Supporting Information

for

Synthesis of the Cancer-Associated KH-1 Antigen by Block Assembly of its Backbone Structure Followed by One-Step Grafting of Three Fucose Residues

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Table of Contents

I. General experimental procedures S1

II. Experimental procedures for the synthesis of **1**-**19** S2

III. NMR and MS spectra of new compounds S17

IV. References S78

I. General Experimental Procedures.

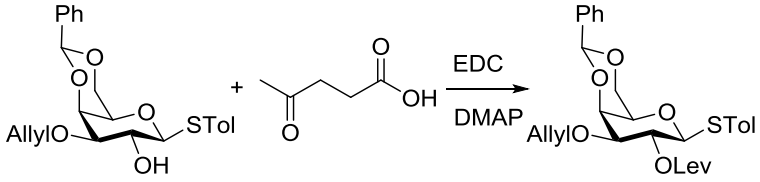
Chemicals and materials were purchased from commercial sources and were used as received without further purification unless otherwise noted. 4Å molecular sieves were flame-dried under high vacuum and used immediately after cooling to rt under a N_2 atmosphere. Analytical TLC was carried out on silica gel 60Å F_{254} plates with detection by a UV detector and/or by charring with 10% (v/v) H_2SO_4 in EtOH. Flash column

chromatography was performed on silica gel 60 (230–400 Mesh). NMR spectra were acquired on a 400, 500 or 600 MHz machine with chemical shifts reported in ppm (δ) and referenced with $CHCl_3$ (^{1}H NMR δ 7.26 ppm) or $CDCl_3$ (^{13}C NMR δ 77.0 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC and ^{1}H–^{13}C HMBC experiments.

II. Experimental procedures for the synthesis of 1-19

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside (7).** It was prepared from galactose according to a literature procedure.[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05-8.02 (m, 2H, ArH), 7.60-7.15 (m, 18H, ArH), 5.56 (t, J = 9.7 Hz, 1H), 5.49 (s, 1 H), 4.81 (d, *J* = 9.7 Hz, 1H), 4.63 (d, *J* = 12.8 Hz, 1H), 4.56 (d, *J* = 12.8 Hz, 1H), 4.39 (d, J = 12.5 Hz, 1H), 4.24 (d, *J* = 2.8 Hz, 1 H), 4.03 (d, *J* = 11.4 Hz, 1H), 3.77 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.50 (s, 1H).

***p*-Tolyl 3-*O*-allyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside (S1).** It was prepared from galactose according to a literature procedure.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.1 Hz, 2H, ArH), 7.39-7.38 (m, 2H, ArH), 7.34-7.32 (m, 3H, ArH), 7.05 (d, *J* = 7.4 Hz, 2H, ArH), 5.95-5.89 (m, 1H, =CH), 5.49 (s, 1H, PhCH), 5.29 (dd, 1H, *J* = 17.2, 1.3 Hz, =C*H*H), 5.19 (dd, 1H, *J* = 17.2, 1.3 Hz, =CH*H*), 4.49 (d, 1H, *J* = 12.9 Hz, H-1), 4.38 (d, 1H, *J* = 13.5 Hz, H-6a), 4.24 (d, 1H, *J* = 3.4 Hz, H-4), 4.22-4.14 (m, 2H, =CH*C*H_2), 4.02 (d, 1H, *J* = 13.5 Hz, H-6b), 3.83 (t, 1H, *J* = 9.9 Hz, H-2), 3.50-3.47 (m, 2H, H-3, H-5), 2.44 (s, 1H, OH), 2.33 (s, 3H, SPhCH_3).

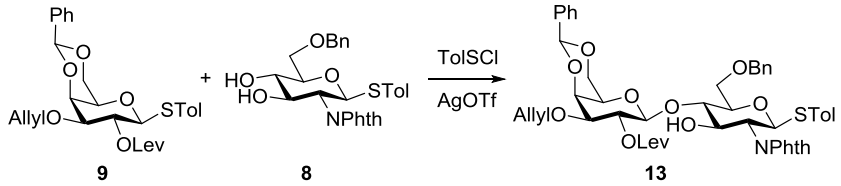


***p*-Tolyl 3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-levulinoyl-1-thio-*β*-D-galactopyranoside (9).** To a solution of **S1** (1.2 g, 3.0 mmol) and levulinic acid (1.04 g, 9.0 mmol) in CH_2Cl_2 (20 mL) were added 4-dimethylaminopyridine (DMAP) (36 mg, 0.3 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (1.4 g, 9.0 mmol) at 0 ^oC. The resulting mixture was allowed to warm to rt and stirred overnight. Upon complete consumption of

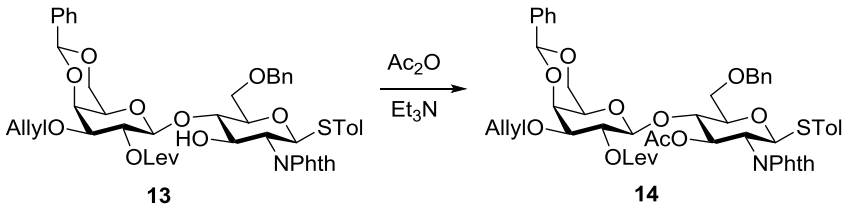
S1 as monitored by TLC, the solution was washed with diluted aq. HCl solution, saturated aq. $NaHCO_3$, water and brine. The organic phase was dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (hexane/EtOAc = 2/1) to afford **9** (1.46 g, 95% yield) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.1 Hz, 2H, ArH), 7.39-7.38 (m, 2H, ArH), 7.33-7.31 (m, 3H, ArH), 7.04 (d, *J* = 8.1 Hz, 2H, ArH), 5.89-5.83 (m, 1H, =CH), 5.48 (s, 1H, PhCH), 5.24 (dd, 1H, *J* = 17.2, 1.3 Hz, =C*H*H), 5.21 (t, 1H, *J* = 9.3 Hz, H-2), 5.16 (dd, 1H, *J* = 17.2, 1.3 Hz, =CH*H*), 4.60 (d, 1H, *J* = 8.1 Hz, H-1), 4.35 (dd, 1H, *J* = 12.2, 1.5 Hz, H-6a), 4.24 (d, 1H, *J* = 3.1 Hz, H-4), 4.13-4.04 (m, 1H, =CH*CH*$_2$), 4.01 (dd, 1H, *J* = 12.2, 1.5 Hz, H-6b), 3.59 (dd, 1H, *J* = 9.4, 3.3 Hz, H-3), 3.47 (s, 1H, H-5), 2.80 (dt, 1H, *J* = 6.7, 6.6 Hz, CH_2), 2.80 (dt, 2H, *J* = 6.7, 6.6 Hz, CH_2), 2.32 (s, 3H, $SPhCH_3$), 2.20 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) *δ* 206.4, 171.0, 138.1, 137.6, 134.7, 134.2, 129.4, 129.0, 128.0, 127.5, 126.6, 117.4, 101.2, 85.3, 78.4, 73.5, 70.7, 70.0, 69.3, 68.7, 38.0, 33.9, 29.9, 28.1, 25.6, 24.9, 21.2. HRMS (MALDI): $[M + Na]^+$ $C_{27}H_{30}O_7SNa^+$ *m*/*z* calcd 521.1604, found 520.9976.

***p*-Tolyl 6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (8).** It was prepared from galactosamine according to a literature procedure.[3] ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.79-6.96 (m, 13 H, ArH), 5.50 (d, *J* = 10.2 Hz), 4.56-4.51 (m, 2 H), 4.29 (dt, 1 H, *J* = 10.2, 4.2 Hz), 4.15 (t, 1 H, *J* = 10.2 Hz), 4.07 (d, 1 H, *J* = 4.2 Hz), 3.99 (d, 1 H, *J* = 4.2 Hz), 3.77-3.69 (m, 2 H), 3.62-3.47 (m, 2 H), 2.25 (s, 3 H).

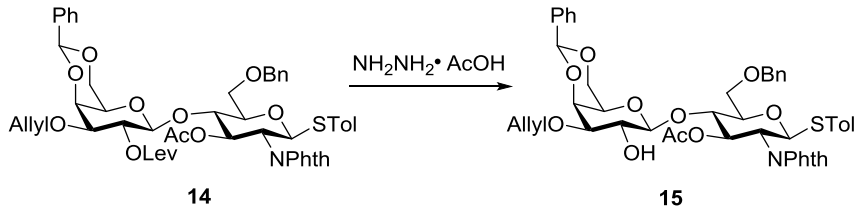
2-Azidoethyl 2,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (6). It was prepared from lactose according to a literature procedure.[3] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38-7.16 (m, 30H, ArH), 5.02 (d, *J* = 10.7 Hz, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.77-4.74 (m, 4H), 4.69 (d, *J* = 11.3 Hz, 1 H), 4.61 (d, *J* = 11.9 Hz, 1 H), 4.56 (d, *J* = 11.9 Hz, 1 H), 4.44-4.38 (m, 4H), 4.28 (d, *J* = 11.9 Hz, 1 H), 4.06-4.03 (m, 1H), 3.96 (t, *J* = 9.7 Hz, 1 H), 3.84 (d, *J* = 2.9 Hz, 1 H), 3.80-3.69 (m, 3H), 3.58-3.40 (m, 10H), 2.18 (d, *J* = 6.5 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$) *δ*.139.0, 138.7, 138.6, 138.4, 138.1, 138.0, 128.4, 128.37, 128.36, 128.3, 128.3, 128.04, 128.00, 127.99, 127.9, 127.74, 127.73, 127.7, 127.68, 127.62, 127.58, 127.55, 127.16, 103.6, 102.7, 82.7, 81.7, 80.6, 76.6, 75.9, 75.3, 75.2, 75.1, 75.0, 74.96, 74.01, 73.4, 73.2, 73.17, 68.2, 68.1, 68.0, 60.0, 50.1.



***p*-Tolyl (3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-levulinoyl-*β*-D-galactopyranosyl)-(1→4)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (13):** Galactosyl donor **9** (124 mg, 0.2 mmol) and freshly activated 4Å MS (1.0 g) in CH_2Cl_2 (5 mL) was stirred at rt for 1 h. The mixture was cooled to -78 ^oC before dry silver triflate (154 mg, 0.6 mmol, 3.0 equiv) in acetonitrile (0.5 mL) was added. After 15 min of stirring, *p*-TolSCl (32 μL, 0.2 mmol) was added. After complete activation of galactosyl donor **9** was confirmed by TLC, a CH_2Cl_2 solution (1 mL) of glucosamine acceptor **8** (100 mg, 0.18 mmol) and TTBP (50 mg, 0.2 mmol) was added to the mixture. The reaction was kept at -78 ^oC and upon completion, which was indicated by the disappearance of **8** (in about 1 h), the mixture was filtered through a pad of Celite. The solid was thoroughly washed with CH_2Cl_2 and the filtrate was combined and washed with saturated solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to afford **13** as a white solid (166 mg, 93% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 7.88-7.82 (m, 2H, ArH), 7.72-7.70 (m, 2H, ArH), 7.43-7.26 (m, 12H, ArH), 7.00 (d, 2H, J = 7.8 Hz, ArH), 5.88-5.82 (m, 1H), 5.57 (d, 1H, J = 10.5 Hz, H-1), 5.45 (s, 1H, PhCH), 5.29-5.26 (m, 2H), 5.19 (dd, 1H, J = 10.7, 1.4 Hz), 4.71 (d, 1H, J = 11.5 Hz), 4.53 (d, 1H, J = 11.5 Hz), 4.46 (d, 1H, J = 8.0 Hz, H-1'), 4.43 (dd, 1H, J = 10.4, 8.2 Hz), 4.24-4.18 (m, 3H), 4.14-4.04 (m, 3H), 3.97 (d, 1H, J = 13.7 Hz), 3.85 (s, 2H), 3.75-3.70 (m, 2H), 3.43 (dd, 1H, J = 10.7, 3.6 Hz), 3.35 (s, 1H), 2.79-2.68 (m, 2H), 2.59-2.56 (m, 2H), 2.27 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.3, 171.1, 168.0, 167.7, 138.5, 138.1, 137.3, 134.6, 134.0, 133.9, 133.5, 131.8, 131.7, 129.6, 128.9, 128.3, 128.0, 127.9, 127.7, 127.6, 126.3, 123.6, 117.4, 101.3, 101.0, 83.4, 80.8, 78.4, 73.5, 72.9, 70.63, 70.62, 70.2, 68.5, 68.4, 66.8, 55.3, 37.7, 29.9, 27.8, 21.1; HRMS (ESI): $[M + Na]^+$ $C_{49}H_{51}NO_{13}SNa^+$ *m/z* calcd 916.2973, found 916.2991.

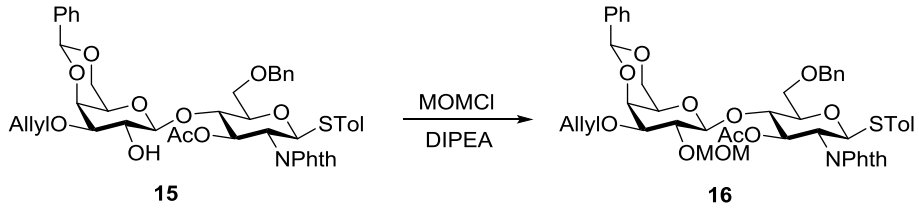


***p*-Tolyl (3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-levulinoyl-*β*-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (14):** Triethylamine (128 uL, 0.93 mmol) was added dropwise in a period of 5 min to a solution of disacchride **13** (165mg, 0.185 mmol) and acetic anhydride (52 uL, 0.56 mmol) in CH_2Cl_2 (10 mL) at 0 ^oC. Then, DMAP (2.5 mg, 0.02 mmol) was added in one portion before the reaction mixture was allowed to warm up to rt. The resulting solution was stirred for 2 h before **13** was completely consumed as indicated by TLC. The solution was washed with diluted aq. HCl solution, saturated aq. $NaHCO_3$, water and brine, and the solvent was removed in vacuum. The residue was purified by flash chromatography (hexane/EtOAc = 3/2) to give **9** (164 mg, yield 95%) as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.86-7.82 (m, 2H, ArH), 7.73-7.69 (m, 2H, ArH), 7.39-7.26 (m, 12H, ArH), 7.02 (d, 2H, J = 7.8 Hz, ArH), 5.88-5.82 (m, 1H, =CH), 5.71 (t, 1H, J = 9.2 Hz, H-3'), 5.67 (d, 1H, J = 10.4 Hz, H-1'), 5.44 (s, 1H, PhCH), 5.26 (dd, 1H, J = 7.2, 1.3 Hz, $=CH_{2a}$), 5.23 (dd, 1H, J = 10.3, 1.5 Hz, $=CH_{2b}$), 5.11 (dd, 1H, J = 10.0, 8.0 Hz, H-2), 4.76 (d, 1H, J = 12.1 Hz, $PhCH_2$), 4.53 (d, 1H, J = 12.0 Hz, $PhCH_2$), 4.48 (d, 1H, J = 8.0 Hz, H-1), 4.27 (t, 1H, J = 10.2 Hz, H-2'), 4.22 (d, 1H, J = 13.1 Hz, H-6a), 4.11 (d, 1H, J = 3.3 Hz, H-4), 4.08 (dd, 1H, J = 13.5, 5.5 Hz, $=CHCH_{2a}$), 4.03-3.91 (m, 4H, $=CHCH_{2b}$, H-6b, H-5', H-6a'), 3.88 (d, 1H, J = 10.9 Hz, H-6b'), 3.74 (d, 1H, J = 9.9 Hz, H-4'), 3.35 (dd, 1H, J = 10.1, 3.5 Hz, H-3), 3.14 (s, 1H, H-5), 2.77-2.74 (m, 2H, CH_2), 2.55-2.51 (m, 2H, CH_2), 2.29 (s, 3H, $PhCH_3$), 2.18 (s, 3H, $COCH_3$), 1.85 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.5, 170.8, 170.5, 167.7, 167.4, 138.4, 138.35, 134.8, 134.2, 134.0, 133.8, 131.8, 131.3, 129.6, 129.0, 128.4, 128.1, 127.8, 127.6, 127.4, 126.5, 123.6, 123.4, 117.1, 101.4, 100.3, 83.0, 79.2, 77.3, 74.8, 73.5, 73.3, 71.7, 70.7, 70.5, 68.7, 68.0, 66.3, 60.0, 54.0, 37.8, 29.9, 29.7, 27.9, 21.1, 20.4; HRMS (ESI): $[M + Na]^+$ $C_{51}H_{53}NO_{14}SNa^+$ *m*/*z* calcd 958.3079, found 958.3066.



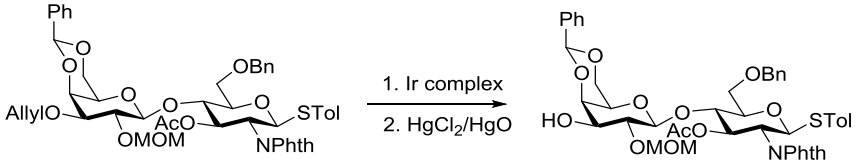
14 **15**

***p*-Tolyl (3-*O*-allyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (15):** Compound **14** (100mg, 0.11 mmol) was dissolved in CH_2Cl_2 and MeOH (4.5 mL/0.5 mL) at rt when hydrazine acetate (492 mg, 5.35 mmol) was added. The resulting mixture was stirred at rt for 4 h before **14** completely disappeared as indicated by TLC. The solution was washed with diluted HCl solution, saturated $NaHCO_3$, water and brine. The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash chromatography (hexane/EtOAc = 1/1) to give **15** (71 mg, yield 80%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85-7.84 (m, 2H, ArH), 7.73-7.72 (m, 2H, ArH), 7.39-7.28 (m, 12H, ArH), 7.02 (d, 2H, J = 7.2 Hz, ArH), 5.96-5.90 (m, 1H, =CH), 5.82 (dd, 1H, J = 10.1, 9.5 Hz, H-3'), 5.66 (d, 1H, J = 10.6 Hz, H-1'), 5.44 (s, 1H, PhCH), 5.29 (dd, 1H, J = 17.3, 1.4 Hz, $=CH_{2a}$), 5.20 (dd, 1H, J = 10.3, 1.8 Hz, $=CH_{2b}$), 4.70 (d, 1H, J = 11.8 Hz, $PhCH_2$), 4.57 (d, 1H, J = 11.4 Hz, $PhCH_2$), 4.36 (d, 1H, J = 7.8 Hz, H-1), 4.30 (t, 1H, J = 10.5 Hz, H-2'), 4.21 (d, 1H, J = 12.3 Hz, H-6a), 4.19-4.17 (m, 1H, $=CHCH_{2a}$), 4.14-4.12 (m, 1H, $=CHCH_{2b}$), 4.10 (d, 1H, J = 3.6 Hz, H-4), 4.05 (t, 1H, J = 9.8 Hz, H-4'), 4.03 (dd, 1H, J = 11.0, 3.1 Hz, H-5'), 3.95 (dd, 1H, J = 12.6, 1.9 Hz, H-6b), 3.89 (dd, 1H, J = 11.3, 1.7 Hz, H-6a'), 3.81-3.76 (m, 2H, H-2, H-6b'), 3.26 (dd, 1H, J = 9.7, 3.5 Hz, H-3), 3.14 (s, 1H, H-5), 2.29 (s, 3H, $PhCH_3$), 1.86 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 170.5, 167.7, 167.3, 138.4, 138.4, 137.8, 134.9, 134.3, 134.0, 133.8, 131.7, 131.3, 129.6, 129.0, 128.3, 128.1, 127.7, 127.6, 127.4, 126.5, 123.5, 117.6, 102.5, 101.3, 83.1, 79.1, 78.9, 75.3, 73.3, 72.9, 71.7, 70.1, 68.9, 68.2, 66.4, 60.0, 54.0, 21.2, 20.5; HRMS (ESI): $[M + Na]^+$ $C_{46}H_{47}NO_{12}SNa^+$ m/z calcd 860.2711, found 860.2720.



15 **16**

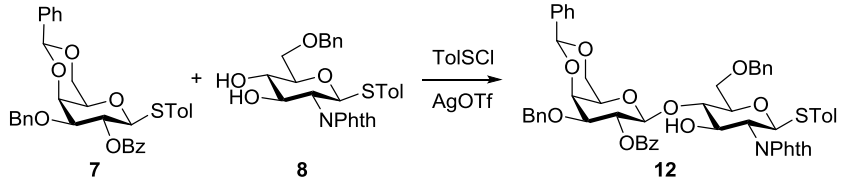
***p*-Tolyl (3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-methoxymethyl-*β*-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (16):** To a solution of **15** (84 mg, 0.1 mmol) and methoxymethyl chloride (23 μL, 0.3 mmol) in anhydrous CH_2Cl_2 (5 mL) was added diisopropylethylamine (0.17 mL, 1.0 mmol) at 0 ^oC, The resulting mixture was allowed to warm up to rt and stirred for 1 h before **15** completely disappeared as indicated by TLC. The solution was washed with diluted HCl solution, saturated $NaHCO_3$, water and brine. The organic phase was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by flash chromatography (hexane/EtOAc = 3/2) to give **16** (68 mg, yield 77%) as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.86-7.84 (m, 2H, ArH), 7.74-7.70 (m, 2H, ArH), 7.39-7.26 (m, 12H, ArH), 7.02 (d, 2H, *J* = 8.0 Hz, ArH), 5.95-5.88 (m, 1H), 5.75 (t, 1H, *J* = 9.7 Hz), 5.67 (d, 1H, *J* = 10.3 Hz, H-1), 5.43 (s, 1H, PhCH), 5.28 (d, 1H, *J* = 17.2 Hz), 5.17 (d, 1H, *J* = 10.6 Hz), 4.78 (d, 1H, *J* = 6.0 Hz), 4.74 (d, 1H, *J* = 6.0 Hz), 4.71 (d, 1H, *J* = 11.6 Hz), 4.57 (d, 1H, *J* = 13.2 Hz), 4.36 (d, 1H, *J* = 7.5 Hz), 4.31 (t, 1H, *J* = 10.2 Hz), 4.21 (d, 1H, *J* = 12.2 Hz), 4.16-4.08 (m, 3H), 4.03 (t, 1H, *J* = 9.6 Hz), 3.99 (dd, 1H, *J* = 11.0, 3.2 Hz), 3.94 (d, 1H, *J* = 12.2 Hz), 3.91 (d, 1H, *J* = 11.0 Hz), 3.72 (d, 1H, *J* = 14.2 Hz), 3.68 (t, 1H, *J* = 9.2 Hz), 3.40 (s, 3H), 3.29 (dd, 1H, *J* = 10.1, 3.3 Hz), 3.01 (s, 3H), 2.29 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 167.8, 167.3, 138.5, 138.4, 137.8, 134.9, 134.3, 134.1, 133.7, 131.7, 131.3, 129.6, 129.0, 128.3, 128.1, 127.6, 127.5, 126.6, 123.6, 123.5, 117.2, 102.2, 101.5, 97.8, 83.2, 79.5, 79.0, 74.9, 74.8, 73.3, 73.2, 71.5, 70.8, 68.8, 68.1, 66.2, 56.3, 54.0, 21.2, 20.5; HRMS (ESI): $[M + Na]^+$ $C_{48}H_{51}NO_{13}SNa^+$ *m*/*z* calcd 904.2973, found 904.2958.



16 **5**

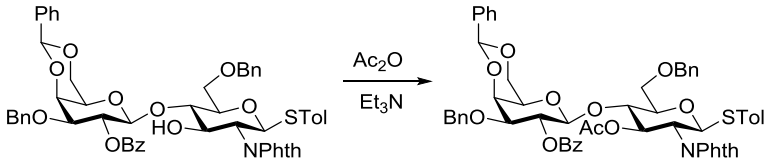
***p*-Tolyl (4,6-*O*-benzylidene-2-*O*-methoxymethyl-*β*-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (5):** Hydrogen gas was slowly bubbled into a solution of $[Ir(COD)(PMePh_2)_2]PF_6$ (7.5 mg 0.009 mmol, 0.15 equiv) in THF at rt until the red color turned into pale yellow (in ca. 2 min). H_2 was exchanged with argon three times before a solution of **16** (53 mg, 0.06

mmol) in THF was added in one portion. The reaction mixture was stirred at rt for 40 min, at which point TLC showed the completion of reaction. The mixture was concentrated in vacuum, and the residue was dissolved in acetone and water (9:1, v/v) before $HgCl_2$ (81 mg, 0.3 mmol, 5.0 equiv) and HgO (2 mg, 0.009 mmol0.15 equiv) were added. In 1 h, the reaction was complete as indicated by TLC. The resulting mixture was filtered and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2 followed by washing with water and brine. The organic phase was concentrated and the residue was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to give **5** as a white solid (40 mg, yield 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H, ArH), 7.74-7.72 (m, 2H, ArH), 7.40-7.30 (m, 12H, ArH), 7.03 (d, 2H, *J* = 8.0 Hz, ArH), 5.77 (t, 1H, *J* = 9.6 Hz), 5.67 (d, 1H, *J* = 10.8 Hz, H-1), 5.47 (s, 1H, PhCH), 4.74 (d, 1H, *J* = 6.3 Hz), 4.70 (d, 1H, *J* = 11.9 Hz), 4.67 (d, 1H, *J* = 6.3 Hz), 4.55 (d, 1H, *J* = 12.3 Hz), 4.37 (d, 1H, *J* = 7.2 Hz), 4.32 (t, 1H, *J* = 10.9 Hz), 4.22 (d, 1H, *J* = 12.4 Hz), 4.10 (s, 1H), 4.02 (t, 1H, *J* = 9.5 Hz), 3.97-3.95 (m, 2H), 3.90 (d, 1H, *J* = 10.2 Hz), 3.73 (d, 1H, *J* = 10.0 Hz), 3.49-3.48 (m, 2H), 3.40 (s, 3H), 3.17-3.15 (m, 2H), 2.30 (s, 3H), 1.9 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 167.9, 167.3, 138.4, 138.3, 137.6, 134.3, 134.1, 133.8, 131.7, 131.3, 129.6, 129.3, 128.4, 128.2, 127.64, 127.63, 127.5, 126.62, 126.61, 123.65, 123.57, 101.7, 101.67, 97.7, 83.3, 79.4, 78.6, 75.3, 75.1, 73.2, 72.1, 71.5, 68.7, 68.0, 66.2, 55.8, 53.9, 21.2, 20.5; HRMS (ESI): $[M + Na]^+$ $C_{45}H_{47}NO_{13}SNa^+$ *m/z* calcd 864.2660, found 864.2670.



***p*-Tolyl (2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (12):** Galactosyl donor **7** (114 mg, 0.2 mmol) and freshly activated 4Å MS (1.0 g) in CH_2Cl_2 (5 mL) was stirred at rt for 1 h. The mixture was cooled to -78 ^{o}C before dry silver triflate (154 mg, 0.6 mmol, 3.0 equiv) in acetonitrile (0.5 mL) was added. After 15 min of stirring, *p*-TolSCl (32 μL, 0.2 mmol) was added. After complete activation of galactosyl donor **7** was confirmed by TLC, a CH_2Cl_2 solution (1 mL) of glucosamine acceptor **8** (100 mg, 0.18

mmol) and TTBP (50 mg, 0.2 mmol) was added to the mixture. The reaction was kept at -78 ^{o}C and upon completion, which was indicated by the disappearance of **8** (in about 1 h), the mixture was filtered through a pad of Celite. The solid was thoroughly washed with CH_2Cl_2 and the filtrate was combined and washed with saturated solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography (hexane/EtOAc = 1/1) to afford **12** as a white solid (155 mg, yield 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, 2H, *J* = 6.8 Hz, ArH), 7.88-7.81 (m, 2H, ArH), 7.71-7.70 (m, 2H, ArH), 7.64 (t, 1H, *J* = 7.2 Hz, ArH), 7.50-7.48 (m, 4H, ArH), 7.35-7.19 (m, 15H, ArH), 6.95 (d, 2H, *J* = 8.2 Hz, ArH), 5.63 (dd, 1H, *J* = 9.5, 8.0 Hz, H-2), 5.51 (d, 1H, *J* = 10.1 Hz, H-1'), 5.46 (s, 1H, PhCH), 4.67 (d, 1H, *J* = 12.7 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = 7.5 Hz, H-1), 4.57 (d, 1H, *J* = 12.5 Hz, $PhCH_2$), 4.45 (dd, 1H, *J* = 10.4, 8.3 Hz, H-2'), 4.30-4.28 (m, 2H, OH, $PhCH_2$), 4.24-4.19 (m, 3H, H-4, H-2', $PhCH_2$), 4.17 (d, 1H, *J* = 12.0 Hz, H-6b), 3.98 (d, 1H, *J* = 11.8 Hz, H-6b'), 3.70 (t, 1H, *J* = 9.1 Hz, H-3'), 3.65 (dd, 1H, *J* = 9.9, 3.2 Hz, H-3), 3.58 (dd, 1H, *J* = 10.1, 3.8 Hz, H-4'), 3.52-3.50 (m, 2H, H-5', H-6b), 3.38 (s, 1H, H-5'), 2.25 (s, 3H, $PhCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 167.7, 164.8, 138.5, 138.0, 137.5, 137.3, 134.0, 133.9, 133.3, 133.27, 131.8, 131.7, 129.9, 129.7, 129.5, 128.9, 128.5, 128.2, 128.1, 128.07, 127.8, 127.7, 127.4, 126.3, 123.6, 123.2, 101.6, 101.1, 83.4, 81.4, 77.9, 76.5, 72.9, 72.4, 70.8, 70.76, 70.5, 68.5, 68.1, 66.8, 55.2, 21.0; HRMS (ESI): $[M + Na]^+$ $C_{55}H_{51}NO_{12}SNa^+$ *m/z* calcd 972.3024, found 972.3016.

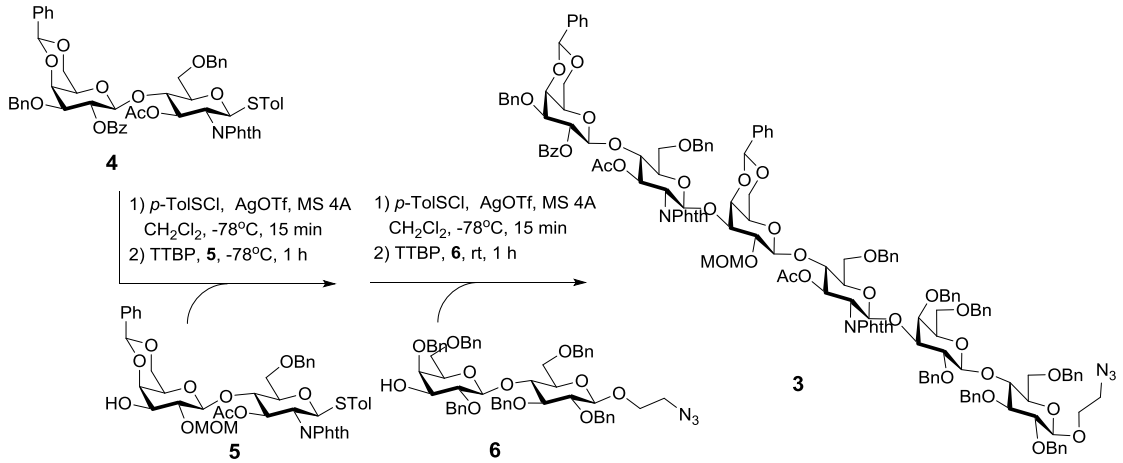


12 **4**

***p*-Tolyl (2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-3--*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-*β*-D-glucopyranoside (4):**

Triethylamine (128 uL, 0.93 mmol) was added dropwise in a period of 5 min to a solution of disacchride **12** (155mg, 0.164 mmol) and acetic anhydride (46 uL, 0.50 mmol) in CH_2Cl_2 (10 mL) at 0 ^{o}C. Then, DMAP (2.5 mg, 0.02 mmol) was added in one portion before the reaction mixture was allowed to warm up to rt. The resulting solution was stirred for 2 h before **12** was completely consumed as indicated by TLC. The solution

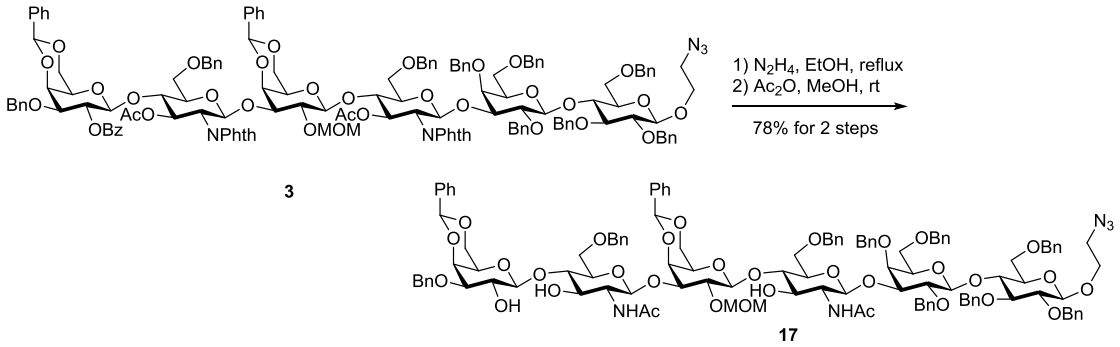
was washed with diluted aq. HCl solution, saturated aq. $NaHCO_3$, water and brine, and the solvent was removed in vacuum. The residue was purified by flash chromatography (hexane/EtOAc = 3/2) to give **4** (151 mg, yield 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, 2H, J = 6.7 Hz, ArH), 7.85-7.81 (m, 2H, ArH), 7.71-7.69 (m, 2H, ArH), 7.59 (t, 1H, J = 7.4 Hz, ArH), 7.46-7.44 (m, 4H, ArH), 7.32-7.18 (m, 15H, ArH), 6.97 (d, 2H, J = 7.7 Hz, ArH), 5.71 (dd, 1H, J = 10.0, 9.2 Hz, H-2), 5.58 (d, 1H, J = 10.1 Hz, H-1'), 5.46 (dd, 1H, J = 9.9, 8.1 Hz, H-3'), 5.44 (s, 1H, PhCH), 4.63 (d, 1H, J = 12.8 Hz, $PhCH_2$), 4.61 (d, 1H, J = 11.8 Hz, $PhCH_2$), 4.60 (d, 1H, J = 7.9 Hz, H-1), 4.53 (d, 1H, J = 12.6 Hz, $PhCH_2$), 4.34 (d, 1H, J = 11.5 Hz, $PhCH_2$), 4.26 (d, 1H, J = 11.5 Hz, H-2'), 4.25 (dd, 1H, J = 11.5 Hz, H-6a), 4.13 (d, 1H, J = 3.2 Hz, H-4), 4.00 (t, 1H, J = 9.6 Hz, H-4'), 3.97 (dd, 1H, J = 12.0, 1.5 Hz, H-6b), 3.68 (dd, 1H, J = 10.8, 3.1 Hz, H-6a'), 3.59-3.53 (m, 3H, H-3, H-5', H-6b'), 3.16 (s, 1H, H-5), 2.25 (s, 3H, $PhCH_3$), 1.76 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 167.6, 167.4, 164.5, 138.4, 138.2, 137.8, 137.6, 134.2, 134.0, 133.6, 133.0, 131.8, 131.3, 129.9, 129.8, 129.5, 129.0, 128.4, 128.3, 128.28, 128.1, 127.7, 127.69, 127.63, 127.6, 126.5, 123.6, 123.4, 101.4, 100.4, 83.1, 78.8, 76.8, 74.8, 73.3, 72.7, 71.7, 71.0, 70.6, 68.7, 67.8, 66.3, 54.0, 21.1, 20.4; HRMS (ESI): $[M + Na]^+$ $C_{57}H_{53}NO_{13}SNa^+$ m/z calcd 1014.3130, found 1014.3160.



2-Azidoethyl (2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-*O*-methoxymethyl-*β*-D-galactopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (3): Galactosyl

donor **4** (150 mg, 0.15mmol) and freshly activated 4Å MS (1.0 g) in CH_2Cl_2 (5 mL) was stirred at rt for 1 h. The mixture was cooled to -78 ^oC before dry silver triflate (116 mg, 0.45 mmol, 3.0 equiv) in acetonitrile (0.5 mL) was added. After 15 min of stirring, *p*-TolSCl (24 μL, 0.15 mmol) was added. After complete activation of **4** was confirmed by TLC, the CH_2Cl_2 solution (1 mL) of disaccharide acceptor **5** (114 mg, 0.136 mmol) and TTBP (37 mg, 0.15 mmol) was added to the reaction mixture. The reaction was kept at -78 ^oC and upon completion, which is indicated by disappearance of **5** (in about 1 h), *p*-TolSCl (21 μL, 0.136 mmol) was added. About 15 min later, TLC indicated the full activation of tetrasacchride donor, and then a CH_2Cl_2 solution (1 mL) of lactose acceptor **6** (142 mg, 0.15 mmol) and TTBP (34 mg, 0.136 mmol) was added. The resulting mixture was allowed to warm to rt and stirred for 1 h before complete consumption of activated tetrasacchride intermediate. The reaction mixture was filtered through Celite. The solid was thoroughly washed with CH_2Cl_2 and the filtrate was washed with saturated solution of $NaHCO_3$. The organic layer was then dried over Na_2SO_4 and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography (hexane/EtOAc=1/1) to afford **3** as a white solid 250 mg (73% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, 2H, *J* = 6.7 Hz, ArH), 7.81 (br, 2H, ArH), 7.70-7.68 (m, 2H, ArH), 7.62-7.57 (m, 2H, ArH), 7.48-7.45 (m, 5H, ArH), 7.36-7.12 (m, 45H, ArH), 7.07-7.05 (m, 6H, ArH), 7.07-7.05 (m, 2H, ArH), 6.87 (t, 2H, *J* = 7.7 Hz, ArH), 5.71-5.67 (m, 2H, H-3', H-3'''), 5.54 (d, 1H, *J* = 8.1 Hz, H-1'), 5.51 (d, 1H, *J* = 8.4 Hz, H-1'''), 5.49 (dd, 1H, *J* = 9.9, 8.1 Hz, H-2), 5.45 (s, 1H, PhCH), 5.22 (s, 1H, PhCH), 5.03 (d, 1H, *J* = 11.4 Hz, $PhCH_2$), 4.88 (d, 1H, *J* = 10.8 Hz, $PhCH_2$), 4.82 (d, 1H, *J* = 10.8 Hz, $PhCH_2$), 4.69-4.53 (m, 7H, H-1, *J* = 8.2 Hz, 6H of $PhCH_2$), 4.49 (d, 1H, *J* = 11.4 Hz, $PhCH_2$), 4.41-4.36 (m, 3H, H-1'''', H-1''''', $PhCH_2$), 4.31-4.22 (m, 7H, H-1'', H-2', H-2''', H-6a'', C*H*HOMe), 4.20-4.09 (m, 6H, H-1'', *J* = 11.5 Hz), 4.05-3.87 (m, 8H, H-5, H-6a, H-4', H-6b'', H-4''', CH*H*OMe), 3.83-3.80 (m, 2H, H-6a''''), 3.72 (d, 1H, *J* = 9.6 Hz, H-6b''''), 3.66-3.40 (m, 14H, H-3, H-5'''', H-6b, C*H*HN$_3$), 3.36-3.28 (m, 6H, CH*H*N$_3$), 3.23 (s, 1H, H-5''), 2.95-2.91 (m, 2H, H-5), 2.91 (s, 3H, OCH_3), 1.85 (s, 3H, $COCH_3$), 1.79 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 170.4, 164.6, 139.4, 138.9, 138.6, 138.4, 138.3, 138.2, 138.1, 138.07, 138.0, 137.7, 137.6, 134.0, 133.1, 133.0, 129.9, 128.7, 128.45, 128.4, 128.3, 128.27, 128.26, 128.24, 128.16, 128.1, 128.07, 128.0, 127.9, 127.8, 127.77, 127.73,

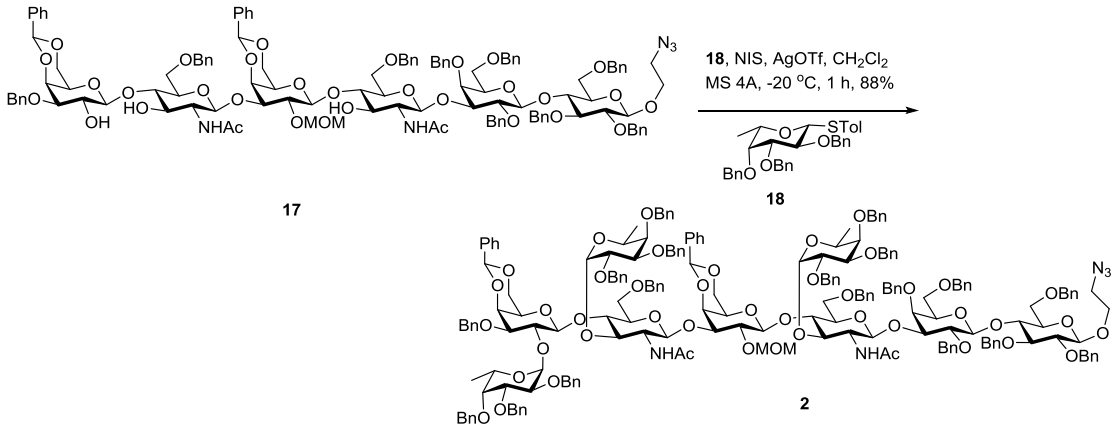
127.67, 127.65, 127.51, 127.49, 127.2, 127.0, 126.7, 126.5, 126.3, 123.3, 103.5 (H-1"", H-1""), 102.4 (H-1"), 101.7, 101.4, 100.7 (H-1), 99.6(H-1', H-1'"), 97.3, 82.8, 82.3, 82.2, 81.5, 78.7, 76.6, 75.9, 75.8, 75.3, 75.2, 75.1, 75.0, 74.8, 74.7, 74.67, 74.4, 74., 73.9, 73.4, 73.3, 73.27, 73.0, 72.9, 72.7, 71.24, 71.18, 70.7, 70.1, 69.0, 68.7, 68.2, 67.9, 67.6, 66.5, 66.1, 55.9, 55.4, 54.9, 50.1, 20.44, 20.4; HRMS (ESI): $[M + Na]^+$ $C_{144}H_{145}N_5O_{37}Na^+$ *m/z* calcd 2558.9511, found 2558.9600.



3 17

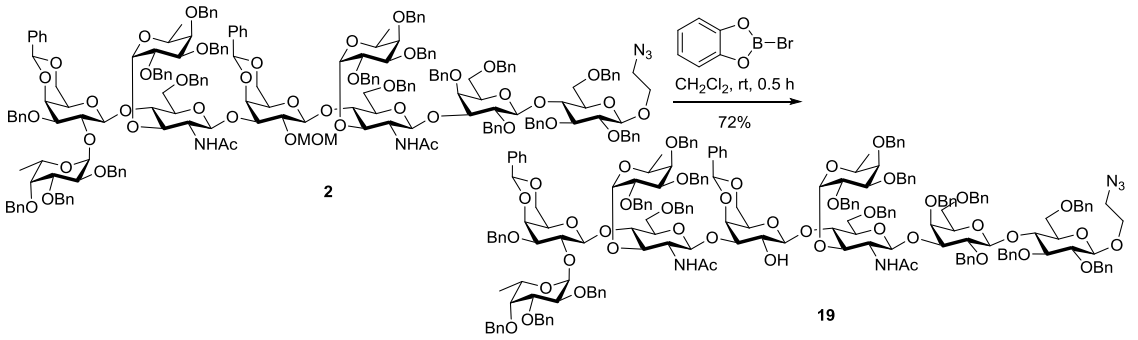
2-Azidoethyl (3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-*O*-methoxymethyl-*β*-D-galactopyranosyl)-(1→4)-(2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (17): After the solution of **3** (0.15 g, 0.06 mmol) and $N_2H_4{\cdot}H_2O$ (3.5 mL) in EtOH (10 mL) was refluxed overnight, MALDI TOF MS showed that all Phth and Bz groups were removed. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 (10 mL). The resulting solution was washed with 1N HCl, saturated $NaHCO_3$, water and brine then dried over Na_2SO_4. The solvent was removed under vacuum and the residue was dissolved in MeOH (5 mL) before anhydrous acetic anhydride (1 mL) was added at rt. The solution was stirred at rt for 1 h, and at this point, MALDI TOF MS showed complete acetylation of the amino groups. The reaction mixture was concentrated in vacuum. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH = 40:1, v/v) to give **17** as a white solid (100 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, 2H, *J* = 7.3 Hz, ArH), 7.45 (d, 2H, *J* = 6.7 Hz, ArH), 7.41-7.13 (m, 50H, ArH), 6.94 (d, 1H, *J* = 4.7 Hz, ArH), 5.92 (br, 1H, NH), 5.42 (s, 1H, PhCH), 5.39 (s, 1H, PhCH), 5.03 (d, 1H, *J* = 11.6 Hz, $PhCH_2$), 5.00 (d, 1H, *J* = 10.6 Hz, $PhCH_2$), 4.96 (d, 1H, *J* = 8.4 Hz, NH), 4.88 (d, 2H, *J* = 11.6 Hz, $PhCH_2$), 4.81-4.75

(m, 4H, H-1', J = 7.3 Hz, $PhCH_2$), 4.73-4.68 (m, 5H, H-1''', J = 7.9 Hz, CH_2OMe), 4.65-4.48 (m, 10H, H-1, J = 8.4 Hz), 4.41 (d, 1H, J = 7.7 Hz, H-1''''), 4.36 (d, 1H, J = 11.4 Hz, $PhCH_2$), 4.35 (d, 1H, J = 8.4 Hz, H-1''''), 4.32 (d, 1H, J = 7.9 Hz, $PhCH_2$), 4.24 (d, 1H, J = 7.9 Hz, H-1''), 4.22-4.08 (m, 11H), 4.00-3.91 (m, 5H), 3.83-3.61 (m, 20H), 3.57-3.34 (m, 20H, OCH_3), 3.30-3.29 (m, 2H), 3.15 (s, 1H), 1.99 (s, 3H, $COCH_3$), 1.57 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 170.2, 139.3, 139.0, 138.6, 138.3, 138.1, 137.8, 129.0, 128.6, 128.3, 127.7, 127.5, 127.1, 126.3, 103.6 (H-1''''), 102.9 (H-1), 102.7 (H-1''''), 102.4 (H-1''), 102.0 (H-1'), 101.6 (H-1'''), 101.1 (PhCH), 100.7 (PhCH), 98.9 (OMOM), 82.7, 81.6, 80.5, 80.1, 78.7, 77.8, 77.5, 76.5, 76.2, 75.7, 75.4, 74.4, 73.4, 72.6, 71.9, 70.2, 69.1, 68.3, 68.1, 67.0, 66.8, 57.6, 56.6, 56.2, 50.9, 31.9, 29.7, 29.3, 23.1, 22.8; HRMS (ESI): $[M + Na]^+$ $C_{121}H_{137}N_5O_{32}Na^+$ m/z calcd 2194.9139, found 2194.9067.



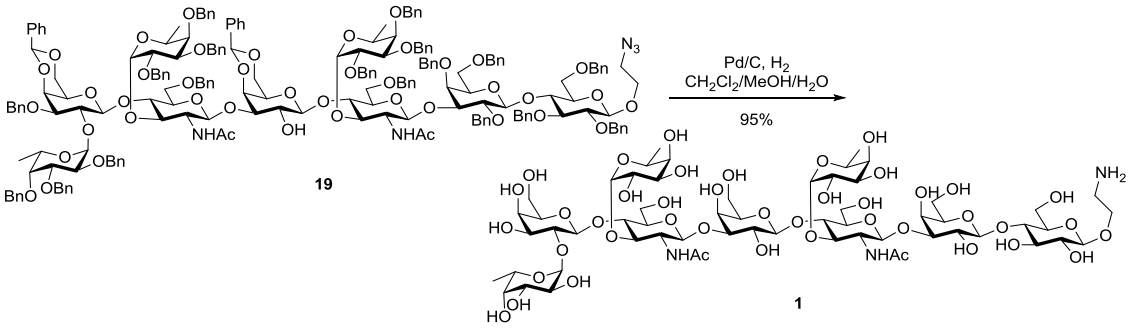
2-Azidoethyl (2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-([2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-*O*-methoxymethyl-*β*-D-galactopyranosyl)-(1→4)-([2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (2): After the mixture of **17** (100 mg, 0.046 mmol), **18** (124 mg, 0.23 mmol) and 4Å MS (1 g) in CH_2Cl_2 (5 mL) was stirred at rt under a N_2 atmosphere for 0.5 h, it was cooled to -50 ^oC. NIS (57 mg, 0.25 mmol) and AgOTf (18 mg, 0.07 mmol) were added in one portion. The mixture was allowed to warm up to -20 ^oC when initiation of the reaction was indicated by the color change. This temperature was maintained for 1 h,

when TLC showed the completion of reaction. Saturated aq. $NaHCO_3$ solution (5 mL) was added to quench the reaction and molecular sieves were removed by filtration. The aqueous phase was separated and extracted with CH_2Cl_2 (3 x 10 mL). The organic phases were combined and washed with saturated aq. Na_2SO_3 solution, dried over Na_2SO_4, and then concentrated in vacuum. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 2:3, v/v) to give **2** (138 mg, 88%) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58-7.55 (m, 4H, ArH), 7.36-7.07 (m, 94H, ArH), 6.97 (d, 2H, *J* = 7.7 Hz, ArH), 5.90 (d, 1H, *J* = 6.1 Hz, NH), 5.63 (d, 1H, *J* = 3.8 Hz, H-1$^{Fuc\text{-}A}$), 5.45 (d, 1H, *J* = 6.5 Hz, H-1$^{GalNAc\text{-}A}$), 5.44 (s, 1H, PhCH), 5.41 (d, 1H, *J* = 8.2 Hz, H-1$^{GalNAc\text{-}B}$), 5.40 (s, 1H, PhCH), 5.30 (d, 1H, *J* = 7.7 Hz, H-1), 5.06 (d, 1H, *J* = 11.8 Hz, $PhCH_2$), 4.99-4.97 (m, 2H, $PhCH_2$), 4.91 (d, 1H, *J* = 11.3 Hz, $PhCH_2$), 4.88-4.85 (m, 3H, *J* = 3.6 Hz, H-1$^{Fuc\text{-}b}$, *J* = 3.0 Hz, H-1$^{Fuc\text{-}C}$, PhC*H*H), 4.80-4.59 (m, 21H, C*H*HOMe), 4.56-4.41 (m, 11H, CH*H*OMe, H-1$^{Gal\text{-}B}$, H-1$^{Gal\text{-}C}$), 4.36-4.22 (m, 10H, H-1$^{Gal\text{-}A}$, H-1^{Glu}), 4.20-4.13 (m, 6H), 4.10-4.05 (m, 5H), 4.02-3.87 (m, 10H), 3.80-3.64 (m, 11H), 3.57-3.44 (m, 10H), 3.38-3.31 (m, 5H), 3.20-3.13 (m, 3H, H-2$^{GalNAc\text{-}B}$), 3.07-3.00 (m, 3H, H-2$^{GalNAc\text{-}A}$), 1.59 (s, 3H, $COCH_3$), 1.29 (d, 3H, *J* = 6.3 Hz, CH_3), 1.22 (s, 3H, $COCH_3$), 1.14 (d, 3H, *J* = 6.0 Hz, CH_3), 1.02 (d, 3H, *J* = 6.5 Hz, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 170.3, 139.54, 139.53, 139.47, 139.3, 139.2, 139.1, 139.0, 138.97, 138.95, 138.94, 138.8, 138.6, 138.3, 138.28, 138.25, 138.23, 138.2, 138.0, 128.8, 128.6, 128.56, 128.49, 128.4, 128.29, 128.27, 128.24, 128.21, 128.19, 128.18, 128.15, 128.12, 128.1, 128.01, 128.0, 127.99, 127.95, 127.93, 127.86, 127.85, 127.83, 127.76, 127.69, 127.65, 127.6, 128.58, 127.55, 127.54, 127.49, 127.48, 127.46, 127.43, 127.39, 127.34, 127.32, 127.29, 127.28, 127.2, 127.18, 127.16, 127.11, 127.09, 127.08, 127.05, 126.86, 126.85, 125.9, 125.8, 103.5 (H-1^{Glu}), 102.5 (H-1$^{Gal\text{-}A}$), 101.1 (H-1$^{Gal\text{-}C}$), 100.7 (H-1$^{GalNAc\text{-}B}$), 100.4 (H-1$^{Gal\text{-}B}$), 99.9 (H-1$^{GalNAc\text{-}A}$), 99.8 (PhCH), 99.7 (PhCH), 98.5 (H-1$^{Fuc\text{-}B}$), 97.7 (H-1$^{Fuc\text{-}C}$), 97.6(H-1$^{Fuc\text{-}A}$), 97.4 (OMOM), 82.8, 82.5, 81.9, 81.6, 81.0, 79.5, 79.3, 79.13, 79.10, 78.8, 78.5, 78.3, 77.1, 76.9, 76.7, 76.2, 75.9, 75.7, 75.6, 75.3, 75.0, 74.98, 74.8, 74.76, 74.74, 74.72, 74.6, 74.4, 74.2, 74.0, 73.8, 73.6, 73.5, 73.43, 73.37, 73.2, 73.0, 72.7, 72.5, 72.4, 72.0, 71.6, 71.4, 71.1, 70.3, 68.2, 68.01, 67.99, 67.0, 66.5, 66.43, 66.4, 66.1, 60.1, 56.1, 50.9, 36.6, 24.7, 23.3, 23.2, 22.9, 16.3, 16.1, 16.0; HRMS (ESI): $[M + 2Na]^{2+}$ $C_{202}H_{221}N_5O_{44}Na_2^{2+}$ *m*/*z* calcd 1733.2497, found 1733.4221.



2-Azidoethyl (2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-([2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-([2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl-(1→3)]-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-(2,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-*β*-D-glucopyranoside (19): B-Bromocatecholborane (16 μL, 1 M in CH_2Cl_2, 0.016 mmol) was added dropwise to a solution of **2** (50 mg, 0.015 mmol) in anhydrous CH_2Cl_2 (5 mL) at 0 ^oC. The mixture was allowed to warm to rt and then stirred for 1 h when **2** disappeared as indicated by TLC. The reaction was quenched by the addition of saturated $NaHCO_3$ solution (2 mL) and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel column chromatography (EtOAc/hexane = 1:1, v/v) to give **19** (35 mg, 72%) as a syrup, which solidified under high vacuum. ^1H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, 2H, J = 8.0 Hz, ArH), 7.53 (d, 2H, J = 7.0 Hz, ArH), 7.34-7.07 (m, 96H, ArH), 6.18 (d, 1H, J = 5.0 Hz, NH), 5.65 (d, 1H, J = 3.1 Hz, H-$1^{Fuc\text{-}A}$), 5.56 (d, 1H, J = 7.8 Hz, H-$1^{GalNAc\text{-}B}$), 5.45 (s, 1H, PhCH), 5.43 (s, 1H, PhCH), 5.23 (d, 1H, J = 6.3 Hz, NH), 5.15 (d, 1H, J = 6.6 Hz, H-$1^{GalNAc\text{-}A}$), 5.09-5.06 (m, 2H, $PhCH_2$), 4.98-4.85 (m, 5H, H-$1^{Fuc\text{-}B}$, H-$1^{Fuc\text{-}C}$, $PhCH_2$), 4.78-4.49 (m, 23H, H-$1^{Gal\text{-}B}$, H-$1^{Gal\text{-}C}$), 4.44-4.37 (m, 3H), 4.34-4.32 (m, 3H, H-$1^{Gal\text{-}A}$, H-1^{Glu}), 4.29-4.20 (m, 6H), 4.17-4.02 (m, 8H), 4.00-3.73 (m, 13H), 3.70-3.63 (m, 6H), 3.59-3.53 (m, 5H), 3.50-3.35 (m, 9H), 3.32-3.30 (m, 2H, H-$2^{GalNAc\text{-}B}$), 3.25 (s, 1H), 3.18-3.10 (m, 3H, H-$2^{GalNAc\text{-}A}$), 3.04 (s, 1H), 3.01 (s, 1H), 1.52 (s, 3H, $COCH_3$), 1.23 (s, 3H, $COCH_3$), 1.22 (d, 3H, J = 6.3 Hz, CH_3), 1.11 (d, 3H, J = 6.0 Hz, CH_3), 0.98 (d, 3H, J = 6.5 Hz, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7, 169.7, 139.6, 139.0, 138.7, 138.3, 138.1, 128.6, 128.3, 128.0, 127.7, 127.5, 127.2, 126.9, 125.8, 103.5, 102.5, 100.1, 99.8,

97.5, 82.8, 81.6, 81.1, 79.2, 78.8, 78.4, 77.9, 76.2, 75.6, 74.8, 74.5, 73.5, 72.5, 72.0, 71.5, 70.9, 70.4, 69.6, 68.3, 68.0, 66.8, 66.5, 60.9, 50.9, 23.2, 23.0, 16.5, 16.4, 16.0; HRMS (ESI): $[M + 2Na]^{2+}$ $C_{200}H_{217}N_5O_{43}Na_2^{2+}$ *m/z* calcd 1711.2366, found 1711.2314.



2-Aminoethyl *α*-L-fucopyranosyl-(1→2)-*β*-D-galactopyranosyl-(1→4)-([*α*-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-*β*-D-galactopyranosyl-(1→4)-([*α*-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-*β*-D-glucopyranosyl)-(1→3)-*β*-D-galactopyranosyl-(1→3)-*β*-D-glucopyranoside (1): The mixture of **19** (20 mg, 5.9 µmol) and 10% Pd/C (8 mg) in CH_2Cl_2/MeOH/H_2O (3:3:1, 3.5 mL) and 3 drops of AcOH was stirred at rt under an H_2 atmosphere at 50 psi for 48 h. The catalyst was removed by filtration through a pad of Celite and the solid was washed with water. The combined filtrate was concentrated in vacuum, and the residue was purified with a Sephadex G-15 gel filtration column using water as the eluent, followed by lyophilization to afford **1** (8.7 mg, 95%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.17 (d, 1H, *J* = 3.5 Hz, H-1), 5.01 (m, 2H, 2 x H-1), 4.78-4.70 (m, 2H), 4.61-4.59 (m, 2H, 2 x H-1), 4.42-4.39 (m, 2H, 2 x H-1), 4.34 (d, 1H, *J* = 7.9 Hz, H-1), 4.32 (d, 1H, *J* = 8.0 Hz, H-1), 4.16-4.12 (m, 1H), 4.05 (d, 1H, *J* = 3.5 Hz), 3.94-3.76 (m, 2H), 3.90-3.38 (m, 44H), 3.22 (t, 1H, *J* = 8.5 Hz), 3.05 (t, 2H, *J* = 6.9 Hz), 1.91 (s, 6H, $COCH_3$), 1.16 (d, 3H, *J* = 6.7 Hz, CH_3), 1.13 (d, 3H, *J* = 6.6 Hz, CH_3), 1.04 (d, 3H, *J* = 6.7 Hz, CH_3); ^{13}C NMR NMR is derived from HMBC and HSQC NMR, which are acquired by indirect methods. (150 MHz, D_2O): δ 174.6, 102.9, 102.4, 102.0, 101.7, 100.1, 99.4, 98.6, 82.1, 81.5, 78.3, 76.3, 75.3, 75.1, 74.8, 74.77, 74.75, 74.4, 73.5, 72.9, 72.6, 71.9, 71.7, 70.5, 69.9, 69.7, 69.1, 68.7, 68.3, 68.2, 68.1, 67.8, 67.7, 66.9, 66.8, 62.4, 61.5, 60.9, 59.9, 59.7, 59.6, 56.0, 46.7, 37.6, 26.7, 22.2, 15.5, 15.2, 8.19. HRMS (ESI): $[M + Na]^+$ $C_{60}H_{103}N_3O_{43}Na^+$ *m/z* calcd 1576.5858, found 1576.6157.

III. NMR and MS spectra of new compounds

Figure S1. ^{1}H NMR of Compound **S1** (600 MHz, $CDCl_3$)

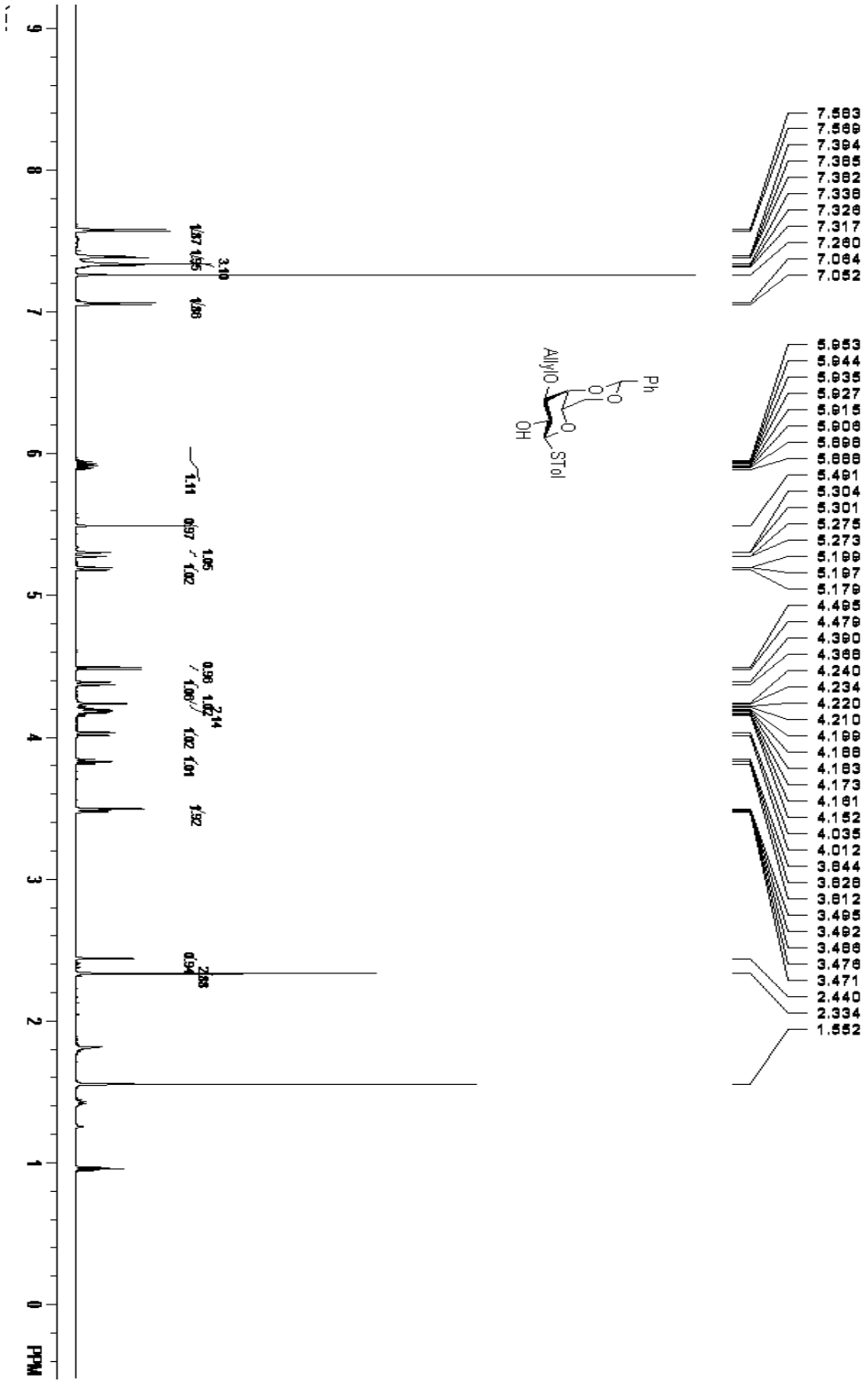


Figure S2.[1]H NMR of Compound **9** (600 MHz, $CDCl_3$)

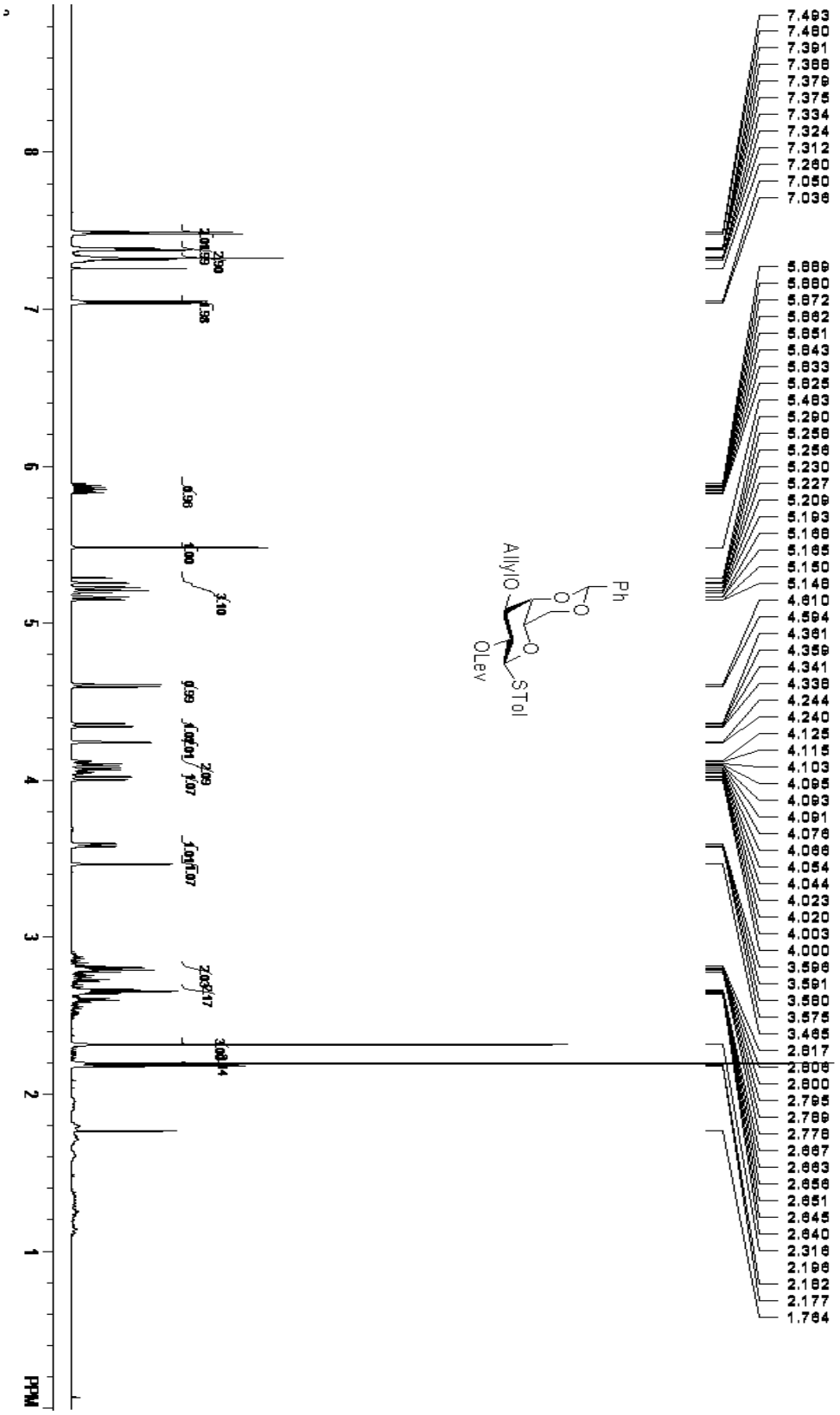


Figure S3. ^{13}C NMR of Compound **9** (600 MHz, $CDCl_3$)

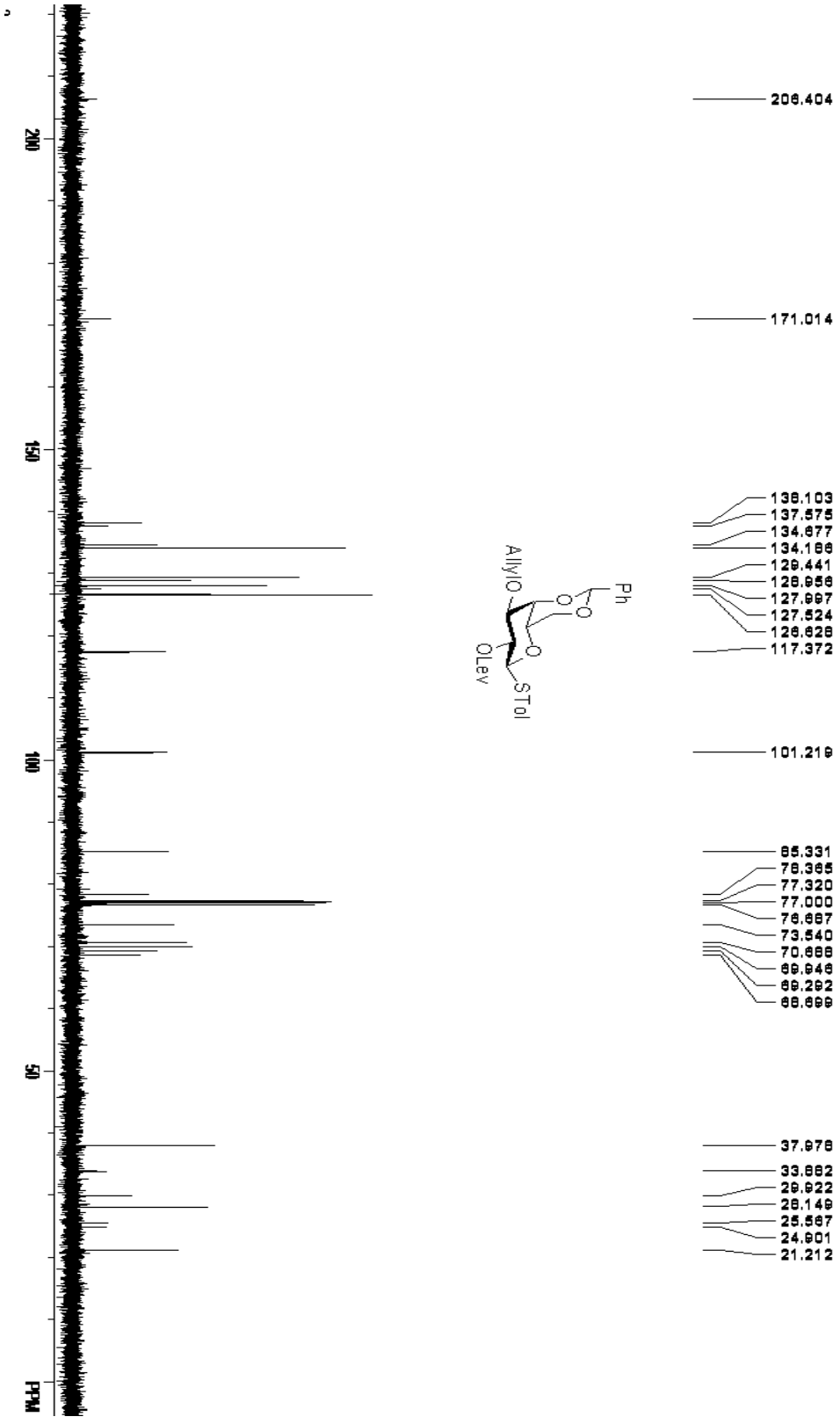


Figure S4. HRMS of Compound **9** (MALDI TOF)

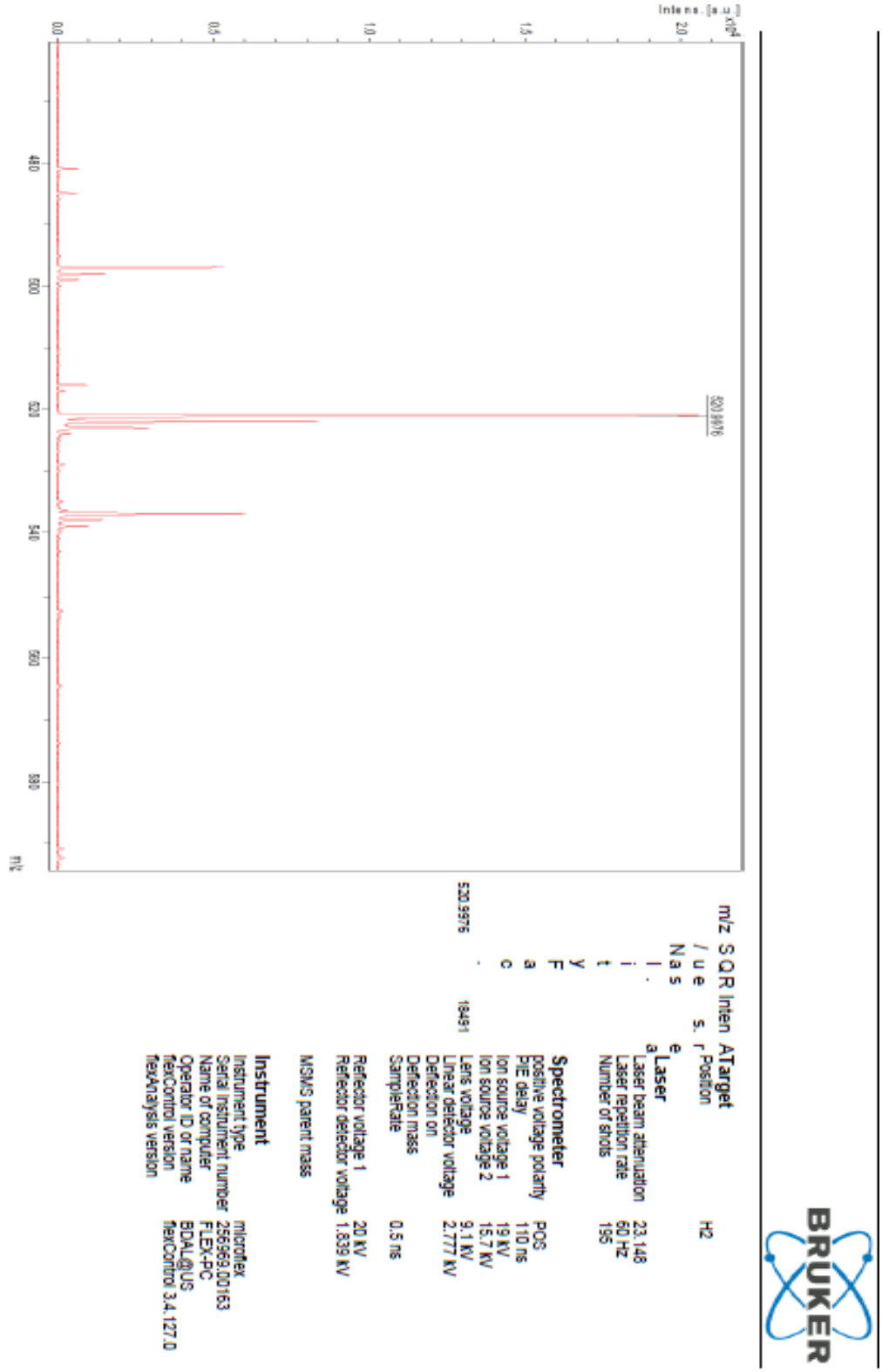


Figure S5. ^{1}H NMR of Compound **6** (600 MHz, $CDCl_3$)

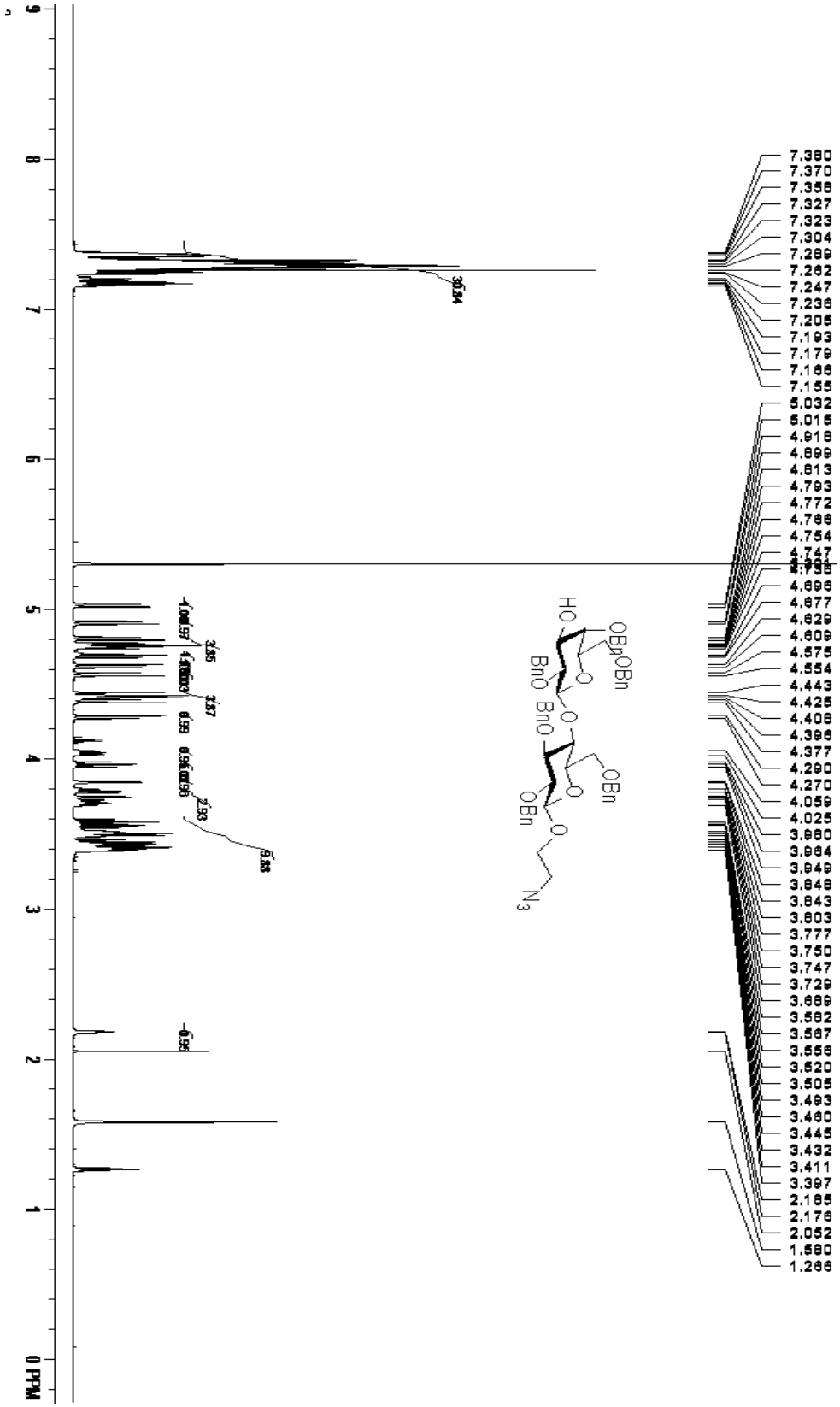


Figure S6. ^{13}C NMR of Compound **6** (600 MHz, $CDCl_3$)

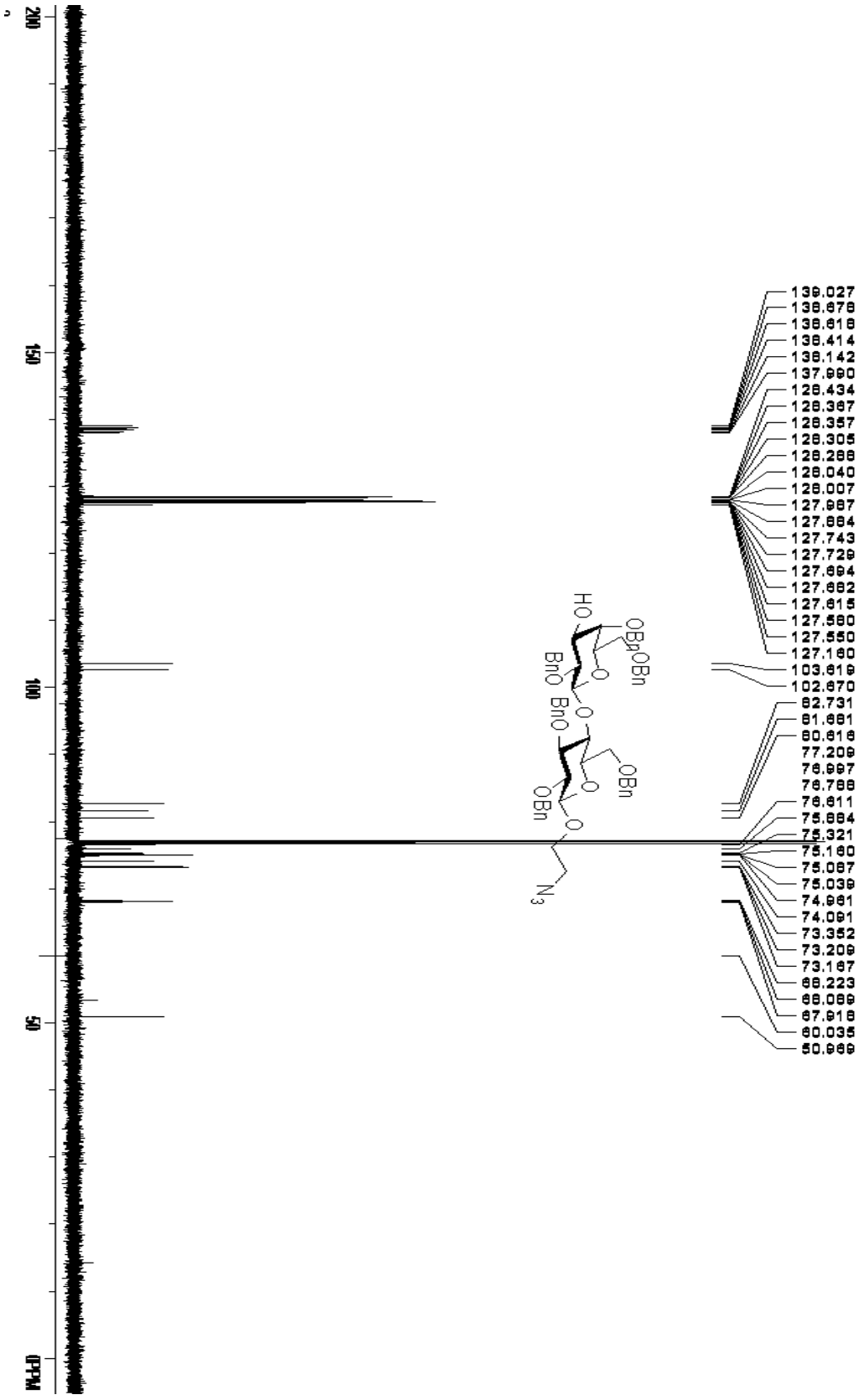


Figure S7. ^{1}H NMR of Compound **13** (600 MHz, $CDCl_3$)

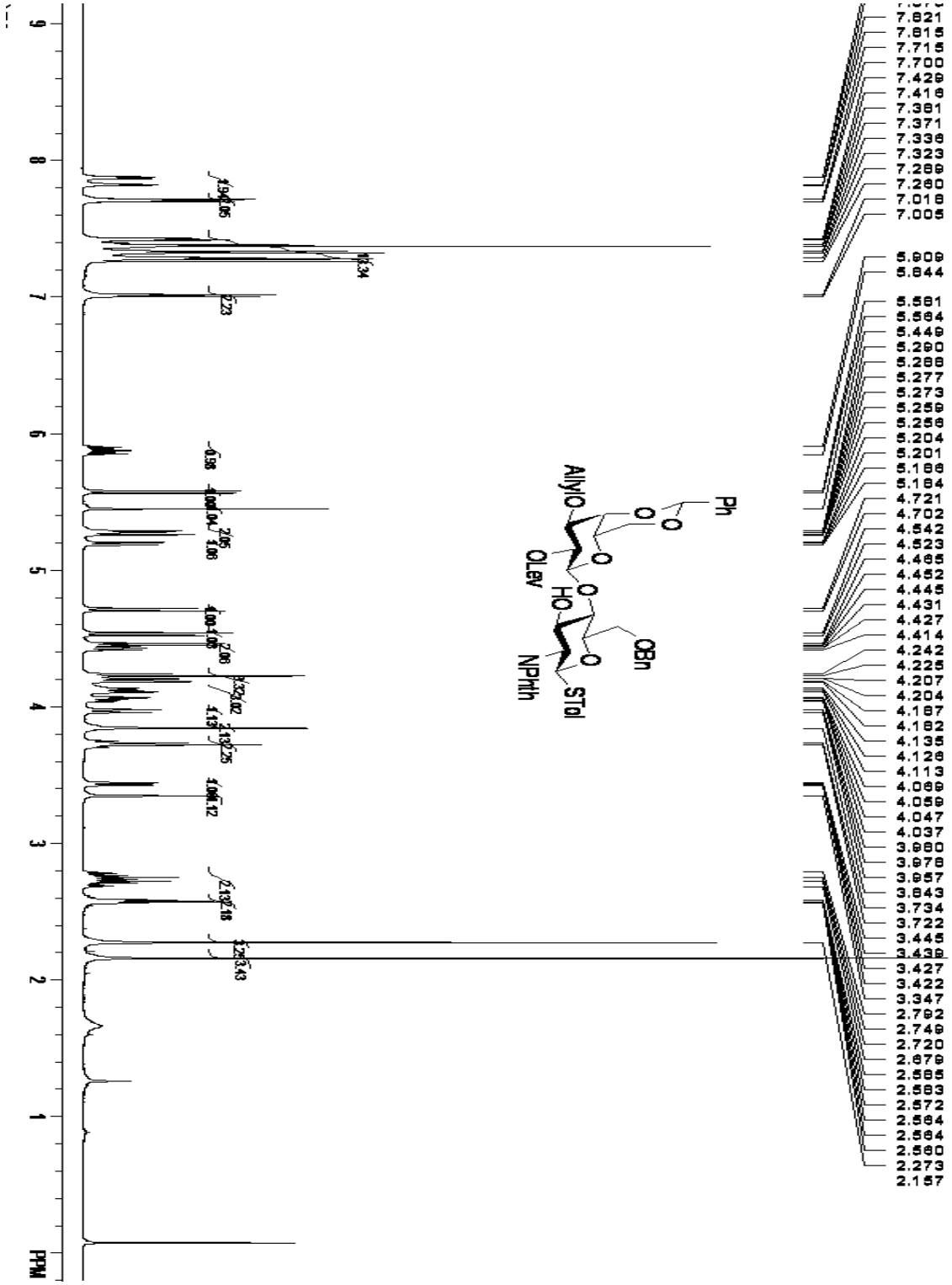


Figure S8. ^{13}C NMR of Compound **13** (600 MHz, $CDCl_3$)

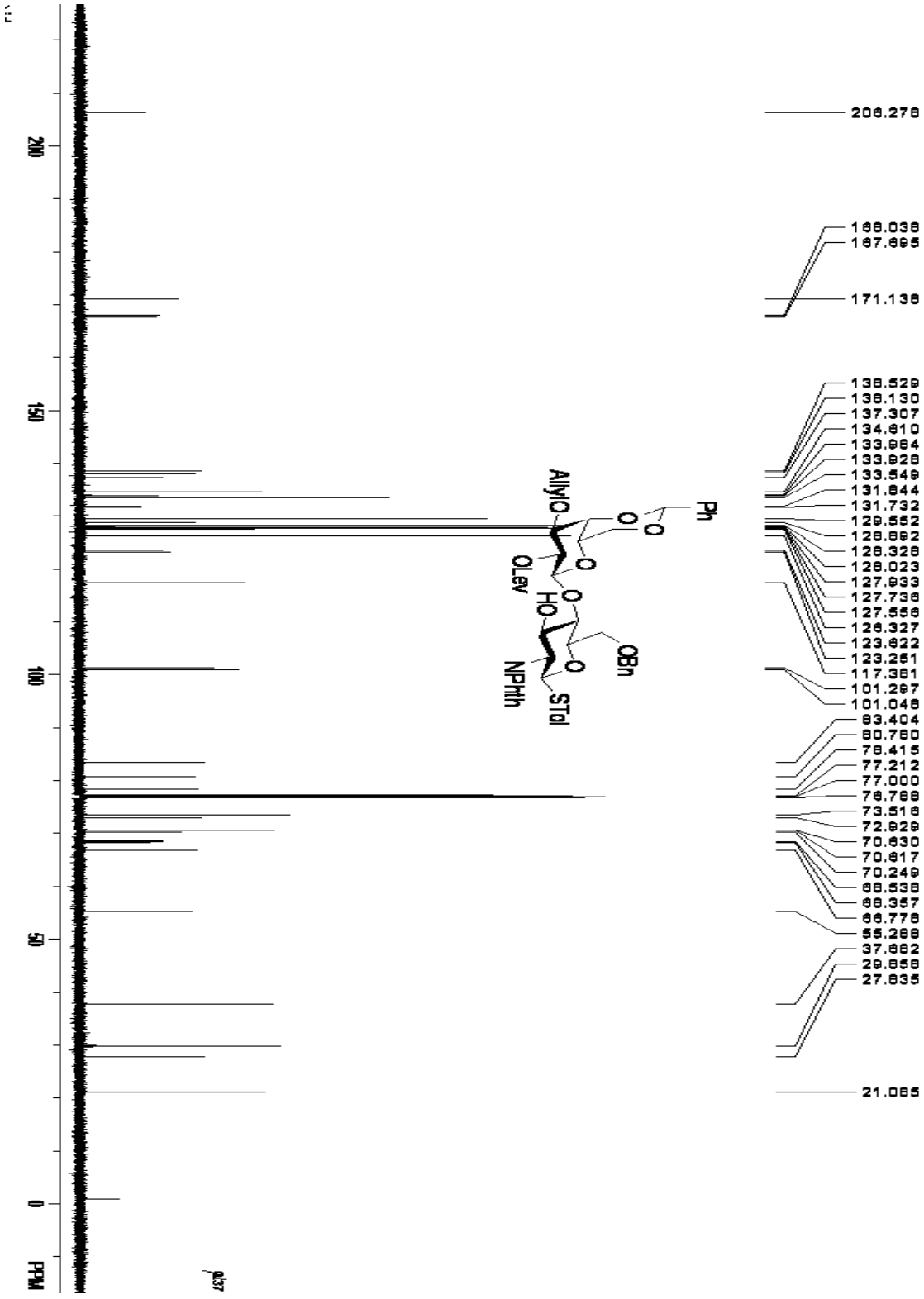


Figure S9. HRMS of Compound **13** (ESI TOF)

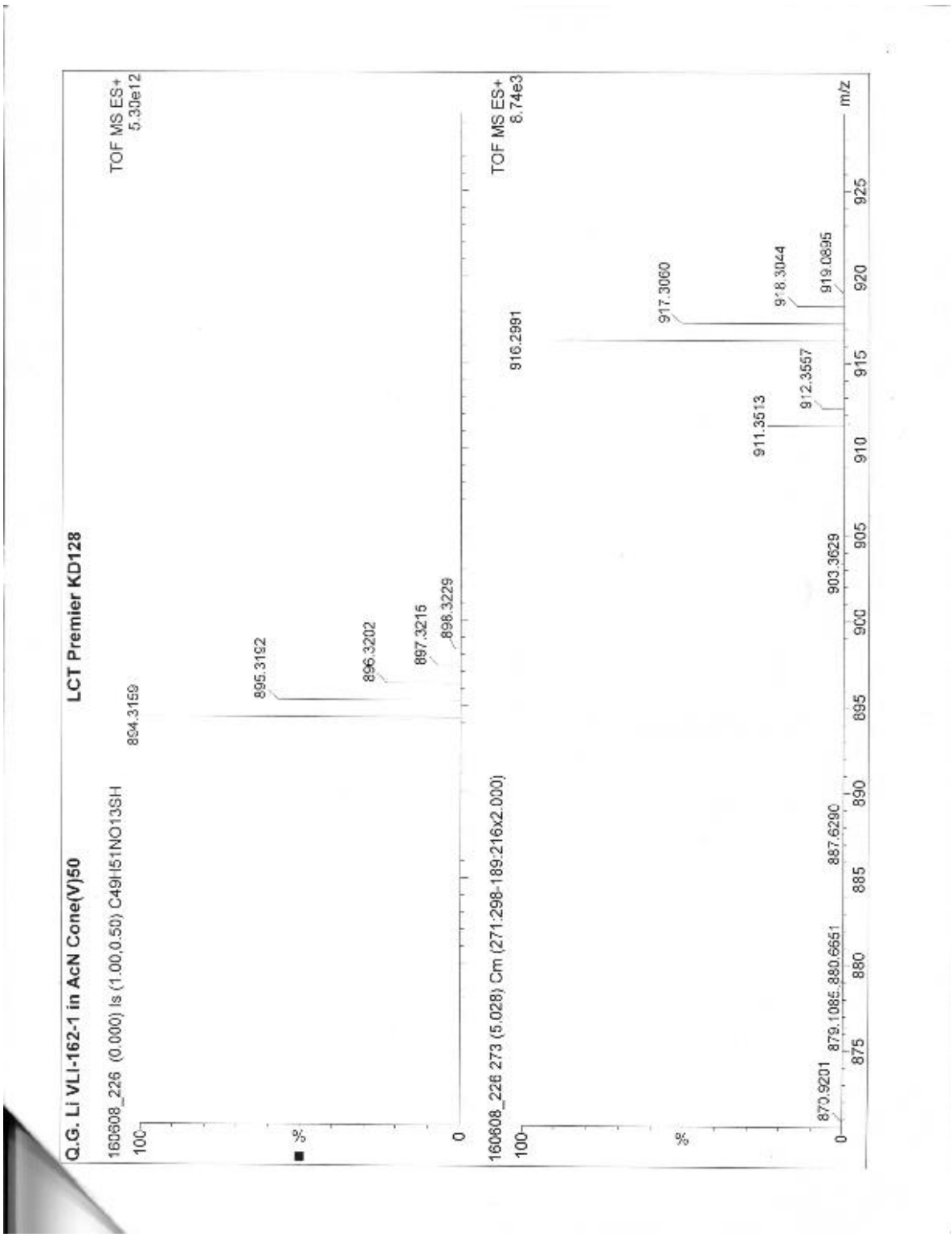


Figure S10. ^{1}H NMR of Compound **14** (600 MHz, $CDCl_3$)

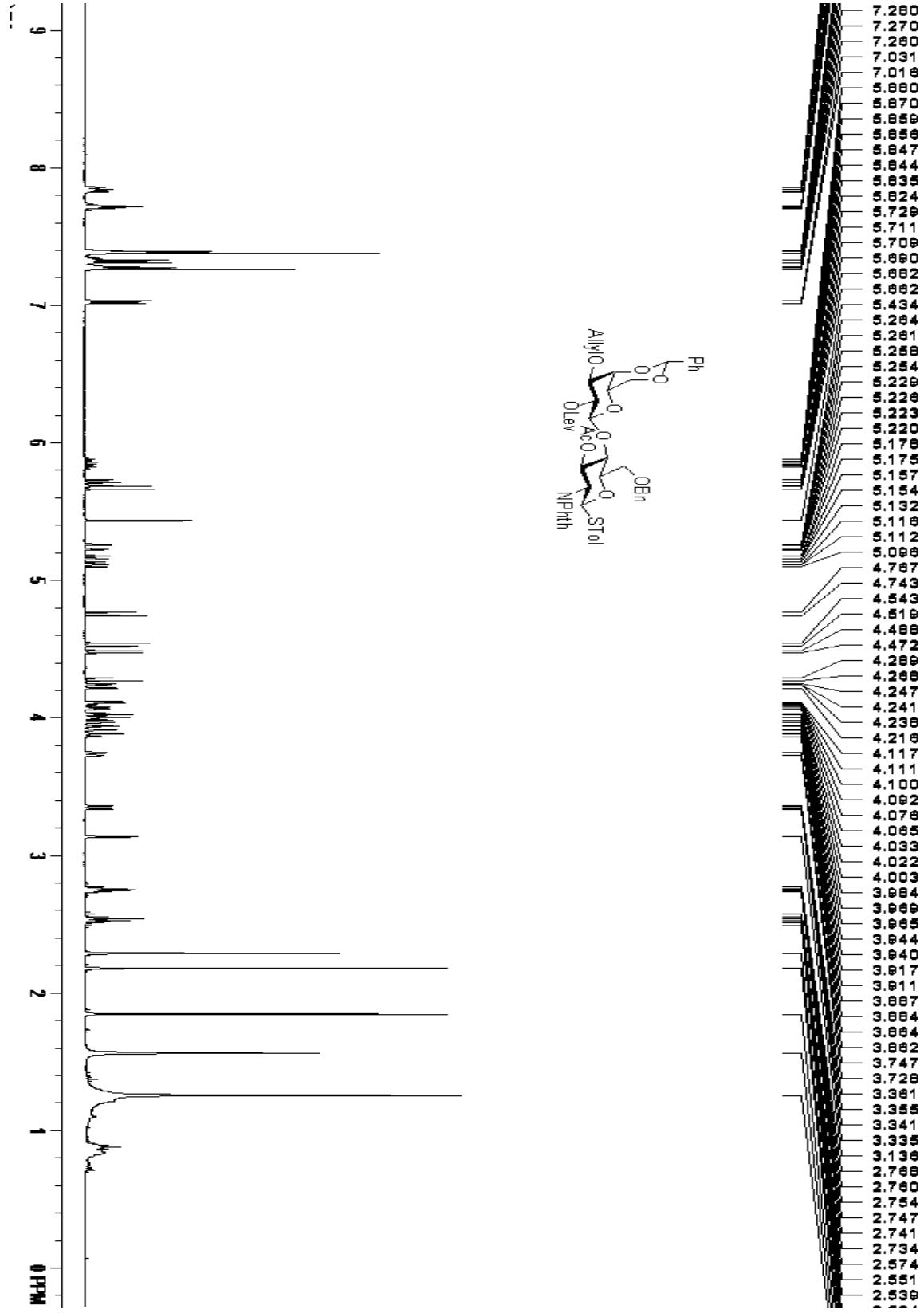


Figure S11. ^{13}C NMR of Compound **14** (600 MHz, $CDCl_3$)

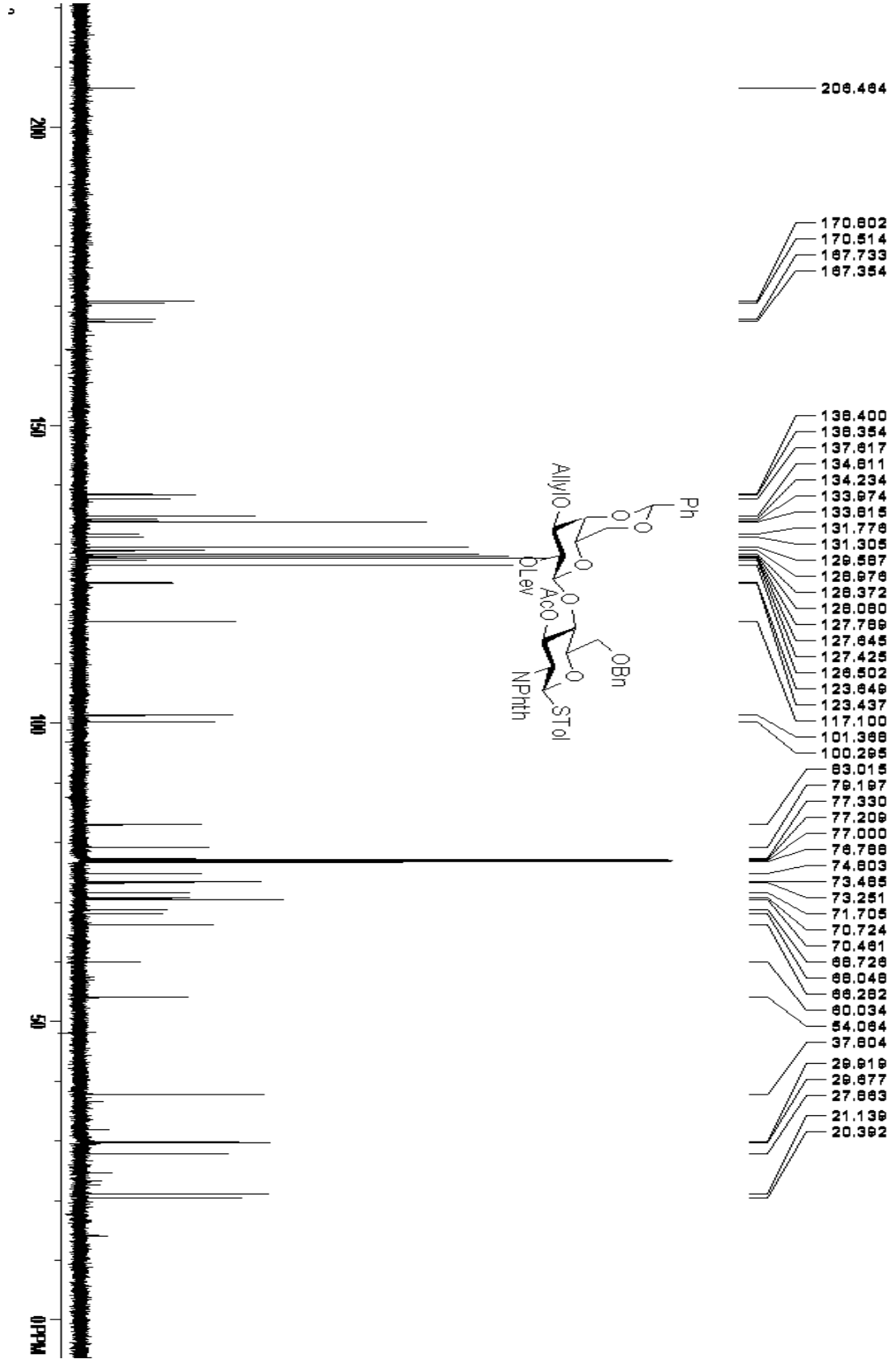


Figure S12. COSY NMR of Compound **14** (500 MHz, $CDCl_3$)

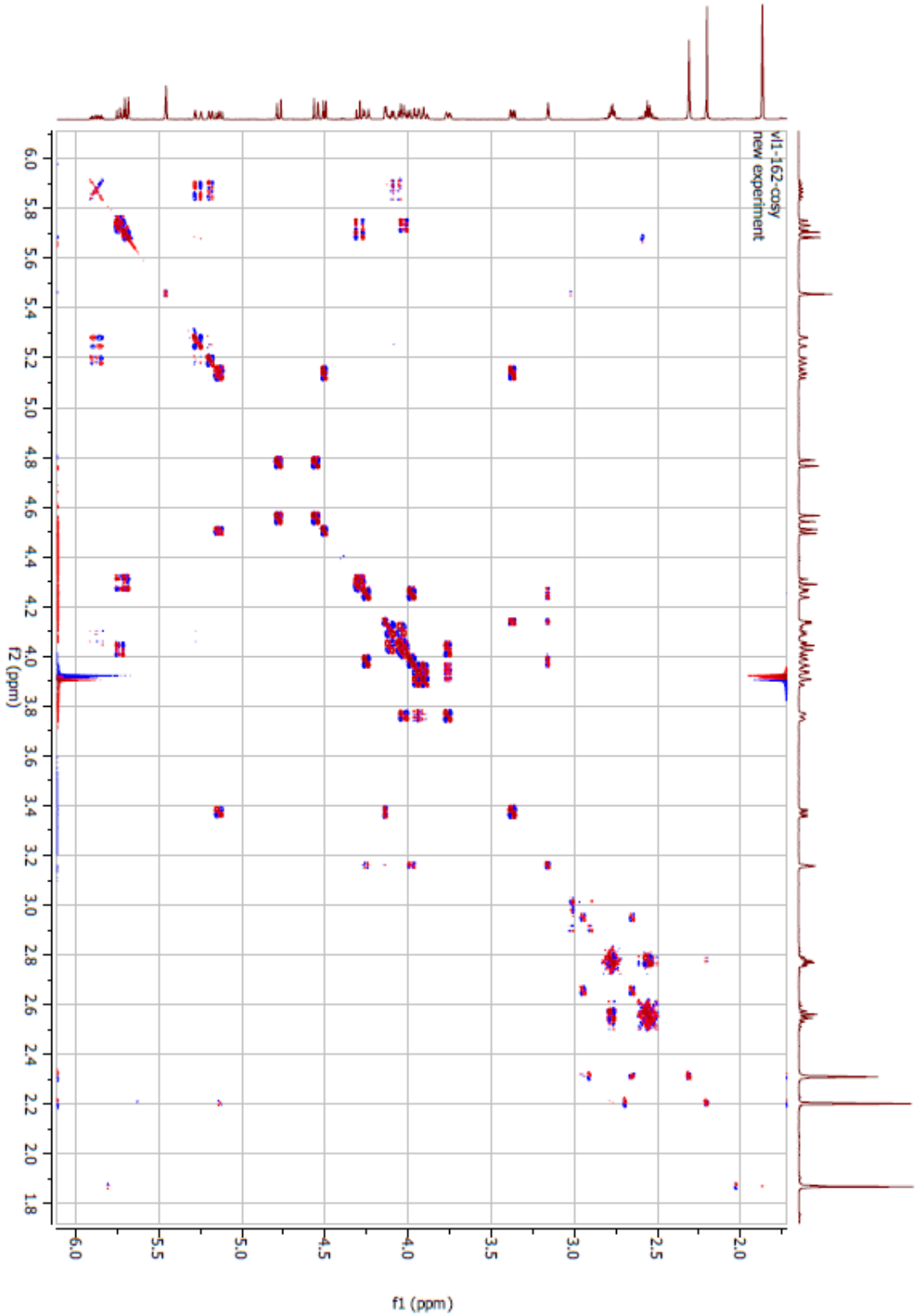


Figure S13. HSQC NMR of Compound **14** (500 MHz, $CDCl_3$)

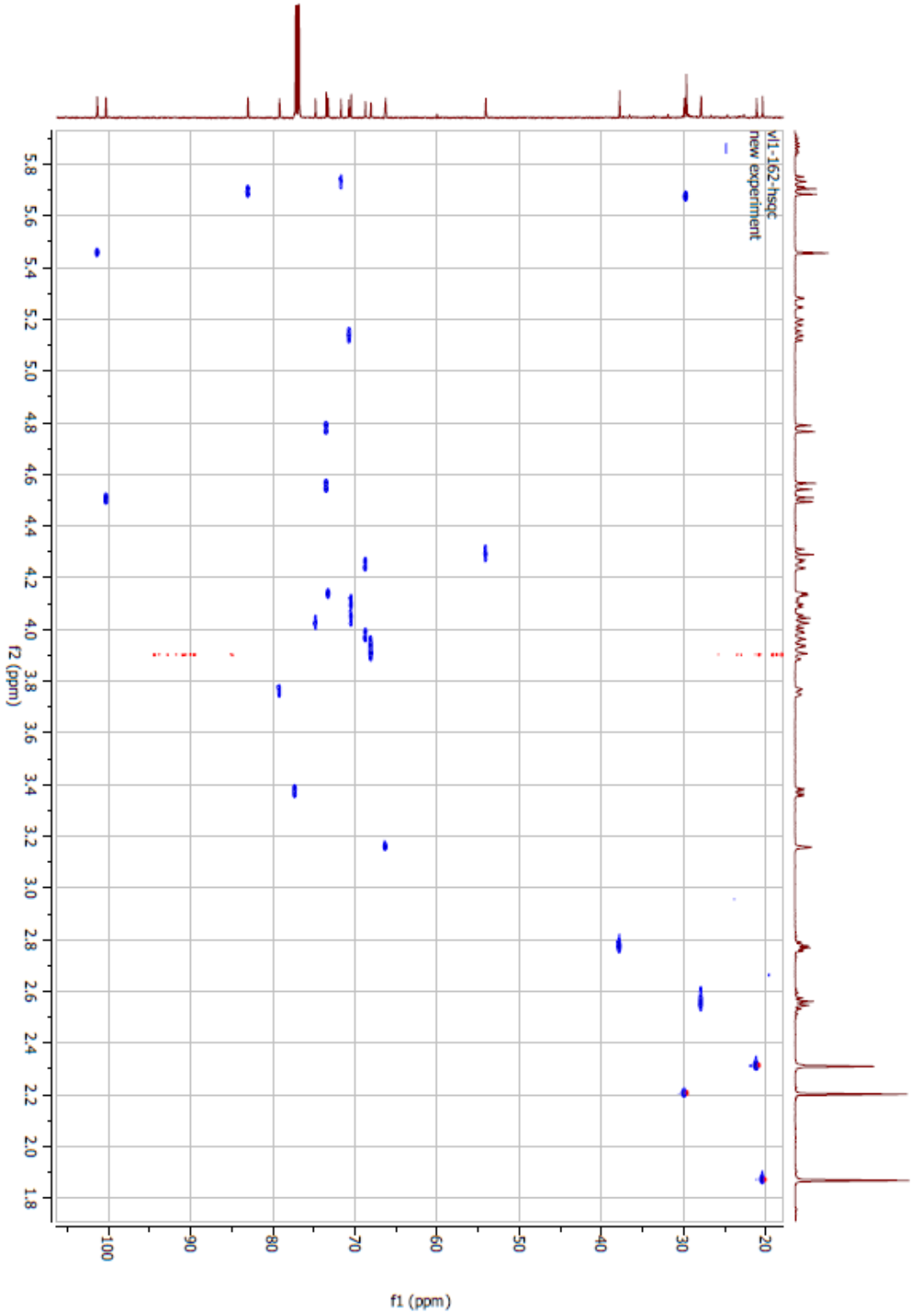


Figure S14. HRMS of Compound **14** (ESI tof)

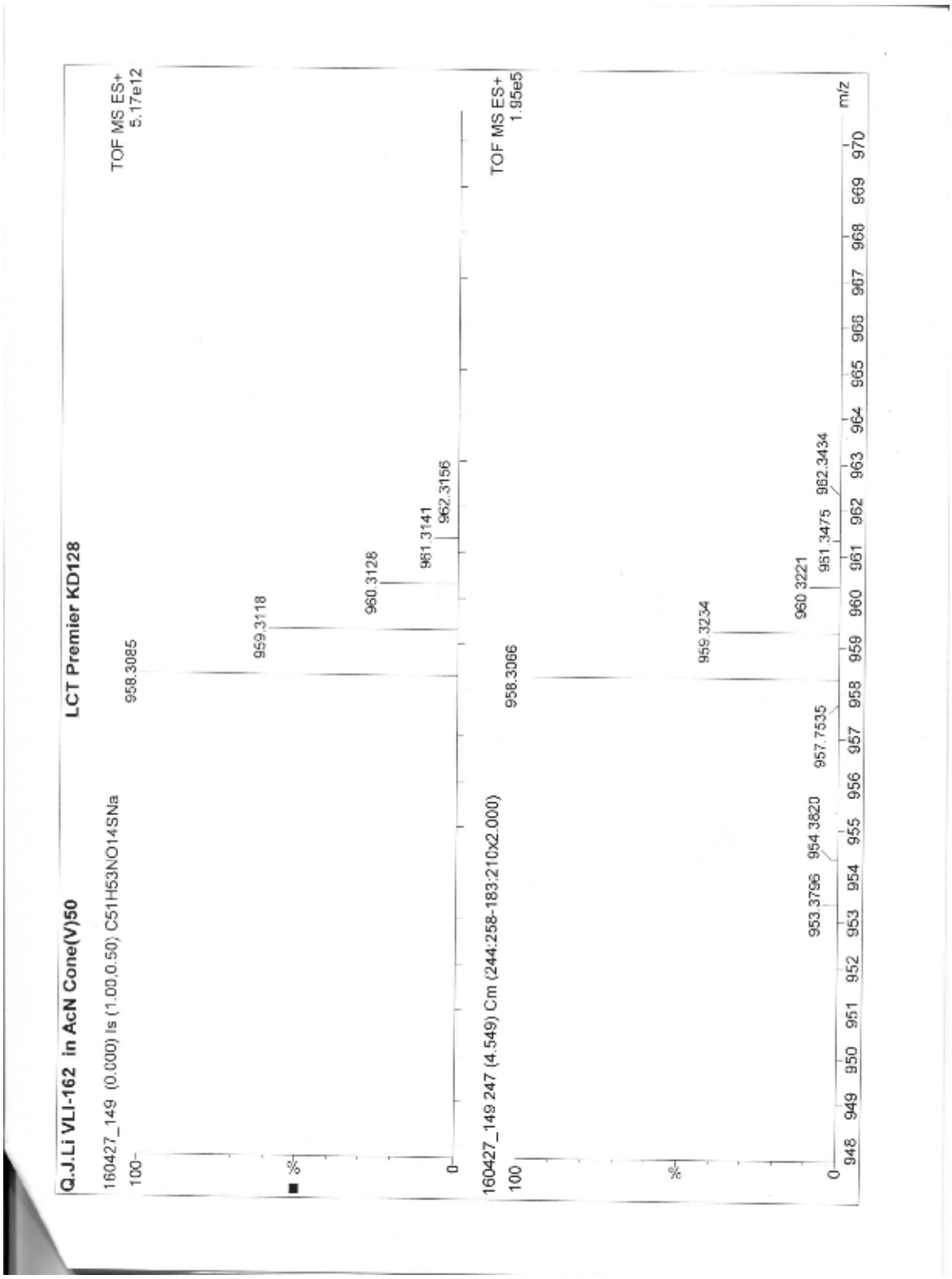


Figure S15. ^{1}H NMR of Compound **15** (600 MHz, $CDCl_3$)

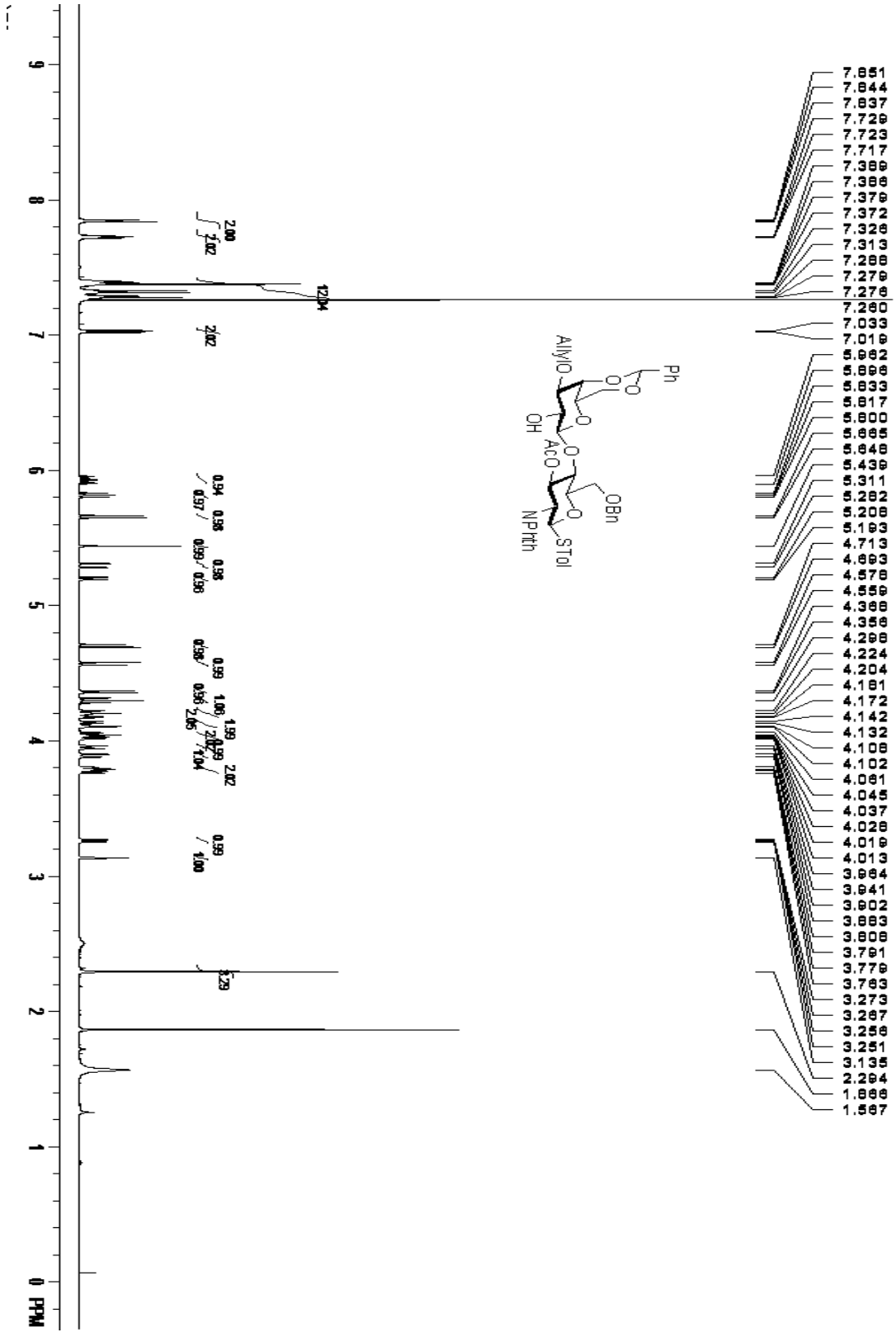


Figure S16. ^{13}C NMR of Compound **15** (600 MHz, $CDCl_3$)

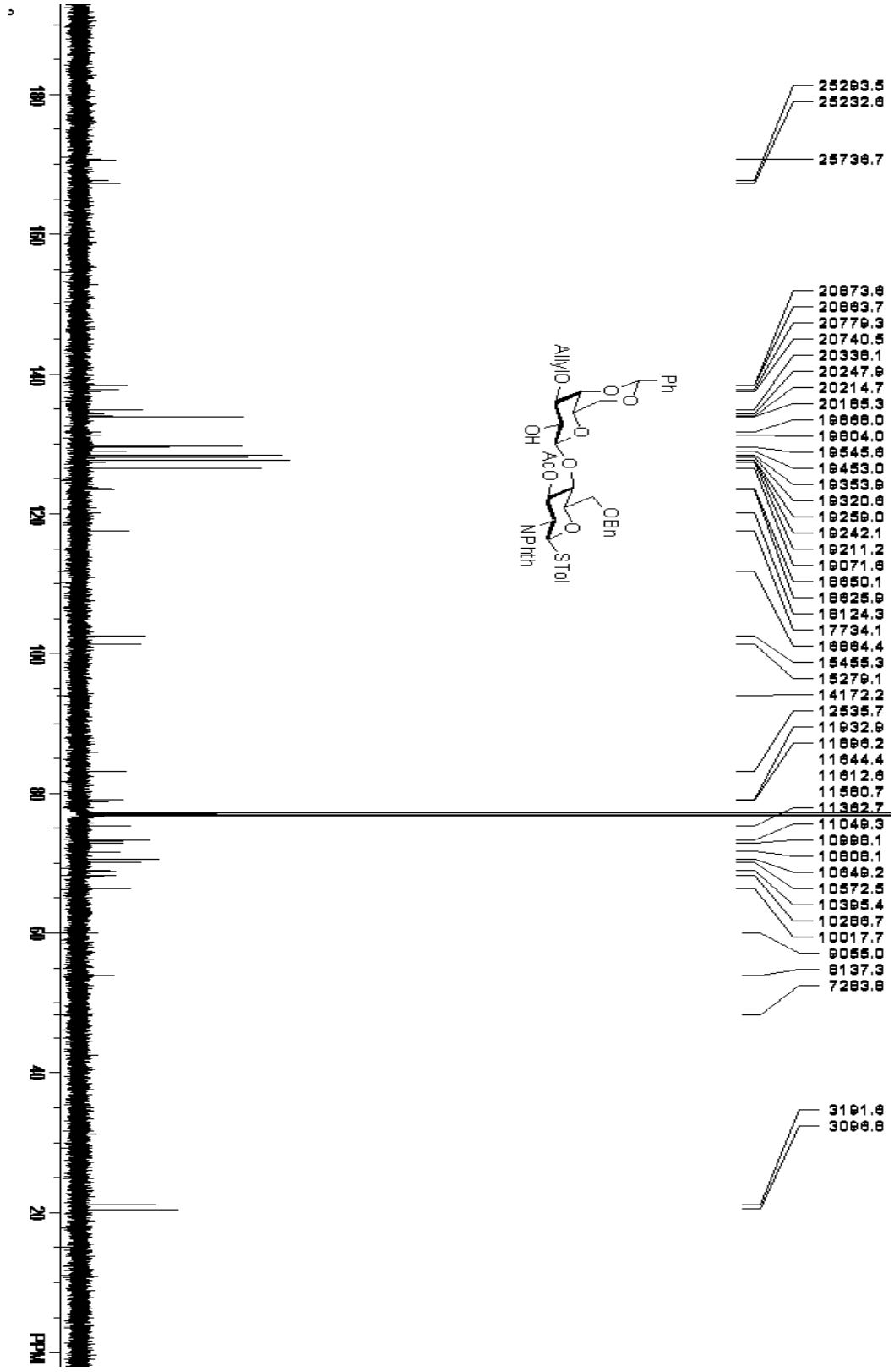


Figure S17. COSY NMR of Compound **15** (600 MHz, $CDCl_3$)

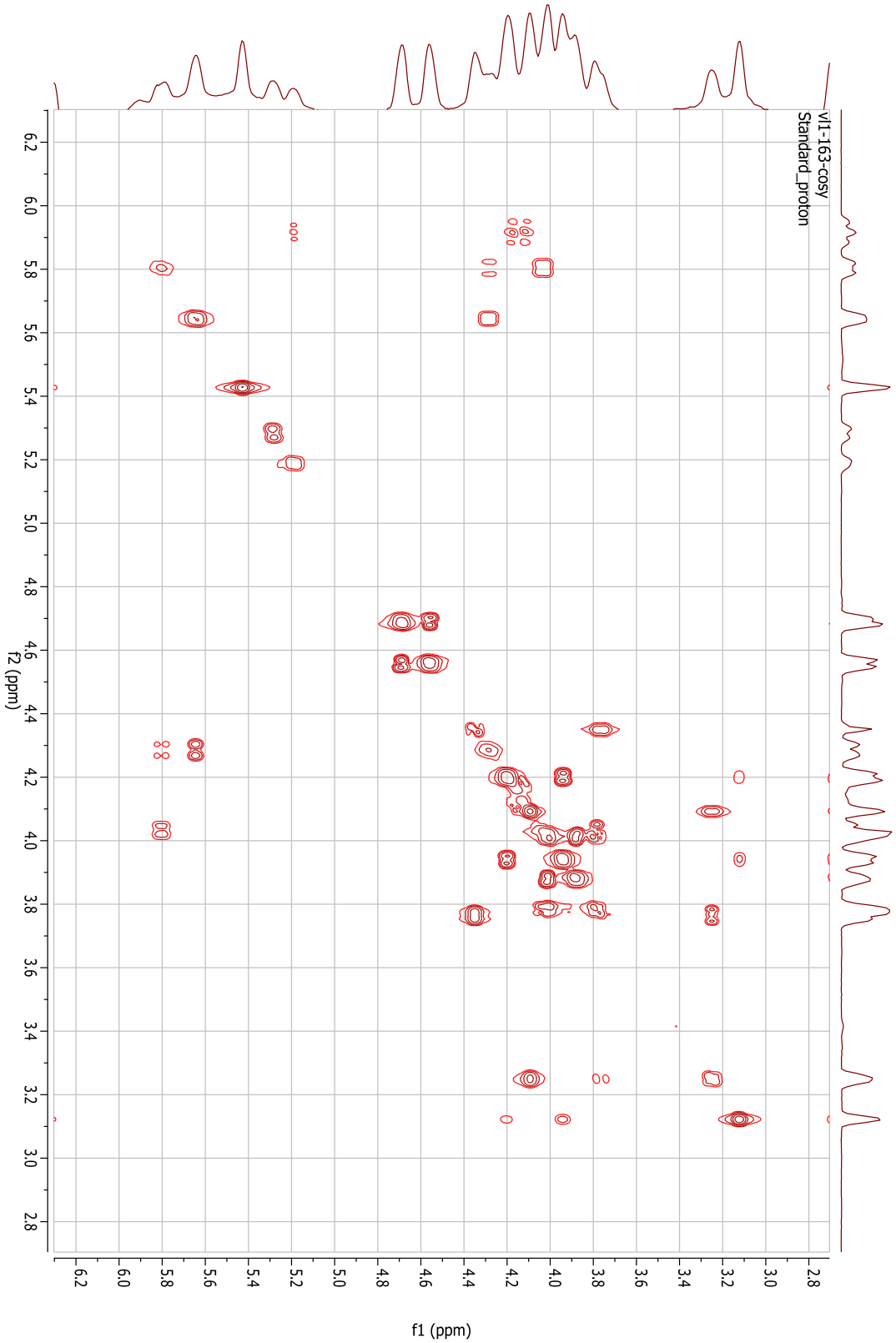


Figure S18. HSQC NMR of Compound **15** (600 MHz, $CDCl_3$)

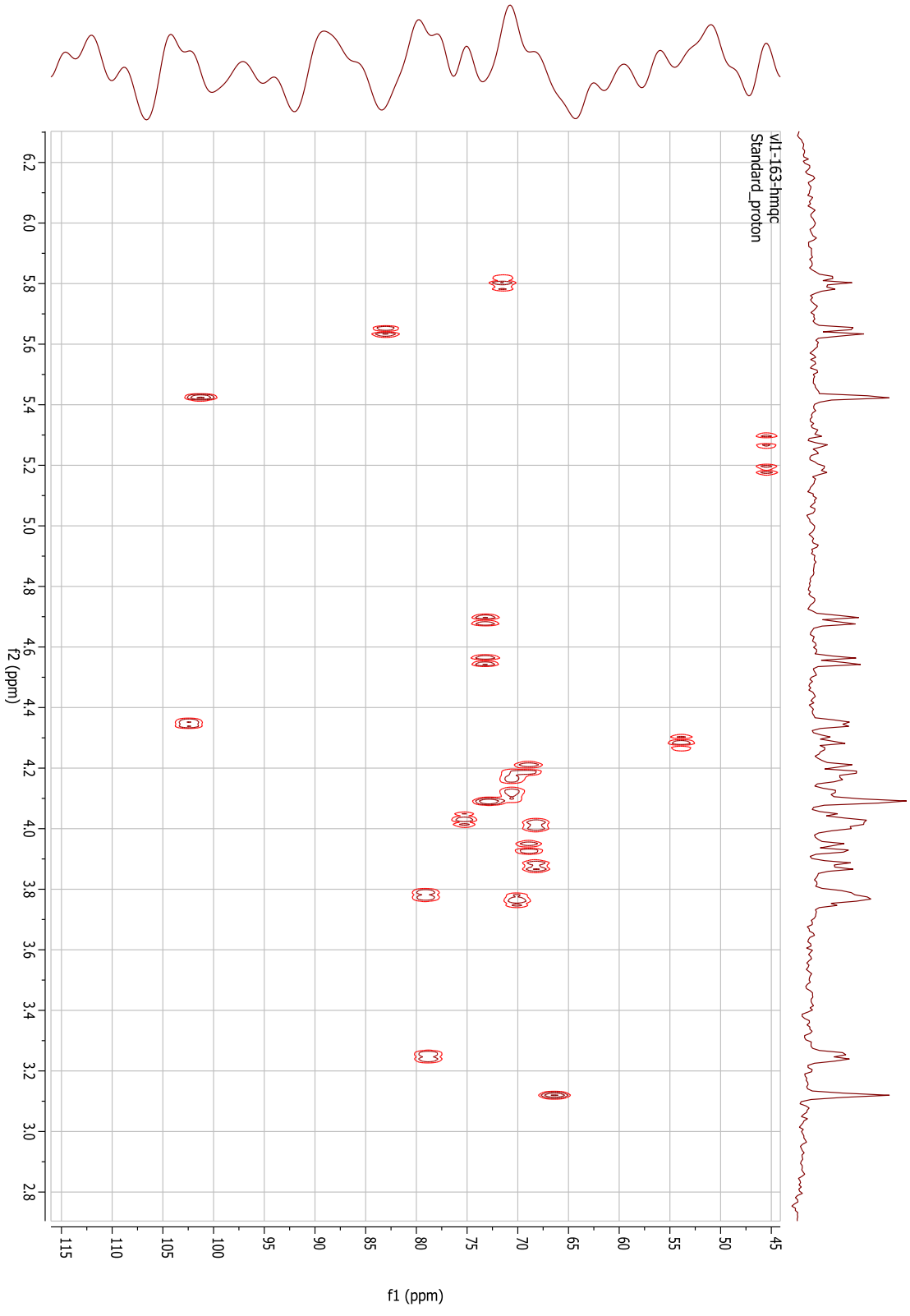


Figure S19. HRMS of Compound **15** (ESI tof)

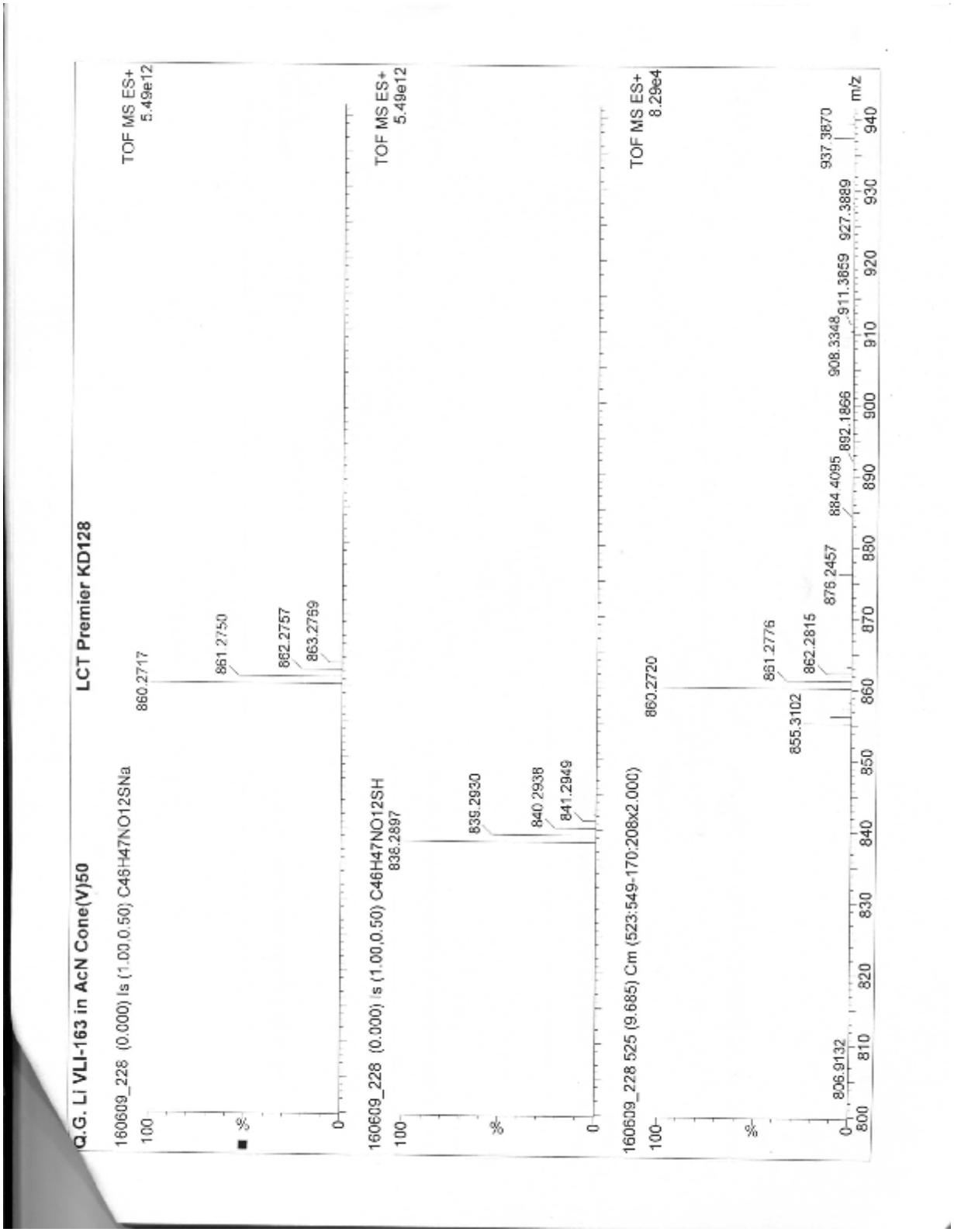


Figure S20. ^{1}H NMR of Compound **16** (600 MHz, $CDCl_3$)

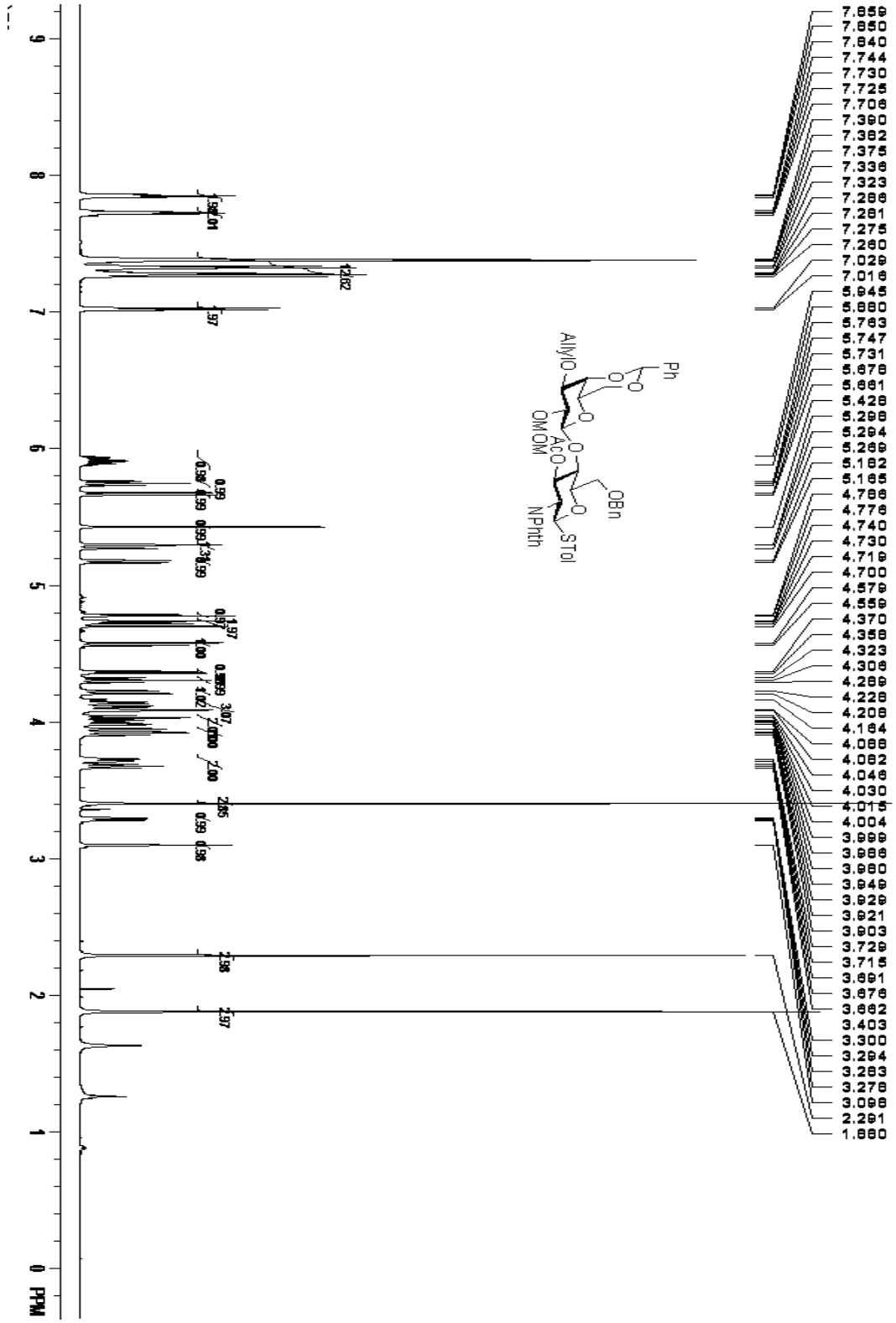


Figure S21. ^{13}C NMR of Compound **16** (600 MHz, $CDCl_3$)

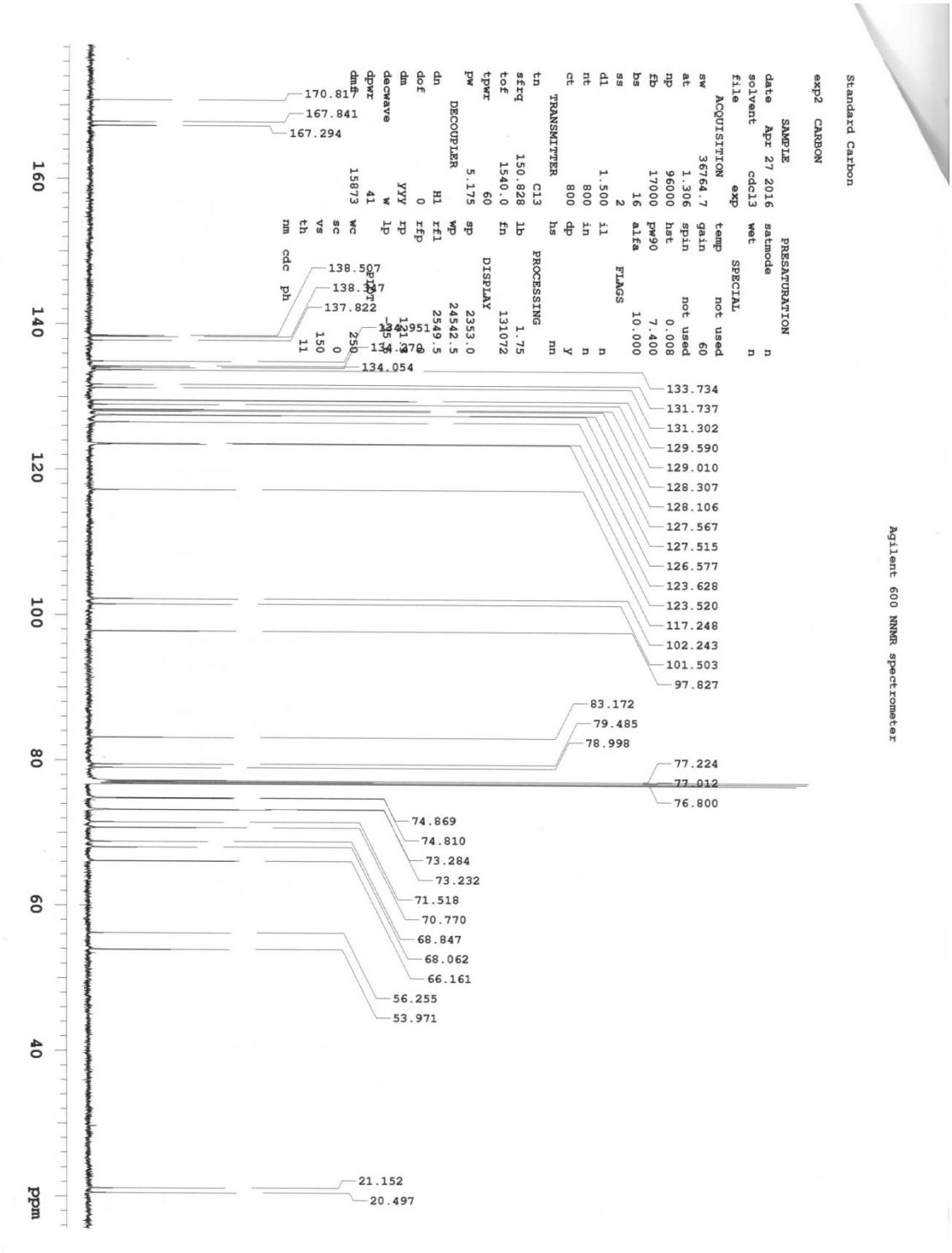


Figure S22. HRMS of Compound **16** (ESI tof)

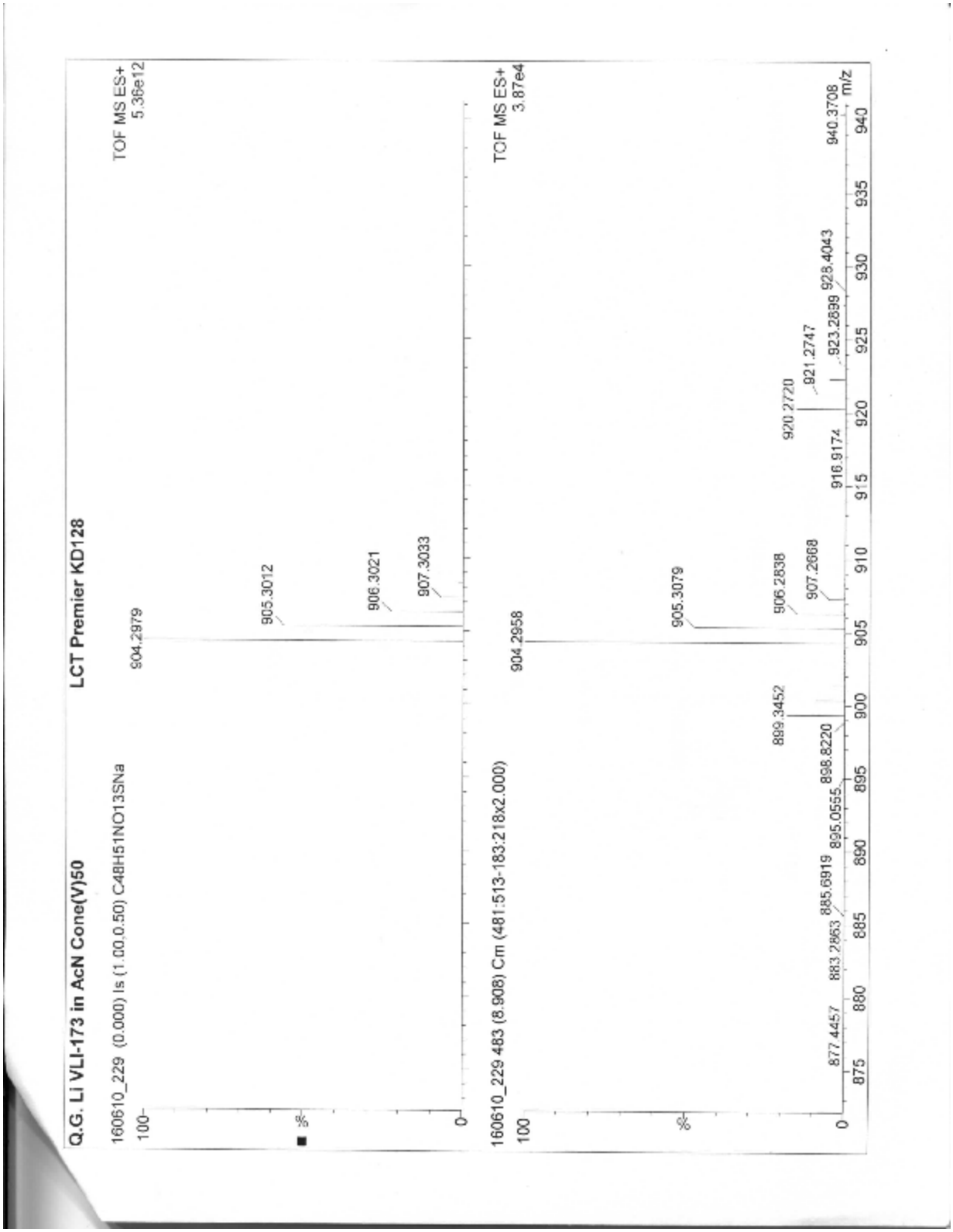


Figure S23. ^{1}H NMR of Compound **5** (600 MHz, $CDCl_3$)

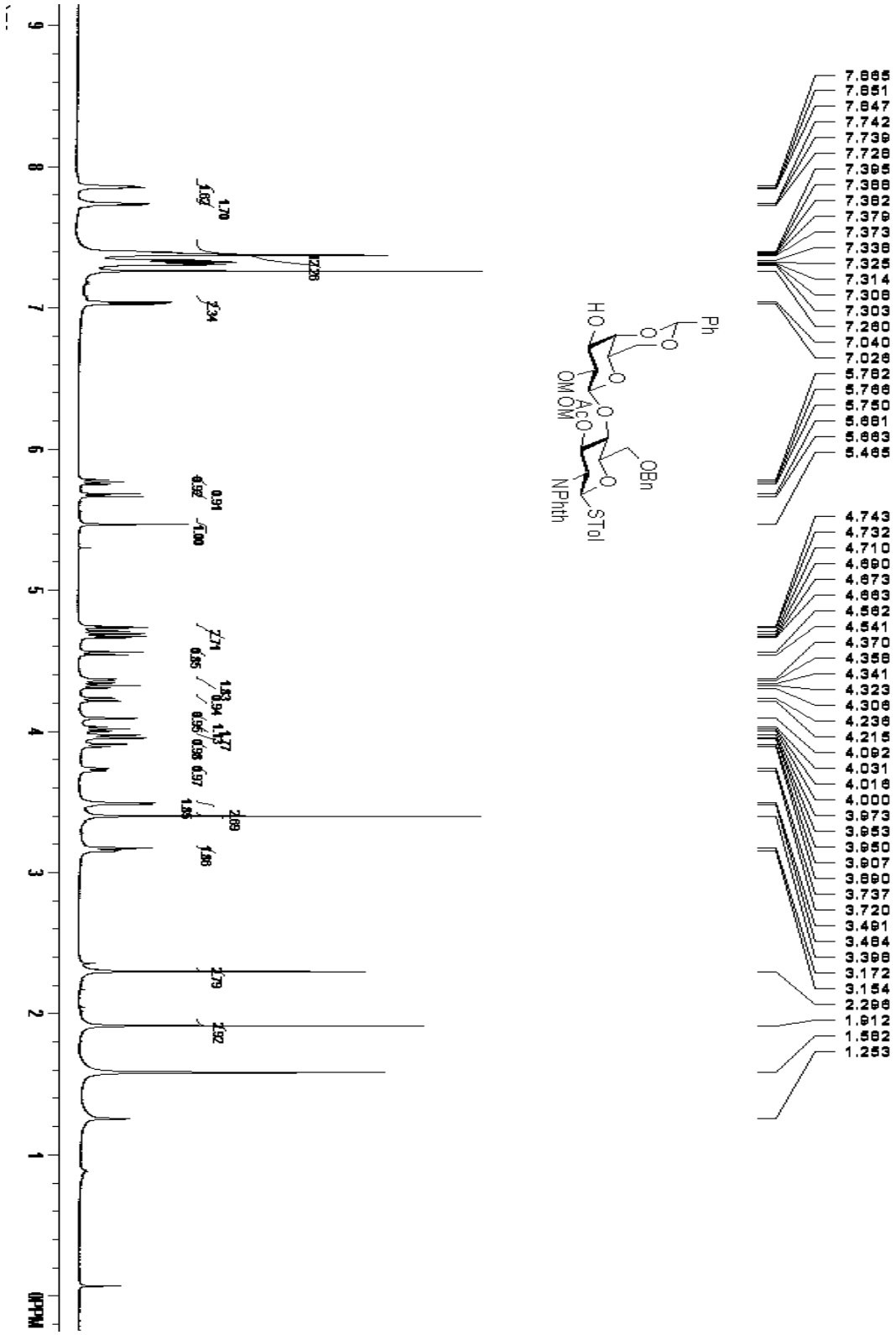


Figure S24. ^{13}C NMR of Compound **5** (600 MHz, $CDCl_3$)

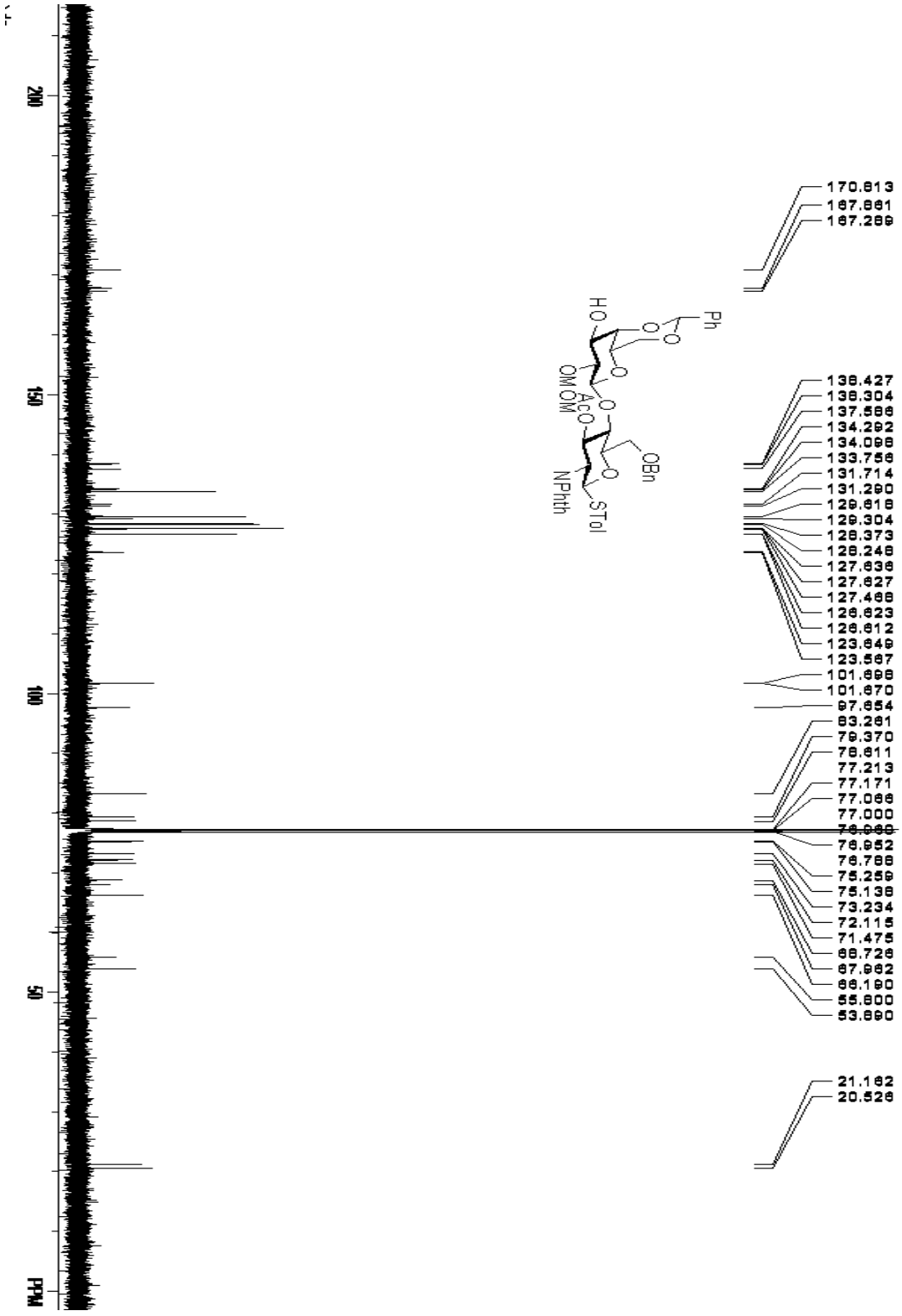


Figure S25. HRMS of Compound **5** (ESI tof)

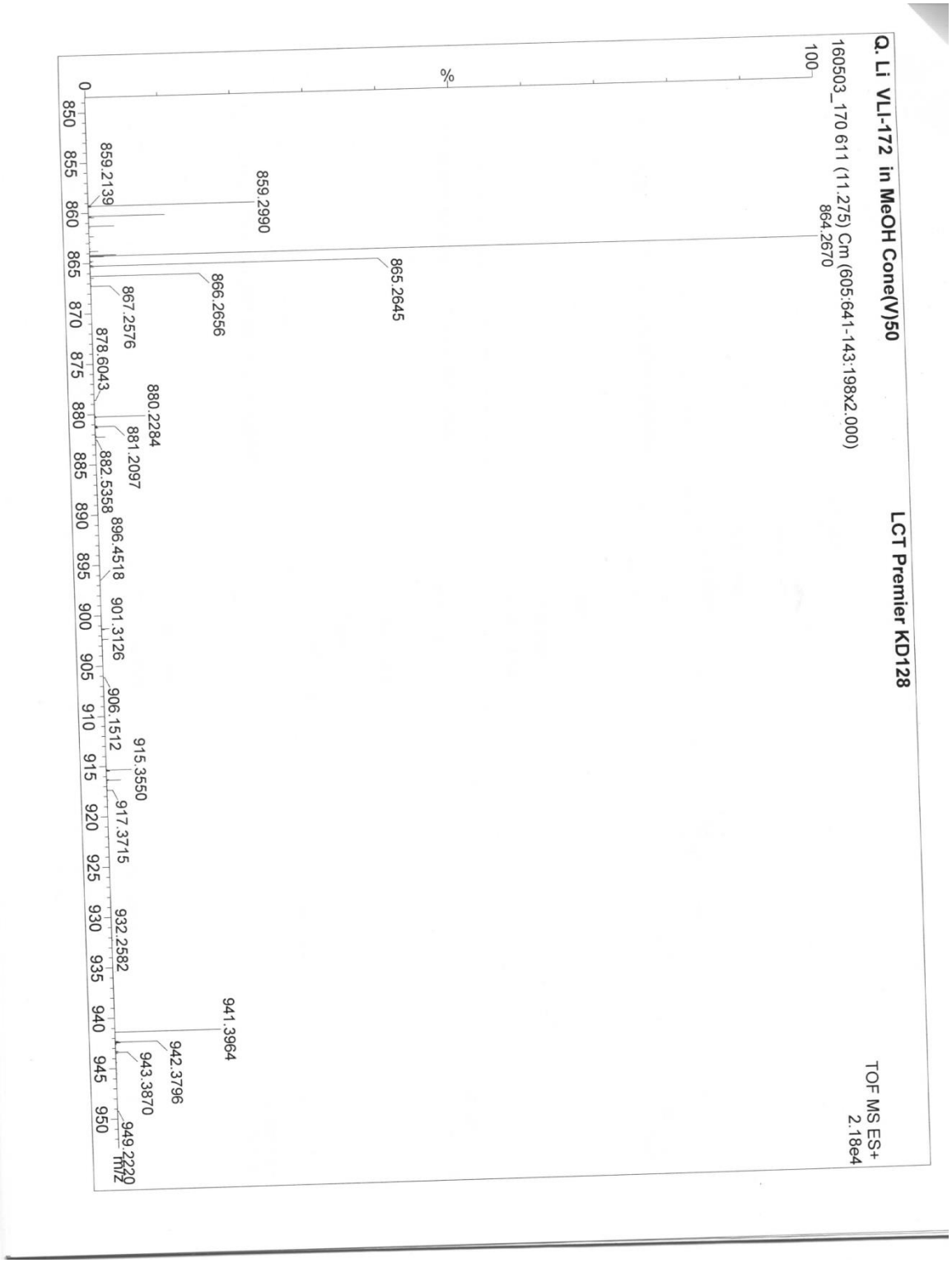


Figure S26. ^{1}H NMR of Compound **12** (600 MHz, $CDCl_3$)

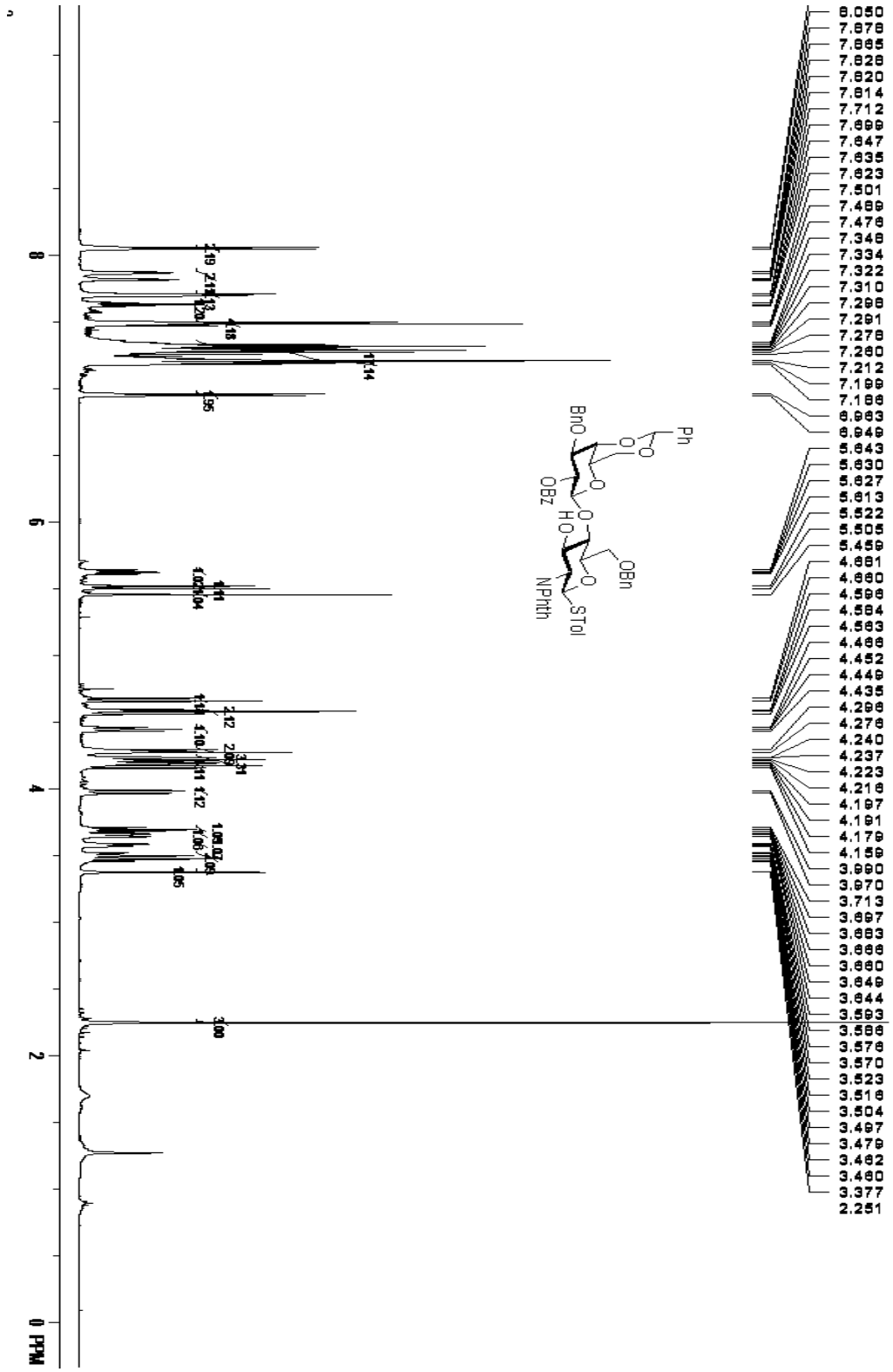


Figure S27. ^{13}C NMR of Compound **12** (600 MHz, $CDCl_3$)

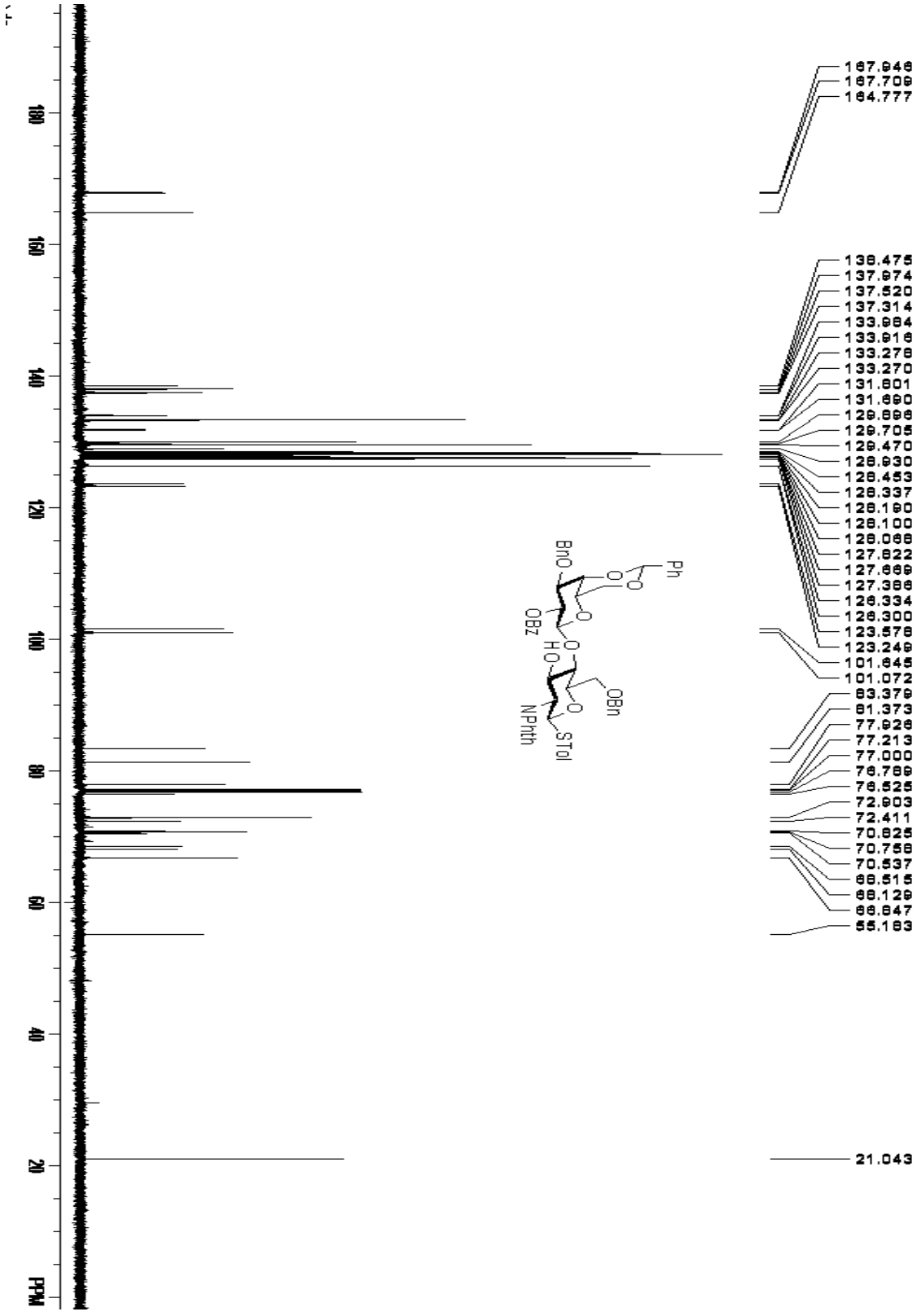


Figure S28. COSY NMR of Compound **12** (600 MHz, $CDCl_3$)

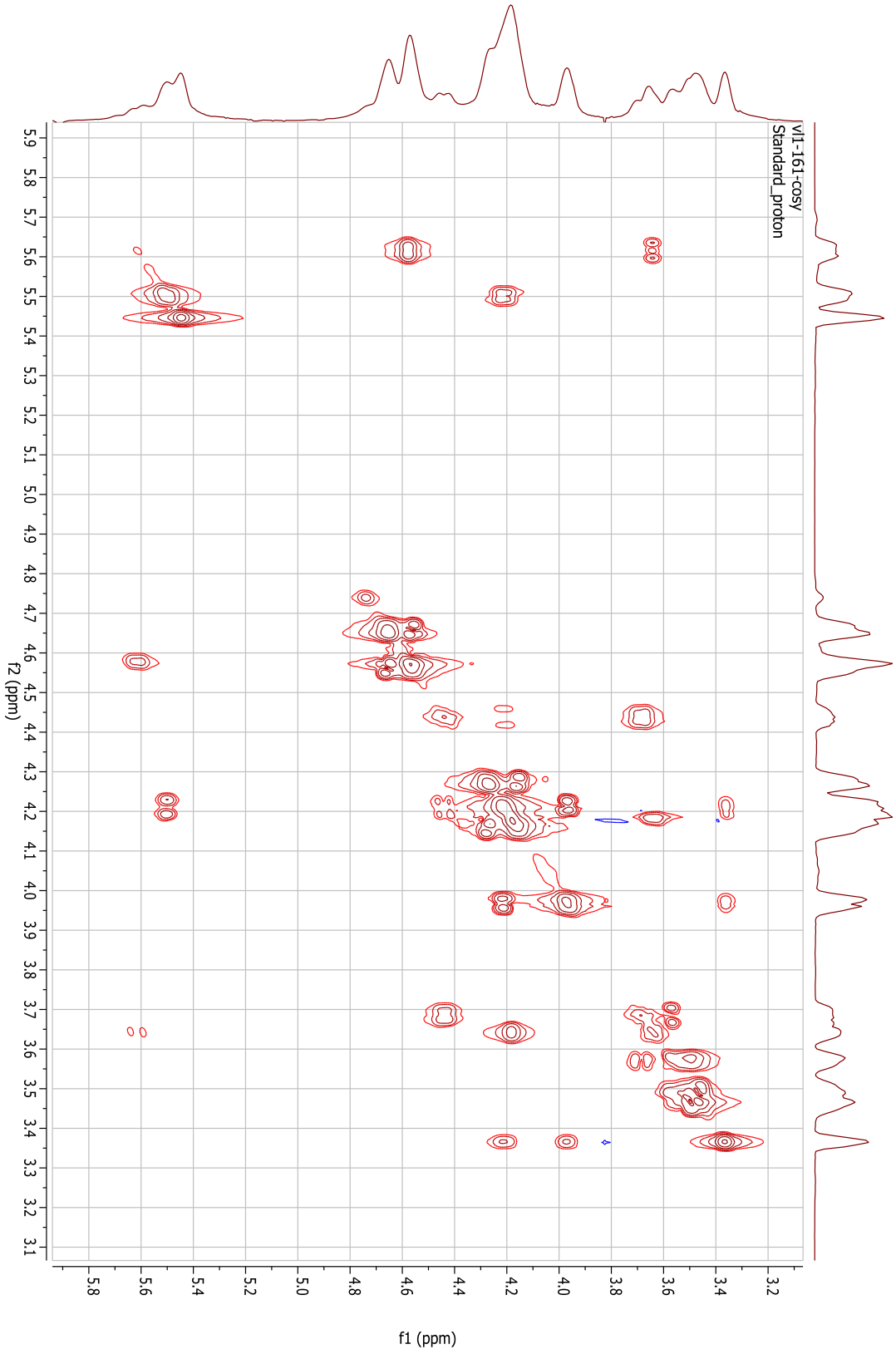


Figure S29. HSQC NMR of Compound **12** (600 MHz, $CDCl_3$)

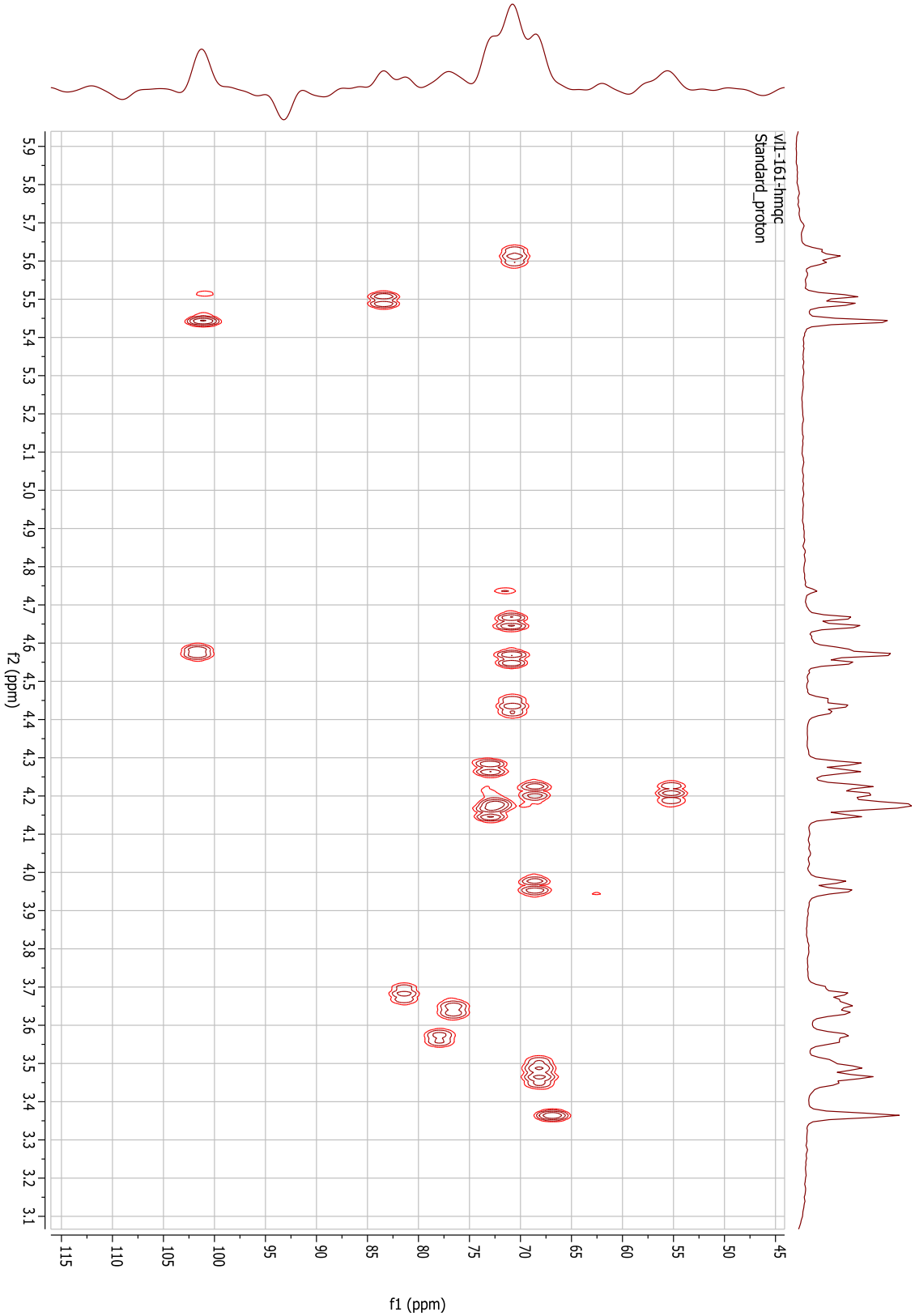


Figure S30. HRMS of Compound **12** (ESI tof)

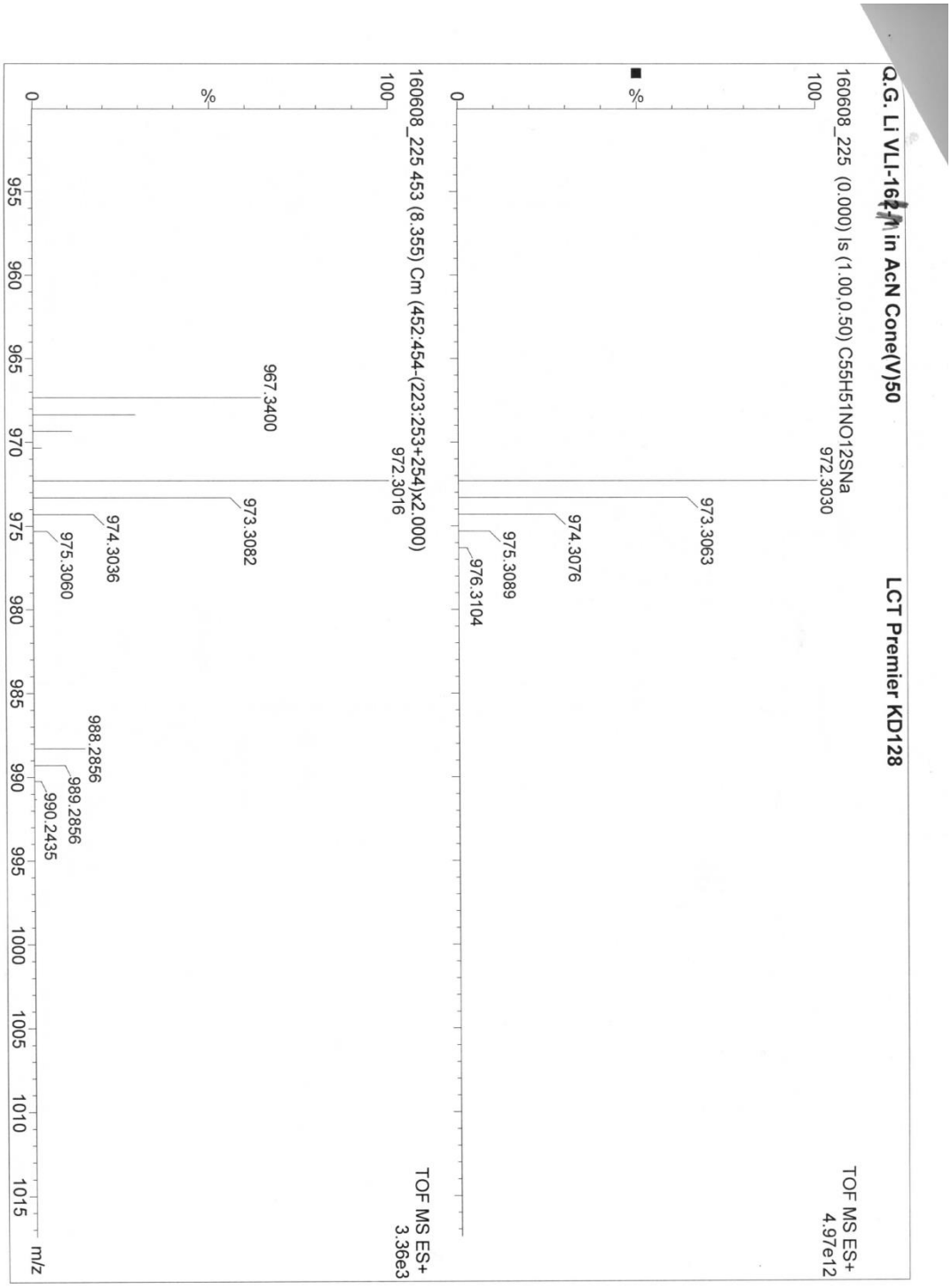


Figure S31. ^{1}H NMR of Compound **4** (600 MHz, $CDCl_3$)

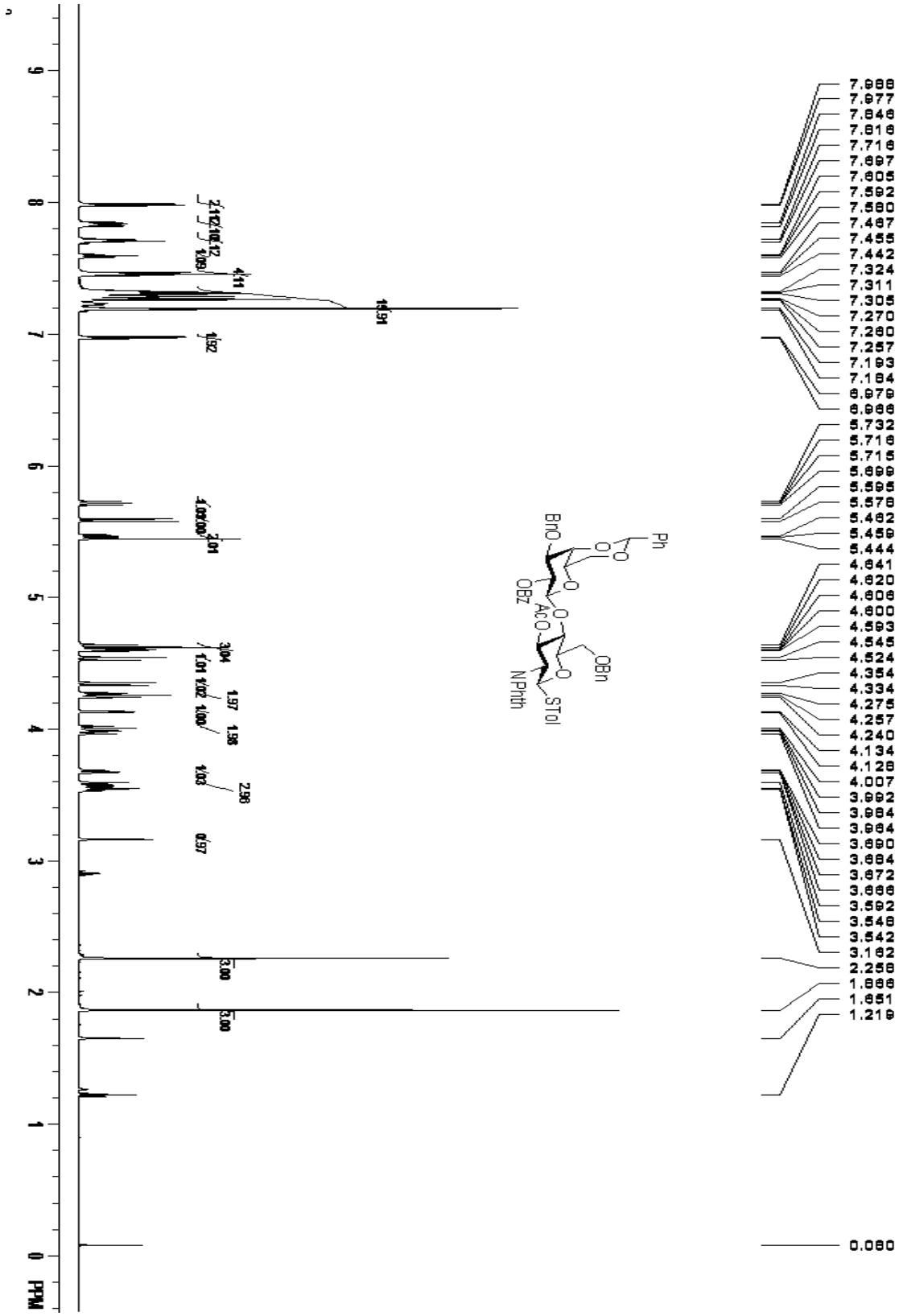


Figure S32. ^{13}C NMR of Compound **4** (600 MHz, $CDCl_3$)

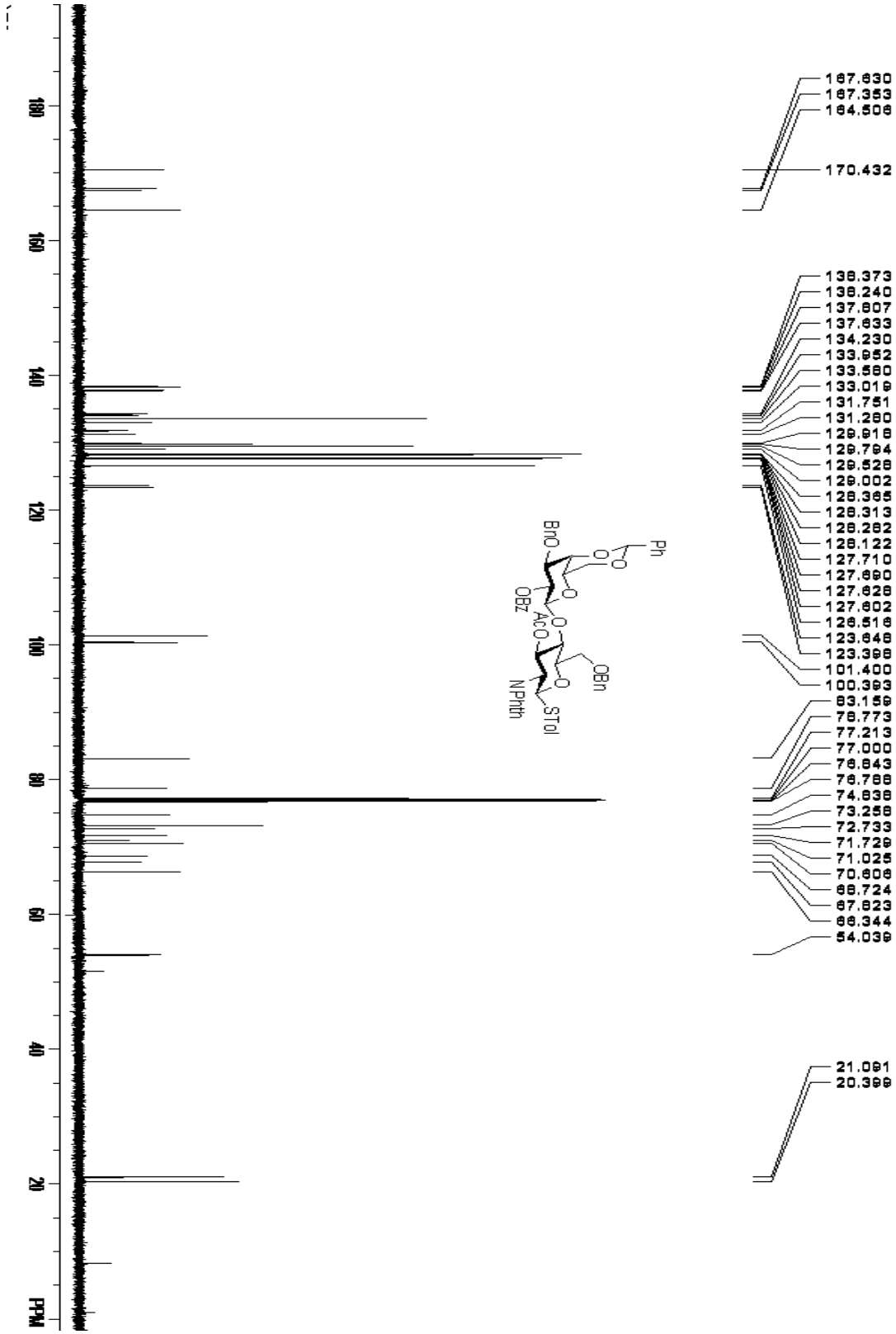


Figure S33. ^{1}H-^{1}H COSY NMR of Compound **4** (600 MHz, $CDCl_3$)

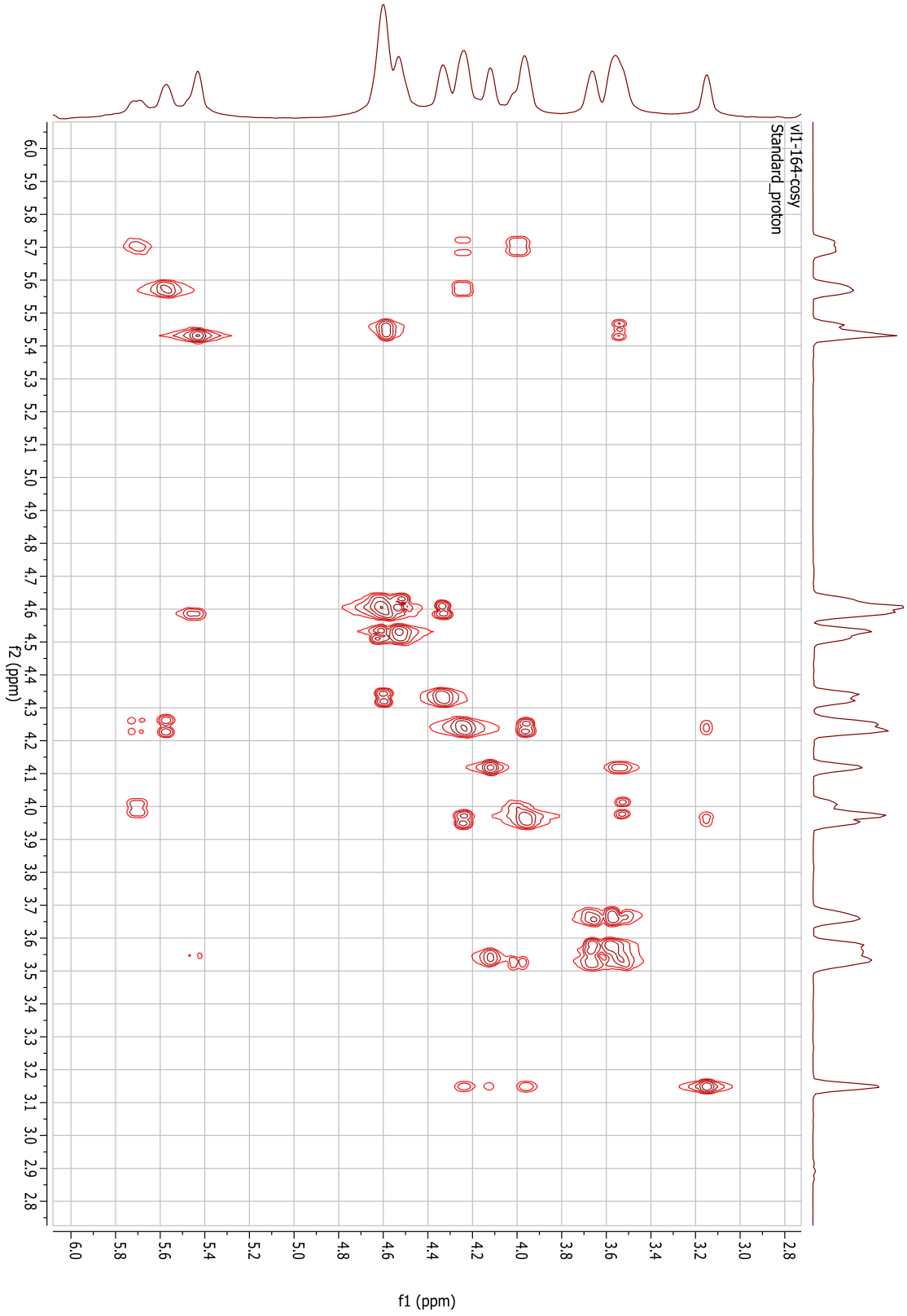


Figure S34. HSQC NMR of Compound **4** (600 MHz, $CDCl_3$)

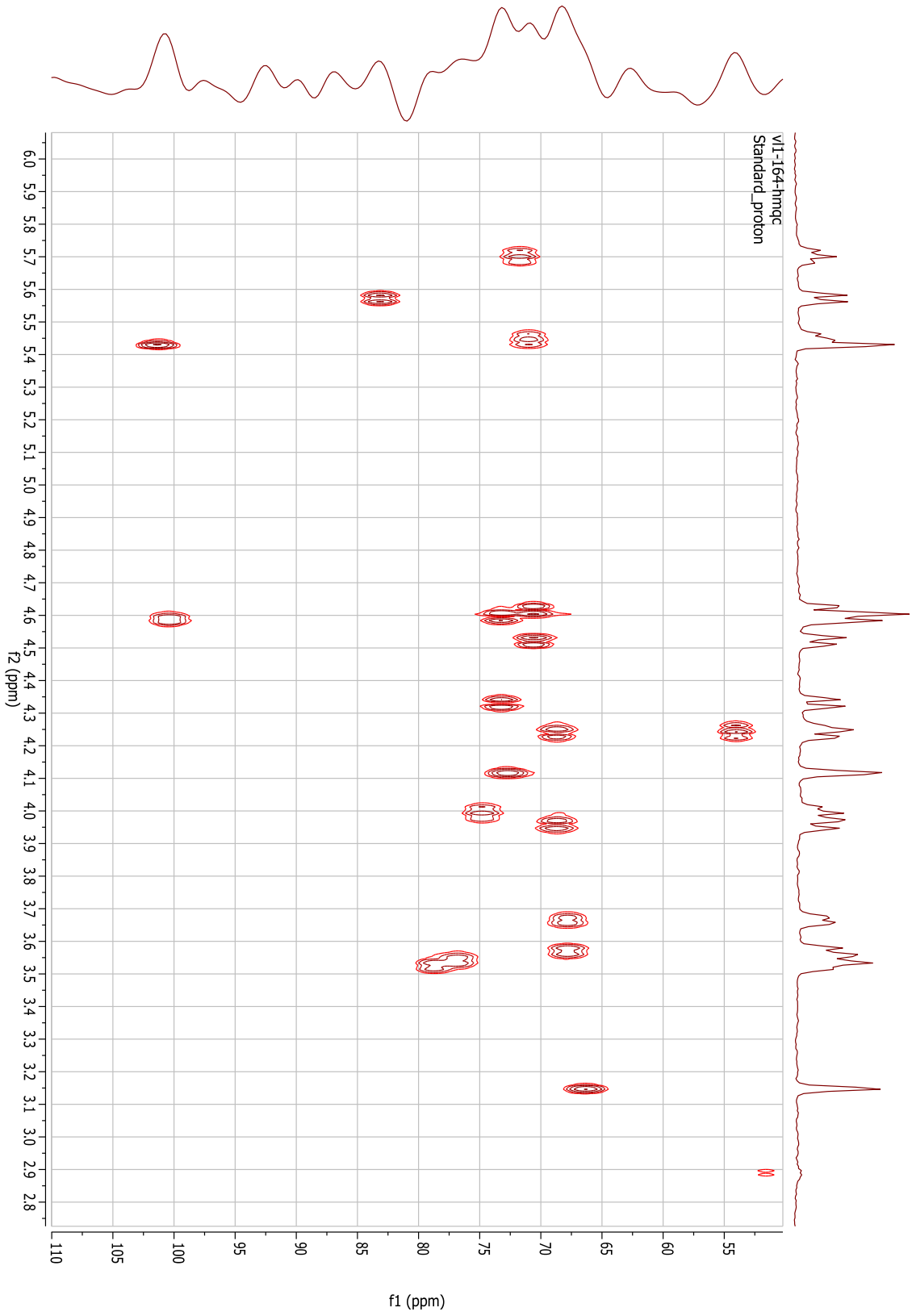


Figure S35. HRMS of Compound **4** (ESI tof)

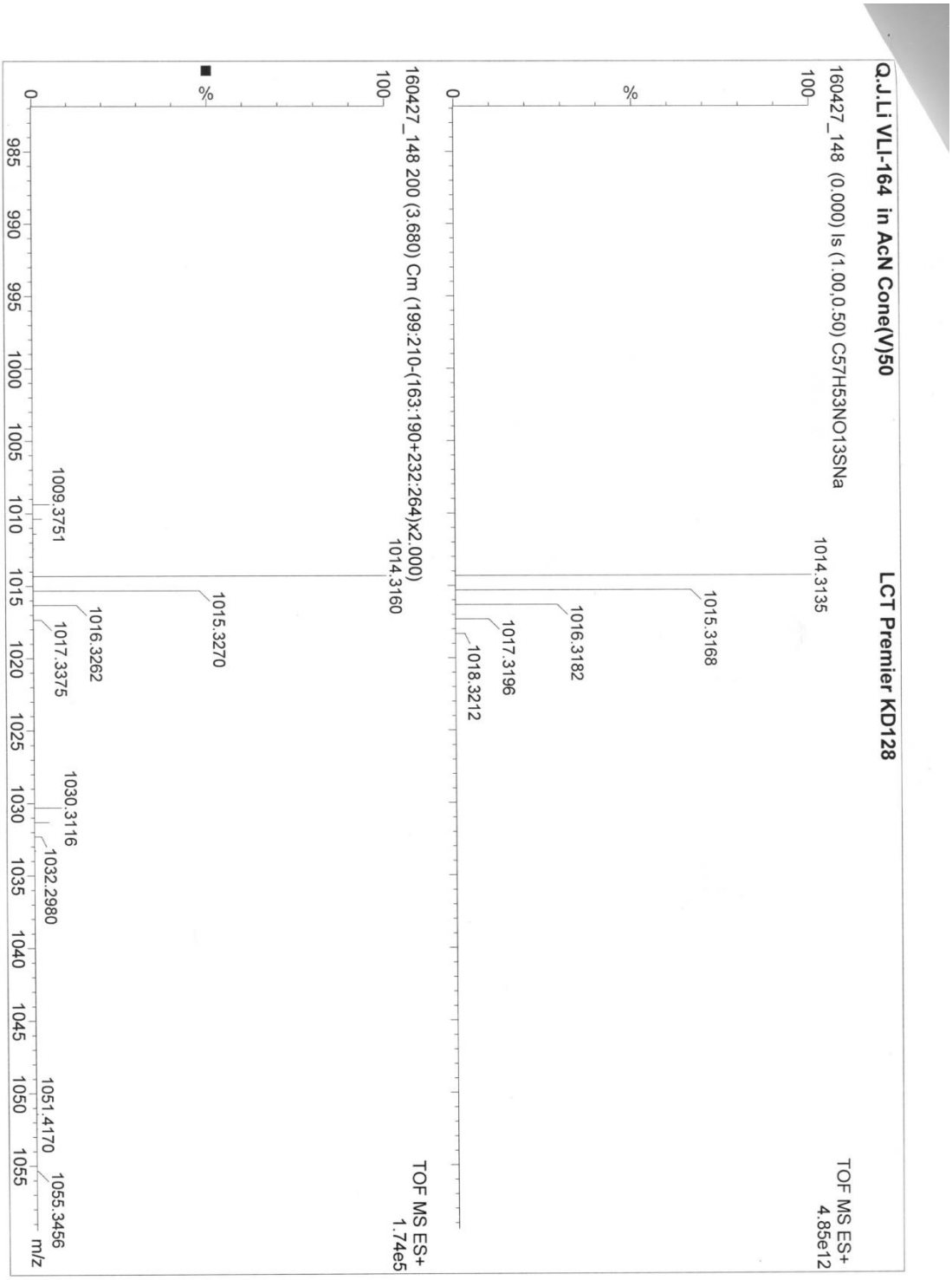


Figure S36. ^{1}H NMR of Compound **3** (600 MHz, $CDCl_3$)

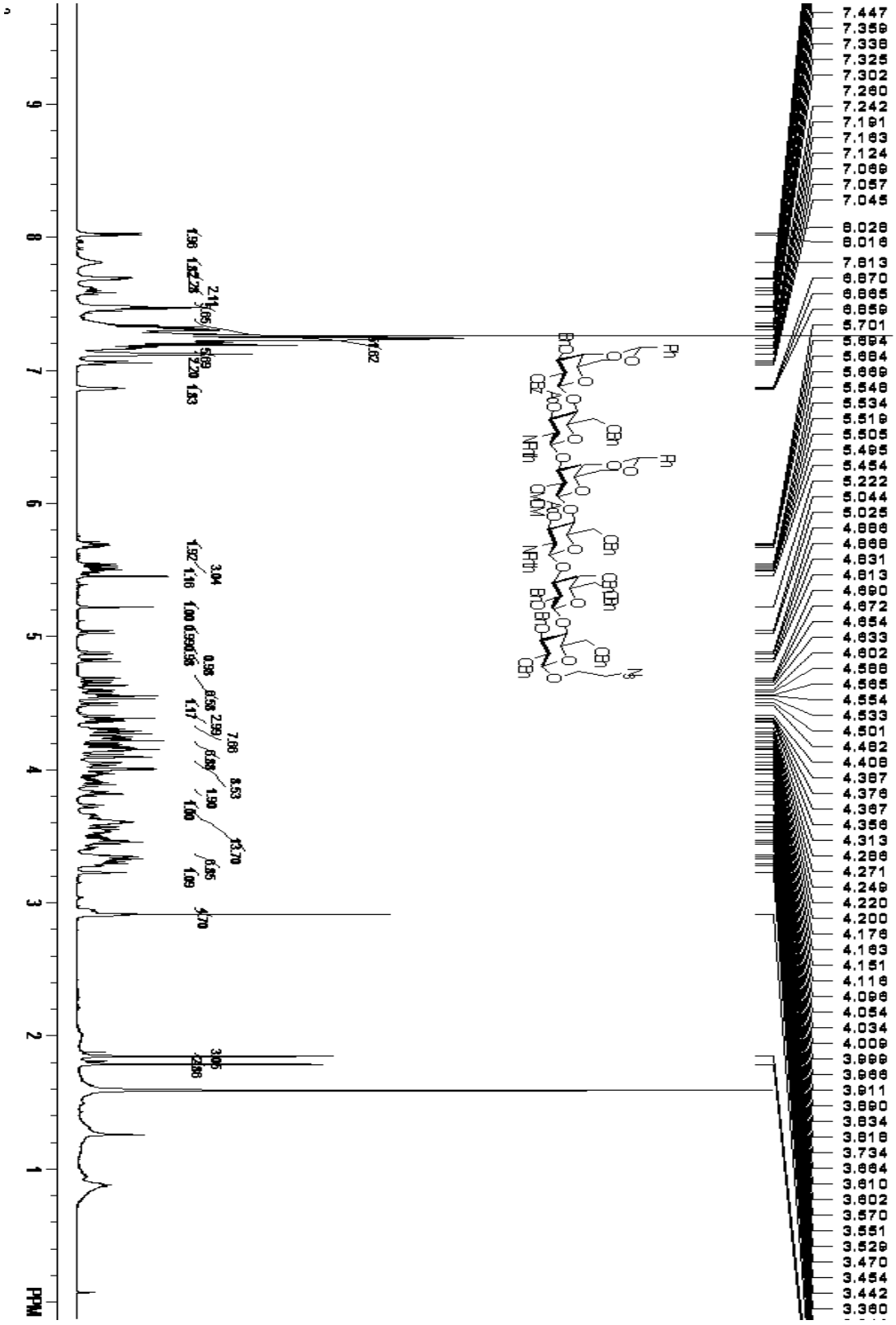


Figure S37. ^{13}C NMR of Compound **3** (600 MHz, $CDCl_3$)

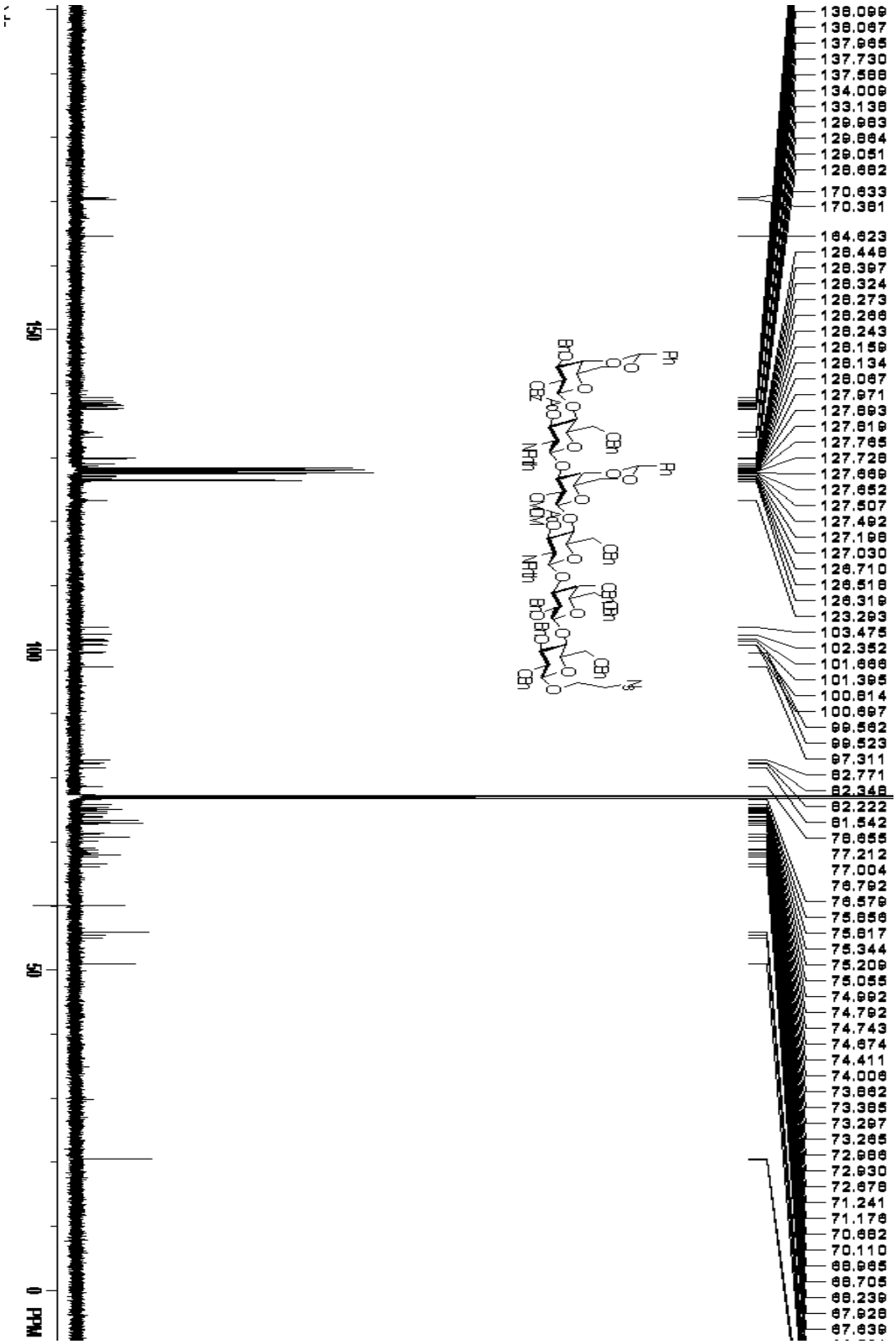


Figure S38. COSY NMR of Compound **3** (600 MHz, $CDCl_3$)

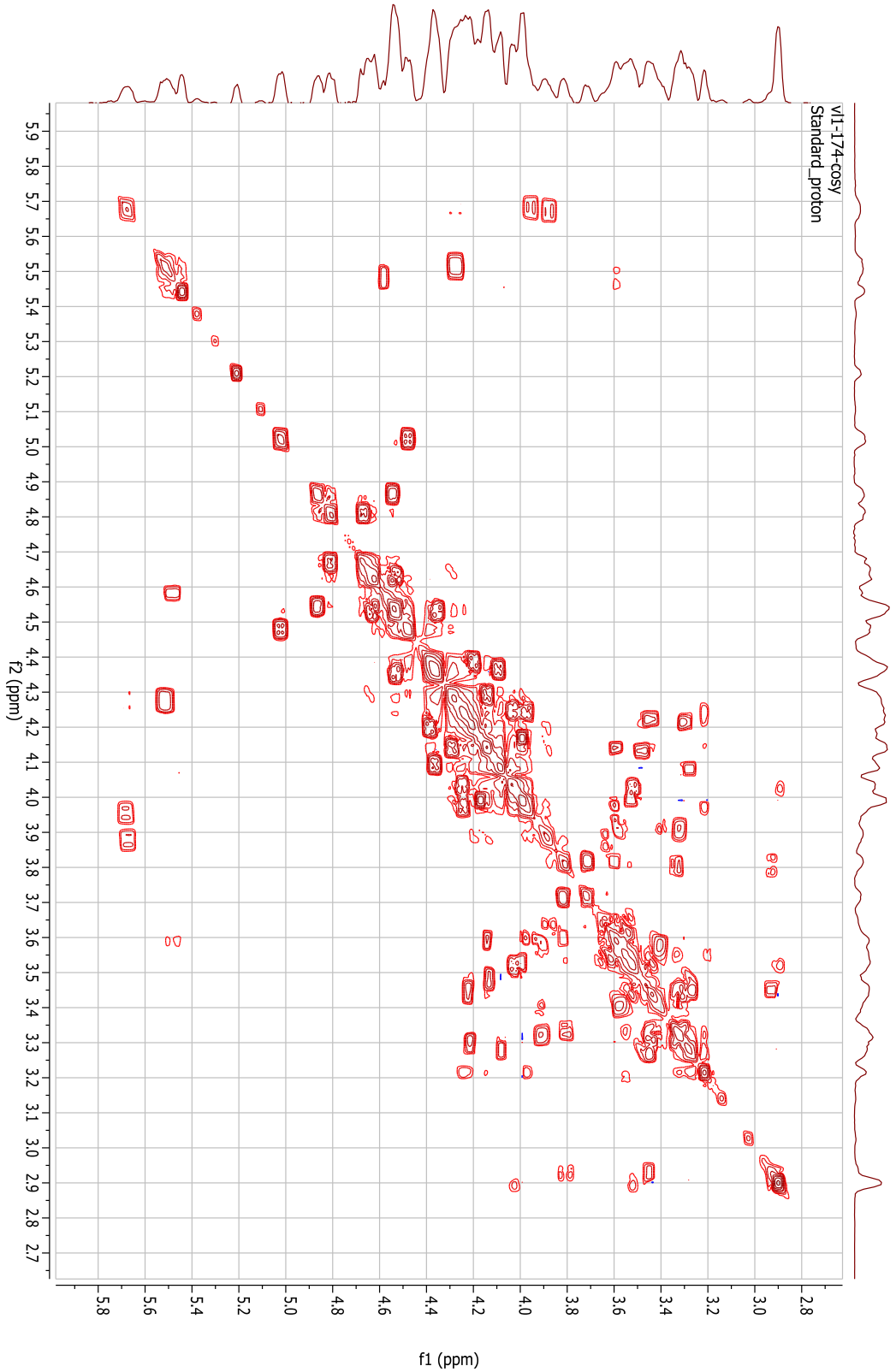


Figure S39. HSQC NMR of Compound **3** (600 MHz, $CDCl_3$)

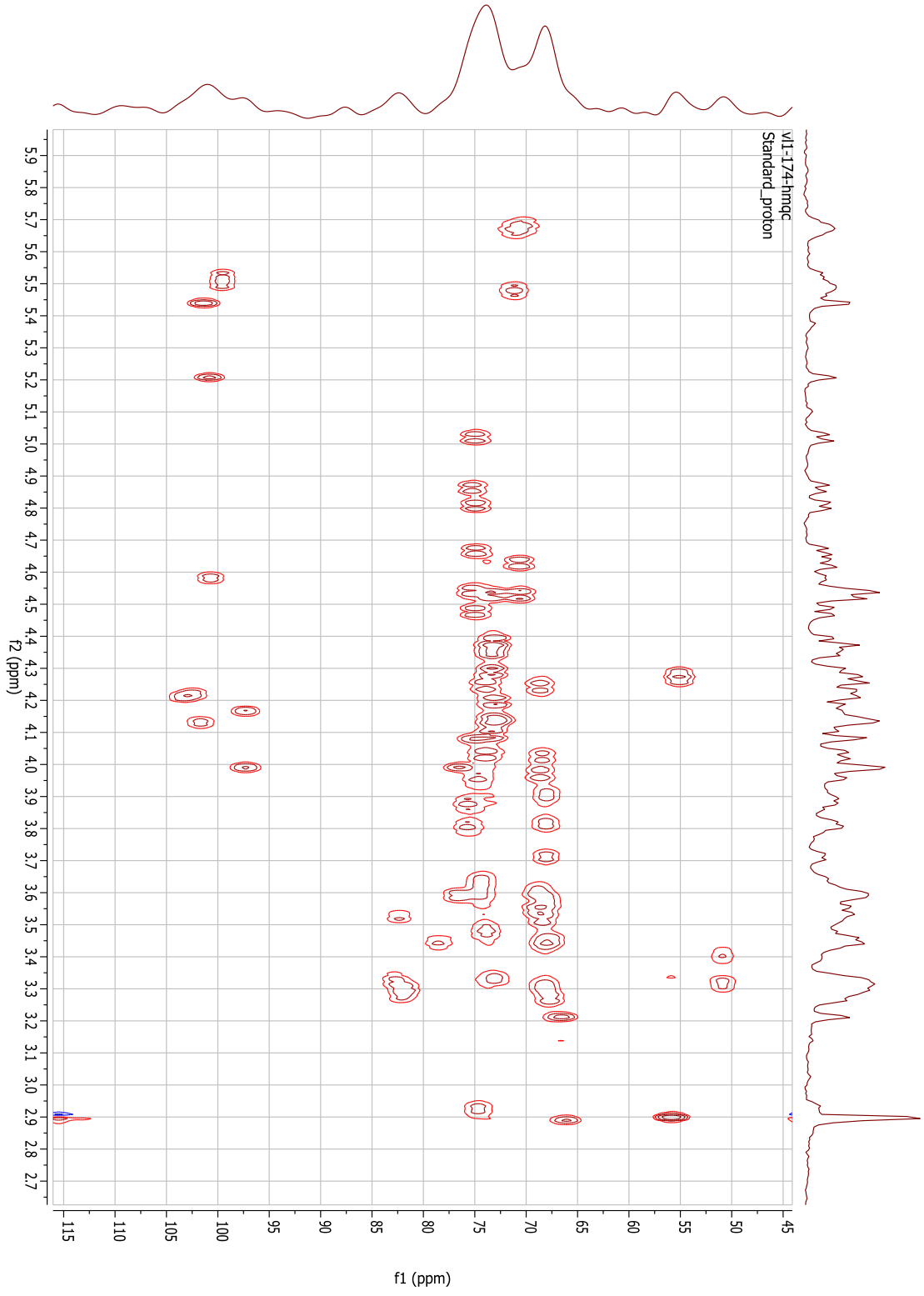


Figure S40. HRMS of Compound **3** (ESI tof)

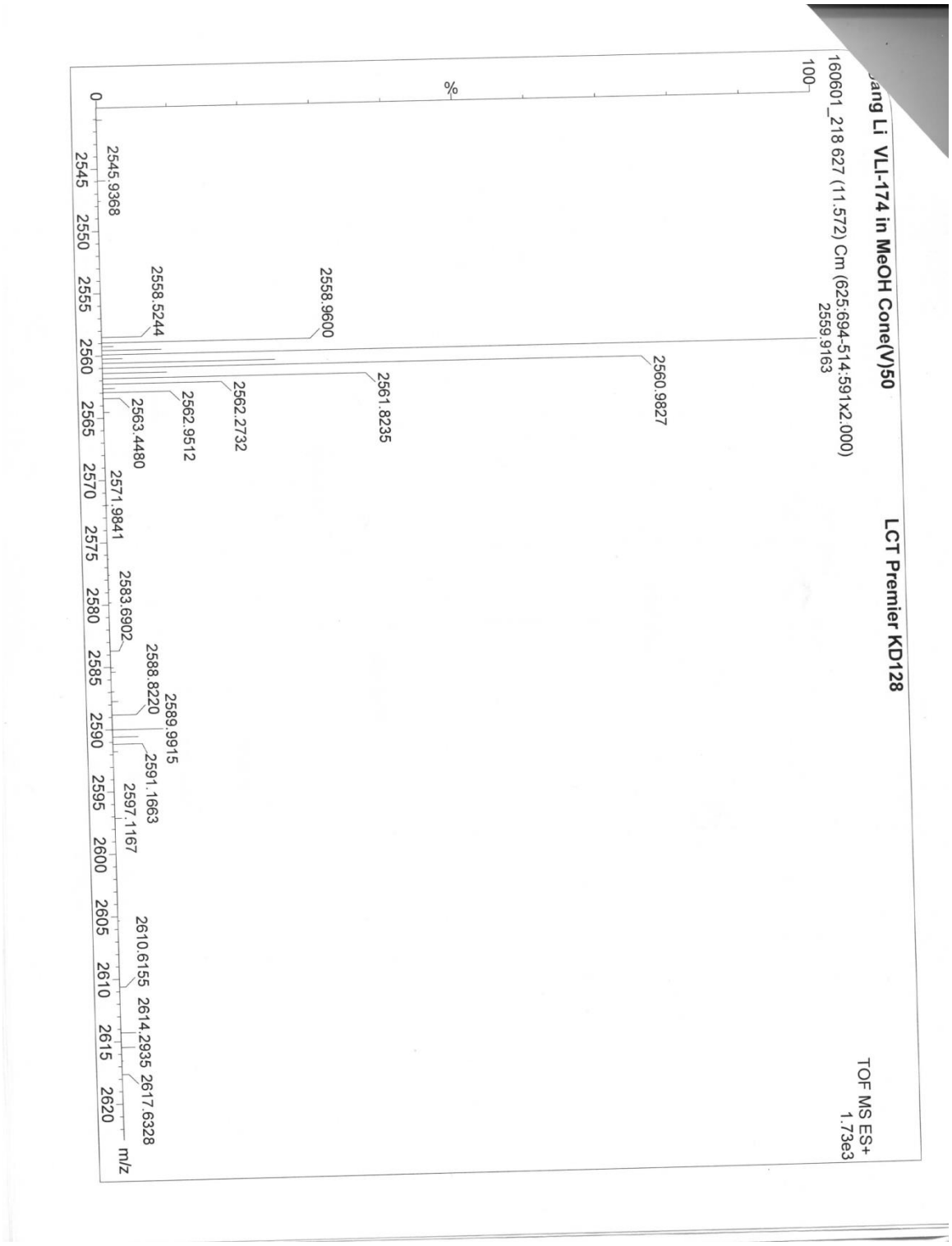


Figure S41. ^{1}H NMR of Compound **17** (600 MHz, $CDCl_3$)

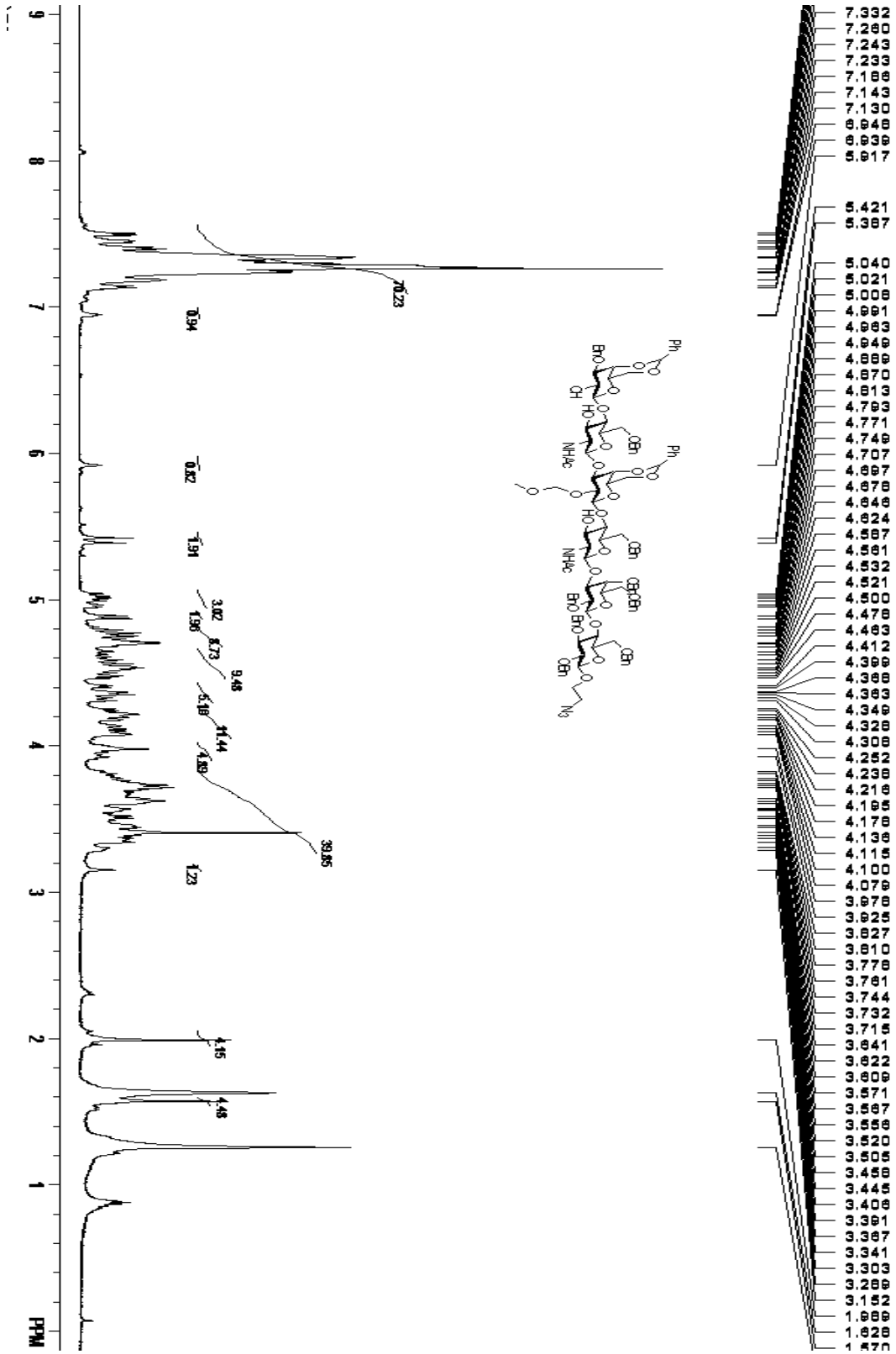


Figure S42. ^{13}C NMR of Compound **17** (600 MHz, $CDCl_3$)

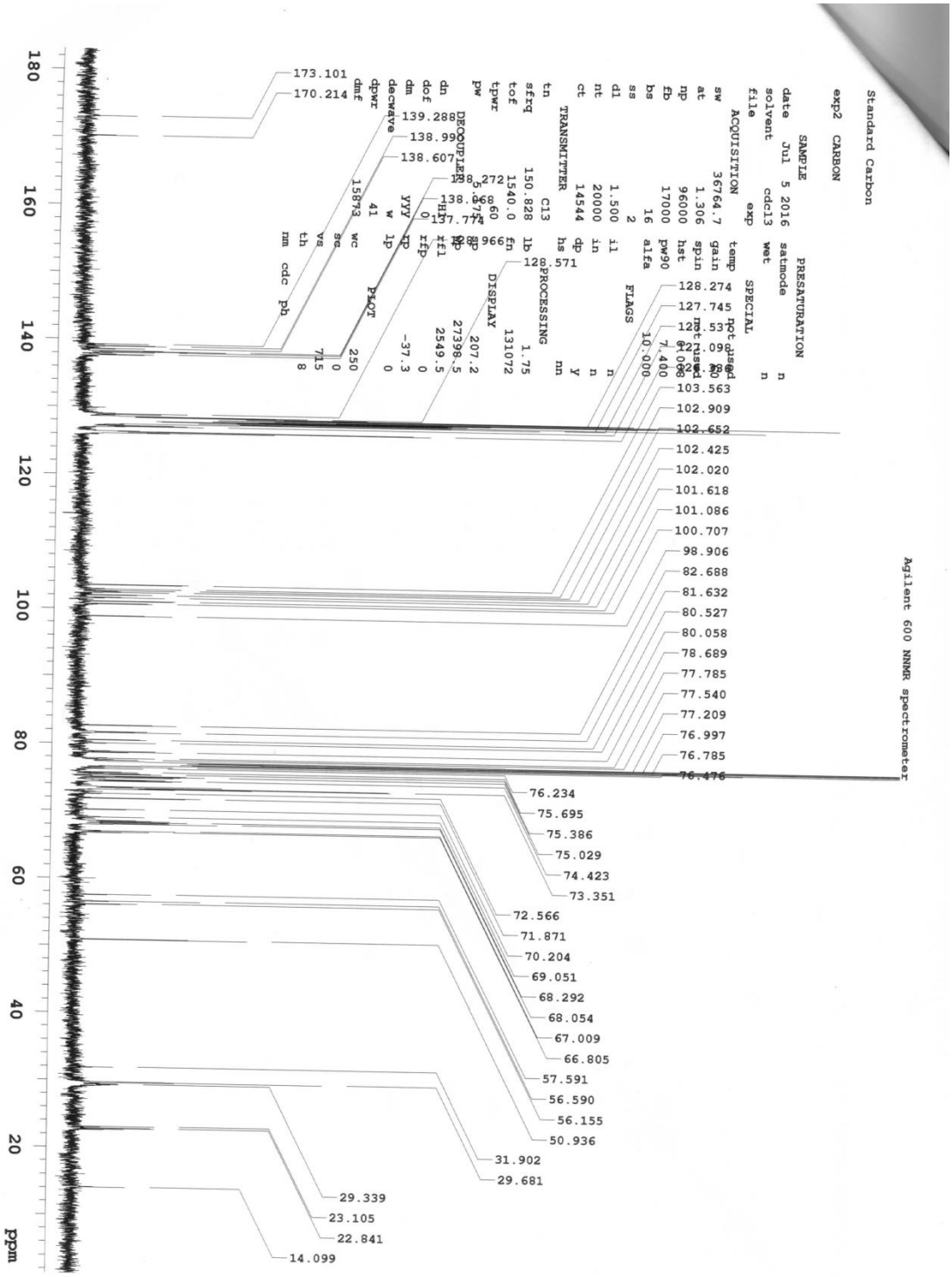


Figure S43. COSY NMR of Compound **17** (600 MHz, $CDCl_3$)

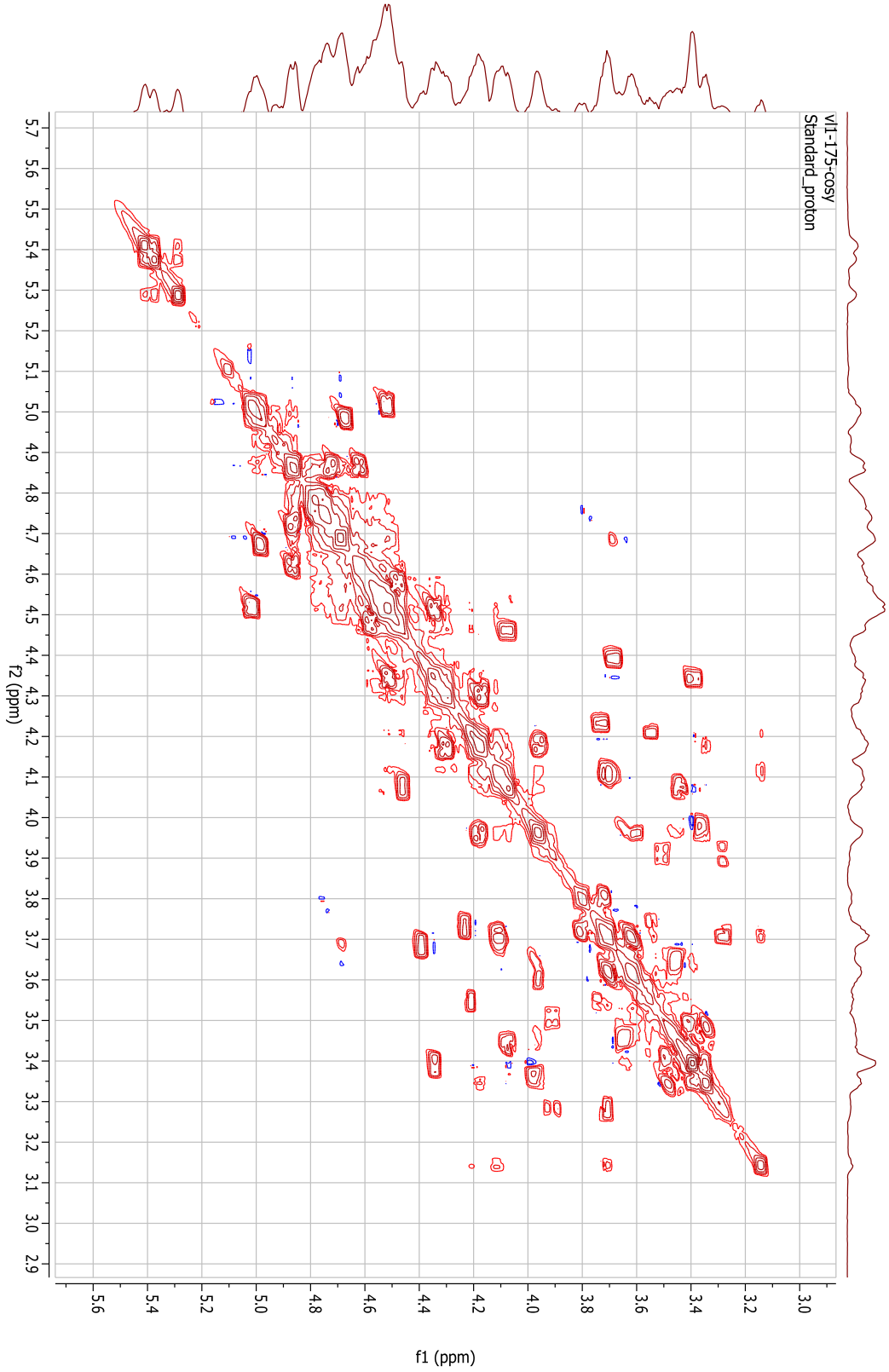


Figure S44. HSQC NMR of Compound **17** (600 MHz, $CDCl_3$)

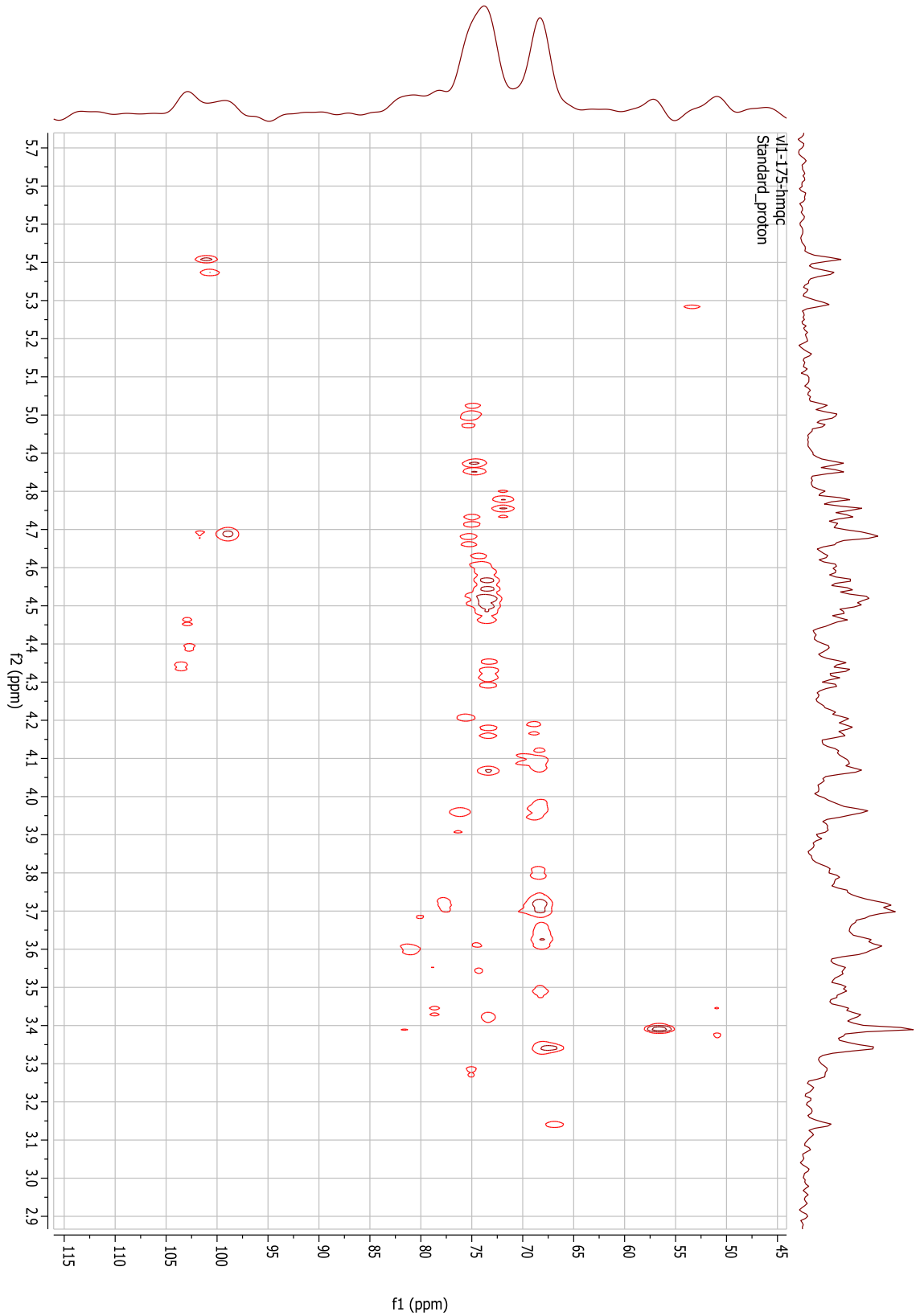


Figure S45. HRMS of Compound **17** (ESI tof)

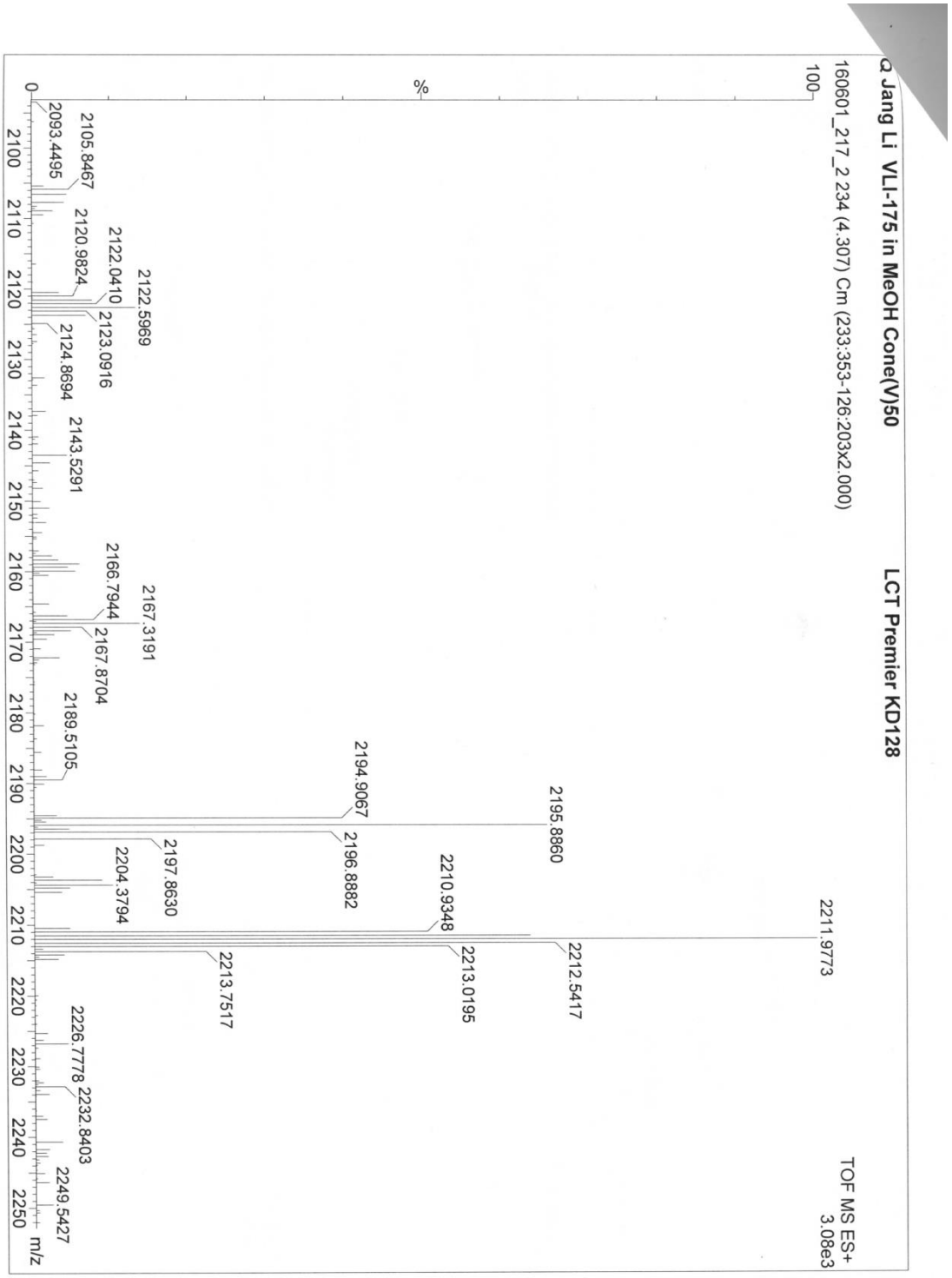


Figure S46. ^{1}H NMR of Compound **2** (600 MHz, $CDCl_3$)

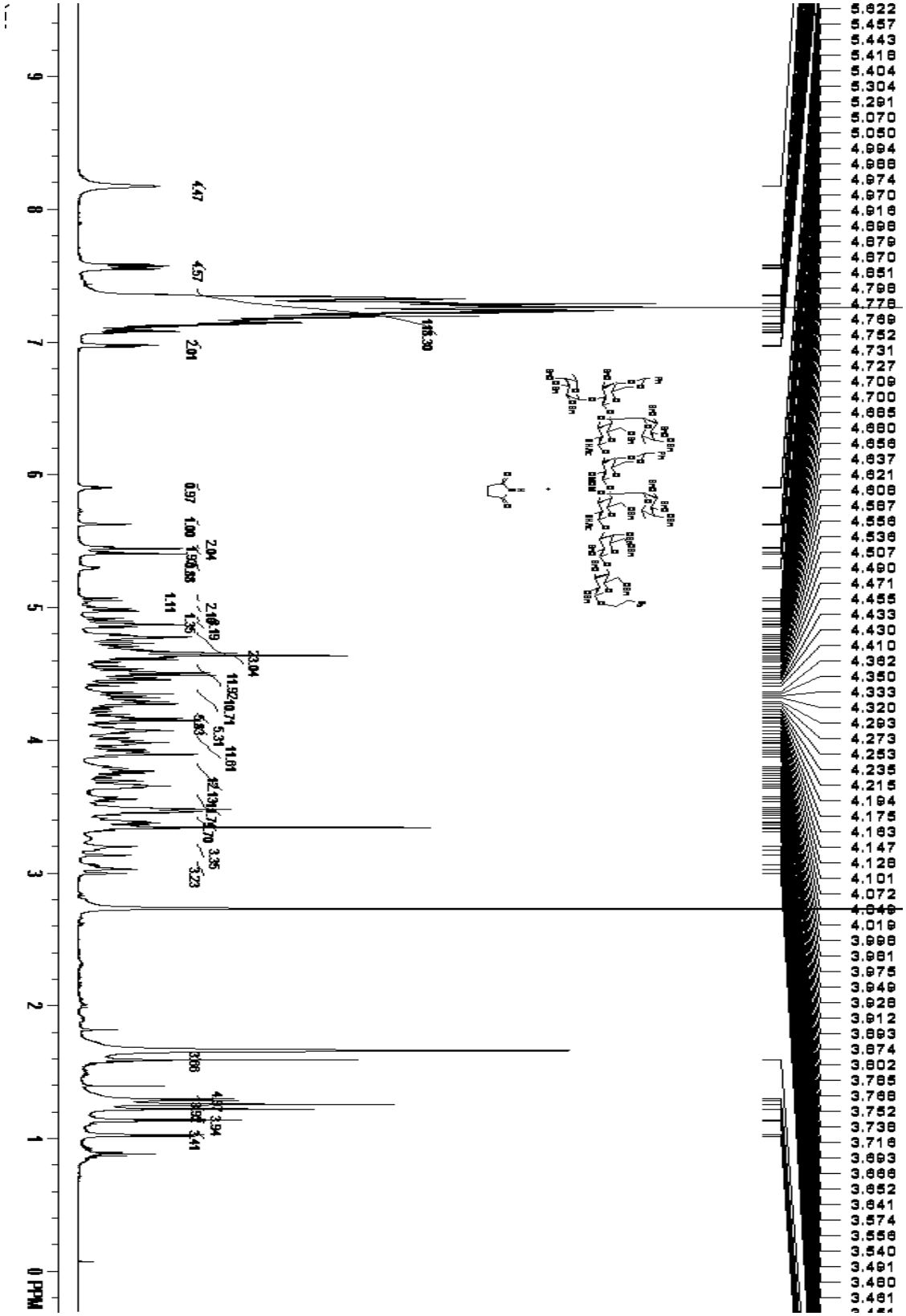


Figure S47. ^{13}C NMR of Compound **2** (600 MHz, $CDCl_3$)

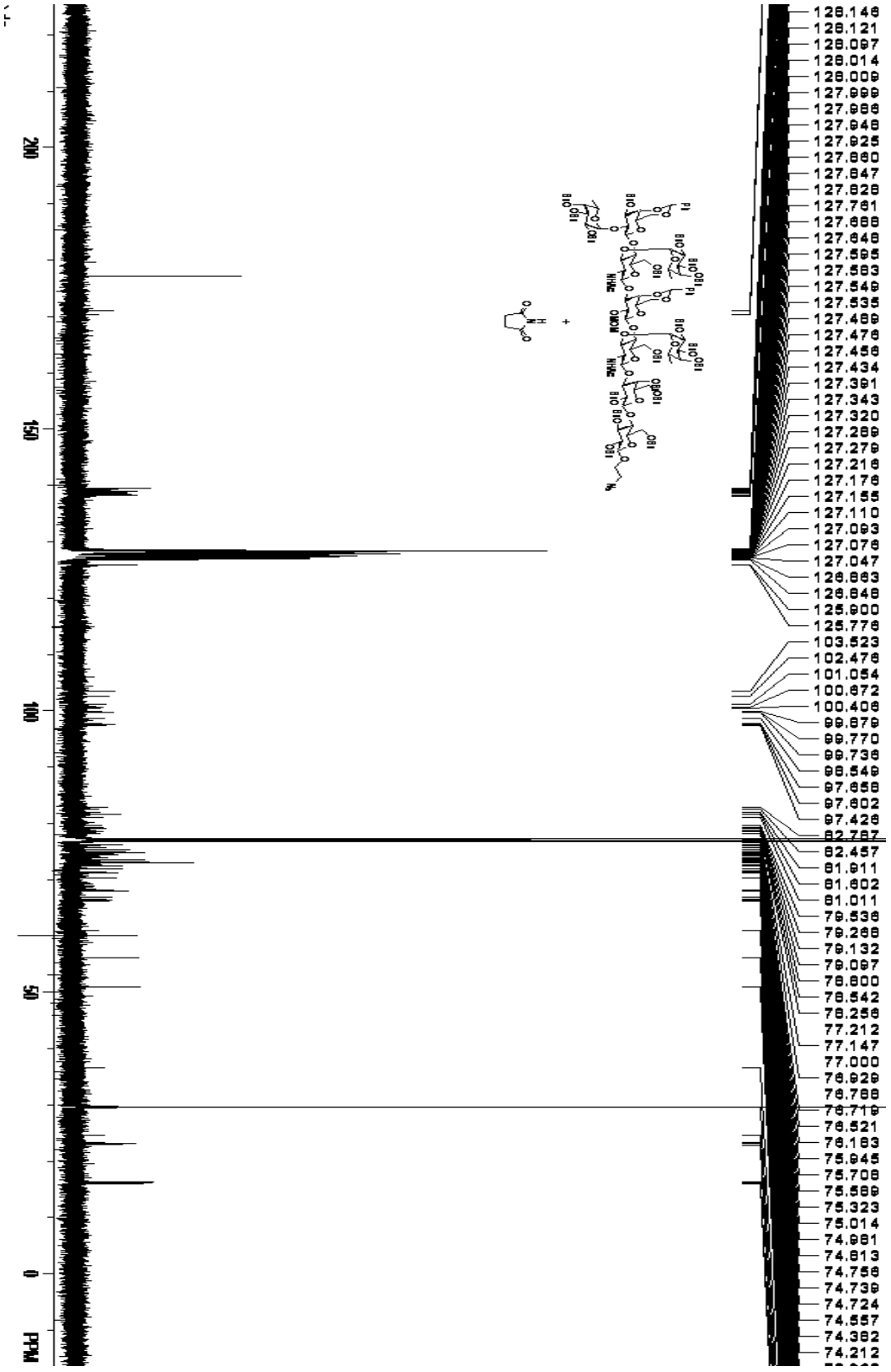


Figure S48. COSY NMR of Compound **2** (600 MHz, $CDCl_3$)

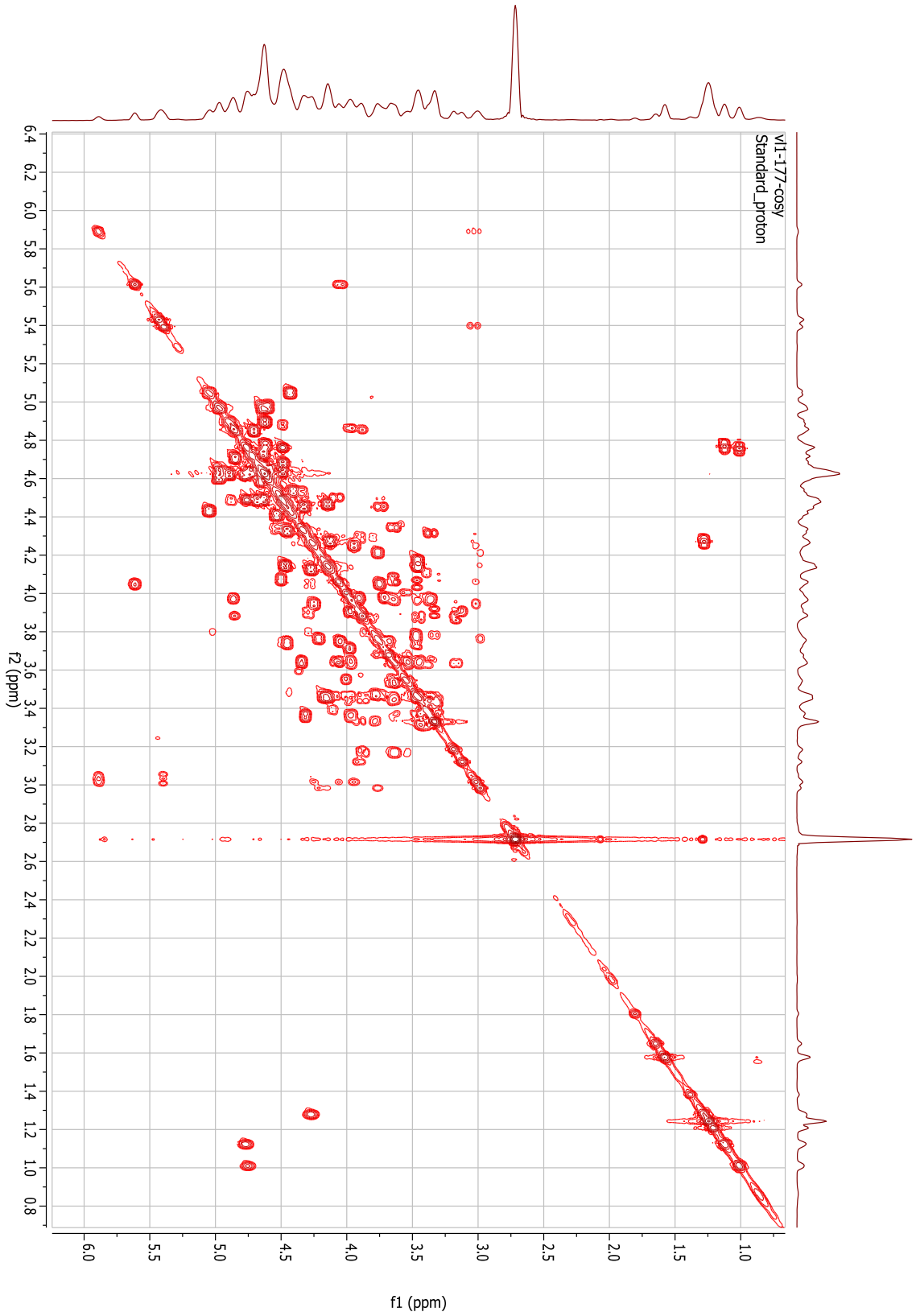


Figure S49. HSQC NMR of Compound **2** (600 MHz, $CDCl_3$)

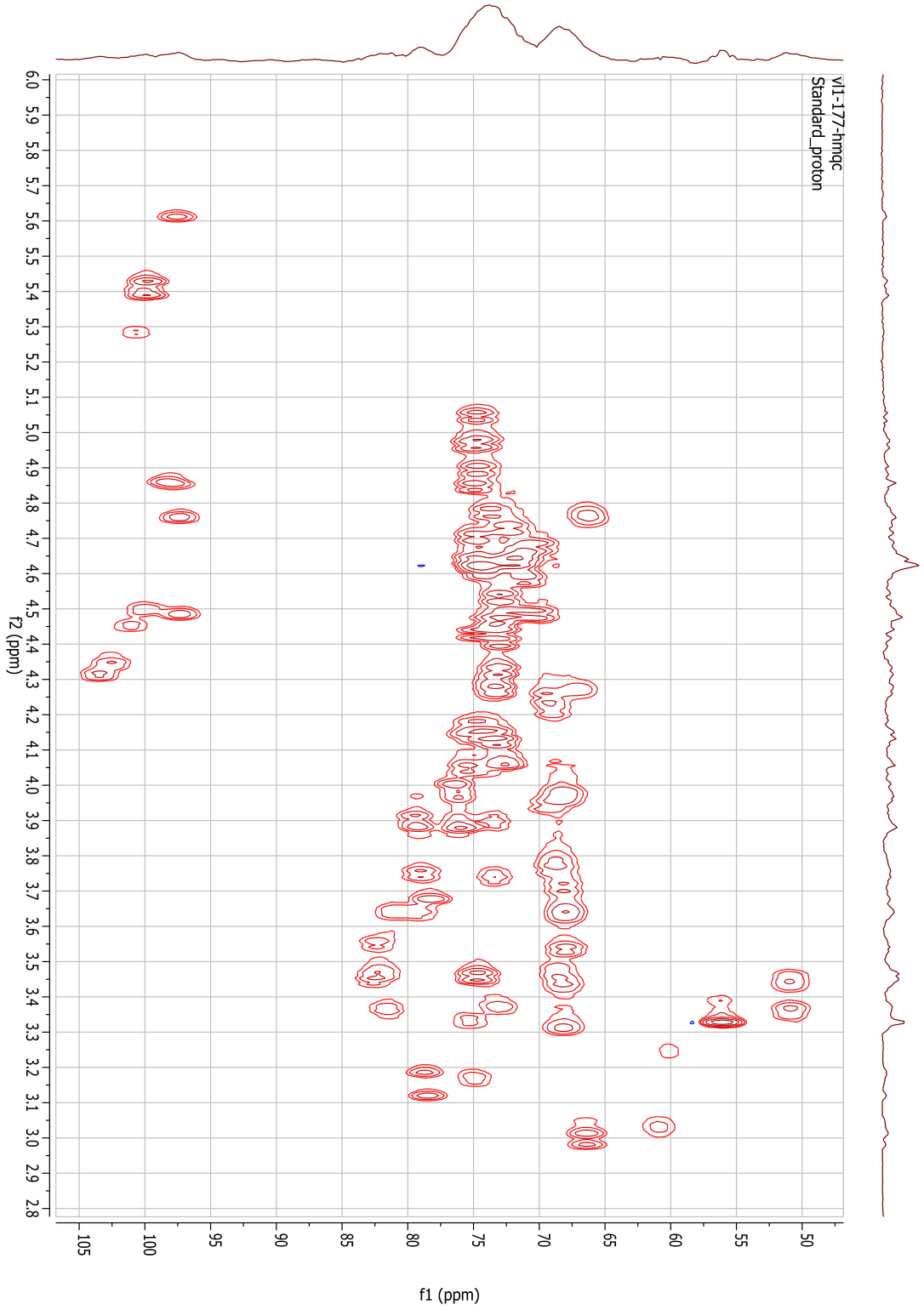


Figure S50. HSQC NMR of Compound **2**, zoom in on anomeric region (600 MHz, $CDCl_3$)

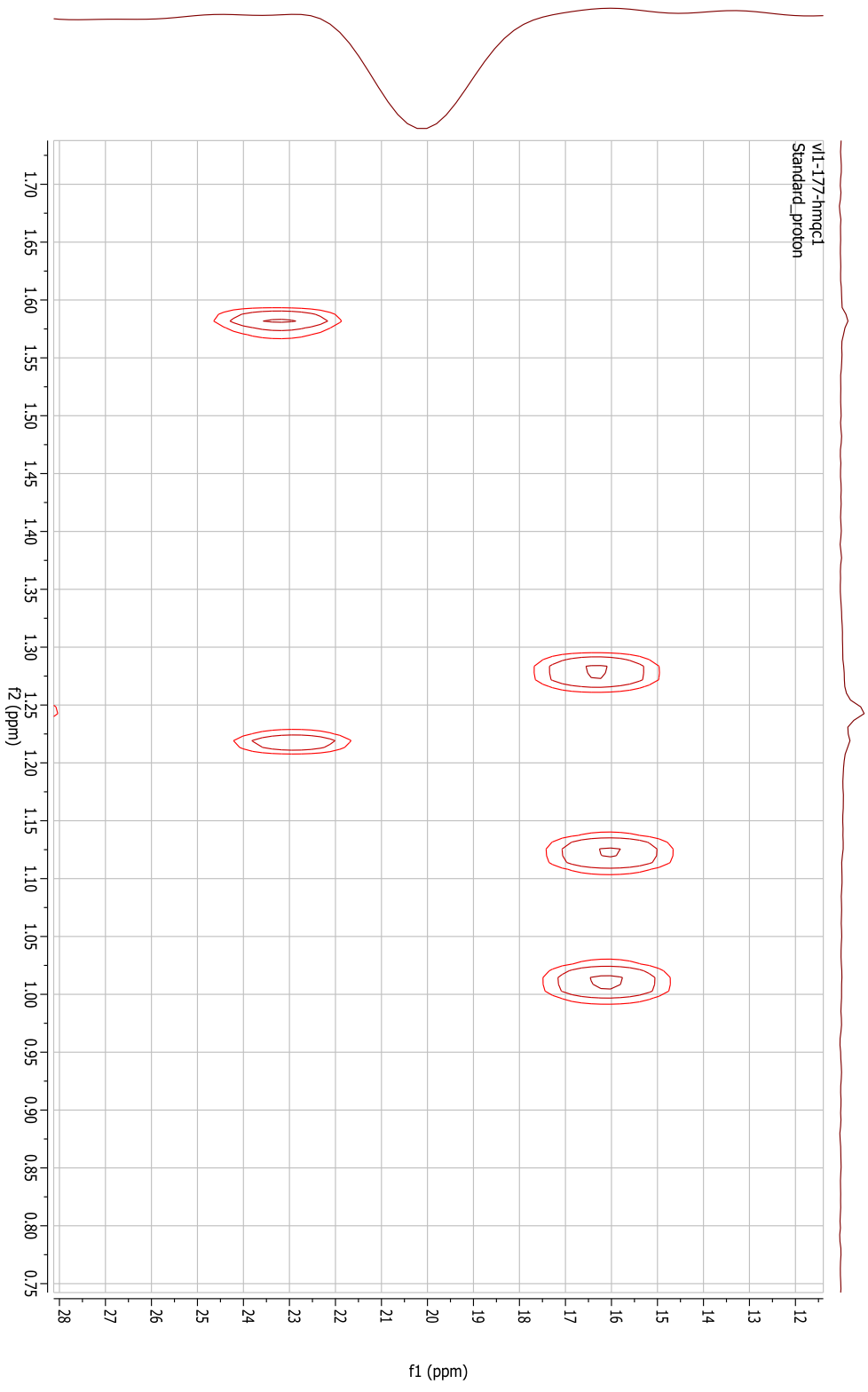


Figure S51. HRMS of Compound **2** (ESI tof)

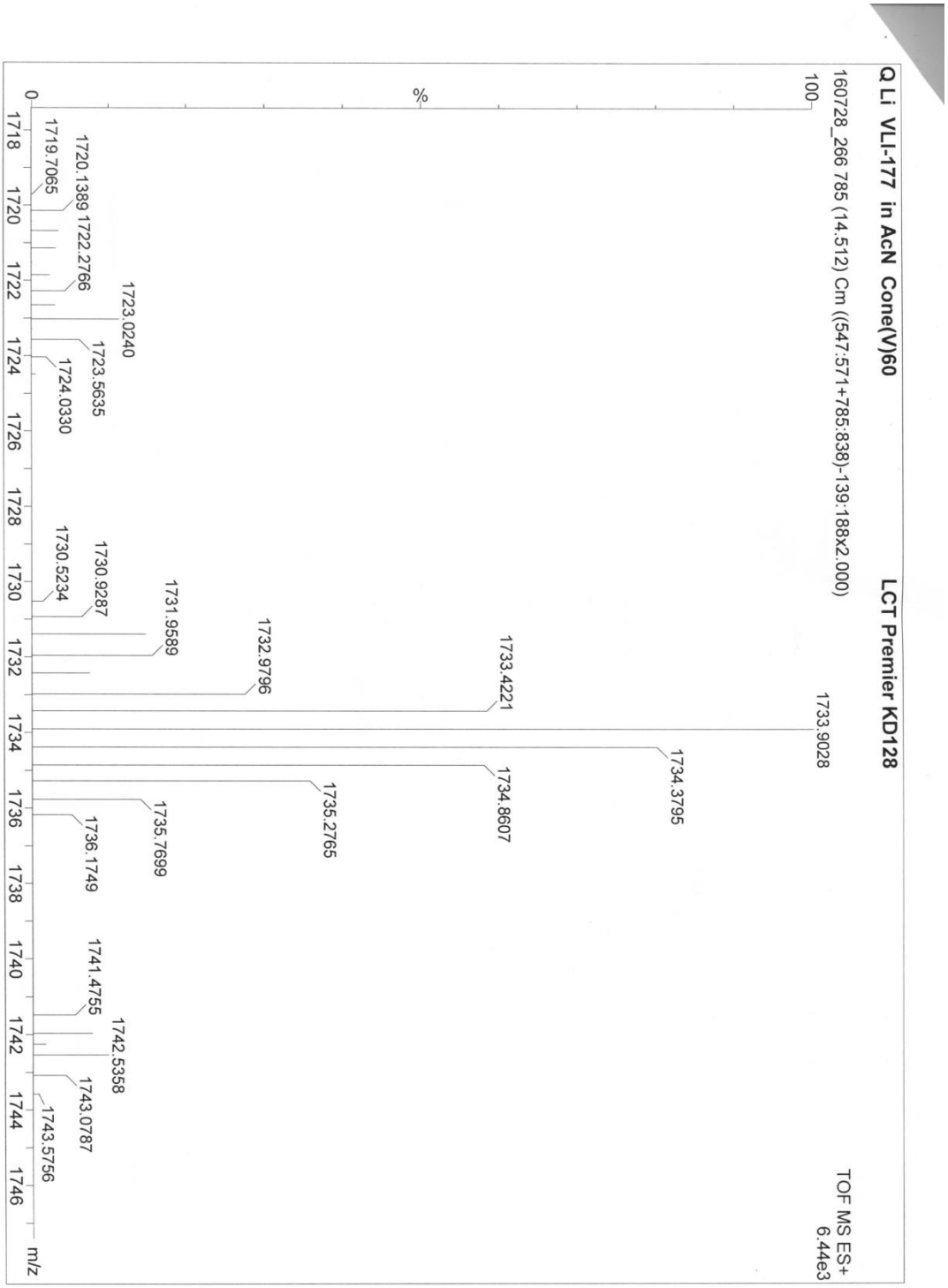


Figure S52. ^{1}H NMR of Compound **19** (600 MHz, $CDCl_3$)

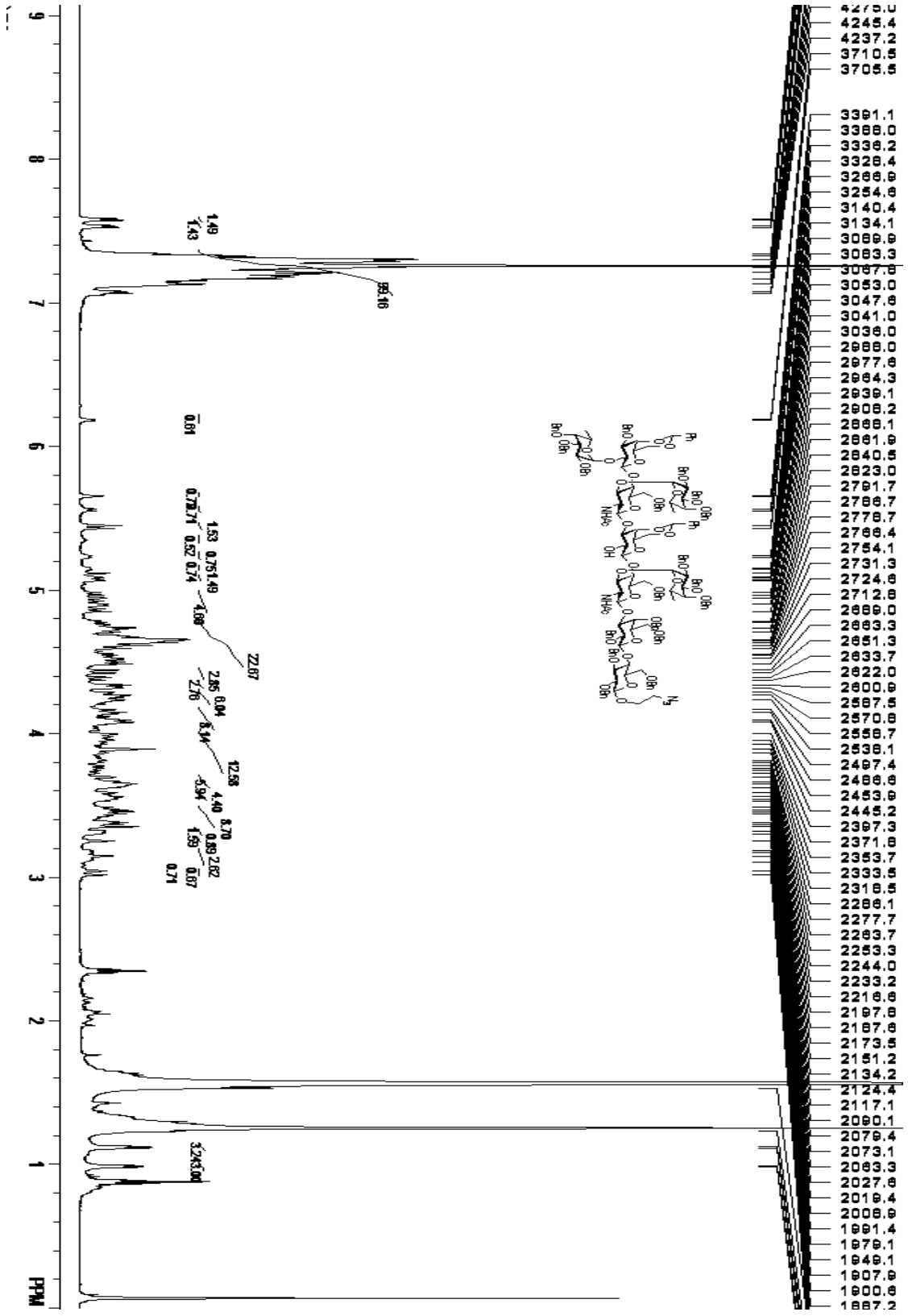


Figure S53. ^{13}C NMR of Compound **19** (600 MHz, $CDCl_3$)

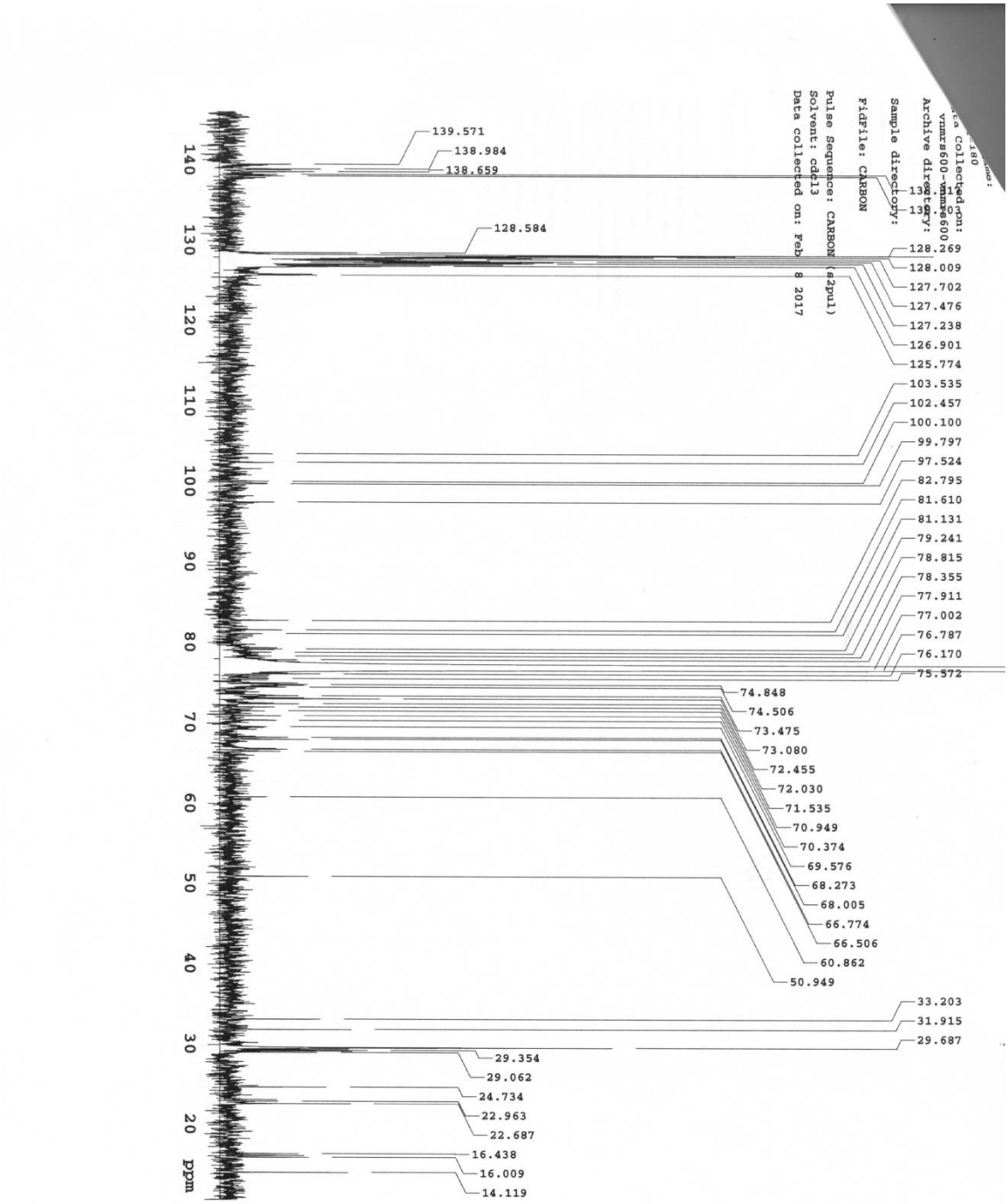


Figure S54. COSY NMR of Compound **19** (600 MHz, $CDCl_3$)

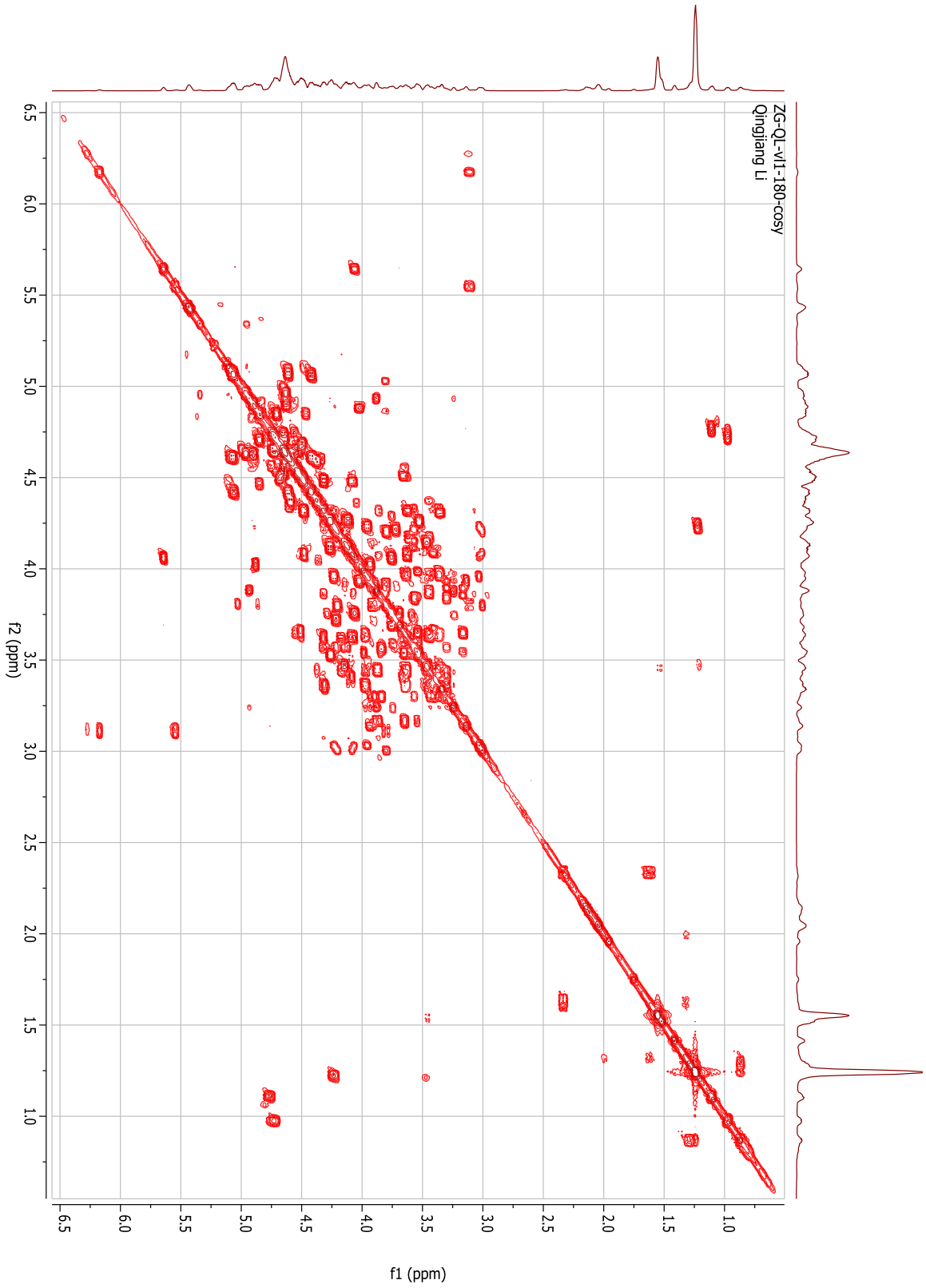


Figure S55. HSQC NMR of Compound **19** (600 MHz, $CDCl_3$)

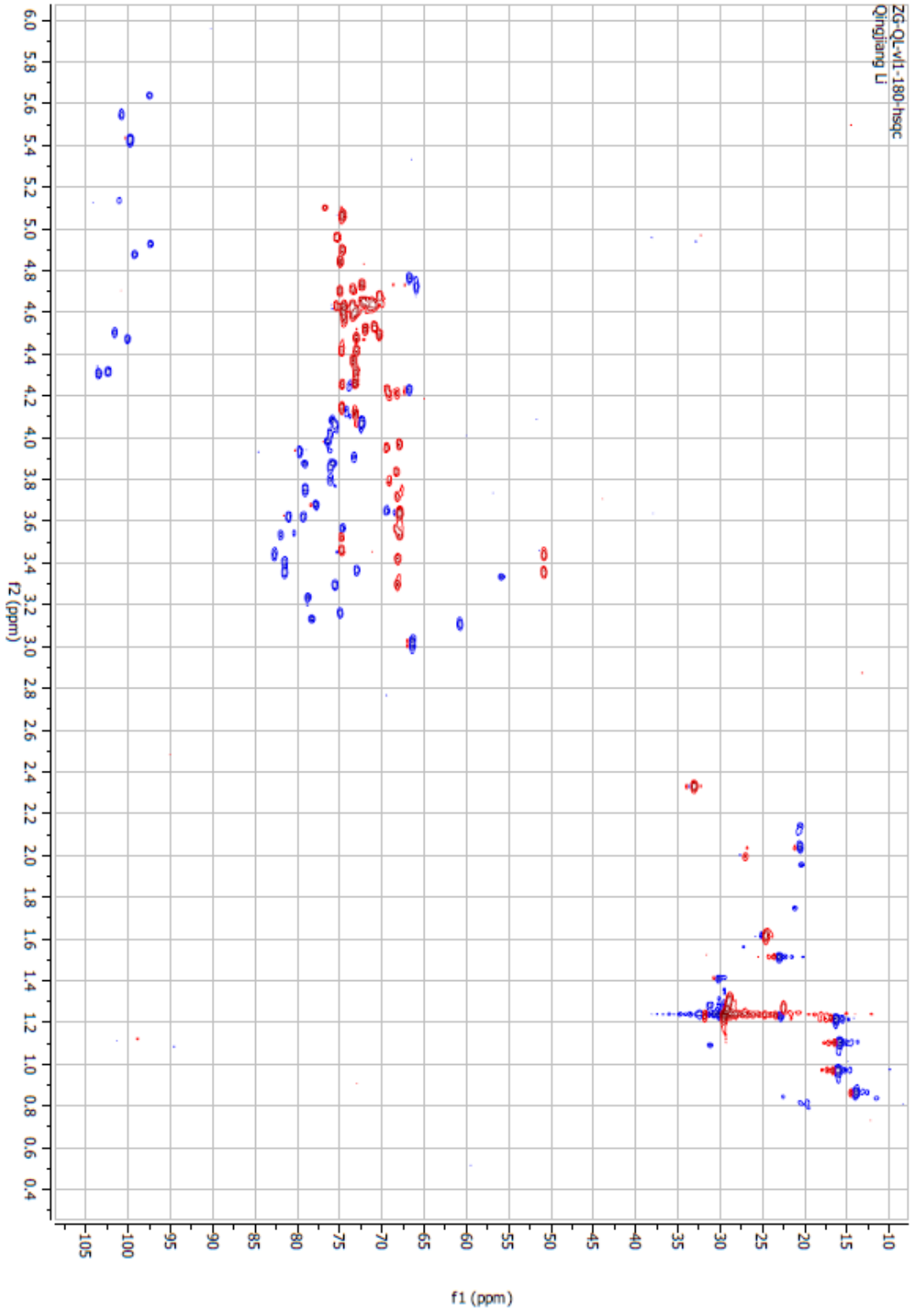


Figure S56. HRMS of Compound **19** (MALDI tof)

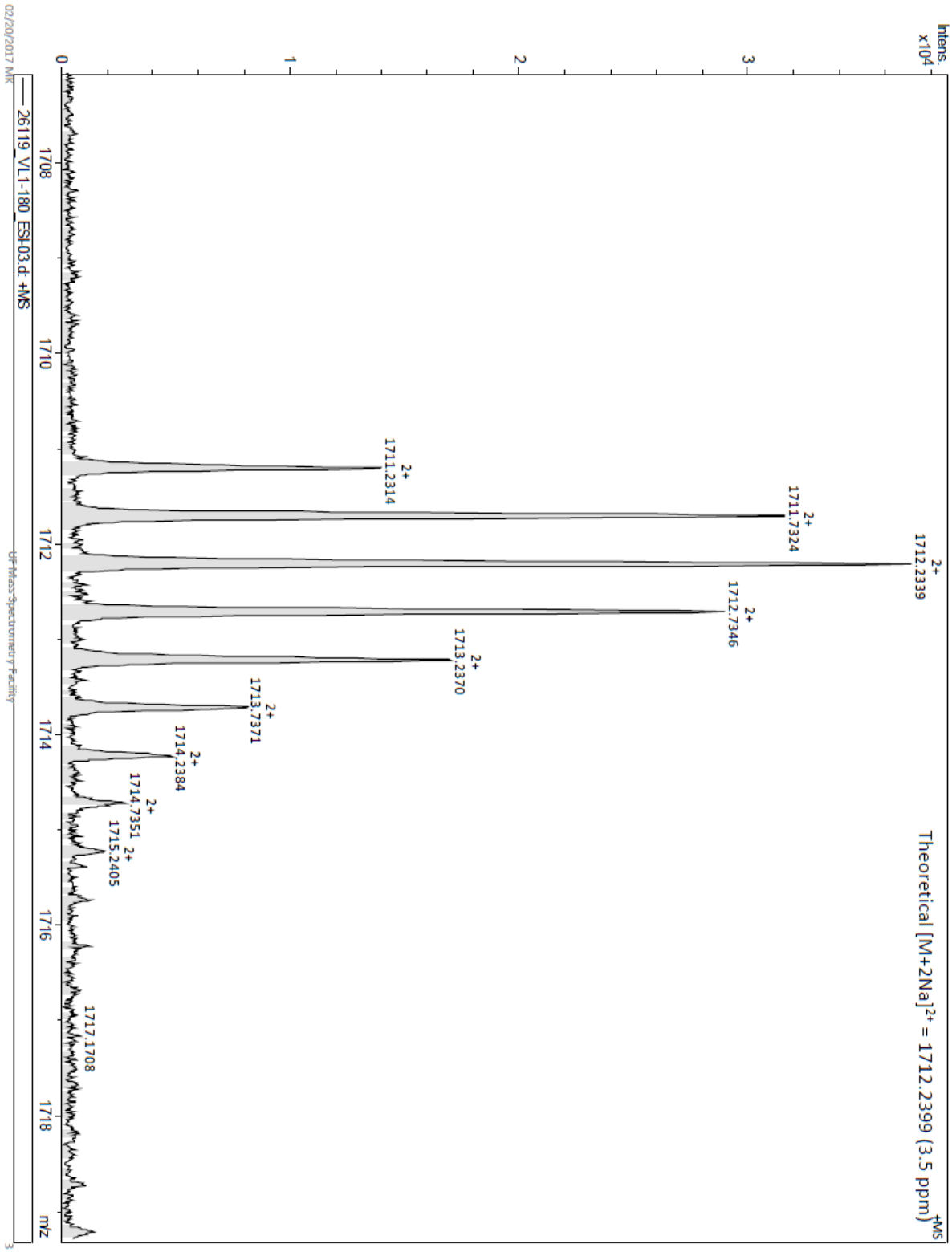


Figure S57. ^{1}H NMR of Compound **1** (600 MHz, D_2O)

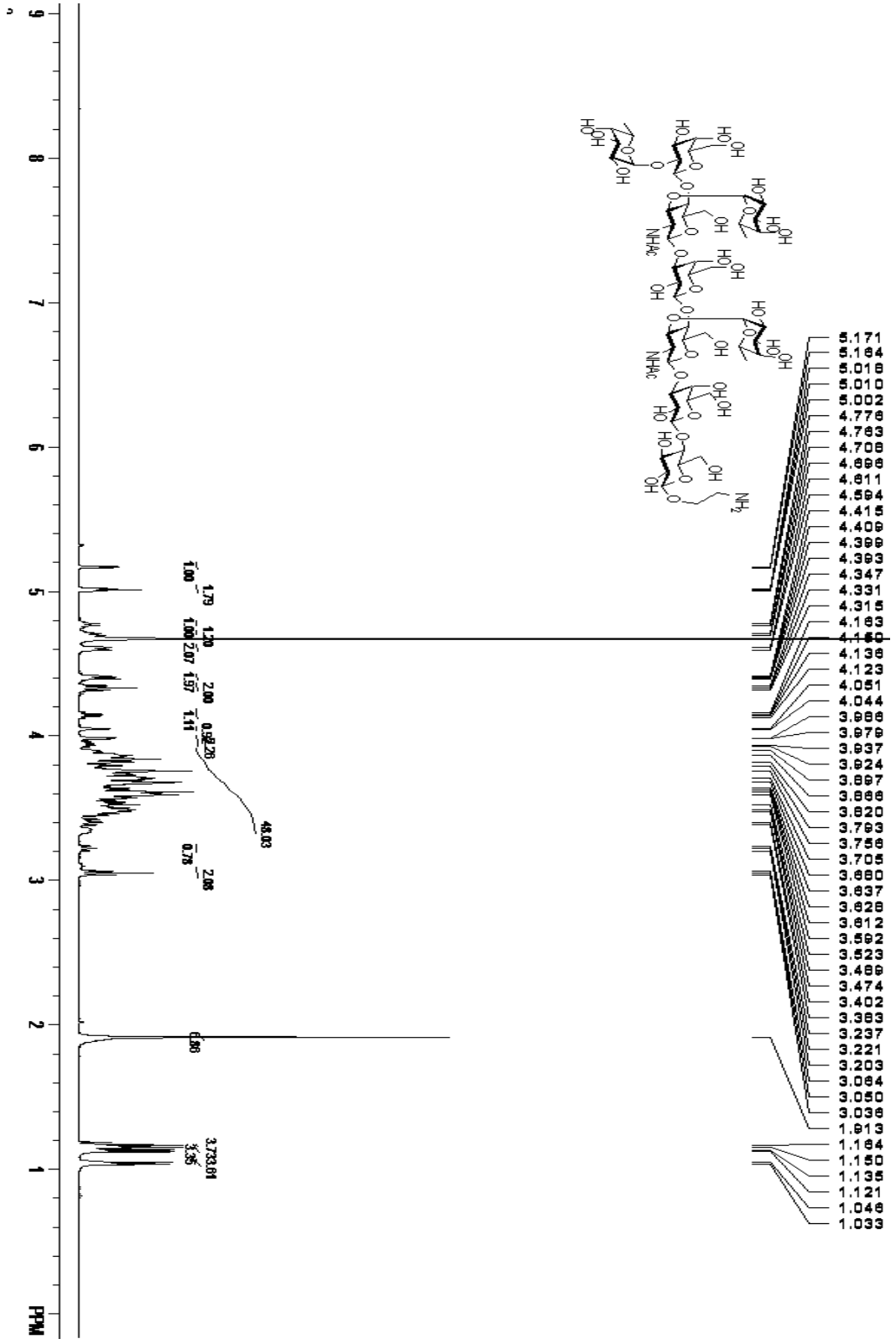


Figure S58. COSY NMR of Compound **1** (600 MHz, D_2O)

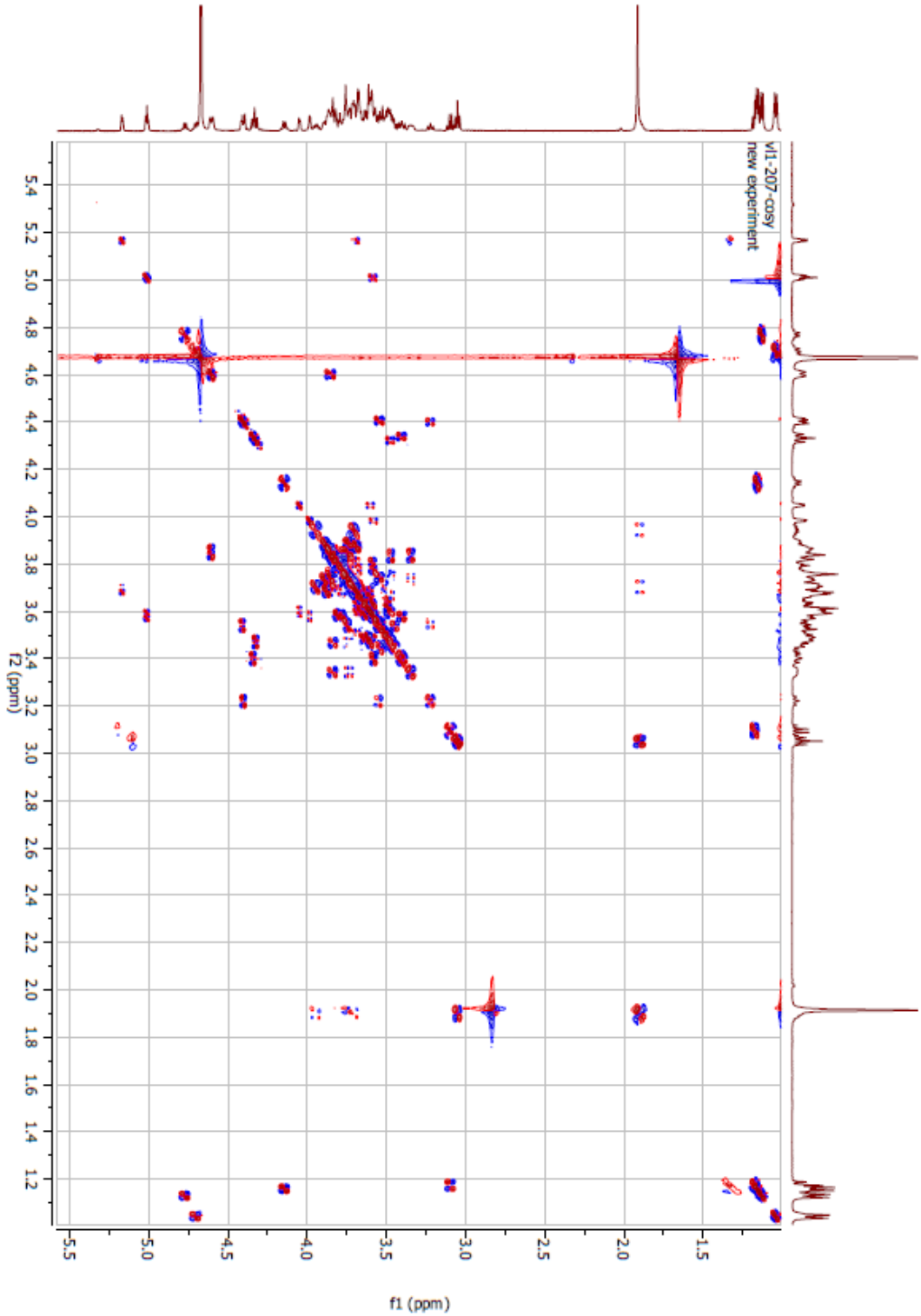


Figure S59. HMBC NMR of Compound **1** (600 MHz, D_2O)

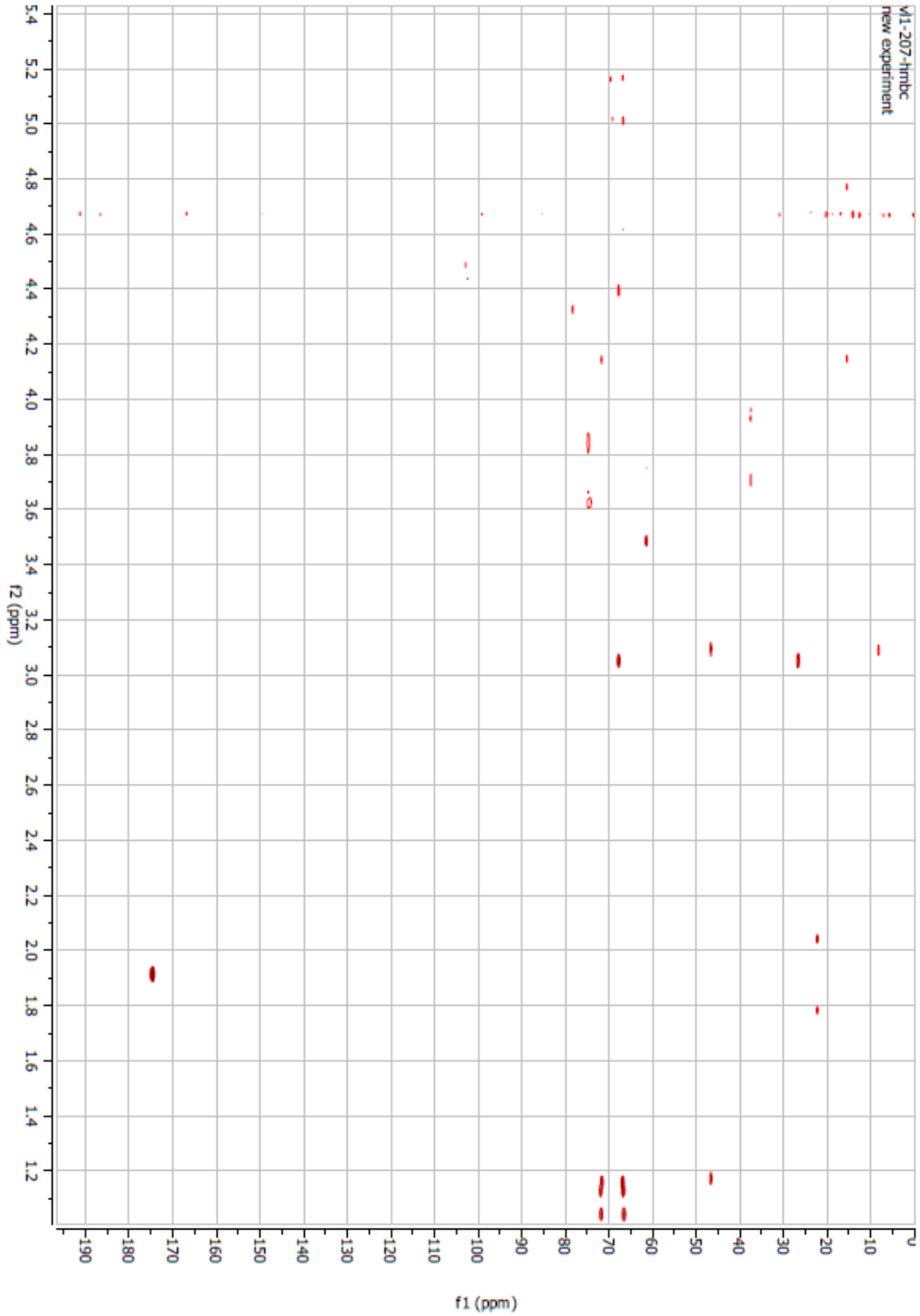


Figure S60. HSQC NMR of Compound **1** (600 MHz, D_2O)

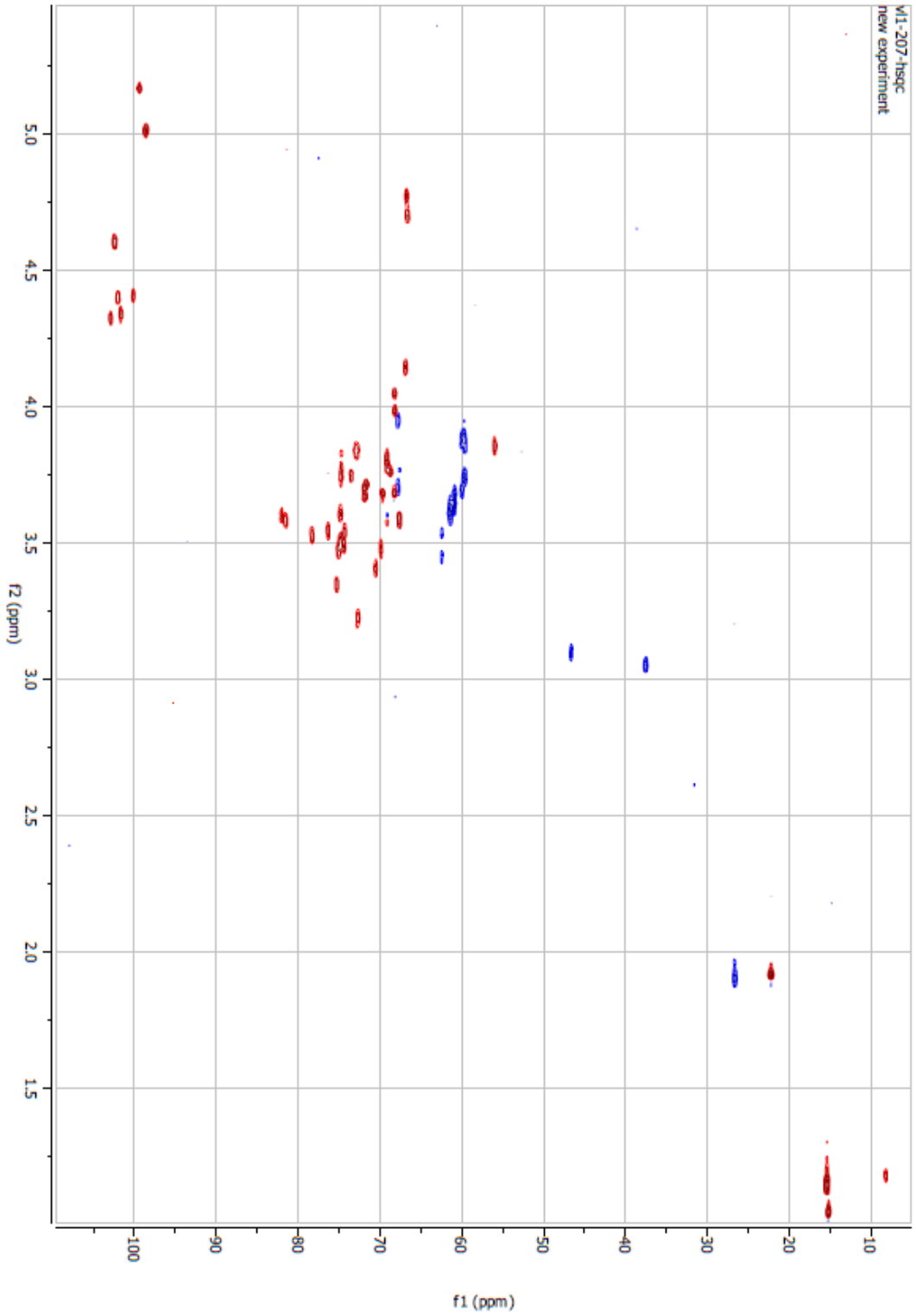


Figure S61. HRMS of Compound **1** (MALDI tof)

IV. References

(1) Taylor, J. G.; Li, X.; Oberthuer, M.; Zhu, W.; Kahne, D. E. *J. Am. Chem. Soc.* **2006**, *128*, 15084-15085.

(2) Yang, B.; Yoshida, K.; Yin, Z.; Dai, H.; Kavunja, H.; El-Dakdouki, M. H.; Sungsuwan, S.; Dulaney, S. B.; Huang, X. *Angew. Chem. Int. Ed.* **2012**, *51*, 10185-10189.

(3) Miermont, A.; Zeng, Y.; Jing, Y.; Ye, X.-S.; Huang, X. *J. Org. Chem.* **2007**, *72*, 8958-8961.