Supporting Information for

Synthesis of a Miniature Lipoarabinomannan

Jian Gao [a], Guochao Liao [a], Lizhen Wang [b], and Zhongwu Guo [a,b,*]

[a] *Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA*

[b] *National Glycoengineering Research Center, Shandong University, Jinan 250100, China*

[*] Corresponding author, E-mail: zwguo@chem.wayne.edu

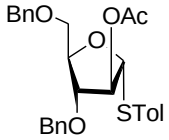
Table of Contents:

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 N_2 atmosphere immediately before use. Analytical TLC was carried out on Silica Gel 60Å F_{254} plates with detection by a UV detector and/or by charring with 15% H_2SO_4 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.

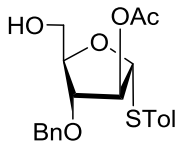
***p*-Tolyl 2-*O*-acetyl-3,5-di-*O*-benzyl-1-thio-α-D-arabinofuranoside (8):**



To a stirred solution of **12** (8.0 g, 25 mmol) in 20 mL of anhydrous CH_2Cl_2 were added AcBr (2.8 mL, 38 mmol) and CH_3OH (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 CH_3OH (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 CH_3OH, and then CH_3ONa in CH_3OH (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 CH_3OH and CH_2Cl_2 (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 CH_3OH before water was added. The aq. phase was extracted with EtOAc (3×50 mL) and the organic layer was combined, dried over Na_2SO_4, 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 CH_2Cl_2. To the mixture was added a catalytic amount of $SnCl_4$ (0.9 mmol, 1M in CH_2Cl_2) 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. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{28}H_{30}O_5SNa$ $[M + Na]^+$, 501.1712; found, 501.1718. ESI MS (*m/z*)*:* found, 501.4.

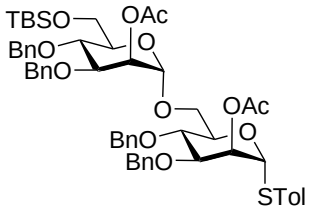
***p*-Tolyl 2-*O*-acetyl-3-*O*-benzyl-5-*O*-*tert*-butydimethylsilyl-1-thio-α-D-arabinofuranoside (9):**



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 1h at rt, quenched with MeOH, diluted with water (100 mL), and extracted with EtOAc (2×100 mL). The organic layer, after being dried with Na_2SO_4, 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 CH_2Cl_2. To the mixture was added a catalytic amount of $SnCl_4$ (0.4 mmol, 1M in CH_2Cl_2) 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. ^{1}H 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 $C_{21}H_{24}O_5SNa$ $[M + Na]^+$, 411.1242; found, 411.1249. ESI MS (*m/z*): found, 411.6.

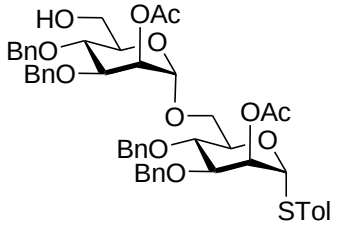
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butydimethylsilyl-α-D-mannopyranosyl)-(1→6)-3,4-di-*O*-benzyl-2-*O*-acetyl-α-D-mannopyranoside (15):**



After a mixture of **10** (1.11 g, 1.78 mmol) and freshly activated molecular sieves 4Å in anhydrous CH_2Cl_2 (20 mL) was stirred at rt for 40 min and then cooled to -78 ˚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 ˚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. ^{1}H 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_{CH} = 172 Hz), 86.59 (Man^{A} C-1, J_{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 $C_{57}H_{70}O_{12}SiSNa$ $[M + Na]^{+}$, 1029.4255; found, 1029.4249.

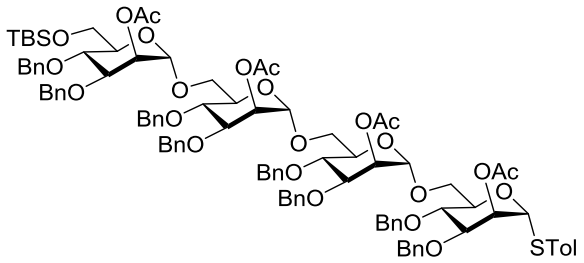
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-3,4-di-*O*-benzyl-2-*O*-acetyl-α-D-mannopyranoside (16):**



After the TBS-protected **15** (760 mg, 0.755 mmol) was dissolved in THF and CH_2Cl_2 (16 mL, 1:1), $Et_3N{\cdot}3HF$ (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

Na_2SO_4, 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. ^{1}H NMR (600 MHz, $CDCl_3$): 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). ^{13}C NMR (150 MHz, $CDCl_3$): 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 $C_{51}H_{56}O_{12}SNa$ [M + Na]$^+$, 915.3390; found, 915.3350.

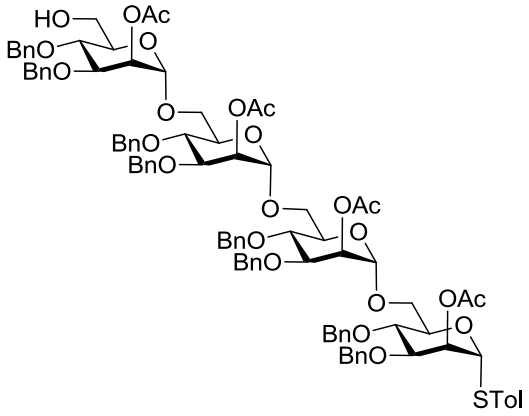
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl-6-*O*-*tert*-butydimethylsilyl-α-D-mannopyranosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-3,4-di-*O*-benzyl-2-*O*-acetyl-α-D-mannopyranoside (17):**



After a mixture of **15** (707 mg, 0.703 mmol) and freshly activated molecular sieves 4Å in anhydrous CH_2Cl_2 (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 μL, 0.703 mmol) 10 min later. The mixture was stirred at -78 ˚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. ^{1}H 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 × Man H-1, 4 × 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 × 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 $C_{101}H_{118}O_{24}SSiNa$ $[M + Na]^+$, 1797.7401; found, 1797.7299.

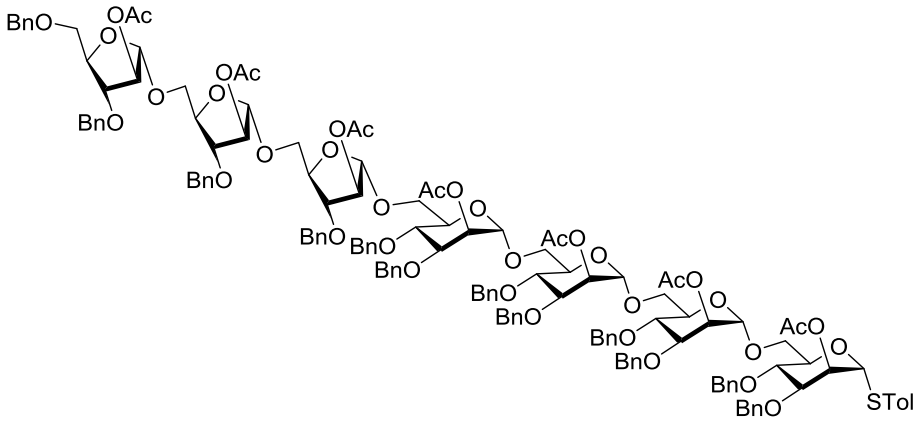
***p*-Tolyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl) -3,4-di-*O*-benzyl-2-*O*-acetyl-α-D-mannopyranoside (7):**



After the TBS-protected **17** (900 mg, 0.507 mmol) was dissolved in THF and CH_2Cl_2 (16 mL, 1:1), $Et_3N{\cdot}3HF$ (495 μL, 3.04 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 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 **7** (724 mg, 86%) as foamy solid. ^{1}H NMR (600 MHz, $CDCl_3$): 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 × Man H-2), 5.38 (s, 1H, Man^A H-1), 4.93-4.86 (m, 7H, 3 × Man H-1, 4 × Bn-CH_2-), 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 × Ac), 2.14 (s, 3H, Ac), 2.12 (s, 3H, Ac). ^{13}C NMR (150 MHz, $CDCl_3$): 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 $C_{95}H_{104}O_{24}SNa$ $[M + Na]^+$, 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):**

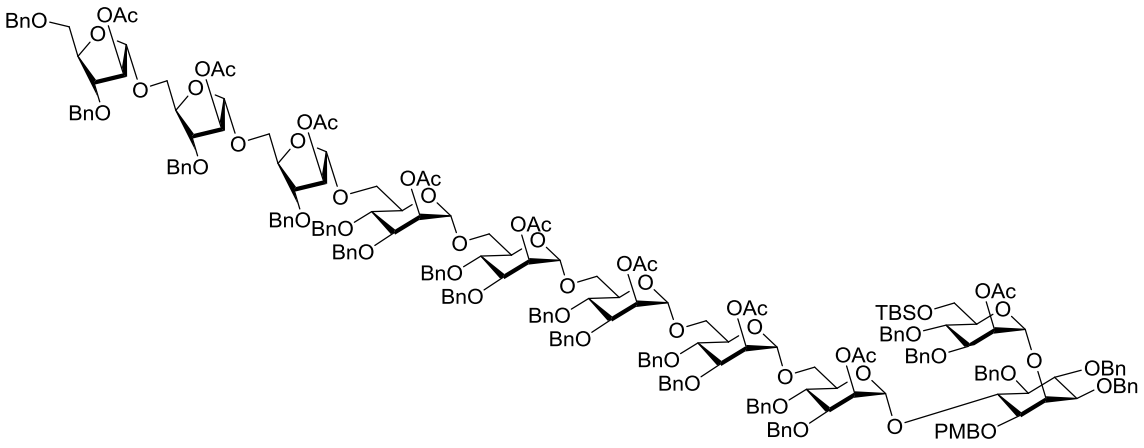


After a mixture of **8** (270 mg, 0.565 mmol) and freshly activated molecular sieves 4Å in anhydrous CH_2Cl_2 (8 mL) was stirred at rt for 40 min and then cooled to -78 ˚C, a solution of AgOTf (436 mg, 1.695 mmol) in acetonitrile (2.5 mL) was added. Ten minutes later, *p*-TolSCl (82 µL, 0.565 mmol) was 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 CH_2Cl_2 (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 CH_2Cl_2 (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 CH_2Cl_2 (3.5 mL). Finally, the reaction was quenched with Et_3N, diluted with CH_2Cl_2, 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. ^{1}H NMR (600 MHz, $CDCl_3$): 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-CH_2-), 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). ^{13}C NMR (150 MHz, $CDCl_3$): 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 $C_{144}H_{158}O_{39}SNa$ $[M + Na]^+$, 2565.9999; found, 2566.0120.

6-*O*-[(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)-(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)]-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):



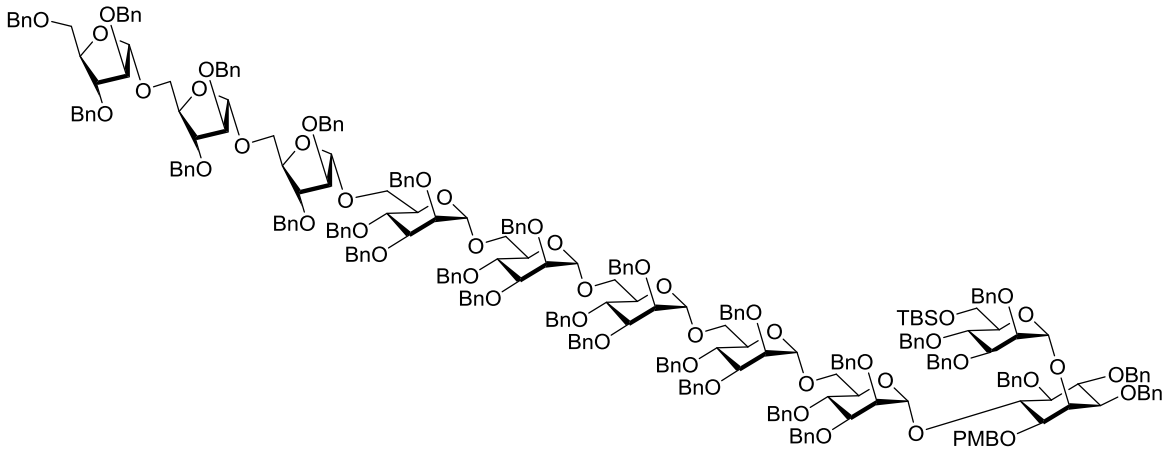
To a solution of **5** (300 mg, 0.118 mmol) in 10 mL of CH_2Cl_2 were added TTBP (88 mg, 0.354 mmol), NIS (53 mg, 0.236 mmol), and AgOTf (61 mg, 0.236 mmol) at 0 ˚C. The

reaction was stirred at rt for 2 h and quenched with saturated aq. $Na_2S_2O_3$ 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%). ^{1}H 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). ^{13}C NMR (150 MHz, $CDCl_3$): 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 $C_{222}H_{250}O_{58}SiNa_2$ $[M + 2Na]^{2+}$, 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*-butyldimethylsil yl-α-D-mannopyranosyl)-1-*O*-(*para*-methoxybenzyl)-D-*myo*-inositol (19):

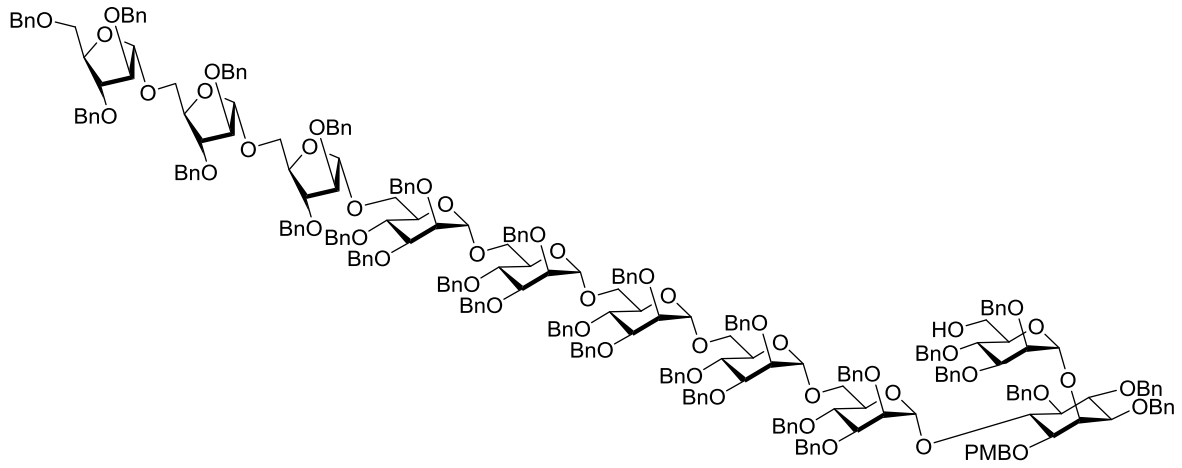


To a solution of **3** (95 mg, 24.5 μmol) in 15 mL of CH_3OH and CH_2Cl_2 (1:2) was added a CH_3ONa solution in CH_3OH (0.5 M) until the pH reached 11. The reaction mixture was stirred at 35 ˚C for 36 h, and the solvent was removed *in vacuo*. The residue was dissolved in a mixture of CH_2Cl_2 and CH_3OH (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 μL, 0.49 mmol) and TBAI (4.1 mg, 11.0 μmol). 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 CH_2Cl_2 (3×50 mL), and the organic layer was dried over Na_2SO_4 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. ^{1}H NMR (600 MHz, $CDCl_3$): 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 × Bn-CH_2-), 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-CH_2-), 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). ^{13}C NMR (150 MHz, $CDCl_3$): 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 $C_{267}H_{286}O_{49}SiNa_2$ $[M + 2Na]^{2+}$, 2174.9; found, 2174.4. MALDI-TOF MS (*m/z*): calcd for $C_{267}H_{286}O_{49}SiNa$ $[M + Na]^{+}$ 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*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-ben

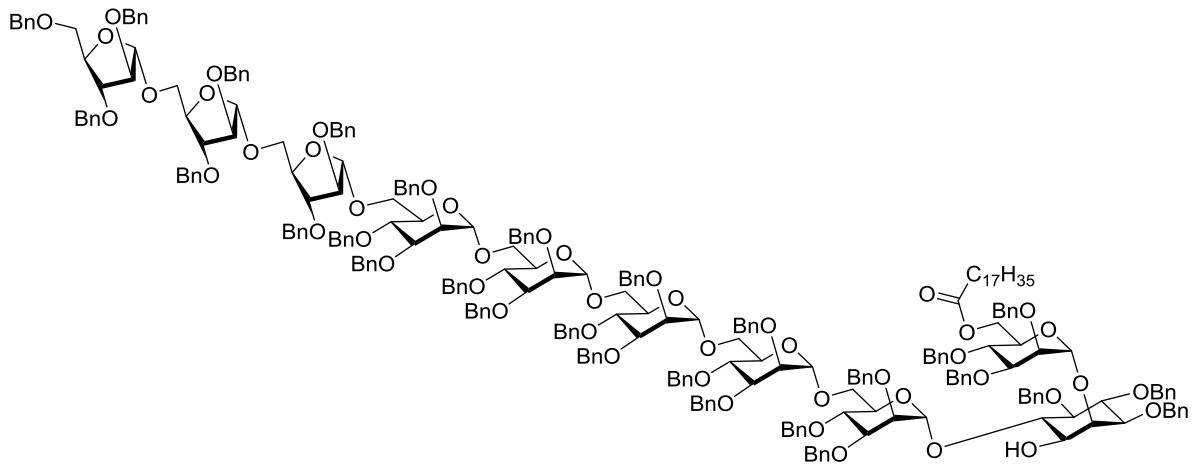
zyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3, 4-tri-*O*-benzyl-α-D-mannopyranosyl)]-2-*O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-1-*O*-(*para*-methoxybenzyl)-D-*myo*-inositol (20):



After the TBS-protected **19** (65.0 mg, 15.1 μmol) was dissolved in THF and CH_2Cl_2 (2 mL, 1:1), $Et_3N{\cdot}3HF$ (49 μL, 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 × 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. ^{1}H 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 × 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 $C_{261}H_{272}O_{49}Na_2$ $[M + 2Na]^{2+}$, 2117.9; found, 2117.2. MALDI-TOF MS (m/z): calcd for $C_{261}H_{272}O_{49}Na$ $[M + Na]^{+}$, 4215.9; found, 4214.6.

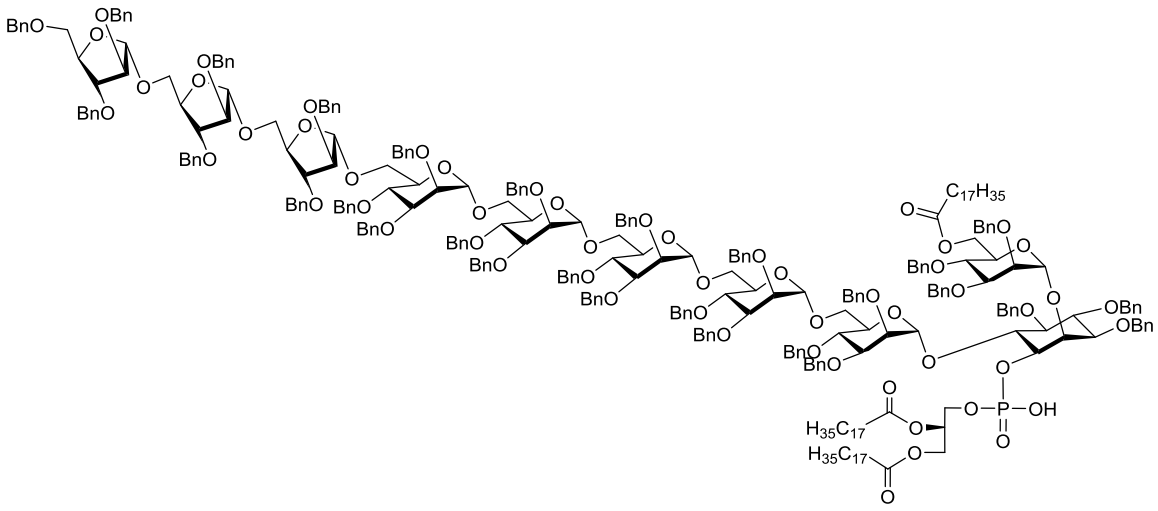
3,4,5-tri-*O*-Benzyl-6-*O*-[(2,3,5-tri-*O*-benzyl-α-D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-arabinosyl)-(1→5)-(2,3-di-*O*-benzyl-α-D-arabinosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)]-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-stearoyl-α-D-mannopyranosyl)-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**: ^{1}H 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 × s, 3H, 3 × Man H-1), 4.85-4.80 (m, 8H, Man^{C} H-1, 7 × 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,

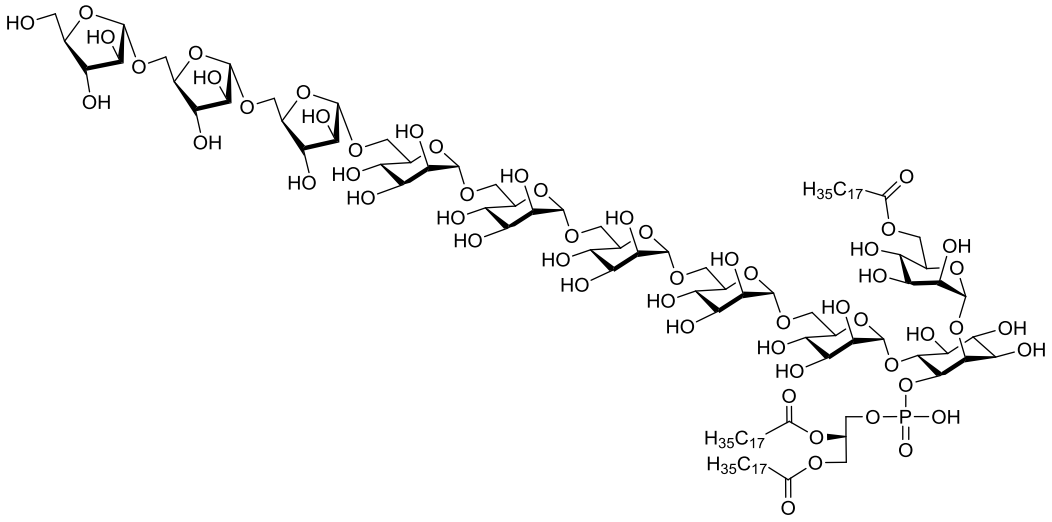
138.26, 138.22, 138.12, 138.05, 138.00, 137.91, 137.81, 137.66, 137.60, 135.48, 129.56, 128.58, 128.48, 128.46, 128.39, 128.33, 128.29, 128.25, 128.22, 128.17, 128.15, 128.12, 128.08, 127.98, 127.89, 127.82, 127.76, 127.71, 127.65, 127.64, 127.58, 127.56, 127.51, 127.48, 127.46, 127.42, 127.41, 127.40, 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 $C_{271}H_{298}O_{49}Na_2$ $[M + 2Na]^{2+}$, 2191.0; found, 2190.9. MALDI-TOF MS (m/z): calcd for $C_{271}H_{298}O_{49}Na$ $[M + Na]^+$, 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):



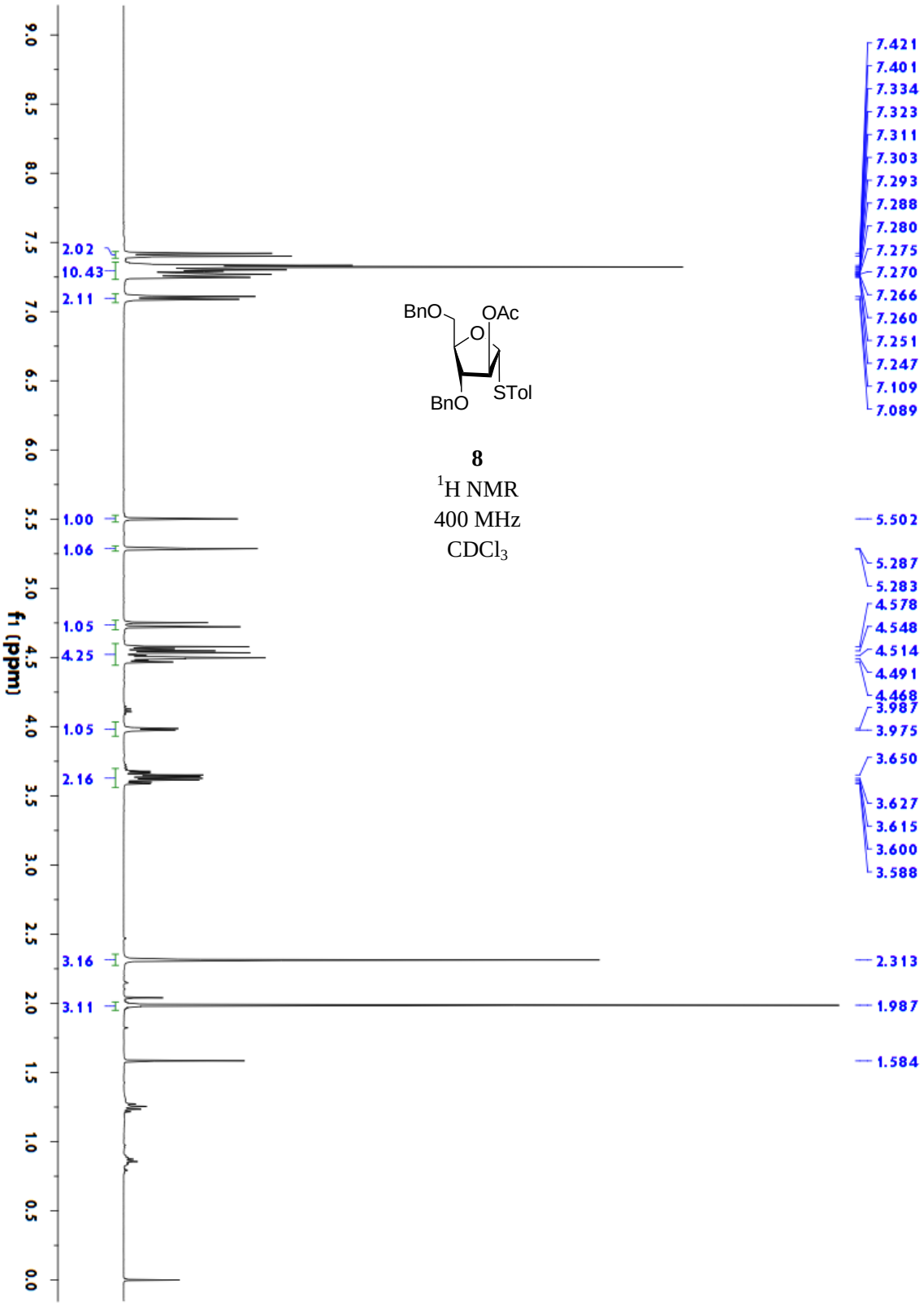
A mixture of **22** (14 mg, 3.2 μmol), freshly prepared glycerylphosphoramidite **4** (13.8 mg, 16.0 μmol) and freshly activated molecular sieves 4Å in 3 mL of CH_2Cl_2 and CH_3CN (2:1) was stirred at rt for 15 min. Then, 1*H*-tetrazole (0.45 M in CH_3CN, 71 μL, 32 μmol) was added to the mixture, which was stirred for another 40 min, before TLC showed the completion of reaction. The mixture was cooled to -20 ˚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 (3×30 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: ^{1}H 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 $C_{317}H_{383}O_{56}NPK$ $[M + K + NH_4]^{2+}$, 2584.8; found, 2584.0.

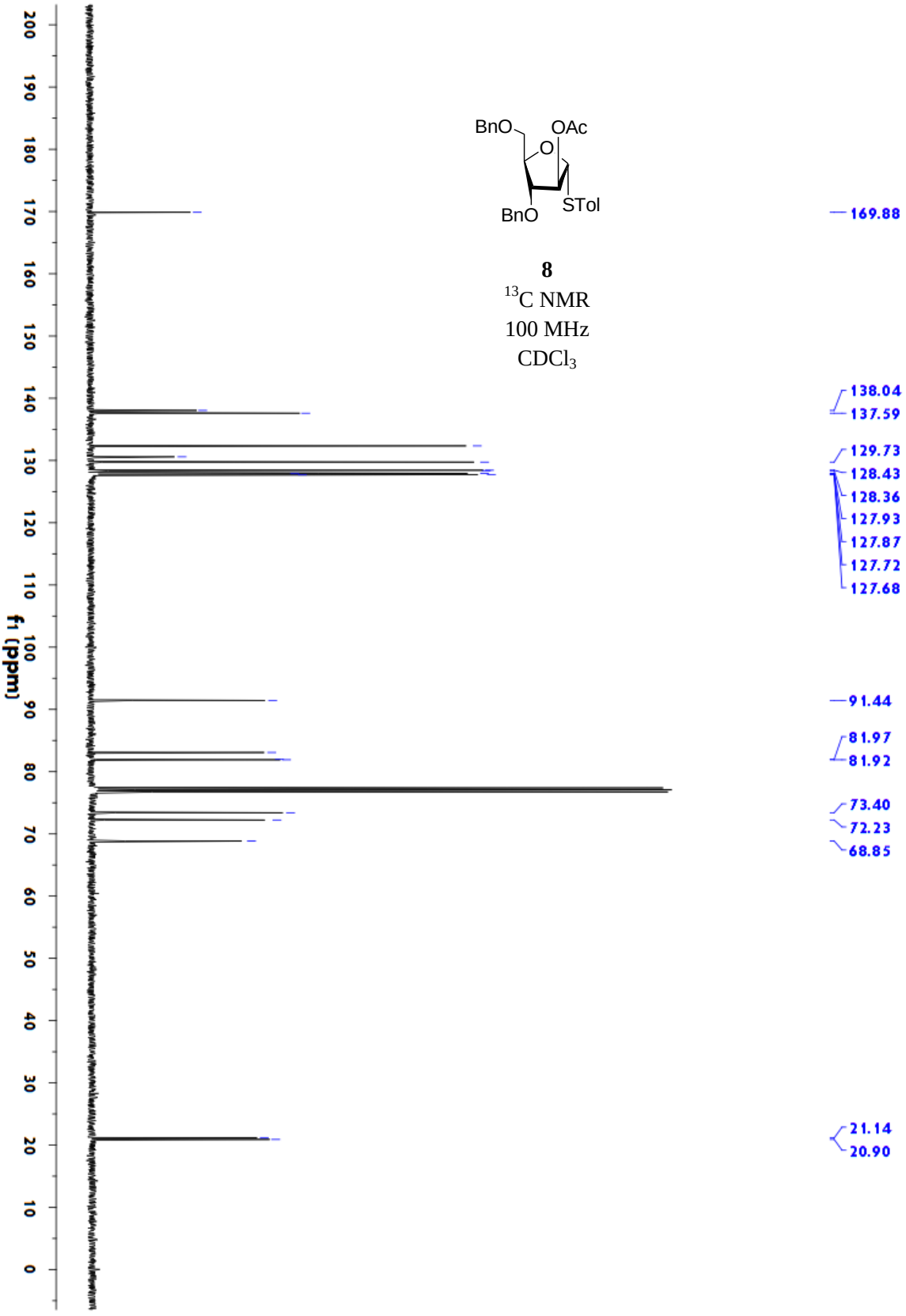
6-*O*-[(α-D-Arabinosyl)-(1→5)-(α-D-arabinosyl)-(1→5)-(α-D-arabinosyl)-(1→6)-(α-D-mannopyranosyl)-(1→6)-(α-D-mannopyranosyl)-(1→6)-(α-D-mannopyranosyl)-(1→6)-(α-D-mannopyranosyl)-(1→6)-(α-D-mannopyranosyl)]-1-*O*-(1,2-di-*O*-stearoyl-*sn*-glycero-3-phosphoryl)-2-*O*-[(6-*O*-stearoyl-α-D-mannopyranosyl)]-D-*myo*-inositol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



The reaction mixture of **2** (11 mg, 2.2 μmol) and 10% Pd/C (8 mg) in $CHCl_3$, MeOH and H_2O (3:3:1, 3.5 mL) was stirred under a H_2 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. ^{1}H NMR (700 MHz, CD_3OD, $CDCl_3$, and D_2O 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). ^{31}P NMR (162 MHz, CD_3OD, $CDCl_3$, and D_2O 3:3:1) δ: 0.67. MALDI-TOF MS (*m/z*): calcd for $C_{114}H_{206}O_{56}PLi$ $[M + Li + H]^{2+}$, 1254.6, found 1254.1.

II. NMR spectra:



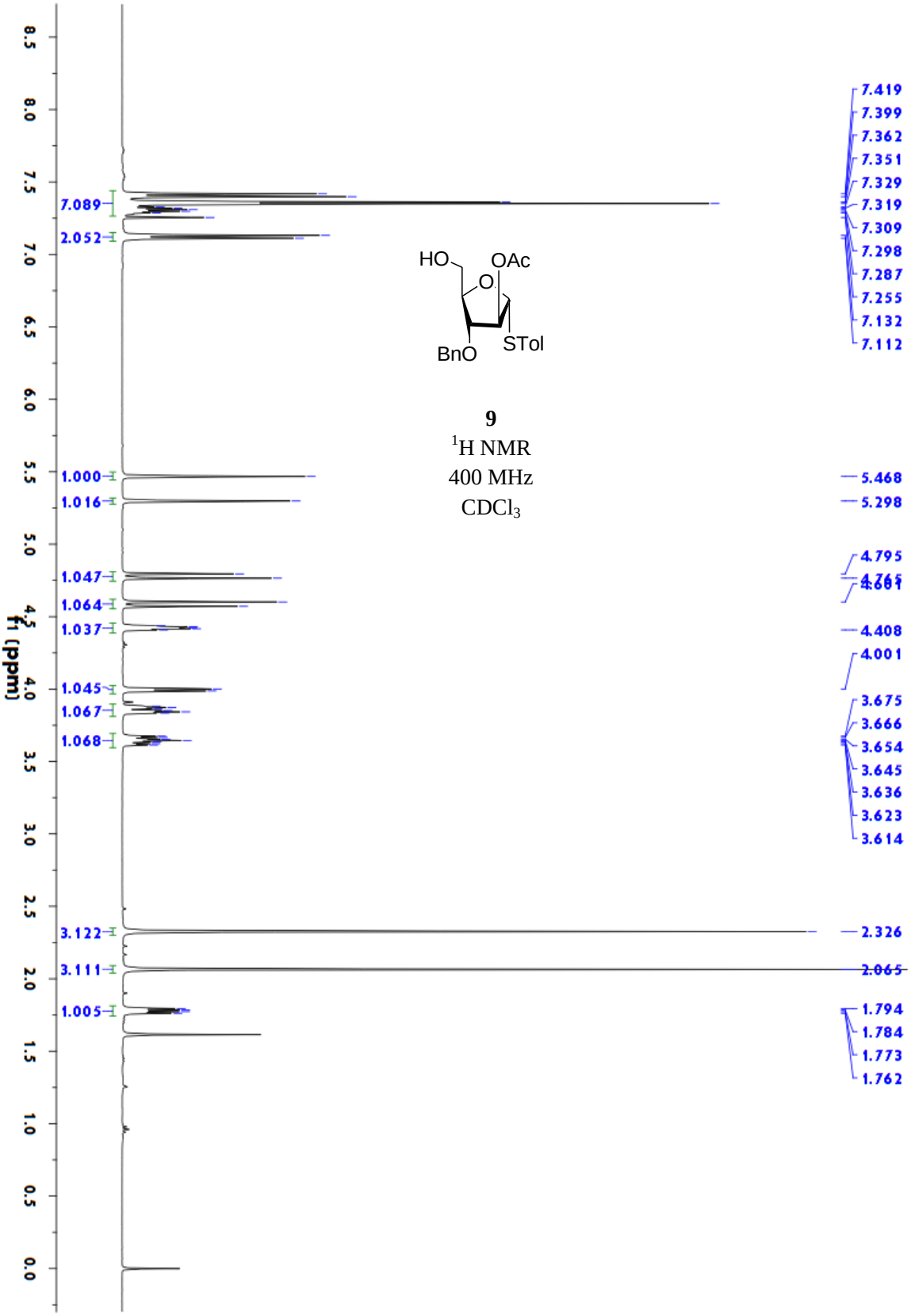


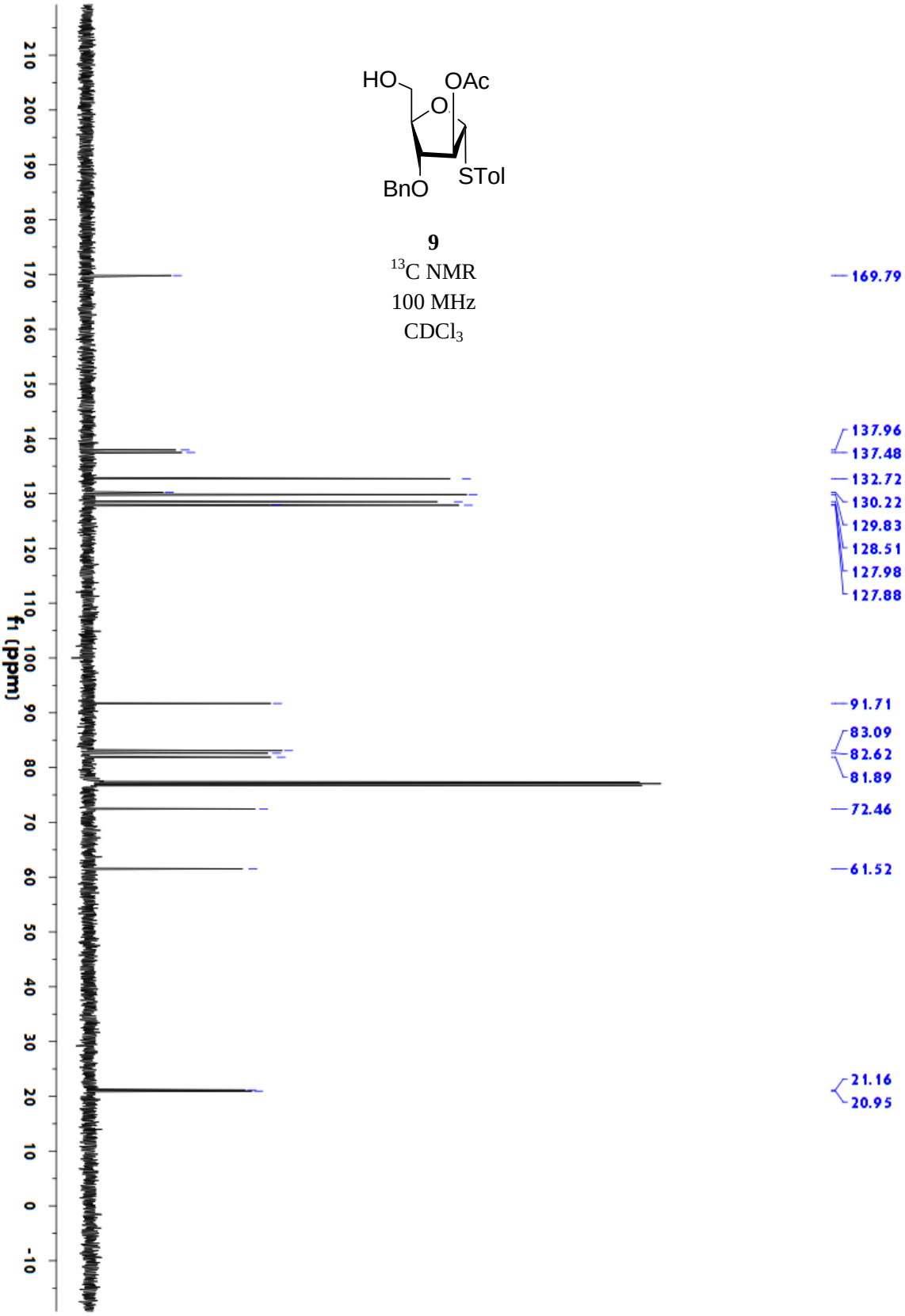
8

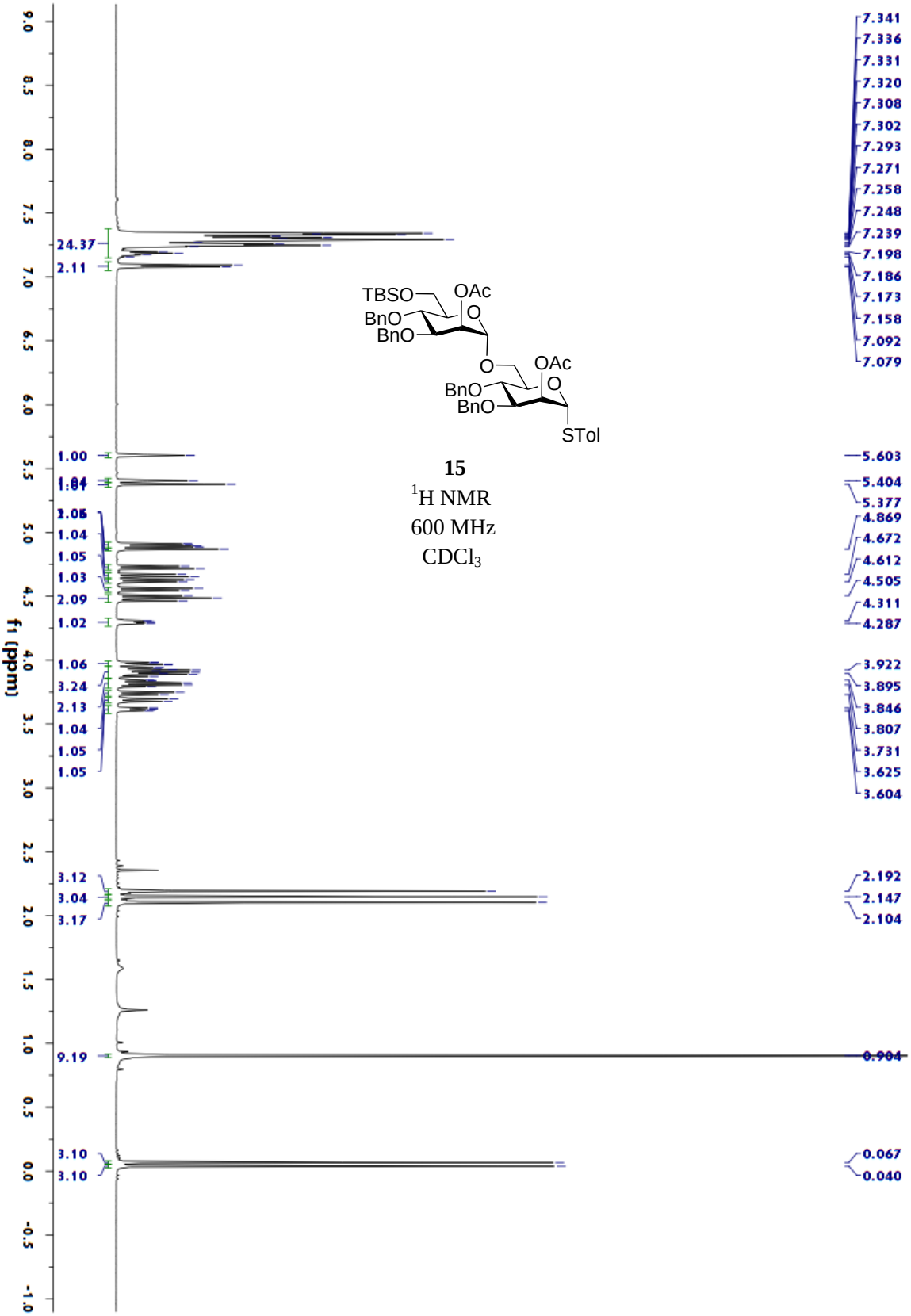
^{13}C NMR

100 MHz

$CDCl_3$


HO
OAc
O
BnO
STol
9
1H NMR
400 MHz
CDCl3
f1 (ppm)
7.089
2.052
1.000
1.016
1.047
1.064
1.037
1.045
1.067
1.068
3.122
3.111
1.005
7.419
7.399
7.362
7.351
7.329
7.319
7.309
7.298
7.287
7.255
7.132
7.112
5.468
5.298
4.795
4.601
4.408
4.001
3.675
3.666
3.654
3.645
3.636
3.623
3.614
2.326
2.065
1.794
1.784
1.773
1.762


HO
OAc
O
BnO
STol
9
13C NMR
100 MHz
CDCl3
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
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

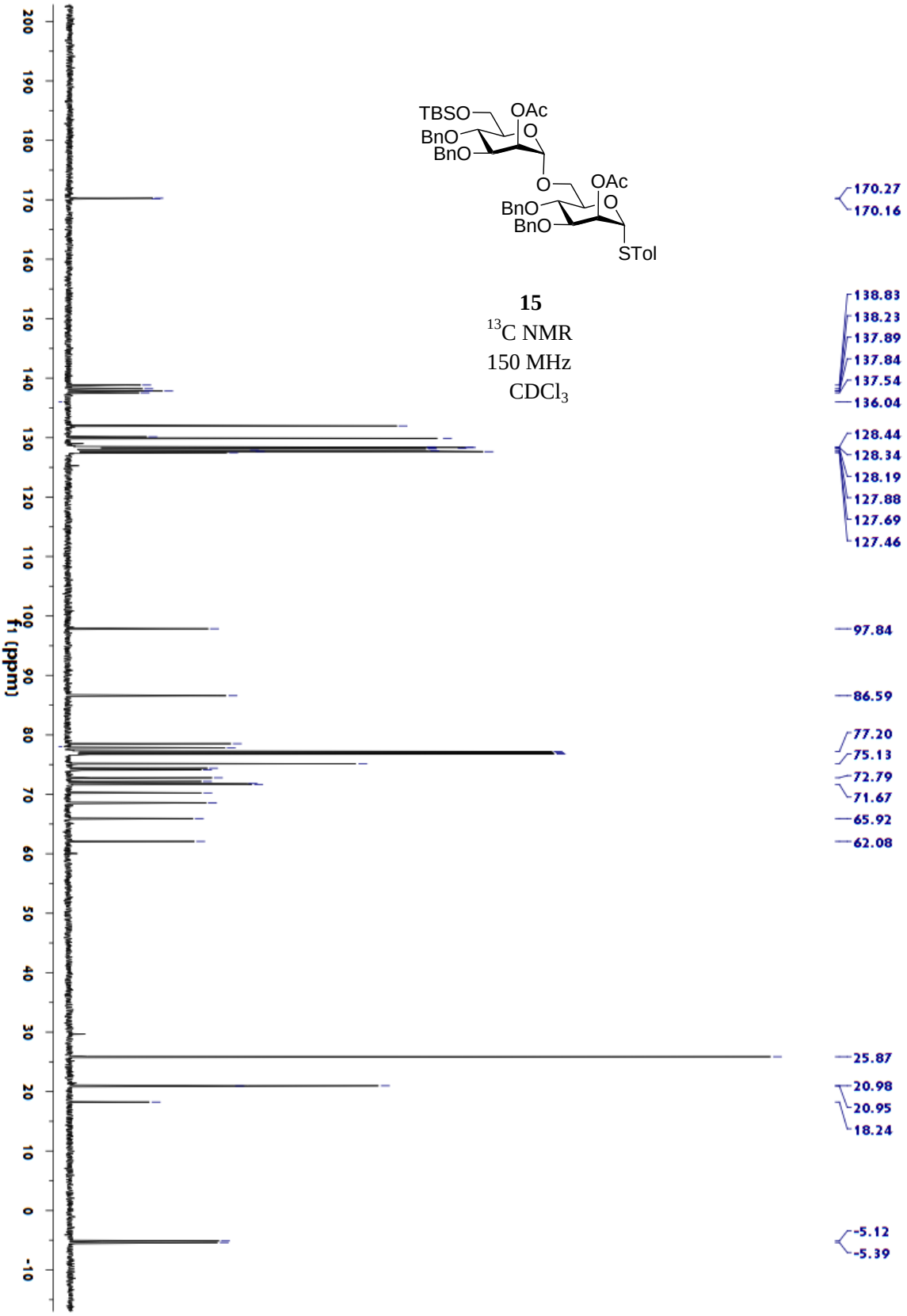


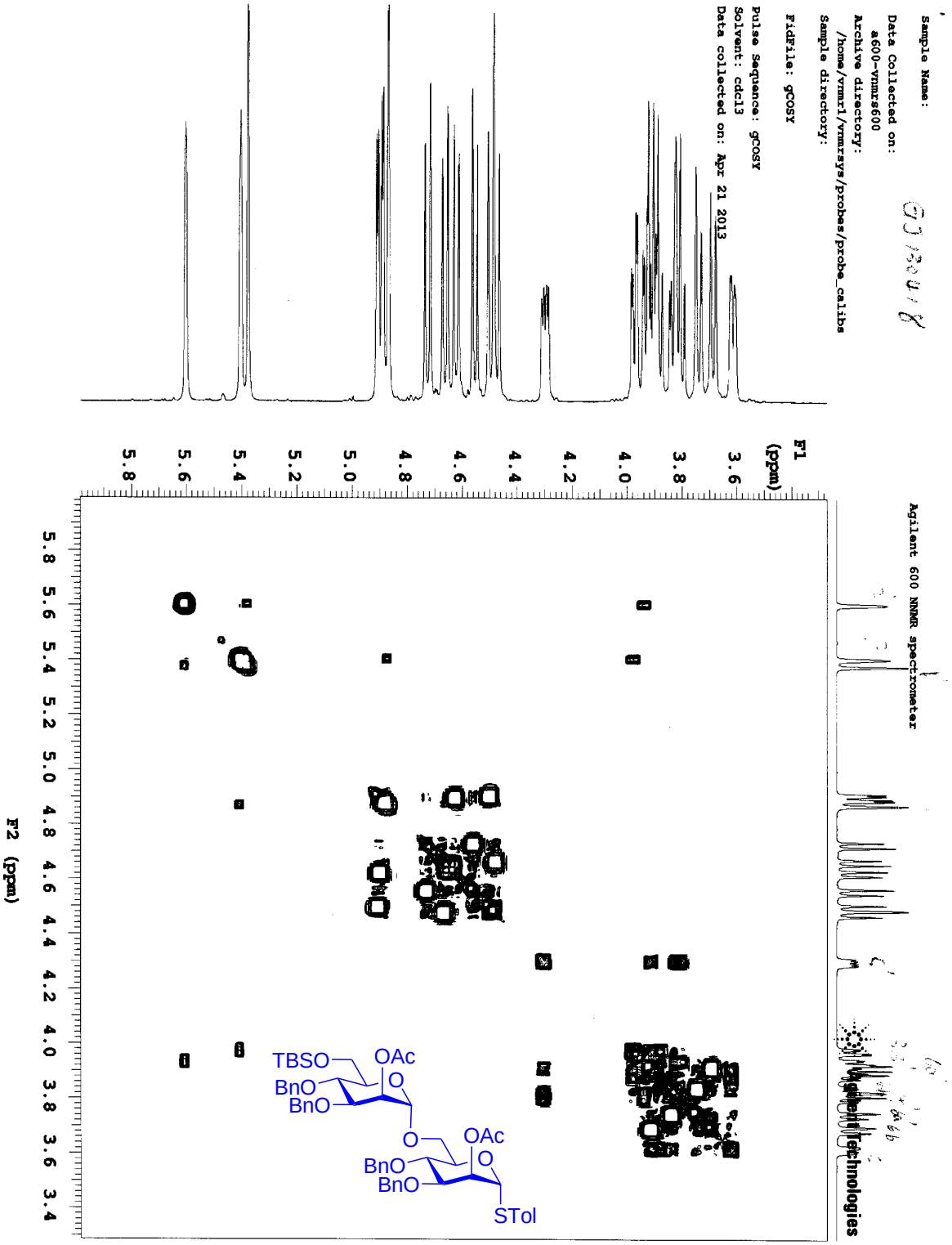
15

^{1}H NMR

600 MHz

$CDCl_3$


TBSO
OAc
BnO
O
BnO
O
OAc
BnO
O
BnO
STol
15
13C NMR
150 MHz
CDCl3
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
170.27
170.16
138.83
138.23
137.89
137.84
137.54
136.04
128.44
128.34
128.19
127.88
127.69
127.46
97.84
86.59
77.20
75.13
72.79
71.67
65.92
62.08
25.87
20.98
20.95
18.24
-5.12
-5.39

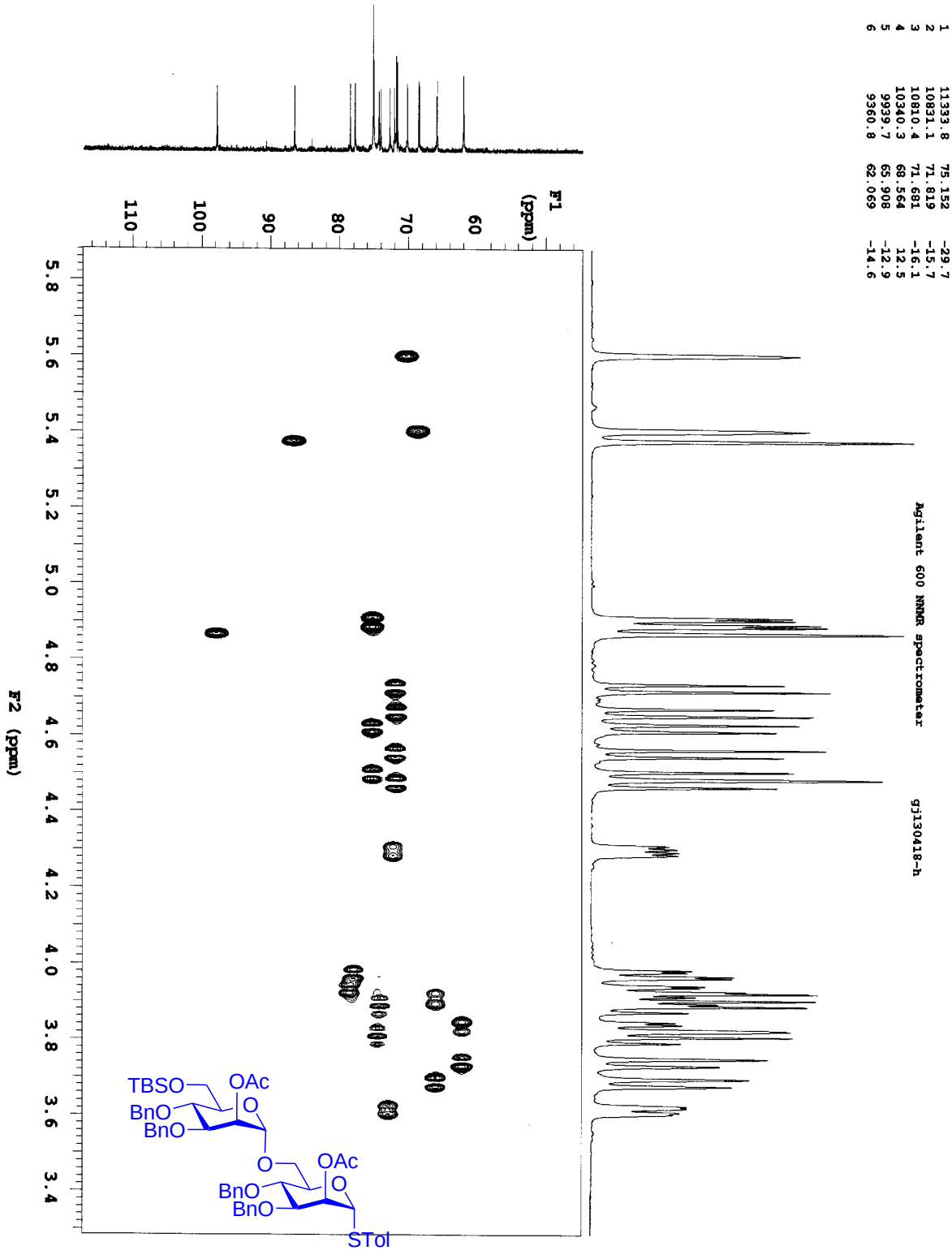


15

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

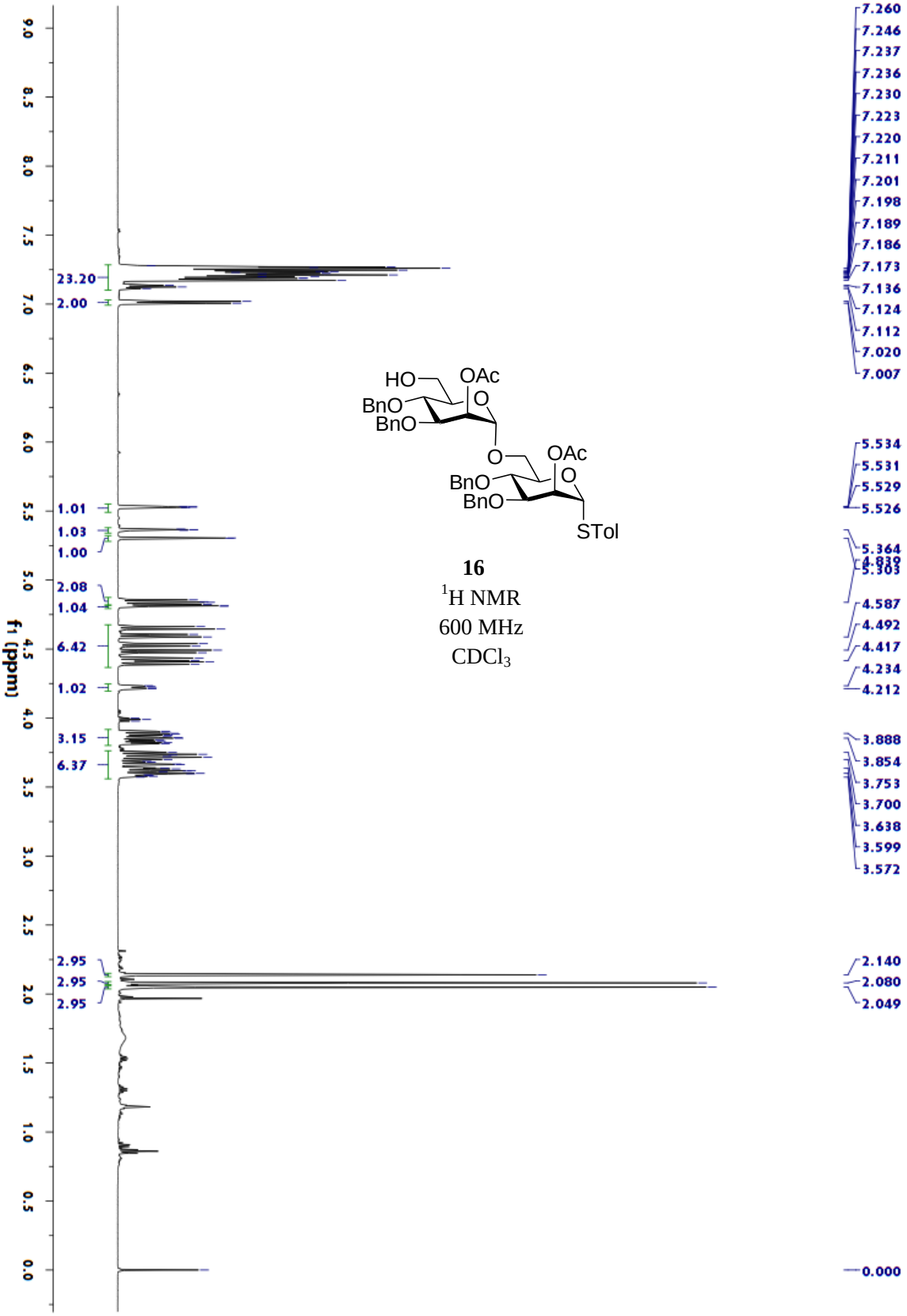


15

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

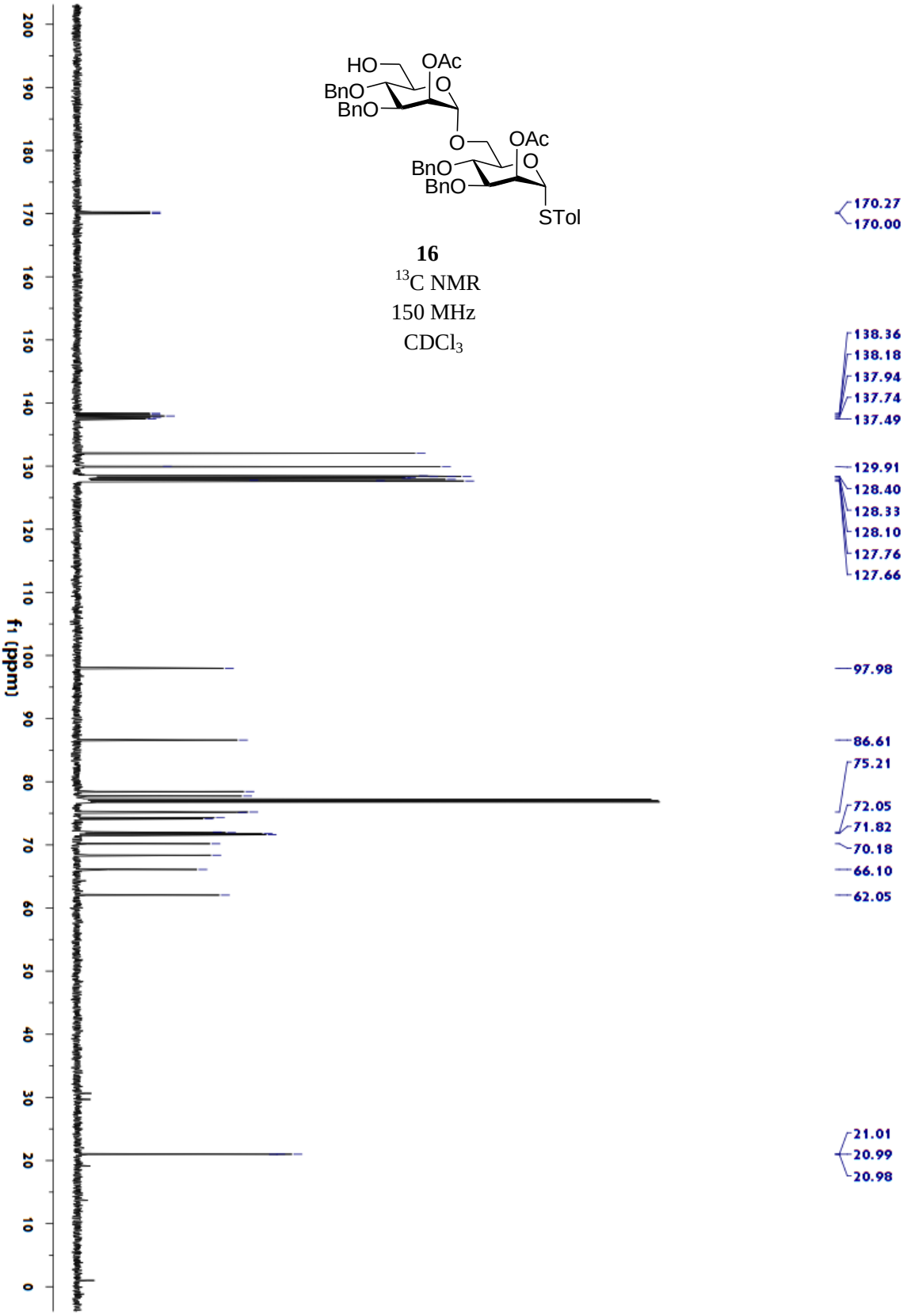


16

^{1}H NMR

600 MHz

$CDCl_3$

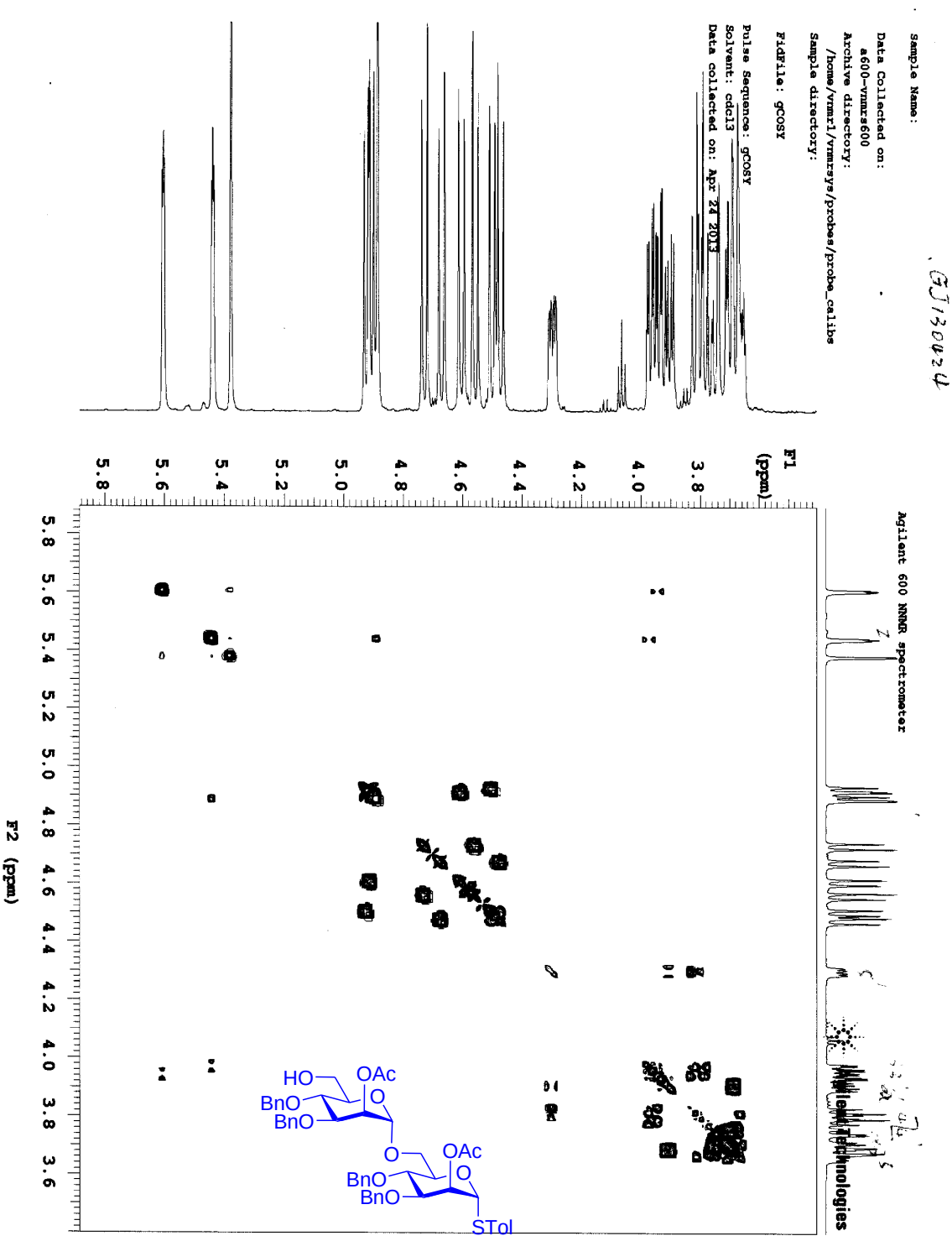


16

^{13}C NMR

150 MHz

$CDCl_3$

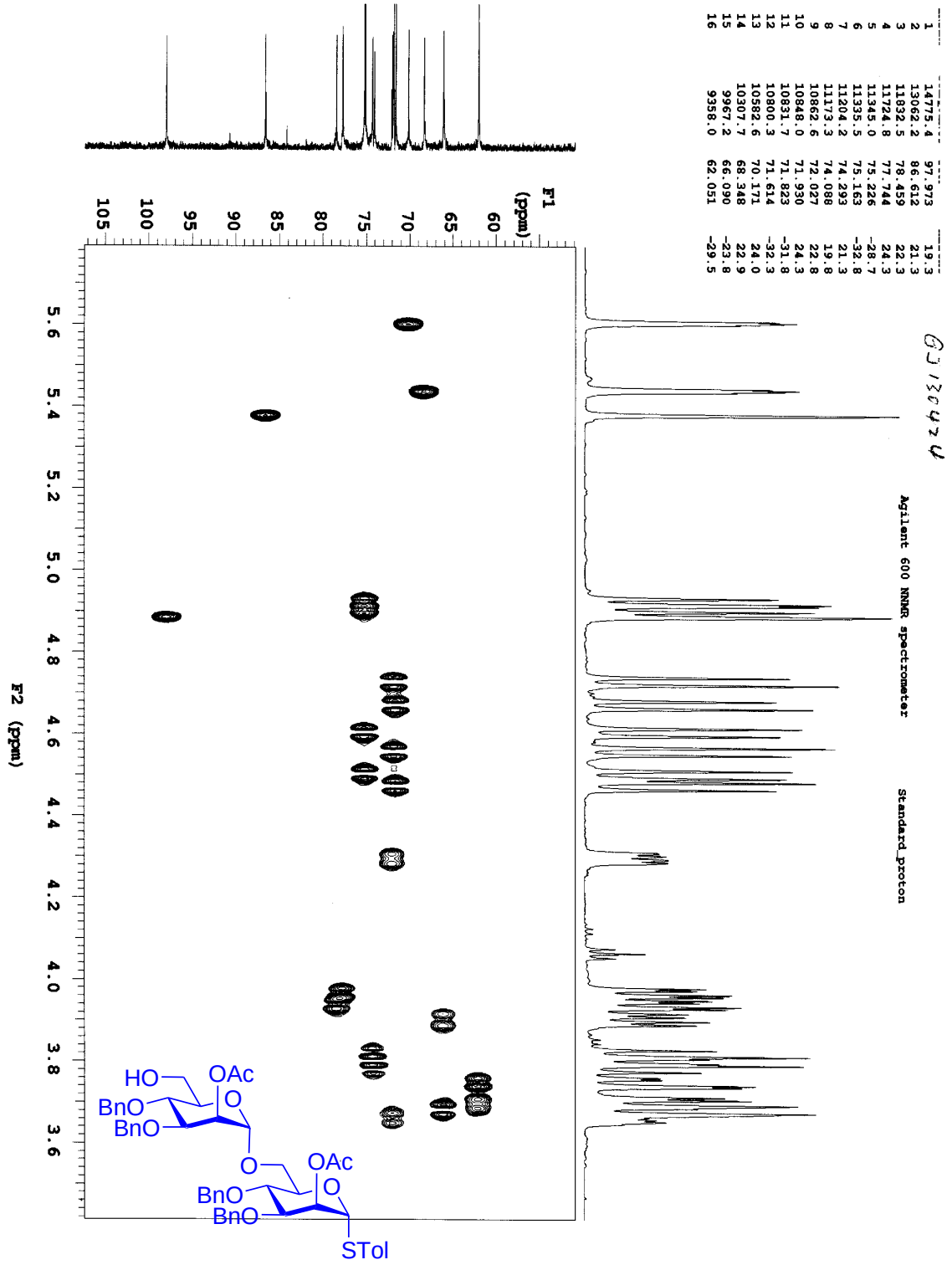


16

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

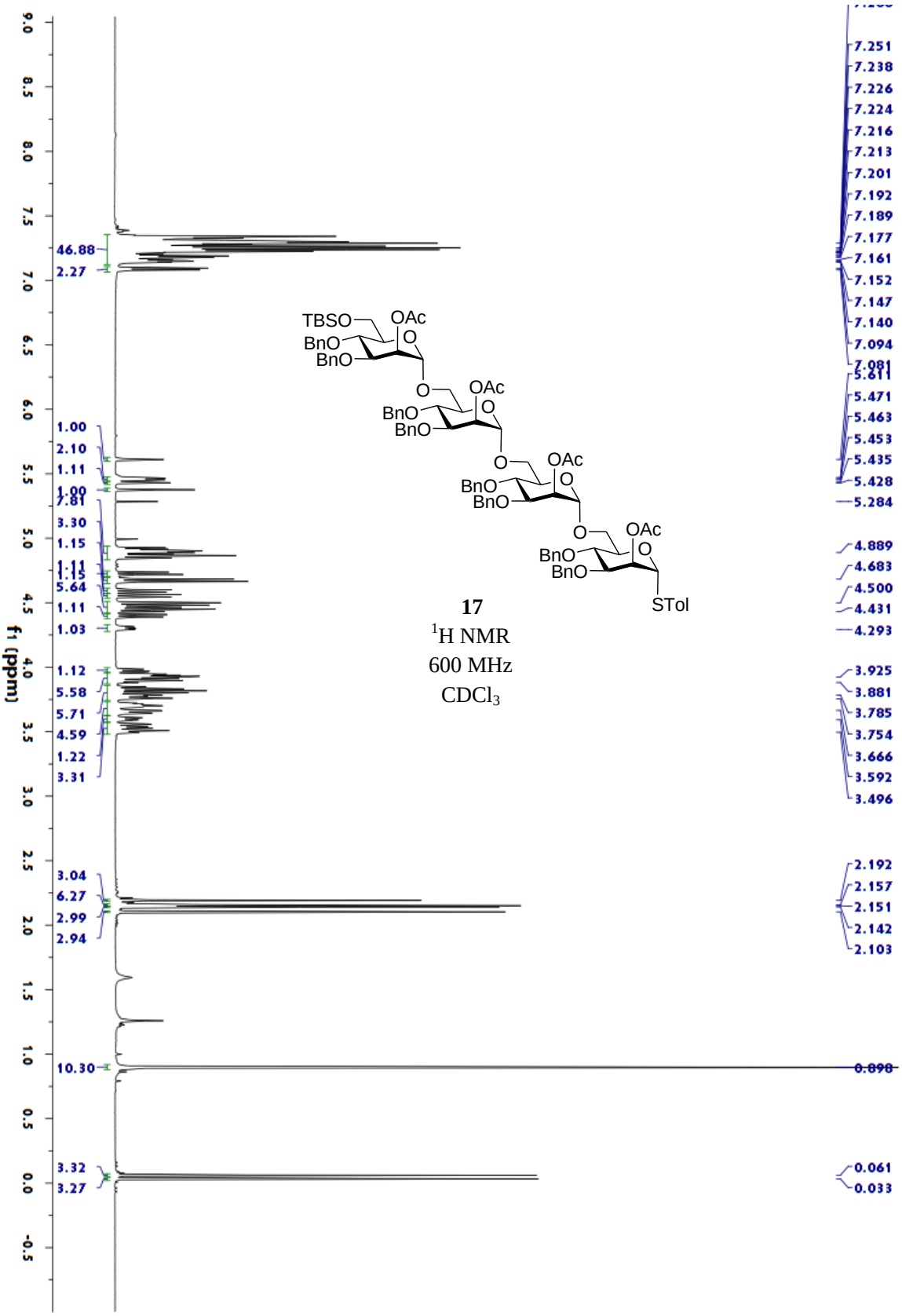


16

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

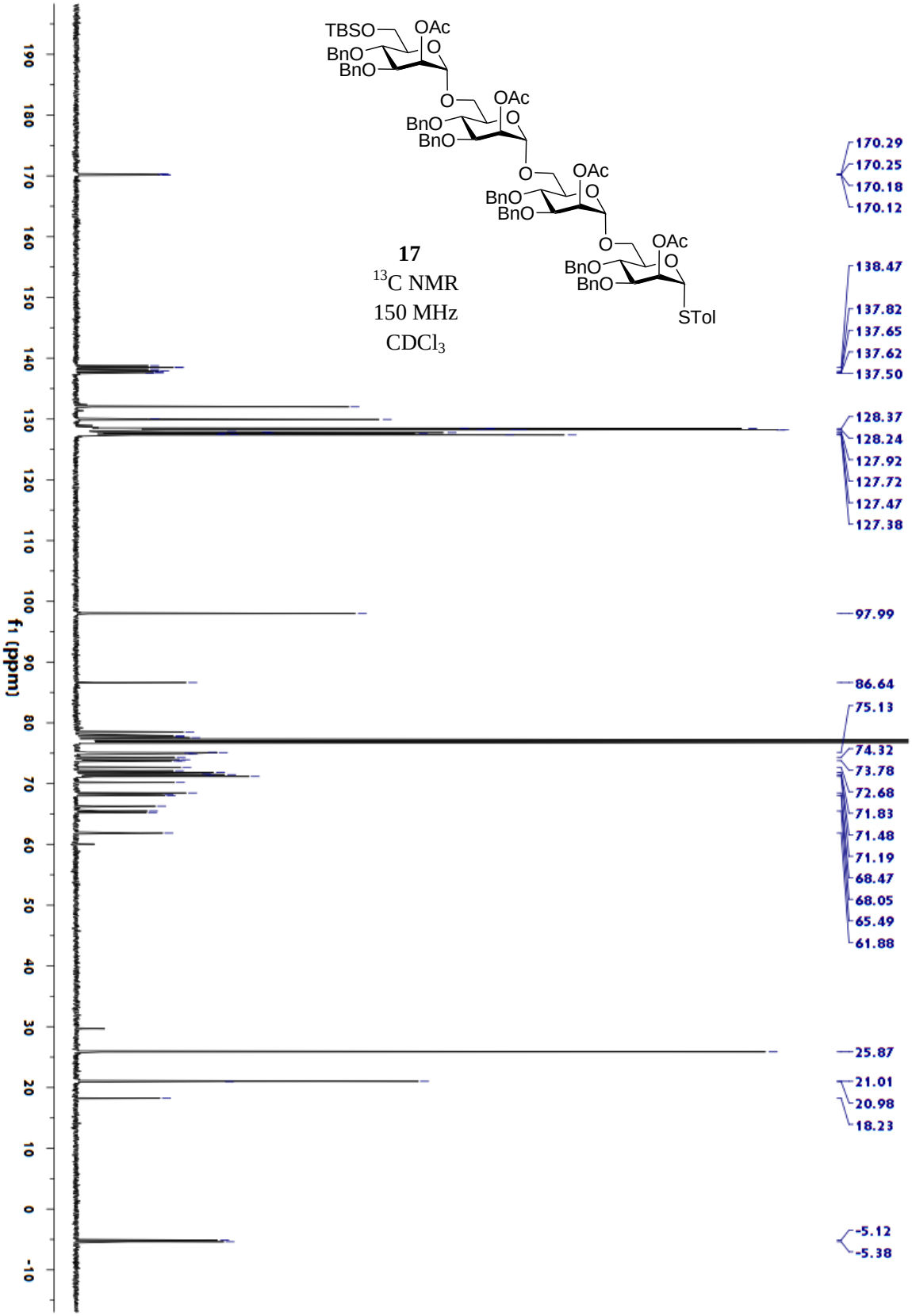


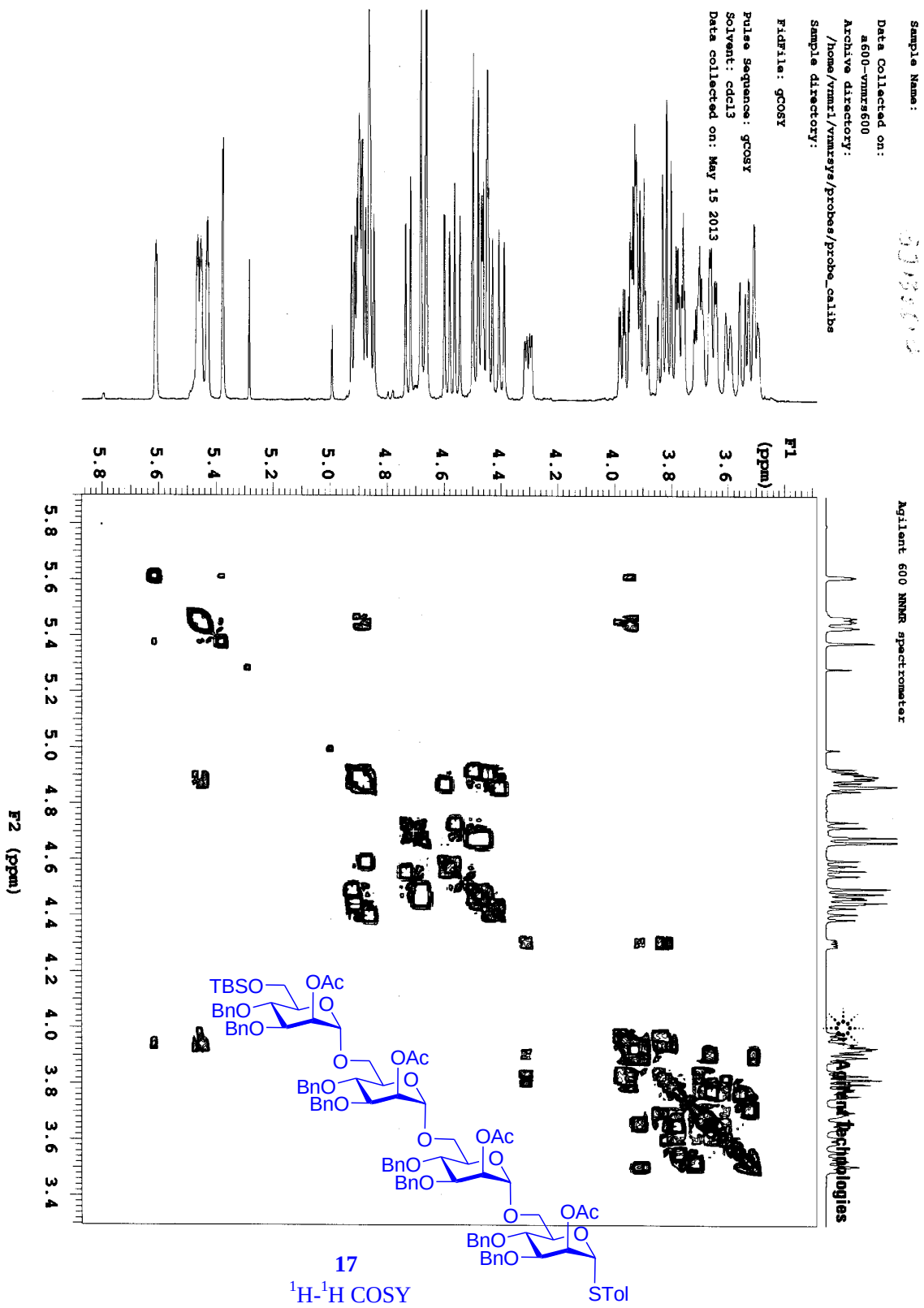
17

^{1}H NMR

600 MHz

$CDCl_3$


TBSO
OAc
BnO
BnO
O
OAc
BnO
BnO
O
OAc
BnO
BnO
O
OAc
BnO
BnO
STol
17
13C NMR
150 MHz
CDCl3
f1 (ppm)
170.29
170.25
170.18
170.12
138.47
137.82
137.65
137.62
137.50
128.37
128.24
127.92
127.72
127.47
127.38
97.99
86.64
75.13
74.32
73.78
72.68
71.83
71.48
71.19
68.47
68.05
65.49
61.88
25.87
21.01
20.98
18.23
-5.12
-5.38

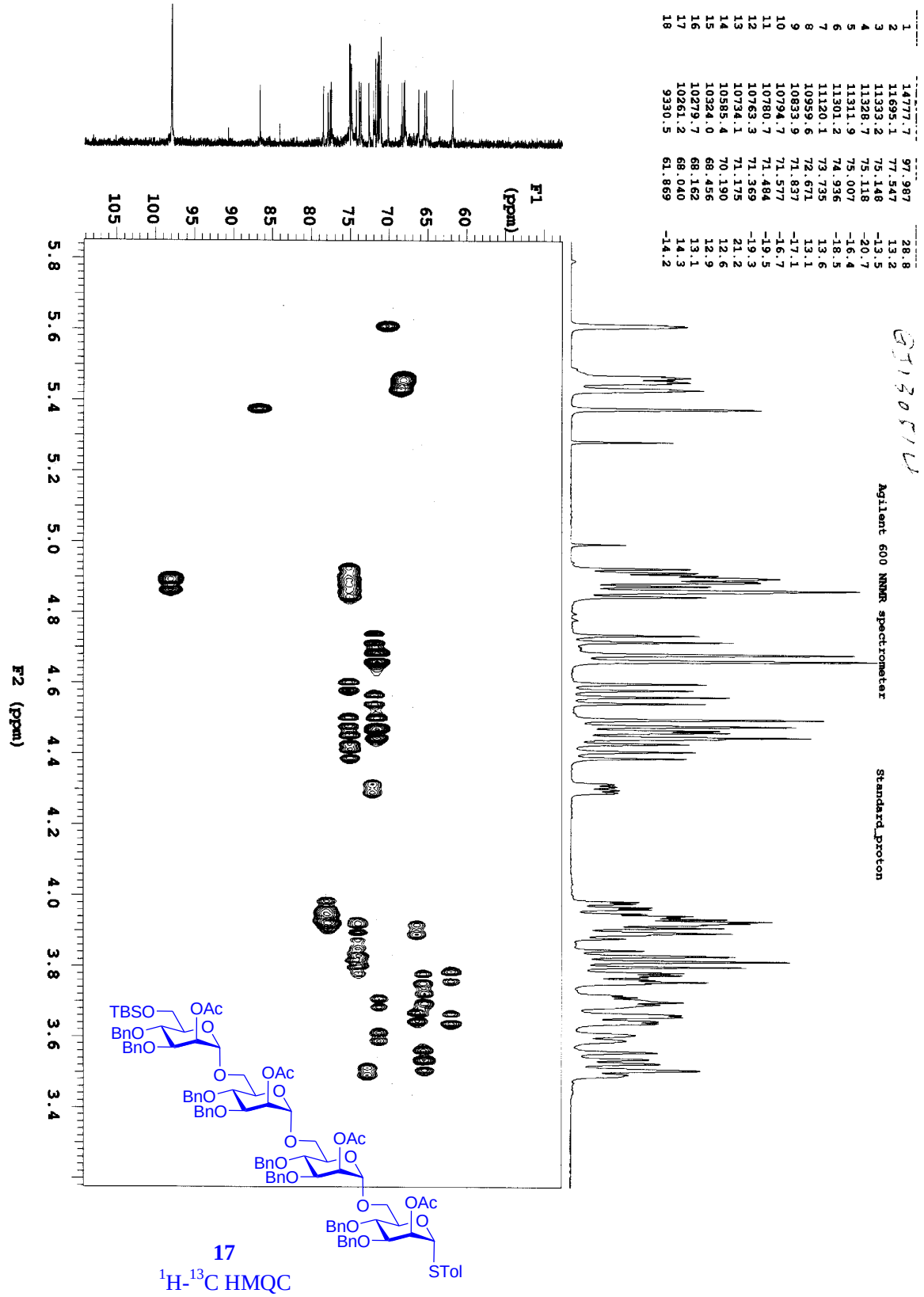


17

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

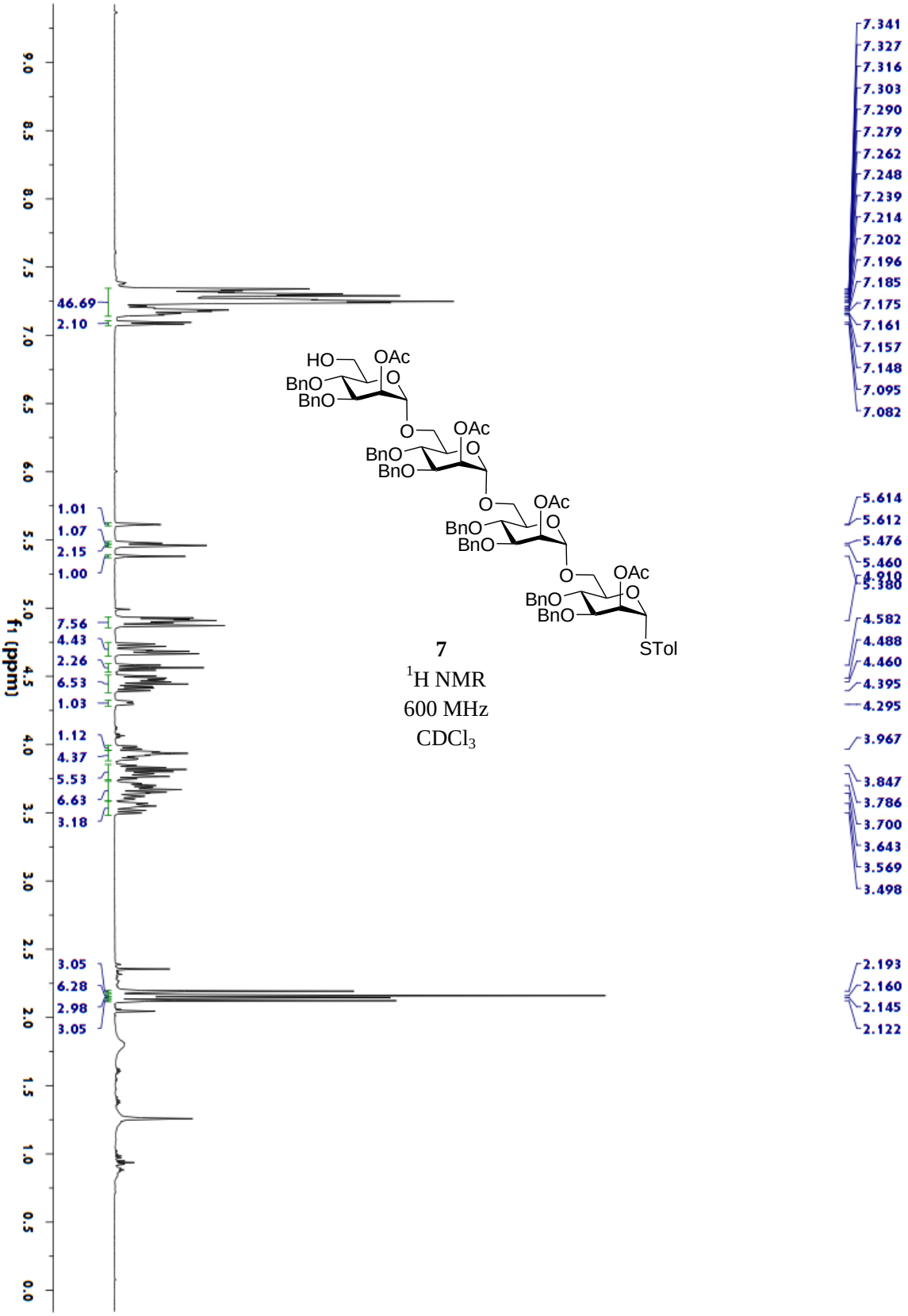


17

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

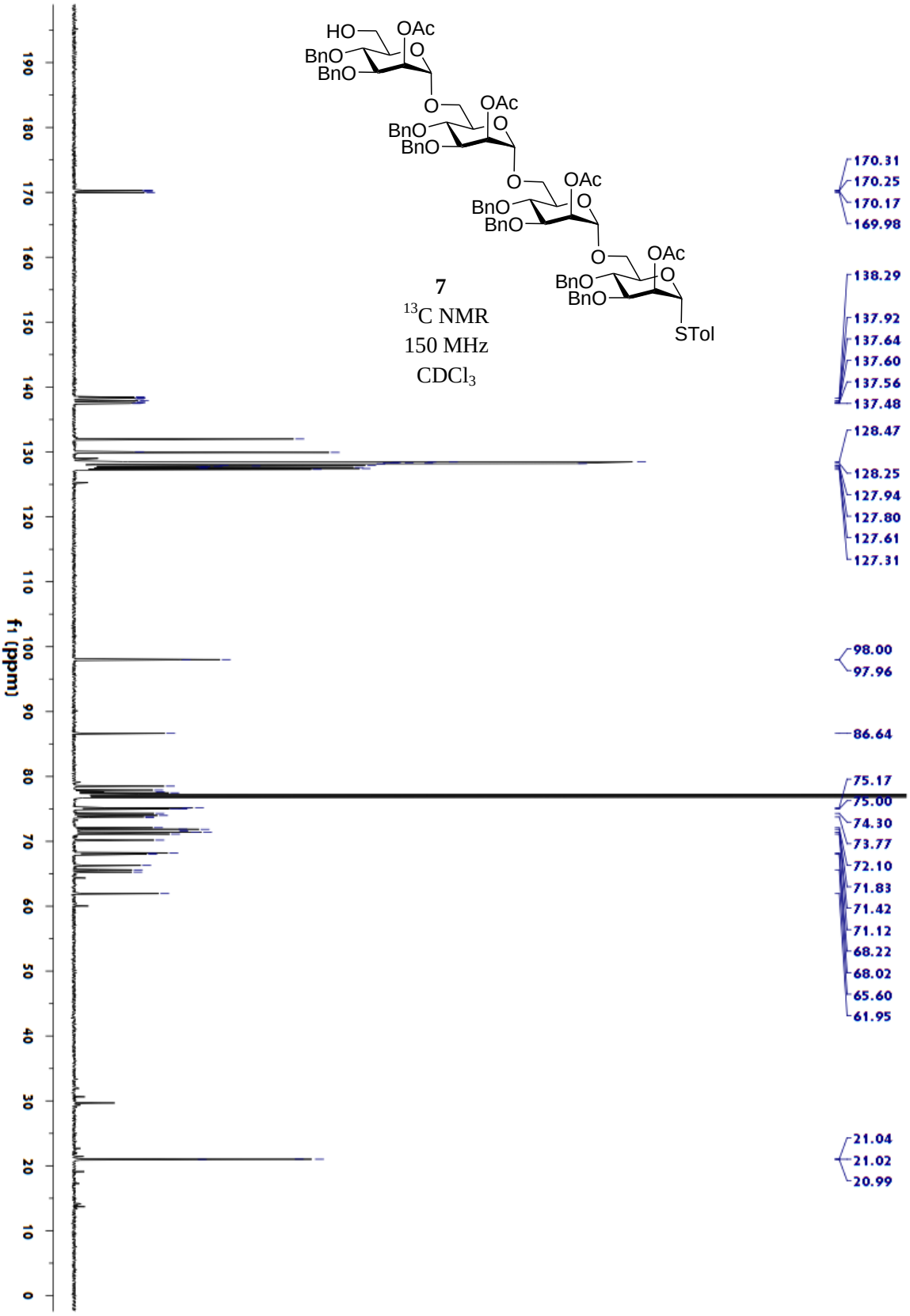


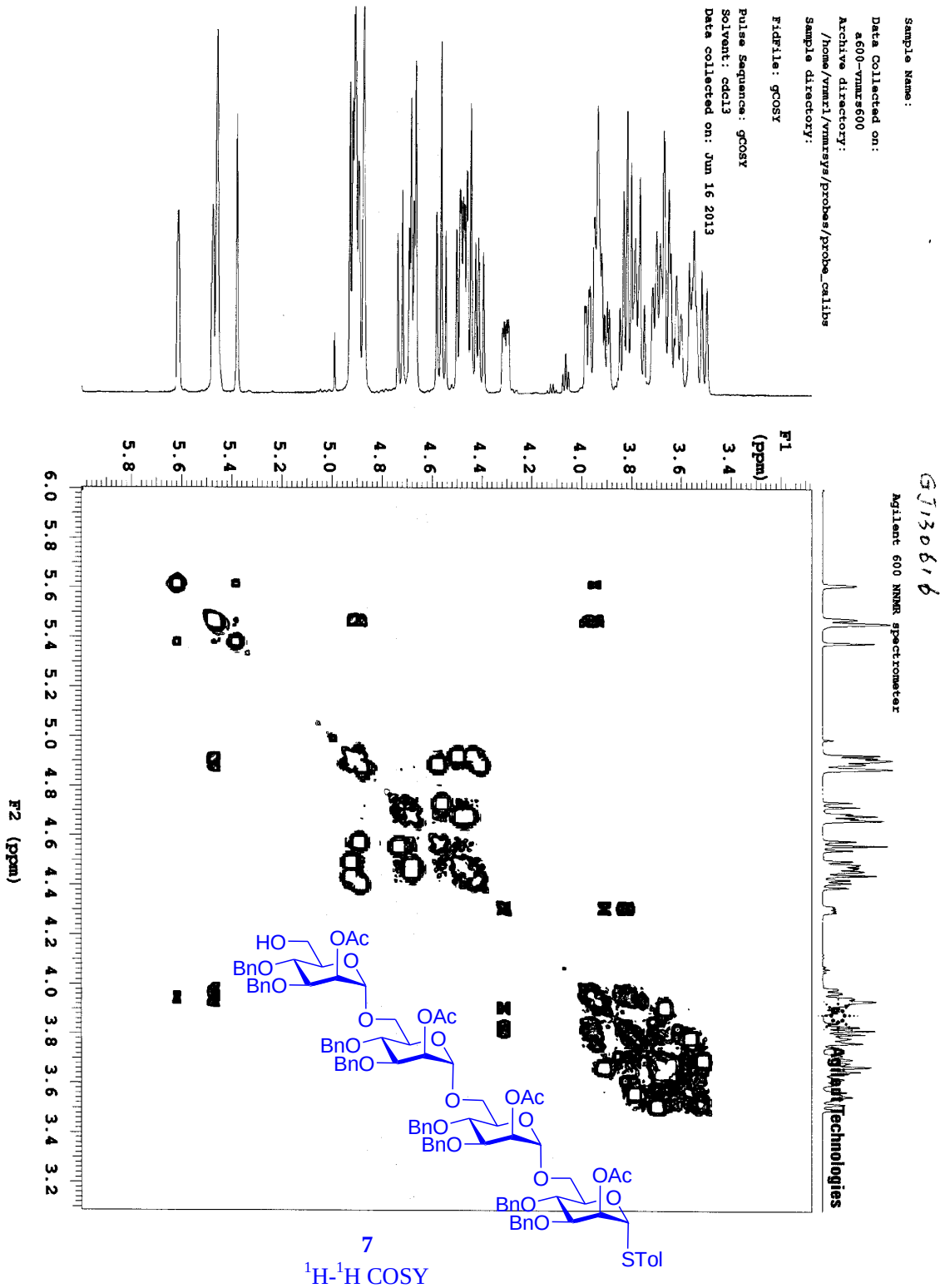
7

^{1}H NMR

600 MHz

$CDCl_3$


HO
OAc
BnO
BnO
O
OAc
BnO
BnO
O
OAc
BnO
BnO
O
OAc
BnO
BnO
STol
7
13C NMR
150 MHz
CDCl3
f1 (ppm)
170.31
170.25
170.17
169.98
138.29
137.92
137.64
137.60
137.56
137.48
128.47
128.25
127.94
127.80
127.61
127.31
98.00
97.96
86.64
75.17
75.00
74.30
73.77
72.10
71.83
71.42
71.12
68.22
68.02
65.60
61.95
21.04
21.02
20.99

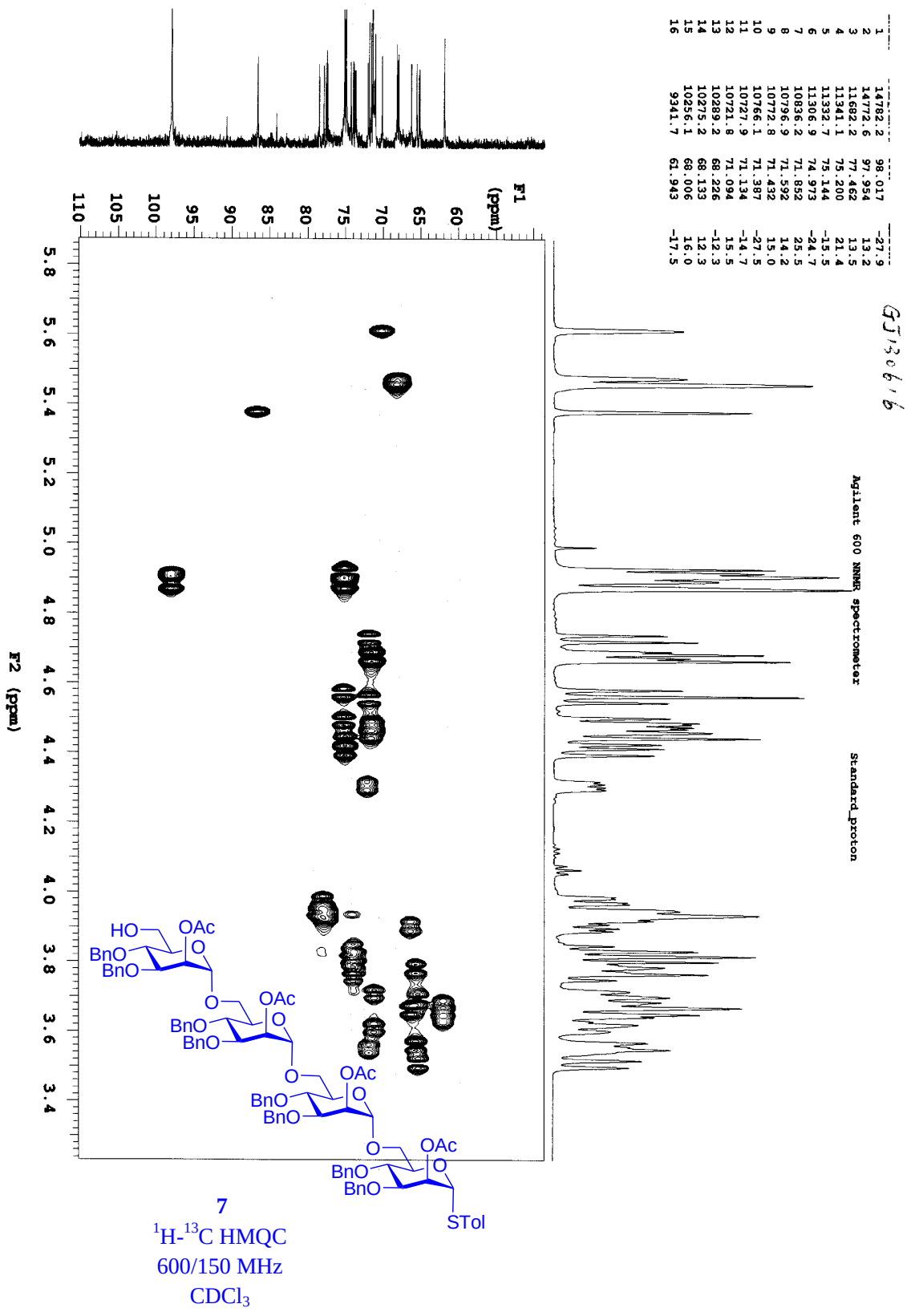


7

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

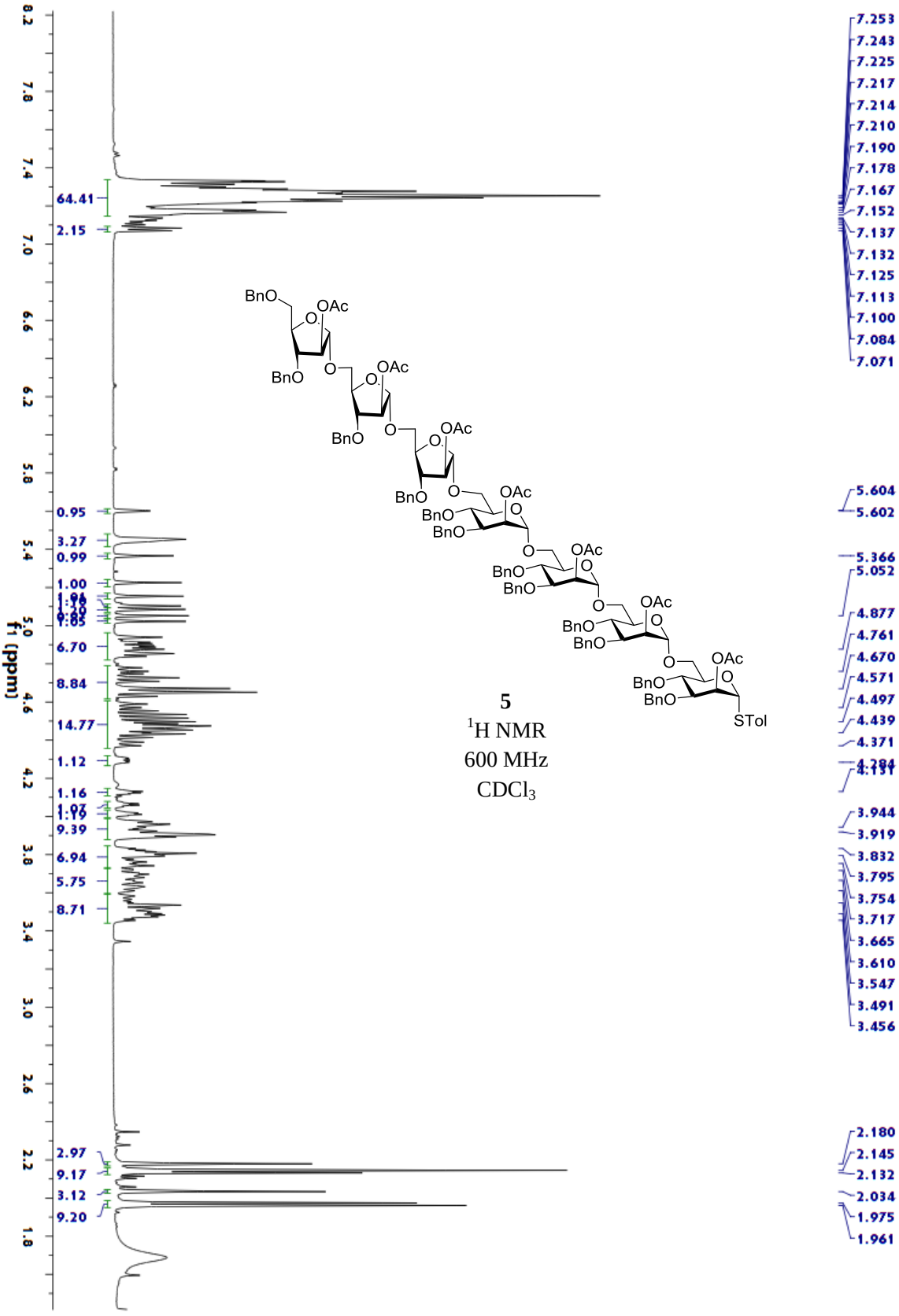


7

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

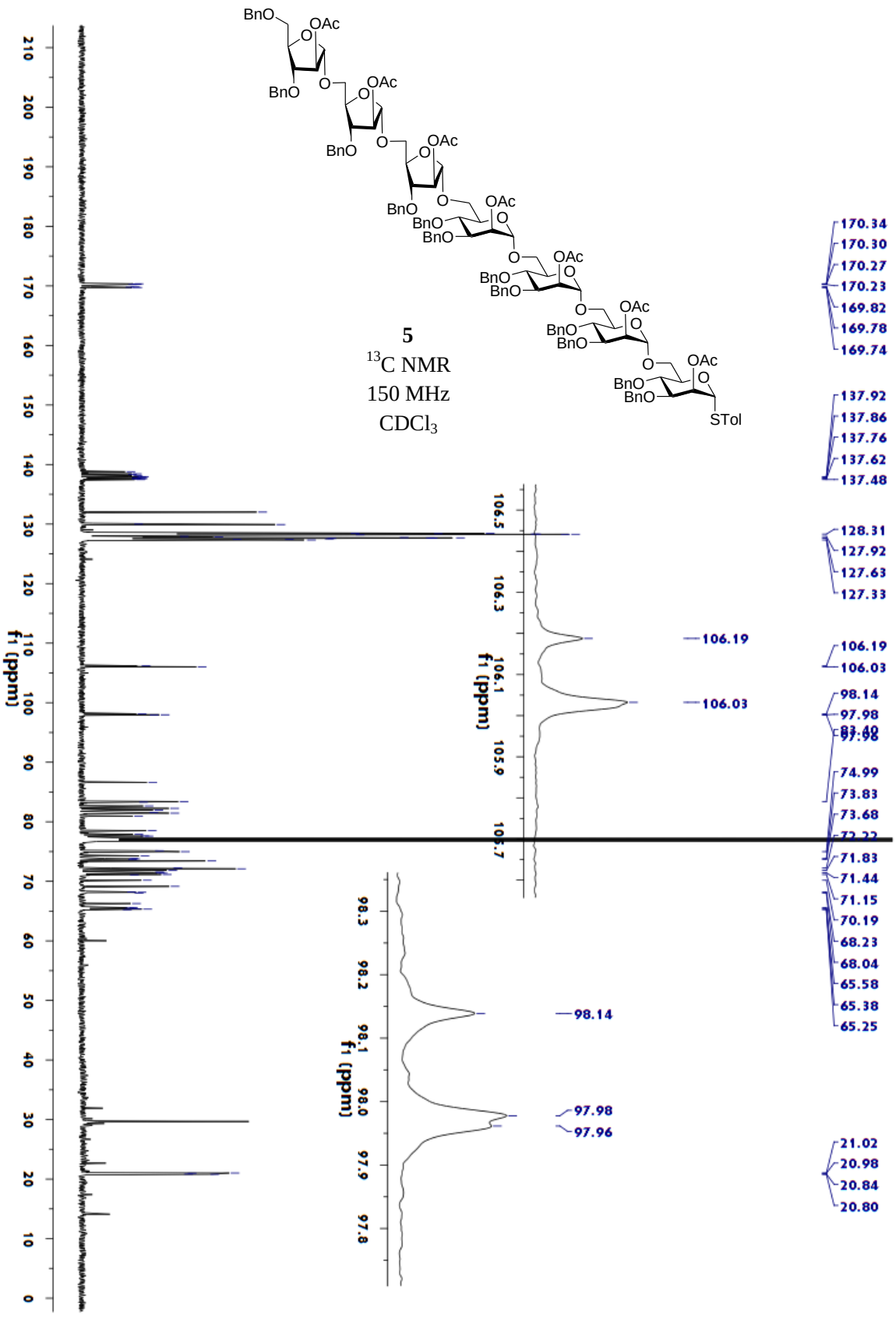


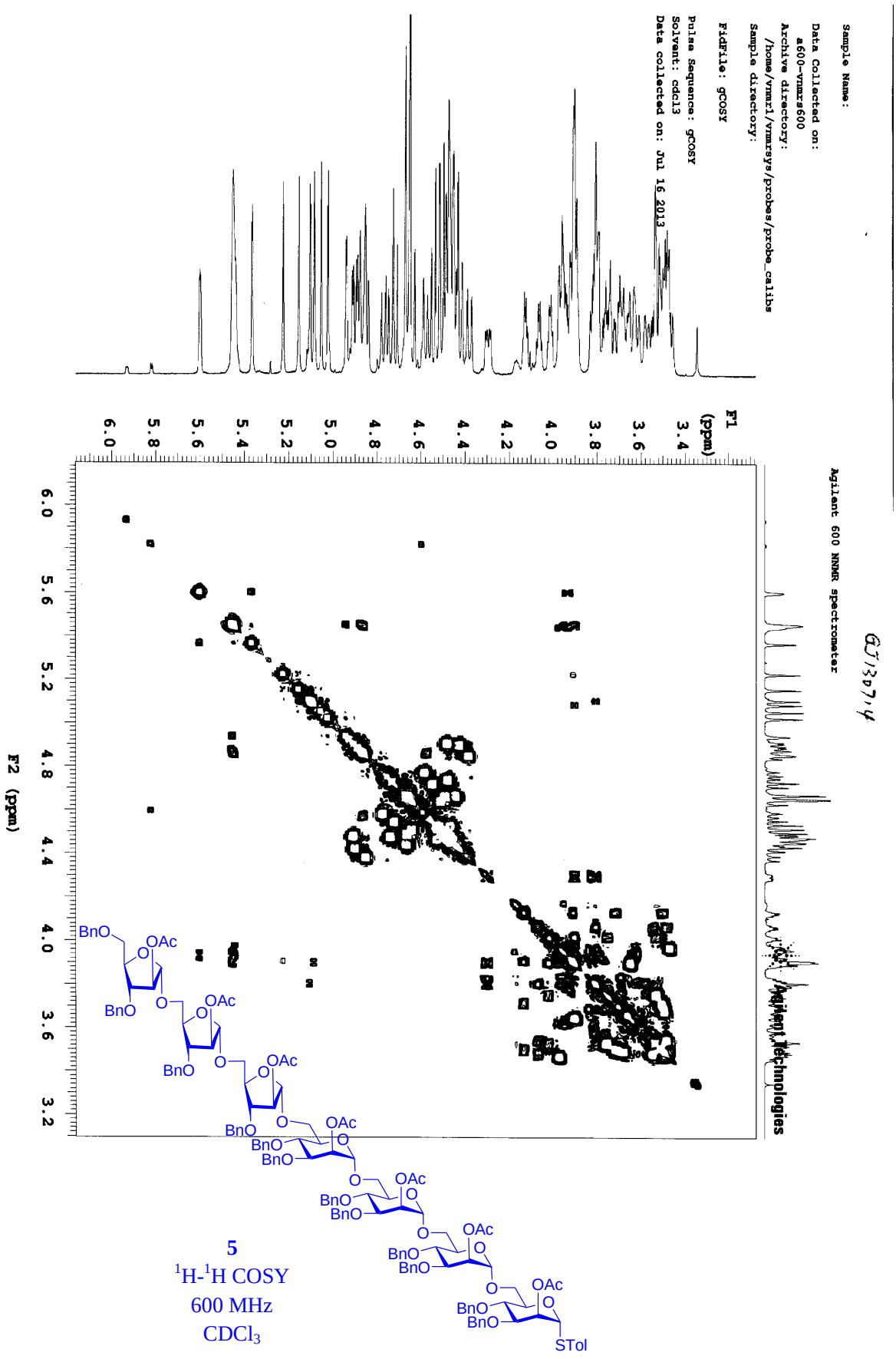
5

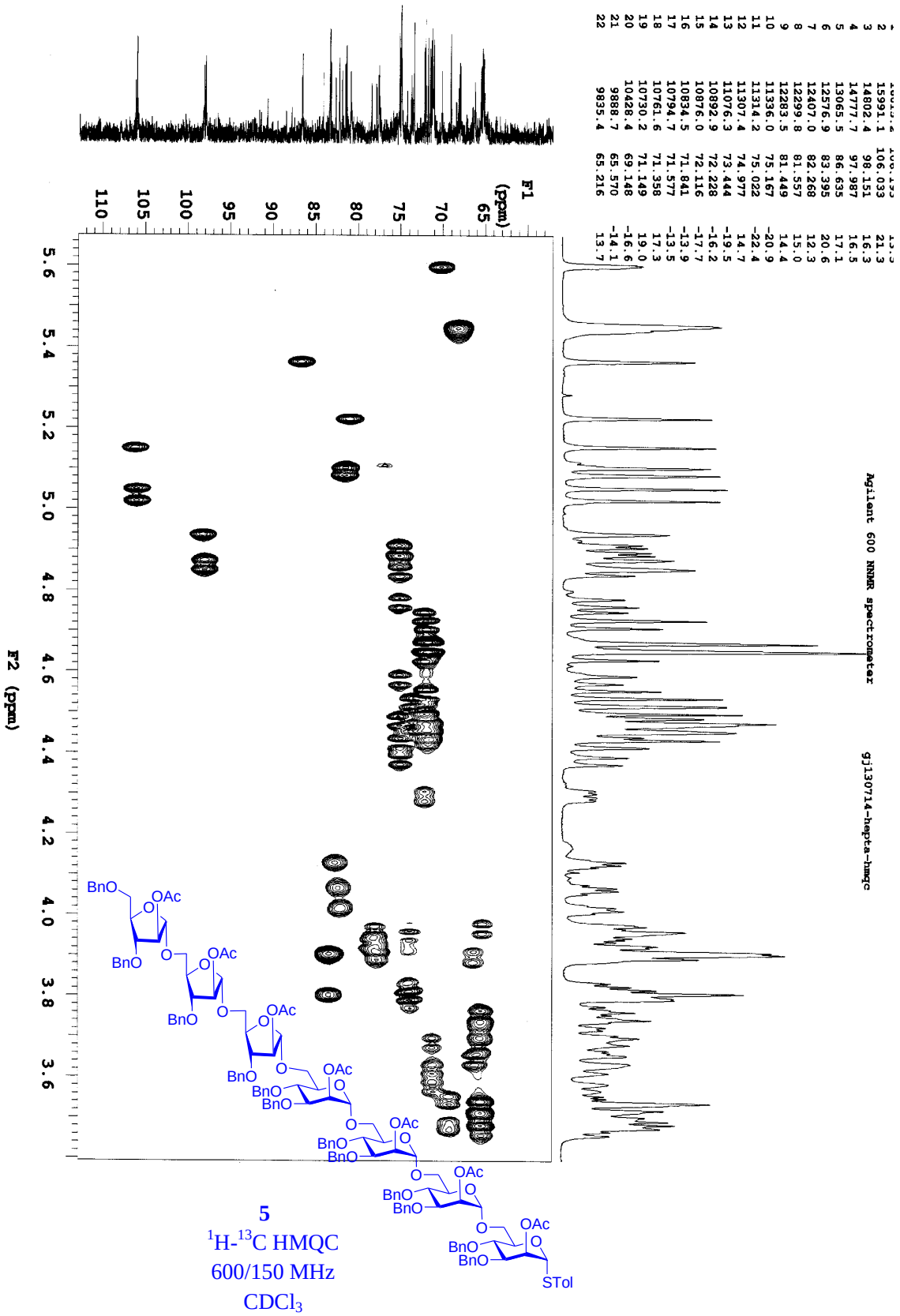
^{1}H NMR

600 MHz

$CDCl_3$


BnO
OAc
O
BnO
STol
5
^{13}C NMR
150 MHz
$CDCl_3$
170.34
170.30
170.27
170.23
169.82
169.78
169.74
137.92
137.86
137.76
137.62
137.48
128.31
127.92
127.63
127.33
106.19
106.03
98.14
97.98
74.99
73.83
73.68
71.83
71.44
71.15
70.19
68.23
68.04
65.58
65.38
65.25
21.02
20.98
20.84
20.80
f1 (ppm)


Sample Name:
Data Collected on:
a600-vnmrs600
Archive directory:
/home/vnmr1/vnmrsys/probes/probe_calibs
Sample directory:
FidFile: gCOSY
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Jul 16 2013
Agilent 600 NMR spectrometer
GJ13D7-4
F1 (ppm)
F2 (ppm)
Agilent Technologies
BnO
OAc
O
STol
5
1H-1H COSY
600 MHz
CDCl3

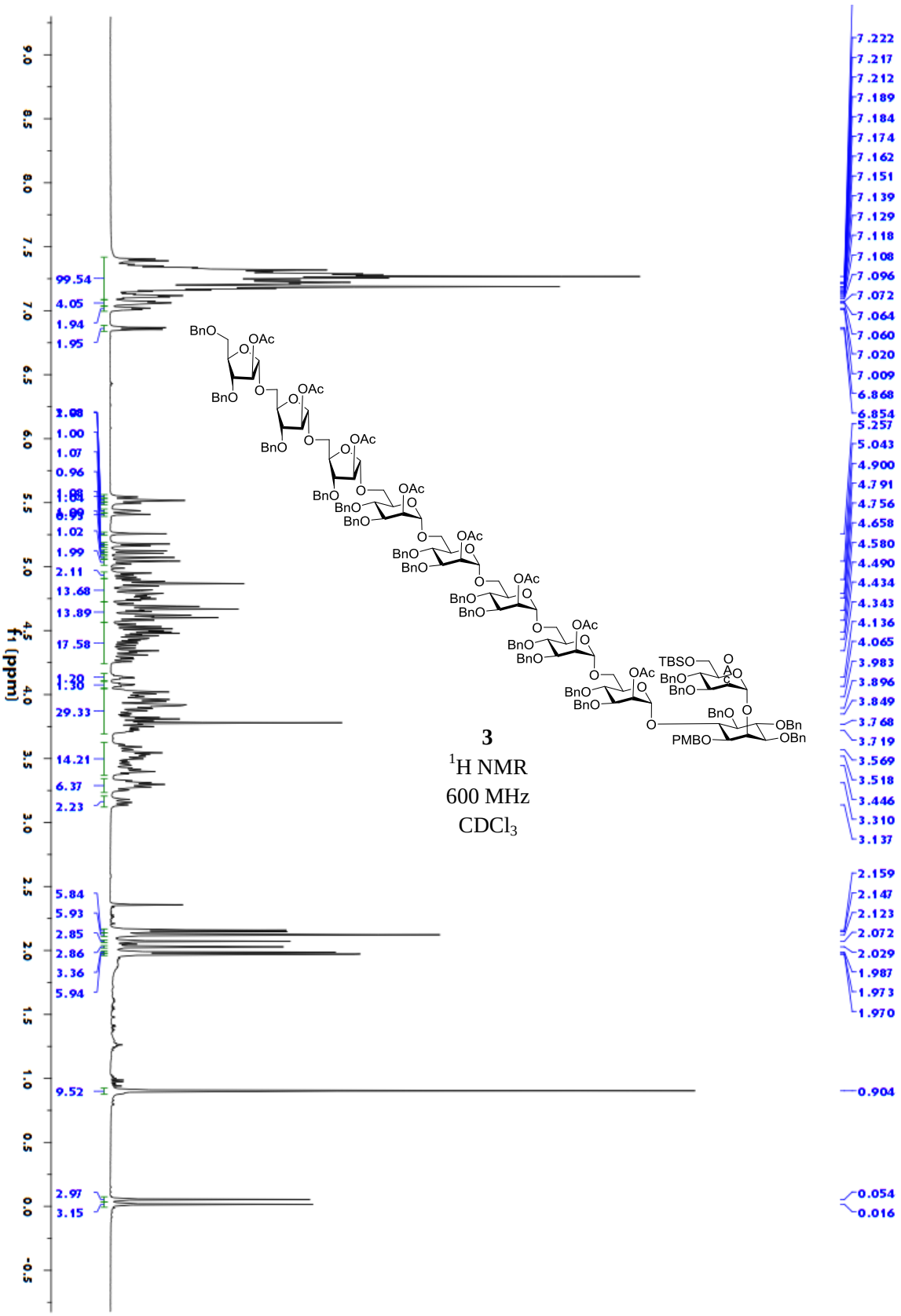


5

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

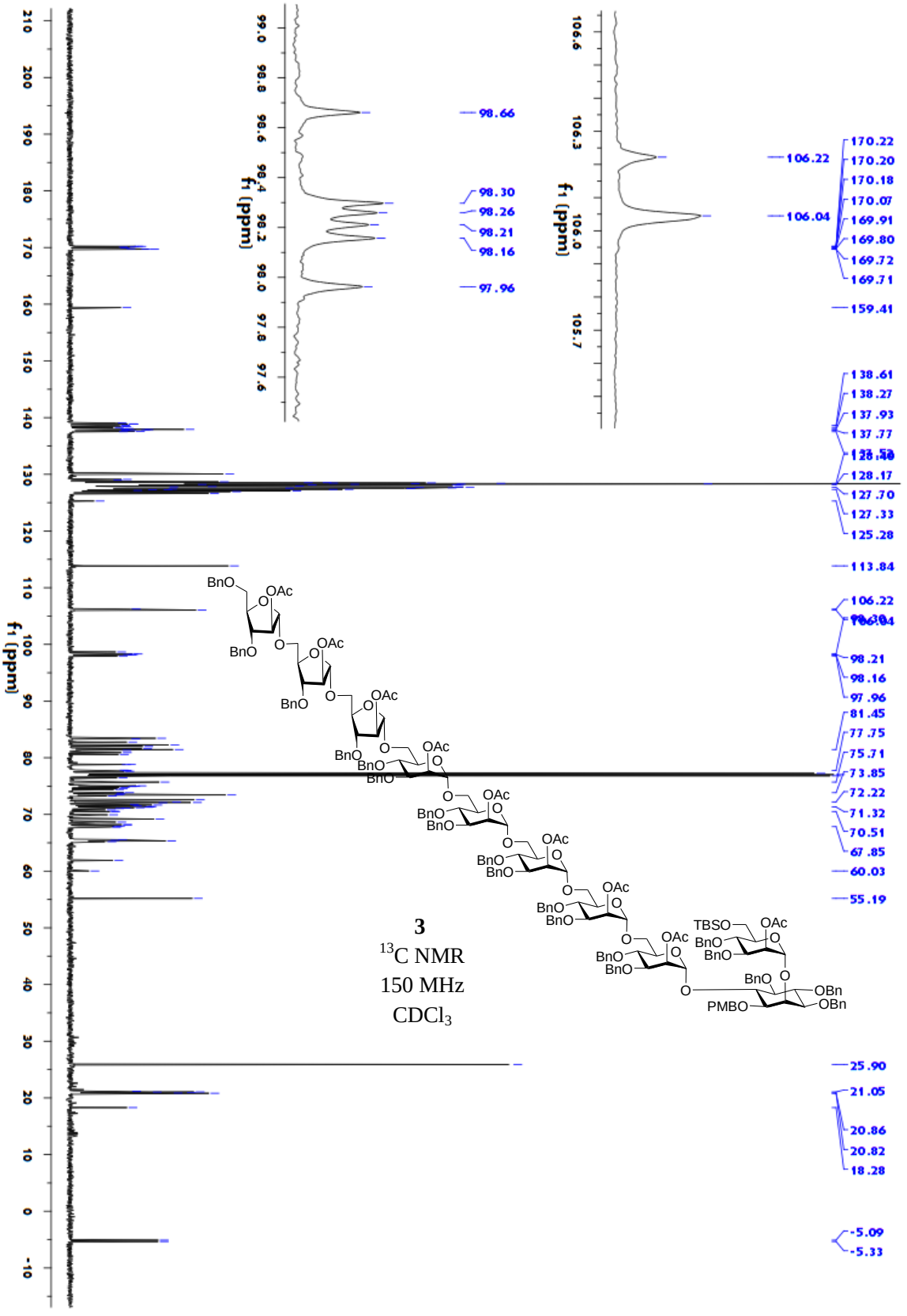


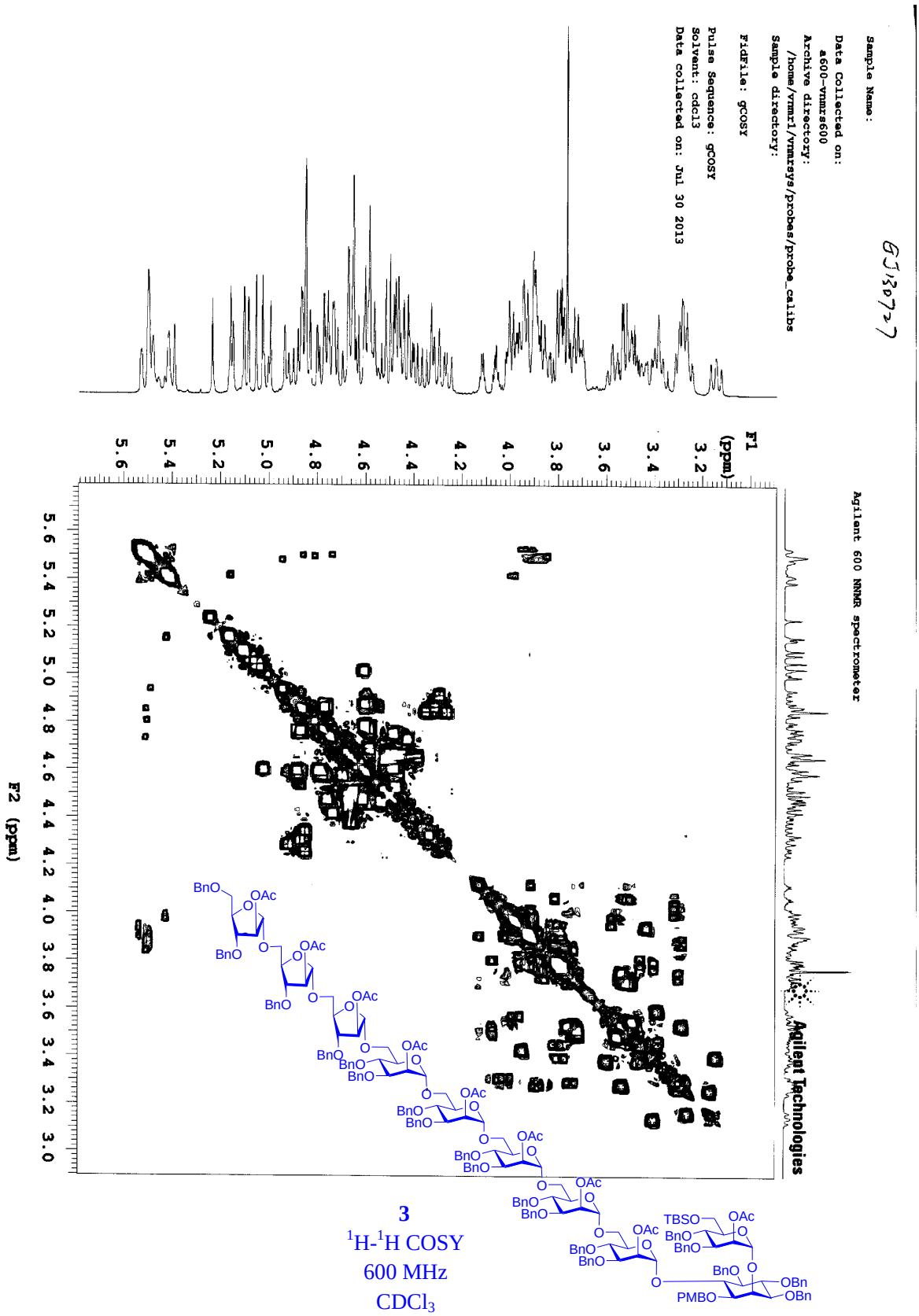
3

^{1}H NMR

600 MHz

$CDCl_3$


3
^{13}C NMR
150 MHz
$CDCl_3$

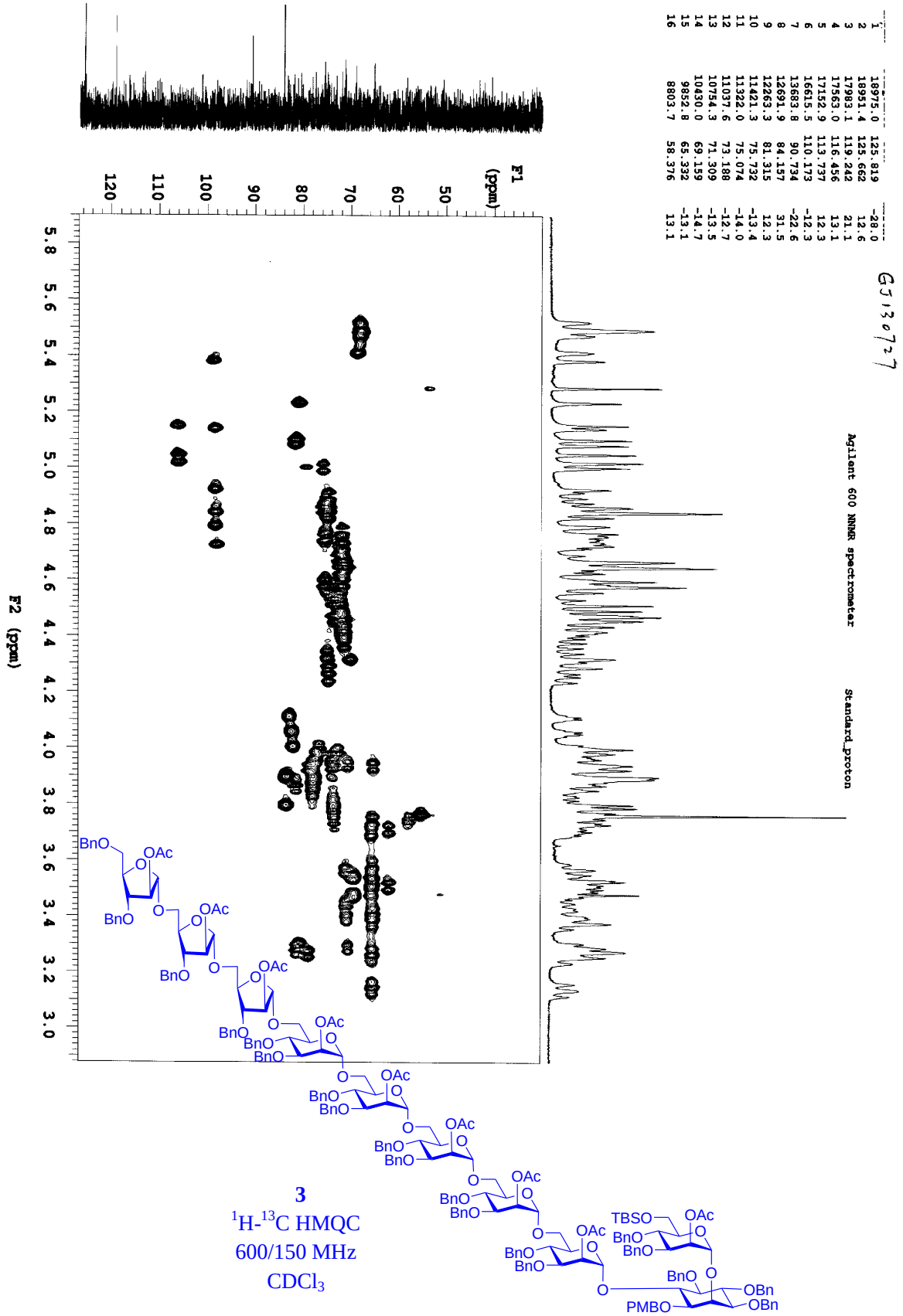


3

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

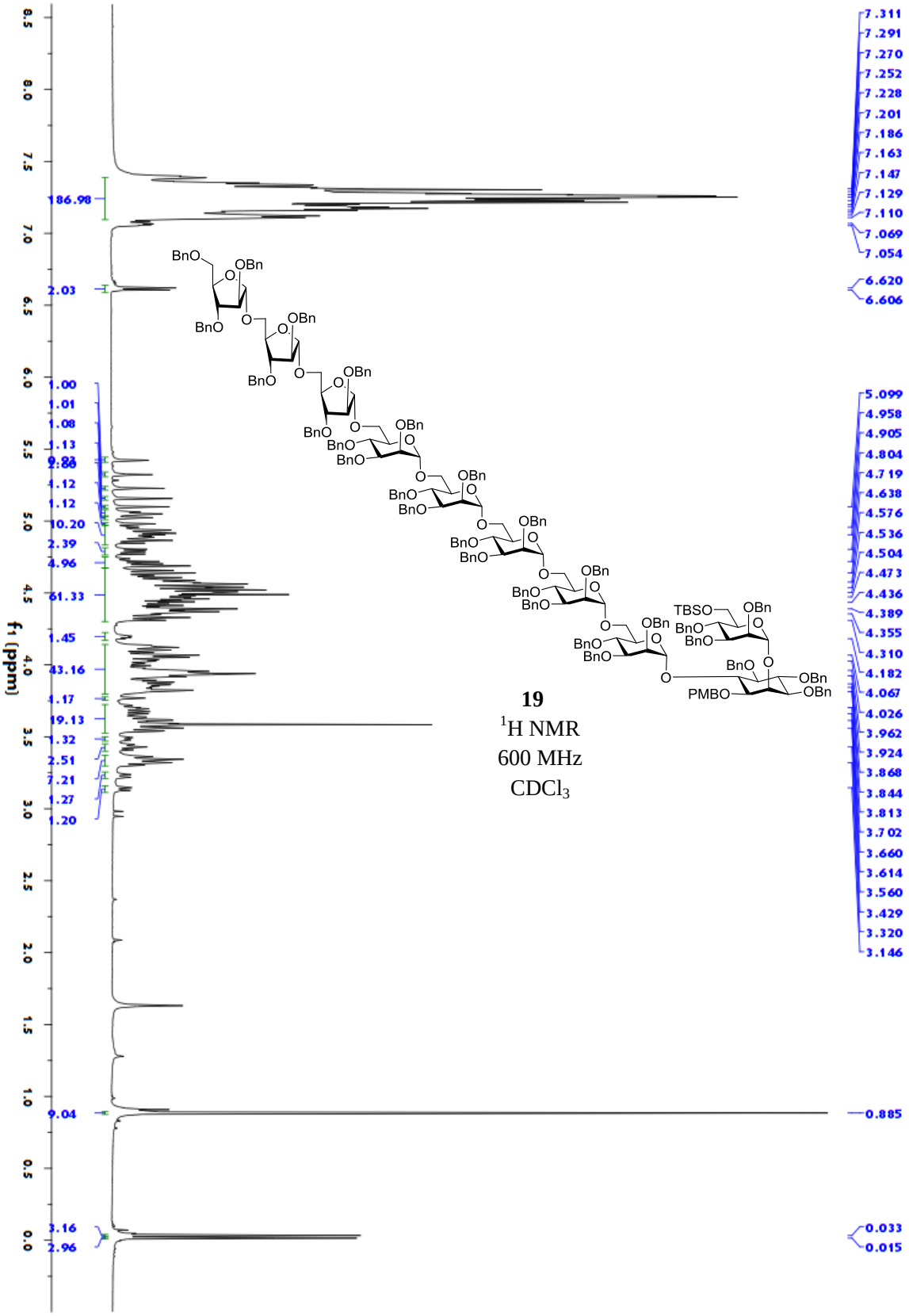


3

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

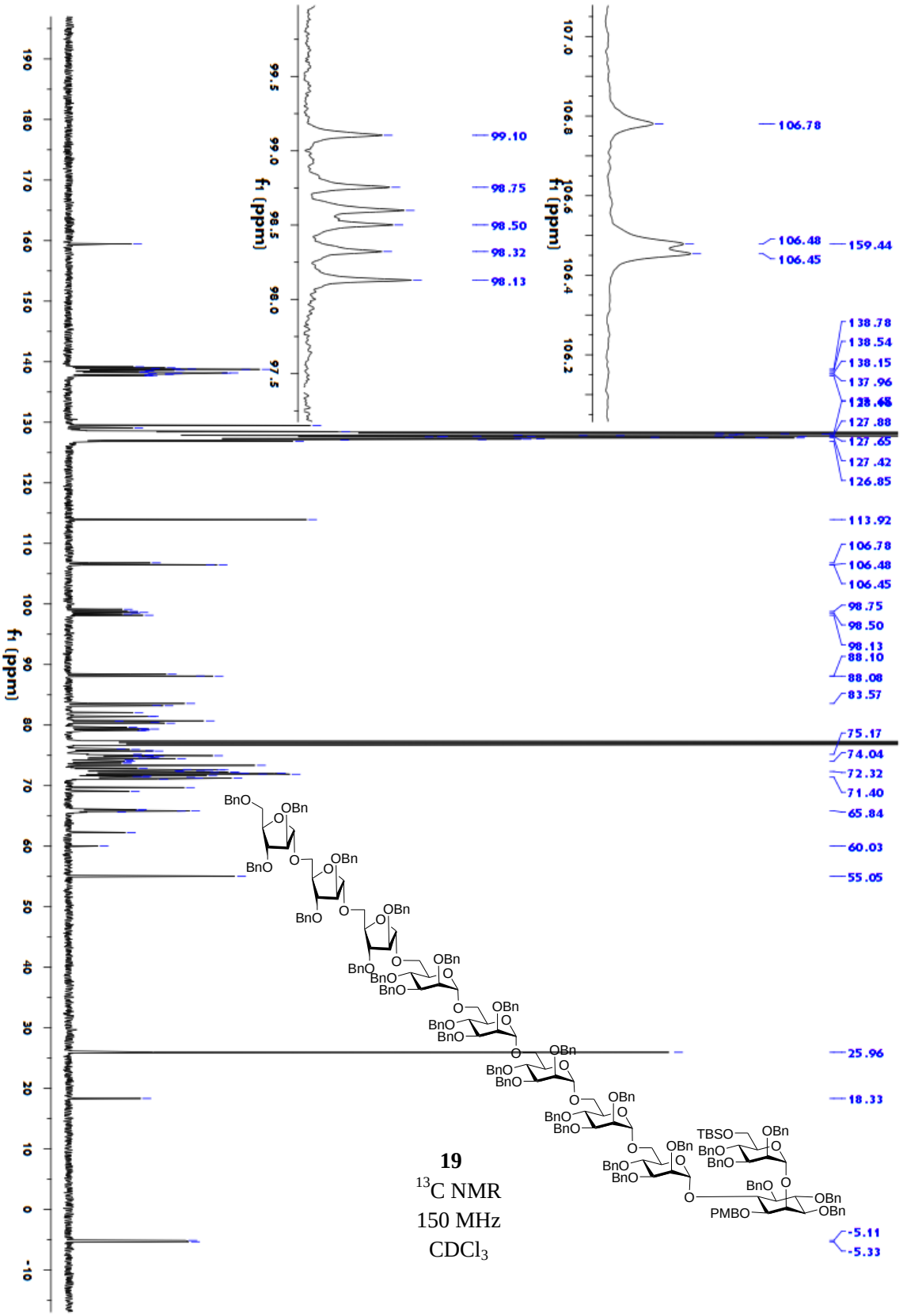


19

^{1}H NMR

600 MHz

$CDCl_3$

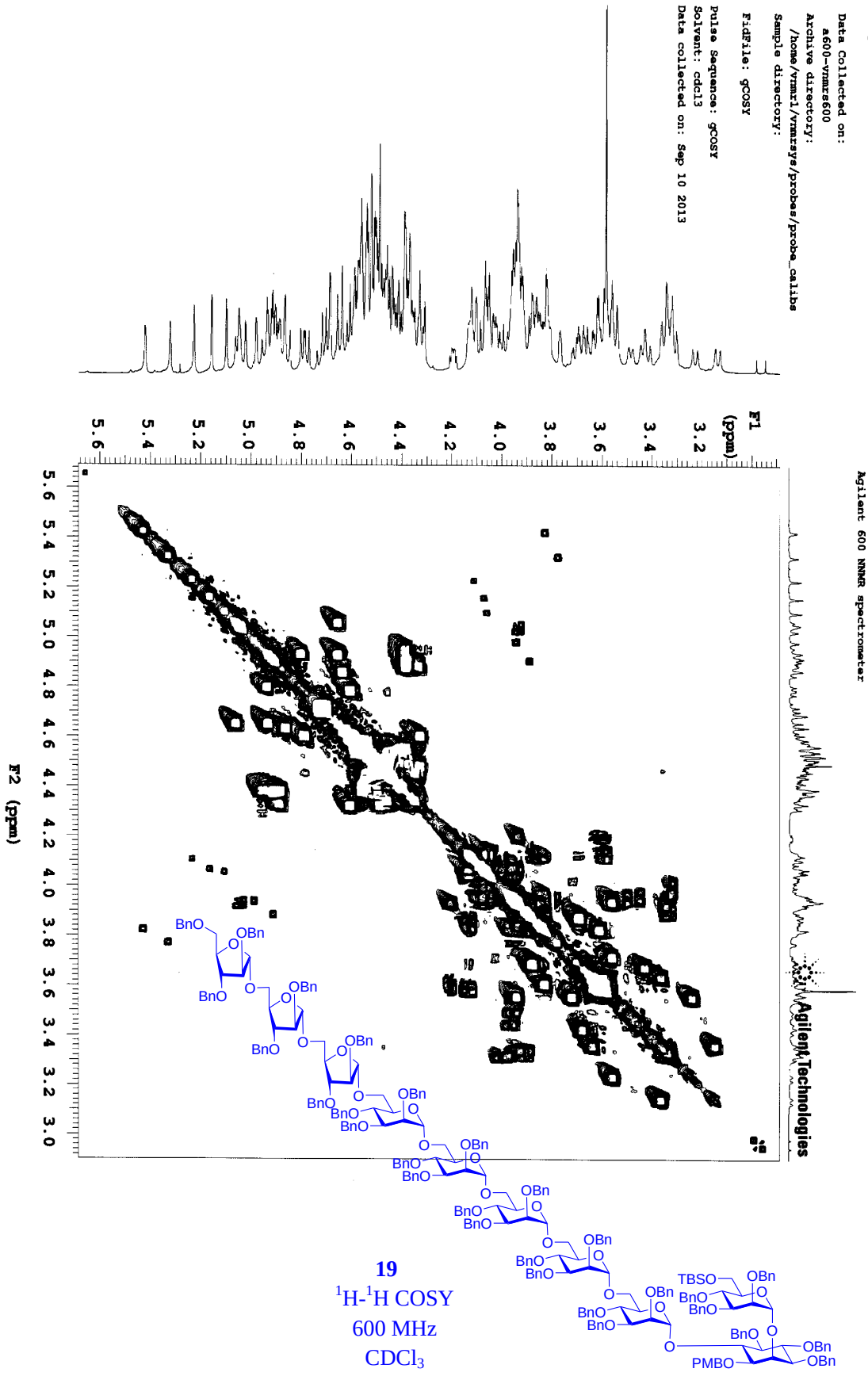


19

^{13}C NMR

150 MHz

$CDCl_3$

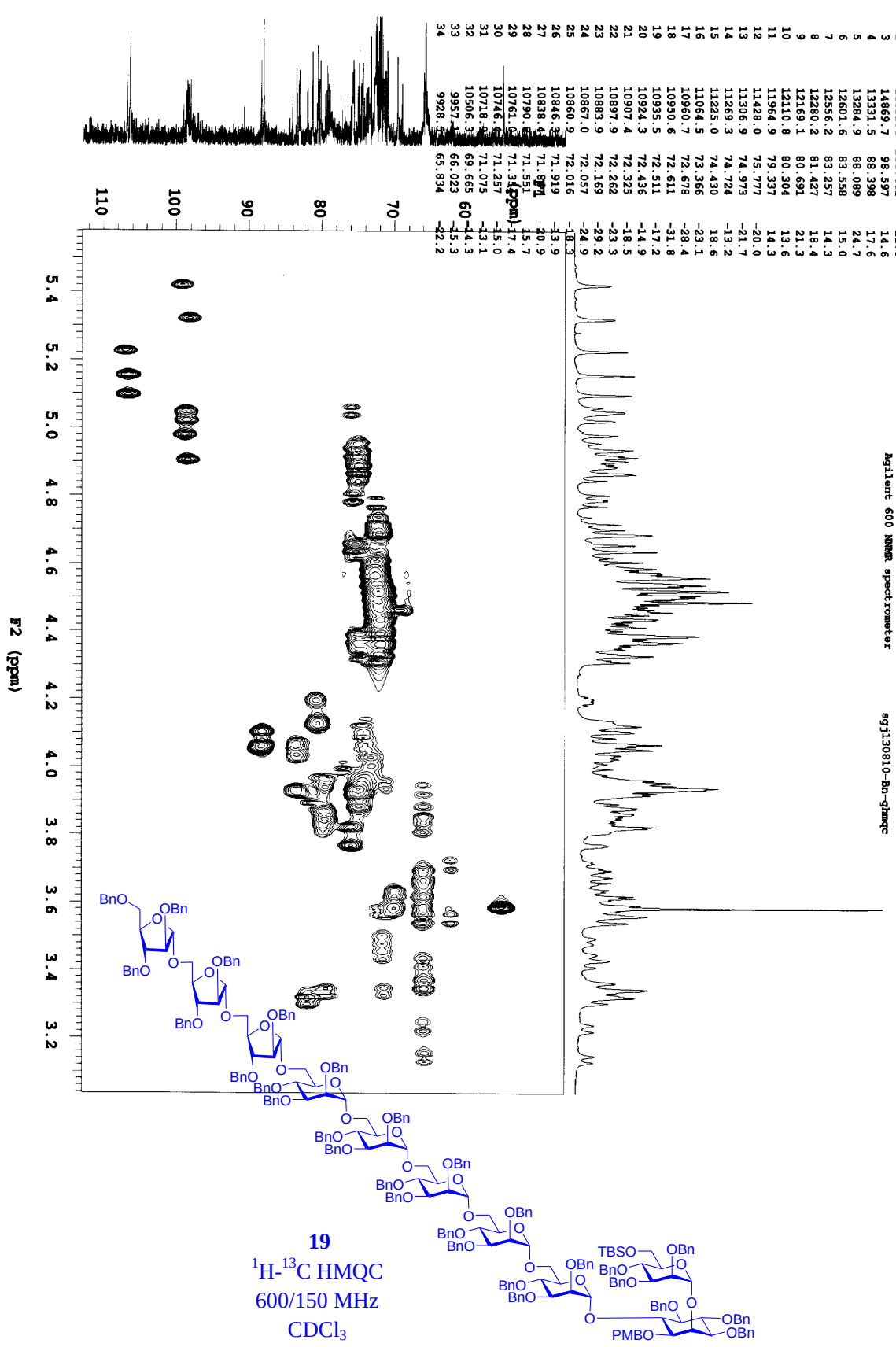


19

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

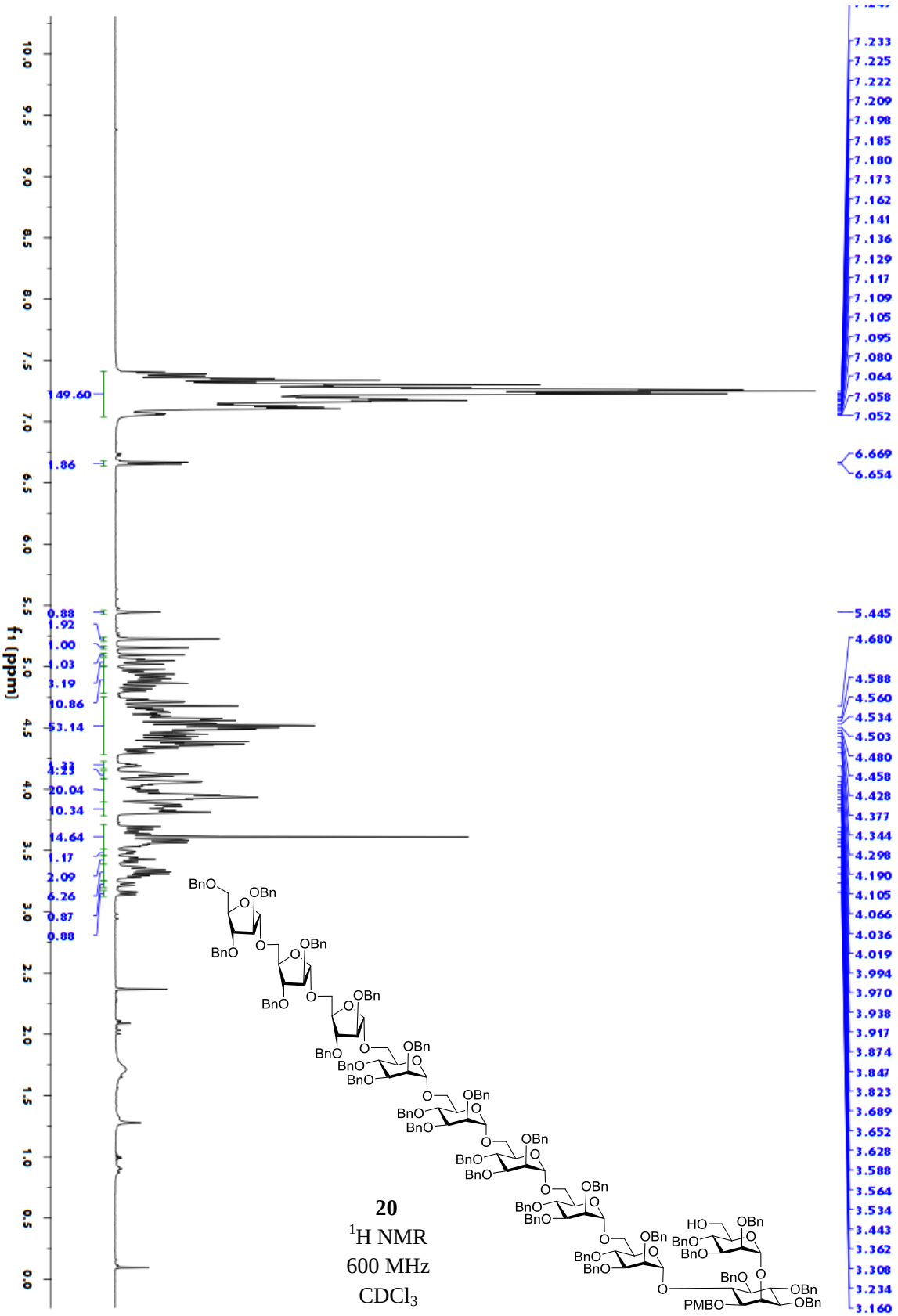


19

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

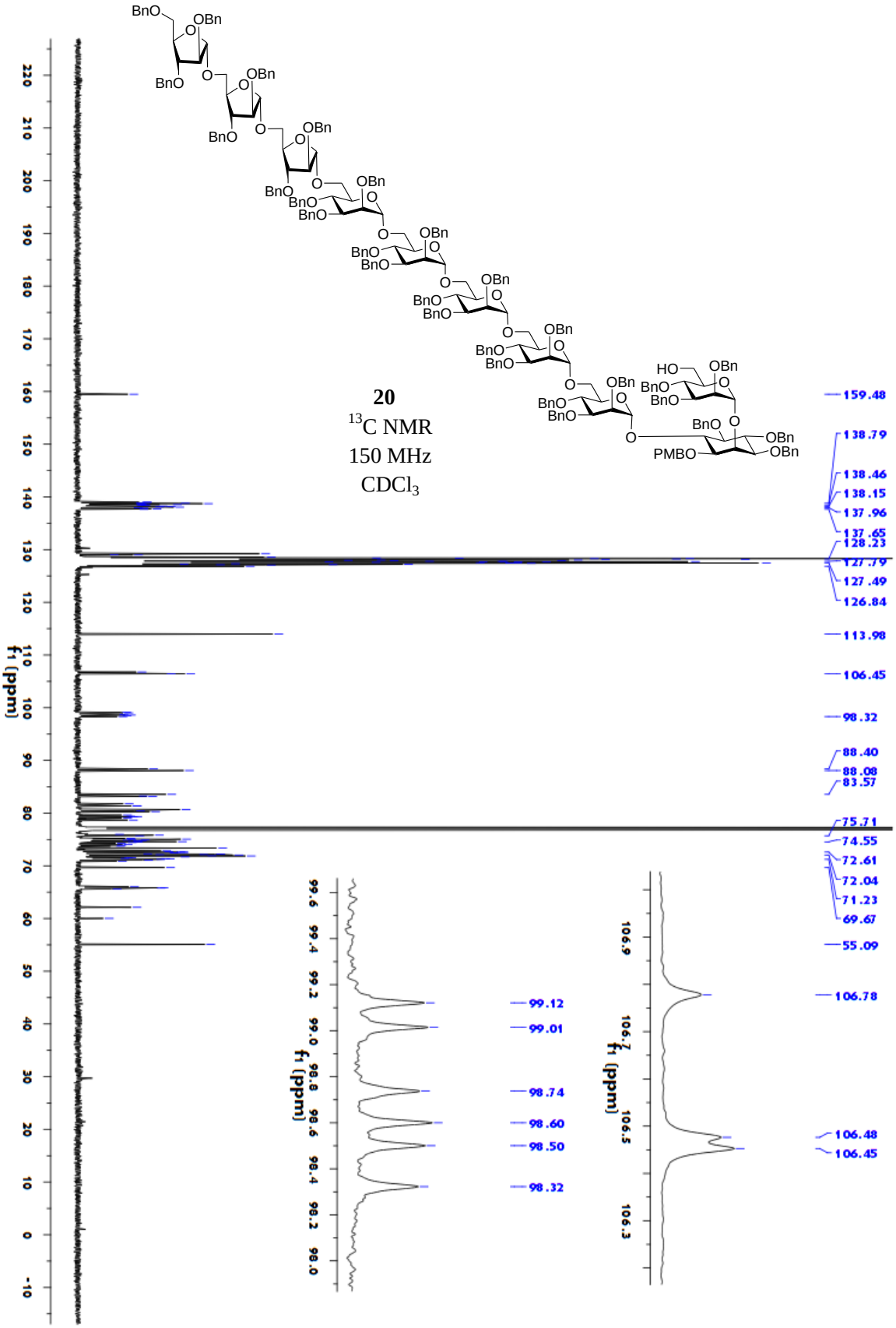


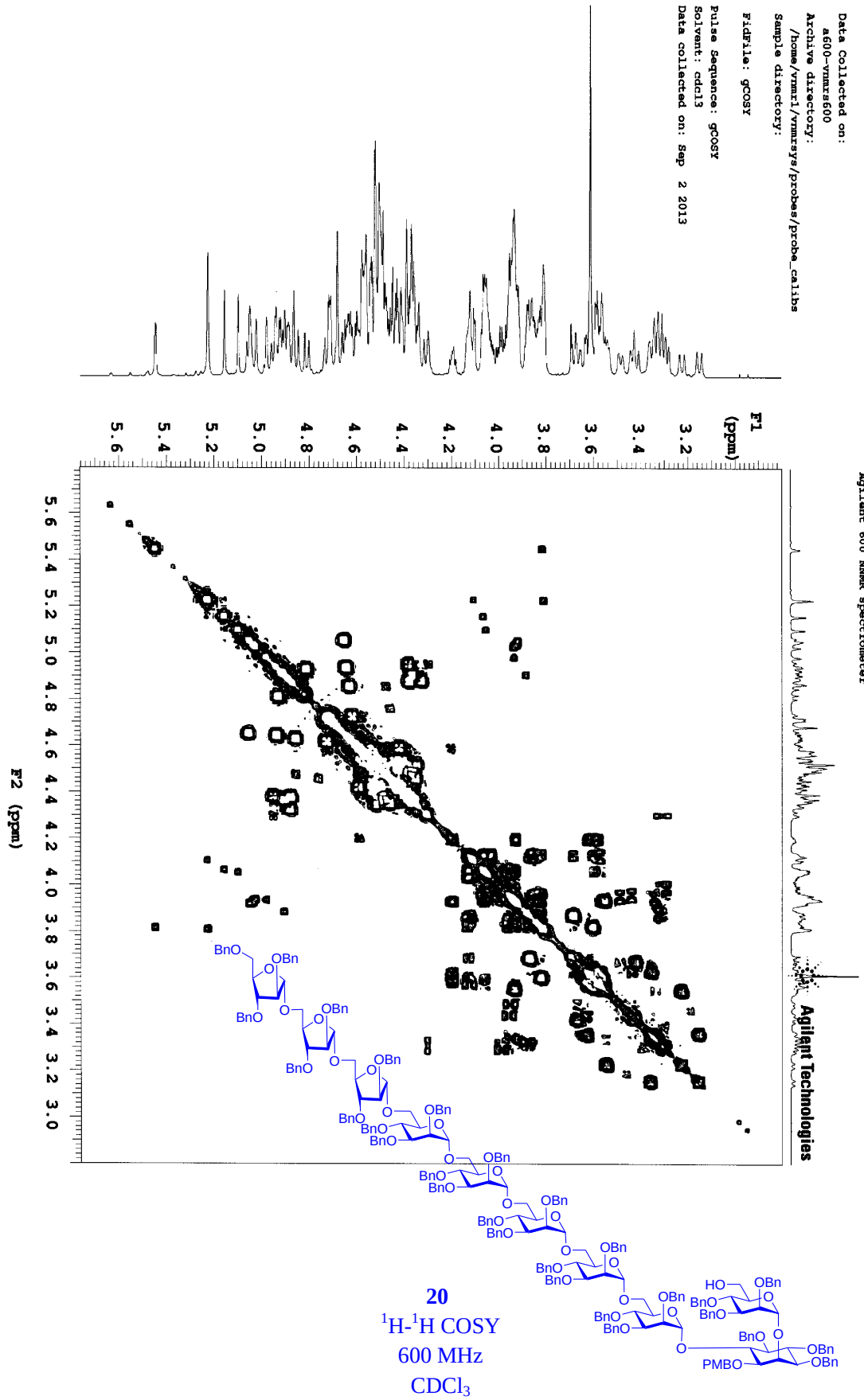
20

^{1}H NMR

600 MHz

$CDCl_3$


20
^{13}C NMR
150 MHz
$CDCl_3$
159.48
138.79
138.46
138.15
137.96
137.65
128.23
127.79
127.49
126.84
113.98
106.45
98.32
88.40
88.08
83.57
75.71
74.55
72.61
72.04
71.23
69.67
55.09
106.78
106.48
106.45
99.12
99.01
98.74
98.60
98.50
98.32
f1 (ppm)

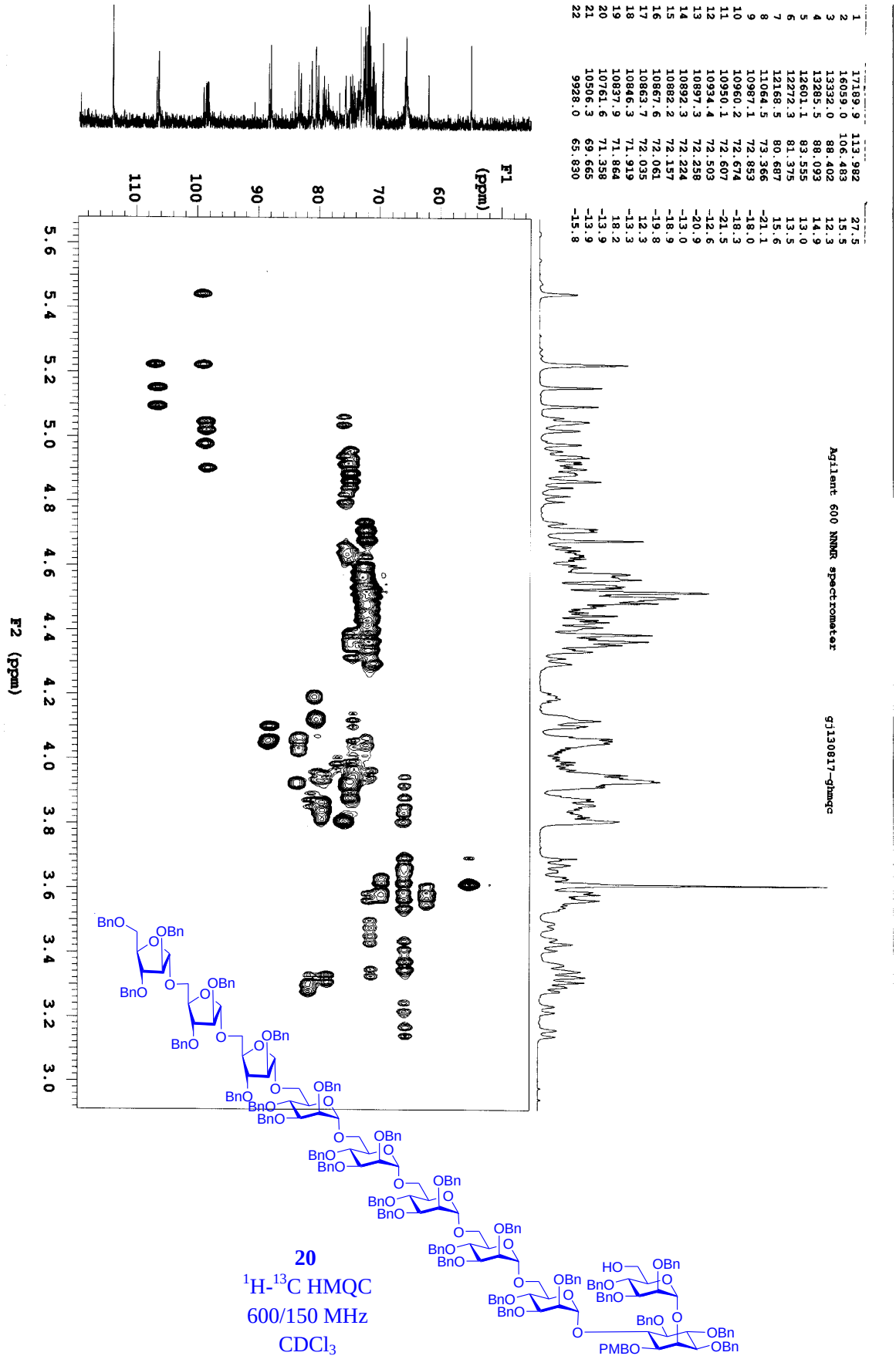


20

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

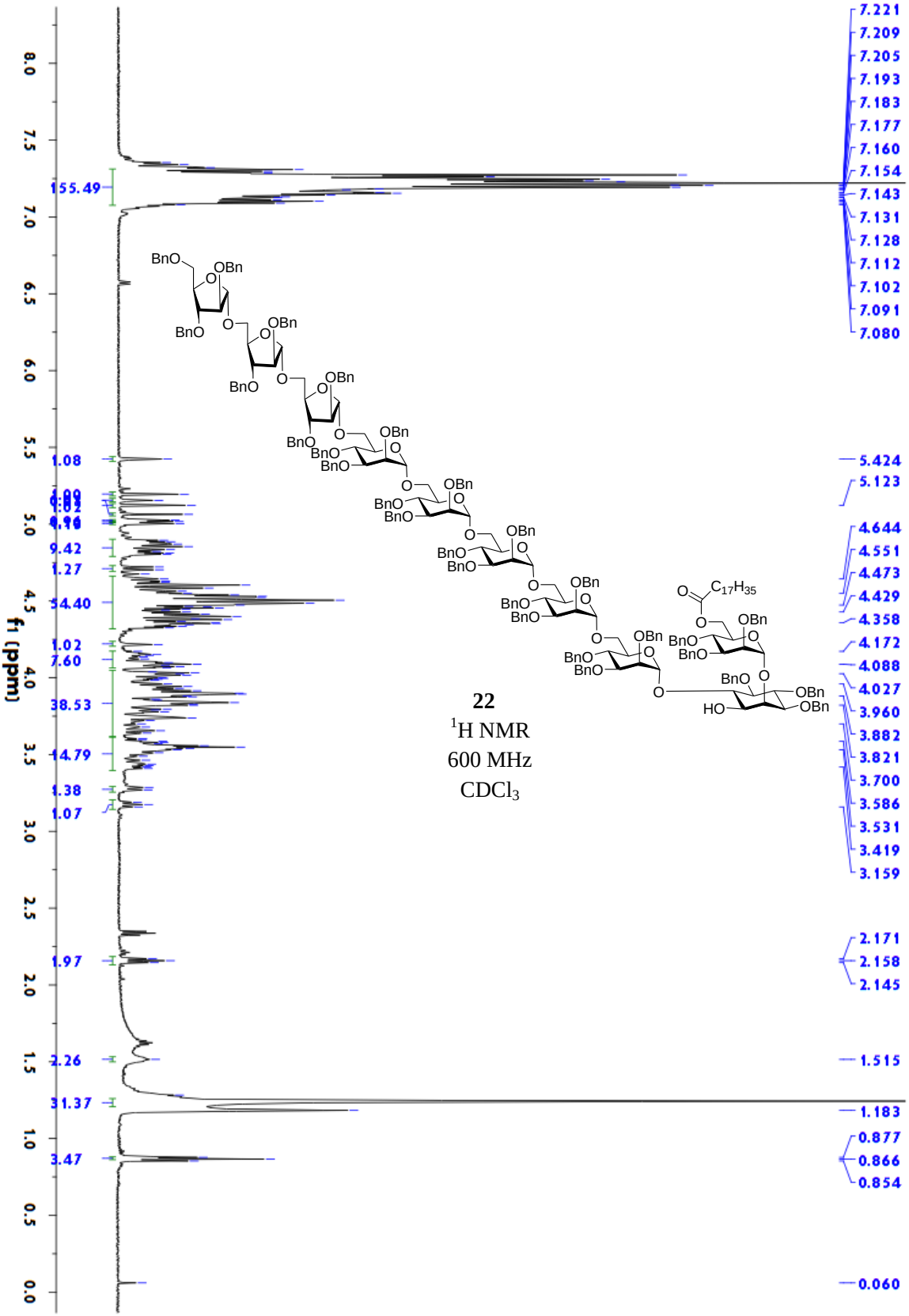


20

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

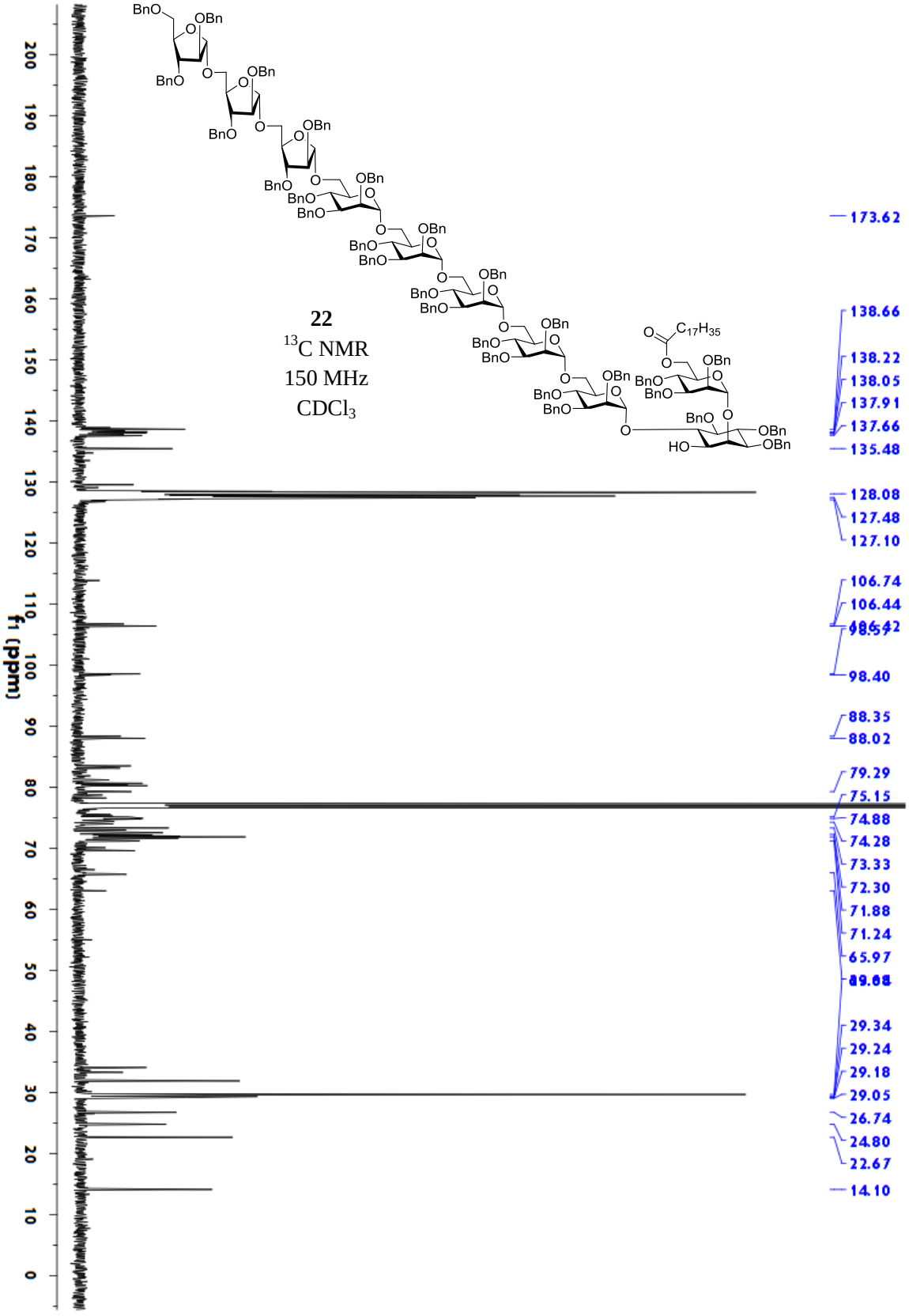


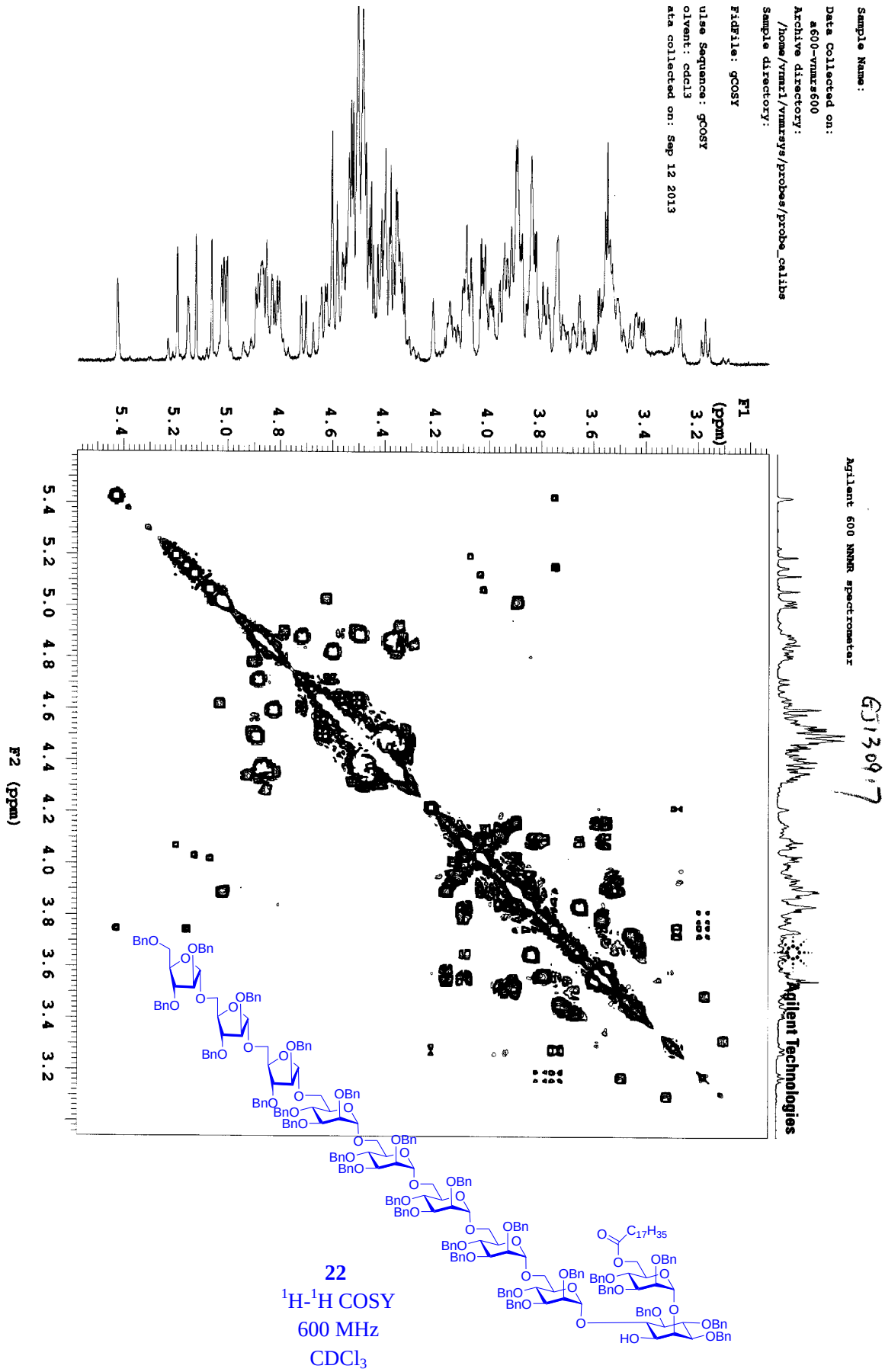
22

^{1}H NMR

600 MHz

$CDCl_3$


22
^{13}C NMR
150 MHz
$CDCl_3$
f1 (ppm)
173.62
138.66
138.22
138.05
137.91
137.66
135.48
128.08
127.48
127.10
106.74
106.44
98.40
88.35
88.02
79.29
75.15
74.88
74.28
73.33
72.30
71.88
71.24
65.97
29.34
29.24
29.18
29.05
26.74
24.80
22.67
14.10

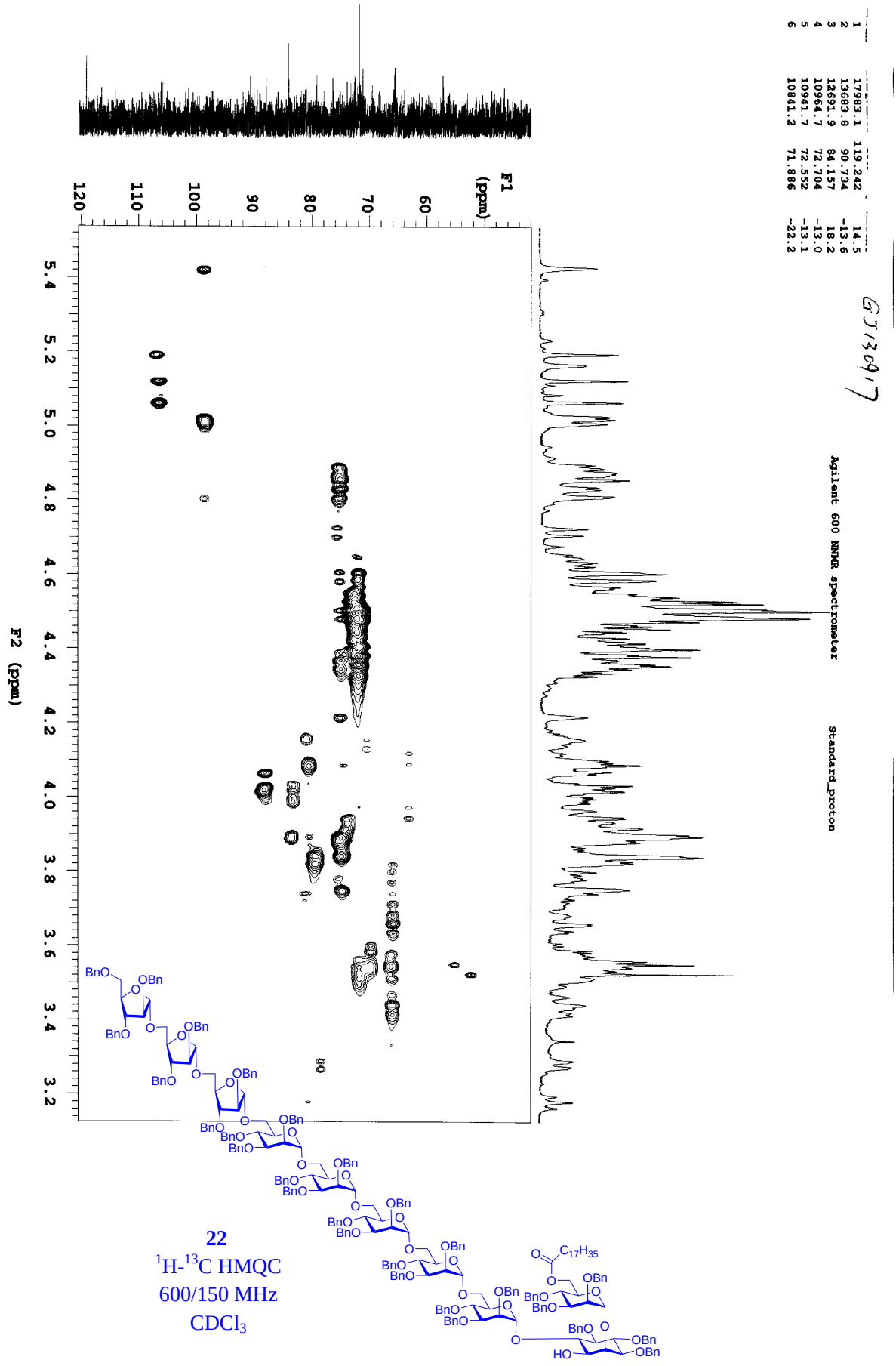


22

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

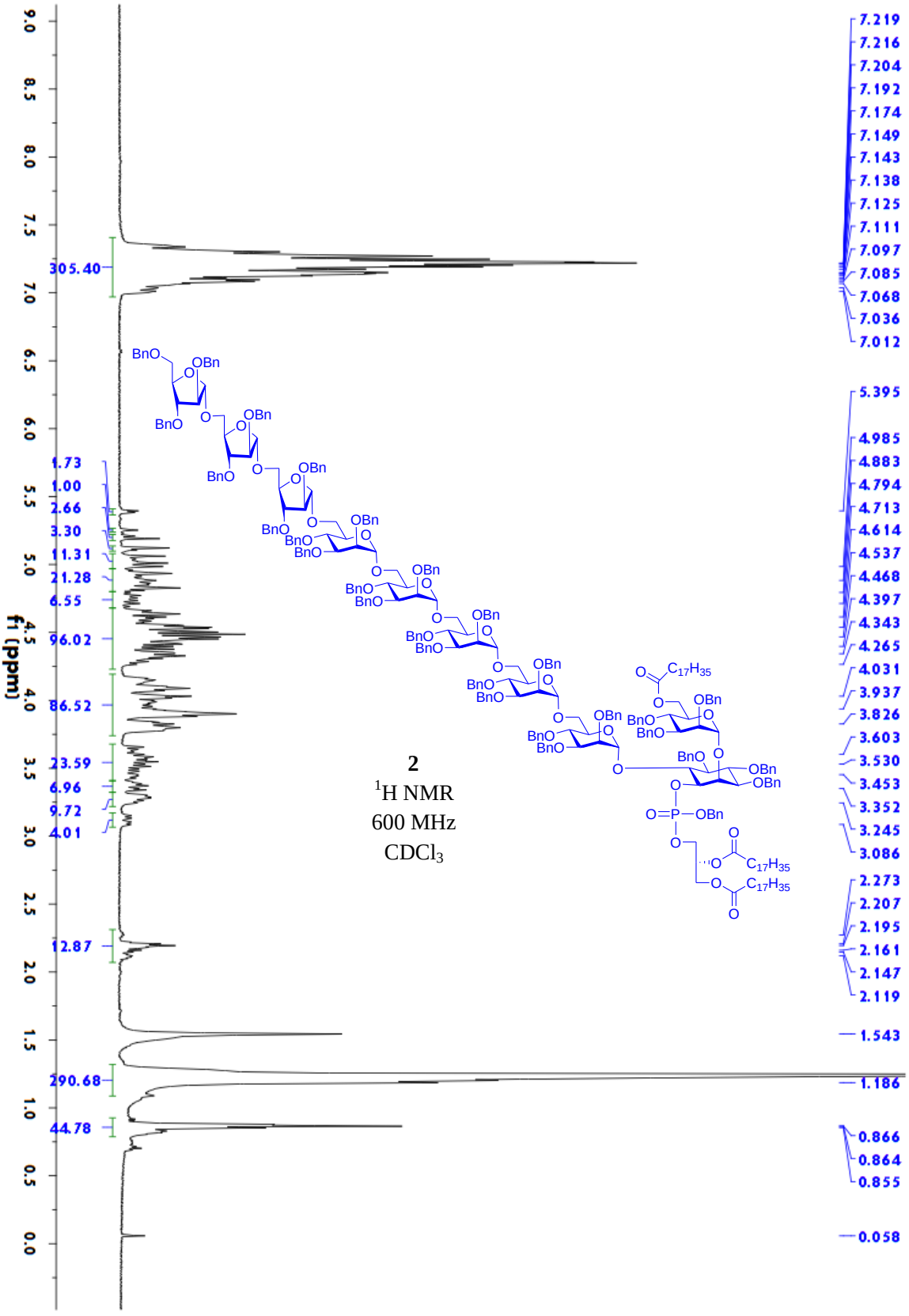


22

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$

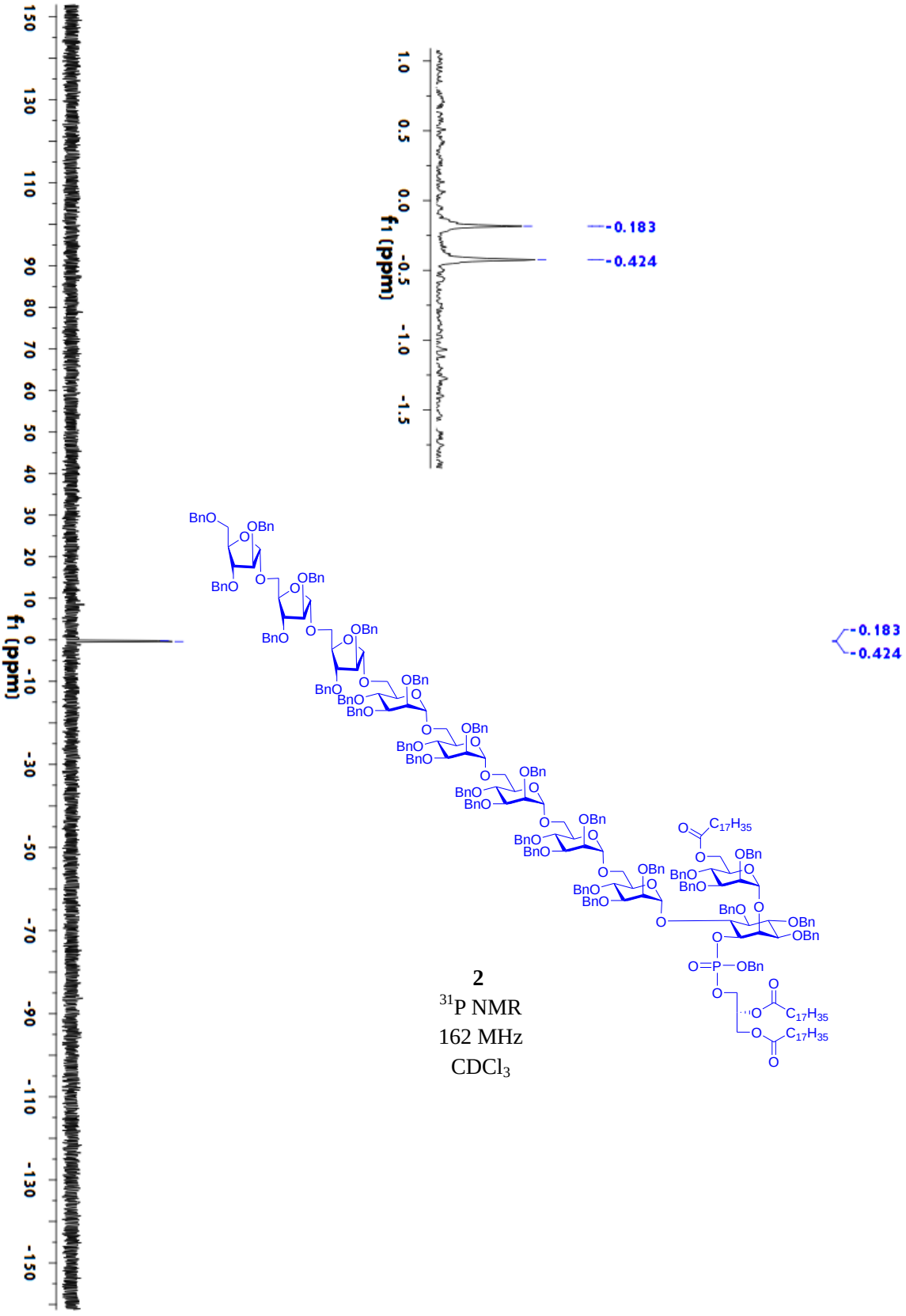


2

^{1}H NMR

600 MHz

$CDCl_3$

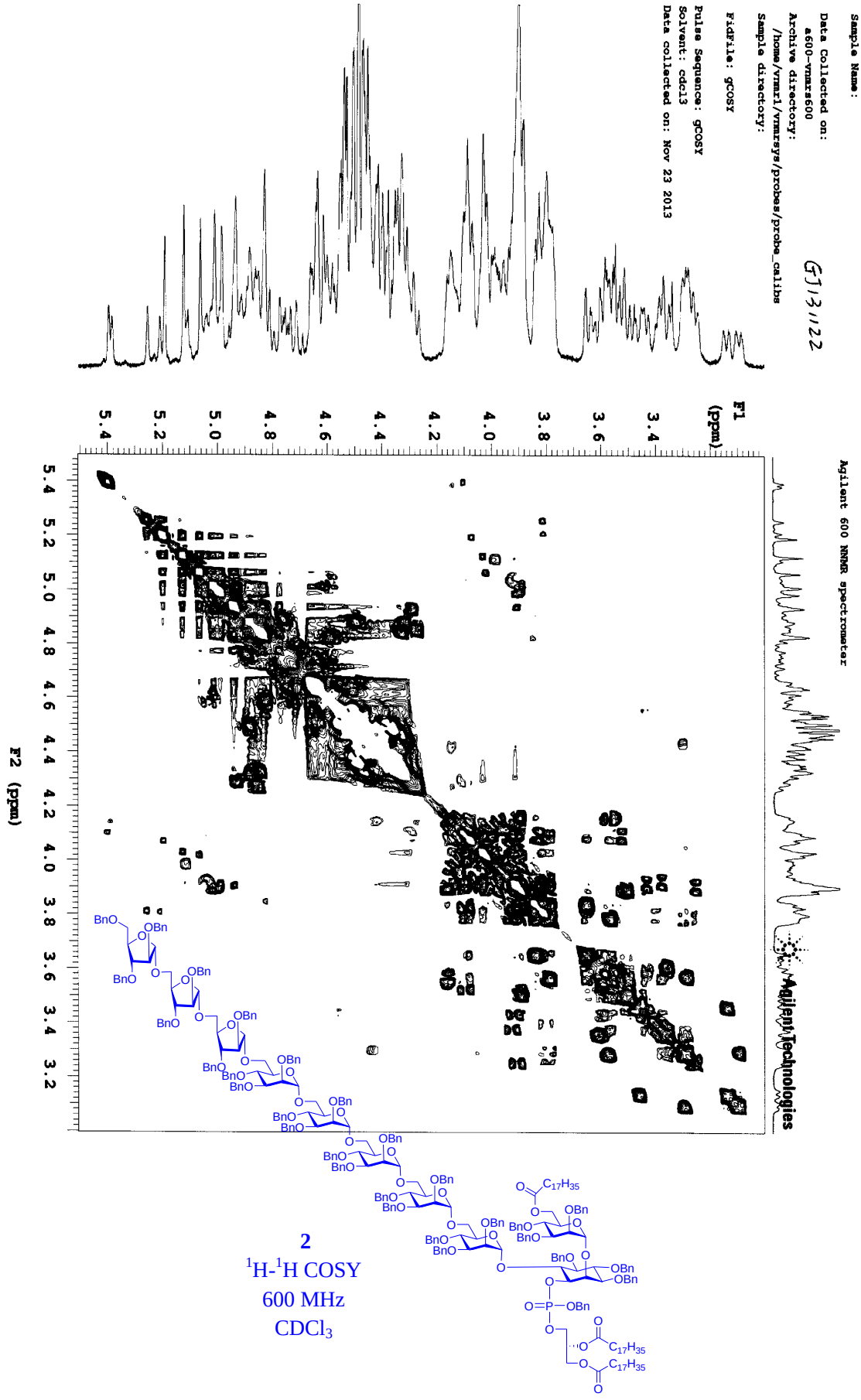


2

^{31}P NMR

162 MHz

$CDCl_3$

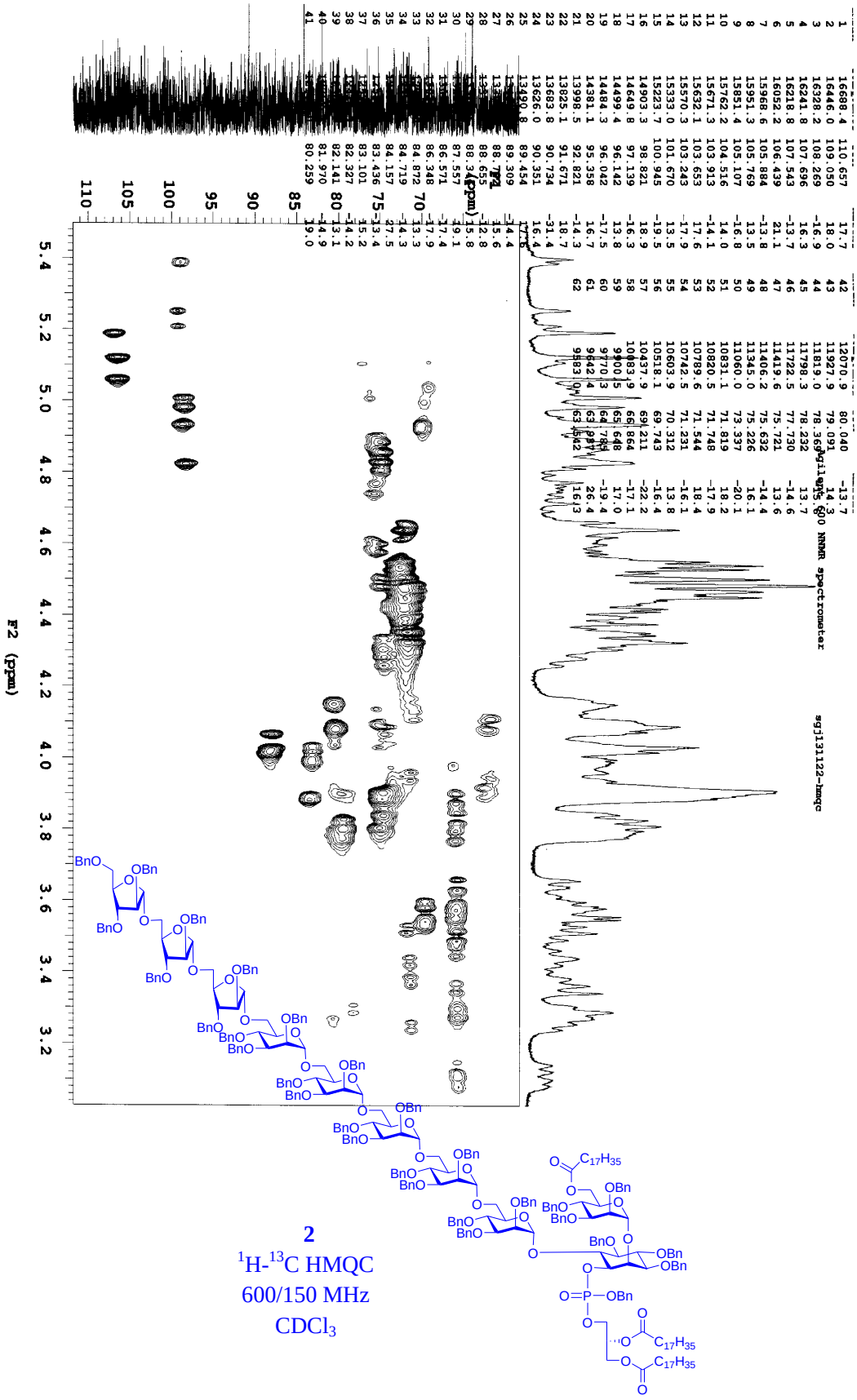


2

^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

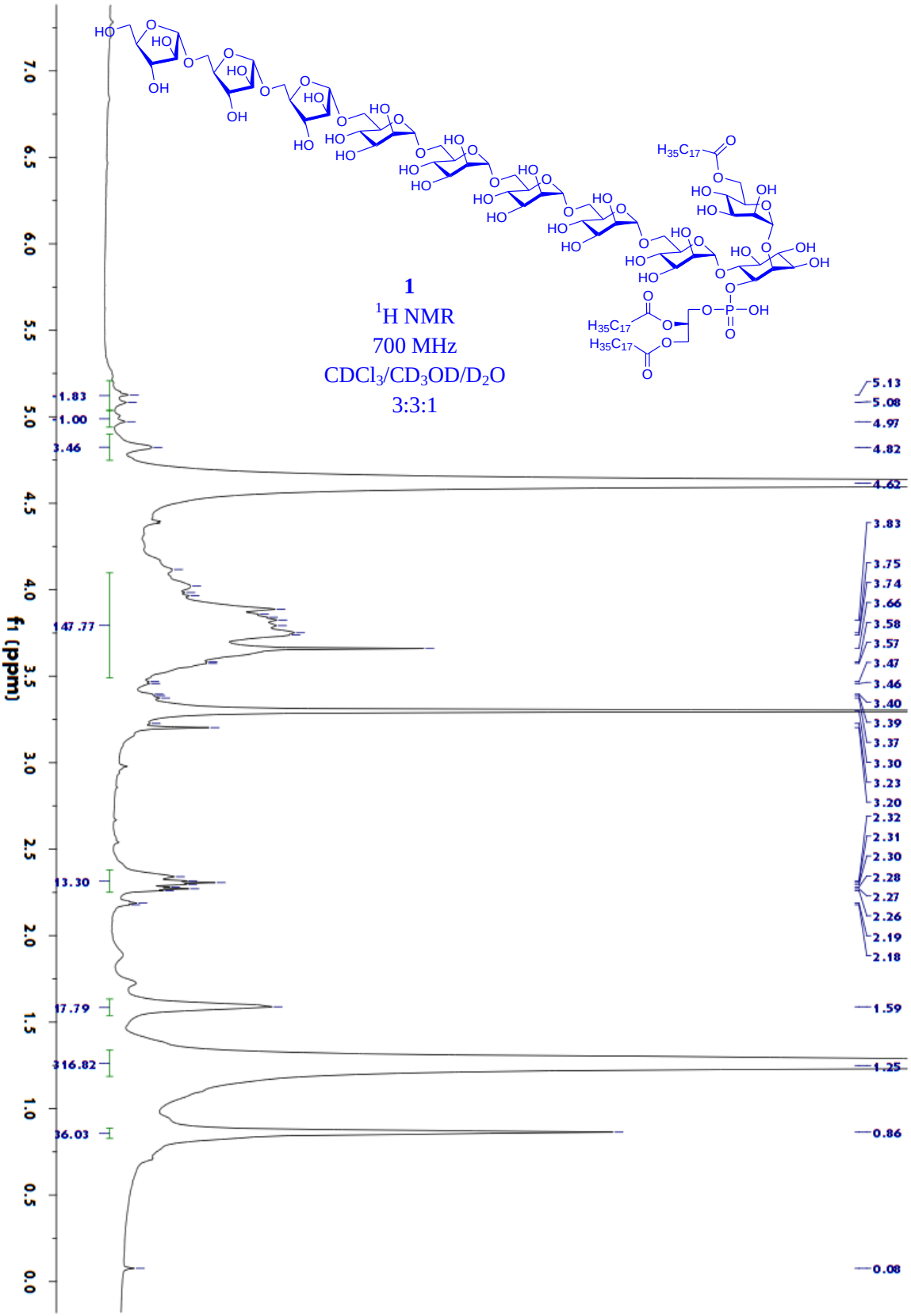


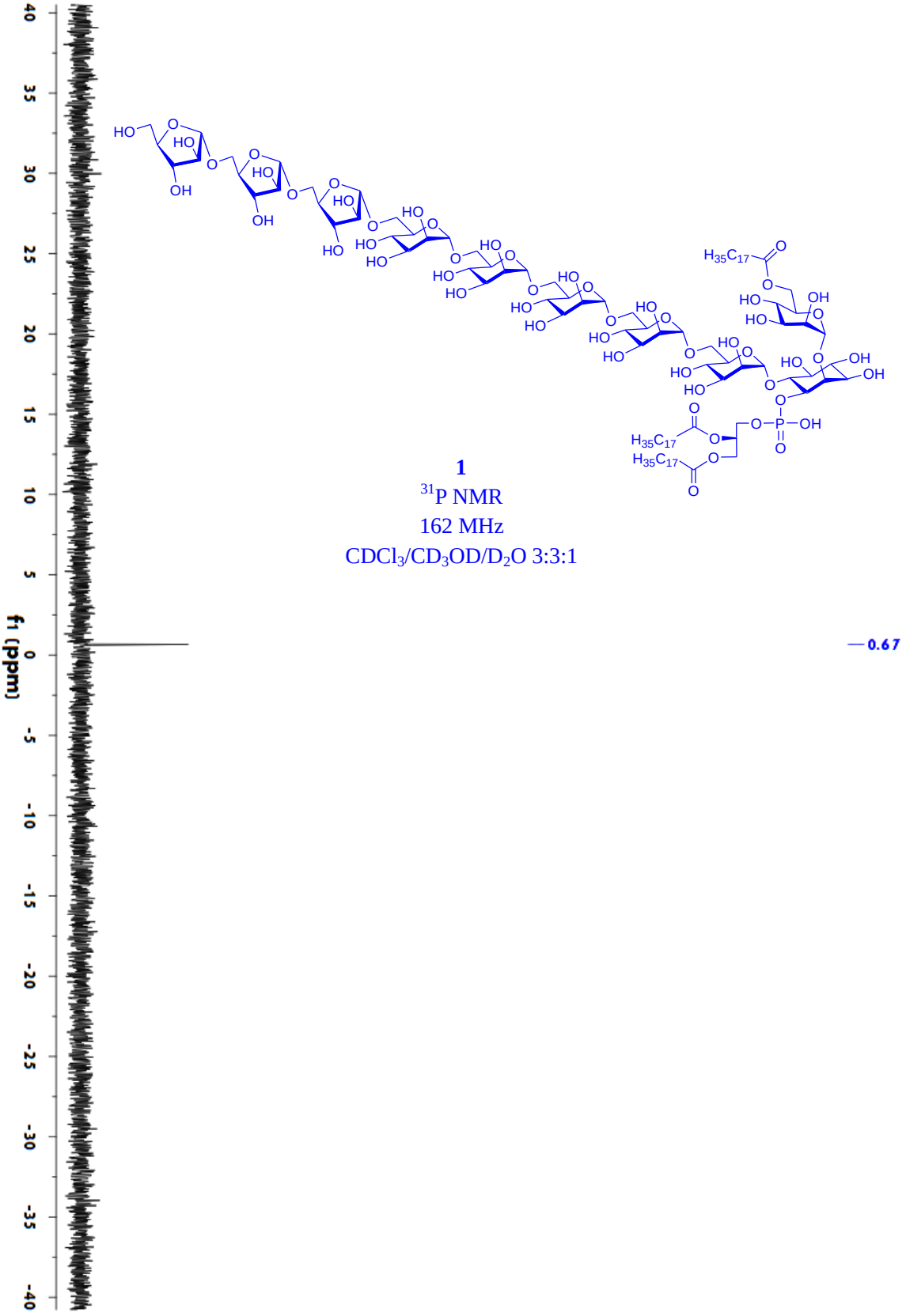
2

^{1}H-^{13}C HMQC

600/150 MHz

$CDCl_3$


1
1H NMR
700 MHz
CDCl3/CD3OD/D2O
3:3:1
f1 (ppm)
1.83
1.00
3.46
147.77
13.30
17.79
16.82
6.03
5.13
5.08
4.97
4.82
4.62
3.83
3.75
3.74
3.66
3.58
3.57
3.47
3.46
3.40
3.39
3.37
3.30
3.23
3.20
2.32
2.31
2.30
2.28
2.27
2.26
2.19
2.18
1.59
1.25
0.86
0.08



1

^{31}P NMR

162 MHz

$CDCl_3/CD_3OD/D_2O$ 3:3:1