Supporting Information

Chemical Synthesis of the Repeating Unit of Type V Group B *Streptococcus* Capsular Polysaccharide

Jian Gao[†] and Zhongwu Guo[‡,*]

[†] National Glycoengineering Research Center and Shandong Provincial Key Laboratory of Carbohydrate Chemistry and Glycobiology, Shandong University, 29 Shanda Nan Lu, Jinan 250010, China

[‡] Department of Chemistry, University of Florida, 214 Leigh Hall, Gainesville, Florida 32611, United States

[*]Corresponding Author E-mail: zguo@chem.ufl.edu

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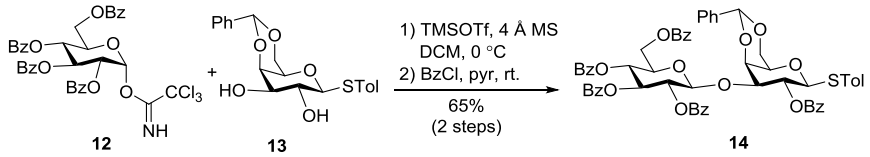
I. Experimental Section

General Experimental Methods: Chemicals and materials were purchased from commercial sources and were used as received without further purification unless otherwise noted. Molecular sieve 4 Å was flame-dried under vacuum and cooled to room temperature under a N_2 atmosphere immediately before use. TLC was carried out on Silica Gel 60 Å F254 plates with detection by a UV detector and/or by charring with 15% H_2SO_4 in EtOH (w/v). Mass spectrometry was recorded on either a high resolution ESI-TOF or a normal resolution MALD-TOF machine. NMR spectra were recorded on a 600 or 700 MHz machine with chemical shifts reported in ppm (δ) downfield from internal tetramethylsilane (TMS) or DHO reference. Signals are described as s (singlet), d (doublet), t (triplet) or m (multiplet), and coupling constants are reported in Hz.

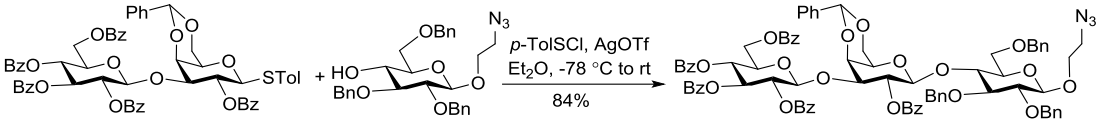
***p*-Tolyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (14):**



To a stirred mixture of **12** (200 mg, 0.271 mmol), **13** (84 mg, 0.226 mmol), and freshly activated MS 4 Å in anhydrous CH_2Cl_2 (4 mL) was slowly added TMSOTf (4.9 μL, 0.027 mmol) under a N_2 atmosphere at 0 °C. After the reaction mixture was stirred under this condition for another 15 min, it was neutralized with Et_3N, filtered, and concentrated. The residue was subjected to flush silica gel column chromatography with EtOAc and hexanes (1:2) as the eluent to give a mixture of two regio-isomers (174 mg, 81% yield) as a foamy solid. This product was then dissolved in pyridine (4 mL), and to the solution was added BzCl (43 μL, 0.366 mmol) at room temperature. After the reaction mixture was stirred for 4 h, it was concentrated under vacuum to give a residue that was purified by silica gel column chromatography with EtOAc and hexanes (1:3) as the eluent to give **14** (156 mg, 65% for two steps) as a foamy solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (d, J = 8.4 Hz, 2H, Ph), 7.88 (d, J = 8.4 Hz, 2H, Ph), 7.70 (dd, J = 9.3, 8.4 Hz, 4H, Ph), 7.58

(t, *J* = 7.8 Hz, 1H, Ph), 7.49 – 7.42 (m, 6H, Ph), 7.39 – 7.23 (m, 13H, Ph), 7.19 (t, *J* = 7.5 Hz, 2H, Ph), 7.04 (t, *J* = 7.5 Hz, 2H, Ph), 6.98 (d, *J* = 7.8 Hz, 2H, Ph), 5.76 (t, *J* = 9.6 Hz, 1H, H-3^{Glc}), 5.61 (t, *J* = 9.8 Hz, 1H, H-4^{Glc}), 5.46 (t, *J* = 8.7 Hz, 1H, H-2^{Glc}), 5.41 – 5.35 (m, 2H, H-2^{Gal}, Ph-C*H*-), 5.09 (d, *J* = 7.8 Hz, 1H, H-1^{Glc}), 4.70 (d, *J* = 9.6 Hz, 1H, H-1^{Gal}), 4.66 (dd, *J* = 12.0, 2.4 Hz, 1H, H-6a^{Glc}), 4.51 (dd, *J* = 12.0, 5.4 Hz, 1H, H-6b^{Glc}), 4.38 (d, *J* = 3.0 Hz, 1H, H-4^{Gal}), 4.26 (d, *J* = 12.0 Hz, 1H, H-6a^{Gal}), 4.09 (m, 2H, H-5^{Glc}, H-3^{Gal}), 3.83 (d, *J* = 12.0 Hz, 1H, H-6b^{Gal}), 3.32 (s, 1H, H-5^{Gal}), 2.28 (s, 3H, Ph-CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.99, 165.69, 165.12, 164.67, 164.45, 138.00, 137.64, 133.88, 133.59, 133.49, 133.44, 133.15, 132.71, 132.62, 130.14, 129.79, 129.72, 129.67, 129.62, 129.51, 129.45, 128.81, 128.76, 128.66, 128.60, 128.45, 128.42, 128.19, 127.98, 127.94, 127.77, 126.56, 101.93 (C-1^{Glc}), 100.96 (Ph-*C*H-), 85.73 (C-1^{Gal}), 79.95, 76.10, 72.87, 72.25, 71.82, 70.16, 69.37, 68.92, 68.76, 62.41, 21.21. HR ESI-TOF MS (m/z): calcd for $C_{61}H_{52}O_{15}SNa$ $[M + Na]^+$, 1079.2925; found, 1079.2880.

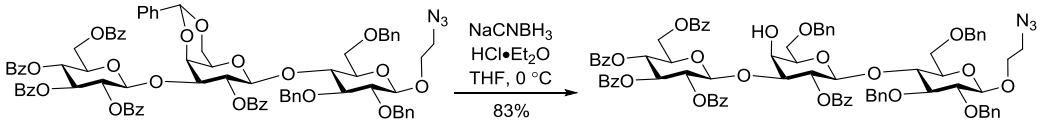
2-Azidoethyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (15):



After a mixture of **14** (110 mg, 0.104 mmol), **9** (49 mg, 0.095 mmol), and freshly activated MS 4 Å in anhydrous diethyl ether (4 mL) was stirred at room temperature for 40 min, it was cooled to −78 °C. Then, a solution of AgOTf (80 mg, 0.312 mmol) in diethyl ether (1.0 mL) was added. Fifteen minutes later, *p*-TolSCl (17 μL, 0.114 mmol) was added through a microsyringe. The reaction mixture was allowed to warm up slowly to room temperature within 1 h and stirred for another 20 min. The reaction was quenched with Et_3N, and the mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated under vacuum, and the residue was purified by silica gel column chromatography with EtOAc and hexanes (1:2) as the eluent to give **15** (116 mg, 84%) as a foamy solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.4 Hz, 2H, Ph), 7.89 (d, *J* = 8.4 Hz, 2H, Ph), 7.70 (d, *J* = 8.4 Hz, 2H, Ph), 7.60 (d, *J* = 7.8 Hz, 2H, Ph), 7.54 (t, *J* = 7.2 Hz,

1H, Ph), 7.51 – 7.47 (m, 3H, Ph), 7.46 – 7.16 (m, 31H, Ph), 7.04 (t, *J* = 7.8 Hz, 2H, Ph), 5.81 (t, *J* = 9.6 Hz, 1H, H-3$^{Glc\text{-}A}$), 5.65 (t, *J* = 9.6 Hz, 1H, H-4$^{Glc\text{-}A}$), 5.47 (t, *J* = 9.6 Hz, 2H, H-2$^{Glc\text{-}A}$, H-2^{Gal}), 5.38 (s, 1H, Ph-C*H*-), 5.09 (d, *J* = 11.4 Hz, 1H, Bn), 5.08 (d, *J* = 7.8 Hz, 1H, H-1$^{Glc\text{-}A}$), 4.84 (d, *J* = 10.8 Hz, 1H, Bn), 4.76 – 4.66 (m, 3H, H-6a$^{Glc\text{-}A}$, 2 × Bn), 4.63 (d, *J* = 7.8 Hz, 1H, H-1^{Gal}), 4.53 – 4.47 (m, 2H, H-6b$^{Glc\text{-}A}$, Bn), 4.27 – 4.10 (m, 2H, H-4^{Gal}, H-1$^{Glc\text{-}B}$), 4.18 (d, *J* = 12.0 Hz, 1H, Bn), 4.17 – 4.11 (m, 2H, H-5$^{Glc\text{-}A}$, H-6a^{Gal}), 3.92 – 3.87 (m, 1H, -OC*H*$_2$CH$_2$-), 3.85 (t, *J* = 9.3 Hz, 1H, H-4$^{Glc\text{-}B}$), 3.76 (dd, *J* = 10.2, 3.0 Hz, 1H, H-3^{Gal}), 3.72 (d, *J* = 12.0 Hz, 1H, H-6b^{Gal}), 3.59 – 3.53 (m, 2H, -OC*H*$_2$CH$_2$-, H-3$^{Glc\text{-}B}$), 3.46 (dd, *J* = 11.0, 4.0 Hz, 1H, H-6a$^{Glc\text{-}B}$), 3.42 – 3.29 (m, 4H, H-6b$^{Glc\text{-}B}$, H-2$^{Glc\text{-}B}$, -CH$_2$C*H*$_2$-N$_3$), 3.11 – 3.05 (m, 1H, H-5$^{Glc\text{-}B}$), 3.03 (s, 1H, H-5^{Gal}). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.99, 165.74, 165.09, 164.67, 164.17, 138.95, 138.54, 138.40, 137.73, 133.50, 133.40, 133.19, 132.77, 132.60, 129.80, 129.70, 129.63, 129.41, 129.35, 129.31, 128.84, 128.69, 128.62, 128.59, 128.55, 128.42, 128.35, 128.27, 128.21, 128.07, 127.96, 127.87, 127.70, 127.45, 127.14, 126.38, 103.39 (C-1$^{Glc\text{-}B}$), 101.76 (C-1$^{Glc\text{-}A}$), 101.00 (C-1^{Gal}), 100.82 (Ph-*C*H-), 82.89, 81.71, 78.68, 77.12, 76.00, 75.65, 74.85, 74.36, 73.25, 72.72, 72.20, 71.85, 70.73, 69.37, 68.44, 68.04, 67.94, 66.65, 62.40, 50.86. HR ESI-TOF MS (m/z): calcd for $C_{83}H_{77}N_3O_{21}Na$ $[M + Na]^+$, 1474.4947; found, 1474.4946.

2-Azidoethyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-(2-*O*-benzoyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16):

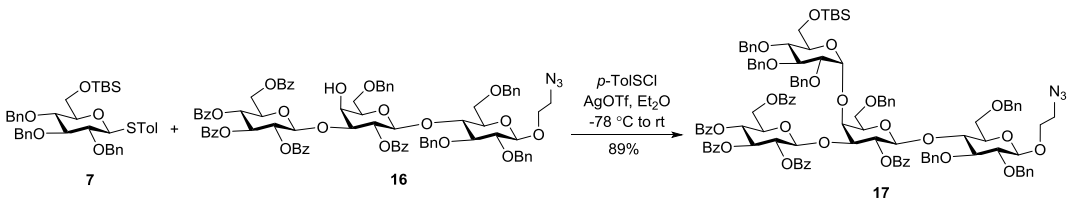


15 **16**

To a stirred mixture of **15** (90 mg, 0.062 mmol), sodium cyanoborohydride (58 mg, 0.930 mmol), and MS 4 Å in THF was added HCl·Et_2O (1 M) slowly at 0 °C until pH reached 2-3. Three hours later, the reaction was quenched with aq. $NaHCO_3$. The solid materials were filtered off and washed with CH_2Cl_2. The organic phases were combined, dried with Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography with EtOAc and hexanes (1:2) as the eluent to produce **16** (75 mg, 83%) as a foamy solid. ^{1}H NMR (600 MHz,

$CDCl_3$) δ: 8.03 (d, J = 7.8 Hz, 2H, Ph), 7.89 (d, J = 8.4 Hz, 2H, Ph), 7.70 (d, J = 8.4 Hz, 2H, Ph), 7.55 – 7.47 (m, 4H, Ph), 7.45 (d, J = 7.8 Hz, 2H, Ph), 7.43 – 7.19 (m, 29H, Ph), 7.16 (t, J = 7.5 Hz, 2H, Ph), 7.09 (t, J = 7.5 Hz, 2H, Ph), 5.81 (t, J = 9.8 Hz, 1H, H-3$^{Glc\text{-}A}$), 5.60 (t, J = 9.6 Hz, 1H, H-4$^{Glc\text{-}A}$), 5.48 (t, J = 8.4 Hz, 1H, H-2$^{Glc\text{-}A}$), 5.43 (t, J = 8.4 Hz, 1H, H-2^{Gal}), 4.98 (d, J = 10.8 Hz, 1H, Bn), 4.93 (d, J = 7.8 Hz, 1H, H-1$^{Glc\text{-}A}$), 4.83 (d, J = 11.4 Hz, 1H, Bn), 4.73 – 4.67 (m, 3H, H-6a$^{Glc\text{-}A}$, Bn), 4.62 (d, J = 8.4 Hz, 1H, H-1^{Gal}), 4.51 (d, J = 12.0 Hz, 1H, Bn), 4.45 (dd, J = 12.0, 6.0 Hz, 1H, H-6b$^{Glc\text{-}A}$), 4.42 (d, J = 12.0 Hz, 1H, Bn), 4.29 (d, J = 12.0 Hz, 1H, Bn), 4.25 – 4.18 (m, 4H, Bn, H-1$^{Glc\text{-}B}$, H-5$^{Glc\text{-}A}$, H-4^{Gal}), 3.92 – 3.88 (m, 1H, -OCH_2CH$_2$-), 3.85 (t, J = 9.3 Hz, 1H, H-4$^{Glc\text{-}B}$), 3.70 (dd, J = 9.6, 3.0 Hz, 1H, H-3^{Gal}), 3.65 – 3.61 (m, 1H, H-6a^{Gal}), 3.59 – 3.55 (m, 1H, -OCH_2CH$_2$-), 3.53 – 3.48 (m, 3H, H-3$^{Glc\text{-}B}$, H-5^{Gal}, H-6b^{Gal}), 3.46 – 3.29 (m, 5H, H-6a,6b$^{Glc\text{-}B}$, H-2$^{Glc\text{-}B}$, -CH$_2$CH_2N3), 3.09 (dd, J = 10.2, 2.4 Hz, 1H, H-5$^{Glc\text{-}B}$), 2.88 (s, 1H, -OH). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.10, 165.69, 165.11, 164.59, 164.33, 139.03, 138.54, 138.29, 138.21, 133.56, 133.39, 133.27, 132.73, 129.82, 129.80, 129.61, 129.49, 129.34, 129.26, 129.17, 128.57, 128.52, 128.44, 128.36, 128.31, 128.24, 128.21, 128.10, 128.04, 127.96, 127.90, 127.68, 127.65, 127.53, 127.49, 127.19, 103.41 (C-1$^{Glc\text{-}B}$), 101.51 (C-1$^{Glc\text{-}A}$), 100.16 (C-1^{Gal}), 82.59, 81.69, 81.54, 76.12, 75.38, 74.88, 74.34, 73.50, 73.38, 73.32, 72.47, 71.59, 71.15, 70.60, 69.39, 68.62, 68.20, 68.03, 67.85, 62.77, 50.88, 26.50. HR ESI-TOF MS (m/z): calcd for $C_{83}H_{79}N_3O_{21}Na$ $[M + Na]^+$, 1476.5104; found, 1476.5099.

2-Azidoethyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-[(2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl)-(1→4)]-(2-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17):

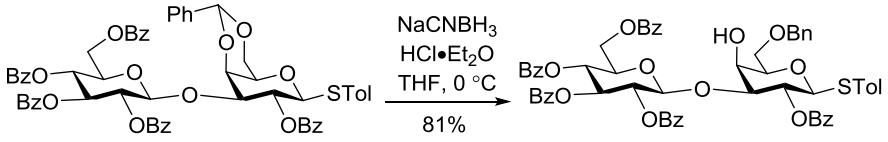


After a mixture of **7** (25.0 mg, 0.037 mmol), **17** (49.3 mg, 0.034 mmol), and freshly activated MS 4 Å in anhydrous diethyl ether (5 mL) was stirred at room temperature for 40 min, it was cooled

to −78 °C. Then, a solution of AgOTf (9.5 mg, 0.037 mmol) in diethyl ether (0.5 mL) was added. Fifteen minutes later, *p*-TolSCl (5.3 μL, 0.037 mmol) was added through a microsyringe. The reaction mixture was allowed to warm up slowly to room temperature within 1 h and stirred for another 20 min. The reaction was quenched with Et_3N, and the mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated under vacuum, and the residue was purified by silica gel column chromatography with EtOAc and hexanes (1:3) as the eluent to give **17** (60.5 mg, 89%) as a foamy solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 – 7.98 (d, J = 8.4 Hz, 2H, Ph), 7.91 (d, J = 8.4 Hz, 2H, Ph), 7.68 (d, J = 8.4 Hz, 2H, Ph), 7.52 – 7.45 (m, 4H, Ph), 7.41 – 7.17 (m, 40H, Ph), 7.17 – 7.04 (m, 8H, Ph), 6.96 (t, J = 8.0 Hz, 2H, Ph), 5.89 (t, J = 9.6 Hz, 1H, H-3$^{Glc\text{-}A}$), 5.61 (t, J = 9.8 Hz, 1H, H-4$^{Glc\text{-}A}$), 5.44 (dd, J = 9.6, 7.8 Hz, 1H, H-2$^{Glc\text{-}A}$), 5.33 (dd, J = 10.2, 7.8 Hz, 1H, H-2^{Gal}), 5.19 (d, J = 3.0 Hz, 1H, H-1$^{Glc\text{-}C}$), 5.10 (d, J = 11.4 Hz, 1H, Bn), 5.08 (d, J = 7.8 Hz, 1H, H-1$^{Glc\text{-}A}$), 4.90 (d, J = 11.4 Hz, 1H, Bn), 4.85 (d, J = 11.4 Hz, 1H, Bn), 4.78 (d, J = 10.8 Hz, 1H, Bn), 4.72 (d, J = 11.4 Hz, 1H, Bn), 4.70 (d, J = 8.4 Hz, 1H, H-1^{Gal}), 4.67 (dd, J = 12.6, 3.0 Hz, 1H, H-6a$^{Glc\text{-}A}$), 4.65 – 4.58 (m, 3H, Bn), 4.56 (d, J = 10.8 Hz, 2H, Bn), 4.54 (dd, J = 12.6, 6.0 Hz, 1H, H-6b$^{Glc\text{-}A}$), 4.46 (d, J = 12.6 Hz, 1H, Bn), 4.31 (d, J = 2.4 Hz, 1H, H-4^{Gal}), 4.26 (m, 2H, H-6a$^{Glc\text{-}C}$, 6b$^{Glc\text{-}C}$), 4.22 (d, J = 7.8 Hz, 1H, H-1$^{Glc\text{-}B}$), 4.21 – 4.16 (m, 3H, Bn, H-5$^{Glc\text{-}A}$), 4.13 (d, J = 9.6 Hz, 1H, H-5$^{Glc\text{-}C}$), 4.01 – 4.04 (m, 2H, Bn, H-3$^{Glc\text{-}C}$), 3.92 – 3.80 (m, 4H, H-4$^{Glc\text{-}C}$, H-4$^{Glc\text{-}B}$, H-6a^{Gal}, -OCH_2CH$_2$-), 3.72 (dd, J = 10.2, 6.6 Hz, 1H, H-6b^{Gal}), 3.67 (d, J = 10.2 Hz, 1H, H-3^{Gal}), 3.58 – 3.52 (m, 3H, H-5^{Gal}, H-3$^{Glc\text{-}B}$, -OCH_2CH$_2$-), 3.44 (dd, J = 9.6, 3.0 Hz, 1H, H-2$^{Glc\text{-}C}$), 3.41 – 3.28 (m, 5H, H-6a,6b$^{Glc\text{-}B}$, H-2$^{Glc\text{-}B}$, -CH$_2$CH_2N$_3$), 3.13 – 3.08 (m, 1H, H-5$^{Glc\text{-}B}$), 0.97 (s, 9H, -*t*Bu), 0.21 (s, 3H, -SiCH$_3$), 0.19 (s, 3H, -SiCH$_3$). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.96, 165.66, 165.16, 164.22, 163.98, 139.38, 139.36, 138.99, 138.62, 138.58, 138.52, 138.38, 133.50, 133.45, 133.17, 132.52, 132.27, 129.84, 129.64, 129.62, 129.29, 129.20, 128.86, 128.69, 128.64, 128.42, 128.33, 128.25, 128.22, 128.18, 128.16, 128.14, 128.12, 128.05, 128.03, 127.92, 127.89, 127.79, 127.70, 127.61, 127.58, 127.43, 127.39, 127.33, 127.28, 127.11, 126.92, 103.28 (C-1$^{Glc\text{-}B}$), 102.97 (C-1$^{Glc\text{-}A}$), 100.73 (C-1^{Gal}), 100.22 (C-1$^{Glc\text{-}C}$), 82.26, 81.81, 81.69, 81.66, 81.53, 79.44, 77.68, 76.89, 75.51, 74.93, 74.79, 74.74, 74.50, 74.22, 73.47, 73.17, 72.94, 72.84, 72.40,

72.33, 72.24, 71.51, 69.66, 69.60, 68.03, 67.98, 62.98, 62.06, 50.88, 26.17, 18.48, -4.67, -5.08. HR ESI-TOF MS (m/z): calcd for $C_{116}H_{121}N_3O_{26}SiNa$ $[M + Na]^+$, 2022.7905; found, 2022.7841.

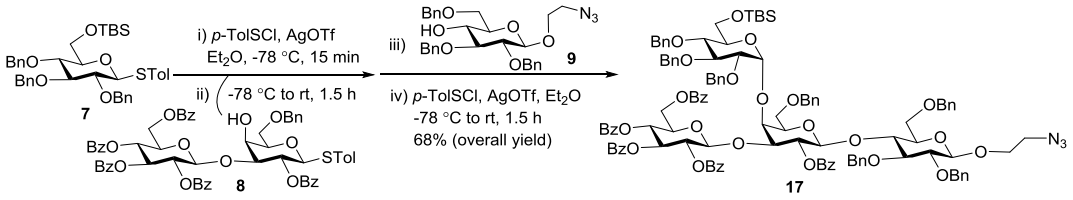
***p*-Tolyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzoyl-6-*O*-benzyl-1-thio-β-D-glucopyranoside (8):**



14 **8**

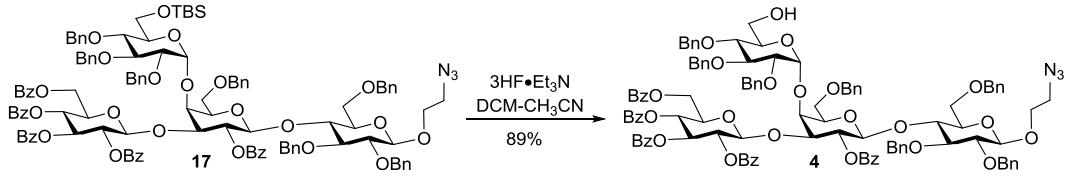
To a stirred mixture of **14** (220 mg, 0.208 mmol), sodium cyanoborohydride (196 mg, 3.125 mmol), and MS 4 Å in THF was added $HCl{\cdot}Et_2O$ (1 M) slowly at 0 °C until pH reached 2-3. Three hours later, the reaction was quenched with aq. $NaHCO_3$, and the solid materials were filtered off and washed with CH_2Cl_2. The combined organic phase was dried and concentrated, and the residue was purified by column chromatography with EtOAc and hexanes (1:2) as the eluent to obtain **8** (179 mg, 81%) as a foamy solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (d, J = 7.2 Hz, 2H, Ph), 7.88 (d, J = 7.2 Hz, 2H, Ph), 7.70 (d, J = 7.2 Hz, 2H, Ph), 7.66 (d, J = 7.2 Hz, 2H, Ph), 7.54 (t, J = 7.5 Hz, 1H, Ph), 7.48 – 7.26 (m, 17H, Ph), 7.22 – 7.17 (m, 4H, Ph), 7.08 (t, J = 7.5 Hz, 2H, Ph), 6.96 (d, J = 7.8 Hz, 2H, Ph), 5.79 (t, J = 9.6 Hz, 1H, H-3^{Glc}), 5.57 (t, J = 9.6 Hz, 1H, H-4^{Glc}), 5.49 (t, J = 9.6 Hz, 1H, H-2^{Glc}), 5.46 (t, J = 9.6 Hz, 1H, H-2^{Gal}), 5.00 (d, J = 7.8 Hz, 1H, H-1^{Glc}), 4.69 – 4.65 (m, 2H, H-6a^{Glc}, H-1^{Gal}), 4.53 – 4.47 (m, 2H, Ph-CH_2), 4.44 (dd, J = 12.0, 6.0 Hz, 1H, H-6b^{Glc}), 4.22 (s, 1H, H-4^{Gal}), 4.17 – 4.12 (m, 1H, H-5^{Glc}), 3.94 (dd, J = 9.6, 3.0 Hz, 1H, H-3^{Gal}), 3.78 (dd, J = 9.6, 3.0 Hz, 1H, H-6a^{Gal}), 3.71 – 3.63 (m, 2H, H-6b^{Gal}, H-5^{Gal}), 2.85 (s, 1H, -OH), 2.25 (s, 3H, Ph-CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 166.05, 165.65, 165.11, 164.68, 164.63, 138.20, 137.70, 133.55, 133.39, 133.24, 132.74, 132.71, 132.60, 129.82, 129.78, 129.62, 129.53, 129.50, 129.47, 129.44, 129.30, 128.58, 128.53, 128.43, 128.36, 128.24, 128.14, 128.03, 127.69, 127.62, 101.40 (C-1^{Glc}), 87.08 (C-1^{Gal}), 82.32, 77.67, 73.56, 72.51, 72.49, 71.59, 69.72, 69.38, 69.14, 68.85, 62.73, 21.09. HR ESI-TOF MS (m/z): calcd for $C_{61}H_{54}O_{15}SNa$ $[M + Na]^+$, 1081.3081; found, 1081.3073.

Preactivation-based one-pot synthesis of 17:



After the mixture of **7** (100 mg, 0.149 mmol) and freshly activated MS 4 Å in anhydrous diethyl ether (20 mL) was stirred at room temperature for 40 min and then cooled to -78 °C, a solution of AgOTf (38 mg, 0.149 mmol) in diethyl ether (1 mL) was added. The mixture was stirred for 10 min, and *p*-TolSCl (22 μL, 0.149 mmol) was added through a microsyringe. Fifteen minutes later, a solution of **8** (143 mg, 0.135 mmol) in anhydrous diethyl ether (2 mL) was added. The reaction was allowed to warm up slowly to room temperature in 1 h, and stirred for another 20 min, before it was cooled to -78 °C. Then, **9** (64 mg, 0.123 mmol) in anhydrous diethyl ether (1 mL), AgOTf (95 mg, 0.369 mmol) in diethyl ether (1 mL), and *p*-TolSCl (18 μL, 0.123 mmol) were added sequentially. The reaction was allowed to warm up slowly to room temperature in 1 h and stirred for another 20 min before it was quenched with Et_3N, diluted with diethyl ether, and then filtered. The filtrate was concentrated under vacuum, and the residue was purified by silica gel column chromatography with EtOAc and hexanes (1:3) as the eluent to produce **17** (167 mg, 68% overall yield for two steps) as a foamy solid. Its spectrometric data were identical to those described above.

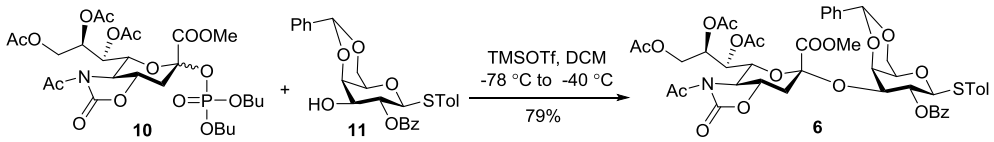
2-Azidoethyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-[(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)]-2-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (4):



To the solution of **17** (140 mg, 0.070 mmol) in CH_2Cl_2 and CH_3CN (V/V, 1:1, 3 mL) was added trimethylamine trihydrofluoride (1 mL). The mixture was stirred at room temperature overnight, and quenched with saturated aq. $NaHCO_3$ solution. The water phase was extracted with CH_2Cl_2

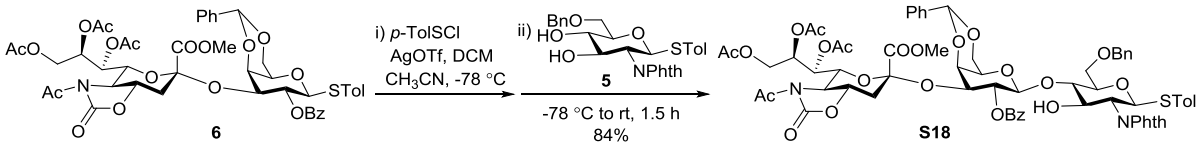
(3 × 40 mL), and the organic layers were combined, dried, and concentrated under vacuum. The residue was purified by silica gel column chromatography with EtOAc and hexanes (1:3) as the eluent to give **4** (117 mg, 89%) as syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.92 (d, J = 8.4 Hz, 2H, Ph), 7.90 (d, J = 7.8 Hz, 2H, Ph), 7.70 (d, J = 8.4 Hz, 2H, Ph), 7.52 – 7.47 (m, 3H, Ph), 7.45 – 7.41 (m, 1H, Ph), 7.37 – 7.33 (m, 4H, Ph), 7.32 – 7.23 (m, 25H, Ph), 7.22 – 7.16 (m, 16H, Ph), 7.11 (t, J = 7.8 Hz, 2H, Ph), 7.08 – 7.04 (m, 3H, Ph), 5.81 (t, J = 9.6 Hz, 1H, H-3$^{Glc\text{-}A}$), 5.62 – 5.56 (m, 2H, H-2,4$^{Glc\text{-}A}$), 5.37 (d, J = 3.6 Hz, 1H, H-1$^{Glc\text{-}C}$), 5.29 (dd, J = 10.2, 7.8 Hz, 1H, H-2^{Gal}), 5.13 (d, J = 11.4 Hz, 1H, Bn), 4.84 (d, J = 11.4 Hz, 1H, Bn), 4.81 (d, J = 7.8 Hz, 1H, H-1$^{Glc\text{-}A}$), 4.77 (d, J = 11.4 Hz, 1H, Bn), 4.73 – 4.57 (m, 9H, H-1^{Gal}, H-6a$^{Glc\text{-}A}$, Bn), 4.54 (dd, J = 12.0, 6.6 Hz, 1H, H-6b$^{Glc\text{-}A}$), 4.43 (d, J = 12.0 Hz, 1H, Bn), 4.27 (d, J = 12.0 Hz, 1H, Bn), 4.22 – 4.19 (m, 2H, H-1$^{Glc\text{-}B}$, H-4^{Gal}), 4.19 – 4.15 (m, 1H, H-5$^{Glc\text{-}A}$), 4.14 – 4.11 (m, 2H, Bn), 4.00 (dt, J = 9.6, 3.6 Hz, 1H, H-5$^{Glc\text{-}C}$), 3.96 (d, J = 12.0 Hz, 1H, H-6a$^{Glc\text{-}C}$), 3.89 – 3.85 (m, 2H, H-3$^{Glc\text{-}C}$, -OCH_2CH$_2$-), 3.83 – 3.75 (m, 3H, H-4$^{Glc\text{-}B}$, H-6b$^{Glc\text{-}C}$, H-6a^{Gal}), 3.68 – 3.62 (m, 2H, H-6b^{Gal}, H-3^{Gal}), 3.59 – 3.49 (m, 5H, H-2$^{Glc\text{-}C}$, H-3$^{Glc\text{-}B}$, H-4$^{Glc\text{-}C}$, H-5^{Gal}, -OCH_2CH$_2$-), 3.40 – 3.27 (m, 5H, H-2$^{Glc\text{-}B}$, H-6a,6b$^{Glc\text{-}B}$, -CH$_2$CH_2N$_3$), 3.13 (s, 1H, -OH), 3.08 (d, J = 9.6 Hz, 1H, H-5$^{Glc\text{-}B}$). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 165.88, 165.76, 165.39, 165.20, 163.92, 139.61, 138.92, 138.67, 138.52, 138.46, 138.41, 138.35, 133.59, 133.47, 133.32, 132.67, 132.58, 129.83, 129.60, 129.54, 129.24, 129.14, 129.08, 128.67, 128.62, 128.52, 128.46, 128.39, 128.31, 128.23, 128.19, 128.18, 128.14, 128.10, 127.97, 127.95, 127.90, 127.77, 127.59, 127.55, 127.43, 127.39, 127.32, 126.74, 103.29 (C-1$^{Glc\text{-}B}$), 102.51 (C-1$^{Glc\text{-}A}$), 100.46 (C-1^{Gal}), 98.74 (C-1$^{Glc\text{-}C}$), 82.73, 82.13, 81.62, 81.15, 80.80, 78.71, 78.15, 75.55, 74.84, 74.81, 74.80, 74.66, 74.15, 73.26, 73.20, 72.60, 72.48, 72.29, 71.47, 71.36, 70.11, 69.70, 68.00, 67.89, 63.07, 61.51, 50.87. HR ESI-TOF MS (m/z): calcd for $C_{110}H_{107}N_3O_{26}Na$ $[M + Na]^+$, 1908.7041; found, 1908.7002.

***p*-Tolyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (6):**



The mixture of **10** (190 mg, 0.285 mmol), **11** (91 mg, 0.190 mmol), and freshly activated MS 4 Å in anhydrous CH_2Cl_2 (5 mL) was stirred under a N_2 atmosphere at room temperature for 3 h and then cooled to -78 °C. TMSOTf (51 μL, 0.285 mmol) was added dropwise using a microsyringe. The reaction mixture was allowed to warm up slowly to -40 °C in 1 h, stirred under the condition for another 20 min, quenched with Et_3N (53 μL, 0.38 mmol), and then filtered. The filtrate was concentrated under vacuum, and the residue was purified by silica gel column chromatography with EtOAc and toluene (1:3) as the eluent to give **6** (140 mg, 79%) as syrup ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.14 – 8.11 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 – 7.44 (m, 4H), 7.40 – 7.32 (m, 5H), 7.03 (d, J = 8.4 Hz, 2H), 5.55 – 5.49 (m, 2H), 5.34 (t, J = 9.6 Hz, 1H), 5.32 (s, 1H), 4.91 (d, J = 9.6 Hz, 1H), 4.57 (dd, J = 9.6, 3.4 Hz, 1H), 4.46 – 4.41 (m, 2H), 4.34 (d, J = 12.0 Hz, 1H), 4.12 (d, J = 12.0 Hz, 1H), 4.07 (d, J = 3.6 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.73 – 3.66 (m, 2H), 3.49 (dd, J = 10.8, 9.6 Hz, 1H), 3.43 (s, 3H), 2.88 (dd, J = 12.0, 3.0 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 2.17 (s, 3H), 2.02 (s, 3H), 1.78 (s, 3H), 1.72 (t, J = 12.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 171.94, 170.90, 170.41, 170.08, 168.66, 164.85, 153.38, 138.15, 137.76, 134.53, 133.09, 130.41, 129.90, 129.40, 129.04, 129.01, 128.93, 128.56, 128.55, 128.43, 128.20, 128.05, 127.18, 126.63, 125.27, 100.87, 96.73, 85.00, 74.92, 74.87, 73.81, 72.86, 71.41, 69.41, 69.19, 68.23, 67.96, 63.73, 58.77, 52.82, 37.00, 24.61, 21.38, 21.26, 20.84, 20.54. (These data agree well with that reported in the literature: C. Hsu, K. Chu, Y. Lin, J. Han, Y. Peng, C. Ren, C. Wu, and C.H. Wong, *Chem. Eur. J.* **2010**, 16, 1754-1760)

_p_-Tolyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (S18):

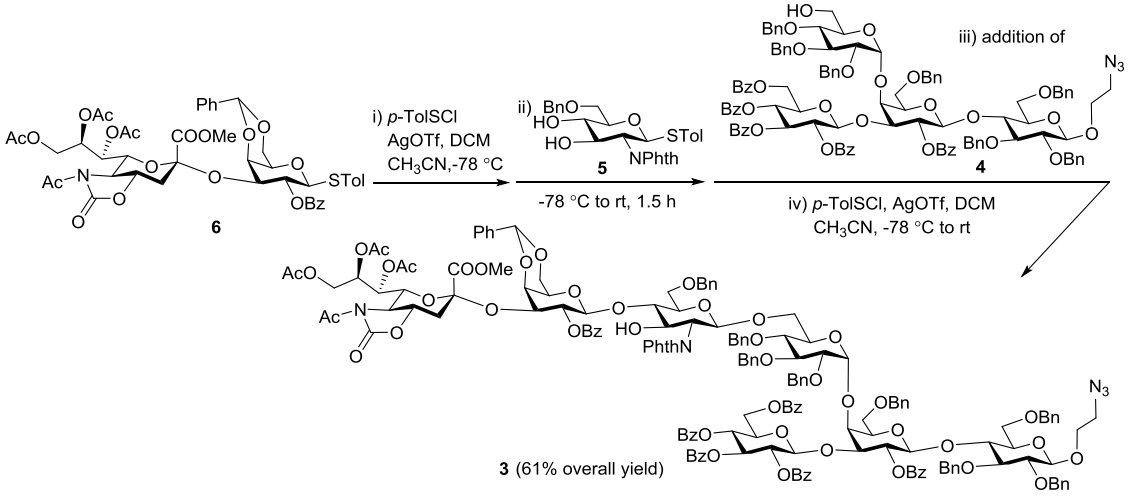


A mixture of **6** (30.0 mg, 0.032 mmol) and freshly activated MS 4 Å in anhydrous CH_2Cl_2 (3 mL) was stirred at room temperature for 40 min and then cooled to -78 °C. A solution of AgOTf (24.7

mg, 0.096 mmol) in acetonitrile (0.5 mL) was added. After 10 min of stirring, *p*-TolSCl (4.6 μL, 0.032 mmol) was added through a microsyringe. Fifteen minutes later, a solution of **5** (14.7 mg, 0.029 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added. The reaction mixture was allowed to warm up slowly to room temperature in 1 h and stirred for another 20 min. The reaction was then quenched with Et_3N, diluted with CH_2Cl_2, and filtered. The filtrate was concentrated in vacuum, and the residue was purified by silica gel column chromatography with EtOAc and toluene (1:3) as the eluent to give **S18** (32.1 mg, 84%) as syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.13 (d, J = 7.8 Hz, 2H, Ph), 7.88 – 7.67 (m, 4H, Ph), 7.60 (t, J = 6.9 Hz, 1H, Ph), 7.47 – 7.42 (t, J = 7.1 Hz, 4H, Ph), 7.34 – 7.25 (m, 7H, Ph), 7.17 – 7.15 (m, 3H, Ph), 6.91 (d, J = 7.8 Hz, 2H, Ph), 5.58 – 5.48 (m, 4H, H-2^{Gal}, H-1^{GlcN}, H-7^{NeuAc}, H-8^{NeuAc}), 5.32 (s, 1H, PhC*H*-), 4.80 (d, J = 7.8 Hz, 1H, H-1^{Gal}), 4.53 (dd, J = 10.2, 3.0 Hz, 1H, H-3^{Gal}), 4.47 – 4.40 (m, 3H, H-3^{GlcN}, H-6^{NeuAc}, H-9^{NeuAc}), 4.24 – 4.10 (m, 6H, H-4^{Gal}, H-5^{Gal}, H-6a^{Gal}, H-2^{GlcN}, Ph-CH_2-), 3.98 (dd, J = 12.0, 7.8 Hz, 1H, H-9^{NeuAc}), 3.74 – 3.59 (m, 4H, H-4^{NeuAc}, H-4^{GlcN}, H-5^{GlcN}, H-6a^{Gal}), 3.56 – 3.47 (m, 3H, H-5^{NeuAc}, H-6a,6b^{GlcN}), 3.36 (s, 3H, -COOCH_3), 2.90 (dd, J = 12.0, 2.4 Hz, 1H, H-3eq^{NeuAc}), 2.43 (s, 3H, -OAc), 2.22 (s, 3H, Ph-CH_3), 2.16 (s, 3H, -OAc), 1.99 (s, 3H, -OAc), 1.94 (s, 3H, -OAc), 1.70 (t, J = 12.6 Hz, 1H, H-3ax^{NeuAc}). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 172.13, 171.00, 170.38, 170.04, 168.46, 167.99, 167.75, 164.78, 153.34, 138.50, 137.92, 137.47, 133.97, 133.91, 133.44, 133.20, 131.85, 131.73, 129.89, 129.82, 129.47, 129.01, 128.59, 128.18, 128.14, 128.11, 127.34, 127.31, 126.38, 123.61, 123.25, 101.52 (C-1^{Gal}), 100.57 (Ph-*C*H-), 96.81, 83.29 (C-1^{GlcN}), 82.05, 78.00, 75.03, 74.79, 72.84, 72.40, 72.13, 71.51, 71.05, 70.07, 68.60, 68.34, 67.76, 66.40, 64.00, 58.77, 55.11, 52.91, 37.18, 24.64, 21.34, 21.06, 20.84, 20.81. HR ESI-TOF MS (m/z): calcd for $C_{67}H_{68}N_2O_{24}SNa$ $[M + Na]^+$, 1339.3780; found, 1339.3838.

Preactivation-based one-pot synthesis of fully protected heptasaccharide 3: 2-Azidoethyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-3,5-dideoxy-D-glycero-α-D- galacto-non-2-ulopyranosylonate)-(2→3)-(2-*O*-benzoyl- 4,6-benzylidene-β-D-galactopyranosyl)-(1→4)-(6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)- (2,3,4-tri-*O*-benzyl-α-D-

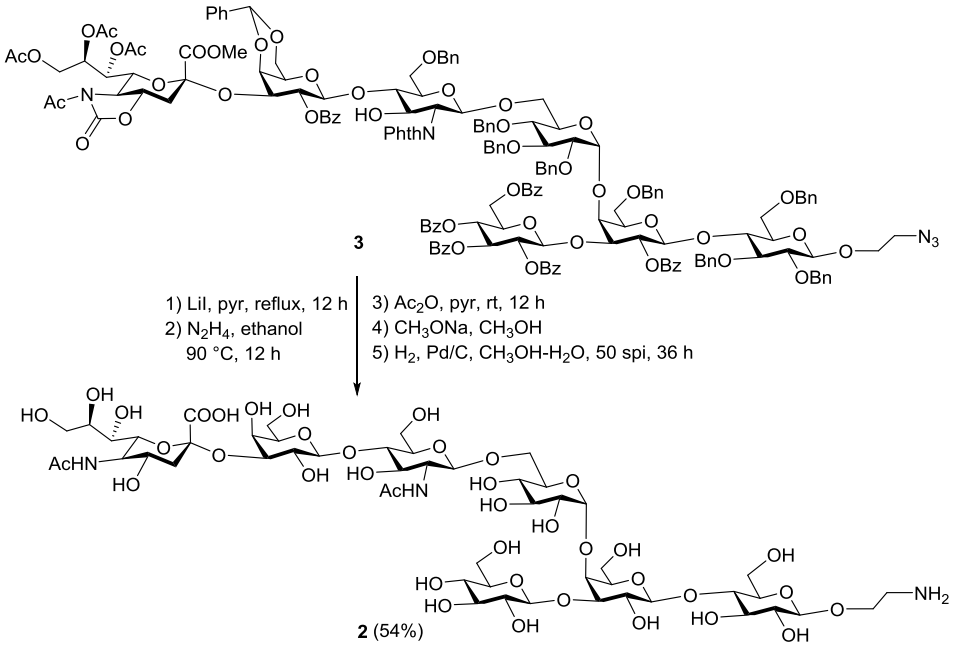
glucopyranosyl)-(1→4)-[(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)]-2-*O*-benzoyl-6-*O*-benzyl-β-D-galactopyranosyl}-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside



A mixture of **6** (60.0 mg, 0.064 mmol) and freshly activated MS 4 Å in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 40 min and then cooled to -78 °C. A solution of AgOTf (49.5 mg, 0.193 mmol) in anhydrous acetonitrile (0.5 mL) was added, and the mixture was stirred for 10 min. Thereafter, *p*-TolSCl (9.3 μL, 0.064 mmol) was added through a microsyringe, and 15 min later, a solution of **5** (29.5 mg, 0.058 mmol) in anhydrous CH_2Cl_2 (1 mL) was added. The reaction was allowed to warm up slowly to room temperature in 1 h, stirred for another 20 min, and then cooled to -78 °C. This was followed by sequential addition of **4** (100.0 mg, 0.053 mmol) in anhydrous CH_2Cl_2 (1 mL), AgOTf (44.9 mg, 0.175 mmol) in CH_3CN (0.5 mL), and *p*-TolSCl (8.4 μL, 0.058 mmol). The reaction mixture was allowed to warm up slowly to room temperature in 1 h, stirred for another 20 min, and then quenched with Et_3N, diluted with CH_2Cl_2, and filtered. The filtrate was concentrated under vacuum, and the residue was purified by silica gel column chromatography with EtOAc and toluene (1:2) as the eluent to provide **3** (99.5 mg, 61% overall yield) as a foamy solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.93 (d, J = 7.2 Hz, 2H, Ph), 7.87 (d, J = 7.8 Hz, 2H, Ph), 7.85 (d, J = 7.8 Hz, 2H, Ph), 7.71 (d, J = 7.8 Hz, 1H, Ph), 7.61 (d, J = 7.8 Hz, 2H, Ph), 7.52 (t, J = 7.5 Hz, 1H, Ph), 7.48 – 7.25 (m, 22H, Ph), 7.24 – 7.07 (m, 38H, Ph), 7.02 – 6.98 (m, 5H, Ph), 6.95 – 6.91 (t, J = 7.2 Hz, 4H, Ph), 5.71 (t, J = 9.6 Hz, 1H, H-3$^{Glc\text{-}A}$), 5.55 – 5.44 (m, 4H, H-7^{NeuAc}, H-8^{NeuAc}, H-4$^{Glc\text{-}A}$, H-2$^{Gal\text{-}B}$), 5.38 – 5.35 (m, 2H, H-2$^{Glc\text{-}A}$, H-1^{GlcN}), 5.33

(s, 1H, Ph-C*H*-), 5.30 (dd, *J* = 9.6, 8.4 Hz, 1H, H-2^{Gal-A}), 4.95 (d, *J* = 11.4 Hz, 1H, Bn), 4.88 (d, *J* = 3.0 Hz, 1H, H-1^{Glc-C}), 4.87 (d, *J* = 8.4 Hz, 1H, H-1^{Glc-A}), 4.83 (d, *J* = 8.4 Hz, 1H, H-1^{Gal-B}), 4.71 (d, *J* = 11.4 Hz, 1H, Bn), 4.65 (d, *J* = 12.0 Hz, 1H, Bn), 4.58 (d, *J* = 7.8 Hz, 1H, H-1^{Gal-A}), 4.55 – 4.50 (m, 2H, H-3^{GlcN}, Bn), 4.46 – 4.31 (m, 13H, H-6^{NeuAc}, H-9^{NeuAc}, H-6b^{Glc-A}, H-3^{Gal-B}, H-2^{GlcN}, Bn), 4.26 – 4.06 (m, 14H, H-1^{Glc-B}, H-4^{Gal-B}, H-4^{Gal-A}, H-6a^{Glc-A}), 4.03 – 3.96 (m, 2H, H-9^{NeuAc}, H-5^{Glc-A}), 3.89 – 3.81 (m, 4H, H-4^{GlcN}, H-3^{Glc-C}, H-5^{GlcN}, -OCH_2-), 3.76 (t, *J* = 9.3 Hz, 1H, H-4^{Glc-B}), 3.73 – 3.67 (m, 3H, H-4^{NeuAc}), 3.65 (dd, *J* = 9.6, 2.4 Hz, 1H, $^{H-3Gal-A}$), 3.60 – 3.42 (m, 8H, H-5^{NeuAc}, H-3^{Glc-B}, -OCH_2-, H-6a,6b^{GlcN}), 3.36 – 3.31 (m, 5H, -COOCH_3, -CH_2-N_3, H-6a^{Glc-B}), 3.29 – 3.20 (m, 4H, H-6b^{Glc-B}, H-2^{Glc-C}, H-2^{Glc-B}, -CH_2-N_3), 3.01 (d, *J* = 10.2 Hz, 1H, H-5^{Glc-B}), 2.84 (dd, *J* = 12.0, 3.0 Hz, 1H, H-3eq^{NeuAc}), 2.43 (s, 3H, -OAc), 2.15 (s, 3H, -OAc), 1.97 (s, 3H, -OAc), 1.90 (s, 3H, -OAc), 1.63 (d, *J* = 12.6 Hz, 1H, H-3ax^{NeuAc}). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 172.02, 170.87, 170.21, 169.93, 168.36, 168.25, 168.00, 165.96, 165.71, 164.90, 164.83, 164.40, 163.86, 153.36, 139.18, 139.01, 138.83, 138.51, 138.47, 138.31, 137.60, 133.52, 133.36, 133.28, 133.23, 133.02, 132.62, 132.24, 131.59, 131.57, 129.83, 129.66, 129.58, 129.51, 129.48, 129.32, 129.21, 128.92, 128.83, 128.51, 128.46, 128.36, 128.28, 128.22, 128.17, 128.06, 127.98, 127.92, 127.85, 127.84, 127.79, 127.74, 127.56, 127.48, 127.43, 127.35, 127.29, 127.19, 126.99, 126.92, 126.82, 126.73, 126.45, 123.34, 123.04, 103.23 (C-1^{Glc-B}), 102.35 (C-1^{Glc-A}), 101.45 (C-1^{Gal-B}), 100.75 (C-1^{Gal-A}), 100.53 (Ph-*C*H-), 99.21 (C-1^{Glc-C}), 98.48 (C-1^{GlcN}), 96.88, 81.92, 81.52, 81.21, 80.30, 79.60, 77.42, 77.09, 76.86, 75.01, 74.79, 74.72, 74.67, 74.42, 74.24, 74.21, 73.66, 73.28, 73.14, 72.96, 72.89, 72.68, 72.25, 72.09, 71.63, 71.40, 71.23, 70.20, 70.11, 69.70, 68.49, 68.43, 68.38, 68.19, 67.92, 66.37, 63.72, 63.19, 58.83, 56.13, 52.86, 50.83, 37.10, 24.63, 21.28, 20.77, 20.74. HR ESI-TOF MS (m/z): calcd for $C_{170}H_{167}N_5O_{50}Na_2$ $[M + 2Na]^{2+}$, 1562.0237; found, 1562.0254.

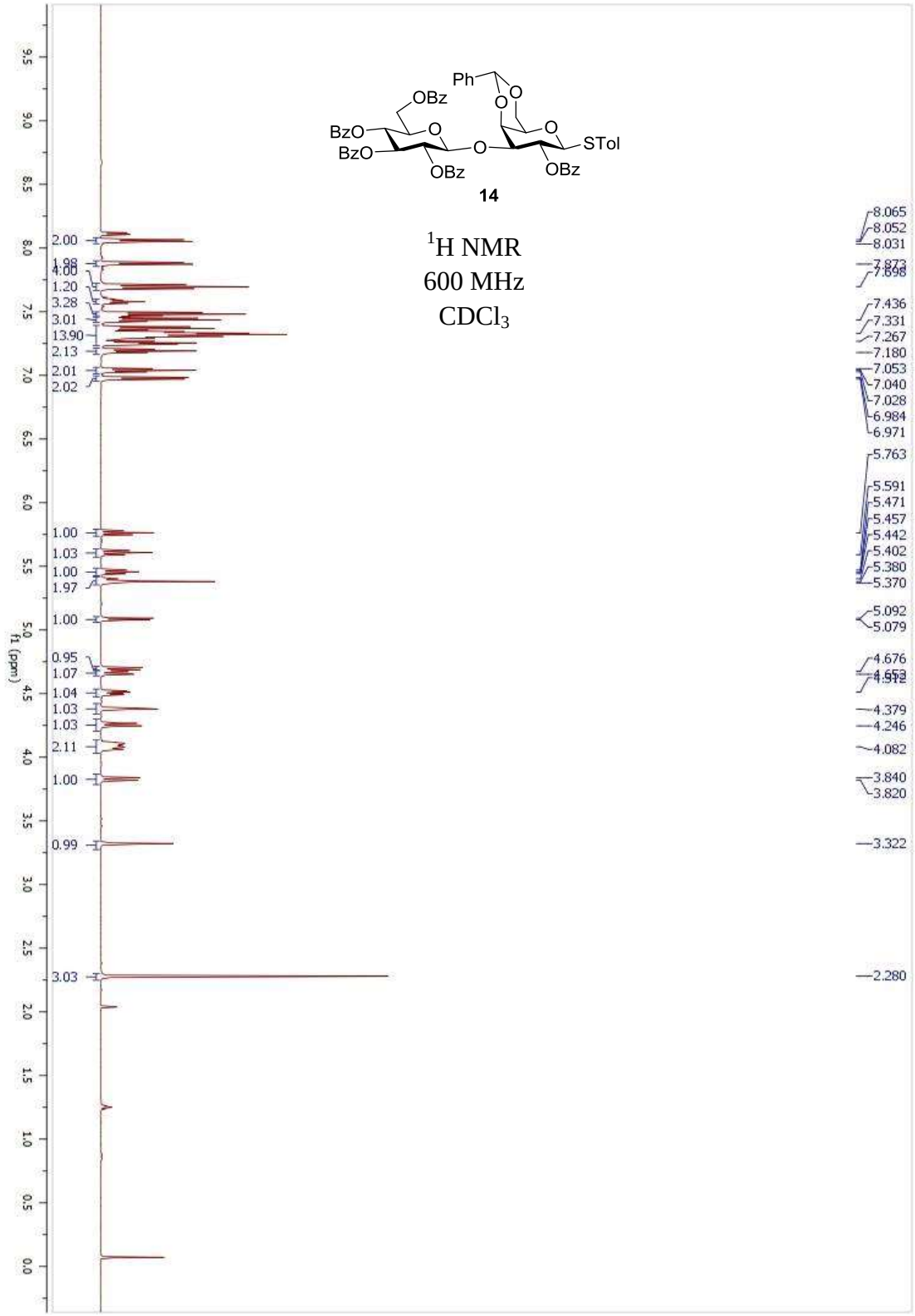
2-Aminoethyl (5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranosylonic acid)-(2→3)-β-D-galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-α-D-glucopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→3)]-β-D- galactopyranosyl-(1→4)-β-D-glucopyranoside (2):

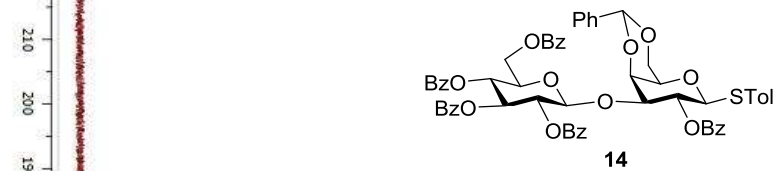


To a solution of **3** (50 mg, 0.016 mmol) in anhydrous pyridine (8 mL) was added lithium iodide (200 mg). The mixture was refluxed with stirring at 120 °C for 12 h under a N_2 atmosphere, and then concentrated and co-evaporated with toluene under vacuum. After the residue was dissolved in ethanol (5 mL), NH_2-NH_2·H_2O (1 mL) was added, and the mixture was stirred under refluxing for 12 h, at which time MALDI-MS indicated the completion of reaction. The reaction mixture was then concentrated and co-evaporated with toluene to afford a solid, which was dissolved in pyridine (5 mL) and Ac_2O (1 mL). After the solution was stirred at room temparature for 12 h, it was concentrated under vacuum. The residue was dissolved in CH_3OH, and to the solution was added CH_3ONa (1M in CH_3OH) until pH reached 10. The reaction mixture was stirred at room temperature for another 6 h, at which time MALDI-MS indicated the completion of reaction. The mixture was neutralized with Amberlyst 15 H^+ resin, filtered, and the filtrate was concentrated under vacuum. The residue was applied to a Sephadex LH-20 gel column for purification using CH_3OH as eluent to give a solid. The solid was dissolved in CH_3OH and H_2O (V/V = 4:1, 5 mL) and then mixed with Pd/C (10 mg). After the mixture was shaken under a H_2 atmosphere at 50 psi for 36 h, it was filtered. The filtrare was concentrated to give a residue, which was purified by a Sephadex G-15 gel column with H_2O as eluent to produce the synthetic target **2** (12 mg, 54% for five steps) as a white solid. ^{1}H NMR (600 MHz, D_2O) δ: 4.72 (d, J = 3.6 Hz, 1H), 4.45 (d, J =

7.8 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 8.4 Hz, 2H), 4.35 (d, *J* = 7.8 Hz, 1H), 4.16 (d, *J* = 10.8 Hz, 1H), 4.09 (s, 1H), 3.97-3.93 (m, 3H), 3.85 – 3.64 (m, 15H), 3.62 – 3.40 (m, 19H), 3.35 – 3.29 (m, 3H), 3.27 – 3.19 (m, 3H), 3.08 (t, *J* = 6.0 Hz, 1H), 2.99 (t, *J* = 8.4 Hz, 1H), 2.59 (dd, *J* = 12.2, 4.5 Hz, 1H), 1.89 (s, 3H), 1.86 (s, 3H), 1.63 (t, *J* = 12.0 Hz, 1H). ^{13}C NMR (150 MHz, D_2O) *δ*: 174.93, 174.41, 173.77, 104.55, 102.86, 102.46, 101.90, 101.40, 99.73, 99.05, 80.88, 79.87, 78.53, 78.02, 75.75, 75.61, 75.46, 75.41, 75.09, 74.71, 74.49, 74.27, 73.48, 72.81, 72.76, 72.49, 72.17, 71.68, 71.46, 71.43, 70.44, 70.01, 69.83, 69.31, 68.82, 68.26, 68.02, 67.39, 67.37, 66.99, 66.98, 62.50, 60.95, 60.85, 60.02, 59.98, 59.89, 54.97, 51.60, 39.56, 39.48, 22.15, 21.95. HR ESI-TOF MS (m/z): calcd for $C_{51}H_{87}N_3O_{39}Na$ $[M + Na]^+$, 1388.4814; found, 1388.4734.

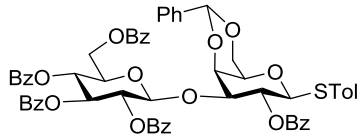
II. NMR and MS Spectra





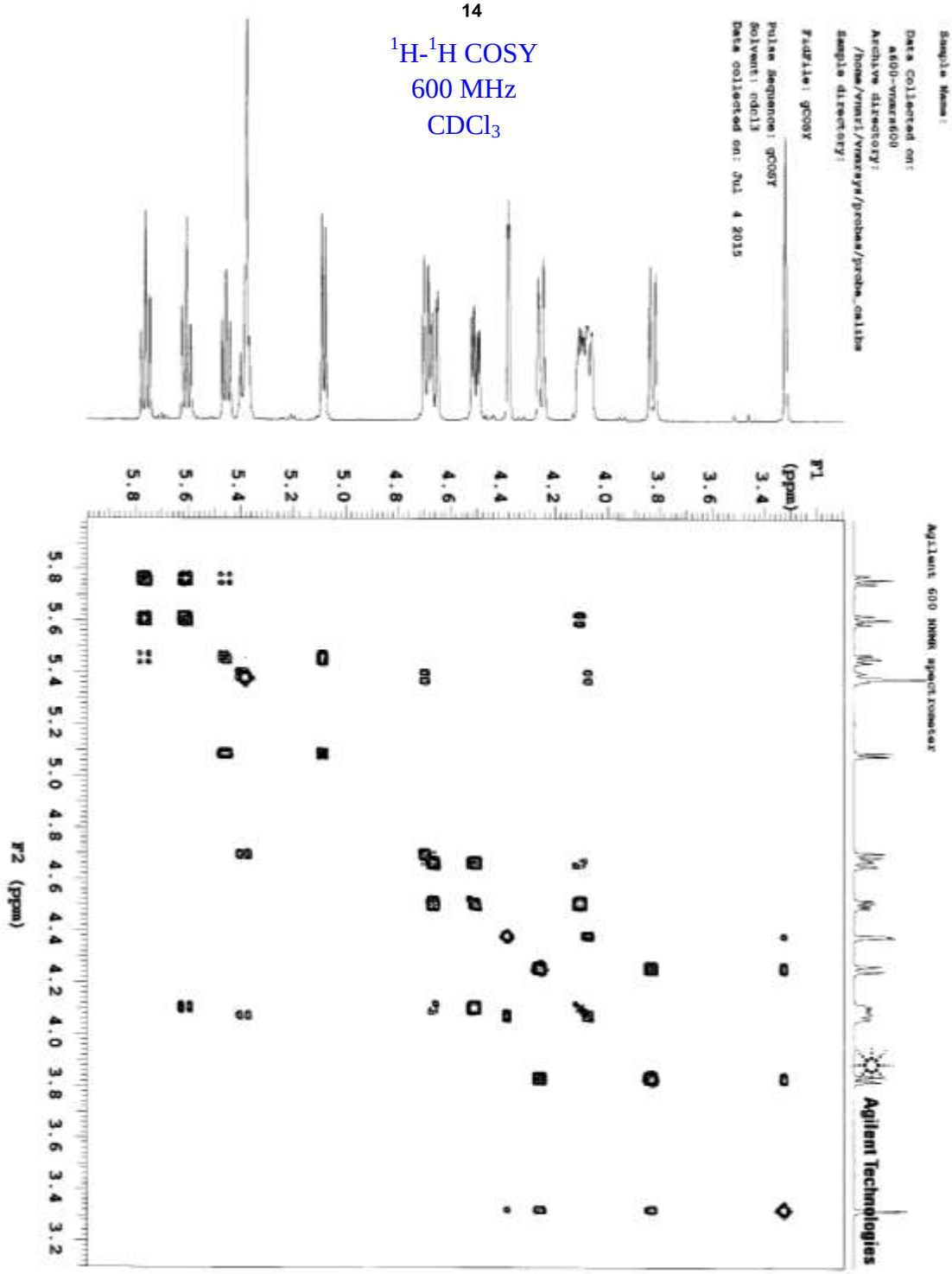
14

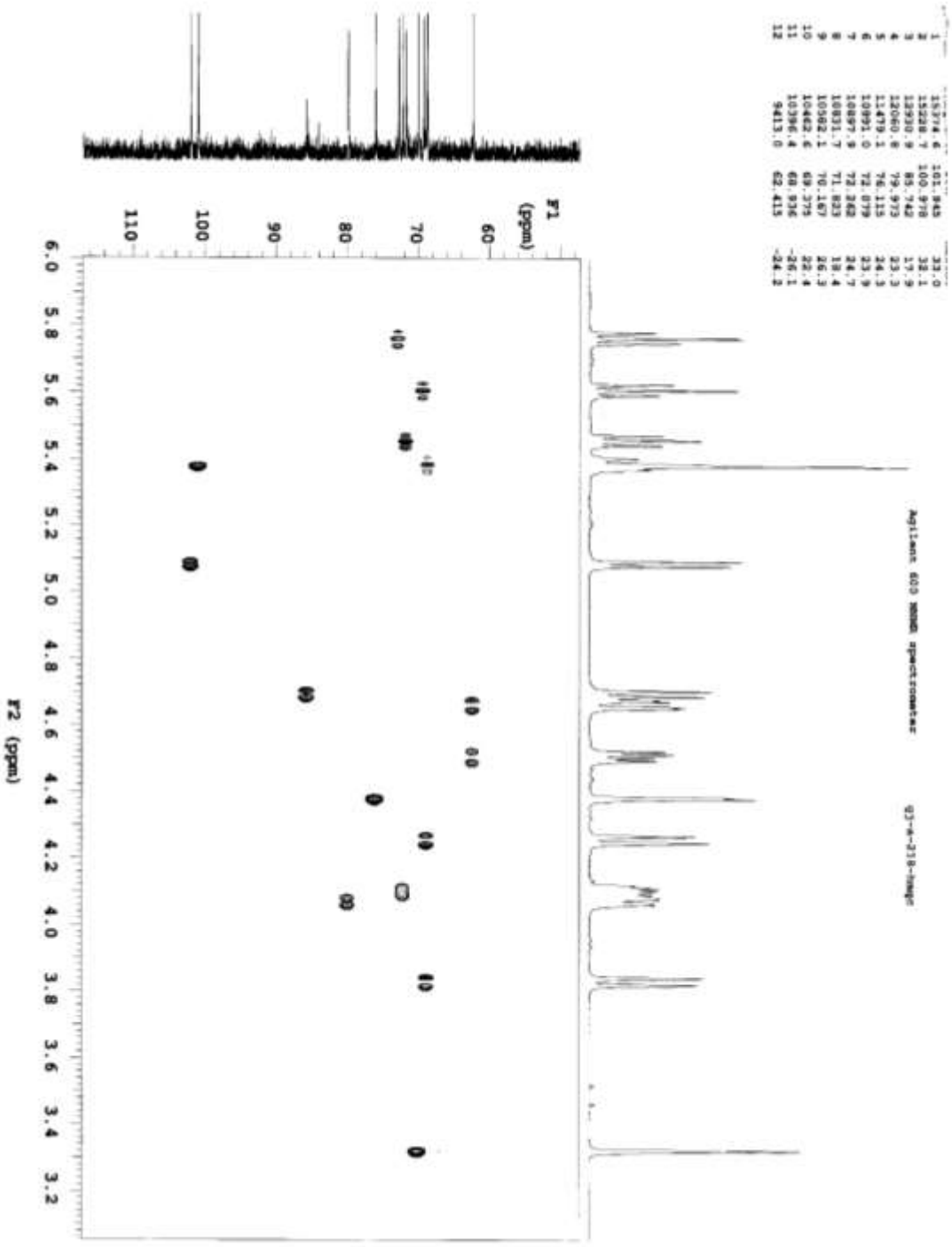
^{13}C NMR
600 MHz
$CDCl_3$

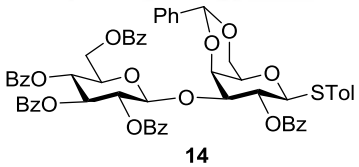


14

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$





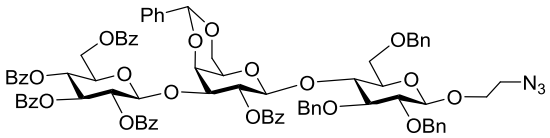


14

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

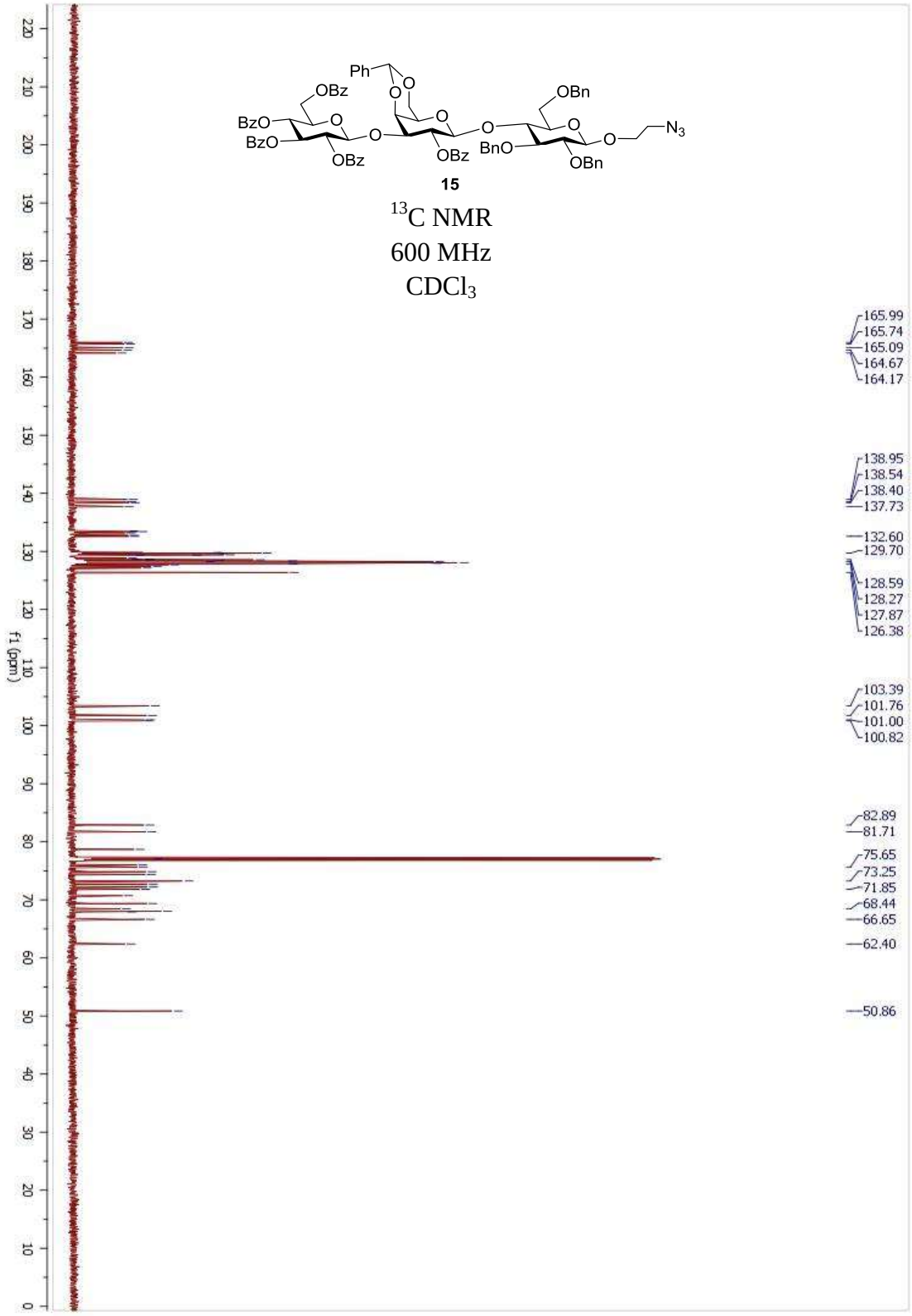
600/150 MHz

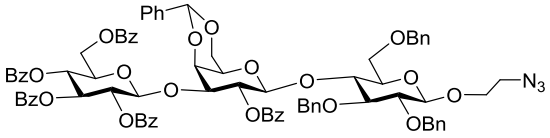
$CDCl_3$



15

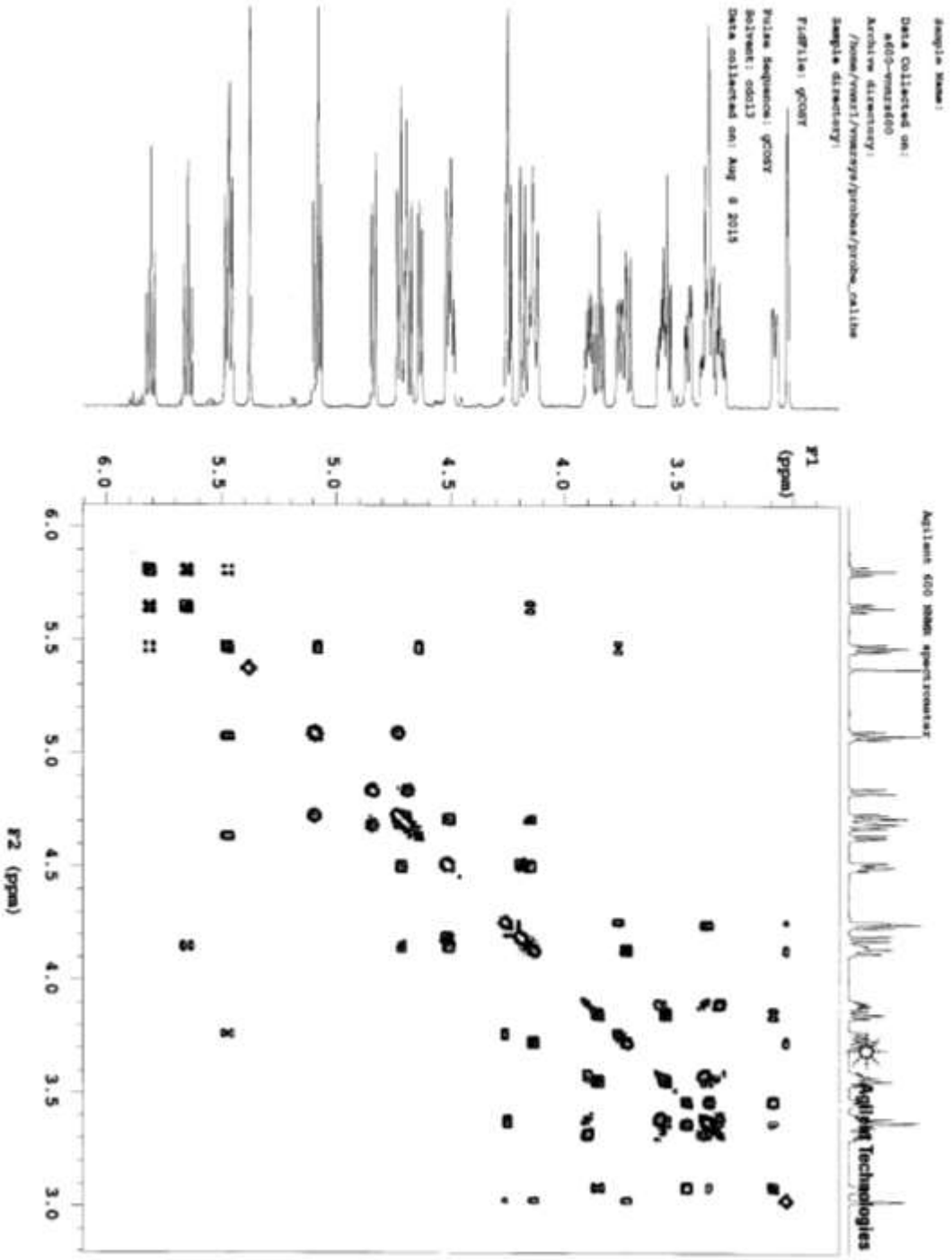
^{1}H NMR
600 MHz
$CDCl_3$

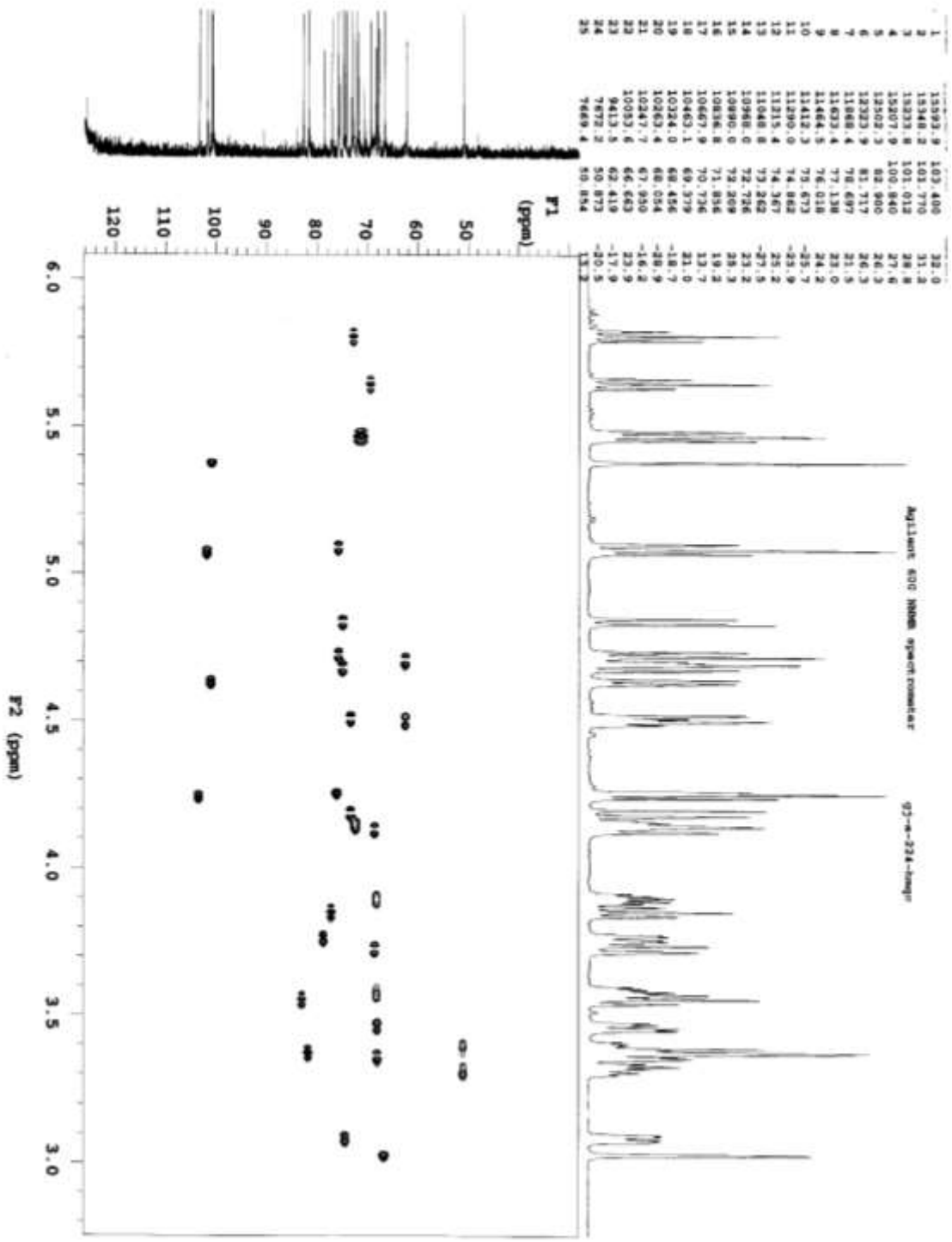

Ph
OBz
BzO
BzO
OBz
OBz
OBn
BnO
OBn
N3
15
13C NMR
600 MHz
CDCl3
f1 (ppm)
165.99
165.74
165.09
164.67
164.17
138.95
138.54
138.40
137.73
132.60
129.70
128.59
128.27
127.87
126.38
103.39
101.76
101.00
100.82
82.89
81.71
75.65
73.25
71.85
68.44
66.65
62.40
50.86

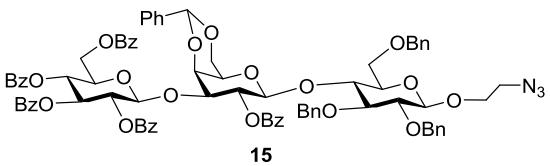


15

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$

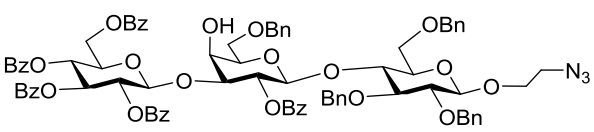






15

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

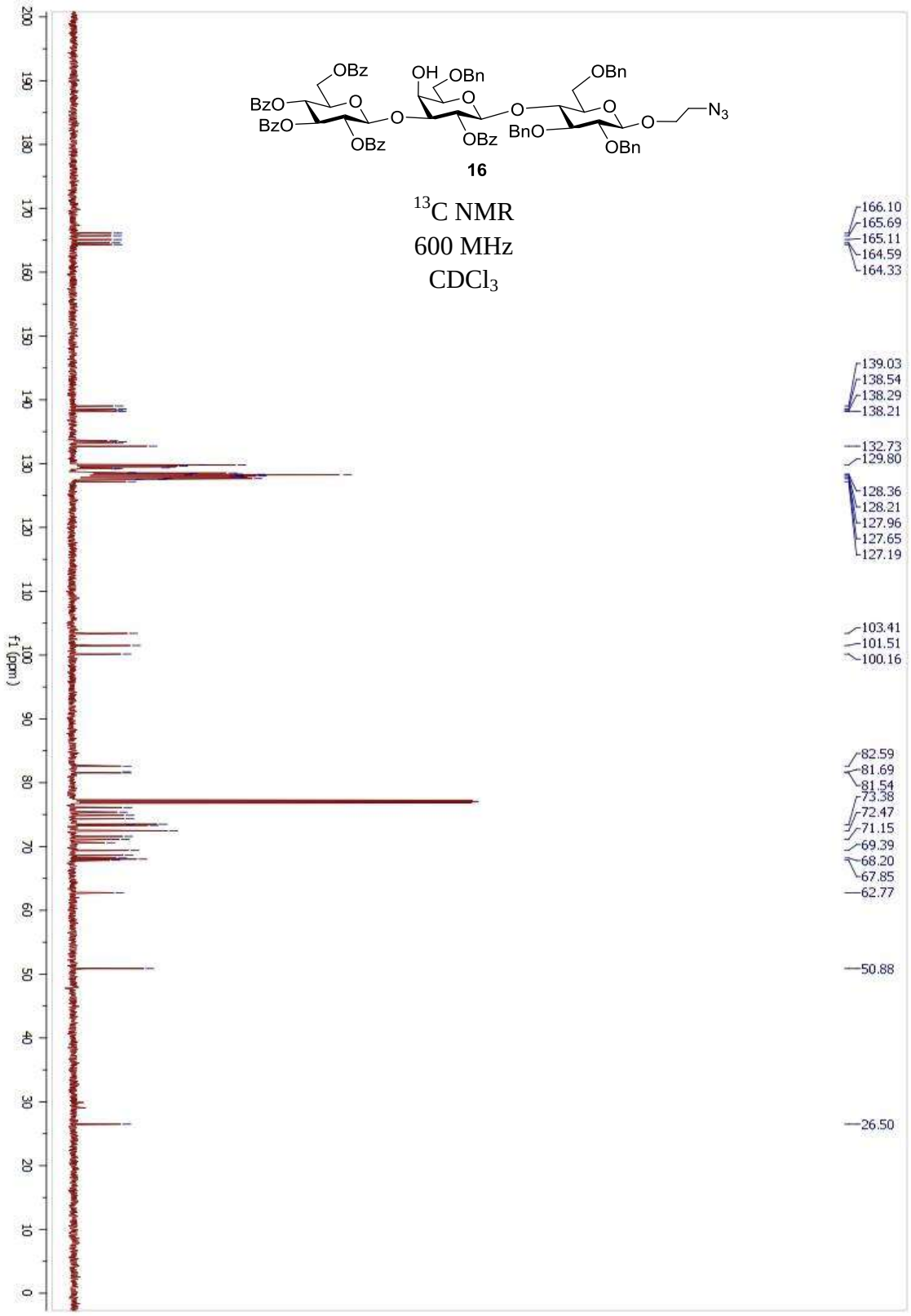


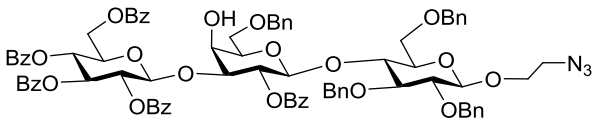
16

^{1}H NMR

600 MHz

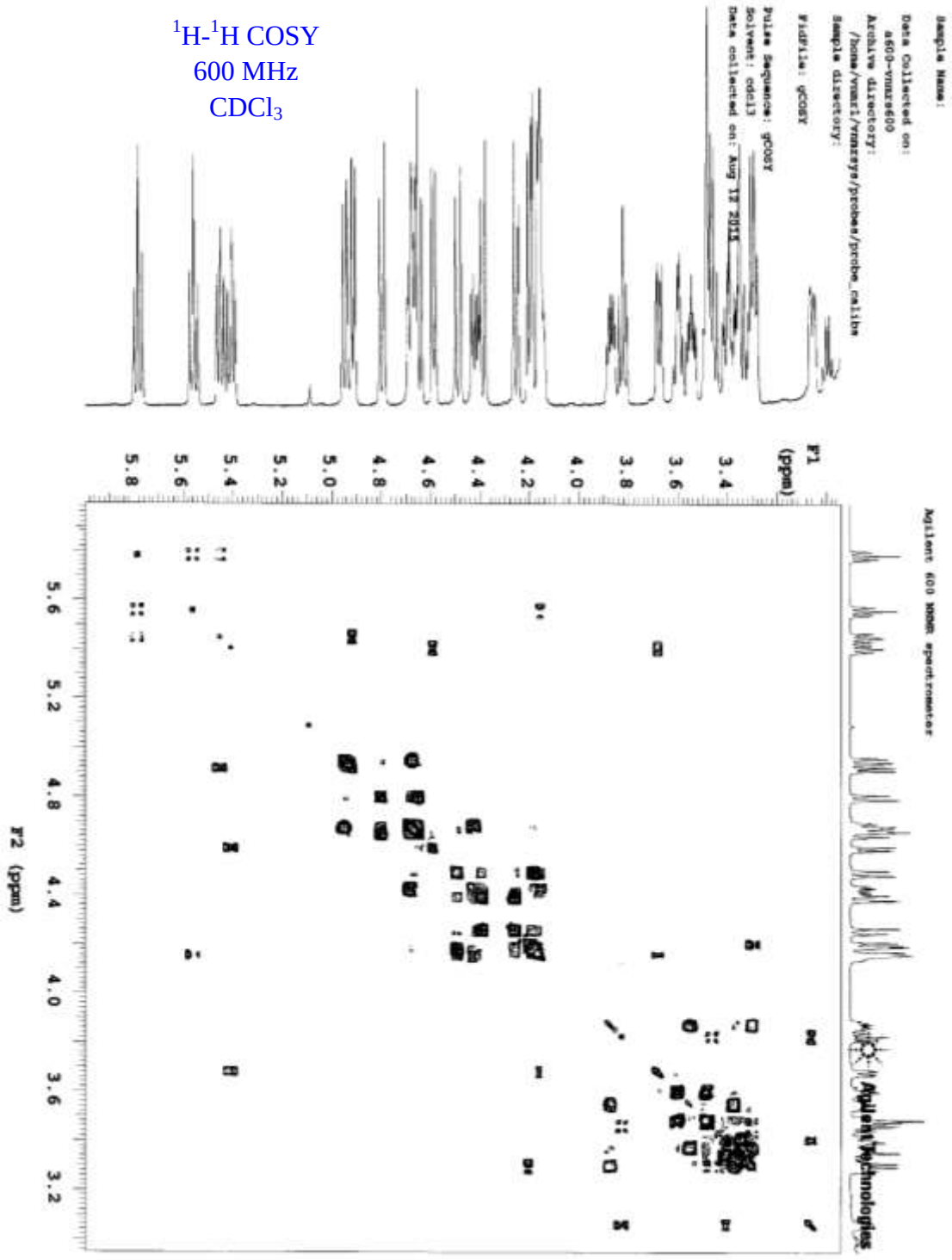
$CDCl_3$

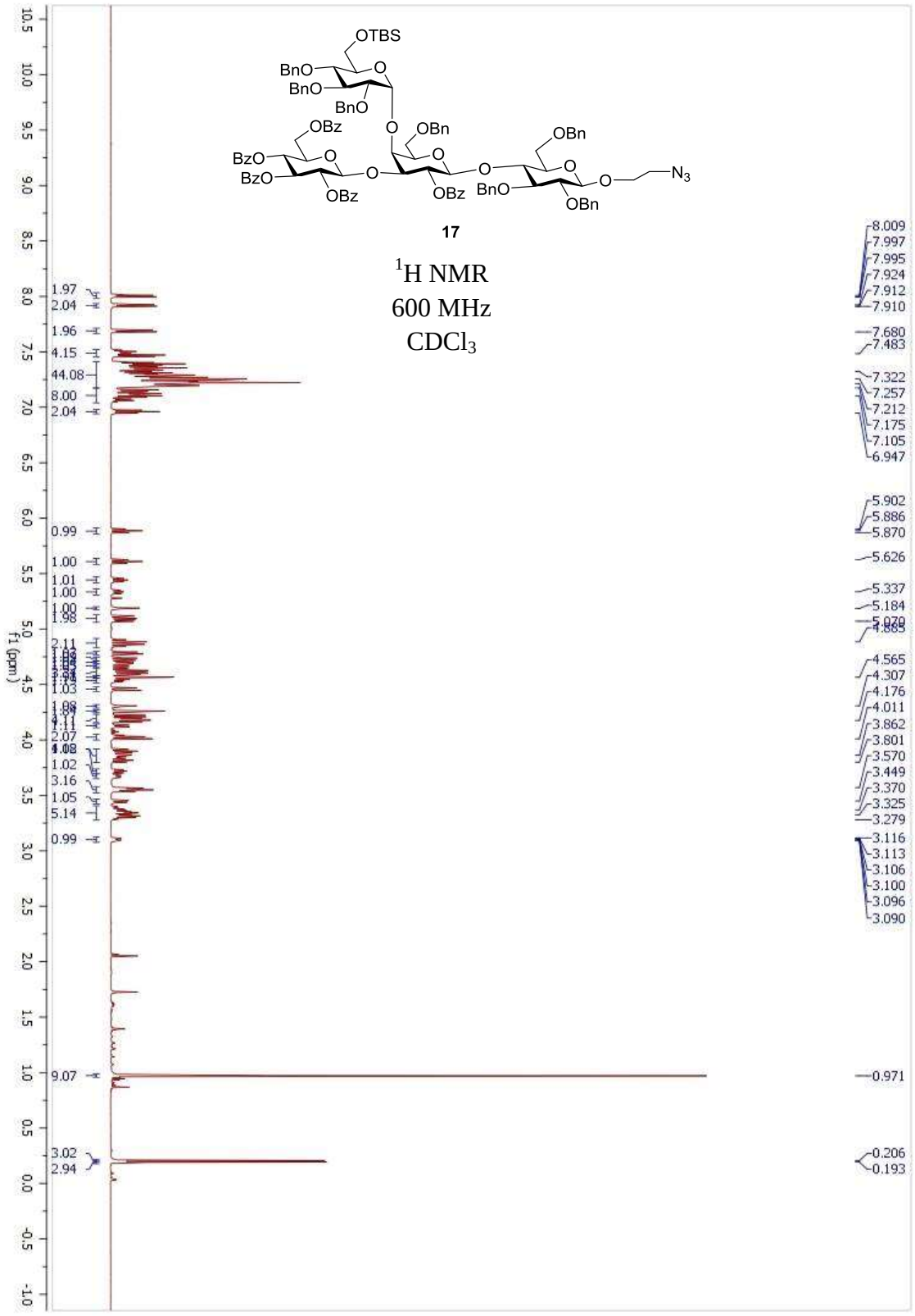

OBz
OH
OBn
OBn
BzO
BzO
OBz
OBz
BnO
OBn
N3
16
13C NMR
600 MHz
CDCl3
f1 (ppm)
166.10
165.69
165.11
164.59
164.33
139.03
138.54
138.29
138.21
132.73
129.80
128.36
128.21
127.96
127.65
127.19
103.41
101.51
100.16
82.59
81.69
81.54
73.38
72.47
71.15
69.39
68.20
67.85
62.77
50.88
26.50



16

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$




OTBS
BnO
BnO
BnO
O
OBz
O
OBn
BzO
BzO
OBz
OBz
BnO
OBn
OBn
N3
17
1H NMR
600 MHz
CDCl3
f1 (ppm)
1.97
2.04
1.96
4.15
44.08
8.00
2.04
0.99
1.00
1.01
1.00
1.00
1.98
1.03
2.07
1.02
3.16
1.05
5.14
0.99
9.07
3.02
2.94
8.009
7.997
7.995
7.924
7.912
7.910
7.680
7.483
7.322
7.257
7.212
7.175
7.105
6.947
5.902
5.886
5.870
5.626
5.337
5.184
5.070
4.885
4.565
4.307
4.176
4.011
3.862
3.801
3.570
3.449
3.370
3.325
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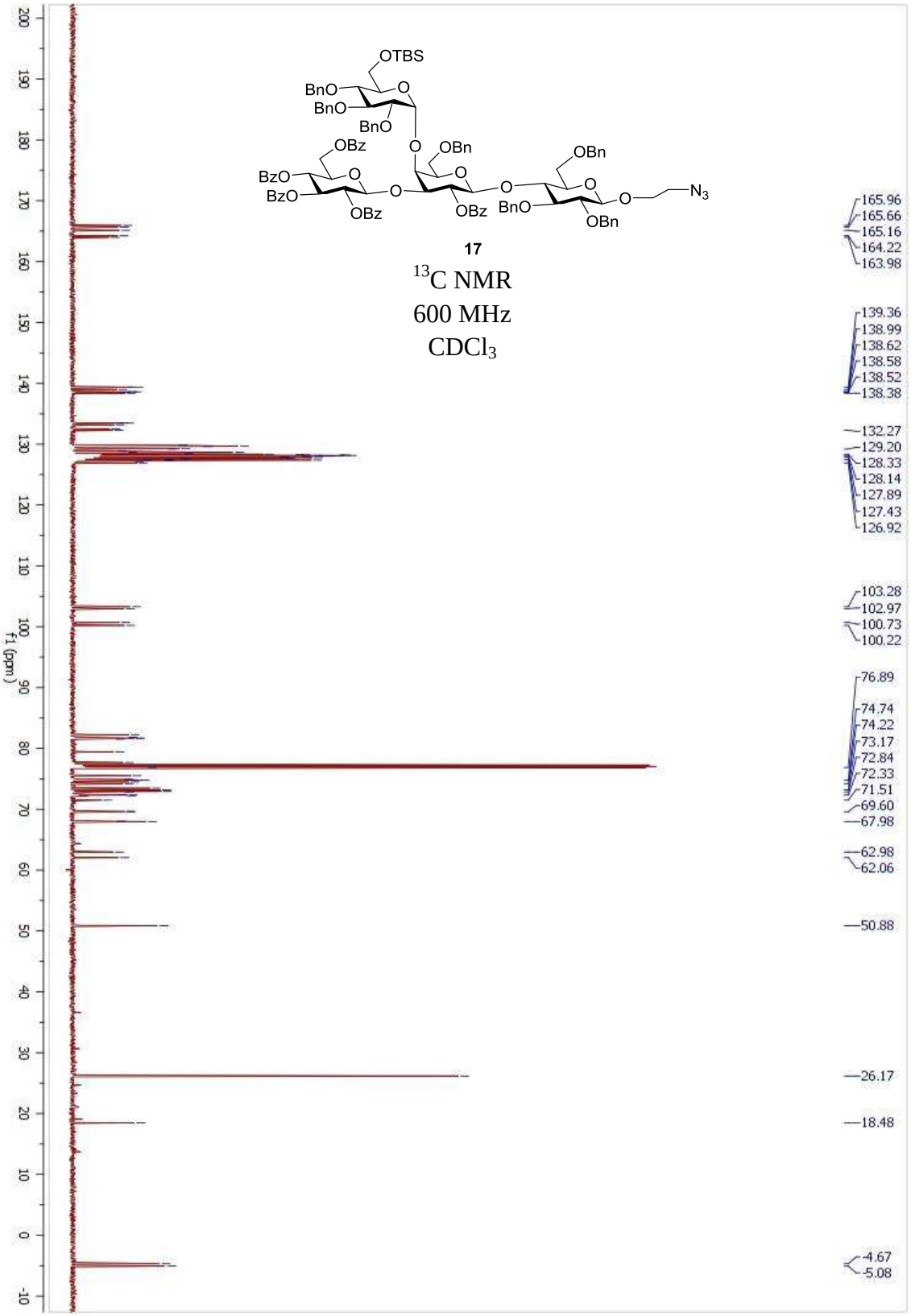
3.116
3.113
3.106
3.100
3.096
3.090
0.971
0.206
0.193


OTBS
BnO
BnO
BnO
O
OBz
O
OBn
BzO
BzO
O
O
O
O
OBz
OBz
OBn
BnO
O
O
N3
OBn
17
13C NMR
600 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
165.96
165.66
165.16
164.22
163.98
139.36
138.99
138.62
138.58
138.52
138.38
132.27
129.20
128.33
128.14
127.89
127.43
126.92
103.28
102.97
100.73
100.22
76.89
74.74
74.22
73.17
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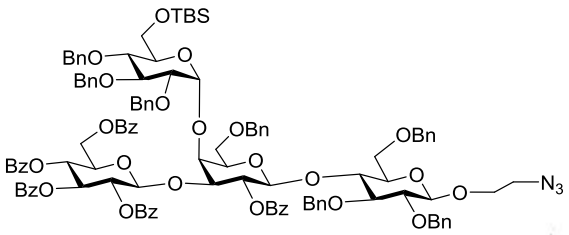
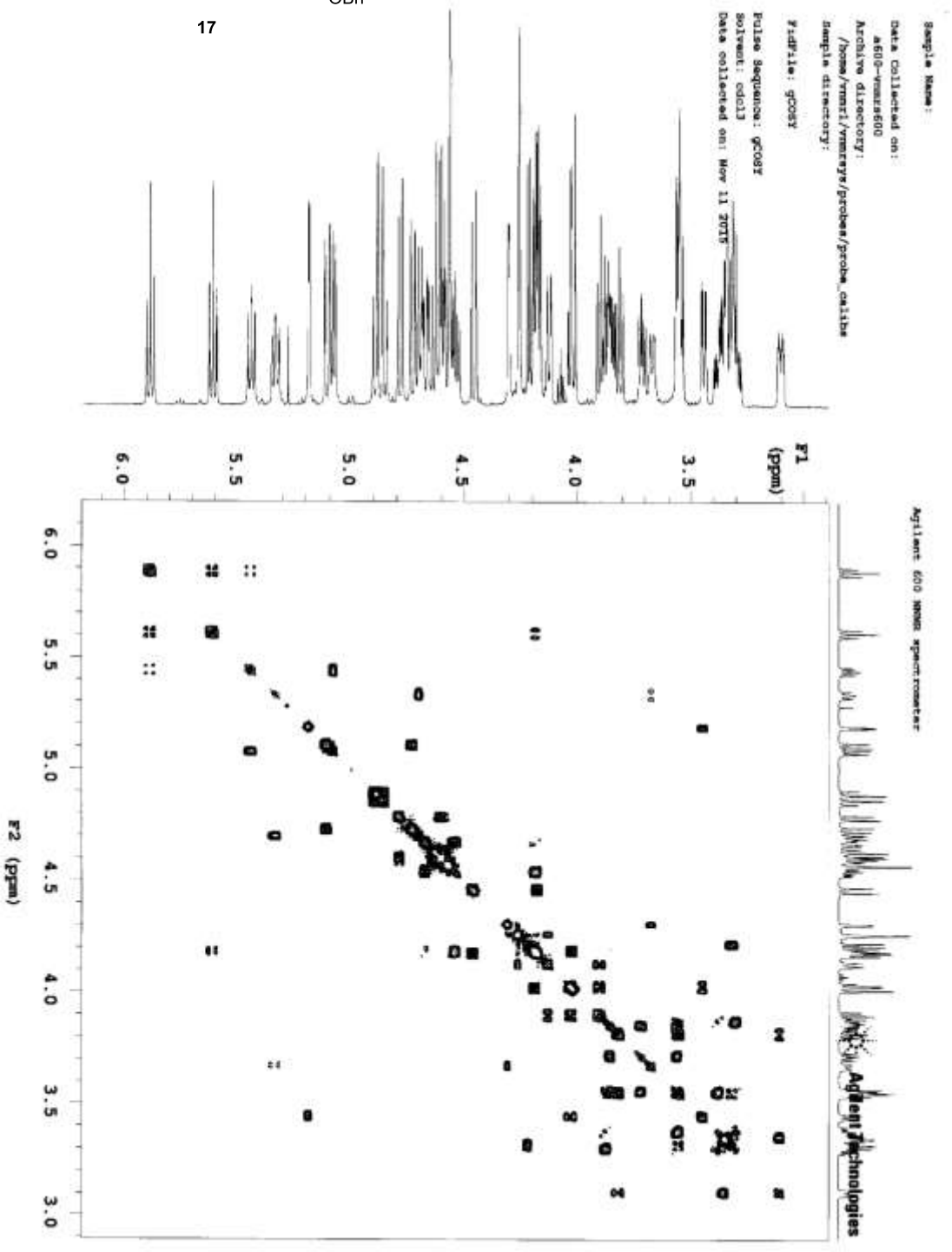
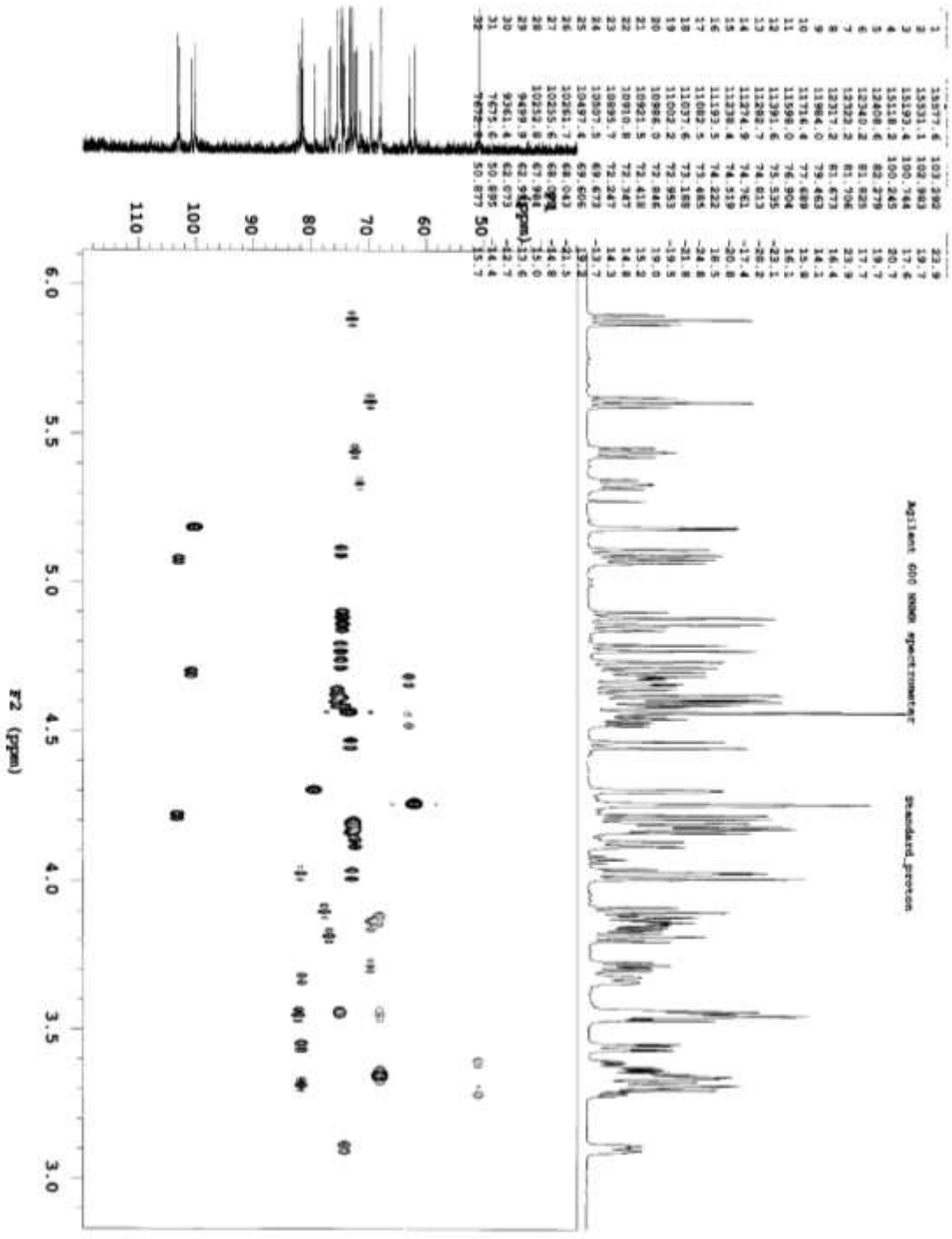
62.98
62.06
50.88
26.17
18.48
-4.67
-5.08

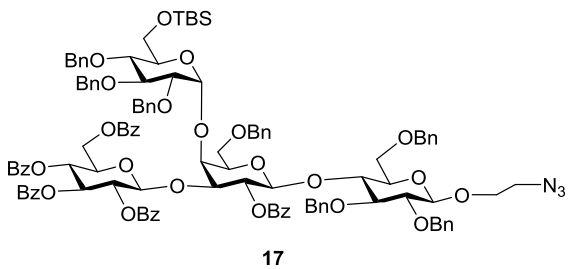


17

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$

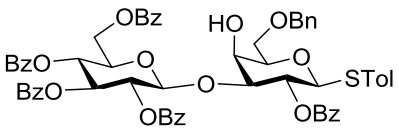






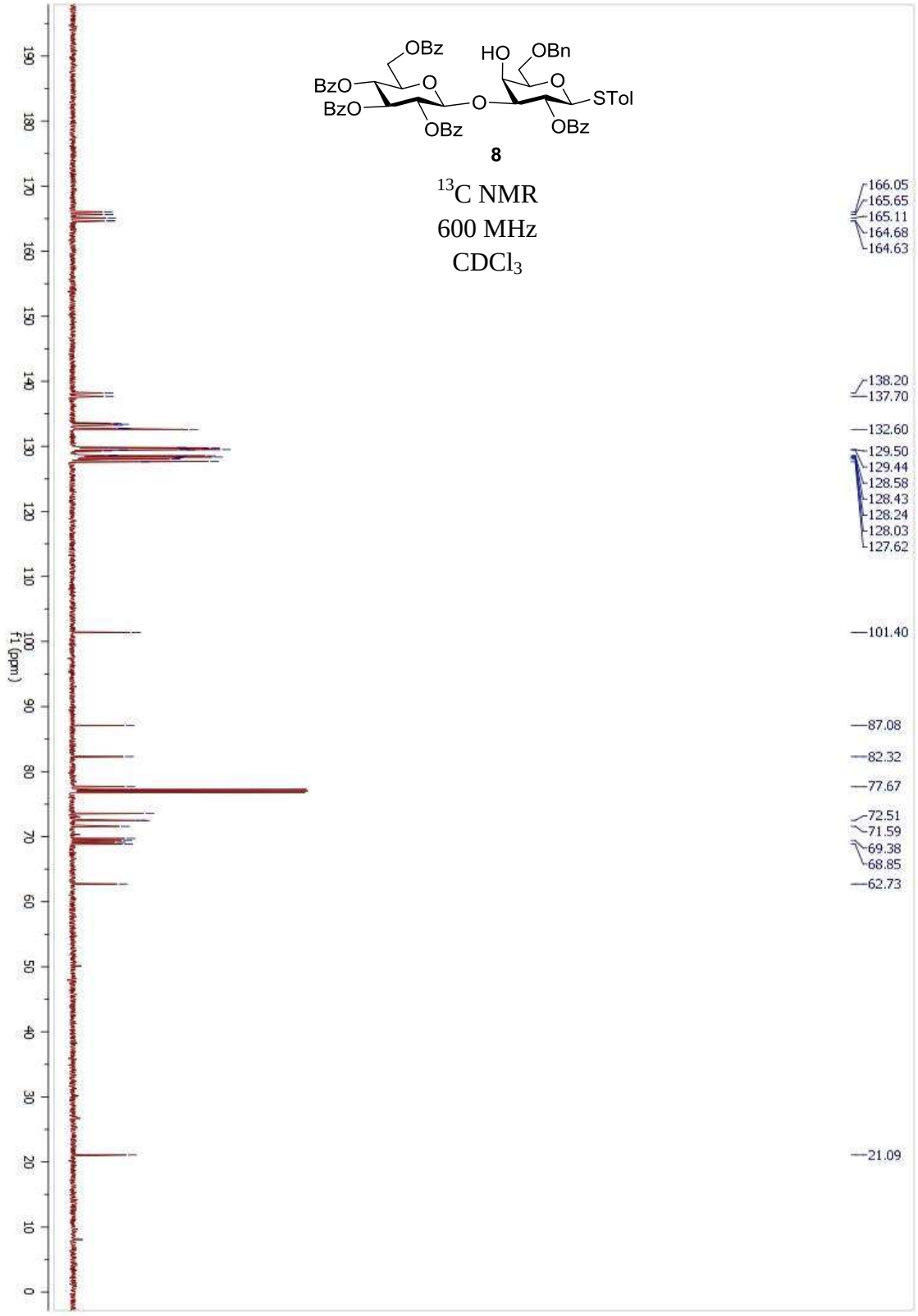
17

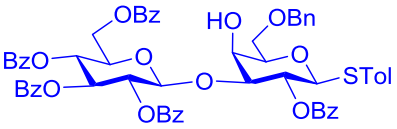
^{1}H-^{13}C HMQC
600/150 MHz
$CDCl_3$



8

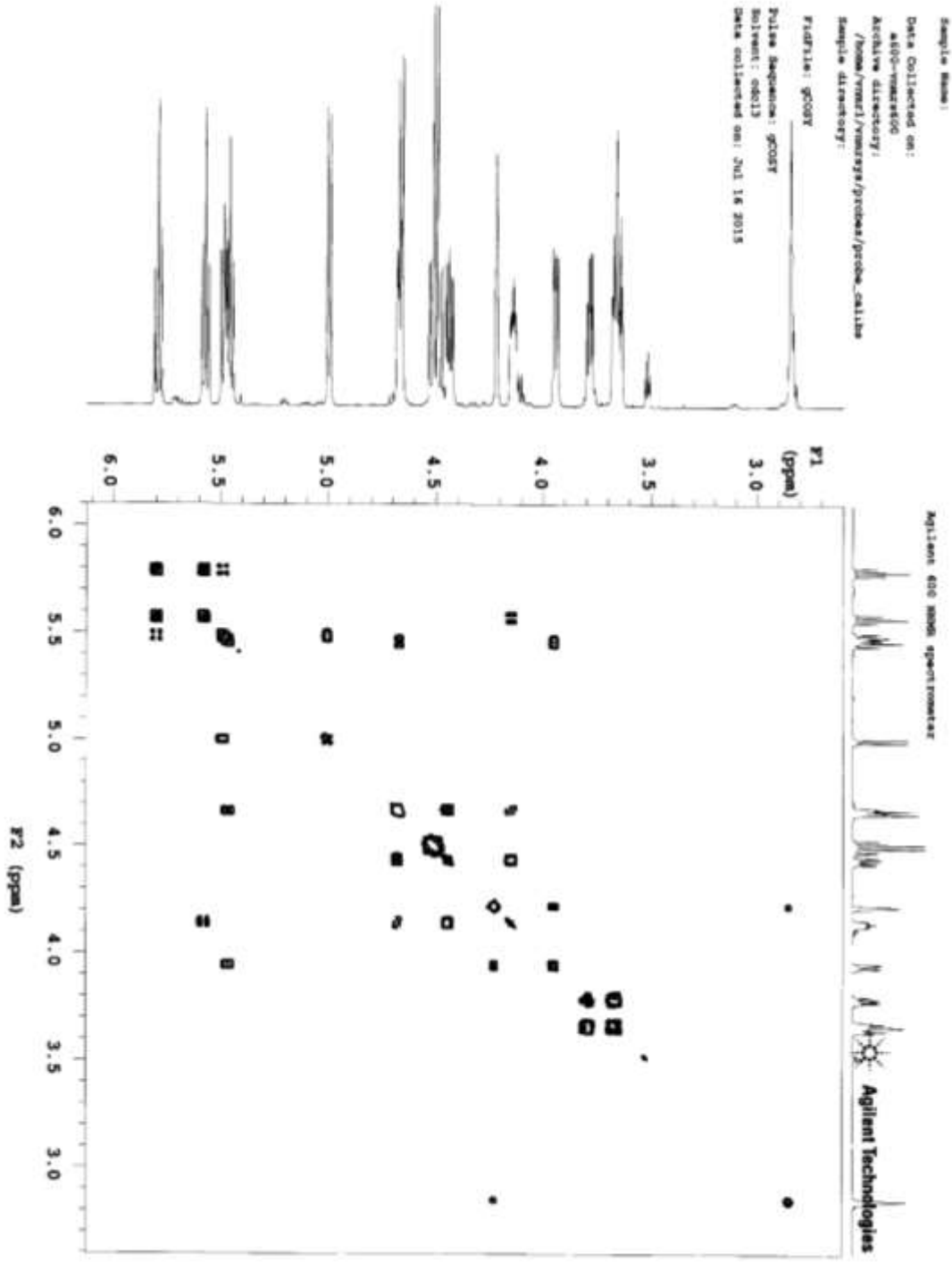
^{1}H NMR
600 MHz
$CDCl_3$

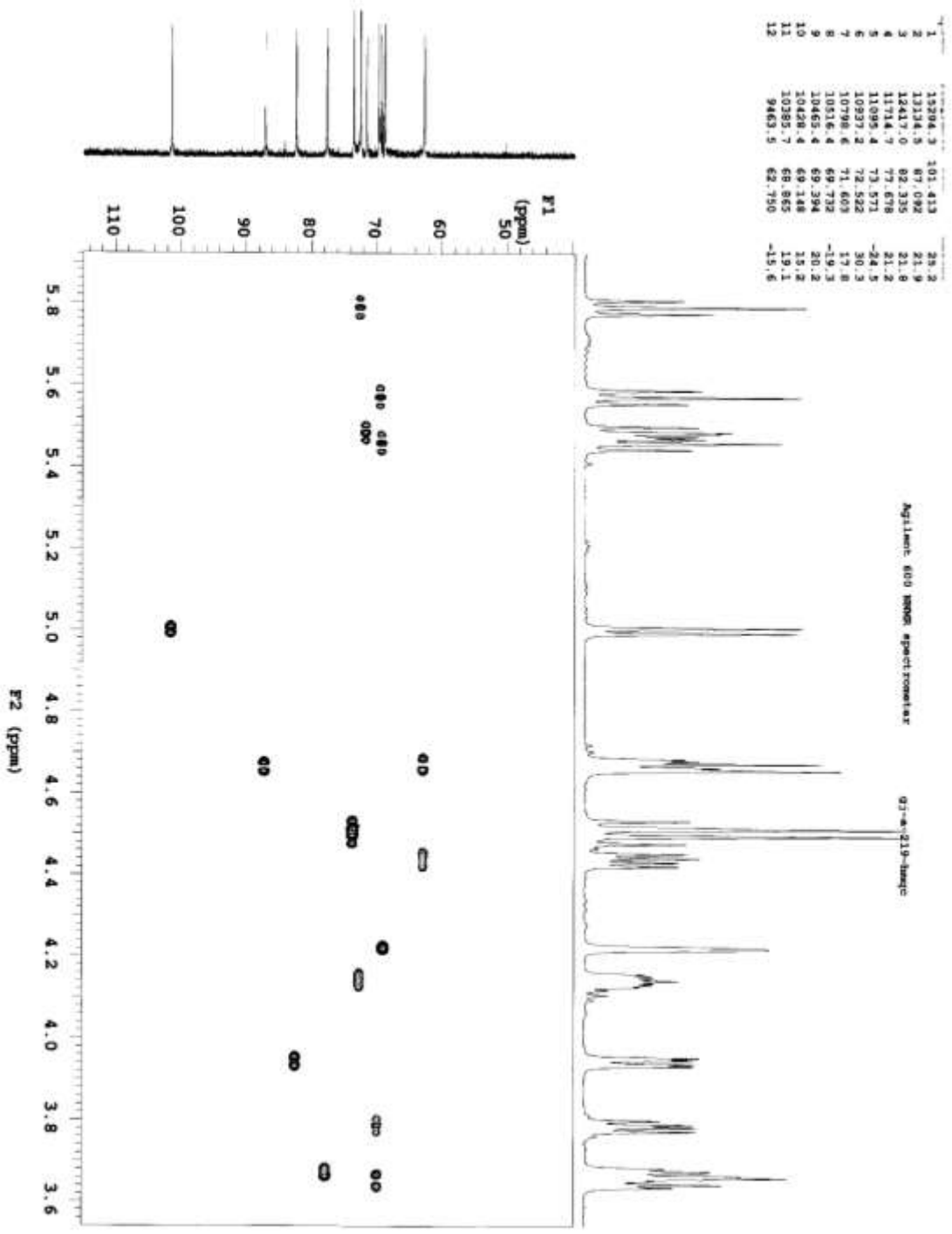

OBz
HO
OBn
BzO
O
O
STol
BzO
OBz
OBz
8
^{13}C NMR
600 MHz
$CDCl_3$
166.05
165.65
165.11
164.68
164.63
138.20
137.70
132.60
129.50
129.44
128.58
128.43
128.24
128.03
127.62
101.40
87.08
82.32
77.67
72.51
71.59
69.38
68.85
62.73
21.09
f1 (ppm)

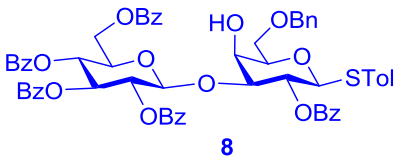


8

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$

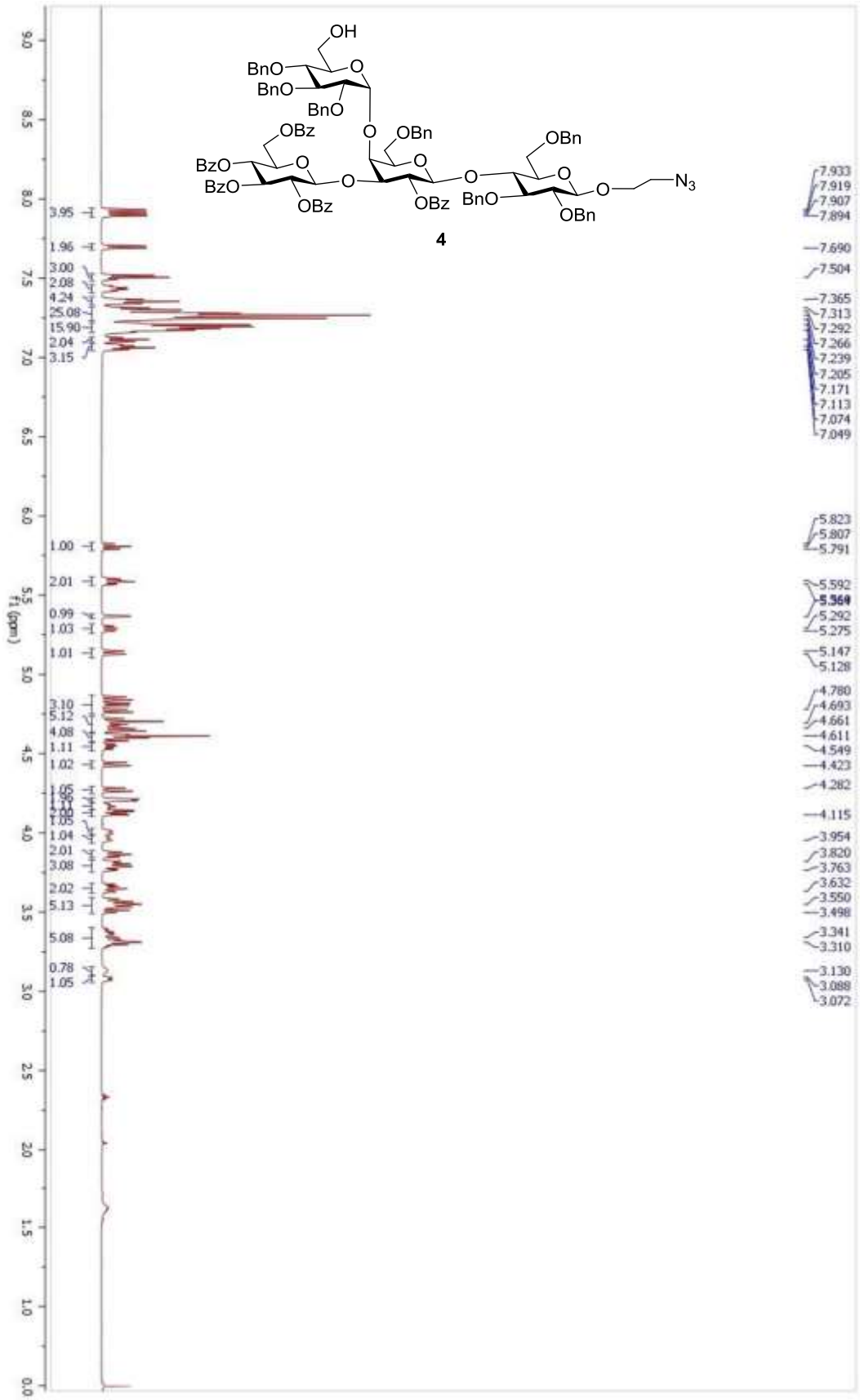


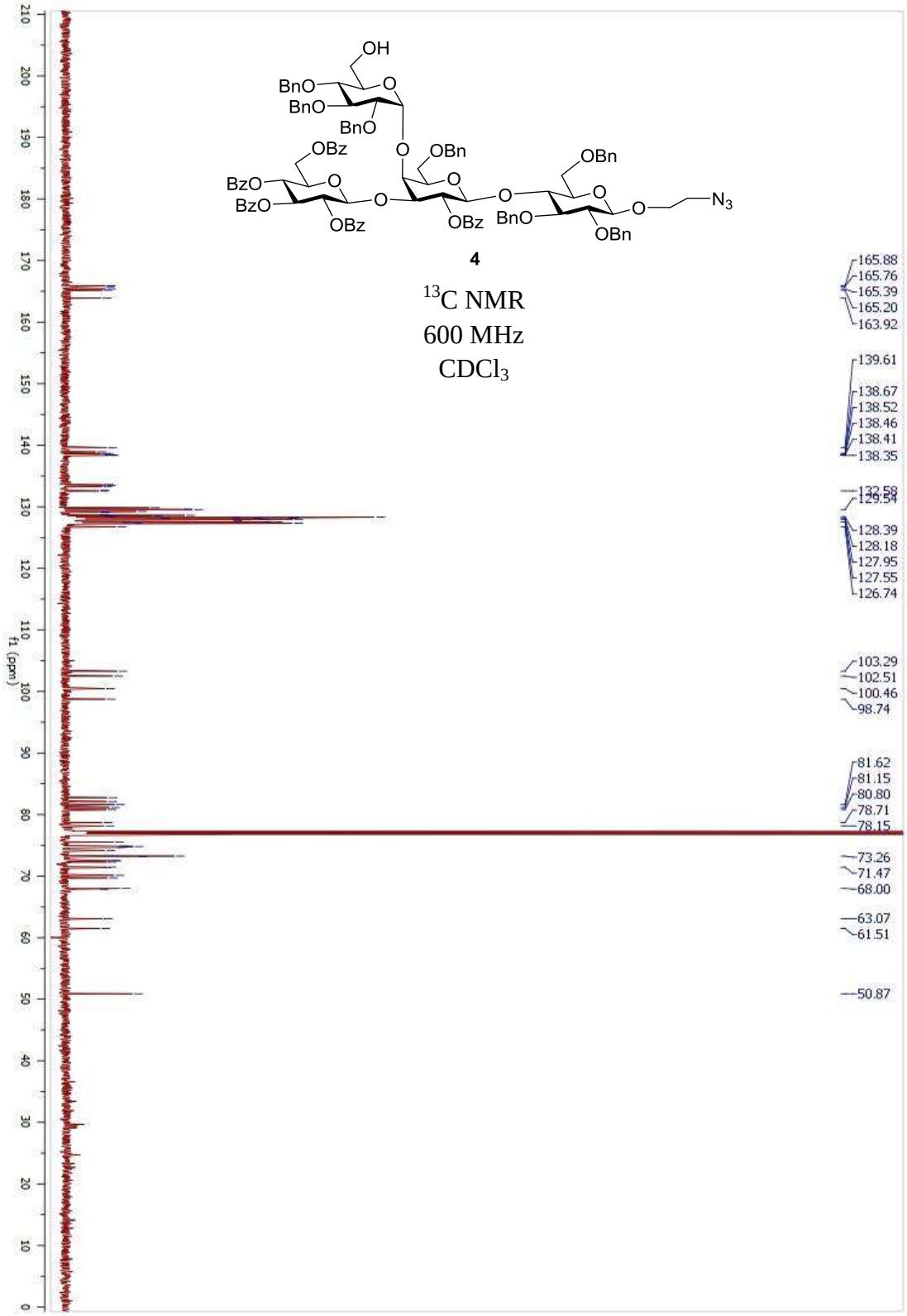




8

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


OH
BnO
BnO
BnO
O
OBz
OBn
BzO
BzO
OBz
OBz
BnO
OBn
N3
4
f1 (ppm)


OH
BnO
BnO
BnO
O
OBz
OBn
BzO
BzO
OBz
OBz
OBn
BnO
OBn
N3
4
13C NMR
600 MHz
CDCl3
f1 (ppm)
165.88
165.76
165.39
165.20
163.92
139.61
138.67
138.52
138.46
138.41
138.35
132.58
129.54
128.39
128.18
127.95
127.55
126.74
103.29
102.51
100.46
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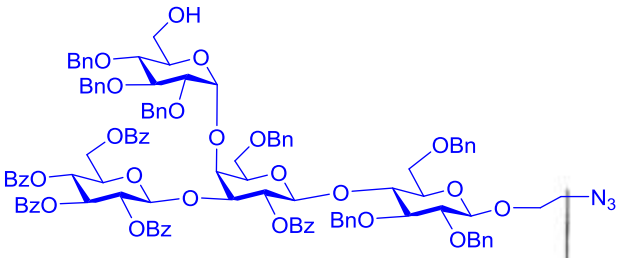
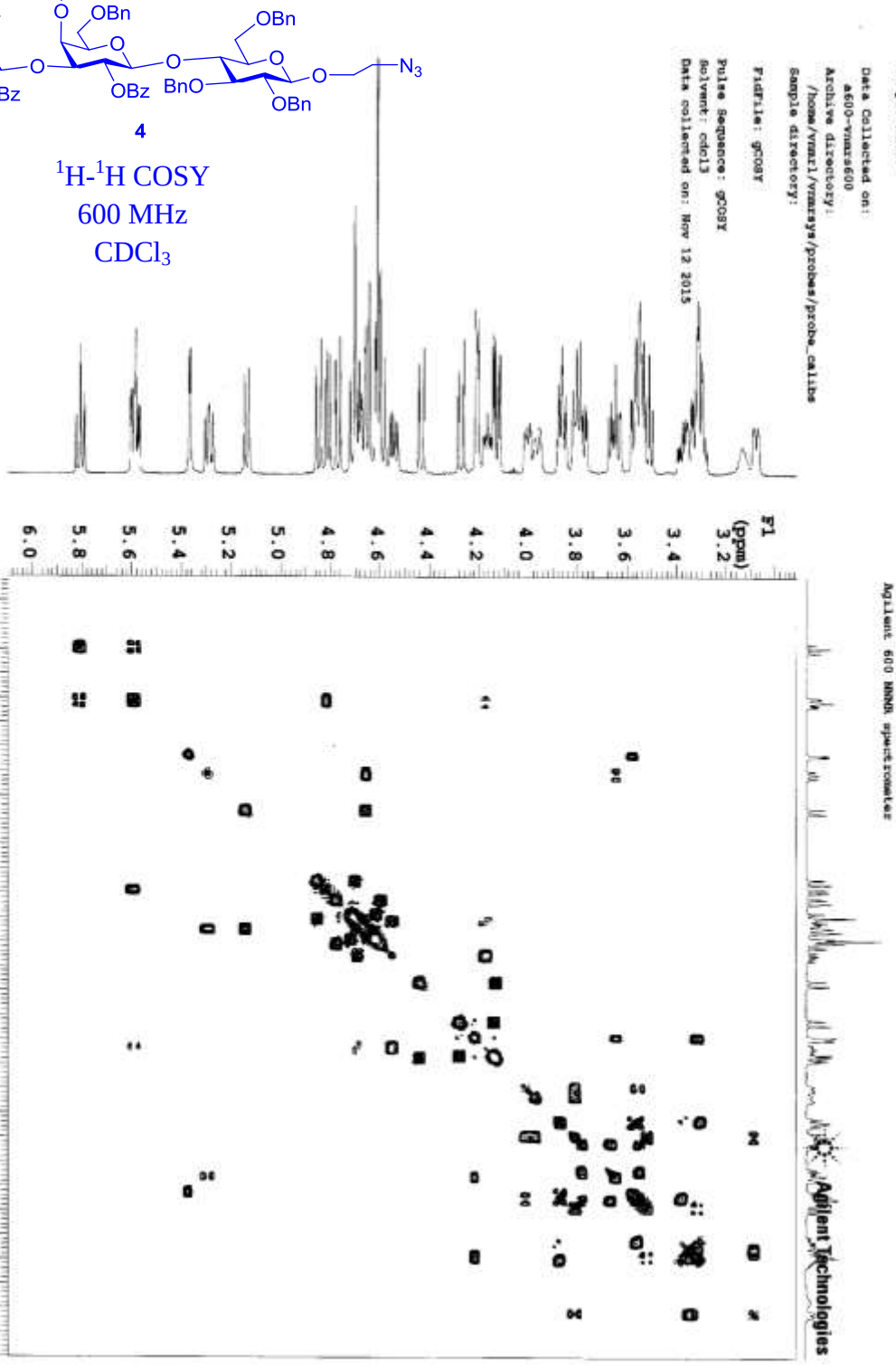
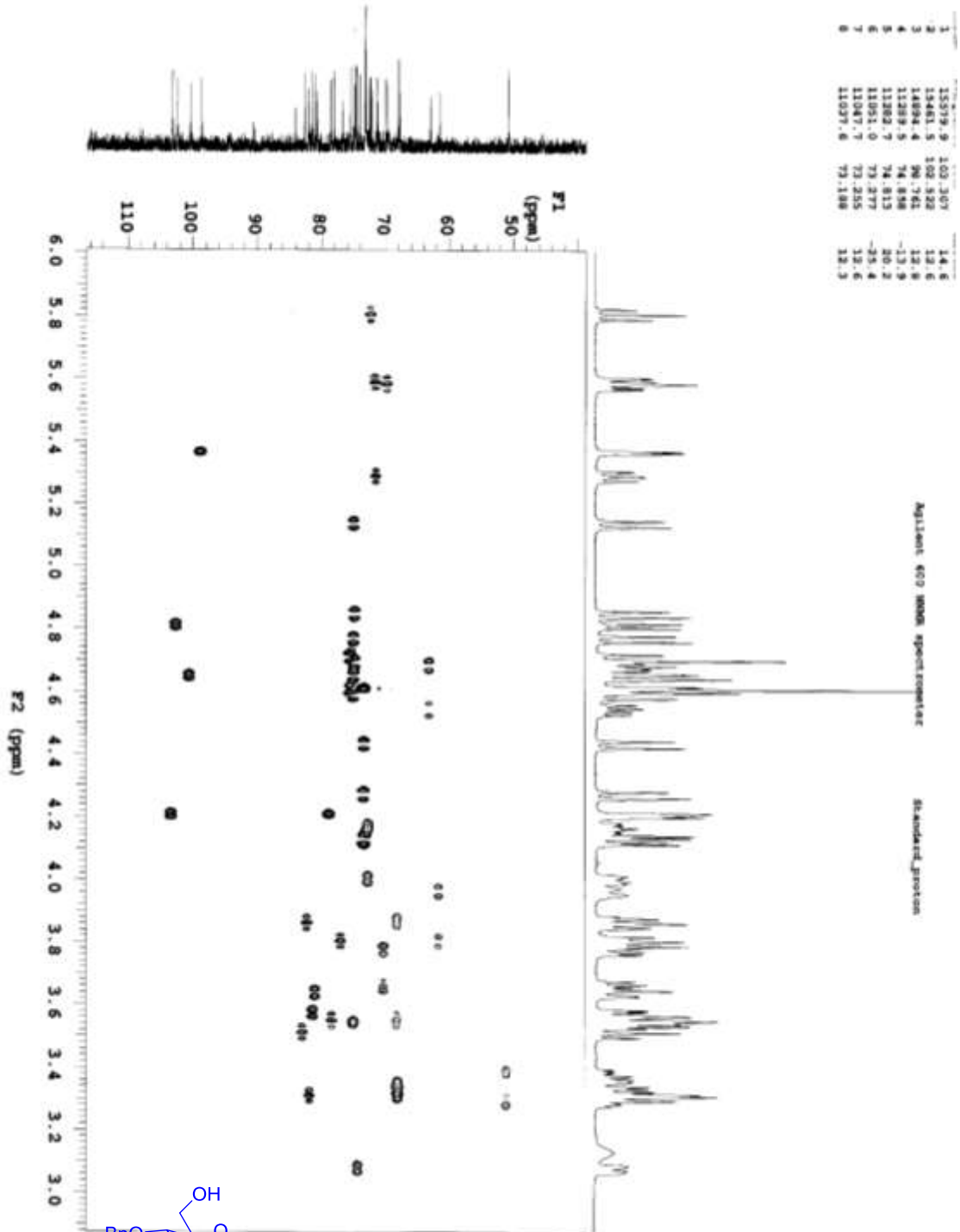
73.26
71.47
68.00
63.07
61.51
50.87

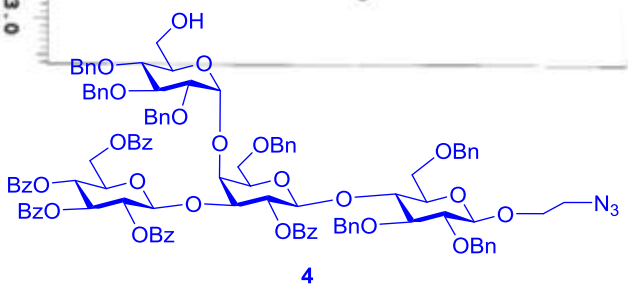


4

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$

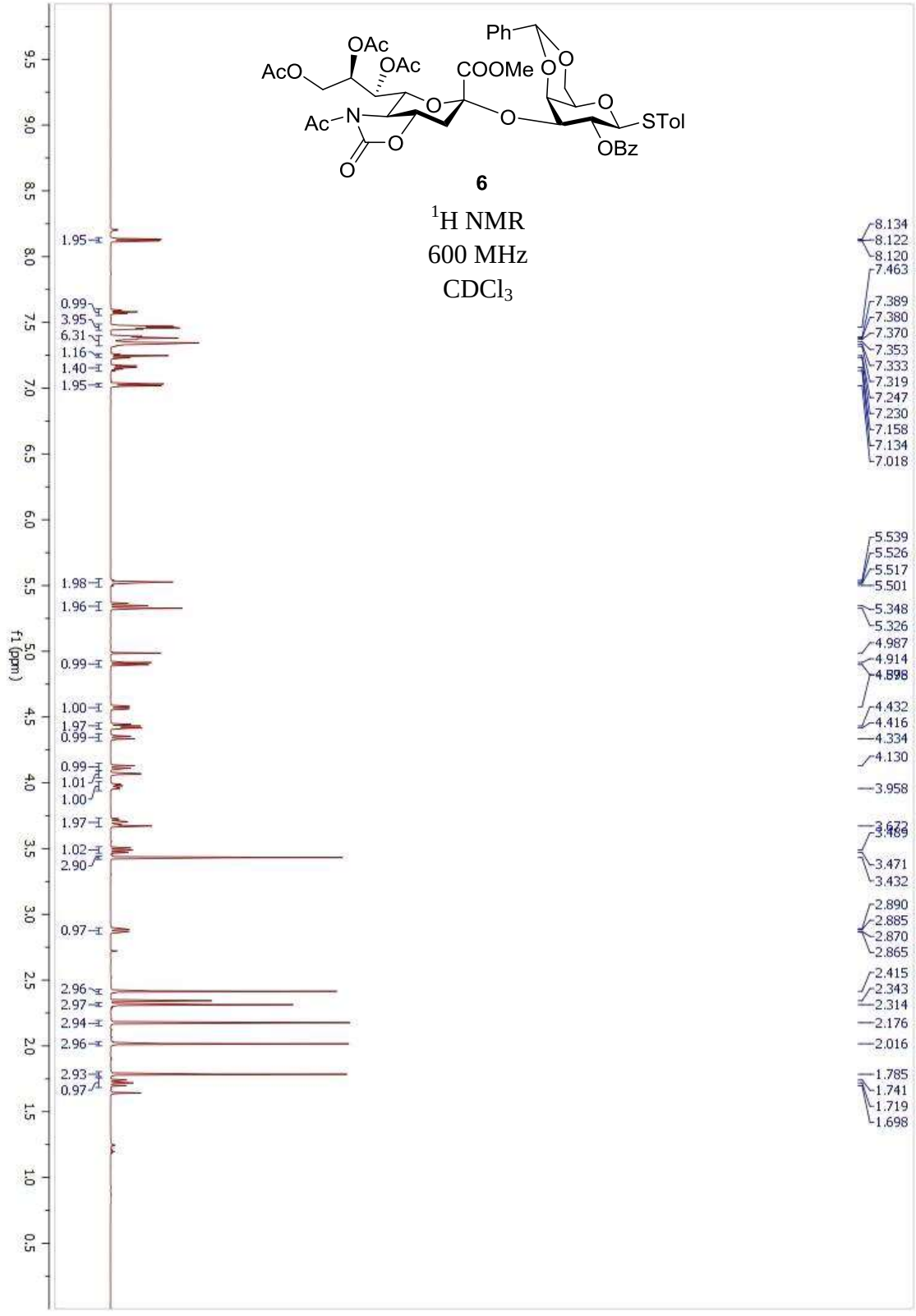


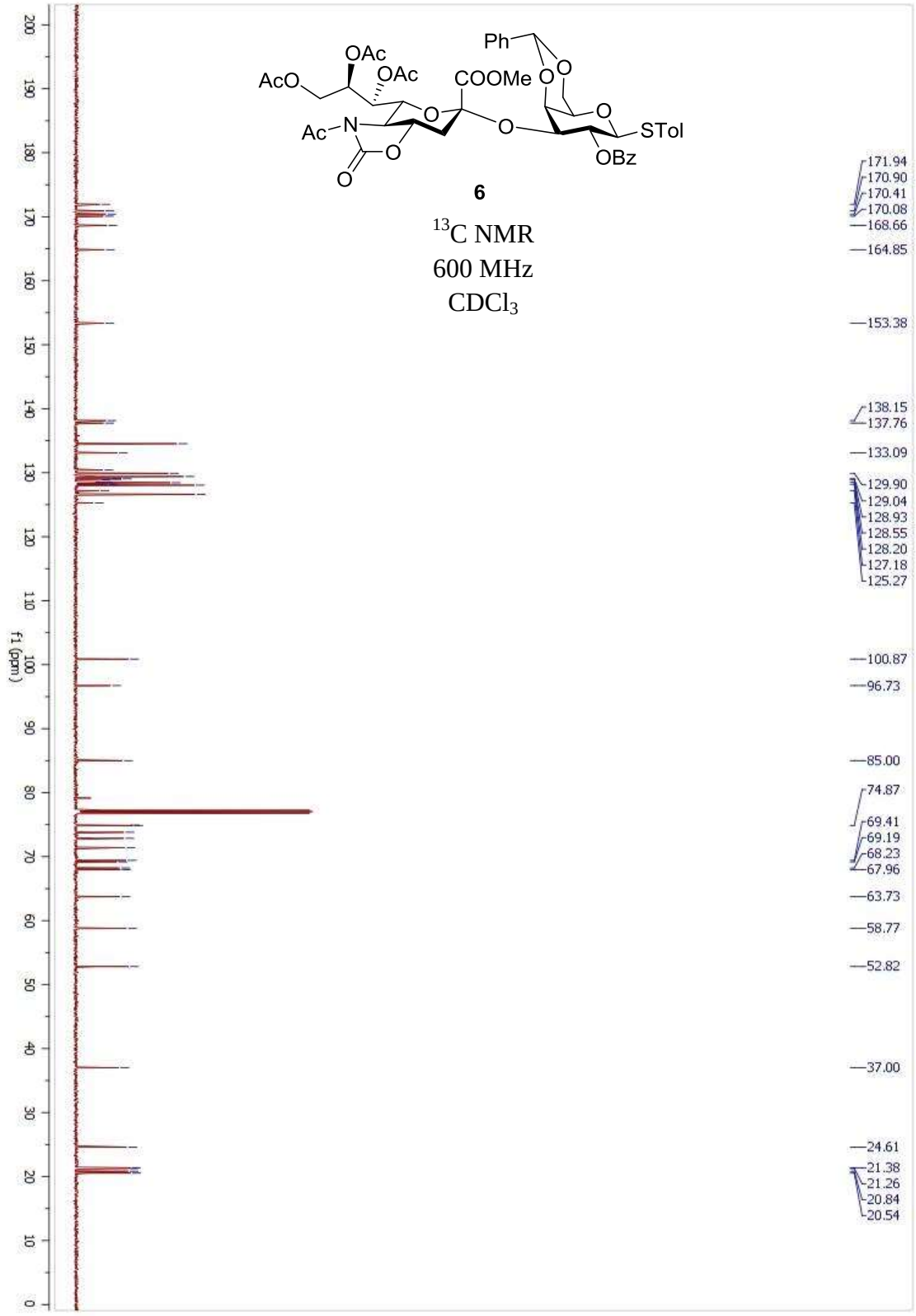


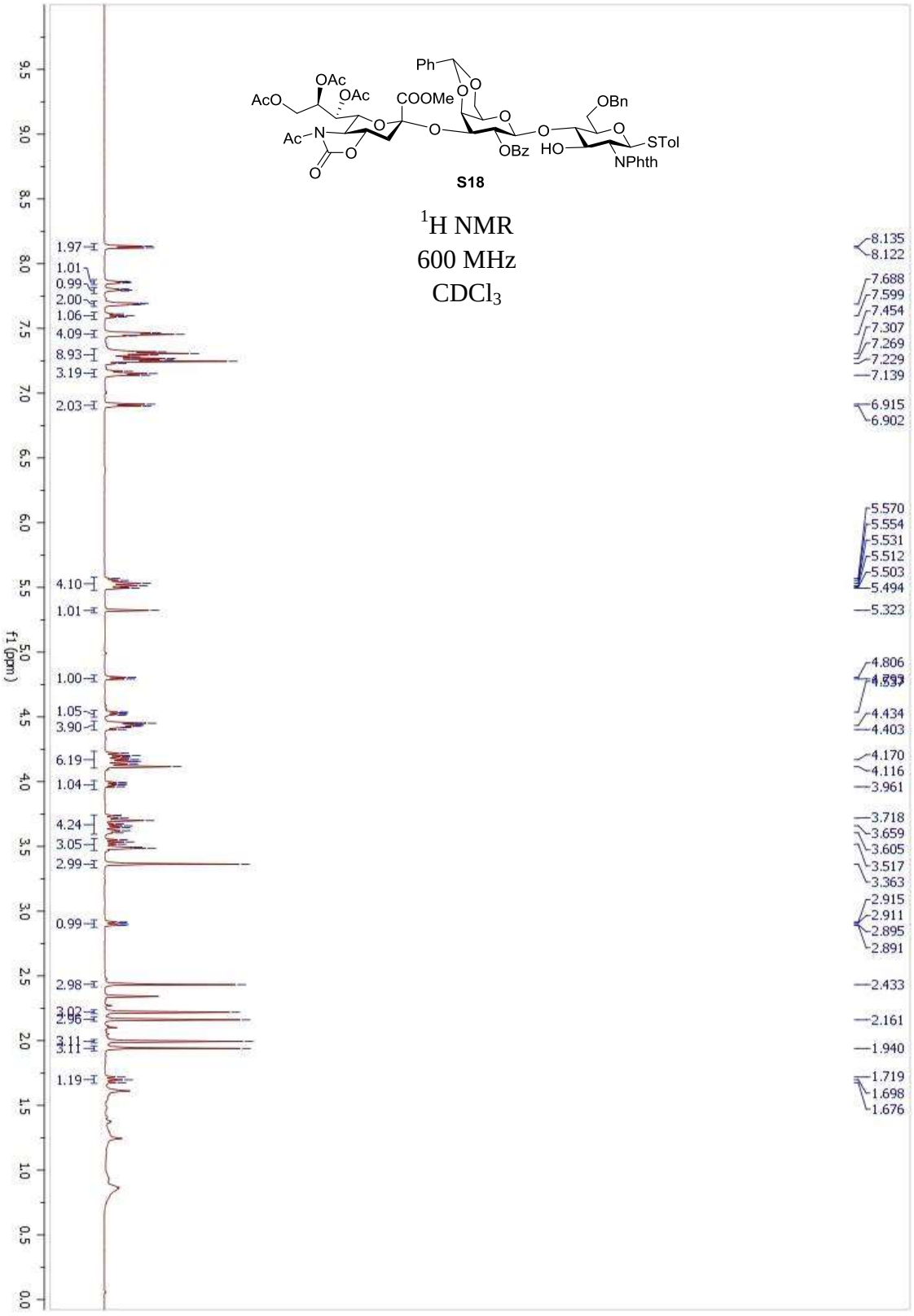


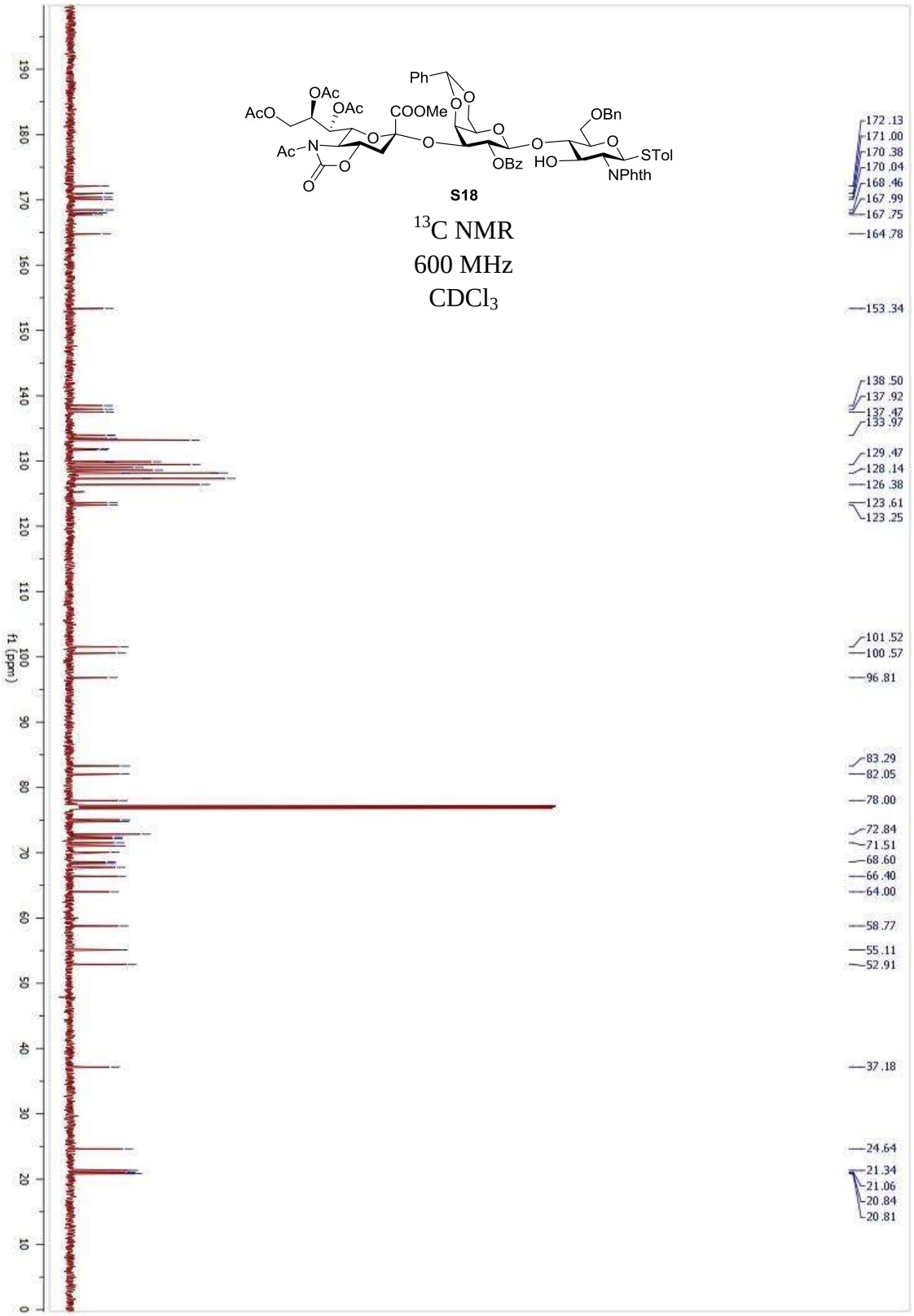
4

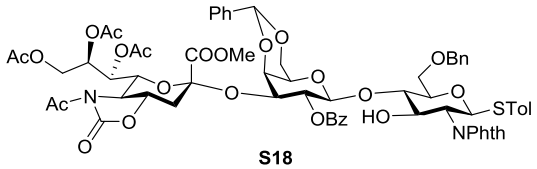
^{1}H-^{13}C HMQC
600/150 MHz
$CDCl_3$


OAc
OAc
AcO
COOMe
Ph
O
Ac
N
O
O
O
O
O
STol
OBz
O
6
1H NMR
600 MHz
CDCl3
f1 (ppm)
1.95
0.99
3.95
6.31
1.16
1.40
1.95
1.98
1.96
0.99
1.00
1.97
0.99
0.99
1.01
1.00
1.97
1.02
2.90
0.97
2.96
2.97
2.94
2.96
2.93
0.97
8.134
8.122
8.120
7.463
7.389
7.380
7.370
7.353
7.333
7.319
7.247
7.230
7.158
7.134
7.018
5.539
5.526
5.517
5.501
5.348
5.326
4.987
4.914
4.432
4.416
4.334
4.130
3.958
3.471
3.432
2.890
2.885
2.870
2.865
2.415
2.343
2.314
2.176
2.016
1.785
1.741
1.719
1.698


OAc
AcO
OAc
COOMe
Ph
O
O
Ac
N
O
O
O
O
STol
OBz
O
6
^{13}C NMR
600 MHz
$CDCl_3$
f1 (ppm)
171.94
170.90
170.41
170.08
168.66
164.85
153.38
138.15
137.76
133.09
129.90
129.04
128.93
128.55
128.20
127.18
125.27
100.87
96.73
85.00
74.87
69.41
69.19
68.23
67.96
63.73
58.77
52.82
37.00
24.61
21.38
21.26
20.84
20.54

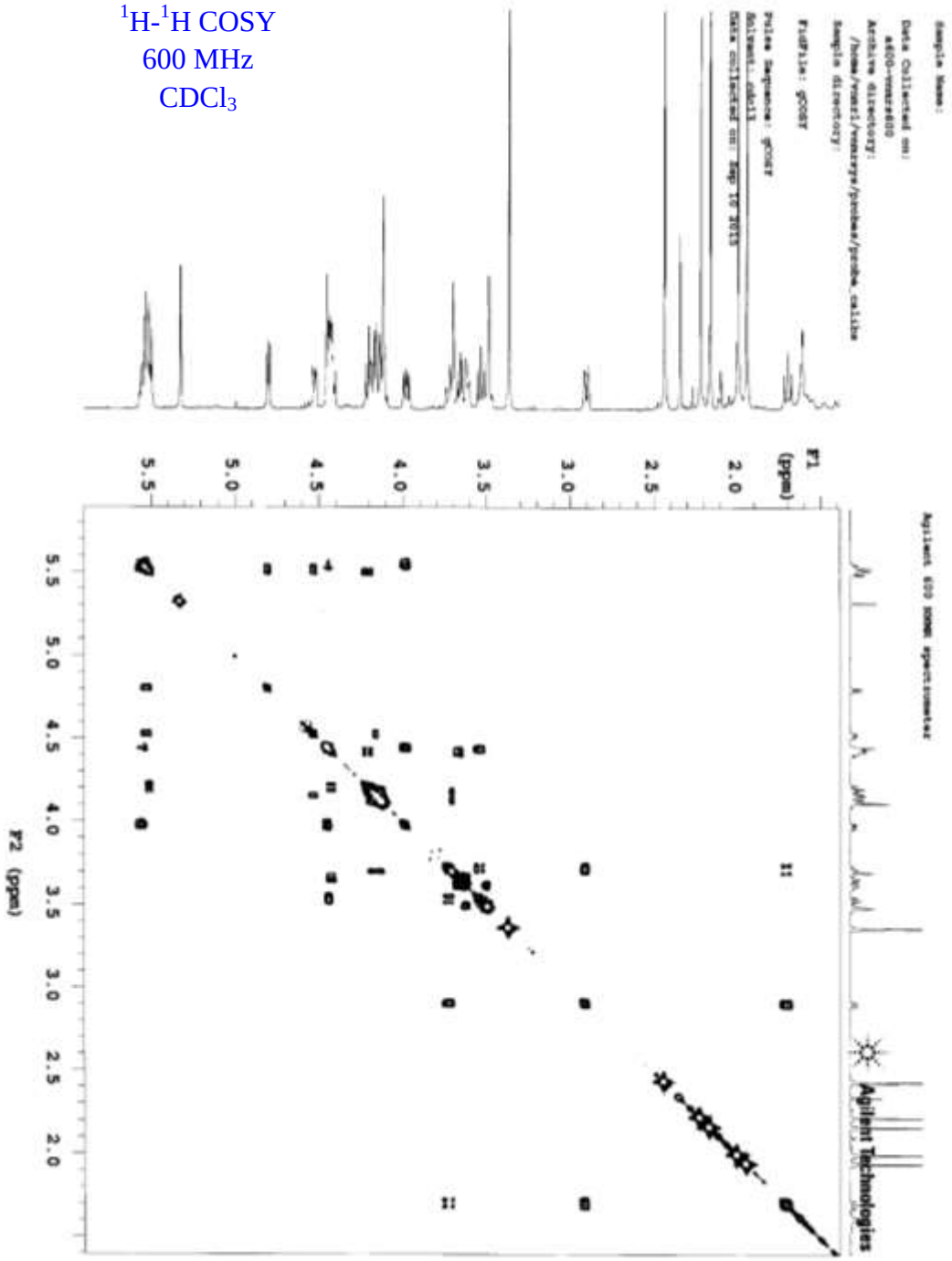

S18
1H NMR
600 MHz
CDCl3
f1 (ppm)

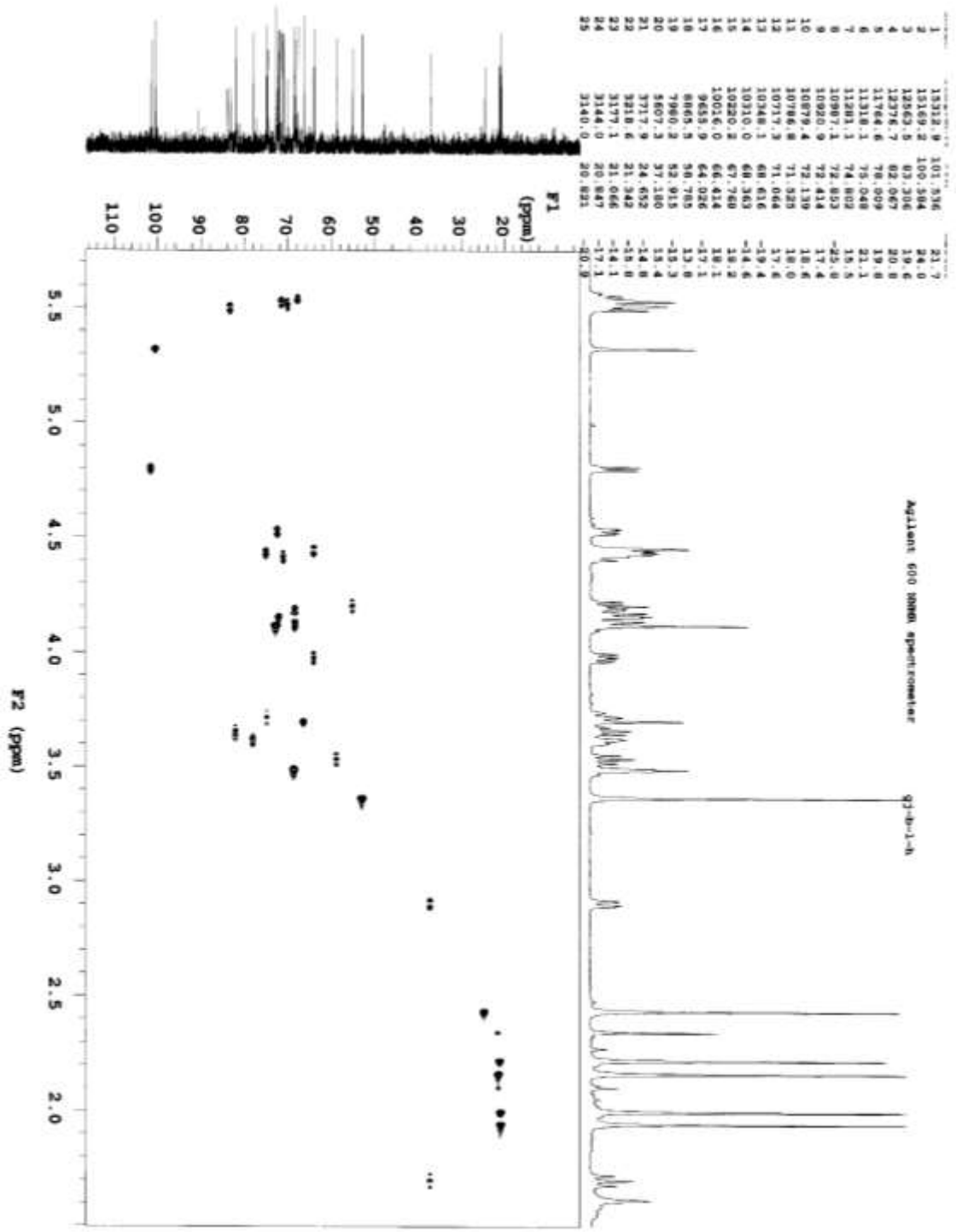

Ph
OAc
AcO
OAc
COOMe
OBn
Ac
N
HO
STol
OBz
NPhth
S18
^{13}C NMR
600 MHz
$CDCl_3$
f1 (ppm)
172.13
171.00
170.38
170.04
168.46
167.99
167.75
164.78
153.34
138.50
137.92
137.47
133.97
129.47
128.14
126.38
123.61
123.25
101.52
100.57
96.81
83.29
82.05
78.00
72.84
71.51
68.60
66.40
64.00
58.77
55.11
52.91
37.18
24.64
21.34
21.06
20.84
20.81

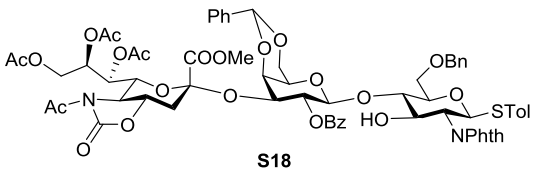


S18

^{1}H-^{1}H COSY
600 MHz
$CDCl_3$

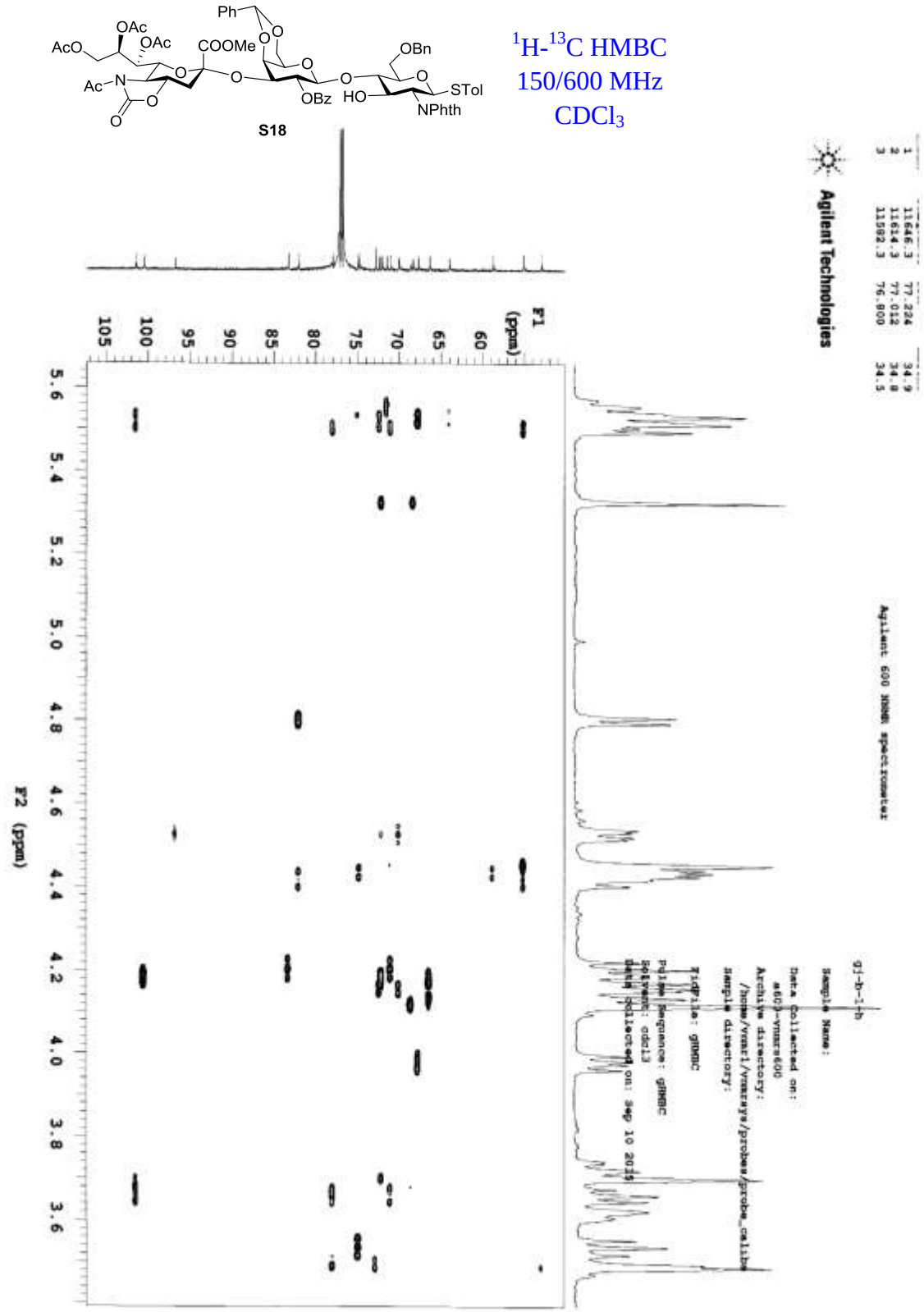


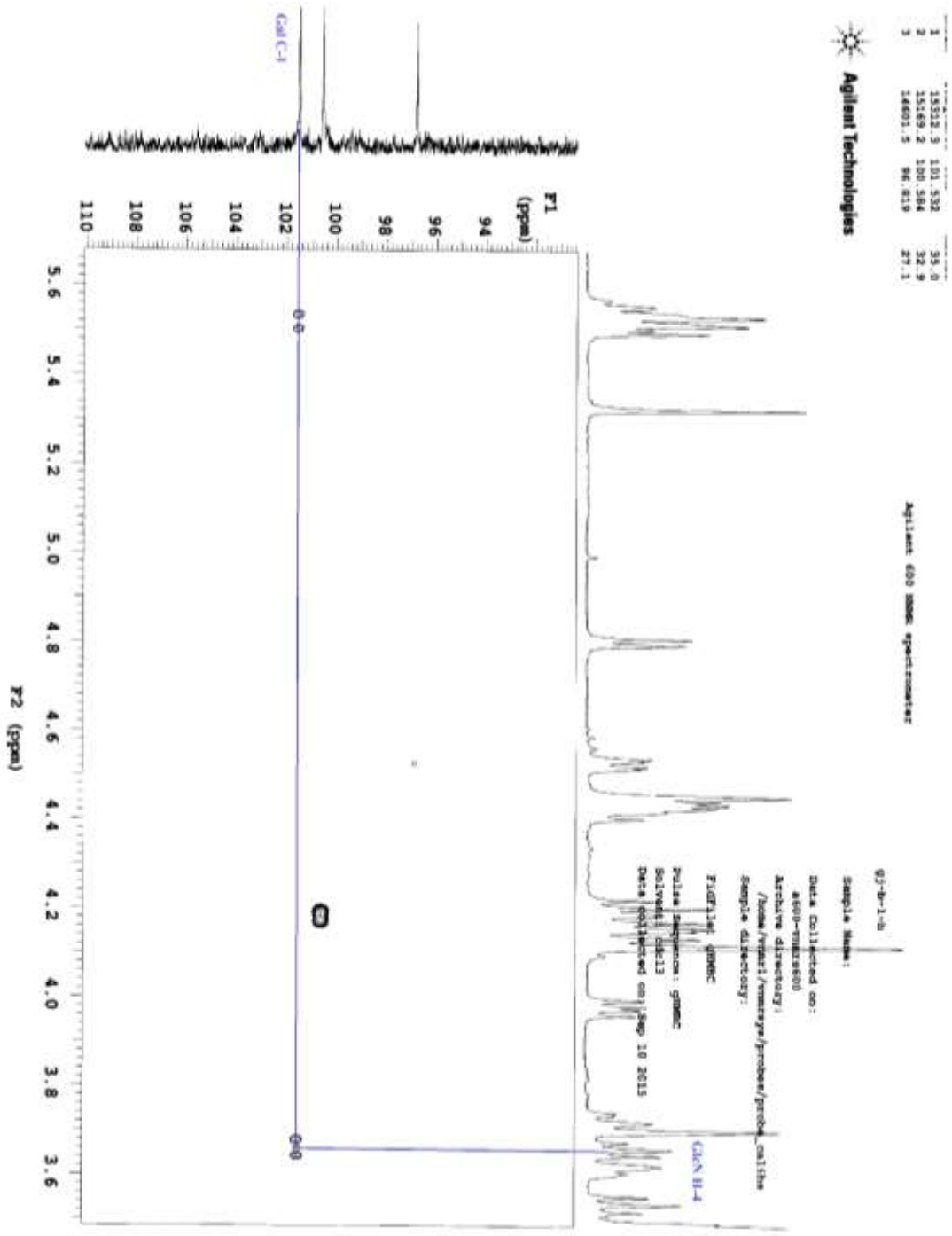


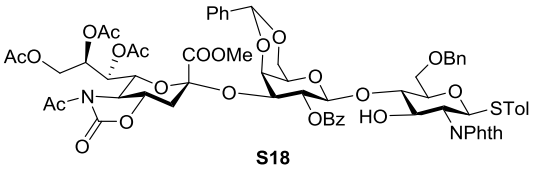


S18

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

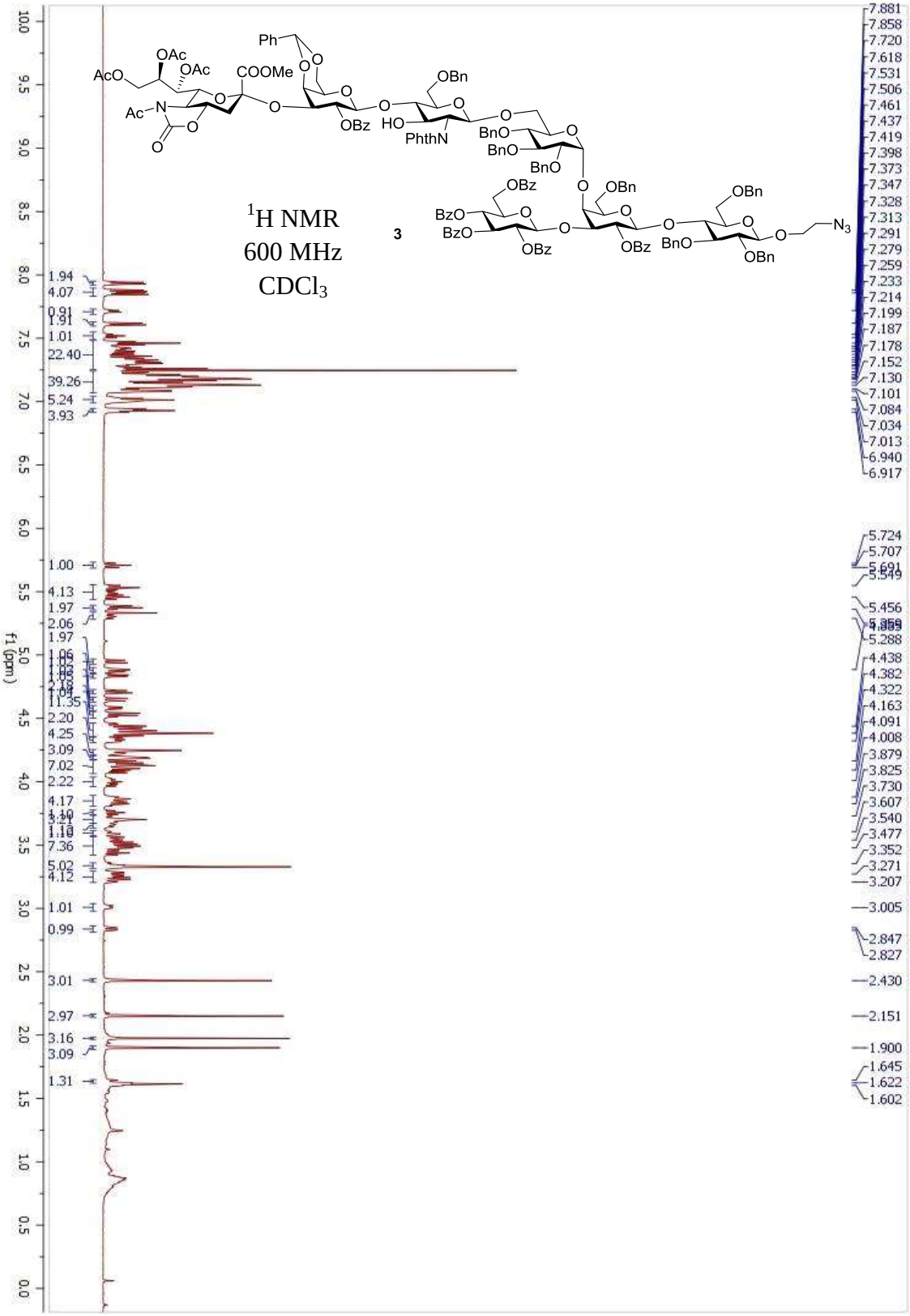

Ph
OAc
AcO
OAc
COOMe
OBn
Ac
N
HO
STol
OBz
NPhth
S18
^{1}H-^{13}C HMBC
150/600 MHz
$CDCl_3$
Agilent Technologies
F1 (ppm)
F2 (ppm)

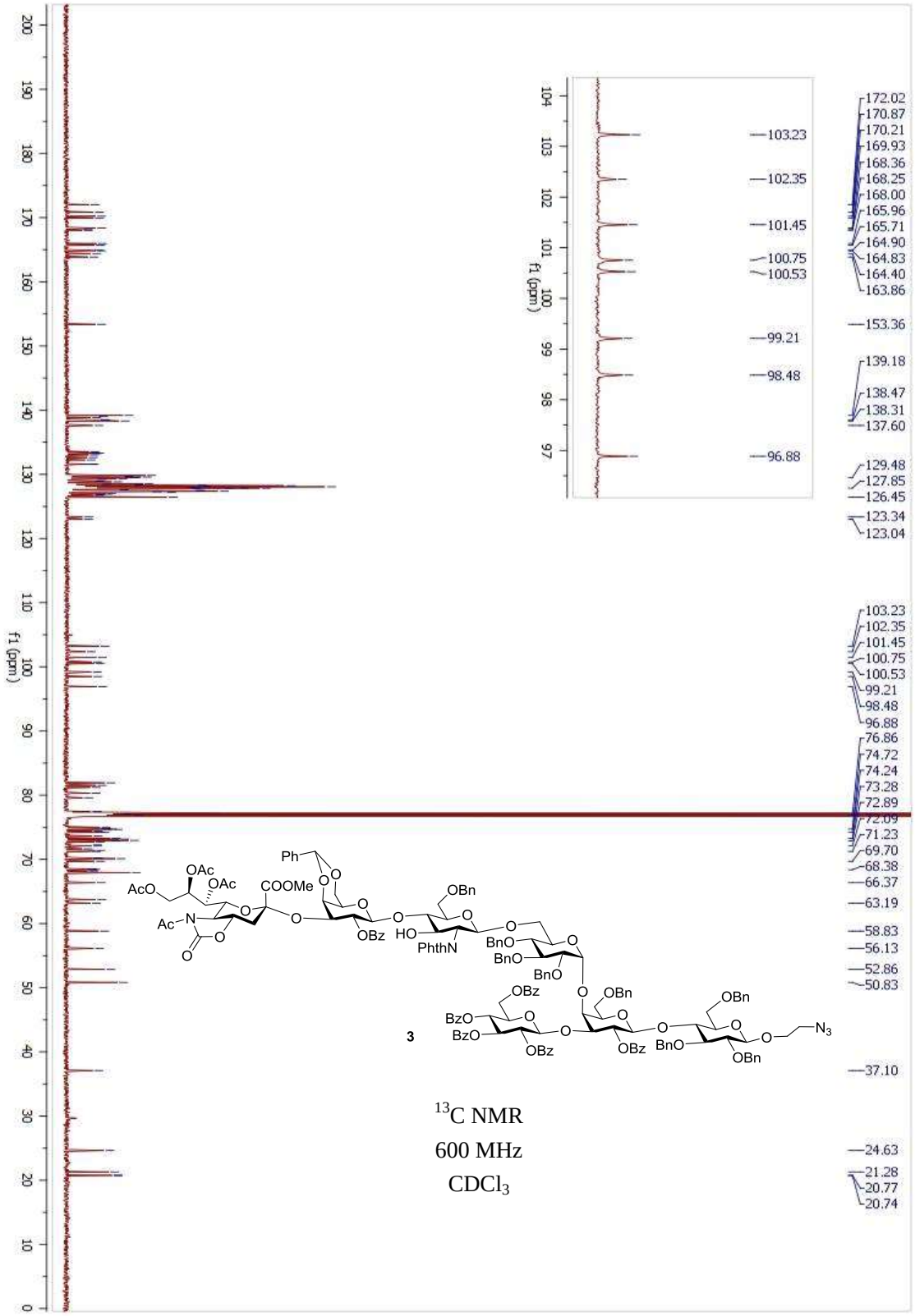




S18

^{1}H-^{13}C HMBC
150/600 MHz
$CDCl_3$

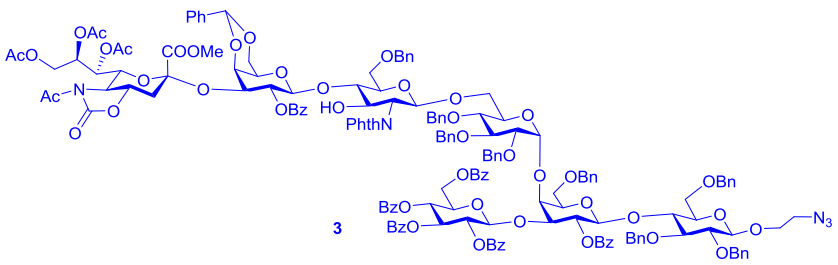

^{1}H NMR
600 MHz
$CDCl_3$
3
f1 (ppm)



^{13}C NMR

600 MHz

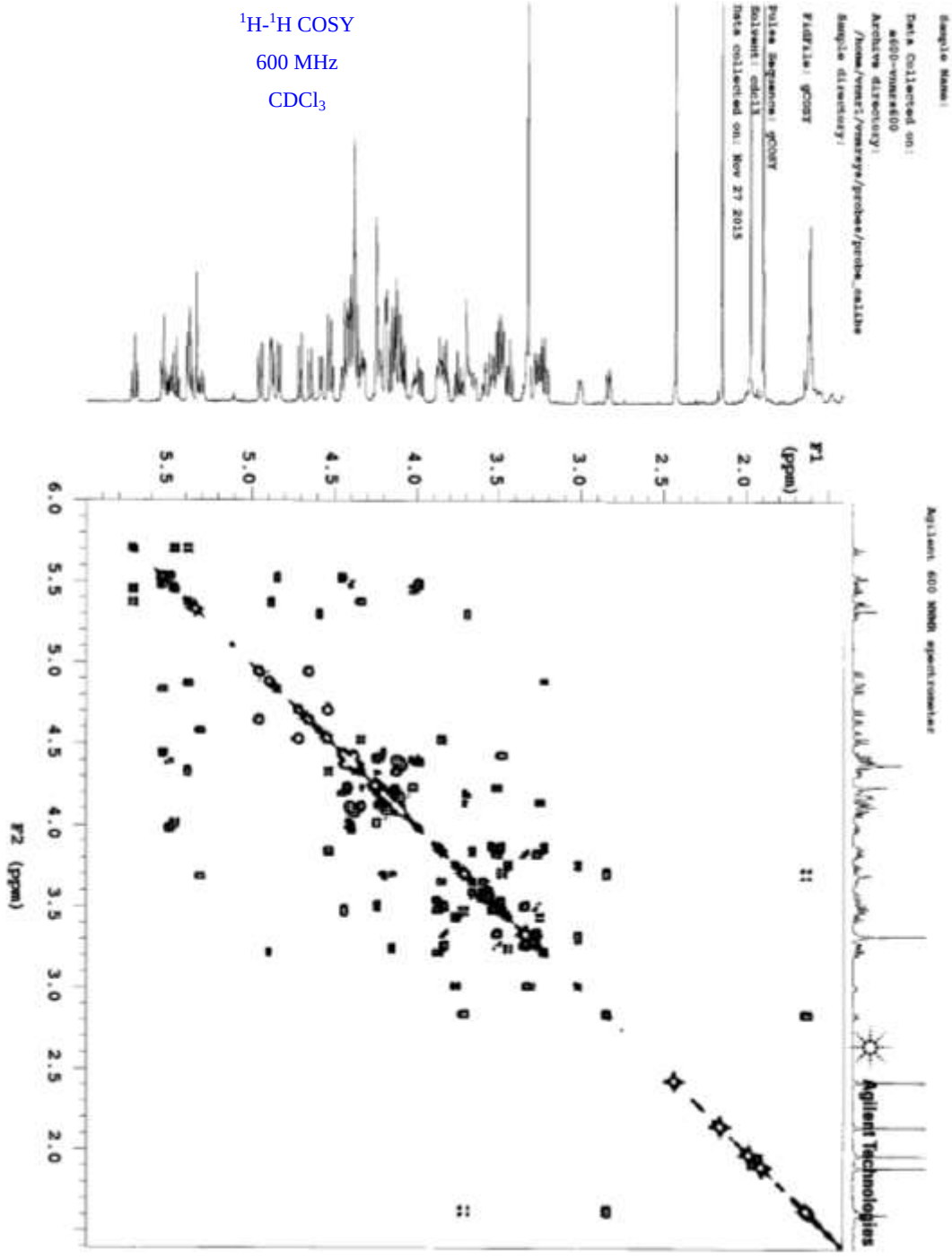
$CDCl_3$

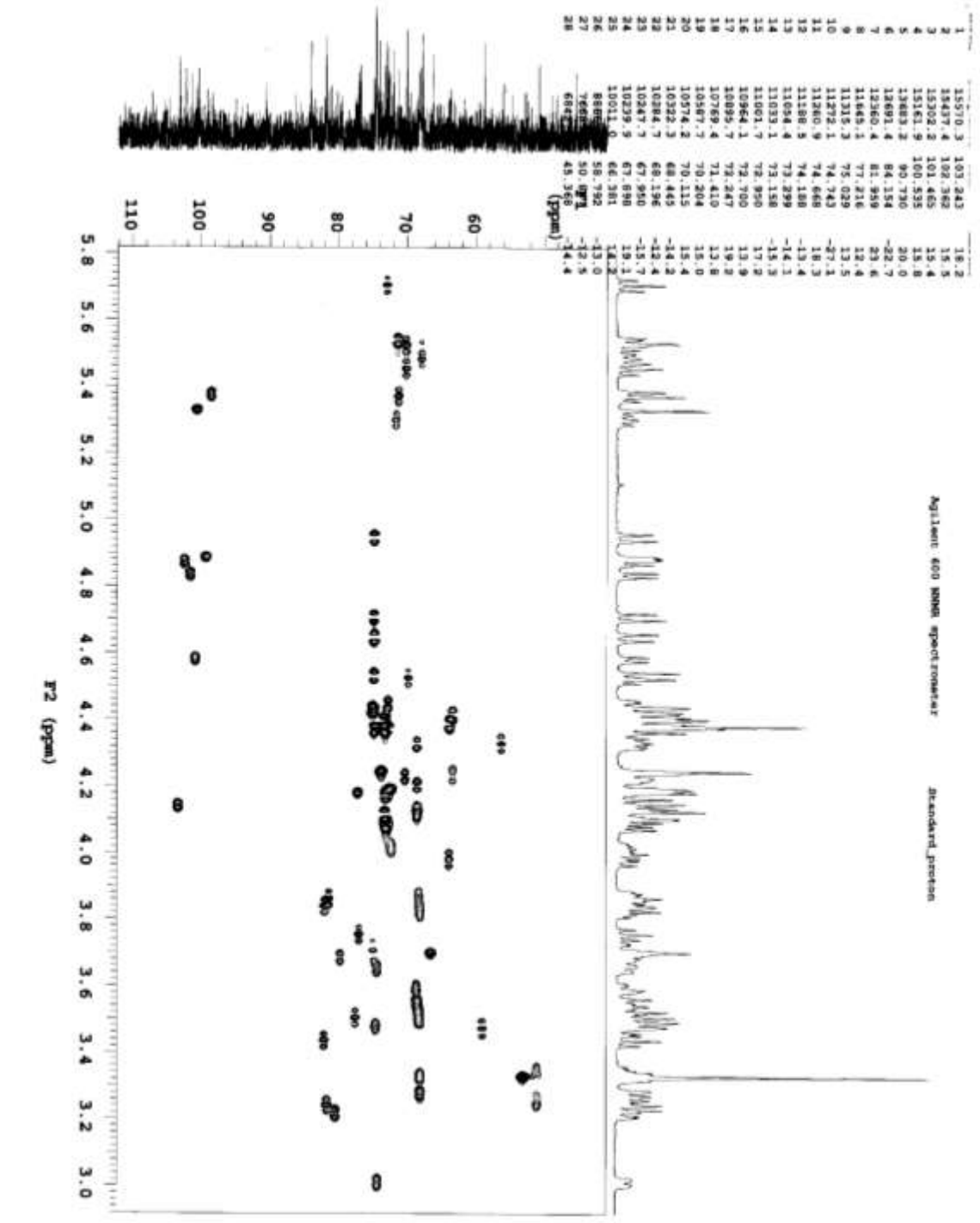


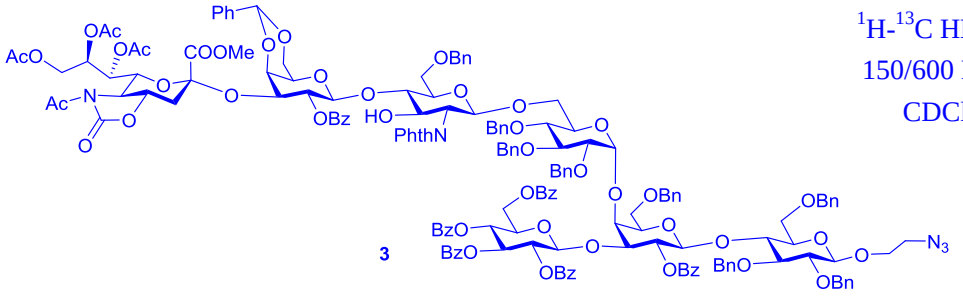
^{1}H-^{1}H COSY

600 MHz

$CDCl_3$

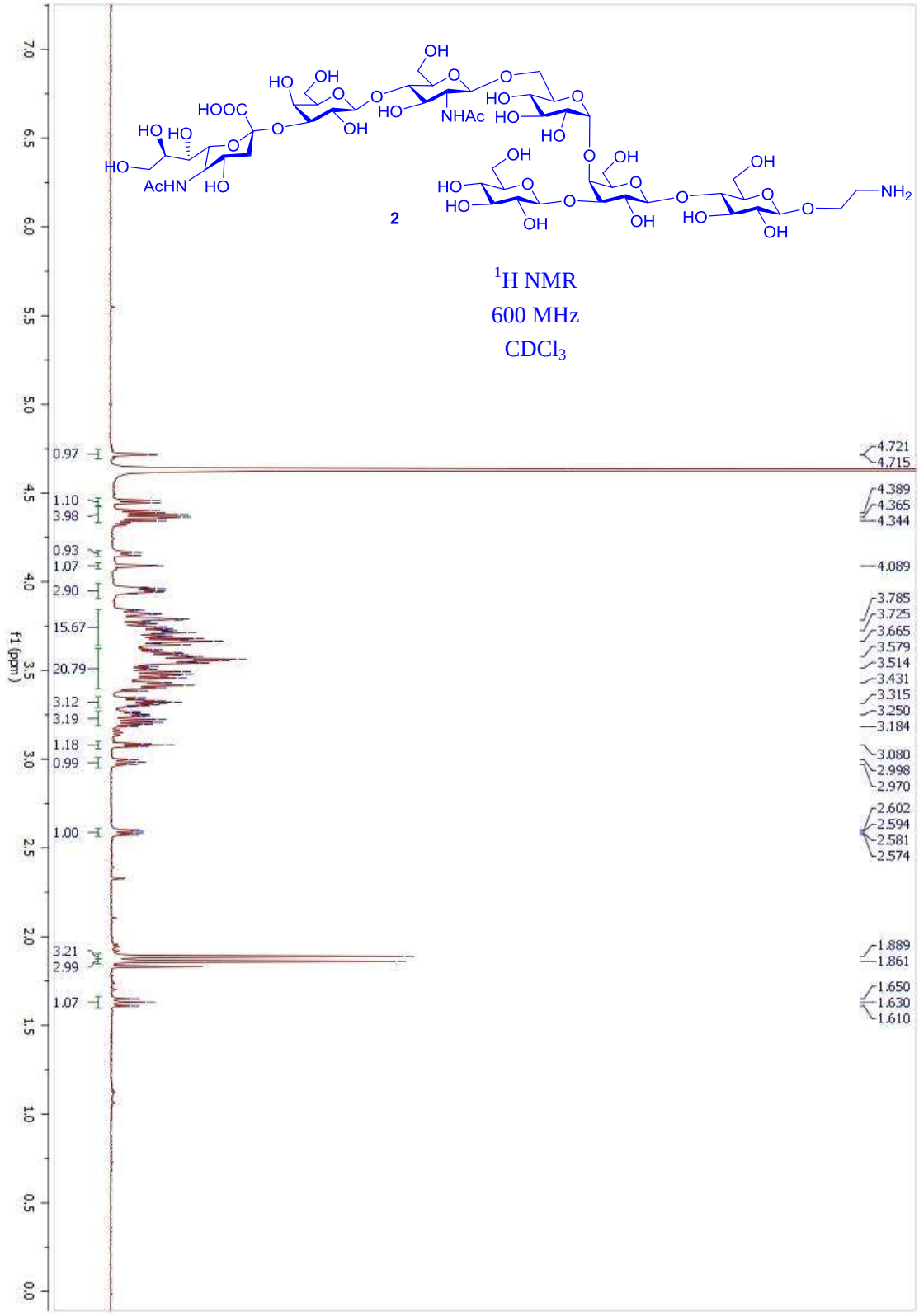


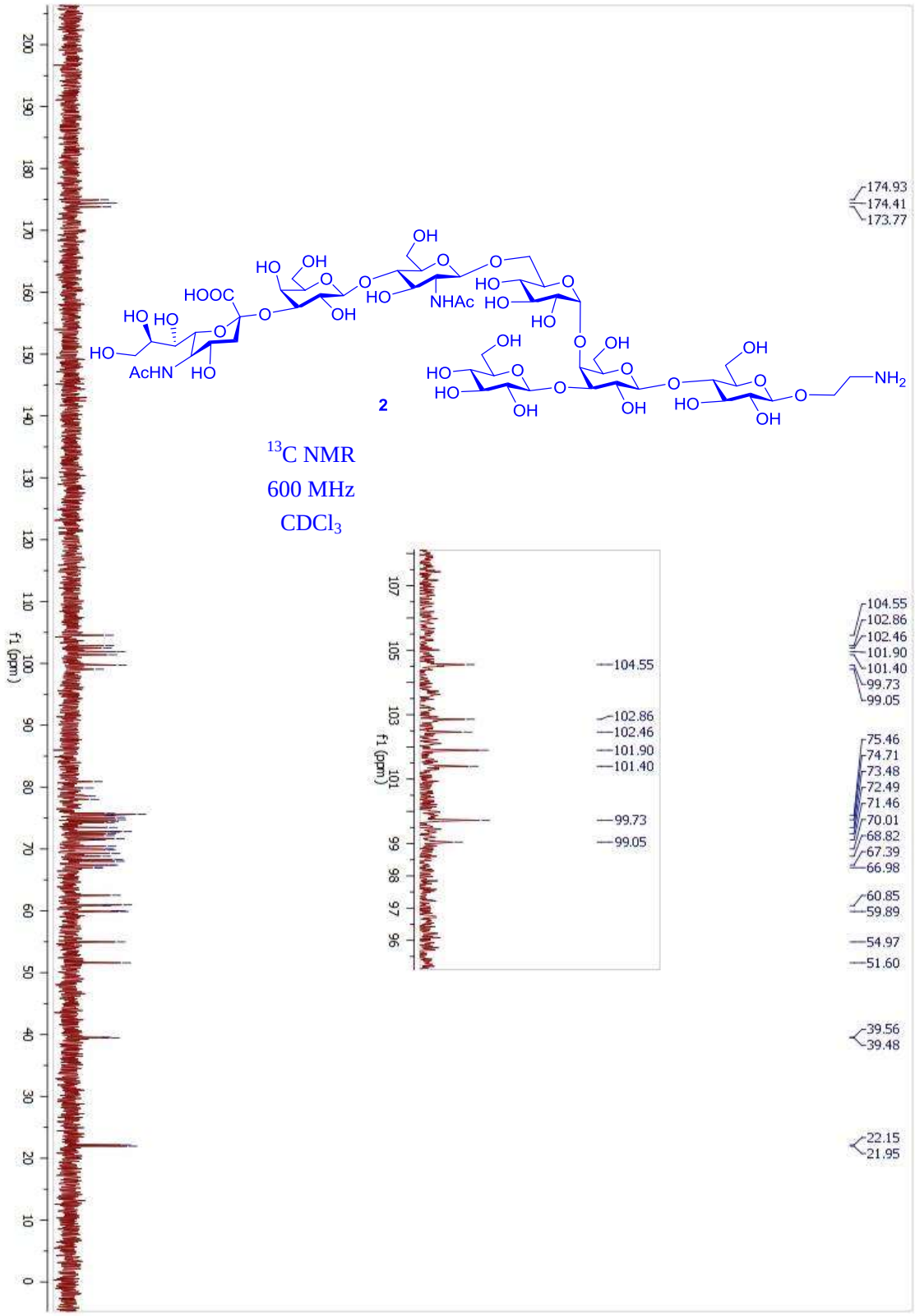


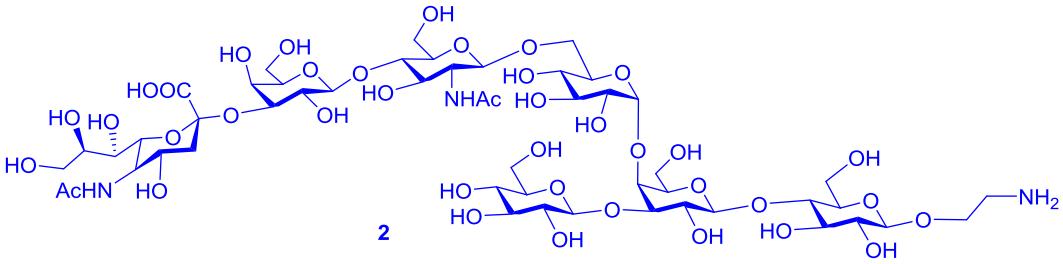


3

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


2
^{1}H NMR
600 MHz
$CDCl_3$
f1 (ppm)
0.97
1.10
3.98
0.93
1.07
2.90
15.67
20.79
3.12
3.19
1.18
0.99
1.00
3.21
2.99
1.07
4.721
4.715
4.389
4.365
4.344
4.089
3.785
3.725
3.665
3.579
3.514
3.431
3.315
3.250
3.184
3.080
2.998
2.970
2.602
2.594
2.581
2.574
1.889
1.861
1.650
1.630
1.610


174.93
174.41
173.77
104.55
102.86
102.46
101.90
101.40
99.73
99.05
75.46
74.71
73.48
72.49
71.46
70.01
68.82
67.39
66.98
60.85
59.89
54.97
51.60
39.56
39.48
22.15
21.95
f1 (ppm)
2
^{13}C NMR
600 MHz
$CDCl_3$

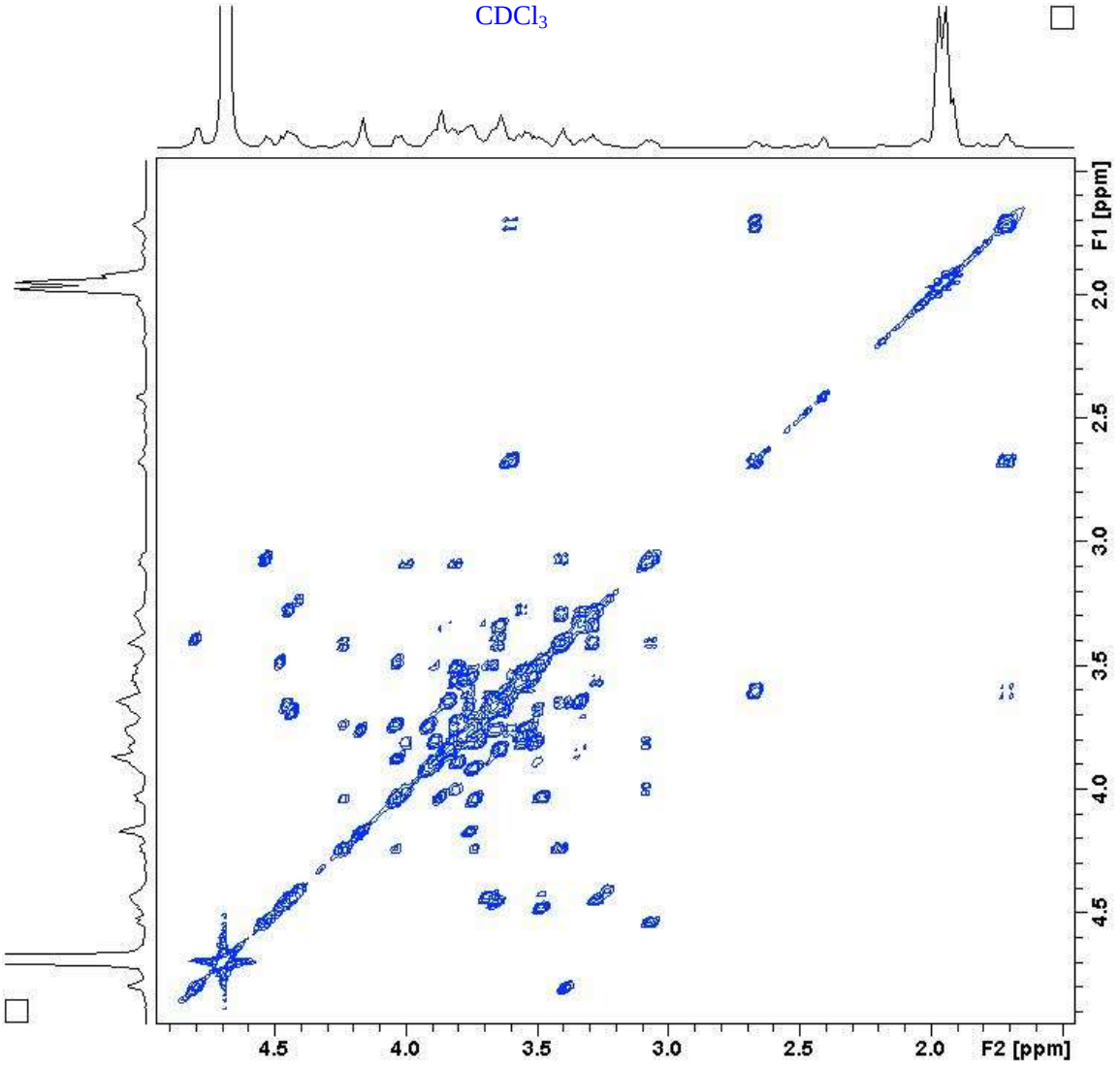


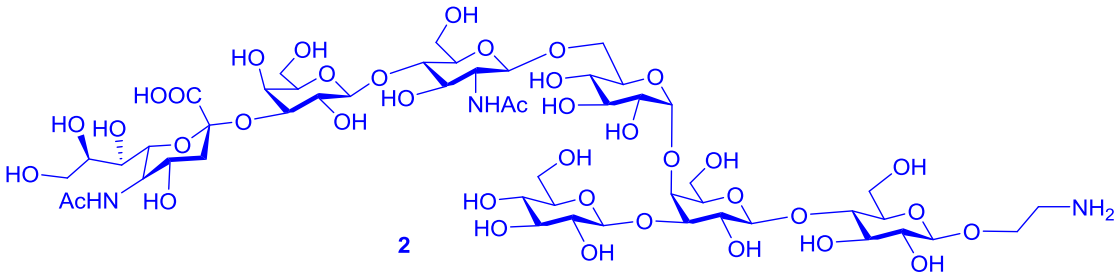
2

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

700 MHz

$CDCl_3$



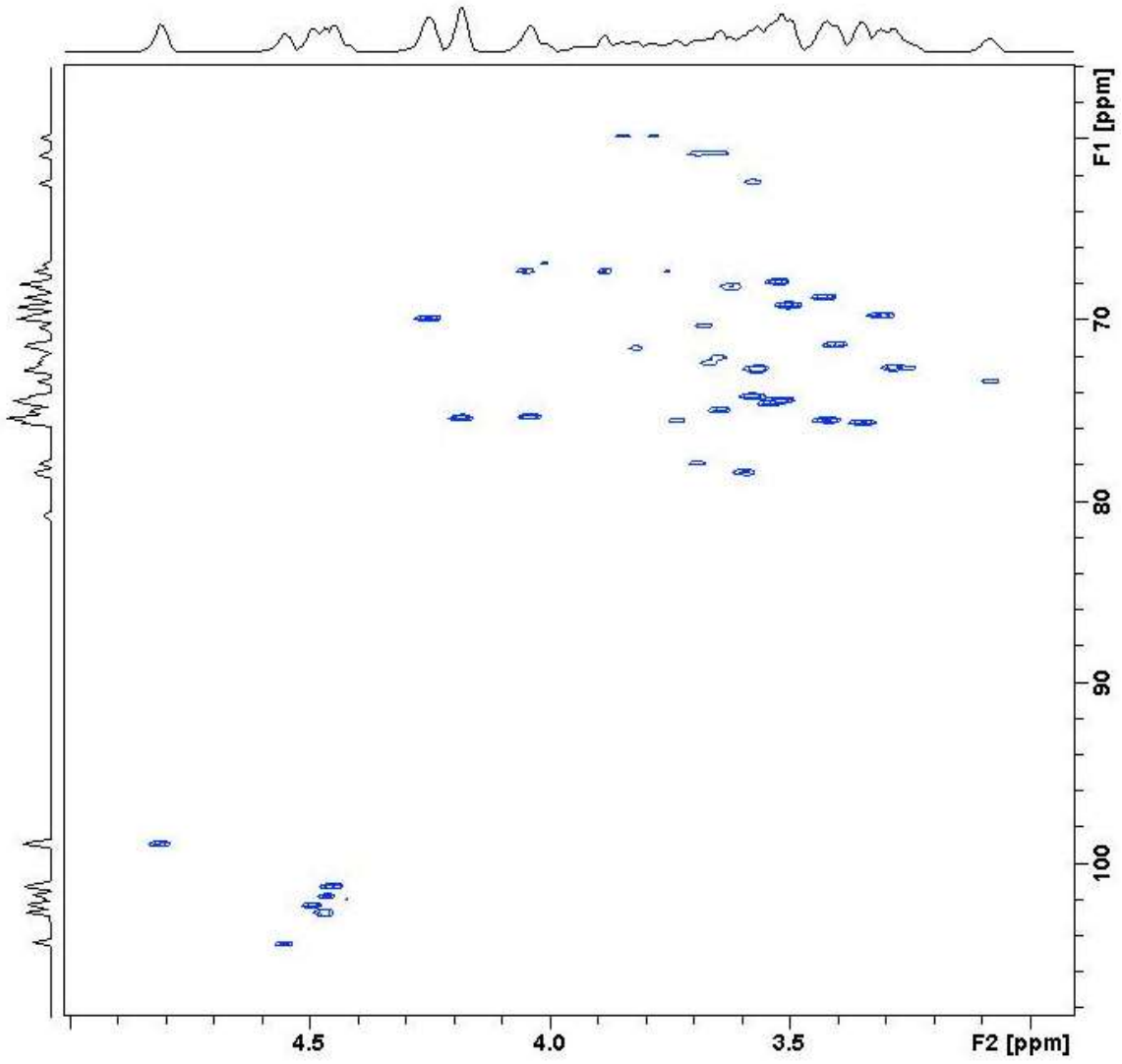


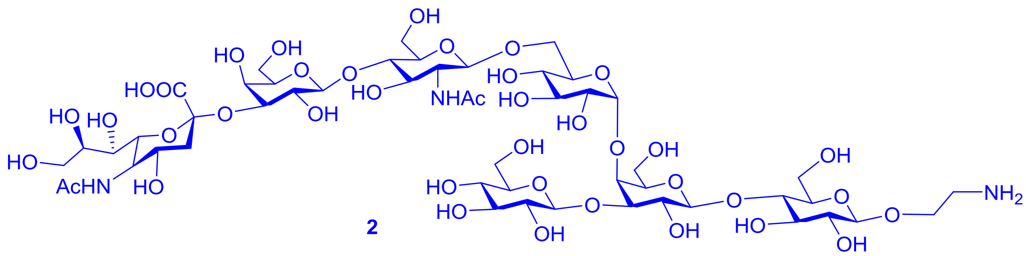
2

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

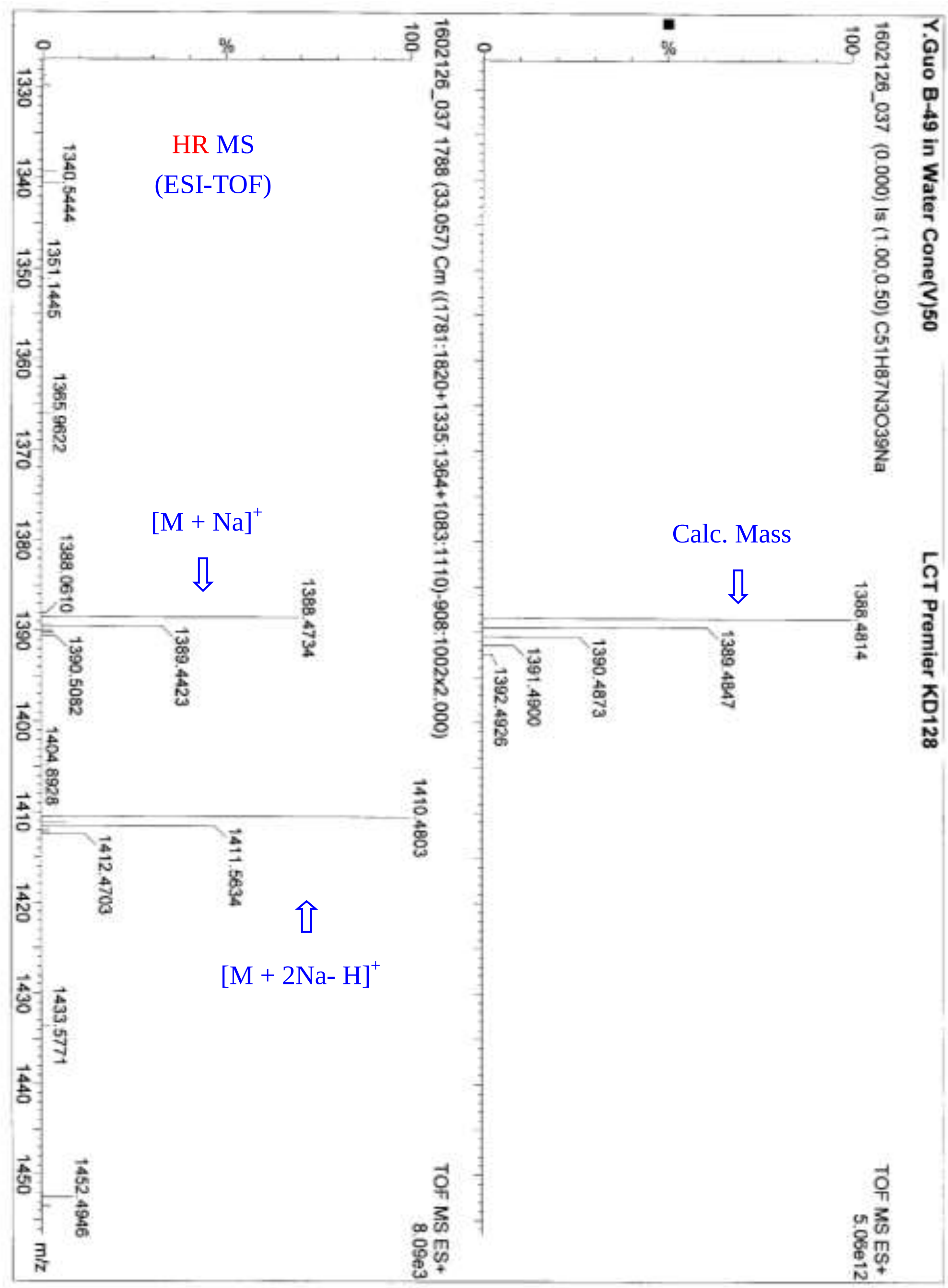
175/700 MHz

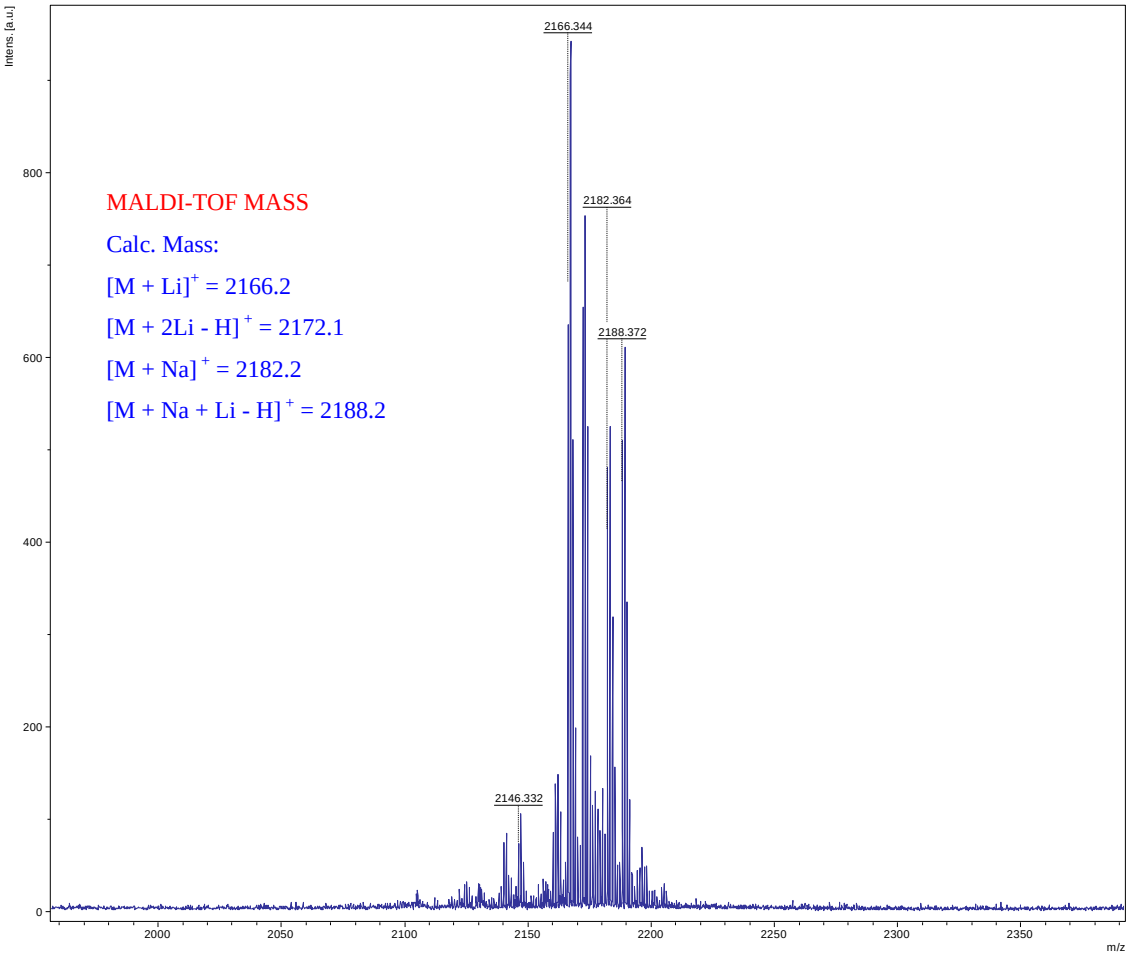
$CDCl_3$

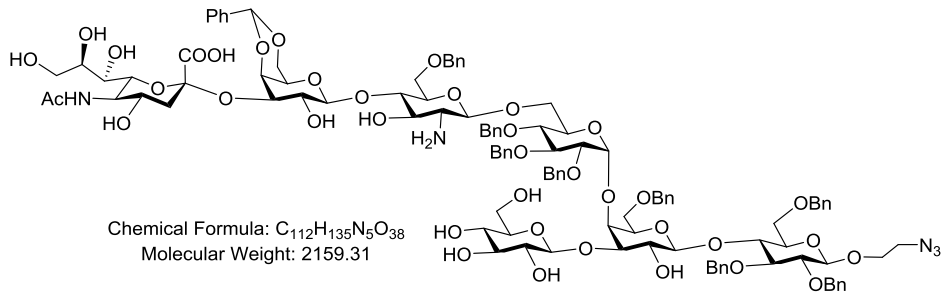



OH
HO
OH
HOOC
HO HO
HO
AcHN
HO
OH
HO
NHAc
HO
HO
HO
OH
OH
HO
HO
OH
OH
OH
HO
OH
NH2

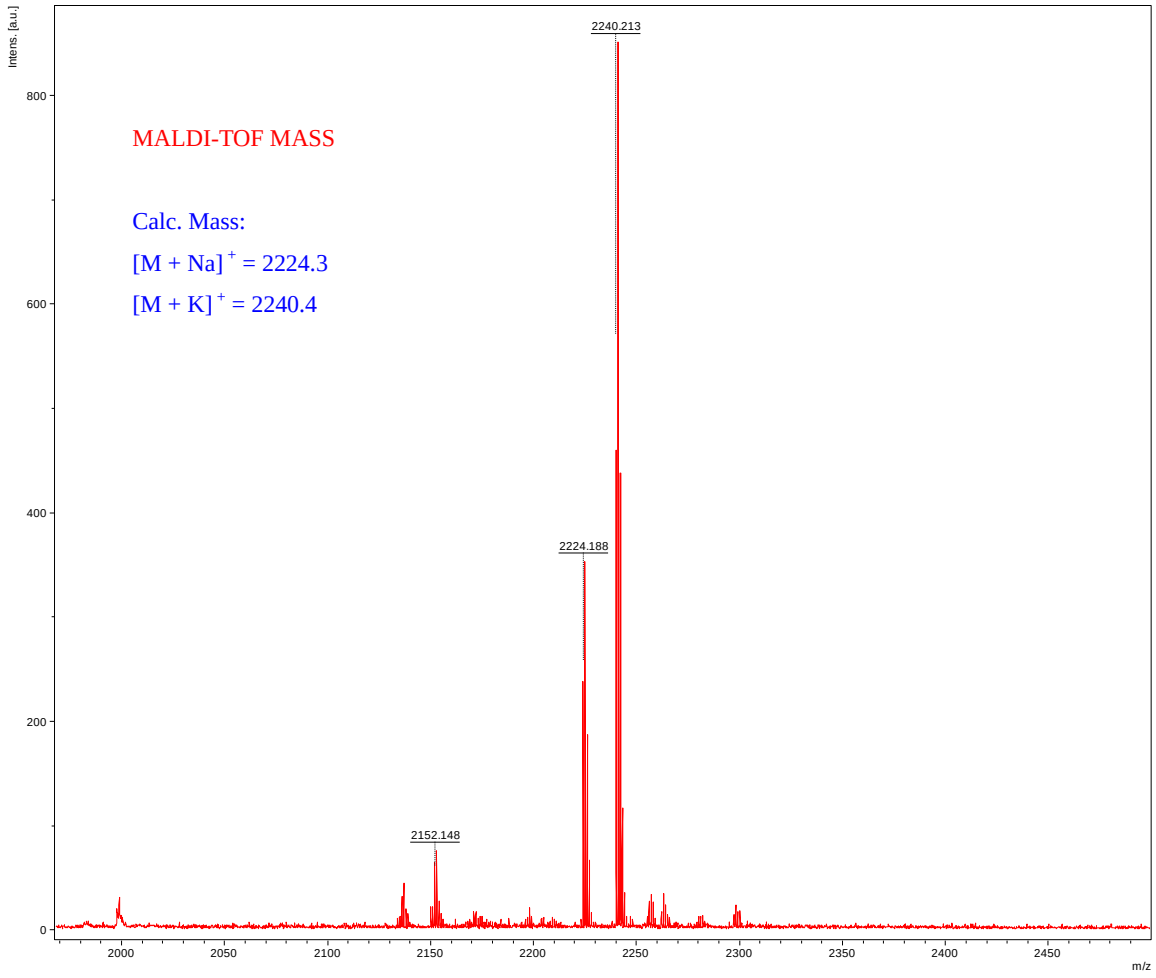
2

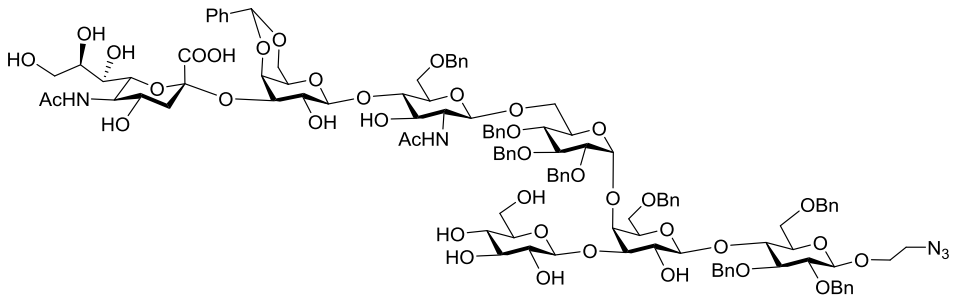

Y.Guo B-49 in Water Cone(V)50
LCT Premier KD128
1602126_037 (0.000) Is (1.00,0.50) C51H87N3O39Na
TOF MS ES+
5.06e12
Calc. Mass
1388.4814
1389.4847
1390.4873
1391.4900
1392.4926
1602126_037 1788 (33.057) Cm ((1781:1820+1335:1364+1083:1110)-908:1002x2.000)
TOF MS ES+
8.09e3
HR MS
(ESI-TOF)
[M + Na]+
[M + 2Na- H]+
1340.5444
1351.1445
1365.9622
1388.0610
1388.4734
1389.4423
1390.5082
1404.8928
1410.4803
1411.5634
1412.4703
1433.5771
1452.4946
m/z





Reaction intermediate after deacylation (the 2nd deprotectin step)





Chemical Formula: $C_{114}H_{137}N_5O_{39}$
Molecular Weight: 2201.3460

Reaction intermediate after selective *N*-acetylation (the 4th deprotectin step)