

Supporting Information for

Synthesis of a Miniature Lipoarabinomannan

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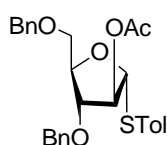
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I. Experimental Section:

General Methods.

Chemicals and materials were obtained from commercial sources, and were used as received without further purification unless otherwise noted. Molecular sieve 4Å was flame-dried under high vacuum and cooled under N₂ atmosphere immediately before use. Analytical TLC was carried out on Silica Gel 60Å F₂₅₄ plates with detection by a UV detector and/or by charring with 15% H₂SO₄ in EtOH (v/v). Mass spectrometry (MS) was performed on a MALDI-TOF MS machine or a high resolution ESI-TOF MS machine. NMR spectra were recorded on a 400, 600 or 700 MHz machine with chemical shifts reported in ppm (δ) downfield from internal tetramethylsilane (TMS) reference. Signals are described as s (singlet), d (doublet), t (triplet), q (quintet) or m (multiplet), and the coupling constants are reported in Hz.

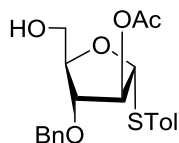
p-Tolyl 2-*O*-acetyl-3,5-di-*O*-benzyl-1-thio- α -D-arabinofuranoside (**8**):



To a stirred solution of **12** (8.0 g, 25 mmol) in 20 mL of anhydrous CH₂Cl₂ were added AcBr (2.8 mL, 38 mmol) and CH₃OH (1.5 mL, 38 mmol) at 0°C. The mixture was stirred at rt for 2 h, when TLC indicated the disappearance of **12**. 2,6-Lutidine (8.7 mL, 75 mmol) and CH₃OH (10 mL) were then added dropwise at rt. Five hours later, the solvent was evaporated *in vacuo* to give a white solid, which was dissolved in 30 mL of CH₃OH, and then CH₃ONa in CH₃OH (1.0 M) was added until the pH reached 10. The reaction mixture was stirred at rt for 3 h, and

the solvent was removed *in vacuo*. The residue was purified by column chromatography with CH₃OH and CH₂Cl₂ (1:15) as the eluent to produce **13** (3.4 g, 65% overall) as colorless syrup. To the solution of **13** (3.4 g, 16.5 mmol) in 20 mL of DMF was slowly added NaH (1.98 g, 49.5 mmol, 60%). Thirty minutes later, BnBr (7.06 g, 41.3 mmol) was added dropwise to the reaction mixture, which was warmed to rt, stirred for another hour and quenched with CH₃OH before water was added. The aq. phase was extracted with EtOAc (3×50 mL) and the organic layer was combined, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography with EtOAc and hexane (1:15) as the eluent to afford colorless syrup (4.5 g, 71%), a part of which (3.5 g, 9.07 mmol) was mixed with *p*-thiocresol (1.35 g, 10.88 mmol) and activated MS 4Å in 20 mL of anhydrous CH₂Cl₂. To the mixture was added a catalytic amount of SnCl₄ (0.9 mmol, 1M in CH₂Cl₂) at 0 °C. The reaction mixture was stirred for 0.5 h, quenched with triethylamine, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with EtOAc and hexane (1:15) as the eluent to afford **8** (3.6 g, 83%) as colorless syrup. ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 8.0 Hz, 2H, Ph), 7.36-7.23 (m, 10H, Ph), 7.10 (d, *J* = 8.0 Hz, 2H, Ph), 5.50 (s, 1H, H-2), 5.29 (t, *J* = 1.6 Hz, 1H, H-1), 4.74 (d, *J* = 12.0 Hz, 1H, Bn), 4.60-4.44 (m, 4H, H-4, Bn), 3.98 (dd, *J* = 4.6, 1H, H-3), 3.63 (m, 2H, H-5, H-5'), 2.31 (s, 3H, Tol), 1.99 (s, 3H, Ac). ¹³C NMR (100 MHz, CDCl₃): δ 169.88, 138.04, 137.59, 132.35, 130.59, 129.73, 128.43, 128.36, 127.93, 127.87, 127.72, 127.68, 91.44, 83.08, 81.97, 81.92, 73.40, 72.23, 68.85, 21.14, 20.90. HR ESI-TOF MS (*m/z*): calcd for C₂₈H₃₀O₅SNa [M + Na]⁺, 501.1712; found, 501.1718. ESI MS (*m/z*): found, 501.4.

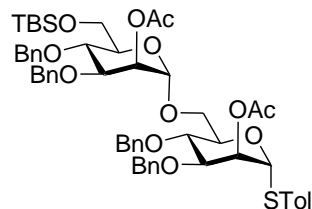
***p*-Tolyl 2-*O*-acetyl-3-*O*-benzyl-5-*O*-*tert*-butyldimethylsilyl-1-thio- α -D-arabinofuranoside (**9**):**



To a solution of **13** (3.0 g, 14.56 mmol) and triethylamine (4.41 g, 43.69 mmol) in 30 mL of pyridine were added TBSCl (2.63 g, 17.48 mmol) and a catalytic amount of DMAP at 0 °C. The reaction mixture was warmed up to rt and stirred for another 5 h. The solution was then concentrated under reduced pressure, and the residue was purified by silica gel column chromatography with EtOAc and hexane (1:4) as the eluent to give a colorless syrup product (3.96 g, 85%). To its solution (1.8 g, 5.63 mmol) in 20 mL of anhydrous DMF was slowly added NaH (450 mg, 11.26 mmol, 60% in oil) at 0 °C. Thirty minutes later, BnBr (1.45 g, 8.45 mmol) was added dropwise. The reaction mixture was warmed to rt slowly and stirred for another 1 h at rt, quenched with MeOH, diluted with water (100 mL), and extracted with EtOAc (2×100 mL). The organic layer, after being dried with Na₂SO₄, was concentrated, and the residue was purified by silica gel column chromatography with EtOAc and hexane (1:10) as the eluent to produce **14** (2.03 g, 88%), a part of which (1.3 g, 3.17 mmol) was mixed with *p*-thiocresol (472 mg, 3.81 mmol), and freshly activated molecular sieves 4Å in 20 mL of anhydrous CH₂Cl₂. To the mixture was added a catalytic amount of SnCl₄ (0.4 mmol, 1M in CH₂Cl₂) at 0 °C. Thirty minutes later, the reaction was quenched with triethylamine, filtered, and concentrated. To a solution of the residue in 20 mL of THF were added TBAF (10 mL, 1M in THF) and AcOH (365 μL, 6.34 mmol). The mixture was stirred at rt for 2 h, when TLC showed completion of the reaction. The solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography with EtOAc and hexane (1:5)

as the eluent to give **9** (886 mg, 72% for two steps) as colorless syrup. ^1H NMR (400 MHz, CDCl_3): δ 7.44-7.26 (m, 7H, Ph), 7.12 (d, $J = 8.0$ Hz, 2H, Ph), 5.47 (s, 1H, H-2), 5.29 (s, 1H, H-1), 4.78 (d, $J = 12.0$ Hz, 1H, Bn), 4.59 (d, $J = 12.0$ Hz, 1H, Bn), 4.45-4.39 (m, 1H, H-4), 3.99 (d, $J = 5.6$ Hz, 1H, H-3), 3.86 (dt, $J = 12.0, 3.6$ Hz, 1H, H-5), 3.64 (m, 1H, H-5'), 2.32 (s, 3H, Tol), 2.06 (s, 3H, Ac). ^{13}C NMR (100 MHz, CDCl_3): δ 169.79, 137.96, 137.48, 132.72, 130.22, 129.83, 128.51, 127.98, 127.88, 91.71, 83.09, 82.62, 81.89, 72.46, 61.52, 21.16, 20.95. HR ESI-TOF MS (m/z): calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5\text{SNa}$ $[\text{M} + \text{Na}]^+$, 411.1242; found, 411.1249. ESI MS (m/z): found, 411.6.

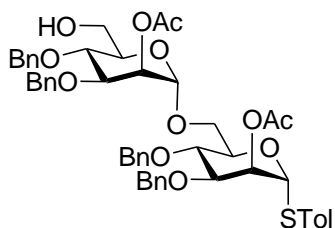
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butydimethylsilyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-3,4-di-*O*-benzyl-2-*O*-acetyl- α -D-mannopyranoside (**15**):**



After a mixture of **10** (1.11 g, 1.78 mmol) and freshly activated molecular sieves 4\AA in anhydrous CH_2Cl_2 (20 mL) was stirred at rt for 40 min and then cooled to $-78\text{ }^\circ\text{C}$, a solution of AgOTf (1.38 g, 5.35 mmol) in acetonitrile (5 mL) was added. Ten minutes later, *p*-TolSCl (257 μL , 1.78 mmol) was added dropwise. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for another 15 min, before a solution of **11** (828 mg, 1.63 mmol) and TTBP (404 mg, 1.63 mmol) in anhydrous CH_2Cl_2 (5.0 mL) was added. The reaction mixture was warmed up to rt slowly in 1 h, stirred for another 20 min, quenched with Et_3N , diluted with CH_2Cl_2 , filtered, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography with a

mixture of EtOAc and toluene (1:30) as the eluent to give **15** (1.39 g, 85%) as syrup. ^1H NMR (600 MHz, CDCl_3): δ 7.38-7.15 (m, 22H, Ph), 7.09 (d, $J = 7.8$ Hz, 2H, Ph), 5.60 (s, 1H, Man^{A} H-2), 5.40 (s, 1H, Man^{B} H-2), 5.37 (s, 1H, Man^{A} H-1), 4.90 (dd, $J = 10.8, 3.6$ Hz, 2H), 4.86 (s, 1H, Man^{B} H-1), 4.73-4.46 (m, 6H), 4.30 (m, 1H), 3.97 (dd, $J = 9.6, 3.0$ Hz, 1H), 3.94-3.87 (m, 3H), 3.84-3.79 (m, 2H), 3.74 (d, $J = 10.8$ Hz, 1H), 3.68 (d, $J = 10.8$ Hz, 1H), 3.61 (dd, $J = 9.6, 3.0$ Hz, 1H), 2.19 (s, 3H, Tol), 2.14 (s, 3H, Ac), 2.10 (s, 3H, Ac), 0.90 (s, 9H, *t*Bu), 0.06 (s, 3H, SiMe), 0.04 (s, 3H, SiMe). ^{13}C NMR (150 MHz, CDCl_3): δ 170.27, 170.16, 138.83, 138.23, 137.89, 137.84, 137.54, 131.97, 129.88, 128.44, 128.37, 128.34, 128.24, 128.19, 128.13, 127.88, 127.76, 127.69, 127.64, 127.63, 127.46, 97.84 (Man^{B} C-1, $J_{\text{CH}} = 172$ Hz), 86.59 (Man^{A} C-1, $J_{\text{CH}} = 169$ Hz), 78.52, 77.83, 75.13, 74.40, 74.09, 72.79, 72.17, 71.81, 71.67, 70.24, 68.58, 65.92, 62.08, 25.87, 20.98, 20.95, 18.24, -5.12, -5.39. HR ESI-TOF MS (m/z): calcd for $\text{C}_{57}\text{H}_{70}\text{O}_{12}\text{SiNa} [\text{M} + \text{Na}]^+$, 1029.4255; found, 1029.4249.

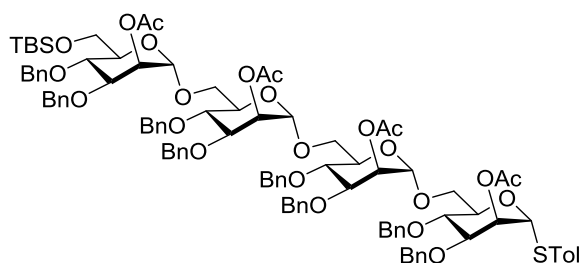
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-3,4-di-*O*-benzyl-2-*O*-acetyl- α -D-mannopyranoside (**16**):**



After the TBS-protected **15** (760 mg, 0.755 mmol) was dissolved in THF and CH_2Cl_2 (16 mL, 1:1), $\text{Et}_3\text{N}\cdot 3\text{HF}$ (740 μL , 4.54 mmol) was added under Argon at rt, and the mixture was stirred at rt overnight. The reaction was quenched with saturated aq. NaHCO_3 , and the water phase was extracted with CH_2Cl_2 (2×100 mL). The organic layer was combined, dried over

Na₂SO₄, and then concentrated under reduced pressure. The residue was finally purified by silica gel column chromatography with EtOAc and toluene (1:10) as the eluent to afford **16** (600 mg, 89%) as foamy solid. ¹H NMR (600 MHz, CDCl₃): δ 7.27-7.11 (m, 22H, Ph), 7.01 (d, *J* = 7.8 Hz, 2H, Ph), 5.53 (dd, *J* = 3.0, 1.8 Hz, 1H, Man^A H-2), 5.36 (dd, *J* = 3.0, 1.8 Hz, 1H, Man^B H-2), 5.30 (d, *J* = 1.2 Hz, 1H, Man^A H-1), 4.84 (dd, *J* = 10.8, 8.4 Hz, 2H), 4.81 (d, *J* = 1.2 Hz, 1H, Man^B H-1), 4.66-4.38 (m, 6H), 4.22 (m, 1H), 3.91-3.81 (m, 3H), 3.76-3.56 (m, 6H), 2.14 (s, 3H, Tol), 2.08 (s, 3H, Ac), 2.04 (s, 3H, Ac). ¹³C NMR (150 MHz, CDCl₃): δ 170.27, 170.00, 138.36, 138.18, 137.94, 137.74, 137.49, 132.06, 129.96, 129.91, 128.46, 128.40, 128.36, 128.33, 128.21, 128.10, 127.90, 127.76, 127.69, 127.66, 97.98 (Man^B C-1), 86.61 (Man^A C-1), 78.45, 77.75, 75.21, 75.14, 74.30, 74.11, 72.05, 71.94, 71.82, 71.61, 70.18, 68.36, 66.10, 62.05, 21.01, 20.99, 20.98. HR ESI-TOF MS (*m/z*): calcd for C₅₁H₅₆O₁₂SNa [M + Na]⁺, 915.3390; found, 915.3350.

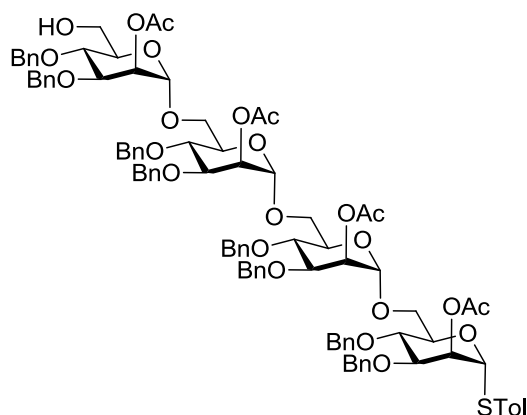
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-3,4-di-*O*-benzyl-2-*O*-acetyl- α -D-mannopyranoside (**17**):**



After a mixture of **15** (707 mg, 0.703 mmol) and freshly activated molecular sieves 4Å in anhydrous CH₂Cl₂ (12 mL) was stirred at rt for 40 min and then cooled to -78 °C, a solution of AgOTf (542 mg, 2.108 mmol) in acetonitrile (4 mL) was added, followed by dropwise

addition of *p*-TolSCl (102 μ L, 0.703 mmol) 10 min later. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for another 15 min, before a solution of **16** (570 mg, 0.639 mmol) and TTBP (200 mg, 0.81 mmol) in anhydrous CH_2Cl_2 (3.0 mL) was added. The reaction mixture was warmed up to rt slowly in 1 h, stirred for another 20 min, quenched with Et_3N , diluted with CH_2Cl_2 , filtered, and then concentrated *in vacuo*. The residue was purified on silica gel column with a mixture of EtOAc and toluene (1:13) as the eluent to give **17** (930 mg, 82%) as foamy solid. ^1H NMR (600 MHz, CDCl_3): δ 7.35-7.12 (m, 42H, Ph), 7.09 (d, $J = 8.0$ Hz, 2H, Ph), 5.61 (dd, $J = 3.0$, 1.8 Hz, 1H, Man^A H-2), 5.46 (dd, $J = 3.0$, 1.8 Hz, 1H, Man H-2), 5.45 (dd, $J = 3.0$, 1.8 Hz, 1H, Man H-2), 5.43 (dd, $J = 3.0$, 1.8 Hz, 1H, Man H-2), 5.37 (s, 1H, Man^A H-1), 4.92-4.83 (m, 7H, 3 \times Man H-1, 4 \times Bn- CH_2 -), 4.72 (d, $J = 10.8$ Hz, 1H), 4.67 (d, $J = 10.8$ Hz, 3H), 4.59 (d, $J = 10.8$ Hz, 1H), 4.55 (d, $J = 11.4$ Hz, 1H), 4.50-4.40 (m, 6H), 4.30 (dd, $J = 9.6$, 4.2 Hz, 1H), 3.97 (dd, $J = 9.6$, 3.0 Hz, 1H), 3.96-3.87 (m, 5H), 3.86-3.74 (m, 5H), 3.72-3.64 (m, 4H), 3.60 (d, $J = 9.6$ Hz, 1H), 3.57-3.48 (m, 3H), 2.19 (s, 3H, Tol), 2.157 (s, 3H, Ac), 2.151 (s, 3H, Ac), 2.14 (s, 3H, Ac), 2.10 (s, 3H, Ac), 0.89 (s, 9H, *t*Bu), 0.06 (s, 3H, SiMe), 0.03 (s, 3H, SiMe). ^{13}C NMR (150 MHz, CDCl_3): δ 170.29, 170.25, 170.18, 170.12, 138.78, 138.48, 138.47, 138.18, 137.90, 137.82, 137.65, 137.62, 137.50, 132.01, 130.03, 129.92, 128.46, 128.44, 128.39, 128.37, 128.28, 128.26, 128.24, 128.21, 128.18, 127.92, 127.80, 127.76, 127.72, 127.68, 127.59, 127.47, 127.43, 127.39, 127.38, 97.99 (3 \times Man C-1), 86.64 (Man^A C-1), 78.52, 77.91, 77.67, 77.55, 75.13, 75.10, 75.00, 74.93, 74.32, 73.92, 73.78, 73.75, 72.68, 72.11, 71.83, 71.57, 71.48, 71.37, 71.19, 70.20, 68.47, 68.17, 68.05, 66.29, 65.49, 65.25, 61.88, 25.87, 21.01, 20.98, 18.23, -5.12, -5.38. HR ESI-TOF MS (m/z): calcd for $\text{C}_{101}\text{H}_{118}\text{O}_{24}\text{SSiNa}[\text{M} + \text{Na}]^+$, 1797.7401; found, 1797.7299.

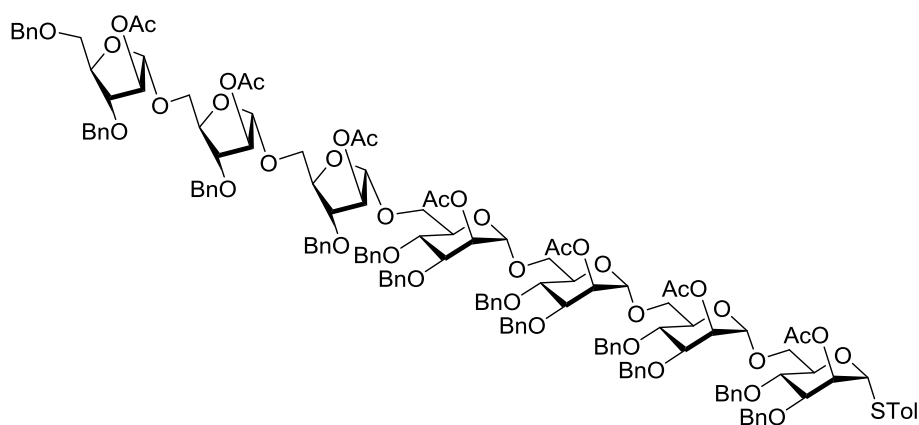
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-3,4-di-*O*-benzyl-2-*O*-acetyl- α -D-mannopyranoside (**7**):**



After the TBS-protected **17** (900 mg, 0.507 mmol) was dissolved in THF and CH₂Cl₂ (16 mL, 1:1), Et₃N·3HF (495 μ L, 3.04 mmol) was added under Argon at rt, and the mixture was stirred at rt overnight. The reaction was quenched with saturated aq. NaHCO₃, and the water phase was extracted with CH₂Cl₂ (2 \times 100 mL). The organic layer was combined, dried over Na₂SO₄, and then concentrated under reduced pressure. The residue was finally purified by silica gel column chromatography with EtOAc and toluene (1:5) as the eluent to afford **7** (724 mg, 86%) as foamy solid. ¹H NMR (600 MHz, CDCl₃): δ 7.34-7.14 (m, 42H, Ph), 7.09 (d, *J* = 7.8 Hz, 2H, Ph), 5.61 (s, 1H, Man^A H-2), 5.47 (s, 1H, Man H-2), 5.46 (s, 2H, 2 \times Man H-2), 5.38 (s, 1H, Man^A H-1), 4.93-4.86 (m, 7H, 3 \times Man H-1, 4 \times Bn-CH₂-), 4.75-4.65 (m, 4H), 4.58-4.53 (m, 2H), 4.51-4.38 (m, 6H), 4.31 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.98 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.96-3.88 (m, 4H), 3.85-3.74 (m, 5H), 3.73-3.59 (m, 6H), 3.58-3.48 (m, 3H), 2.19 (s, 3H, Tol), 2.16 (s, 6H, 2 \times Ac), 2.14 (s, 3H, Ac), 2.12 (s, 3H, Ac). ¹³C NMR (150 MHz, CDCl₃): δ 170.31, 170.25, 170.17, 169.98, 138.48, 138.39, 138.29, 138.18, 137.92, 137.64, 137.60,

137.56, 137.48, 132.01, 130.02, 129.93, 128.47, 128.46, 128.43, 128.38, 128.34, 128.32, 128.29, 128.25, 128.22, 128.17, 127.94, 127.91, 127.85, 127.80, 127.71, 127.68, 127.61, 127.48, 127.45, 127.31, 98.00 (2 × Man C-1), 97.96 (Man C-1), 86.64 (Man^A C-1), 78.50, 77.91, 77.62, 77.47, 75.17, 75.14, 75.00, 74.97, 74.30, 73.98, 73.77, 73.71, 72.10, 71.86, 71.83, 71.57, 71.42, 71.39, 71.12, 70.19, 68.22, 68.15, 68.02, 66.29, 65.60, 65.26, 61.95, 21.04, 21.02, 20.99. HR ESI-TOF MS (*m/z*): calcd for C₉₅H₁₀₄O₂₄SNa [M + Na]⁺, 1683.6536; found, 1683.6420.

***p*-Tolyl (2-*O*-acetyl-3,5-di-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2-*O*-acetyl-3-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2-*O*-acetyl-3-*O*-benzyl- α -D-arabinosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl- α -D-mannopyranosyl)-3,4-di-*O*-benzyl-2-*O*-acetyl- α -D-mannopyranoside (5):**

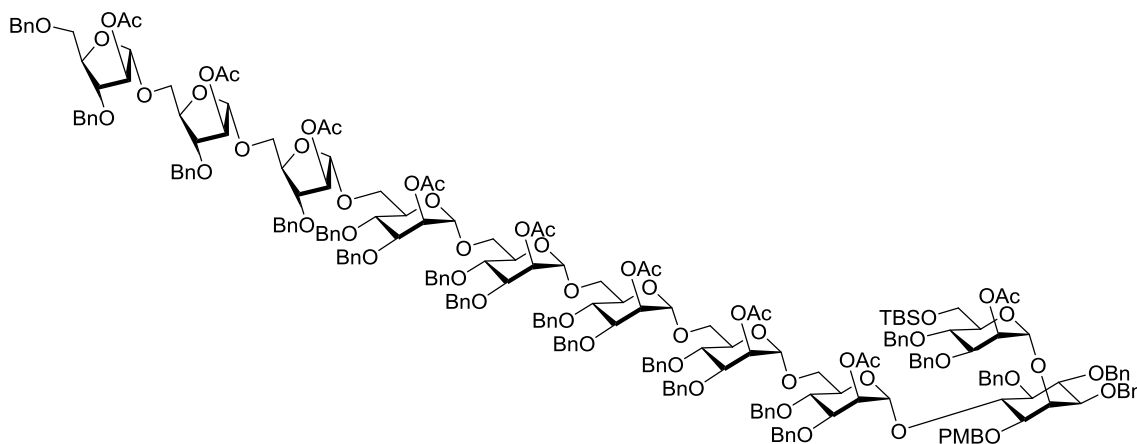


After a mixture of **8** (270 mg, 0.565 mmol) and freshly activated molecular sieves 4Å in anhydrous CH₂Cl₂ (8 mL) was stirred at rt for 40 min and then cooled to -78 °C, a solution of AgOTf (436 mg, 1.695 mmol) in acetonitrile (2.5 mL) was added. Ten minutes later, *p*-TolSCl (82 μL, 0.565 mmol) was added dropwise. The mixture was stirred at -78 °C for

another 15 min, before a solution of **9** (199 mg, 0.514 mmol) and TTBP (127 mg, 0.514 mmol) in anhydrous CH₂Cl₂ (2.0 mL) was added. The reaction mixture was warmed up to rt slowly in 1 h, stirred for another 20 min, and then cooled to -78 °C again. This was followed by another glycosylation by the same protocol using AgOTf (396 mg, 1.542 mmol) in acetonitrile (2.0 mL), *p*-TolSCl (74 μL, 0.514 mmol), **9** (181 mg, 0.467 mmol) and TTBP (116 mg, 0.467 mmol) in anhydrous CH₂Cl₂ (2.0 mL). Thereafter, another glycosylation was achieved with **7** (705 mg, 0.425 mmol) as the glycosyl donor following the same protocol using AgOTf (360 mg, 1.401 mmol) in acetonitrile (2.0 mL), *p*-TolSCl (68 μL, 0.467 mmol), and **7** and TTBP (105 mg, 0.425 mmol) in anhydrous CH₂Cl₂ (3.5 mL). Finally, the reaction was quenched with Et₃N, diluted with CH₂Cl₂, filtered, and concentrated *in vacuum*. The residue was purified by silica gel column chromatography with EtOAc and toluene (1:5) as the eluent to give **5** (443 mg, 41% overall) as a foamy solid. ¹H NMR (600 MHz, CDCl₃): δ 7.34-7.15 (m, 62H, Ph), 7.08 (d, *J* = 8.0 Hz, 2H, Ph), 5.60 (s, 1H, Man^A H-2), 5.45 (m, 3H, 3 × Man H-2), 5.37 (s, 1H, Man^A H-1), 5.22 (s, 1H, Ara^A H-2), 5.15 (s, 1H, Ara^A H-1), 5.10 (s, 1H, Ara H-2), 5.08 (s, 1H, Ara H-2), 5.05 (s, 1H, Ara H-1), 5.02 (s, 1H, Ara H-1), 4.96 (s, 1H, Man^B H-1), 4.94-4.82 (m, 5H, 2 × Man H-1, 3 × Bn-CH₂-), 4.77-4.62 (m, 8H), 4.60-4.36 (m, 13H), 4.30 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.12 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.06 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.01 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.99-3.88 (m, 8H), 3.85-3.44 (m, 20H), 2.18 (s, 3H, Tol), 2.14 (s, 6H, 2 × Ac), 2.13 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.96 (s, 6H, 2 × Ac). ¹³C NMR (150 MHz, CDCl₃): δ 170.34, 170.30, 170.27, 170.23, 169.82, 169.78, 169.74, 138.79, 138.44, 138.37, 138.14, 137.92, 137.89, 137.86, 137.81, 137.76, 137.65, 137.62, 137.59, 137.48, 132.01, 129.99, 129.92, 128.46, 128.44, 128.38, 128.31, 128.30, 128.28,

128.23, 128.19, 127.92, 127.82, 127.73, 127.69, 127.67, 127.63, 127.59, 127.51, 127.45, 127.41, 127.33, 106.19 (Ara^A C-1), 106.03 (2 × Ara C-1), 98.14 (Man^B C-1), 97.98 (Man C-1), 97.96 (Man C-1), 86.62 (Man^A C-1), 83.40, 83.31, 82.65, 82.25, 81.95, 81.55, 81.45, 80.96, 78.50, 77.89, 77.63, 77.59, 75.14, 74.99, 74.30, 73.83, 73.77, 73.68, 73.43, 72.22, 72.11, 71.83, 71.56, 71.44, 71.37, 71.15, 71.10, 70.19, 69.16, 68.23, 68.16, 68.04, 66.28, 65.58, 65.49, 65.38, 65.34, 65.25, 21.02, 20.98, 20.84, 20.80. HR ESI-TOF MS (m/z): calcd for C₁₄₄H₁₅₈O₃₉SNa [M + Na]⁺, 2565.9999; found, 2566.0120.

6-O-[(2-O-Acetyl-3,5-di-O-benzyl- α -D-arabinosyl)-(1 \rightarrow 5)-(2-O-acetyl-3-O-benzyl- α -D-arabinosyl)-(1 \rightarrow 5)-(2-O-acetyl-3-O-benzyl- α -D-arabinosyl)-(1 \rightarrow 6)-(2-O-acetyl-3,4-di-O-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-O-acetyl-3,4-di-O-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-O-acetyl-3,4-di-O-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2-O-acetyl-3,4-di-O-benzyl- α -D-mannopyranosyl)]-2-O-(2-O-acetyl-3,4-di-O-benzyl-6-O-*tert*-butyldimethylsilyl- α -D-mannopyranosyl)-3,4,5-tri-O-benzyl-1-O-(*para*-methoxybenzyl)-D-*myo*-inositol (3):



To a solution of **5** (300 mg, 0.118 mmol) in 10 mL of CH₂Cl₂ were added TTBP (88 mg, 0.354 mmol), NIS (53 mg, 0.236 mmol), and AgOTf (61 mg, 0.236 mmol) at 0 °C. The

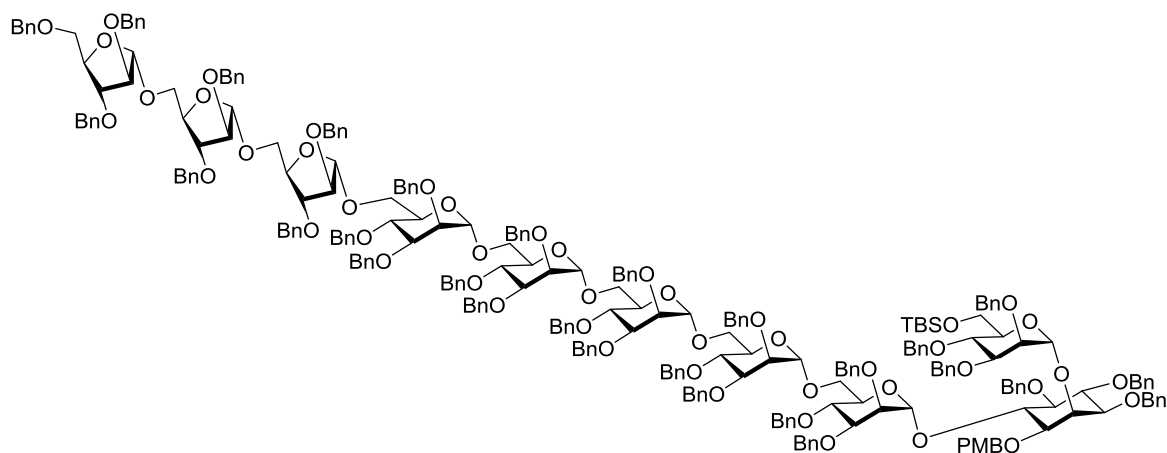
reaction was stirred at rt for 2 h and quenched with saturated aq. $\text{Na}_2\text{S}_2\text{O}_3$ at 0 °C. The mixture was diluted with saturated aq. NaCl and extracted with CH_2Cl_2 (2×70 mL). The organic layer was combined, dried over Na_2SO_4 , and then condensed under reduced pressure. The mixture was purified by silica gel column chromatography with EtOAc and toluene (1:6) as the eluent to produce a foamy solid. To a solution of this product in 10 mL of anhydrous CH_2Cl_2 were added DBU (8.8 μL , 59 μmol) and CCl_3CN (59 μL , 0.59 mmol) at 0 °C. The reaction mixture was stirred for 1 h, and concentrated *in vacuo* to afford a residue, which was purified on a Et_3N -neutralized silica gel column with EtOAc and toluene (1:10) as the eluent to produce **18** (228 mg, 75% for two steps) as a foamy solid, which was directly used in the next step without further purification. To the stirred mixture of **18** (199 mg, 77 μmol), **6** (80 mg, 55 μmol), and molecular sieves 4Å in anhydrous CH_2Cl_2 (5 mL) was added TMSOTf (1.4 μL , 7.7 μmol) under an N_2 atmosphere at 0 °C. The mixture was stirred for another 30 min, before TLC indicated the completion of the reaction. The mixture was neutralized with Et_3N , filtered, and concentrated. The residue was subjected to silica column chromatography with EtOAc and toluene (1:6) as the eluent to afford **3** as colorless syrup (168 mg, 79%). ^1H NMR (600 MHz, CDCl_3): δ 7.42-7.09 (m, 91H, Ph), 7.08-7.04 (m, 4H, Ph), 7.01 (d, $J = 6.6$ Hz, 2H, Ph), 6.86 (d, $J = 8.4$ Hz, 2H, Ph), 5.54 (s, 1H, Man^{A} H-2), 5.52 (s, 3H, 3 × Man H-2), 5.49 (s, 1H, Man H-2), 5.43 (s, 1H, Man^{B} H-2), 5.40 (s, 1H, Man^{A} H-1), 5.25 (s, 1H, Ara^{A} H-2), 5.17 (s, 1H, Ara^{A} H-1), 5.16 (s, 1H, Man^{B} H-1), 5.12 (s, 1H, Ara H-2), 5.10 (s, 1H, Ara H-2), 5.07 (s, 1H, Ara H-1), 5.05-5.02 (m, 2H, Ara H-1, 1 × Bn- CH_2 -), 4.95-4.24 (m, 43H, 4 × Man H-1, 39 × Bn- CH_2 -), 4.15-4.11 (m, 1H), 4.09-4.05 (m, 1H), 4.04-3.69 (m, 27H), 3.61-3.38 (m, 14H), 3.34 -3.23 (m, 6H), 3.20-3.12 (m, 2H), 2.15 (s, 3H, Ac), 2.14 (s, 3H, Ac),

2.12 (s, 6H, 2 × Ac), 2.07 (s, 3H, Ac), 2.02 (s, 3H, Ac), 1.98 (s, 3H, Ac), 1.973 (s, 3H, Ac), 1.970 (s, 3H, Ac), 0.90 (s, 9H, *t*Bu), 0.05 (s, 3H, SiMe), 0.01 (s, 3H, SiMe). ¹³C NMR (150 MHz, CDCl₃): δ 170.22, 170.20, 170.18, 170.07, 169.91, 169.80, 169.72, 169.71, 169.70, 159.41, 139.04, 138.90, 138.88, 138.61, 138.52, 138.44, 138.27, 138.07, 138.02, 137.93, 137.88, 137.86, 137.77, 137.70, 137.56, 137.52, 130.05, 129.10, 129.02, 128.67, 128.52, 128.51, 128.47, 128.45, 128.40, 128.37, 128.33, 128.31, 128.28, 128.24, 128.21, 128.17, 128.11, 128.05, 127.96, 127.84, 127.79, 127.73, 127.70, 127.67, 127.63, 127.56, 127.48, 127.38, 127.35, 127.33, 127.30, 127.27, 127.16, 127.09, 126.95, 126.64, 125.28, 113.84, 106.22 (Ara^A C-1), 106.04 (2 × Ara C-1), 98.66 (Man^A C-1), 98.30 (Man^B C-1), 98.26 (Man C-1), 98.21 (Man C-1), 98.16 (Man C-1), 97.96 (Man C-1), 83.44, 83.34, 82.76, 82.29, 81.99, 81.58, 81.45, 81.32, 80.91, 80.59, 78.81, 78.79, 77.81, 77.75, 77.68, 77.62, 76.44, 75.71, 75.06, 74.97, 74.93, 74.75, 74.59, 74.40, 73.85, 73.77, 73.58, 73.52, 73.44, 73.27, 72.59, 72.22, 72.11, 72.07, 71.70, 71.66, 71.52, 71.41, 71.32, 71.28, 71.19, 71.10, 71.04, 70.81, 70.55, 70.51, 69.94, 69.18, 68.66, 68.20, 68.18, 67.94, 67.85, 67.76, 65.57, 65.44, 65.33, 65.22, 61.90, 60.03, 55.19, 25.90, 21.14, 21.05, 21.02, 20.97, 20.86, 20.82, 18.28, -5.09, -5.33. HR ESI-TOF MS (*m/z*): calcd for C₂₂₂H₂₅₀O₅₈SiNa₂ [M + 2Na]²⁺, 1958.8089; found, 1958.8101.

3,4,5-tri-*O*-Benzyl-6-*O*-[(2,3,5-tri-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,

4-tri-*O*-benzyl- α -D-mannopyranosyl]-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl

yl- α -D-mannopyranosyl)-1-*O*-(*para*-methoxybenzyl)-D-*myo*-inositol (19**):**

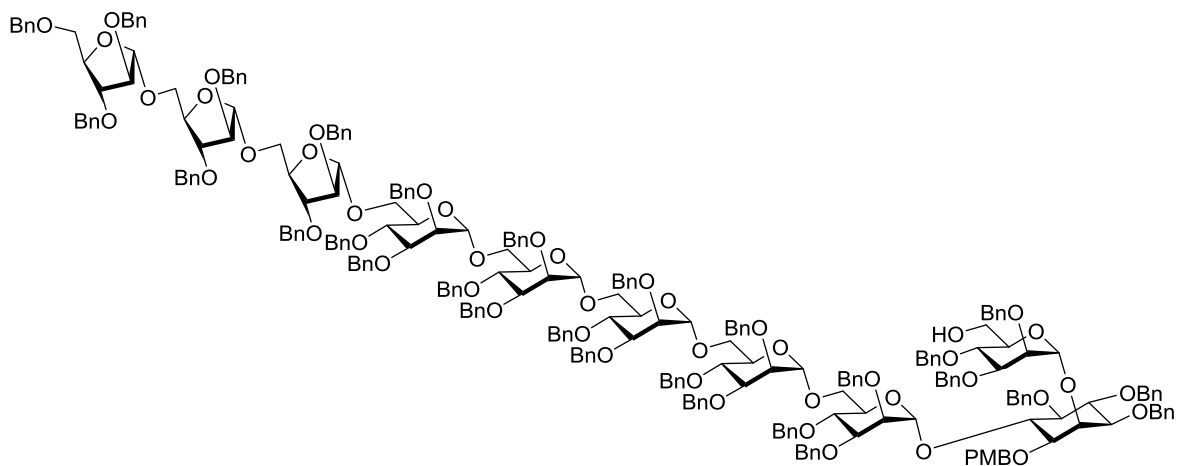


To a solution of **3** (95 mg, 24.5 μ mol) in 15 mL of CH₃OH and CH₂Cl₂ (1:2) was added a CH₃ONa solution in CH₃OH (0.5 M) until the pH reached 11. The reaction mixture was stirred at 35 °C for 36 h, and the solvent was removed *in vacuo*. The residue was dissolved in a mixture of CH₂Cl₂ and CH₃OH (1:10) and filtered. The filtrate was concentrated *in vacuo* to afford an intermediate that was directly applied to the next reaction. To a solution of this intermediate in anhydrous DMF was added BnBr (58 μ L, 0.49 mmol) and TBAI (4.1 mg, 11.0 μ mol). Ten minutes later, NaH was added (6.9 mg, 0.287 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1.5 h, before TLC showed the completion of reaction. MeOH was then slowly added to quench the reaction before water was added. The aqueous phase was extracted with CH₂Cl₂ (3 \times 50 mL), and the organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography with EtOAc and toluene (1:14) as the eluent to give **19** (80 mg, 76% for two steps) as colorless syrup. ¹H NMR (600 MHz, CDCl₃): δ 7.41-7.04 (m, 142H, Ph), 6.61 (d, *J* = 8.4 Hz, 2H, Ph), 5.42 (s, 1H, Man^A H-1), 5.32 (s, 1H, Man^B H-1), 5.23 (s, 1H, Ara^A H-1), 5.16 (s, 1H, Ara H-1), 5.10 (s, 1H, Ara H-1), 5.07-5.04 (m, 2H, Man H-1, 1 \times Bn-CH₂-), 5.02 (s, 1H, Man H-1), 4.98 (s,

1H, Man H-1), 4.97-4.30 (m, 58H, Man^C H-1, 57 × Bn-CH₂-), 4.23-4.17 (m, 1H), 4.16-3.29 (m, 57H), 3.23 (d, *J* = 11.4 Hz, 1H), 3.14 (d, *J* = 10.8 Hz, 1H), 0.88 (s, 9H, *t*Bu), 0.03 (s, 3H, SiMe), 0.02 (s, 3H, SiMe). ¹³C NMR (150 MHz, CDCl₃): δ 159.44, 139.16, 139.01, 138.84, 138.80, 138.78, 138.72, 138.71, 138.60, 138.54, 138.48, 138.33, 138.26, 138.15, 138.13, 138.10, 138.06, 137.96, 137.94, 137.86, 137.71, 137.65, 129.48, 129.06, 128.48, 128.35, 128.32, 128.29, 128.27, 128.25, 128.24, 128.16, 128.14, 128.11, 128.08, 128.03, 127.99, 127.93, 127.88, 127.79, 127.77, 127.75, 127.73, 127.70, 127.67, 127.65, 127.63, 127.59, 127.58, 127.52, 127.50, 127.45, 127.42, 127.41, 127.34, 127.26, 127.21, 127.13, 127.06, 126.85, 113.92, 106.78 (Ara^A C-1), 106.48 (Ara C-1), 106.45 (Ara C-1), 99.10 (Man^A C-1), 98.75 (Man^B C-1), 98.60 (Man C-1), 98.50 (Man C-1), 98.32 (Man C-1), 98.13 (Man^C C-1), 88.40, 88.10, 88.08, 83.57, 83.26, 83.19, 82.06, 81.44, 81.40, 80.69, 80.64, 80.47, 80.29, 79.61, 79.41, 79.34, 79.30, 79.15, 79.04, 76.08, 75.96, 75.75, 75.70, 75.17, 75.04, 74.99, 74.94, 74.85, 74.80, 74.70, 74.59, 74.55, 74.43, 74.26, 74.04, 73.90, 73.73, 73.35, 72.88, 72.67, 72.61, 72.58, 72.55, 72.51, 72.43, 72.32, 72.25, 72.17, 72.15, 72.05, 72.01, 71.91, 71.87, 71.70, 71.56, 71.50, 71.40, 71.35, 71.25, 71.22, 71.07, 69.67, 69.07, 66.03, 65.90, 65.84, 65.78, 65.63, 62.25, 60.03, 55.05, 25.96, 18.33, -5.11, -5.33. ESI-TOF MS (*m/z*): calcd for C₂₆₇H₂₈₆O₄₉SiNa₂ [M + 2Na]²⁺, 2174.9; found, 2174.4. MALDI-TOF MS (*m/z*): calcd for C₂₆₇H₂₈₆O₄₉SiNa [M + Na]⁺ 4330.1; found, 4329.5.

3,4,5-tri-*O*-Benzyl-6-*O*-[(2,3,5-tri-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-ben

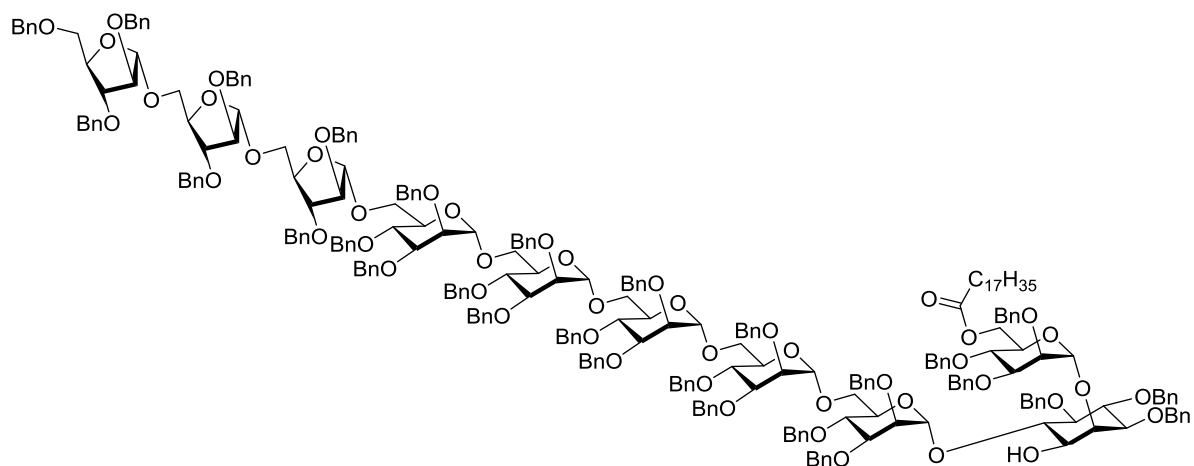
zyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)]-2-*O*-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-1-*O*-(*para*-methoxybenzyl)-D-*myo*-inositol (20**):**



After the TBS-protected **19** (65.0 mg, 15.1 μ mol) was dissolved in THF and CH_2Cl_2 (2 mL, 1:1), $\text{Et}_3\text{N}\cdot 3\text{HF}$ (49 μ L, 0.30 mmol) was added under Argon at rt, and the mixture was stirred at rt overnight. The reaction was quenched with saturated aq. NaHCO_3 , and the water phase was extracted with CH_2Cl_2 (2 \times 40 mL). The organic layer was combined, dried over Na_2SO_4 , and then concentrated under reduced pressure. The residue was finally purified by silica gel column chromatography with EtOAc and toluene (1:5) as the eluent to afford **20** (57.6 mg, 91%) as colorless syrup. ^1H NMR (600 MHz, CDCl_3): δ 7.41-7.04 (m, 142H, Ph), 6.66 (d, J = 9.0 Hz, 2H, Ph), 5.44 (s, 1H, Man^{A} H-1), 5.23 (s, 2H, Man^{B} H-1, Ara^{A} H-1), 5.15 (s, 1H, Ara H-1), 5.09 (s, 1H, Ara H-1), 5.07-5.04 (m, 2H, 2 \times Man H-1), 5.02 (s, 1H, Man H-1), 5.00-4.28 (m, 59H, Man^{C} H-1), 4.20-4.18 (dd, J = 10.3, 5.3 Hz, 1H), 4.13-4.09 (m, 4H), 4.08-3.90 (m, 20H), 3.88-3.80 (m, 10H), 3.70-3.52 (m, 14H), 3.48 (d, J = 9.0 Hz, 1H), 3.44-3.40 (t, J = 10.4 Hz, 2H), 3.38-3.27 (m, 6H), 3.22 (d, J = 11.4 Hz, 1H), 3.15 (d, J = 11.4 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ 159.48, 138.99, 138.98, 138.82, 138.79, 138.73,

138.67, 138.59, 138.54, 138.48, 138.46, 138.38, 138.25, 138.15, 138.11, 138.06, 137.96, 137.86, 137.71, 137.65, 129.20, 129.02, 129.00, 128.56, 128.41, 128.37, 128.35, 128.31, 128.29, 128.27, 128.23, 128.16, 128.14, 128.10, 128.08, 128.03, 128.01, 127.97, 127.92, 127.88, 127.79, 127.77, 127.75, 127.73, 127.70, 127.67, 127.66, 127.65, 127.59, 127.52, 127.49, 127.46, 127.44, 127.40, 127.32, 127.26, 127.20, 127.15, 127.12, 127.06, 126.84, 113.98, 106.78 (Ara^A C-1), 106.48 (Ara C-1), 106.45 (Ara C-1), 99.12 (Man^A C-1), 99.01 (Man^B C-1), 98.74 (Man C-1), 98.60 (Man C-1), 98.50 (Man C-1), 98.32 (Man^C C-1), 88.40, 88.08, 83.57, 83.26, 83.19, 81.78, 81.38, 81.34, 80.68, 80.47, 80.29, 79.63, 79.42, 79.34, 79.31, 79.05, 78.69, 77.23, 77.02, 76.81, 75.98, 75.81, 75.71, 75.17, 75.05, 75.00, 74.93, 74.87, 74.80, 74.70, 74.59, 74.55, 74.43, 74.26, 74.04, 73.90, 73.74, 73.35, 72.84, 72.67, 72.61, 72.58, 72.56, 72.50, 72.47, 72.28, 72.24, 72.14, 72.12, 72.04, 71.91, 71.87, 71.70, 71.56, 71.51, 71.41, 71.35, 71.28, 71.23, 71.09, 70.86, 69.67, 66.02, 65.83, 65.78, 65.63, 62.13, 60.03, 55.09. ESI-TOF MS (*m/z*): calcd for C₂₆₁H₂₇₂O₄₉Na₂ [M + 2Na]²⁺, 2117.9; found, 2117.2. MALDI-TOF MS (*m/z*): calcd for C₂₆₁H₂₇₂O₄₉Na [M + Na]⁺, 4215.9; found, 4214.6.

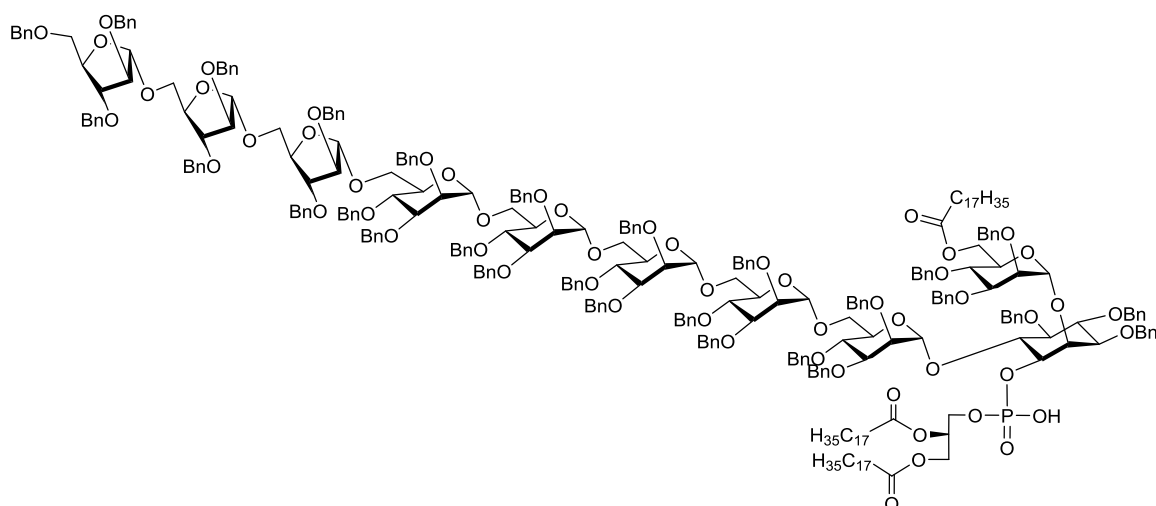
3,4,5-tri-*O*-Benzyl-6-*O*-[(2,3,5-tri-*O*-benzyl- α -D-arabinosyl)-(1 \rightarrow 5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1 \rightarrow 5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1 \rightarrow 6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)]-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-stearoyl- α -D-mannopyranosyl)-D-*myo*-inositol (22):



After a solution of **20** (50 mg, 12.0 μmol), stearic acid (17.0 mg, 60.0 μmol), DCC (12.4 mg, 60.0 μmol) and DMAP (1.5 mg, 12.0 mmol) in anhydrous CH_2Cl_2 (7 mL) was stirred at rt overnight, it was filtered off, and the filtrate was condensed *in vacuo*. The residue was briefly purified by silica gel column chromatography with EtOAc and toluene: (1:15) as the eluent of to give **21** (47.6 mg, 89%) as a foamy solid, which was directly subjected to the next step of reaction. Compound **21** (40 mg, 8.9 μmol) was dissolved in 4 mL of 2% TFA in CH_2Cl_2 , and the solution was stirred for about 6 h with TLC detection once every 2 h. The solution was then co-evaporated with toluene for 3 times to remove TFA thoroughly. The residue was purified by silica gel column chromatography with EtOAc and toluene (1:12) as the eluent to give **22** (21 mg, 54%) as a foamy solid, as well as recovered **21** (11.6 mg). **22**: ^1H NMR (600 MHz, CDCl_3): δ 7.31-7.08 (m, 140H, Ph), 52.42 (s, 1H, Man^A H-1), 5.19 (s, 1H, Ara^A H-1), 5.15 (s, 1H, Man^B H-1), 5.12 (s, 1H, Ara H-1), 5.06 (s, 1H, Ara H-1), 5.03-5.00 (3 \times s, 3H, 3 \times Man H-1), 4.85-4.80 (m, 8H, Man^C H-1, 7 \times Bn), 4.71 (d, $J = 10.8$ Hz, 1H), 4.66-4.32 (m, 48H), 4.22 (s, 1H), 4.17-3.40 (m, 54H), 3.28 (d, $J = 9.6$ Hz, 1H), 3.17 (t, $J = 9.0$ Hz, 1H), 2.16 (t, $J = 7.8$ Hz, 2H), 1.52-1.45 (m, 2H), 1.28-1.18 (m, 28H), 0.87 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 173.62, 138.92, 138.72, 138.66, 138.52, 138.43, 138.36, 138.32,

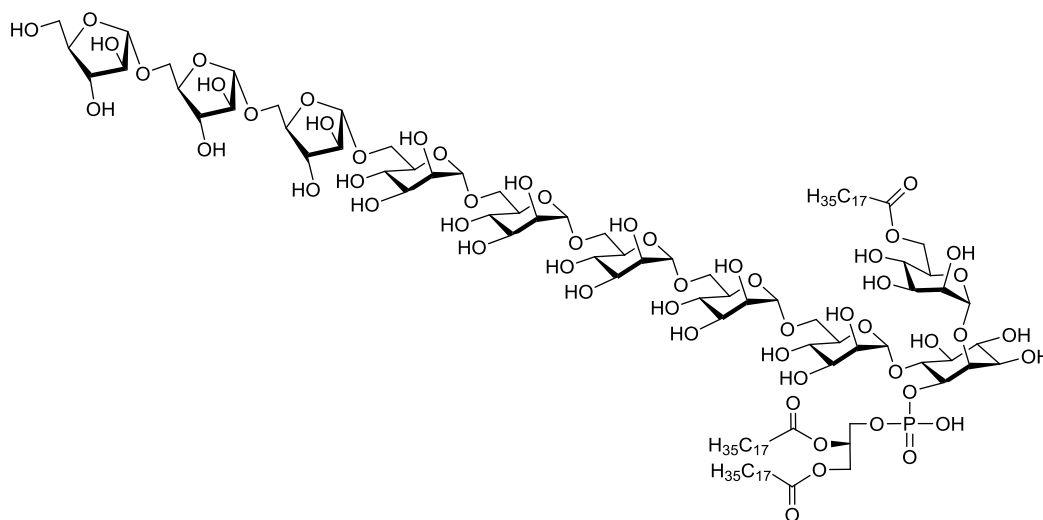
138.26, 138.22, 138.12, 138.05, 138.00, 137.91, 137.81, 137.66, 137.60, 135.48, 129.56, 128.58, 128.48, 128.46, 128.39, 128.33, 128.29, 128.25, 128.22, 128.17, 128.15, 128.12, 128.08, 127.98, 127.89, 127.82, 127.76, 127.71, 127.65, 127.64, 127.58, 127.56, 127.51, 127.48, 127.46, 127.42, 127.41, 127.40, 127.36, 127.34, 127.30, 127.29, 127.27, 127.21, 127.10, 106.74 (Ara^A C-1), 106.44 (Ara C-1), 106.42 (Ara C-1), 98.57 (Man^A C-1, Man^B C-1), 98.54 (3 × Man C-1), 98.40 (Man^C C-1), 88.35, 88.02, 83.50, 83.20, 83.13, 81.21, 80.65, 80.44, 80.26, 79.38, 79.29, 78.74, 78.26, 75.53, 75.32, 75.15, 75.12, 75.06, 74.99, 74.92, 74.88, 74.80, 74.71, 74.51, 74.39, 74.28, 74.13, 74.04, 74.00, 73.92, 73.33, 73.00, 72.65, 72.55, 72.47, 72.30, 72.22, 72.12, 72.02, 71.96, 71.88, 71.84, 71.66, 71.57, 71.34, 71.24, 71.15, 70.11, 69.62, 66.50, 65.97, 65.84, 65.82, 65.76, 65.73, 63.04, 34.11, 31.90, 29.68, 29.65, 29.48, 29.34, 29.24, 29.18, 29.05, 24.80, 22.67, 14.10. ESI-TOF MS (*m/z*): calcd for C₂₇₁H₂₉₈O₄₉Na₂ [M + 2Na]²⁺, 2191.0; found, 2190.9. MALDI-TOF MS (*m/z*): calcd for C₂₇₁H₂₉₈O₄₉Na [M + Na]⁺, 4362.2; found, 4362.3.

3,4,5-tri-*O*-Benzyl-6-*O*-[(2,3,5-tri-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl- α -D-arabinosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl- α -D-mannopyranosyl)]-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-stearoyl- α -D-mannopyranosyl)-1-*O*-(1,2-di-*O*-stearoyl-*sn*-glycero-3-benzylphosphoryl)-D-*myo*-inositol (2):



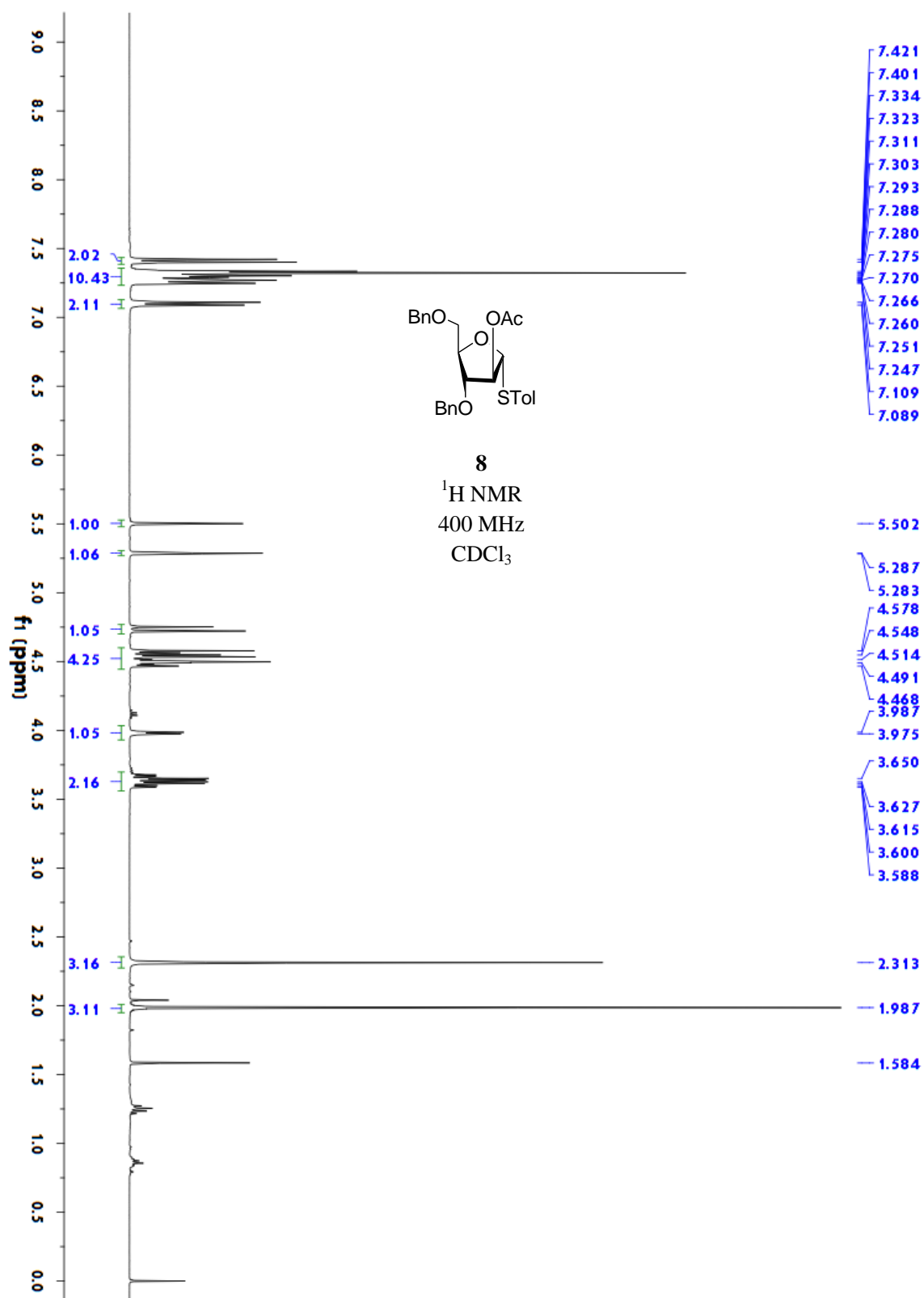
A mixture of **22** (14 mg, 3.2 μmol), freshly prepared glycerylphosphoramidite **4** (13.8 mg, 16.0 μmol) and freshly activated molecular sieves 4 \AA in 3 mL of CH_2Cl_2 and CH_3CN (2:1) was stirred at rt for 15 min. Then, 1*H*-tetrazole (0.45 M in CH_3CN , 71 μL , 32 μmol) was added to the mixture, which was stirred for another 40 min, before TLC showed the completion of reaction. The mixture was cooled to $-20\text{ }^\circ\text{C}$, and *m*-CPBA (2.8 mg, 16.0 μmol) was added. The reaction was slowly warmed to rt in 1 h, and then quenched with saturated aq. NaS_2O_3 . The water phase was extracted with CH_2Cl_2 (3 \times 30 mL), and the organic phase was combined, dried over Na_2SO_4 and concentrated *in vacuo*. Finally, the residue was purified by silica gel column chromatography with EtOAc and toluene (1:15) as the eluent to afford **2** (11.6 mg, 70%) as syrup. For one stereoisomer: ^1H NMR (600 MHz, CDCl_3): δ 5.39 (s, 1H, Man^A H-1), 5.25 (s, 1H, Man^B H-1), 5.19 (s, 1H, Ara^A H-1), 5.12 (s, 1H, Ara H-1), 5.06 (s, 1H, Ara H-1), 5.01 (s, 1H, Man^C H-1), 4.98 (s, 1H, Man^D H-1), 4.93 (s, 1H, Man^E H-1), 4.82 (s, 1H, Man^F H-1). ^{31}P NMR (162 MHz, CDCl_3) δ -0.42, -0.18. ^{13}C NMR (150 MHz, CDCl_3): δ 106.65 (Ara^A C-1), 106.32 (Ara^C C-1), 106.29 (Ara^D C-1), 99.02 (Man^A C-1), 98.71 (Man^B C-1), 98.51 (Man^C C-1), 98.38 (Man^D C-1), 98.25 (Man^E C-1), 97.89 (Man^F C-1). ESI-TOF MS (*m/z*): calcd for $\text{C}_{317}\text{H}_{383}\text{O}_{56}\text{NPK}$ [$\text{M} + \text{K} + \text{NH}_4$] $^{2+}$, 2584.8; found, 2584.0.

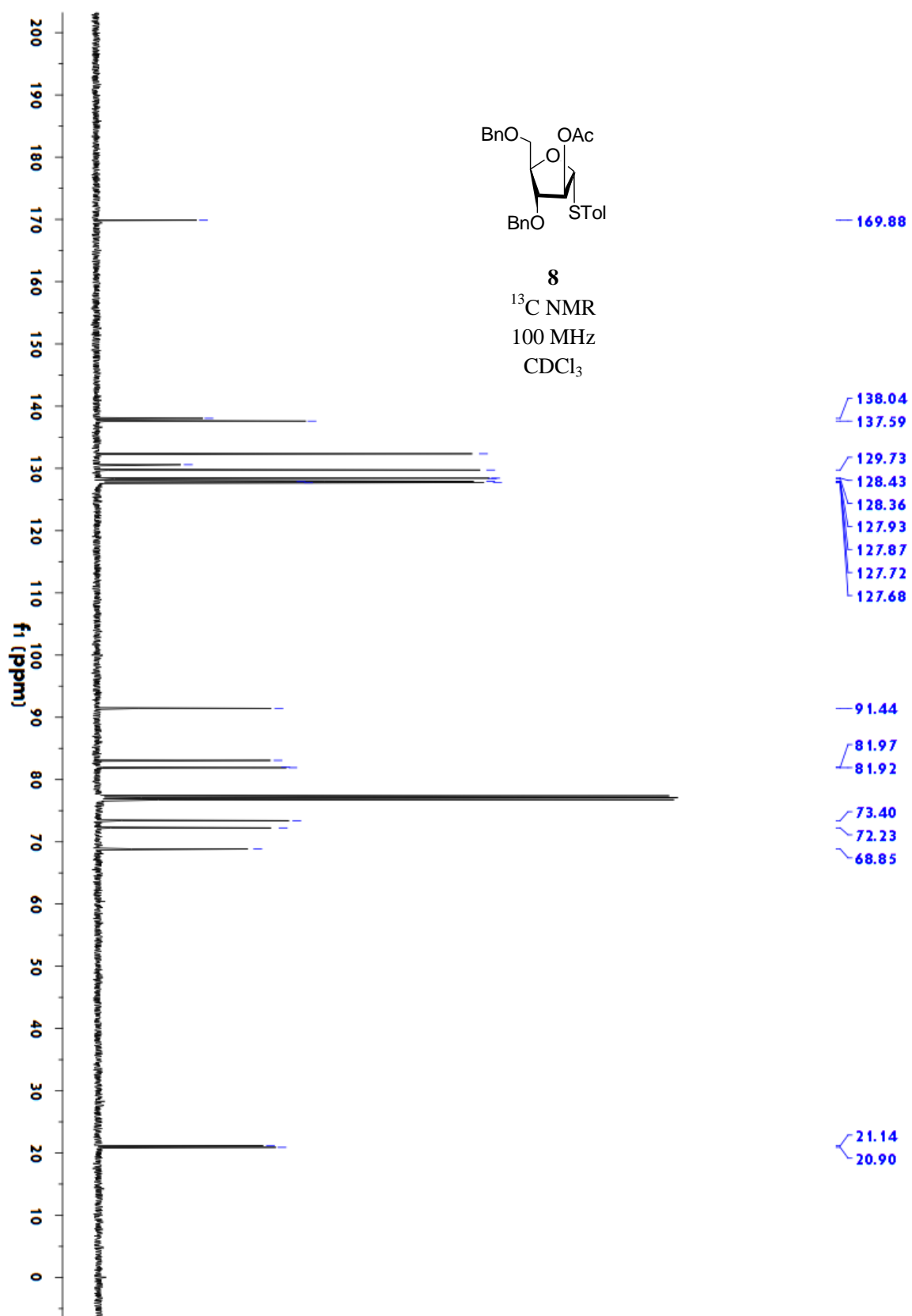
6-O-[(α -D-Arabinosyl)-(1 \rightarrow 5)-(α -D-arabinosyl)-(1 \rightarrow 5)-(α -D-arabinosyl)-(1 \rightarrow 6)-(α -D-mannopyranosyl)-(1 \rightarrow 6)-(α -D-mannopyranosyl)-(1 \rightarrow 6)-(α -D-mannopyranosyl)-(1 \rightarrow 6)-(α -D-mannopyranosyl)-(1 \rightarrow 6)-(α -D-mannopyranosyl)]-1-O-(1,2-di-O-stearoyl-*sn*-glycero-3-phosphoryl)-2-O-[(6-O-stearoyl- α -D-mannopyranosyl)]-D-*myo*-inositol (1):

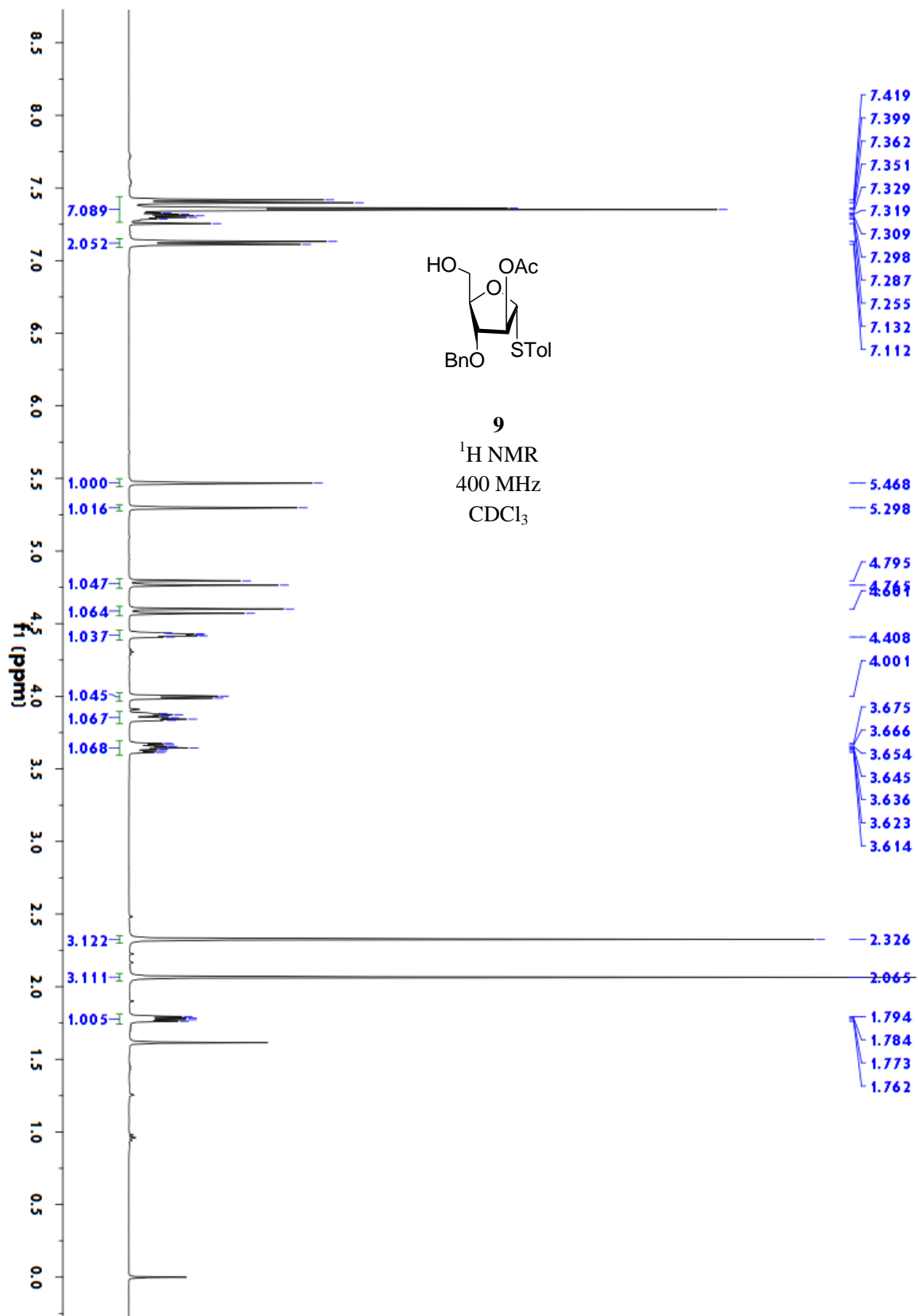


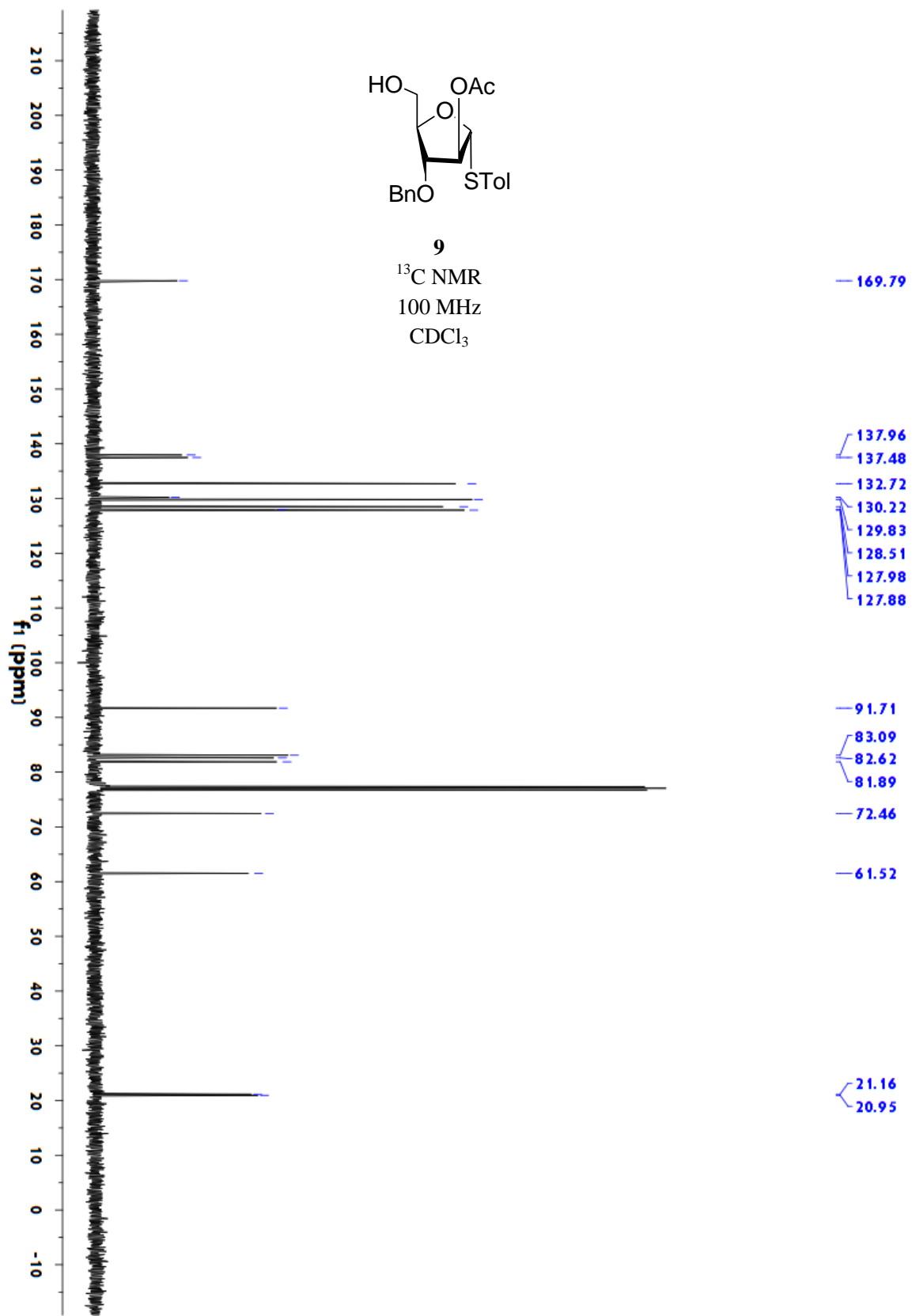
The reaction mixture of **2** (11 mg, 2.2 μ mol) and 10% Pd/C (8 mg) in CHCl₃, MeOH and H₂O (3:3:1, 3.5 mL) was stirred under a H₂ atmosphere (50 psi) for 4 days. The solution was filtered off, and the filtrate was concentrated *in vacuo* to afford the target molecule **1** (4.0 mg, 74%) as an off-white solid. ¹H NMR (700 MHz, CD₃OD, CDCl₃, and D₂O 3:3:1) δ : 5.13 (s, 1H), 5.08 (s, 1H), 4.97 (s, 1H), 4.82 (s, 4H), 2.36-2.18 (m, 6H), 1.64-1.56 (m, 6H), 1.38-1.15 (m, 84H), 0.78-0.88 (m, 6H). ³¹P NMR (162 MHz, CD₃OD, CDCl₃, and D₂O 3:3:1) δ : 0.67. MALDI-TOF MS (*m/z*): calcd for C₁₁₄H₂₀₆O₅₆PLi [M + Li + H]²⁺, 1254.6, found 1254.1.

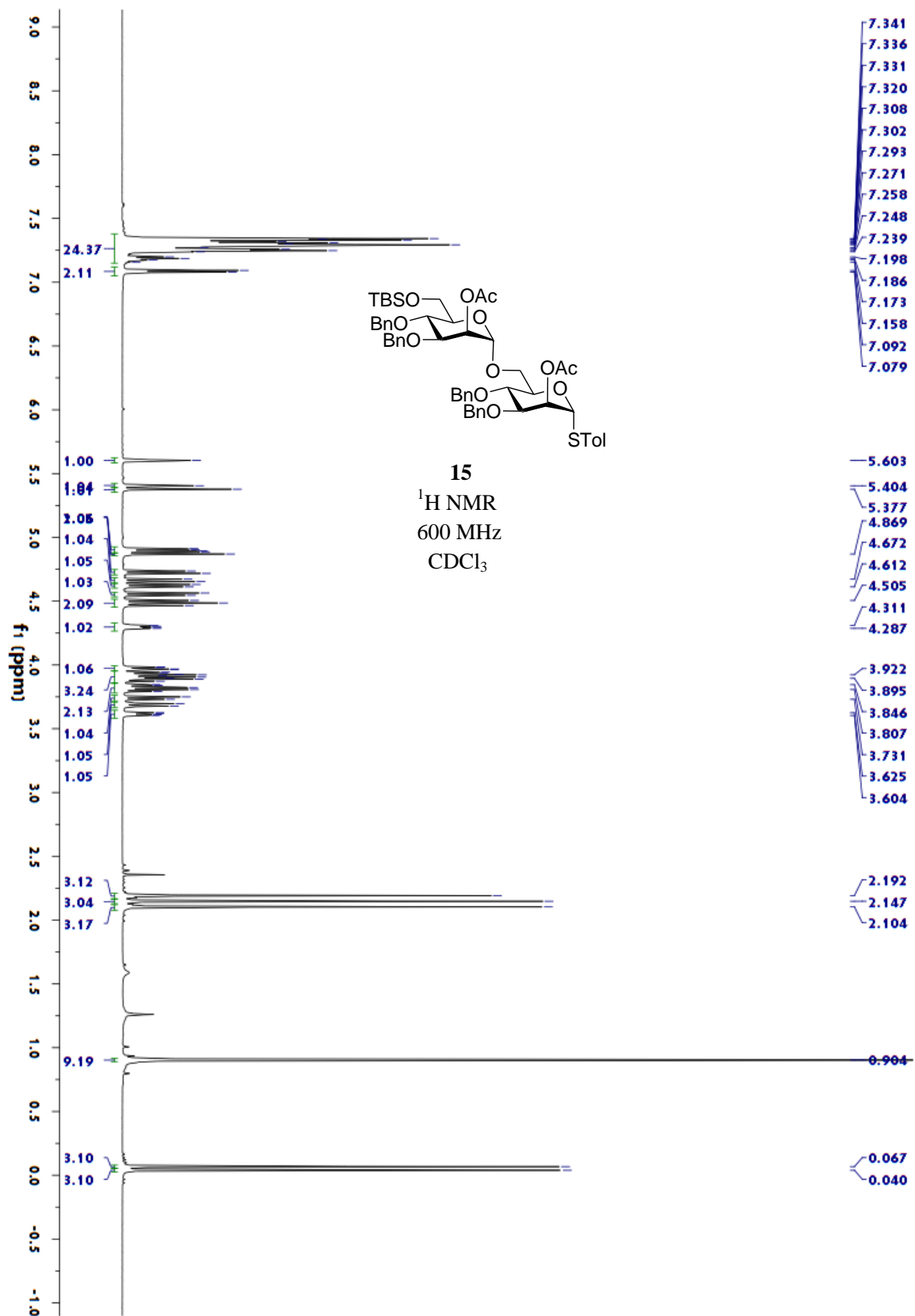
II. NMR spectra:

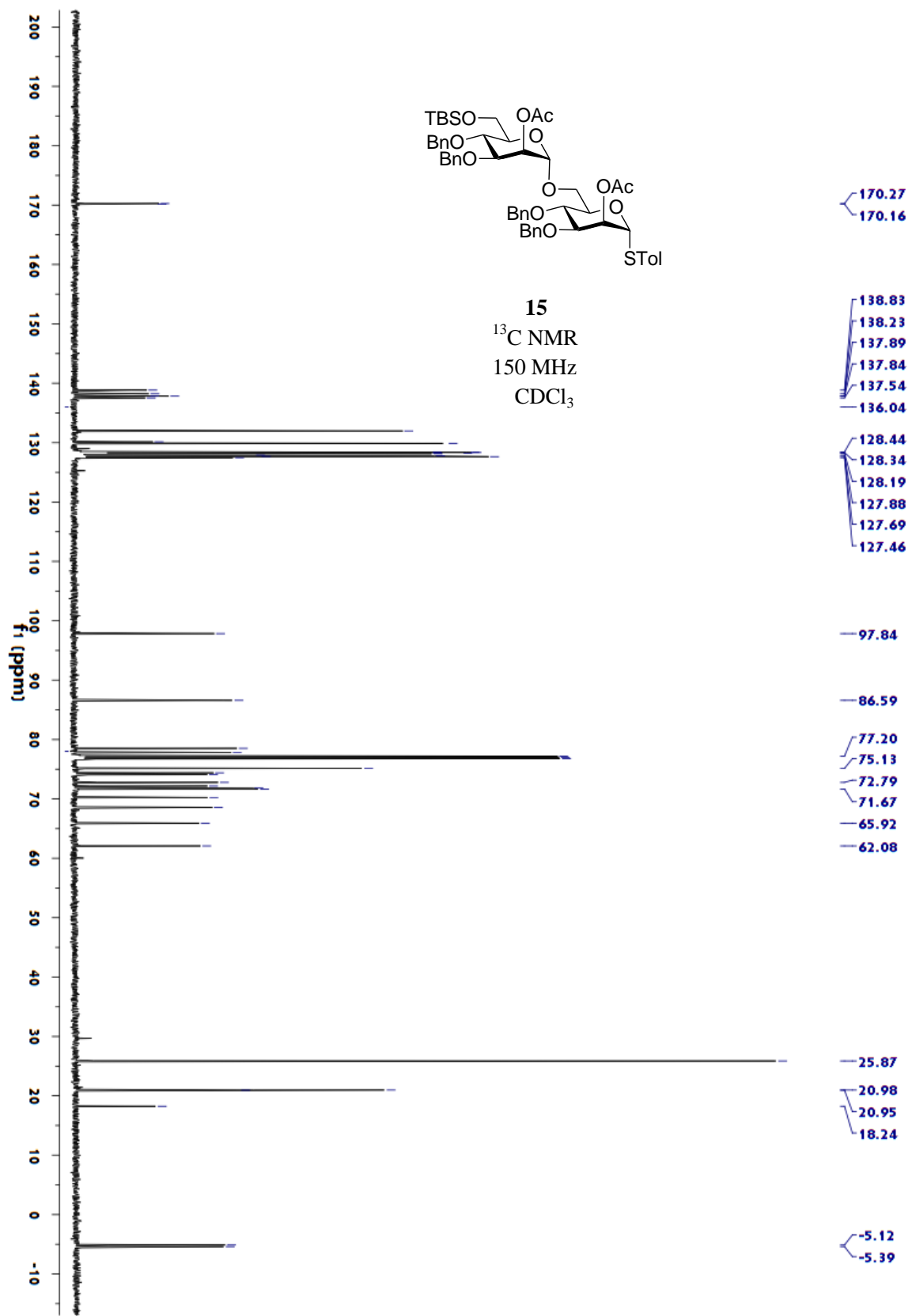












00130018

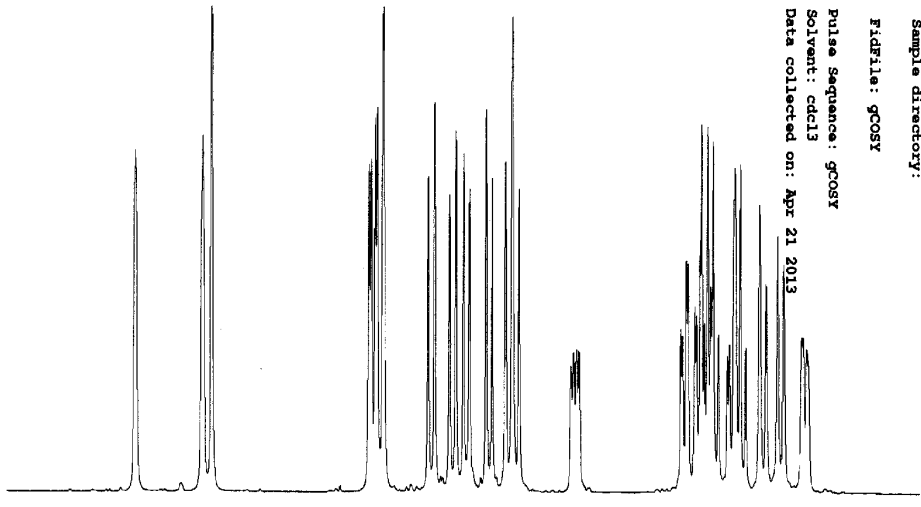
Sample Name:
Data Collected on:
#600-ymmr600
Archive directory:
/home/ymmr1/ymmrays/probes/probe_caliba
Sample directory:

FidFile: gCOSY

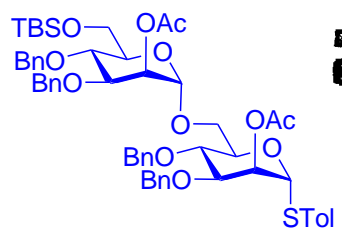
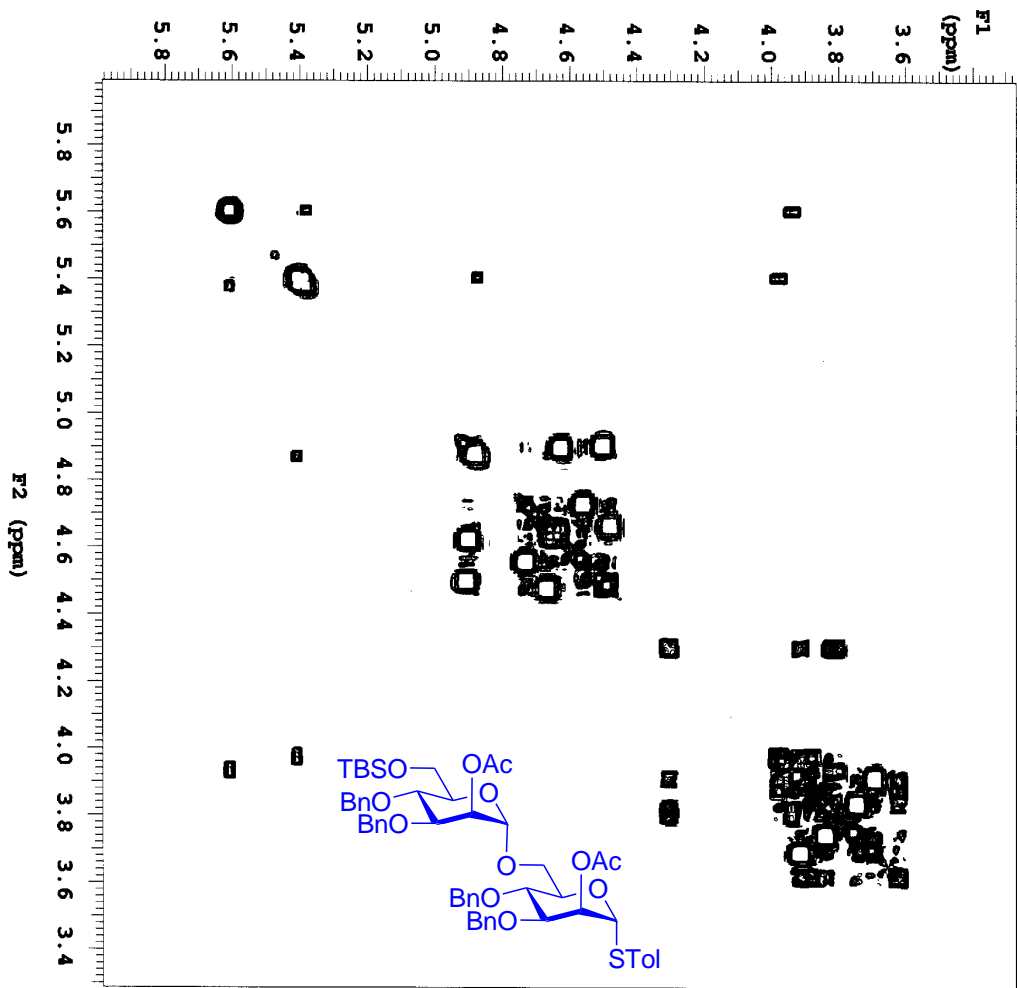
Pulse Sequence: gCOSY

Solvent: cdcl3

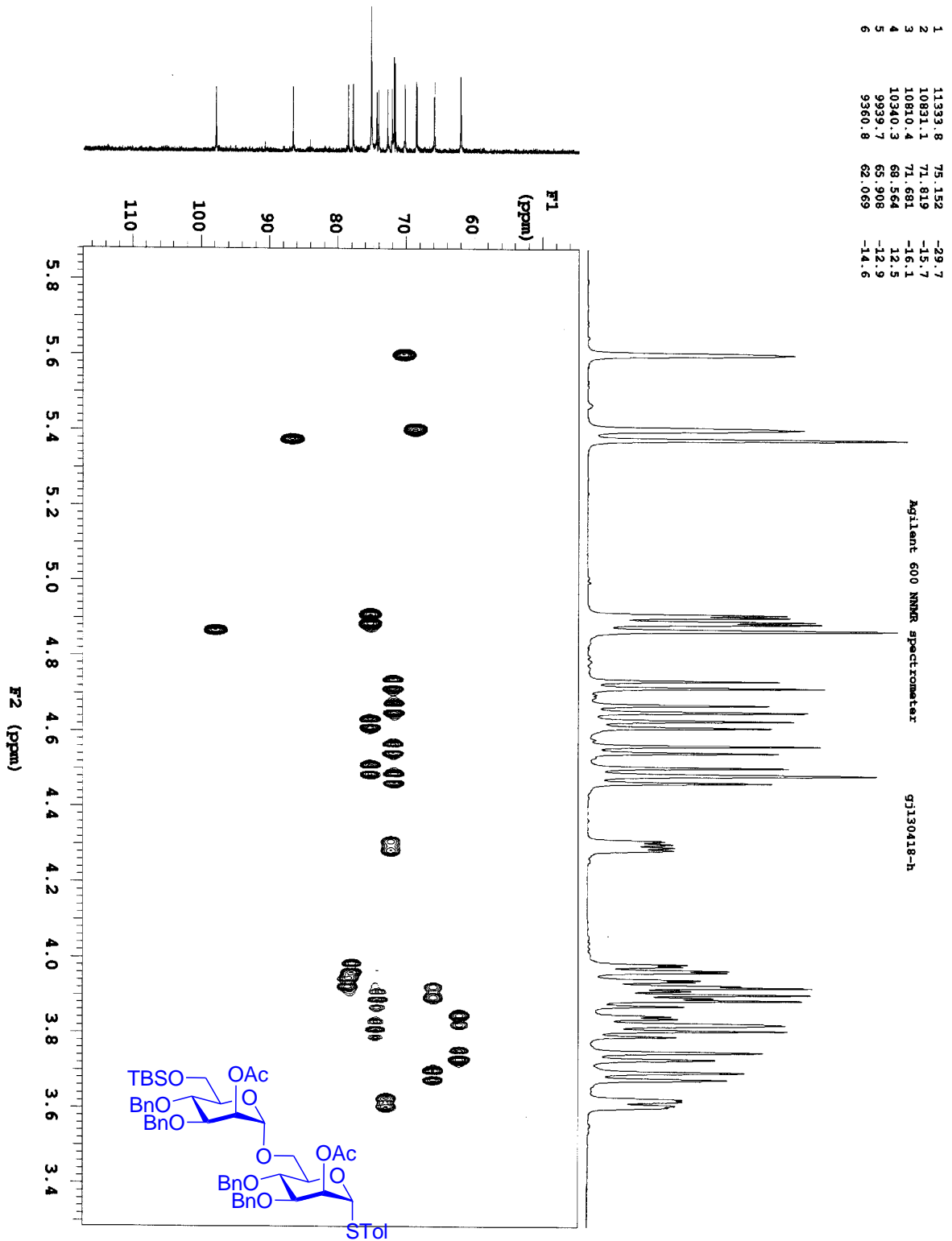
Data collected on: Apr 21 2013

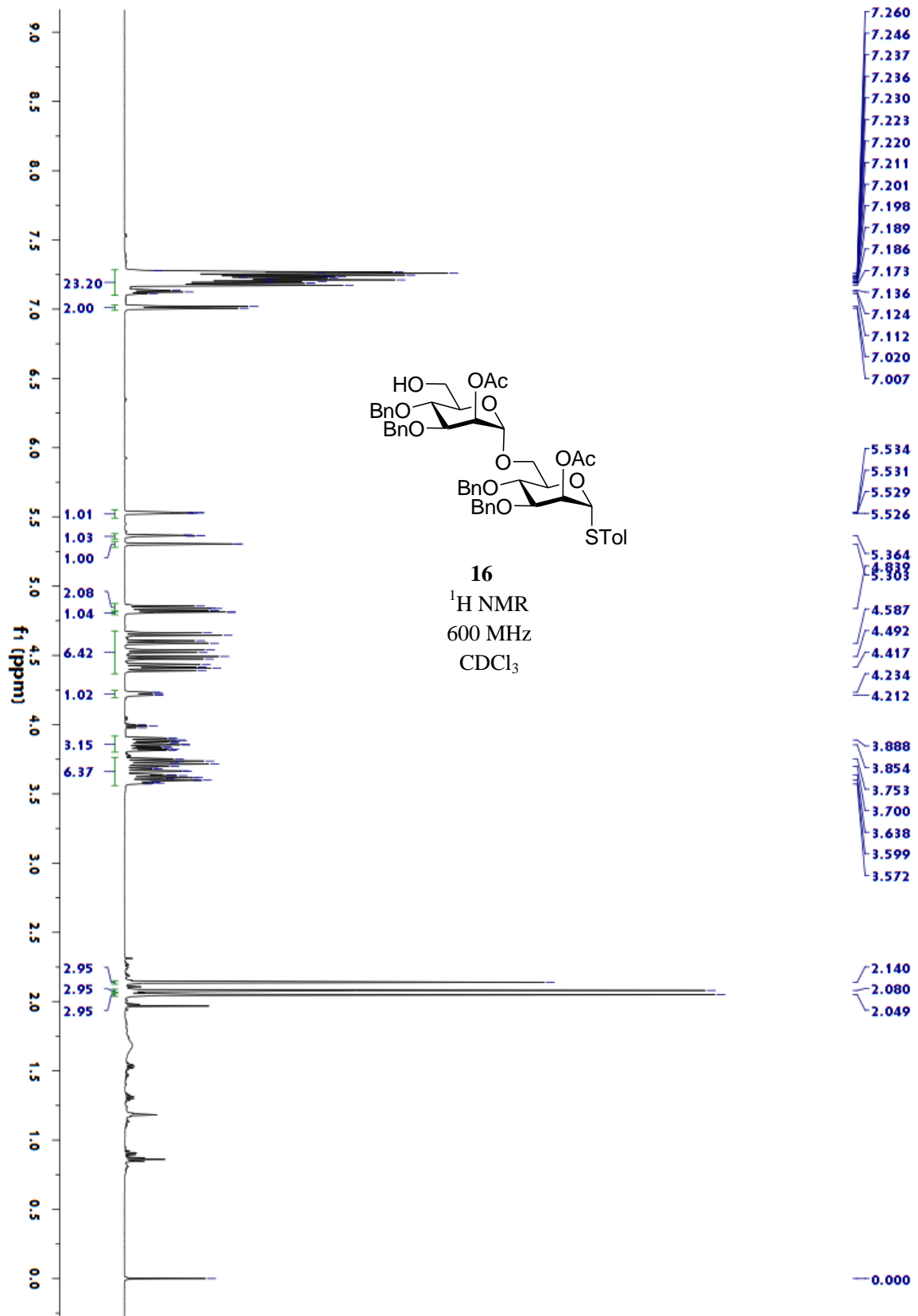


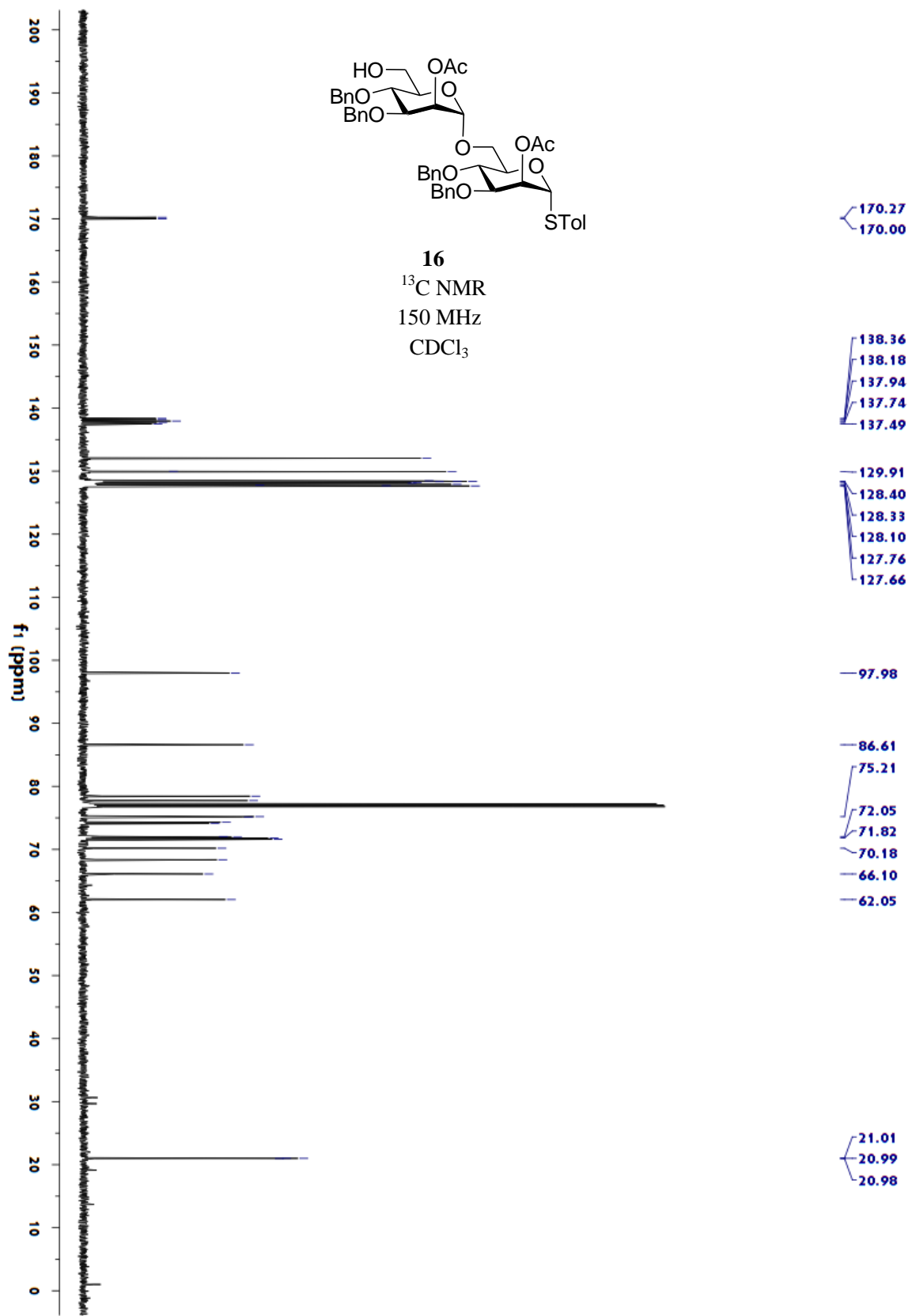
Agilent 600 NMR spectrometer



15
¹H-¹H COSY
600 MHz
CDCl₃



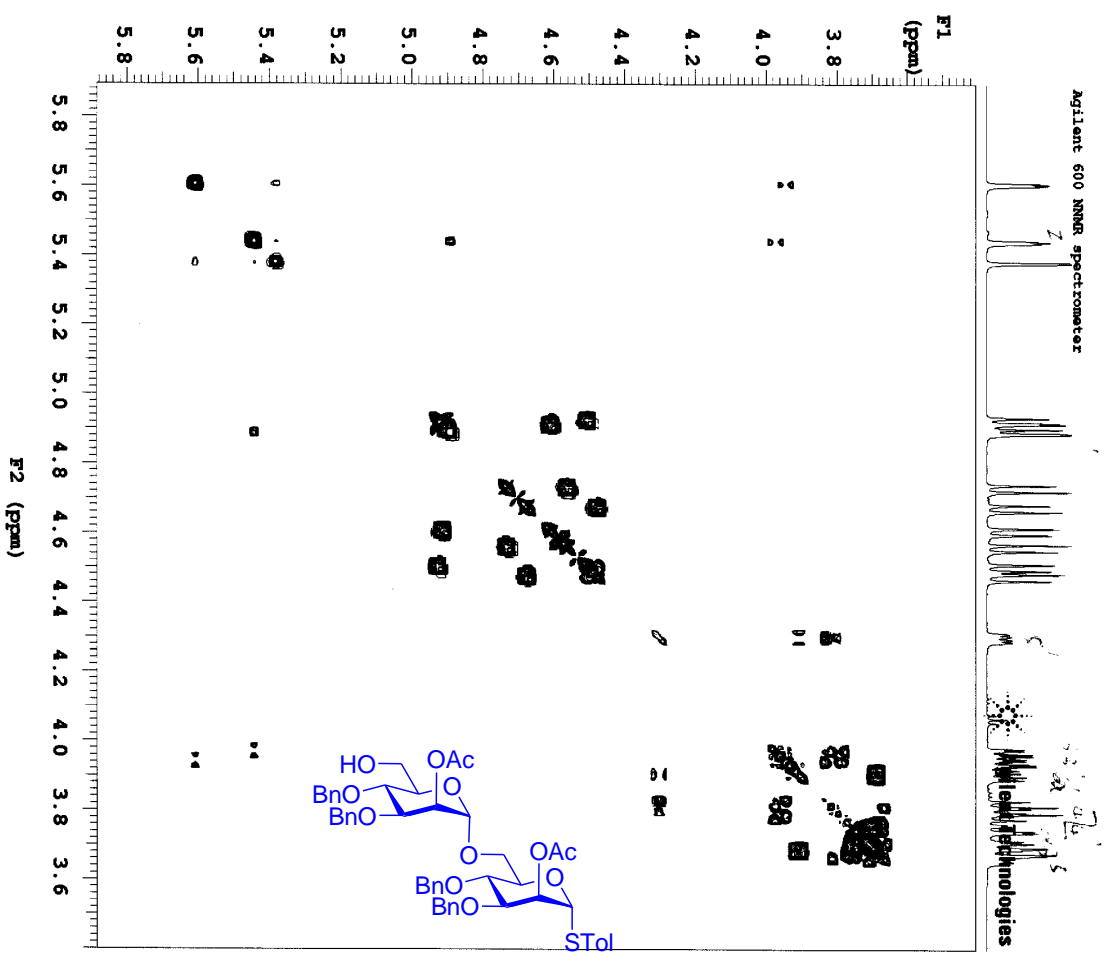
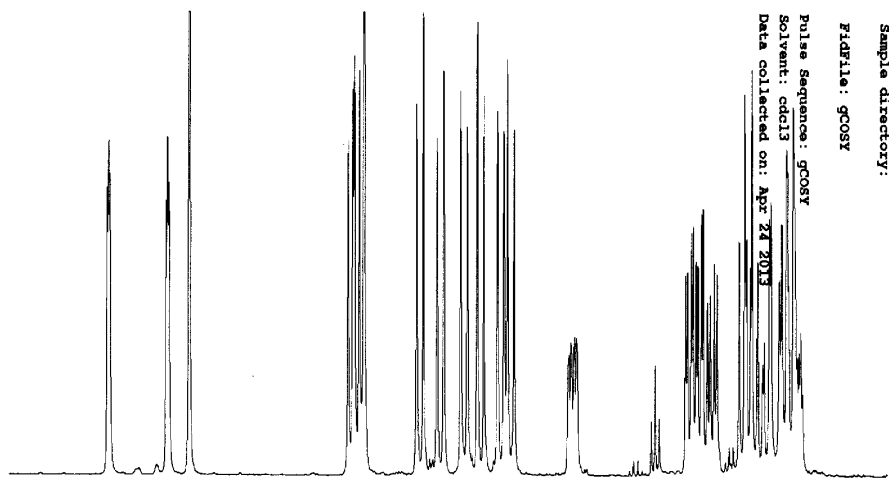




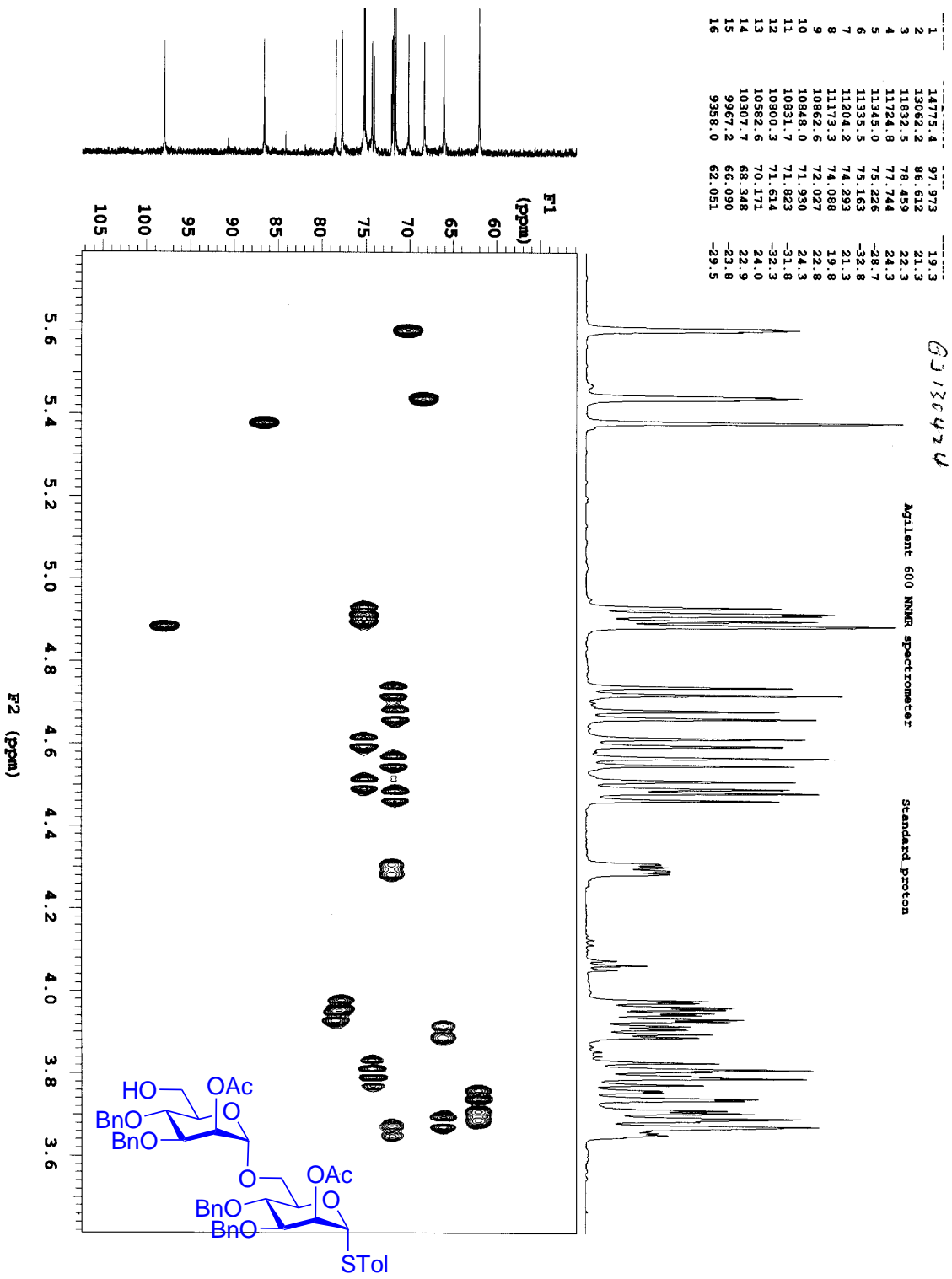
5130424

Sample Name:
Data Collected on:
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Archive directory:
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Sample directory:

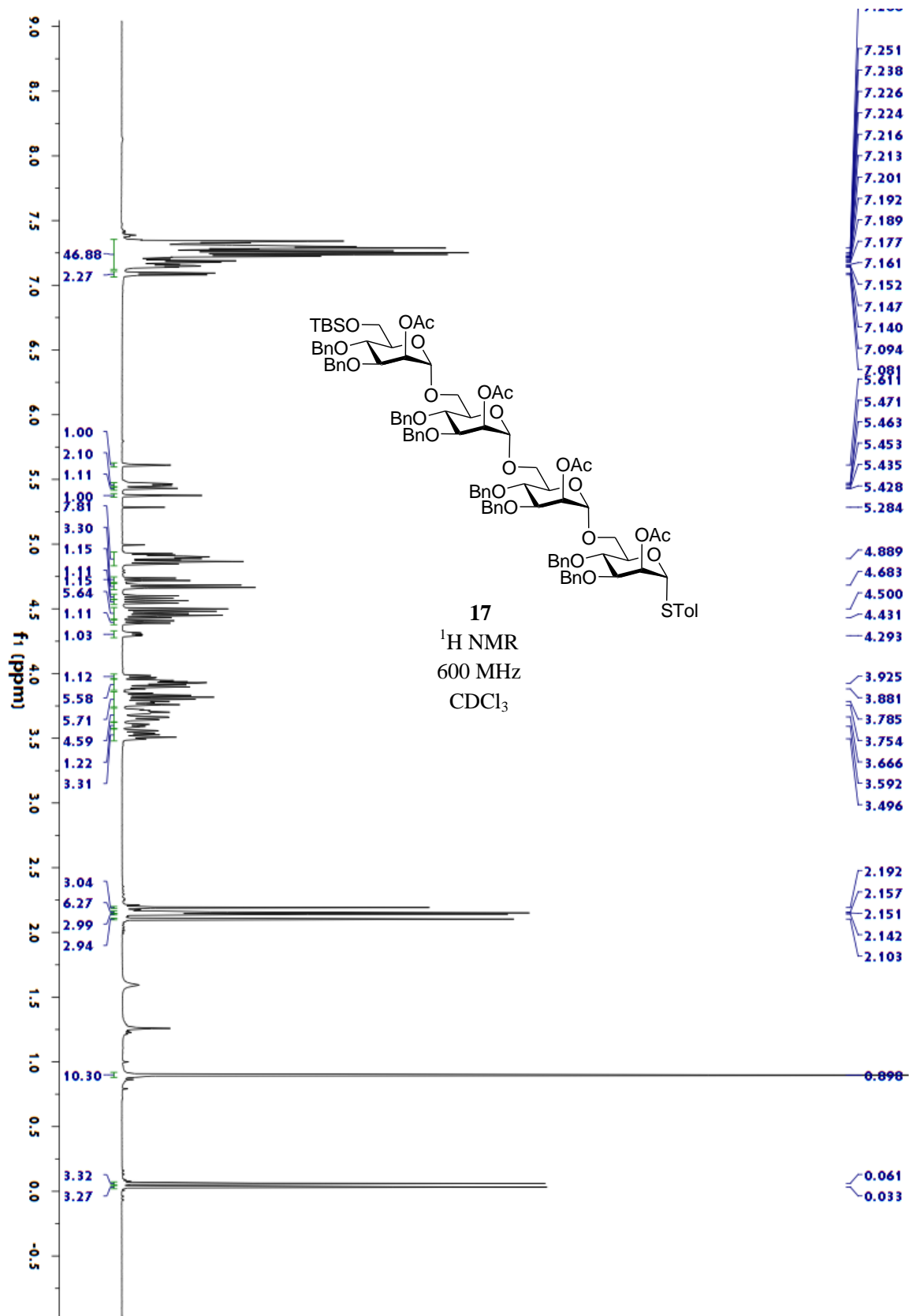
Pulse Sequence: gcosy
Solvent: cdcl3
Data collected on: Apr 24 2013

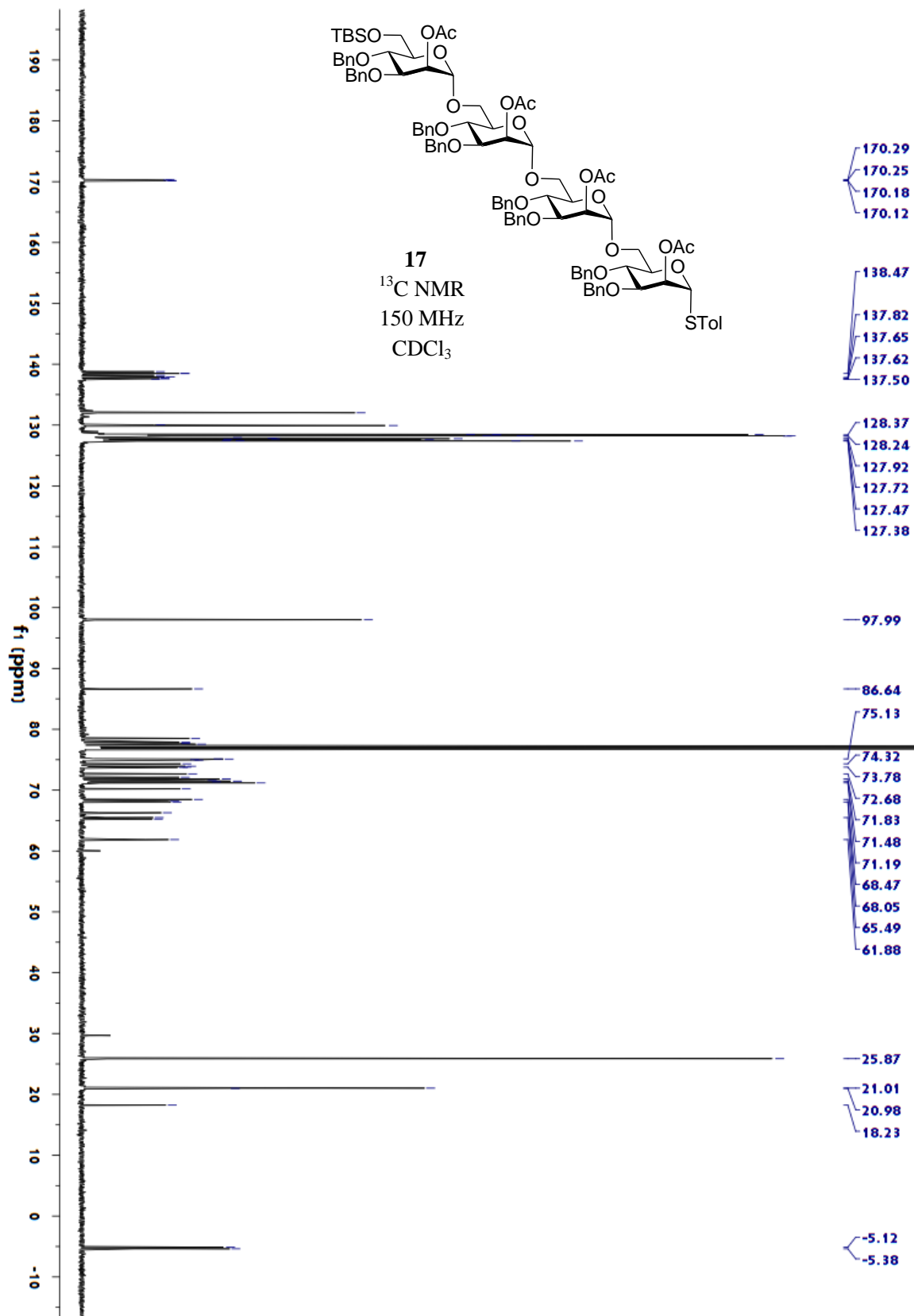


16
¹H-¹H COSY
600 MHz
CDCl₃



16
 ^1H - ^{13}C HMQC
 600/150 MHz
 CDCl_3





009902

Sample Name:

Data Collected on:

a600-vnmr5600

Archive directory:

/home/vnmr1/vnmr5600/probes/probe_calibs

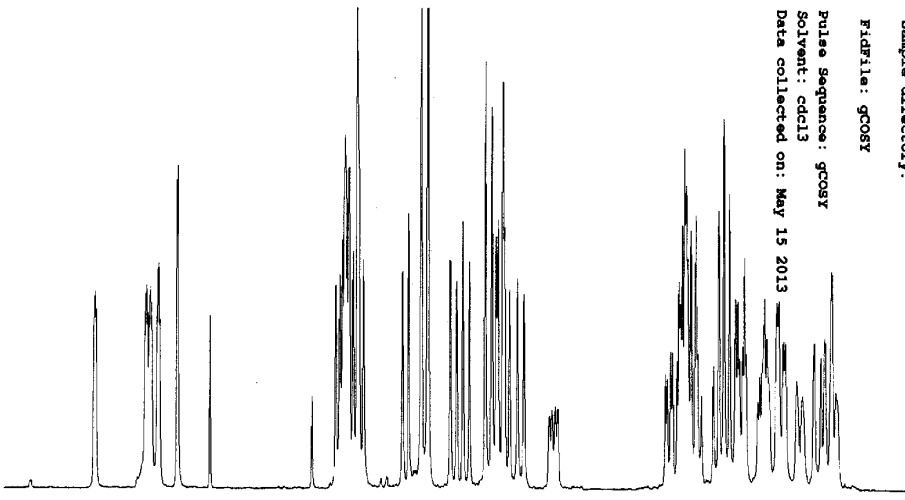
Sample directory:

Filefile: gCOSY

Pulse Sequence: gcosy

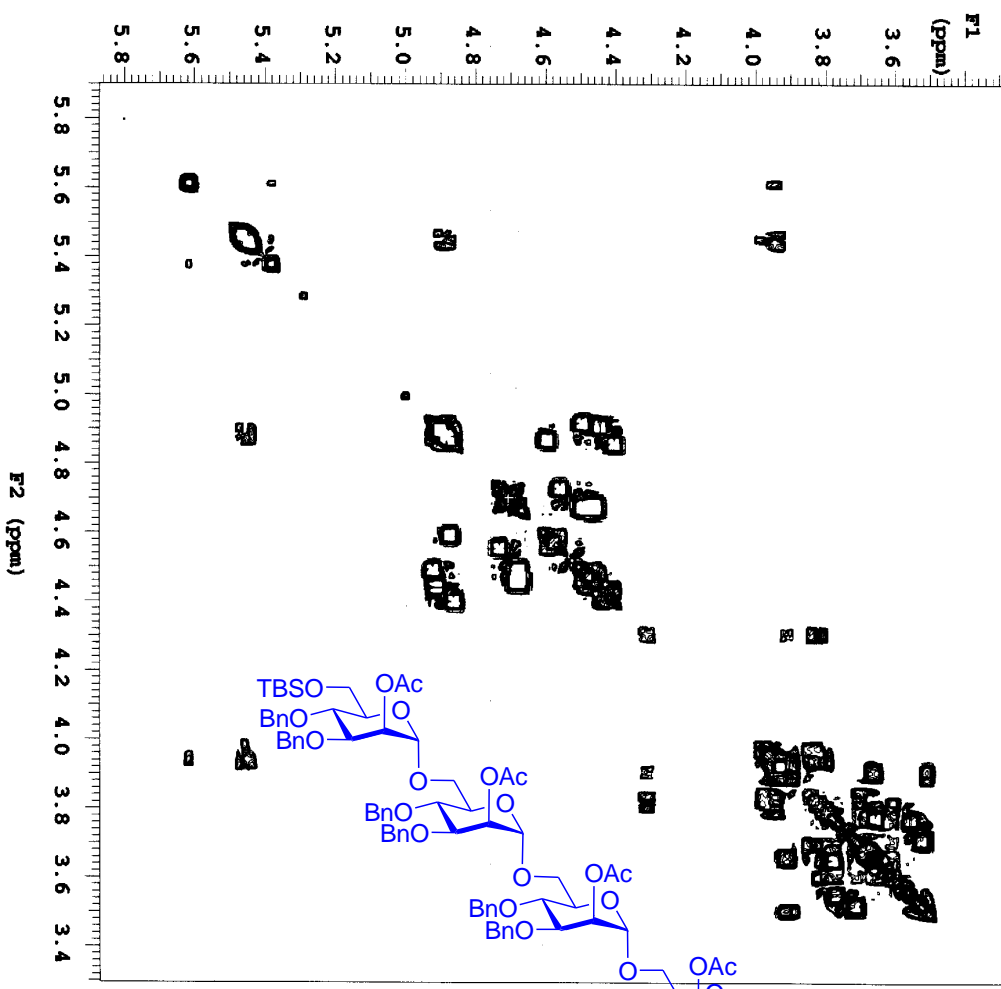
Solvent: cdcl3

Data collected on: May 15 2013

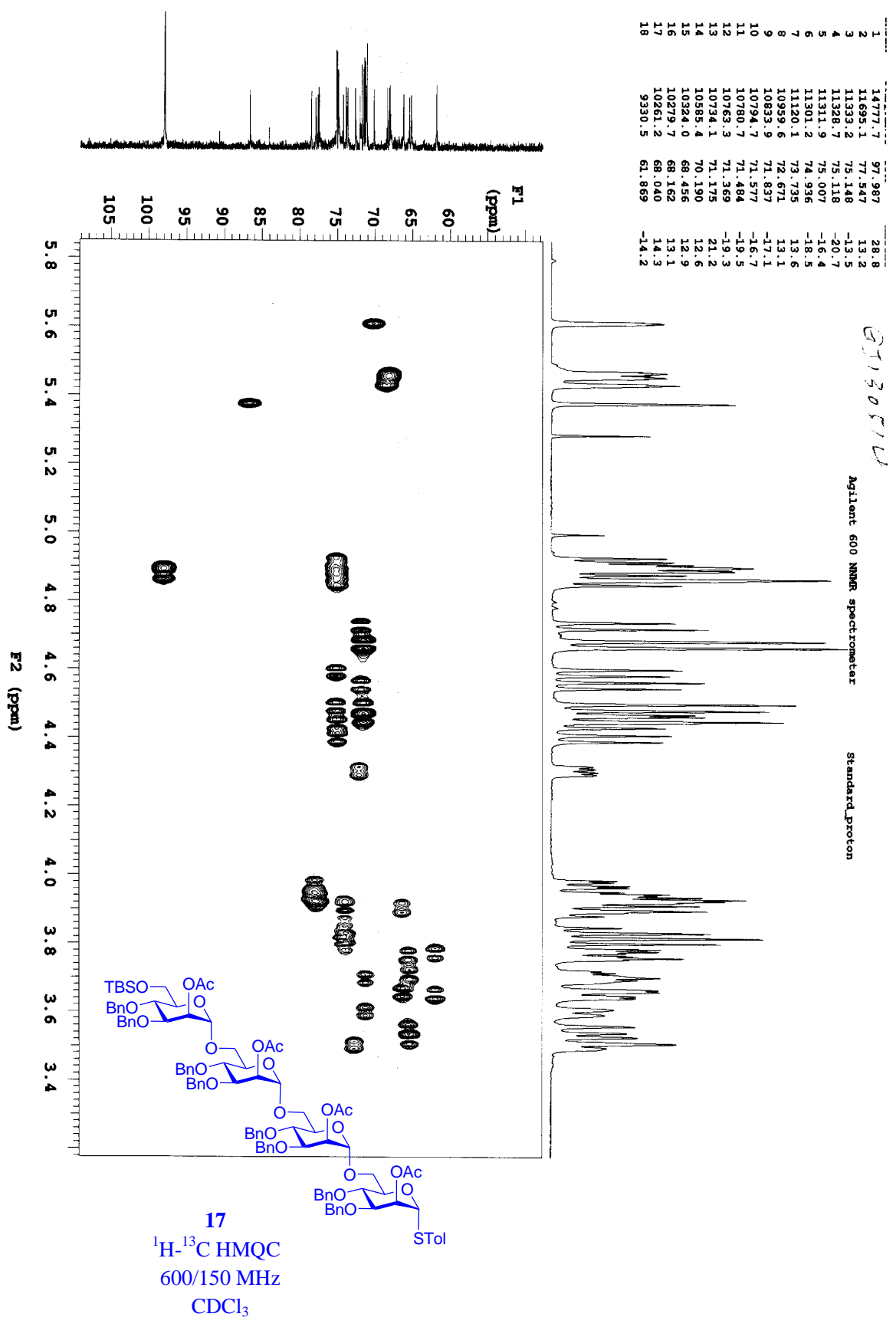


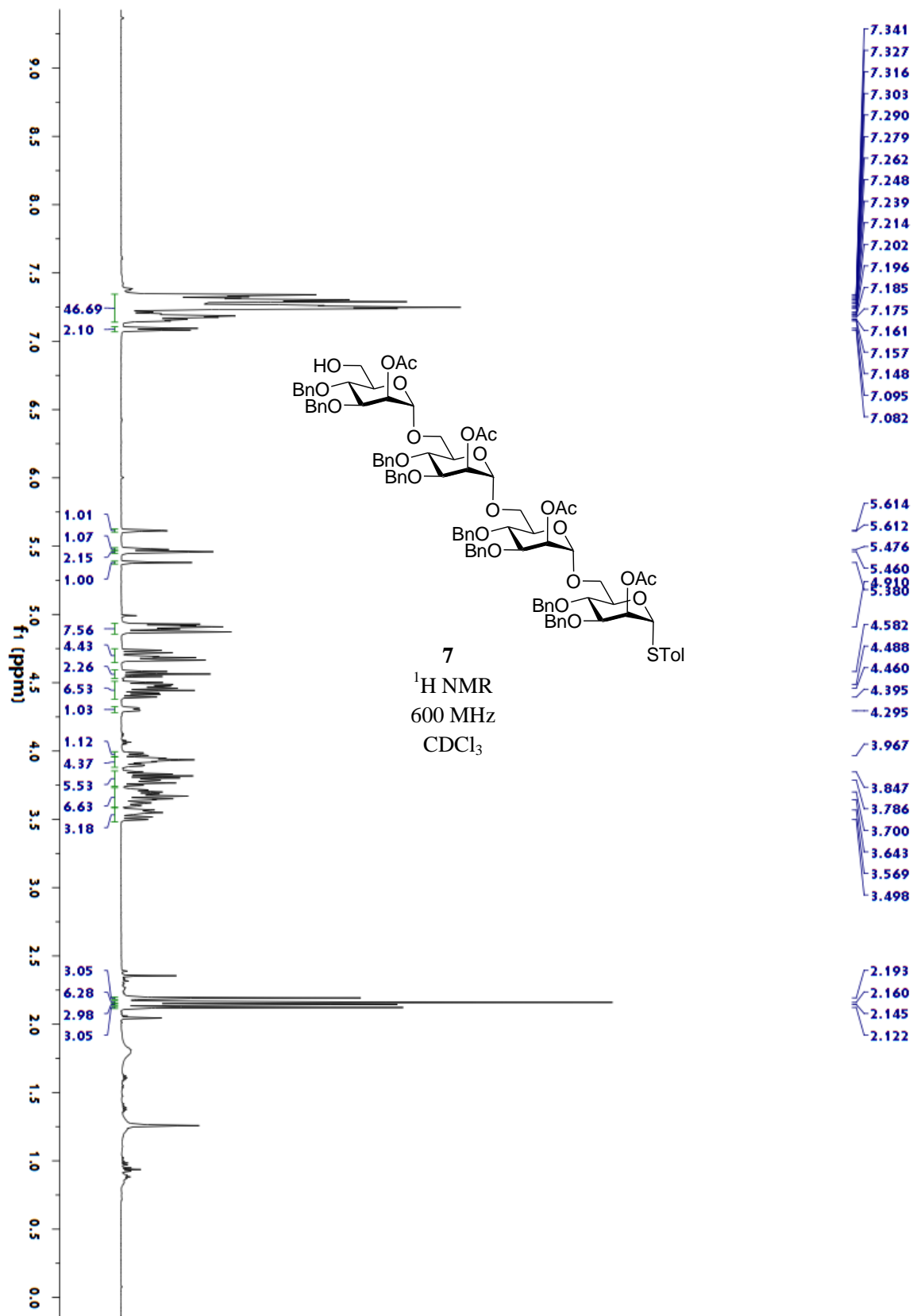
Agilent 600 NMR spectrometer

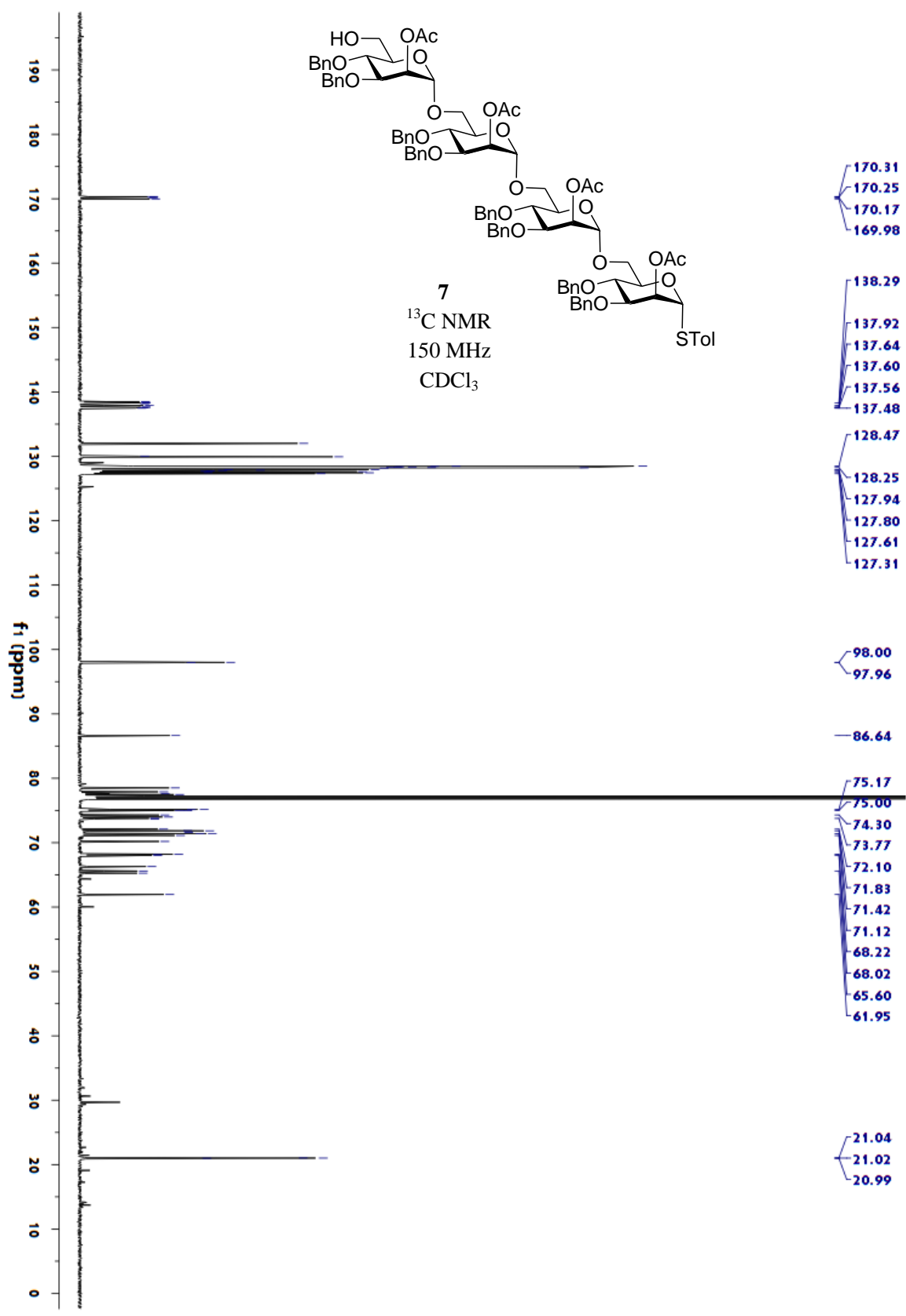
Agilent Technologies



17
¹H-¹H COSY
600 MHz
CDCl₃





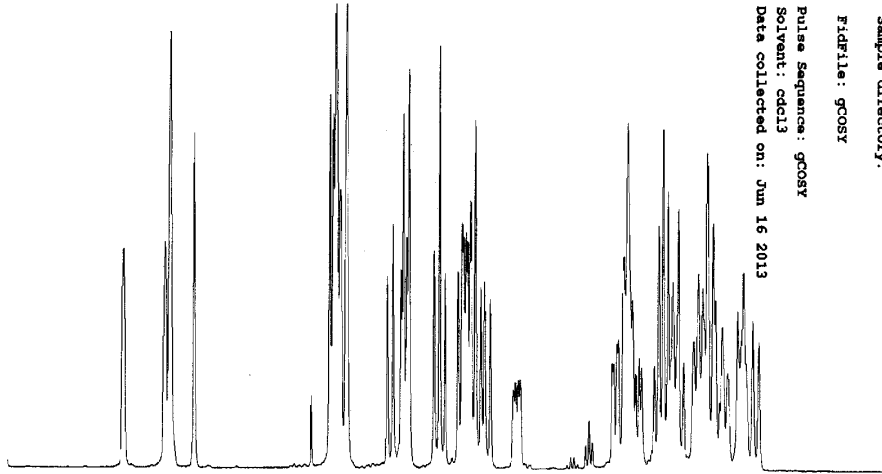


Sample Name:

Data Collected on:
#600-ymms600
Archive directory:
/home/ymml/ymmsys/probes/probe_calibs
Sample directory:

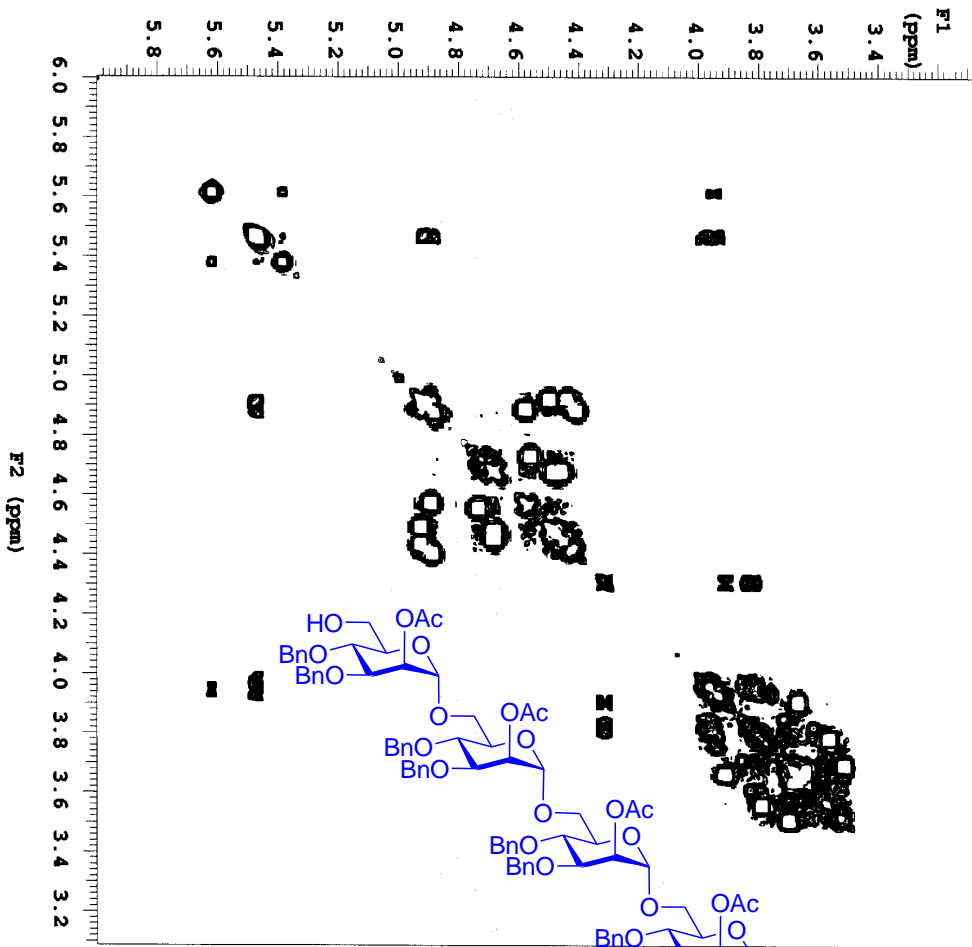
Fidfile: gcosy

Pulse Sequence: gcosy
Solvent: cdcl3
Data collected on: Jun 16 2013



GJ130616

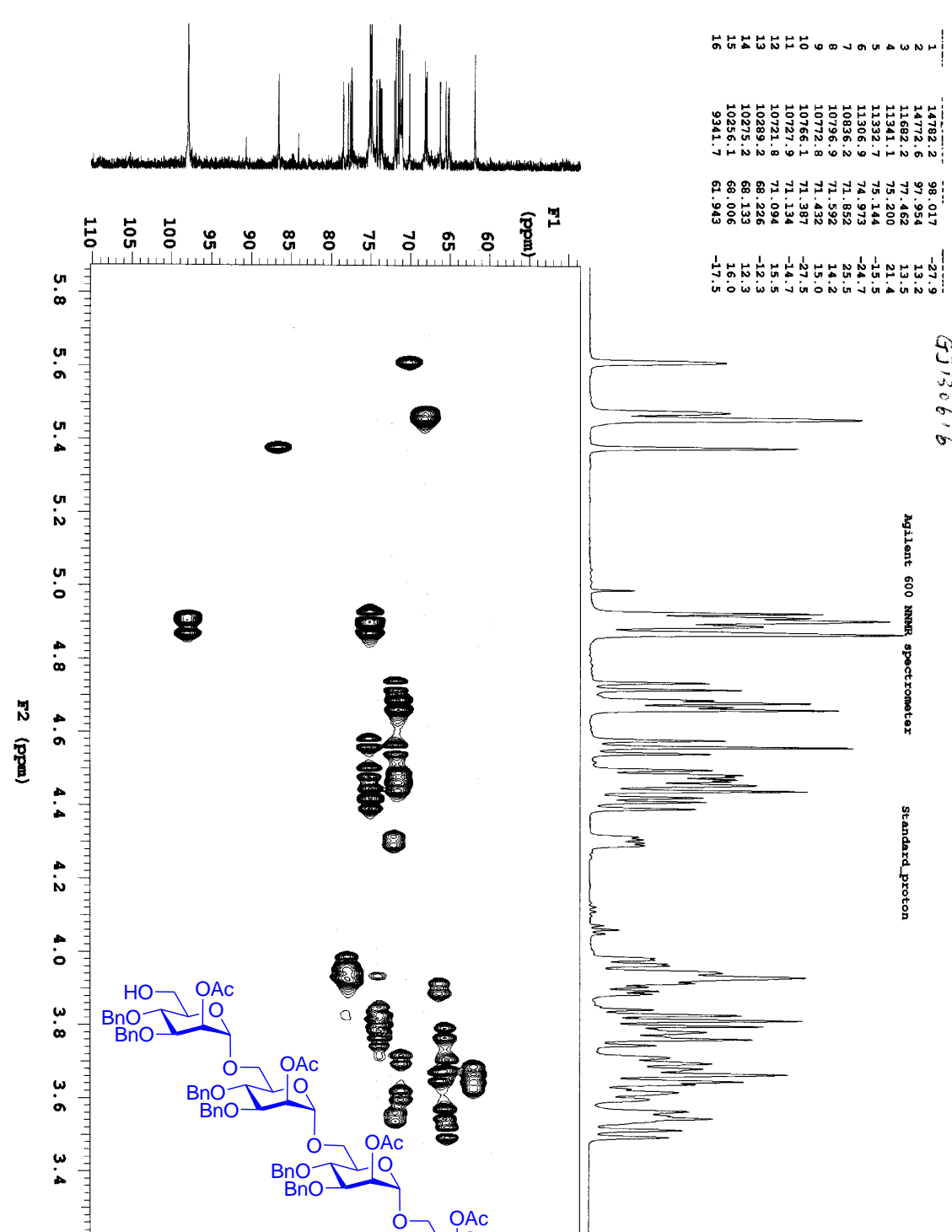
Agilent 600 NMR spectrometer



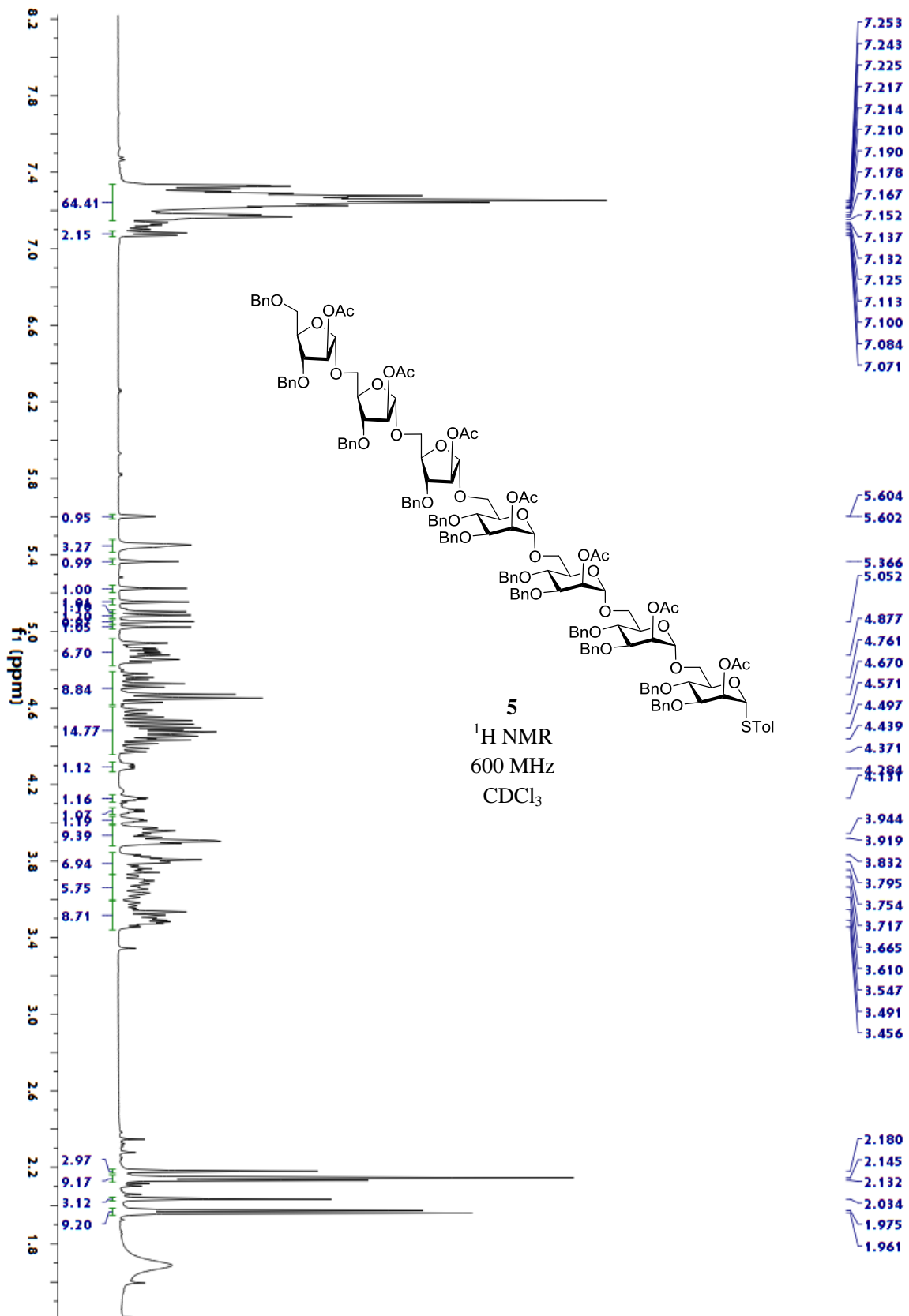
7
¹H-¹H COSY
600 MHz
CDCl₃

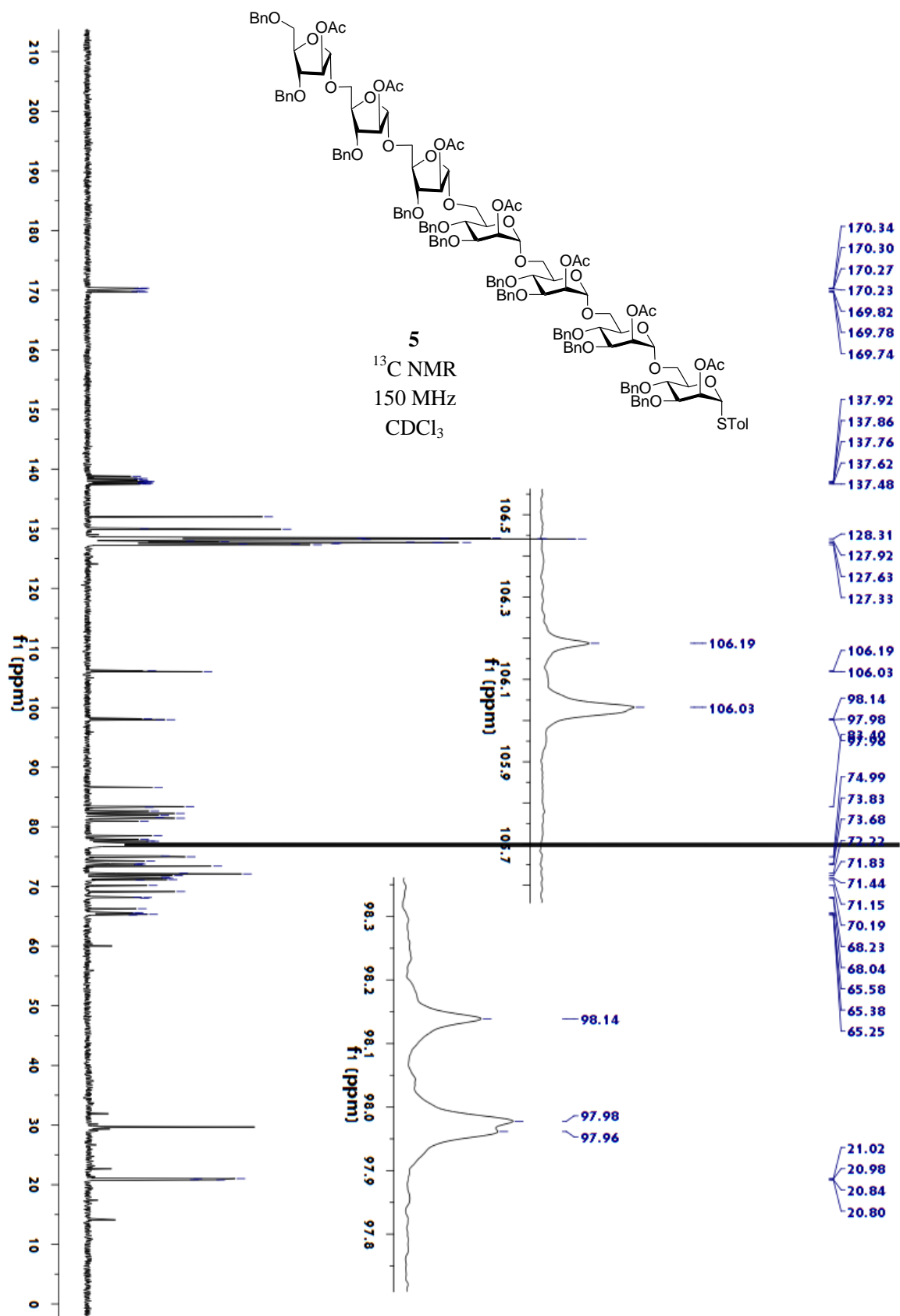
GJ130616

Peak #	Chemical Shift (ppm)	Integration
1	14782.2	98.017
2	14772.6	97.954
3	11682.2	77.462
4	11341.1	75.200
5	11332.7	75.144
6	11306.9	74.973
7	10836.2	71.852
8	10796.9	71.592
9	10772.8	71.432
10	10766.1	71.387
11	10727.9	71.134
12	10721.8	71.094
13	10289.2	68.226
14	10275.2	68.133
15	10256.1	68.006
16	9341.7	61.943



7
 $^1\text{H}-^{13}\text{C}$ HMQC
600/150 MHz
 CDCl_3
STol



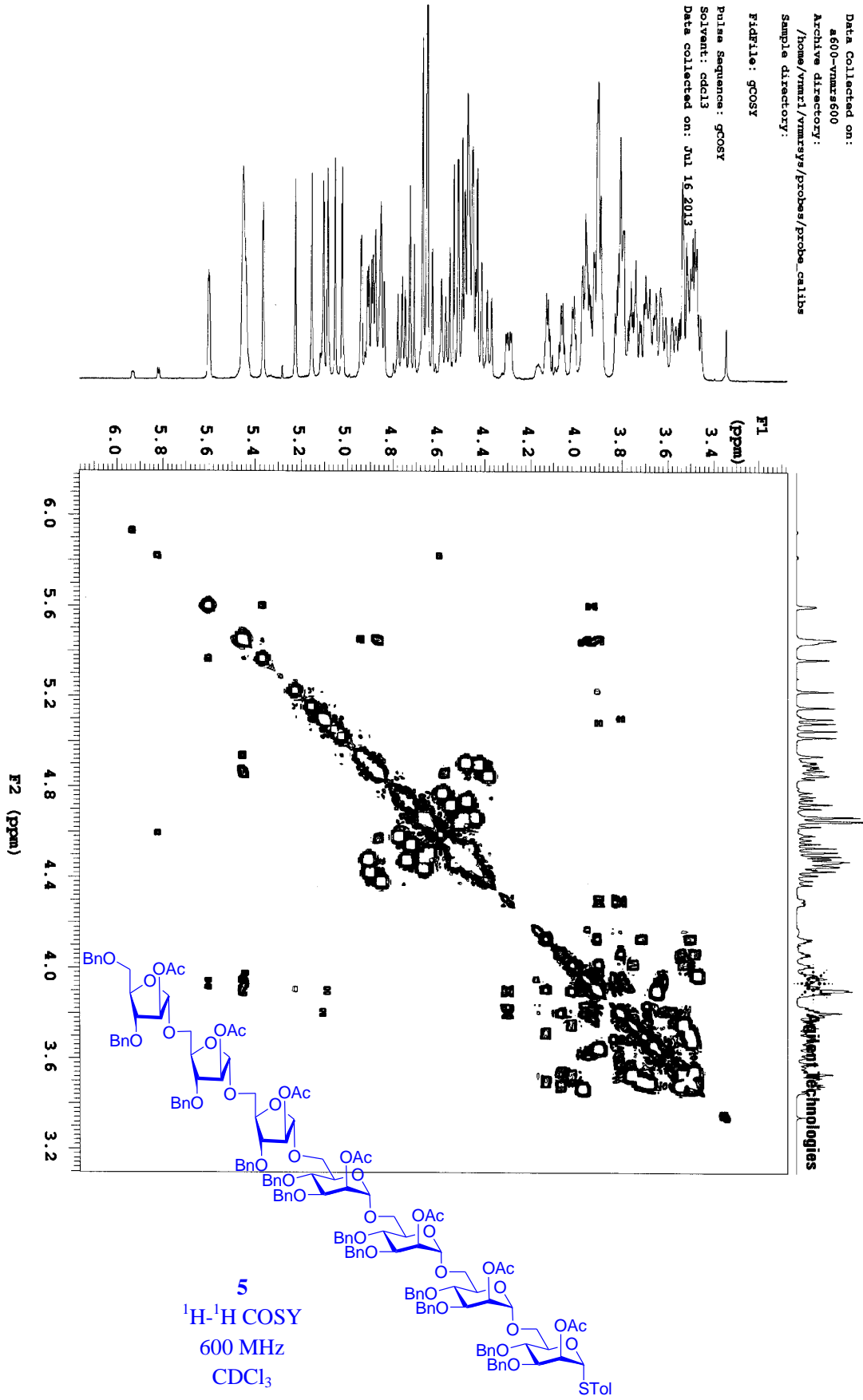


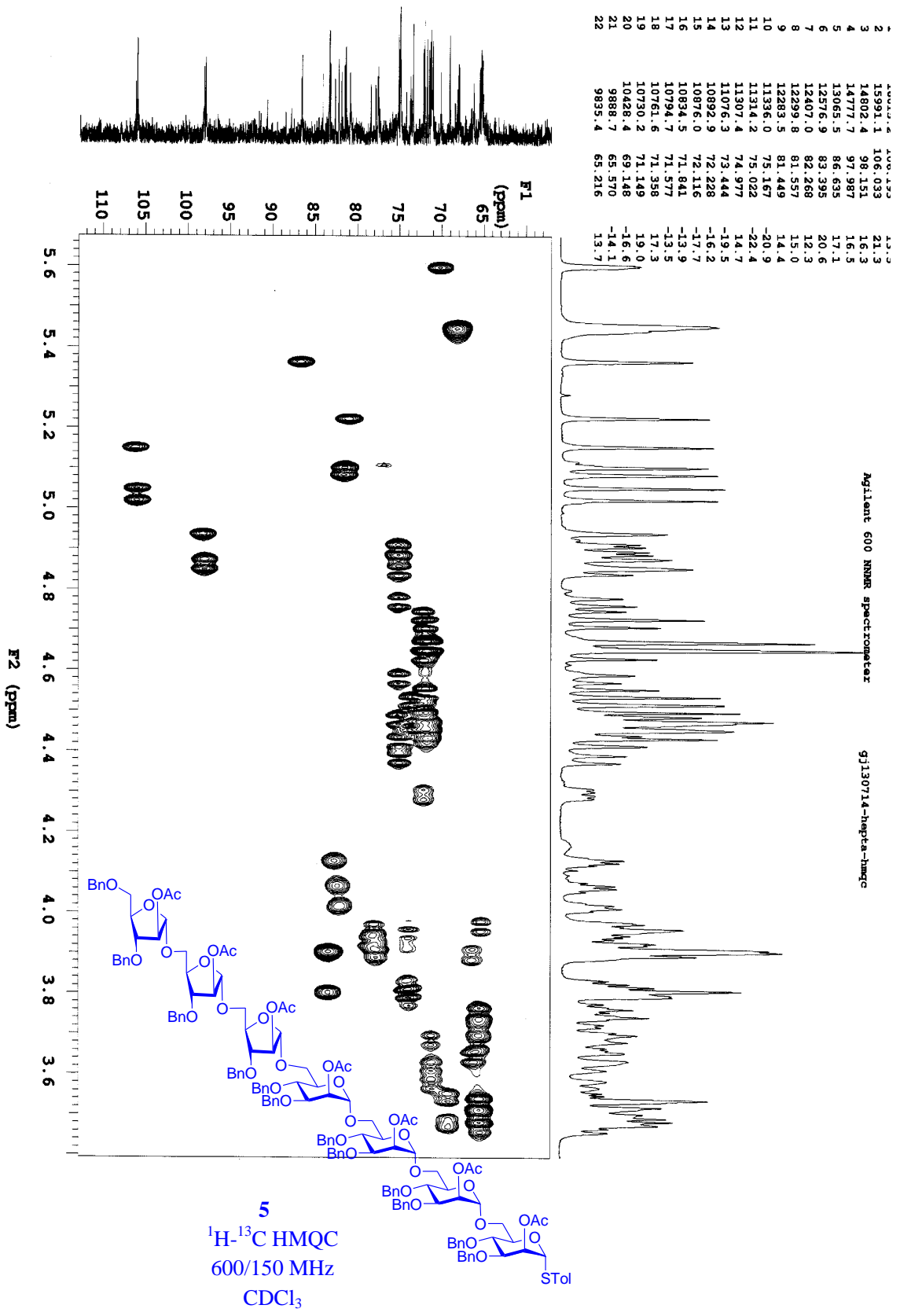
07130714

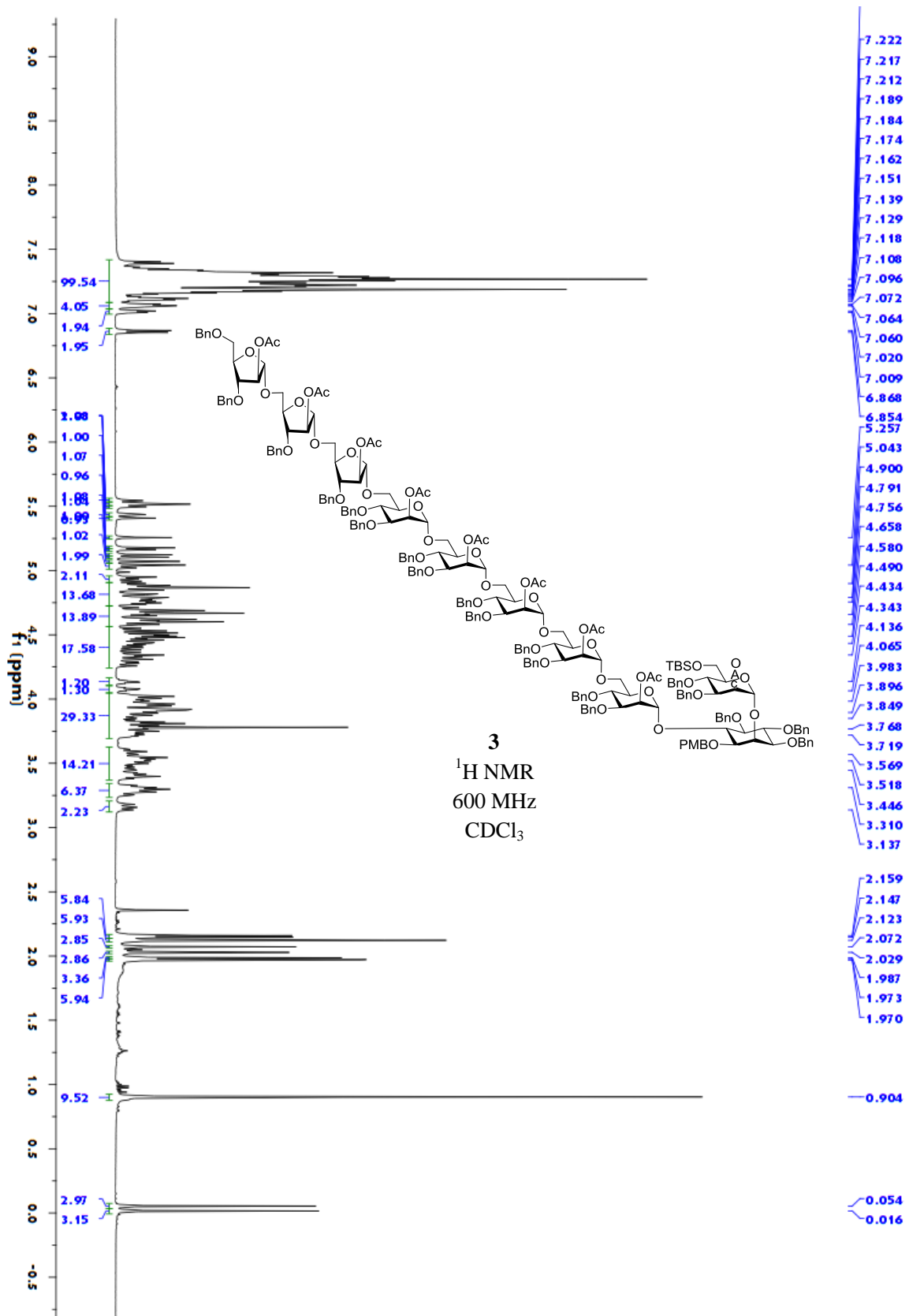
Agilent 600 NMR spectrometer

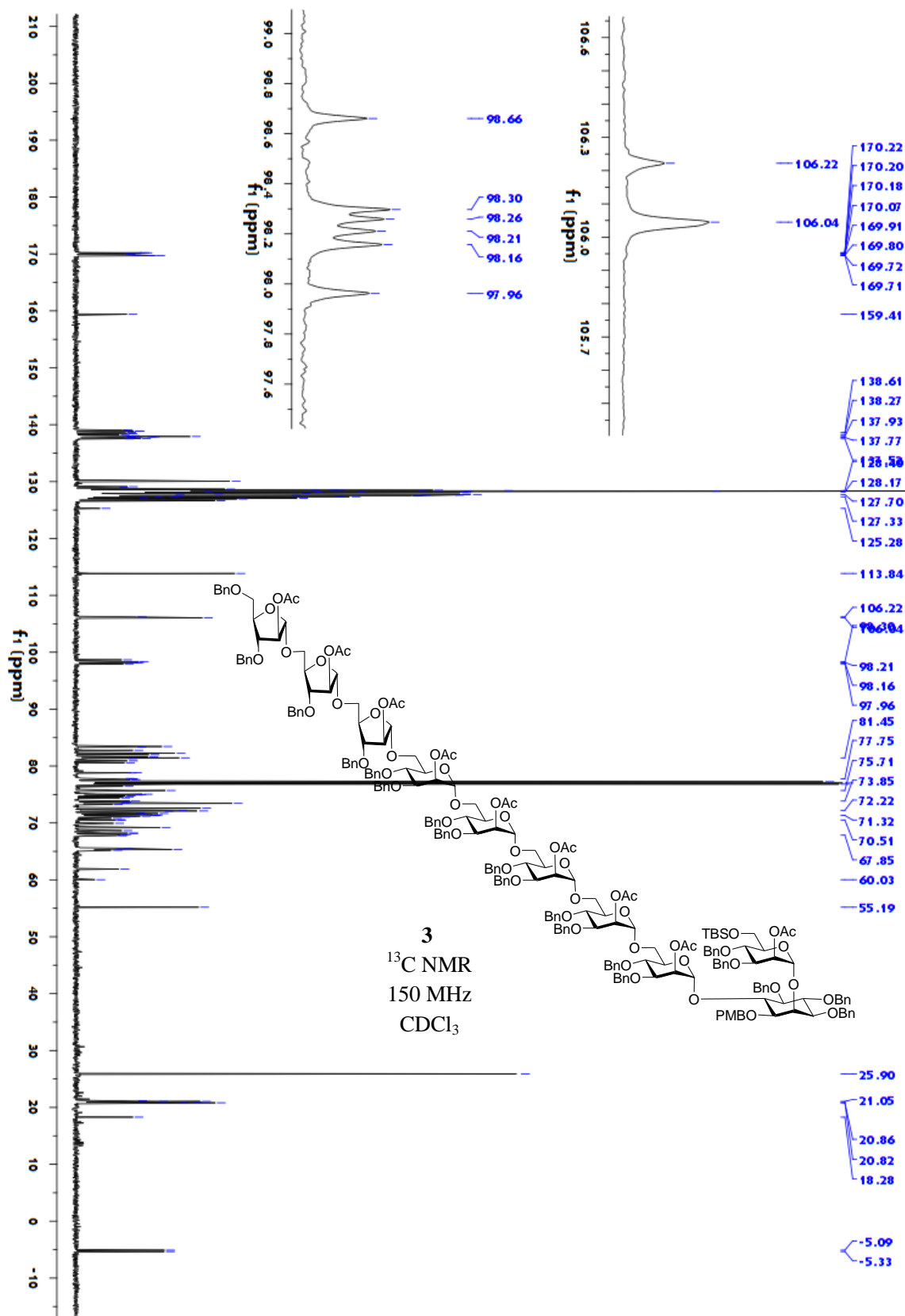
Sample Name:
Data Collected on:
a60-vmr600
Archive directory:
/home/vmr1/vmrays/probes/probe_calibs
Sample directory:

Fidfile: gcossy
Pulse Sequence: gcossy
Solvent: cdcl3
Data collected on: Jul 16 2013









GJ130727

Sample Name:

Data Collected on:

4600-Vnmr600

Archive directory:

/home/vnmr1/vnmrsys/probes/probe_calibs

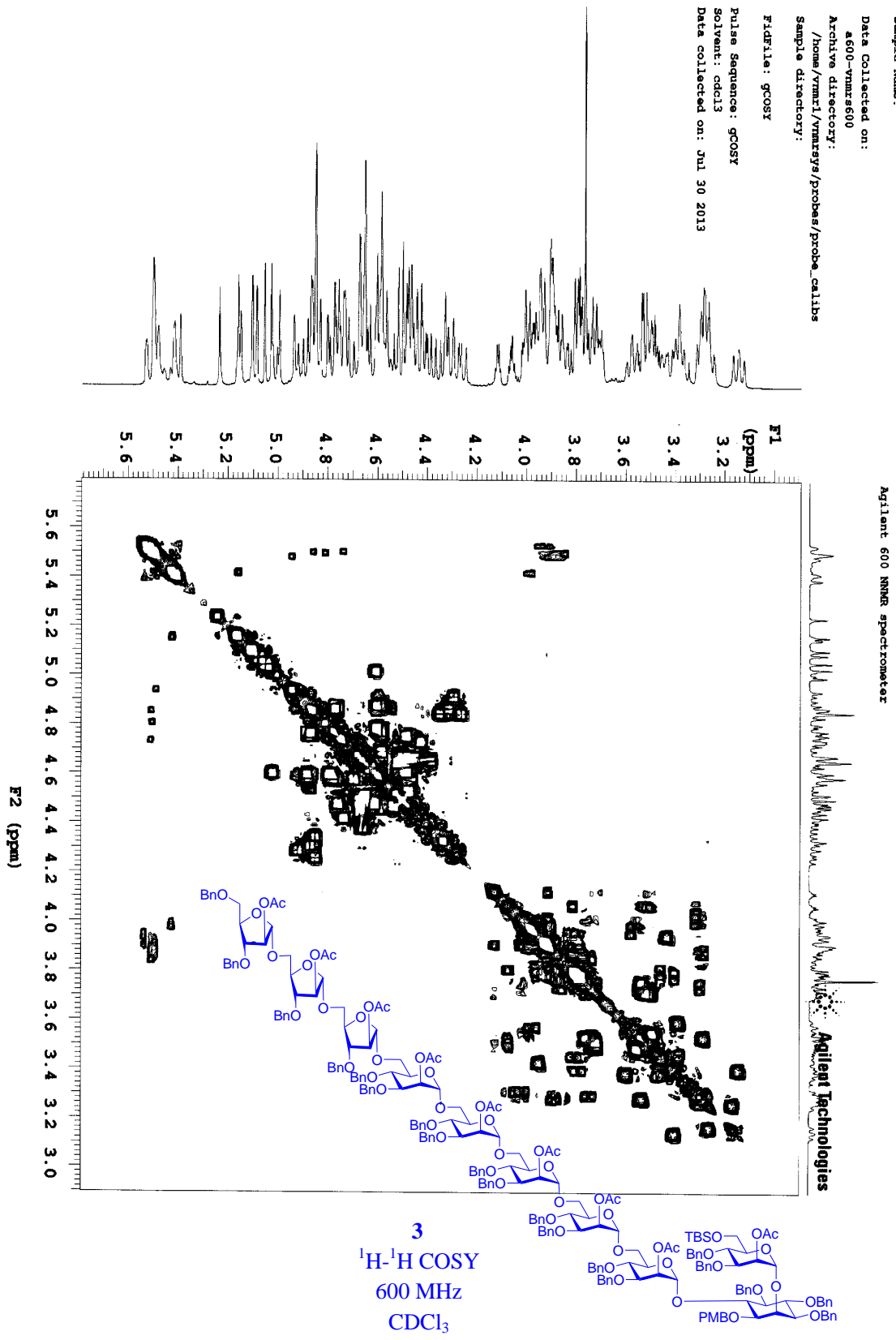
Sample directory:

Fidfile: gc051

Pulse Sequence: gc051

Solvent: cdcl3

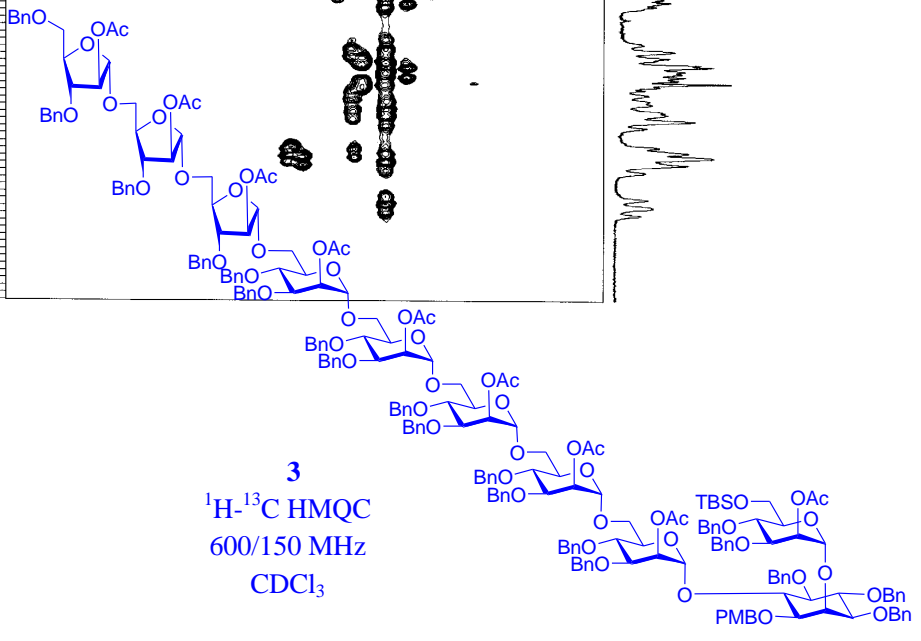
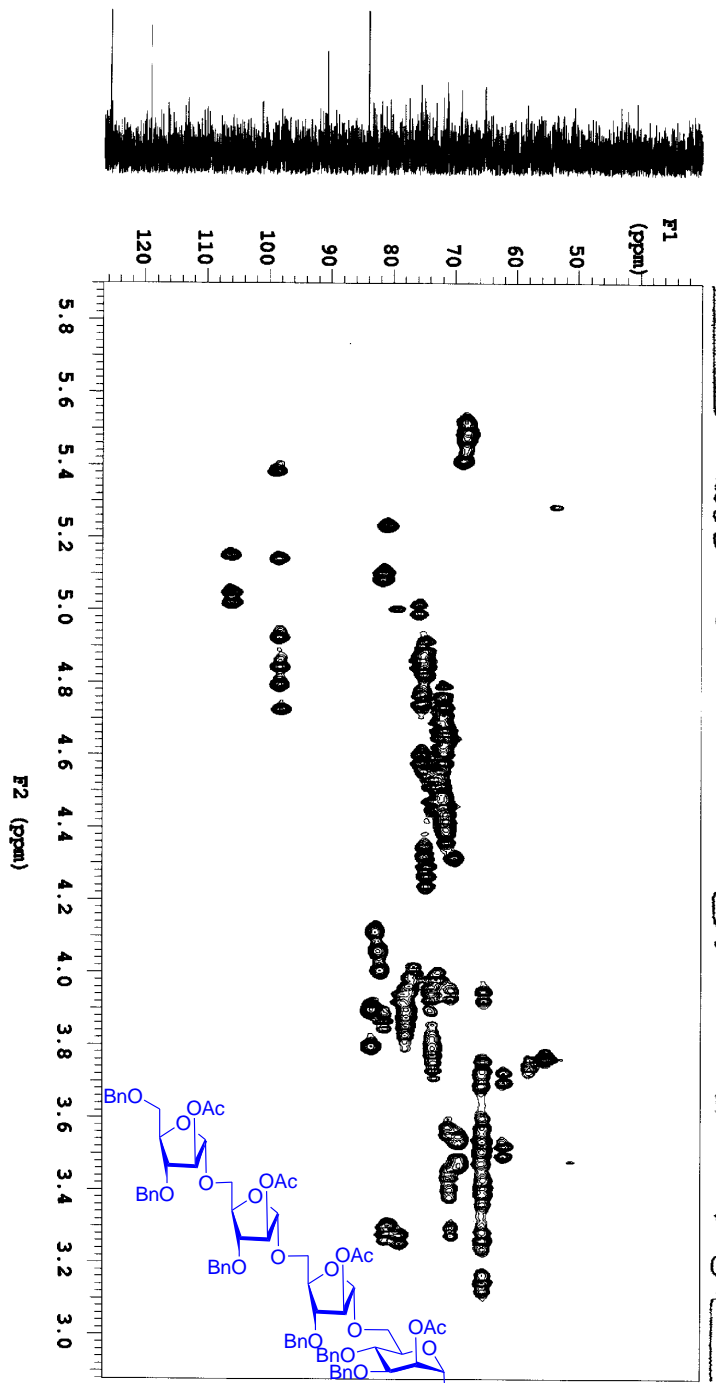
Data collected on: Jul 30 2013

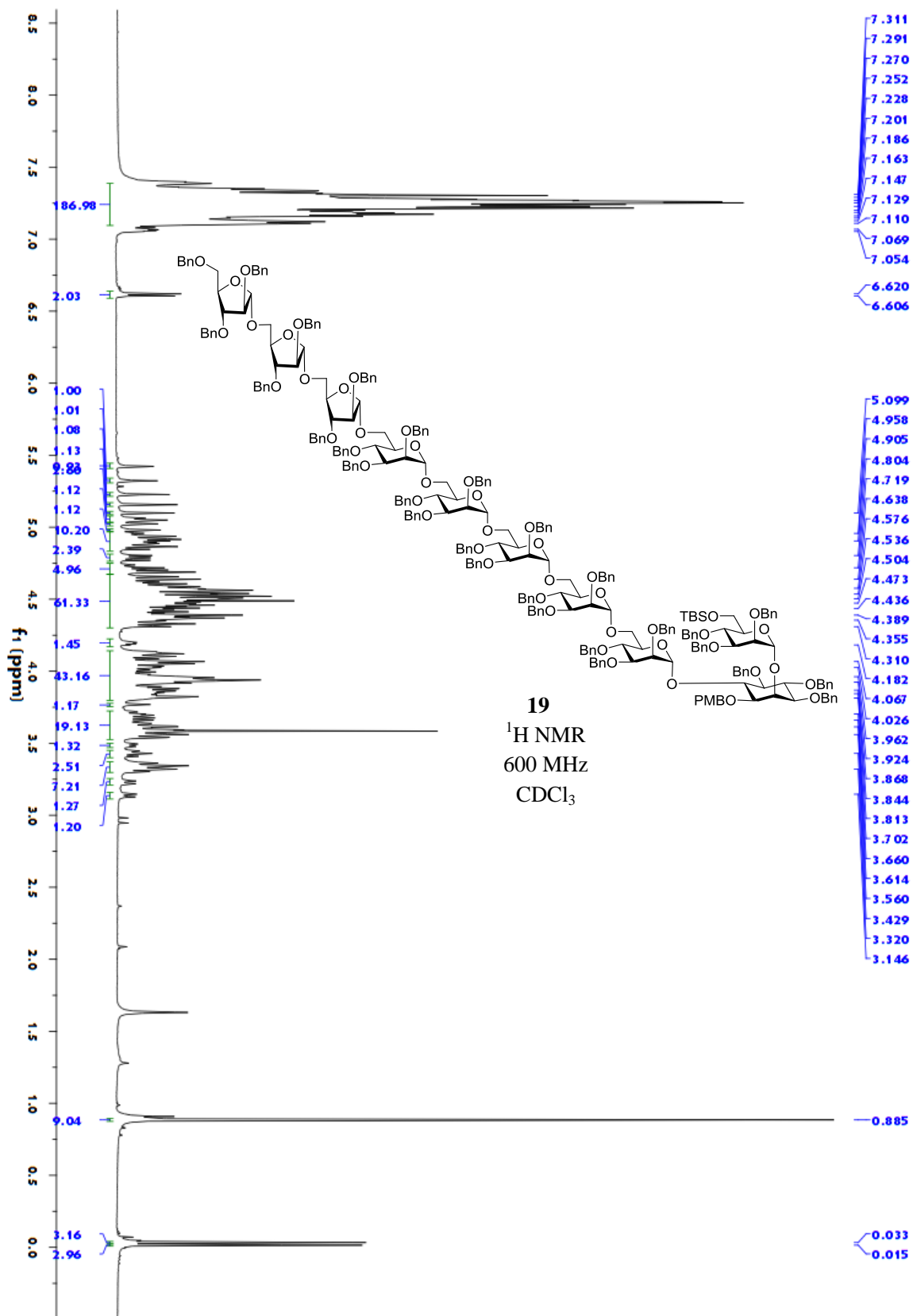


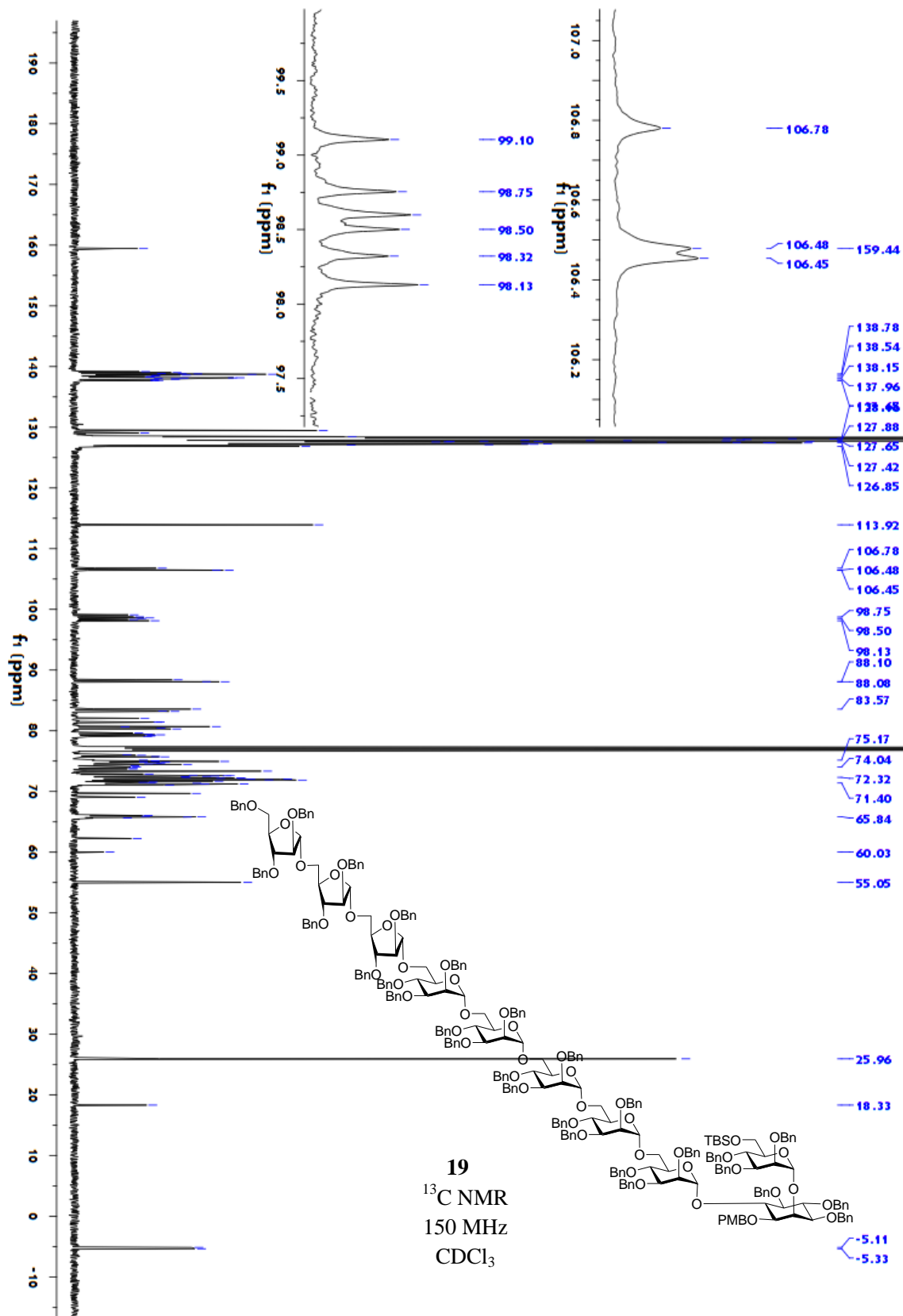
G5130727

1	18975.0	125.819	-28.0
2	18951.4	125.662	12.6
3	17983.1	119.242	21.1
4	17563.0	116.456	13.1
5	17152.9	113.737	12.3
6	16615.5	110.173	-12.3
7	15683.8	90.734	-22.6
8	12891.9	84.157	31.5
9	12663.3	81.315	12.5
10	11821.3	75.732	-13.4
11	11322.0	75.074	-14.0
12	11037.6	73.188	-12.7
13	10754.3	71.309	-13.5
14	10430.0	69.159	-14.7
15	9852.8	65.332	-13.1
16	8803.7	58.376	13.1

Agilent 600 NMR spectrometer
Standard, proton







GJ130810

Sample Name:

Data Collected on:

4600-vmr600

Archive directory:

/home/vmr1/vmr600/probes/probe_caliba

Sample directory:

File: gc057

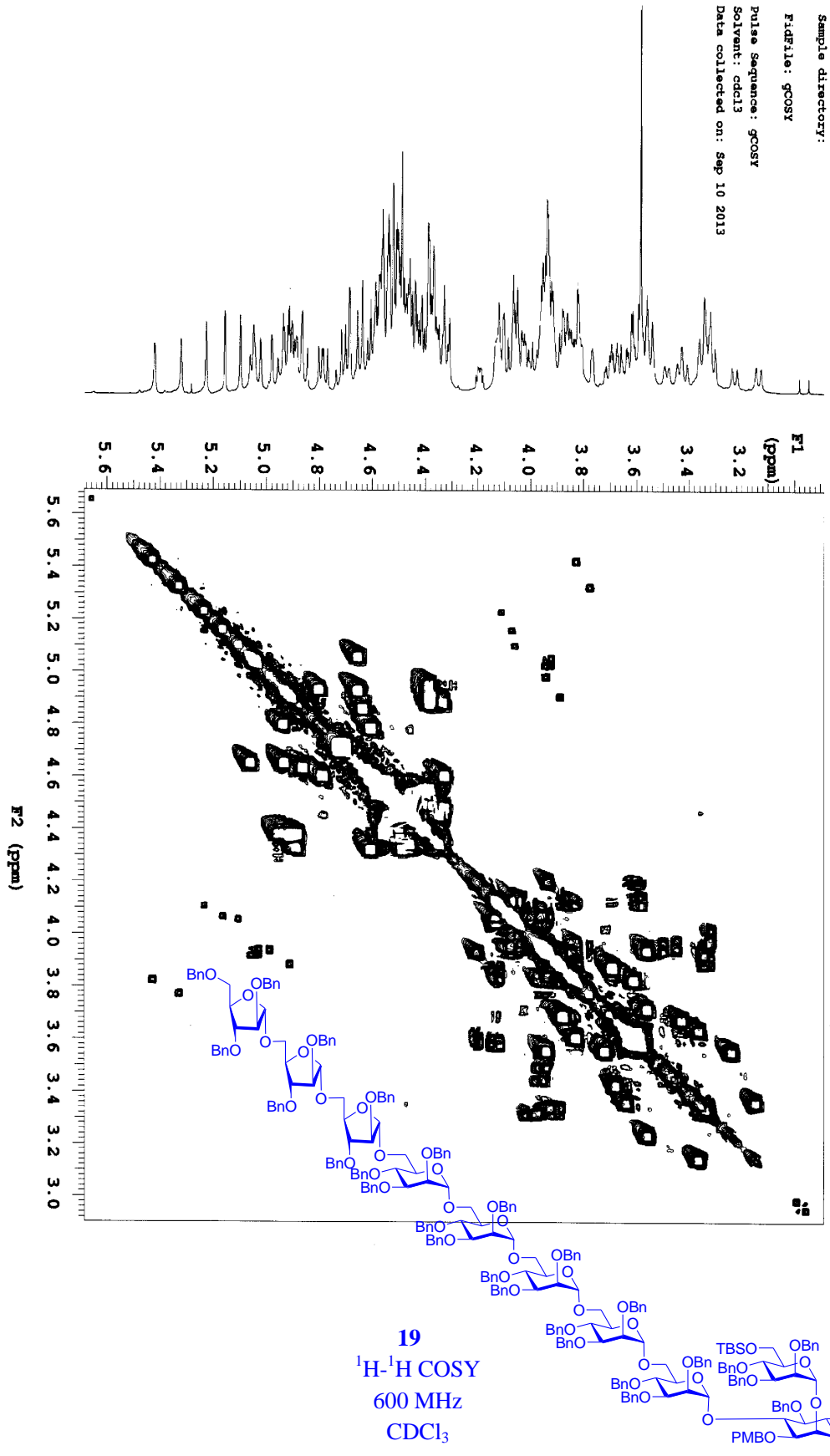
Pulse Sequence: gc057

Solvent: cdcl3

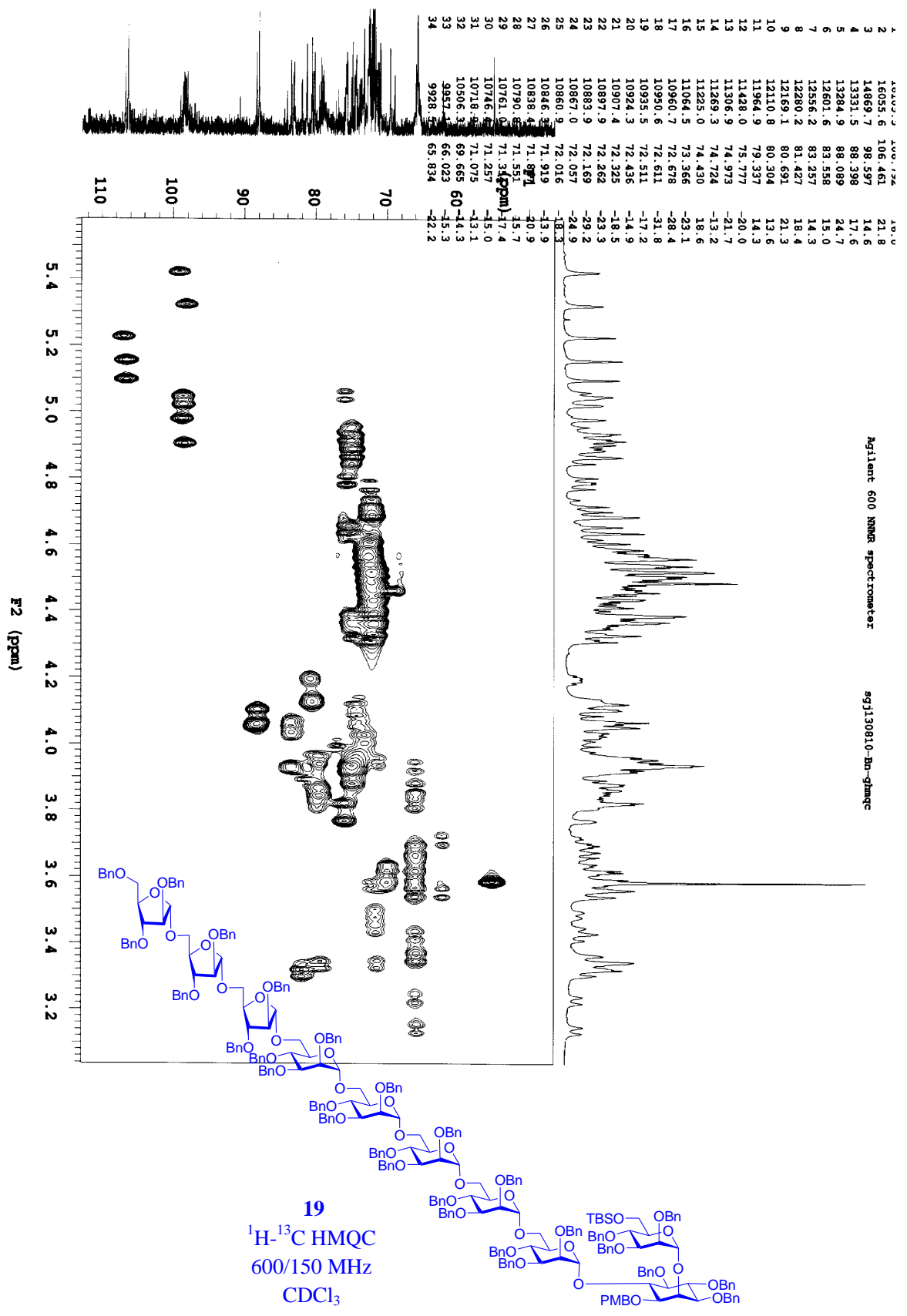
Data collected on: Sep 10 2013

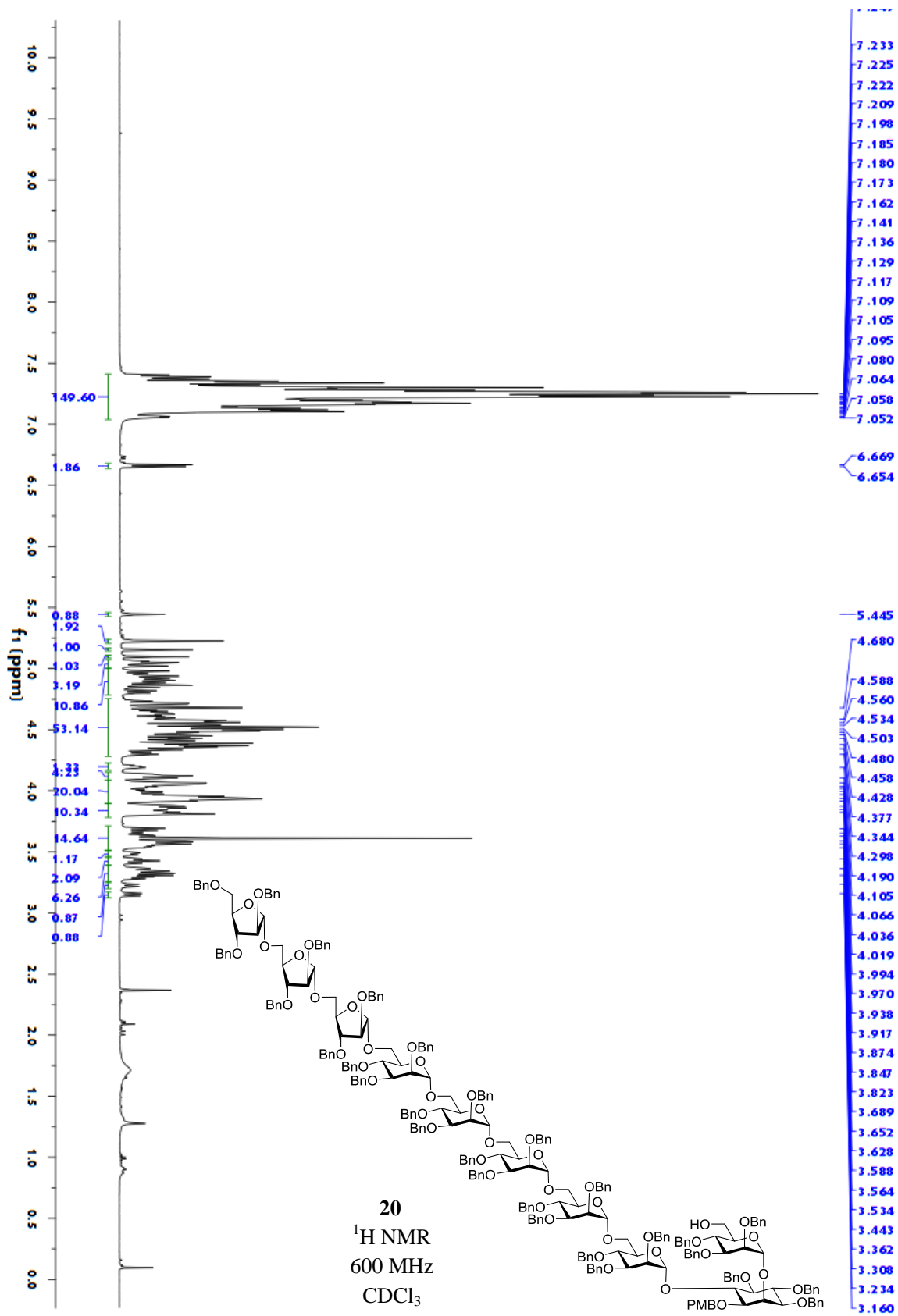
Agilent 600 NMR spectrometer

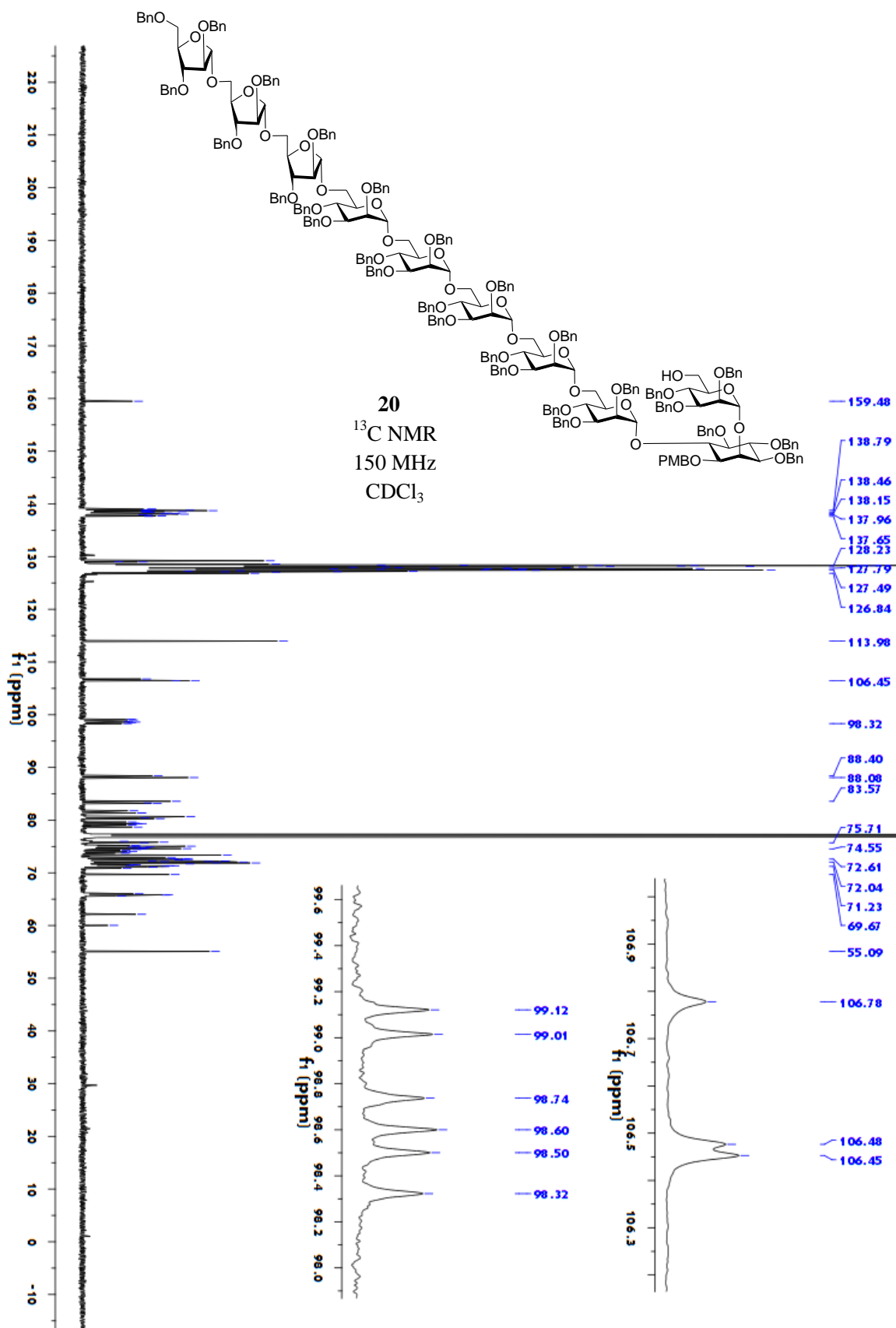
Agilent Technologies



19
 $^1\text{H}-^1\text{H}$ COSY
600 MHz
 CDCl_3

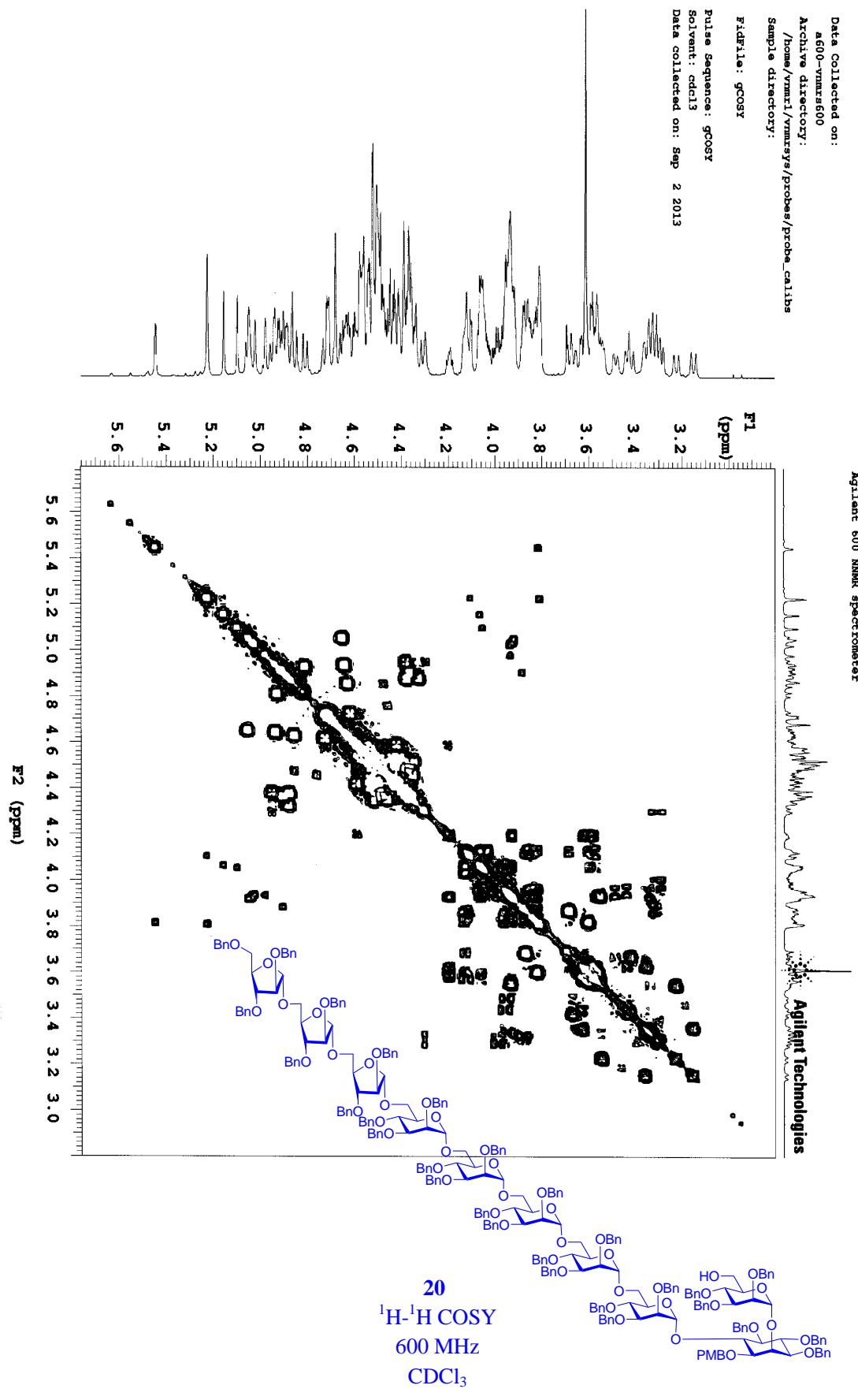


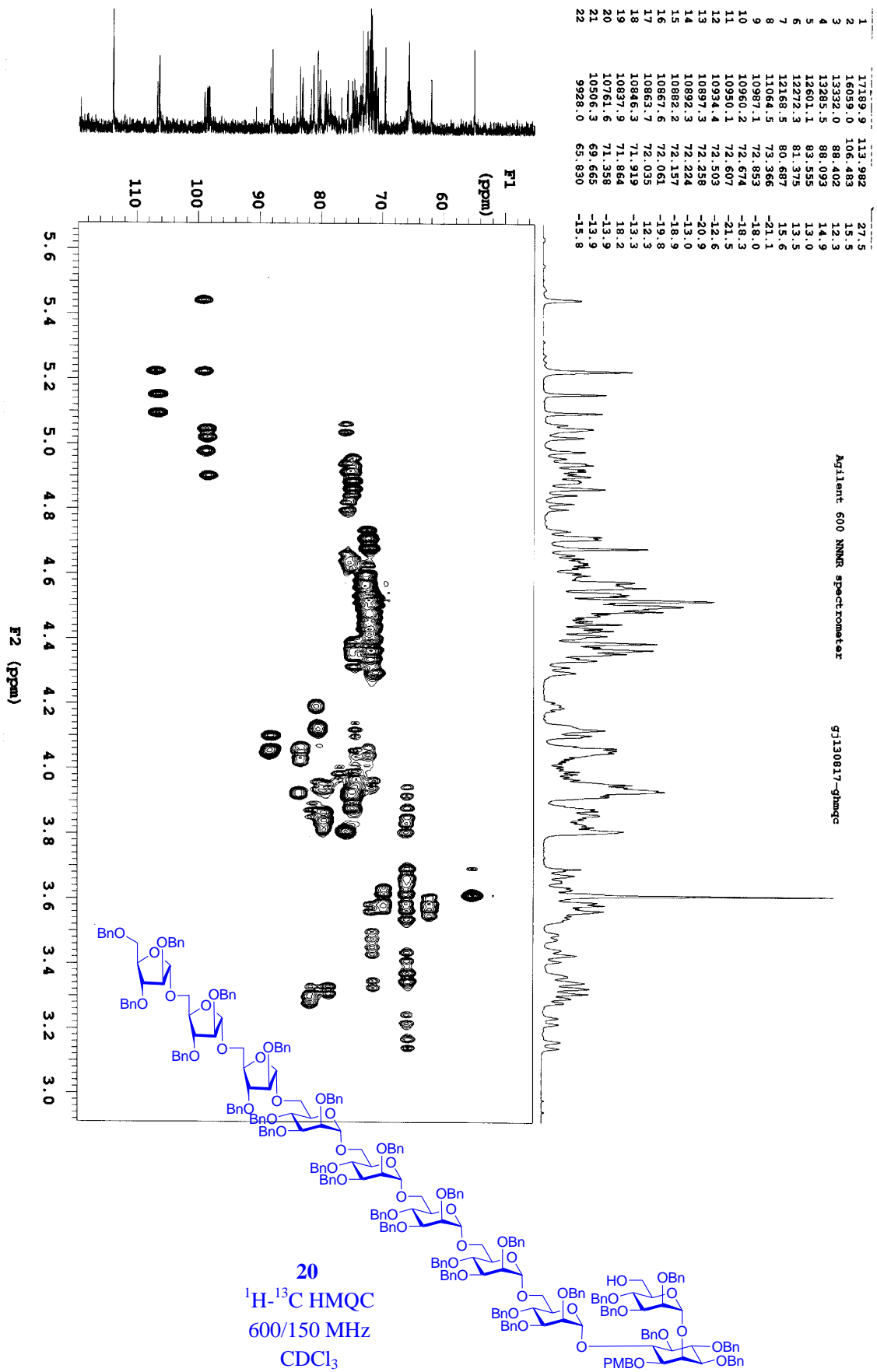


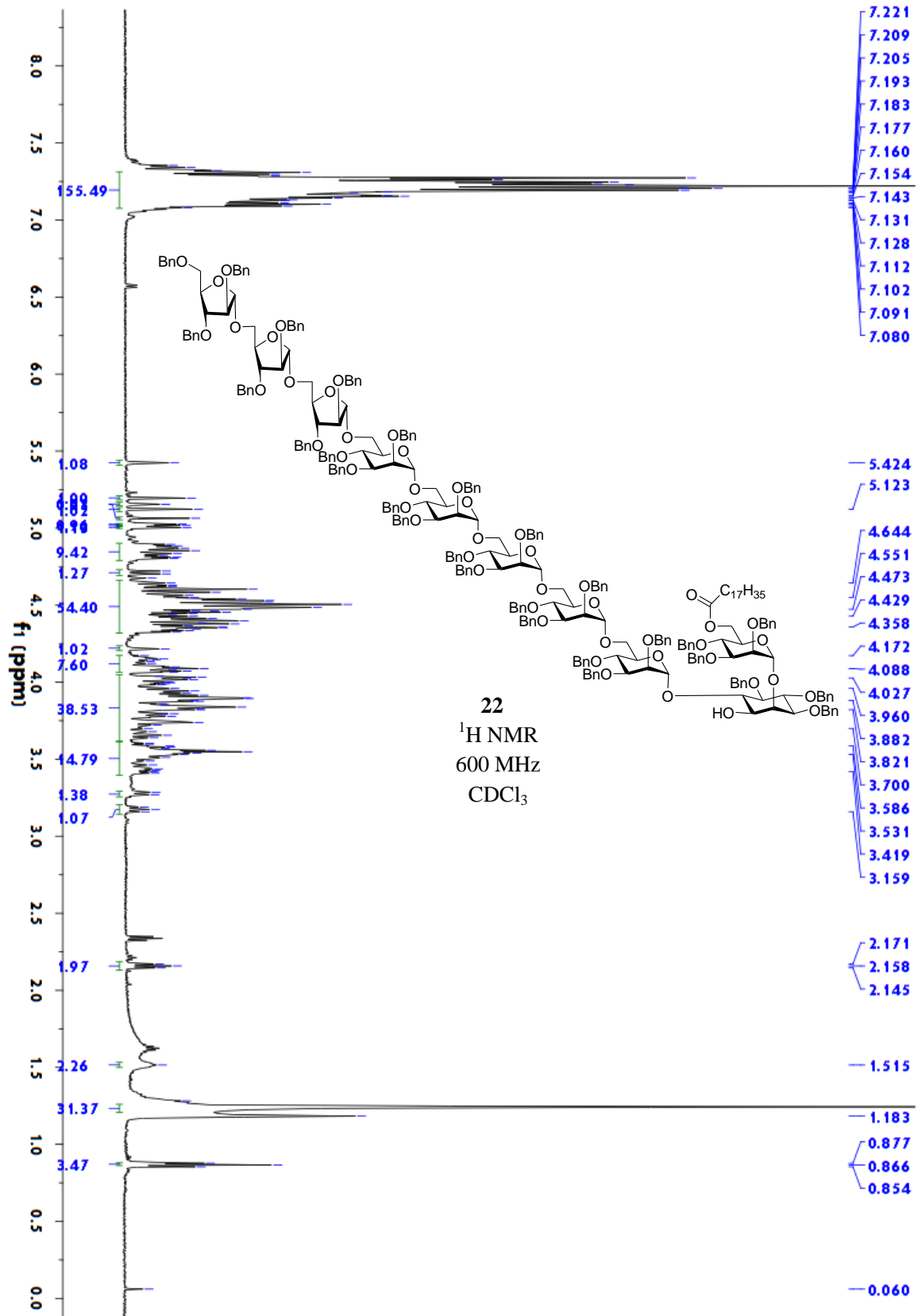


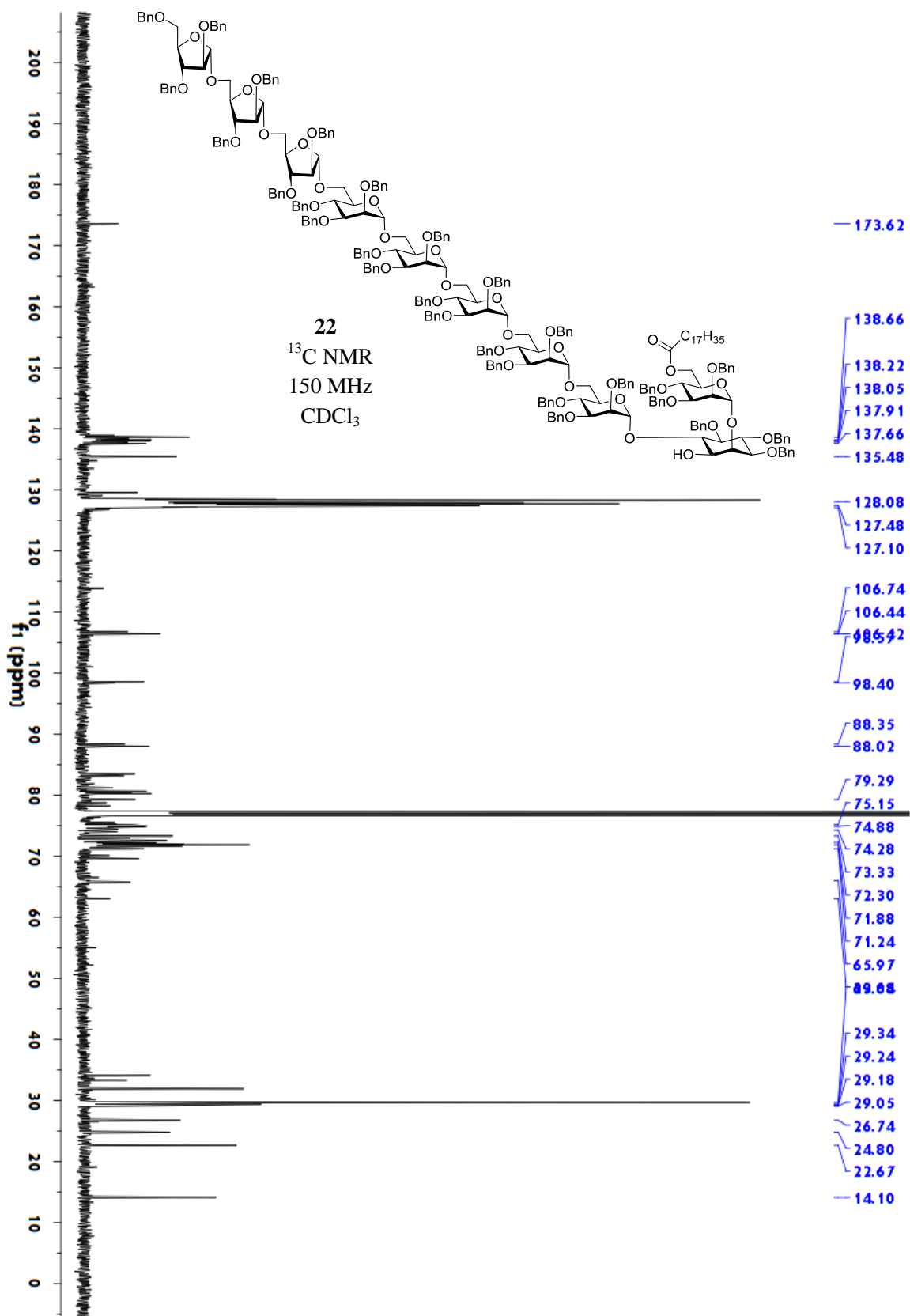
Sample Name:
 Data Collected on:
 4600-vnmr6600
 Archive directory:
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 Sample directory:
 FIDFile: gcOSY
 Pulse Sequence: gcOSY
 Solvent: cdcl3
 Data collected on: Sep 2 2013

Agilent 600 NMR spectrometer









Sample Name:

Data Collected on:

600-nmr600

Archive directory:

/home/vmr1/vmrays/probes/probe_calibs

Sample directory:

Fidfile: gc057

ulse Sequence: gc057

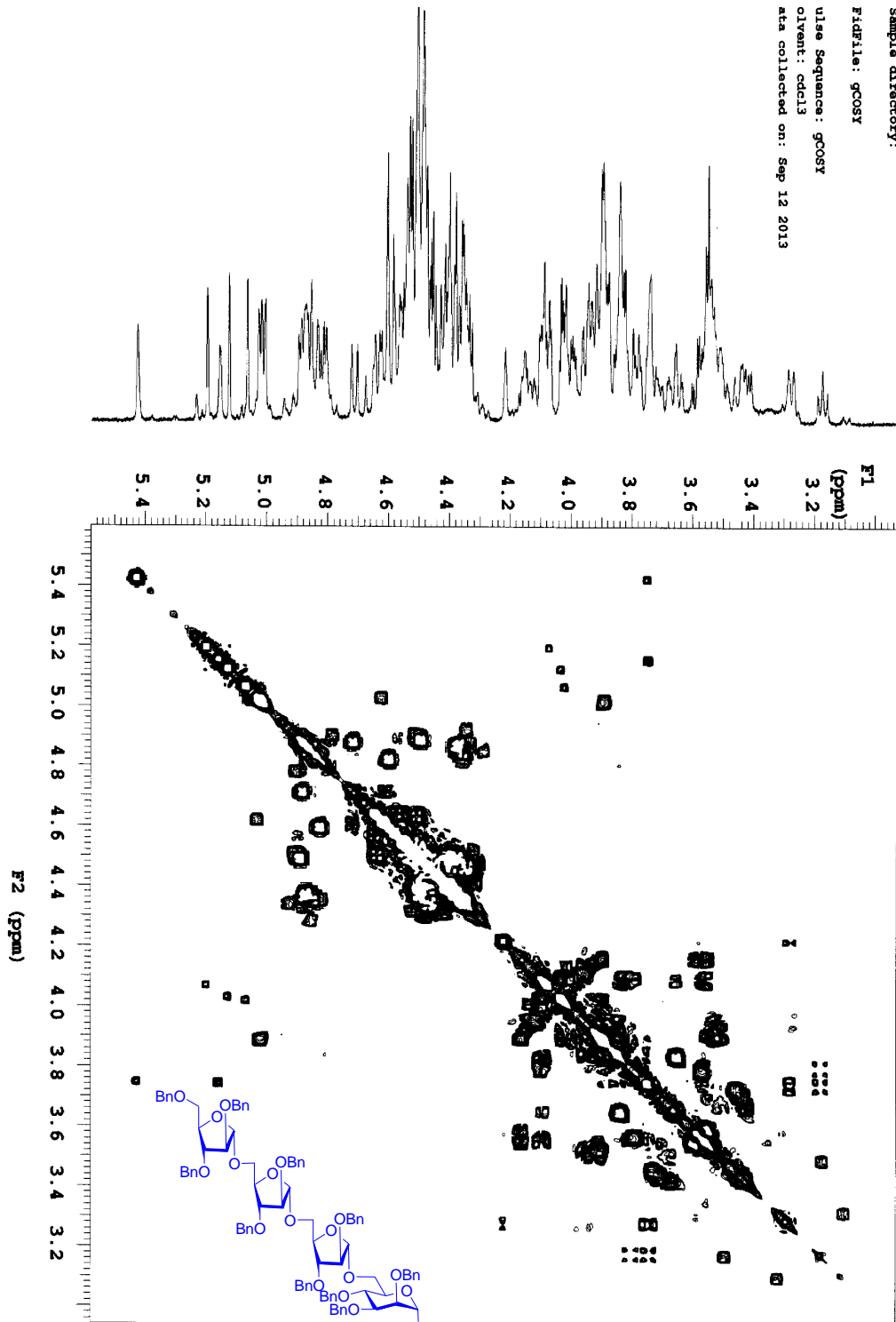
olvent: cdcl3

ata collected on: Sep 12 2013

Agilent 600 NMR spectrometer

613097

Agilent Technologies



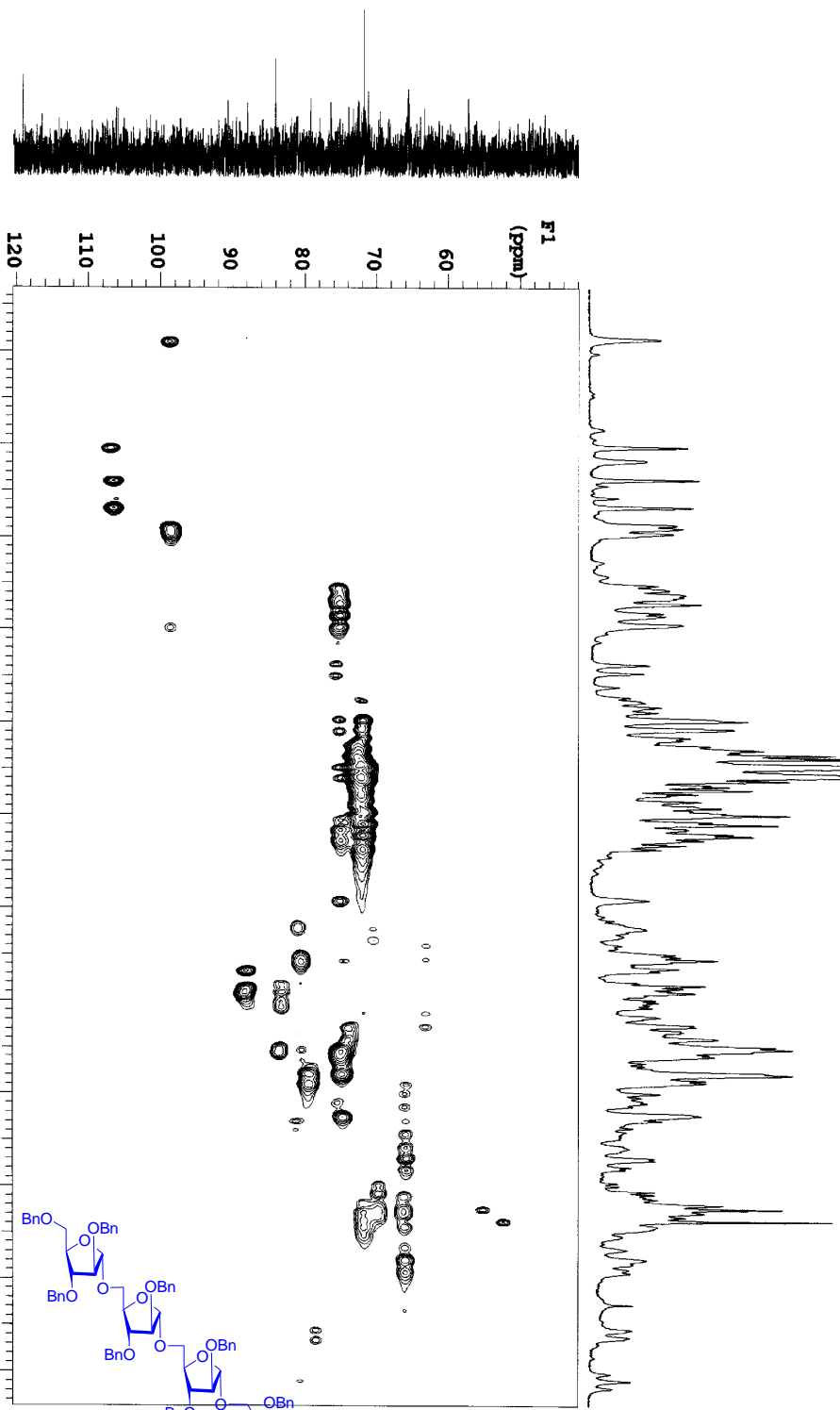
22
 $^1\text{H}-^1\text{H}$ COSY
600 MHz
 CDCl_3

1	17983.1	119.242	14.5
2	13683.8	90.734	-13.6
3	12691.9	84.157	18.2
4	10964.7	72.704	-13.0
5	10941.7	72.552	-13.1
6	10841.2	71.886	-22.2

GJ130917

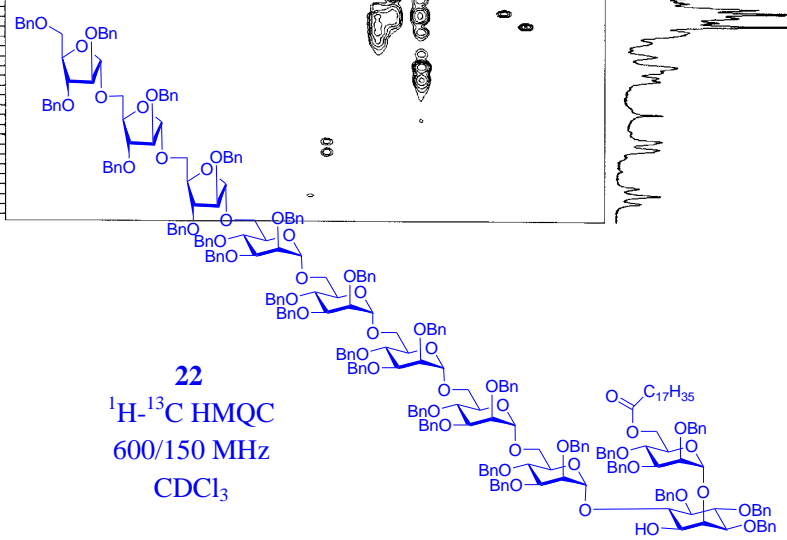
Agilent 600 NMR spectrometer

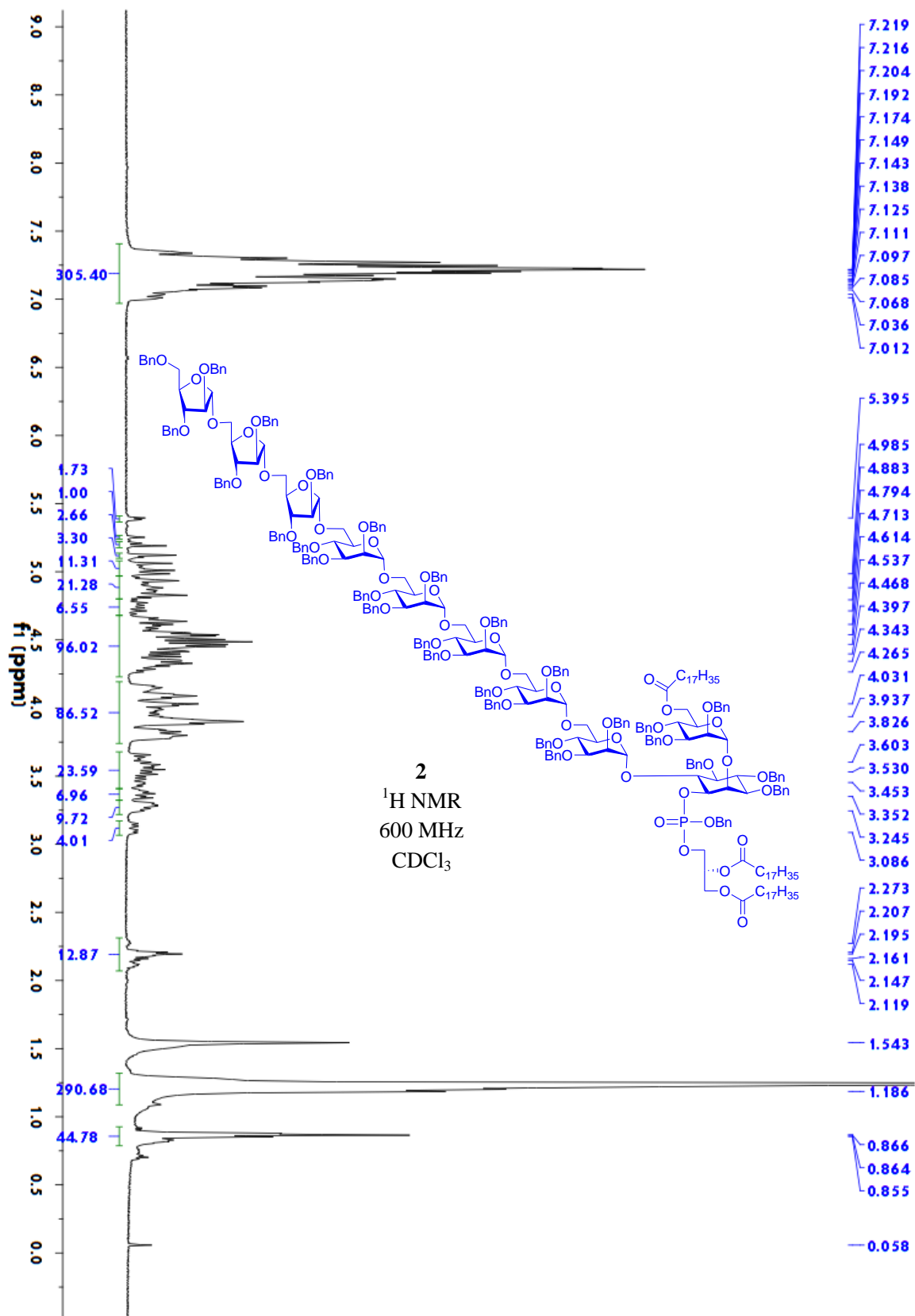
Standard_proton



F1 (ppm)

F2 (ppm)





Sample Name :

Data Collected on:

600-nmr600

Archive directory:

/home/vrnari/vrnarsys/probes/probe_calibs

Sample directory:

Fidfile: gcosy

Pulse Sequence: gcosy

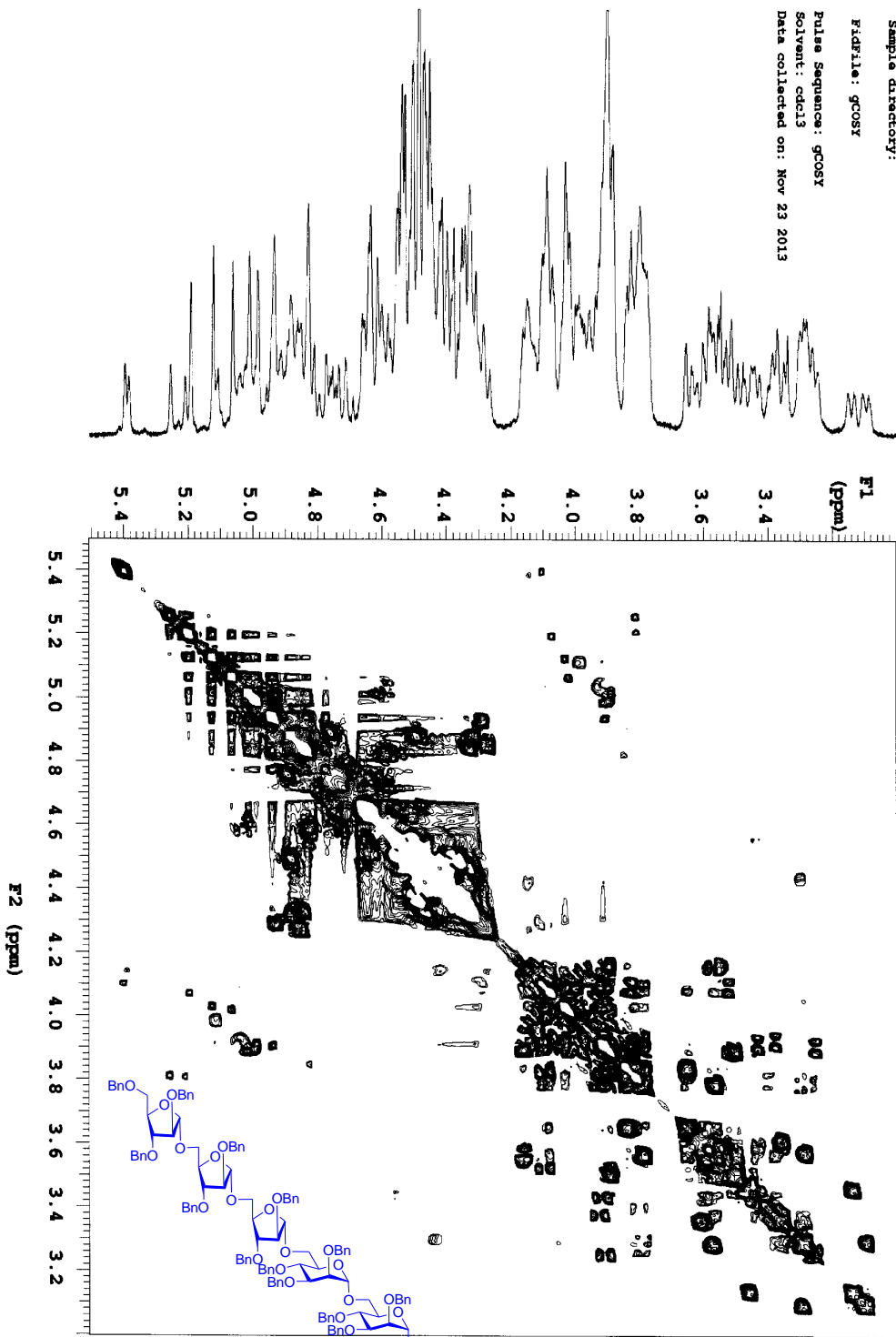
Solvent: cdcl3

Data collected on: Nov 23 2013

GJ131122

Agilent 600 NMR spectrometer

Agilent Technologies



2
 $^1\text{H}-^1\text{H}$ COSY
600 MHz
 CDCl_3

