Supporting Information

Chemical Synthesis of the Tumor-Associated Globo H Antigen

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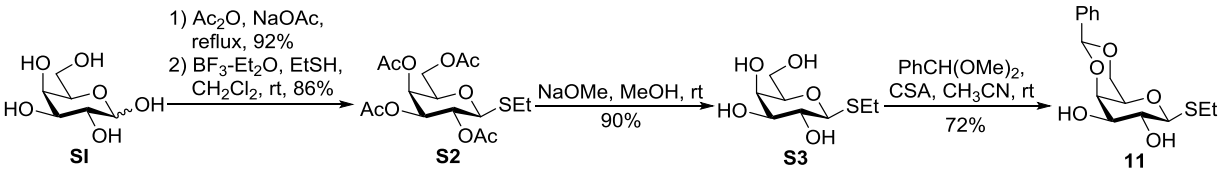
Table of Contents

Supplementary Experimental Section

General Methods. Chemicals and materials were obtained from commercial sources and were used as received without further purification unless otherwise noted. 4Å molecular sieves (MS) were flame-dried under high vacuum and used immediately after cooling under a N_2 atmosphere. Analytical TLC was carried out on silica gel 60Å F_{254} plates with detection by a UV detector and/or by charring with 15% (v/v) H_2SO_4 in EtOH. NMR spectra were recorded on a 400, 500, or 600 MHz machine with chemical shifts reported in ppm (δ) downfield from tetramethylsilane (TMS) that was used as an internal reference.



Ethyl 2,3,4,6-tetra-*O*-Acetyl-1-thio-β-D-galactopyranoside S2.[1] After a mixture of D-galactose **S1** (10.0 g, 55.5 mmol), anhydrous NaOAc (5.9 g, 72.2 mmol) and Ac_2O (50 ml) was stirred at 80 ^oC for 4 h, with the reaction progress monitored by TLC, it was cooled to rt and then poured into cold saturated aq. $NaHCO_3$ solution. The mixture was stirred at 0 ^oC for 1.5 h and extracted with CH_2Cl_2. The organic layer was separated and dried over Na_2SO_4. The solvent was removed

in vacuum and the residue was purified by silica gel column chromatography (AcOEt/petroleum ether. 1:4, v/v) to give the peracetylated galactose (19.8 g, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 5.69 (d, *J* = 8.1 Hz, 1 H, H-1), 5.42 (d, *J* = 3.2 Hz, 1 H, H-4), 5.33 (t, *J* = 8.1 Hz, 1 H, H-2), 5.07 (dd, *J* = 10.5, 4.0 Hz, 1 H, H-3), 4.19-4.08 (m, 2 H, H-6, H-6'), 4.07-4.02 (m, 1 H, H-5), 2.10 (s, 3 H, O<u>Ac</u>), 2.06 (s, 6 H, O<u>Ac</u>), 2.01 (s, 3 H, O<u>Ac</u>), 1.97 (s, 3 H, O<u>Ac</u>). The product (19.0 g, 48.7 mmol) and ethanethiol (5.41 mL, 73.0 mmol) were dissolved in anhydrous CH_2Cl_2 (120 mL) at 0 ^{o}C, and then $BF_3{\cdot}Et_2O$ (12.0 mL, 97.4 mmol) was added dropwise. The solution was stitted at 0 ^{o}C until when TLC showed the completion of the reaction. The reaction mixture was washed with saturated aq. $NaHCO_3$ solution and brine and dried over Na_2SO_4, and the organic phase was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (AcOEt/petroleum ether. 1:4, v/v) to give **S2** (16.4 g, 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (d, *J* = 3.2 Hz, 1 H, H-4), 5.19 (t, J = 9.7 Hz, 1 H, H-2), 5.01 (dd, *J* = 9.7, 3.2 Hz, 1 H, H-3), 4.46 (d, *J* = 11.3 Hz, 1 H, H-1), 4.16-4.03 (m, 2 H, H-6, H-6'), 3.90 (t, J = 6.5 Hz, 1 H, H-5), 2.77-2.60 (m, 2 H, S<u>CH$_2$</u>CH$_3$), 2.11 (s, 3 H, O<u>Ac</u>), 2.03 (s, 3 H, O<u>Ac</u>), 2.03 (s, 3 H, O<u>Ac</u>), 1.94 (s, 3 H, O<u>Ac</u>), 1.25 (t, J = 6.5 Hz, 3 H, SCH$_2$<u>CH$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.2, 170.0, 169.5, 84.0, 74.3, 71.6, 67.2, 67.1, 61.4, 24.3, 20.8, 20.6, 20.5, 20.4, 14.8.

Ethyl 1-Thio-β-D-galactopyranoside S3.[2] After **S2** (16.0 g, 40.8 mmol) was dissolved in MeOH (70 mL), a CH_3ONa/CH_3OH solution (0.4 M) was added until pH reached 9. The reaction was stirred at rt for 3 h. When TLC showed the completion of reaction, the solution was neutralized with Amberlyst (H^+) resin to pH 6-7, and then concentrated in vacuum. The residue was purified by flash column chromatography (MeOH/CH_2Cl_2, 1:5, v/v) to afford **S3** (8.2 g, 90%) as a white solid. ^{1}H NMR (400 MHz, CD_3OD): δ 4.32 (d, *J* = 9.7 Hz, 1 H, H-1), 3.88 (d, *J* = 3.2 Hz, 1 H, H-4), 3.77-3.64 (m, 2 H, H-6, H-6`), 3.52 (t, J = 8.1 Hz, 1 H, H-2), 3.46 (dd, *J* = 9.7, 3.2 Hz, 1 H, H-3), 3.33-3.29 (m, 1 H, H-5), 2.83-2.65 (m, 2 H, S<u>CH$_2$</u>CH$_3$), 1.28 (t, J = 6.5 Hz, 3 H SCH$_2$<u>CH$_3$</u>); ^{13}C NMR (100 MHz, CD_3OD): δ 86.0, 79.2, 74.8, 69.9, 69.1, 61.2, 23.5, 14.1.

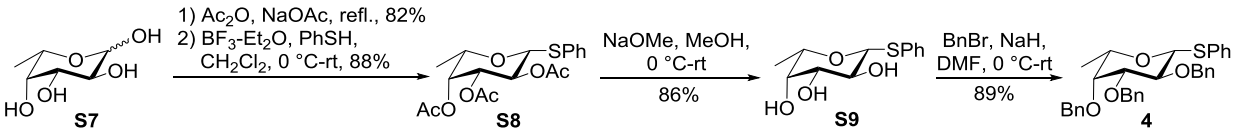
Ethyl 4:6-*O*-Phenylmethylene-1-thio-β-D-galactopyranoside 11.[3] To the solution of **S3** (8.0 g, 35.7 mmol) in anhydrous CH_3CN (30 mL) were added benzaldehyde dimethyl acetal (6.45 mL, 42.8 mmol) and CSA (2.0 g, 8.9 mmol) at rt, and the reaction was stirred at rt with occasional vacuum application until TLC showed that the reaction was completed. Then the reaction was quenched with Et_3N (2.47 mL, 17.8 mmol) and diluted with CH_2Cl_2 (60 mL). The solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography (MeOH/CH_2Cl_2, 1:10, v/v) to give **11** (8.02 g, 72%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 2 H, ArH), 7.42-7.38 (m, 3 H, ArH), 5.53 (s, 1 H, CHPh), 4.34 (d, *J* = 8.8 Hz, 1 H, H-1), 4.33 (d, *J* = 12.8 Hz, 1 H, H-6), 4.25 (d, *J* = 3.2 Hz, 1 H, H-4), 4.03 (d, *J* = 12.8 Hz, 1 H, H-6`), 3.81 (t, J = 8.8 Hz, 1 H, H-2), 3.68 (dd, *J* = 10.0, 4.4 Hz, 1 H, H-3), 3.53-3.50 (m, 1 H, H-5), 2.88-2.69 (m, 2 H, S<u>CH$_2$</u>CH$_3$), 2.51 (bs, 2 -OH), 1.34 (t, J = 6.5 Hz, 3 H, SCH$_2$<u>CH$_3$</u>); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 129.3, 128.3, 126.4, 101.5, 85.3, 75.6, 73.9, 70.1, 69.7, 69.3, 23.5, 14.1.

2-Deoxy-2-phthalimido-β-D-galactopyranose tetraacetate S5.[4] After the suspension of D-galactosamine hydrochloride **S4** (5.0 g, 23.3 mmol), $Na_2CO_3{\cdot}H_2O$ (2.5 g 23.3 mmol) and phthalic anhydride (3.5 g, 23.3 mmol) in H_2O (50 ml) was stirred at rt for 3 h, the resultant clear solution (pH 3.0; initial pH 8.5) was cooled to -78 ^oC and lyophilized to offer a pale yellow solid residue (9.16 g). This residue was suspended in a mixture of pyridine (200 ml) and acetic anhydride (100 ml) at 0 ^oC and was stirred for 20 h. Acetic anhydride and pyridine were evaporated in vacuum, and the residue was co-evaporated with toluene (10 ml) twice, and finally subjected to silica gel chromatography (EtOAc/toluene 1:9, v/v) to obtain **S5** (8.18 g, 74%) as a white solid along. ^1H NMR (400 MHz, $CDCl_3$): δ 7.90-7.80 (m, 2 H, ArH), 7.78-7.71 (m, 2 H, ArH), 6.52 (dd, *J* = 11.3, 3.2 Hz, 1 H, H-3), 6.34 (d, *J* = 6.8 Hz, 1 H, H-1), 5.66 (d, *J* = 3.2 Hz, 1 H, H-4), 4.90 (dd, J = 11.3, 3.2 Hz, H-2), 4.49 (t, J = 8.1 Hz, 1 H, H-5), 4.17-4.11 (m, 2 H, H-6, H-6'), 2.18 (s, 3 H, OAc), 2.05 (s, 6 H, 2×OAc), 1.88 (s, 3 H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 169.83, 169.81, 169.29, 167.5, 166.8, 134.0, 133.9, 129.2, 123.3, 123.2, 83.9, 74.1, 68.4, 66.5, 61.2, 49.7, 20.7, 20.3, 20.2, 20.1.

***para*-Tolyl 3,4,6-tri-*O*-Acetyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside S6.**[5] To the stirred solution of **S5** (5.0 g, 10.4 mmol) and *p*-toluenethiol (1.95 g, 15.7 mmol) in anhydrous CH_2Cl_2 (30 mL) at 0 ^oC was added $BF_3{\cdot}Et_2O$ (1.6 mL, 12.6 mmol) dropwise. When TLC showed the completion of reaction, the reaction mixture was washed with saturated aq. $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuum. The residue was purified by flash column chromatography (EtOAc/hexane 1:4, v/v) to give **S6** (4.96 g, 88%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89-7.80 (m, 2 H, ArH), 7.79-7.70 (m, 2 H, ArH), 7.33-7.26 (m, 2 H, ArH), 7.09-7.01 (m, 2 H, ArH), 5.79 (dd, *J* = 11.3, 3.2 Hz, 1 H, H-3), 5.63 (d, *J* = 9.7 Hz, 1 H, H-1), 5.47 (d, *J* = 3.2 Hz, 1 H, H-4), 4.49 (t, J = 11.3 Hz, 1 H, H-2), 4.25-4.18 (m, 1 H, H-6), 4.17-4.1 (m, 1 H, H-6'), 4.10-4.05 (m, 1 H, H-5), 2.29 (s, 3 H, SPh$\underline{CH_3}$), 2.16 (s, 3 H, OAc), 2.03 (s, 6 H, 2×OAc), 1.81 (s, 3 H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 169.7, 167.9, 167.2, 138.4, 134.4, 134.3, 133.4, 133.2, 131.5, 131.2, 129.7, 129.6, 128.0, 123.7, 123.6, 84.3, 74.5, 68.8, 66.9, 61.5, 50.1, 20.1, 20.7, 20.6, 20.5.

***para*-Tolyl 2-Deoxy-4:6-*O*-phenylmethylene-2-phthalimido-1-thio-β-D-galactopyranoside 8.** To a solution of **S6** (4.9 g, 9.1 mmol) in MeOH (25 mL) was added a CH_3ONa/CH_3OH solution (0.4 M) until pH reached 9.5. The reaction mixture was stirred at rt 4 h. When TLC showed the completion of reaction, it was neutralized to pH 6-7 with Amberlyst (H^+) resin and concentrated in vacuum. The residue was purified by flash column chromatography ($MeOH/CH_2Cl_2$, 1:8, v/v) to give a solid compound (3.43 g, 91%), which is directly used in next reaction. After the product was dissolved in anhydrous CH_3CN (40 mL), benzaldehyde dimethyl acetal (1.5 mL, 9.8 mmol) and CSA (0.48 g, 2.05 mmol) were added. The reaction was stirred at rt with occasional vacuum

application until TLC showed the completion reaction. It was quenched with Et_3N (0.57 mL, 4.1 mmol) and diluted with CH_2Cl_2 (30 mL). The solution was then washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography (MeOH/CH_2Cl_2, 1:13, v/v) to give **8** (3.4 g, 83%) as a light yellow solid. $[\alpha]_D^{25}$ = -28.72° (*c* 3.33, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.81 (m, 2 H, ArH), 7.75-7.71 (m, 2 H, ArH), 7.50-7.46 (m, 2 H, ArH), 7.45-7.38 (m, 5 H, ArH), 7.08 (d, *J* = 8.1 Hz, 1 H, ArH), 5.62 (d, *J* = 9.7 Hz, 1 H, H-1), 5.56 (s, 1 H, CHPh), 4.49 (dd, *J* = 9.7, 3.2 Hz, 1 H, H-3), 4.43 (t, J = 9.7 Hz, 1 H, H-2), 4.41 (d, *J* = 12.9 Hz, 1 H, H-6), 4.28 (d, *J* = 3.2 Hz, 1 H, H-4), 4.06 (d, *J* = 12.9 Hz, 1 H, H-6'), 3.68 (s, 1 H, H-5), 2.41 (bs, 1 H, -OH), 2.35 (s, 3 H, SPh$\underline{CH_3}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 167.8, 138.3, 137.4, 134.1, 131.9, 131.7, 129.5, 129.4, 128.3, 127.3, 126.7, 123.6, 123.2, 101.6, 82.7, 75.0, 70.1, 69.4, 68.7, 53.2, 21.3; HRMS (ESI TOF): calcd. for $C_{28}H_{25}NNaO_6$ $[M+Na]^+$ *m/z*, 526.1300; found, 526.1302.

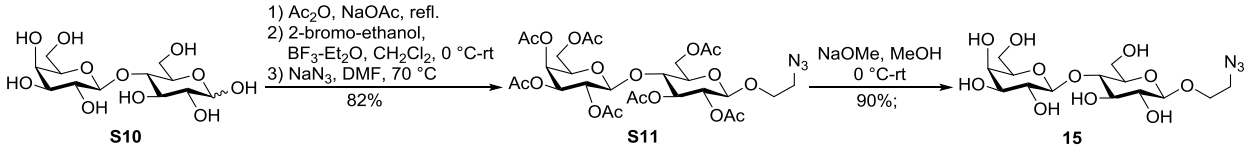


Phenyl 2,3,6-tri-*O*-Acetyl-β-L-fucopyranoside S8.[6] A mixture of L-fucose (4.0 g, 24.36 mmol) anhydrous NaOAc (2.6 g, 31.37 mmol) and Ac_2O (30 ml) was stirred at 70 °C for 8 h with the reaction progress monitored by TLC. After the reaction was completed, it was cooled to rt and them was poured into cold saturated aq. $NaHCO_3$ solution. After the mixture was stirred for 1.5 h, it was extracted with CH_2Cl_2, and the organic phase was dried over Na_2SO_4. After the solvent was removed in vacuum, the residue was purified by flash silica gel column chromatography (AcOEt/toluene. 1:4, v/v) to give the peracetylated fucose (6.63 g, 81.9%) as sticky syrup. This product (1.3 g, 3.9 mmol) and benzentethiol (1.6 mL, 15.6 mmol) were dissolved in anhydrous CH_2Cl_2 (15 mL), and to this solution was then added $BF_3{\cdot}Et_2O$ (0.73 mL, 5.87 mmol) at 0 °C. When TLC showed the completion of reaction, it was quenched and washed with saturated aq. $NaHCO_3$ solution and brine, dried over Na_2SO_4, and then concentrated. The residue was purified by flash column chromatography (EtOAc/Hexane 1:5, v/v) to afford **S8** (1.38 g, 88%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53-7.48 (m, 2 H, ArH), 7.34-7.26 (m, 3 H, ArH), 5.26 (d, *J* = 3.0 Hz, 1 H, H-4), 5.22 (t, *J* = 9.8 Hz, 1 H, H-2), 5.05 (dd, *J* = 9.8, 3.0 Hz, 1 H, H-3), 4.70 (d, *J* = 10.4 Hz, 1 H, H-1), 3.83 (q, J = 6.7 Hz, 1 H, H-5), 2.13 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 1.96 (s, 3 H, OAc), 1.23 (d, J = 6.7 Hz, 3 H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.8, 170.1, 169.5, 132.9, 132.3, 128.9, 127.9, 86.4, 73.1, 72.4, 70.3, 67.3, 20.9, 20.7, 20.6, 16.5.

Phenyl β-L-Fucopyranoside S9.[7] To the solution of **S8** (1.35 g, 3.37 mmol) dissolved in MeOH (10 mL) was added a CH_3ONa/CH_3OH solution (0.4 M) until pH reached 9.5. The solution was stirred at rt for 2 h. When TLC showed the completion reaction, it was neutralized to pH 6-7 with Amberlyst (H^+) resin and then concentrated in vacuum. The residue was finally purified by flash column chromatography (MeOH/CH_2Cl_2, 1:9, v/v) to give **S9** (0.73 g, 86%) as a yellowish solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54-7.48 (m, 2 H, ArH), 7.34-7.26 (m, 3 H, ArH), 4.56 (d, *J* =

9.8 Hz, 1 H, H-1), 4.04 (bs, 3 -OH), 3.82 (d, *J* = 2.9 Hz, 1 H, H-3), 3.77 (t, *J* = 9.8 Hz, 1 H, H-2), 3.66 (dd, *J* = 9.8, 2.9 Hz, 1 H, H-4), 3.59 (q, J = 6.8 Hz, 1 H, H-5), 1.30 (d, *J* = 6.8 Hz, 3 H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.4, 131.84, 131.8, 128.9, 127.5, 88.6, 75.2, 74.7, 71.7, 70.0, 16.7.

Phenyl 2,3,6-tri-*O*-Phenylmethyl-β-L-fucopyranoside 4.[6] After a mixture of **S9** (0.70 g, 2.73 mmol) and NaH (230 mg, 9.6 mmol) in DMF (10 mL) was stirred at 0 ^{o}C for 45 min, BnBr (1.62 mL, 13.67 mmol) was added at 0 ^{o}C. Thereafter, the mixture was stirred for another 6 h. When TLC showed the completion of reaction, it was quenched with H_2O at 0 ^{o}C, and the mixture was diluted with EtOAc. The aq. layer was washed with EtOAc (5 x 5 mL) followed by drying over Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography (acetone/hexane 1:10, v/v) to give **4** (1.28 g, 89%) as colorless syrup. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66-7.62 (m, 2 H, ArH), 7.46-7.31 (m, 15 H, ArH), 7.28-7.23 (m, 3 H, ArH), 5.06 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.85 (d, J = 10.4 Hz, 1 H, CH_2Ph), 4.79 (s, 2 H, CH_2Ph), 4.78 (d, J = 10.4 Hz, 1 H, CH_2Ph), 4.73 (d, *J* = 11.6 Hz, 1 H, CH_2Ph), 4.66 (d, *J* = 9.8 Hz, 1 H, H-1), 3.99 (t, *J* = 9.8 Hz, 1 H, H-2), 3.69 (d, *J* = 3.1 Hz, 1 H, H-3), 3.65 (dd, *J* = 9.2, 3.1 Hz, 1 H, H-4), 3.60-3.56 (m, 1 H, H-5), 1.32 (d, *J* = 6.1 Hz, 3 H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8, 138.5, 138.4, 134.4, 131.6, 128.8, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.0, 87.6, 84.6, 77.4, 77.2, 76.7, 75.6, 74.7, 72.9, 17.4; HRMS (ESI TOF): calcd. for $C_{33}H_{34}NaO_4S$ $[M+Na]^+$ *m/z*, 549.2076; found, 549.2063.



2-Azidoethyl 2,3,4,6-tetra-*O*-Acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-β-D-glucopyranoside S11.[8] Lactose **S10** was converted into **S11** according to a literature procedure in three steps in an 82% (8.01 g) overall yield.

2-Azidoethyl β-D-Galactopyranosyl-(1→4)-β-D-glucopyranoside 15.[9] To the solution of **S11** (8.0 g, 11.33 mmol) dissolved in MeOH (60 mL) was added a CH_3ONa/CH_3OH solution (0.4 M) until pH reached 10. The solution was stirred at rt for 12 h. When TLC showed the completion reaction, it was neutralized to pH 6-7 with Amberlyst (H^+) resin and concentrated in vacuum. The residue was finally purified by flash column chromatography ($MeOH/CH_2Cl_2$, 1:4, v/v) to give **15** (4.18 g, 90%) as a white solid. ^{1}H NMR (400 MHz, CD_3OD): δ 4.37 (d, J = 8.1 Hz, 1 H, H-1'), 4.35 (d, *J* = 7.8 Hz, 1 H, H-1), 4.05-3.98 (m, 1 H, $OCH_2\underline{CH_2}N_3$), 3.95-3.66 (m, 6 H, $OCH_2\underline{CH_2}N_3$, H-6a', H-6b', H-4, H-4', H-6b), 3.62-3.39 (m, 8 H, H-5, H-2, H-3, H-6a, H-3', H-5', $O\underline{CH_2}CH_2N_3$), 3.32-3.24 (m, 1 H, H-2'); ^{13}C NMR (100 MHz, CD_3OD): δ 103.7, 102.9, 79.2, 75.7, 75.1, 75.0, 73.4, 73.3, 71.1, 68.9, 68.0, 61.1, 60.5, 50.6.

Supplementary References

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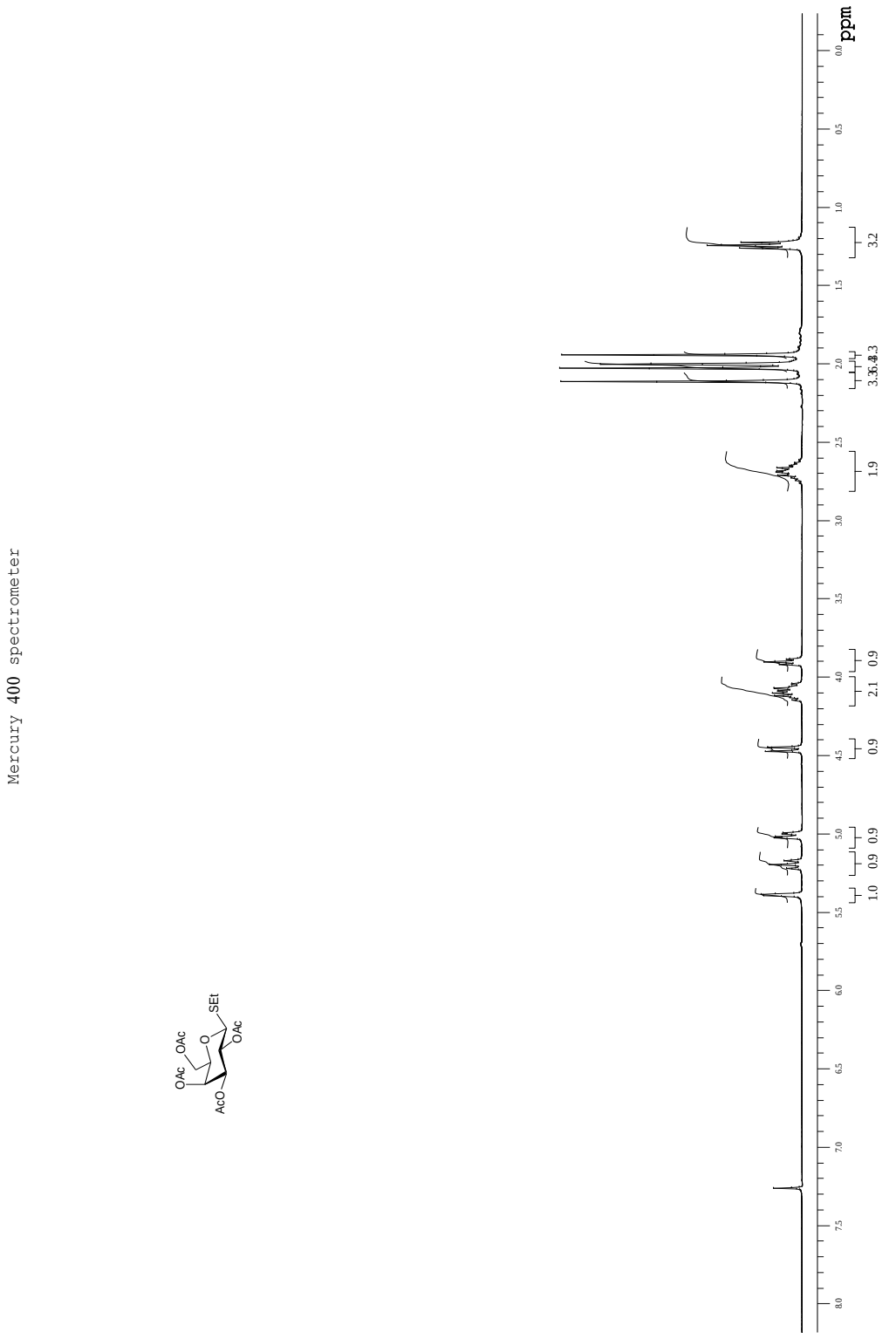
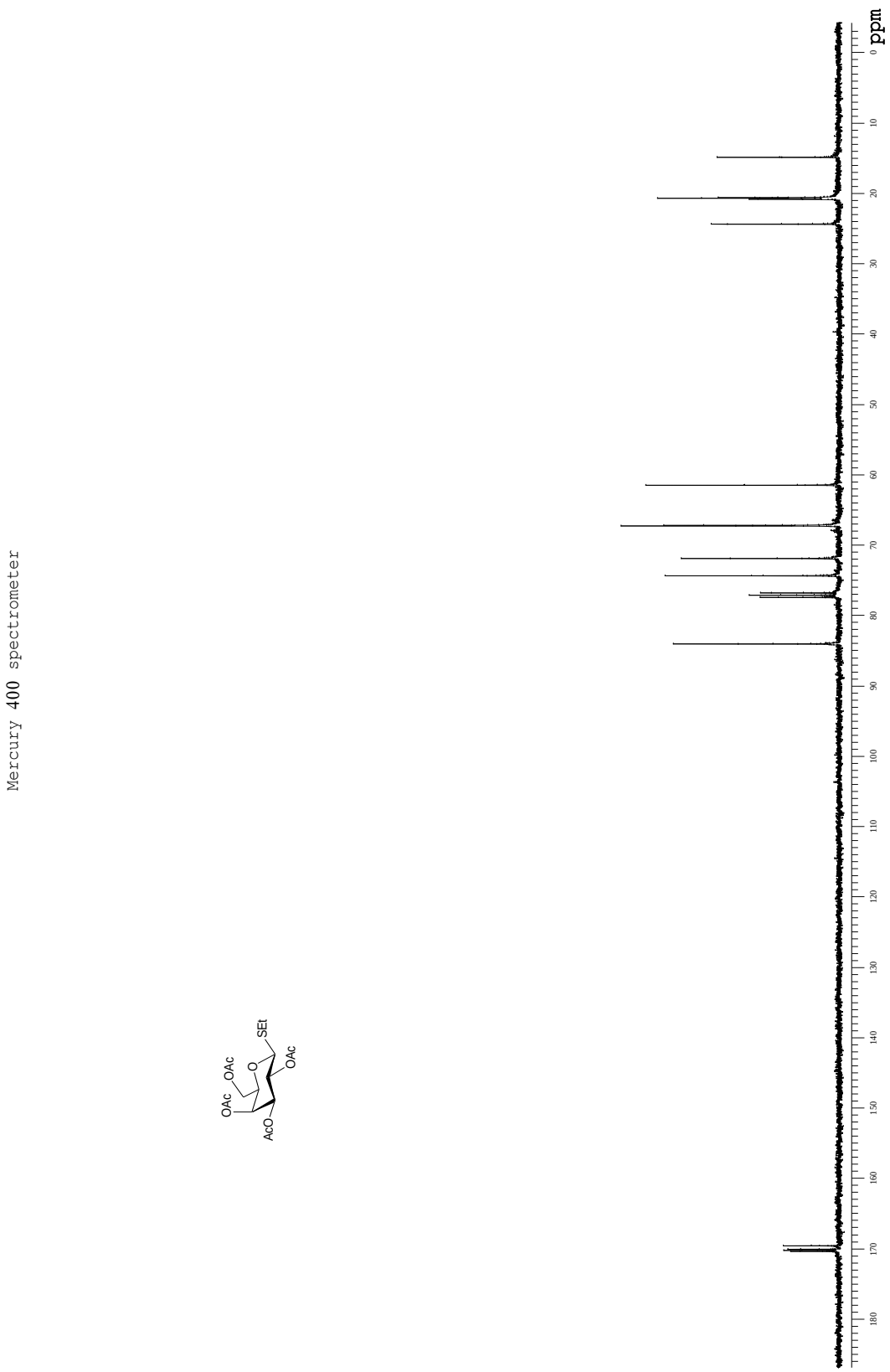
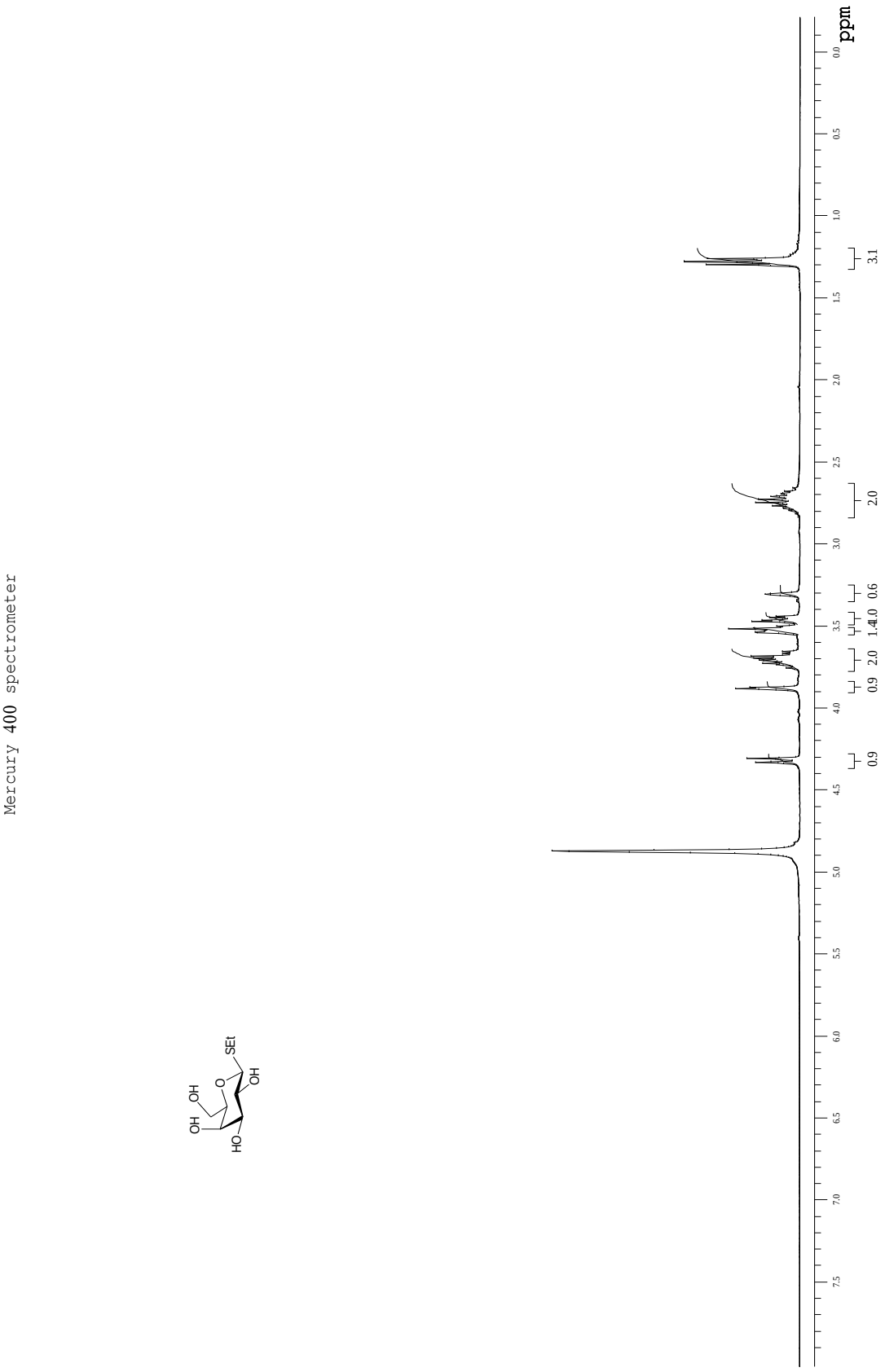
Compound NMR and MS Spectra



^{1}H NMR Spectrum of compound **S2** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of compound **S2** ($CDCl_3$, 400 MHz)



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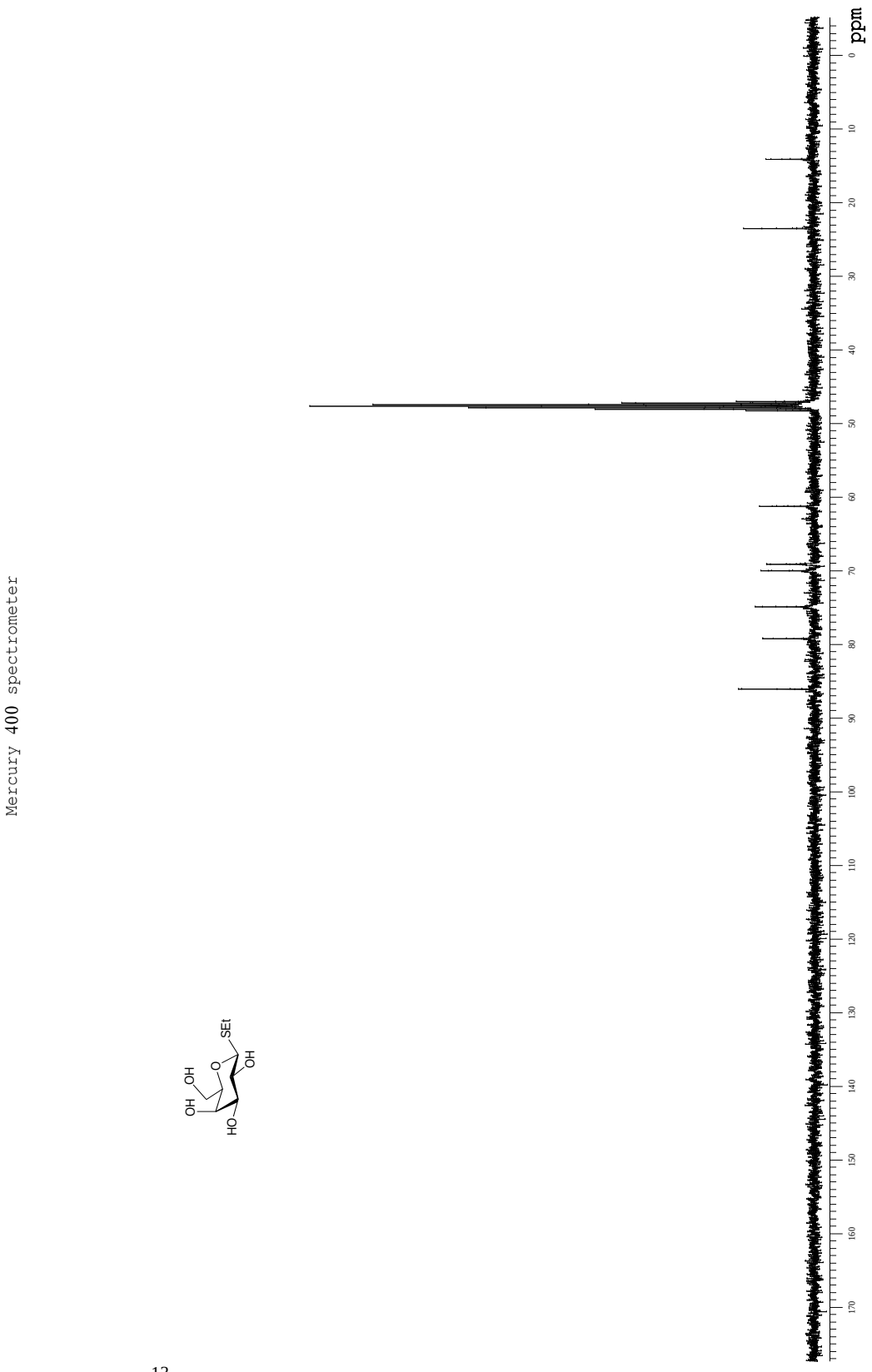
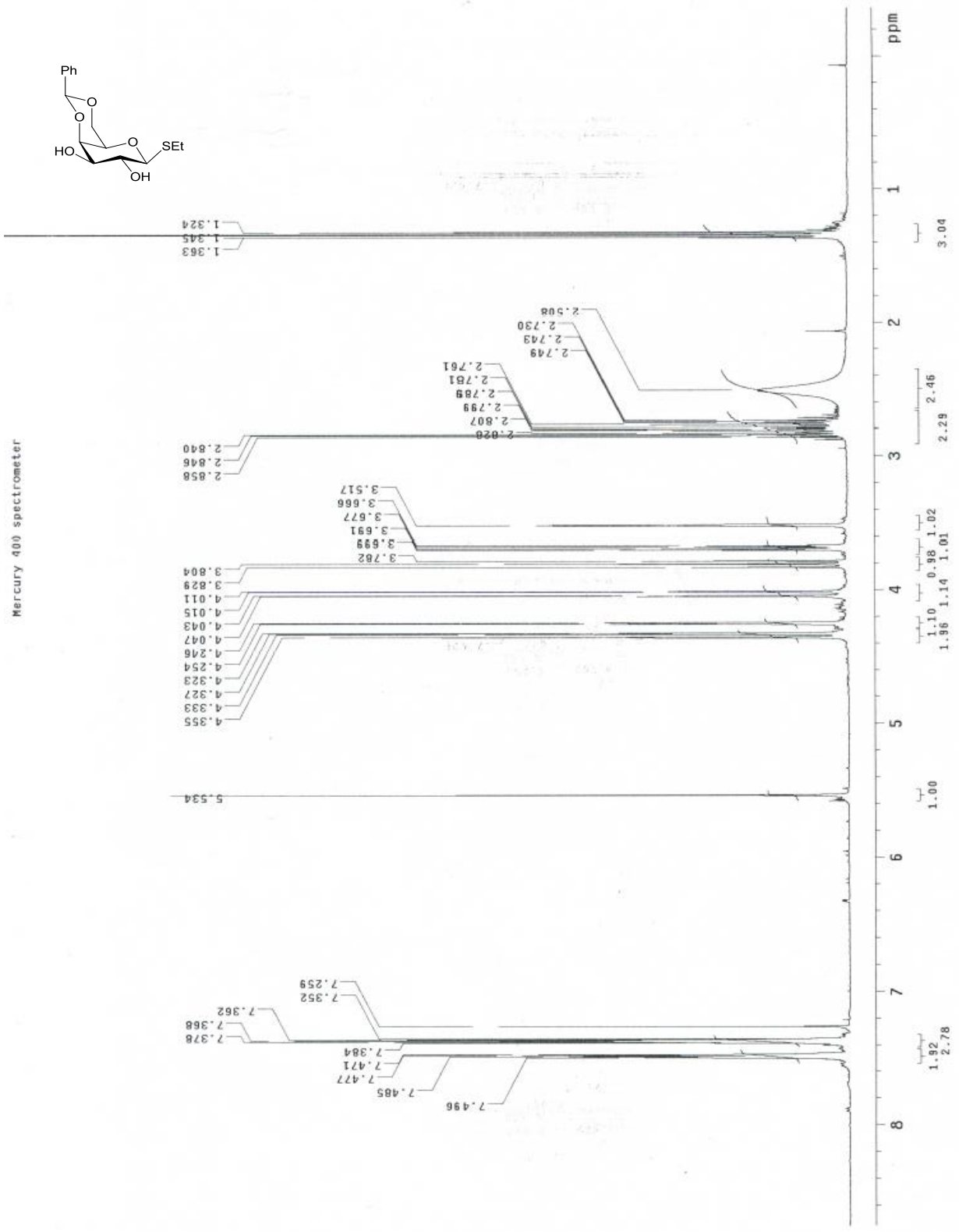
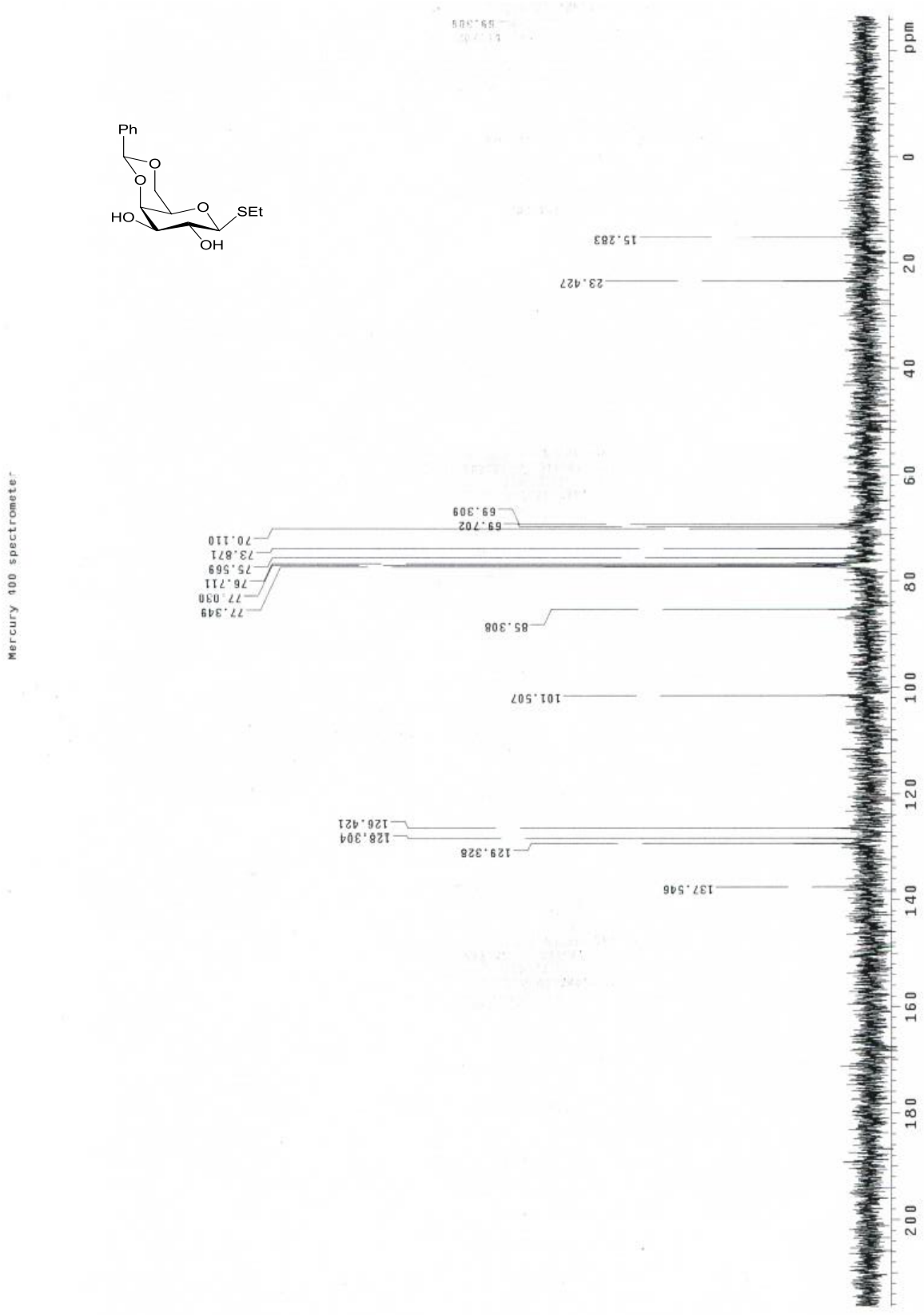


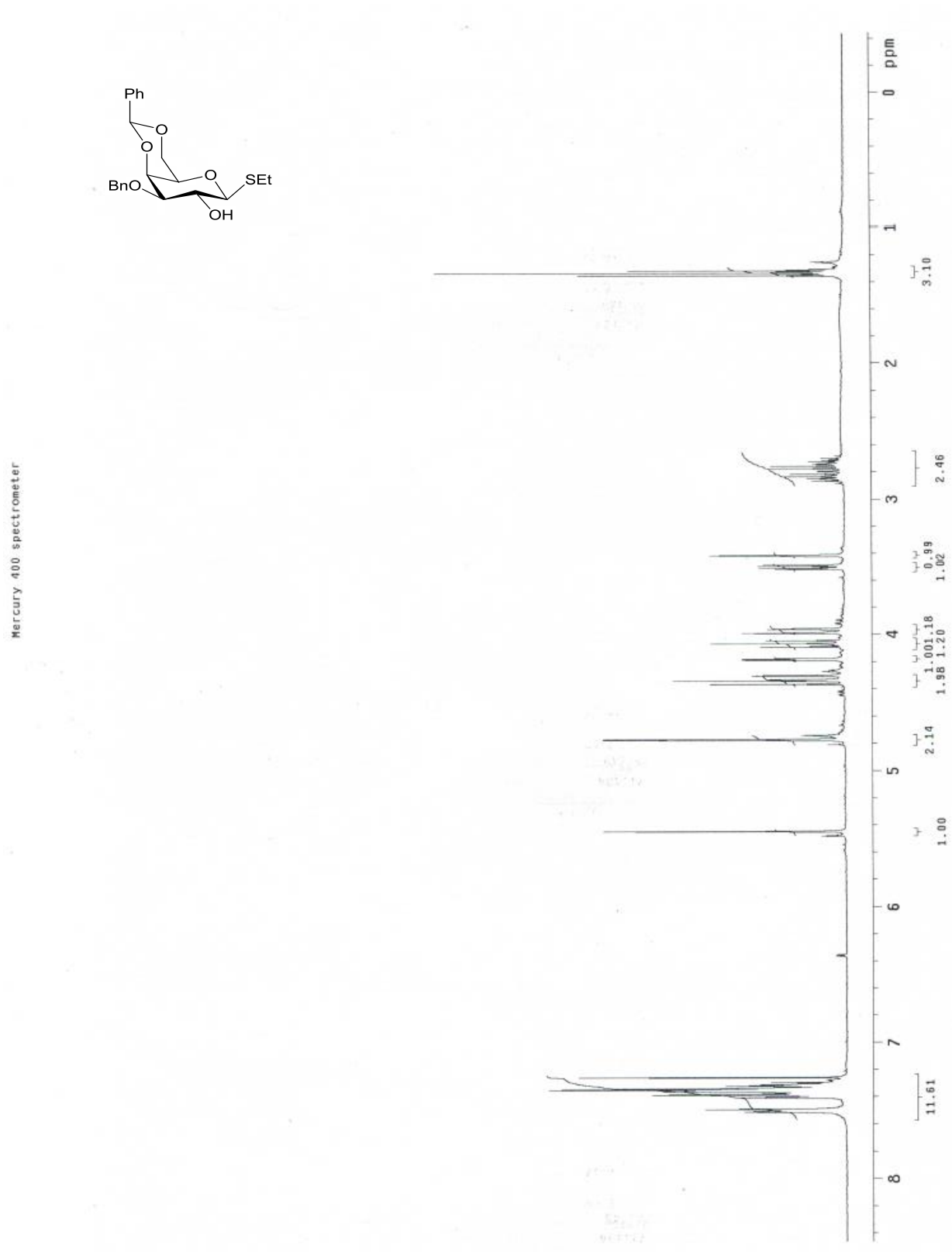
^{13}C NMR Spectrum of compound **S3** (CD_3OD, 400 MHz)



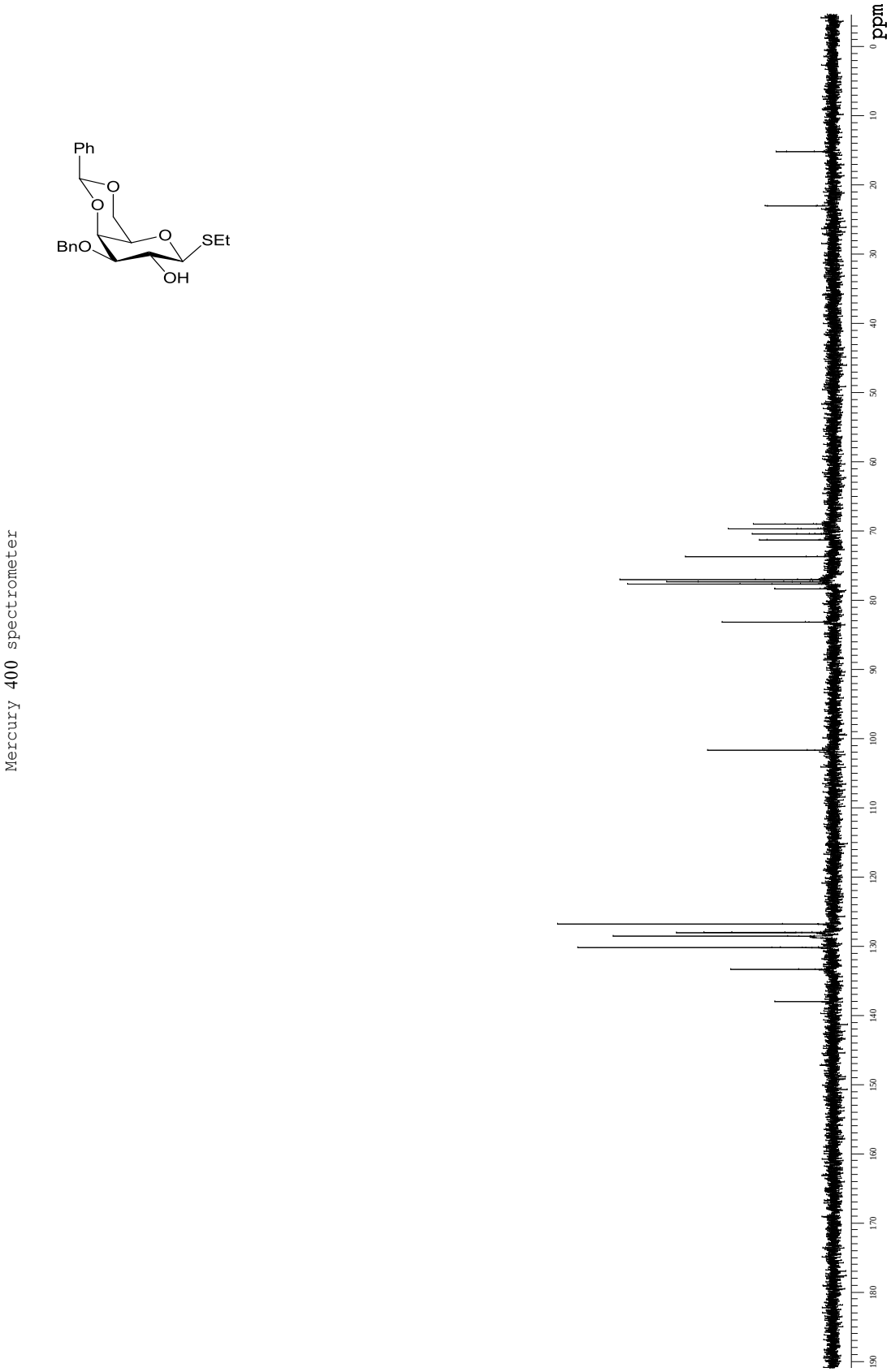
^{1}H NMR Spectrum of compound **11** ($CDCl_3$, 400 MHz)



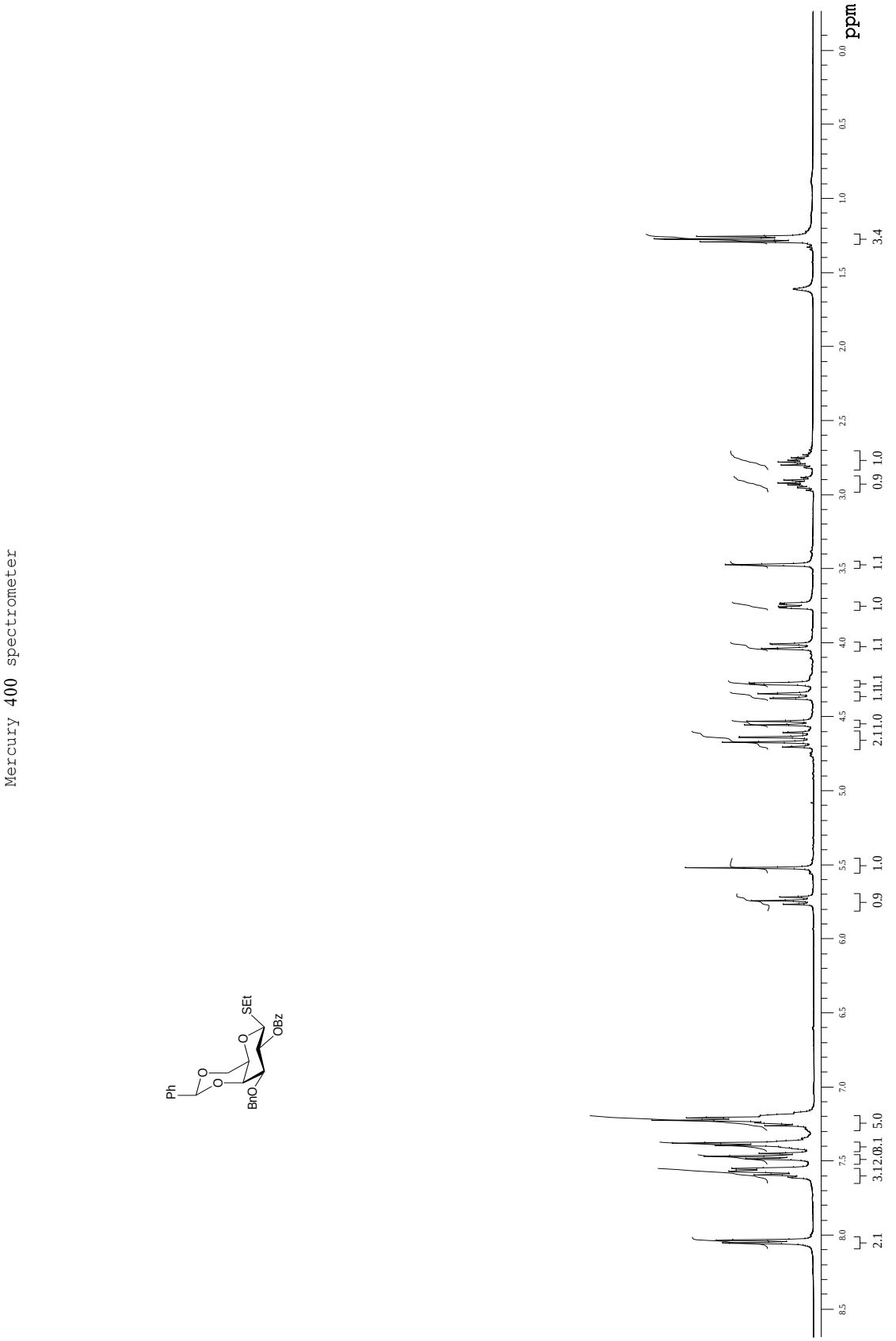
^{13}C NMR Spectrum of compound **11** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of compound **12** ($CDCl_3$, 400 MHz)

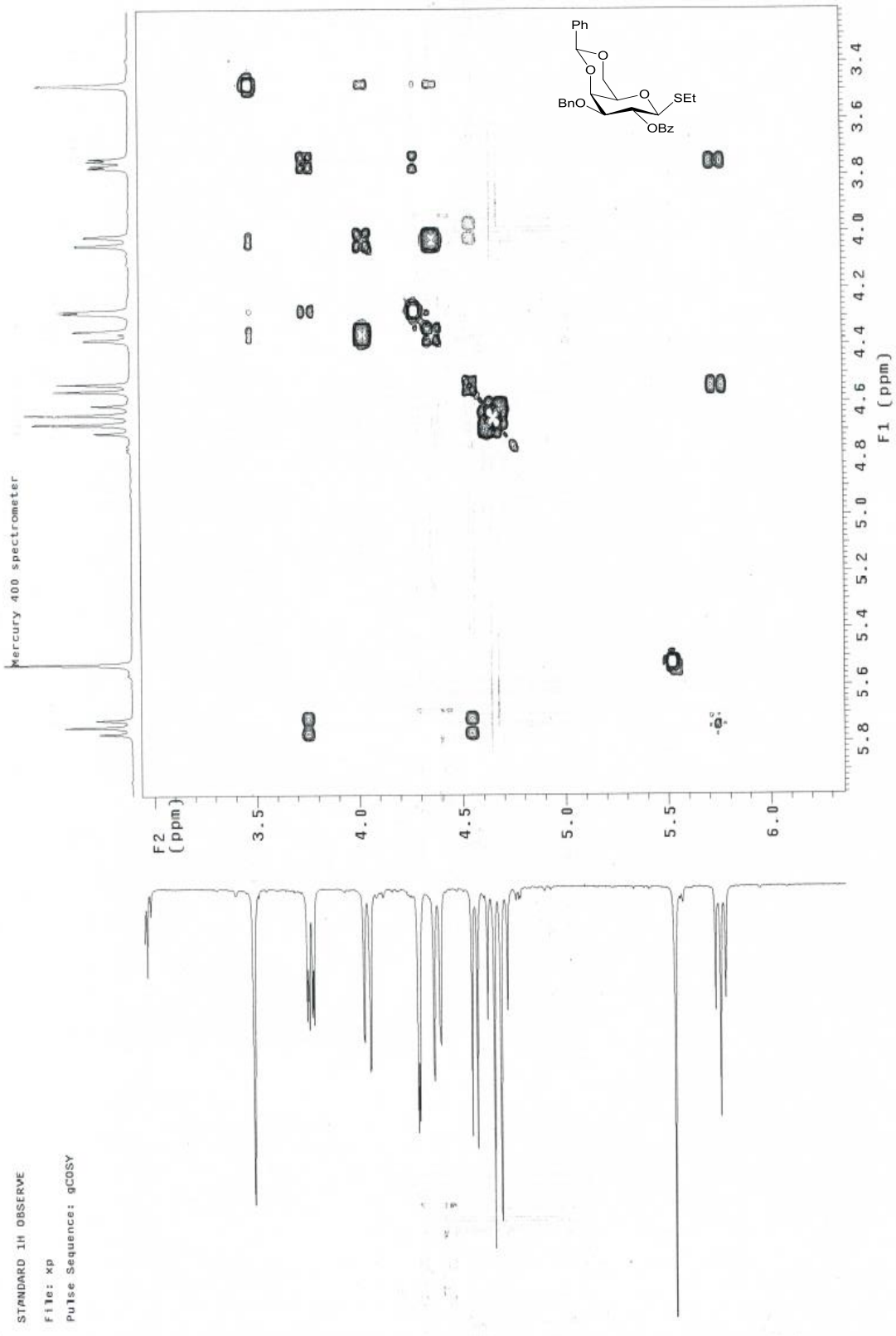


^{13}C NMR Spectrum of compound **12** ($CDCl_3$, 400 MHz)

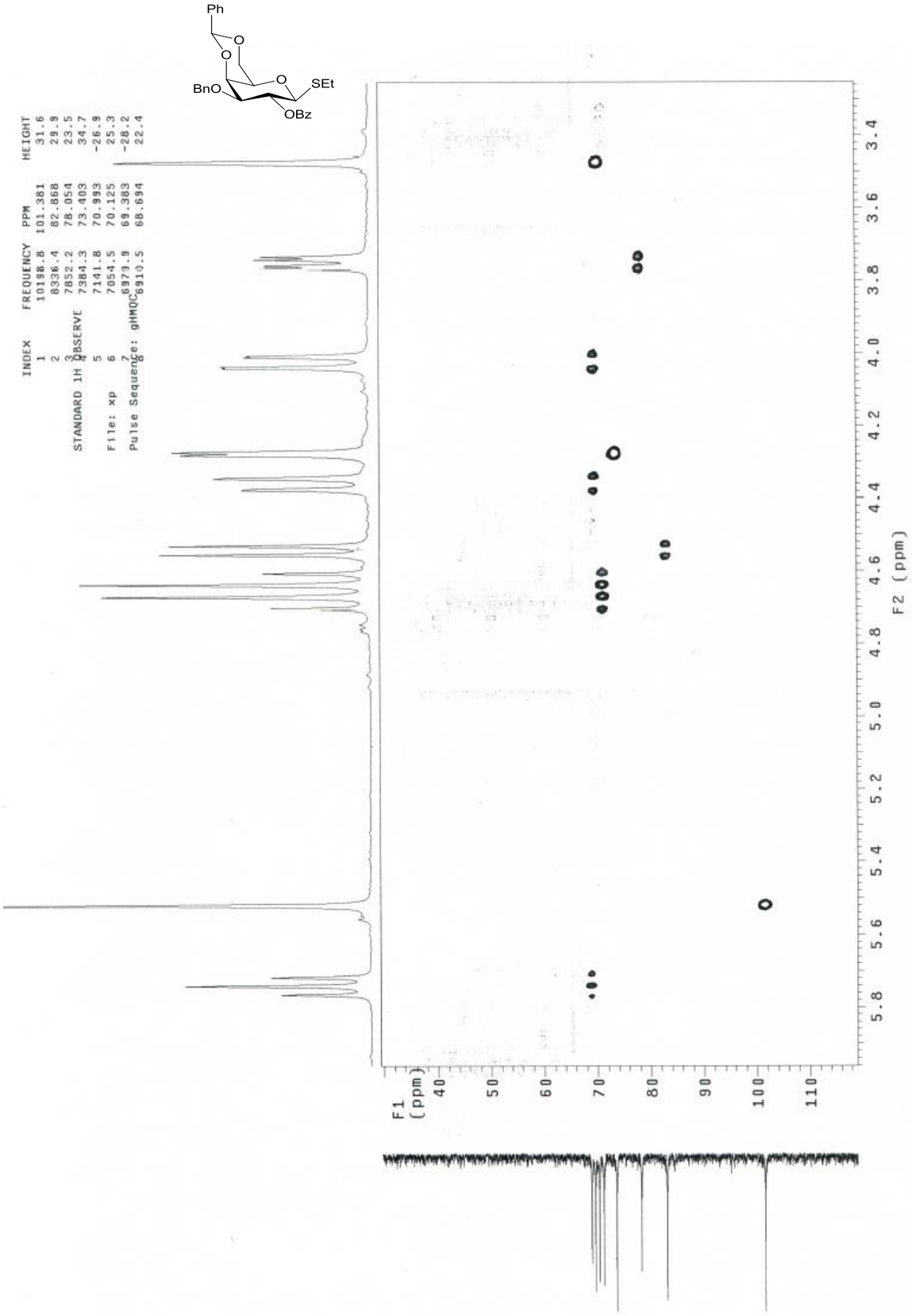


^{1}H NMR Spectrum of compound **7** ($CDCl_3$, 400 MHz)

^{13}C NMR Spectrum of compound **7** ($CDCl_3$, 400 MHz)



^{1}H-^{1}H COSY Spectrum of compound **7** ($CDCl_3$, 400 MHz)

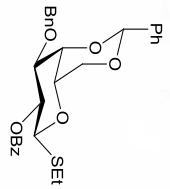


^{1}H-^{13}C HMQC NMR Spectrum of compound **7** ($CDCl_3$, 400/100 MHz)

Elemental Composition Report

Single Mass Analysis

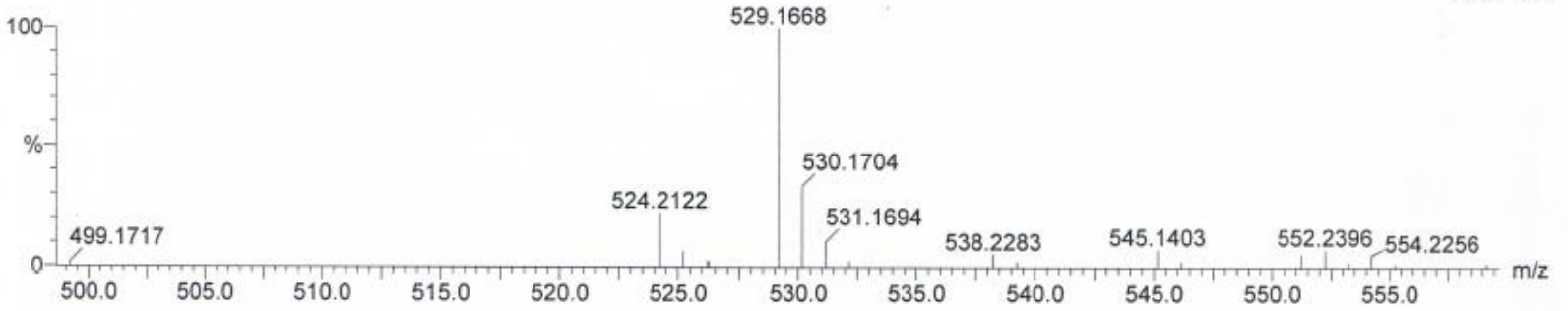
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6



Monoisotopic Mass, Even Electron Ions
4185 formula(e) evaluated with 19 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-10 O: 0-30 23Na: 0-1 S: 1-2
SATADRU MANDAL SSM-Gal-OBz(SEt)

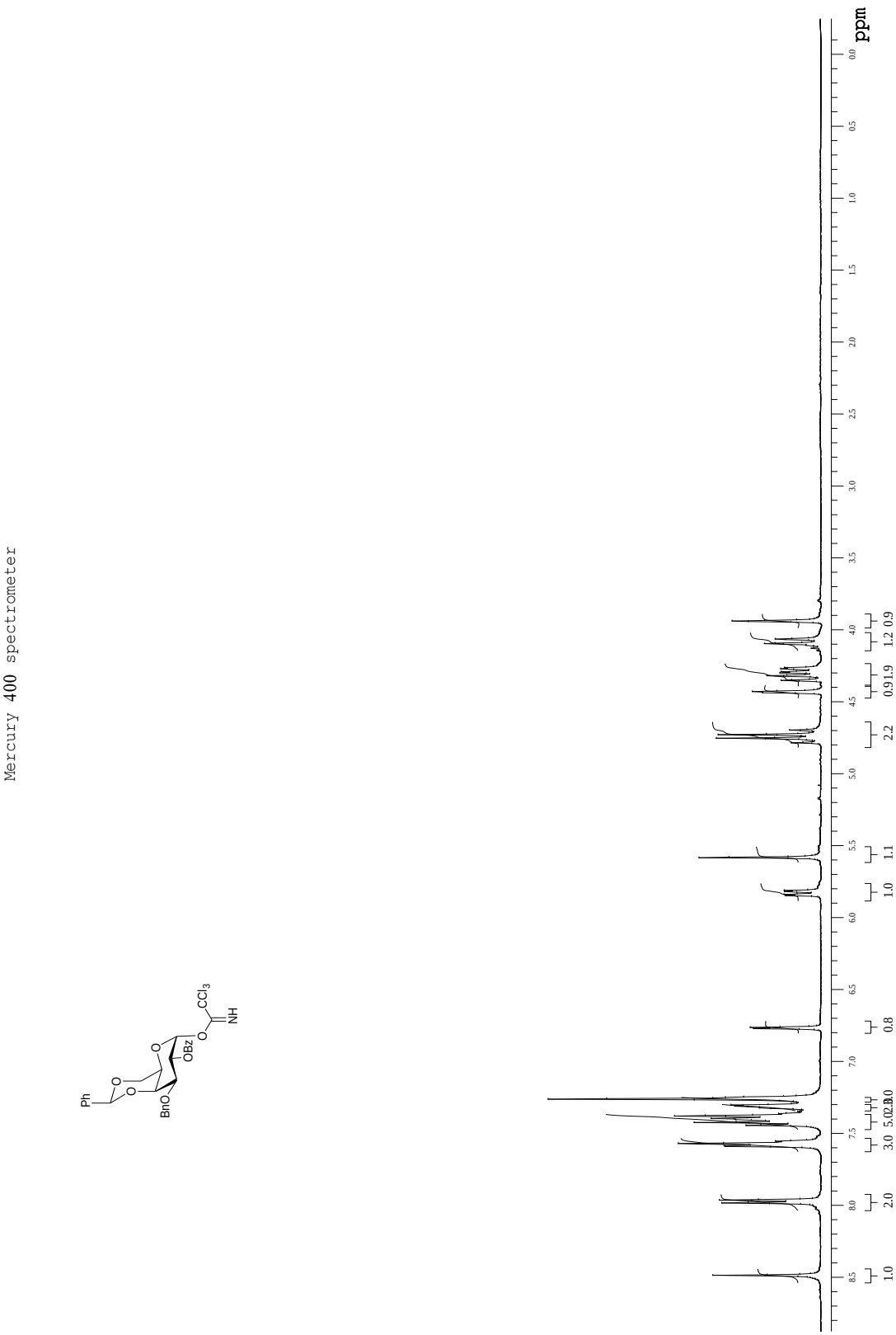
2013_0129_3051_2 14 (0.283) Cm (11:18-1:9x2.000)

LCT2008-07b.pro 2010-cif.splLCT Premier
1: TOF MS ES+
1.48e+004

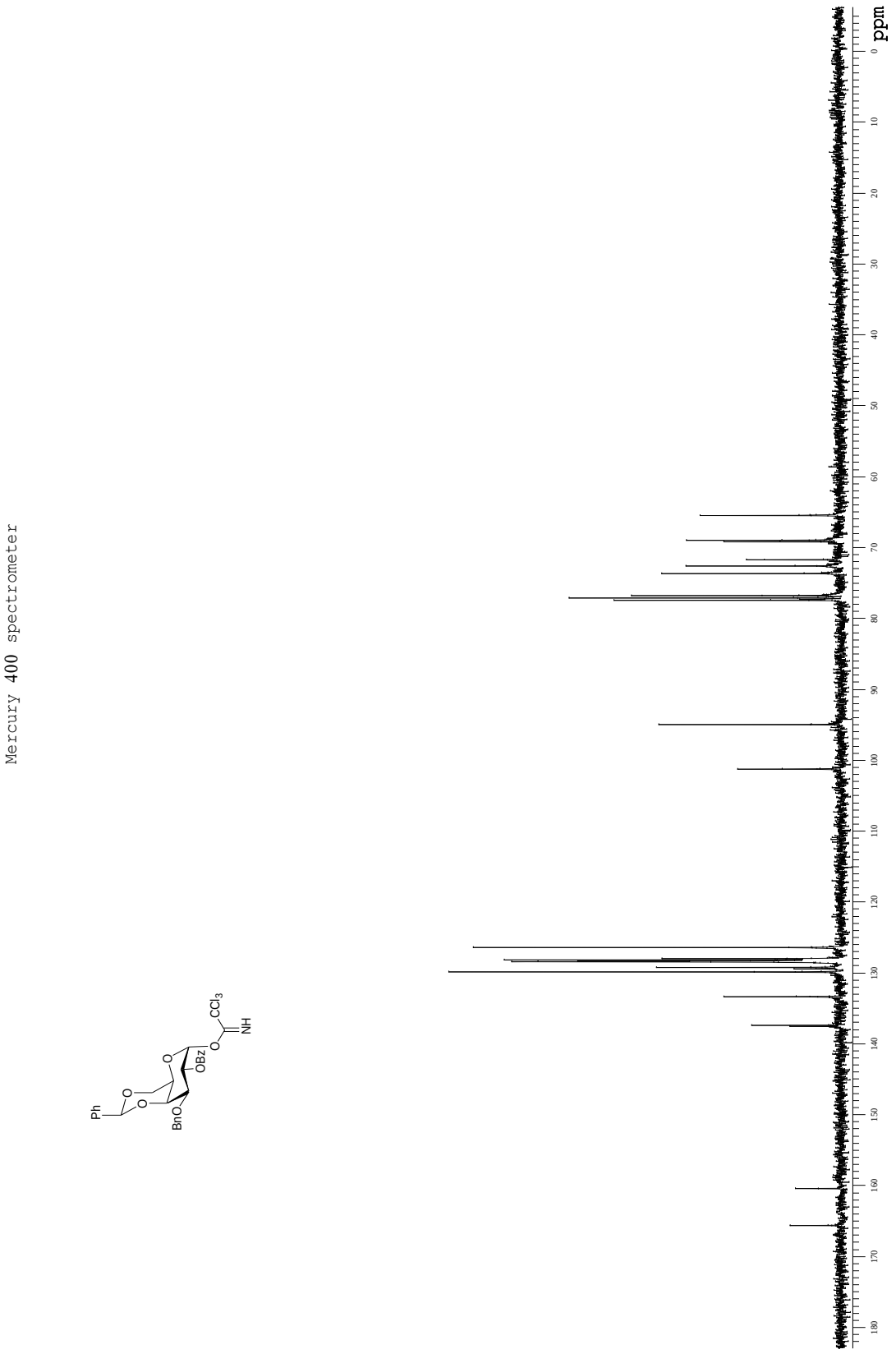


Minimum:				-1.5			
Maximum:		50.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
529.1668	529.1674	-0.6	-1.1	19.5	30.1	1.1	C30 H26 N4 O2 23Na S
	529.1671	-0.3	-0.6	23.5	30.1	1.1	C28 H21 N10 S
	529.1661	0.7	1.3	14.5	31.2	2.2	C29 H30 O6 23Na S
	529.1658	1.0	1.9	18.5	31.5	2.5	C27 H25 N6 O4 S
	529.1679	-1.1	-2.1	1.5	32.5	3.5	C17 H34 N2 O13 23Na S

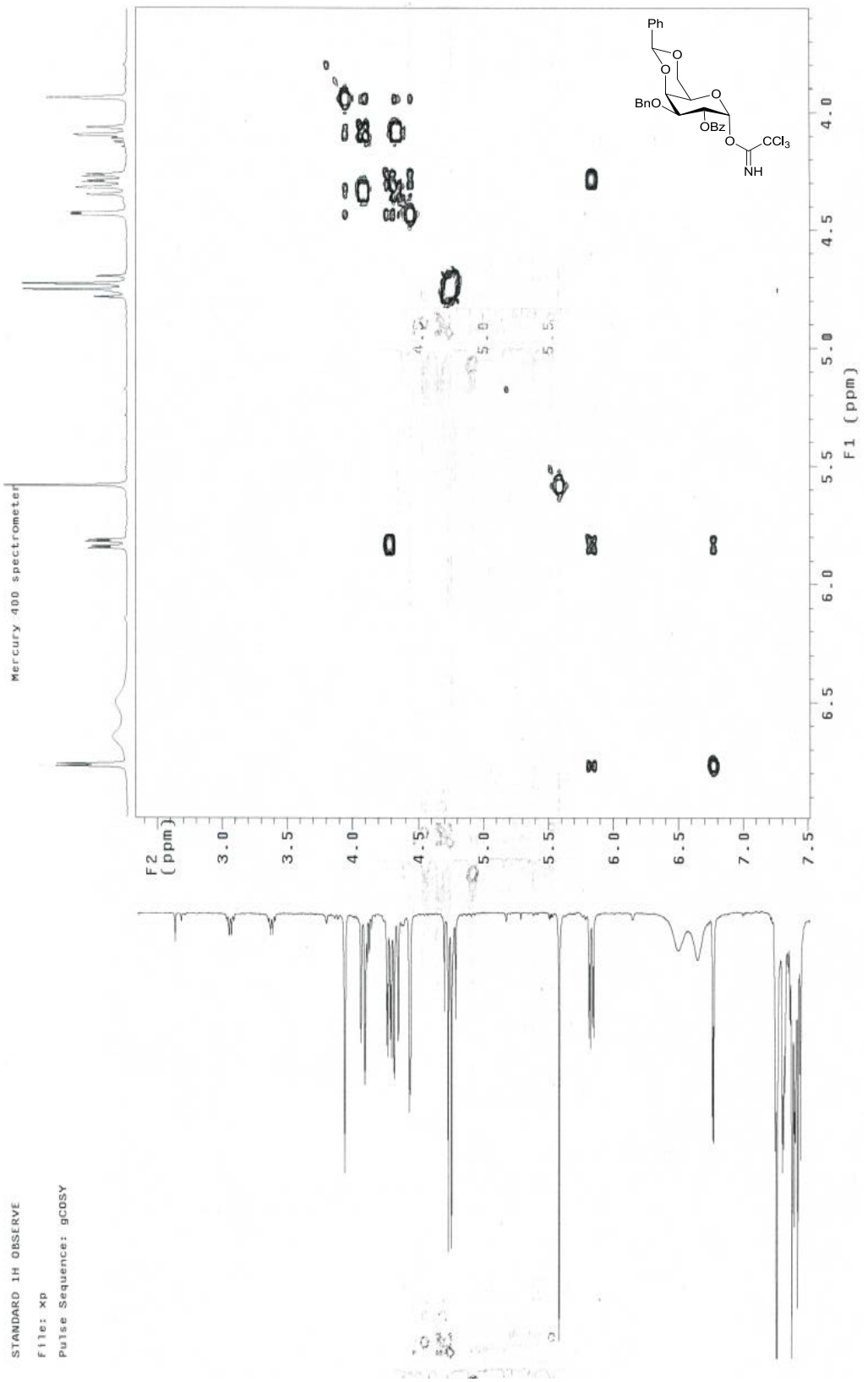
HRMS (ESI MS) spectrum of compound **7**



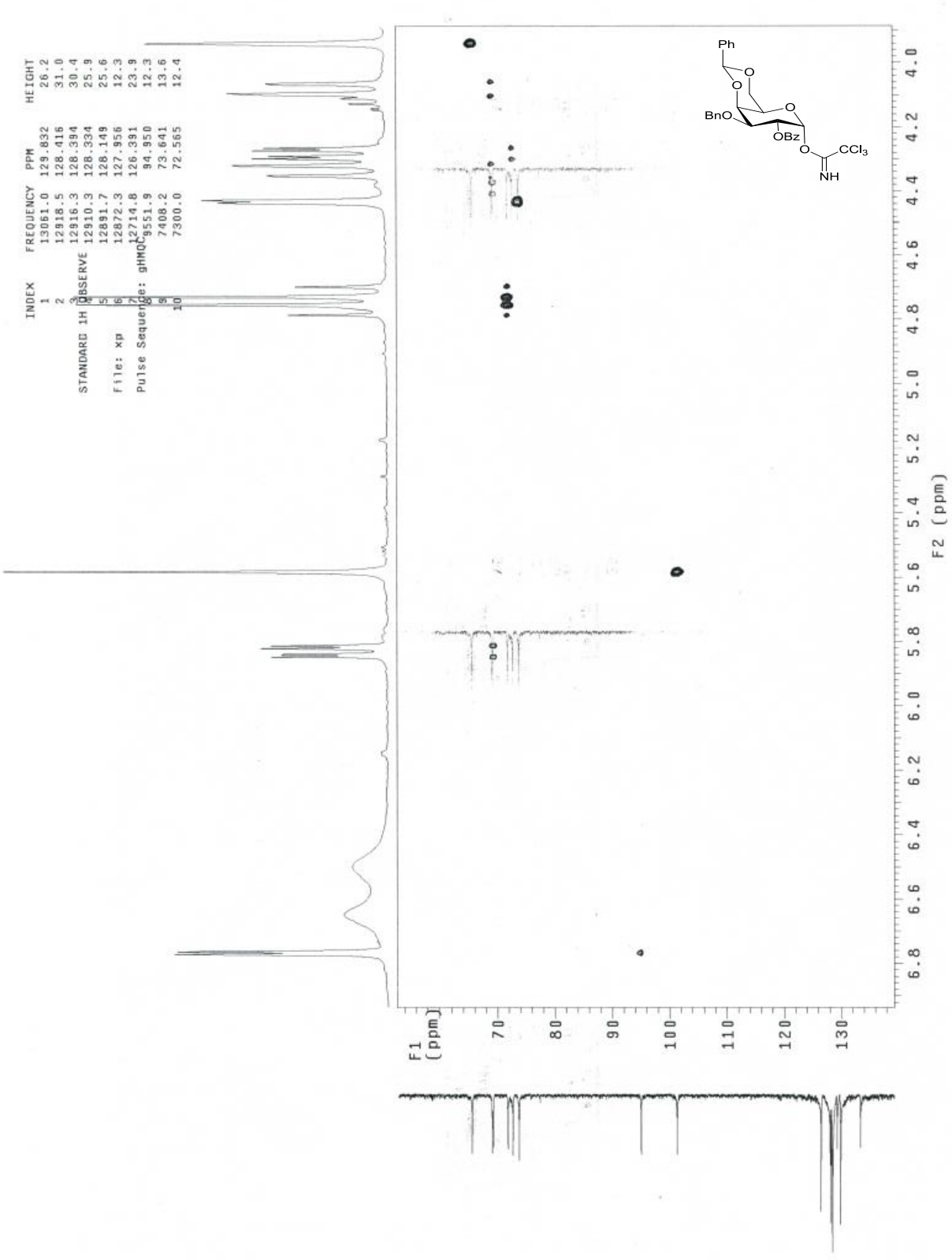
^{1}H NMR Spectrum of compound **19** ($CDCl_3$, 400 MHz)



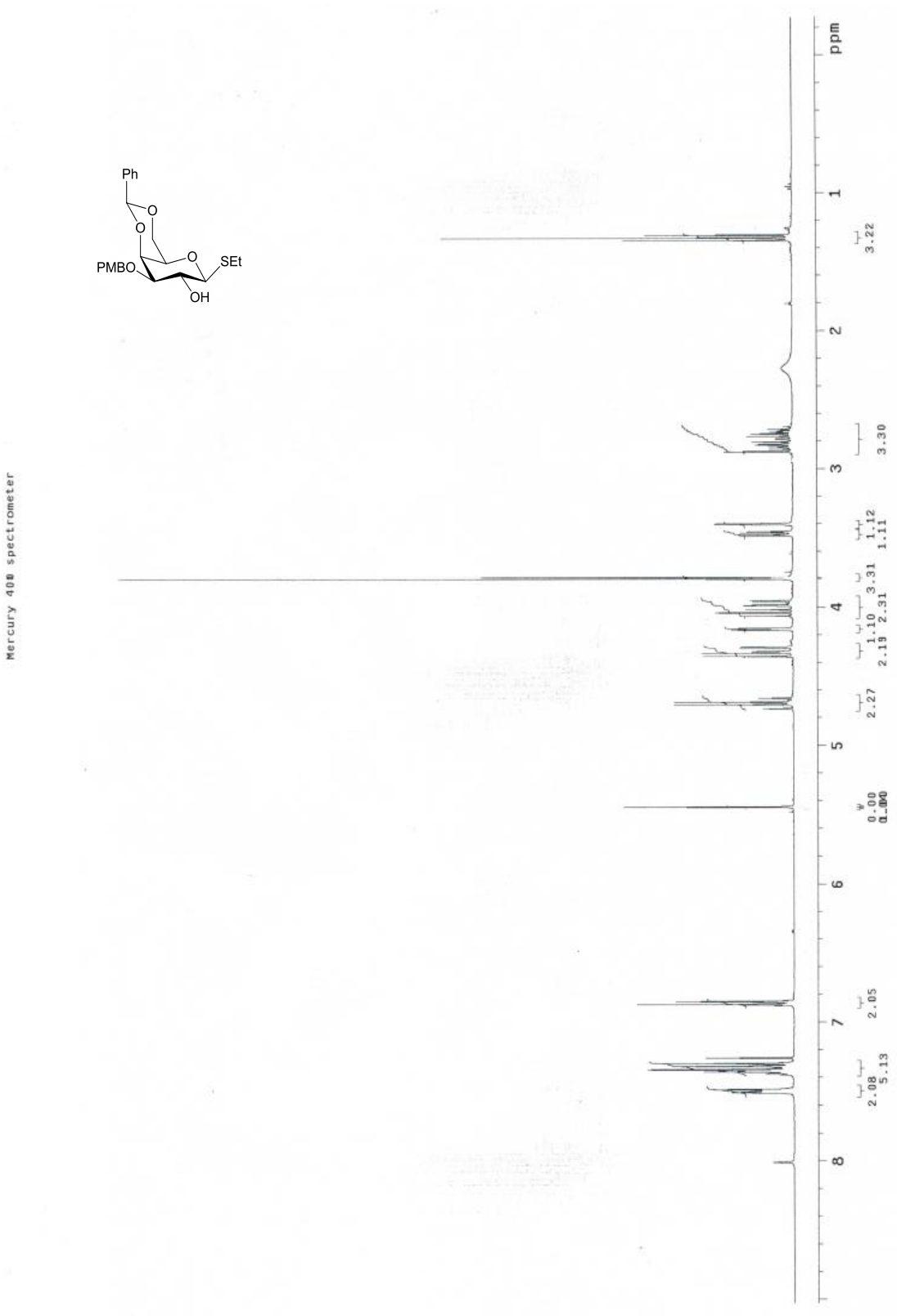
^{13}C NMR Spectrum of compound **19** ($CDCl_3$, 400 MHz)



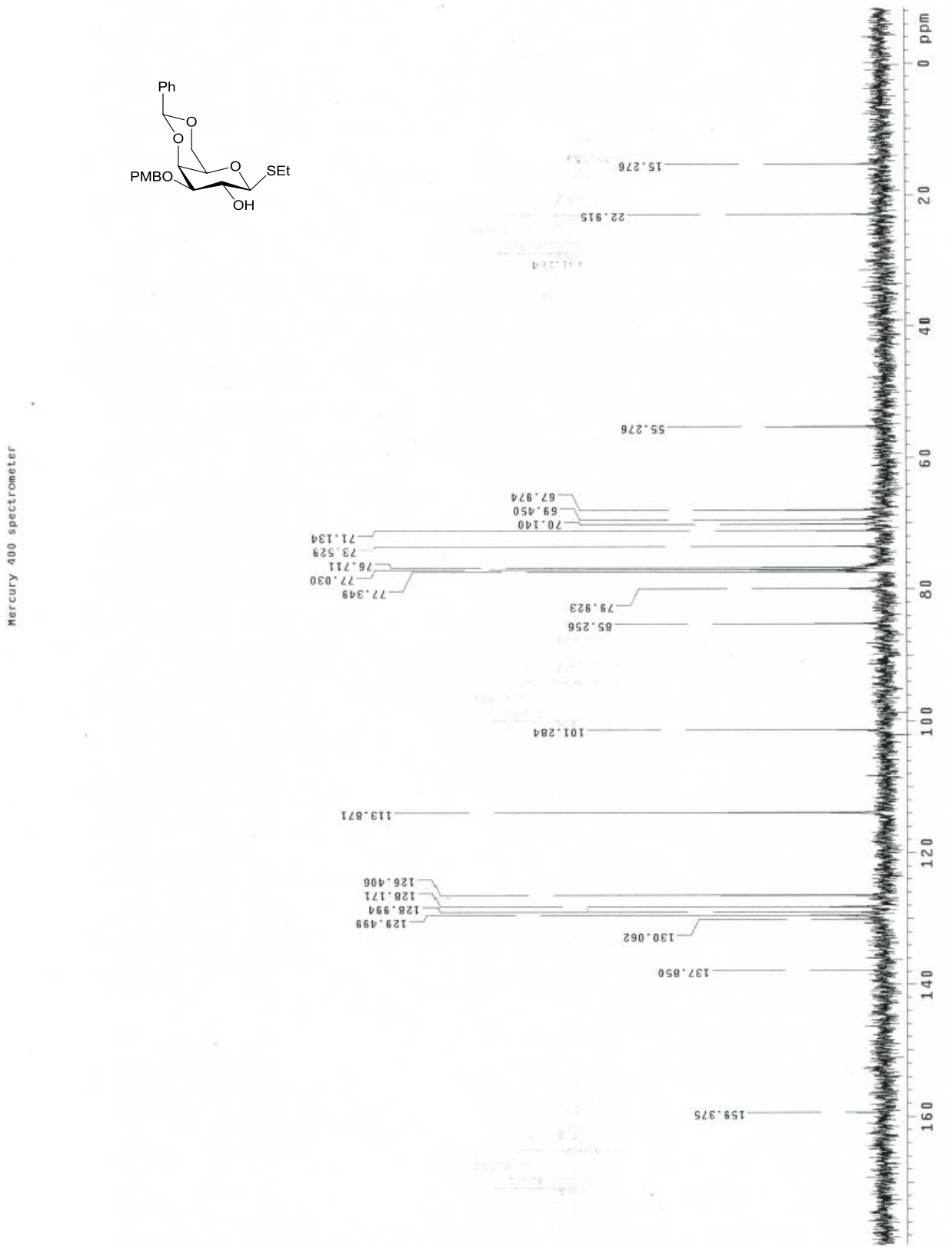
^{1}H-^{1}H COSY Spectrum of compound **19** ($CDCl_3$, 400 MHz)



^{1}H-^{13}C HMQC NMR Spectrum of compound **19** ($CDCl_3$, 400/100 MHz)

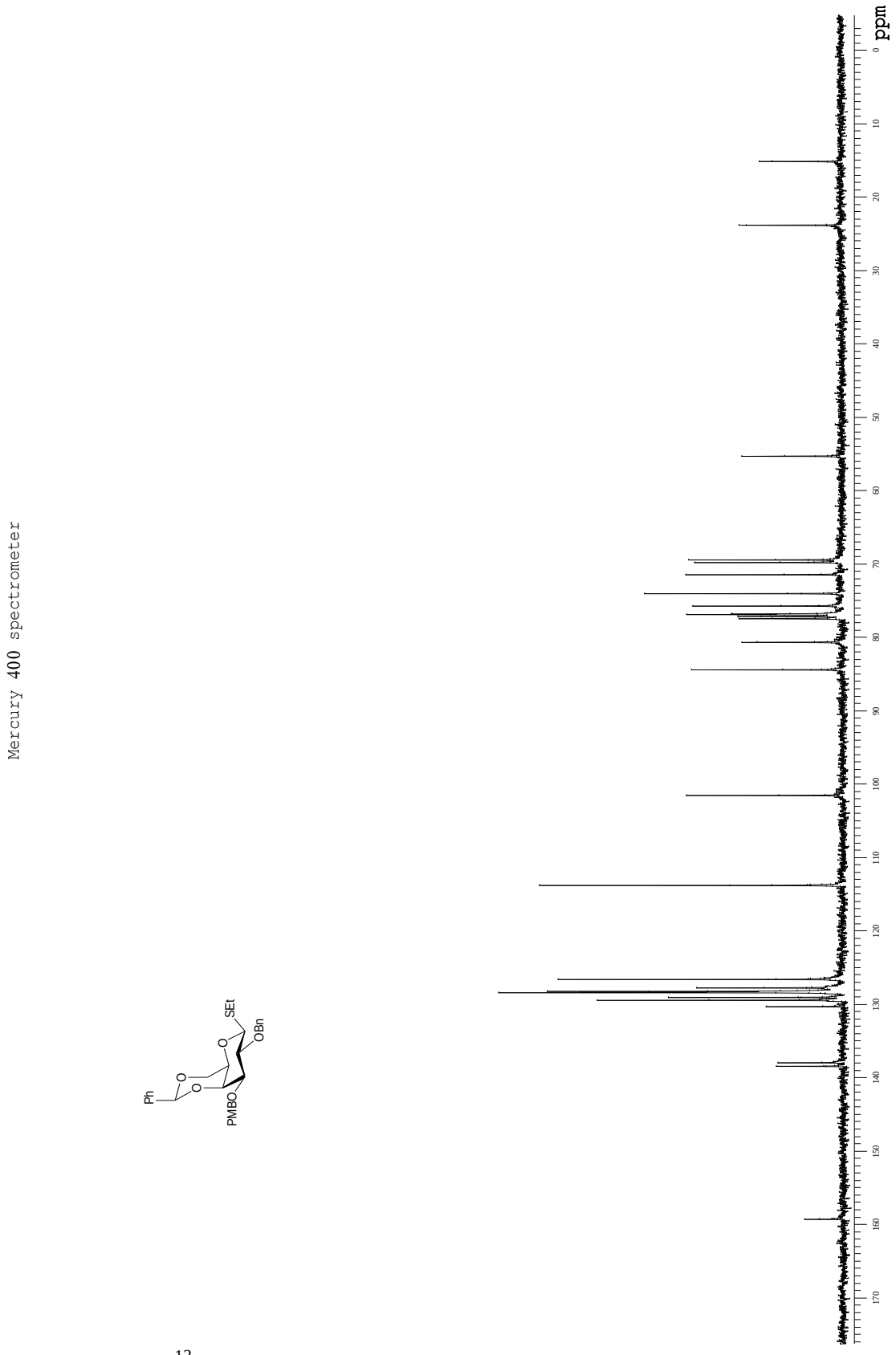


^{1}H NMR Spectrum of compound **13** ($CDCl_3$, 400 MHz)

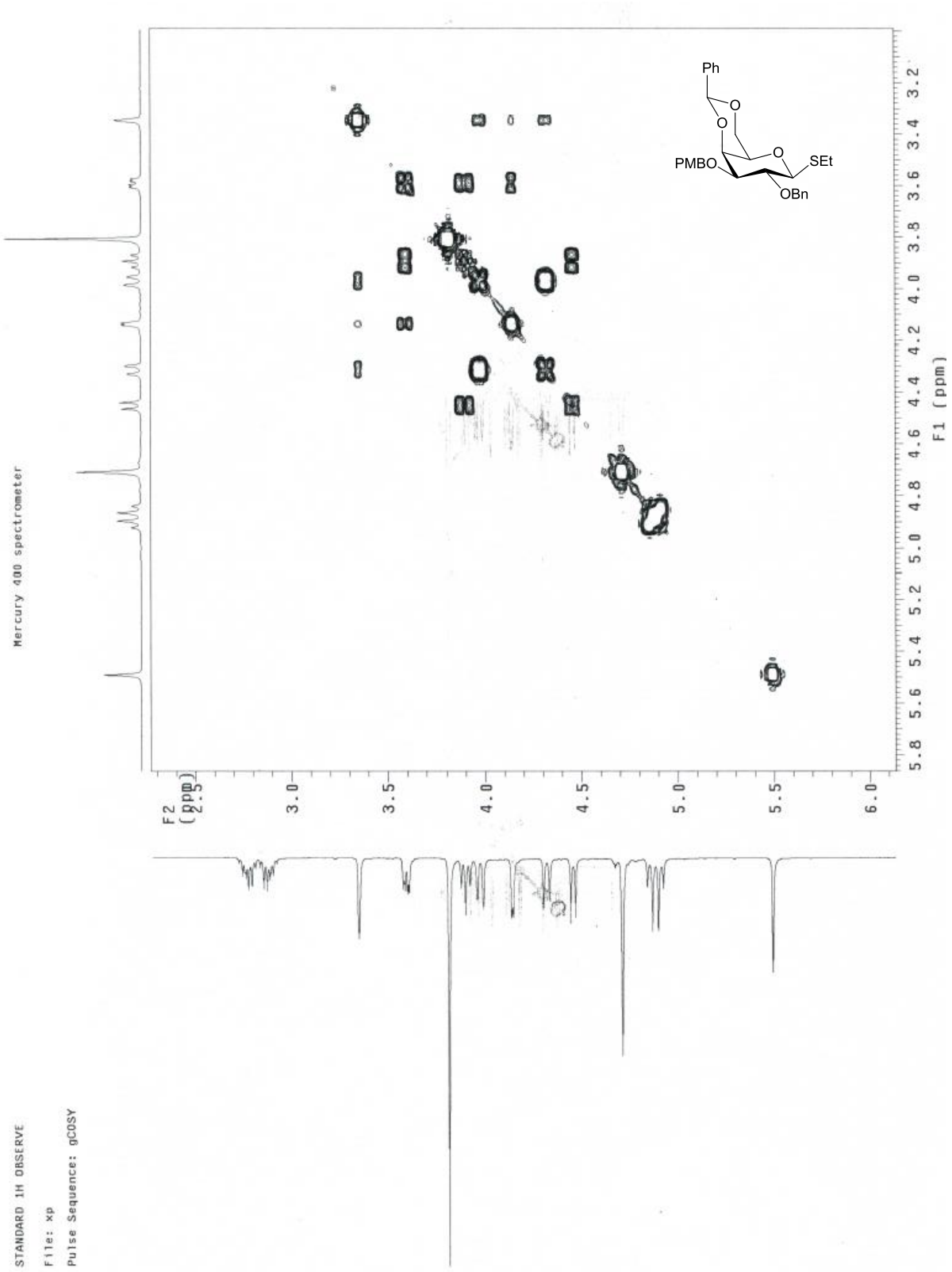


^{13}C NMR Spectrum of compound **13** ($CDCl_3$, 400 MHz)

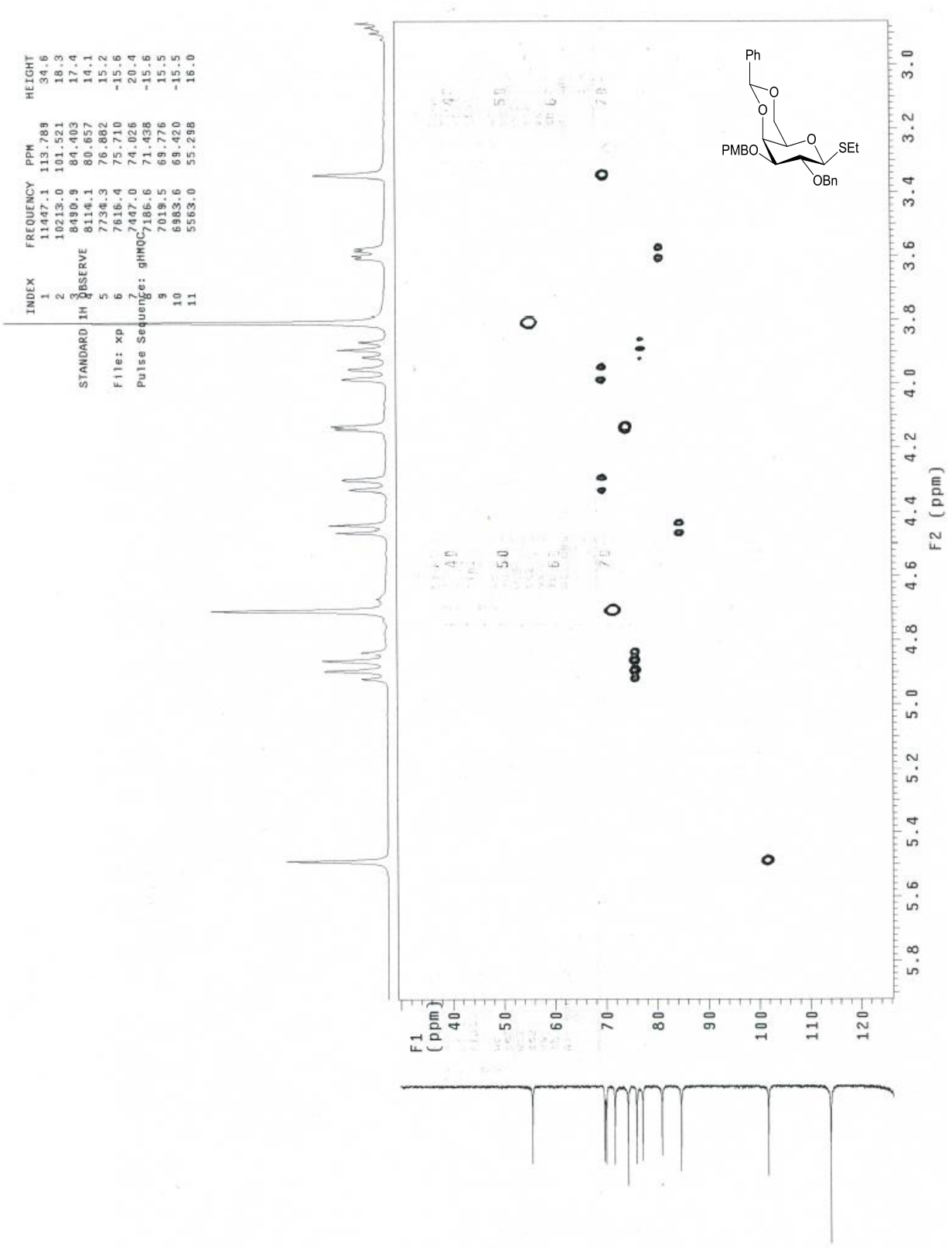
^{1}H NMR Spectrum of compound **14** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of compound **14** ($CDCl_3$, 400 MHz)



^{1}H-^{1}H COSY Spectrum of compound **14** ($CDCl_3$, 400 MHz)

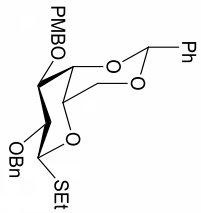


^{1}H-^{13}C HMQC NMR Spectrum of compound **14** ($CDCl_3$, 400/100 MHz)

Elemental Composition Report

Single Mass Analysis

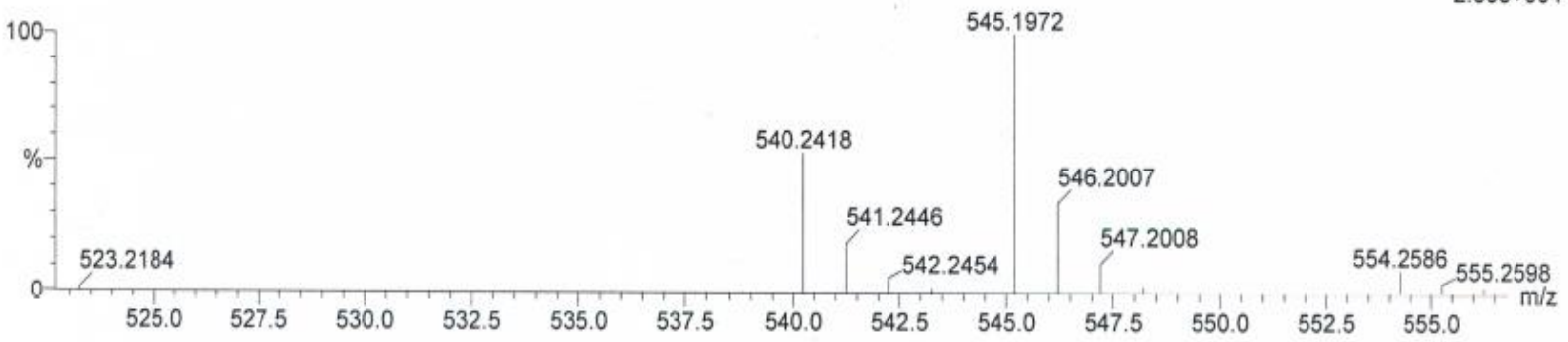
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6



Monoisotopic Mass, Even Electron Ions
1325 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-1000 N: 0-3 O: 0-15 23Na: 0-1 S: 1-2
SATADRU MANDAL SSM-Gal-PMB(SEt)

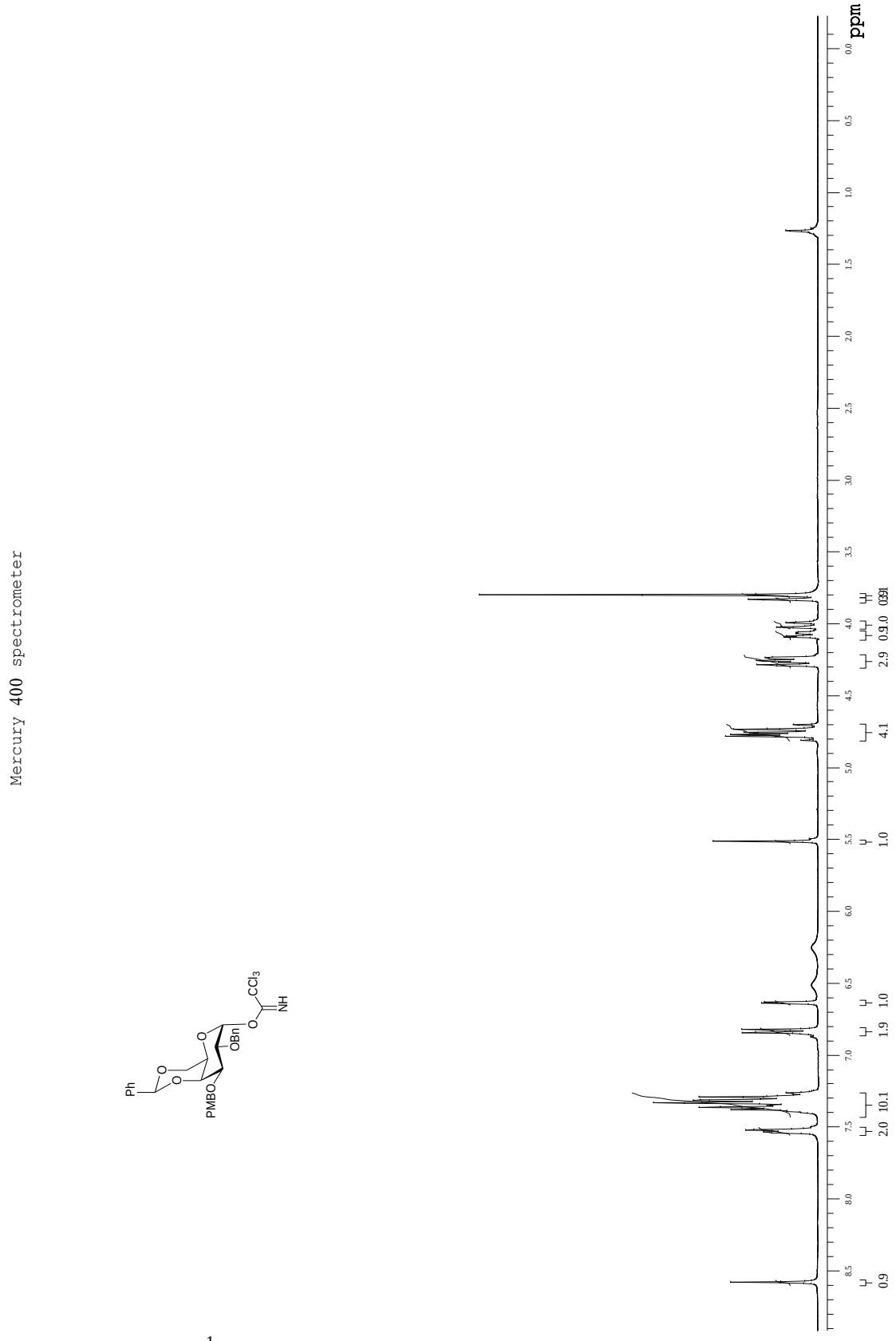
2013_0130_3058 26 (0.548) Cm (26:33-1:8x2.000)

LCT2008-07b.pro 2010-cif.splLCT Premier
1: TOF MS ES+
2.36e+004

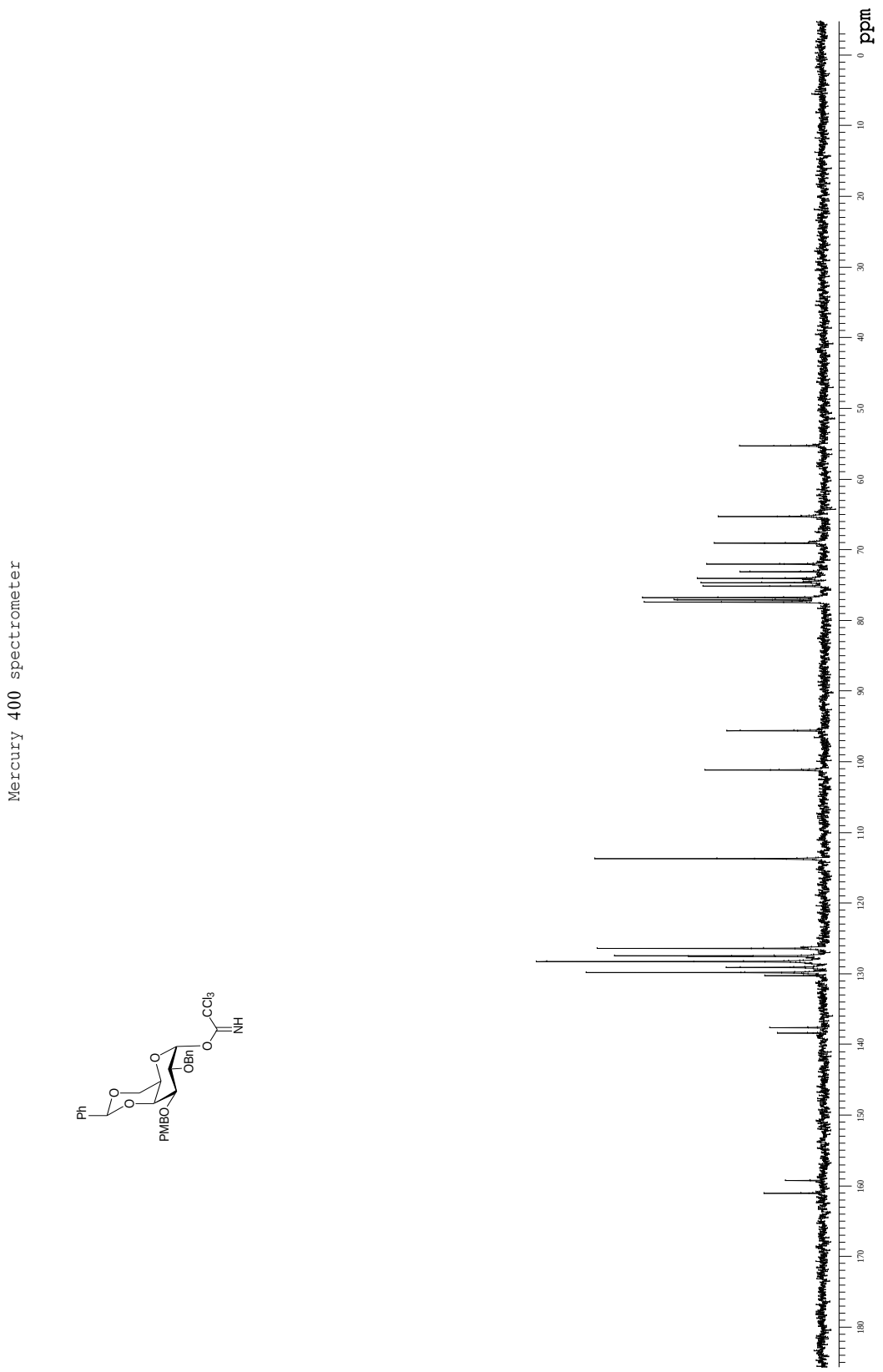


Minimum:				-1.5			
Maximum:		50.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
545.1972	545.1974	-0.2	-0.4	13.5	35.9	0.3	C30 H34 O6 23Na S
	545.1958	1.4	2.6	12.5	37.9	2.2	C27 H33 N2 O8 S
	545.1998	-2.6	-4.8	16.5	38.3	2.7	C32 H33 O6 S
	545.1992	-2.0	-3.7	0.5	38.4	2.8	C18 H38 N2 O13 23Na S

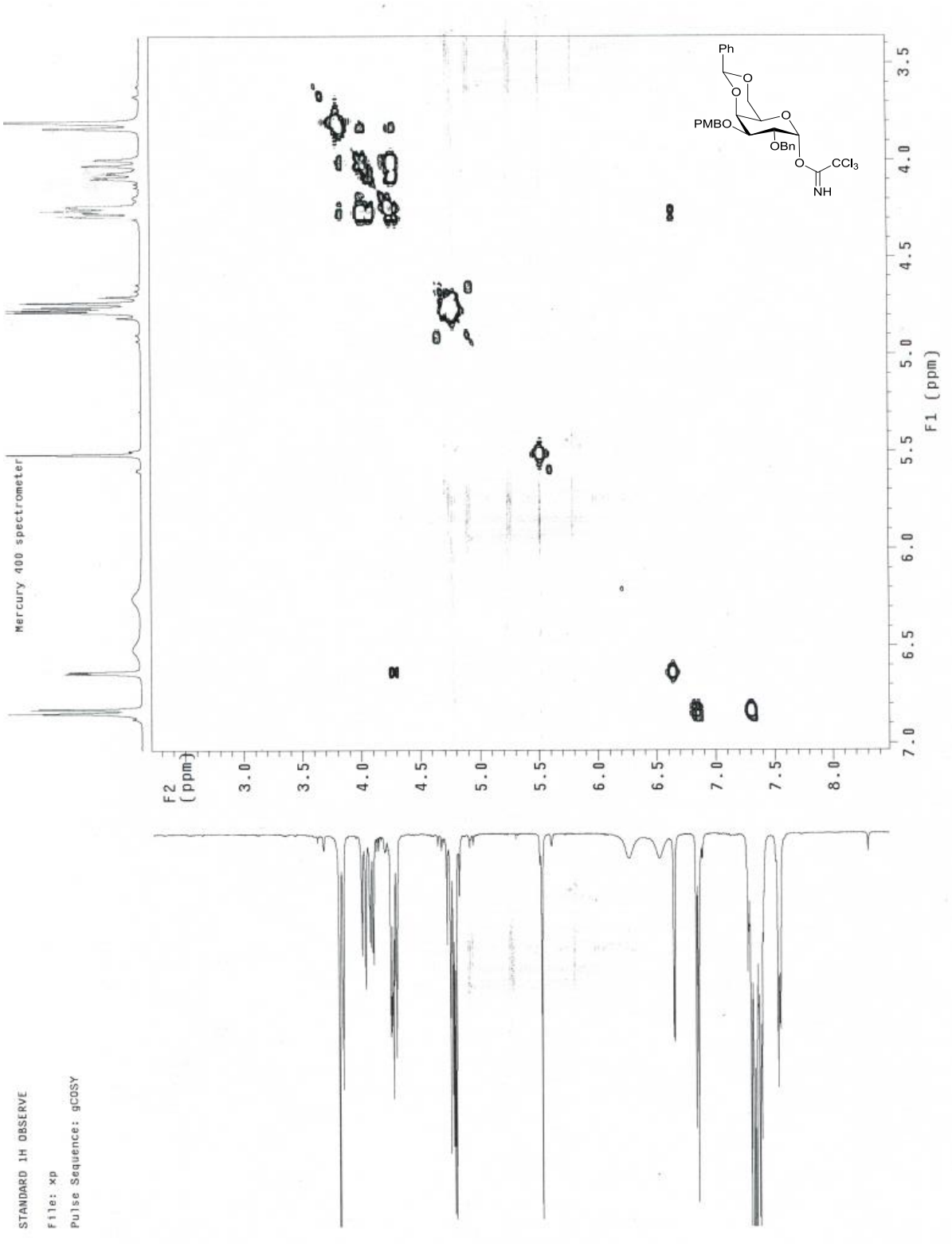
HRMS (ESI MS) spectrum of compound **14**



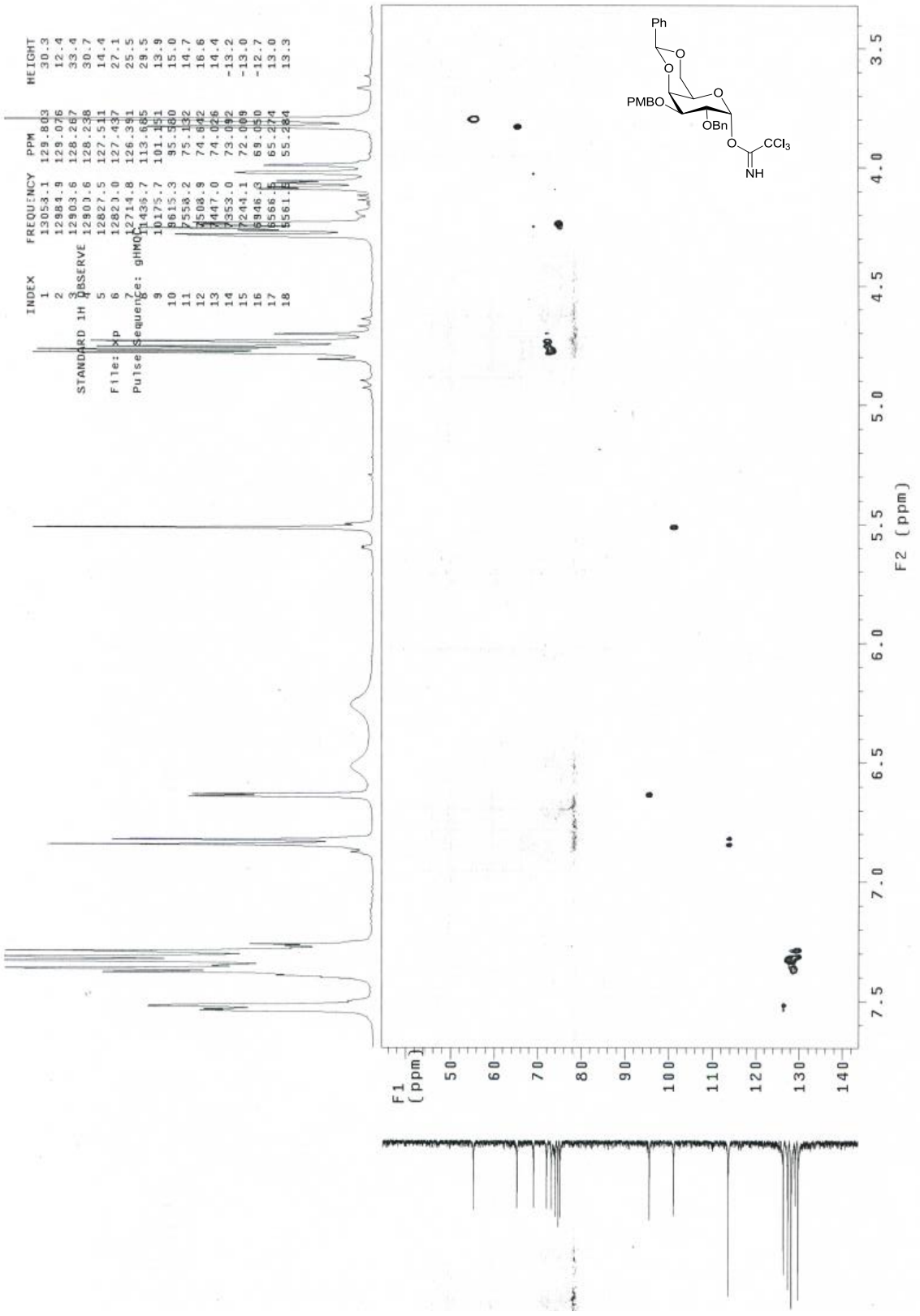
^{1}H NMR Spectrum of compound **9** ($CDCl_3$, 400 MHz)



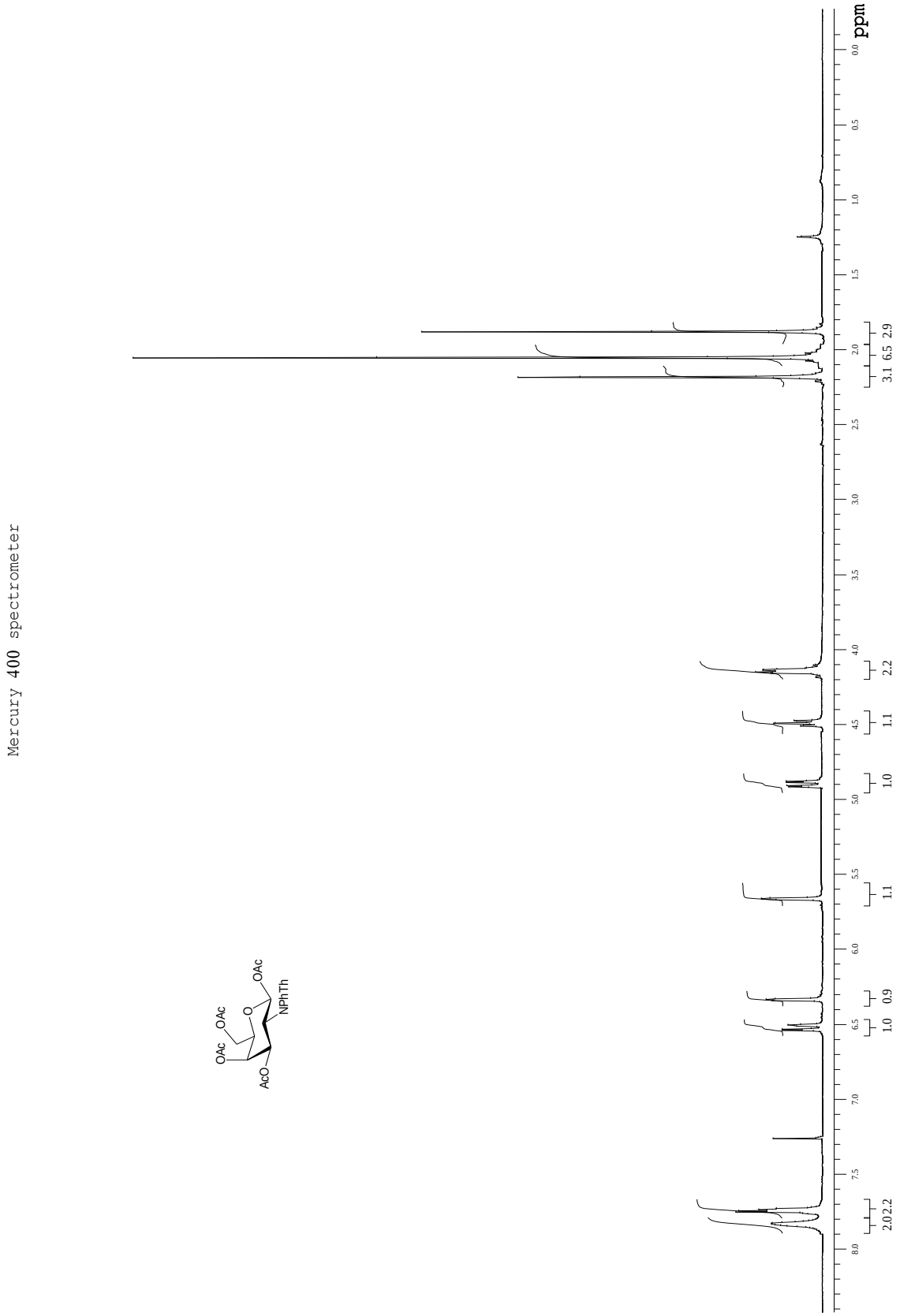
^{13}C NMR Spectrum of compound **9** ($CDCl_3$, 400 MHz)



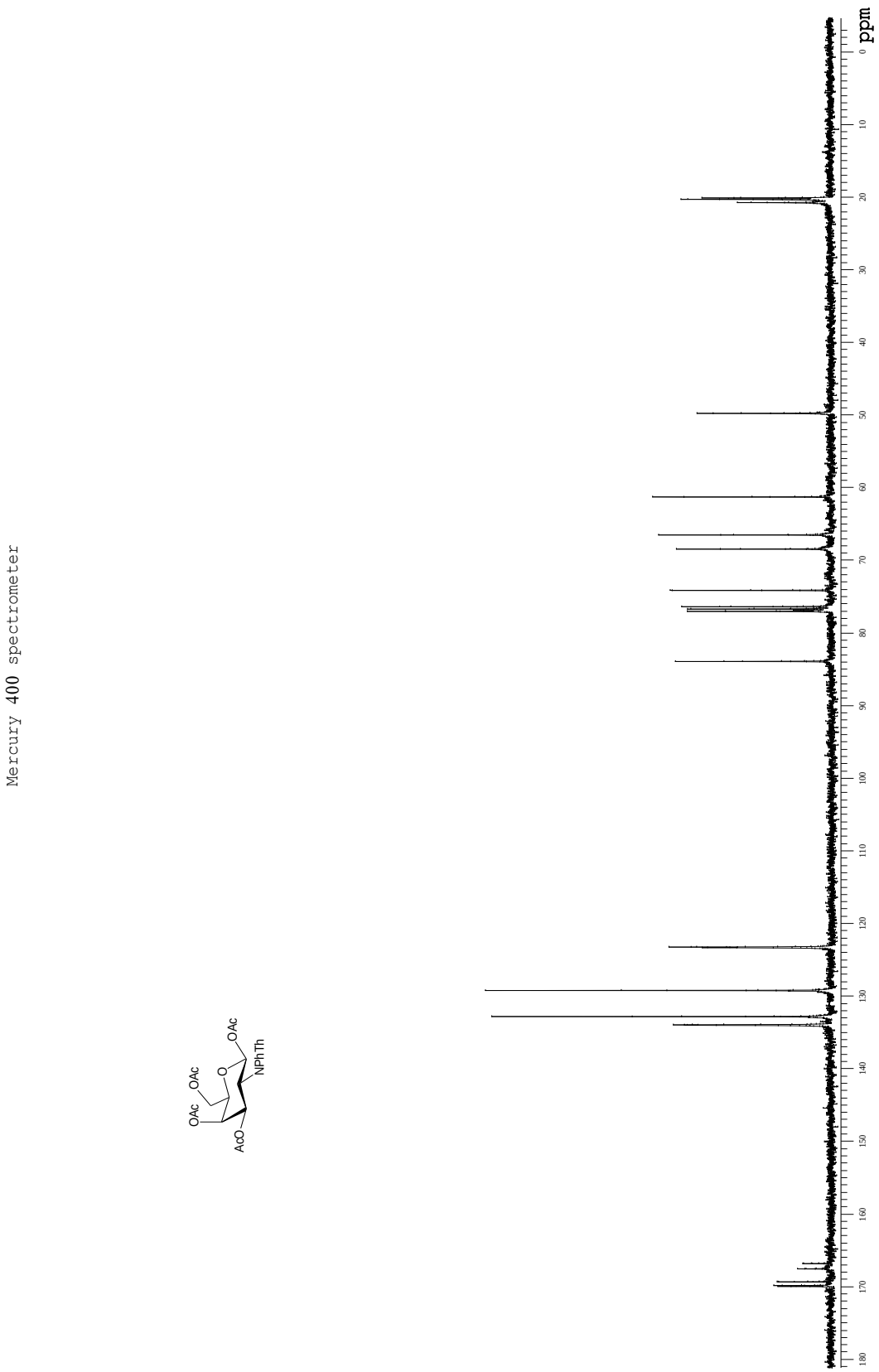
^{1}H-^{1}H COSY Spectrum of compound **9** ($CDCl_3$, 400 MHz)



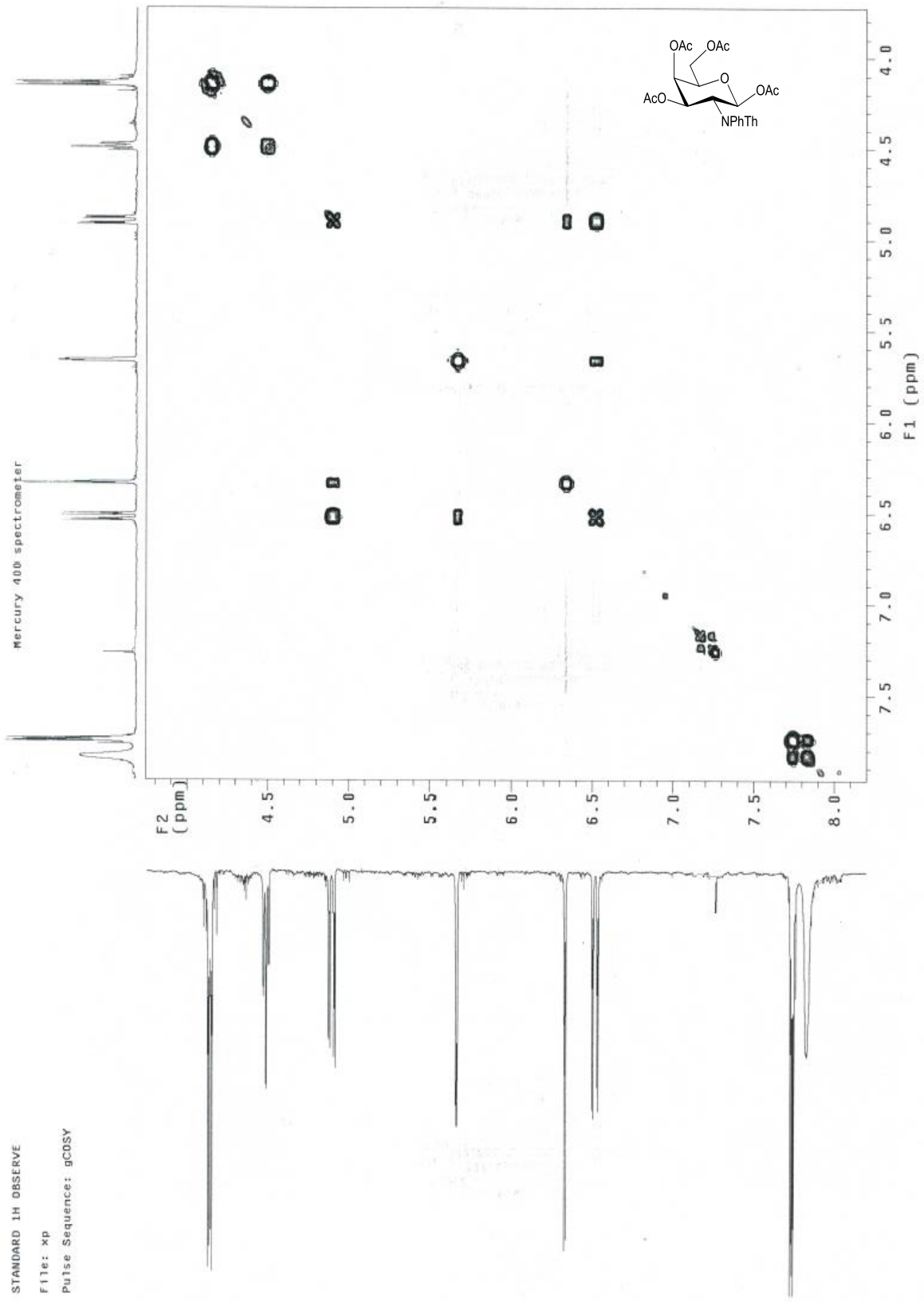
^{1}H-^{13}C HMQC NMR Spectrum of compound **9** ($CDCl_3$, 400/100 MHz)



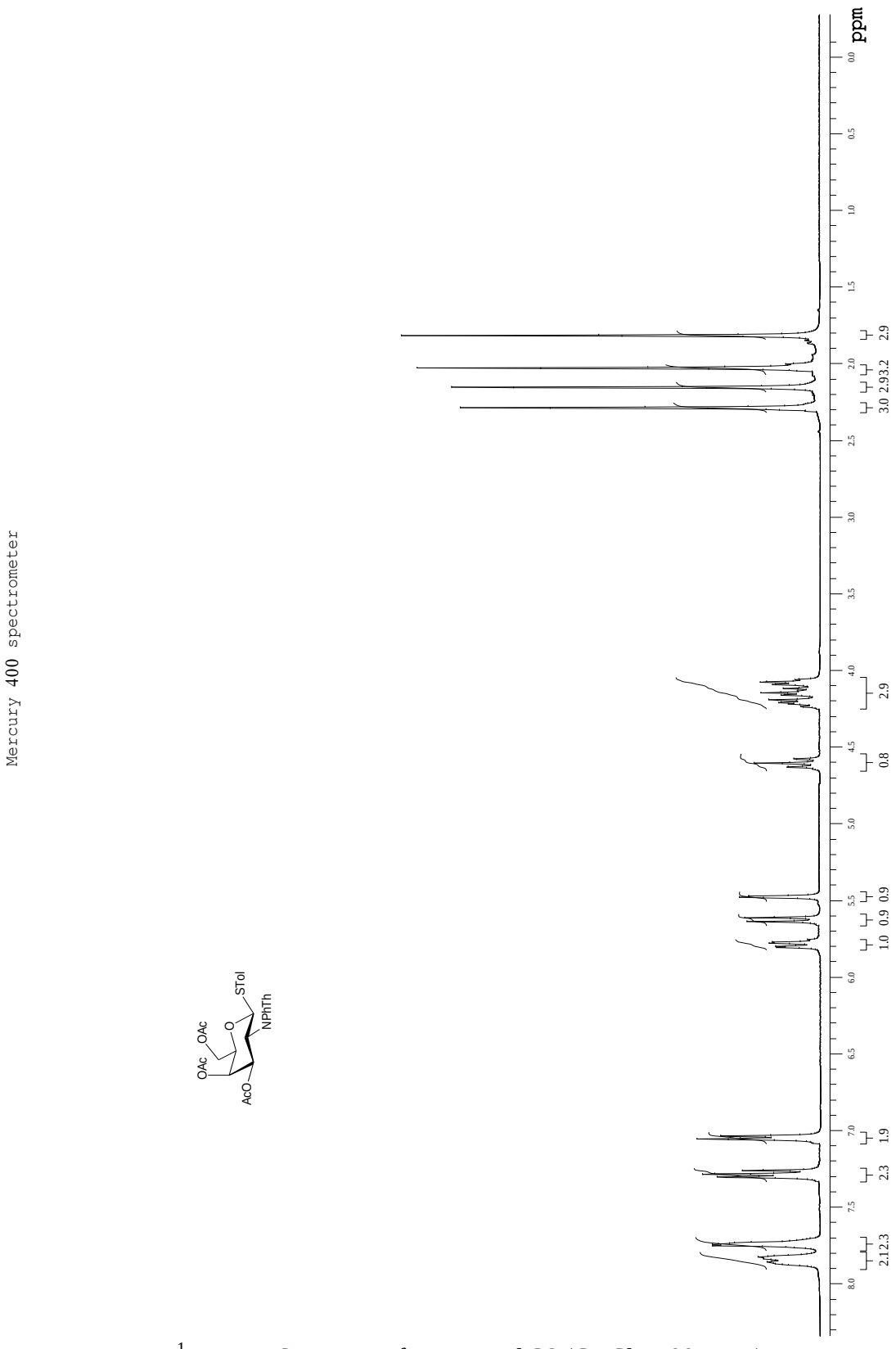
^{1}H NMR Spectrum of compound **S5** ($CDCl_3$, 400 MHz)



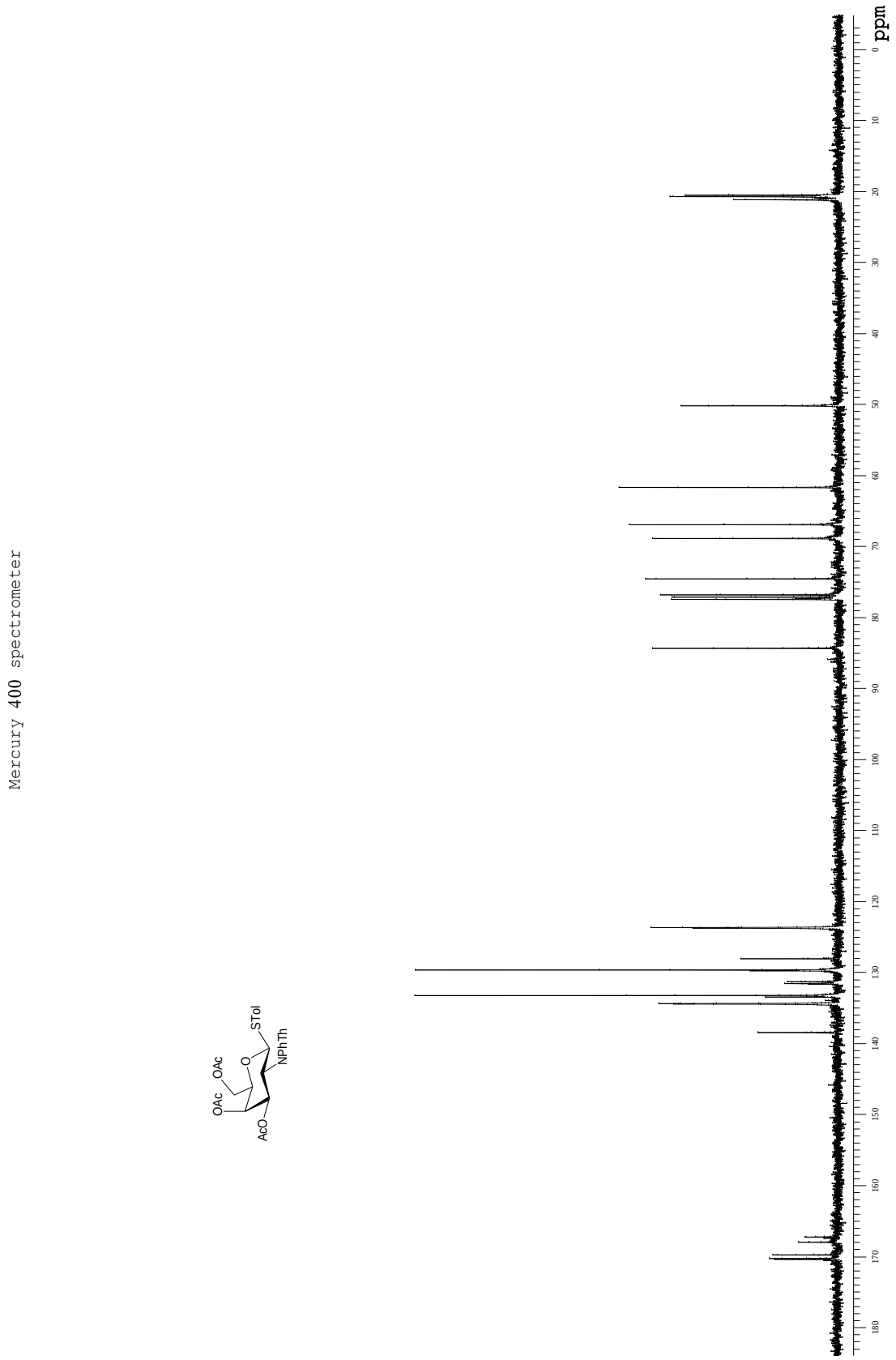
^{13}C NMR Spectrum of compound **S5** ($CDCl_3$, 400 MHz)



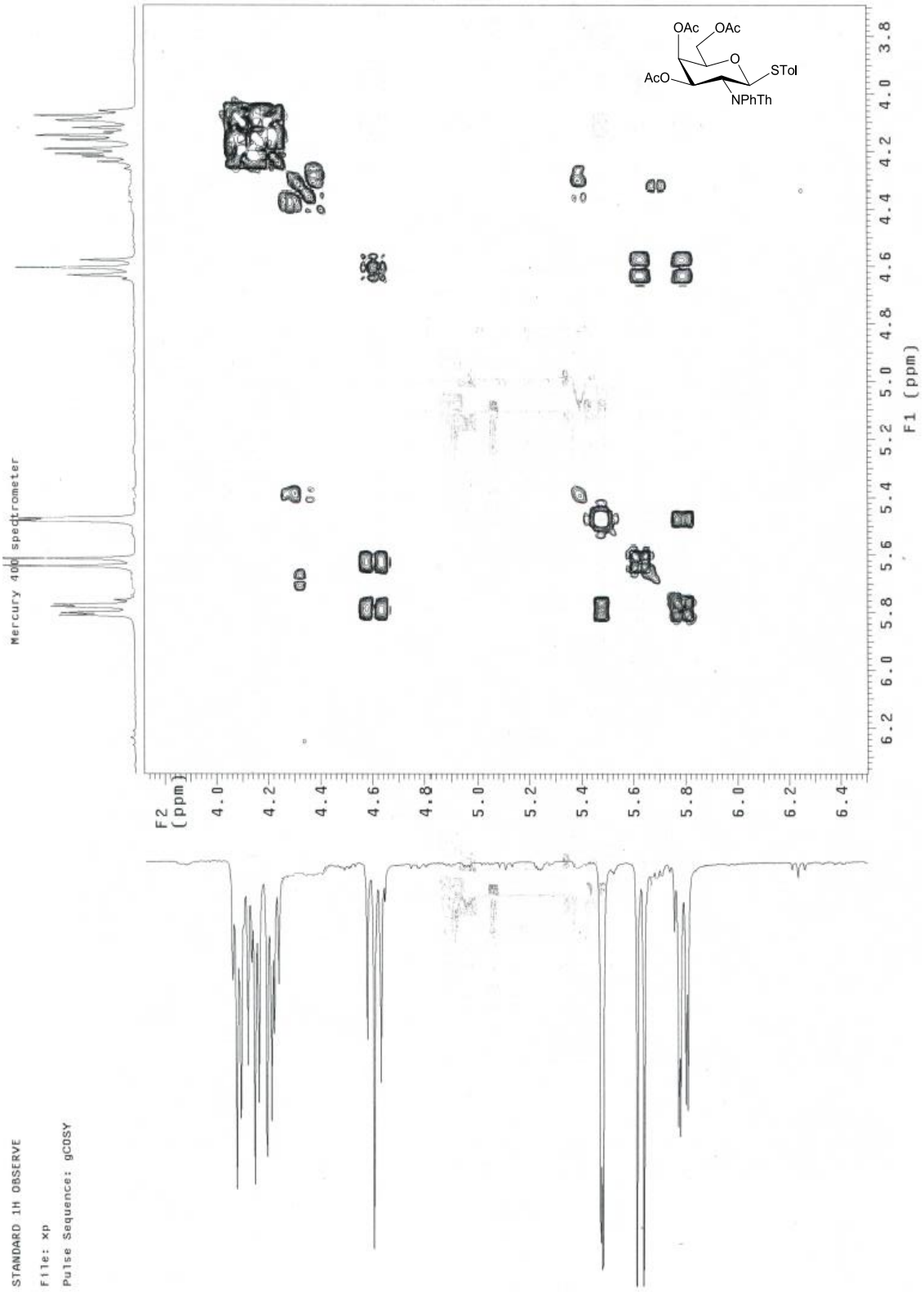
^{1}H-^{1}H COSY Spectrum of compound **S5** ($CDCl_3$, 400 MHz)



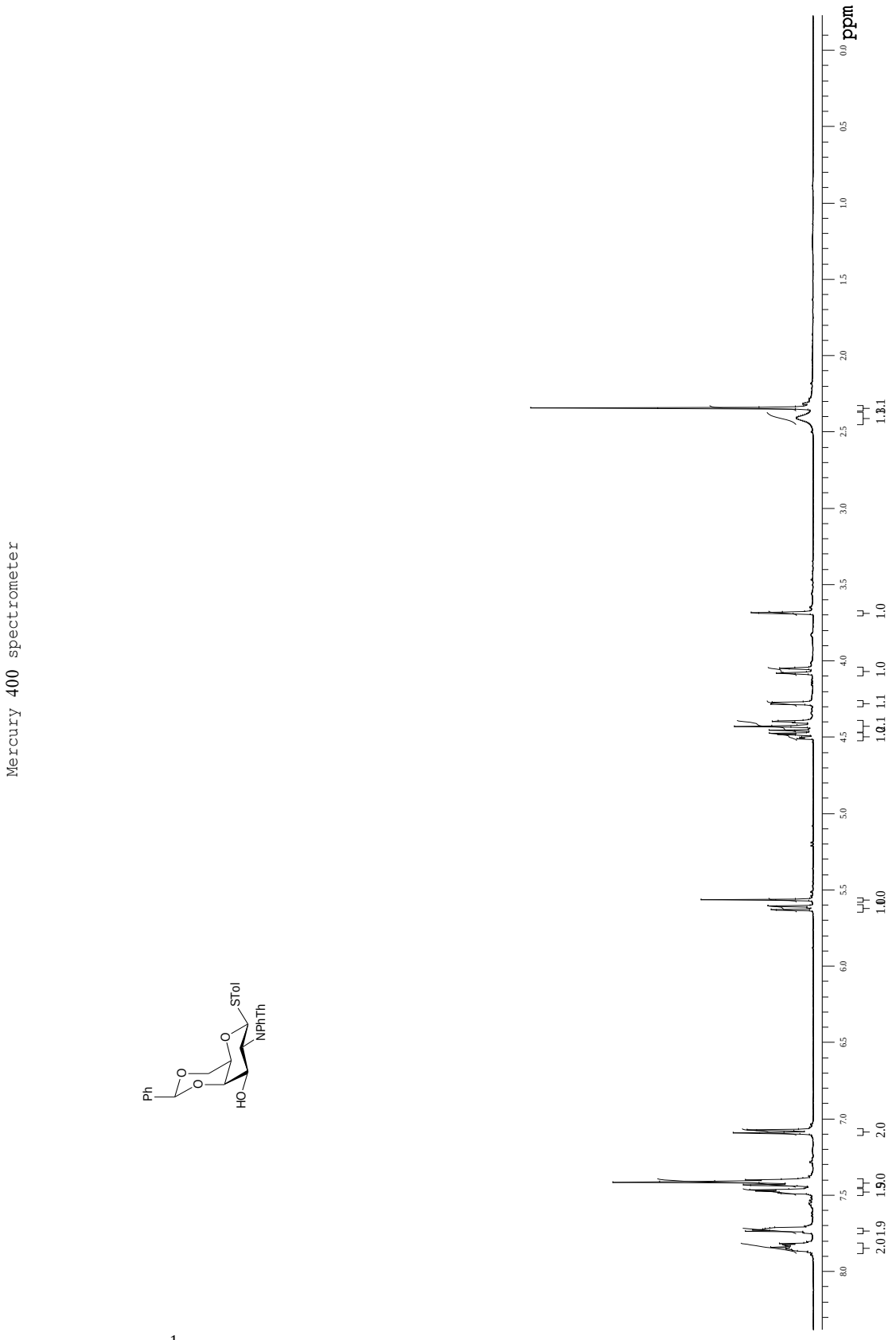
^{1}H NMR Spectrum of compound **S6** ($CDCl_3$, 400 MHz)



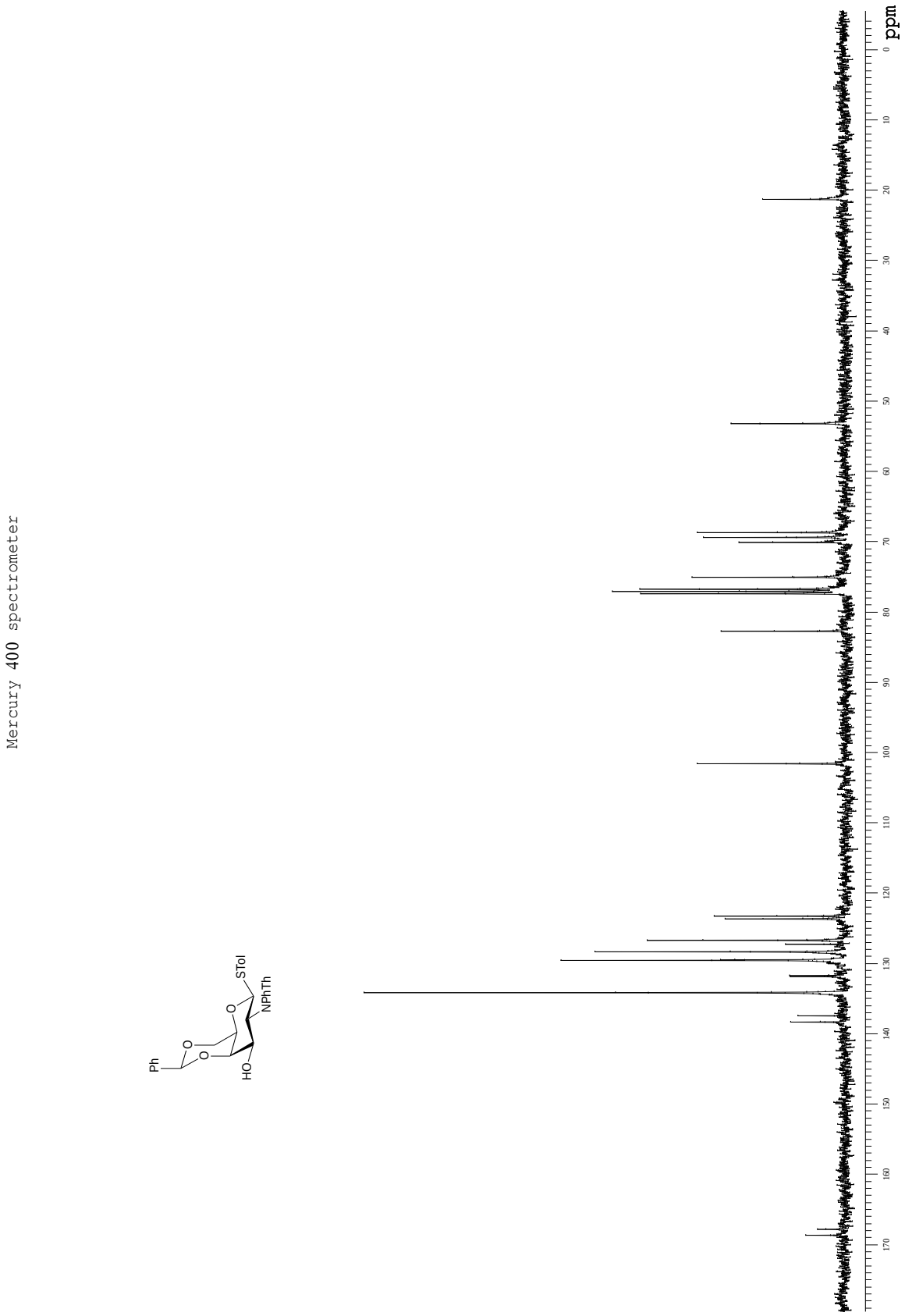
^{13}C NMR Spectrum of compound **S6** ($CDCl_3$, 400 MHz)



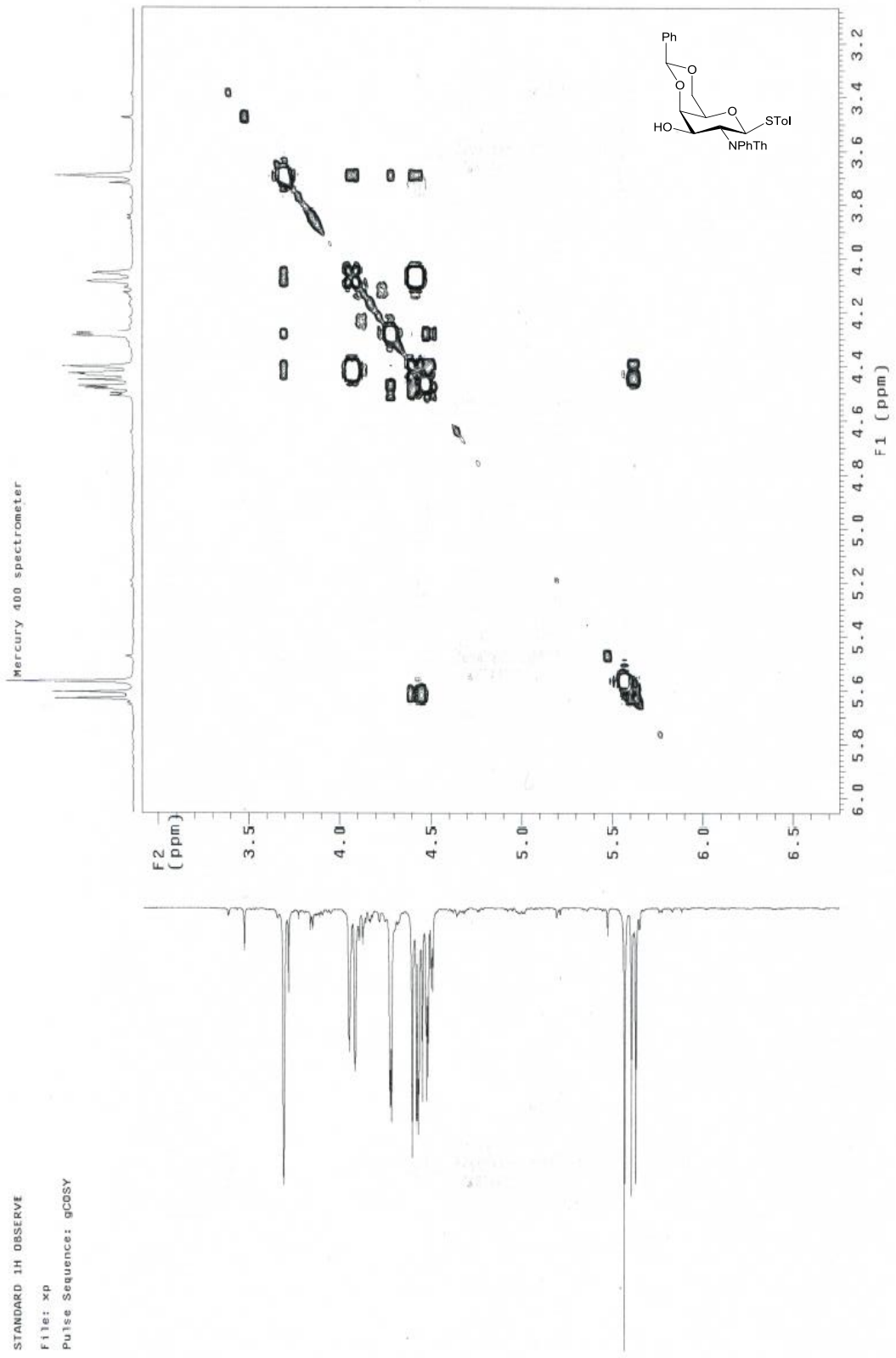
^{1}H-^{1}H COSY Spectrum of compound **S6** ($CDCl_3$, 400 MHz)



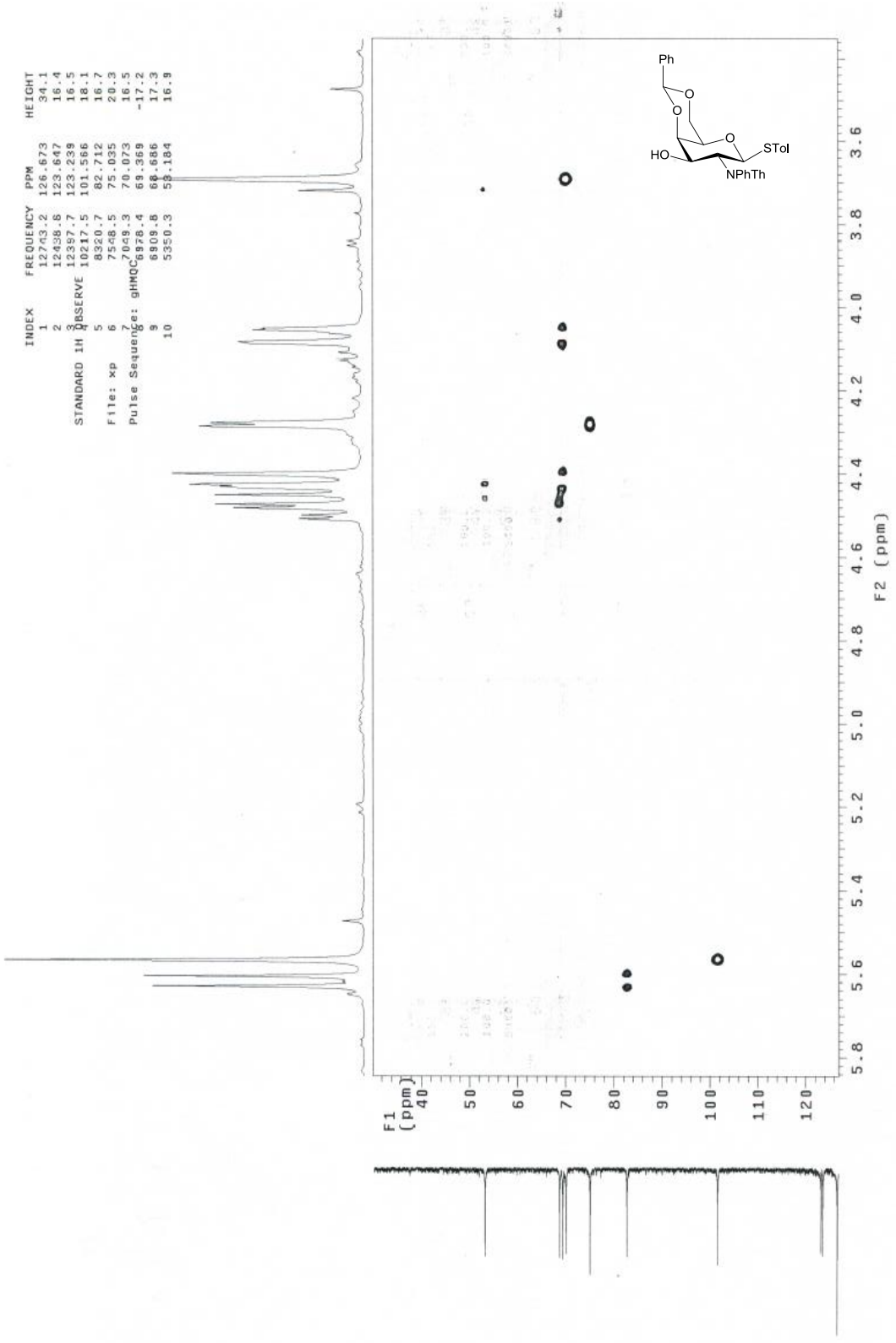
^{1}H NMR Spectrum of compound **8** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of compound **8** ($CDCl_3$, 400 MHz)

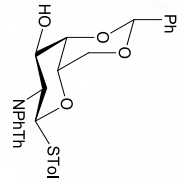


^{1}H-^{1}H COSY Spectrum of compound **8** ($CDCl_3$, 400 MHz)



^{1}H-^{13}C HMQC NMR Spectrum of compound **8** ($CDCl_3$, 400/100 MHz)

Elemental Composition Report



Single Mass Analysis

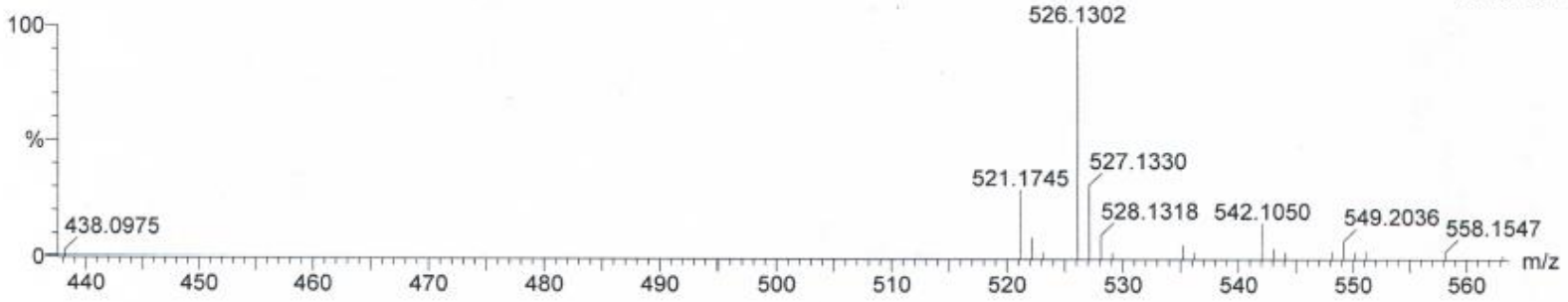
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
1271 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-1000 N: 0-3 O: 0-15 23Na: 0-1 S: 1-2

SATADRU MANDAL SSM-Gal-Amine-Acceptor

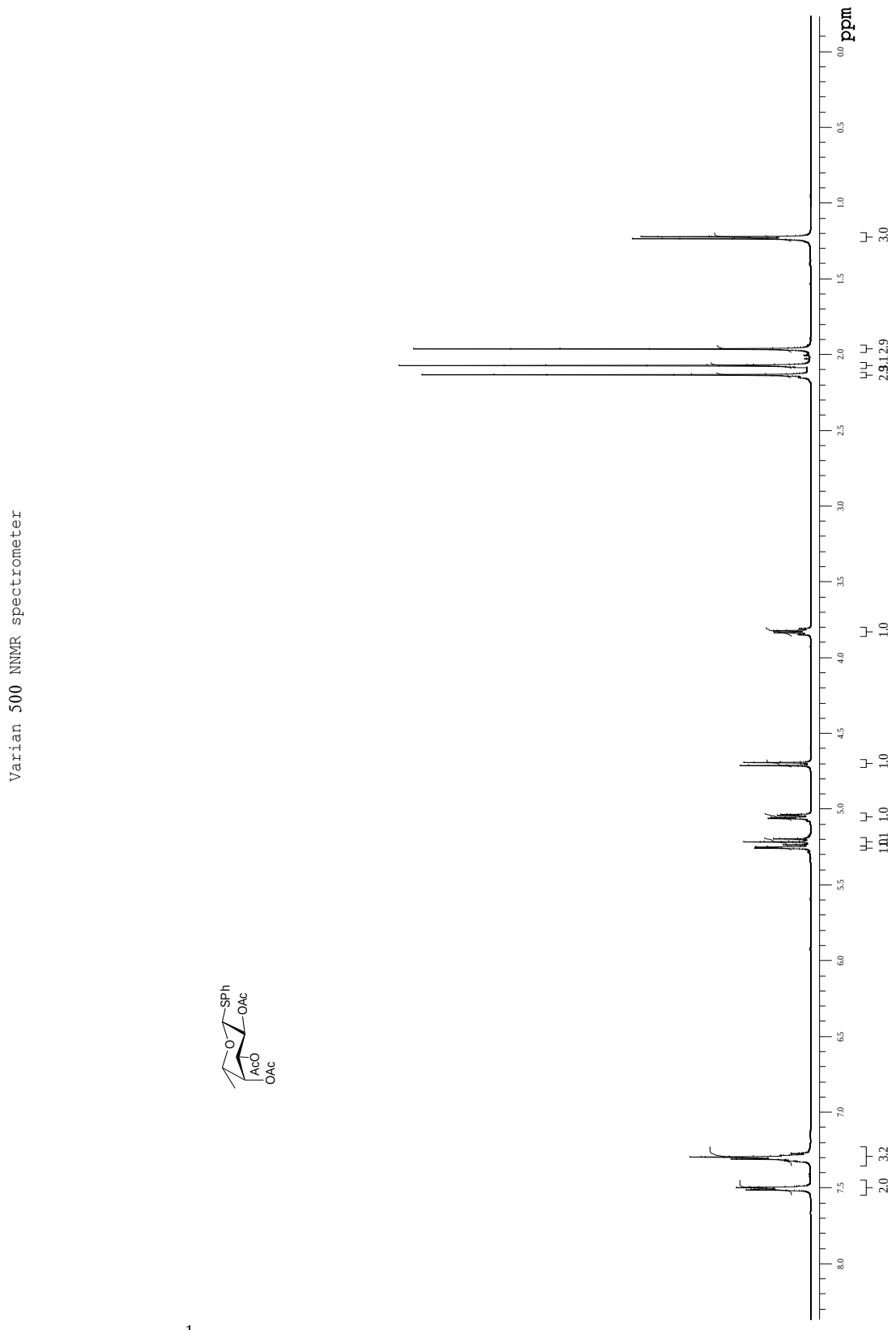
2013_0130_3056 20 (0.405) Cm (20:25-1:8x2.000)

LCT2008-07b.pro 2010-cif.splLCT Premier
1: TOF MS ES+
1.64e+004

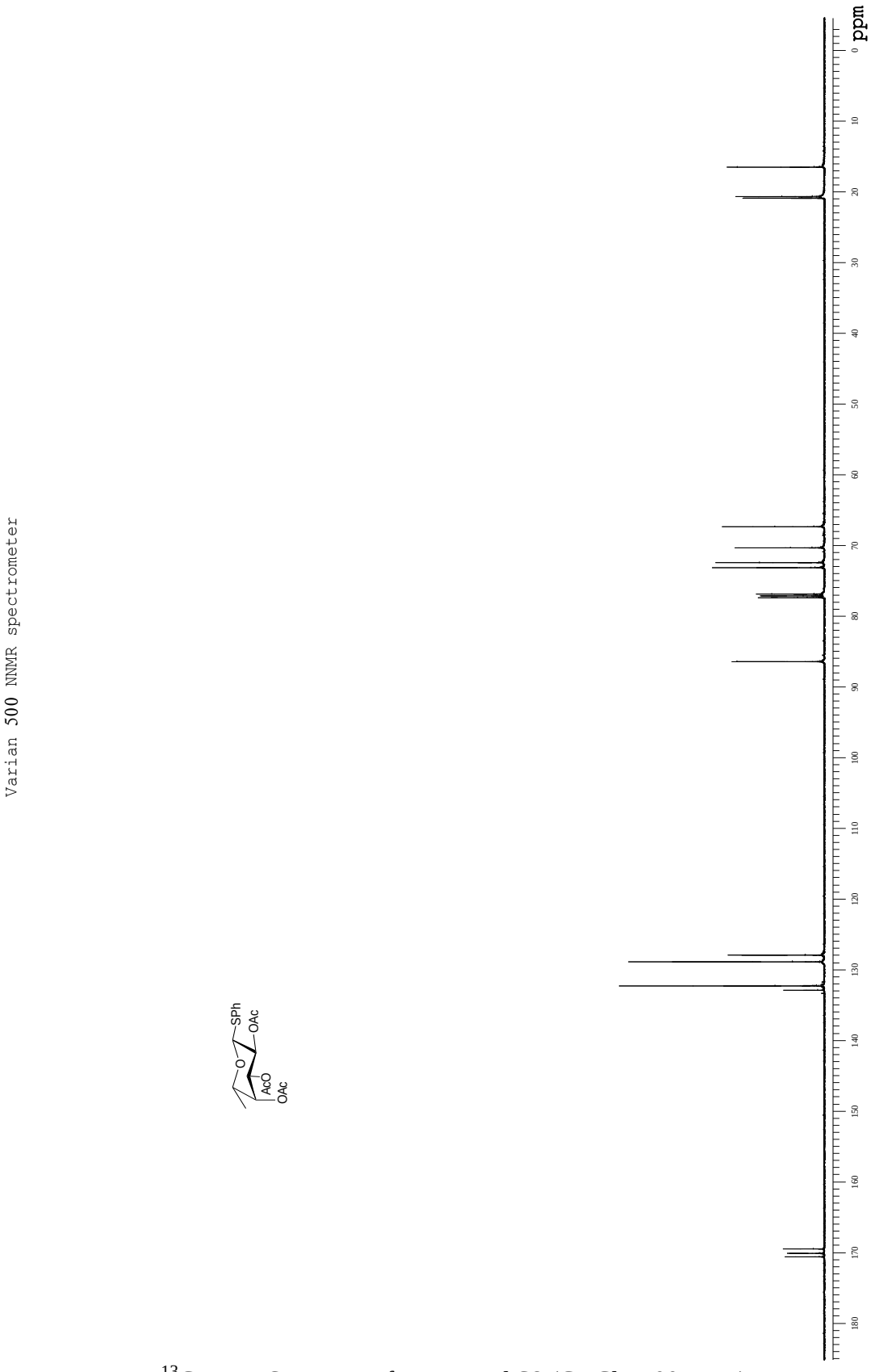


Minimum:				-1.5			
Maximum:		50.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
526.1302	526.1300	0.2	0.4	16.5	31.3	0.4	C28 H25 N O6 23Na S
	526.1284	1.8	3.4	15.5	32.6	1.7	C25 H24 N3 O8 S
	526.1319	-1.7	-3.2	3.5	33.0	2.1	C16 H29 N3 O13 23Na S

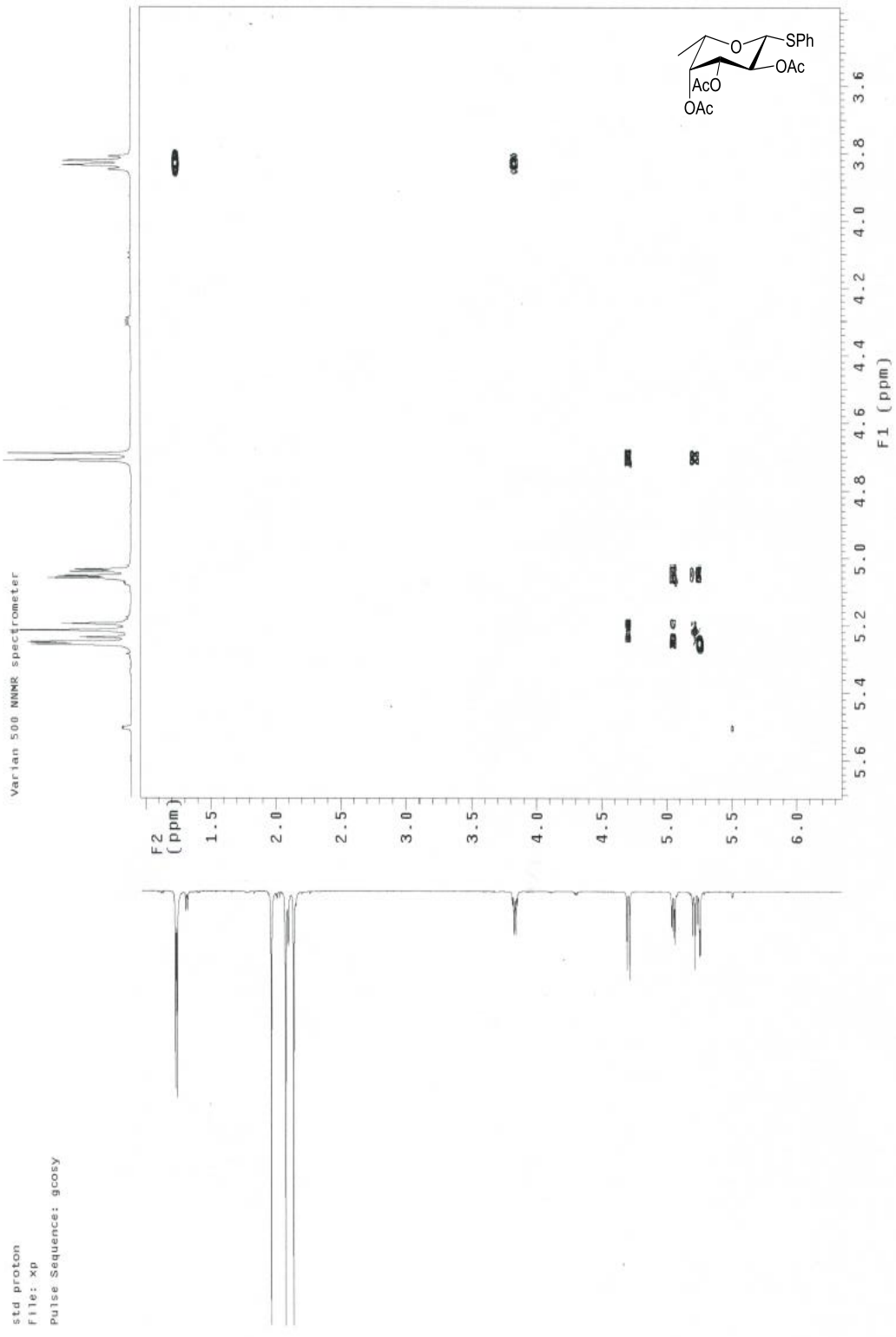
HRMS (ESI MS) spectrum of compound **8**



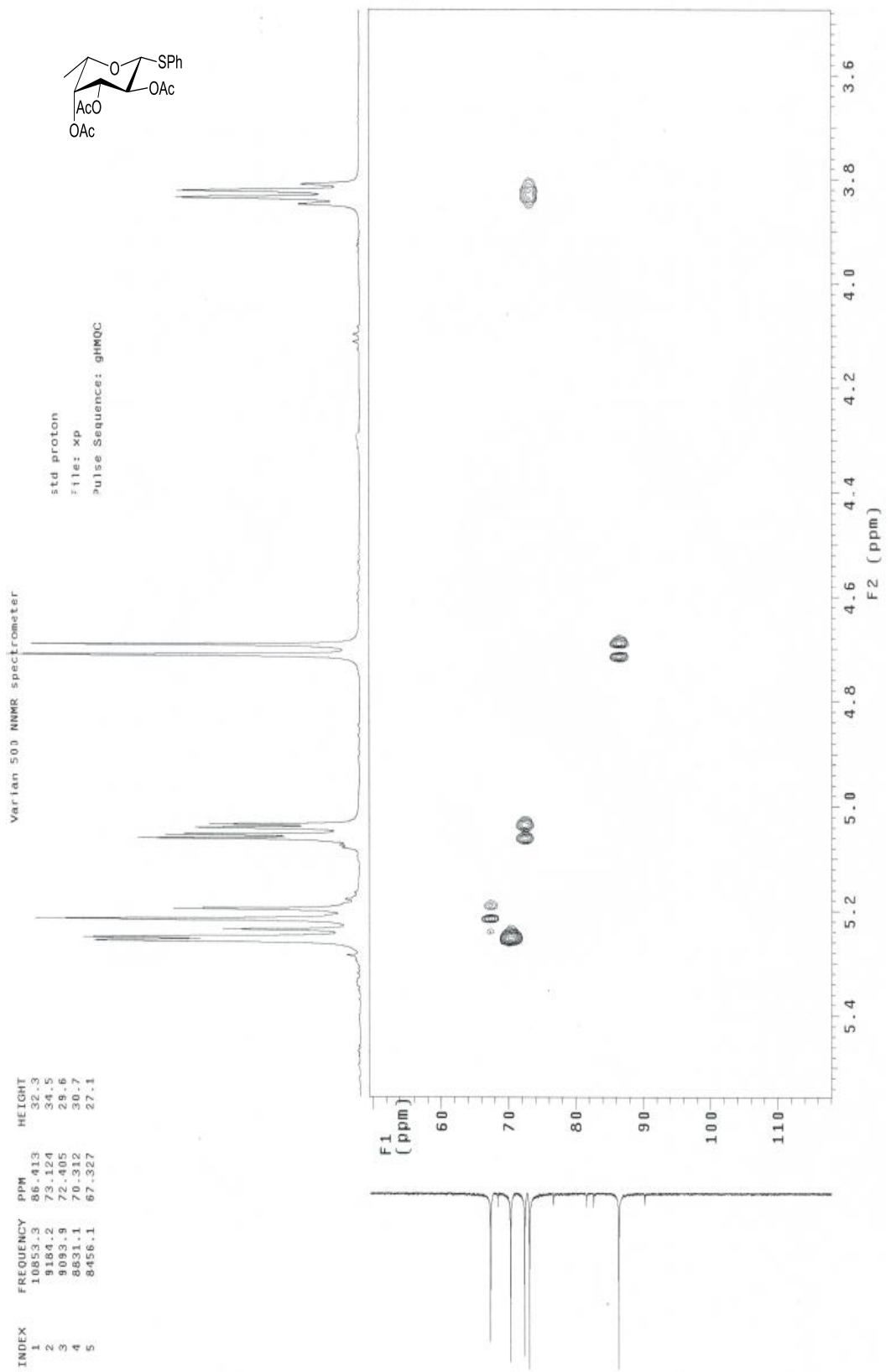
^{1}H NMR Spectrum of compound **S8** ($CDCl_3$, 500 MHz)



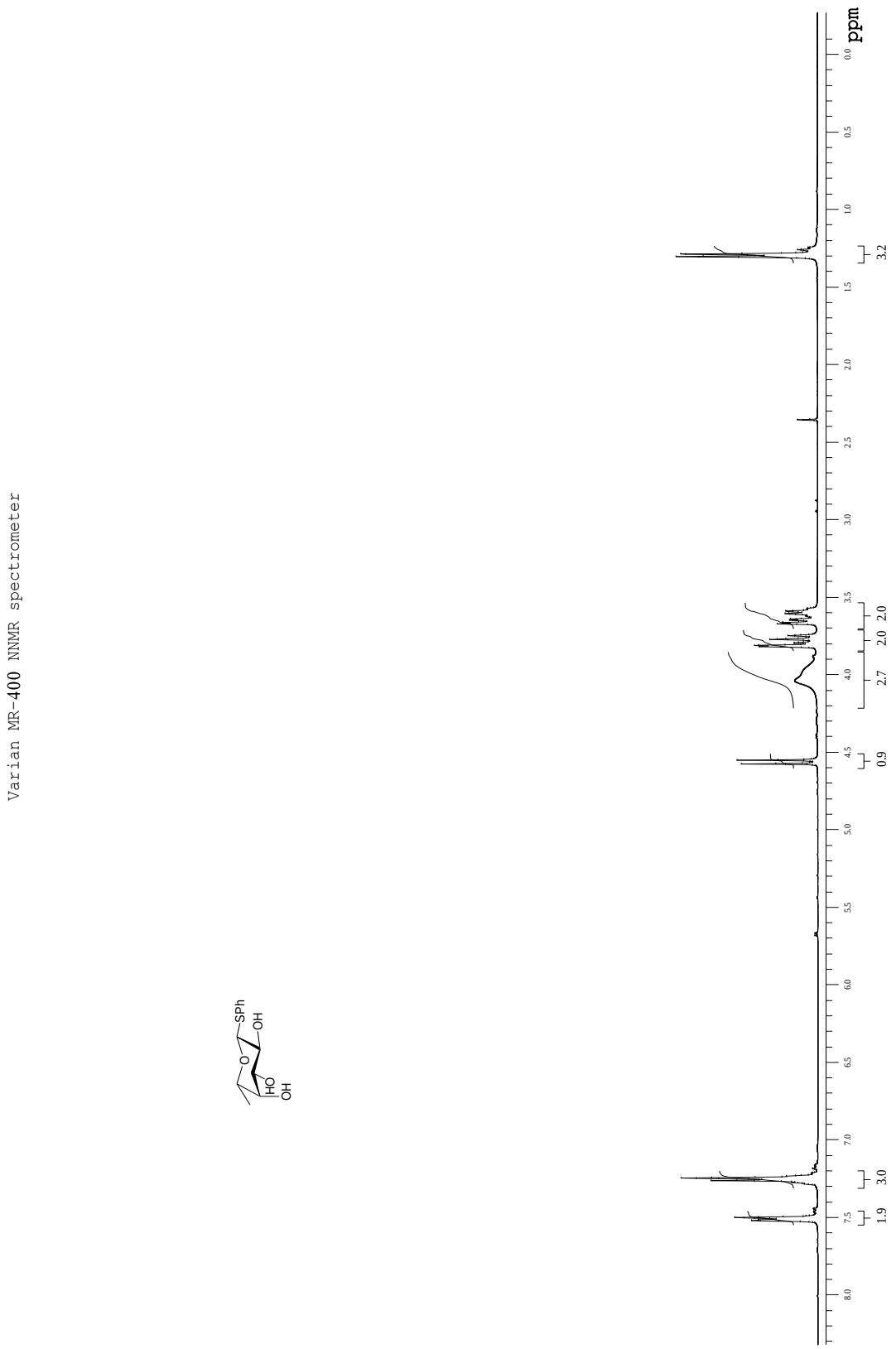
^{13}C NMR Spectrum of compound **S8** ($CDCl_3$, 500 MHz)



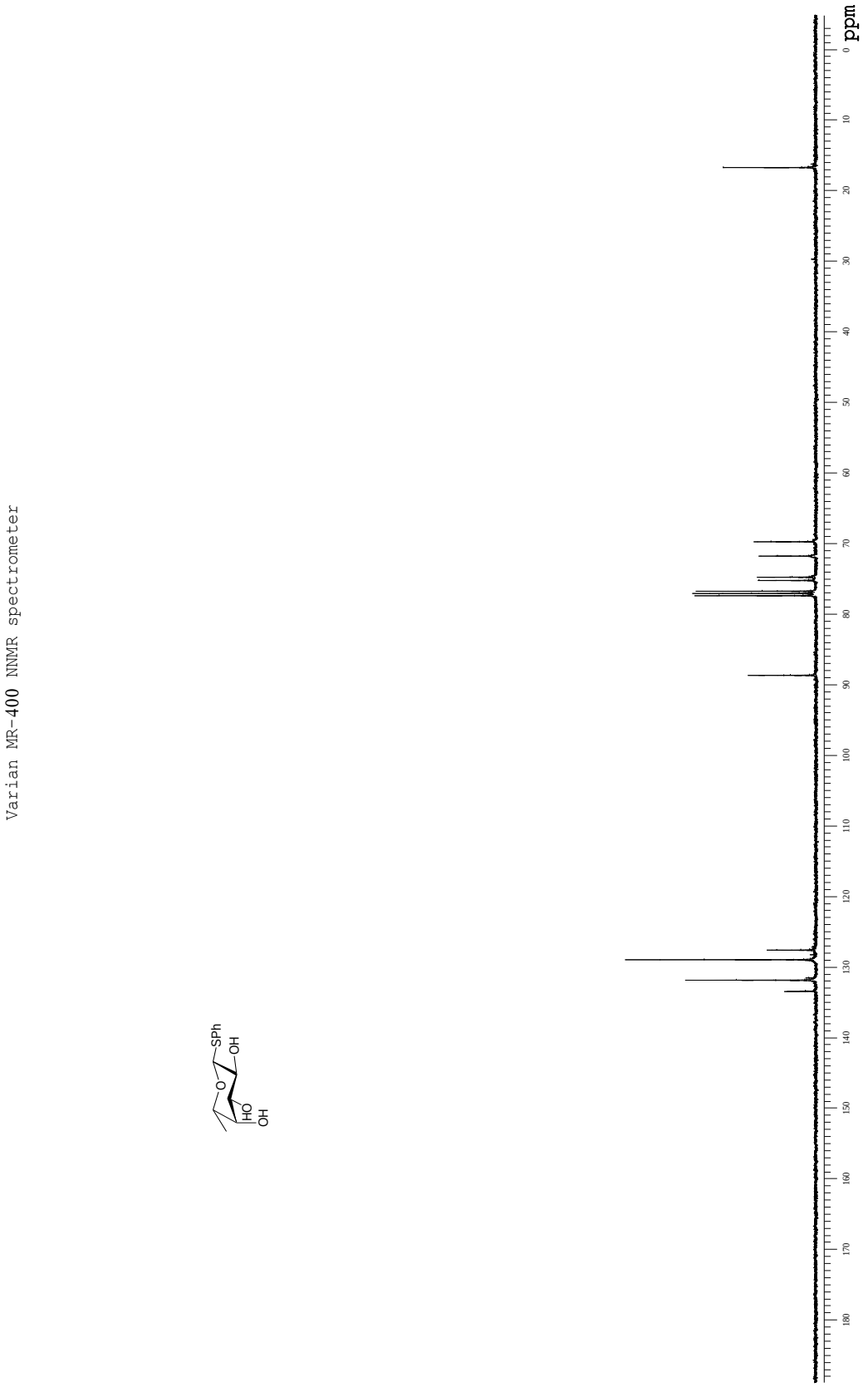
^{1}H-^{1}H COSY Spectrum of compound **S8** ($CDCl_3$, 500 MHz)



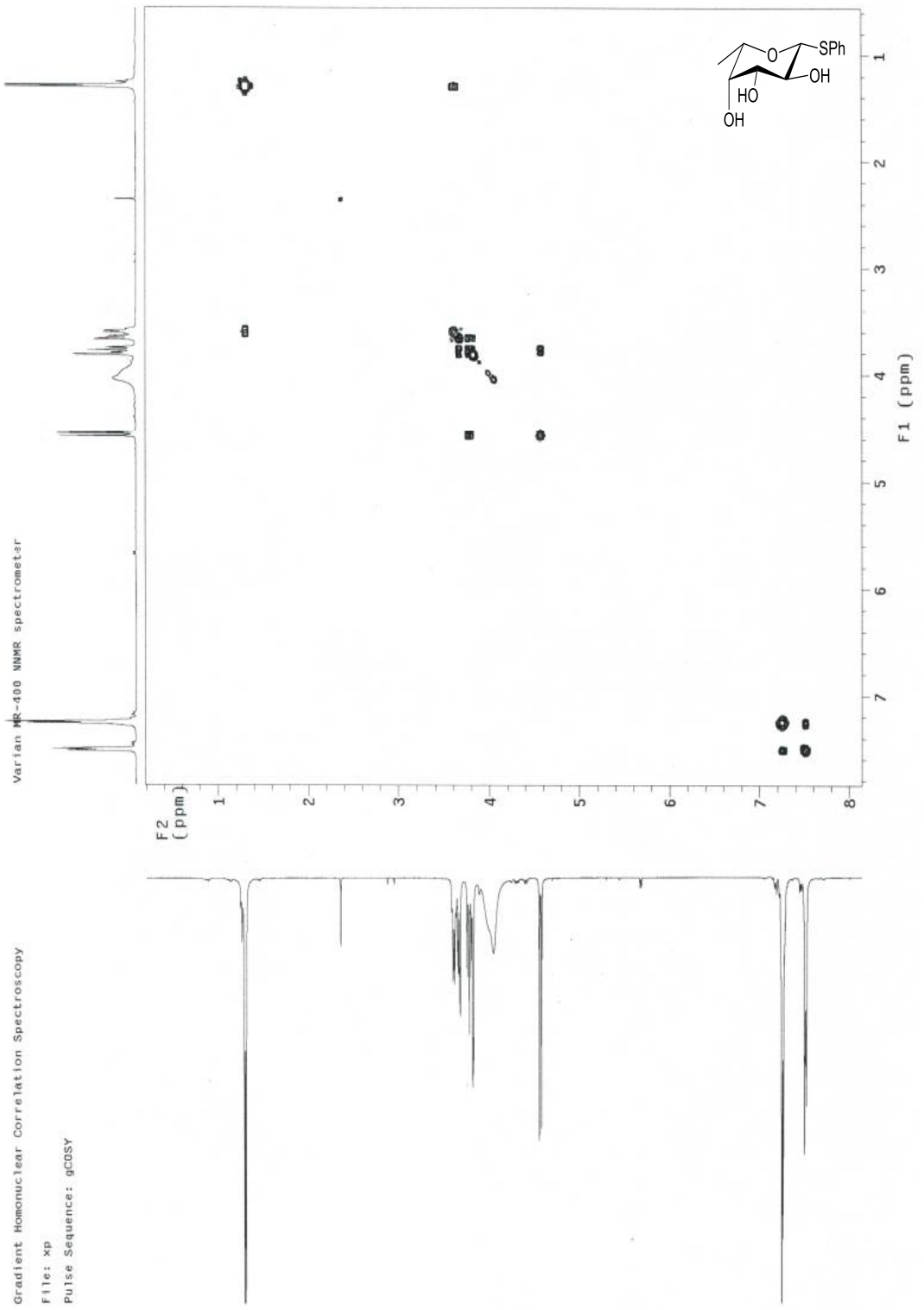
^{1}H-^{13}C HMQC NMR Spectrum of compound **S8** ($CDCl_3$, 500/125 MHz)



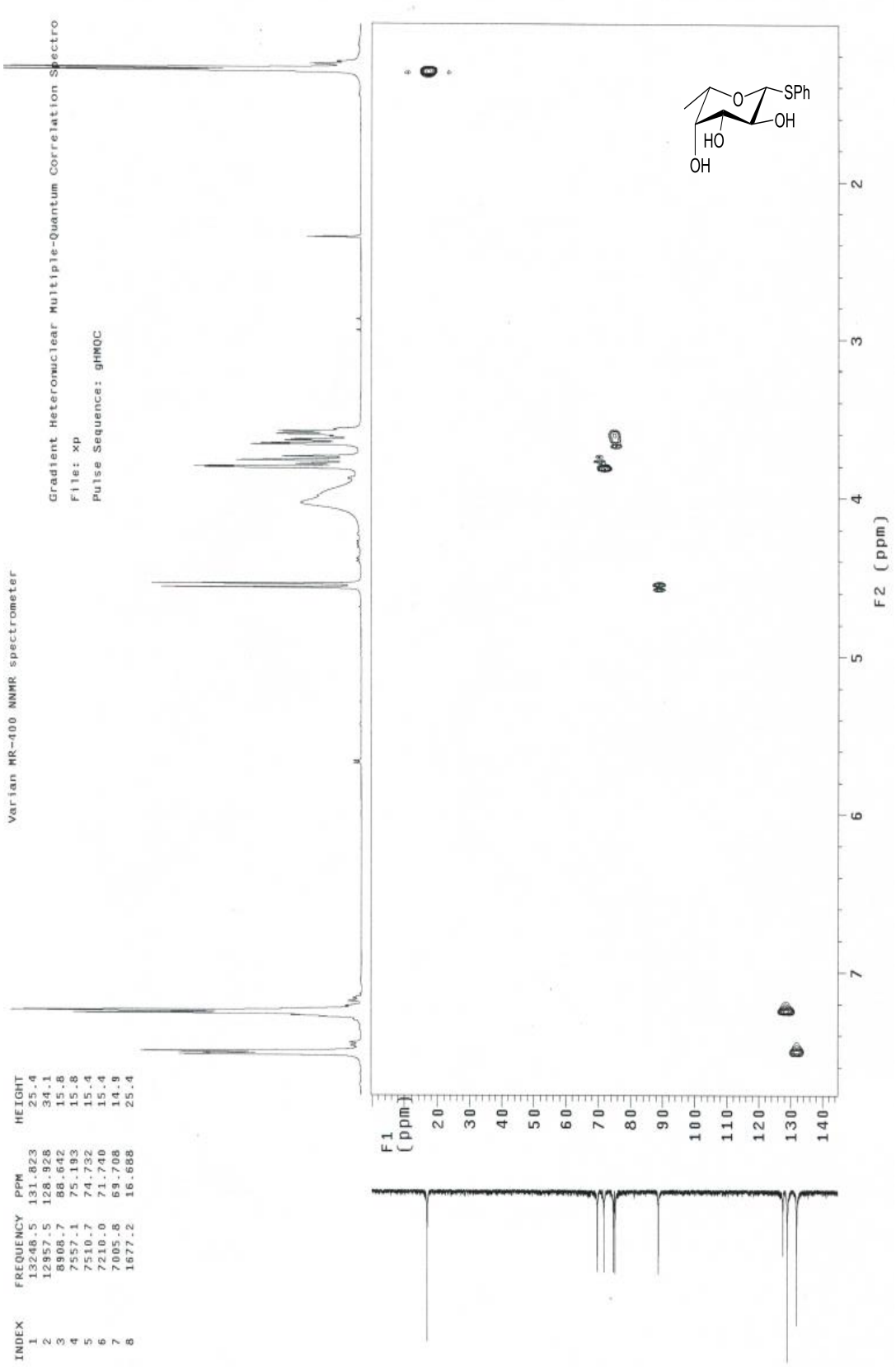
^{1}H NMR Spectrum of compound **S9** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of compound **S9** ($CDCl_3$, 400 MHz)

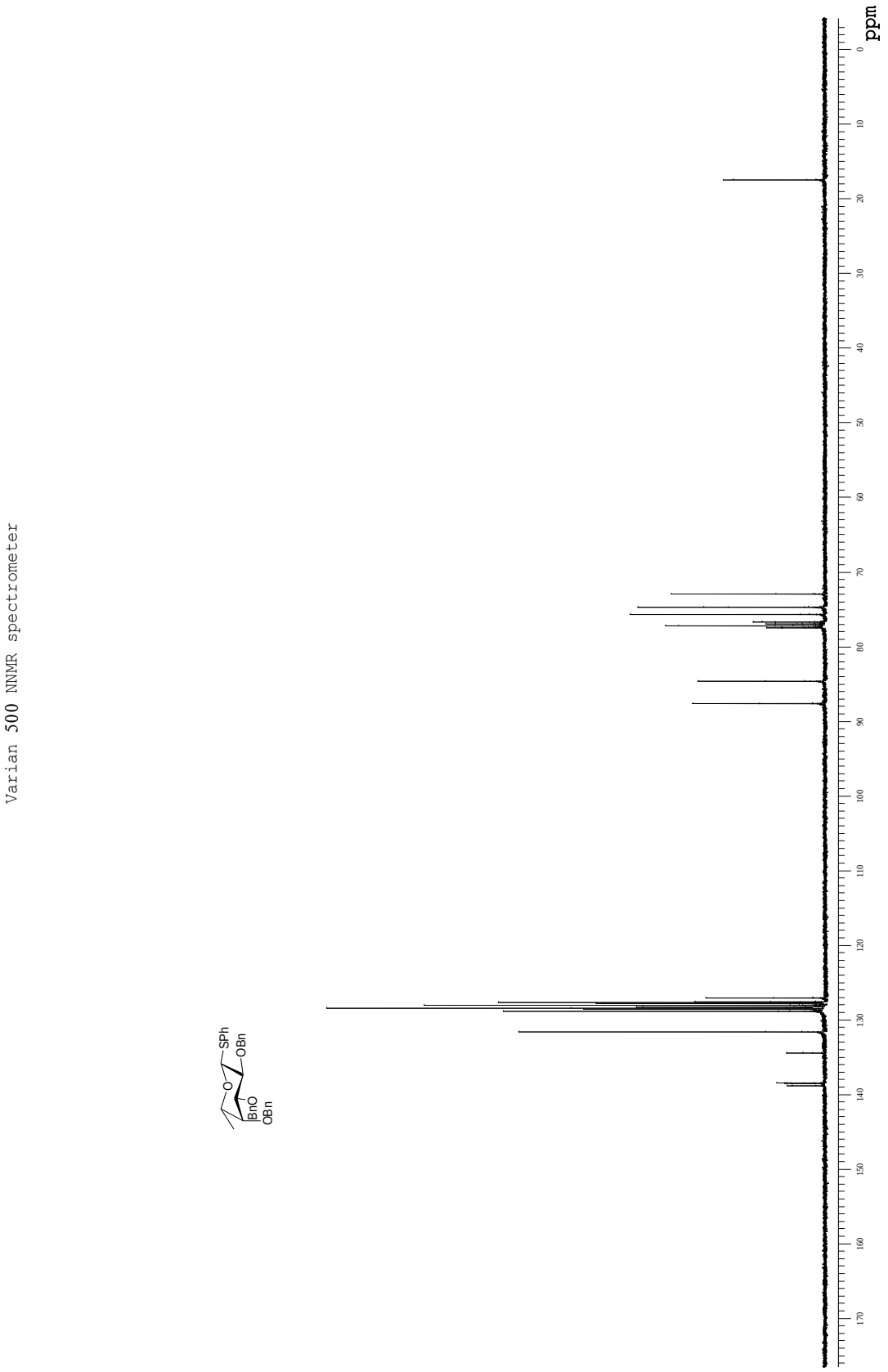


^{1}H-^{1}H COSY Spectrum of compound **S9** ($CDCl_3$, 400 MHz)

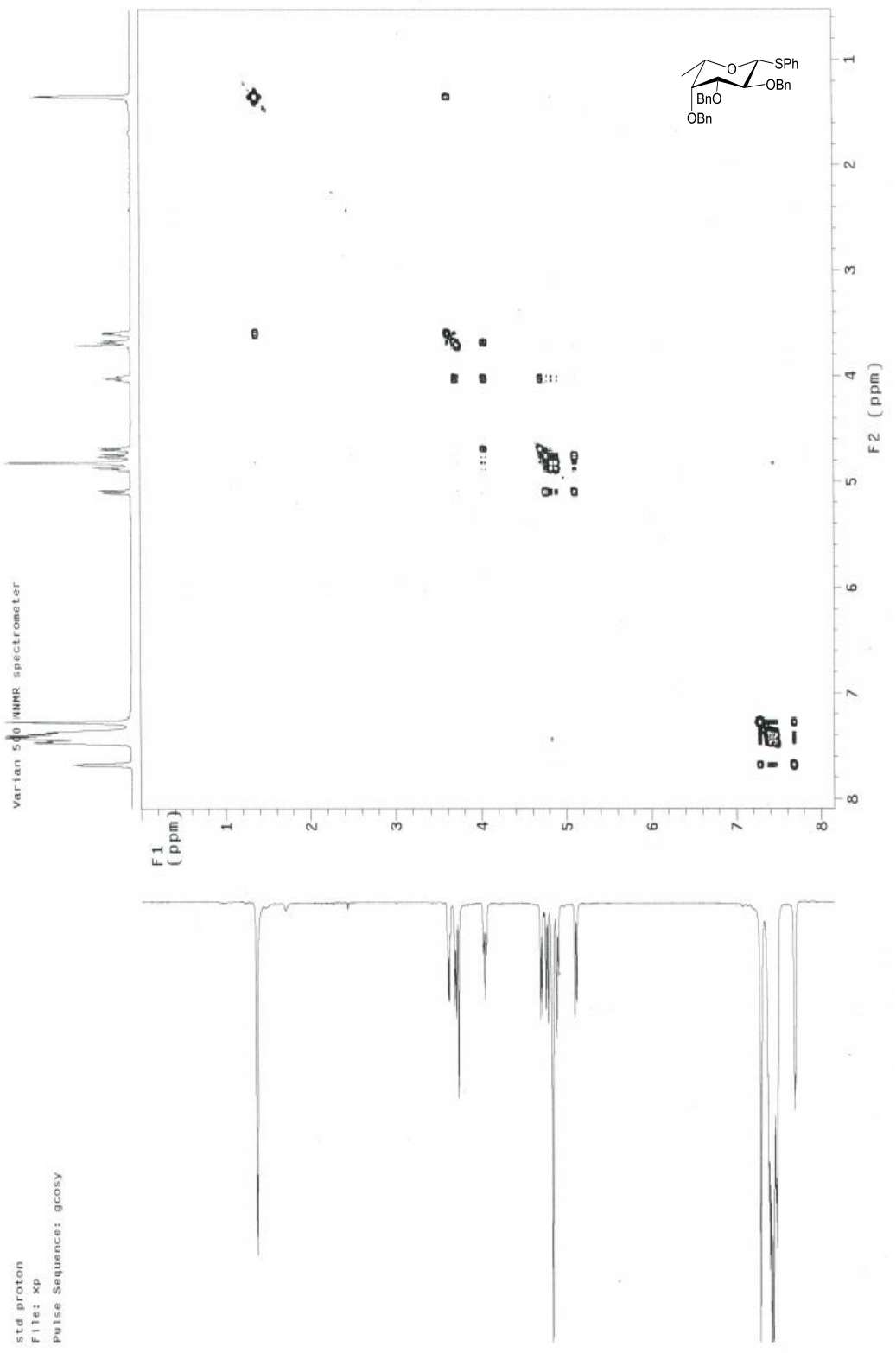


^{1}H-^{13}C HMQC NMR Spectrum of compound **S9** ($CDCl_3$, 400/100 MHz)

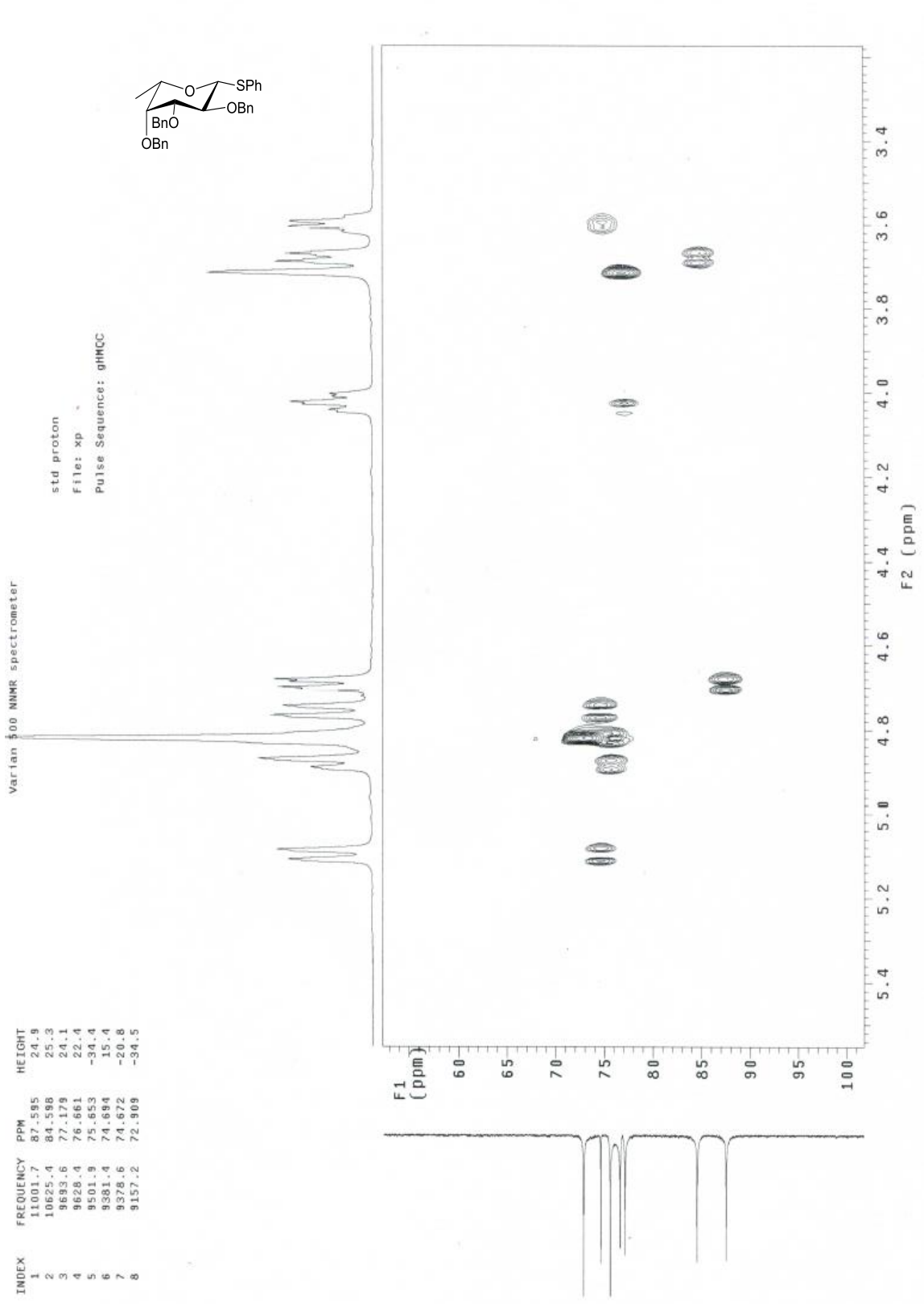
^{1}H NMR Spectrum of compound **4** ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of compound **4** ($CDCl_3$, 500 MHz)

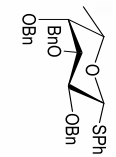


^{1}H-^{1}H COSY Spectrum of compound **4** ($CDCl_3$, 500 MHz)



^{1}H-^{13}C HMQC NMR Spectrum of compound **4** ($CDCl_3$, 500/125 MHz)

Elemental Composition Report **Page 1**

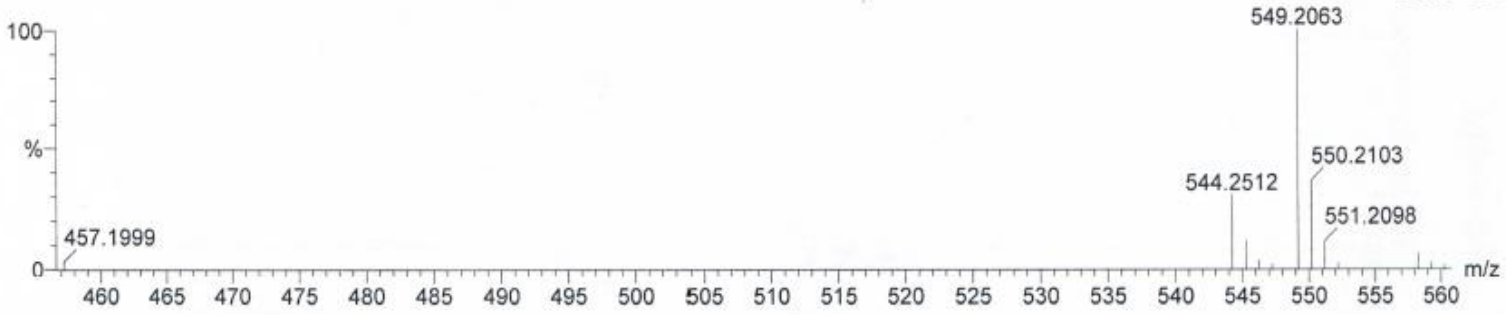


Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

Monoisotopic Mass, Even Electron Ions
1007 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-1000 N: 0-3 O: 0-10 23Na: 0-1 S: 1-2
SATADRU MANDAL SSM-F-SPh

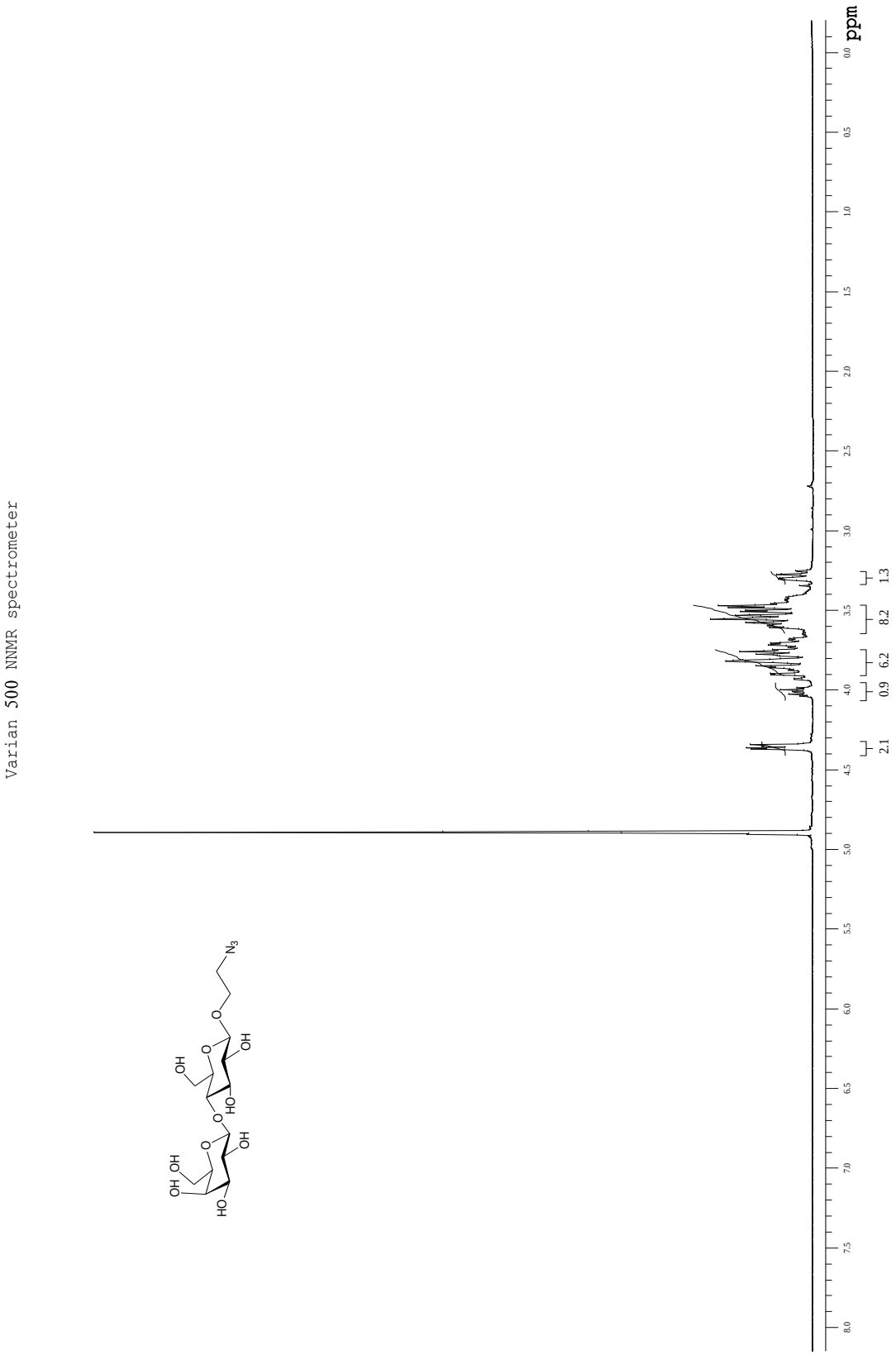
LCT2008-07b.pro 2010-cif.splLCT Premier
1: TOF MS ES+
5.84e+004

2013_0131_3060 22 (0.460) Cm (22:29-1:8x2.000)

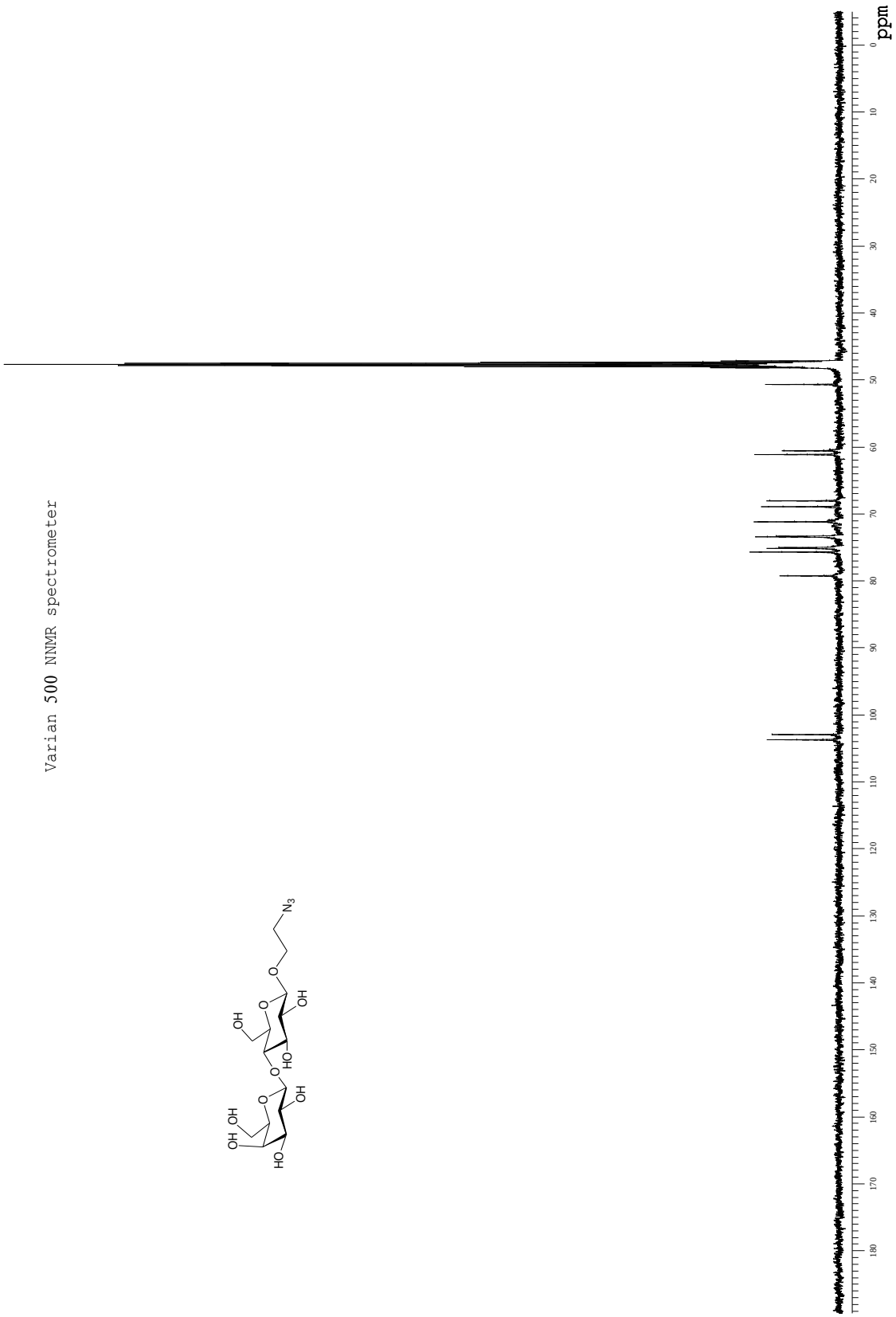


Minimum:				-1.5			
Maximum:		50.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
549.2063	549.2076	-1.3	-2.4	16.5	42.6	0.5	C33 H34 O4 23Na S
	549.2059	0.4	0.7	15.5	43.2	1.0	C30 H33 N2 O6 S
	549.2069	-0.6	-1.1	7.5	49.2	7.1	C25 H38 N2 O6 23Na S2

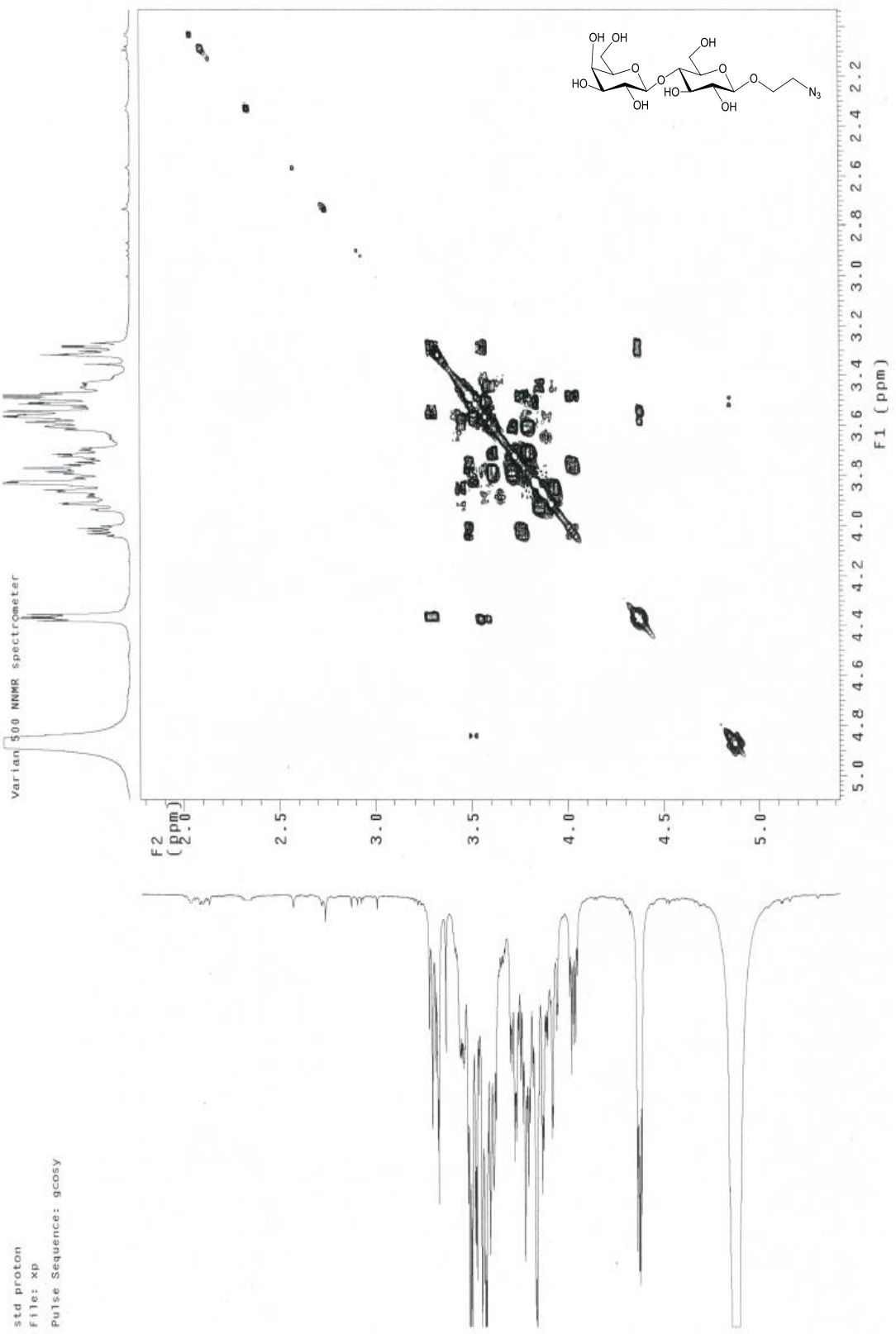
HRMS (ESI MS) spectrum of compound **4**



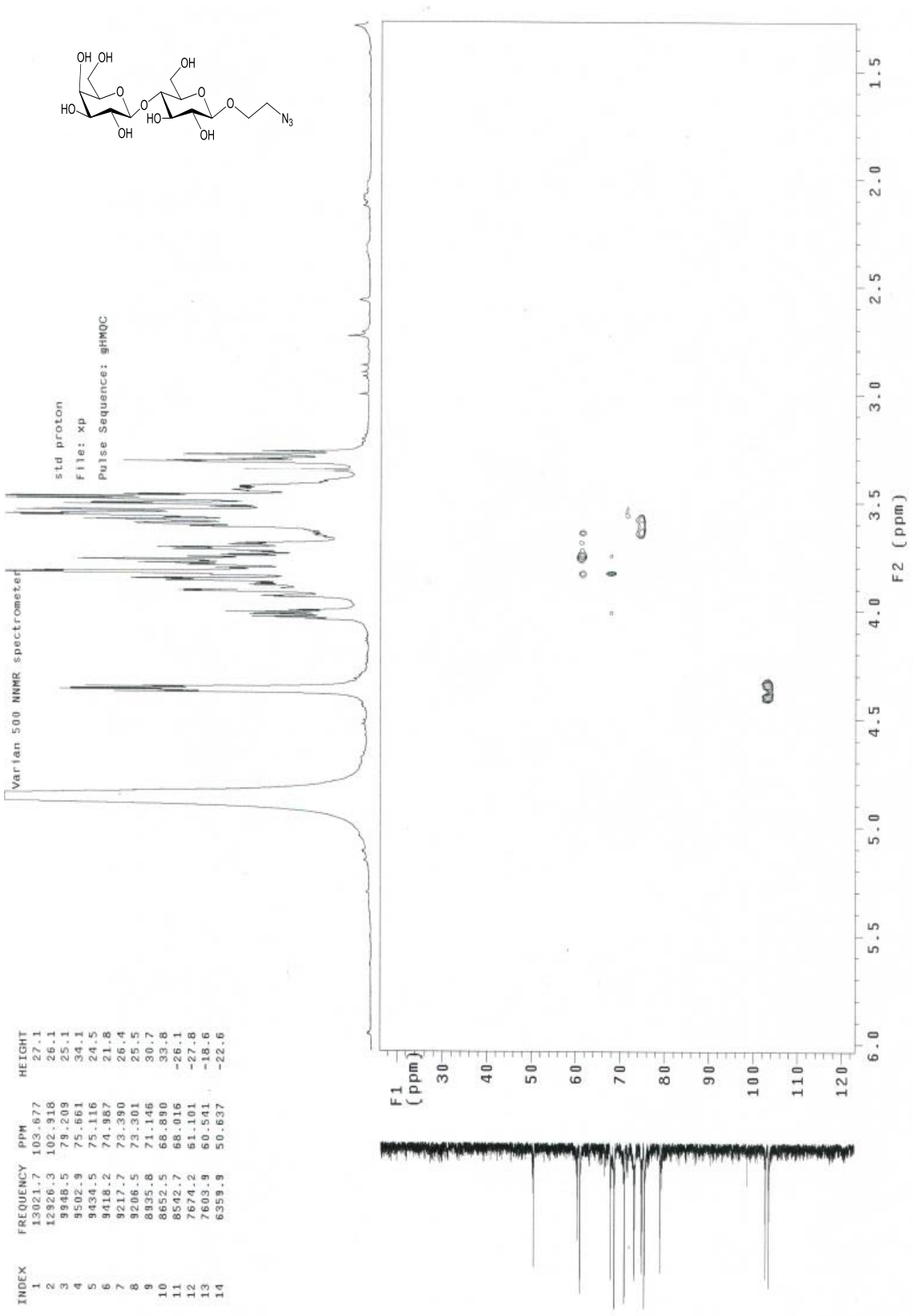
^{1}H NMR Spectrum of compound **15** (CD_3OD, 500 MHz)



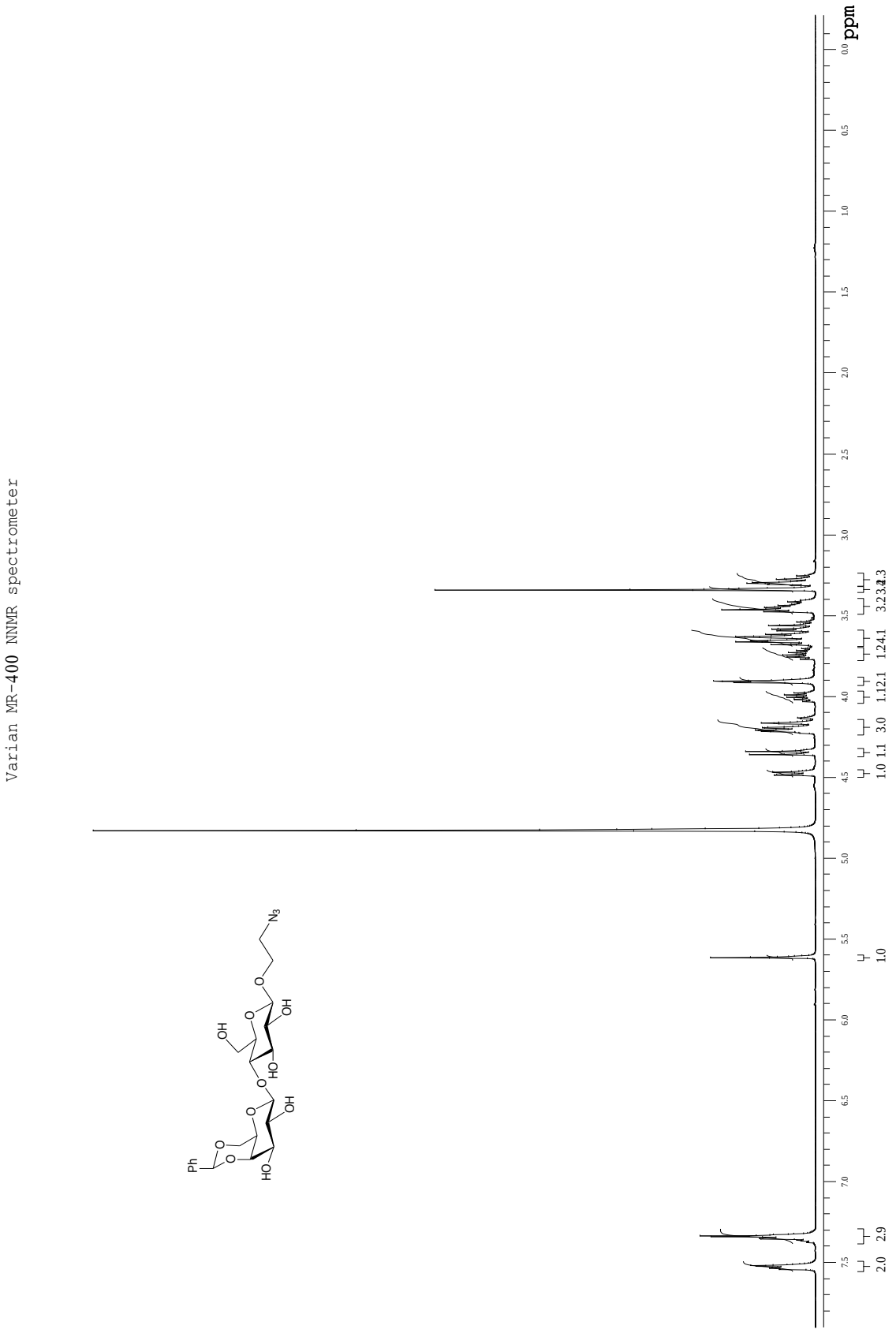
^{13}C NMR Spectrum of compound **15** (CD_3OD, 500 MHz)



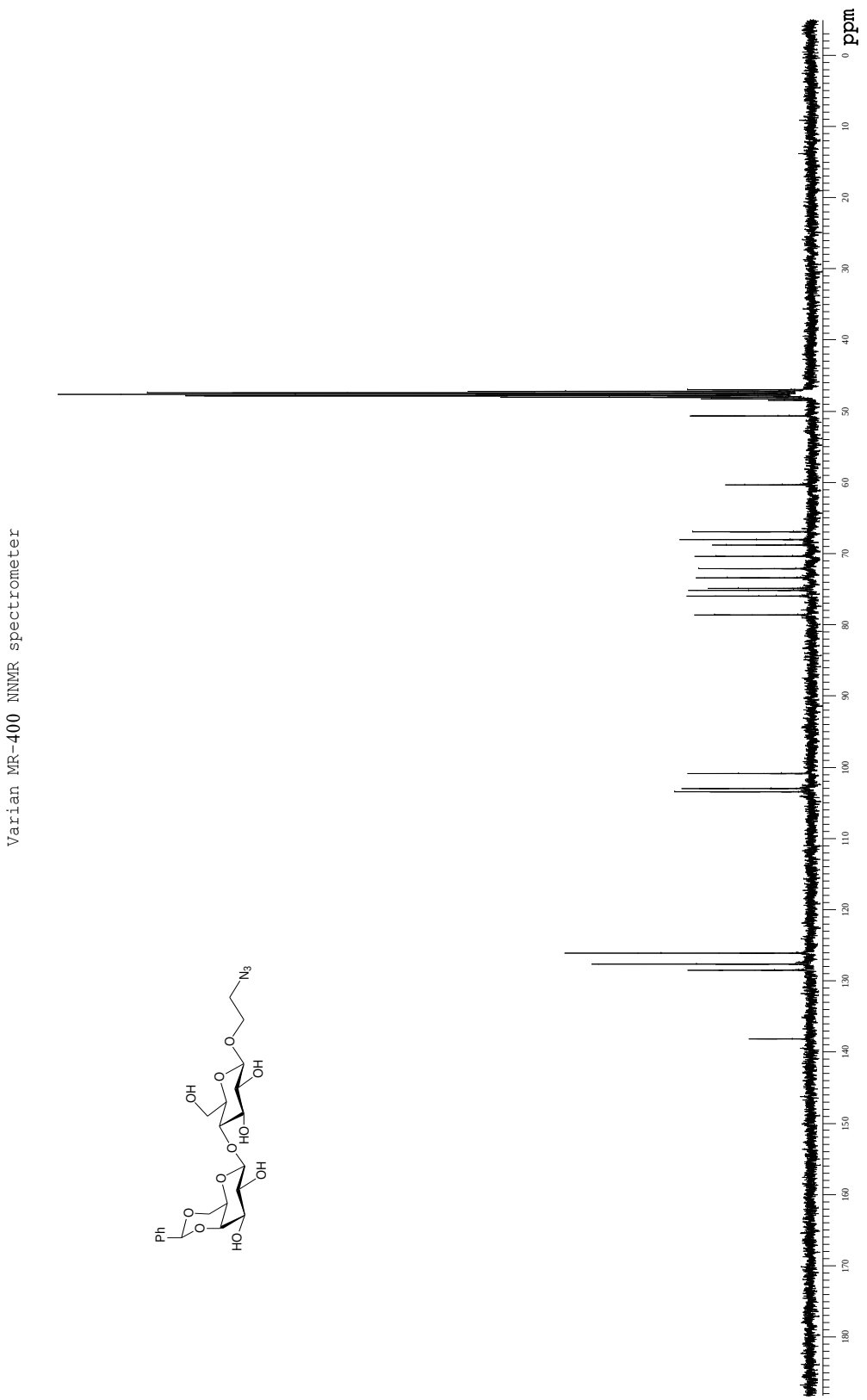
^{1}H-^{1}H COSY Spectrum of compound **15** (CD_3OD, 500 MHz)



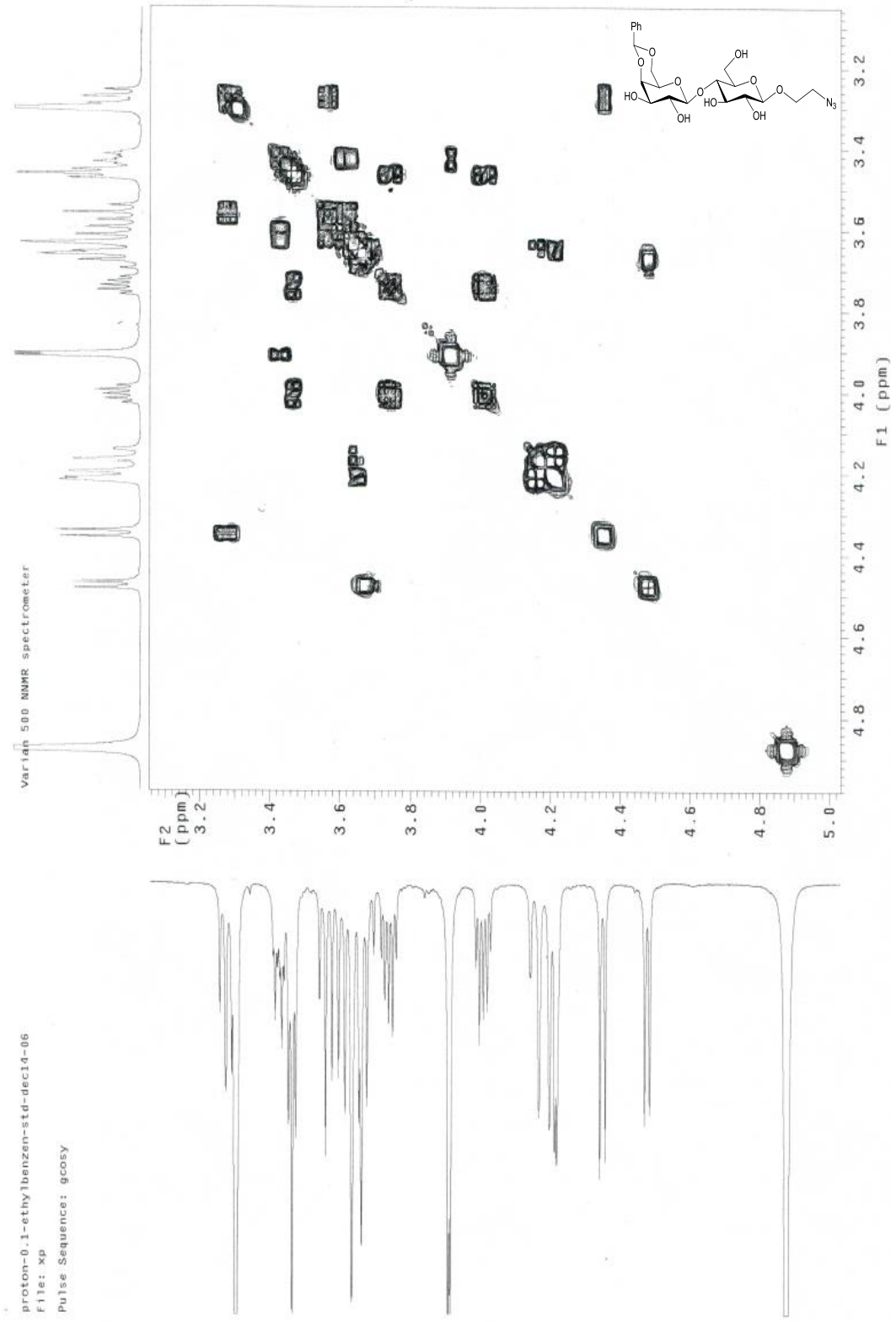
^{1}H-^{13}C HMQC NMR Spectrum of compound **15** (CD_3OD, 500/125 MHz)



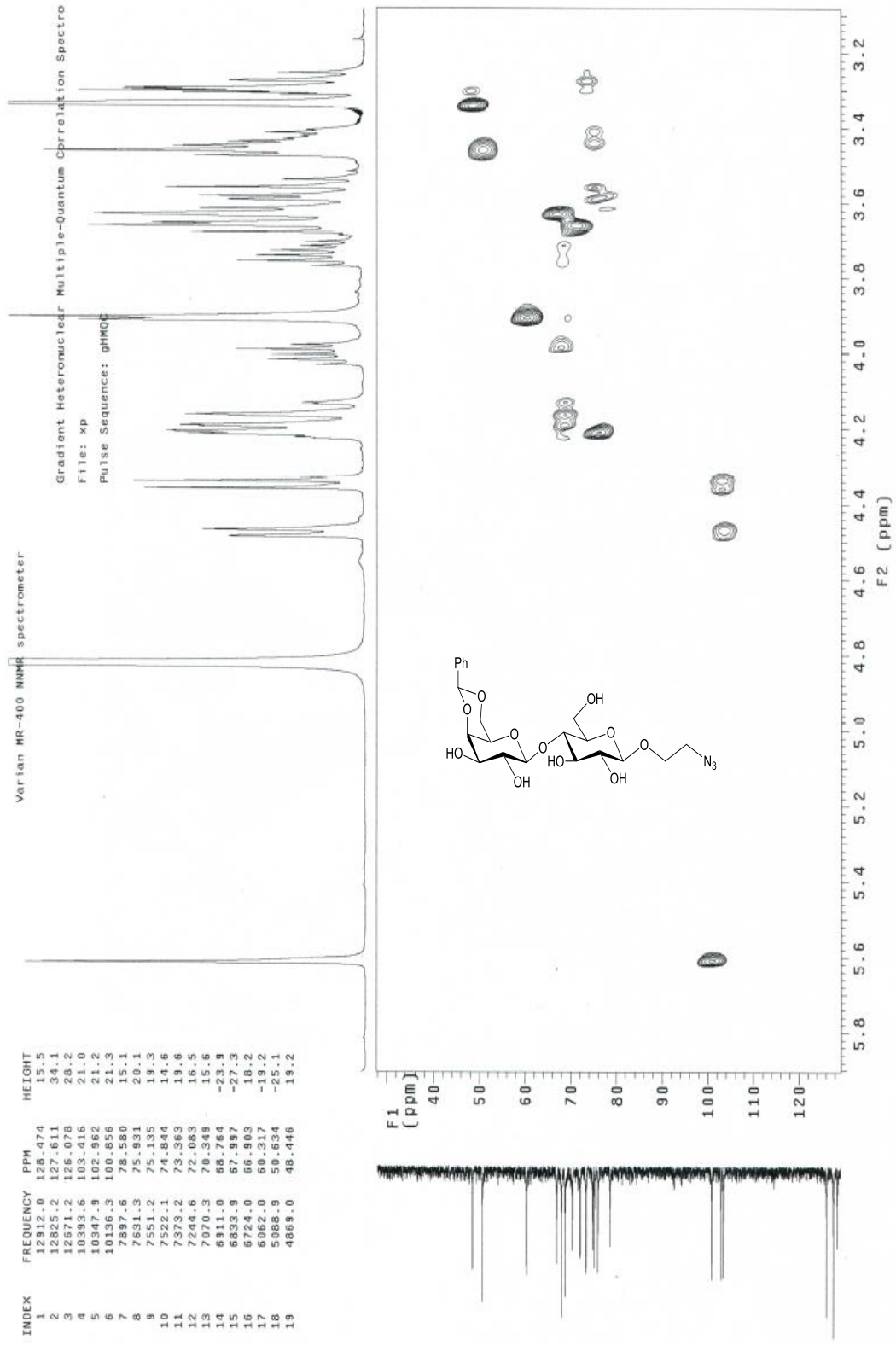
^{1}H NMR Spectrum of compound **16** (CD_3OD, 400 MHz)



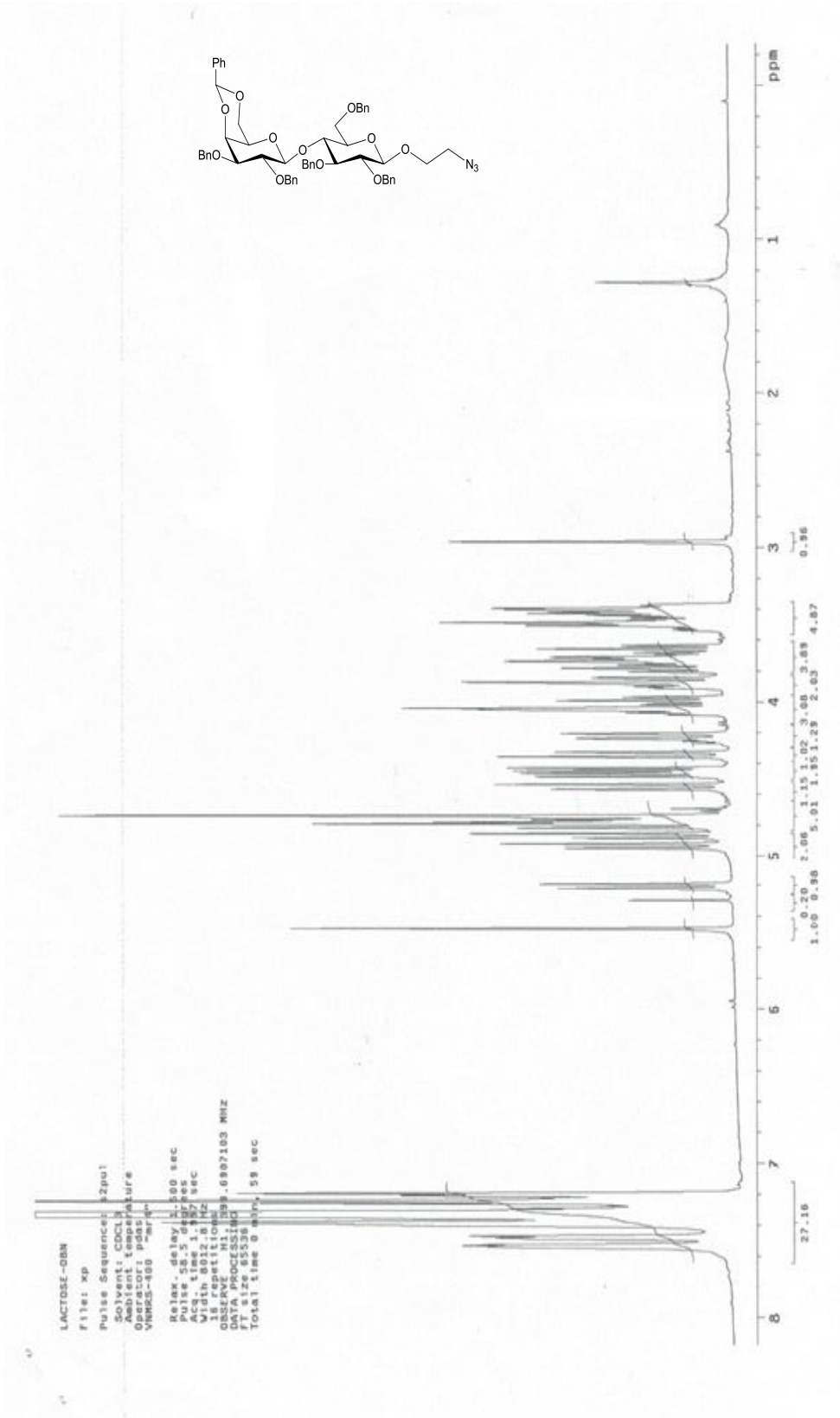
^{13}C NMR Spectrum of compound **16** (CD_3OD, 400 MHz)



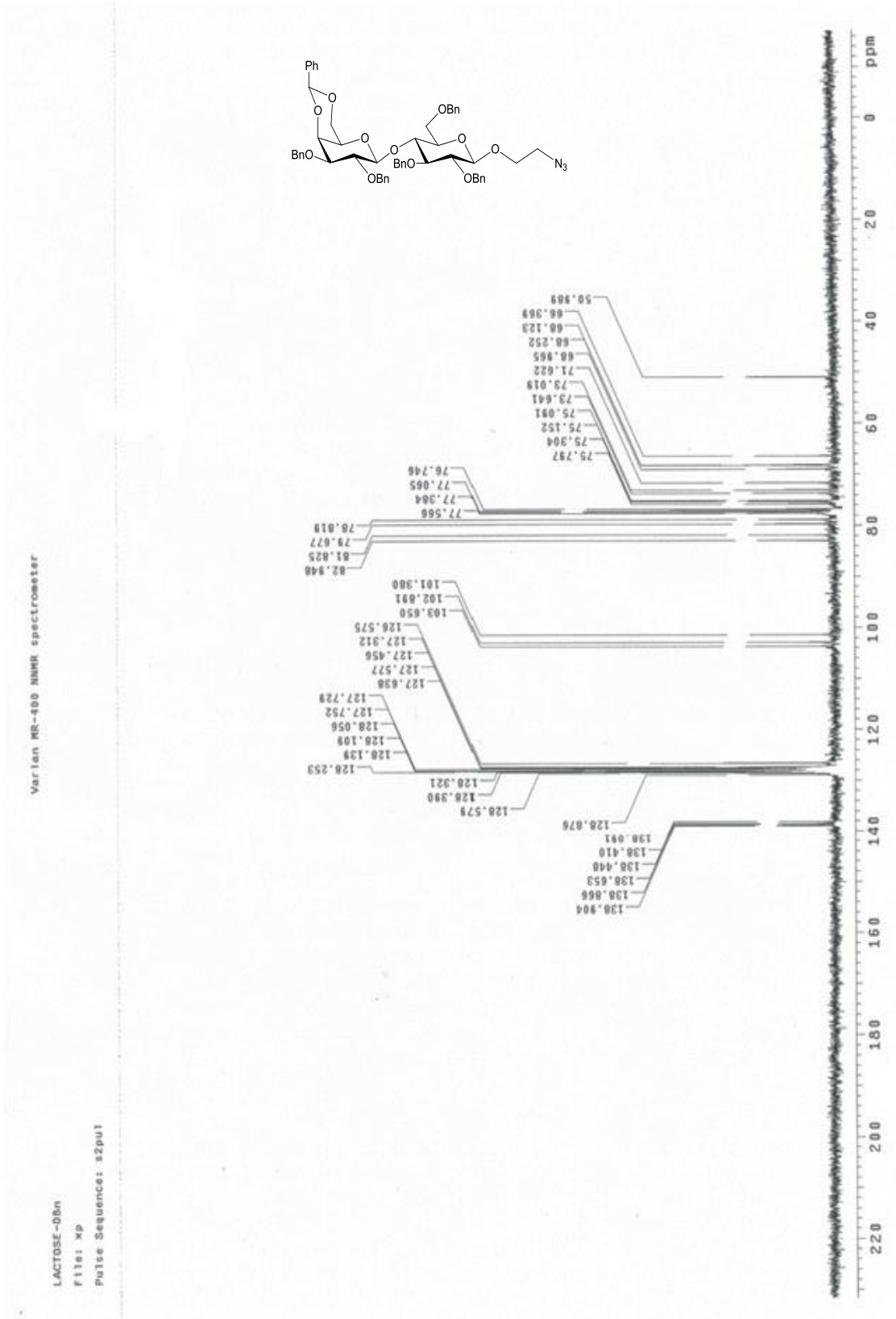
^{1}H-^{1}H COSY Spectrum of compound **16** (CD_3OD, 500 MHz)



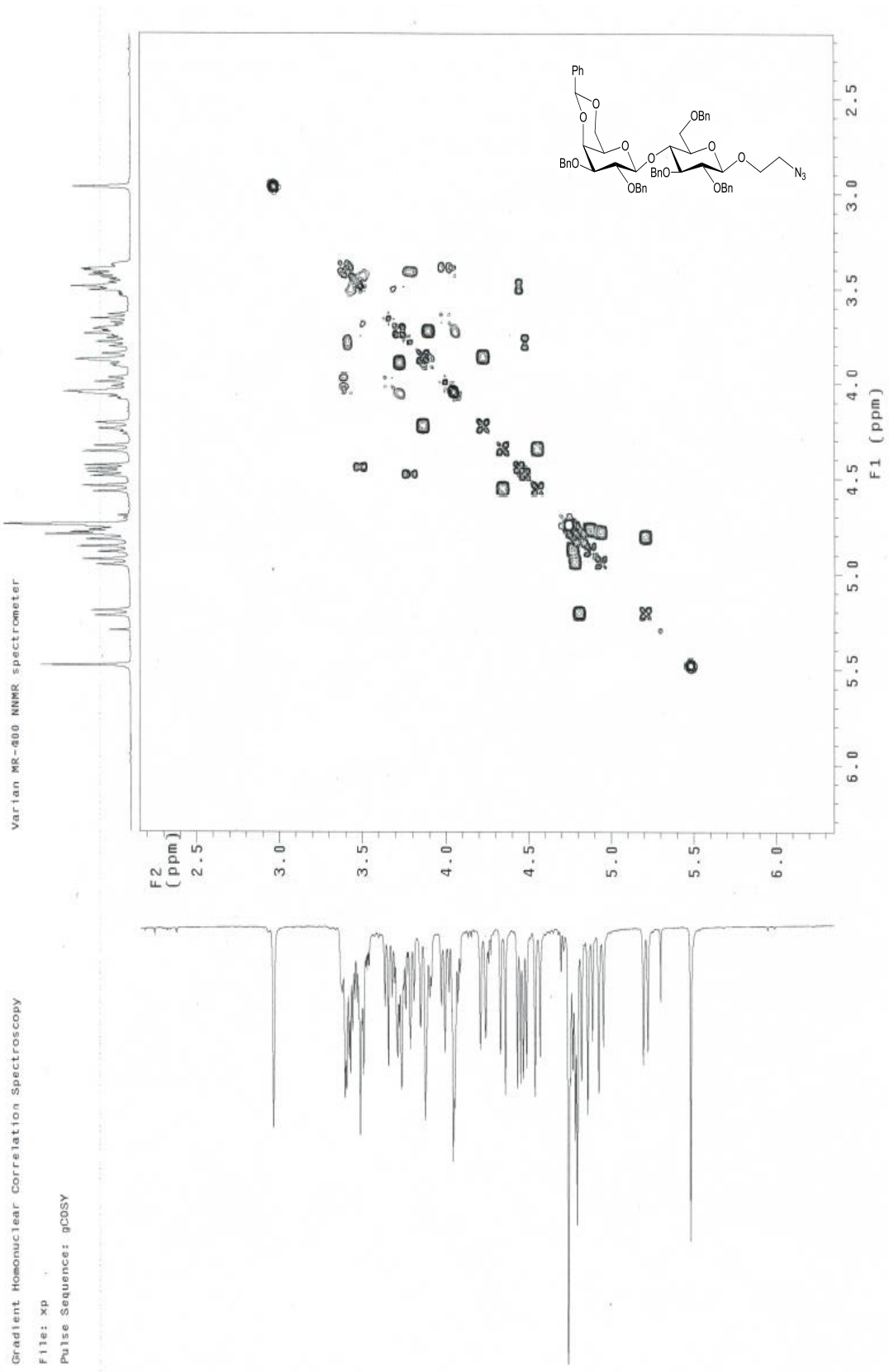
^{1}H-^{13}C HMQC NMR Spectrum of compound **16** (CD_3OD, 400/100 MHz)



^{1}H NMR Spectrum of compound **17** ($CDCl_3$, 400 MHz)

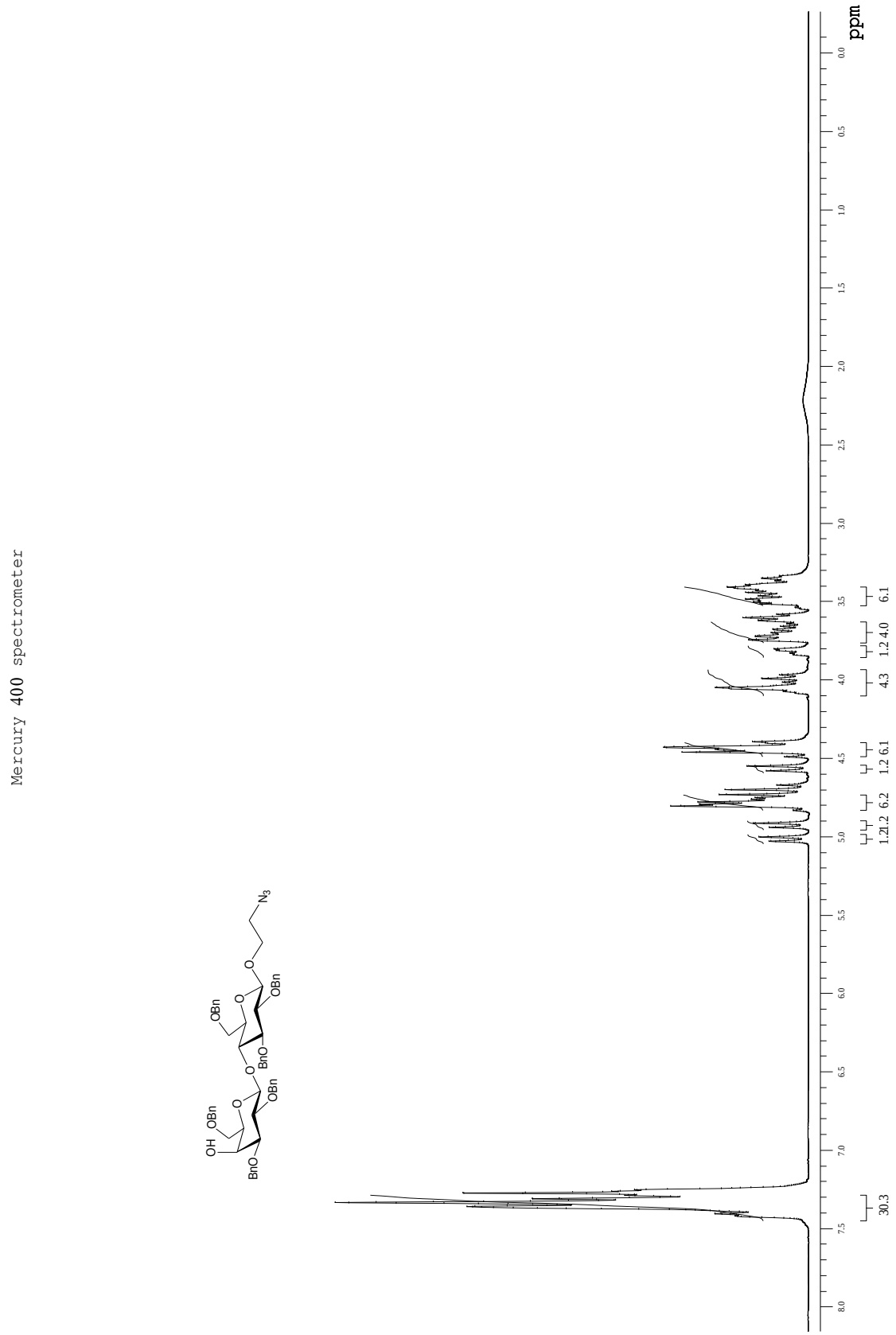


^{13}C NMR Spectrum of compound **17** ($CDCl_3$, 400 MHz)

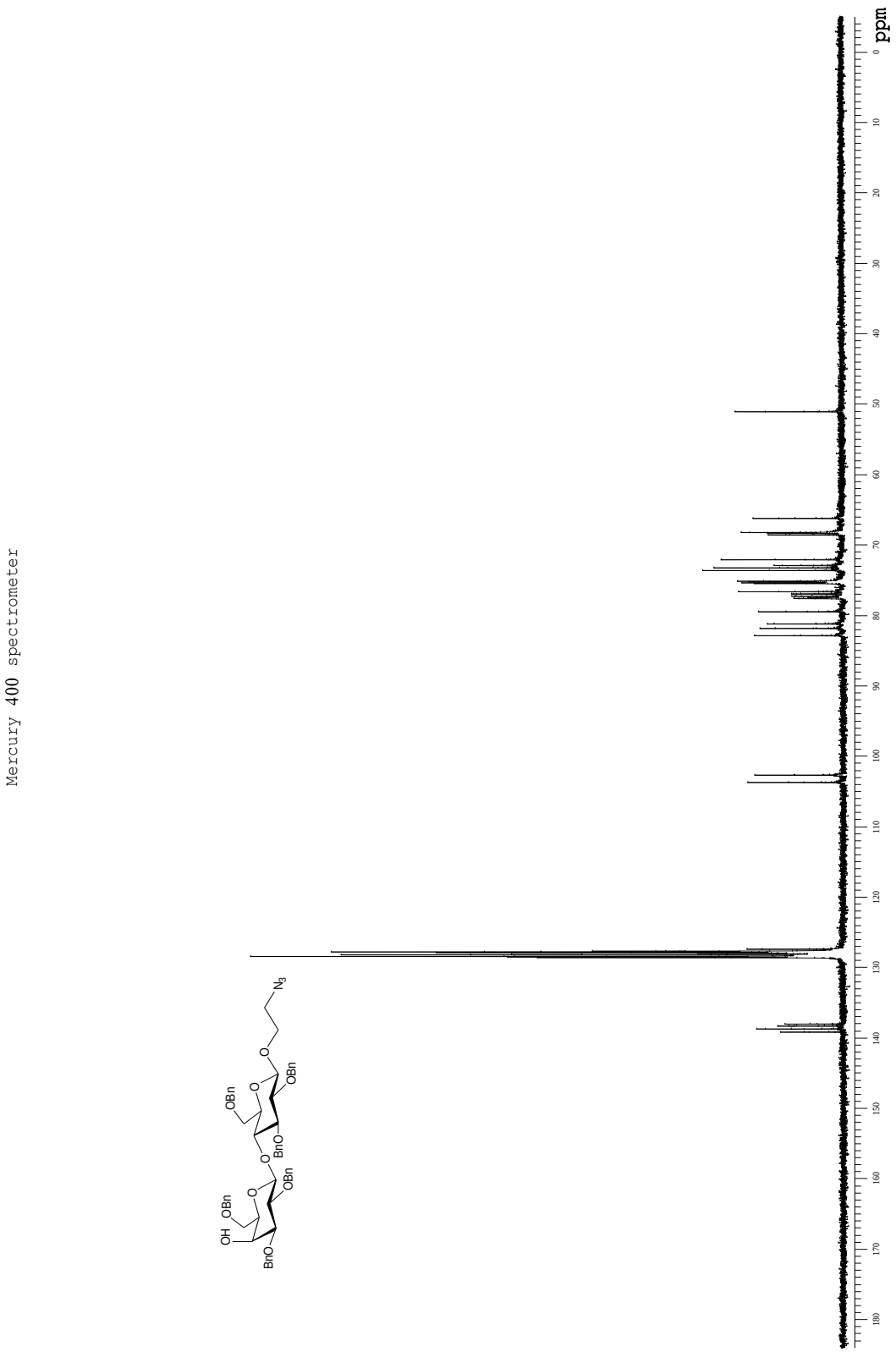


^{1}H-^{1}H COSY Spectrum of compound **17** ($CDCl_3$, 400 MHz)

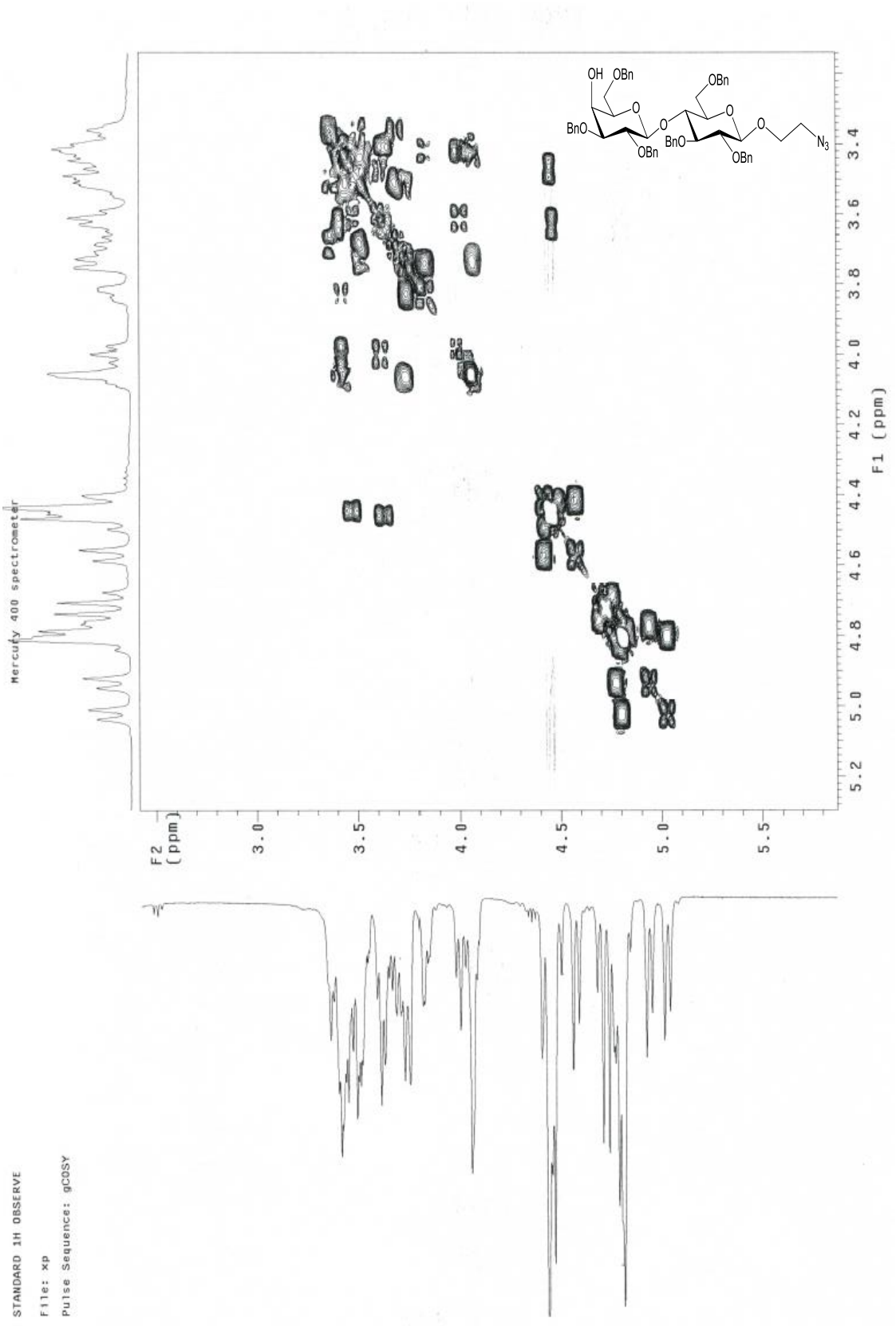
MALTI-TOF MS spectrum of compound **17**



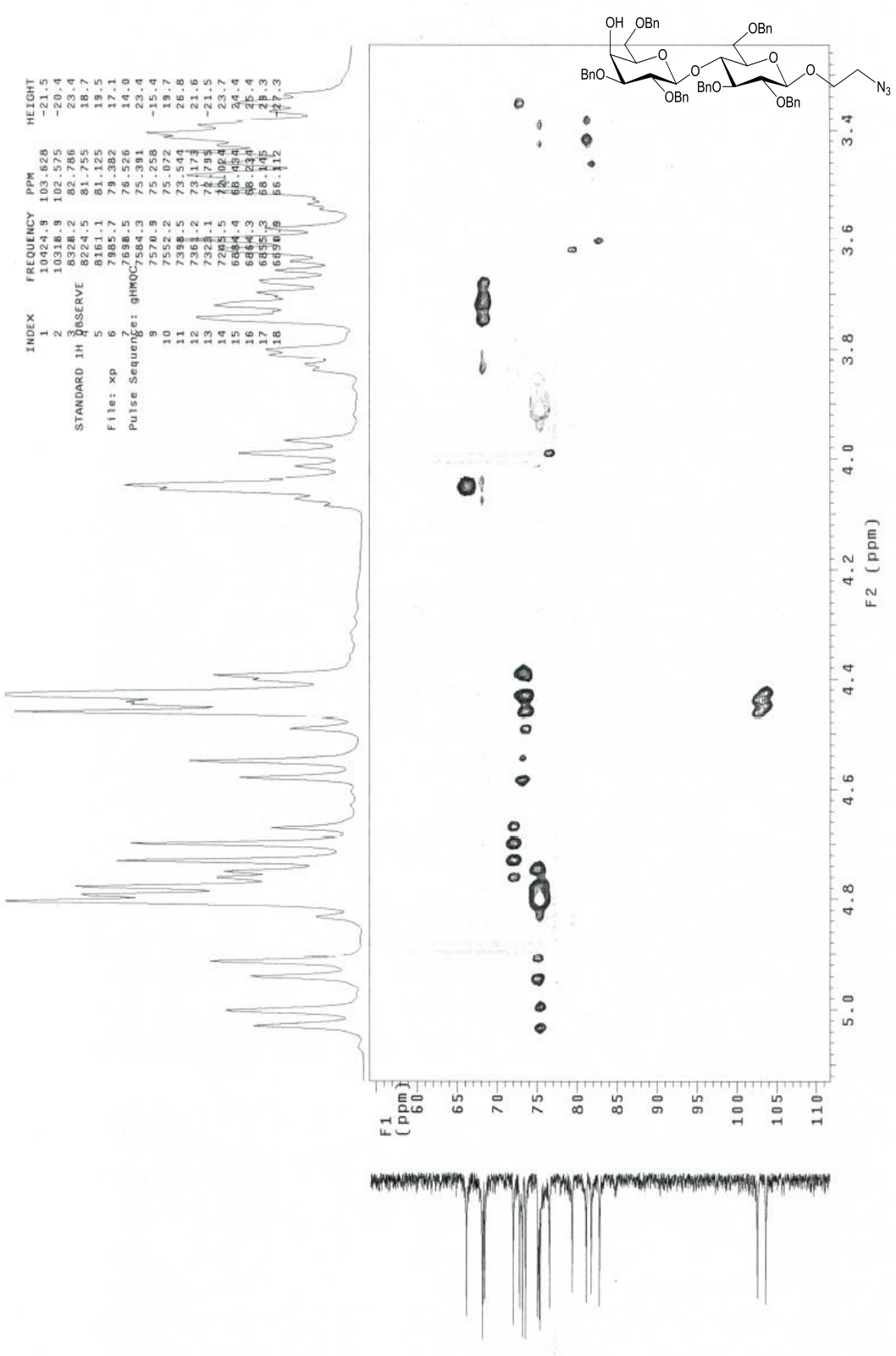
^{1}H NMR Spectrum of compound **10** ($CDCl_3$, 400 MHz)



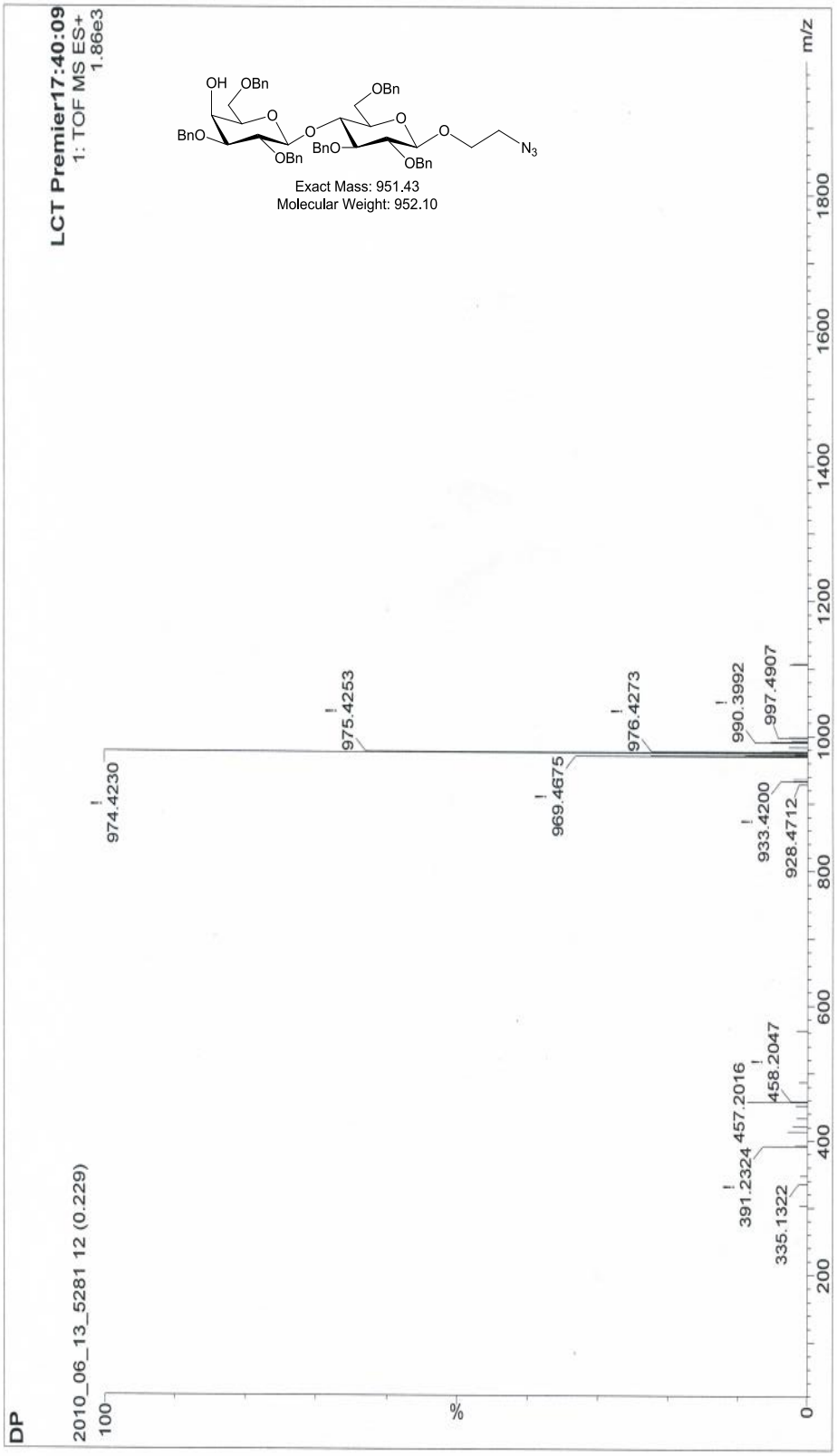
^{13}C NMR Spectrum of compound **10** ($CDCl_3$, 400 MHz)



^{1}H-^{1}H COSY Spectrum of compound **10** ($CDCl_3$, 400 MHz)

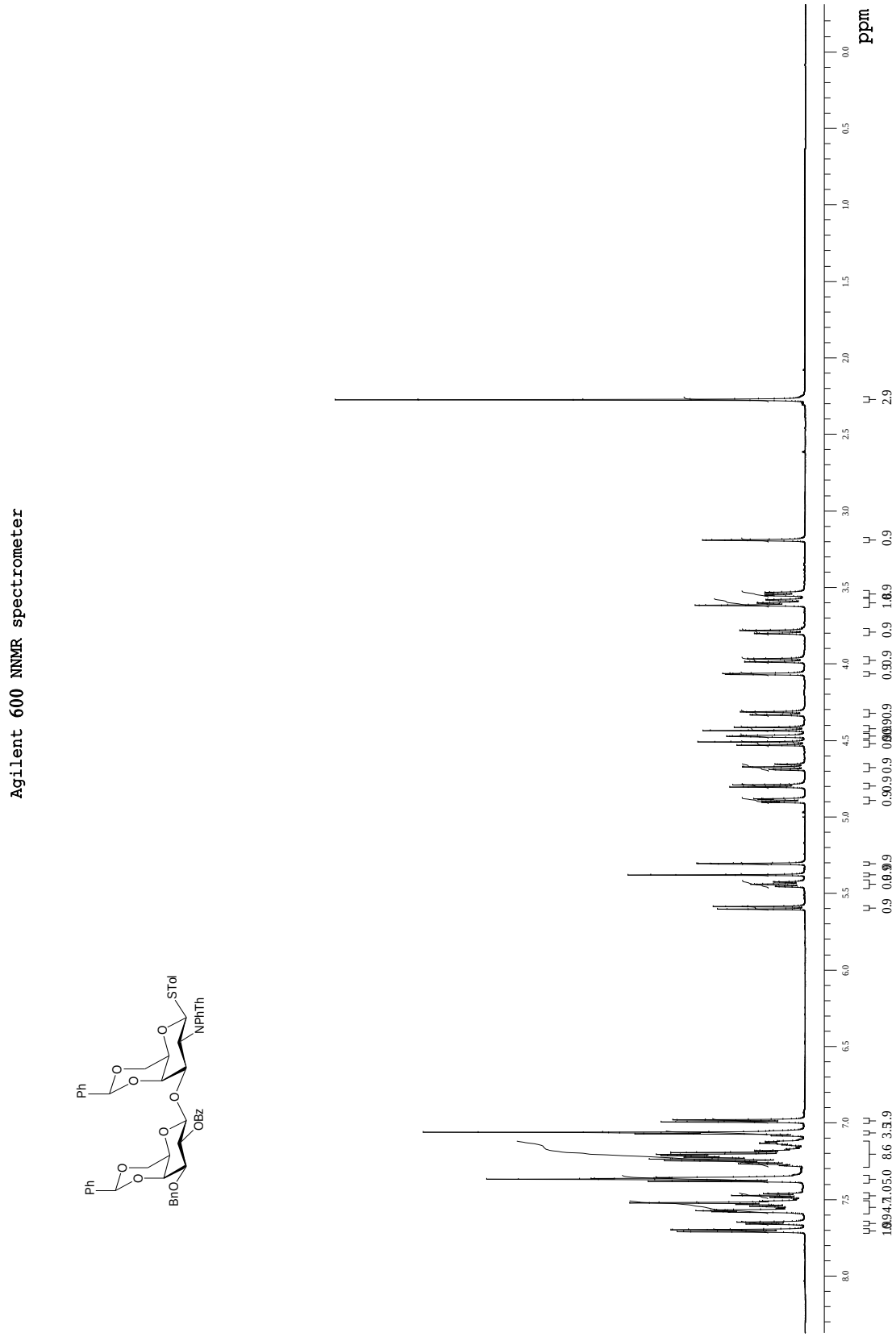


^{1}H-^{13}C HMQC NMR Spectrum of compound **10** ($CDCl_3$, 400/100 MHz)

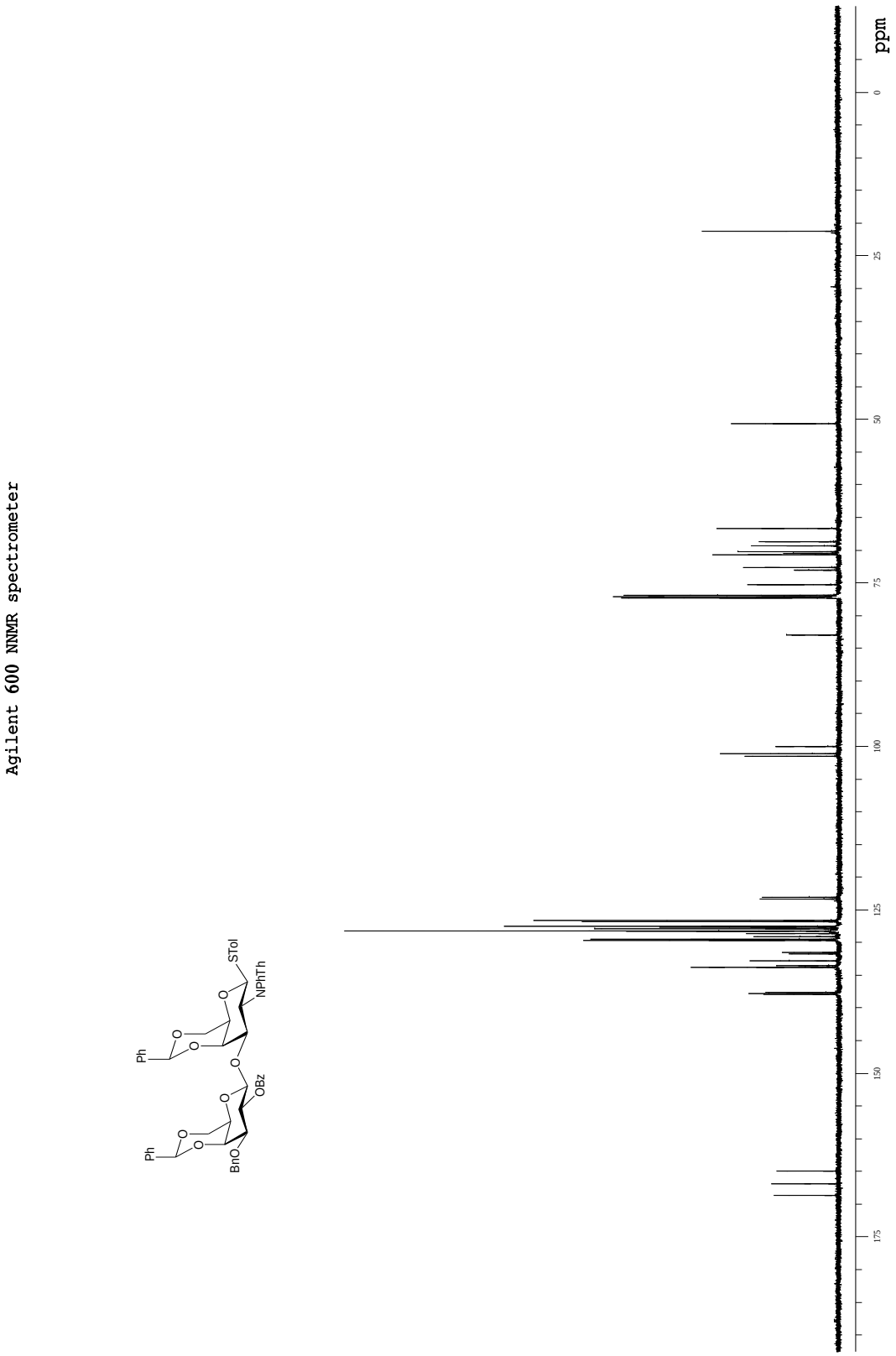


ESI MS spectrum of compound **10**

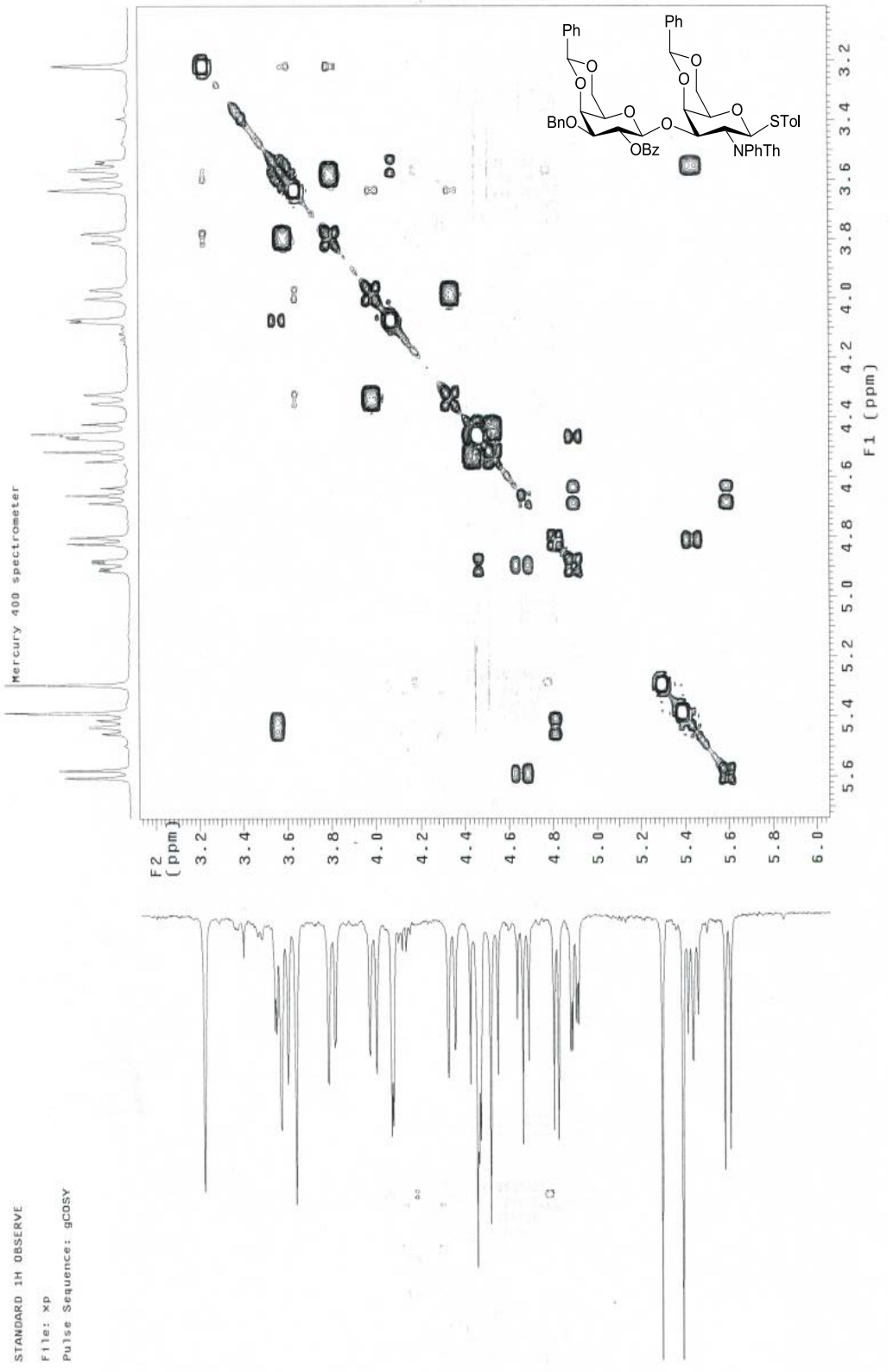
HRMS (ESI MS) spectrum of compound **10**



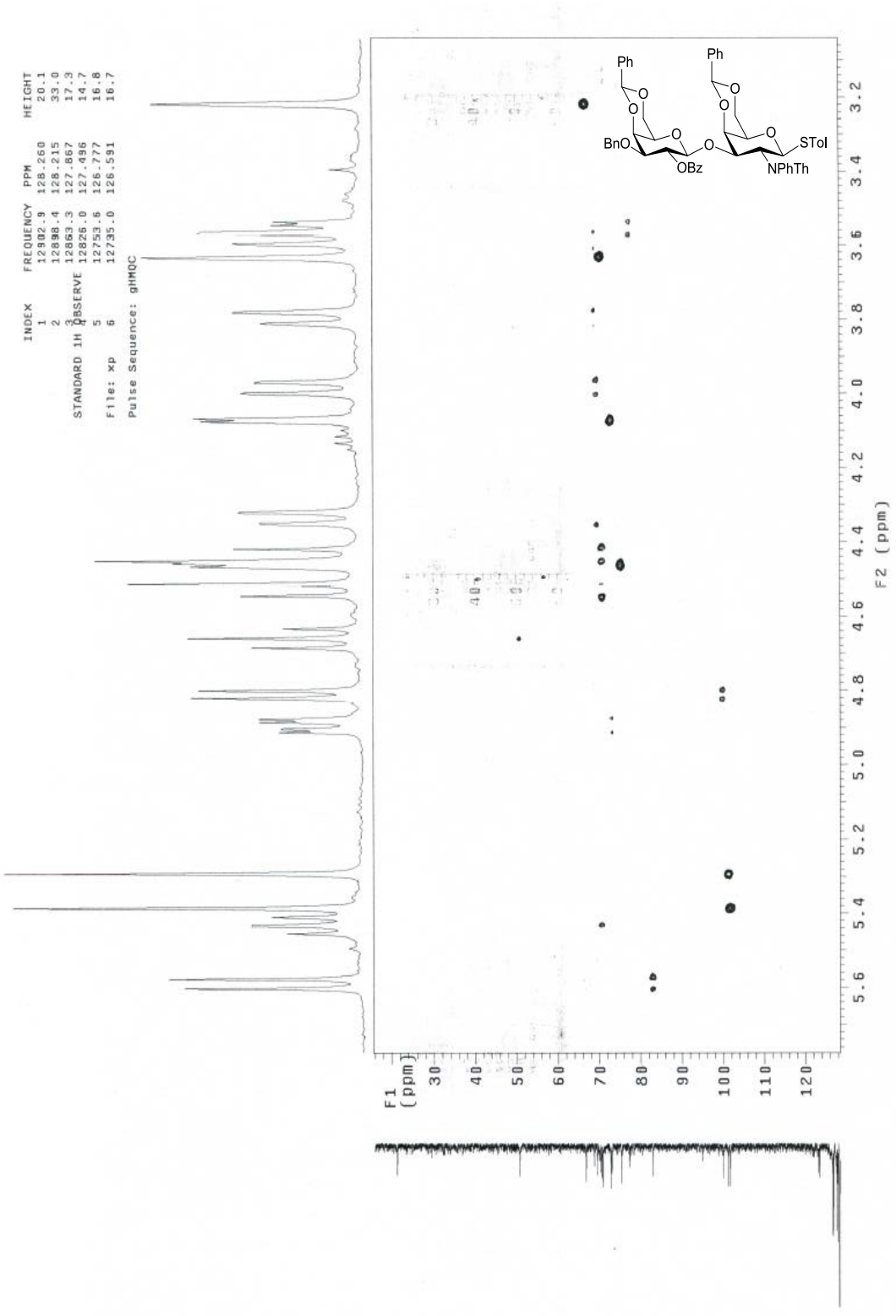
^{1}H NMR Spectrum of compound **5** ($CDCl_3$, 600 MHz)



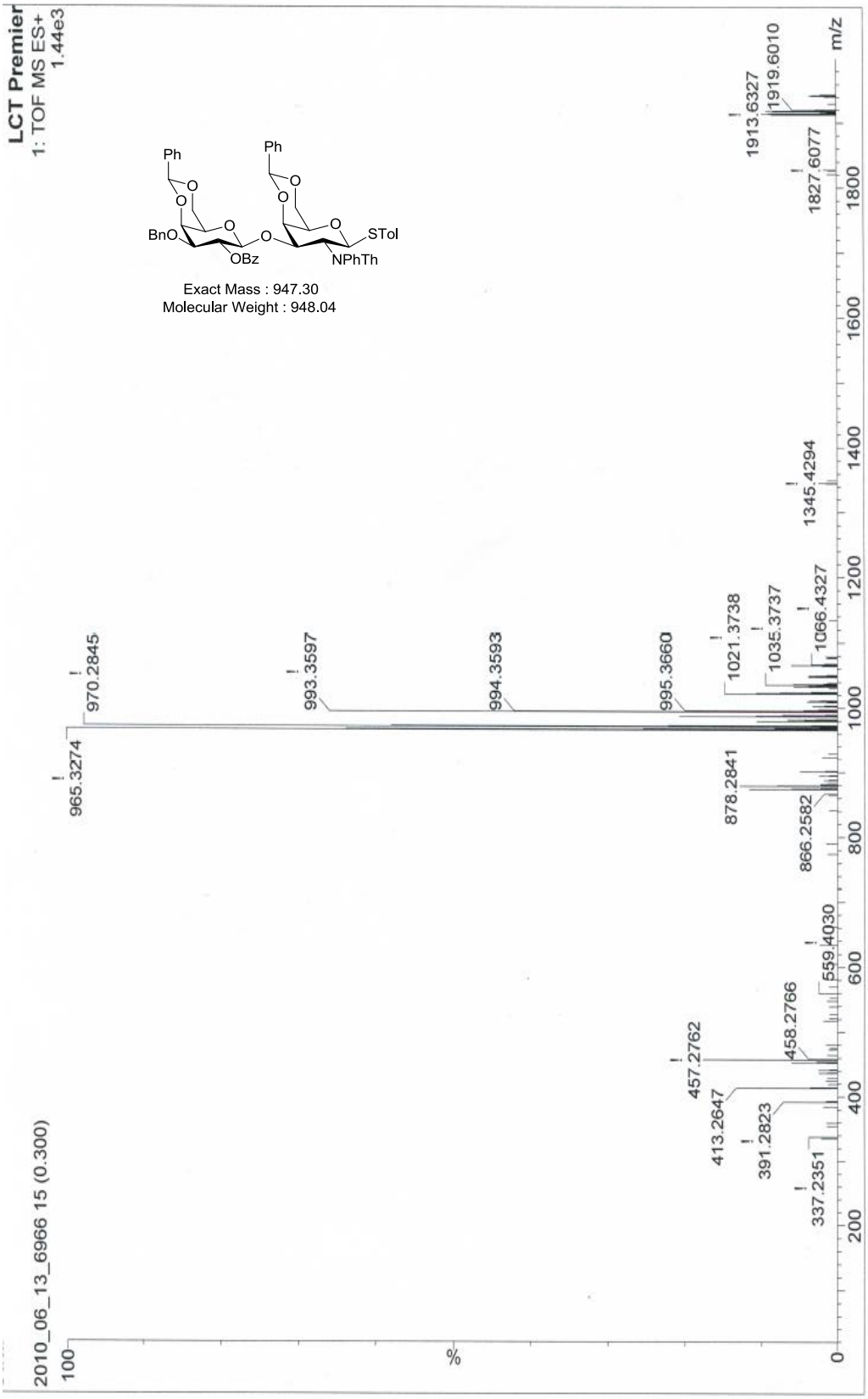
^{13}C NMR Spectrum of compound **5** ($CDCl_3$, 600 MHz)



^{1}H-^{1}H COSY Spectrum of compound **5** ($CDCl_3$, 400 MHz)

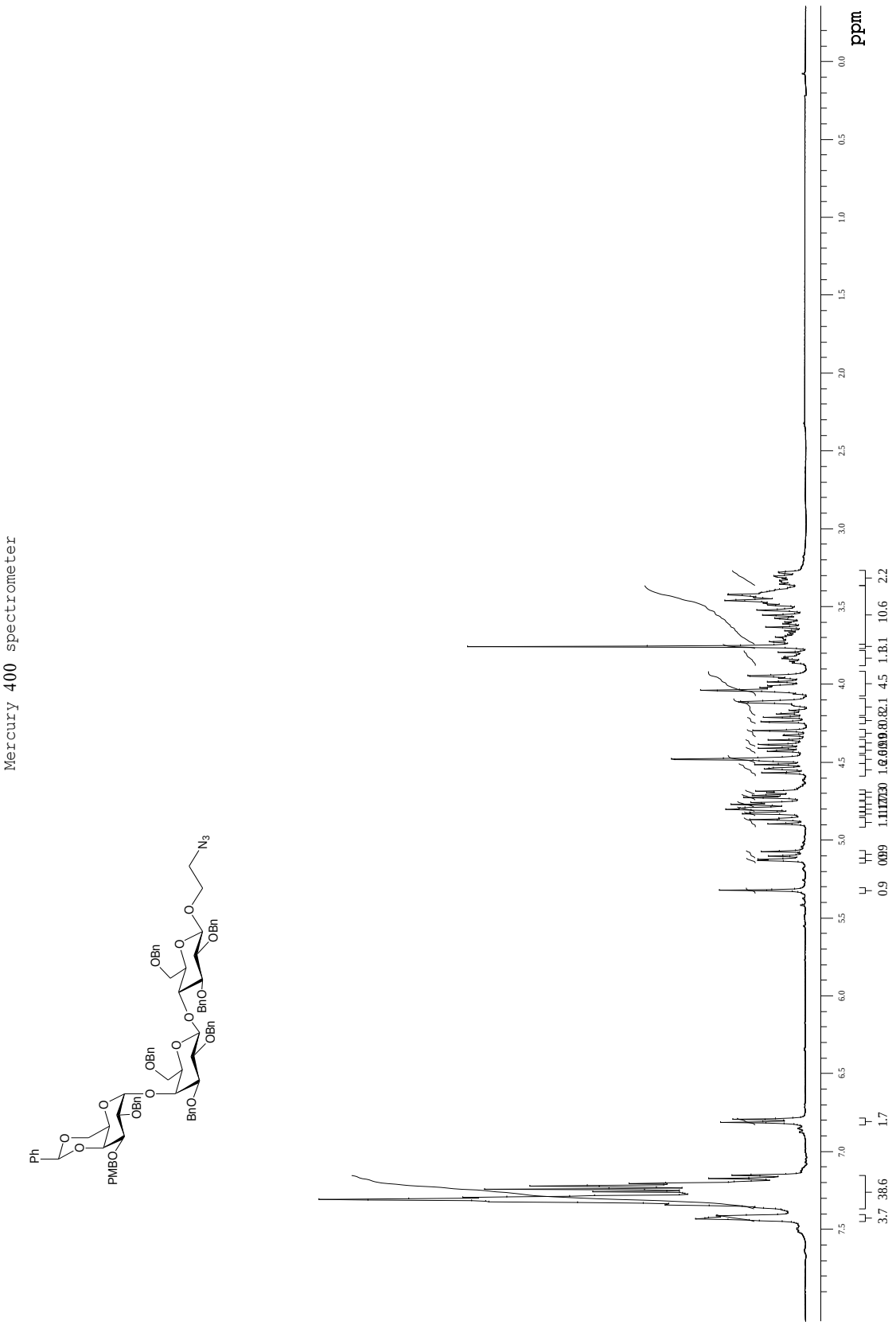


^{1}H-^{13}C HMQC NMR Spectrum of compound **5** ($CDCl_3$, 400/100 MHz)

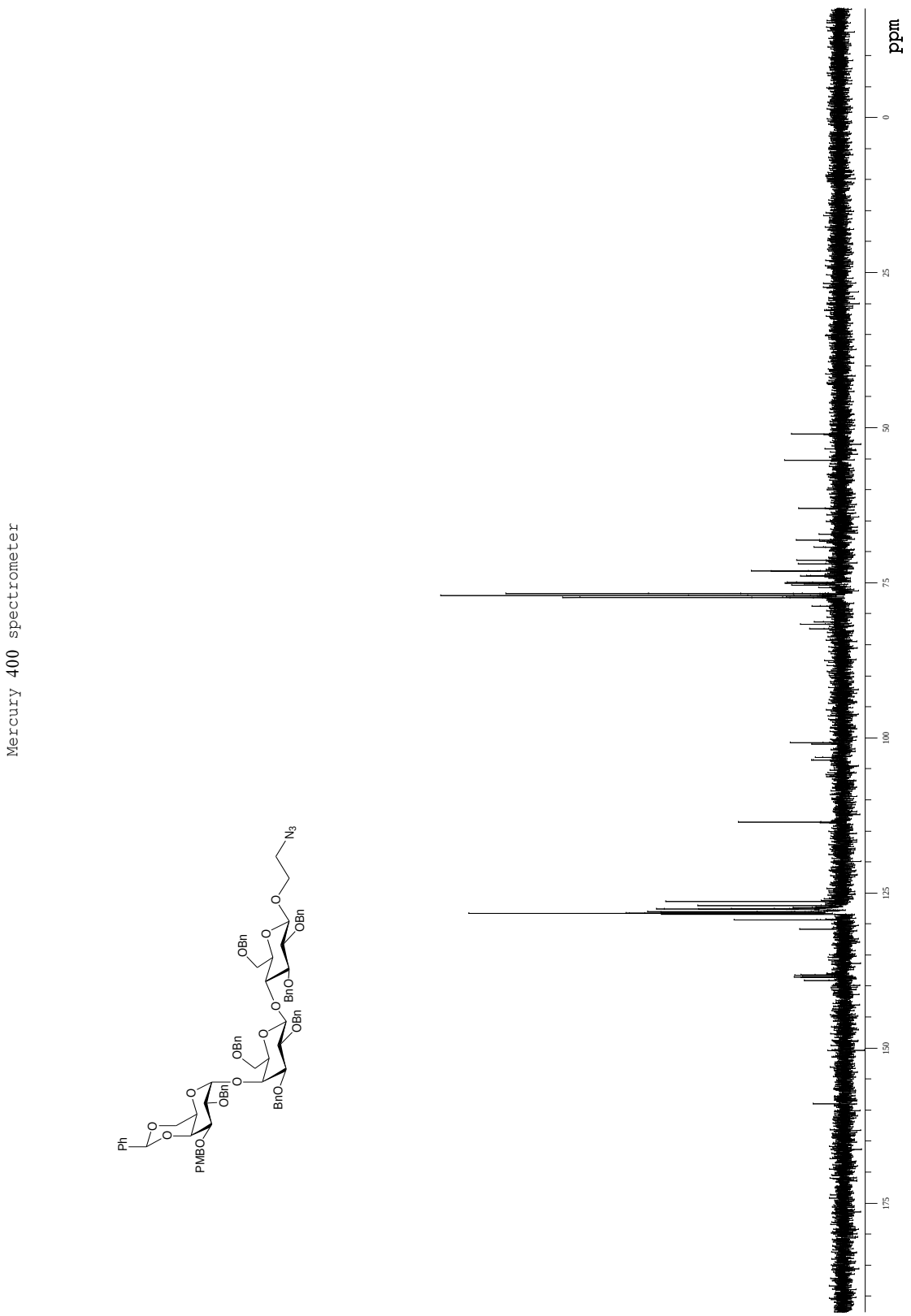


ESI MS spectrum of compound **5**

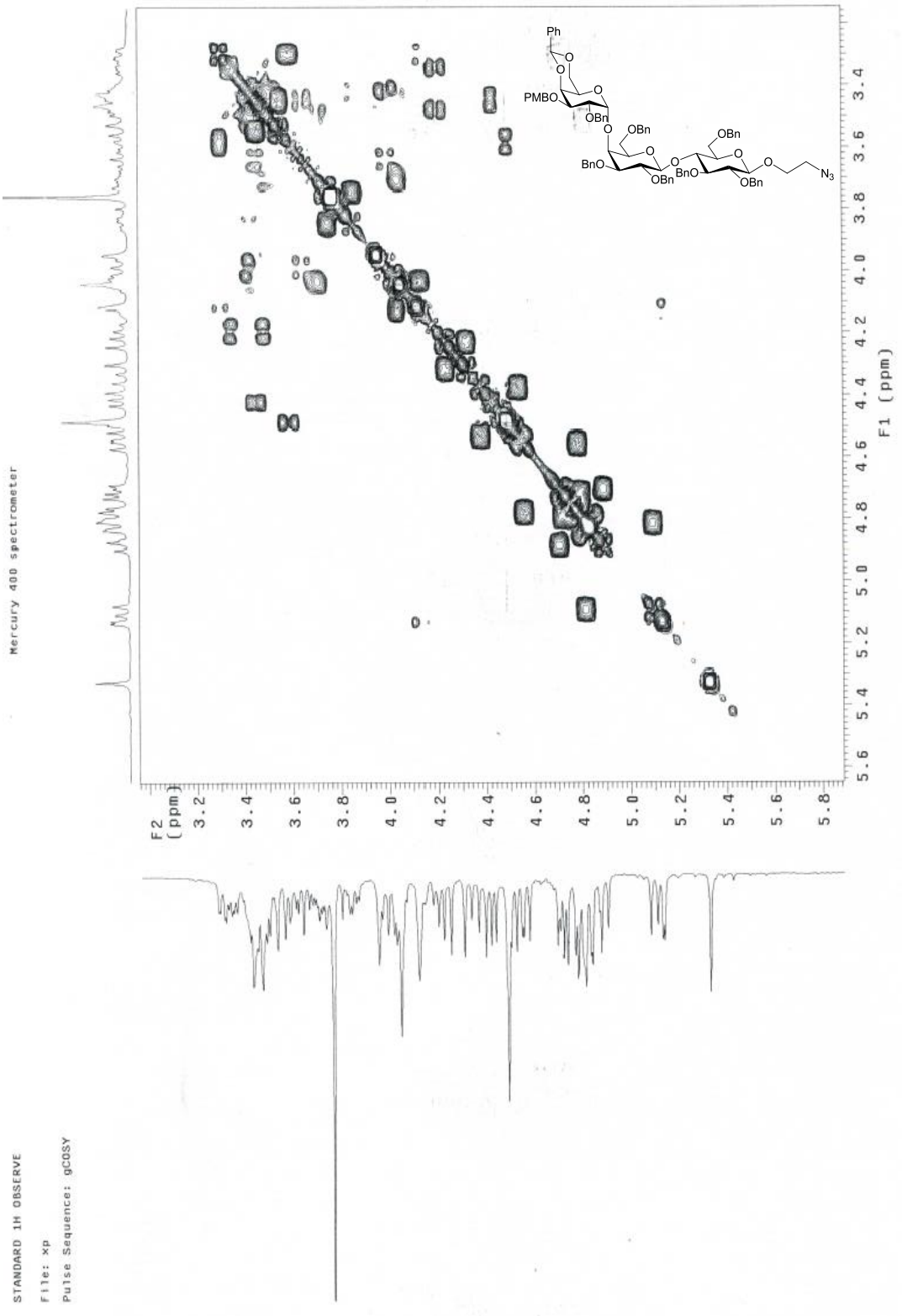
HRMS (ESI MS) spectrum of compound **5**



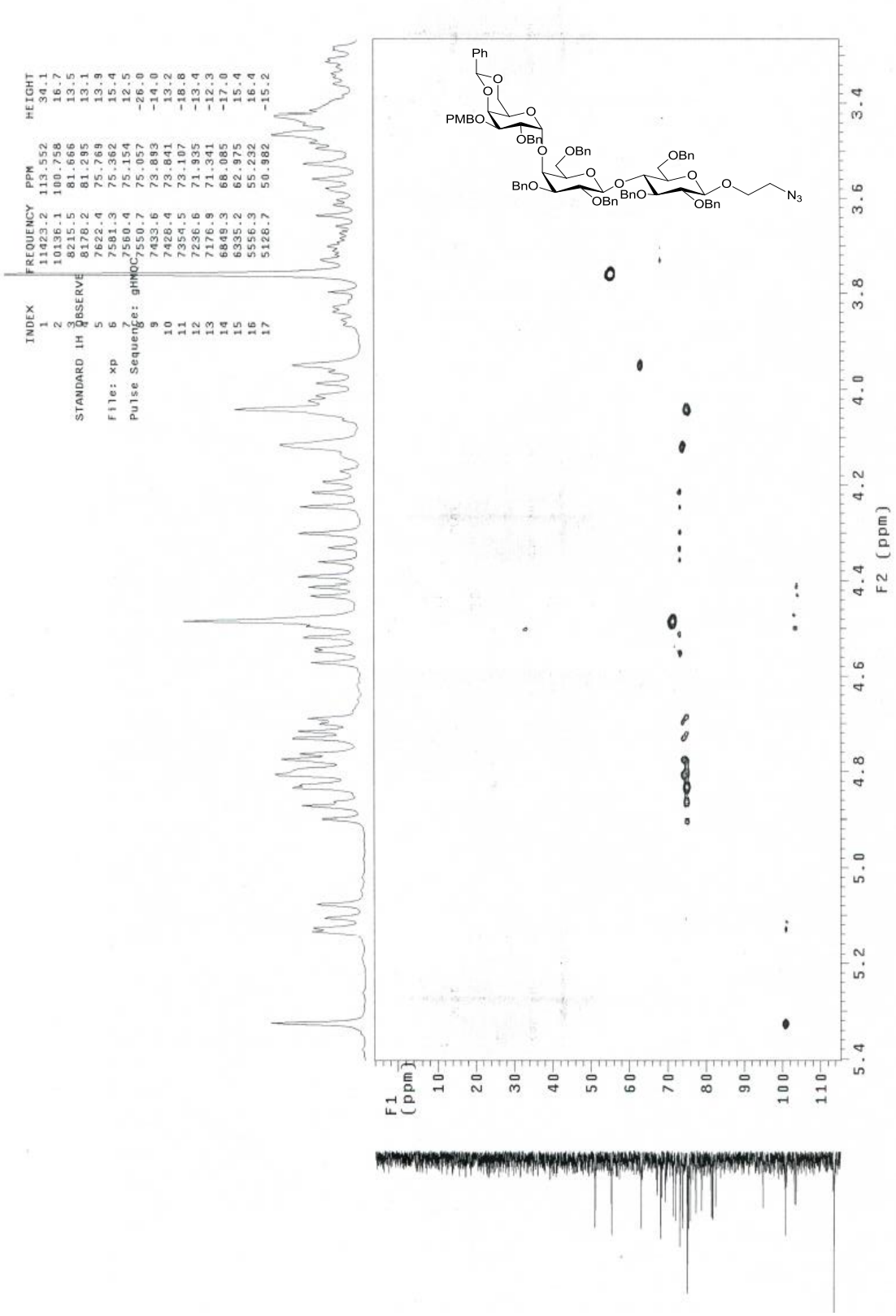
^{1}H NMR Spectrum of compound **6** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of compound **6** ($CDCl_3$, 400 MHz)



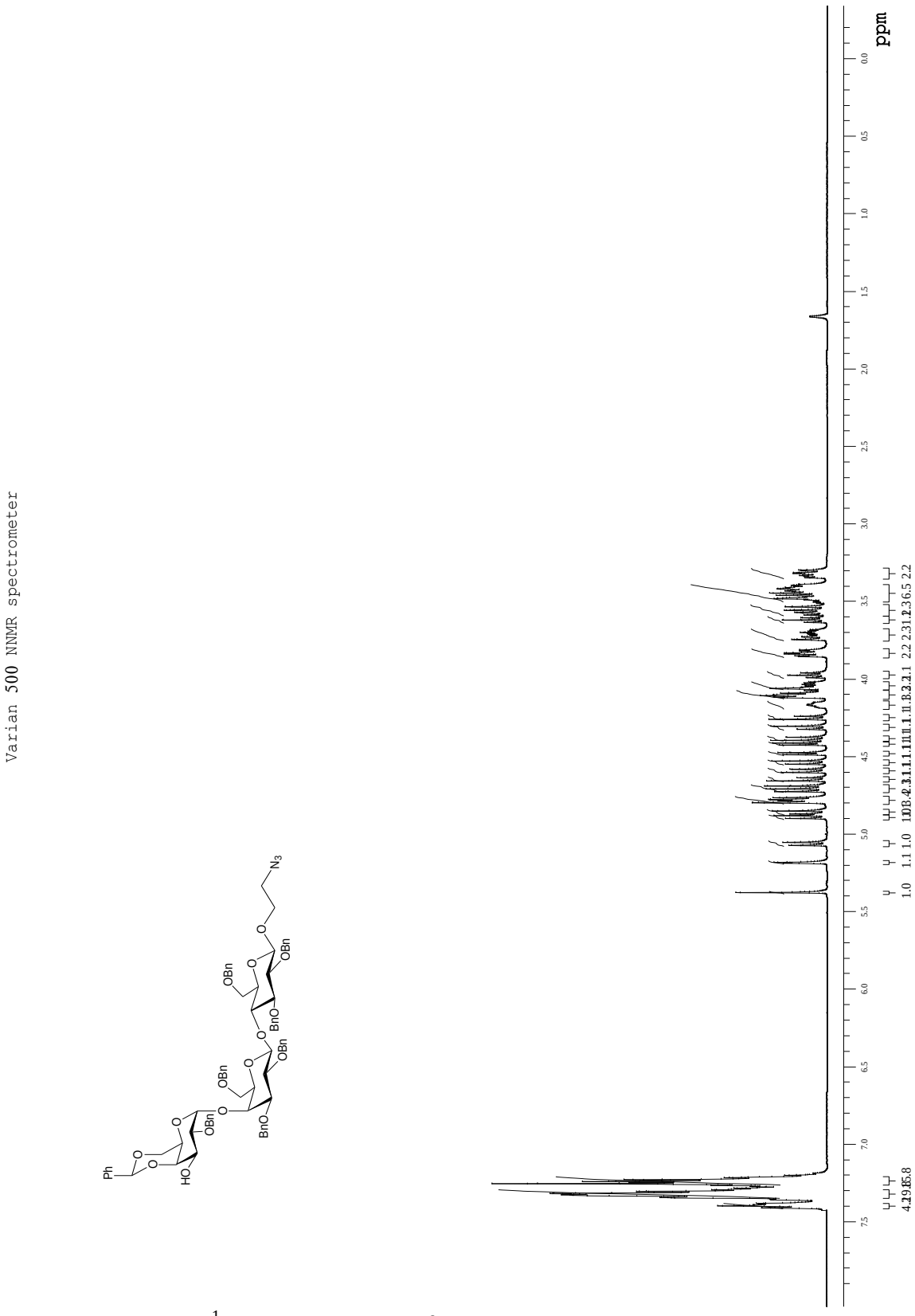
^{1}H-^{1}H COSY Spectrum of compound **6** ($CDCl_3$, 400 MHz)



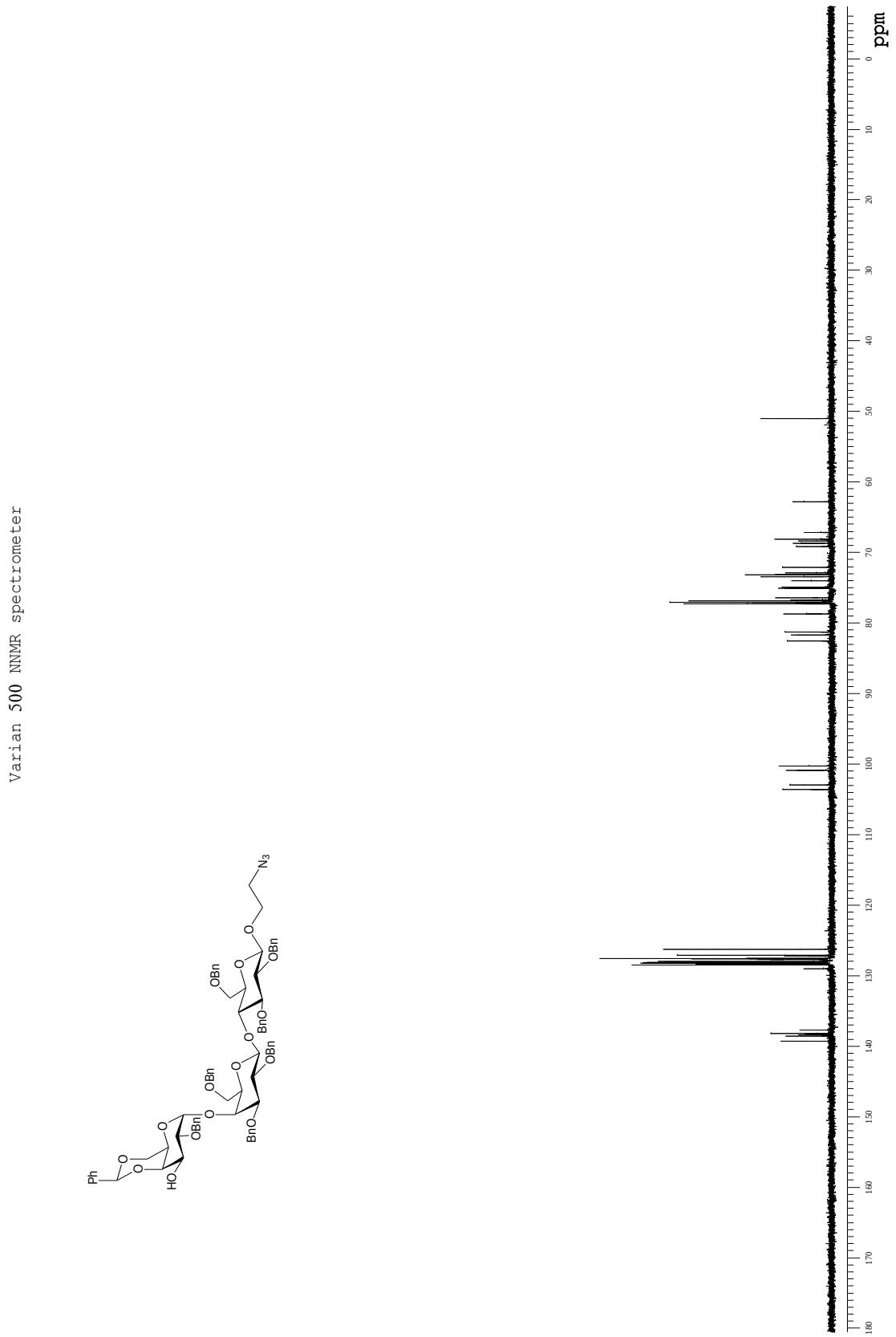
^{1}H-^{13}C HMQC NMR Spectrum of compound **6** ($CDCl_3$, 400/100 MHz)

MALTI-TOF MS spectrum of compound **6**

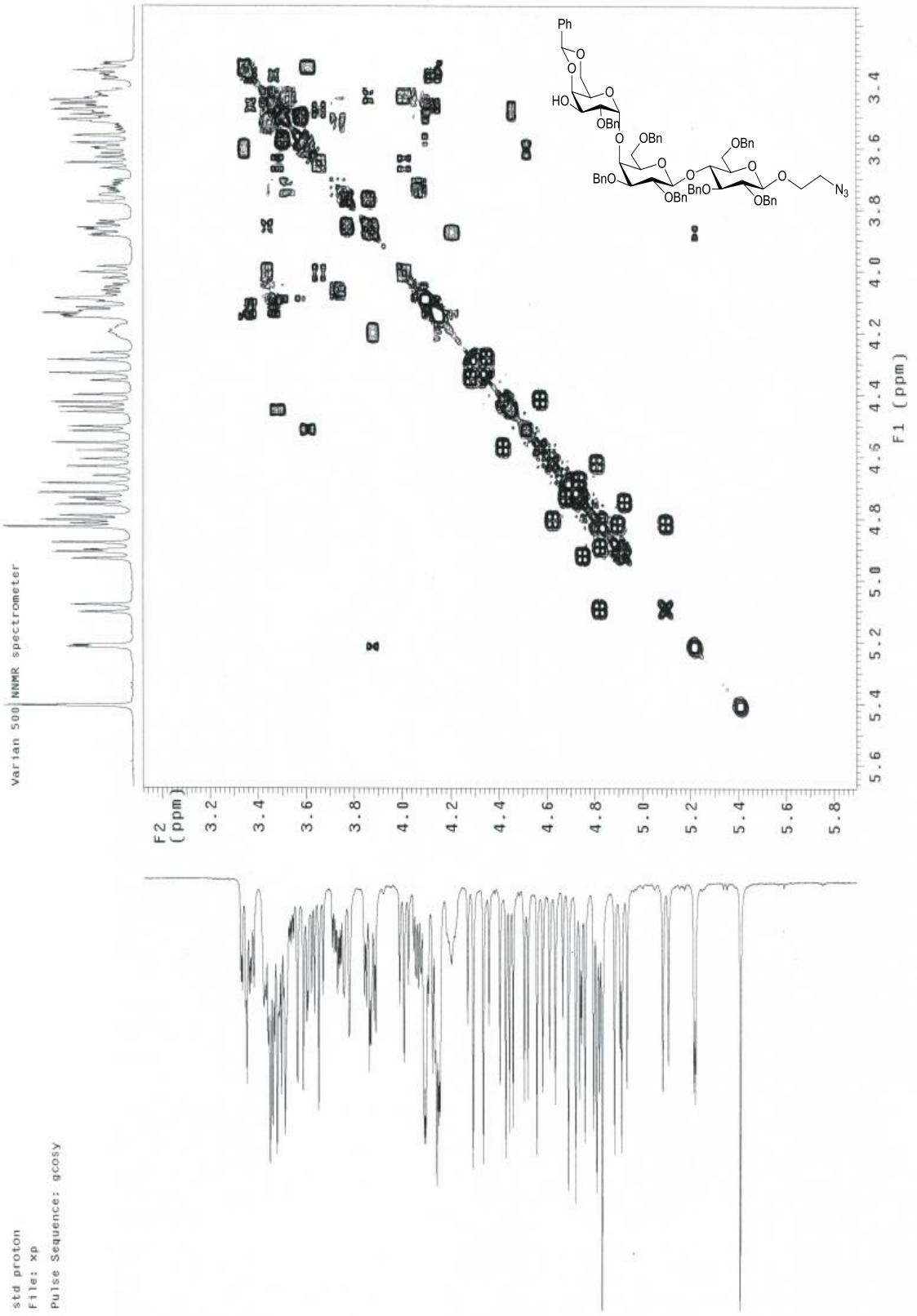
HRMS (ESI MS) spectrum of compound **6**



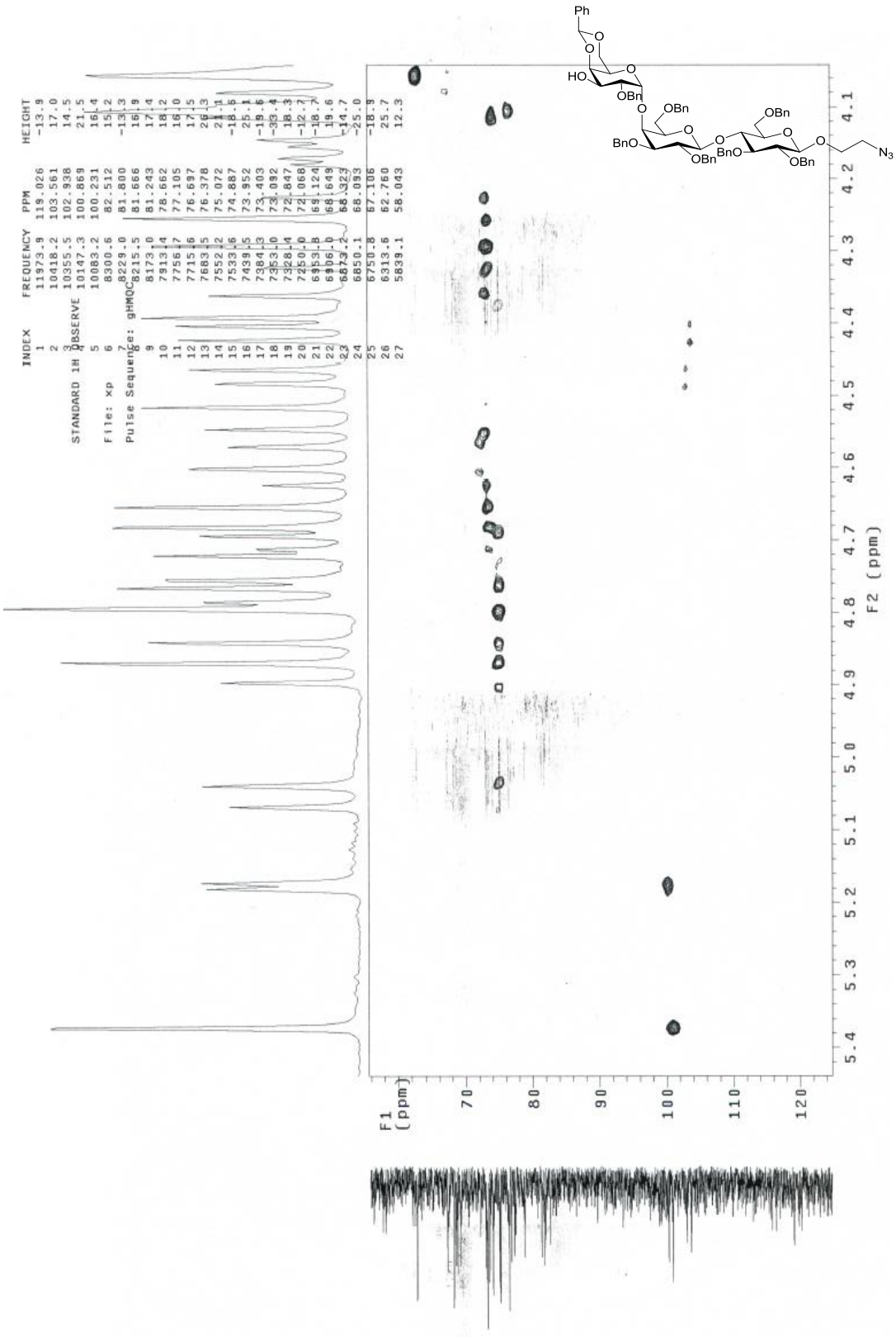
^{1}H NMR Spectrum of compound **20** ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of compound **20** ($CDCl_3$, 500 MHz)



^{1}H-^{1}H COSY Spectrum of compound **20** ($CDCl_3$, 500 MHz)

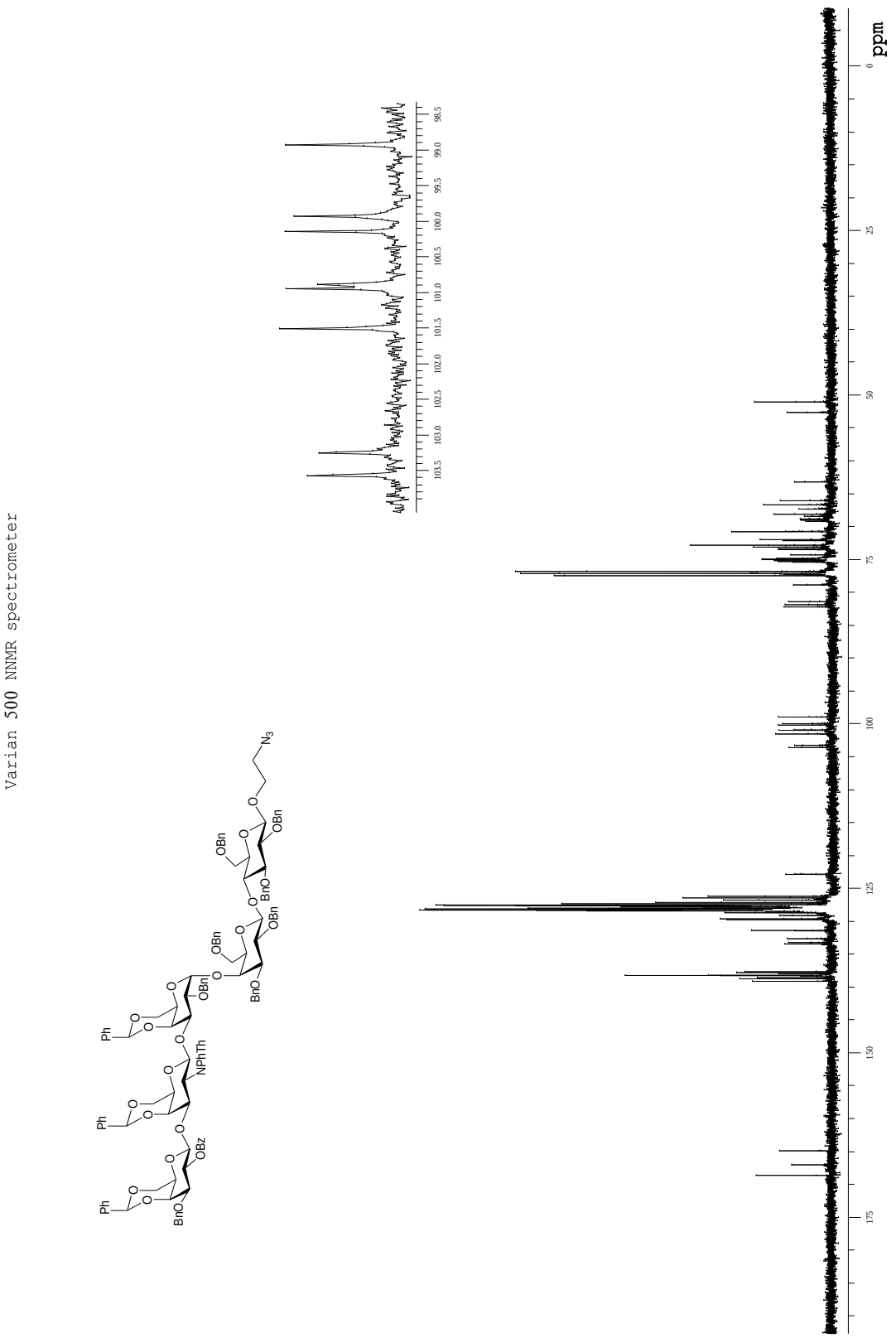


^{1}H-^{13}C HMQC NMR Spectrum of compound **20** ($CDCl_3$, 500/125 MHz)

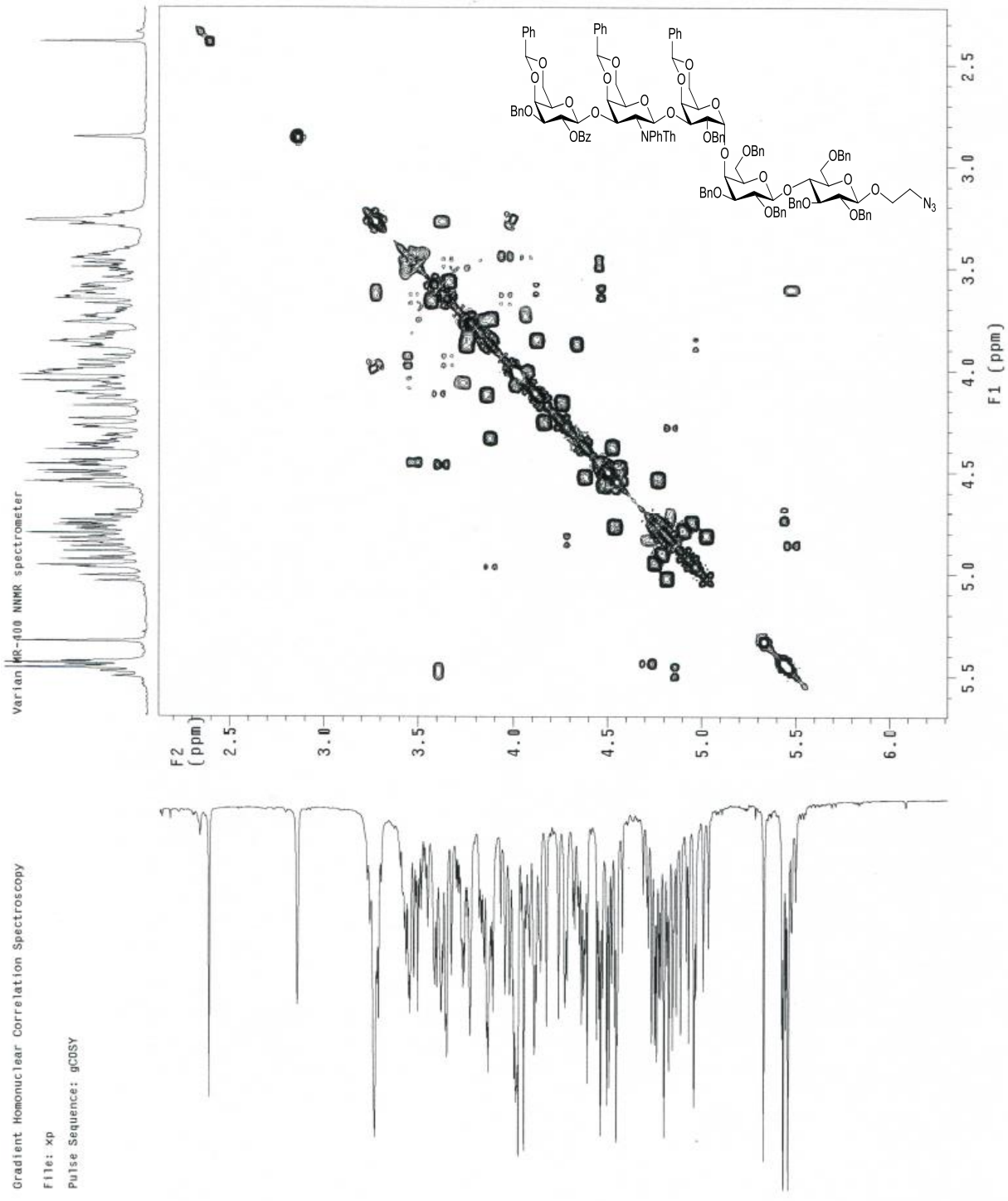
MALTI-TOF MS spectrum of compound **20**

HRMS (ESI MS) spectrum of compound **20**.

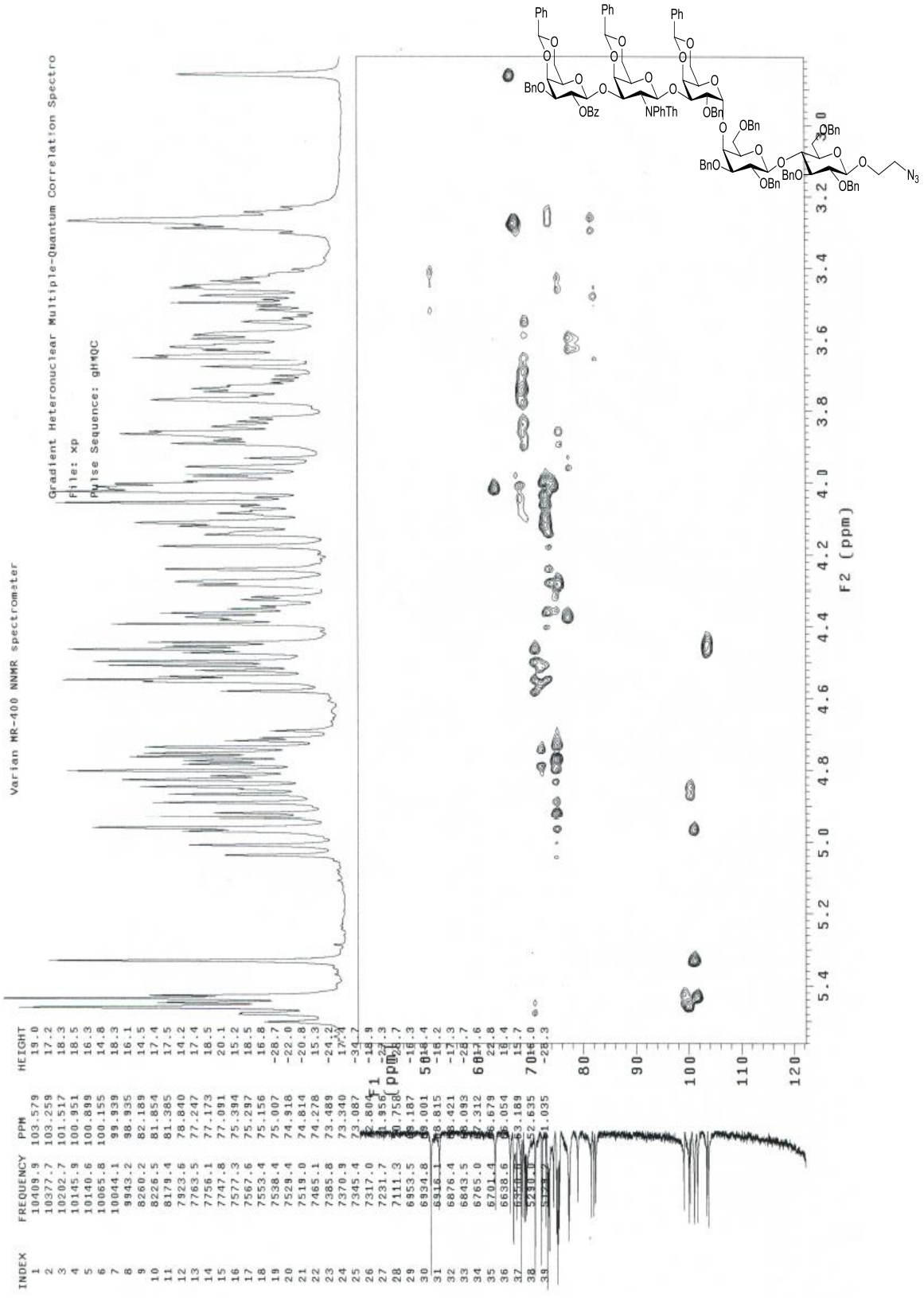
^{1}H NMR Spectrum of compound **3** ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of compound **3** ($CDCl_3$, 500 MHz)



^{1}H-^{1}H COSY Spectrum of compound **3** ($CDCl_3$, 400 MHz)

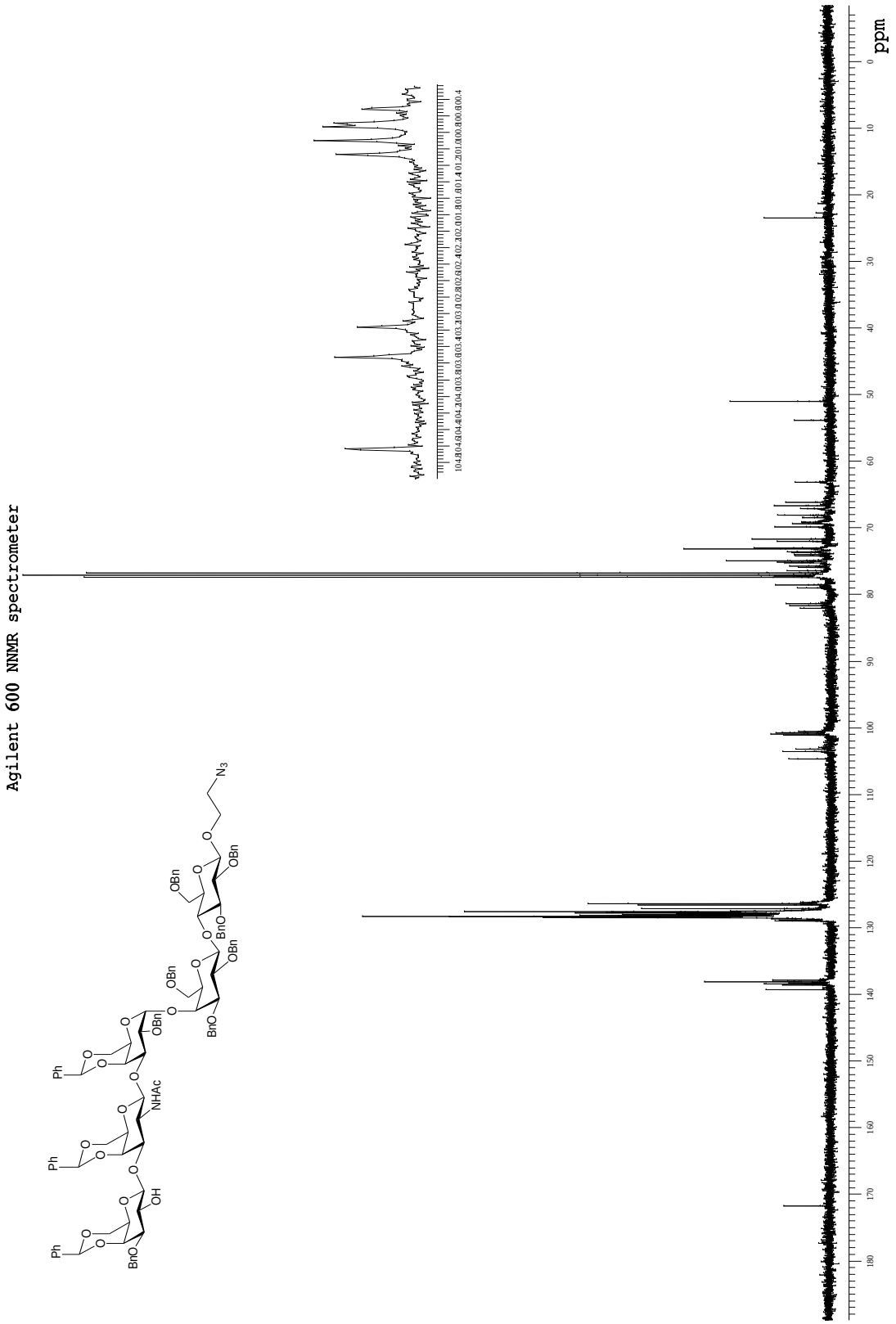


^{1}H-^{13}C HMQC NMR Spectrum of compound **3** ($CDCl_3$, 400/100 MHz)

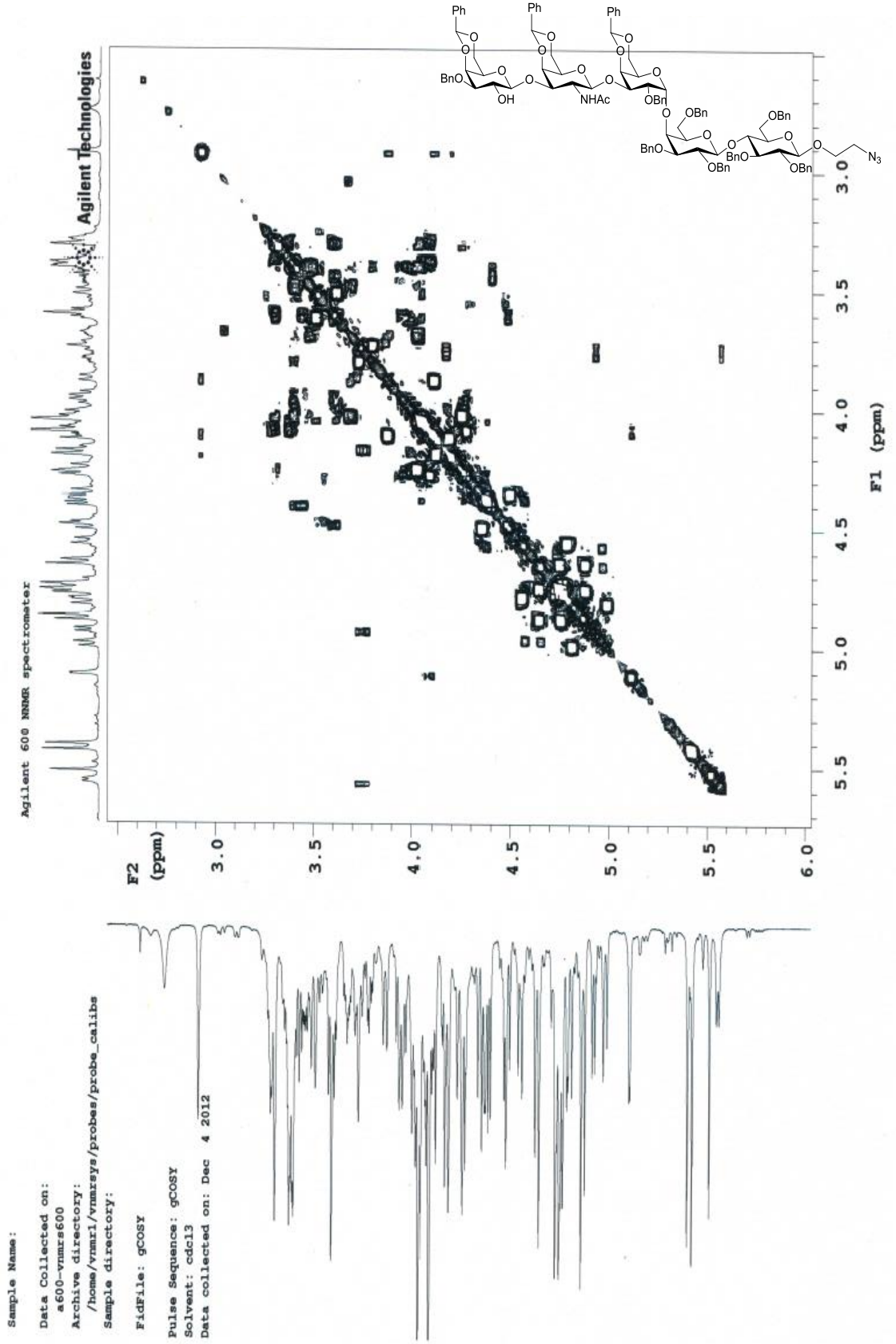
MALTI-TOF MS spectrum of compound **3**

HRMS (ESI MS) spectrum of compound **3**.

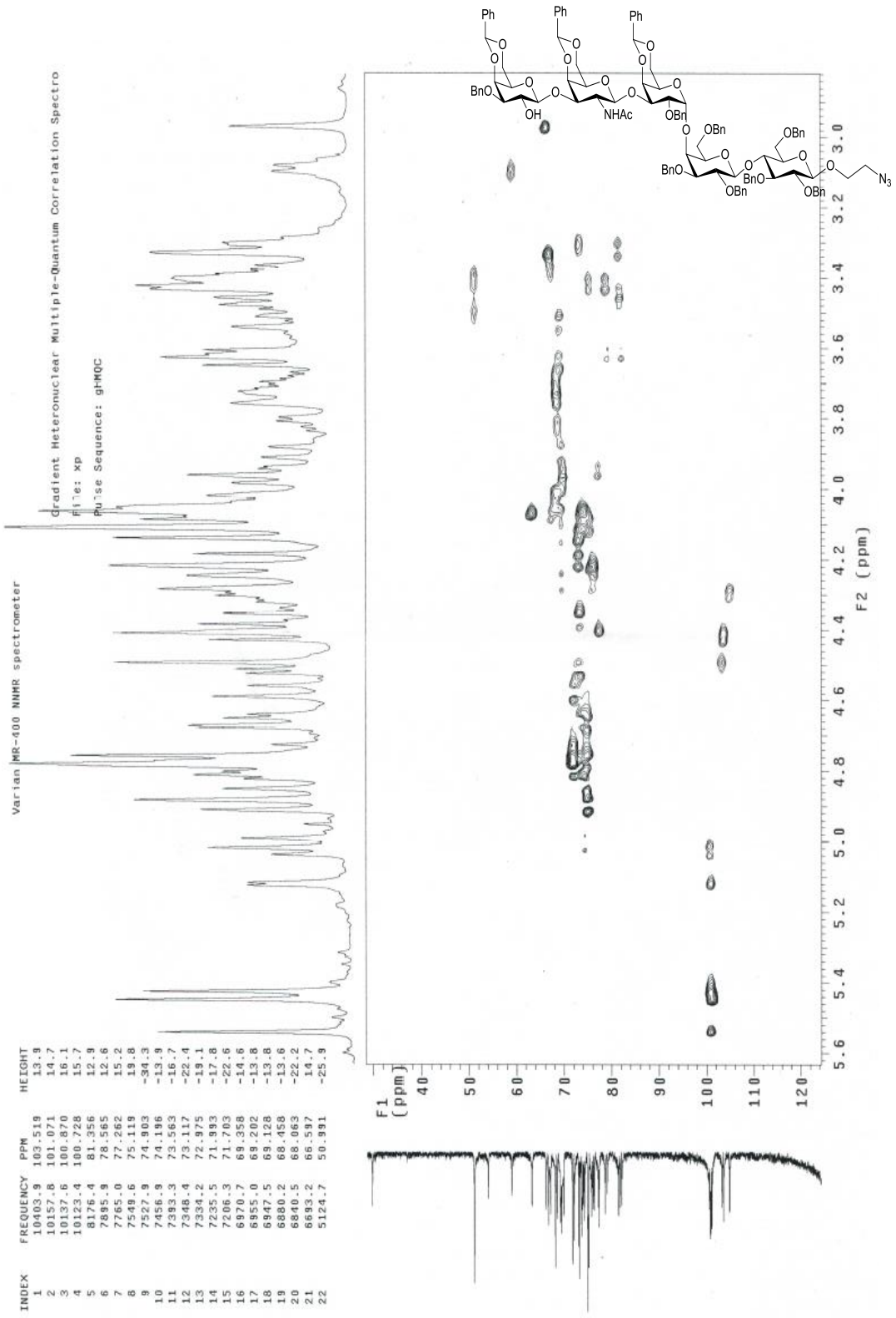
^{1}H NMR Spectrum of compound **21** ($CDCl_3$, 600 MHz)



^{13}C NMR Spectrum of compound **21** ($CDCl_3$, 600 MHz)



^{1}H-^{1}H COSY Spectrum of compound **21** ($CDCl_3$, 600 MHz)



^{1}H-^{13}C HMQC NMR Spectrum of compound **21** ($CDCl_3$, 400/100 MHz)

MALTI-TOF MS spectrum of compound **21**

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 6

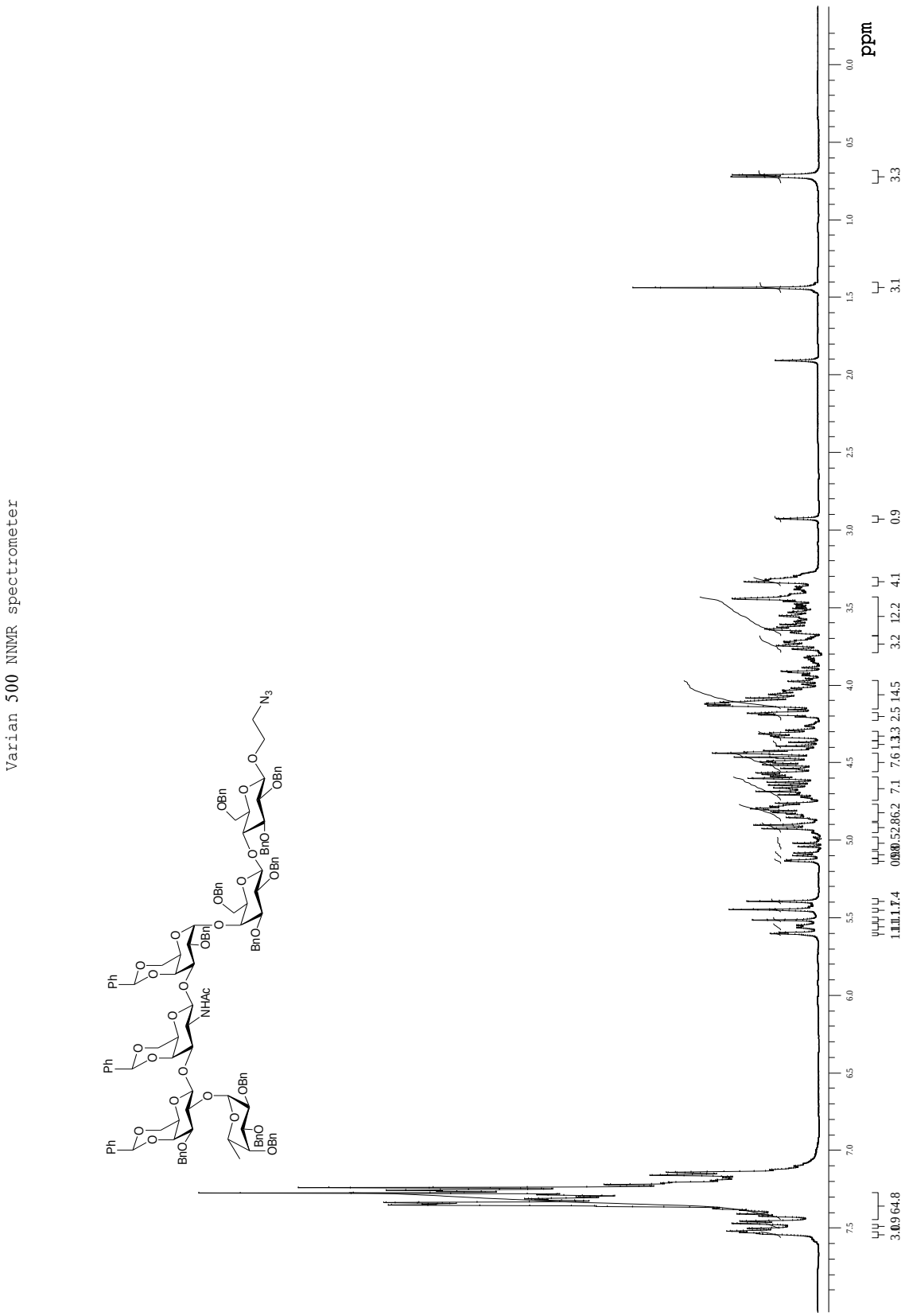
Monoisotopic Mass, Even Electron Ions
421 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-111 H: 0-1000 N: 0-4 O: 0-26 23Na: 0-1
SATARDU S MANDAL SSM-OH-NHAc-Penta

2013_0218_3105 16 (0.317) Cm (16:20-1:7x2.000)

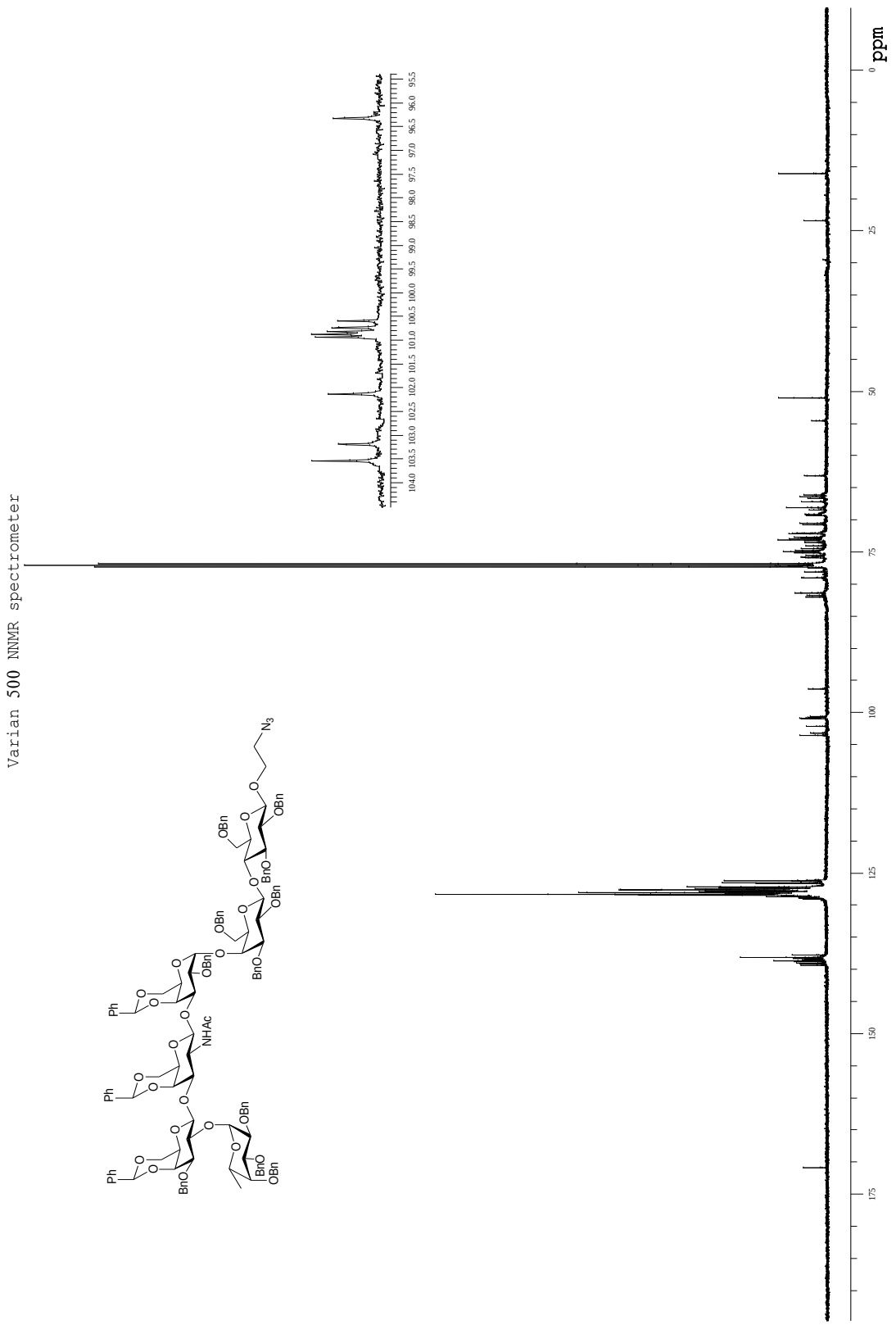
LCT2008-07b.pro 2010-cif.spiLCT Premier
1: TOF MS ES+
6.31e+002

Minimum:					-1.5				
Maximum:		50.0	5.0		100.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
1945.8005	1945.7932	7.3	3.8	54.5	26.4	0.0	C111 H118 N4 O26 23Na		

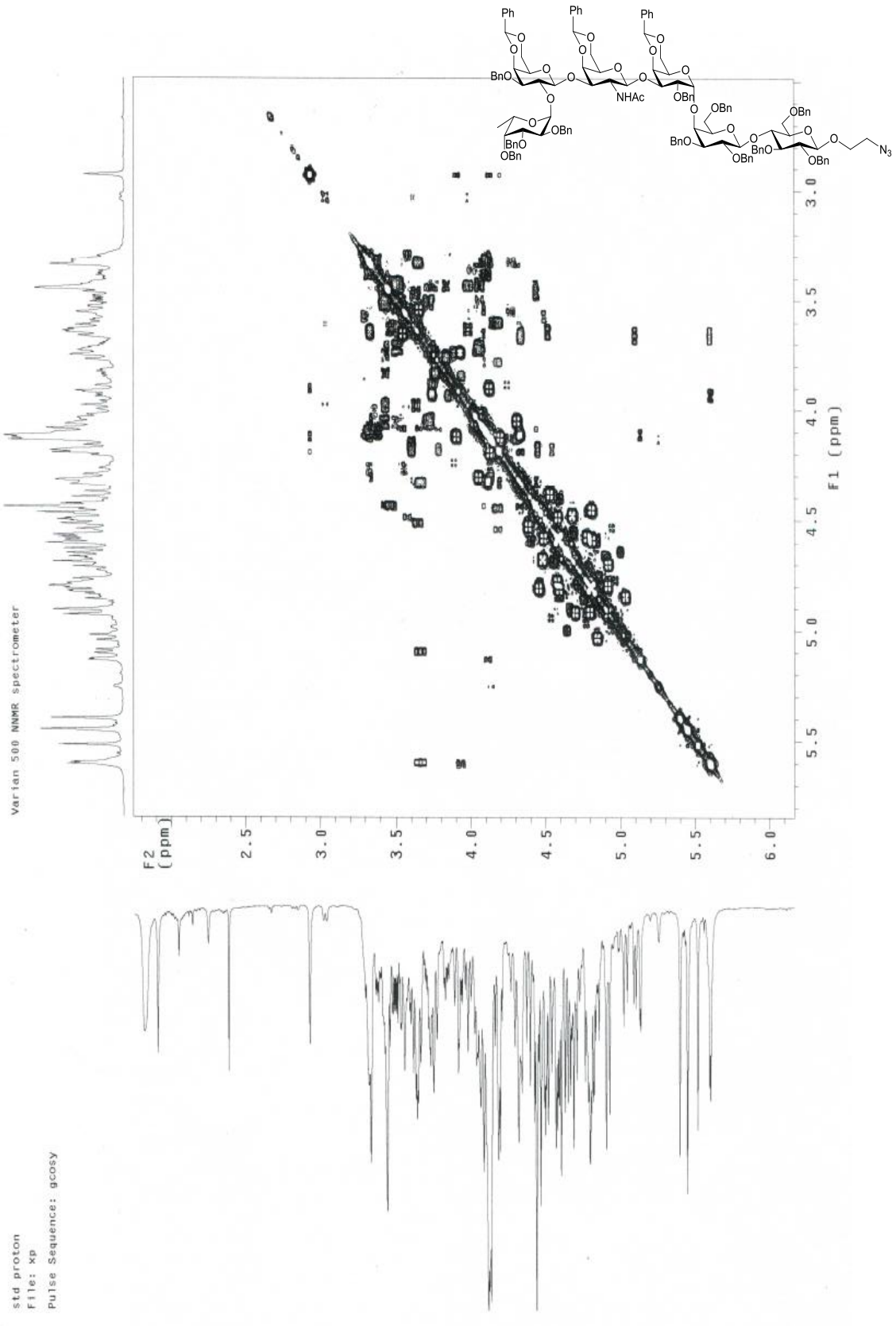
HRMS (ESI MS) spectrum of compound **21**.



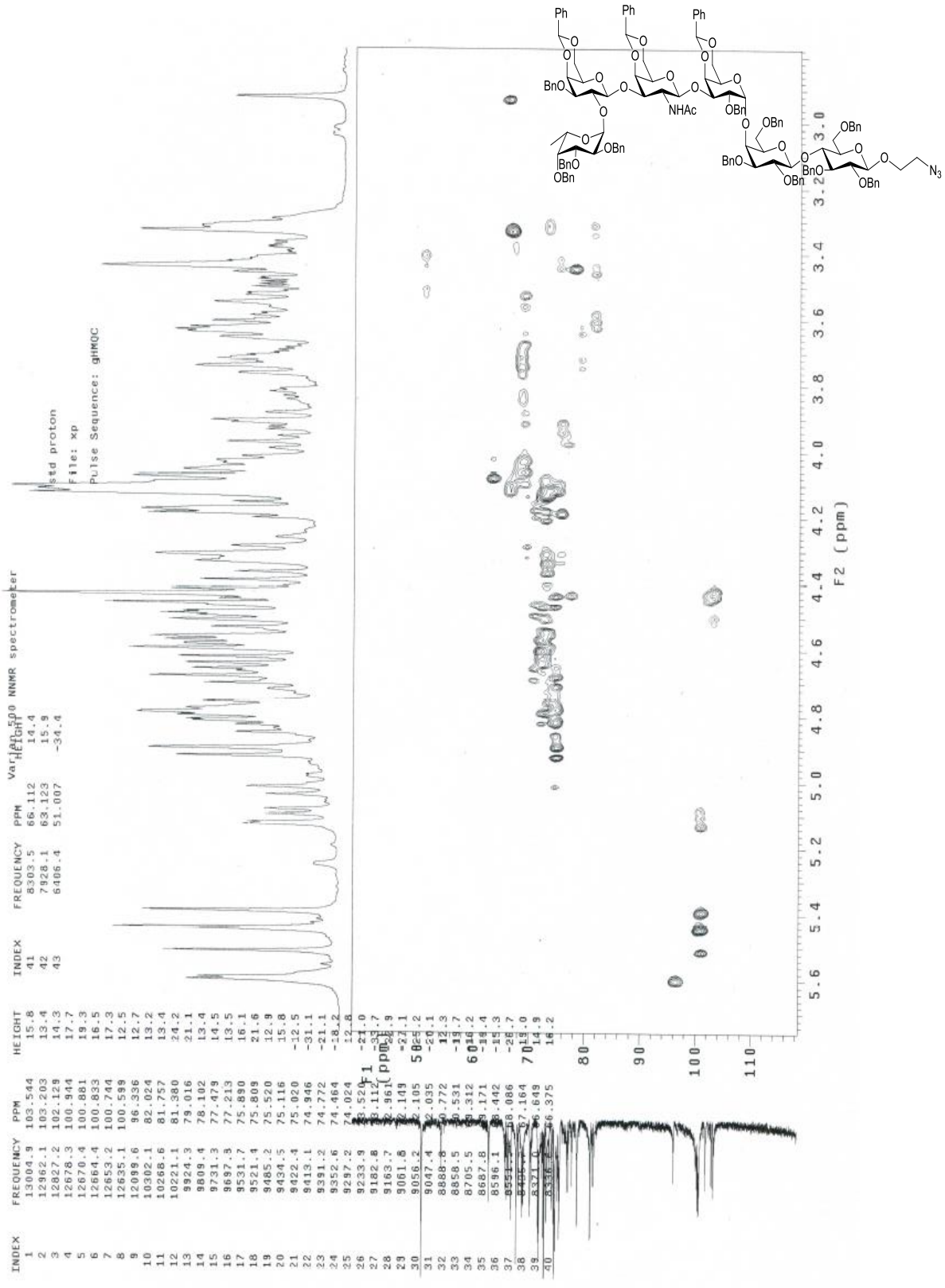
^{1}H NMR Spectrum of compound **22** ($CDCl_3$, 500 MHz)



^{13}C NMR Spectrum of compound **22** ($CDCl_3$, 500 MHz)



^{1}H-^{1}H COSY Spectrum of compound **22** ($CDCl_3$, 500 MHz)

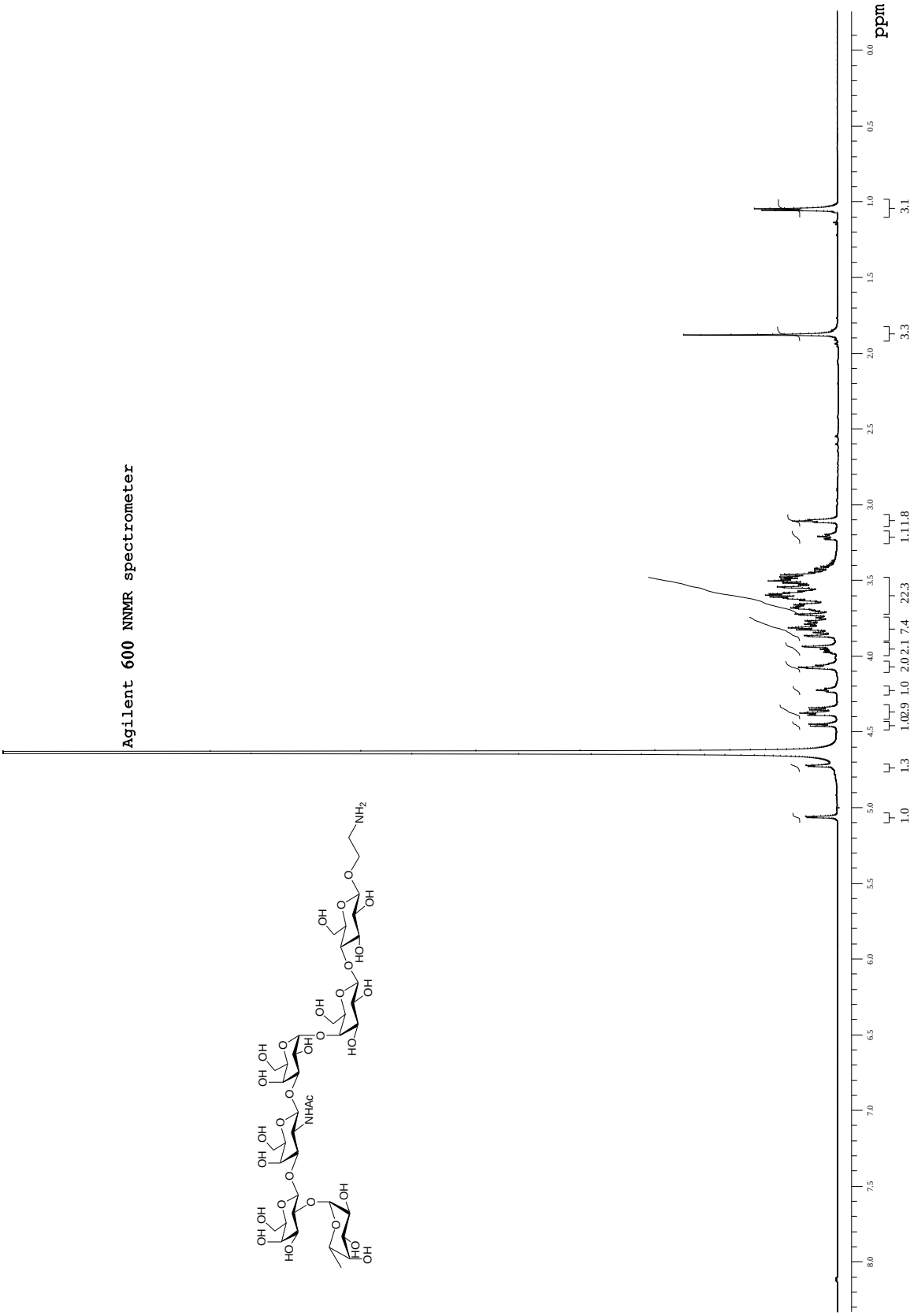


^{1}H-^{13}C HMQC NMR Spectrum of compound **22** ($CDCl_3$, 500/125 MHz)

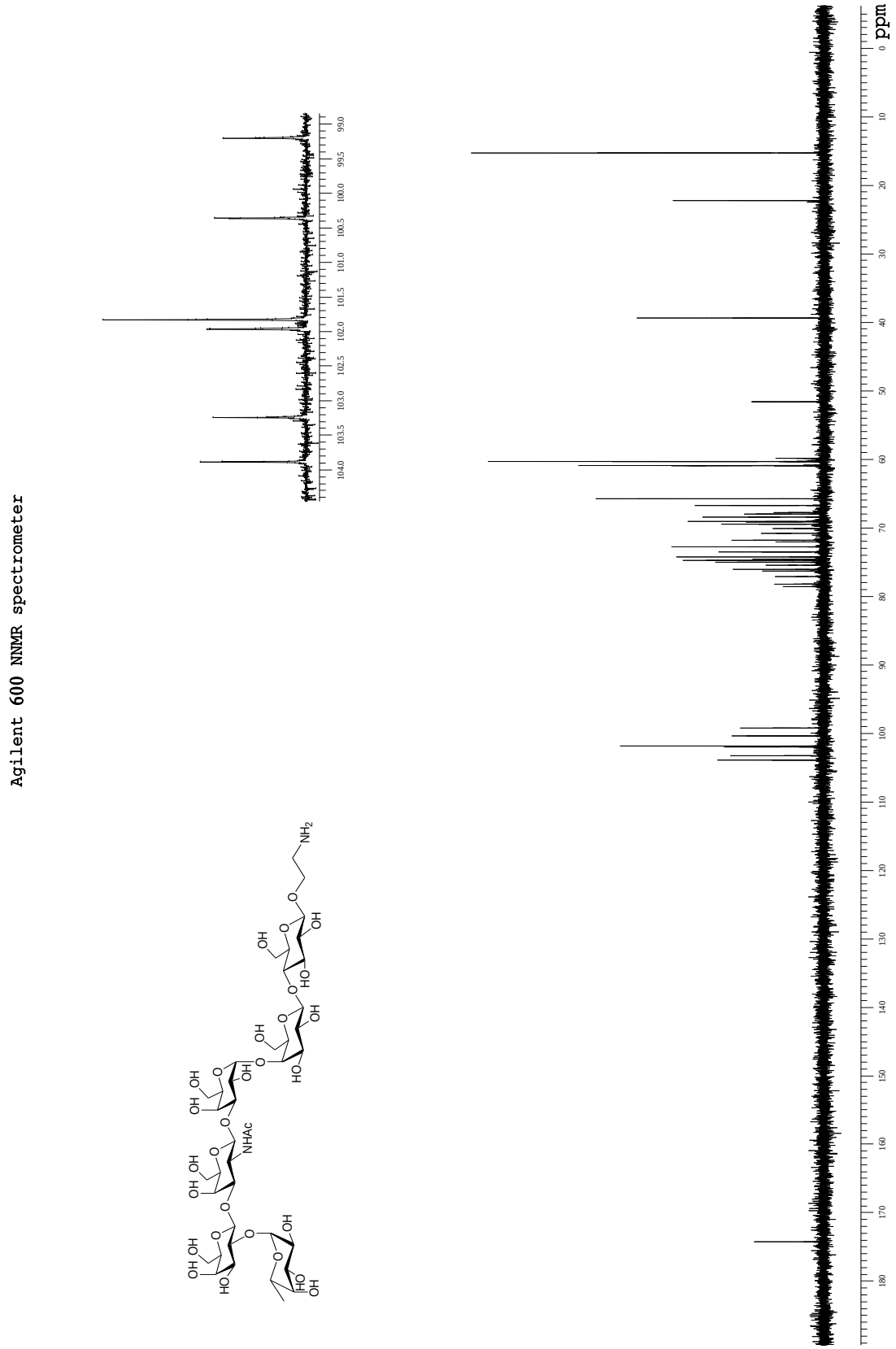
MALTI-TOF MS spectrum of compound **22**

HRMS (ESI MS) spectrum of compound **22**.

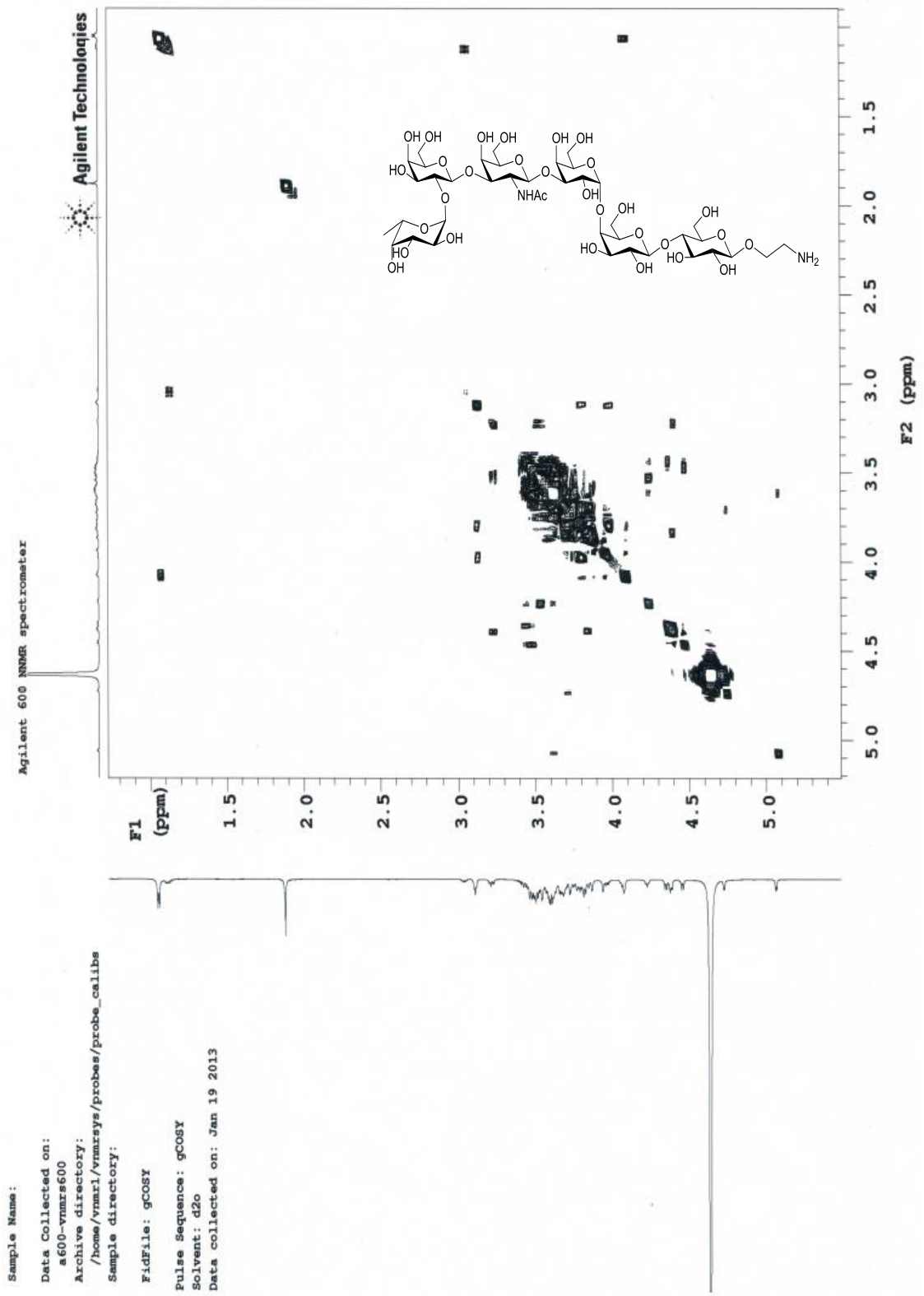
MALTI-TOF MS spectrum of compound **22a**



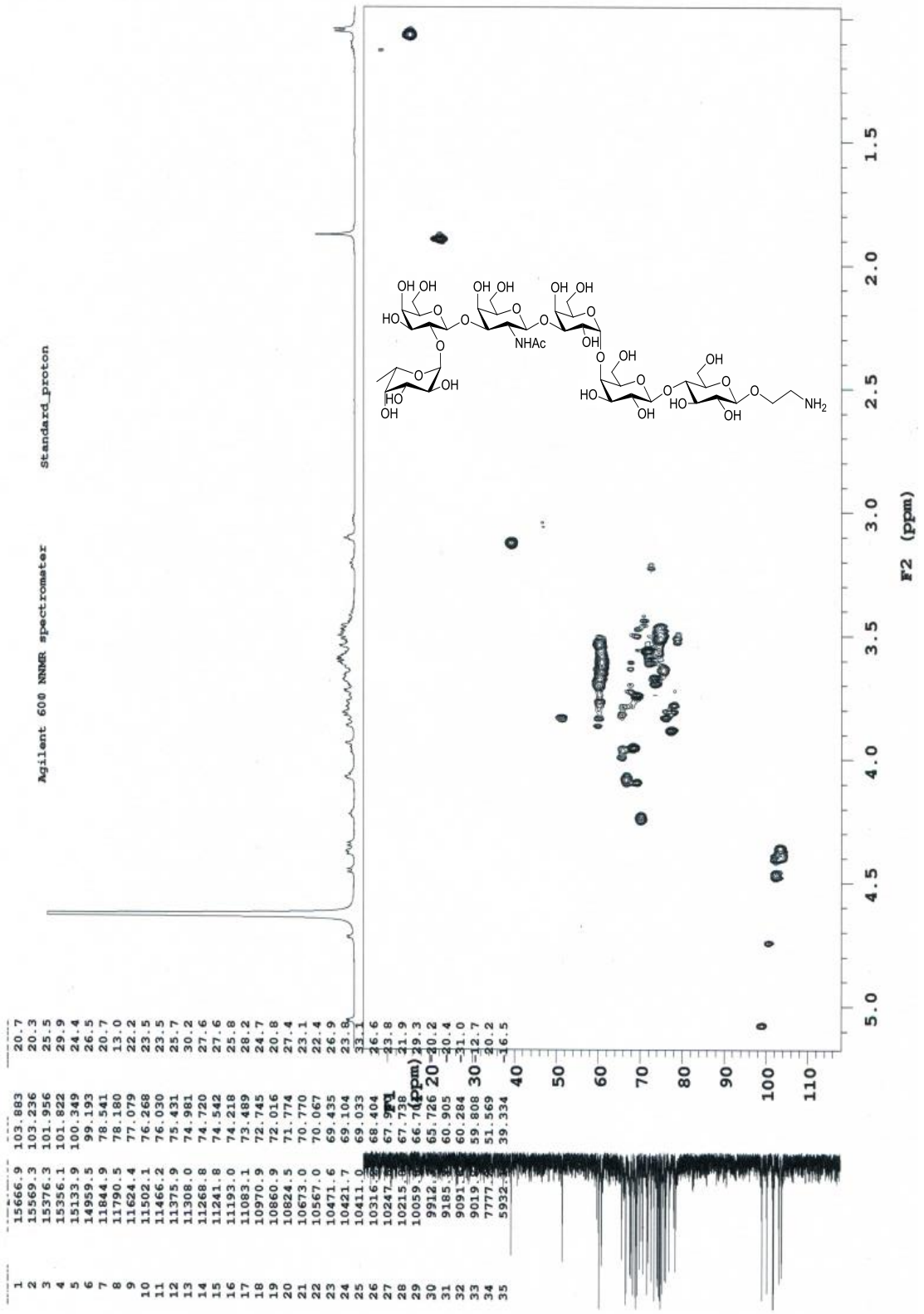
^{1}H NMR Spectrum of compound **2** (D_2O, 600 MHz)



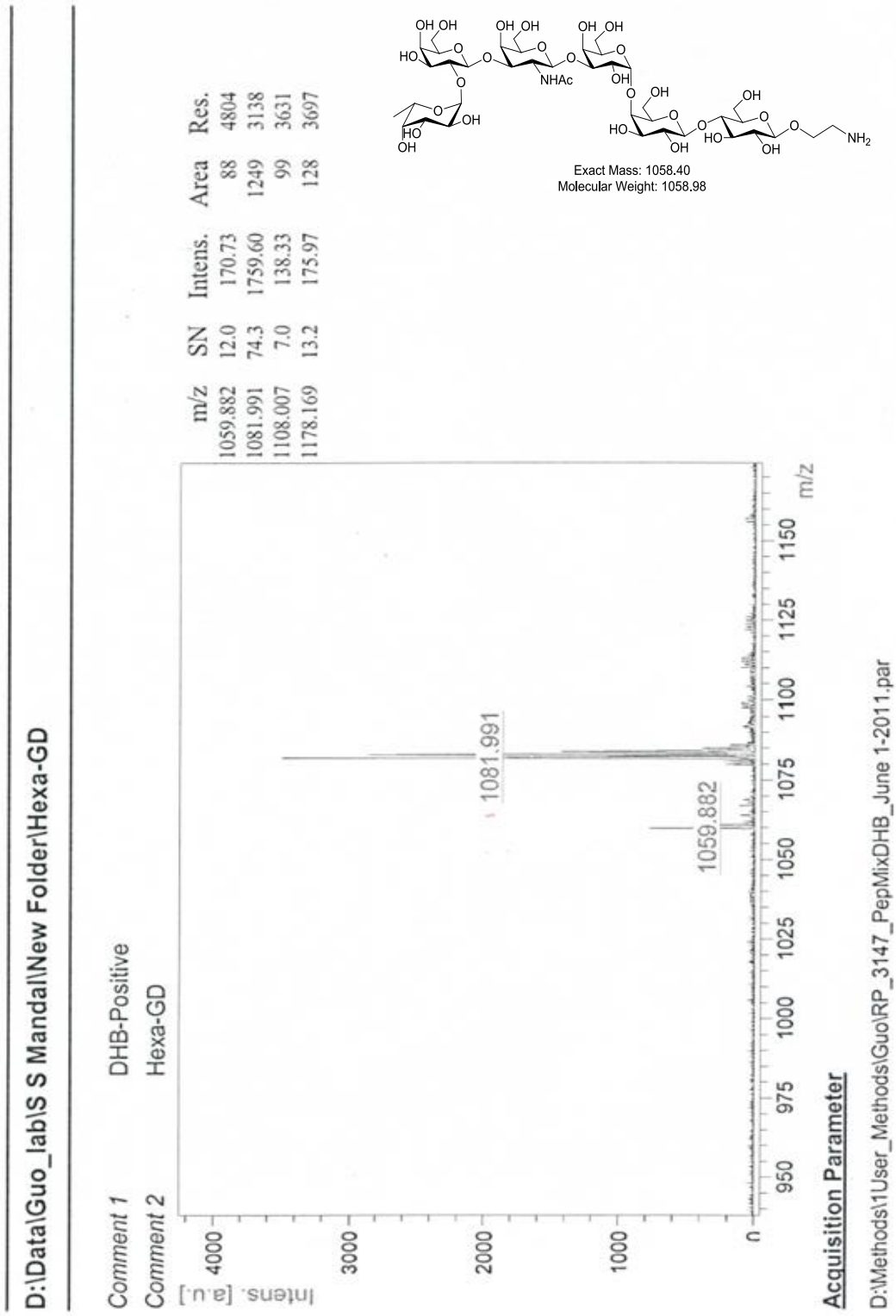
^{13}C NMR Spectrum of compound **2** (D_2O, 600 MHz)



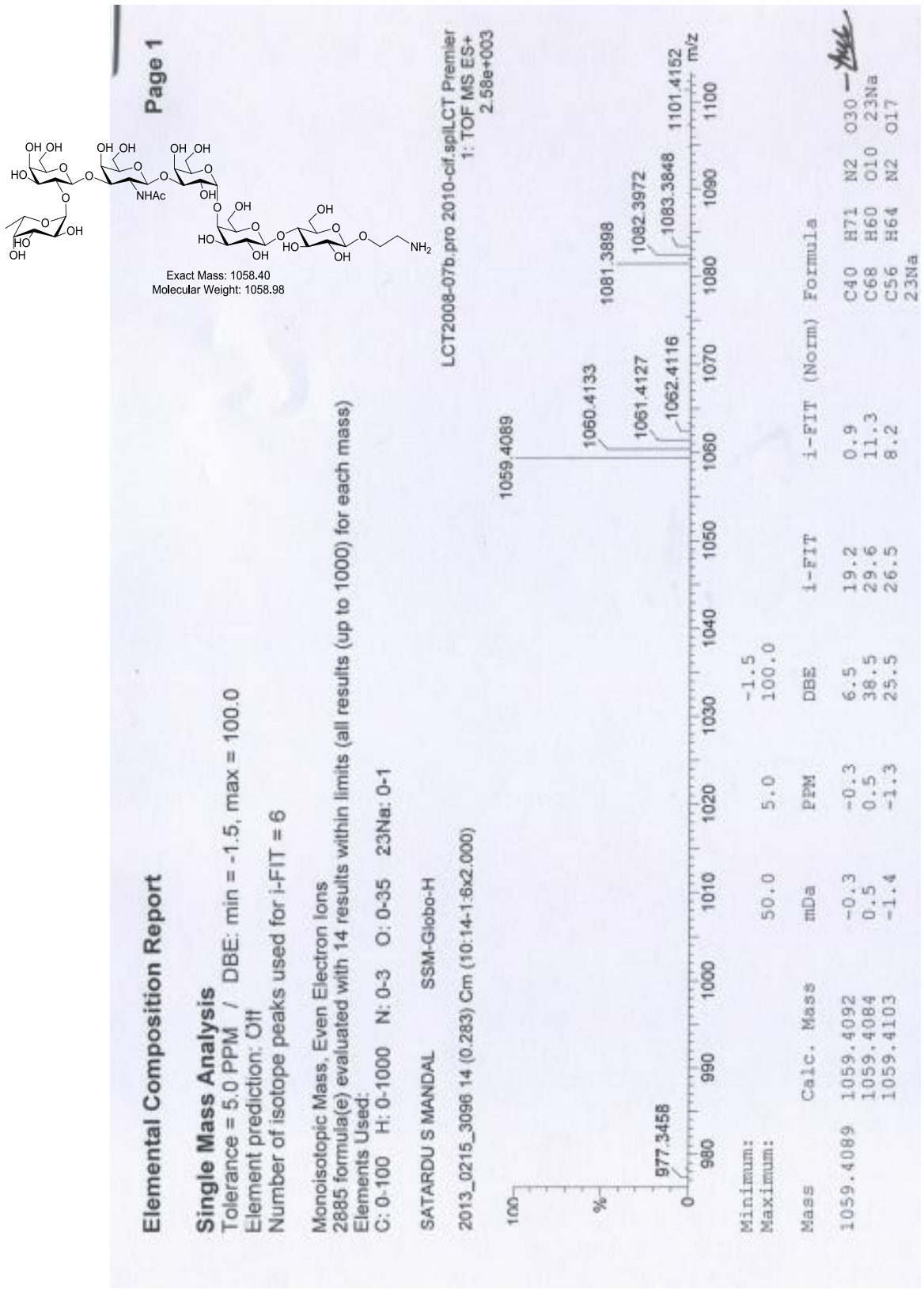
^{1}H-^{1}H COSY Spectrum of compound **2** (D_2O, 600 MHz)



^{1}H-^{13}C HMQC NMR Spectrum of compound **2** (D_2O, 600/150 MHz)



MALTI-TOF MS spectrum of compound **2**



HRMS (ESI MS) spectrum of compound **2**