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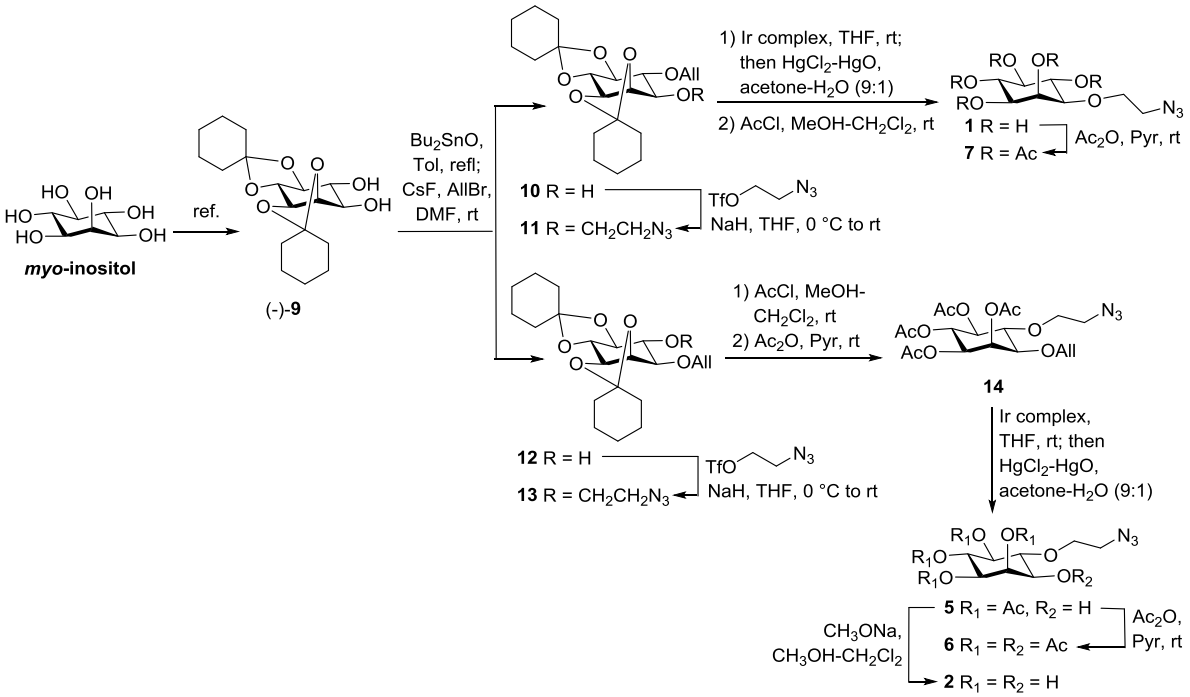
I. Experimental Section

Methods for the synthesis of inositol derivatives

General methods. Chemical and materials were purchased from commercial sources, and 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 F254 plates with detection by a UV detector and/or by charring with 20% phosphomolybdic acid in EtOH (w/v). Mass spectrometry (MS) was performed on a high resolution ESI-TOF MS machine. NMR spectra were recorded on a 500 and 600 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.

Scheme S1. Synthesis of azide-labeled *myo*-inositol analogs **1**-**2** and **5**-**7**



4-*O*-Allyl-1,2:5,6-di-*O*-cyclohexylidene-D-*myo*-inositol (10) and 3-*O*-Allyl-1,2:5,6-di-*O*-cyclohexylidene-D-*myo*-inositol (12). A reaction mixture of (-)-**9**[1] (4.0 g, 11.8 mmol) and Bu_2SnO (4.4 g, 17.7 mmol) in 60 mL of toluene was refluxed with azeotropic removal of water for 6 h. After the reaction was cooled to room temperature, toluene was removed under reduced pressure. To the residue were dissolved in anhydrous DMF (30 mL), followed by addition of CsF (5.38 g, 35.4 mmol) and allyl bromide (1.5 mL, 17.7 mmol). The reaction mixture was stirred at room temperature under a N_2 atmosphere for 24 h, at the end of which time TLC indicated the completion of reaction. The solution was diluted with ethyl acetate and washed with saturated aq. NaCl solution. The organic layer was dried with Na_2SO_4 and concentrated in vacuum. Column chromatograph of the residue with ethyl acetate and hexane (1:5) as eluent gave **10** (2.86 g, 64%) or **12** (939 mg, 21%) as colorless syrup. The NMR data of **10** were in accordance with that of the reported:[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.93-5.86 (m, 1H, All), 5.29 (dd, J = 17.0, 1.5 Hz, 1H, All), 5.17 (dd, J = 10.5, 1.5 Hz, 1H, All), 4.39 (dd, J = 7.5, 3.5 Hz, 1H, H-2), 4.31 (t, J = 7.5 Hz, 1H, H-1), 4.20 (dd, J = 13.0, 5.5 Hz, 1H, All), 4.15-4.08 (m, 2H, All, H-6), 3.94 (m, 1H, H-3), 3.79 (dd, J = 7.8, 1.8 Hz, 1H, H-4), 3.45 (dd, J = 10.5, 7.8 Hz, 1H, H-5), 2.59 (s, 1H, OH), 1.71-1.31 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.5, 117.5, 113.1, 111.4, 79.9, 78.9, 76.8, 76.6, 75.4, 72.3, 70.8, 36.8, 36.7, 36.5, 33.6, 25.3, 25.2, 24.0, 23.9, 23.8, 23.5. Compound **12:** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.98-5.90 (m, 1H, All), 5.30 (dd, J = 17.5, 1.0 Hz, 1H, All), 5.21 (d, J = 10.3 Hz, 1H, All), 4.48 (t, J = 5.0 Hz, 1H, H-2), 4.24-4.21 (m, 2H, H-1), 4.14 (dd, J = 13.0, 6.0 Hz, 1H), 4.03 (dd, J = 10.0, 6.5 Hz, 1H, H-4), 3.76 (t, J = 10.0 Hz, 1H, H-6), 3.52 (dd, J = 6.5, 4.5 Hz, 1H, H-3), 3.32 (t, J = 10.0 Hz, 1H, H-5), 2.58 (s, 1H), 1.75-1.36 (m, 20H). ^{13}C NMR (150 MHz,

$CDCl_3$) δ: 134.6, 118.1, 113.1, 111.3, 80.9, 78.8, 77.6, 76.3, 74.3, 72.4, 72.0, 37.8, 36.7, 36.5, 35.2, 25.2, 25.1, 24.1, 23.79, 23.78, 23.74. HR MS (ESI-TOF) *m/z*: calcd for $C_{21}H_{32}O_6Na$ [M + Na]$^+$ 403.2097, found 403.2114.

3-*O*-Azidoethyl-4-*O*-Allyl-1,2:5,6-di-*O*-cyclohexylidene-D-*myo*-inositol (11). A solution of **10** (200 mg, 0.526 mmol) in 15 mL of anhydrous THF was mixed with NaH (51 mg, 2.105 mmol) and 2-azidoethyl trifluoromethanesulfonate (459 mg, 2.105 mmol) at 0 ºC under a N_2 atmosphere. After the mixture was stirred at room temperature for 1 h, excessive NaH was quenched with saturated aq. NaCl solution, and the mixture was diluted with ethyl acetate. The organic layer, after being washed with saturated aq. NaCl solution, was dried with Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column with ethyl acetate and hexane (1:15) as eluent to afford **11** (208 mg, 88%) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.94-5.87 (m, 1H, All), 5.30 (dd, *J* = 17.2, 1.6 Hz, 1H, All), 5.18 (dd, *J* = 10.4, 1.3 Hz, 1H, All), 4.37 (dd, *J* = 6.9, 3.9 Hz, 1H, H-2), 4.28 (t, *J* = 7.2 Hz, 1H, H-1), 4.22 (dd, *J* = 13.2, 4.8 Hz, 1H, All), 4.11 (dd, *J* = 13.2, 5.4 Hz, 1H, All), 4.04 (dd, *J* = 10.8, 7.8 Hz, 1H, H-6), 3.86-3.82 (m, 1H), 3.79 (dd, *J* = 7.8, 3.0 Hz, 1H, H-4), 3.76-3.72 (m, 1H), 3.62 (t, *J* = 3.0 Hz, 1H, H-3), 3.42-3.37 (m, 2H, H-5), 3.30-3.26 (m, 1H), 1.74-1.36 (m, 20H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 134.4, 117.2, 112.9, 111.5, 81.1, 79.6, 78.6, 76.7, 76.4, 74.9, 70.76, 70.74, 50.9, 36.6, 36.5, 36.4, 34.4, 25.1, 25.0, 23.9, 23.7, 23.7, 23.5. HR MS (ESI-TOF) *m/z*: calcd for $C_{23}H_{35}N_3O_6Na$ [M + Na]$^+$ 472.2424, found 472.2421.

3-*O*-Azidoethyl-D-*myo*-inositol (1). A solution of $[Ir(COD)(PMePh_2)_2]PF_6$ (68 mg, 0.080 mmol) in 5 mL of anhydrous THF was stirred at room temperature under a H_2 atmosphere until the red color turned to pale yellow in about 10 min. The H_2 was exchanged

with argon thoroughly (three times) before the solution of compound **11** (180 mg, 0.401 mmol) in 5 mL anhydrous THF was added slowly. The reaction mixture was stirred at room temperature for 30 min, at the end of which TLC indicated the completion of reaction. The reaction mixture was concentrated under reduced pressure, and after the residue was dissolved in acetone and water (10 mL, 9:1, v/v), the solution were treated with $HgCl_2$ (545 mg, 2.01 mmol) and HgO (9 mg, 0.04 mmol). Fifteen minutes later, the mixture was concentrated and purified by silica gel column chromatograpgy with ethyl acetate and hexane (1:2) to afford the intermediate product as syrup. It was dissolved in CH_3OH-CH_2Cl_2 (12 mL, 1:3, v/v), followed by addition of acetyl chloride (32 μL). The solution was stirred at room temperature for 2 h. Triethylamine (123 μL) was added to quench the reaction. The solution was concentrated under vacuum, and the residue was purified by silica gel column chromatograpgy with CH_3OH and CH_2Cl_2 (1:4) as eluent to give **1** as colorless syrup (72 mg, 72% for two steps). ^{1}H NMR (600 MHz, CD_3OD) δ: 4.12 (t, J = 2.7 Hz, 1H, H-2), 3.83-3.78 (m, 1H), 3.74-3.72 (m, 1H), 3.70 (t, J = 9.6 Hz, 1H, H-4), 3.60 (t, J = 9.6 Hz, 1H, H-6), 3.49-3.40 (m, 2H), 3.31 (dd, J = 9.6, 2.7 Hz,1H, H-1), 3.17-3.13 (m, 2H, H-3, H-5). ^{13}C NMR (150 MHz, CD_3OD) δ: 82.4, 76.6, 74.2, 73.8, 73.4, 71.2, 70.1, 52.3. HR MS (ESI-TOF) *m/z*: calcd for $C_{16}H_{30}N_6O_{12}Na$ $[2M + Na]^+$ 521.1819, found 521.1812.

1,2,4,5,6-Penta-*O*-acetyl-3-*O*-azidoethyl-D-*myo*-inositol (7). To a solution of **1** (30 mg, 0.12 mmol) in 5 mL of pyridine was added Ac_2O (300 μL) at room temperature. The mixture was stirred overnight and then concentrated under vacuum. The residue was purified by silica gel column chromatography with ethyl acetate and hexane (1:2) as eluent to give **7** (50 mg, 90%) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.69 (t, J = 3.0 Hz, 1H, H-2),

5.48 (t, *J* = 10.2 Hz, 1H, H-6), 5.40 (t, *J* = 10.2 Hz, 1H, H-4), 5.11 (t, *J* = 10.2 Hz, 1H, H-5), 4.94 (dd, *J* = 10.2, 3.0 Hz, 1H, H-1), 3.79-3.76 (m, 1H), 3.58 (dd, *J* = 10.2, 3.0 Hz, 1H, H-3), 3.53-3.50 (m, 1H), 3.33-3.22 (m, 2H), 2.19 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.00 (3 × s, 9H, 3 × OAc). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 170.3, 170.15, 170.11, 169.9, 169.8, 76.4, 71.4, 71.0, 69.7, 69.6, 69.3, 66.9, 50.9, 21.0, 20.9, 20.78, 20.75, 20.72. HR MS (ESI-TOF) *m/z*: calcd for $C_{18}H_{25}N_3O_{11}Na$ $[M + Na]^+$ 482.1387, found 482.1410.

3-*O*-Allyl-4-*O*-azidoethyl-1,2:5,6-di-*O*-cyclohexylidene-D-*myo*-inositol (13). The azido ethyl group was attached to the 3-*O*-position of compound **12** (850 mg, 2.24 mmol) by the same procedure described for the synthesis of **11** to give **13** (844 mg, 84%) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) *δ*: 5.91-5.85 (m, 1H, All), 5.28 (dd, *J* = 17.4, 1.2 Hz, 1H, All), 5.16 (d, *J* = 10.2 Hz, 1H, All), 4.35 (dd, *J* = 6.6, 4.2 Hz, 1H, H-2), 4.27 (t, *J* = 7.2 Hz, 1H, H-1), 4.15 (d, *J* = 5.4 Hz, 2H, All), 4.02 (dd, *J* = 10.2, 7.2 Hz, 1H, H-6), 3.89-3.85 (m, 1H), 3.77-3.74 (m, 1H), 3.71 (dd, *J* = 7.8, 3.0 Hz, 1H, H-4), 3.63 (t, *J* = 3.6 Hz, 1H, H-3), 3.41-3.36 (m, 2H, H-5), 3.32-3.28 (m, 1H), 1.72-1.35 (m, 20H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*: 134.7, 117.2, 112.9, 111.5, 80.7, 79.3, 78.3, 77.0, 76.3, 74.8, 72.5, 69.1, 50.6, 36.6, 36.5, 36.4, 34.5, 25.1, 25.0, 23.9, 23.67, 23.66, 23.6. HR MS (ESI-TOF) *m/z*: calcd for $C_{23}H_{35}N_3O_6Na$ $[M + Na]^+$ 472.2424, found 403.2439.

1,2,5,6-Tetra-*O*-acetyl-3-*O*-allyl-4-*O*-azidoethyl-D-*myo*-inositol (14). The removal of the two cyclohexyl ketals in **13** (800 mg, 1.78 mmol) followed the same procedure described for the synthesis of **1**, which offered the intermediate product as colorless syrup, which was then dissolved in pyridine (20 mL) and Ac_2O (4 mL) at room temperature. The solution was stirred overnight and then concentrated under vacuum. The residue was purified by silica gel

column chromatograpgy with ethyl acetate and hexane (1:2) as eluent to give **14** (603 mg, 74% for two steps) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.85-5.79 (m, 1H, All), 5.61 (t, *J* = 3.0 Hz, 1H, H-2), 5.36 (t, *J* = 10.2 Hz, 1H, H-6), 5.25 (dd, *J* = 17.4, 1.2 Hz, 1H, All), 5.17 (dd, *J* = 10.4, 1.2 Hz, 1H, All), 5.04 (t, *J* = 10.2 Hz, 1H, H-5), 4.88 (dd, *J* = 10.8, 3.0 Hz, 1H, H-1), 4.09 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.00-3.92 (m, 2H), 3.69-3.65 (m, 2H, H-4), 3.49 (dd, *J* = 9.6, 3.0 Hz, 1H, H-3), 3.31-3.29 (m, 2H), 2.14 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 169.9, 169.8, 169.7, 133.7, 118.0, 79.1, 76.8, 72.2, 71.9, 71.2, 69.7, 69.1, 67.2, 51.1, 20.8, 20.7, 20.6, 20.5. HR MS (ESI-TOF) *m/z*: calcd for $C_{19}H_{27}N_3O_{10}Na$ $[M + Na]^+$ 480.1594, found 480.1603.

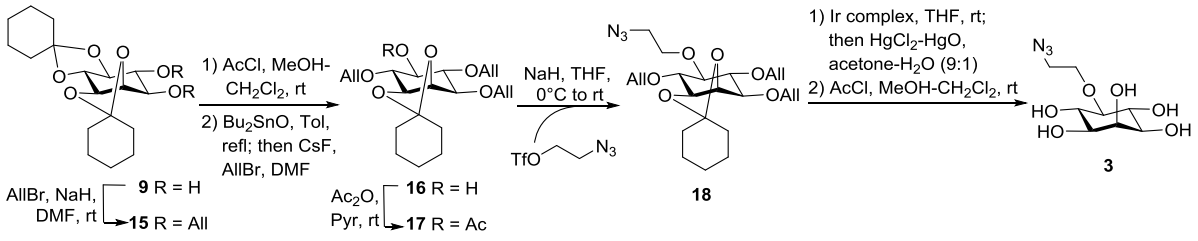
1,2,5,6-Tetra-*O*-acetyl-4-*O*-azidoethyl-D-*myo*-inositol (5). The removal of the All group in **14** (550 mg, 1.20 mmol) followed the same procedure for the synthesis of **1**, which offered **5** (432 mg, 86%) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.54 (t, *J* = 2.7 Hz, 1H, H-2), 5.33 (t, *J* = 10.2 Hz, 1H, H-6), 5.05 (t, *J* = 10.2 Hz, 1H, H-5), 4.91 (dd, *J* = 10.5, 2.8 Hz, 1H, H-1), 3.84-3.75 (m, 3H, H-3), 3.65 (t, *J* = 9.6 Hz, 1H, H-4), 3.38 (t, *J* = 4.8 Hz, 2H), 3.19 (d, *J* = 3.6 Hz, 1H, OH), 2.13 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.94 (s, 3H, OAc). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 170.5, 170.2, 170.1, 170.0, 80.4, 72.7, 71.7, 70.3, 70.1, 69.7, 69.4, 51.5, 21.0, 20.9, 20.76, 20.70. HR MS (ESI-TOF) *m/z*: calcd for $C_{16}H_{23}N_3O_{10}Na$ $[M + Na]^+$ 440.1281, found 440.1287.

1,2,4,5,6-Penta-*O*-acetyl-4-*O*-azidoethyl-D-*myo*-inositol (6). Acetylation of **5** (45 mg, 0.108 mmol) followed the same procedure for the synthesis of **7**, which offered **6** as colorless syrup (47 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.55 (t, *J* = 2.8 Hz, 1H, H-2), 5.37 (t, *J* = 10.2 Hz, 1H, H-6), 5.12 (t, *J* = 9.6 Hz, 1H, H-5), 5.05 (dd, *J* = 10.2, 2.8 Hz, 1H,

H-1), 4.99 (dd, *J* = 10.2, 2.8 Hz, 1H, H-3), 3.84 (t, *J* = 10.2 Hz, 1H, H-4), 3.74-3.66 (m, 2H), 3.32-3.25 (m, 2H), 2.16 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.96 (s, 3H, OAc). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 170.3, 169.9, 169.7, 169.53, 169.51, 77.6, 72.5, 71.6, 70.4, 70.1, 68.7, 68.6, 51.2, 21.0, 20.89, 20.85, 20.80, 20.7. HR MS (ESI-TOF) *m/z*: calcd for $C_{18}H_{25}N_3O_{11}Na$ $[M + Na]^+$ 482.1387, found 482.1396.

4-*O*-Azidoethyl-D-*myo*-inositol (2). To a solution of **5** (50 mg, 0.12 mmol) in CH_2Cl_2 and CH_3OH (1:1, 10 mL) was added a CH_3ONa solution (0.5 M in CH_3OH) until the pH reached 10. The mixture was stirred at room temperature for 3 h, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatograpgy with CH_3OH and CH_2Cl_2 (1:4) as eluent to give **2** as colorless syrup (27 mg, 89%). ^{1}H NMR (600 MHz, CD_3OD) δ: 3.99-3.93 (m, 3H), 3.62 (t, *J* = 9.6 Hz, 1H), 3.46-3.43 (m, 4H), 3.33 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.26-3.23 (m, 1H). ^{13}C NMR (150 MHz, CD_3OD) δ: 84.0, 76.4, 74.5, 74.4, 73.4, 73.3, 72.7, 52.5. HR MS (ESI-TOF) *m/z*: calcd for $C_{16}H_{30}N_6O_{12}Na$ $[2M + Na]^+$ 521.1819, found 521.1846.

Scheme S2. Synthesis of compound **3**



3,4-Di-*O*-allyl-1,2:5,6-di-*O*-cyclohexylidene-D-*myo*-inositol (15). To a solution of **9** (300 mg, 0.882 mmol) in 10 mL of anhydrous DMF was added NaH (85 mg, 3.53 mmol) and

AllBr (305 μL, 3.53 mmol) at 0 ºC under a N_2 atmosphere. One hour later, the reaction was quenched with saturated aq. NaCl solution. The organic layer, after washing with saturated aq. NaCl solution, was dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with ethyl acetate and hexane (1:15) as eluent to give **15** (322 mg, 87%) as colorless syrup. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.93-5.84 (m, 2H, All), 5.31-5.26 (m, 2H, All), 5.19-5.13 (m, 2H, All), 4.35 (dd, J = 6.6, 3.6 Hz, 1H, H-2), 4.28 (t, J = 7.2 Hz, 1H, H-1), 4.19 (dd, J = 13.2, 5.4 Hz, 1H, All), 4.15-4.08 (m, 3H, All), 4.07 (dd, J = 10.8, 7.2 Hz, 1H, H-6), 3.75 (dd, J = 7.8, 3.0 Hz, 1H, H-4), 3.63 (t, J = 3.0 Hz, 1H, H-3), 3.42 (dd, J = 10.8, 7.8 Hz, 1H, H-5), 1.72-1.36 (m, 20H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 135.0, 134.7, 117.3, 113.0, 111.8, 79.7, 79.4, 78.8, 77.1, 76.7, 75.2, 72.6, 70.9, 36.9, 36.8, 36.5, 34.9, 25.4, 25.3, 24.2, 23.95, 23.92, 23.8. HR MS (ESI-TOF) *m/z*: calcd for $C_{24}H_{36}O_6Na$ $[2M + Na]^+$ 443.2410, found 443.2415.

3,4,6-Tri-*O*-allyl-1,2-*O*-cyclohexylidene-D-*myo*-inositol (16). A solution of **15** (290 mg, 0.69 mmol) in CH_3OH-CH_2Cl_2 (1:3, 20 mL) was stirred with acetyl chloride (15 μL) at room temperature for 10 min. After the mixture was quenched with triethylamine (70 μL), the solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography with ethyl acetate and hexane (1:2) as eluent to give colorless syrup. Regioselective allylation of this product followed the same procedure for the synthesis of **10**, which offered **16** as colorless syrup (113 mg, 43% for two steps).^{1}H NMR (600 MHz, $CDCl_3$) δ: 5.95-5.86 (m, 3H, All), 5.28-5.24 (m, 3H, All), 5.17-5.12 (m, 3H, All), 4.38-4.29 (m, 3H, All-2H, H-2), 4.24-4.15 (m, 4H, All), 4.01 (t, J = 6.3 Hz, 1H, H-1), 3.60 (t, J = 8.4 Hz, 1H, H-4), 3.55-3.51 (m, 2H, H-3, H-6), 3.36 (dt, J = 9.6, 8.4 Hz, 1H, H-5), 2.67 (d, J = 1.8 Hz,

1H, OH), 1.78-1.28 (m, 10H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 135.15, 135.11, 135.0, 117.6, 117.4, 117.2, 110.7, 81.6, 80.2, 78.7, 77.3, 74.3, 73.6, 73.3, 72.5, 72.2, 37.4, 35.3, 25.2, 24.1, 23.7. HR MS (ESI-TOF) *m/z*: calcd for $C_{21}H_{32}O_6Na$ $[M + Na]^+$ 403.2097, found 403.2127.

3,4,6-Tri-*O*-allyl-5-*O*-acetyl-1,2-*O*-cyclohexylidene-D-*myo*-inositol (17). To confirm the structure of compound **16**, it (5.0 mg, 0.013 mmol) was acylated by the same procedure as described above to obtain compound **17** (5.2 mg, 94%) as colorless syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.98-5.82 (m, 3H, All), 5.33-5.13 (m, 6H, All), 4.90 (t, J = 10.2 Hz, 1H, H-5), 4.42 (dd, J = 5.7, 3.8 Hz, 1H, H-2), 4.28-4.20 (m, 4H, All), 4.17-4.11 (m, 3H, All, H-1), 3.74 (t, J = 8.5 Hz, 1H, H-6), 3.67 (dd, J = 8.5, 3.8 Hz, 1H, H-3), 3.63 (dd, J = 9.0, 6.5 Hz, 1H, H-4), 2.09 (s, 3H), 1.81-1.35 (m, 10H). HR MS (ESI-TOF) *m/z*: calcd for $C_{23}H_{34}O_7Na$ $[M + Na]^+$ 445.2202, found 445.2200. The ^{1}H NMR and ^{1}H-^{1}H COSY spectra of **17** showed a significant downfield shift (δ 4.90 ppm) of the H-5 signal compared to the corresponding H-5 signal of **16** (δ 3.36 ppm).

3,4,6-Tri-*O*-allyl-5-*O*-azidoethyl-1,2-*O*-cyclohexylidene-D-*myo*-inositol (18). Installation of the azidoethyl group at the 5-O-position of **16** (95 mg, 0.25 mmol) followed the same procedure described for the synthesis of **11**, which gave **18** (98 mg, 87%) as colorless syrup. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.03-5.90 (m, 3H, All), 5.33-5.28 (m, 3H, All), 5.21-5.16 (m, 3H, All), 4.39-4.31 (m, 3H, All-2H, H-2), 4.28-4.20 (m, 4H, All), 4.02 (dd, J = 7.0, 6.6 Hz, 1H, H-1), 3.92-3.87 (m, 2H), 3.68 (t, J = 8.7 Hz, 1H, H-4), 3.58 (dd, J = 10.0, 7.0 Hz, 1H, H-6), 3.53 (dd, J = 8.5, 4.0 Hz, 1H, H-3), 3.43-3.36 (m, 2H), 3.12 (dd, J = 10.0, 8.5 Hz, 1H, H-5), 1.81-1.30 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.5, 135.4, 135.2, 117.6, 117.0, 116.9, 110.7, 83.1, 82.4, 80.4, 79.0, 77.2, 77.1, 74.3, 74.1, 73.1, 72.5, 71.9, 51.6, 37.6, 35.4,

25.3, 24.1, 23.8. HR MS (ESI-TOF) *m/z*: calcd for $C_{23}H_{35}N_3O_6Na$ $[M + Na]^+$ 472.2424, found 472.2416.

5-*O*-Azidoethyl-D-*myo*-inositol (3). The removal of the All groups in compound **18** (70 mg, 0.156 mmol) followed the same procedure used for the synthesis of **5**, which offered the intermediate product as colorless syrup, which was dissolved in CH_3OH-CH_2Cl_2 (1:3, 12 mL) and then treated with acetyl chloride (15 μL) at room temperature for 2 h. After the reaction was quenched with triethylamine (60μL), the solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography with CH_3OH-CH_2Cl_2 (1:4) as eluent to give **3** as colorless syrup (23 mg, 58% for two steps). ^{1}H NMR (600 MHz, CD_3OD) δ: 3.95-3.91 (m, 3H), 3.67 (t, J = 9.6 Hz, 2H), 3.42 (t, J = 5.4 Hz, 2H), 3.34-3.33 (m, 2H), 2.97 (t, J = 9.6 Hz, 1H). ^{13}C NMR (150 MHz, CD_3OD) δ: 86.0, 74.2, 74.0, 73.6, 72.7, 52.5. HR MS (ESI-TOF) *m/z*: calcd for $C_{16}H_{30}N_6O_{12}Na$ $[2M + Na]^+$ 521.1819, found 521.1811.

Protocols for cell metabolic engineering and related analysis

Metabolic engineering of yeast cells with the inositol derivatives. *Saccharomyces cerevisiae* ATCC 204508 cells were cultivated in YPAD medium containing 0.4 g/L adenine sulfate, 20 g/L glucose, 10 g/L yeast extract, and 20 g/L peptone. After 24 h of cultivation at 30 ˚C, the cells were transferred in a 1% (v/v) ratio into YPAD medium supplemented with or without an inositol derivative (3 mM). After incubation for another 14 h at 30 ˚C, the cells were harvested by centrifugation at 10,000 rpm for 1 min. The resulting cell pellets were then washed with phosphate buffered saline (PBS buffer, pH7.4) and incubated with *Arthrobacter luteus* lyticase (Sigma) at 25 ˚C for 10~20 min. The cells were collected by centrifugation at 10,000 rpm for 1 min and washed with PBS plus 2% BSA (bovine serum albumin), which were ready for click reactions described below.

Metabolic engineering of cancer cells with the inositol derivatives. Cancer cell lines A549, K562, Hela, SKM28 and MCF-7 were cultivated in Dulbecco's Modified Eagle's Medium (DMEM, ATCC® 30-2002™) supplemented with 100 U/mL penicillin-streptomycin (Gibco®) and 10% fetal bovine serum (FBS, Gibco®) under an atmosphere of 5% CO_2 and 95% air at 37 °C. After 3-4 days of growth, 5~6 × 10^6 cells were transferred into 20 mL of 10% FBS/DMEM medium supplemented with or without an inositol derivative (100~200 μM) and the mixture was incubated at 37 °C for 1~2 days. Thereafter, the cells were harvested by centrifugation at 3,500 rpm for 1 min, fixed in 4% paraformaldehyde for 15 min, and washed three times with 2% BSA/PBS, which were ready for click reactions described below.

Click reaction to label cell with biotin and fluorescent staining of the labeled cells. Yeast or cancer cells (1 × 10^6) prepared above were suspended in 250 μL of the click reaction solutions containing 0.1 mM Biotin-PEG_4-alkyne **4** (Sigma), 2 mM $CuSO_4$ and 10 mM sodium ascorbate (Sigma) in 50 mM Tris-HCl buffer (pH 7.4).[3,4] The reaction mixture was incubated at room temperature for 30 min and quenched with 1 mL of 2% BSA/PBS.[3] Then, the cells were washed six times and stained with 100 μL of 0.5 μg/mL streptavidin-APC (Invitrogen) for 30 min followed by washing with 2% BSA/PBS for three times.

Analytical and imaging flow cytometry. Analytical flow cytometry was performed on a BD LSR II (BD Biosciences, San Jose, CA) cytometer and analyzed using FlowJo software (TreStar, Ashland, OR). Imaging flow cytometry was performed on an Amnis ImageStreamX Mark II (EMD Millipore, Billerica, MA) imaging cytometer with a single camera system, 60x magnification using 405 nm (25.00 mW), 642 nm (9.00 mW), and 758 nm (1.00 mW) lasers. Samples were counterstained with DAPI nuclear marker at the time of acquisition. Analysis was performed using IDEAS software (Amnis, Seattle, WA). Analytical and imaging flow cytometry was performed in the Microscopy, Imaging, and Cytometry Resources (MICR) core at the Karmanos Cancer Institute, Wayne State University.

Confocal microscopy analysis. A549 cells were inoculated in glass bottom cell culture dishes (Φ20mm, NEST®). About 2×10^5 cells (per dish) were cultured in 1 mL of 10% FBS/DMEM with or without 200 μM of **5**. After growth for 1 day at 37 °C, the cells adherent to the bottom of the dishes were fixed with 4% paraformaldehyde for 15 min, washed with 2% BSA/PBS 3 times, and then subjected to click reaction and fluorescent staining as described above. The resulting cells were stained with DAPI for 5 min, and then the samples were analyzed by laser scanning confocal microscopy (Zeiss LSM700, Germany). DAPI and APC were excited at 405 nm and 639 nm, respectively.

Western blotting analysis of GPI-anchored proteins. A549 cells were cultured in 10% FBS/DMEM medium with or without **5** (200 μM), harvested, and washed three times with PBS buffer (pH 7.4). About 10×10^6 cells were re-suspended in PBS buffer (1 mL) supplemented with 5 mM of $CaCl_2$ and $MgCl_2$ and were then divided into two equal groups, which were treated with or without 0.8 U of phosphatidylinositol-specific phospholipase C (PI-PLC) from *Bacillus cereus* (Invitrogen, USA).[5] After incubation at 20 °C for 1 h, the cells were removed by centrifugation, and the supernatant was then treated with ultrafiltration (3 kDa cutoff membrane, Millipore), washed twice with 50 mM Tris-HCl buffer (pH 7.4), and finally concentrated to 30 μL. A volume of the concentrated supernatant (10 μL) was used for click reaction with a solution (25 μL) containing tris(2-carboxyethyl)phosphine hydrochloride (TCEP, 1 mM), tris[(1-benzyl-1-H-1,2,3-triazol-4-yl)methyl]amine (TBTA, 0.1 mM), $CuSO_4$ (1 mM) and Biotin-PEG_4-alkyne (0.1 mM).[6] The reaction was gently vortexed and incubated at room temperature for 1 h.[6]

The reaction mixture were subsequently loaded onto SDS-PAGE and then subjected to Western blotting for analysis. The proteins in the gel were transferred onto a PVDF membrane (Millipore, USA) by means of a Transfer Cell (Bio-Rad, USA). The membrane bearing proteins was washed with TBST buffer (10 mM Tris-Cl, 150 mM NaCl, 0.1% v/v Tween 20, pH 7.5) and incubated in blocking solution (2% BSA in TBST buffer) for 1 h.

Then it was washed three times with TBST buffer and incubated with streptavidin-peroxidase conjugate (Proteintech, USA. 1:2000 dilution) in blocking solution for 30 min. The resulting membrane was washed five times with TBST buffer and then detected by incubation with ECL (enhanced chemiluminescence) substrate (Thermo Scientific, USA). The reaction result was scanned with a ProteinSimple imaging system (USA).

II. Supplementary Figures

S. cerevisiae ATCC 204508 cells were cultivated in YPAD medium supplemented with or without and inositol derivative of **1-7** (3 mM). After 14 h of incubation at 30 ˚C, the cells were collected and treated with lyticase for partial hydrolysis of the β-(1→3)-glucan in the yeast cell wall. This treatment would facilitate exogenous reagents to approach membrane proteins on the cell surface. After lyticase treatment, the cells were subjected to click reaction with Biotin-PEG_4-alkyne **4** and then staining with streptavidin-APC. The cell-associated MFI (mean fluorescent intensity) was quantified by flow cytometry. The cells in the control group were subjected to the same procedure except for the absence of an inositol derivative.

Figure S1a showed that the MFIs of the yeast cells treated with **1**-**3** were not obviously higher than that of cells in the control group, suggesting that **1**-**3** could not be effectively incorporated by the yeast cells in their GPI biosynthesis. **Figure S1b** showed that yeast cells were effectively labeled by the fluorescent tag after treatment with **5**-**7** and that the MFI of the stained yeast cells treated with **5** was more than one thousand folds higher than that of cells in the control group.

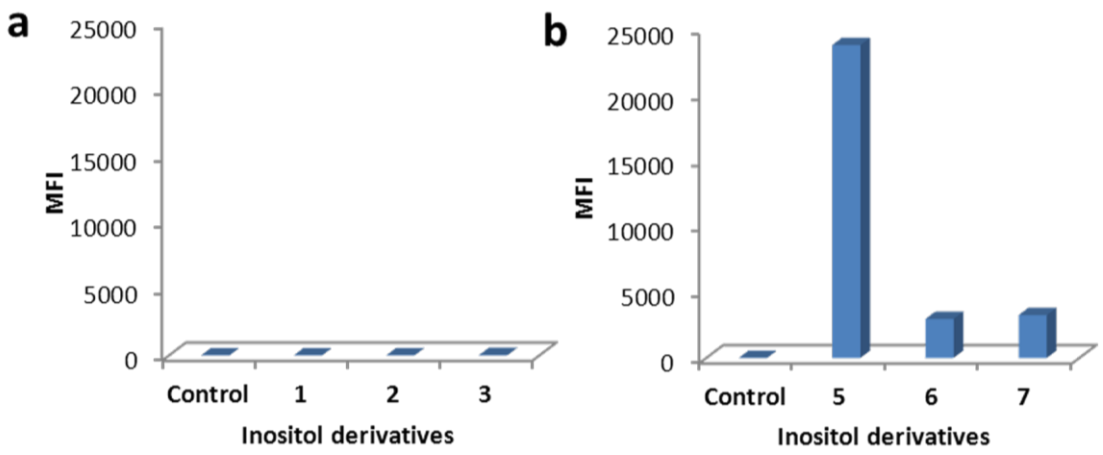


Figure S1. The results of metabolic engineering of GPIs and GPI-anchored proteins on *S. cerevisiae* ATCC 204508 cells with inositol derivatives **1-3** and **5-7.** (a) MFI values of the yeast cells treated with **1-3**. (b) MFI values of the yeast cells treated with **5-7**.

To probe the application scope of the new metabolic engineering strategy, it was then assessed with a human lung carcinoma cell line A549. In this context, the A549 cells were inoculated in 10% FBS/DMEM medium supplemented with or without an inositol derivative of **5-7** at 200 μM. This concentration was determined according to the reported protocols for the metabolic engineering of glycans on cancer cells.[4] After 2 days of incubation at 37 ˚C, the treated cells were harvested and fixed in 4% paraformaldehyde for 15 min. The cells were then subjected to click reaction with Biotin-PEG_4-alkyne **4**, which was followed by staining with streptavidin-APC. The fluorescence intensity of the cells was subsequently analyzed by flow cytometry. Cells in the control group were subjected to the same procedures except for the absence of an inositol derivative.

Figure S2 showed that the MFI values of A549 cells treated with **5** and **6**/**7** were *ca.* 30 and 16 folds, respectively, higher than that of the control. Moreover, partially acetylated **5** was once again more efficient than peracetylated **6** for cell metabolic engineering. **Figure S3** showed the flow distribution of cells in the control group (blue) or cells treated with **5** (red) according to their fluorescence intensities.

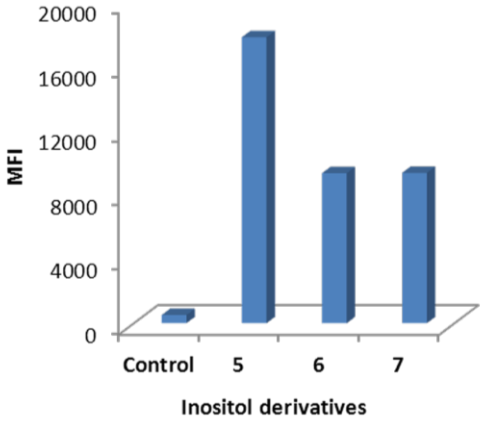


Figure S2. The results of metabolic engineering of GPIs and GPI-anchored proteins on A549 cells with inositol derivatives **5-7.**

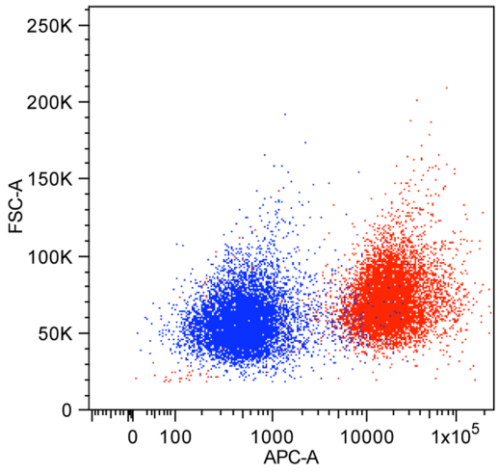


Figure S3. Dot plot analysis of A549 cells treated with **5.** The blue and red dots represent the untreated and **5**-treated cells, respectively.

A competitive inhibition experiment was performed to further verify the incorporation of inositol derivative **5** in the GPI biosynthetic pathway in the above experiments. A549 cells were inoculated in 10% FBS/DMEM medium supplemented with **5** together with 0, 100, 200 μM of **8**, respectively. After 1 day of incubation at 37 ˚C, the treated cells were harvested and fixed in 4% paraformaldehyde for 15 min. Thereafter, the cells were subjected to click reaction with Biotin-PEG_4-alkyne **4** and then staining with streptavidin-APC. The MFI of treated cells was analyzed by flow cytometry. A549 cells in the control group were subjected to the same procedures except for the absence of **5** and **8**.

Figure S4 showed that the **5**-treated cells showed decreased MFI values in the presence of increased concentrations of **8** from 0 to 200 μM. The results suggested that **8** could competitively inhibit cell incorporation of **5** and thereby cell labeling.

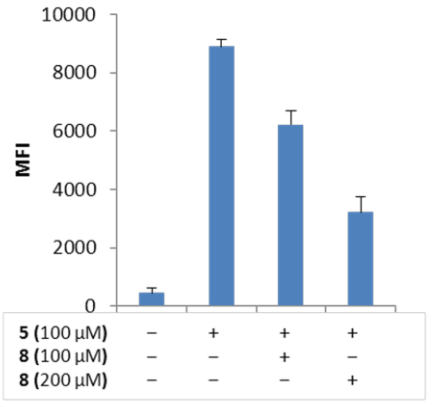


Figure S4. The influence of **8** on metabolically engineered labeling of GPIs and GPI-anchored proteins on A549 cells by **5.**

The influence of concentration of **5** and incubation time on the metabolic engineering of GPI-anchored proteins expressed on A549 cells was also evaluated. Compound **5** was first tested at concentrations ranging from 50 to 500 μM. The labeling of **5**-treated A549 cells was dependent on the concentrations of **5**, as the MFI values was increased with the increase of the concentration of **5** within 300 μM. However, at and beyond 400 μM, no cell growth could be observed, as the compound inhibited cell growth at higher concentrations. Combined with the results of the **5**-treated cell growth and MFI values, 100 μM and 200 μM concentrations were optimal for cell labeling and the labeling processes at these concentrations were traced within two days.

A549 cells were cultured with 100 μM or 200 μM of **5** for 1 or 2 days at 37 ˚C. The cells treated with 200 μM of **5** for showed significant shift of the fluorescent peak to the right as compared to the cells treated with 100 μM of **5 (Figures S5a** and **S5b**), confirming that the intensity of cell labeling was dependent upon the concentration of **5**. Moreover, **Figure S5c** also showed that the cells incubated with 100 μM or 200 μM of **5** had increased MFI values

with the extension of incubation time. Thus, the cells treated with 200 μM of **5** exhibited the highest MFI increase after 2 days of incubation under the tested conditions. However, under this condition, the cell growth decreased by about 30% (**Figure S5d**). Data in **Figure S5d** also indicated that 100 μM of **5** did not exhibit obvious inhibition on the cell growth while showing high efficiency for cell metabolic engineering.

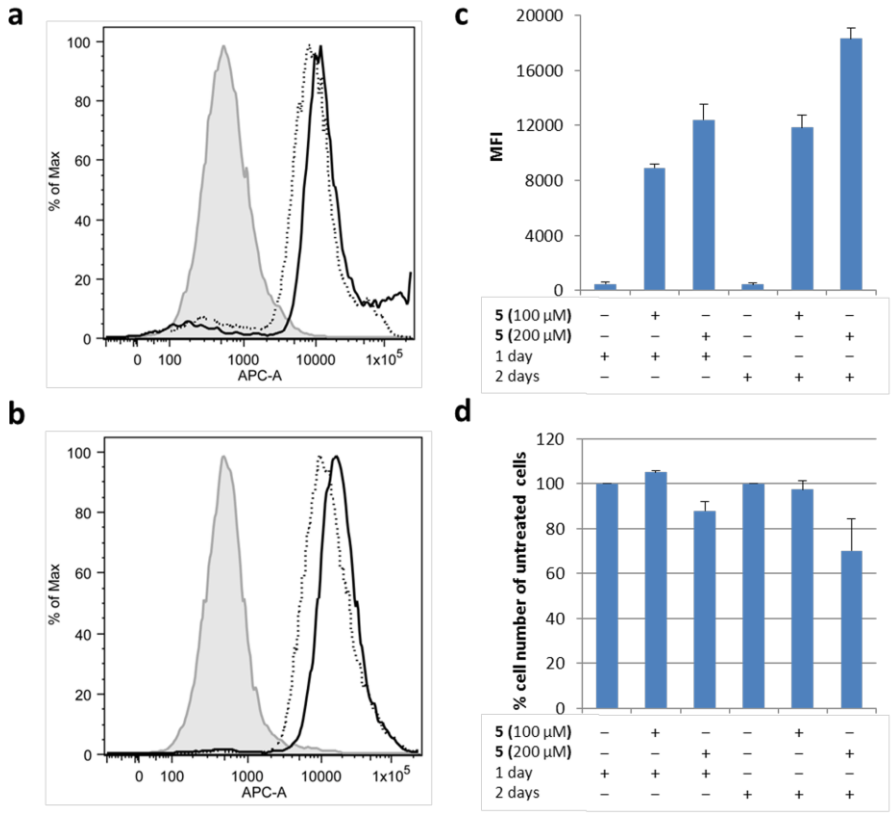


Figure S5. The influence of the concentration of **5** and incubation time on the metabolic engineering of GPIs and GPI-anchored proteins on A549 cells. (a) and (b) Flow cytometry results of A549 cells incubated with different concentration of **5** for 1 day and 2 days, respectively. The concentrations of **5** are 0 μM (filled histogram), 100 μM (dotted line), and 200 μM (solid line), respectively. (c) MFI values of A549 cells treated with **5** for 1 day or 2 days. (d) Cell growth analysis of **5**-treated A549 cells.

GPI-anchored proteins on **5**-treated A549 cells were analyzed after being released from the cell surface on incubation with PI-PLC. The amount of GPI-anchored protein PLAP (with

observed molecular mass of ca. 70 kDa) in the supernatant of cells treated with PI-PLC was significantly higher than that of cells without PI-PLC treatment (**Figure S6a**,), confirming the cleavage and release of GPI-anchored PLAP by PI-PLC. A549 cells treated with or without **5** were also subjected to treatment with or without PI-PLC, and the resultant supernatants were then reacted with Biotin-PEG_4-alkyne and probed using streptavidin-peroxidase for Western blotting, and the results are illustrated in **Figure S6b**. Clearly, the supernatant of cells treated with both **5** and PI-PLC (central lane) showed a series of protein bands that were not observed in the supernatants of cells treated with PI-PLC but without **5** (left lane) or cells treated with **5** but without PI-PLC (right lane). Note: the very faint protein bands for the supernatants of cells treated with **5** but without PI-PLC might be due to the residual activities of endogenous phospholipases, while these bands were not observed at all for cells cultured without **5**. All of the results confirmed that on treatment with **5**, A549 cell expressed azide-labeled GPI-anchored proteins that can be released by PI-PLC and further modified by click reaction.

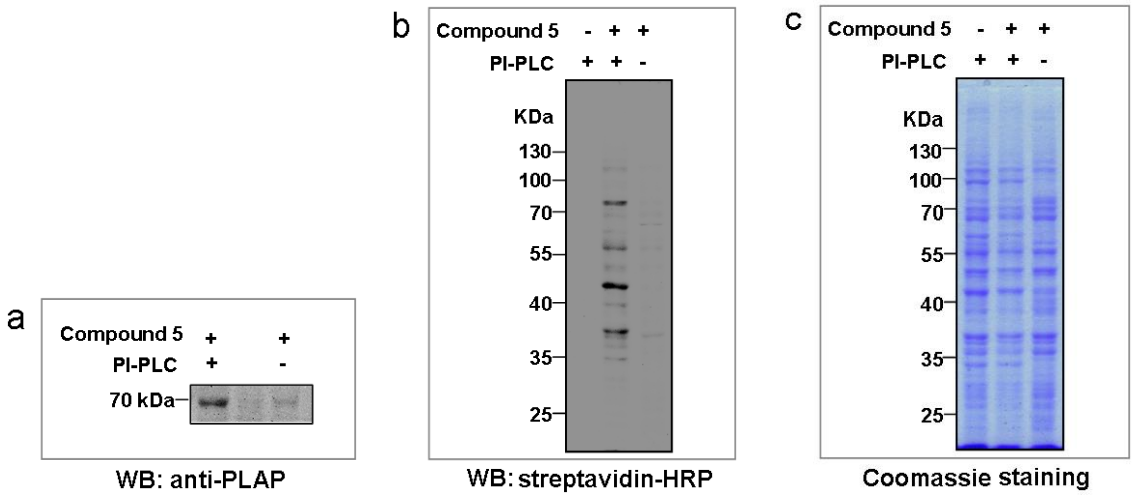


Figure S6. Western blotting analysis of GPI-anchored proteins released from **5**-treated A549 cells. (a) Detection of PLAP in the supernatants of cells treated with or without PI-PLC using anti-PLAP antibody (Abcam, United Kingdom). (b) Detection of GPI-anchored proteins in the

supernatants of cells treated with PI-PLC but not **5** (left lane), with **5** and PI-PLC (central lane), and with **5** but not PI-PLC (right lane) by click reaction with Biotin-PEG_4-alkyne and then probing with streptavidin-HRP (horseradish peroxidase). (c) Coomassie staining of the gel to show total proteins loaded to each lane in (b).

Four other cancer cell lines, K562, Hela, SKM28 and MCF-7, were also treated with **5**. In all of the cases, cells were inoculated in 10% FBS/DMEM medium supplemented with or without 100 μM of **5**. After 2 days of incubation at 37 ˚C, they were harvested and fixed in 4% paraformaldehyde for 15 min, and then subjected to click reaction with **4** and staining with streptavidin-APC. The cells were finally analyzed by analytical and imaging flow cytometry.

Figures S7-S10a and **S7-S10b** showed that all of the cell lines were effectively labeled after treatment with **5**. **Figures S7-S10c** further revealed that the bright red fluorescence was concentrated on the cell surface, confirming that the azido group was indeed delivered onto the cell membrane to allow for surface click reaction and subsequently the attachment of a fluorescent tag.

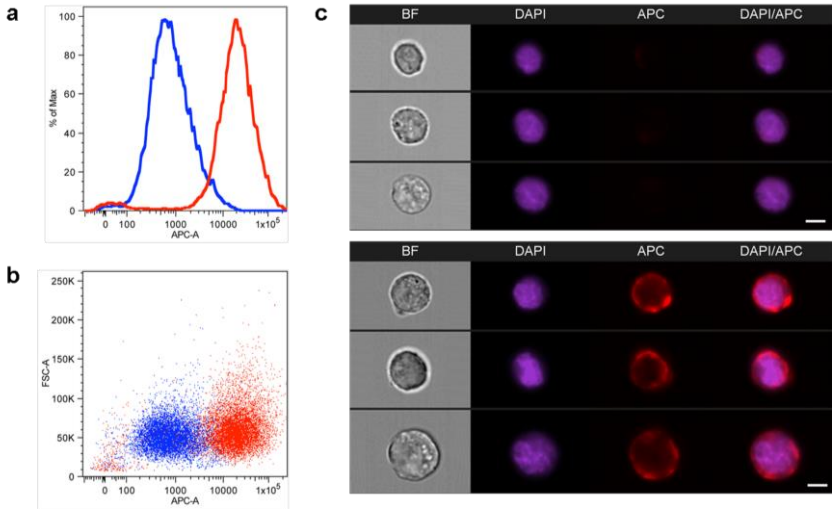


Figure S7. Analysis of labeled GPIs and GPI-anchored proteins expressed on K562 cells treated with **5.** (a) Histogram of the untreated (blue) and **5**-treated (red) cells. (b) Dot plot of the untreated (blue) and **5**-treated (red) cells. (c) Representative images of the untreated (upper) and **5**-treated (lower) cells, respectively (the white scale bar is 7 μm).

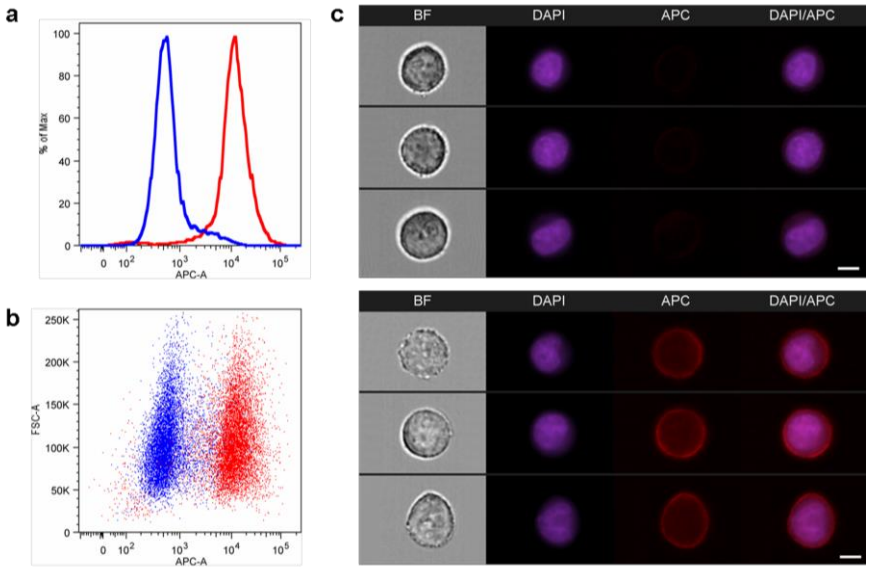


Figure S8. Analysis of labeled GPIs and GPI-anchored proteins expressed on Hela cells treated with **5.** (a) Histogram of the untreated (blue) and **5**-treated (red) cells. (b) Dot plot of the untreated (blue) and **5**-treated (red) cells. (c) Representative images of the untreated (upper) and **5**-treated (lower) cells, respectively (the white scale bar is 7 μm).

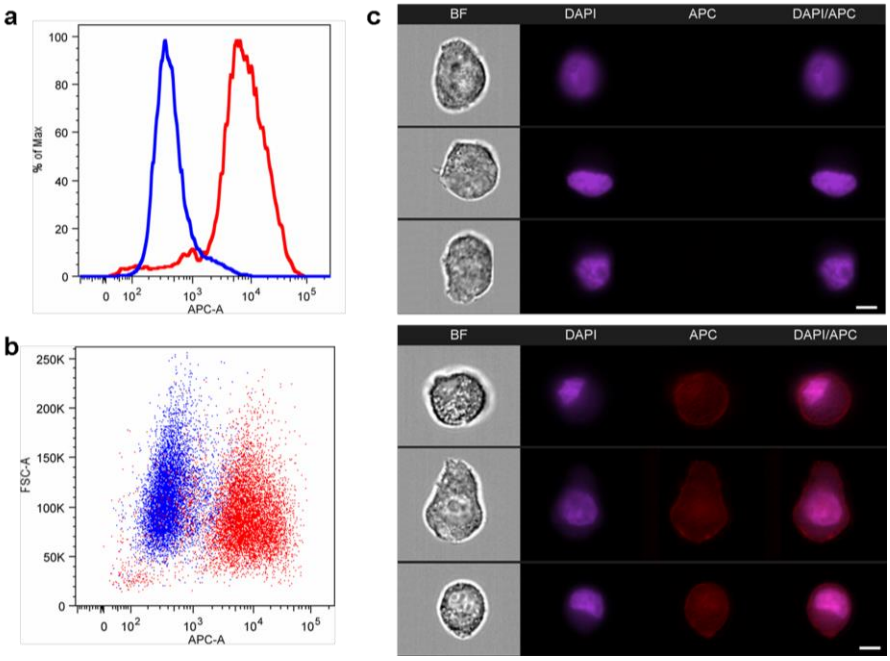


Figure S9. Analysis of labeled GPIs and GPI-anchored proteins expressed on SKM28 cells treated with **5.** (a) Histogram of the untreated (blue) and **5**-treated (red) cells. (b) Dot plot of the untreated (blue) and **5**-treated (red) cells. (c) Representative images of the untreated (upper) and **5**-treated (lower) cells, respectively (the white scale bar is 7 μm).

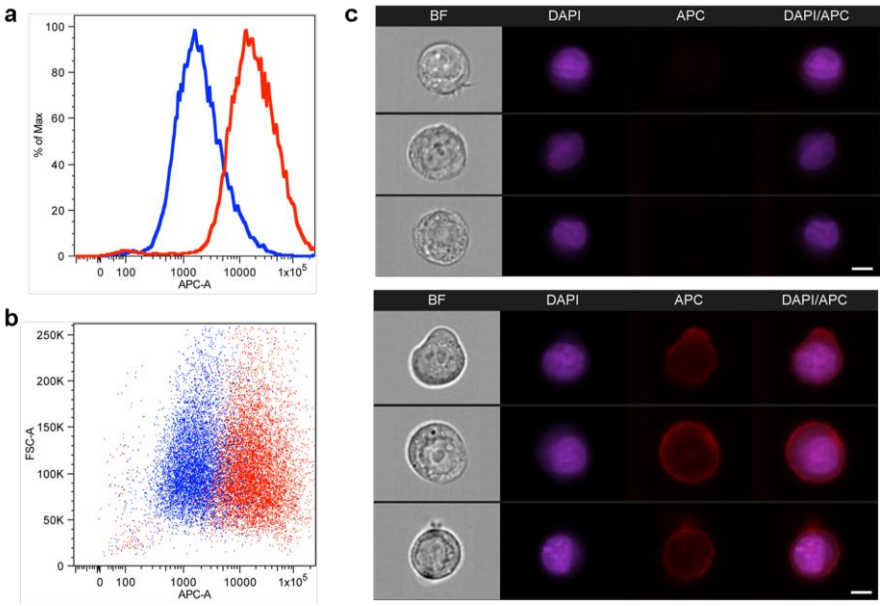
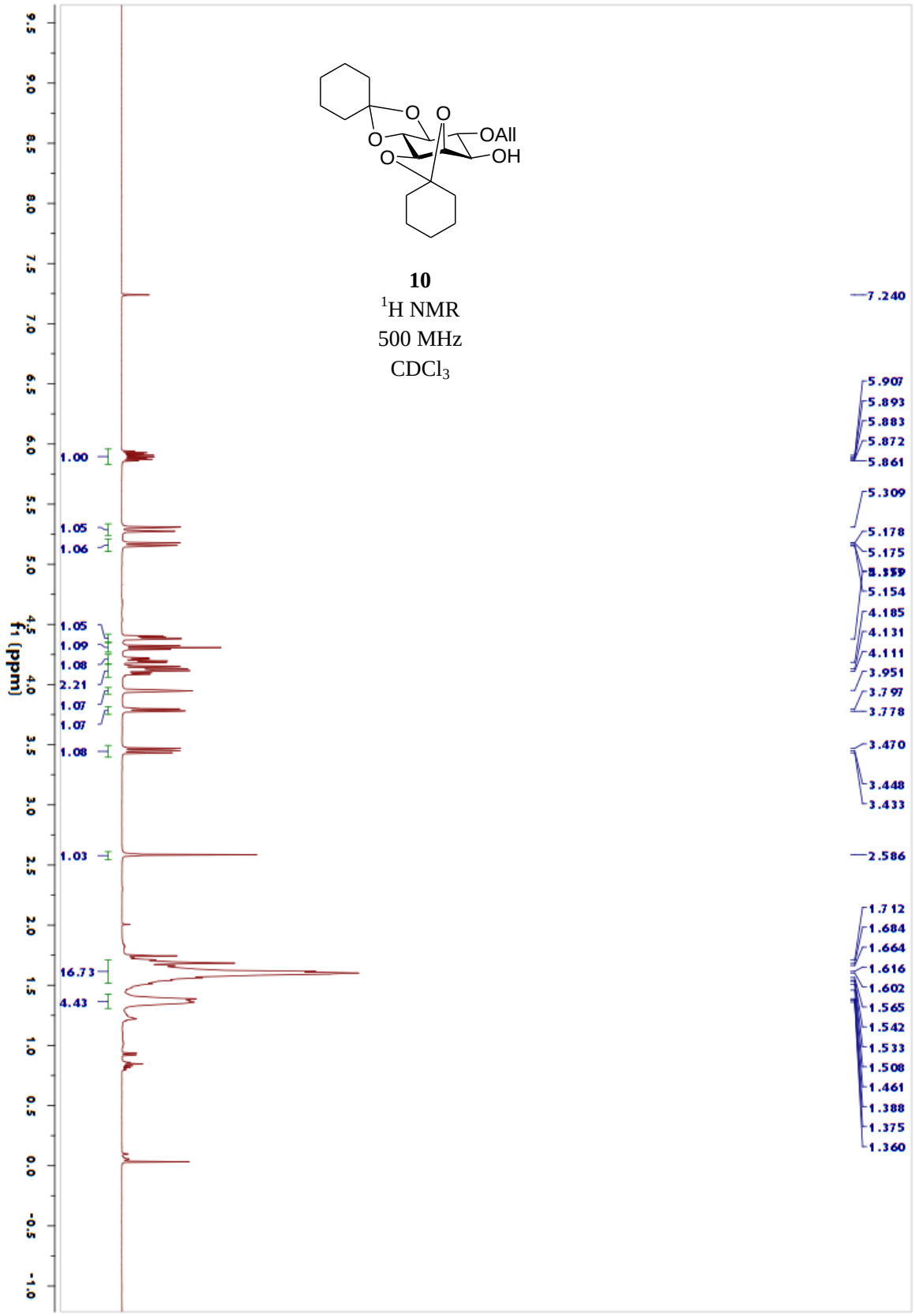
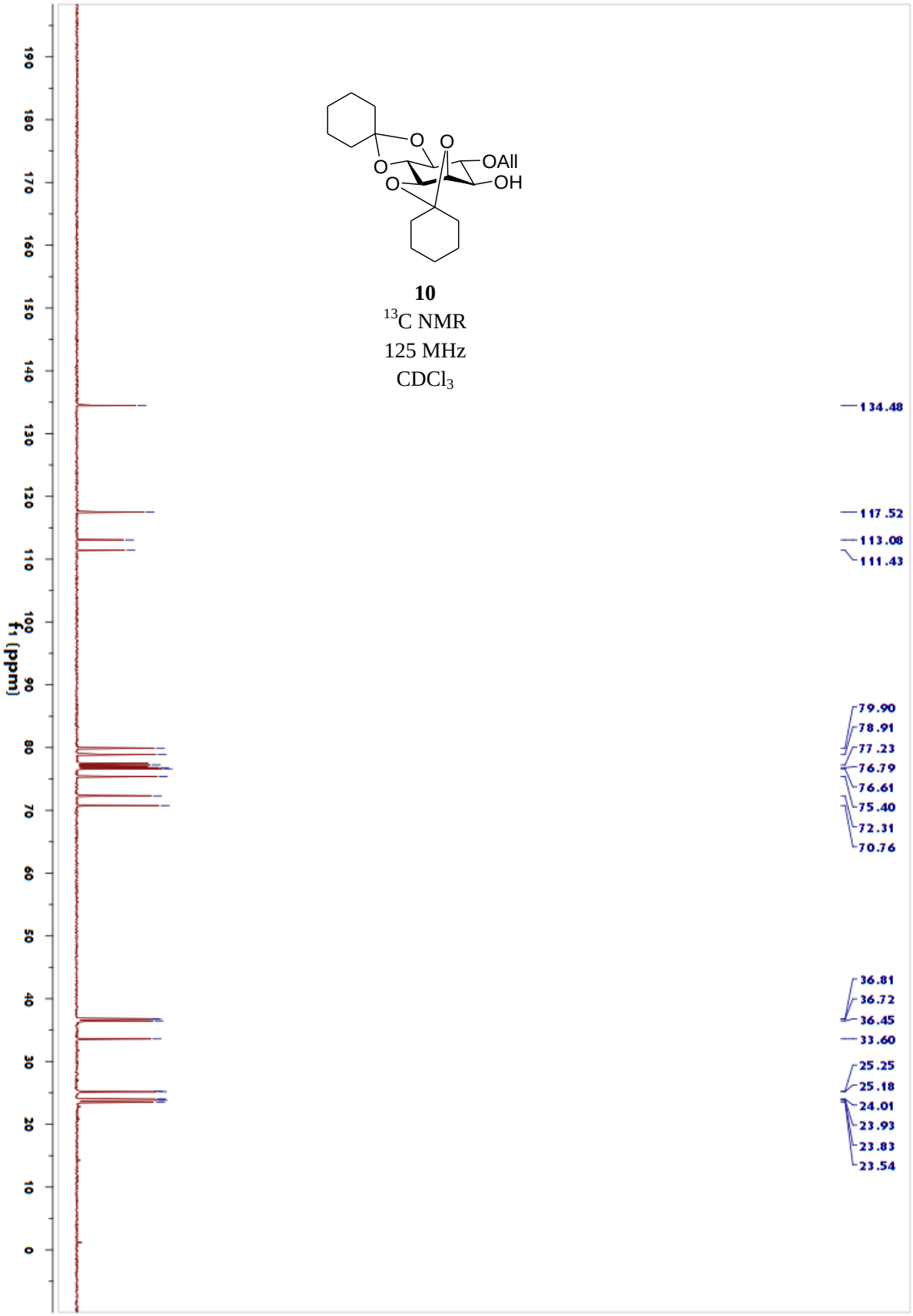


Figure S10. Analysis of labeled GPIs and GPI-anchored proteins expressed on MCF-7 cells treated with **5.** (a) Histogram of the untreated (blue) and **5**-treated (red) cells. (b) Dot plot of the untreated (blue) and **5**-treated (red) cells. (c) Representative images of the untreated (upper) and **5**-treated (lower) cells, respectively (the white scale bar is 7 μm).

III. NMR Spectra



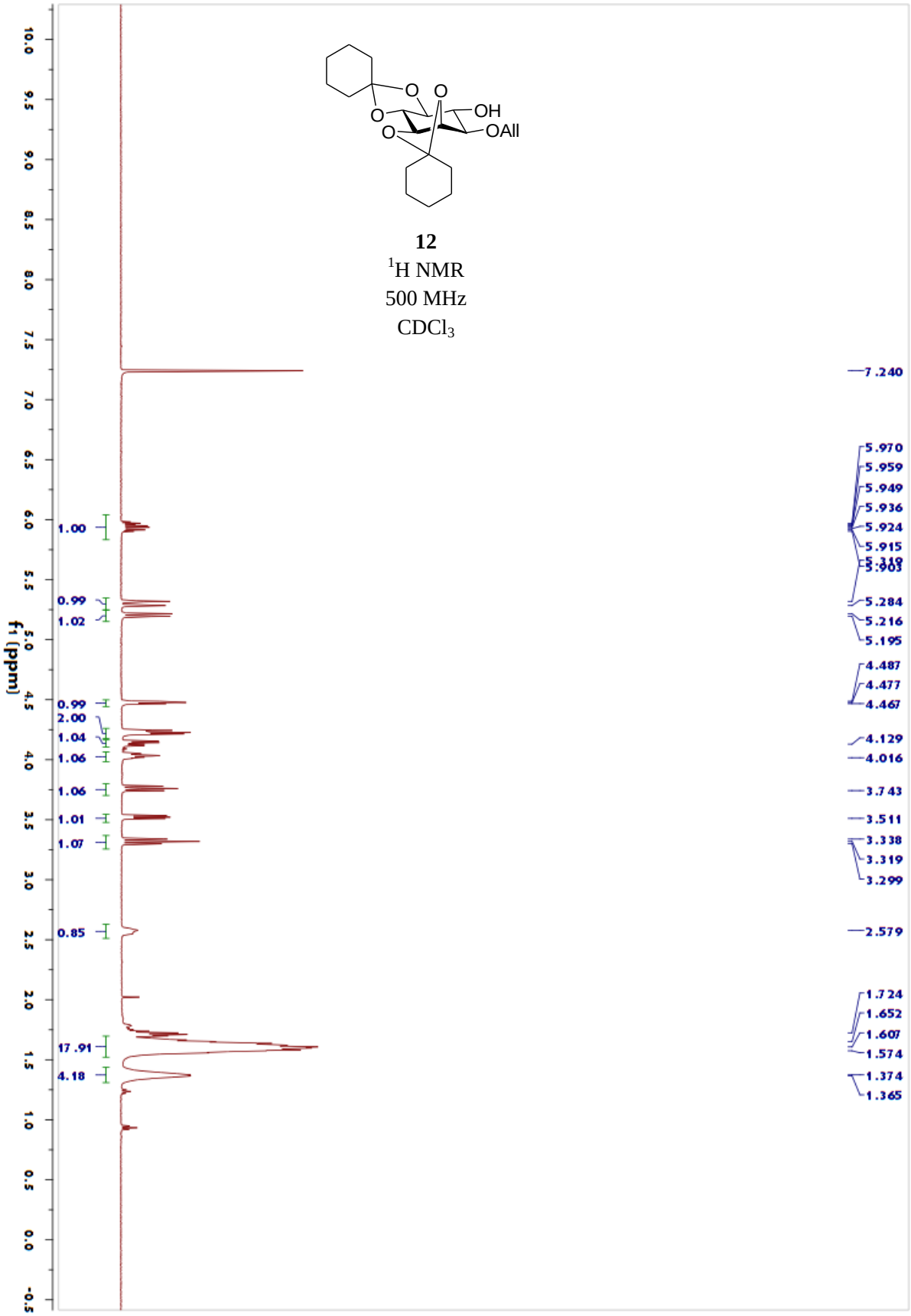


10

^{13}C NMR

125 MHz

$CDCl_3$

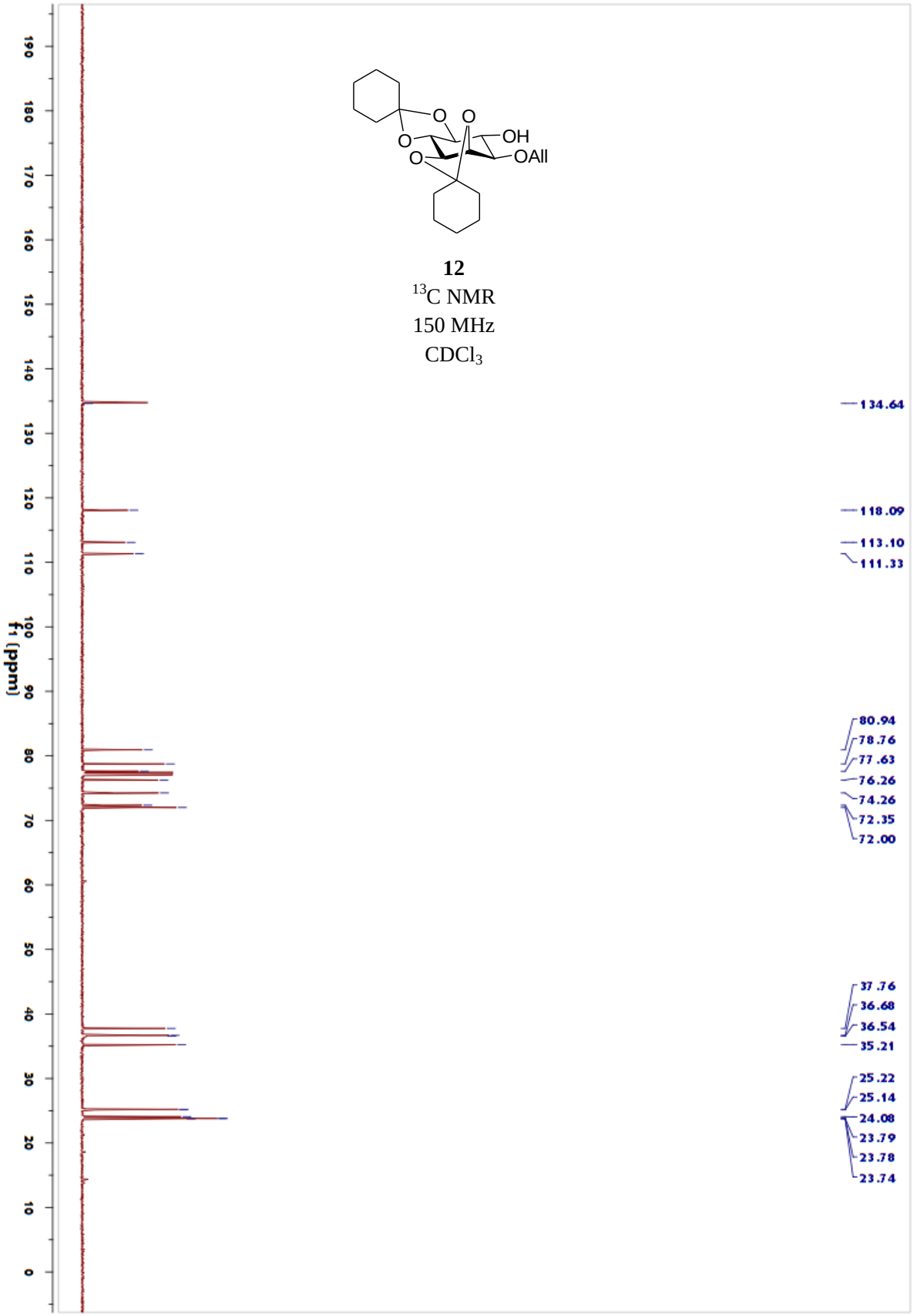


12

^{1}H NMR

500 MHz

$CDCl_3$

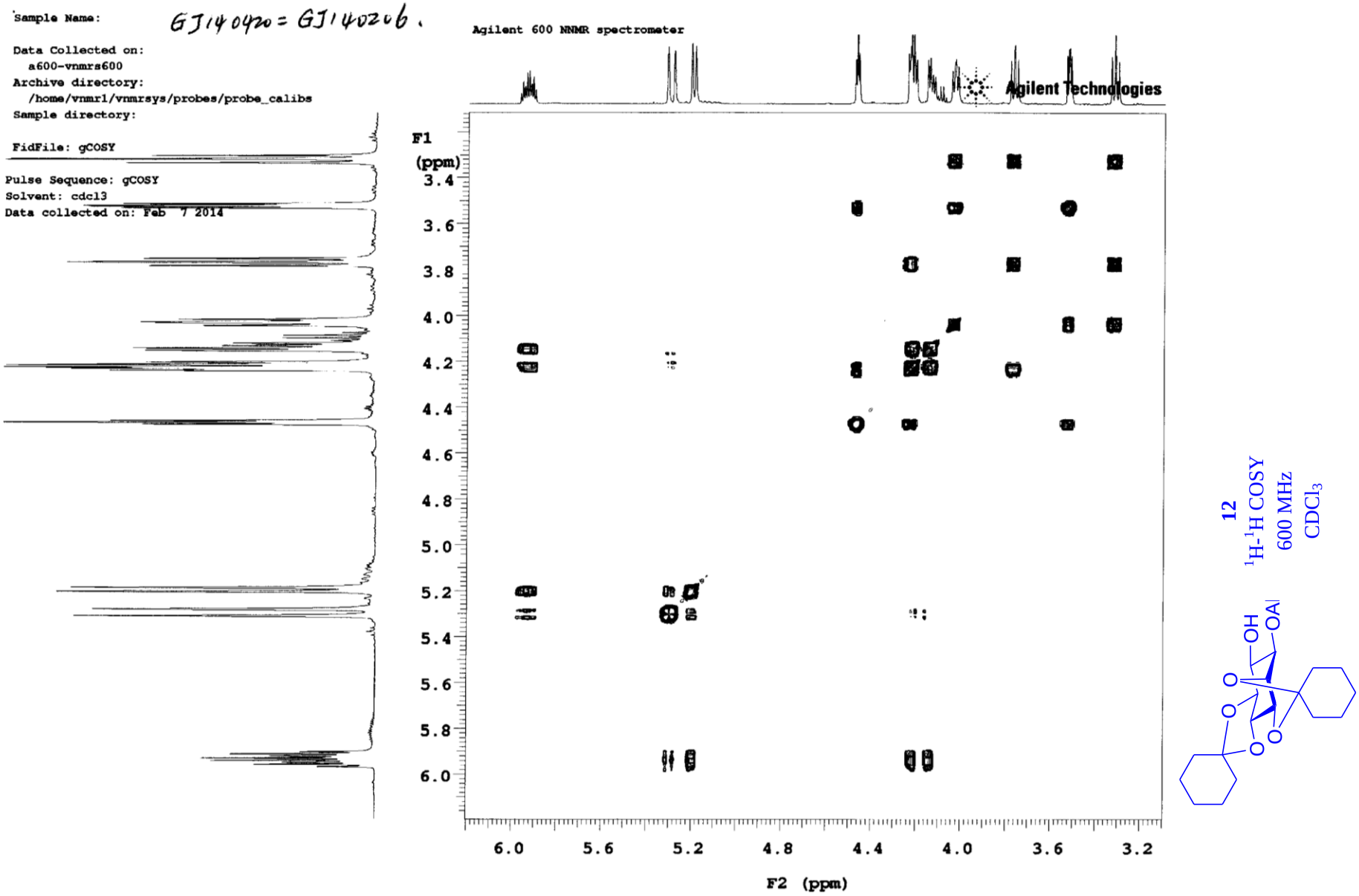


12

^{13}C NMR

150 MHz

$CDCl_3$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Data collected on: Feb 7 2014
Agilent 600 NNMR spectrometer
Agilent Technologies
F1
(ppm)
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3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.6
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4.0
3.6
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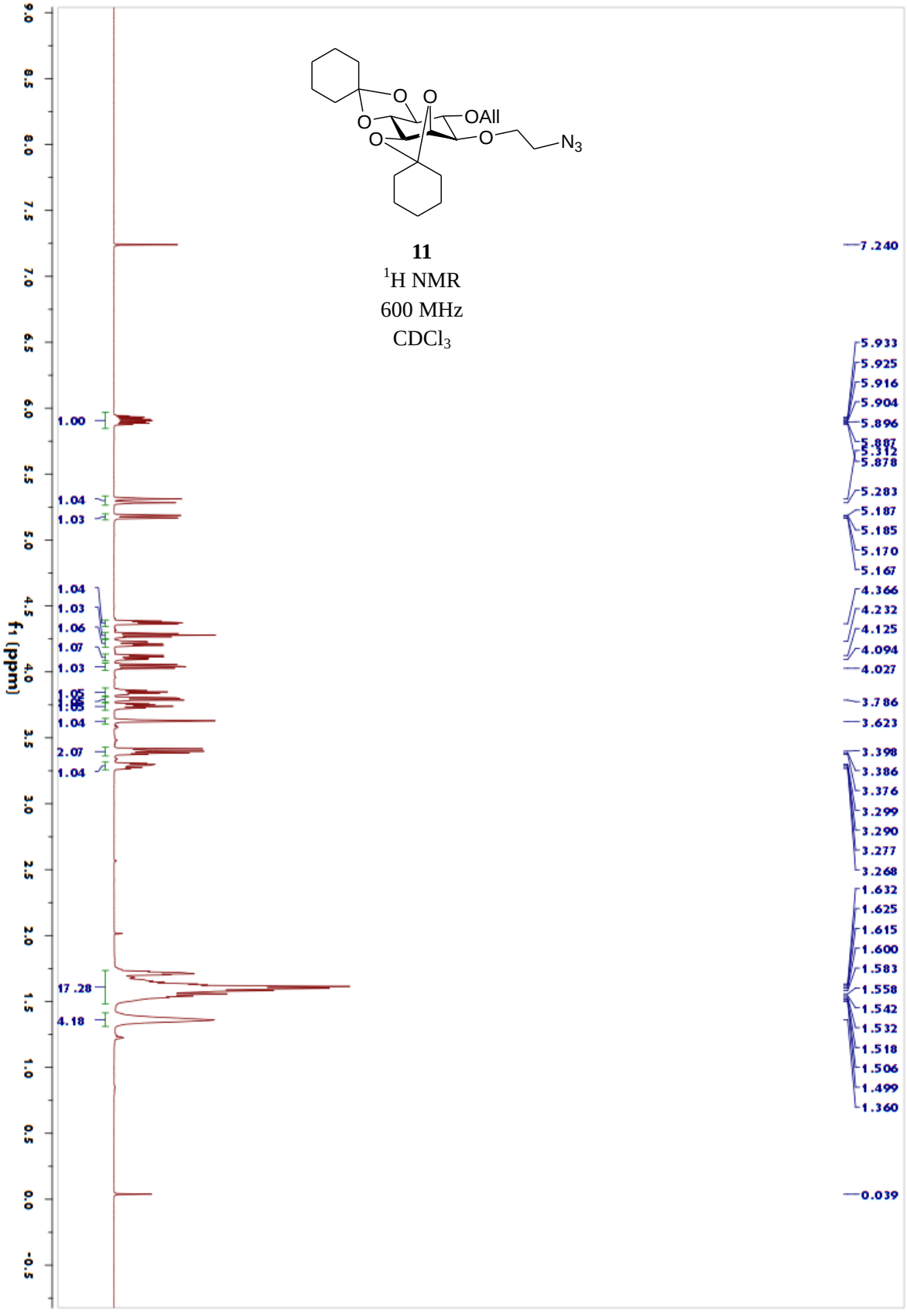
O
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N3
11
1H NMR
600 MHz
CDCl3
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1.03
1.06
1.07
1.03
1.05
1.04
2.07
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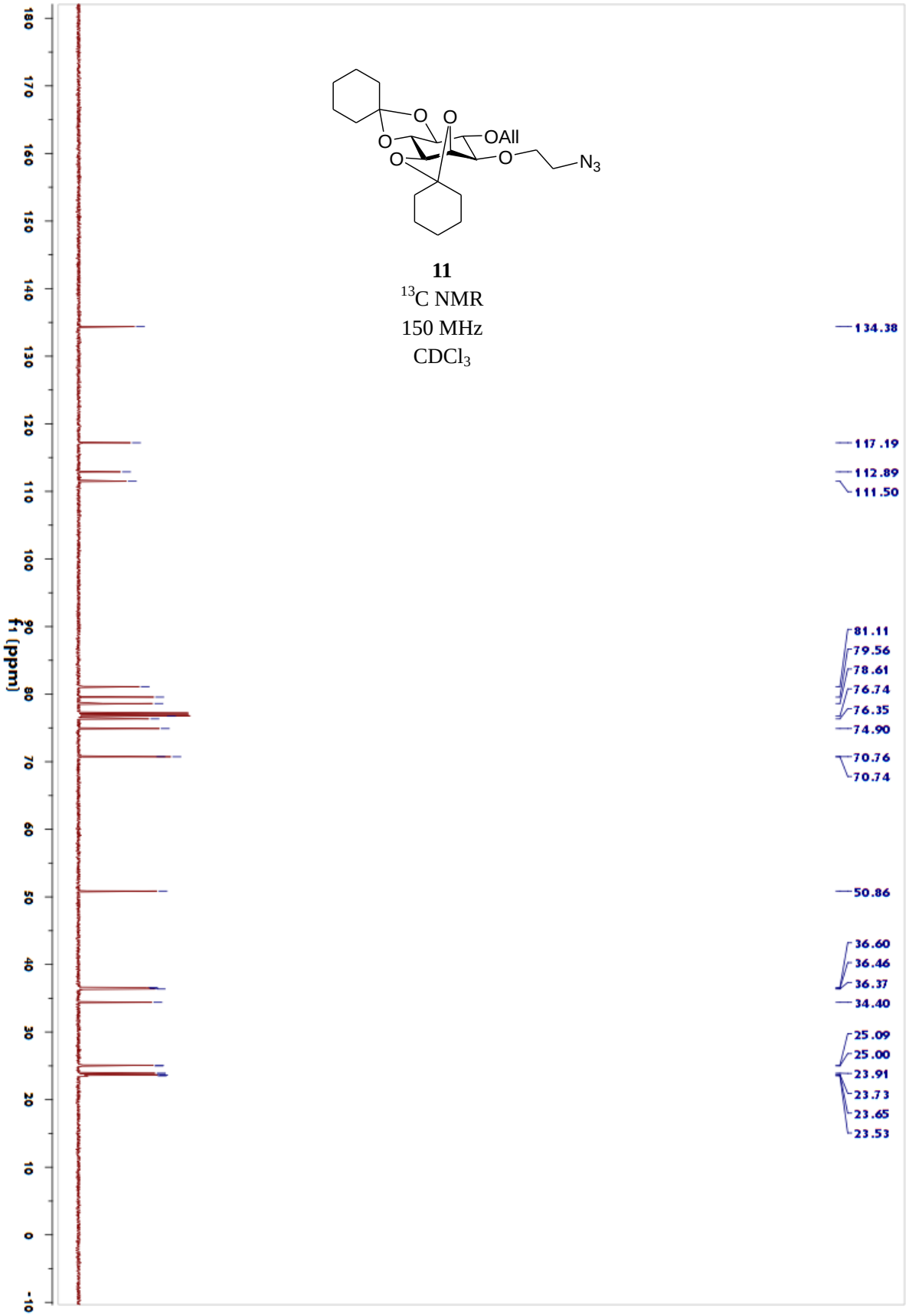
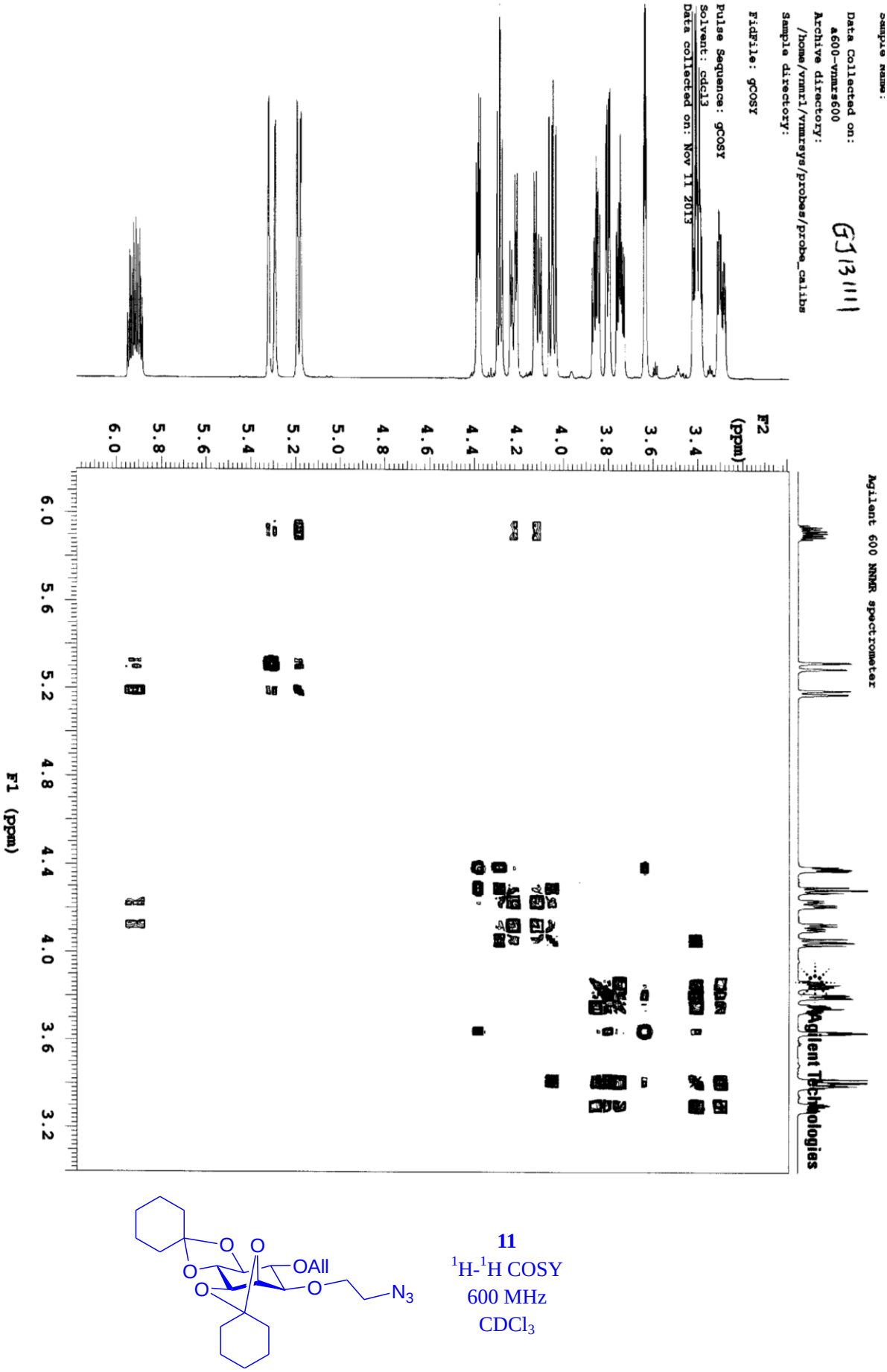


11

^{13}C NMR

150 MHz

$CDCl_3$

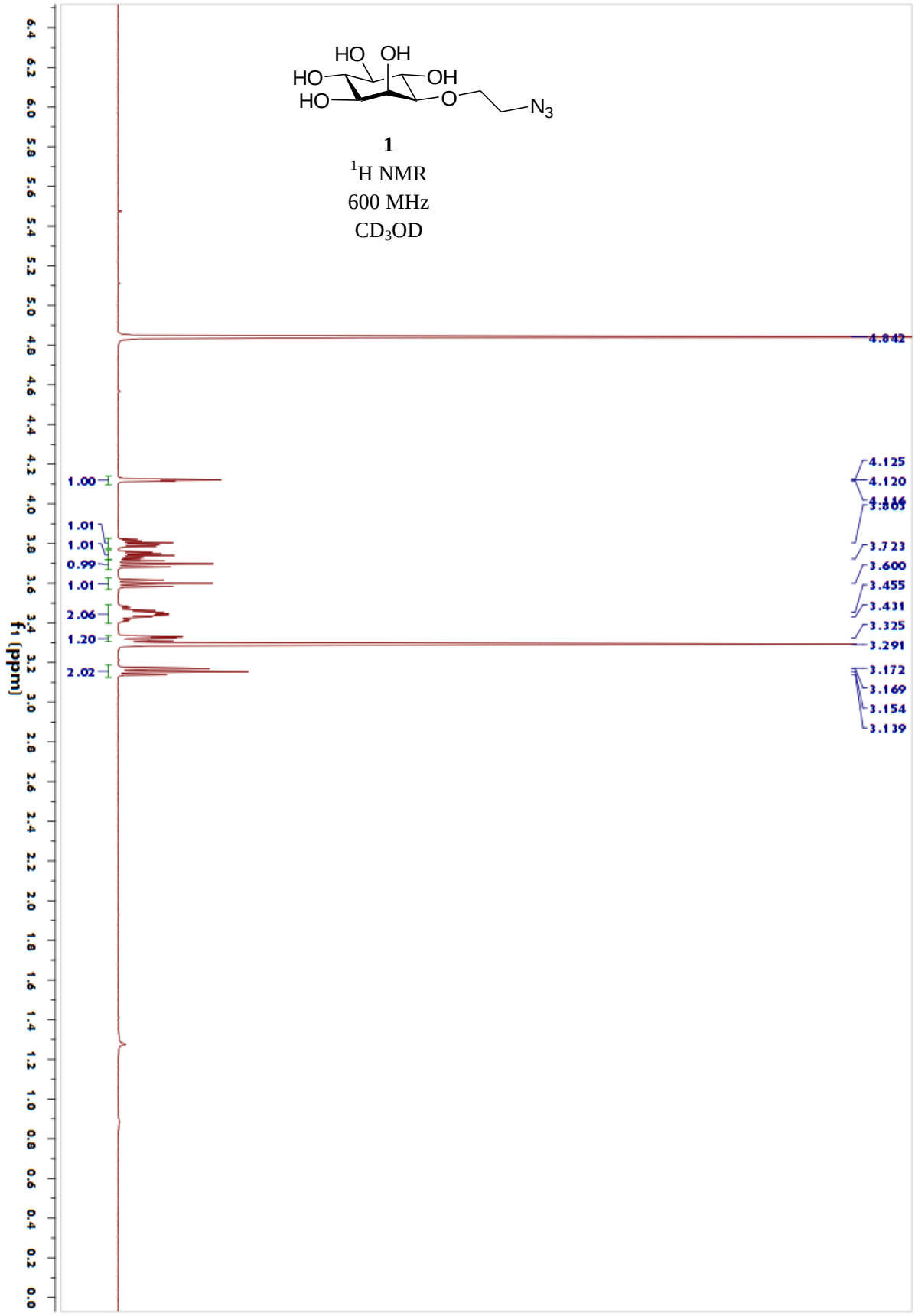


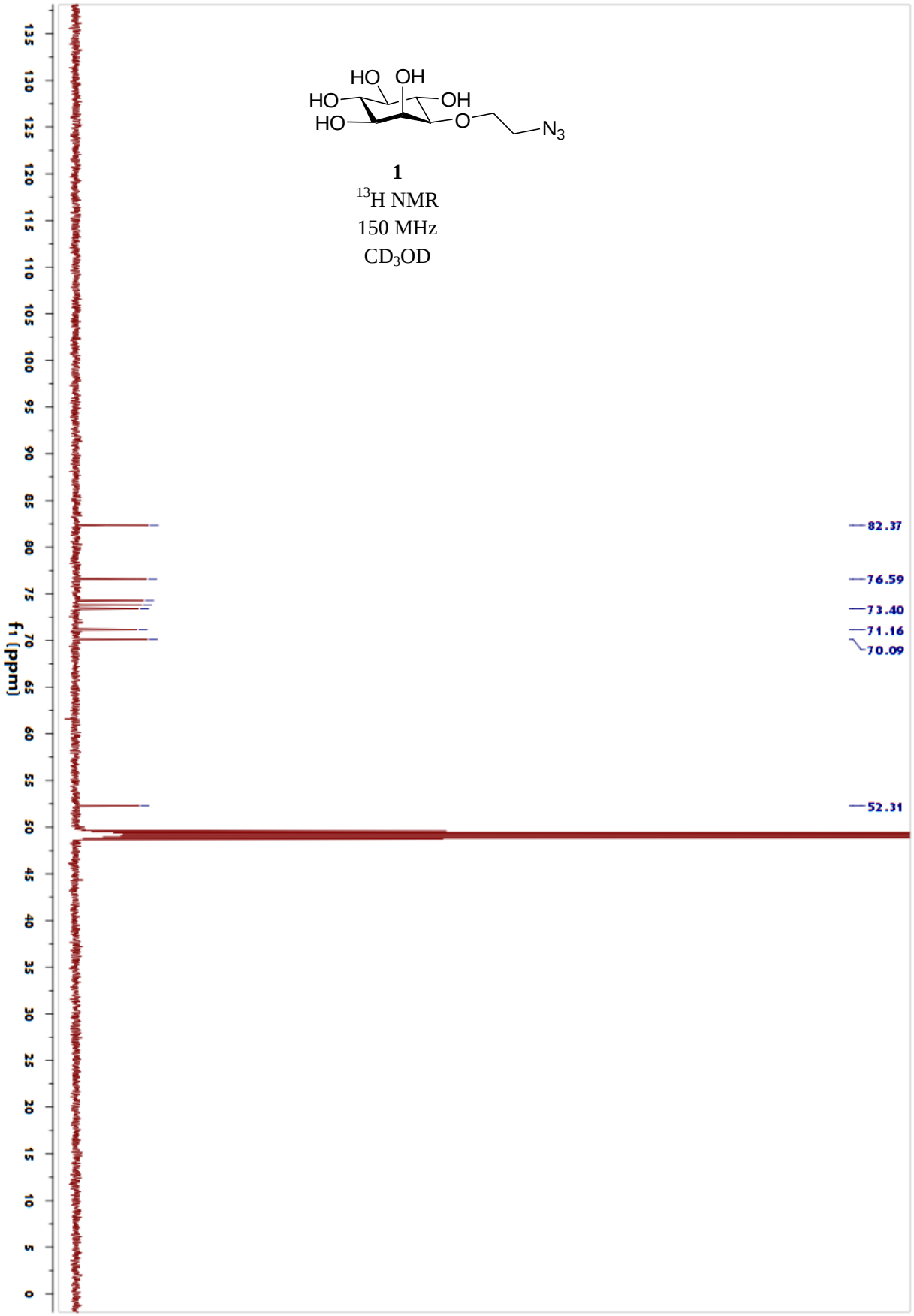
11

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

600 MHz

$CDCl_3$


HO
OH
HO
OH
HO
O
N3
1
1H NMR
600 MHz
CD3OD
4.842
4.125
4.120
3.723
3.600
3.455
3.431
3.325
3.291
3.172
3.169
3.154
3.139
1.00
1.01
1.01
0.99
1.01
2.06
1.20
2.02
f1 (ppm)

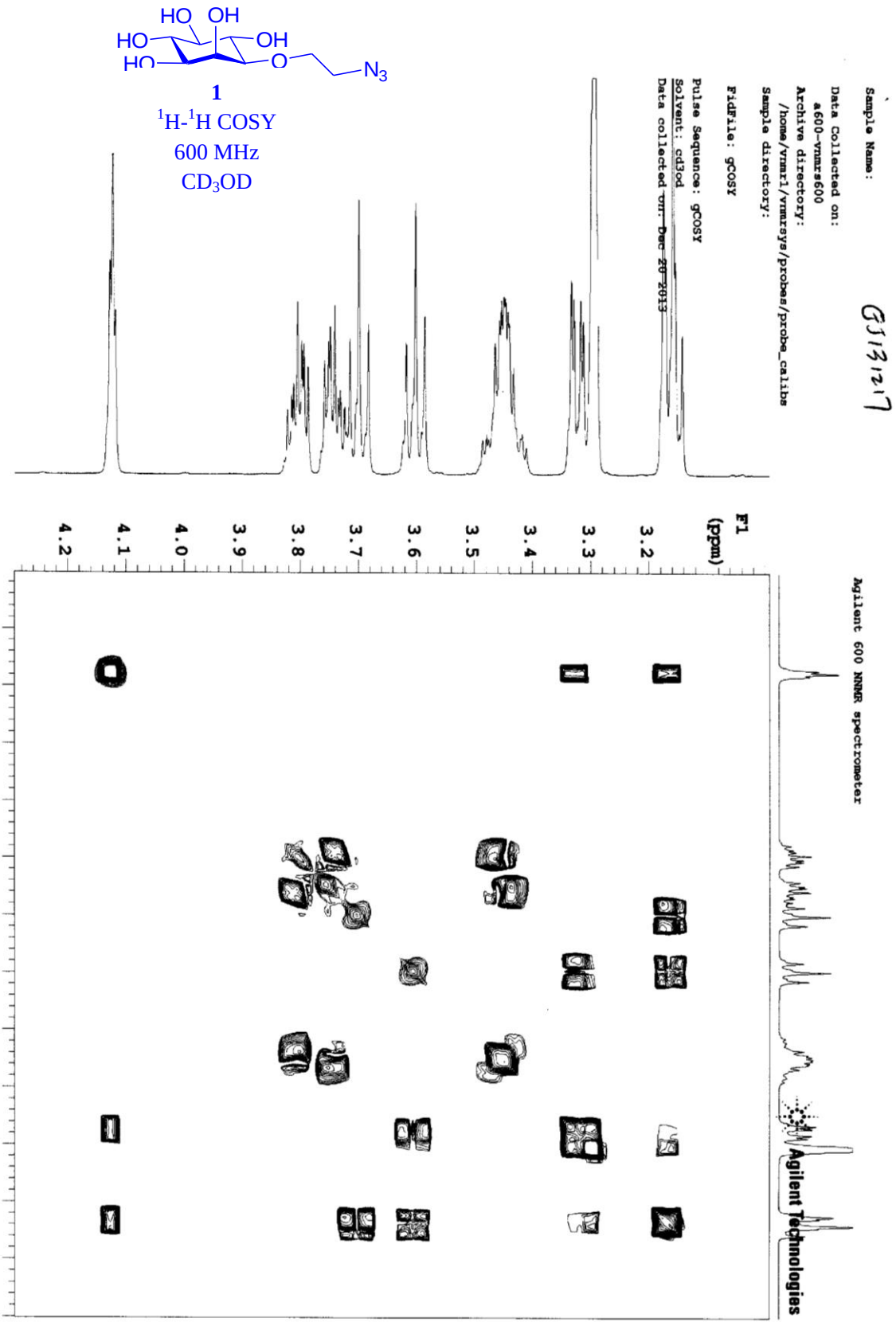


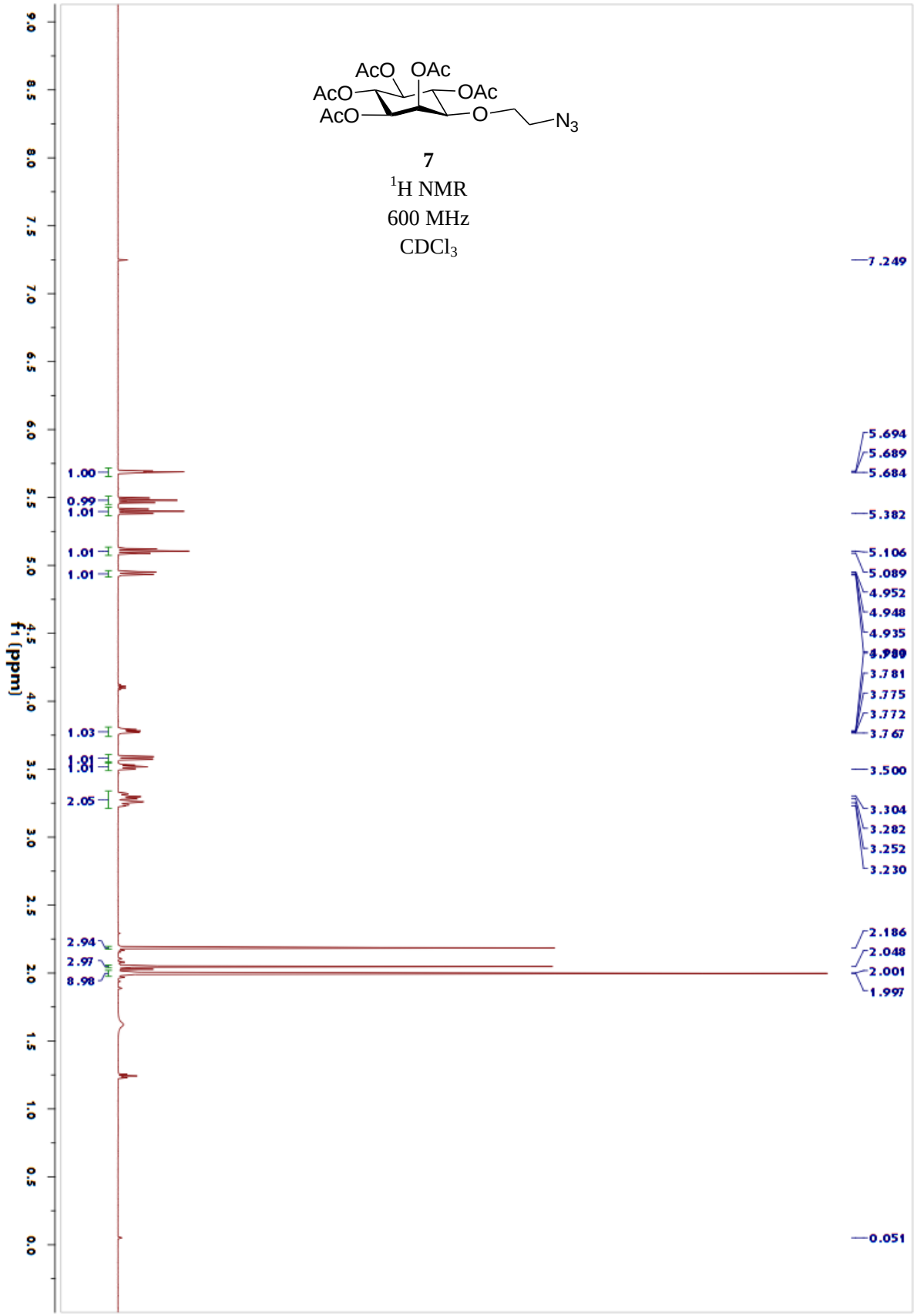
1

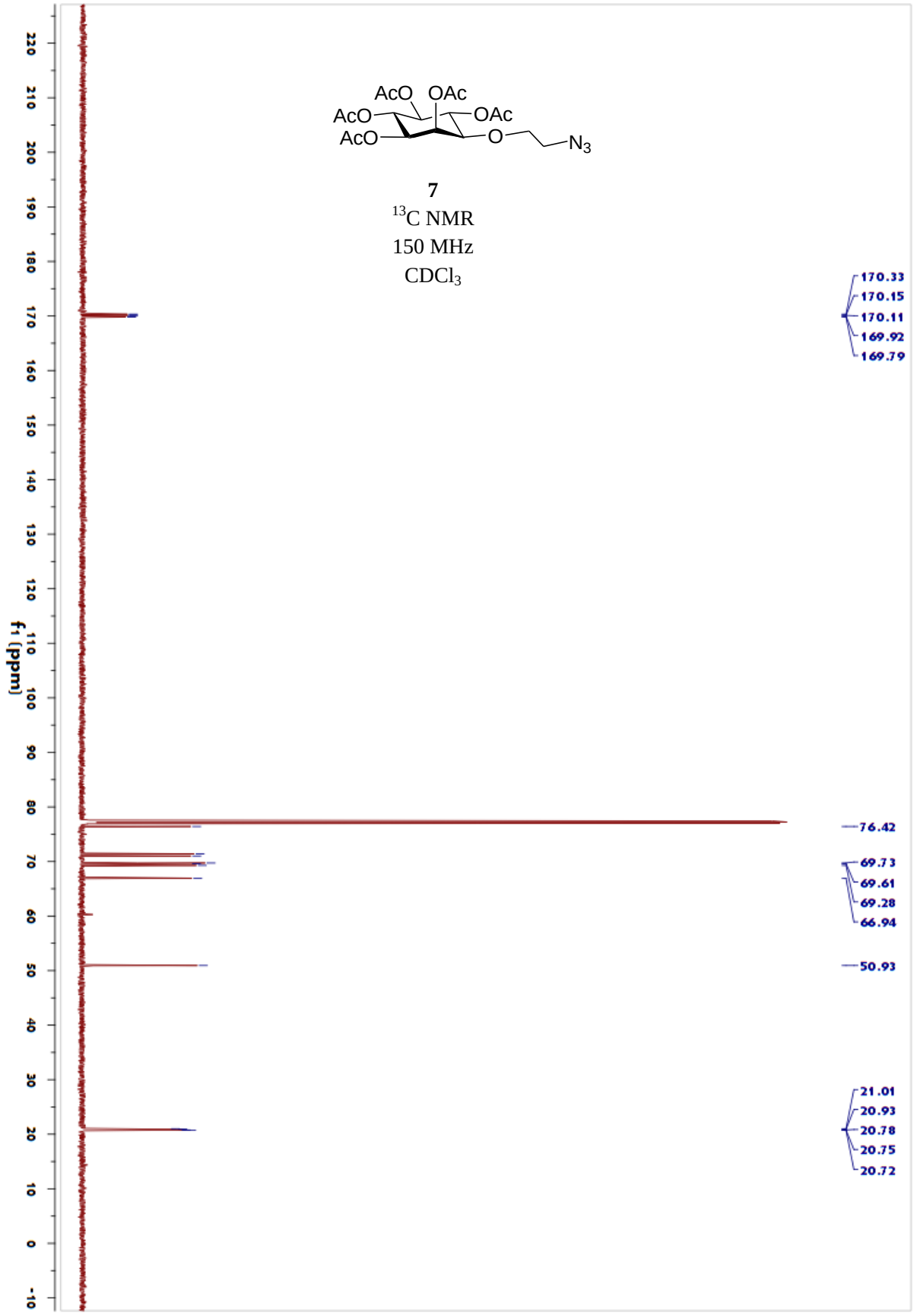
^{13}H NMR

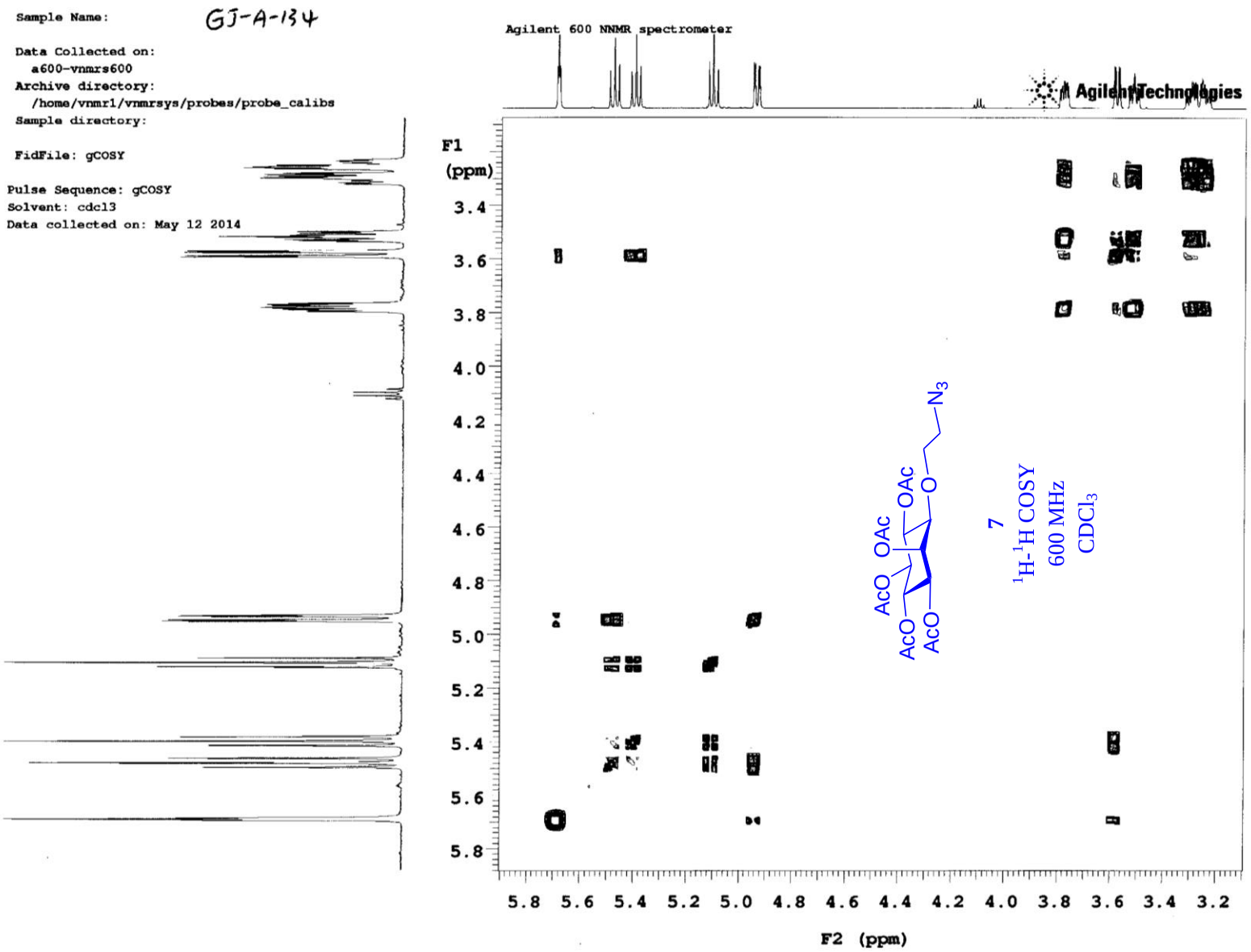
150 MHz

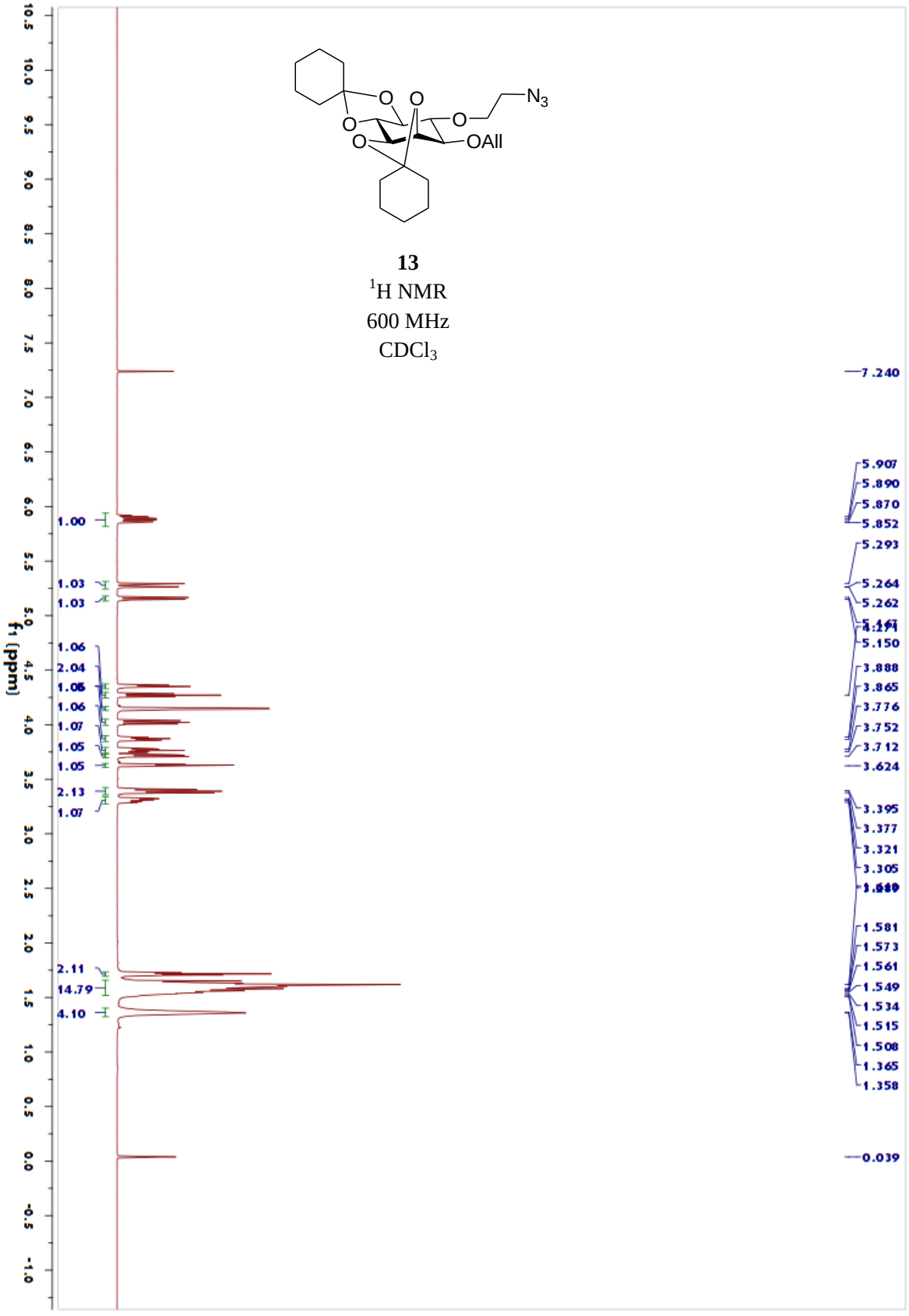
CD_3OD


HO
OH
HO
OH
HO
O
N3
1
1H-1H COSY
600 MHz
CD3OD
Sample Name:
GJ131217
Data Collected on:
a600-vnmrs600
Archive directory:
/home/vnmr1/vnmrsys/probes/probe_calibs
Sample directory:
FidFile: gCOSY
Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Dec 20 2013
Agilent 600 NMR spectrometer
Agilent Technologies
F1 (ppm)
F2 (ppm)


AcO
OAc
AcO
OAc
AcO
O
N3
7
1H NMR
600 MHz
CDCl3
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.00
0.99
1.01
1.01
1.01
1.03
1.01
1.01
2.05
2.94
2.97
8.98
7.249
5.694
5.689
5.684
5.382
5.106
5.089
4.952
4.948
4.935
4.930
3.781
3.775
3.772
3.767
3.500
3.304
3.282
3.252
3.230
2.186
2.048
2.001
1.997
0.051


AcO
OAc
AcO
OAc
AcO
O
N3
7
13C NMR
150 MHz
CDCl3
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
170.33
170.15
170.11
169.92
169.79
76.42
69.73
69.61
69.28
66.94
50.93
21.01
20.93
20.78
20.75
20.72


Sample Name: GJ-A-134
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: May 12 2014
Agilent 600 NNMR spectrometer
Agilent Technologies
F1 (ppm)
F2 (ppm)
AcO
OAc
AcO
OAc
O
N3
7
1H-1H COSY
600 MHz
CDCl3

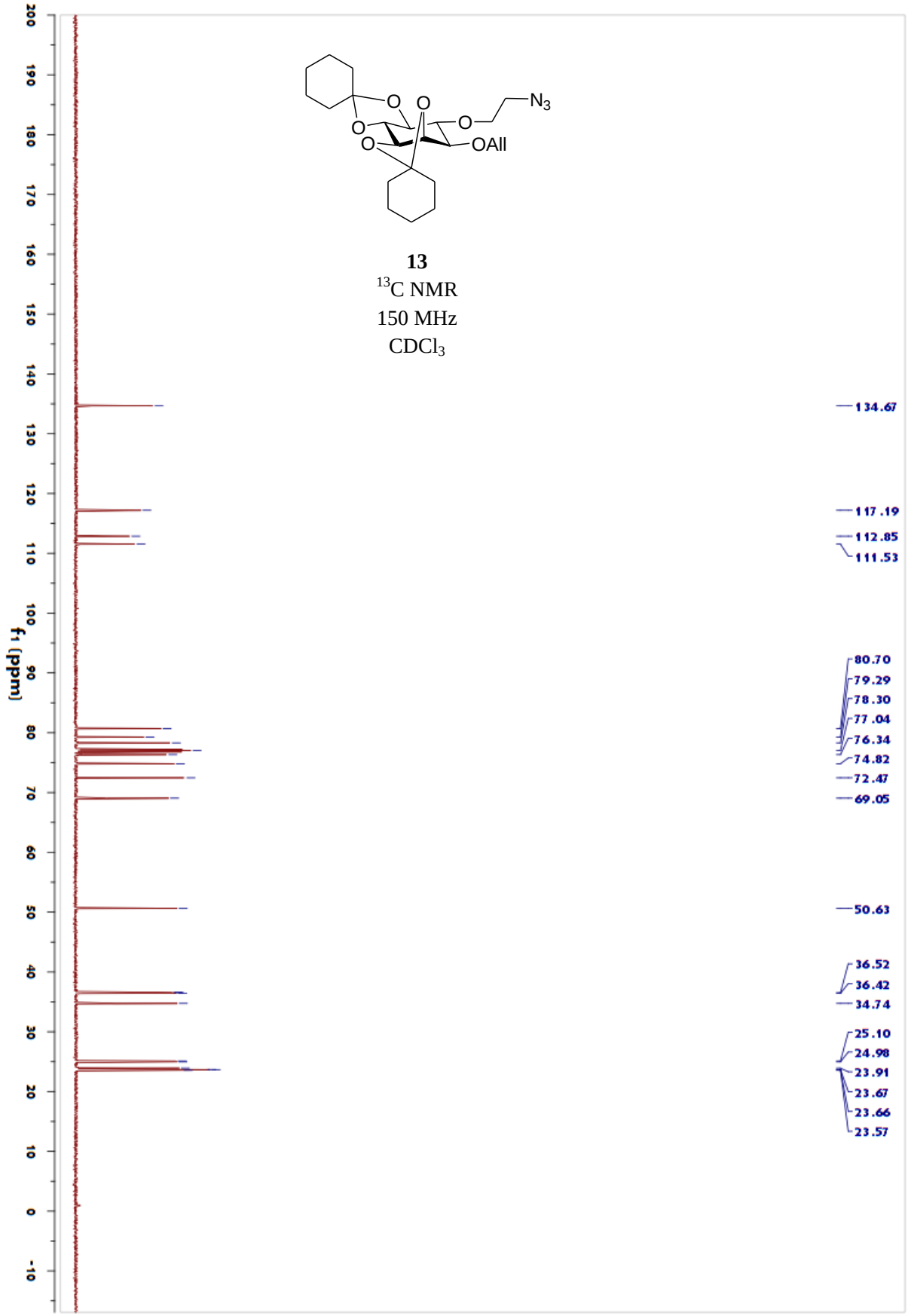


13

^{1}H NMR

600 MHz

$CDCl_3$

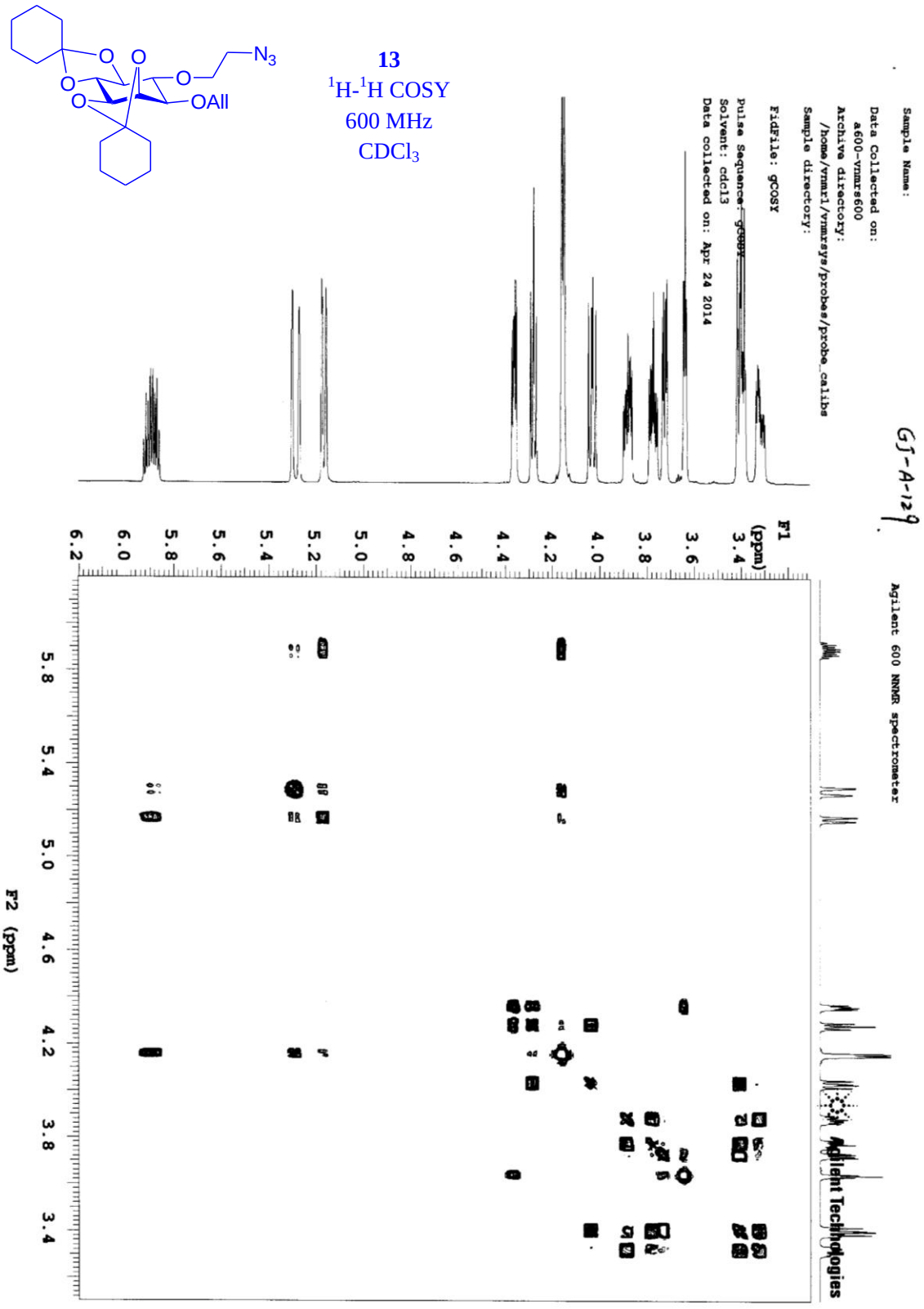


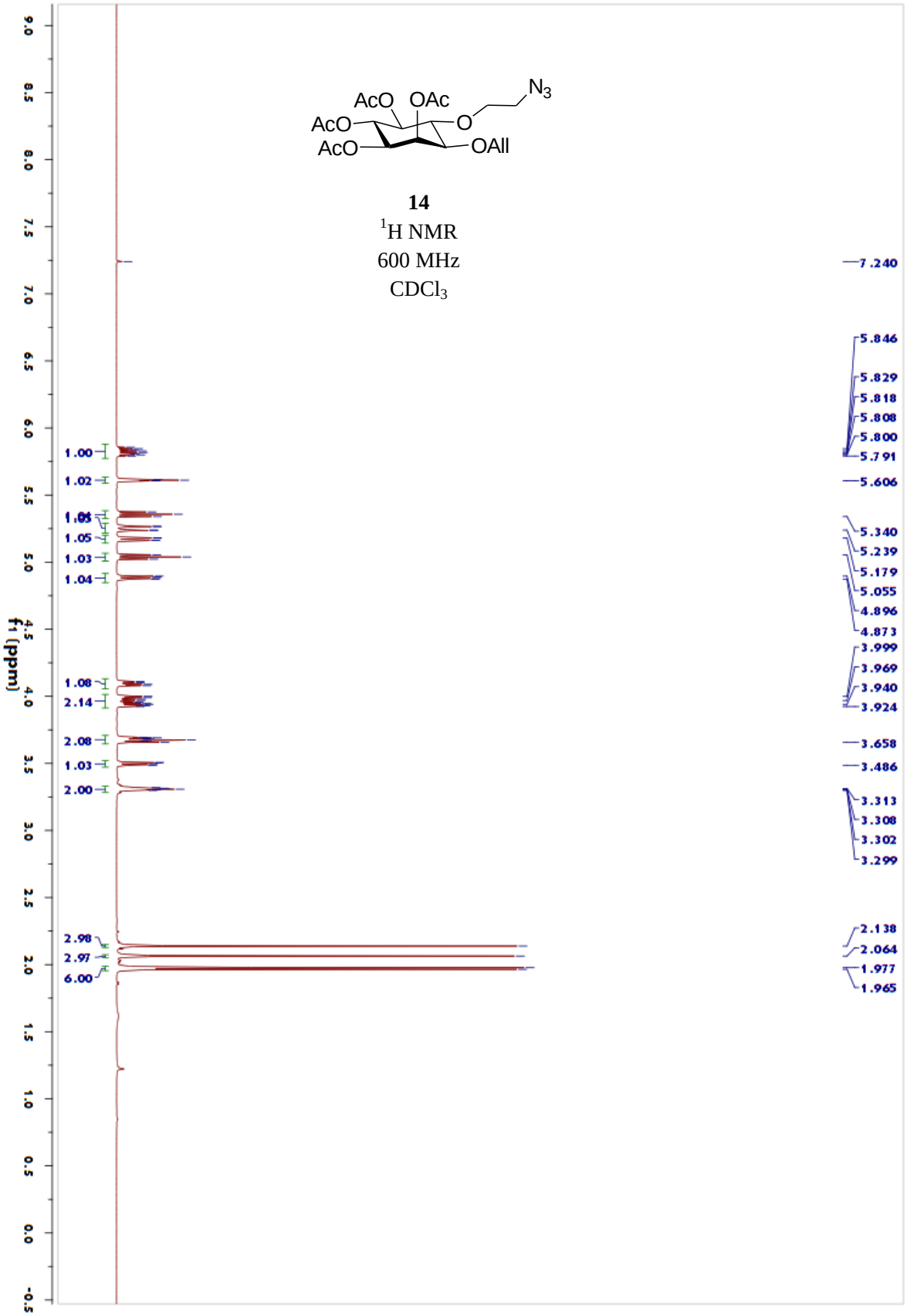
13

^{13}C NMR

150 MHz

$CDCl_3$


N3
O
OAll
13
1H-1H COSY
600 MHz
CDCl3
Sample Name:
GJ-A-129
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: Apr 24 2014
Agilent 600 NMR spectrometer
F1 (ppm)
F2 (ppm)
Agilent Technologies

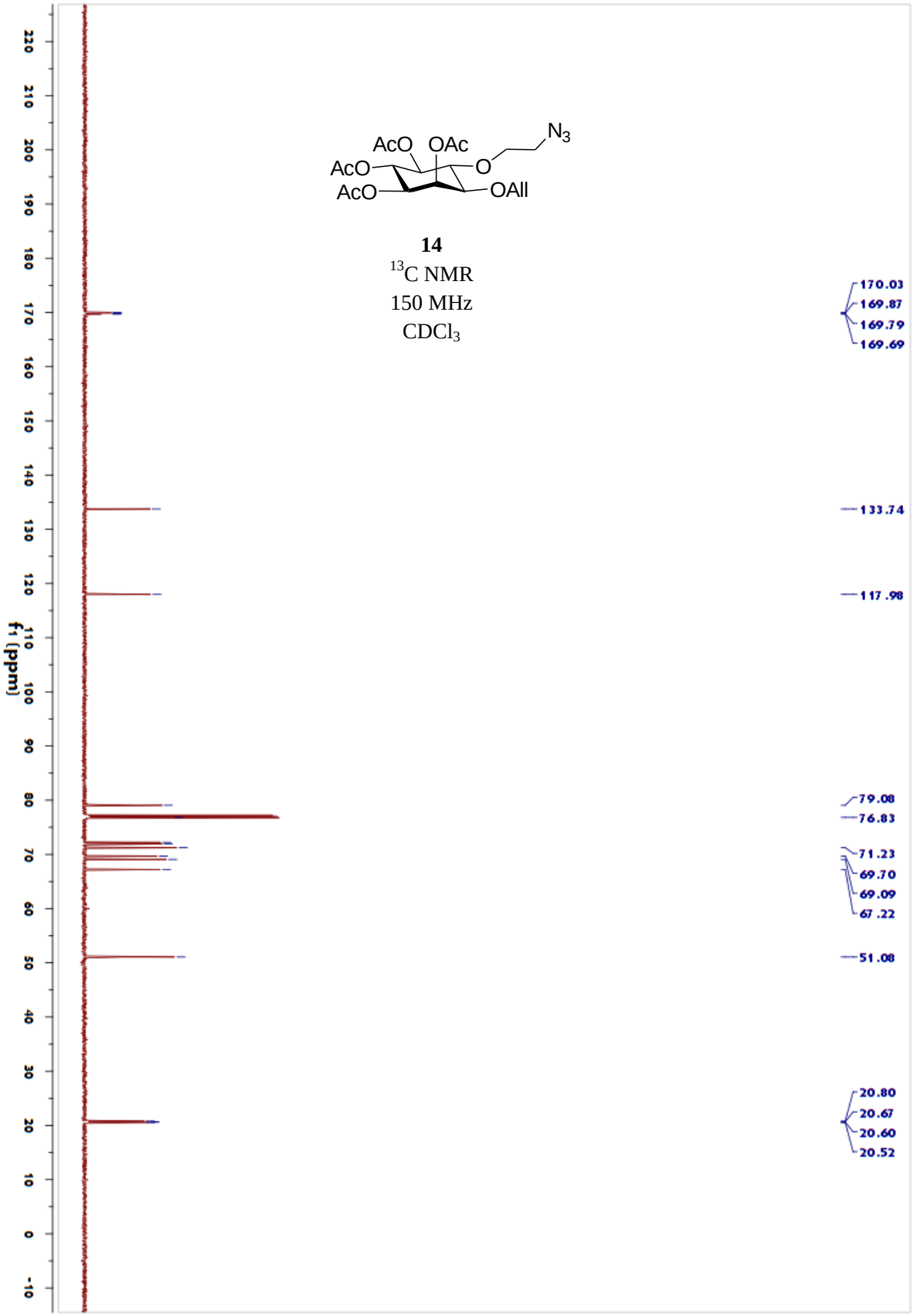


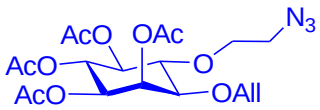
14

^{1}H NMR

600 MHz

$CDCl_3$


AcO
OAc
AcO
O
N3
AcO
OAll
14
13C NMR
150 MHz
CDCl3
170.03
169.87
169.79
169.69
133.74
117.98
79.08
76.83
71.23
69.70
69.09
67.22
51.08
20.80
20.67
20.60
20.52
f1 (ppm)

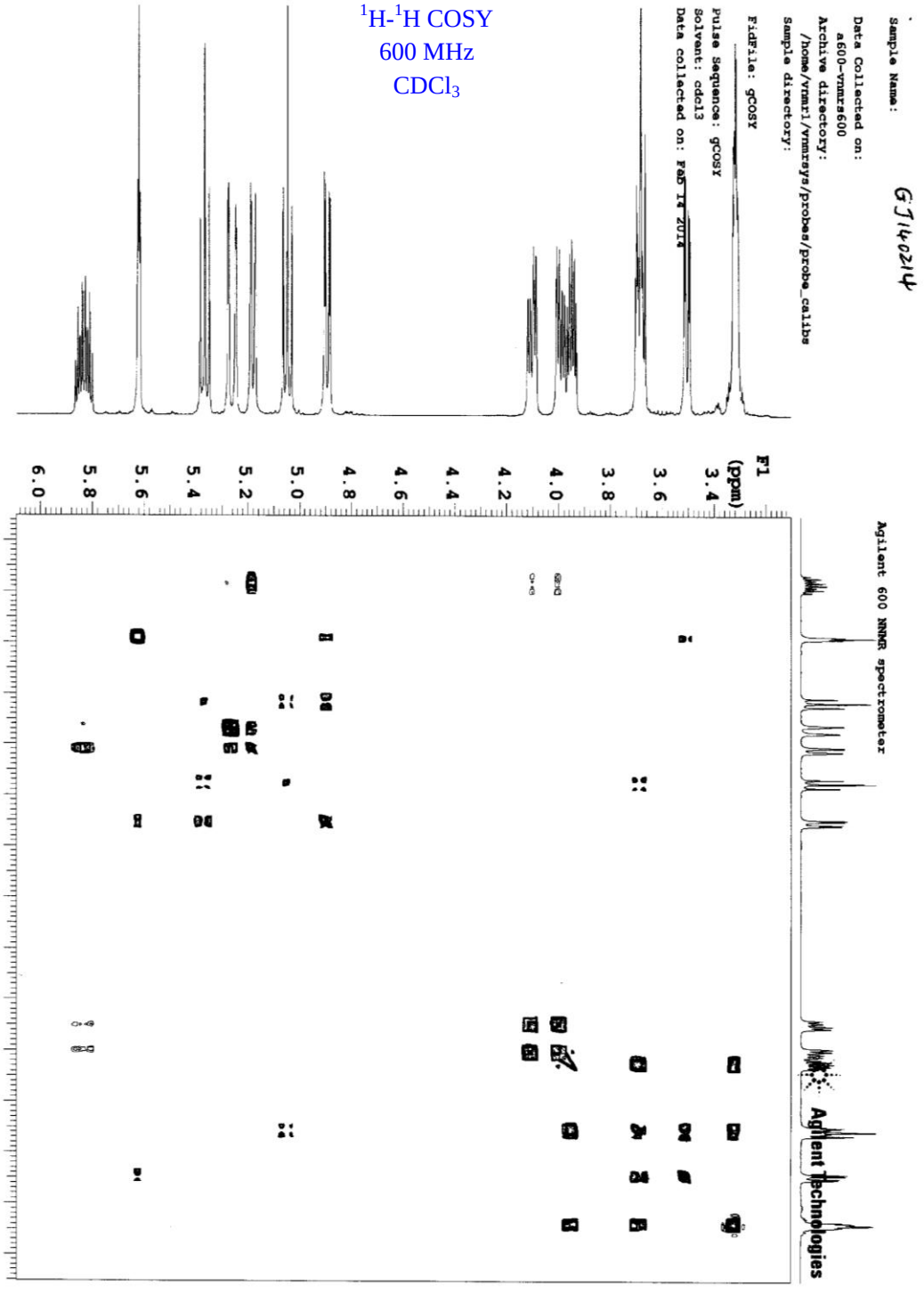


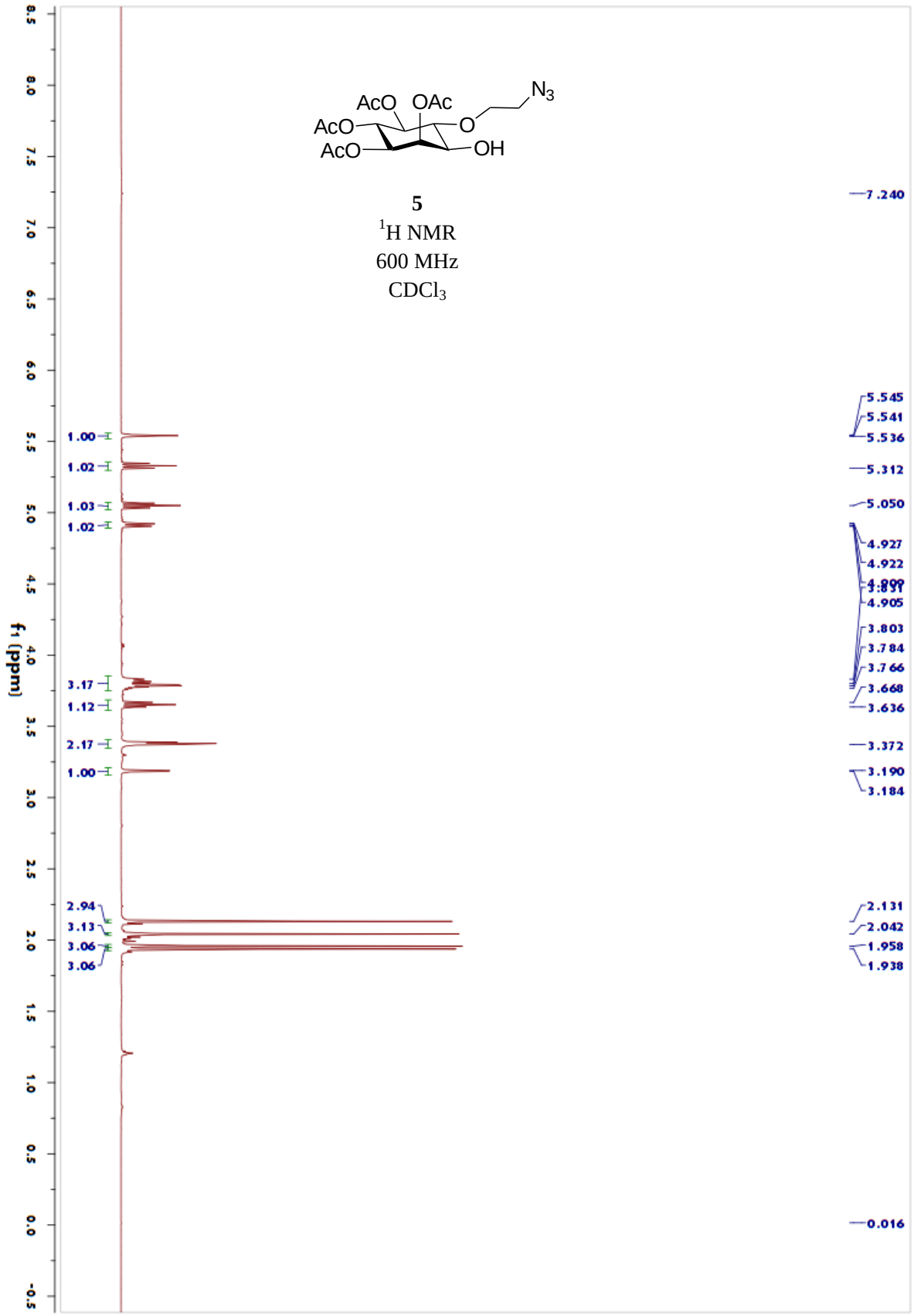
14

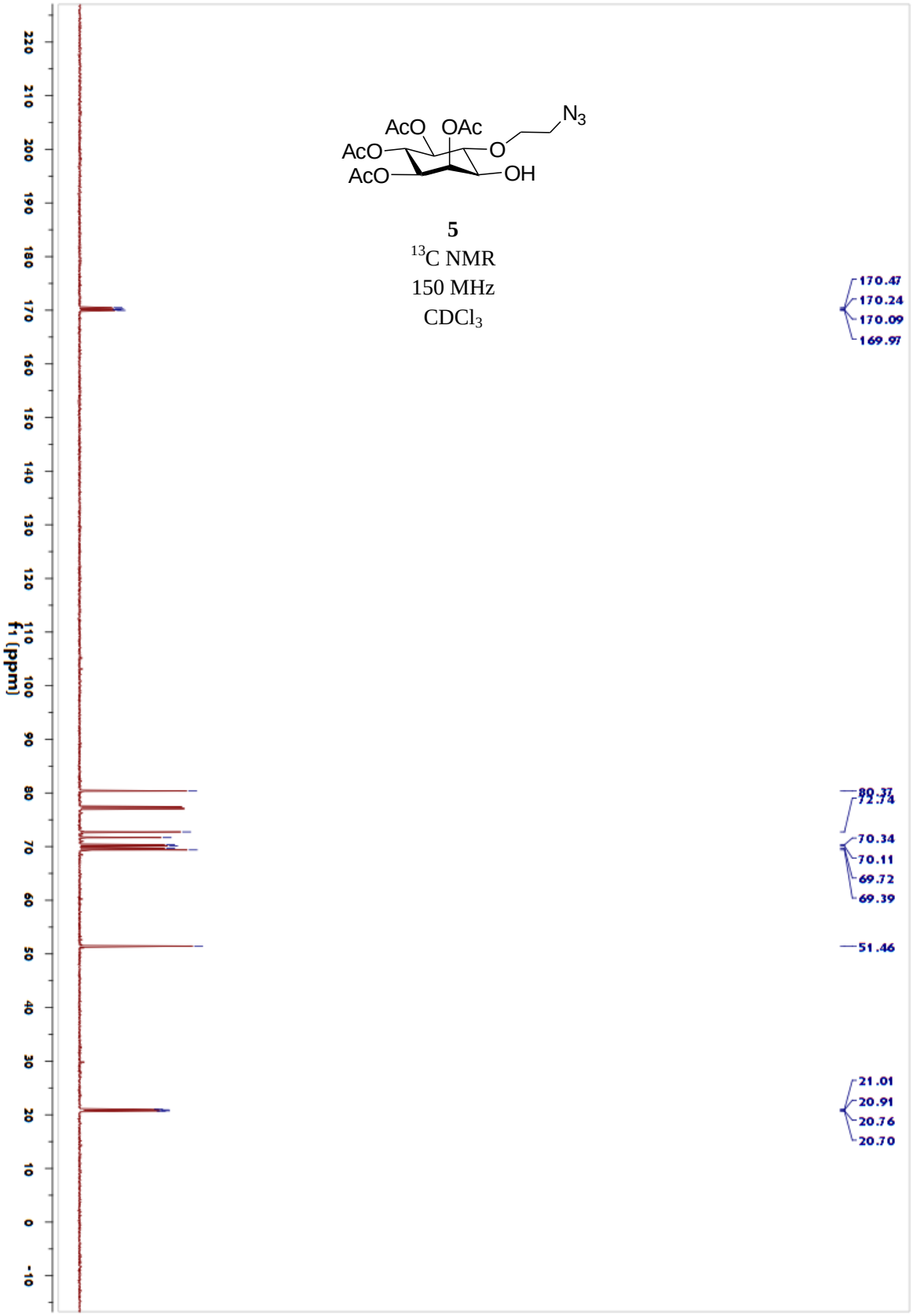
^{1}H-^{1}H COSY

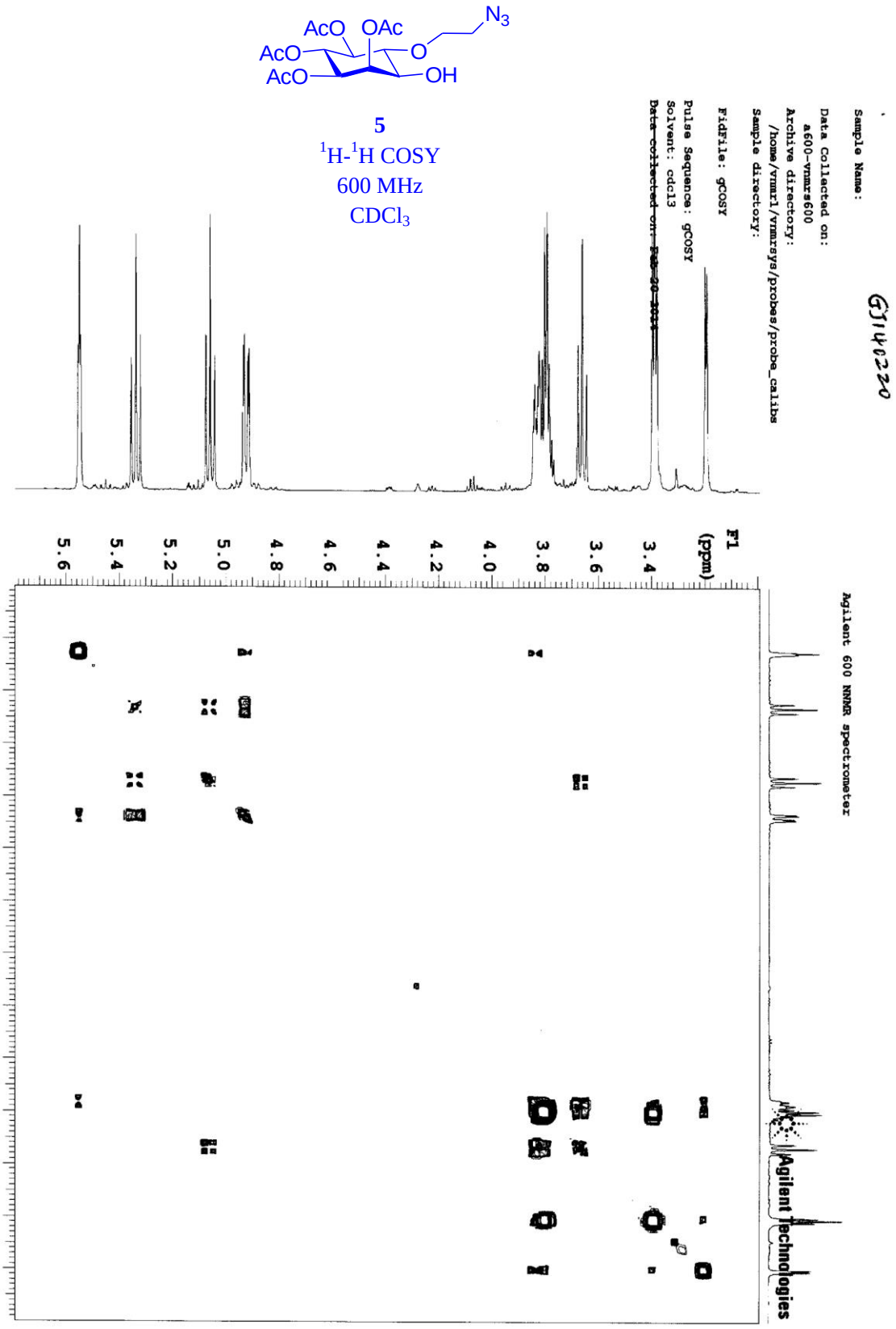
600 MHz

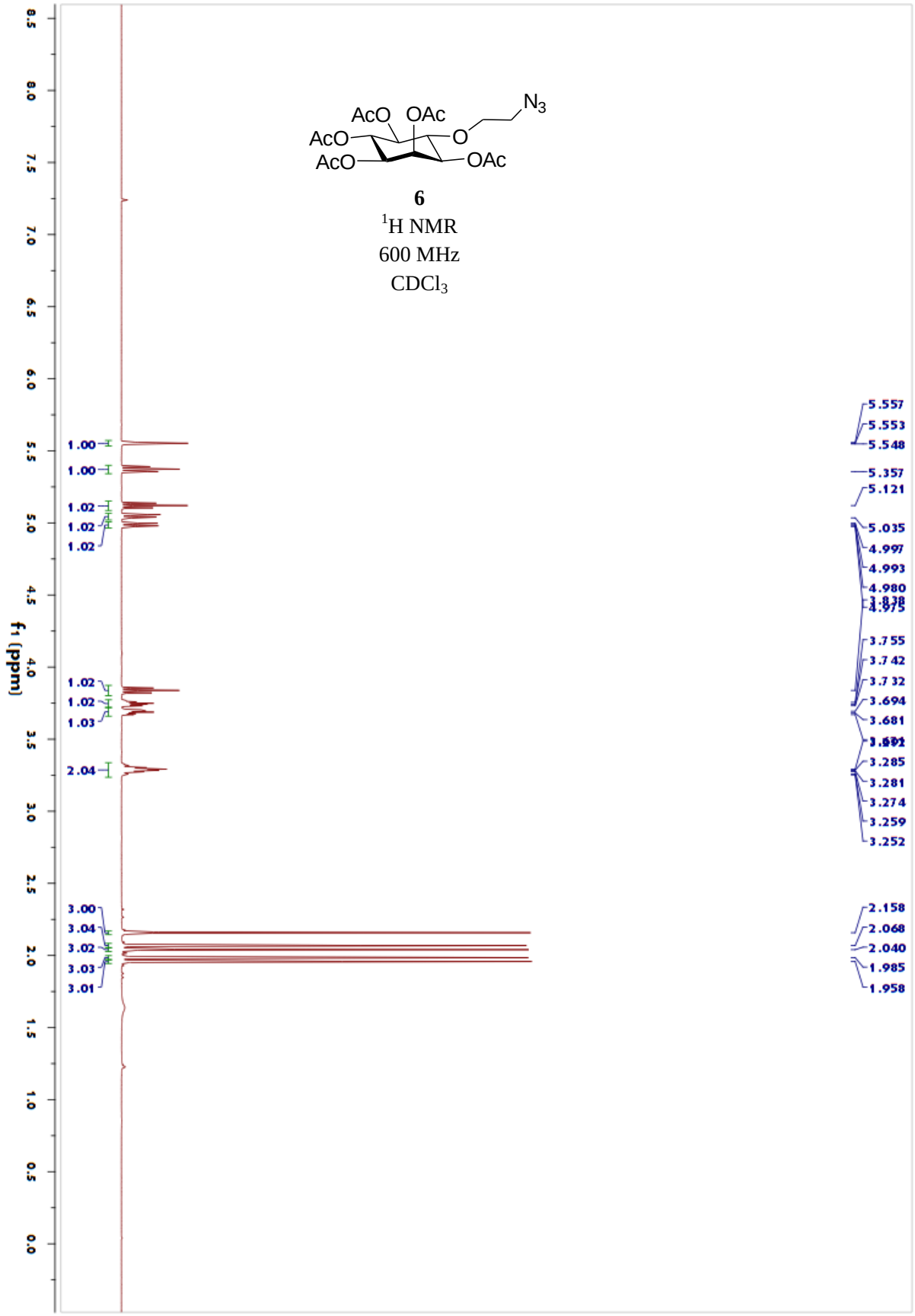
$CDCl_3$

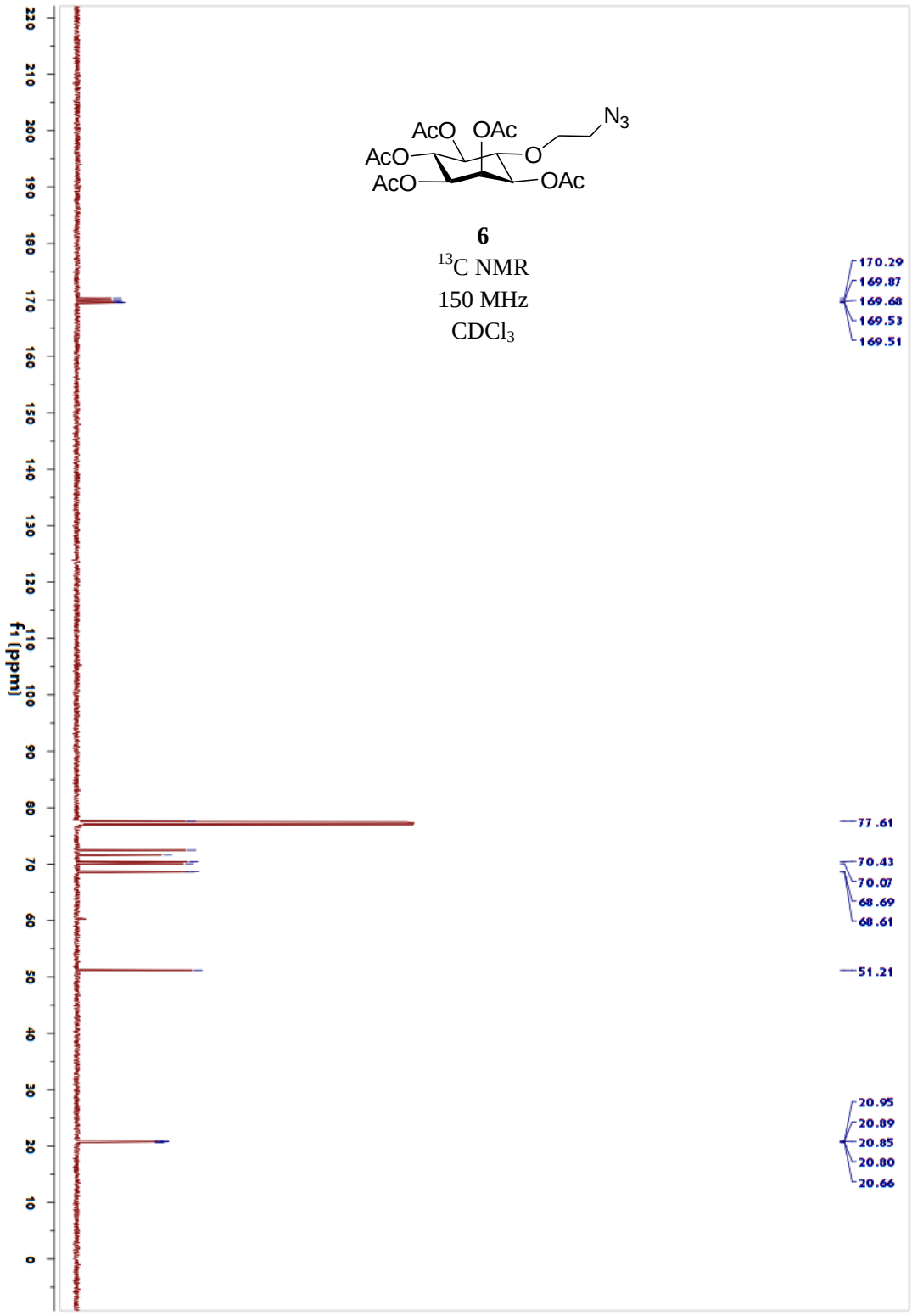


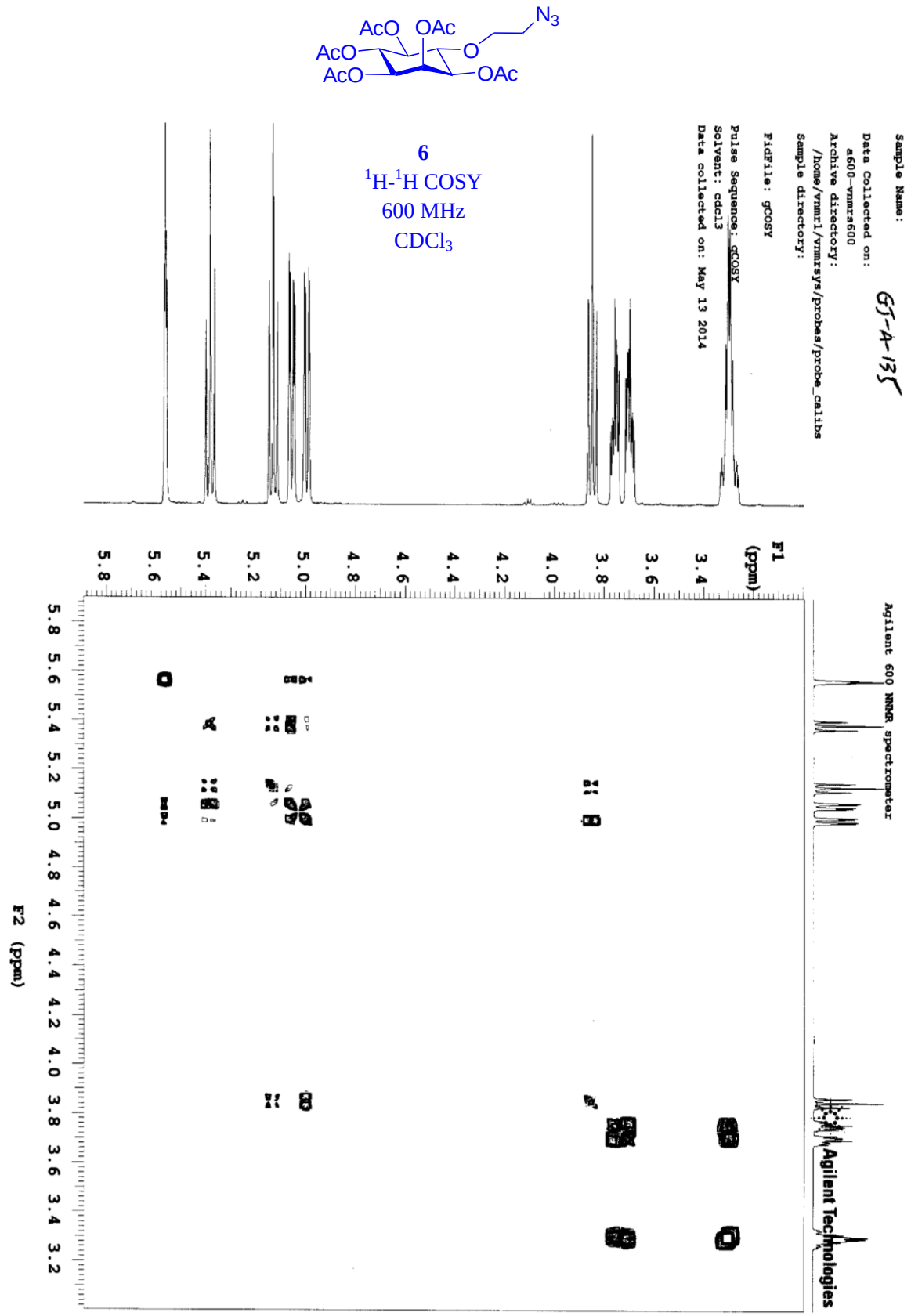

AcO
OAc
AcO
O
N3
AcO
OH
5
1H NMR
600 MHz
CDCl3
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1.00
1.02
1.03
1.02
3.17
1.12
2.17
1.00
2.94
3.13
3.06
3.06
7.240
5.545
5.541
5.536
5.312
5.050
4.927
4.922
4.905
3.803
3.784
3.766
3.668
3.636
3.372
3.190
3.184
2.131
2.042
1.958
1.938
0.016

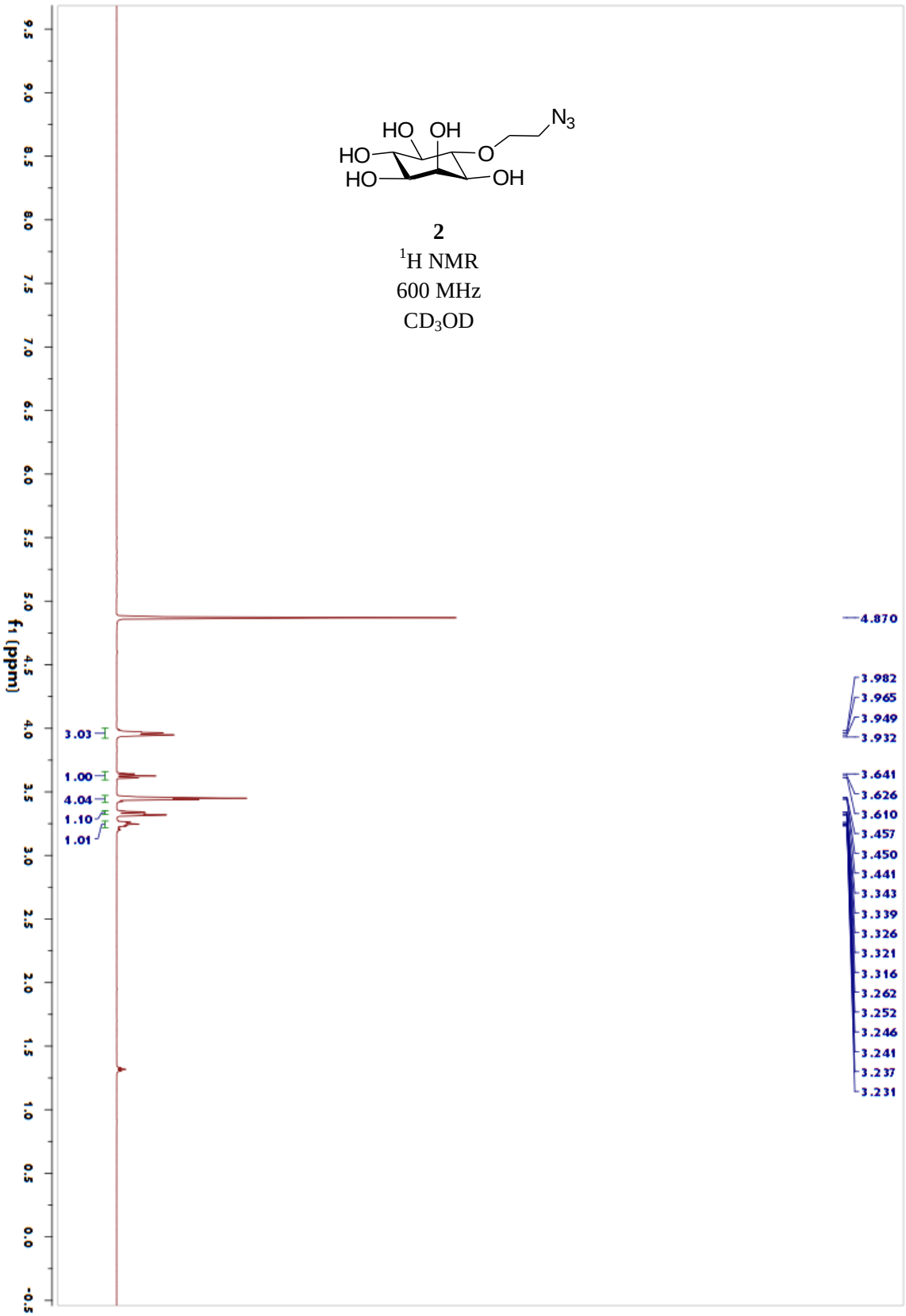

AcO
OAc
AcO
O
N3
AcO
OH
5
13C NMR
150 MHz
CDCl3
170.47
170.24
170.09
169.97
80.37
72.74
70.34
70.11
69.72
69.39
51.46
21.01
20.91
20.76
20.70
f1 (ppm)

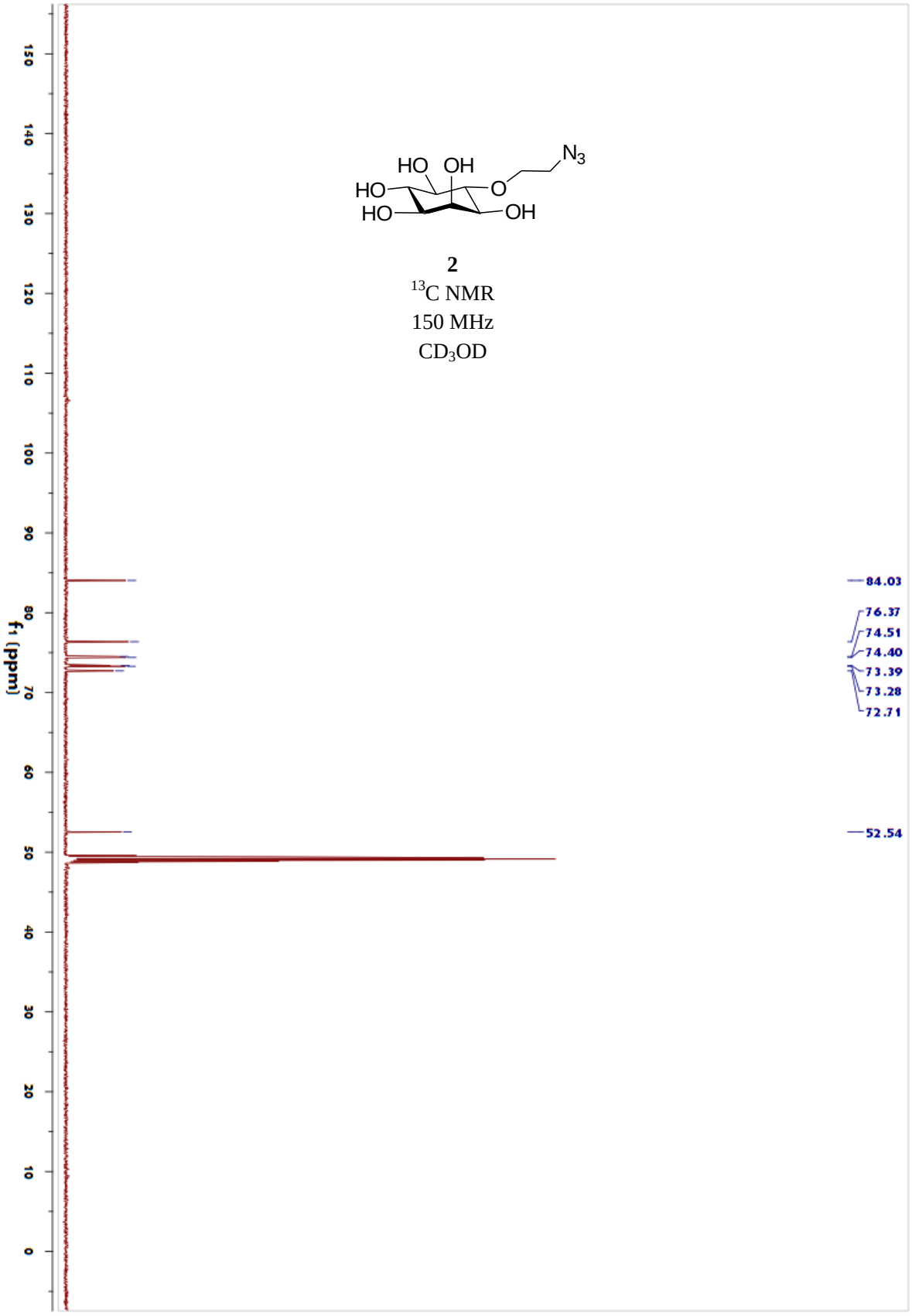

AcO
OAc
AcO
AcO
O
N3
OH
5
1H-1H COSY
600 MHz
CDCl3
Sample Name:
GJ140220
Data Collected on:
a600-vnmrs600
Archive directory:
/home/vnmrl/vnmrsys/probes/probe_calibs
Sample directory:
FidFile: gCOSY
Pulse Sequence: gCOSY
Solvent: cdcl3
Agilent 600 NMR spectrometer
F1 (ppm)
F2 (ppm)
Agilent Technologies


AcO
OAc
AcO
O
N3
AcO
OAc
6
1H NMR
600 MHz
CDCl3
f1 (ppm)
1.00
1.00
1.02
1.02
1.02
1.02
1.02
1.03
2.04
3.00
3.04
3.02
3.03
3.01
5.557
5.553
5.548
5.357
5.121
5.035
4.997
4.993
4.980
4.975
3.755
3.742
3.732
3.694
3.681
3.285
3.281
3.274
3.259
3.252
2.158
2.068
2.040
1.985
1.958


AcO
OAc
AcO
O
N3
AcO
OAc
6
13C NMR
150 MHz
CDCl3
170.29
169.87
169.68
169.53
169.51
77.61
70.43
70.07
68.69
68.61
51.21
20.95
20.89
20.85
20.80
20.66
f1 (ppm)


AcO
OAc
AcO
O
N3
AcO
OAc
6
1H-1H COSY
600 MHz
CDCl3
Sample Name:
GJ-A-135
Data Collected on:
a600-vnmrs600
Archive directory:
/home/vnmrl/vnmrsys/probes/probe_calibs
Sample directory:
FidFile: gCOSY
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: May 13 2014
Agilent 600 NMNR spectrometer
F1 (ppm)
F2 (ppm)
Agilent Technologies


HO
OH
HO
O
HO
OH
N3
2
1H NMR
600 MHz
CD3OD
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
3.03
1.00
4.04
1.10
1.01
4.870
3.982
3.965
3.949
3.932
3.641
3.626
3.610
3.457
3.450
3.441
3.343
3.339
3.326
3.321
3.316
3.262
3.252
3.246
3.241
3.237
3.231

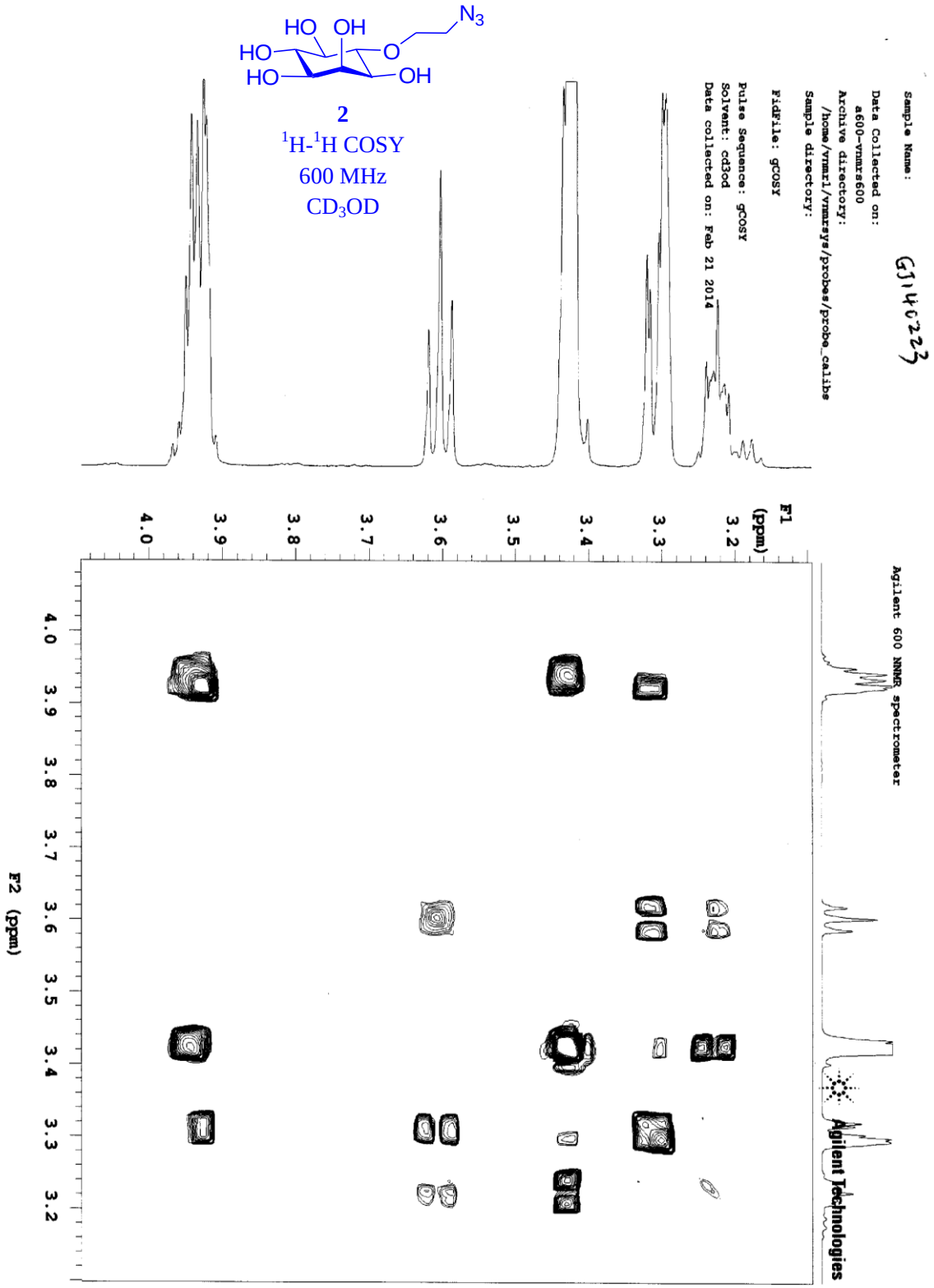


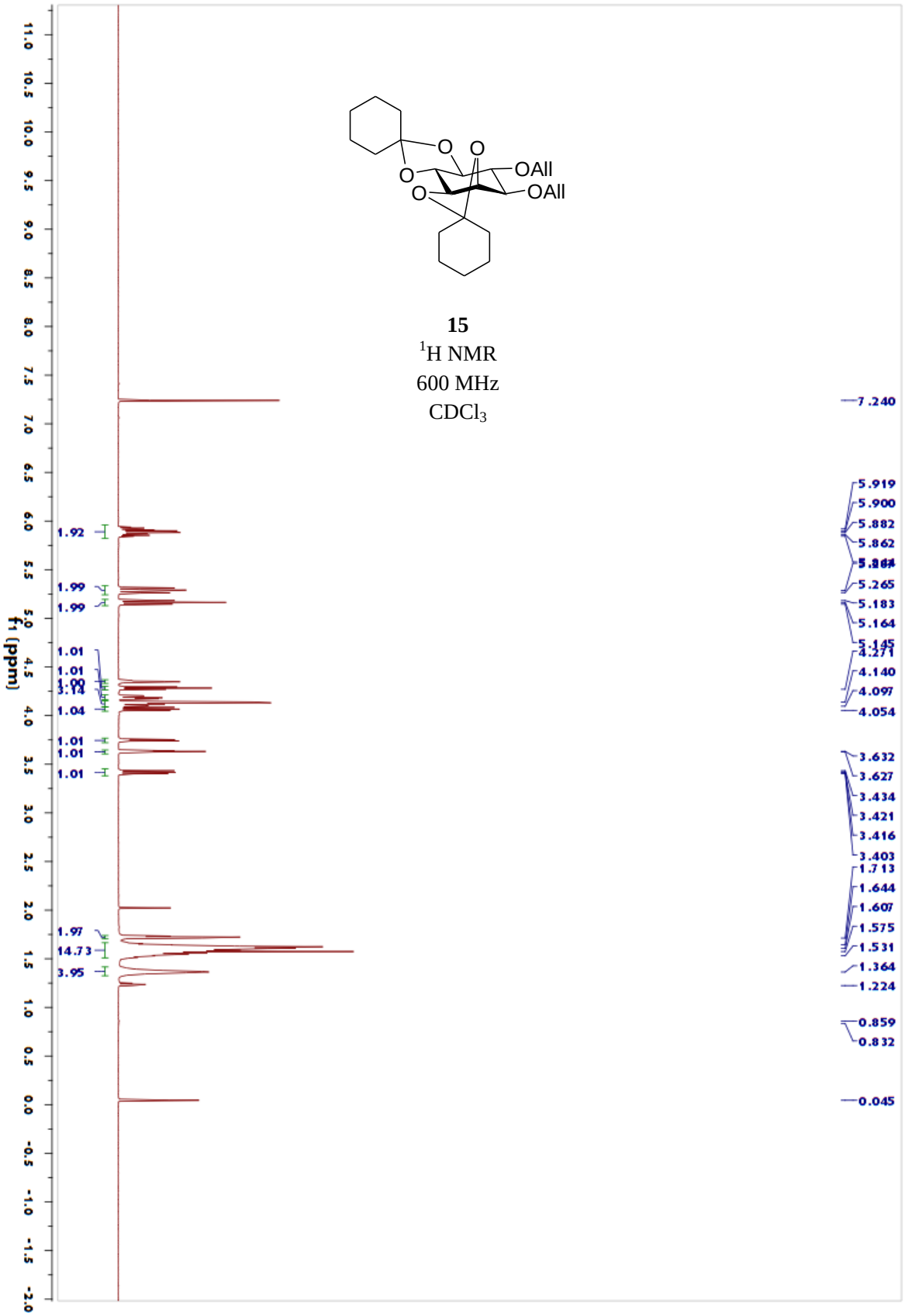
2

^{13}C NMR

150 MHz

CD_3OD


HO
OH
HO
O
HO
OH
N3
2
1H-1H COSY
600 MHz
CD3OD
Sample Name:
GJ140223
Data Collected on:
a600-vnmrs600
Archive directory:
/home/vnmr1/vnmrsys/probes/probe_calibs
Sample directory:
FidFile: gCOSY
Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Feb 21 2014
F1 (ppm)
F2 (ppm)
Agilent 600 NMR spectrometer
Agilent Technologies

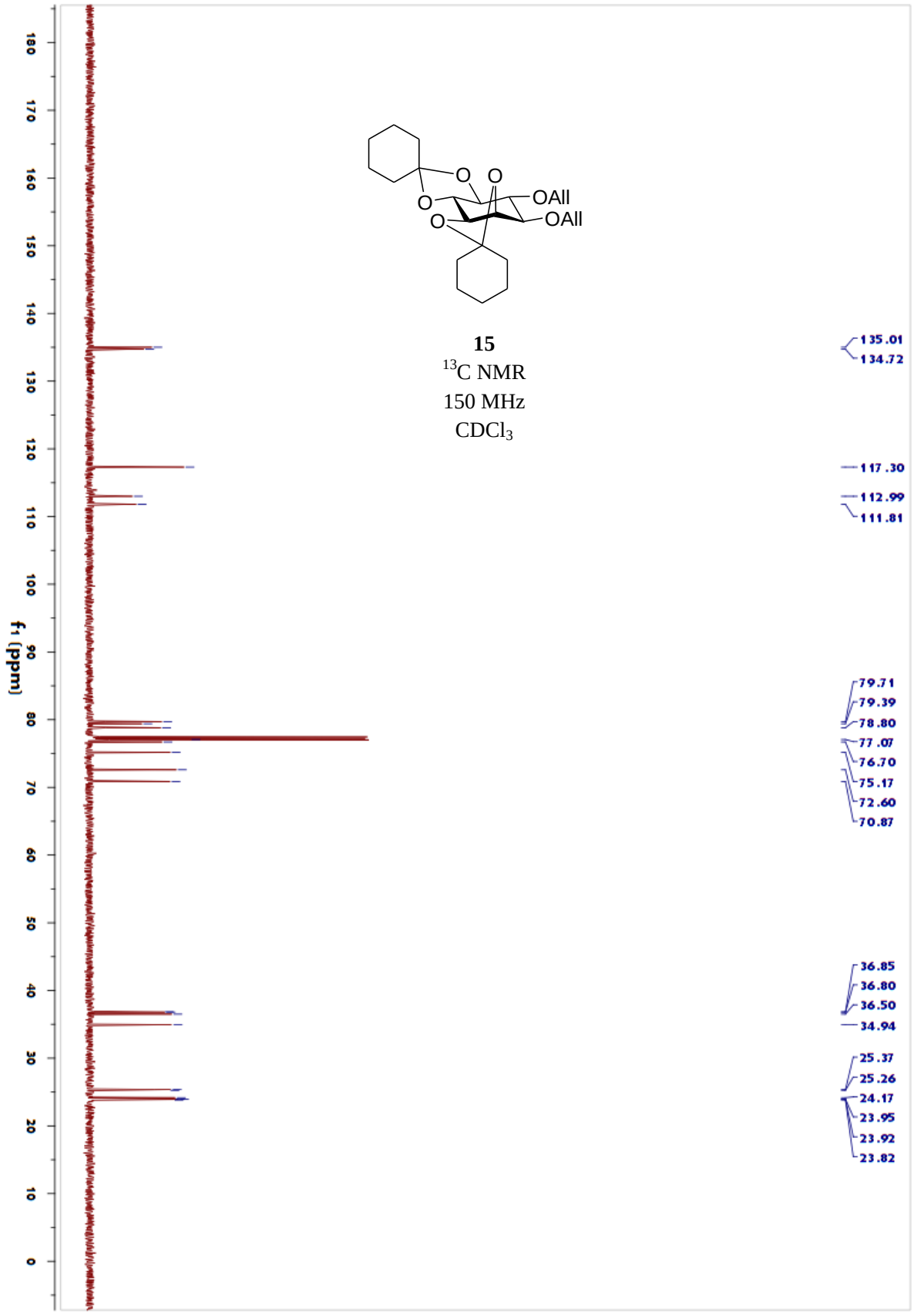


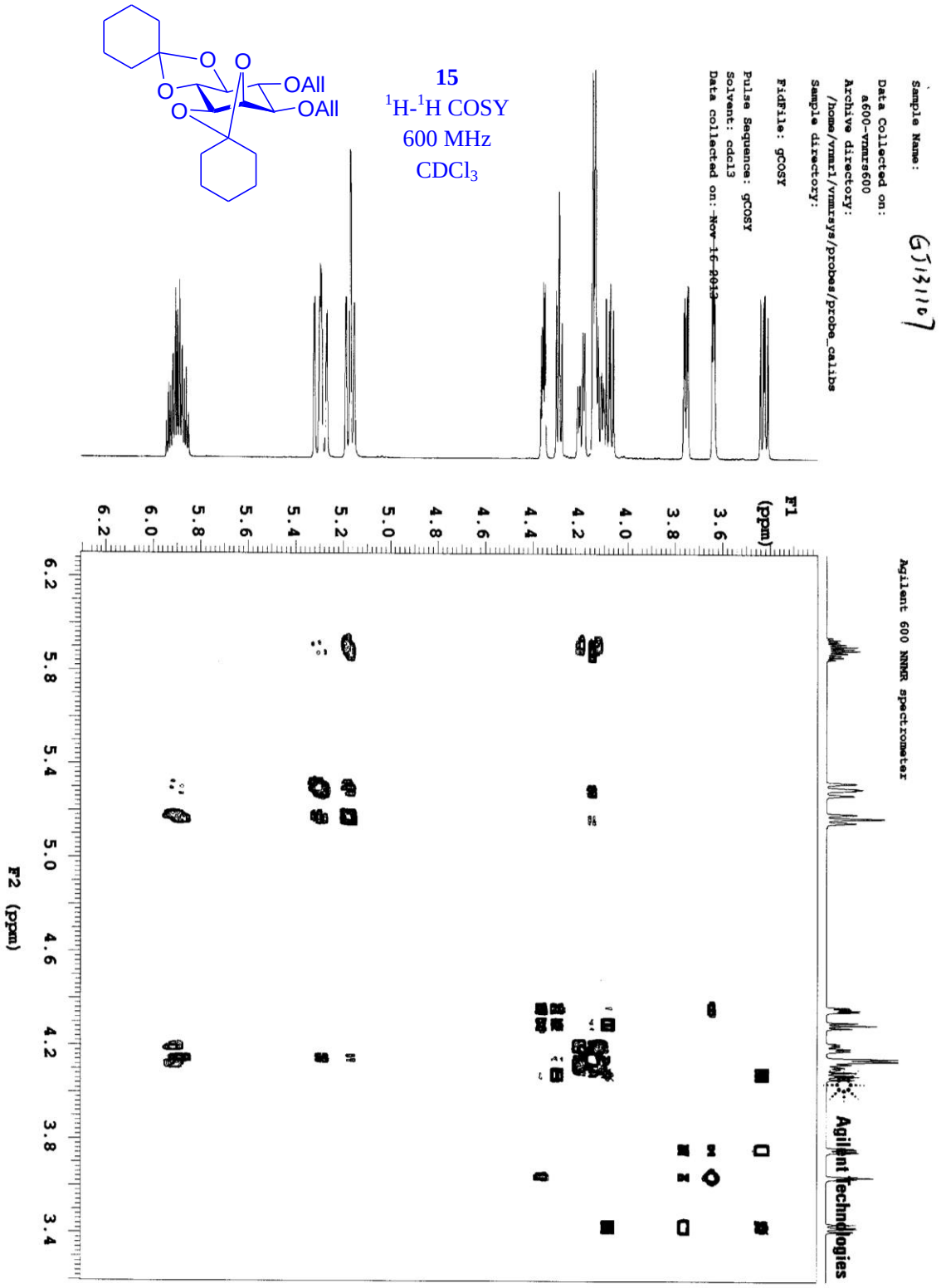
15

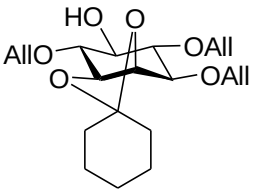
^{1}H NMR

600 MHz

$CDCl_3$


O
O
O
O
OAll
OAll
15
^{13}C NMR
150 MHz
$CDCl_3$
f1 (ppm)
135.01
134.72
117.30
112.99
111.81
79.71
79.39
78.80
77.07
76.70
75.17
72.60
70.87
36.85
36.80
36.50
34.94
25.37
25.26
24.17
23.95
23.92
23.82


OAll
OAll
15
^{1}H-^{1}H COSY
600 MHz
$CDCl_3$
Sample Name: GJ12107
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: Nov 16 2012
Agilent 600 NMR spectrometer
Agilent Technologies
F1 (ppm)
F2 (ppm)

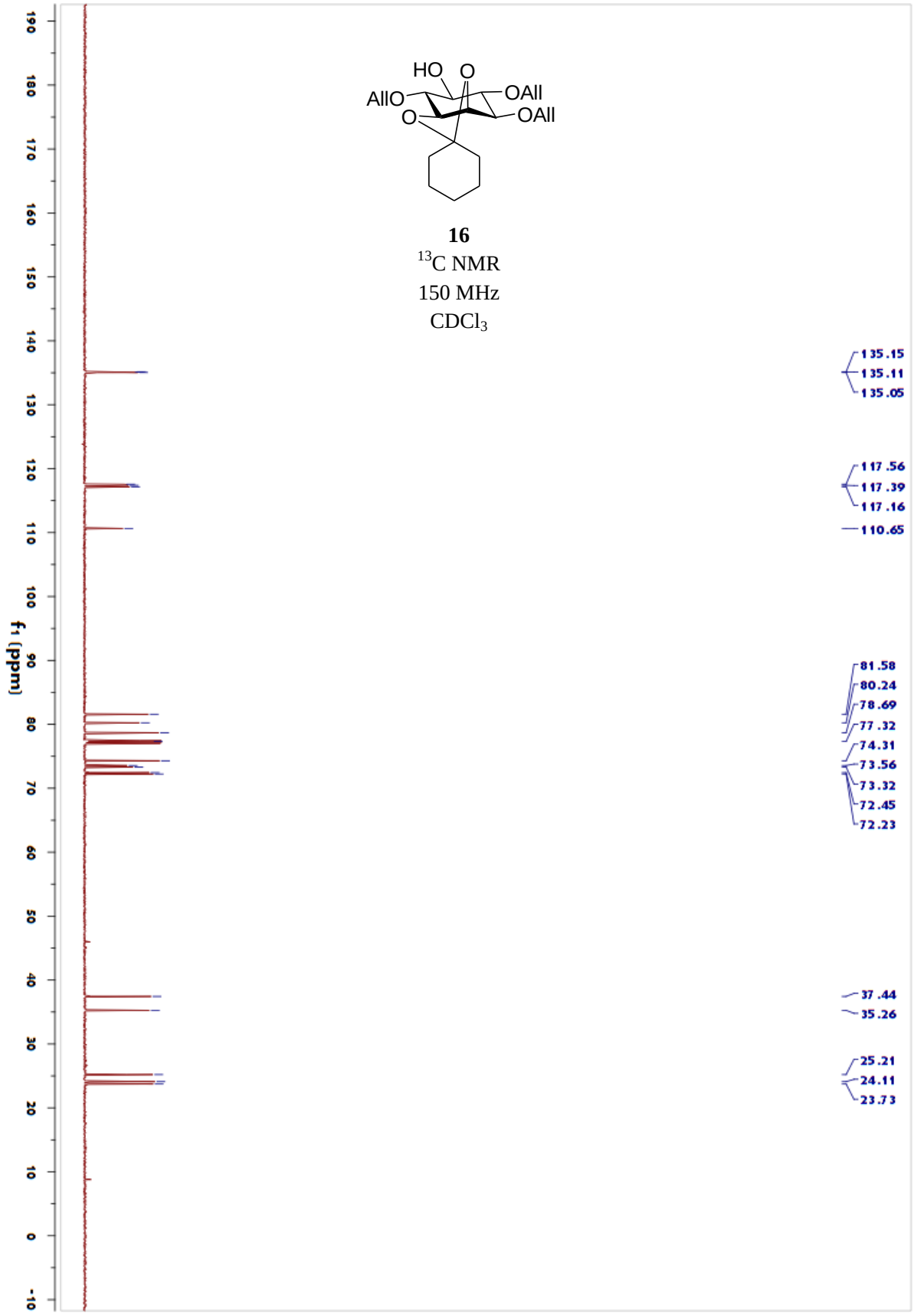


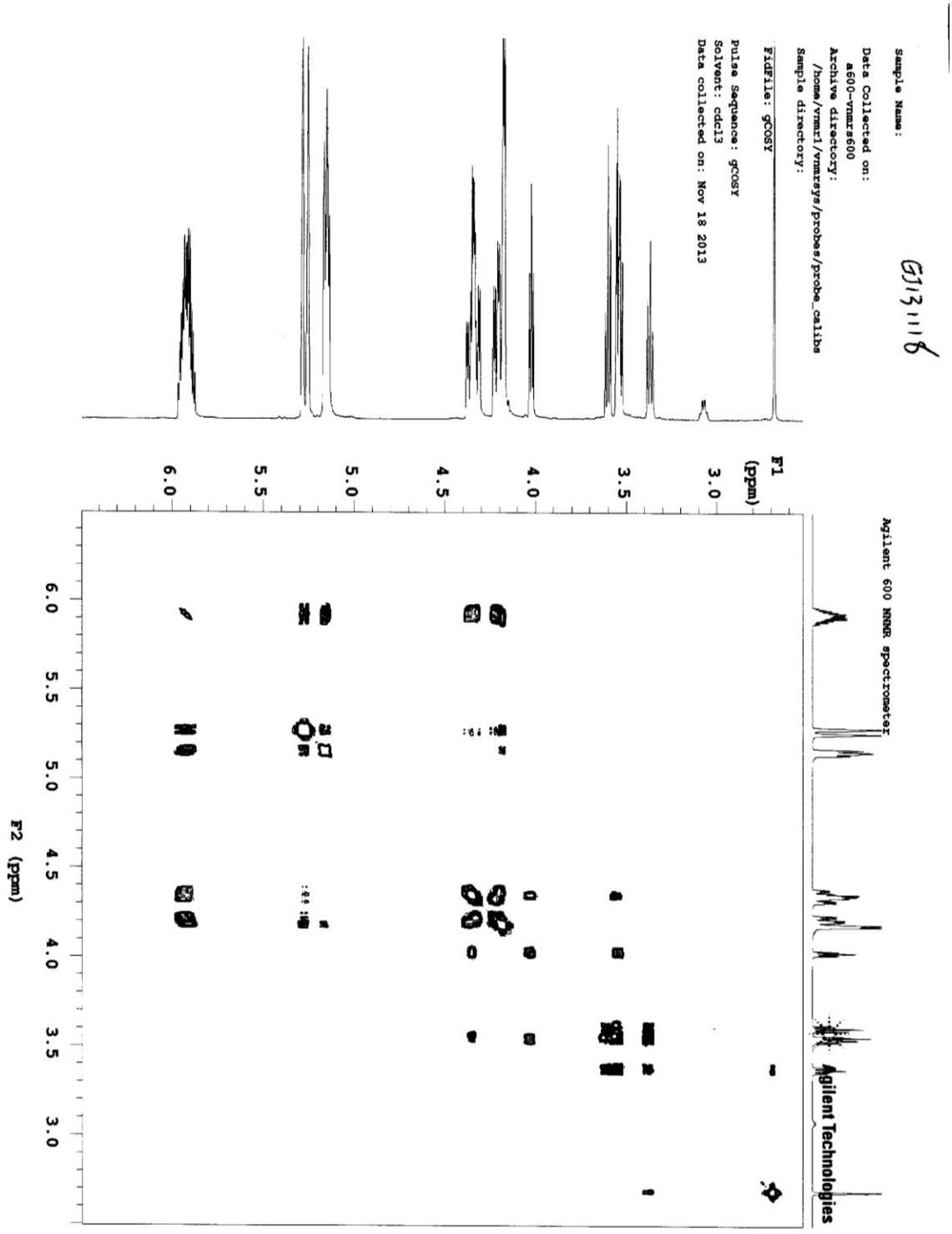
16

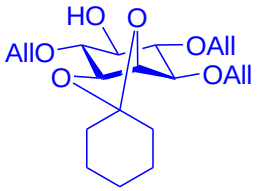
^{1}H NMR

600 MHz

$CDCl_3$


HO
O
AllO
OAll
O
OAll
16
13C NMR
150 MHz
CDCl3
f1 (ppm)
135.15
135.11
135.05
117.56
117.39
117.16
110.65
81.58
80.24
78.69
77.32
74.31
73.56
73.32
72.45
72.23
37.44
35.26
25.21
24.11
23.73



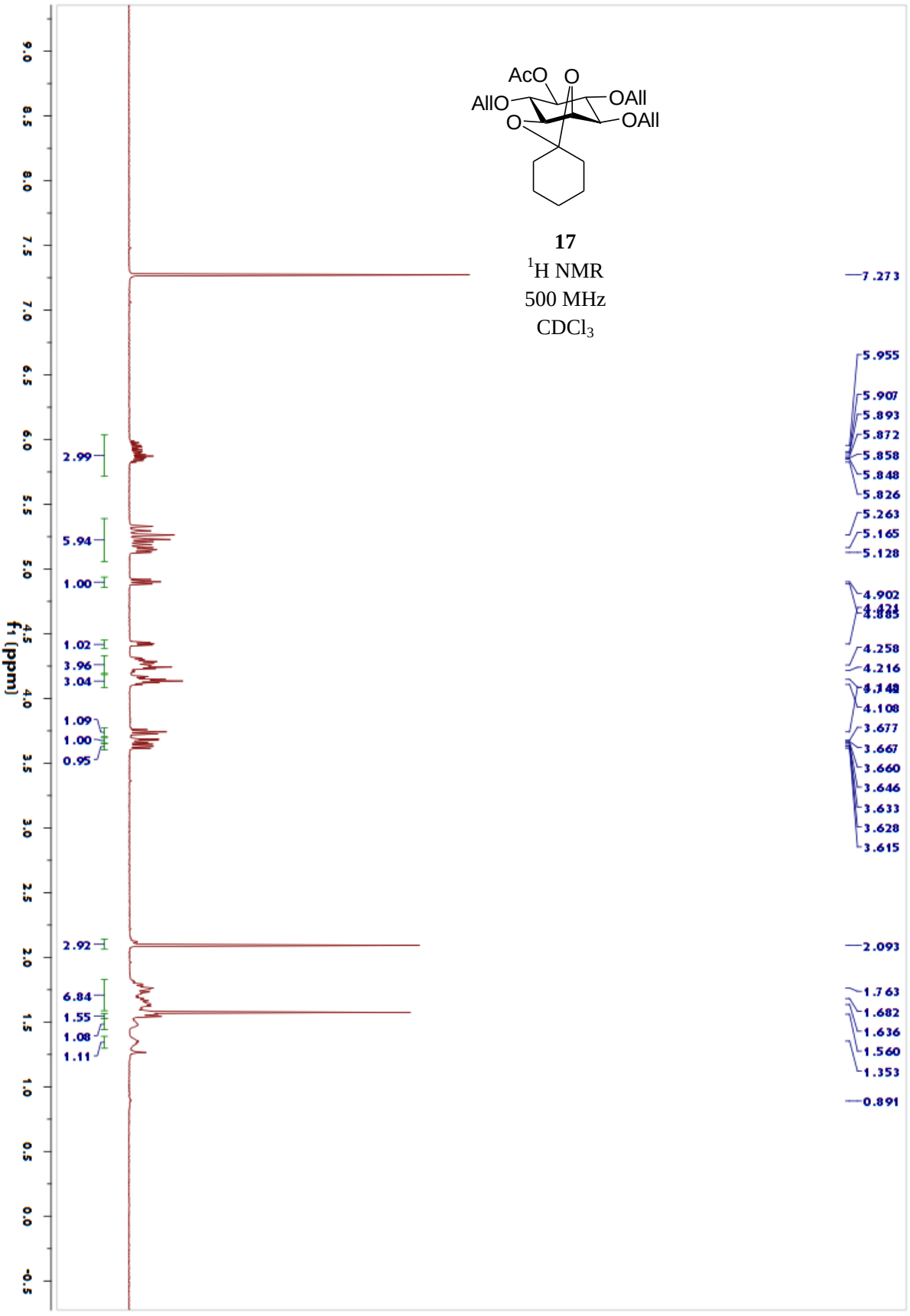


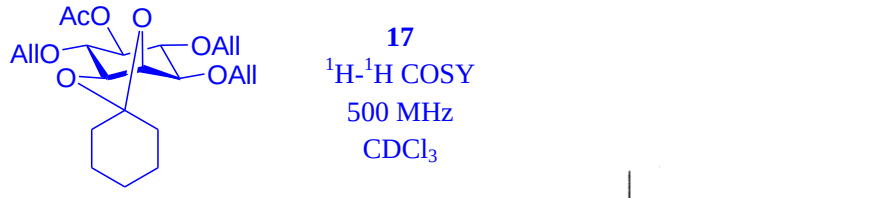
16

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

600 MHz

$CDCl_3$


AcO
O
AllO
OAll
O
OAll
17
1H NMR
500 MHz
CDCl3
f1 (ppm)
7.273
5.955
5.907
5.893
5.872
5.858
5.848
5.826
5.263
5.165
5.128
4.902
4.258
4.216
4.108
3.677
3.667
3.660
3.646
3.633
3.628
3.615
2.093
1.763
1.682
1.636
1.560
1.353
0.891
2.99
5.94
1.00
1.02
3.96
3.04
1.09
1.00
0.95
2.92
6.84
1.55
1.08
1.11

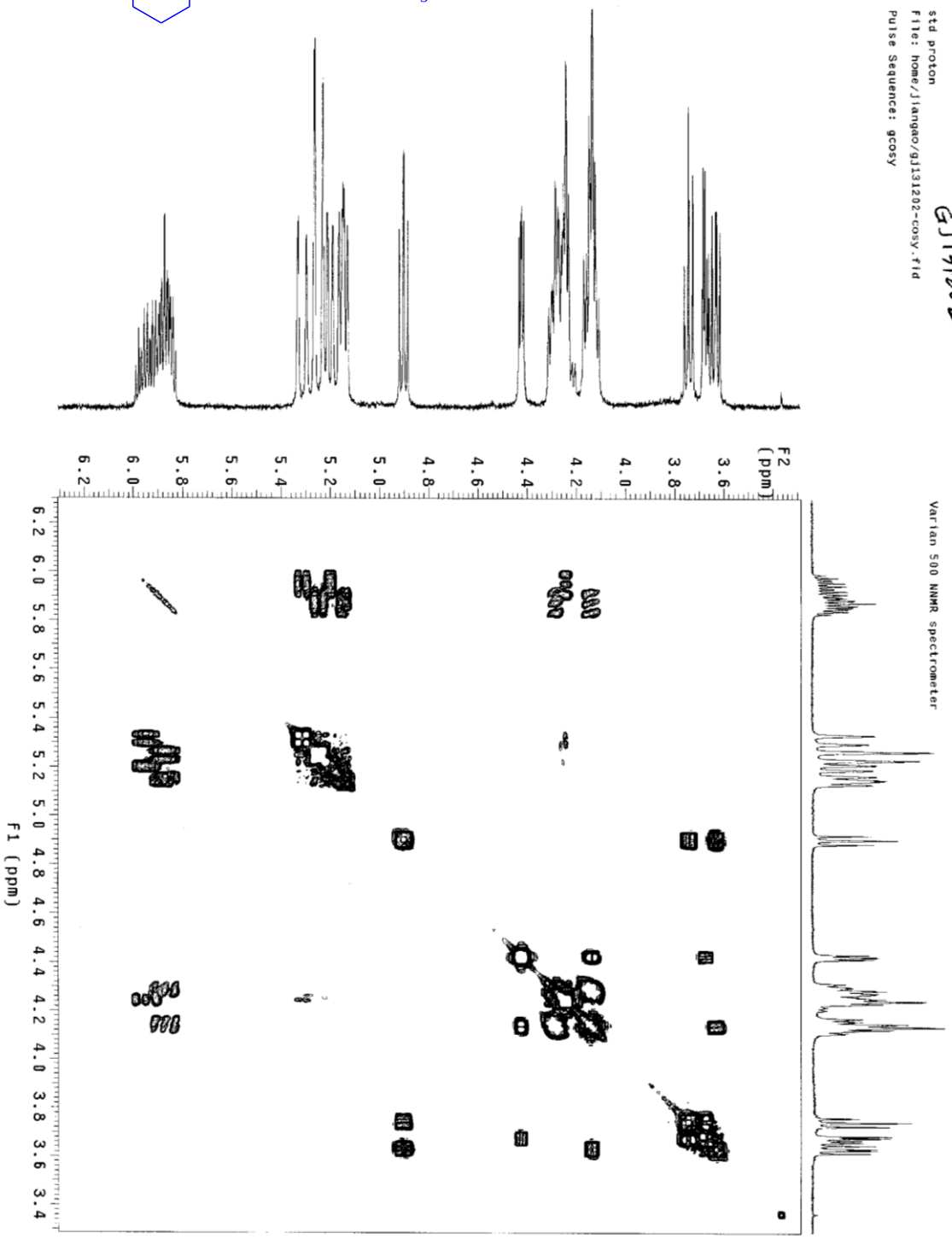


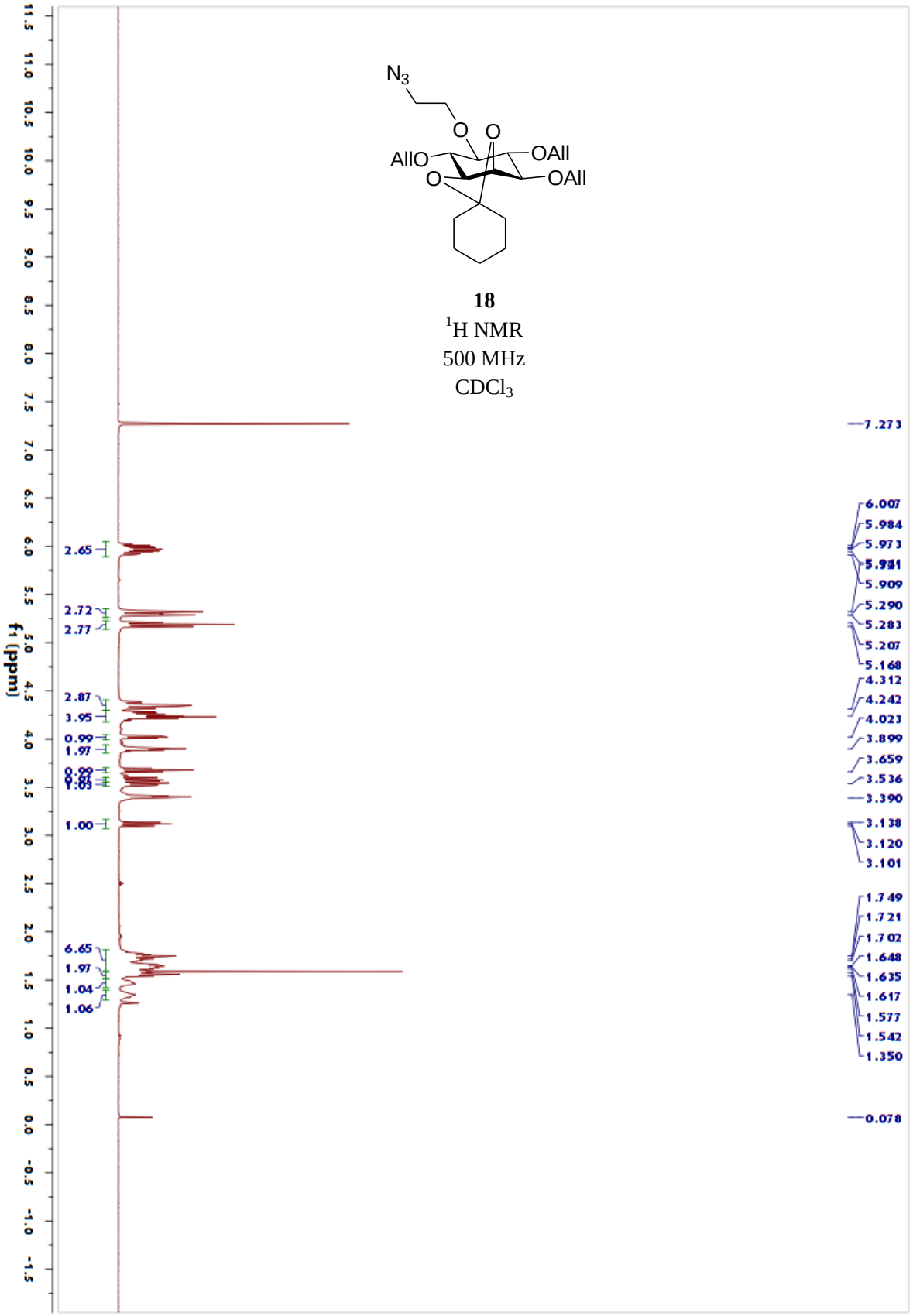
17

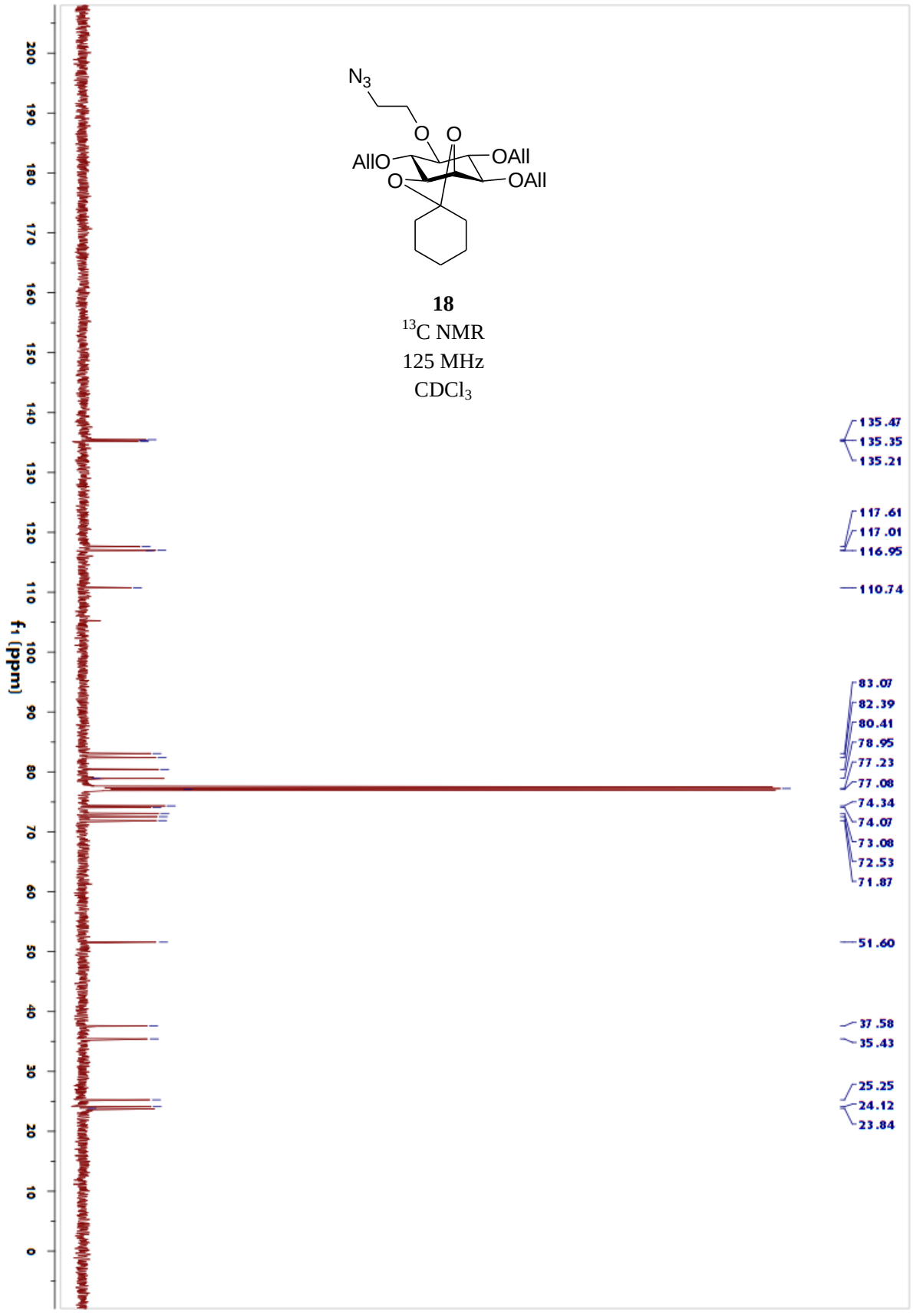
^{1}H-^{1}H COSY

500 MHz

$CDCl_3$




N3
O
O
AllO
OAll
O
OAll
18
1H NMR
500 MHz
CDCl3
f1 (ppm)
7.273
6.007
5.984
5.973
5.909
5.290
5.283
5.207
5.168
4.312
4.242
4.023
3.899
3.659
3.536
3.390
3.138
3.120
3.101
1.749
1.721
1.702
1.648
1.635
1.617
1.577
1.542
1.350
0.078
2.65
2.72
2.77
2.87
3.95
0.99
1.97
1.00
6.65
1.97
1.04
1.06

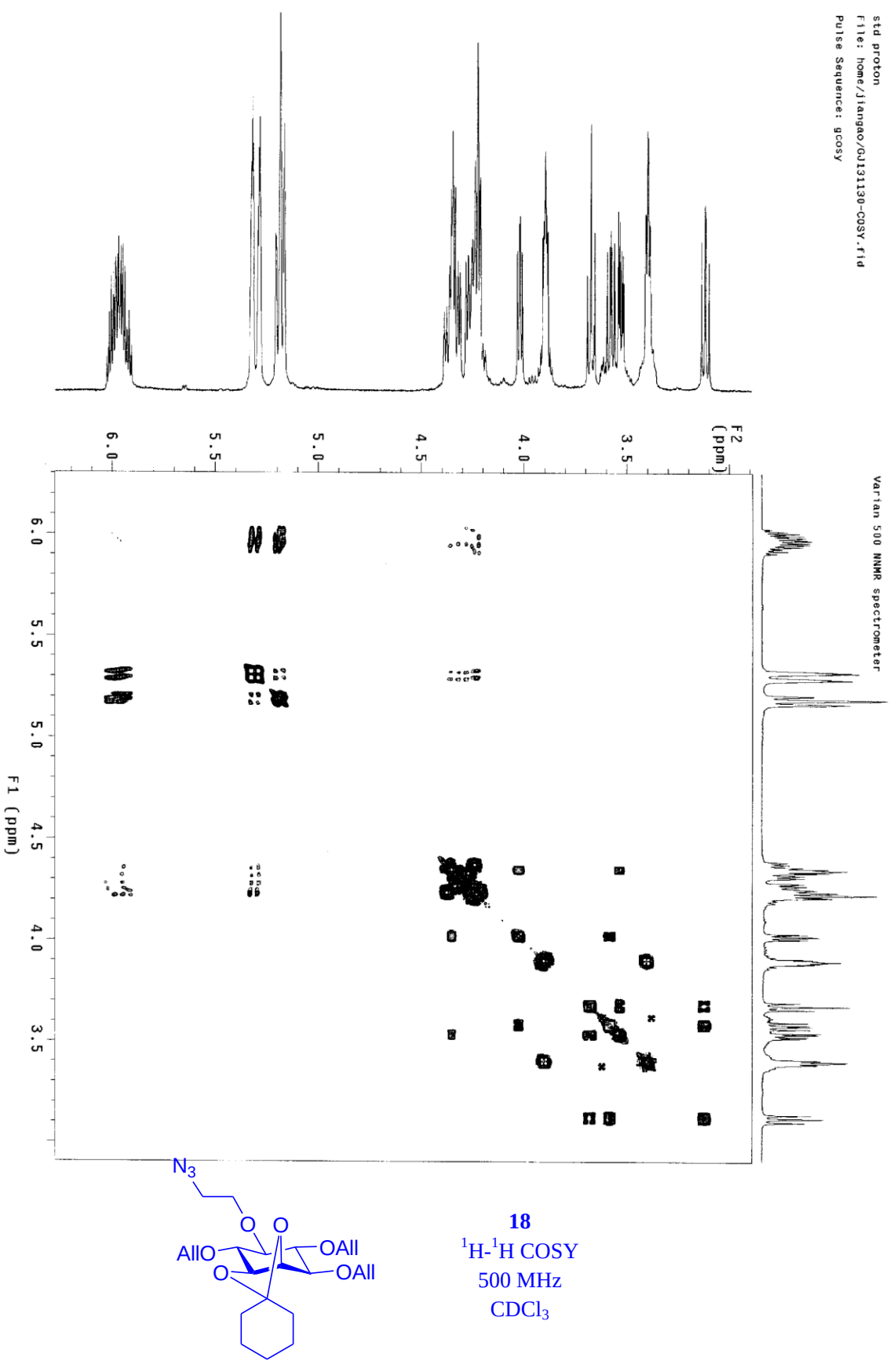


18

^{13}C NMR

125 MHz

$CDCl_3$

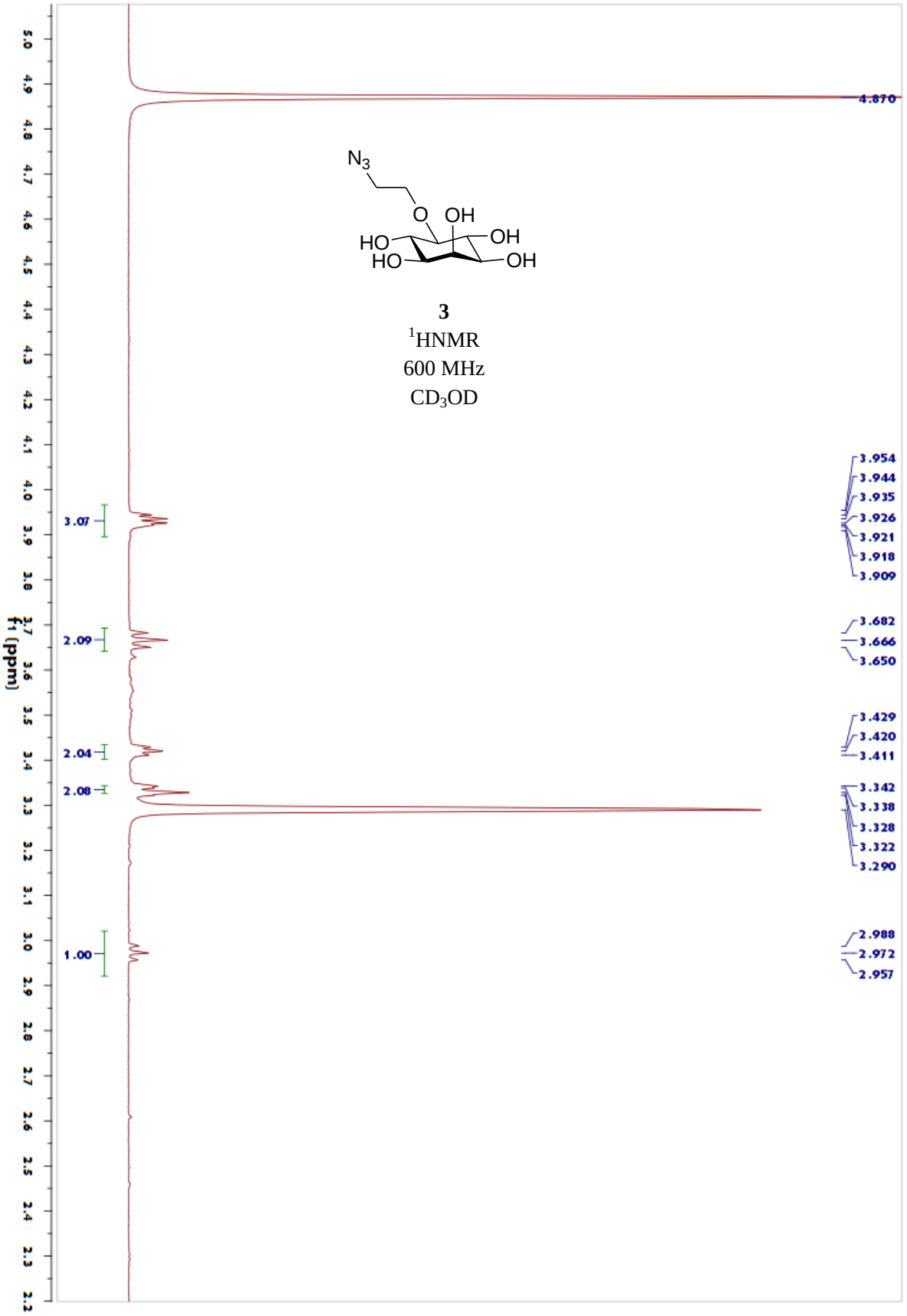


18

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

500 MHz

$CDCl_3$

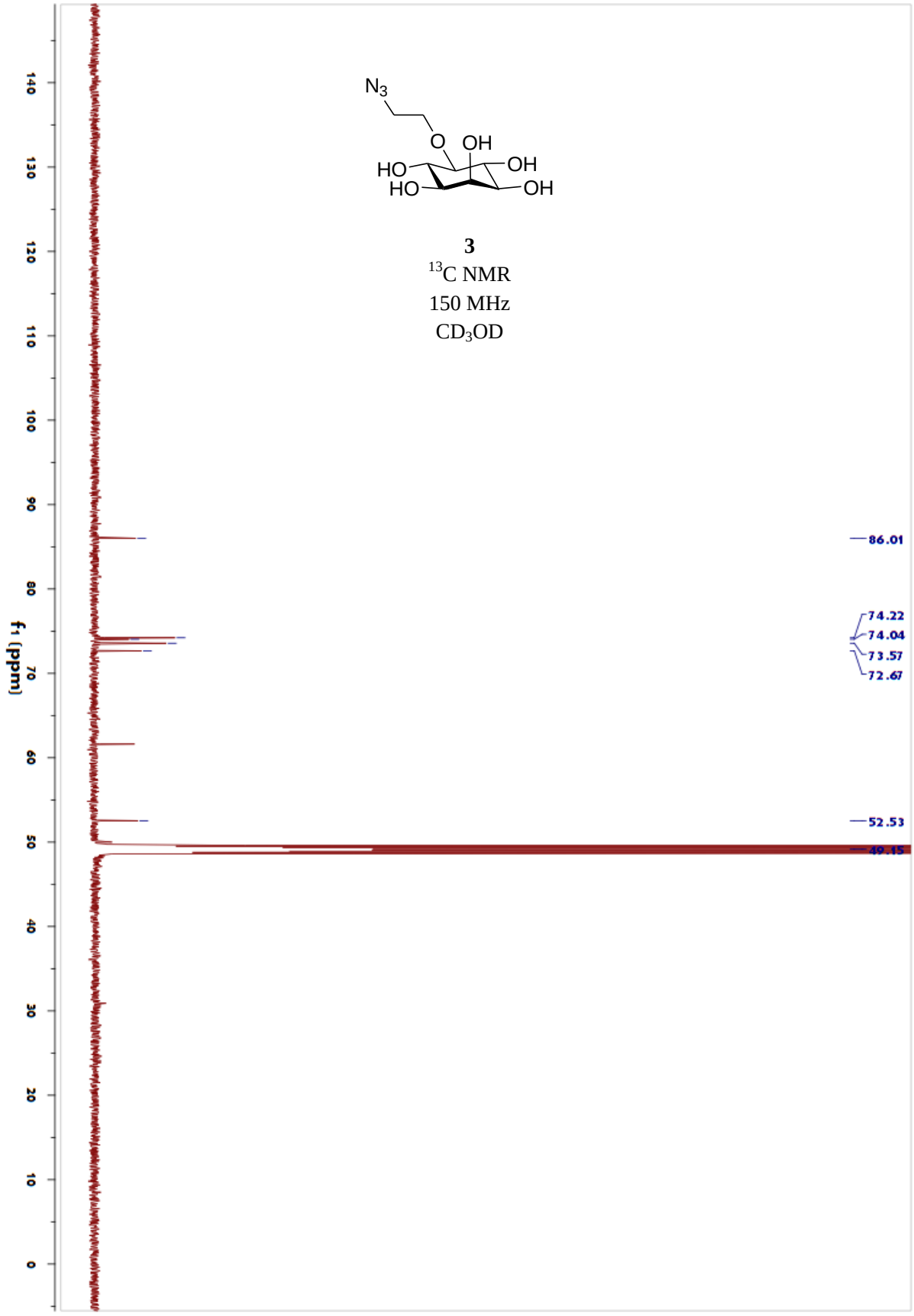


3

^{1}HNMR

600 MHz

CD_3OD

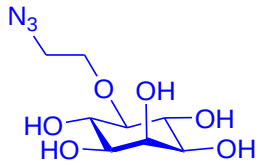

N3
O
OH
HO
OH
HO
OH
3
13C NMR
150 MHz
CD3OD
86.01
74.22
74.04
73.57
72.67
52.53
49.15
f1 (ppm)

3

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

600 MHz

CD_3OD



IV. Supplementary References

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