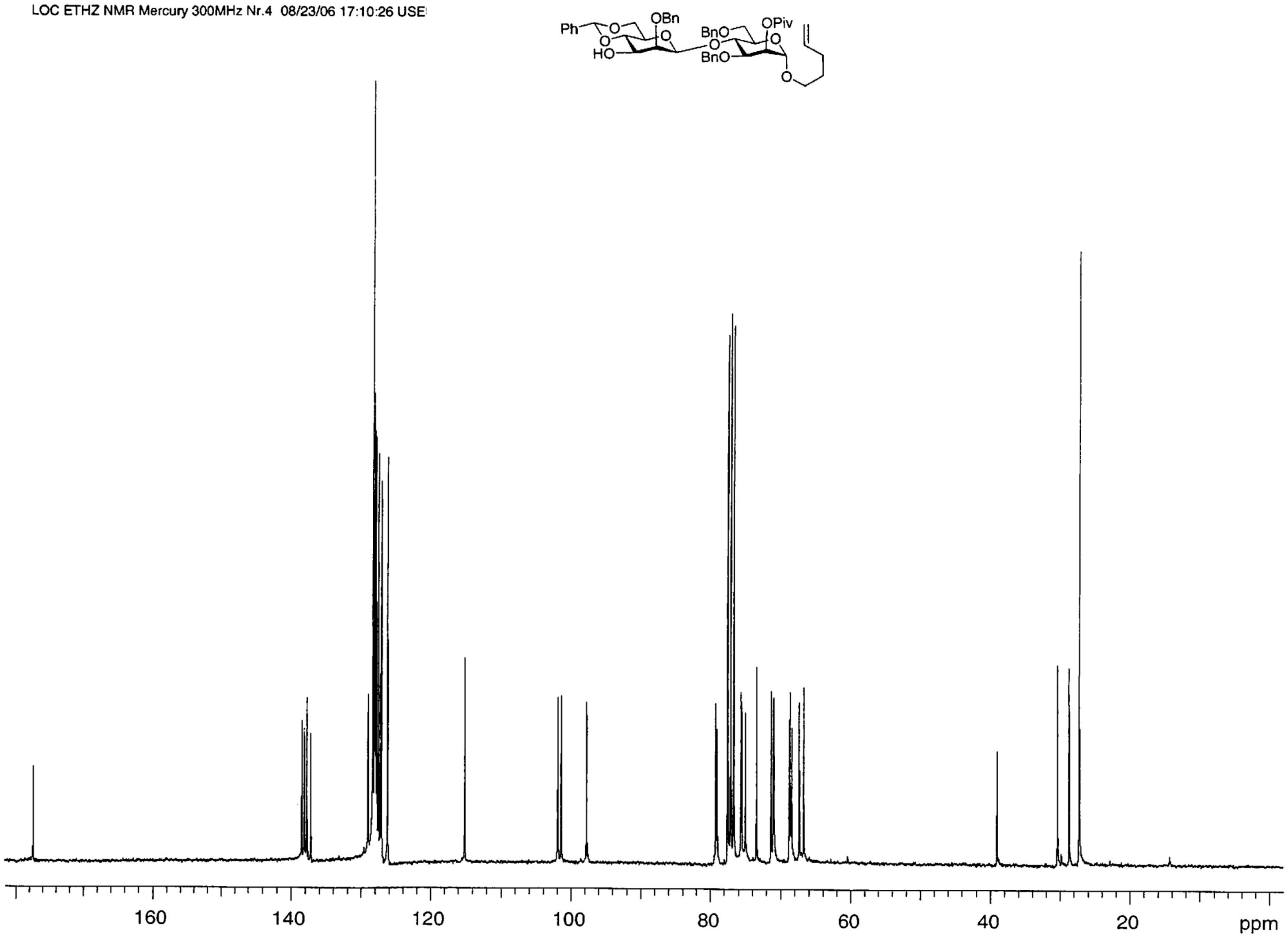

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 08
Ph
O
O
OBn
O
TIPSO
BnO
O
BnO
OPiv
O
ppm
180
160
140
120
100
80
60
40
20

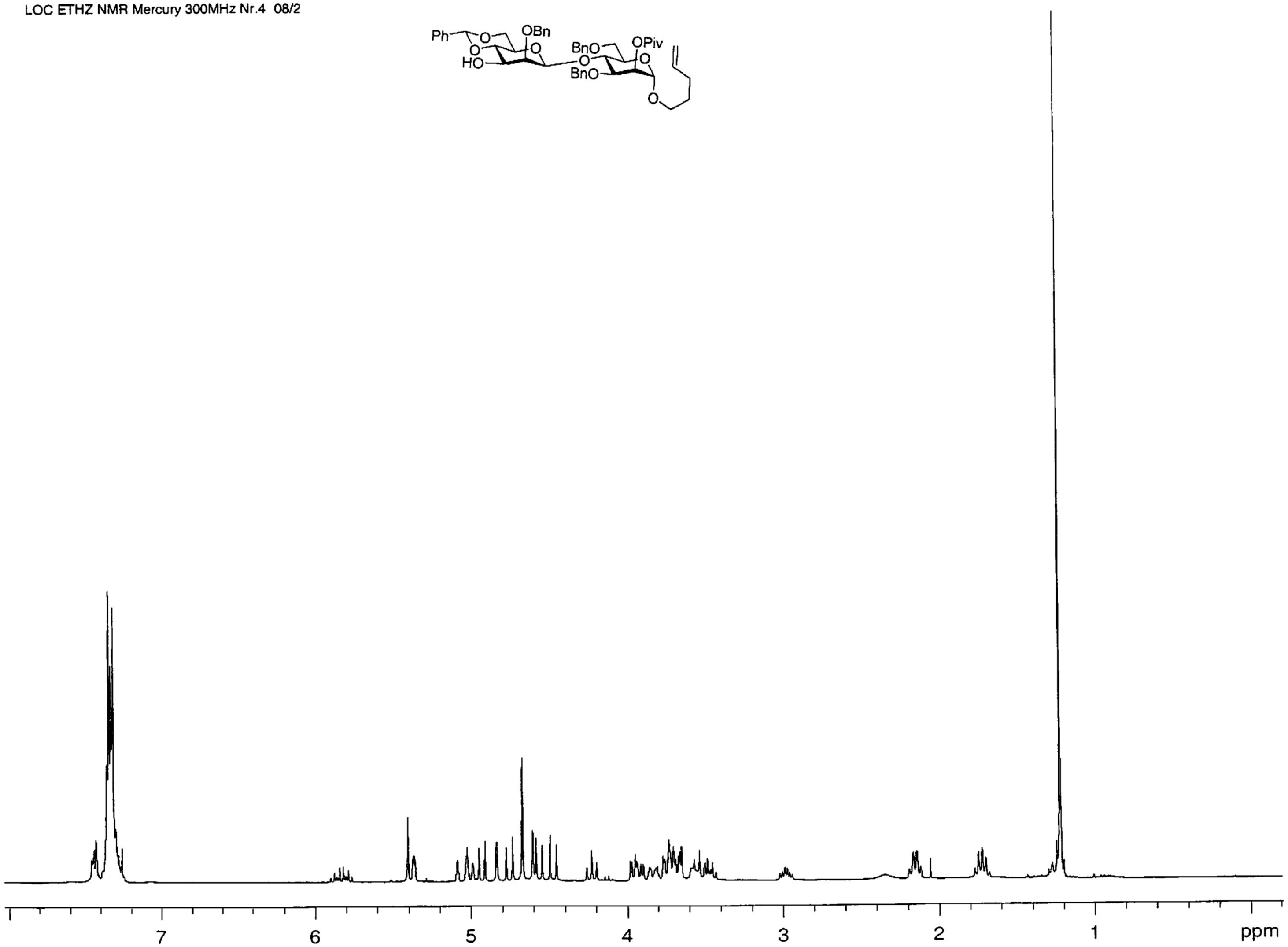
LOC ETHZ NMR Mercury-vx 300MHz Nr.6 08/23/06

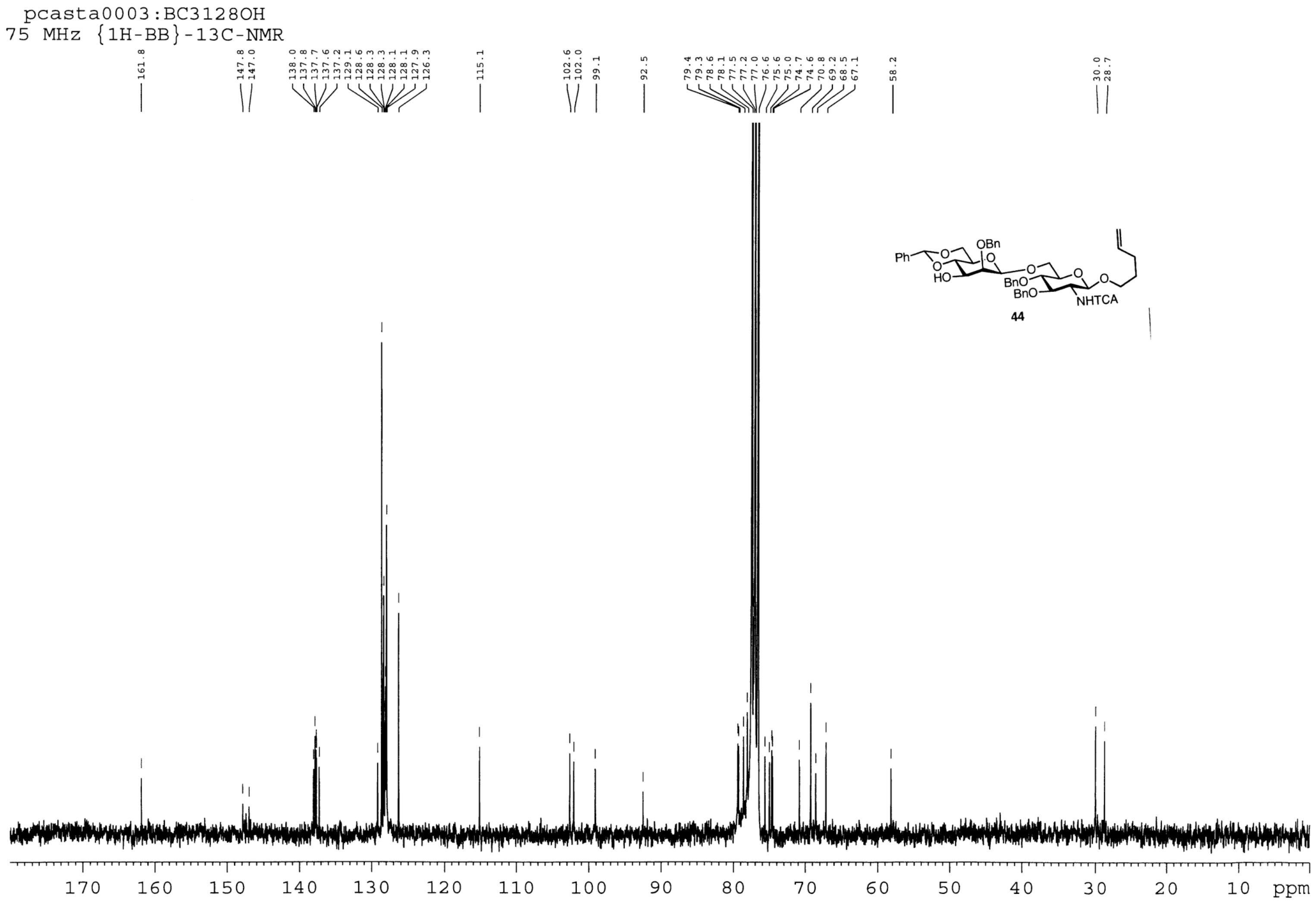


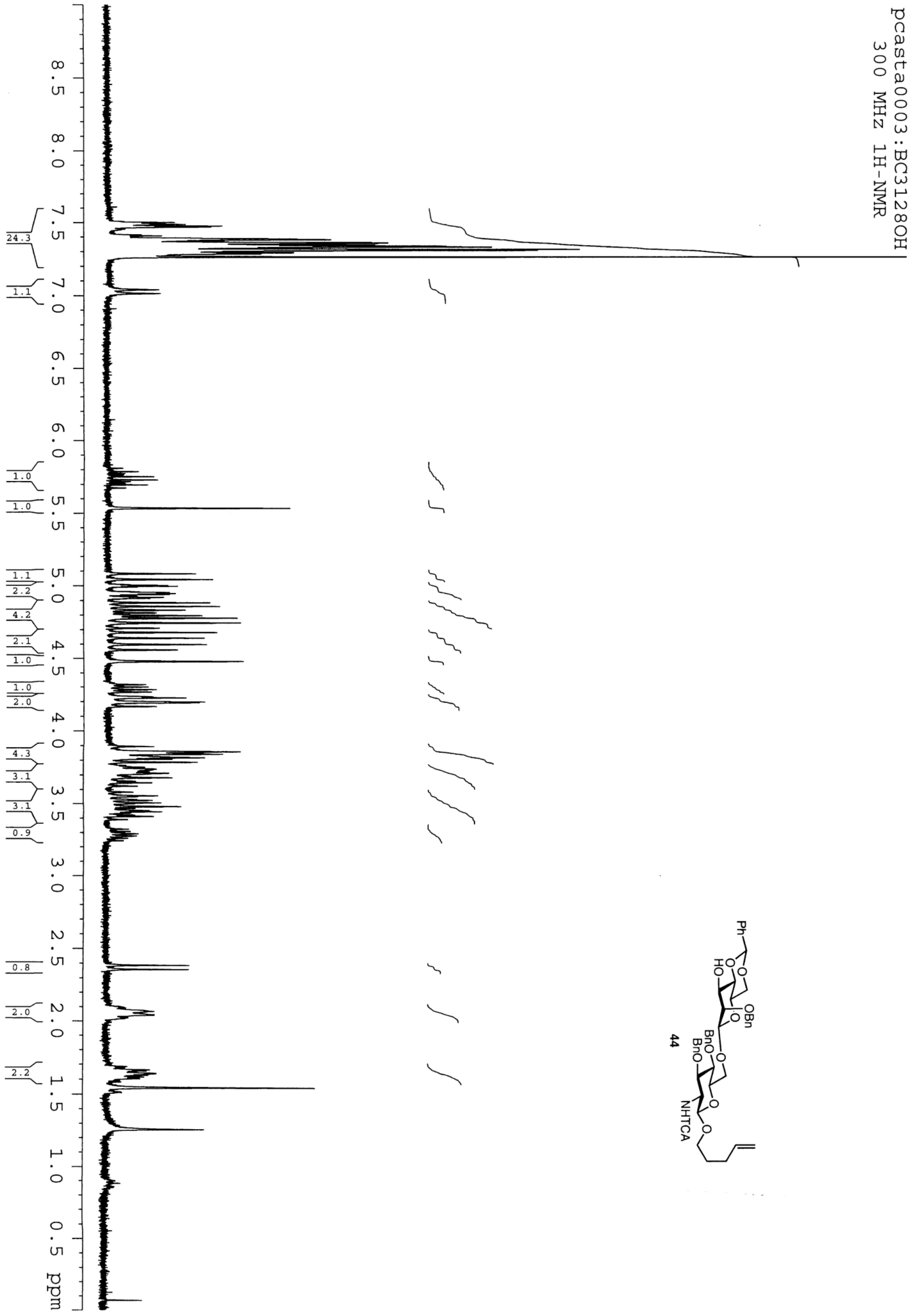

LOC ETHZ NMR Mercury 300MHz Nr.4 08/23/0
Ph
OBn
O
TIPSO
BnO
OBn
OTBS
N_3
ppm
160
140
120
100
80
60
40
20

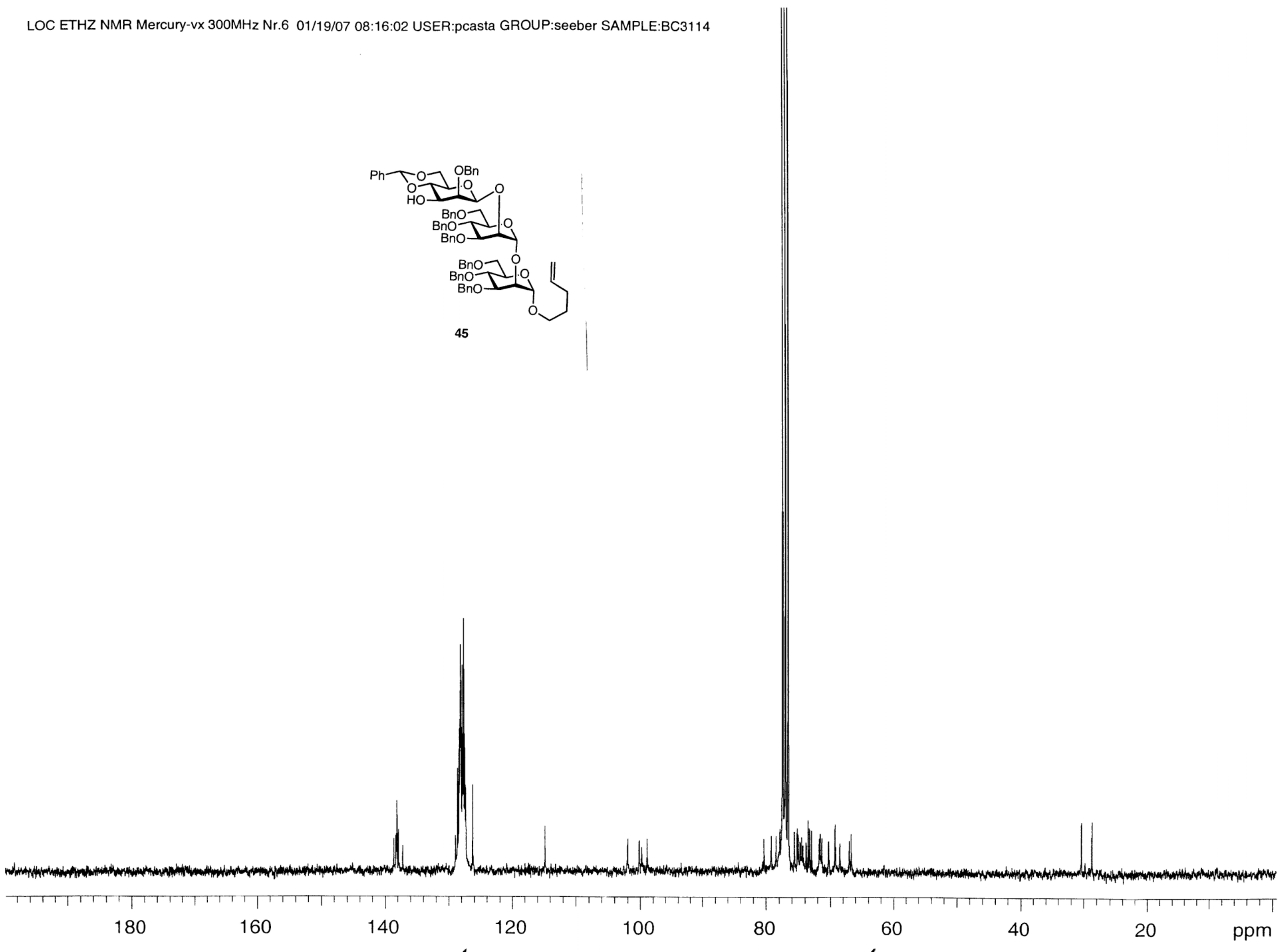

LOC ETHZ NMR Mercury 300MHz Nr.4 08/23/0
Ph
OBn
TIPSO
BnO
OBn
OTBS
N$_3$
8
7
6
5
4
3
2
1
ppm

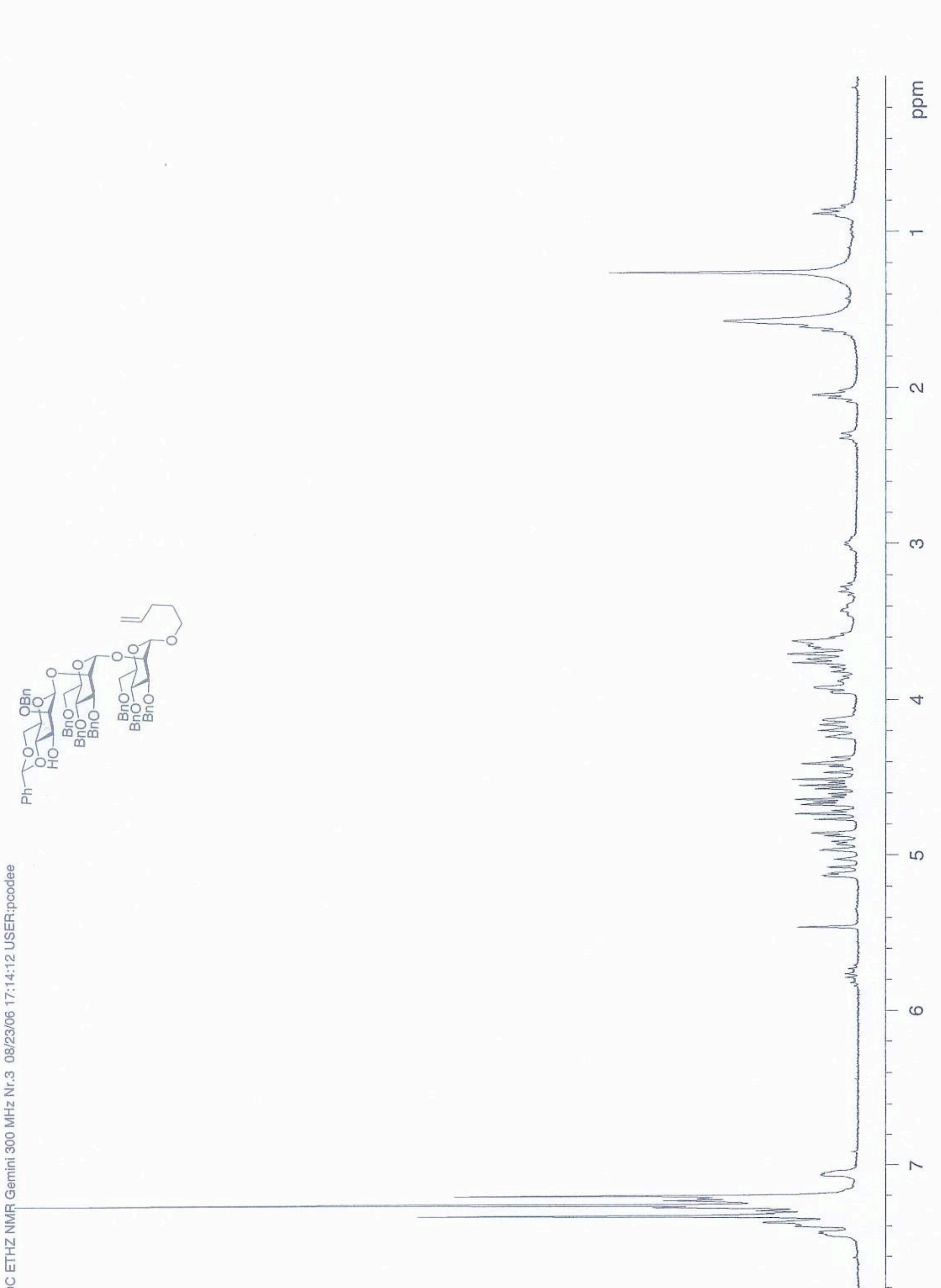

LOC ETHZ NMR Mercury 300MHz Nr.4 08/23/06 17:10:26 USE
Ph
O
HO
OBn
O
BnO
O
BnO
OPiv
O
O
160
140
120
100
80
60
40
20
ppm

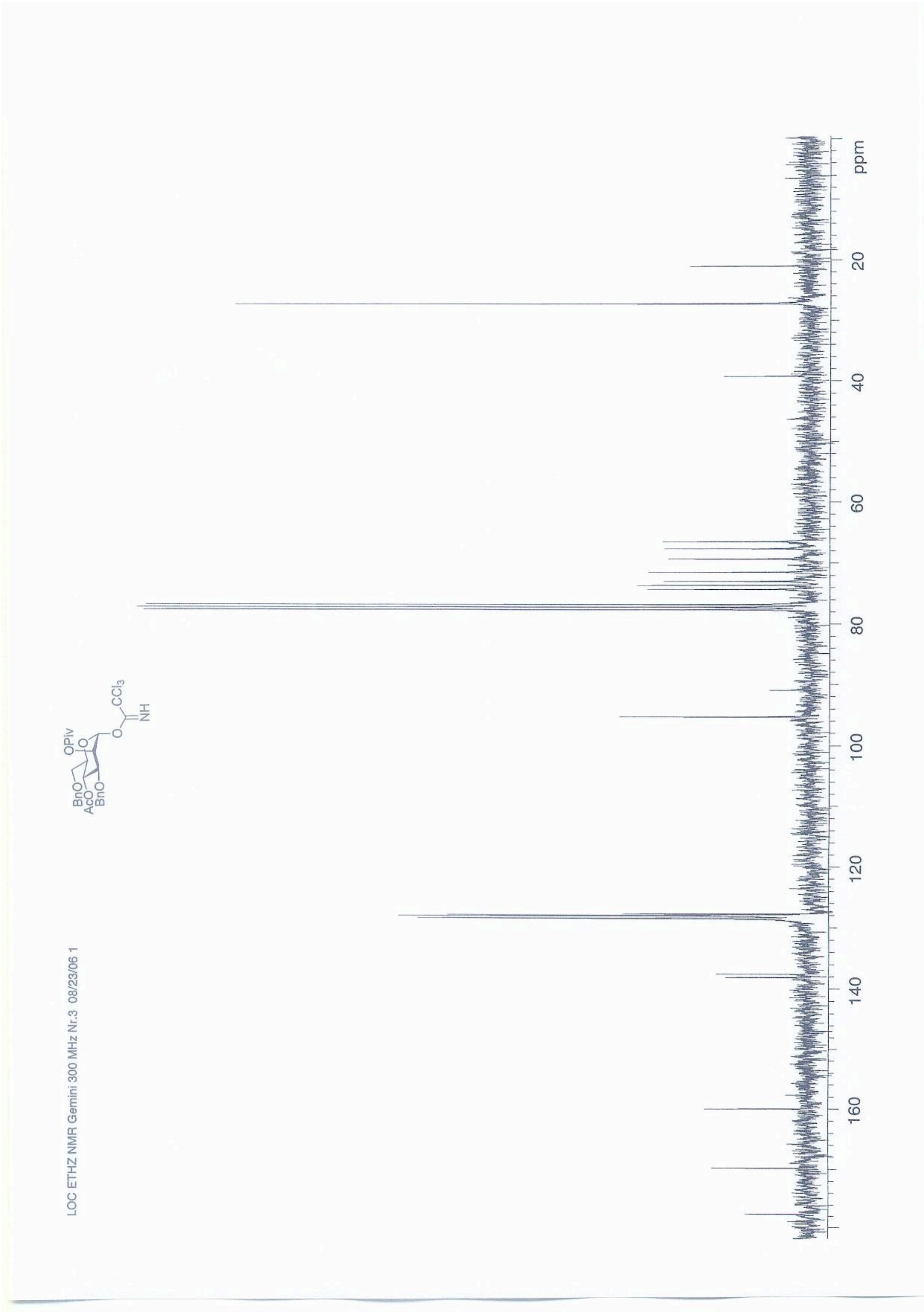

LOC ETHZ NMR Mercury 300MHz Nr.4 08/2
Ph
O
O
OBn
O
HO
BnO
O
BnO
OPiv
O
O
7
6
5
4
3
2
1
ppm

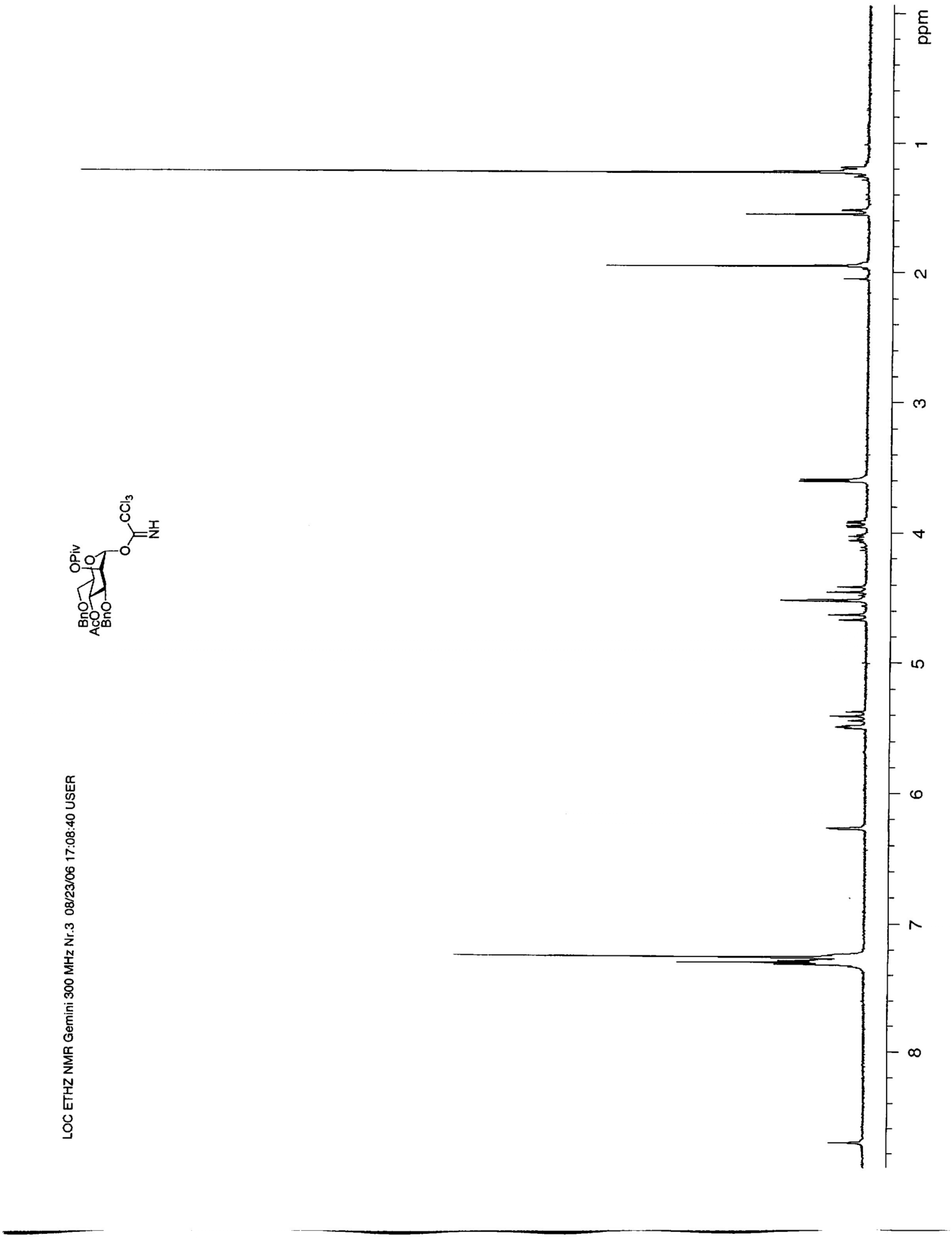

pcasta0003:BC3128OH
75 MHz {1H-BB}-13C-NMR
161.8
147.8
147.0
138.0
137.8
137.7
137.6
137.2
129.1
128.6
128.3
128.3
128.1
128.1
127.9
126.3
115.1
102.6
102.0
99.1
92.5
79.4
79.3
78.6
78.1
77.5
77.2
77.0
76.6
75.6
75.0
74.7
74.6
70.8
69.2
68.5
67.1
58.2
30.0
28.7
Ph
O
OBn
HO
BnO
BnO
NHTCA
44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

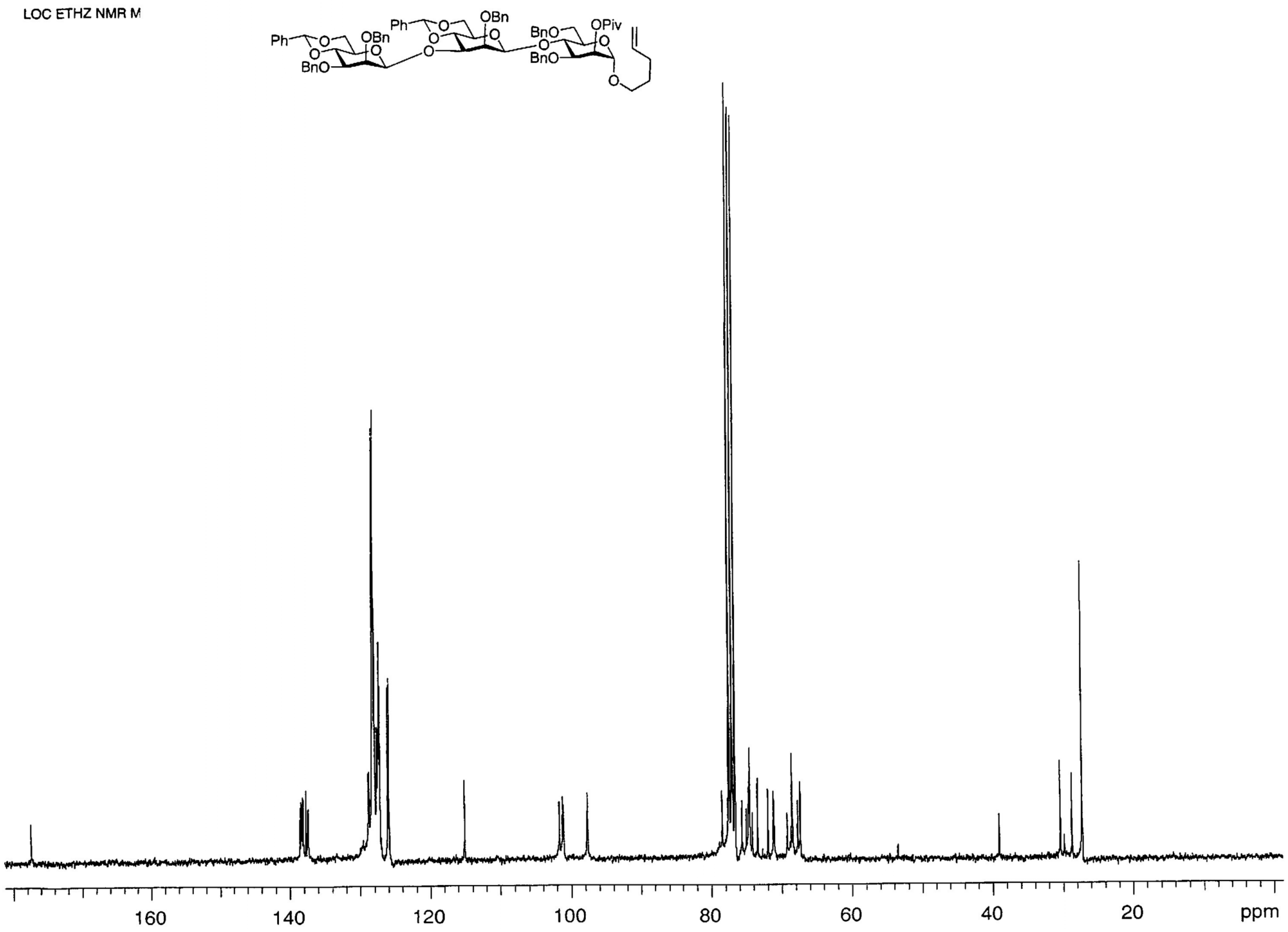

pcasta0003:BC3128OH
300 MHz 1H-NMR
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
24.3
1.1
1.0
1.0
1.1
2.2
4.2
2.1
1.0
1.0
2.0
4.3
3.1
3.1
0.9
0.8
2.0
2.2
Ph
O
O
HO
OBn
O
BnO
BnO
O
O
NHTCA
44


LOC ETHZ NMR Mercury-vx 300MHz Nr.6 01/19/07 08:16:02 USER:pcasta GROUP:seeber SAMPLE:BC3114
Ph
O
O
OBn
O
O
HO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
O
O
45
180
160
140
120
100
80
60
40
20
ppm

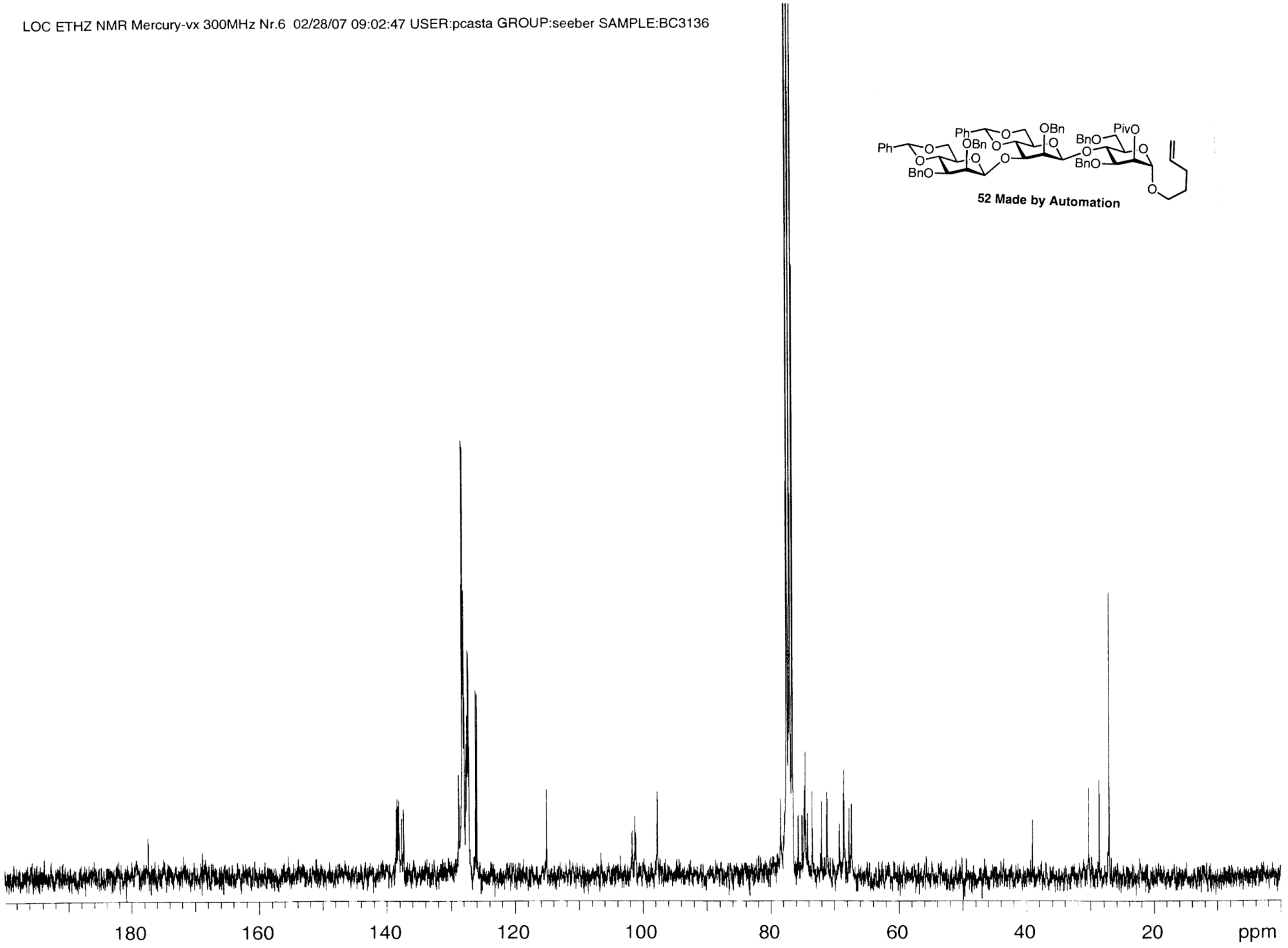

LOC ETHZ NMR Gemini 300 MHz Nr.3 08/23/06 17:14:12 USER:pcodee
Ph
O
O
HO
OBn
O
BnO
BnO
BnO
O
BnO
BnO
BnO
O
ppm
8
7
6
5
4
3
2
1

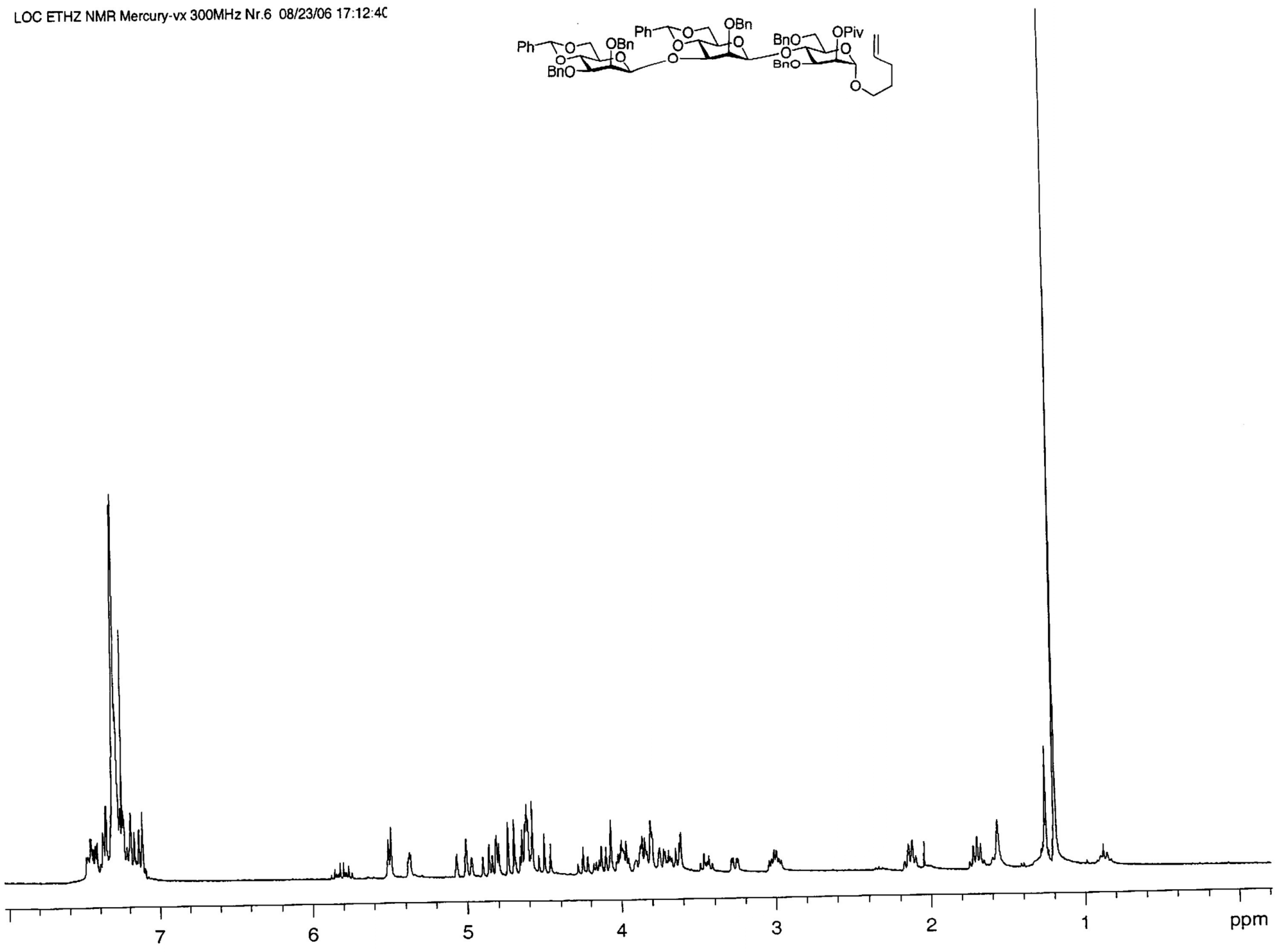

LOC ETHZ NMR Gemini 300 MHz Nr.3 08/23/06 1
BnO
AcO
BnO
OPiv
O
O
CCl3
NH
160
140
120
100
80
60
40
20
ppm


LOC ETHZ NMR Gemini 300 MHz Nr.3 08/23/06 17:08:40 USER
OPiv
BnO
AcO
BnO
O
O
CCl3
NH
ppm
1
2
3
4
5
6
7
8

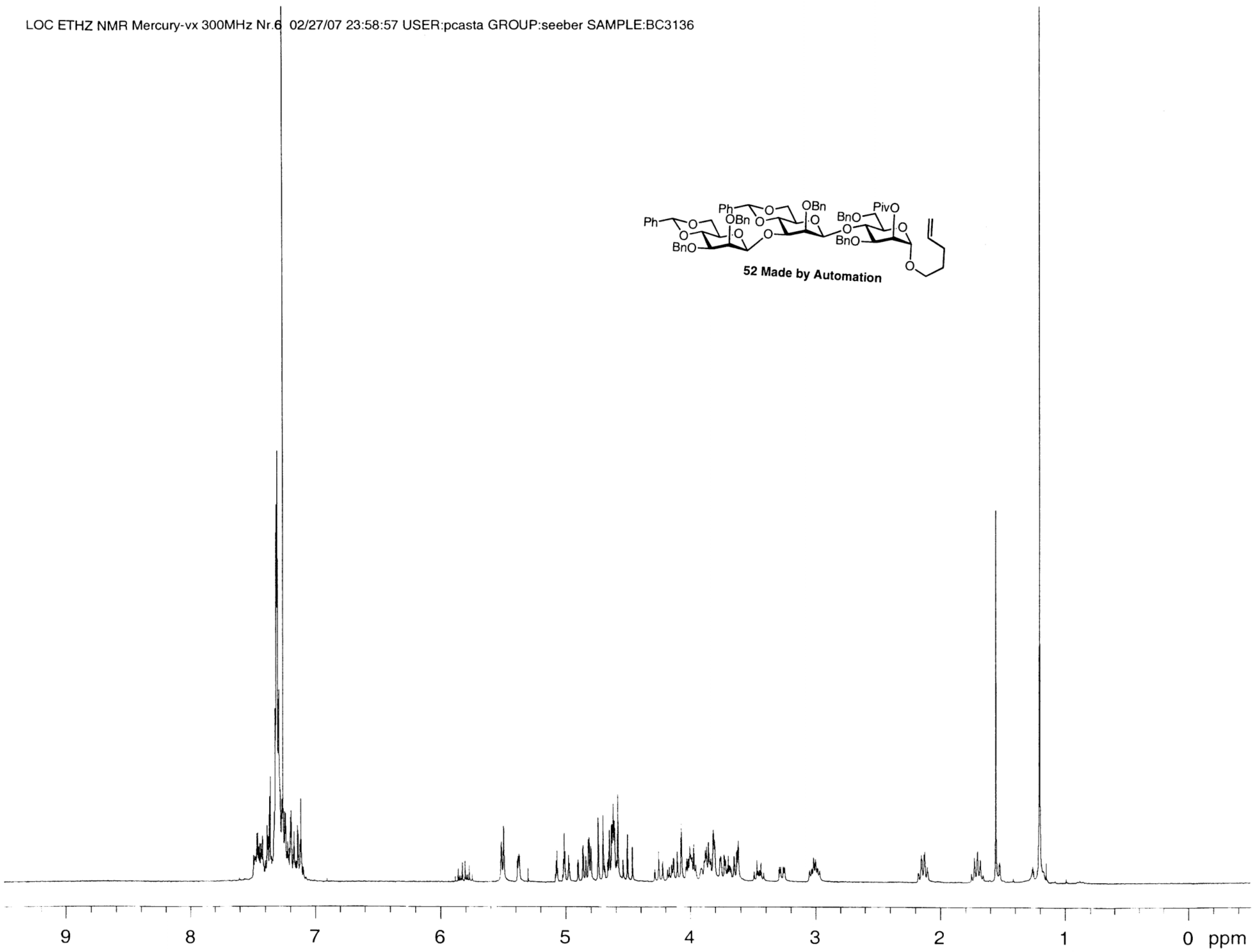

LOC ETHZ NMR M
Ph
O
O
OBn
O
BnO
Ph
O
O
OBn
O
O
BnO
O
BnO
OPiv
O
BnO
O
O
160
140
120
100
80
60
40
20
ppm

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 02/28/07 09:02:47 USER:pcasta GROUP:seeber SAMPLE:BC3136




LOC ETHZ NMR Mercury-vx 300MHz Nr.6 08/23/06 17:12:40
Ph
OBn
BnO
Ph
OBn
BnO
OPiv
BnO
7
6
5
4
3
2
1
ppm

LOC ETHZ NMR Mercury-vx 300MHz Nr.6 02/27/07 23:58:57 USER:pcasta GROUP:seeber SAMPLE:BC3136



52 Made by Automation