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Supporting Information

Synthetic Phenolic Glycolipids for Application in Diagnostic Tests for Leprosy

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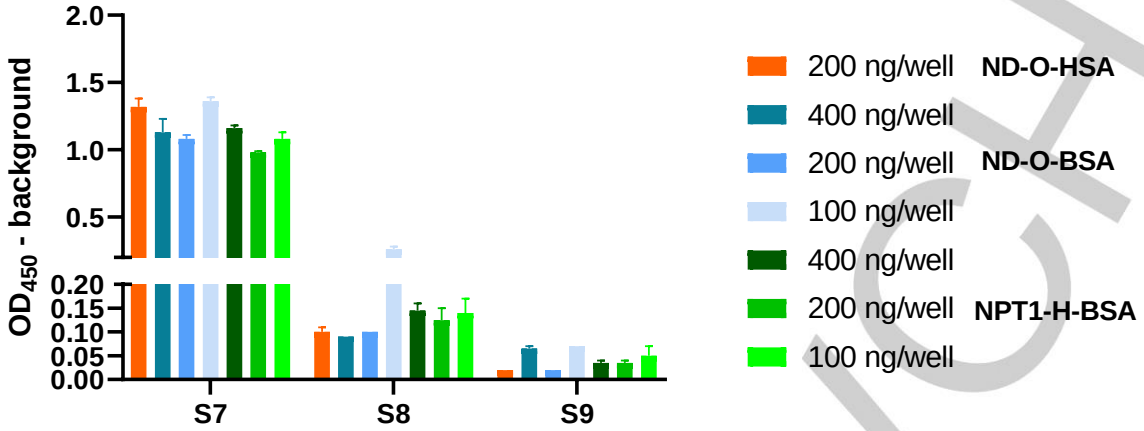
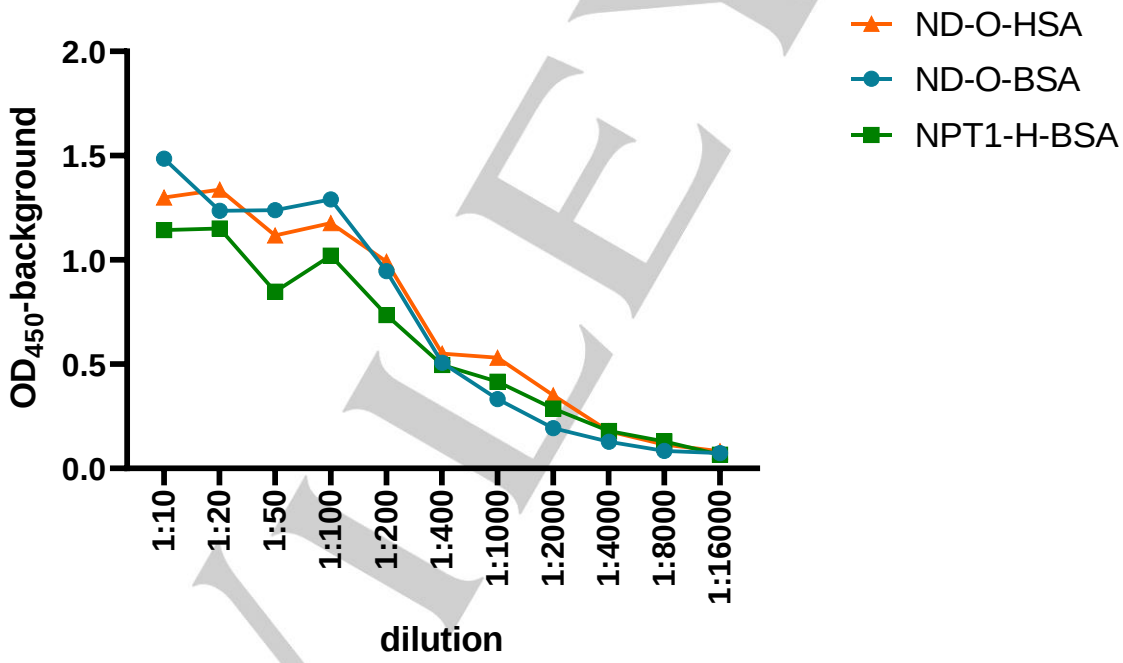
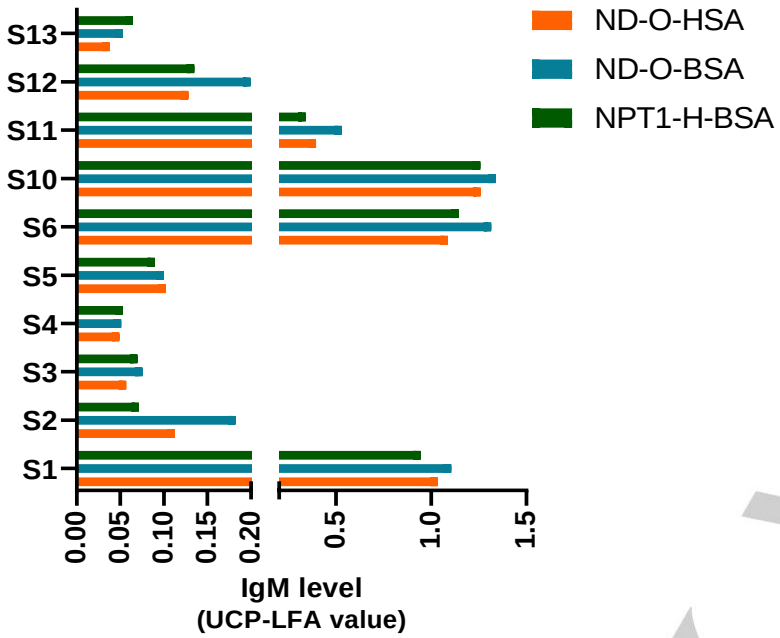


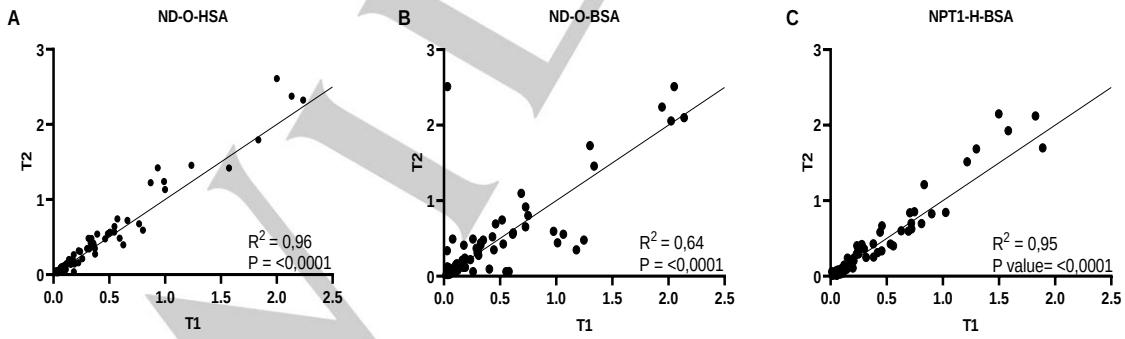
Supplementary Figure S1: Evaluation of different ELISA coating concentrations of synthetic PGL conjugates. Different coating concentrations (400, 200 and 100 ng/well) were tested for the newly synthesized ND-O-BSA (blue) and NPT1-H-BSA (green) compared to the coating concentration used in the routine PGL-I ELISA (200 ng/well of ND-O-HSA; orange). Three samples with known IgM antibody levels to ND-O-HSA were tested for the different concentrations; a positive sample with high levels of ND-O-HSA specific IgM (S7) and control samples from areas were leprosy is endemic (S8) and not endemic (S9). According to the routine PGL-I ELISA protocol samples were diluted 1:400. The final readout of the ELISA is the OD_{450}-background (*y*-axis).



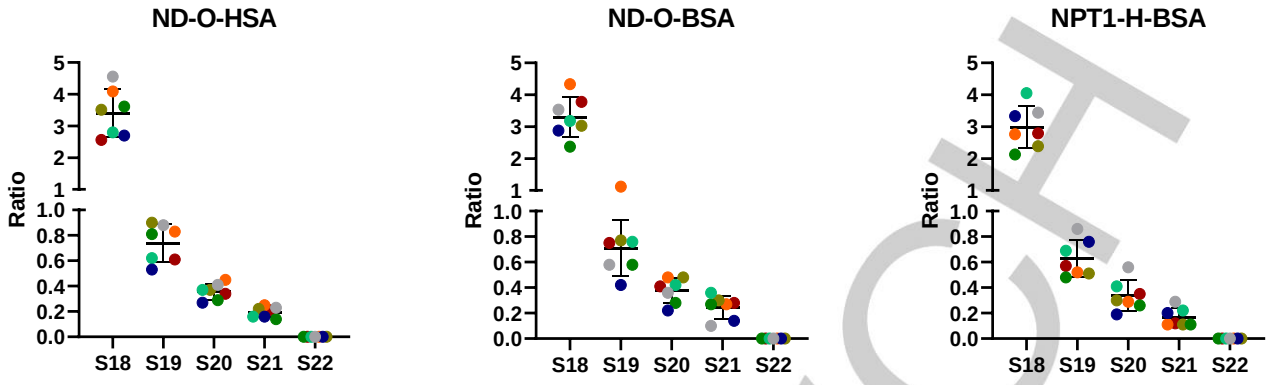
Supplementary Figure S2: Evaluation of antibody titration curves for three synthetic PGL conjugates. The IgM antibody titer curve has been determined for the three different synthetic PGL conjugates using a positive control sample (S7) (ND-O-HSA: orange line, ND-O-BSA: blue line and NPT1-H-BSA: green line). The coating concentration used is 200 ng/well as determined in Supplementary Figure S1. The sample dilution ranges from a 1:10 to 1:16000. The final readout of the ELISA is the OD_{450}-background (*y*-axis).



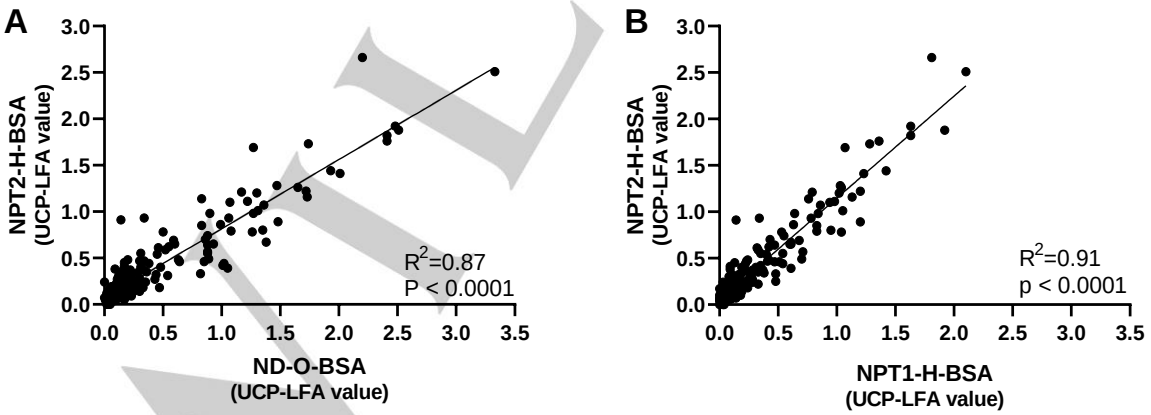
Supplementary Figure S3: Three synthetic PGLs (ND-O-HSA, ND-O-BSA and NPT1-H-BSA) applied to the up-converting phosphor lateral flow assay (UCP-LFA). IgM levels (UCP-LFA value) of 10 leprosy patients as determined using the UCP-LFA with ND-O-BSA (blue) and NPT1-H-BSA (green) highly correlate with the IgM levels detected using ND-O-HSA UCP-LFA (orange).



Supplementary Figure S4: Stability of the ND-O-HSA, ND-O-BSA and NPT1-H-BSA UCP-LFA assessed after one month. The IgM antibody levels (UCP-LFA value) detected using the three different UCP-LFAs (ND-O-HSA: A, ND-O-BSA: B and NPT1-H-BSA: C) assessed in 92 samples at two different timepoints. T2 (y-axis) was tested one month after T1 (x-axis). The correlation was determined for the UCP-LFA values observed at each timepoint.



Supplementary Figure S5: Stability of the ND-O-HSA, ND-O-BSA and NPT1-H-BSA UCP-LFA. Of five serum samples of leprosy patients the UCP-LFA values were generated from two to thirteen months (m) after production of the strips (2m, 3m, 4m, 6m, 7m, 10m and 13m). The UCP-LFA values correspond to the level of PGL-I specific IgM in the sample. UCP-LFA strips with three different Test lines were produced, using either ND-O-HSA, ND-O-BSA or NPT1-H-BSA as synthetic PGL-I. UCP-LFA values obtained at 2m (red) 3m (orange), 4m (yellow), 6m (green), 7m (light blue), 10m (dark blue) and 13 months (grey) (*y*-axis) are depicted per sample and the mean UCP-LFA value is indicated by the horizontal bar. Error bars represent the standard deviation.



Supplementary Figure S6: Correlation of NPT2-H-BSA UCP-LFA with ND-O-BSA and NPT1-H-BSA UCP-LFA. (A) Correlation of IgM levels (UCP-LFA value) determined by NPT2-H-BSA UCP-LFA (*y*-axis) and ND-O-BSA UCP-LFA (*x*-axis). (B) Correlation of IgM levels (UCP-LFA value) determined by NPT2-H-BSA UCP-LFA (*y*-axis) and NPT1-H-BSA UCP-LFA (*x*-axis).

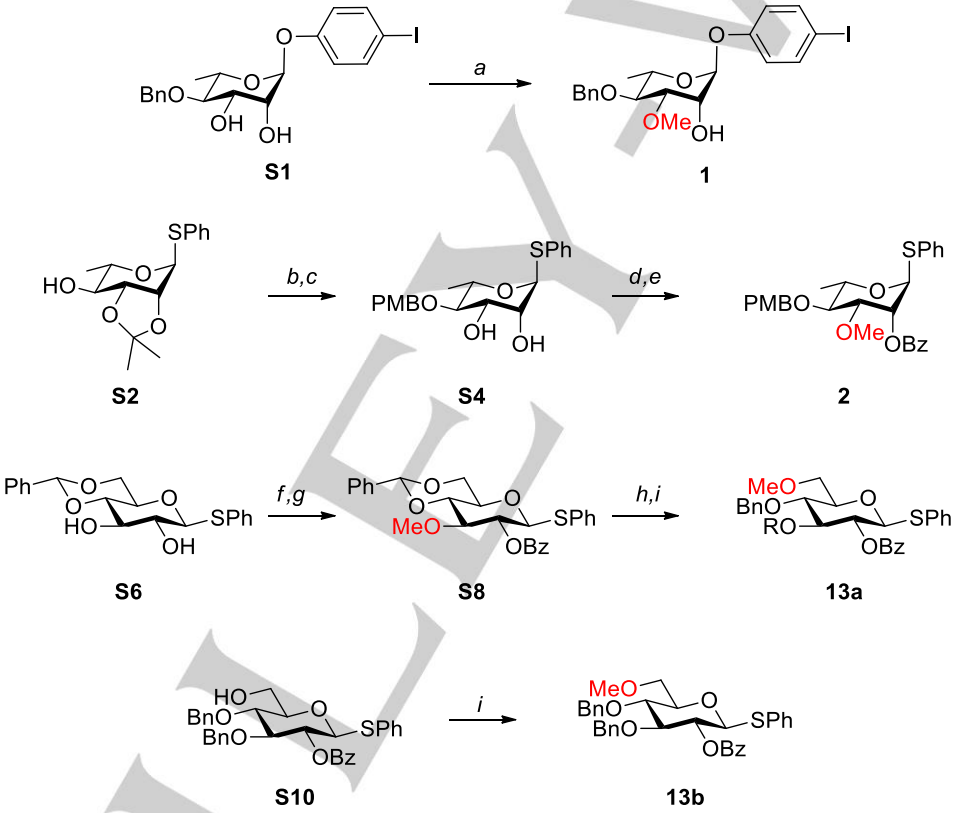
Synthesis of PGL conjugates

General procedures

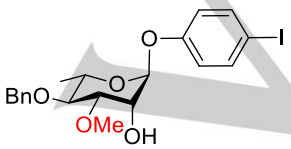
All reactions were carried out in oven-dried glassware (80 °C). Prior to reactions, traces of water and solvent were removed by co-evaporation with toluene where appropriate. Reactions sensitive to air or moisture were carried out under a nitrogen atmosphere (balloon). Commercially available reagents and solvents (Aldrich Chemistry, Honeywell, Merck, Ficher Scientific, Biosolve, Fluka, VWR Chemicals, Acros Organics, Fluorochem, Brunschwig, Carbosynth) were used as received unless stated otherwise. Solvents for reactions were reagent grade and dried by storage over flame dried 4 Å molecular sieves when needed. Tf_2O used in glycosylations was dried by distillation over P_2O_5 and stored in a Schlenk flask at -20 °C.

Reaction progress was monitored using aluminium-supported silica gel TLC plates (Merck, Kieselgel 60, F254); visualization was carried out by irradiation with UV light (254 nm), followed by spraying with 20% H_2SO_4 in EtOH (v/v) or $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% H_2SO_4, followed by charring. Additional analysis with TLC-MS was used when needed. Column chromatography was carried out using silica gel (Fluka, 40-63 µm mesh).

NMR spectra were recorded at ambient temperature on a Brucker AV-400LIQ spectrometer. Samples were prepared in $CDCl_3$ unless stated otherwise. Chemical shifts (δ) are reported in ppm relative to Me_4Si (δ; 0.00 ppm) or residual solvent signals. ^{13}C-APT spectra are ^{1}H decoupled and structural assignment was achieved using HH-COSY and HSQC 2D experiments. Coupling constants of anomeric carbon atoms ($J_{1H,C1}$) were determined using HMBC-GATED experiments. MALDI measurements were carried out with a Bruker Autoflex Speed™ LRF.

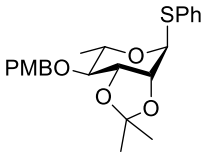


*Scheme 1. Building block synthesis. Reagents and conditions: (a) 1. Bu_2SnO, toluene reflux, 2. MeI, CsF, DMF, 91%, (b) NaH, PMBCl, DMF, 98%, (c) AcOH/H_2O (4:1), 45 °C, 88%, (d) 1. Bu_2SnO, toluene reflux, 2. MeI, CsF, DMF, 93%, (e) BzCl, pyridine, DCM, 94%, (f) 1. Bu_2SnO, toluene reflux, 2. MeI, CsF, DMF, 76%, (g) BzCl, DMAP, pyridine, 82% (h) $BH_3{\cdot}THF$, TMSOTf, DCM, 96% (i) NaH, MeI, DMF, 72% (**13a**), 79% (**13b**).*

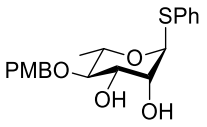


4-iodophenyl 3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (1) Compound **S1**[1] (4.56 g, 10 mmol, 1.0 eq) was dissolved in toluene (500 mL, 0.02 M) and Bu_2SnO (2.74 g, 11 mmol, 1.1 eq) was added to the solution. The mixture was refluxed for 2 hours and then concentrated. The mixture was then dissolved in dry DMF (100 mL, 0.1 M) and CsF (1.82 g, 12 mmol, 1.2 eq) and MeI (0.81 mL, 13 mmol, 1.3 eq) were added. The reaction was allowed to stir for 22 hours after which it was quenched by addition of H_2O and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and

concentrated. Purification by means of column chromatography (pentane-Et_2O 1:1) gave the title compound (4.28 g, 9.1 mmol, 91%, 10:1 mixture of regioisomers) as a clear oil. $[\alpha]_D^{25}$ -79.9 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz) δ: 7.57-7.54 (m, 2H, CH_{arom}); 7.36-7.24 (m, 5H, CH_{arom}); 6.84-6.80 (m, 2H, CH_{arom}); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 4.86 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.63 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.21 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.76-3.71 (m, 2H, H-3, H-5); 3.56 (s, 3H, OCH_3); 3.44 (t, 1H, *J* = 5.2 Hz, H-4); 2.74 (bs, 1H, 2-O*H*); 1.24 (d, 3H *J* = 6.4 Hz, H-6); ^{13}C-APT NMR (101 MHz) δ: 156.0 ($C_{q,arom}$); 138.5 (*C*H_{arom}); 138.4 ($C_{q,arom}$); 128.5, 128.1, 127.9, 118.6 (*C*H_{arom}); 97.1 (C-1); 84.8 (*C*-I_{arom}); 81.5 (C-3); 79.7 (C-4); 75.4 (*C*$H_{2,Bn}$); 68.2 (C-5); 67.8 (C-2); 57.8 (O*C*H_3); 18.0 (C-6). IR (thin film, cm^{-1}): 1026, 1095, 1133, 1177, 1233, 1452, 1484, 2927, 3408. HRMS calculated for $C_{20}H_{23}IO_5Na$ 493.0488 $[M+Na]^+$; found 493.0479.

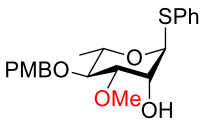


Phenyl 2,3-*O*-isopropylidene-4-*O*-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (S3) Compound **S2**[1] (7.45 g, 25 mmol, 1.0 eq) was dissolved in dry DMF (250 mL, 0.1 M) and PMBCl (4.8 mL, 35 mmol, 1.4 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 1.40 g, 35 mmol, 1.4 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was quenched by addition of H_2O, and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 9:1) gave the title compound (10.2 g, 24.5 mmol, 98%) as a pale oil. $[\alpha]_D^{25}$ -148.8 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz) δ: 7.46-7.43 (m, 2H, CH_{arom}); 7.29-7.19 (m, 5H, CH_{arom}); 6.87-6.84 (m, 2H, CH_{arom}); 5.74 (s, 1H, H-1); 4.84 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.56 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.35-4.28 (m, 2H, H-2, H-3); 4.16-4.11 (m, 1H, H-5); 3.73 (s, 3H, C$H_{3,PMB}$); 3.28 (dd, 1H, *J* = 7.0, 9.8 Hz, H-4); 1.51 (s, 3H, C(CH_3)$_2$); 1.36 (s, 3H, C(CH_3)$_2$); 1.21 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.3, 133.7 ($C_{q,arom}$); 131.8 (*C*H_{arom}); 130.4 ($C_{q,arom}$); 130.3, 129.7, 129.1, 127.6, 113.8 (*C*H_{arom}); 109.5 (*C*(CH$_3$)$_2$); 83.8 (C-1); 81.0 (C-4); 78.4 (C-3); 76.7 (C-2); 72.7 (PhCH_2); 55.1 (*C*$H_{3,PMB}$); 28.0, 26.5 (C(*C*H_3)$_2$); 17.7 (C-6). IR (thin film, cm^{-1}): 1035, 1057, 1086, 1108, 1220, 1248, 1513. HRMS calculated for $C_{23}H_{28}O_5SNa$ 439.1555 $[M+Na]^+$; found 439.1553.

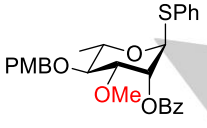


Phenyl 4-*O*-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (S4)

Compound **S3** (9.04 g, 21.7 mmol, 1.0 eq.) was dissolved in AcOH/H_2O (4:1, 500 mL, 0.04 M) and stirred at 45 °C for 3h. The solvent was evaporated until a thick oil was formed. The oil was co-evaporated three times with toluene to give the title compound (8.16 g, 21.7 mmol, 100%) as a slightly yellow oil. $[\alpha]_D^{25}$ -70.8 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz) δ: 7.45-7.42 (m, 2H, CH_{arom}); 7.31-7.22 (m, 5H, CH_{arom}); 6.91-6.88 (m, 2H, CH_{arom}); 5.46 (d, 1H, *J* = 1.6 Hz, H-1); 4.71-4.63 (m, 2H, C$H_{2,PMB}$); 4.23-4.16 (m, 2H, H-2, H-5); 3.89 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.80 (s, 3H, C$H_{3,PMB}$); 3.41 (t, 1H, *J* = 9.2 Hz, H-4); 1.34 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.6, 134.3 ($C_{q,arom}$); 131.4 (*C*H_{arom}); 130.3 ($C_{q,arom}$); 129.8, 129.3, 127.5, 114.2 (*C*H_{arom}); 87.5 (C-1); 81.5 (C-4); 74.9 (PhCH_2); 72.7 (C-2); 72.0 (C-3); 68.8 (C-5); 55.4 (*C*$H_{3,PMB}$); 18.0 (C-6). IR (thin film, cm^{-1}): 1036, 1065, 1097, 1250, 1513, 3328. HRMS calculated for $C_{20}H_{24}O_5SNa$ 399.1242 $[M+Na]^+$; found 399.1244.

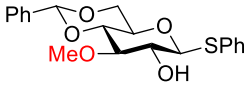


Phenyl 3-*O*-methyl-4-*O*-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (S5) Compound **S4** (8.16 g, 21.7 mmol, 1.0 eq) was dissolved in toluene (500 mL, 0.04 M) and Bu_2SnO (5.94 g, 23.9 mmol, 1.1 eq) was added to the solution. The mixture was refluxed for 2 hours and then concentrated. The mixture was then dissolved in dry DMF (220 mL, 0.1 M) and CsF (3.96 g, 26 mmol, 1.2 eq) and MeI (1.8 mL, 28.2 mmol, 1.3 eq) were added. The reaction was allowed to stir for 20 hours after which it was quenched by addition of H_2O and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:1) gave the title compound (7.88 g, 20.2 mmol, 93%, 10:1 mixture of regioisomers) as a pale oil. $[\alpha]_D^{25}$ = -113.8 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz) δ: 7.47-7.43 (m, 2H, CH_{arom}); 7.32-7.22 (m, 5H, CH_{arom}); 6.90-6.87 (m, 2H, CH_{arom}); 5.53 (d, 1H, *J* = 1.6 Hz, H-1); 4.78 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.56 (d, 1H, *J* = 10.4 Hz, PhCH*H*); 4.29 (dd, 1H, *J* = 1.6, 3.6 Hz, H-2); 4.18-4.14 (m, 1H, H-5); 3.80 (s, 3H, C$H_{3,PMB}$); 3.56 (dd, 1H, *J* = 3.6, 9.2 Hz, H-3); 3.52 (s, 3H, OCH_3); 3.43 (t, 1H, *J* = 9.2 Hz, H-4); 2.74 (d, 1H, *J* = 4.8 Hz, 2-O*H*); 1.28 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.4, 134.3 ($C_{q,arom}$); 131.4 (*C*H_{arom}); 130.6 ($C_{q,arom}$); 129.8, 129.1, 127.4, 114.0 (*C*H_{arom}); 87.2 (C-1); 82.1 (C-3); 79.7 (C-4); 75.0 (PhCH_2); 69.5 (C-2); 68.7 (C-5); 57.6 (O*C*H_3); 55.4 (*C*$H_{3,PMB}$); 17.9 (C-6). IR (thin film, cm^{-1}): 1035, 1083, 1097, 1249, 1513, 3450. HRMS calculated for $C_{21}H_{26}O_5SNa$ 413.1394 $[M+Na]^+$; found 413.1399.

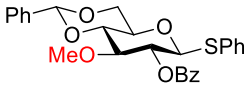


Phenyl 2-*O*-benzoyl-3-*O*-methyl-4-*O*-(4-methoxybenzyl)-1-thio-α-L-rhamnopyranoside (2) Compound **S5** (0.15 g, 0.37 mmol, 1.0 eq) was dissolved in pyridine (1.9 mL, 0.2 M) and BzCl (86 µL, 0.74 mmol, 2.0 eq) was added to the solution. A catalytic amount of DMAP was added and the mixture was allowed to stir for 2 hours. The reaction was quenched by addition of MeOH and concentrated. The resulting oil was dissolved in Et_2O and washed with 1M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated. Purification by means of column chromatography (pentane-Et_2O 9:1) gave the title compound (7.88 g, 20.2 mmol, 93%) as a pale oil. $[\alpha]_D^{25}$ -120.2 (c 1.0, $CHCl_3$). ^1H NMR (400 MHz) δ: 8.07-8.03 (m, 2H, CH_{arom}); 7.58-7.54 (m, 1H, CH_{arom}); 7.48-7.42 (m, 4H, CH_{arom}); 7.32-7.21 (m, 5H, CH_{arom}); 6.89 (d, 2H, *J* = 8.4 Hz, CH_{arom}); 5.82 (d, 1H, *J* = 1.6 Hz, H-2); 5.55 (s, 1H, H-1); 4.74 (dd, 2H, *J* = 10.6, 95.8 Hz, PhCH_2); 4.30-4.26 (m, 1H, H-5); 3.78-3.74 (m, 4H, H-3, C$H_{3,PMB}$); 3.57 (t, 1H, *J* = 9.4 Hz, H-4); 3.50 (s, 3H, OCH_3); 1.37 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.7 (*C*O_{Bz}); 159.4, 134.1 ($C_{q,arom}$); 133.4, 131.8 (*C*H_{arom}); 130.6 ($C_{q,arom}$); 130.0 (*C*H_{arom});

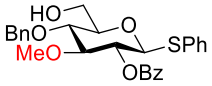
129.9 ($C_{q,arom}$); 129.2, 128.5, 127.7, 113.9 (CH_{arom}); 86.2 (C-1); 80.8 (C-3); 79.8 (C-4); 75.1 (PhCH_2); 70.8 (C-2); 69.1 (C-5); 57.6 (OCH_3); 55.3 ($CH_{3,PMB}$); 18.1 (C-6). IR (thin film, cm^{-1}): 1070, 1093, 1109, 1251, 1267, 1513, 1722. HRMS calculated for $C_{28}H_{30}O_6SNa$ 517.1661 $[M+Na]^+$; found 517.1663.



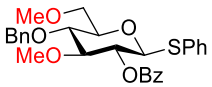
Phenyl 3-*O*-methyl-4,6-*O*-benzylidene-1-thio-ß-D-glucopyranoside (S7) After co-evaporation with toluene, compound **S6** [2] (3.60 g, 10 mmol, 1.0 eq) was dissolved in toluene (500 mL, 0.02 M). To the solution was added Bu_2SnO (2.70 g, 11 mmol, 1.1 eq.) and refluxed for 2 hours after which it was concentrated. The residue was dissolved in dry DMF (100 mL, 0.1 M) and MeI (0.8 mL, 13 mmol, 1.3 eq.) along with CsF (1.82 g, 12 mmol, 1.2 eq.) were added. The reaction mixture was stirred overnight after which it was quenched with H_2O. The aqueous phase was extracted with Et_2O (3x) after which the combined organic layers were washed with brine, dried with $MgSO_4$, filtered and concentrated. Purification by means of column chromatography (pentane-EtOAc, 7:3) gave the title compound (2.86 g, 7.64 mmol, 76%) as a white solid. ^{1}H NMR (400 MHz) δ: 7.56-7.52 (m, 2H, CH_{arom}); 7.49-7.46 (m, 2H, CH_{arom}); 7.39-7.26 (m, 6H, CH_{arom}); 5.54 (s, 1H, PhC*H*); 4.66-4.63 (m, 1H, H-1); 4.38 (dd, 1H, *J* = 4.8, 10.4 Hz, H-6); 3.78 (t, 1H, *J* = 10.2 Hz, H-6); 3.67 (s, 3H, OC*H*3); 3.61-3.44 (m, 4H, H-2, H-3, H-4, H-5); 2.68 (s, 1H, 2-O*H*). ^{13}C NMR (100 MHz) δ: 137.2 ($C_{q,arom}$); 133.3 (CH_{arom}); 131.4 ($C_{q,arom}$); 129.2, 129.2, 128.6, 128.4, 126.1 (CH_{arom}); 101.4 (PhCH); 88.6 (C-1); 83.7 (C-3); 81.2 (C-4); 72.3 (C-2); 70.8 (C-5); 68.7 (C-6); 61.2 (OCH_3). Spectroscopic data were in accordance with those previously reported in the literature[3].



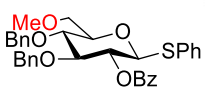
Phenyl 2-*O*-benzoyl-3-*O*-methyl-4,6-*O*-benzylidene-1-thio-ß-D-glucopyranoside (S8) To a solution of compound **S7** (2.30 g, 6.14 mmol, 1.0 eq.) in pyridine (15.3 mL, 0.4 M), BzCl (1.4 mL, 12.3 mmol, 2.0 eq.) was added dropwise to the mixture after which it was stirred for 4.5 h. The reaction was quenched with H_2O, the aqueous phase extracted with Et_2O (3x), the combined organic layers washed with 1M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated. Recrystallization of the residue from EtOH afforded the title compound (2.42 g, 5.06 mmol, 82%) as a white solid. $[\alpha]_D^{25}$ 13.4 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.11-8.09 (m, 2H, CH_{arom}); 7.61 (t, 1H, *J* = 7.4 Hz, CH_{arom}); 7.50-7.43 (m, 8H, CH_{arom}); 7.40-7.35 (m, 2H, CH_{arom}); 7.31-7.25 (m, 2H, CH_{arom}); 5.59 (s, 1H, PhC*H*); 5.23 (dd, 1H, *J* = 8.4, 9.2 Hz, H-2); 4.89 (d, 1H, *J* = 10.0 Hz, H-1); 4.44-4.40 (m, 1H, H-6); 3.84 (t, 1H, *J* = 10.2 Hz, H-6); 3.77-3.67 (m, 2H, H-3, H-4); 3.61-3.55 (m, 1H, H-5); 3.51 (s, 3H, OCH_3). ^{13}C-APT NMR (101 MHz) δ: 165.3 (CO_{Bz}); 137.2 ($C_{q,arom}$); 133.4, 132.9 (CH_{arom}); 132.5 ($C_{q,arom}$); 130.0 (CH_{arom}); 129.9 ($C_{q,arom}$); 129.2, 129.1, 128.6, 128.4, 128.3, 126.2 (CH_{arom}); 101.1 (PhC*H*); 87.2 (C-1); 82.4 (C-3); 81.1 (C-4); 72.3 (C-2); 70.8 (C-5); 68.7 (C-6); 60.9 (OCH_3). IR (thin film, cm^{-1}): 1026, 1069, 1093, 1178, 1268, 1727, 3451. HRMS calculated for $C_{27}H_{26}O_6SNa$ 501.1348 $[M+Na]^+$; found 501.1342.



Phenyl 2-*O*-benzoyl-3-*O*-methyl-4-*O*-benzyl-1-thio-ß-D-glucopyranoside (S9) Compound **S8** (2.35 g, 4.91 mmol, 1.0 eq.) was co-evaporated with toluene (3x) under N_2 atmosphere before it was dissolved in dry DCM (24.6 mL, 0.2 M). A 1M solution of BH_3·THF (24.6 mL, 24.6 mmol, 5 eq.) in THF was added dropwise to the solution after which TMSOTf (0.13 mL, 0.74 mmol, 0.15 eq.) was added to the mixture. The reaction mixture was stirred for 5 h and slowly quenched with NEt_3 (2.8 mL) followed by MeOH, which was added until the formation of H_2 ceased. The mixture was concentrated and co-evaporated with MeOH (2x). Purification by column chromatography (pentane-Et_2O 7:3) gave the title compound (2.08 g, 4.33 mmol, 88%) as a white solid. $[\alpha]_D^{25}$ 32 (c 0.4, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.12-8.10 (m, 2H, CH_{arom}); 7.62-7.58 (m, 1H, CH_{arom}); 7.50-7.46 (m, 2H, CH_{arom}); 7.43-7.41 (m, 2H, CH_{arom}); 7.37-7.25 (m, 8H, CH_{arom}); 5.22-5.17 (m, 1H, H-2); 4.87-4.81 (m, 2H, H-1, PhC*H*H); 4.66 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 3.92-3.88 (m, 1H, H-6); 3.75-3.68 (m, 1H, H-6); 3.62-3.59 (m, 2H, H-3, H-4); 3.51 (s, 3H, OCH_3); 3.50-3.47 (m, 1H, H-5); 1.98 (bs, 1H, 6-O*H*). ^{13}C-APT NMR (101 MHz) δ: 165.4 (CO_{Bz}); 138.0 ($C_{q,arom}$); 133.5 (CH_{arom}); 132.9 ($C_{q,arom}$) 132.4, 132.0, 130.1 (CH_{arom}); 129.9 ($C_{q,arom}$); 129.2, 128.7, 128.5, 128.4, 128.2, 128.1, 127.8 (CH_{arom}); 86.6 (C-3); 86.3 (C-1); 79.7 (C-5); 77.2 (C-4); 75.2 (PhCH_2); 72.8 (C-2); 62.3 (C-6); 61.1 (OCH_3). IR (thin film, cm^{-1}): 1027, 1070, 1092, 1178, 1266, 1452, 1727, 3470. HRMS calculated for $C_{27}H_{28}O_6SNa$ 503.1504 $[M+Na]^+$; found 503.1499.

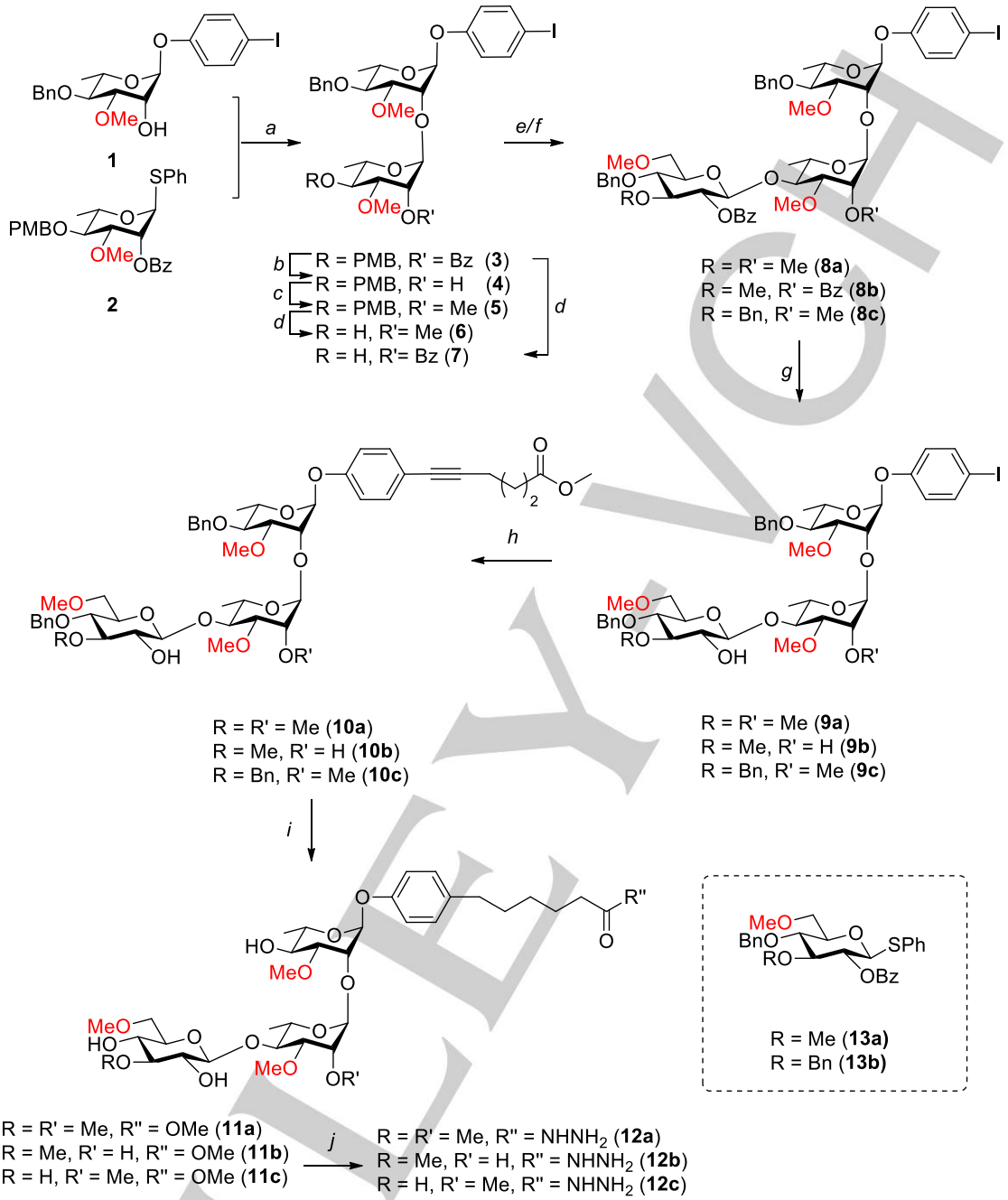


Phenyl 2-*O*-benzoyl-3,6-di-*O*-methyl-4-*O*-benzyl-1-thio-ß-D-glucopyranoside (13a) Compound **S9** (0.60 g, 1.25 mmol, 1.0 eq.) was dried by co-evaporation with toluene and dissolved in dry DMF (12.5 mL, 0.1 M). The solution was cooled to 0 °C after which MeI (0.16 mL, 2.51 mmol, 2.0 eq.) was added. The reaction mixture was stirred for 5 minutes before NaH (60%, 84 mg, 2.51 mmol, 2.0 eq.) was added and stirred at rt for 5.5 hours. The reaction was quenched with H_2O, the aqueous phase extracted with Et_2O (3x), the organic layers washed with brine, dried with $MgSO_4$ and concentrated. Purification by column chromatography (pentane-Et_2O, 17:3) gave the title compound (0.45 g, 0.91 mmol, 72%) as a white solid. $[\alpha]_D^{25}$ 33.6 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.11-8.09 (m, 2H, CH_{arom}); 7.59-7.55 (m, 1H, CH_{arom}); 7.47-7.43 (m, 4H, CH_{arom}); 7.35-7.21 (m, 8H, CH_{arom}); 5.23 (t, 1H, *J* = 9.4 Hz, H-2); 4.85 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.78 (d, 1H, *J* = 10.0 Hz, H-1); 4.64 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 3.70-3.49 (m, 7H, H-3, H-4, H-5, H-6, OCH_3); 3.38 (s, 3H, OCH_3). ^{13}C-APT NMR (101 MHz) δ: 165.2 (CO_{Bz}); 138.1, 133.5 ($C_{q,arom}$); 133.3, 132.1, 129.9, 128.9, 128.5, 128.5, 128.1, 127.9, 127.7 (CH_{arom}); 86.6 (C-1); 86.5 (C-4); 79.2 (C-3); 77.5 (C-5); 75.0 (PhCH_2); 72.6 (C-2); 71.3 (C-6); 60.9, 59.5 (OCH_3). IR (thin film, cm^{-1}): 1027, 1070, 1093, 1143, 1178, 1265, 1452, 1730. HRMS calculated for $C_{28}H_{30}O_6SNa$ 517.1661 $[M+Na]^+$; found 517.1655.

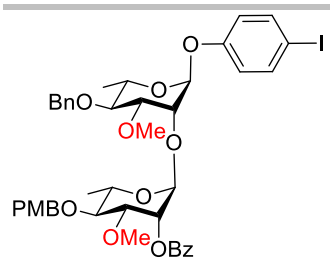


Phenyl 2-*O*-benzoyl-3-*O*-methyl-3,4-di-*O*-benzyl-1-thio-ß-D-glucopyranoside (13b) Compound **S10**[4] (2.48 g, 4.31 mmol, 1.0 eq) was dried by co-evaporation with toluene and dissolved in dry DMF (43.1 mL, 0.1 M).

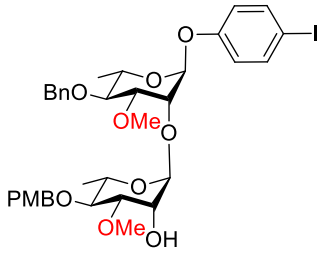
The solution was cooled to 0 °C after which MeI (mL, 2.51 mmol, 2.0 eq.) was added. The reaction mixture was stirred for 5 minutes before NaH (60%, 0.29 g, 8.62 mmol, 2.0 eq.) was added and stirred at rt for 5 hours. The reaction was quenched with H_2O, the aqueous phase extracted with Et_2O (3x), the organic layers washed with brine, dried with $MgSO_4$ and concentrated. Purification by column chromatography (pentane-Et_2O, 4:1) gave the title compound (0.45 g, 0.91 mmol, 79%) as a white solid. $[\alpha]_D^{25}$ 41.3 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.02 (d, 2H, *J* = 8.0 Hz, C*H*$_{arom}$); 7.57 (t, 1H, *J* = 7.4 Hz, C*H*$_{arom}$); 7.46-7.42 (m, 4H, C*H*$_{arom}$); 7.35-7.23 (m, 8H, C*H*$_{arom}$); 7.11 (s, 5H, C*H*$_{arom}$); 5.29 (t, 1H, *J* = 9.4 Hz, H-2); 4.84 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.79-4.72 (m, 2H, H-1, PhC*H*H); 4.66-4.63 (m, 2H, PhCH*H*, PhCH*H*); 3.84 (t, 1H, *J* = 9.4 Hz, H-3); 3.77-3.63 (m, 3H, H-4, H-6); 3.57-3.54 (m, 1H, H-5); 3.39 (s, 3H, OC*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 165.3 (*C*O$_{Bz}$); 138.1, 137.8, 133.4 (C$_{q,arom}$); 133.3, 132.4, 130.0, 128.9, 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.8 (*C*H$_{arom}$); 86.6 (C-1); 84.3 (C-3); 79.4 (C-5); 77.8 (C-4); 75.4, 75.2 (Ph*C*H$_2$); 72.6 (C-2); 71.3 (C-6); 59.6 (O*C*H$_3$). IR (thin film, cm^{-1}): 1000, 1026, 1069, 1090, 1140, 1178, 1205, 1264, 1315, 1452, 1482, 1727. HRMS calculated for $C_{34}H_{34}O_6SNa$ 593.1974 $[M+Na]^+$; found 593.1968.



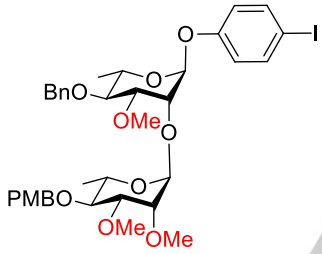
Scheme 1. Trisaccharide synthesis. Reagents and conditions: (a) Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 66%, (b) Na, MeOH/THF, 97%, (c) NaH, MeI, DMF, 95%, (d) HCl/HFIP, HFIP/DCM, 93% (**14**), 100% (**15**), (e) Donor **13a**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 93% (**8a**), 88% (**8b**), (f) Donor **13b**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 100% (**8c**), (g) Na, MeOH/THF, 99% (**9a**), 84% (**9b**), 97% (**9c**), (h) Methyl hex-5-ynoate, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, 99% (**10a**), 77% (**10b**), 82% (**10c**), (i) Pd/C, H_2, THF/MeOH, 100% (**11a**), 82% (**11b**), 90% (**11c**), (j) $N_2H_4{\cdot}H_2O$, EtOH, 89% (**12a**), 100% (**12b**). 84% (**12c**).



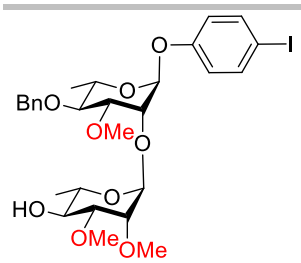
4-iodophenyl 2-*O*-(2-*O*-benzoyl-3-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (3) Donor **2** (396 mg, 0.80 mmol, 1.0 eq), Ph_2SO (210 mg, 1.04 mmol, 1.3 eq) and TTBP (497 mg, 2.0 mmol, 2.5 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (16 mL, 0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -70 °C after which Tf_2O (175 µL, 1.04 mmol, 1.3 eq) was added to the solution. After stirring for 30 minutes, acceptor **1** (752 mg, 1.60 mmol, 2.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (4 mL, 0.4 M) and added to the solution at -65 °C. After stirring for 2.5 hours the reaction reached -40 °C and was quenched by addition of NEt_3 (1 mL). The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 4:1) gave the title compound (451 mg, 0.53 mmol, 66%) as a clear oil. $[\alpha]_D^{25}$ -33.2 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.10-8.08 (m, 2H, C*H*$_{arom}$); 7.60-7.54 (m, 3H, C*H*$_{arom}$); 7.50-7.46 (m, 2H, C*H*$_{arom}$); 7.38-7.25 (m, 7H, C*H*$_{arom}$); 6.89 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 6.79 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.70 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 5.45 (d, 1H, *J* = 2.0 Hz, H-1); 5.17 (d, 1H, *J* = 1.6 Hz, H-1'); 4.92 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.84 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.66 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.59 (d, 1H, *J* = 10.4 Hz, PhCH*H*); 4.20 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.89-3.75 (m, 6H, H-3, H-3', H-5', C*H*$_{3,PMB}$); 3.71-3.67 (m, 1H, H-5); 3.53-3.45 (m, 8H, H-4, H-4', OC*H*$_3$); 1.34 (d, 3H, *J* = 6.0 Hz, H-6'); 1.24 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.8 (*C*O$_{Bz}$); 159.5, 156.1, 138.5 (C$_{q,arom}$); 138.5, 133.3 (*C*H$_{arom}$); 130.6 (C$_{q,arom}$); 130.1, 130.0, 128.6, 128.5, 128.2, 127.8, 118.6, 113.9 (*C*H$_{arom}$); 99.4 (C-1'); 96.9 (C-1); 84.8 (*C*-I$_{arom}$); 81.4 (C-3'); 80.1 (C-3); 79.9 (C-4'); 79.7 (C-4); 75.4, 75.2 (Ph*C*H$_2$); 73.5 (C-2); 69.2 (C-2'); 68.8 (C-5); 68.5 (C-5'); 58.1, 57.8 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 18.3 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1042, 1072, 1098, 1118, 1233, 1268, 1452, 1484, 1514, 1724. HRMS calculated for $C_{42}H_{47}IO_{11}Na$ 877.2061 $[M+Na]^+$; found 877.2055.



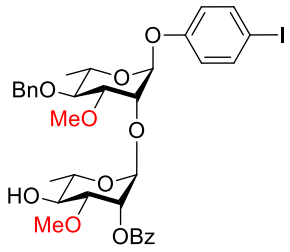
4-iodophenyl 2-*O*-(3-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (4) Compound **3** (451 mg, 0.53 mmol, 1.0 eq) was dissolved in THF (2.6 mL, 0.2 M). A small piece of sodium was dissolved in MeOH and 2.6 mL of this solution was added. The reaction was stirred for 2 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (384 mg, 0.51 mmol, 97%) as a pale oil. $[\alpha]_D^{25}$ -63.7 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.57-7.53 (m, 2H, C*H*$_{arom}$); 7.34-7.25 (m, 7H, C*H*$_{arom}$); 6.91-6.87 (m, 2H, C*H*$_{arom}$); 6.80-6.76 (m, 2H, C*H*$_{arom}$); 5.42 (d, 1H, *J* = 2.0 Hz, H-1); 5.13 (d, 1H, *J* = 1.6 Hz, H-1'); 4.88 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.78 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.61 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.56 (d, 1H, *J* = 10.4 Hz, PhCH*H*); 4.21-4.19(m, 2H, H-2, H-2'); 3.81 (s, 3H, C*H*$_{3,PMB}$); 3.79-3.74 (m, 2H, H-3, H-5); 3.70-3.66 (m, 1H, H-5'); 3.60 (dd, 1H, *J* = 3.4, 9.0 Hz, H-3'); 3.57 (s, 3H, OC*H*$_3$); 3.53 (s, 3H, OC*H*$_3$); 3.43-3.34 (m, 2H, H-4, H-4'); 1.27 (d, 3H, *J* = 6.0 Hz, H-6'); 1.22 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.5, 156.1, 138.5 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 130.6 (C$_{q,arom}$); 129.9, 128.5, 128.1, 127.9, 118.6, 114.0 (*C*H$_{arom}$); 100.9 (C-1'); 96.9 (C-1); 84.8 (*C*-I$_{arom}$); 81.5 (C-3); 81.4 (C-3'); 80.1 (C-4); 79.6 (C-4'); 785.4, 75.1 (Ph*C*H$_2$); 73.4 (C-2); 68.7 (C-5'); 68.1 (C-2'); 68.0 (C-5); 58.1, 57.7 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 18.1 (C-6'); 18.0 (C-6). IR (thin film, cm^{-1}): 1045, 1070, 1113, 1139, 1233, 1249, 1484, 1513, 3484. HRMS calculated for $C_{36}H_{43}IO_{10}Na$ 773.1799 $[M+Na]^+$; found 773.1809.



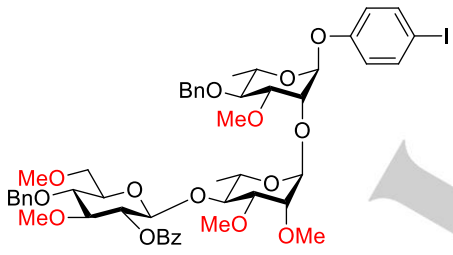
4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (5) Compound **4** (196 mg, 0.26 mmol, 1.0 eq) was dissolved in dry DMF (2.6 mL, 0.1 M) and MeI (32 µL, 0.52 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 16 mg, 0.39 mmol, 1.5 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was quenched by addition of H_2O, and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:1) gave the title compound (207 mg, 0.26 mmol, 100%) as a pale oil. $[\alpha]_D^{25}$ -70.7 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.57-7.53 (m, 2H, C*H*$_{arom}$); 7.33-7.26 (m, 7H, C*H*$_{arom}$); 6.90-6.86 (m, 2H, C*H*$_{arom}$); 6.80-6.76 (m, 2H, C*H*$_{arom}$); 5.39 (d, 1H, *J* = 1.6 Hz, H-1); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 4.88 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.83 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.64 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.54 (d, 1H, *J* = 10.4 Hz, PhCH*H*); 4.19 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.80 (s, 3H, C*H*$_{3,PMB}$); 3.77-3.55 (m, 14H, H-2', H-3, H-3', H-5, H-5', OC*H*$_3$); 3.46-3.38 (m, 2H, H-4, H-4'); 1.27 (d, 3H, *J* = 6.0 Hz, H-6'); 1.22 (d, 1H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.4, 156.1 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 130.8 (C$_{q,arom}$); 129.9, 128.5, 128.1, 127.9, 118.6, 114.0 (*C*H$_{arom}$); 98.9 (C-1'); 97.0 (C-1); 84.8 (*C*-I$_{arom}$); 81.7 (C-3); 81.2 (C-3'); 80.2 (C-4); 80.0 (C-4'); 77.6 (C-2'); 75.3, 75.2 (Ph*C*H$_2$); 68.8 (C-5); 68.6 (C-5'); 59.2, 58.2, 58.1 (O*C*H$_3$); 55.4 (O*C*H$_{3,PMB}$); 18.1 (C-6); 18.1 (C-6'). IR (thin film, cm^{-1}): 1035, 1052, 1072, 1093, 1120, 1173, 1233, 1248, 1484, 1514. HRMS calculated for $C_{36}H_{45}IO_{10}Na$ 787.1955 $[M+Na]^+$; found 787.19450.



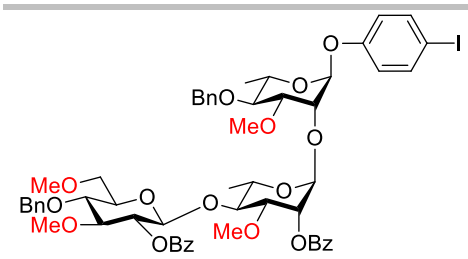
4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (6) Compound **5** (199 mg, 0.26 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 2.6 mL, 0.1 M) after which a solution of HCl in HFIP (0.13 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, indicated by a dark purple colour, the reaction was quenched by addition of sat. aq. $NaHCO_3$. The mixture was diluted with DCM, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (155 mg, 0.24 mmol, 93%) as a pale oil. $[\alpha]_D^{25}$ -75.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.35-7.28 (m, 5H, C*H*$_{arom}$); 6.83-6.79 (m, 2H, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.18 (d, 1H, *J* = 1.6 Hz, H-1'); 4.77 (dd, 2H, *J* = 10.8, 65.6 Hz, PhC*H*$_2$); 4.22 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.79-3.70 (m, 4H, H-2', H-3, H-5, H-5'); 3.62-3.40 (m, 12H, H-3', H-4, H-4', OC*H*$_3$); 2.34 (bs, 4'-OH); 1.30 (d, 3H, *J* = 6.4 Hz, H-6); 1.25 (d, 3H, *J* = 6.0 Hz, H-6'). ^{13}C-APT NMR (101 MHz) δ: 156.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.4 (C$_{q,arom}$); 128.5, 128.1, 127.9, 118.6 (*C*H$_{arom}$); 99.1 (C-1'); 97.0 (C-1); 84.9 (*C*-I$_{arom}$); 81.6 (C-3); 80.8 (C-3'); 80.0 (C-4); 75.9 (C-2'); 75.2 (Ph*C*H$_2$); 73.5 (C-2); 71.7 (C-4'); 68.9 (C-5'); 68.8 (C-5); 59.1, 58.2, 57.1 (O*C*H$_3$); 18.2 (C-6'); 17.9 (C-6). IR (thin film, cm^{-1}): 1013, 1017, 1032, 1050, 1073, 1089, 1122, 1139, 1233, 1262, 1484, 2909, 2929, 3481. HRMS calculated for $C_{28}H_{37}IO_9Na$ 667.1380 [M+Na]$^+$; found 667.1374.



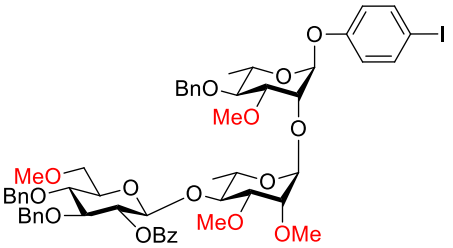
4-iodophenyl 2-*O*-(2-*O*-benzoyl-3-*O*-methyl-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (7) Compound **3** (88 mg, 0.10 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 1 mL, 0.1 M) after which a solution of HCl in HFIP (50 µL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, indicated by a dark purple colour, the reaction was quenched by addition of sat. aq. $NaHCO_3$. The mixture was diluted with DCM, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:1) gave the title compound (80 mg, 0.10 mmol, 100%) as a pale oil. $[\alpha]_D^{25}$ -57.1 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.09-8.06 (m, 2H, C*H*$_{arom}$); 7.60-7.55 (m, 3H, C*H*$_{arom}$); 7.48-7.44 (m, 2H, C*H*$_{arom}$); 7.39-7.25 (m, 5H, C*H*$_{arom}$); 6.83-6.80 (m, 2H, C*H*$_{arom}$); 5.70 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.22 (d, 1H, *J* = 1.6 Hz, H-1'); 4.80 (dd, 2H, *J* = 11.0, 103.4 Hz, PhC*H*$_2$); 4.24 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.90-3.86 (m, 1H, H-5'); 3.79 (dd, 1H, *J* = 2.8, 9.2 Hz, H-3); 3.75-3.62 (m, 3H, H-3', H-4', H-5); 3.56-3.47 (m, 7H, H-4, OC*H*$_3$); 2.60 (bs, 1H, 4'-O*H*); 1.37 (d, 3H, *J* = 6.0 Hz, H-6'); 1.27 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.7 (*C*O$_{Bz}$); 156.1, 138.5 (C$_{q,arom}$); 138.5, 133.4, 130.0 (*C*H$_{arom}$); 129.8 (C$_{q,arom}$); 128.6, 128.5, 128.2, 127.9, 118.6 (*C*H$_{arom}$); 99.6 (C-1'); 97.0 (C-1); 84.9 (*C*-I$_{arom}$); 81.4 (C-3); 79.9 (C-4); 79.6 (C-3'); 75.4 (C-2); 73.6 (C-4'); 68.9 (C-5); 68.9 (C-5'); 68.0 (C-2'); 58.2, 57.5 (O*C*H$_3$); 18.2 (C-6); 18.1 (C-6'). IR (thin film, cm^{-1}): 1040, 1073, 1096, 1119, 1176, 1202, 1232, 1271, 1316, 1385, 1452, 1484, 1585, 1724, 2931, 3446. HRMS calculated for $C_{34}H_{39}IO_{10}Na$ 757.1486 [M+Na]$^+$; found 757.1480.



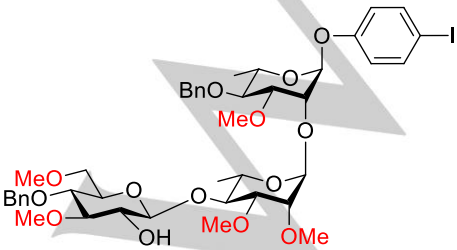
4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzoyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (8a) Donor **13a** (103 mg, 0.21 mmol, 1.5 eq), Ph_2SO (50 mg, 0.23 mmol, 1.7 eq) and TTBP (103 mg, 0.42 mmol, 3.0 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (2.8 mL, 0.08 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -60 °C after which Tf_2O (35 µL, 0.23 mmol, 1.7 eq) was added to the solution. After stirring for 30 minutes, acceptor **6** (90 mg, 0.14 mmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.4 mL, 0.4 M) and added to the solution. After stirring for 1.5 hours the reaction was quenched by addition of NEt_3 (0.14 mL). The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (140 mg, 0.14 mmol, 98%) as a slightly yellow oil. $[\alpha]_D^{25}$ -74.9 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.16-8.14 (m, 2H, C*H*$_{arom}$); 7.58-7.56 (m, 3H, C*H*$_{arom}$); 7.47 (t, 1H, *J* = 7.8 Hz, C*H*$_{arom}$); 7.36-7.26 (m, 11H, C*H*$_{arom}$); 6.82-6.80 (m, 2H, C*H*$_{arom}$); 5.40 (d, 1H, *J* = 1.6 Hz, H-1); 5.17-5.12 (m, 2H, H-1', H-2''); 4.85-4.80 (m, 3H, H-1'', PhC*H*H, PhC*H*H); 4.66 (d, 1H, *J* = 11.2 Hz), PhCH*H*); 4.58 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.17 (dd, 1H, *J* = 2.0, 2.8 Hz); 3.74-3.39 (m, 19H, H-2', H-3, H-3', H-3'', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 3.35-3.30 (m, 2H, H-4, H-4'); 3.13 (s, 3H, OC*H*$_3$); 1.29 (d, 3H, *J* = 6.0 Hz, H-6'); 1.20 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.3 (*C*O$_{Bz}$); 156.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.5, 138.4 (C$_{q,arom}$); 133.2 (*C*H$_{arom}$); 130.3 (C$_{q,arom}$); 130.0, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 118.6 (*C*H$_{arom}$); 101.4 (C-1''); 98.4 (C-1'); 96.8 (C-1''); 85.4 (C-3''); 84.8 (*C*-I$_{arom}$); 81.8 (C-3); 80.5 (C-4'); 80.0 (C-4); 77.7 (C-3'); 77.5 (C-4''); 76.6 (C-2'); 75.2, 75.0 (Ph*C*H$_2$); 74.9 (C-5''); 74.3 (C-2''); 73.1 (C-2); 71.2 (C-6''); 68.8 (C-5'); 68.0 (C-5); 60.8, 59.8, 59.0, 58.3, 57.2 (O*C*H$_3$); 18.1 (C-6 and C-6'). IR (thin film, cm^{-1}): 1027, 1055, 1072, 1092, 1119, 1140, 1233, 1268, 1484, 1734, 2928. HRMS calculated for $C_{50}H_{61}IO_{15}Na$ 1051.2953 [M+Na]$^+$; found 1051.2947.



4-iodophenyl 2-*O*-(2-*O*-benzoyl-3-*O*-methyl-4-*O*-(2-*O*-benzoyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (8b) Donor **13a** (69 g, 0.14 mmol, 1.5 eq), Ph_2SO (37 mg, 0.18 mmol, 2.0 eq) and TTBP (86 mg, 0.35 mmol, 3.8 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (2.8 mL, 0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -60 °C after which Tf_2O (30 µL, 0.18 mmol, 2.0 eq) was added to the solution. After stirring for 30 minutes, acceptor **3** (68 mg, 93 µmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.3 mL, 0.3 M) and added to the solution. After stirring for 2 hours the reaction was quenched by addition of NEt_3 (0.1 mL). The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 3:7) gave the title compound (92 mg, 82 µmol, 88%) as a pale oil. $[\alpha]_D^{25}$ -42.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.14-8.12 (m, 2H, C*H*$_{arom}$); 8.07-8.05 (m, 2H, C*H*$_{arom}$); 7.59-7.54 (m, 4H, C*H*$_{arom}$); 7.49-7.42 (m, 4H, C*H*$_{arom}$); 7.35-7.25 (m, 10H, C*H*$_{arom}$); 6.81 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 2.0 Hz, H-1); 5.16-5.14 (m, 2H, H-1', H-2''); 4.87-4.83 (m, 3H, H-1'', PhC*H*H, PhC*H*H); 4.65 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.59 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.18 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.72-3.53 (m, 7H, H-3, H-4', H-4'', H-5, H-5', H-6''); 3.52-3.40 (m, 13H, H-3', H-3'', H-4, H-5'', OC*H*$_3$); 3.10 (s, 3H, OC*H*$_3$); 1.38 (d, 3H, *J* = 6.4 Hz, H-6'); 1.23 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.7, 165.3 (*C*O$_{Bz}$); 138.5 (*C*H$_{arom}$); 138.3 (C$_{q,arom}$); 133.4, 133.3 (*C*H$_{arom}$); 130.2 (C$_{q,arom}$); 130.1, 130.0, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 118.7 (*C*H$_{arom}$); 101.5 (C-1''); 99.1 (C-1'); 96.8 (C-1); 85.4 (C-3''); 84.9 (*C*-I$_{arom}$); 81.5 (C-3); 79.9 (C-4); 79.4 (C-3'); 78.2 (C-4'); 77.6 (C-4''); 75.3, 75.0 (PhC*H*$_2$); 74.9 (C-5''); 74.2 (C-2''); 73.0 (C-2); 71.5 (C-6''); 68.9 (C-5); 68.4 (C-2'); 68.0 (C-5'); 60.8, 59.8, 58.2, 57.4 (OC*H*$_3$); 18.3 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1000, 1027, 1070, 1096, 1112, 1140, 1178, 1233, 1268, 1452, 1484, 1723, 2931. HRMS calculated for $C_{56}H_{63}IO_{16}Na$ 1141.3059 $[M+Na]^+$; found 1141.3064.

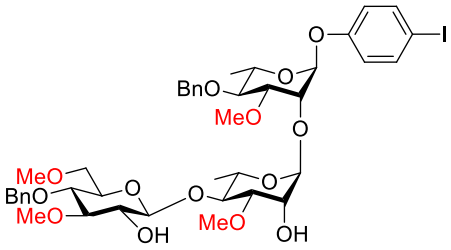


4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (8c) Donor **13b** (204 mg, 0.41 mmol, 1.5 eq), Ph_2SO (92 mg, 0.45 mmol, 1.7 eq) and TTBP (205 mg, 0.83 mmol, 3.0 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (5.5 mL, 0.07 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -70 °C after which Tf_2O (76 µL, 0.45 mmol, 1.7 eq) was added to the solution. After stirring for 20 minutes, acceptor **6** (177 mg, 0.27 mmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.6 mL, 0.4 M) and added to the solution. After stirring for 1 hour the reaction was quenched by addition of pyridine (0.28 mL). The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (284 g, 0.26 mmol, 93%) as a slightly yellow oil. $[\alpha]_D^{25}$ -76.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.12-8.10 (m, 2H, C*H*$_{arom}$); 7.62-7.58 (m, 3H, C*H*$_{arom}$); 7.49-7.45 (m, 2H, C*H*$_{arom}$); 7.37-7.32 (m, 10H, C*H*$_{arom}$); 7.16-7.13 (m, 5H, C*H*$_{arom}$); 6.85-6.83 (m, 2H, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 2.0 Hz, H-1); 5.27 (t, 1H, *J* = 8.4 Hz, H-2''); 5.16 (d, 1H, *J* = 2.0 Hz, H-1'); 4.88-4.84 (m, 3H, H-1'', PhC*H*H, PhC*H*H); 4.79 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.72-4.67 (m, 2H, PhCH*H*, PhCH*H*); 4.61 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.21 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.83-3.62 (m, 9H, H-2', H-3, H-3', H-3'', H-4'', H-5, H-5', H-6''); 3.55 (s, 3H, OC*H*$_3$); 3.50 (s, 4H, H-5'', OC*H*$_3$); 3.43 (s, OC*H*$_3$); 3.38-3.30 (m, 2H, H-4, H-4'); 3.15 (s, 3H, OC*H*$_3$); 1.33 (d, 3H, *J* = 5.6 Hz, H-6'); 1.24 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.2 (*C*O$_{Bz}$); 156.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.3, 138.1 (C$_{q,arom}$); 133.1 (*C*H$_{arom}$); 130.3 (C$_{q,arom}$); 130.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 118.6 (*C*H$_{arom}$); 101.5 (C-1''); 98.4 (C-1'); 96.8 (C-1); 84.8 (*C*-I$_{arom}$); 83.1 (C-3''); 81.8 (C-4''); 80.5 (C-4); 80.0 (C-4'); 78.1 (C-3); 77.7 (C-3'); 76.6 (C-2'); 75.2, 75.2, 75.1 (PhC*H*$_2$); 75.0 (C-5''); 74.3 (C-2''); 73.1 (C-2); 71.2 (C-6''); 68.8 (C-5'); 68.0 (C-5); 59.9, 59.0, 58.2, 57.2 (OC*H*$_3$); 18.1 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1000, 1027, 1055, 1072, 1095, 1120, 1140, 1233, 1268, 1452, 1484, 1731, 2931. HRMS calculated for $C_{56}H_{65}IO_{15}Na$ 1127.3266 $[M+Na]^+$; found 1127.3260.

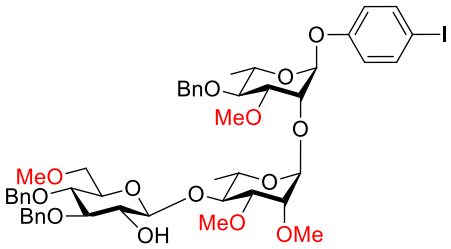


4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (9a) Compound **8a** (102 mg, 0.1 mmol, 1.0 eq) was dissolved in THF (0.49 mL, 0.2 M) and the solution was diluted with MeOH (0.49 mL). A small piece of sodium was added to the solution and the reaction was stirred for 2 hours. The reaction was then quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x), the organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (92 mg, 0.1 mmol, 100%) as a pale oil. $[\alpha]_D^{25}$ -27.4 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.58-7.56 (m, 2H, C*H*$_{arom}$); 7.36-7.26 (m, 10H, C*H*$_{arom}$); 6.82-6.79 (m, 2H, C*H*$_{arom}$); 5.40 (d, 1H, *J* = 1.6 Hz, H-1); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 4.89-4.83 (m, 2H, PhC*H*H, PhC*H*H); 4.66-4.60 (m, 2H, PhCH*H*, PhCH*H*); 4.37 (d, 1H, *J* = 8.0 Hz, H-1''); 4.18 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2);

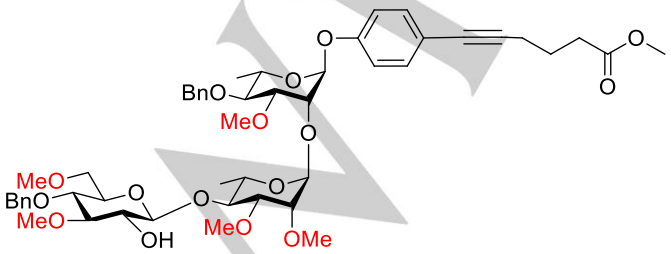
3.90 (bs, 1H, 2''-O*H*); 3.79-3.75 (m, 3H, H-2', H-3, H-5); 3.71-3.58 (m, 6H, H-3', H-5', H-5'', OCH_3); 3.56-3.50 (m, 11H, H-4'', H-6'', OCH_3); 3.46-3.36 (m, 6H, H-2'', H-4, H-4', OCH_3); 3.29 (t, 1H, *J* = 8.8 Hz, H-3''); 1.35 (d, 3H, *J* = 6.4 Hz, H-6); 1.25 (d, 3H, *J* = 6.4 Hz, H-6'). ^{13}C-APT NMR (101 MHz) δ: 156.0 ($C_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.4 ($C_{q,arom}$); 128.6, 128.5, 128.1, 128.1, 127.9, 118.6 (*C*H$_{arom}$); 105.8 (C-1''); 98.8 (C-1'); 96.9 (C-1); 86.4 (C-3''); 84.9 (*C*-I$_{arom}$); 81.8 (C-5''); 81.6 (C-3); 80.3 (C-3'); 80.0 (C-4); 77.3 (C-4''); 75.8 (C-2'); 75.6 (C-2''); 75.3 (PhCH$_2$); 75.2 (C-4'); 75.0 (PhCH$_2$); 71.3 (C-6''); 68.7 (C-5'); 68.4 (C-5); 61.0, 59.5, 59.1, 58.3, 56.7 (OCH$_3$); 18.2 (C-6'); 17.7 (C-6). IR (thin film, cm^{-1}): 1000, 1002, 1030, 1032, 1052, 1071, 1120, 1233, 1455, 1485, 2896, 2923, 3445. HRMS calculated for $C_{43}H_{57}IO_{14}Na$ 947.2691 [M+Na]$^+$; found 947.2709.



4-iodophenyl 2-*O*-(3-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (9b) Compound **8b** (90 mg, 80 µmol, 1.0 eq) was dissolved in THF (0.4 mL, 0.2 M). A small piece of sodium was dissolved in MeOH and 0.4 mL of this solution was added. The reaction was stirred for 4 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (DCM-EtOAc 7:3) gave the title compound (61 mg, 67 µmol, 84%) as a pale oil. $[\alpha]_D^{25}$ -65.2 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.36-7.28 (m, 10H, C*H*$_{arom}$); 6.82-6.79 (m, 2H, C*H*$_{arom}$); 5.41 (d, 1H, *J* = 1.6 Hz, H-1); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 4.89-4.86 (t, 2H, *J* = 11.0 Hz, PhC*H*H, PhC*H*H); 4.64-4.61 (m, 2H, PhCH*H*, PhCH*H*); 4.35 (d, 1H, *J* = 7.6 Hz, H-1''); 4.25 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2'); 4.19 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.85-3.79 (m, 1H, H-5'); 3.78-3.59 (m, 9H, H-3, H-3', H-4', H-5, H-6'', OCH_3); 3.55-3.50 (m, 7H, H-4'', OCH_3); 3.47-3.36 (m, 7H, H-2'', H-5'', OCH_3); 3.30 (t, 1H, *J* = 9.2 Hz, H-3''); 1.35 (d, 3H, *J* = 6.4 Hz, H-6'); 1.24 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.0 ($C_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.5, 138.4 ($C_{q,arom}$); 128.6, 128.5, 128.1, 128.1, 127.9, 127.9, 118.6 (*C*H$_{arom}$); 105.7 (C-1''); 100.8 (C-1'); 96.9 (C-1); 86.2 (C-3''); 84.9 (*C*-I$_{arom}$); 81.5 (C-3); 81.2 (C-4'); 80.6 (C-3'); 80.1 (C-4); 77.3 (C-4''); 75.6 (C-2''); 75.3 (PhCH$_2$); 75.3 (C-5''); 75.0 (PhCH$_2$); 73.6 (C-2); 71.3 (C-6''); 68.7 (C-5); 67.9 (C-5'); 66.9 (C-2'); 61.1, 59.5, 58.2, 56.9 (OCH$_3$); 18.1 (C-6); 17.6 (C-6'). IR (thin film, cm^{-1}): 1069, 1116, 1232, 1454, 1484, 2928, 3451. HRMS calculated for $C_{42}H_{55}IO_{14}Na$ 933.2534 [M+Na]$^+$; found 933.2529.

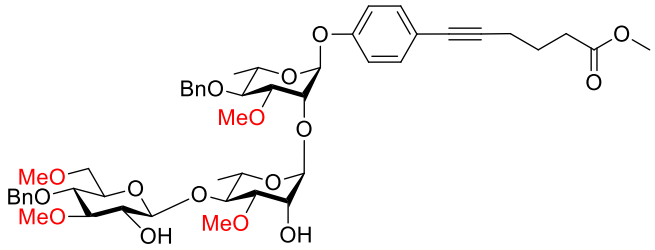


4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (9c) Compound **8c** (95 mg, 86 µmol, 1.0 eq) was dissolved in THF (0.8 mL, 0.1 M) and the solution was diluted with MeOH (0.8 mL). A small piece of sodium was added to the solution and the reaction was stirred for 2 hours. The reaction was then quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x), the organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (85 mg, 85 µmol, 99%) as a pale oil. $[\alpha]_D^{25}$ -41.4 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.58-7.55 (m, 2H, C*H*$_{arom}$); 7.42-7.40 (m, 1H, C*H*$_{arom}$); 7.37-7.25 (m, 14H, C*H*$_{arom}$); 6.82-6.79 (m, 2H, C*H*$_{arom}$); 5.41 (d, 1H, *J* = 2.0 Hz, H-1); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 5.02 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.89-4.82 (m, 3H, PhC*H*H, PhC*H*H, PhCH*H*); 4.66-4.59 (m, 2H, PhCH*H*, PhCH*H*); 4.40 (d, 1H, *J* = 6.8 Hz, H-1''); 4.19 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.79-3.72 (m, 4H, H-2', H-3, H-5', 2''-O*H*); 3.70-3.51 (m, 17H, H-2'', H-3', H-3'', H-4'', H-5, H-5'', H-6'', OCH_3); 3.42-3.38 (m, 2H, H-4, H-4'); 3.35 (s, 3H, OCH_3); 1.36 (d, 3H, *J* = 6.4 Hz, H-6); 1.25 (d, 3H, *J* = 6.4 Hz, H-6'); ^{13}C-APT NMR (101 MHz) δ: 156.0, 139.0 ($C_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.4 ($C_{q,arom}$); 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 118.6 (*C*H$_{arom}$); 105.7 (C-1''); 98.8 (C-1'); 96.9 (C-1); 84.8 (*C*-I$_{arom}$); 84.8 (C-4''); 81.7 (C-3''); 81.6 (C-3); 80.3 (C-3'); 80.0 (C-4'); 77.1 (C-2''); 76.2 (C-4); 75.8 (C-2'); 75.2 (C-5''); 75.2, 75.2, 75.0 (PhCH$_2$); 73.7 (C-2); 71.3 (C-6''); 68.7 (C-5'); 68.4 (C-5); 59.5, 59.1, 58.3, 56.7 (OCH$_3$); 18.2 (C-6'); 17.7 (C-6). IR (thin film, cm^{-1}): 1053, 1070, 1089, 1119, 1232, 1454, 1484, 2928, 3454. HRMS calculated for $C_{49}H_{61}IO_{14}Na$ 1023.3004 [M+Na]$^+$; found 1023.2998.

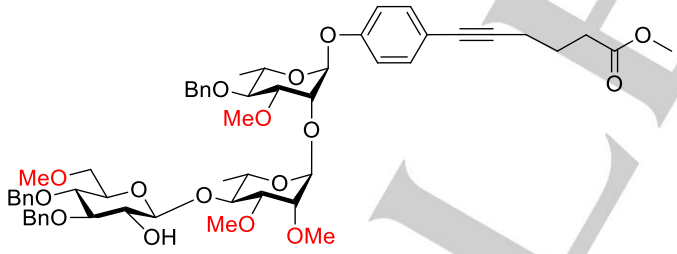


Methyl 6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)phenylhex-5-ynoate (10a) Compound **9a** (67 mg, 72 µmol, 1.0 eq) was dissolved in freshly distilled NEt_3 (2 mL, 0.04 M) together with methyl hex-5-ynoate (28 µL, 0.22 mmol, 3.0 eq). A cocktail of $Pd(PPh_3)_2Cl_2$ (28 mg), PPh_3 (22 mg) and CuI (15 mg) in freshly distilled NEt_3 was stirred for 15 minutes at 40 °C . Of this cocktail 0.18 mL was added to the reaction mixture, amounting to 0.1 eq $Pd(PPh_3)_2Cl_2$, 0.2 eq PPh_3 and 0.2 eq CuI. The reaction was left to stir overnight at 40 °C after which it was diluted with Et_2O and washed with 1 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by column chromatography (DCM-EtOAc 6:4) gave the title compound (66 mg, 72 µmol, 99%) as a yellow oil. $[\alpha]_D^{25}$ -56.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.36-7.26 (m, 12H, C*H*-$_{arom}$); 6.95-6.92 (m, 2H, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 4.90-4.83 (m, 2H, PhC*H*H, PhC*H*H); 4.66-4.60 (m, 2H, PhCH*H*, PhCH*H*); 4.38 (d, 1H, *J* = 7.6 Hz, H-1''); 4.19 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.90 (bs, 1H, 2''-O*H*); 3.79-

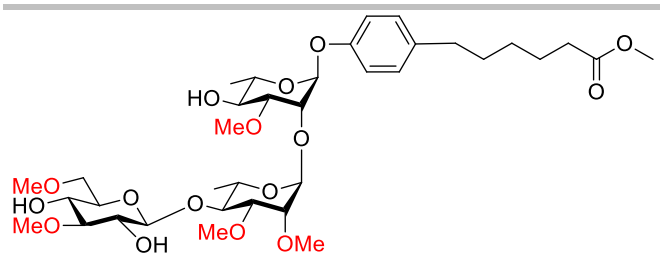
3.70 (m, 3H, H-2', H-3, H-5); 3.69-3.66 (m, 9H, H-3', H-5', H-5'', OCH_3, COOCH_3); 3.64-3.59 (m, 2H, H-6''); 3.56-3.50 (m, 10H, H-4'', OCH_3); 3.46-3.37 (m, 6H, H-2'', H-4, H-4', OCH_3); 3.36 (s, 3H, OCH_3); 3.29 (t, 1H, *J* = 8.6 Hz, H-3''); 2.53-2.45 (m, 4H, C$H_{2,linker}$, C$H_{2,linker}$); 1.95-1.90 (m, 2H, C$H_{2,linker}$); 1.36 (d, 3H, *J* = 6.0 Hz, H-6); 1.24 (d, 3H, *J* = 6.4 Hz, H-6'). ^{13}C-APT NMR (101 Mz) δ: 173.8 (*C*OOCH$_3$); 155.6, 138.4, 138.4 (C$_{q,arom}$); 133.0, 128.7, 128.5, 128.5, 128.1, 128.1, 127.9 (*C*H$_{arom}$); 117.6 (C$_{q,arom}$); 116.1 (*C*H$_{arom}$); 105.8 (H-1''); 98.8 (C-1'); 87.8 (C$_{q,alkyne}$); 86.4 (C-3''); 81.8 (C-3); 81.6 (C-5''); 81.0 (C$_{q,alkyne}$); 80.3 (C-3'); 80.1 (C-2''); 77.3 (C-4''); 75.8 (C-2'); 75.6 (C-4); 75.2 (C-4'); 75.2, 75.0 (Ph*C*H$_2$); 73.7 (C-2); 71.3 (C-6''); 68.7 (C-5'); 68.4 (C-5); 61.0, 59.5, 59.1, 58.3, 56.7 (O*C*H$_3$); 51.7 (COO*C*H$_3$); 33.0, 24.0, 19.0 (*C*H$_{2,linker}$); 18.1 (C-6'); 17.7 (C-6). IR (thin film, cm^{-1}): 1005, 1016, 1030, 1053, 1070, 1088, 1120, 1140, 1233, 1507, 1739, 2930, 3420. HRMS calculated for $C_{50}H_{66}O_{16}Na$ 945.4249 [M+Na]$^+$; found 945.4244.



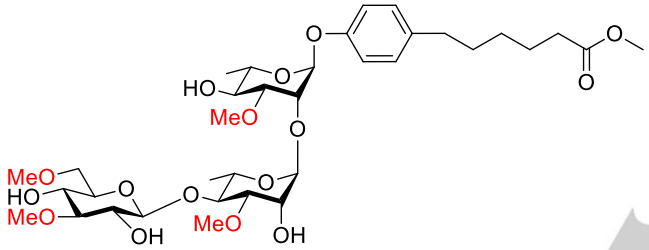
Methyl 6-(4-(2-*O*-(3-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)phenylhex-5-ynoate (10b) Compound **9b** (61 mg, 67 µmol, 1.0 eq) was dissolved in freshly distilled NEt$_3$ (1 mL, 0.07 M) together with methyl hex-5-ynoate (28 µL, 0.20 mmol, 3.0 eq). A cocktail of Pd(PPh$_3$)$_2$Cl$_2$ (14 mg), PPh$_3$ (11 mg) and CuI (7 mg) in freshly distilled NEt$_3$ was stirred for 15 minutes at 40 °C . Of this cocktail 0.34 mL was added to the reaction mixture, amounting to 0.1 eq Pd(PPh$_3$)$_2$Cl$_2$, 0.2 eq PPh$_3$ and 0.2 eq CuI. The reaction was left to stir overnight at 40 °C after which it was diluted with Et$_2$O, filtered over celite and washed with 1 M HCl, sat. aq. NaHCO$_3$ and brine. The organic layer was dried with MgSO$_4$, filtered and concentrated. The product was purified by column chromatography (DCM-EtOAc 7:3) gave the title compound (47 mg, 52 µmol, 77%) as a yellow oil. [α]$_D^{25}$ -60.5 (c 1.0, CHCl$_3$). ^{1}H NMR (400 MHz) δ: 7.36-7.26 (m, 12H, C*H*$_{arom}$); 6.93 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 2.0 Hz, H-1); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 4.89-4.84 (m, 2H, PhC*H*H, PhC*H*H); 4.64-61 (m, 2H, PhCH*H*, PhCH*H*); 4.35 (d, 1H, *J* = 7.6 Hz, H-1''); 4.25 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 4.20 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.88-3.80 (m, 1H, H-5'); 3.78 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.71-3.60 (m, 11H, H-3', H-4', H-5, H-6'', COOCH_3, OCH_3); 3.54-3.50 (m, 7H, H-4'', OCH_3); 3.47-3.36 (m, 6H, H-2'', H-4, H-5'', OCH_3); 3.30 (t, 1H, *J* = 9.0 Hz, H-3''); 2.51 (t, 2H, *J* = 7.4 Hz, C$H_{2,linker}$); 2.47 (t, 2H, *J* = 6.8 Hz, C$H_{2,linker}$); 1.92 (quint, 2H, *J* = 7.2 Hz, C$H_{2,linker}$); 1.35 (d, 3H, *J* = 6.0 Hz, H-6'); 1.24 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 173.8 (*C*OOCH$_3$); 155.6, 138.5, 138.4 (C$_{q,arom}$); 133.1, 128.6, 128.5, 128.1, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 117.6 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 105.7 (C-1''); 100.8 (C-1'); 96.8 (C-1); 87.9 (C$_{q,alkyne}$); 86.3 (C-3''); 81.6 (C-3); 81.2 (C-4'); 81.1 (C$_{q,alkyne}$); 80.7 (C-3'); 80.1 (C-4); 77.4 (C-4''); 75.6 (C-2''); 75.3 (C-5''); 75.0 (Ph*C*H$_2$, Ph*C*H$_2$); 73.6 (C-2); 71.3 (C-6''); 68.7 (C-5); 67.9 (C-5'); 66.9 (C-2'); 61.1, 59.5, 58.2, 57.0 (O*C*H$_3$); 51.8 (COO*C*H$_3$); 33.1, 24.1, 19.0 (*C*H$_{2,linker}$); 18.2 (C-6); 17.6 (C-6'). IR (thin film, cm^{-1}): 1049, 1069, 1139, 1233, 1454, 1508, 1560, 1736, 2923, 3464. HRMS calculated for $C_{49}H_{64}O_{16}Na$ 931.4092 [M+Na]$^+$; found 931.4087.



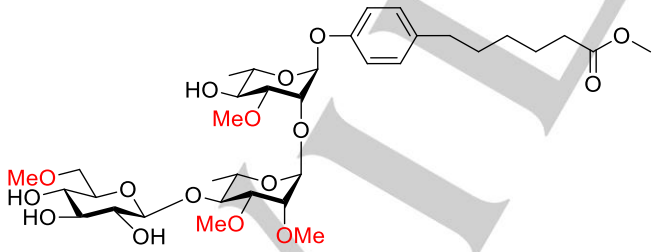
Methyl 6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)phenylhex-5-ynoate (10c) Compound **9c** (85 mg, 85 µmol, 1.0 eq) was dissolved in freshly distilled NEt$_3$ (1.79 mL, 0.05 M) together with methyl hex-5-ynoate (33 µL, 0.26 mmol, 3.0 eq). A cocktail of Pd(PPh$_3$)$_2$Cl$_2$ (28 mg), PPh$_3$ (22 mg) and CuI (15 mg) in freshly distilled NEt$_3$ was stirred for 15 minutes at 40 °C . Of this cocktail 0.21 mL was added to the reaction mixture, amounting to 0.1 eq Pd(PPh$_3$)$_2$Cl$_2$, 0.2 eq PPh$_3$ and 0.2 eq CuI. The reaction was left to stir overnight at 40 °C after which it was diluted with Et$_2$O and washed with 1 M HCl, sat. aq. NaHCO$_3$ and brine. The organic layer was dried with MgSO$_4$, filtered and concentrated. The product was purified by column chromatography (DCM-EtOAc 7:3) gave the title compound (70 mg, 70 µmol, 82%) as a yellow oil. [α]$_D^{25}$ -67.5 (c 1.0, CHCl$_3$). ^{1}H NMR (400 MHz) δ: 7.42-7.26 (m, 17H, C*H*$_{arom}$); 6.93 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 2.0 Hz, H-1); 5.16 (d, 1H, *J* = 1.6 Hz, H-1'); 5.02 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.90-4.82 (m, 3H, PhCH*H*, PhC*H*H, PhC*H*H); 4.66-4.59 (m, 2H, PhCH*H*, PhCH*H*); 4.40 (d, 1H, *J* = 6.8 Hz, H-1''); 4.19 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.83-3.65 (m, 4H, H-2', H-3, H-5', 2"-O*H*); 3.62-3.53 (m, 20H, H-2'', H-3', H-3'', H-4, H-4'', H-5, H-6'', OCH_3); 3.42-3.38 (m, 2H, H-4', H-5''); 3.35 (s, 3H, OCH_3); 2.53-2.45 (m, 4H, C$H_{2,Linker}$); 1.95-1.90 (m, 2H, C$H_{2,Linker}$); 1.36 (d, 3H, *J* = 6.0 Hz, H-6'); 1.25 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 173.8 (*C*OOCH$_3$); 155.6, 139.1, 138.5, 138.4 (C$_{q,arom}$); 133.1, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.6 (*C*H$_{arom}$); 117.6 (C$_{q,arom}$); 116.1 (*C*H$_{arom}$); 105.7 (C-1''); 96.8 (C-1'); 96.8 (C-1); 87.9 (C$_{q,alkyne}$); 84.8 (C-4''); 81.7 (C-3); 81.6 (C-3'); 81.1 (C$_{q,alkyne}$); 80.4 (C-3''); 80.1 (C-4'); 77.3 (C-2''); 76.2 (C-4); 75.9 (C-2'); 75.3 (C-5''); 75.2, 75.2, 75.0 (Ph*C*H$_2$); 73.8 (C-2); 71.4 (C-6''); 68.7 (C-5); 68.4 (C-5'); 59.5, 59.1, 58.3, 56.7 (O*C*H$_3$); 51.7 (COO*C*H$_3$); 33.0, 24.1, 19.0 (*C*H$_{2,Linker}$); 18.2 (C-6); 17.8 (C-6'). IR (thin film, cm^{-1}): 1000, 1055, 1070, 1120, 1203, 1233, 1286, 1454, 1507, 1605, 1736, 2932, 3453. HRMS calculated for $C_{56}H_{70}O_{16}Na$ 1021.4562 [M+Na]$^+$; found 1021.4556.



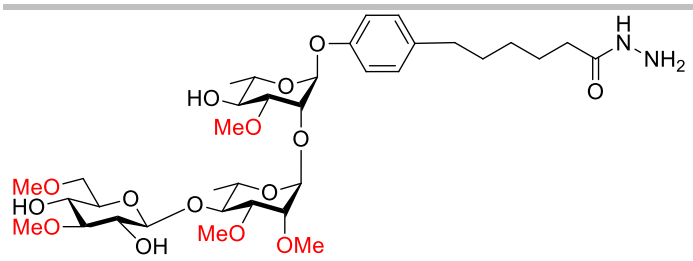
Methyl 6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranosyl)phenylhexanoate (11a) Compound **10a** (66 mg, 72 µmol, 1.0 eq) was dissolved in a mixture of THF and MeOH (1:1, 3 mL, 0.03 M) and the solution was purged with N_2. Palladium on carbon (10%, 15 mg, 14 µmol, 0.2 eq) was added to the solution. The solution was then purged with H_2 and stirred for 40 hours under H_2 atmosphere. The mixture was then purged with N_2, diluted with EtOAc, filtered over celite and concentrated. Purification by means of column chromatography (MeOH-DCM 1:9) gave the title compound (53 mg, 72 µmol, 100%) as a pale oil. $[\alpha]_D^{25}$ -46.6 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.09 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.97-6.94 (m, 2H, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 1.6 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.41 (d, 1H, *J* = 7.6 Hz, H-1''); 4.23 (dd, 1H, *J* = 2.0, 2.4 Hz, H-1); 3.90 (bs, 1H, 2''-O*H*); 3.79-3.72 (m, 3H, H-2', H-5, H-5'); 3.68-3.60 (m, 11H, H-3, H-3', H-4', H-6'', OC*H*$_3$, COOC*H*$_3$); 3.58-3.49 (m, 11H, H-4, H-4'', OC*H*$_3$); 3.48-3.38 (m, 5H, H-2'', H-5'', OC*H*$_3$); 3.17 (t, 1H, *J* = 9.0 Hz, H-3''); 2.56 (t, 2H, *J* = 7.8 Hz, C*H*$_{2,linker}$); 2.31 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 1.70-1.57 (m, 4H, C*H*$_{2,linker}$, C*H*$_{2,linker}$); 1.40-1.27 (m, 5H, C*H*$_{2,linker}$, H-6'); 1.25 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 174.4 (*C*OOCH$_3$); 154.3, 136.5 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 105.7 (C-1''); 98.5 (C-1'); 97.4 (C-1); 85.6 (C-3''); 81.7, 81.5 (C-3 and C-3'); 80.3 (C-4'); 75.8 (C-2'); 75.1, 74.2 (C-2'' and C-5''); 72.9 (C-6''); 72.2 (C-2); 71.9 (C-4); 71.2 (C-4''); 69.1, 68.4 (C-5 and C-5'); 60.7, 59.7, 59.2, 57.8, 56.7 (O*C*H$_3$); 51.6 (COO*C*H$_3$); 35.0, 34.1, 31.3, 28.8, 24.9 (*C*H$_{2,linker}$); 17.9 (C-6); 17.7 (C-6'). IR (thin film, cm^{-1}): 1009, 1067, 1120, 1201, 1228, 1454 1510, 1736, 1933, 3436. HRMS calculated for $C_{36}H_{58}O_{16}Na$ 769.3623 [M+Na]$^+$; found 769.3617.



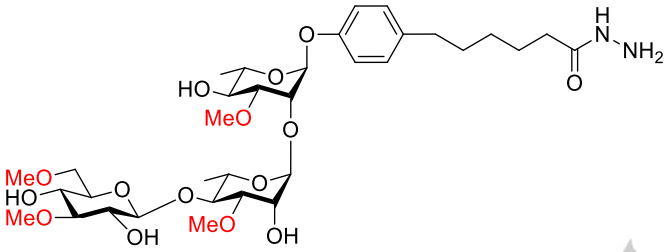
Methyl (6-(4-(2-*O*-(3-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-L-rhamnopyranosyl)phenylhexanoate (11b) Compound **10b** (35 mg, 38 µmol, 1.0 eq) was dissolved in a mixture of THF and MeOH (1:1, 3.8 mL, 0.01 M) and the solution was purged with N_2. Palladium on carbon (10%, 8 mg, 8 µmol, 0.2 eq) was added to the solution. The solution was then purged with H_2 and stirred overnight under H_2 atmosphere. The mixture was then purged with N_2, diluted with EtOAc, filtered over celite and concentrated. Purification by means of column chromatography (MeOH-DCM 3:17) gave the title compound (23 mg, 31 µmol, 82%) as a pale oil. $[\alpha]_D^{25}$ -63.0 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.09 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.94 (dd, 2H, *J* = 2.2, 6.6 Hz, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 1.6 Hz, H-1); 5.08 (d, 1H, *J* = 1.6 Hz, H-1'); 4.39 (d, 1H, *J* = 8.0 Hz, H-1''); 4.22-4.19 (m, 2H, H-2, H-2'); 3.83-3.72 (m, 2H, H-5, H-5'); 3.69-3.53 (m, 13H, H-3, H-3', H-4, H-4', H-4'', H-6'', COOC*H*$_3$, OC*H*$_3$); 3.51 (s, 6H, OC*H*$_3$); 3.45-3.39 (m, 5H, H-2'', H-5'', OC*H*$_3$); 3.18 (t, 1H, *J* = 9.0 Hz, H-3''); 2.91 (bs, 1H, O*H*); 2.56 (t, 2H, *J* = 7.8 Hz, C*H*$_{2,linker}$); 2.42 (bs, 1H, O*H*); 2.31 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 1.70-1.57 (m, 4H, C*H*$_{2,linker}$); 1.40-1.32 (m, 5H, H-6, C*H*$_{2,linker}$); 1.27 (d, 3H, *J* = 6.4 Hz, H-6'). ^{13}C-APT NMR (101 MHz) δ: 174.4 (*C*OOCH$_3$); 154.4, 136.5 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 105.6 (C-1''); 100.7 (C-1'); 97.4 (C-1''); 85.5 (C-3''); 81.3, 81.1 (C-3 and C-3'); 75.2, 74.3 (C-2'' and C-5''); 72.9 (C-6''); 72.5 (C-2); 71.8 (C-4); 71.3 (C-4''); 69.1 (C-5); 67.9 (C-5'); 66.9 (C-2'); 60.7, 59.8, 57.7, 56.9 (O*C*H$_3$); 51.6 (COO*C*H$_3$); 35.0, 34.1, 31.4, 28.9, 24.9 (*C*H$_{2,linker}$); 17.9 (C-6); 17.6 (C-6'). IR (thin film, cm^{-1}): 1013, 1065, 1122, 1202, 1228, 1261, 1455, 1510, 1736, 2858, 2931, 3426. HRMS calculated for $C_{35}H_{56}O_{16}Na$ 755.3466 [M+Na]$^+$; found 755.3457.



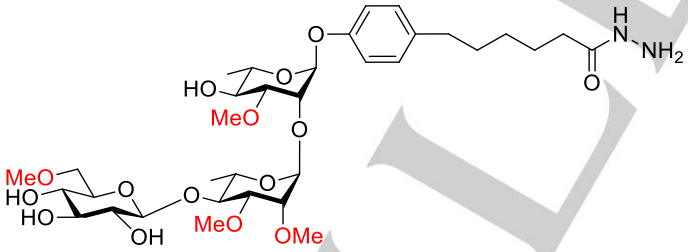
Methyl (6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranosyl)phenylhexanoate (11c) Compound **10c** (70 mg, 70 µmol, 1.0 eq) was dissolved in a mixture of THF and MeOH (1:1, 7 mL, 0.01 M) and the solution was purged with N_2. Palladium on carbon (10%, 15 mg, 14 µmol, 0.2 eq) was added to the solution. The solution was then purged with H_2 and stirred overnight under H_2 atmosphere. The mixture was then purged with N_2, diluted with EtOAc, filtered over celite and concentrated. Purification by means of column chromatography (MeOH-DCM 3:17) gave the title compound (46 mg, 63 µmol, 90%) as a pale oil. $[\alpha]_D^{25}$ -51.6 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.96-6.94 (m, 2H, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.45 (d, 1H, *J* = 7.6 Hz, H-1''); 4.22 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.79-3.72 (m, 3H, H-2', H-5, H-5'); 3.70-3.61 (m, 8H, H-3, H-3', H-4, H-6'', COOC*H*$_3$); 3.58-3.48 (m, 12H, H-3'', H-4', H-5'', OC*H*$_3$); 3.45-3.34 (m, 5H, H-2'', H-4'', OC*H*$_3$); 2.56 (t, 2H, *J* = 7.8 Hz, C*H*$_{2,linker}$); 2.31 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 1.70-1.57 (m, 4H, C*H*$_{2,linker}$, C*H*$_{2,linker}$); 1.40-1.32 (m, 5H, H-6, C*H*$_{2,linker}$); 1.27 (d, 3H, *J* = 6.0 Hz, H-6'). ^{13}C-APT NMR (101 MHz) δ: 174.4 (*C*OOCH$_3$); 154.3, 136.5 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 105.2 (C-1''); 98.5 (C-1'); 97.4 (C-1); 81.5, 81.3 (C-3 and C-3'); 80.2 (C-4); 76.6 (C-3''); 75.9 (C-2'); 74.8 (C-2''); 74.3 (C-4''); 72.9 (C-6''); 72.3 (C-2); 71.9 (C-4'); 71.5 (C-5''); 69.1, 68.3 (C-5 and C-5'); 59.8, 59.1, 57.8, 56.7 (O*C*H$_3$); 51.6 (COO*C*H$_3$); 35.0, 34.1, 31.3, 28.8, 24.9 (*C*H$_{2,linker}$); 17.9, 17.7 (C-6 and C-6'). IR (thin film, cm^{-1}): 1007, 1067, 1118, 1201, 1229, 1457, 1508, 1736, 2931, 3413. HRMS calculated for $C_{35}H_{56}O_{16}Na$ 755.3466 [M+Na]$^+$; found 755.3461.



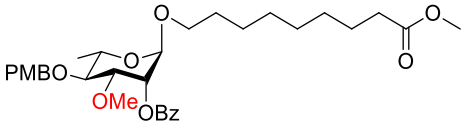
6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranosyl)phenyl)hexanohydrazide (12a) Compound **11a** (51 mg, 68 µmol, 1.0 eq) was dissolved in a mixture of EtOH and $N_2H_4 \cdot H_2O$ (1:2, 3 mL, 0.02 M) and stirred for 3 hours after which it was concentrated. Purification by means of column chromatography (MeOH-DCM 1:9) gave the title compound (45 mg, 60 µmol, 82%) as a pale oil. $[\alpha]_D^{25}$ -64.5 (c 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.94-6.92 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 2.0 Hz, H-1); 5.09 (d, 1H, *J* = 2.0 Hz, H-1'); 4.54 (d, 1H, *J* = 8.0 Hz, H-1''); 4.22 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.78-3.74 (m, 2H, H-2', H-5'); 3.68-3.54 (m, 12H, H-3, H-3', H-4', H-5, H-6'', OC*H*$_3$, COOC*H*$_3$); 3.49-3.44 (m, 7H, H-4, OC*H*$_3$); 3.37 (s, 3H, OC*H*$_3$); 3.34-3.29 (m, 2H, H-4'', H-5''); 3.19 (t, 1H, *J* = 7.6 Hz, H-2''); 3.09 (t, 1H, *J* = 8.4 Hz, H-3''); 2.55 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 2.13 (t, 2H, *J* = 7.4 Hz, C*H*$_{2,linker}$); 1.62-1.58 (m, 4H, C*H*$_{2,linker}$); 1.32-1.27 (m, 4H, C*H*$_{2,linker}$); 1.24-1.21 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 175.3 (*C*ONHNH$_2$); 155.9, 137.8 (C$_{q,arom}$); 130.5, 117.4 (*C*H$_{arom}$); 104.8 (C-1''); 100.4 (C-1'); 98.9 (C-1); 87.6 (C-3''); 82.1, 81.9 (C-3 and C-3'); 79.1 (C-4'); 77.7 (C-2''); 76.7 (C-5''); 76.0 (C-2); 75.4 (C-2''); 73.3 (C-4); 73.0 (C-6''); 71.2 (C-4''); 70.7 (C-5); 69.1 (C-5'); 61.0, 59.8, 59.1, 58.5, 57.5 (O*C*H$_3$); 35.8, 34.9, 32.4, 29.7, 26.7 (*C*H$_{2,linker}$); 18.3, 18.2 (C-6 and C-6'). IR (thin film, cm^{-1}): 1068, 1119, 1201, 1228, 1294, 1387, 1452, 1510, 2931, 3398. HRMS calculated for $C_{35}H_{58}N_2O_{15}Na$ 769.3735 [M+Na]$^+$; found 769.3729.



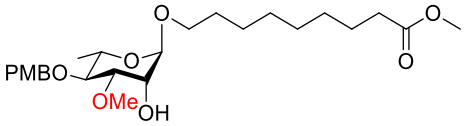
6-(4-(2-*O*-(3-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranosyl)phenyl)hexanohydrazide (12b) Compound **11b** (23 mg, 31 µmol, 1.0 eq) was dissolved in a mixture of EtOH and $N_2H_4 \cdot H_2O$ (1:2, 3 mL, 0.01 M) and stirred for 3 hours after which it was concentrated. Purification by means of column chromatography (MeOH-DCM 1:4) gave the title compound (23 mg, 31 µmol, 100%) as a pale oil. $[\alpha]_D^{25}$ -52.9 (c 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.93 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 4.98 (d, 1H, *J* = 1.6 Hz, H-1'); 4.56 (d, 1H, *J* = 8.0 Hz, H-1''); 4.20 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 4.13 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2'); 3.80-3.76 (m, 1H, H-5'); 3.70-3.45 (m, 15H, H-3, H-3', H-4, H-5, H-6'', OC*H*$_3$); 3.37-3.29 (m, 5, H-4'', H-5'', OC*H*$_3$); 3.20 (dd, 1H, *J* = 7.8, 9.0 Hz, H-2''); 3.07 (t, 1H, *J* = 8.2 Hz, H-3''); 2.55 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 2.13 (t, 2H, *J* = 7.4 Hz, C*H*$_{2,linker}$); 1.64-1.58 (m, 4H, C*H*$_{2,linker}$); 1.39-1.21 (m, 8H, H-6, H-6', C*H*$_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 175.4 (*C*ONHNH$_2$); 155.9, 137.8 (C$_{q,arom}$); 130.5, 117.4 (*C*H$_{arom}$); 105.0 (C-1''); 103.5 (C-1'); 98.9 (C-1); 87.6 (C-3''); 82.1 (C-3'); 81.7 (C-3); 79.1 (C-4'); 76.8 (C-5''); 75.7 (C-2); 75.5 (C-2''); 73.2 (C-4); 73.0 (C-6''); 71.2 (C-4''); 70.7 (C-5); 69.1 (C-5'); 67.8 (C-2'); 60.9, 59.8, 58.3, 57.0 (O*C*H$_3$); 35.8, 34.9, 32.4, 29.7, 26.7 (*C*H$_{2,linker}$); 18.2 (C-6); 18.2 (C-6'). IR (thin film, cm^{-1}): 1017, 1063, 1116, 1228, 1248, 1268, 1454, 1510, 1637, 2926, 3386. HRMS calculated for $C_{34}H_{56}N_2O_{15}Na$ 755.3578 [M+Na]$^+$; found 733.3754.



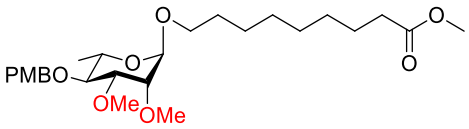
6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranosyl)phenyl)hexanohydrazide (12c) Compound **11c** (46 mg, 63 µmol, 1.0 eq) was dissolved in a mixture of EtOH and $N_2H_4 \cdot H_2O$ (1:2, 3 mL, 0.02 M) and stirred for 3 hours after which it was concentrated. Purification by means of column chromatography (MeOH-DCM 1:4) gave the title compound (39 mg, 53 µmol, 84%) as a pale oil. $[\alpha]_D^{25}$ -42.9 (c 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.95-6.92 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.54 (d, 1H, *J* = 7.6 Hz, H-1''); 4.22 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.78-3.74 (m, 2H, H-2, H-5); 3.70-3.54 (m, 9H, H-3, H-3', H-4, H-5, H-6'', OC*H*$_3$); 3.49-3.44 (m, 7H, H-4', OC*H*$_3$); 3.37-3.24 (m, 6H, H-3'', H-4'', H-5'', OC*H*$_3$); 3.15 (dd, 1H, *J* = 8.0, 8.8 Hz, H-2''); 2.55 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 2.13 (t, 2H, *J* = 7.4 Hz, C*H*$_{2,linker}$); 1.66-1.56 (m, 4H, C*H*$_{2,linker}$, C*H*$_{2,linker}$); 1.36-1.27 (m, 2H, C*H*$_{2,linker}$); 1.25-1.21 (m, 6H, H-6, H-6'); ^{13}C-APT NMR (101 MHz) δ: 175.3 (*C*OOCH$_3$); 155.9, 137.8 (C$_{q,arom}$); 130.5, 117.4 (*C*H$_{arom}$); 104.8 (C-1''); 100.4 (C-1'); 98.9 (C-1); 82.1, 81.9 (C-3 and C-3'); 79.0 (C-4); 77.9 (C-4''); 77.7 (C-2'); 76.9 (C-3''); 76.0 (C-2); 75.5 (C-2''); 73.3 (C-4'); 73.1(C-6''); 71.7 (C-5''); 70.7 (C-5'); 69.1 (C-5); 59.8, 59.1, 58.5, 57.5 (O*C*H$_3$); 35.8, 32.4, 29.7, 26.7 (*C*H$_{2,linker}$); 18.3 (C-6); 18.2 (C-6'). IR (thin film, cm^{-1}): 1012, 1066, 1116, 1201, 1228, 1387, 1457, 1510, 1656, 1731, 2932, 3380. HRMS calculated for $C_{34}H_{57}N_2O_{15}$ 733.3759 [M+H]$^+$; found 733.37462.



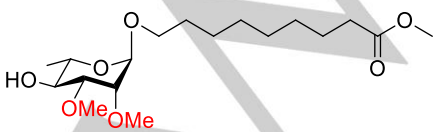
Methyl 9-(2-*O*-benzoyl-3-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)nonanoate (14) Donor **2** (148 mg, 0.30 mmol, 1.0 eq), Ph_2SO (79 mg, 0.39 mmol, 1.3 eq) and TTBP (186 mg, 0.75 mmol, 2.5 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (6 mL, 0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -60 °C after which Tf_2O (65 µL, 0.39 mmol, 1.3 eq) was added. After stirring for 30 minutes, methyl 9-hydroxylnonanoate[5] (282 mg, 1.5 mmol, 5.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (3.8 mL, 0.4 M) and added to the solution. After stirring for 1 hour the reaction was quenched by addition of NEt_3 (0.3 mL). The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 4:1) gave the title compound (136 mg, 0.24 mmol, 79%) as a pale oil. $[\alpha]_D^{25}$ -5.6 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.11-8.09 (m, 2H, C*H*$_{arom}$); 7.58-7.56 (m, 1H, C*H*$_{arom}$); 7.48-7.44 (m, 2H, C*H*$_{arom}$); 7.31-7.26 (m, 2H, C*H*$_{arom}$); 6.90-6.86 (m, 2H, C*H*$_{arom}$); 5.52 (dd, 1H, *J* = 1.8, 3.4 Hz, H-2); 4.85-4.81 (m, 2H, H-1, PhC*H*H); 3.80-3.75 (m, 5H, H-3, H-5, OC*H*$_3$); 3.68-3.62 (m, 4H, C*H*H$_{linker}$, OC*H*$_3$); 3.48-3.37 (m, 5H, H-4, CH*H*$_{linker}$, OC*H*$_3$); 2.30 (t, 2H, *J* = 7.4 Hz, C*H*$_{2,linker}$); 1.64-1.53 (m, 4H, C*H*$_{2,linker}$); 1.35-1.26 (m, 12H, H-6, C*H*$_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.4 (*C*OOCH$_3$); 165.9 (*C*O$_{Bz}$); 159.4 (C$_{q,arom}$); 133.3 (*C*H$_{arom}$); 130.8, 130.1 (C$_{q,arom}$); 130.0, 129.9, 128.5, 113.9 (*C*H$_{arom}$); 97.7 (C-1); 80.4 (C-4); 79.9 (C-3); 75.1 (Ph*C*H$_2$); 69.3 (C-2); 68.0 (O*C*H$_{2,linker}$); 67.6 (C-5); 57.5 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 34.2, 29.5, 29.3, 29.2, 29.2, 26.2, 25.0 (*C*H$_{2,linker}$); 18.3 (C-6). IR (thin film, cm^{-1}): 1003, 1027, 1070, 1099, 1112, 1173, 1193, 1251, 1269, 1319, 1364, 1452, 1514, 1724, 2855, 2925. HRMS calculated for $C_{32}H_{44}O_9Na$ 595.2883 $[M+Na]^+$; found 595.2879.



Methyl 9-(3-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)nonanoate (15) Compound **14** (264 mg, 0.46 mmol, 1.0 eq) was dissolved in THF (2.3 mL, 0.2 M). A small piece of sodium was dissolved in MeOH and 2.3 mL of this solution was added and the reaction was stirred for 2 hours. The reaction was then quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x), the organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (Et_2O) gave the title compound (210 mg, 0.45 mmol, 97%) as a pale oil. $[\alpha]_D^{25}$ -36.5 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.30-7.26 (m, 2H, C*H*$_{arom}$); 6.90-6.86 (m, 2H, C*H*$_{arom}$); 4.78 (s, 1H, H-1); 4.66 (dd, 2H, *J* = 10.6, 87.4 Hz, PhC*H*$_2$); 4.02 (dd, 1H, *J* = 1.6, 3.6 Hz, H-2); 3.81 (s, 3H, C*H*$_{3,PMB}$); 3.69-3.59 (m, 5H, H-5, OC*H*H$_{linker}$, COOC*H*$_3$); 3.56-3.51 (m, 4H, H-3, OC*H*$_3$); 3.41-3.31 (m, 2H, H-4, OCH*H*$_{linker}$); 2.41 (bs, 1H, 2-O*H*); 2.30 (t, 2H, *J* = 7.4 Hz, C*H*$_{2,linker}$); 1.61 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,linker}$); 1.53 (t, 2H, *J* = 6.6 Hz, C*H*$_{2,linker}$); 1.29-1.27 (m, 11H, H-6, C*H*$_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.5 (*C*OOCH$_3$); 159.4, 130.8 (C$_{q,arom}$); 129.8, 113.9 (*C*H$_{arom}$); 99.1 (C-1); 81.9 (C-3); 79.7 (C-4); 75.1 (Ph*C*H$_2$); 68.2 (C-2); 67.7 (O*C*H$_{2,linker}$); 67.2 (C-5); 57.6 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 51.6 (COO*C*H$_3$); 34.2, 29.6, 29.3, 29.3, 29.2, 26.2, 25.1 (*C*H$_{2,linker}$); 18.0 (C-6). IR (thin film, cm^{-1}): 1073, 1079, 1083, 1109, 1113, 1251, 1457, 1514, 1734, 2916, 3490. HRMS calculated for $C_{25}H_{40}O_8Na$ 491.2621 $[M+Na]^+$; found 491.2615.

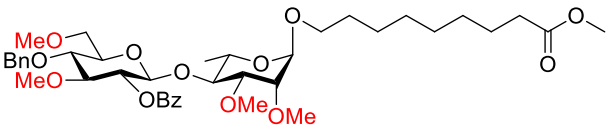


Methyl 9-(2,3-di-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)nonanoate (16) Compound **15** (105 mg, 0.22 mmol, 1.0 eq) was dissolved in dry DMF (1.5 mL, 0.15 M) and MeI (42 µL, 0.67 mmol, 3.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 27 mg, 0.67 mmol, 3.0 eq) was then added. The reaction mixture was warmed to rt while stirring for 1 hour after which it was quenched by addition of MeOH, and partitioned between water and Et_2O. The aqueous layer was extracted with Et_2O (3x) and the organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 4:6) gave the title compound (98 mg, 0.20 mmol, 91%) as a pale oil. $[\alpha]_D^{25}$ -41.5 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.30-7.27 (m, 2H, C*H*$_{arom}$); 6.89-6.86 (m, 2H, C*H*$_{arom}$); 4.83 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.81 (s, 1H, H-1); 4.53 (d, 1H, *J* = 10.4 Hz, PhCH*H*); 3.80 (s, 3H, C*H*$_{3,PMB}$); 3.66-3.42 (m, 13H, H-2, H-3, H-5, OC*H*H$_{linker}$, COOC*H*$_3$, OC*H*$_3$); 3.40-3.34 (m, 2H, H-4, OCH*H*$_{linker}$); 2.30 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,linker}$); 1.62 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,linker}$); 1.54 (t, 2H, *J* = 6.4 Hz, C*H*$_{2,linker}$); 1.30-1.27 (m, 11H, H-6, C*H*$_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.4 (*C*OOCH$_3$); 159.3, 131.0 (C$_{q,arom}$); 129.8, 113.9 (*C*H$_{arom}$); 96.9 (C-1); 81.7 (C-3); 80.3 (C-4); 77.7 (C-2); 75.1 (*C*H$_{3,PMB}$); 67.7 (O*C*H$_{2,linker}$); 67.7 (C-5); 59.2, 57.9 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 51.6 (COO*C*H$_3$); 34.2, 29.6, 29.3, 29.3, 29.2, 26.2, 25.0 (*C*H$_{2,linker}$); 18.0 (C-6). IR (thin film, cm^{-1}): 1036, 1072, 1093, 1120, 1142, 1173, 1198, 1249, 1457, 1464, 1514, 1739, 2932. HRMS calculated for $C_{26}H_{42}O_8Na$ 505.2777 $[M+Na]^+$; found 505.2771.

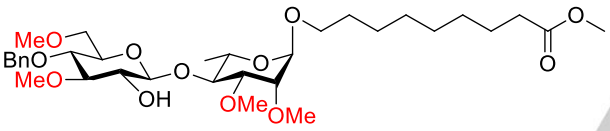


Methyl 9-(2,3-di-*O*-methyl-α-L-rhamnopyranosyl)nonanoate[6] (17) Compound **16** (98 mg, 0.20 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 2 mL, 0.1 M) after which a solution of HCl in HFIP (0.1 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, indicated by a dark purple colour, the reaction was quenched by addition of sat. aq. $NaHCO_3$. The mixture was diluted with DCM, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 1:4) gave the title compound (70 mg, 0.19 mmol, 95%) as a pale oil. ^{1}H NMR (400 MHz) δ: 4.85 (d, 1H, *J* = 1.2 Hz, H-1); 3.70-3.60 (m, 6H, H-2, H-5, OC*H*H$_{linker}$, COOC*H*$_3$); 3.56 (t, 1H, *J* = 9.4 Hz, H-4); 3.50 (s, 3H, OC*H*$_3$); 3.47 (s, 3H, OC*H*$_3$); 3.44-3.37 (m, 2H, H-3, OCH*H*$_{linker}$); 2.31 (t, 2H, *J* = 7.6 Hz, OC*H*$_{2,linker}$); 1.64-

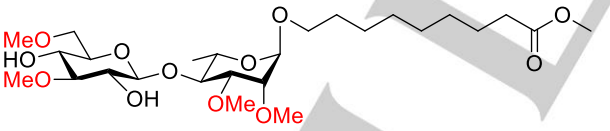
1.54 (m, 4H, C$H_{2,linker}$); 1.38-1.31 (m, 11H, H-6, C$H_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.5 (C$OOCH_3$); 97.2 (C-1); 81.2 (C-3); 76.1 (C-2); 71.9 (C-4); 68.2 (C-5); 67.8 (O$CH_{2,linker}$); 59.1, 57.1 (OCH_3); 51.6 (COOCH_3); 34.2, 29.6, 29.4, 29.3, 29.2, 26.3, 25.1 (C$H_{2,linker}$); 17.8 (C-6).



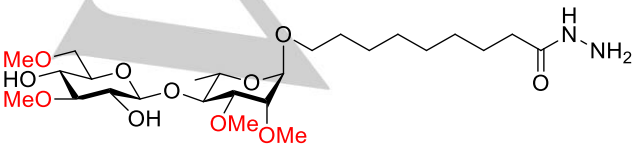
Methyl 9-(2,3-di-*O*-methyl-4-O-(2-*O*-benzoyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)nonanoate (18) Donor **13a** (230 mg, 0.47 mmol, 1.5 eq), Ph_2SO (123 mg, 0.61 mmol, 2.0 eq) and TTBP (291 mg, 1.17 mmol, 3.8 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (9 mL, 0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -60 °C after which Tf_2O (102 µL, 0.61 mmol, 2.0 eq) was added to the solution. After stirring for 30 minutes, acceptor **17** (122 mg, 0.31 mmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.75 mL, 0.4 M) and added to the solution. After stirring for 1.5 hours the reaction was quenched by addition of NEt_3 (0.3 mL). The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 7:3) gave the title compound (194 mg, 0.26 mmol, 84%) as a pale oil. $[\alpha]_D^{25}$ -29.5 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 8.14-8.12 (m, 2H, CH_{arom}); 7.59-7.55 (m, 1H, CH_{arom}); 7.47-7.44 (m, 2H, CH_{arom}); 7.35-7.27 (m, 5H, CH_{arom}); 5.14 (dd, 1H, *J* = 8.0, 9.6 Hz, H-2'); 4.85-4.82 (m, 2H, H-1', PhC*H*H); 4.77 (d, 1H, *J* = 1.6 Hz, H-1); 4.66 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 3.72-3.40 (m, 21H, H-2, H-3, H-3', H-4', H-5, H-5', H-6', OCH_{linker}, COOCH_3, OCH_3); 3.34-3.27 (m, 2H, H-4, OCHH_{linker}); 3.08 (s, 3H, OCH_3); 2.30 (t, 2H, *J* = 7.4 Hz, C$H_{2,linker}$); 1.62 (t, 2H, *J* = 7.2 Hz, C$H_{2,linker}$); 1.52 (t, 2H, 6.6 Hz, C$H_{2,linker}$); 1.31-1.25 (m, 11H, H-6, C$H_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.4 (C$OOCH_3$); 165.3 (CO_{Bz}); 138.4 (C$_{q,arom}$); 133.1 (CH_{arom}); 130.3 (C$_{q,arom}$); 129.9, 128.5, 128.5, 128.2, 127.9 (CH_{arom}); 101.4 (C-1'); 96.6 (C-1); 85.3 (C-3'); 80.9 (C-4); 77.8 (C-5'); 77.5 (C-3); 76.6 (C-2); 75.0 (PhCH_2); 74.8 (C-4'); 74.3 (C-2'); 71.2 (C-6'); 67.8 (O$CH_{2,linker}$); 60.8, 59.8, 59.0, 56.7 (OCH_3); 51.6 (COOCH_3); 34.2, 29.8, 29.4, 29.3, 29.2, 29.2, 26.1, 25.0 (C$H_{2,linker}$); 18.0 (C-6). IR (thin film, cm^{-1}): 1029, 1057, 1072, 1090, 1116, 1143, 1268, 1733. HRMS calculated for $C_{40}H_{58}O_{13}Na$ 769.3775 $[M+Na]^+$; found 769.3770.



Methyl 9-(2,3-di-*O*-methyl-4-O-(3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)nonanoate (19) Compound **18** (116 mg, 0.155 mmol, 1.0 eq) was dissolved in THF (0.8 mL, 0.2 M). A small piece of sodium was dissolved in MeOH and 0.8 mL of this solution was added. The reaction was stirred for 2 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated. Purification by means of column chromatography (pentane-Et_2O 3:7) gave the title compound (82 mg, 0.128 mmol, 82%) as a pale oil. $[\alpha]_D^{25}$ -21.7 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.34-7.27 (m, 5H, CH_{arom}); 4.86-4.82 (m, 2H, H-1, PhC*H*H); 4.61 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.37 (d, 1H, *J* = 7.6 Hz, H-1'); 3.91 (bs, 1H, 2'-O*H*); 3.68-3.54 (m, 13H, H-2, H-3, H-4, H-5, H-6', OCH_3, COOCH_3); 3.51-3.35 (m, 13H, H-2', H-4', H-5', OCH_3); 3.28 (t, 1H, *J* = 9.0 Hz, H-3'); 2.31 (t, 2H, *J* = 7.6 Hz, C$H_{2,linker}$); 1.65-1.35 (m, 4H, C$H_{2,linker}$); 1.31-1.23 (m, 11H, H-6, C$H_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.4 (C$OOCH_3$); 138.4 (C$_{q,arom}$); 128.5, 128.1, 127.9 (CH_{arom}); 105.8 (C-1'); 96.9 (C-1); 86.5 (C-3'); 82.0 (C-3); 80.7 (C-4); 77.3 (C-4'); 76.0 (C-2); 75.6 (C-2'); 75.2 (C-5'); 75.0 (PhCH_2); 71.3 (C-6'); 67.9 (O$CH_{2,linker}$); 67.6 (C-5); 61.0, 59.5, 59.1 56.6 (OCH_3); 51.6 (COOCH_3); 34.2, 29.6, 29.3, 29.2, 29.2, 26.2, 25.0 (C$H_{2,linker}$); 17.7 (C-6). IR (thin film, cm^{-1}): 1029, 1070, 1118, 1143, 1192, 1251, 1269, 1454, 1736, 2856, 2928, 3476. HRMS calculated for $C_{33}H_{54}O_{12}Na$ 665.3513 $[M+Na]^+$; found 665.3500.



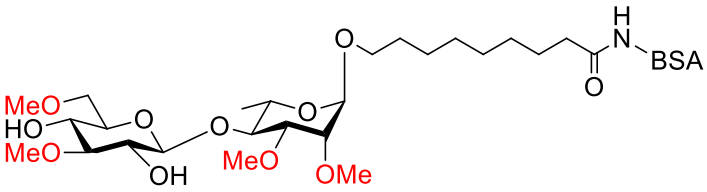
Methyl 9-(2,3-di-*O*-methyl-4-O-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)nonanoate[6] (20) Compound **19** (49 mg, 76 µmol, 1.0 eq) was dissolved in THF (1.5 mL, 0.05 M) and the solution was purged with N_2. Palladium on carbon (10%, 8 mg, 7.6 µmol, 0.1 eq) was added to the solution. The solution was then purged with H_2 and stirred overnight under H_2 atmosphere. The mixture was then purged with N_2, diluted with EtOAc, filtered over celite and concentrated. Purification by means of column chromatography (MeOH-DCM 1:19) gave the title compound (40 mg, 72 µmol, 95%) as a pale oil. ^{1}H NMR (400 MHz) δ: 7.34-7.27 (m, 5H, CH_{arom}); 4.86-4.82 (m, 2H, H-1, PhC*H*H); 4.61 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.37 (d, 1H, *J* = 7.6 Hz, H-1'); 3.91 (bs, 1H, 2'-O*H*); 3.68-3.54 (m, 13H, H-2, H-3, H-4, H-5, H-6', OCH_3, COOCH_3); 3.51-3.35 (m, 13H, H-2', H-4', H-5', OCH_3, OCH_3, OCH_3,); 3.28 (t, 1H, *J* = 9.0 Hz, H-3'); 2.31 (t, 2H, *J* = 7.6 Hz, C$H_{2,linker}$); 1.65-1.35 (m, 4H, C$H_{2,linker}$); 1.31-1.23 (m, 11H, H-6, C$H_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 174.4 (C$OOCH_3$); 138.4 (C$_{q,arom}$); 128.5, 128.1, 127.9 (CH_{arom}); 105.8 (C-1'); 96.9 (C-1); 86.5 (C-3'); 82.0 (C-3); 80.7 (C-4); 77.3 (C-4'); 76.0 (C-2); 75.6 (C-2'); 75.2 (C-5'); 75.0 (PhCH_2); 71.3 (C-6'); 67.9 (O$CH_{2,linker}$); 67.6 (C-5); 61.0, 59.5, 59.1 56.6 (OCH_3); 51.6 (COOCH_3); 34.2, 29.6, 29.3, 29.2, 29.2, 26.2, 25.0 (C$H_{2,linker}$); 17.7 (C-6).



9-(2,3-di-*O*-methyl-4-O-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)nonanohydrazide[6] (21) Compound **20** (17 mg, 31 µmol, 1.0 eq) was dissolved in a mixture of EtOH and $N_2H_4 \cdot H_2O$ (1:2, 1.5 mL, 0.02 M) and stirred for 3 hours after which it was concentrated. Purification by means of column

chromatography (MeOH-DCM 1:9) gave the title compound (17 mg, 31 µmol, 100%) as a pale oil. ^{1}H NMR (400 MHz, CD_3OD) δ: 4.80 (d, 1H, *J* = 1.6 Hz, H-1); 4.53 (d, 1H, *J* = 7.6 Hz, H-1'); 3.68-3.54 (m, 9H, H-2, H-3, H-4, H-6', OC*H*H$_{linker}$, OC*H*$_3$); 3.44-3.40 (m, 7H, OCH*H*$_{linker}$, OC*H*$_3$, OC*H*$_3$); 3.37 (s, 3H, OC*H*$_3$); 3.35-3.20 (m, 2H, H-4', H-5'); 3.18 (dd, 1H, *J* = 8.0, 9.2 Hz, H-2''); 3.06 (dd, 1H, *J* = 8.4, 9.2 Hz, H-3'); 2.13 (t, 2H, *J* = 7.4 Hz, C*H*$_{2,linker}$); 1.63-1.54 (m, 4H, C*H*$_{2,linker}$); 1.39-1.21 (m, 11H, H-6, C*H*$_{2,linker}$). ^{13}C-APT NMR (101 MHz) δ: 175.3 (*C*ONHNH$_2$); 104.9 (C-1'); 98.3 (C-1); 87.6 (C-3'); 82.4 (C-3); 79.4 (C-4); 77.8 (C-2); 76.7 (C-5'); 75.5 (C-2'); 73.0 (C-6'); 71.2 (C-4'); 68.8 (O*C*H$_{2,linker}$); 68.5 (C-5); 61.0, 59.8, 59.1 (O*C*H$_3$); 35.0, 30.6, 30.3, 30.2, 29.3, 26.8 (*C*H$_{2,linker}$); 18.3 (C-6).

MALDIs



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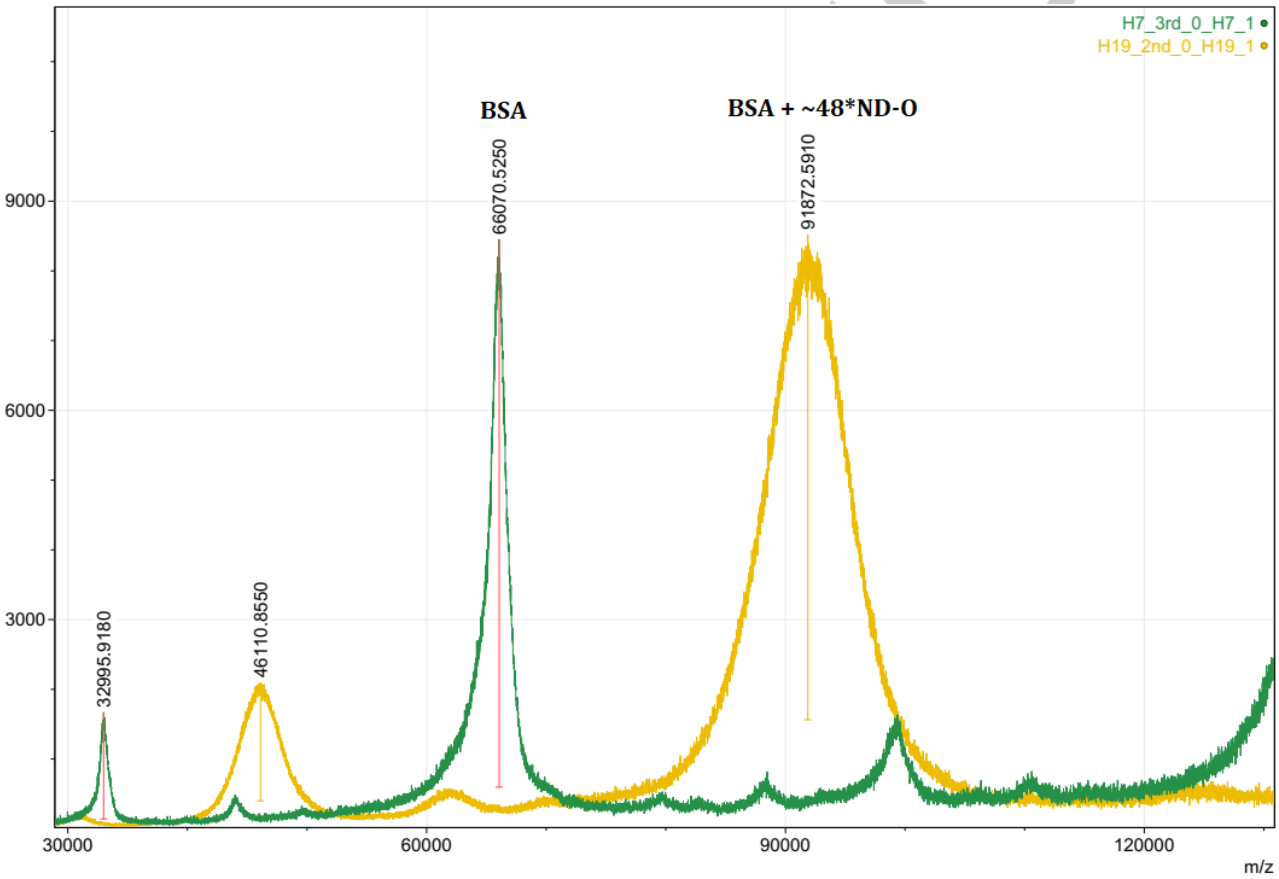

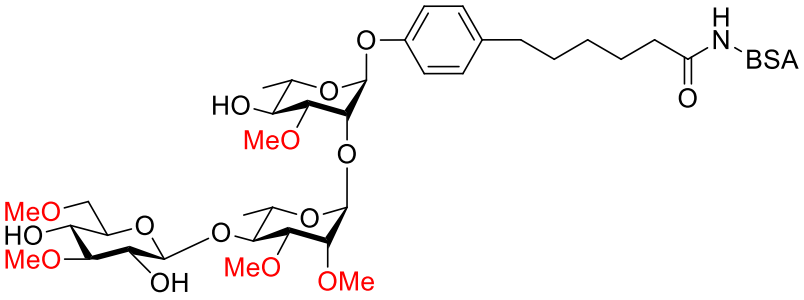
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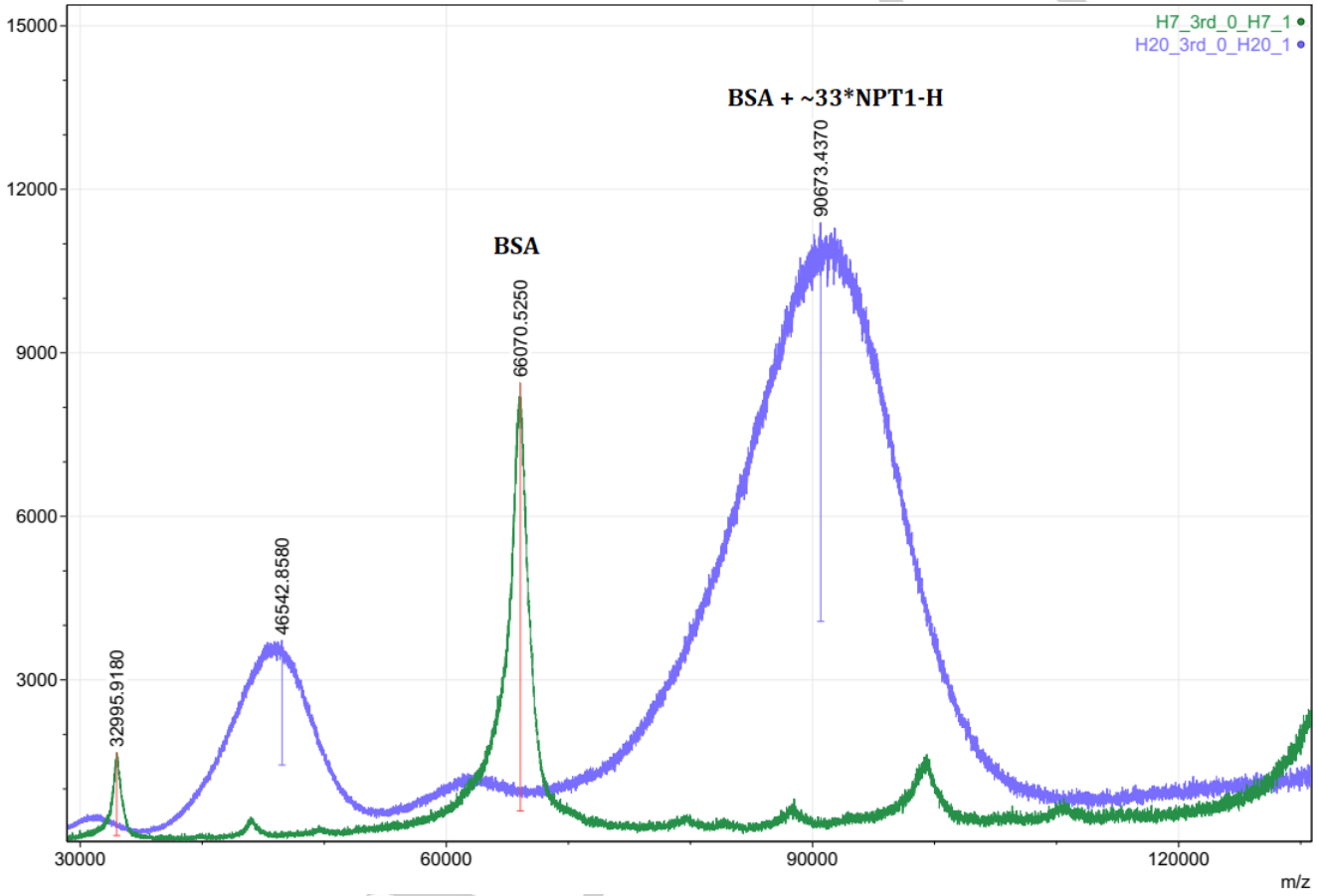
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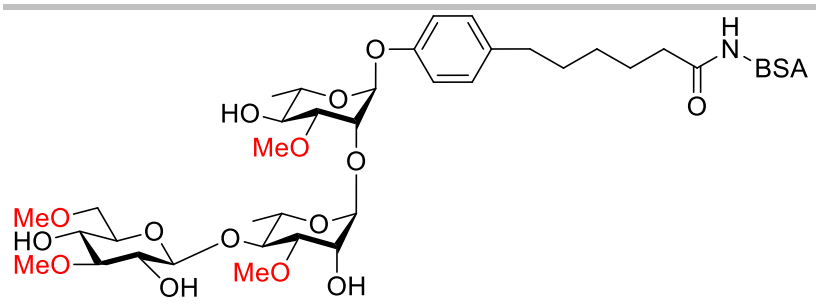
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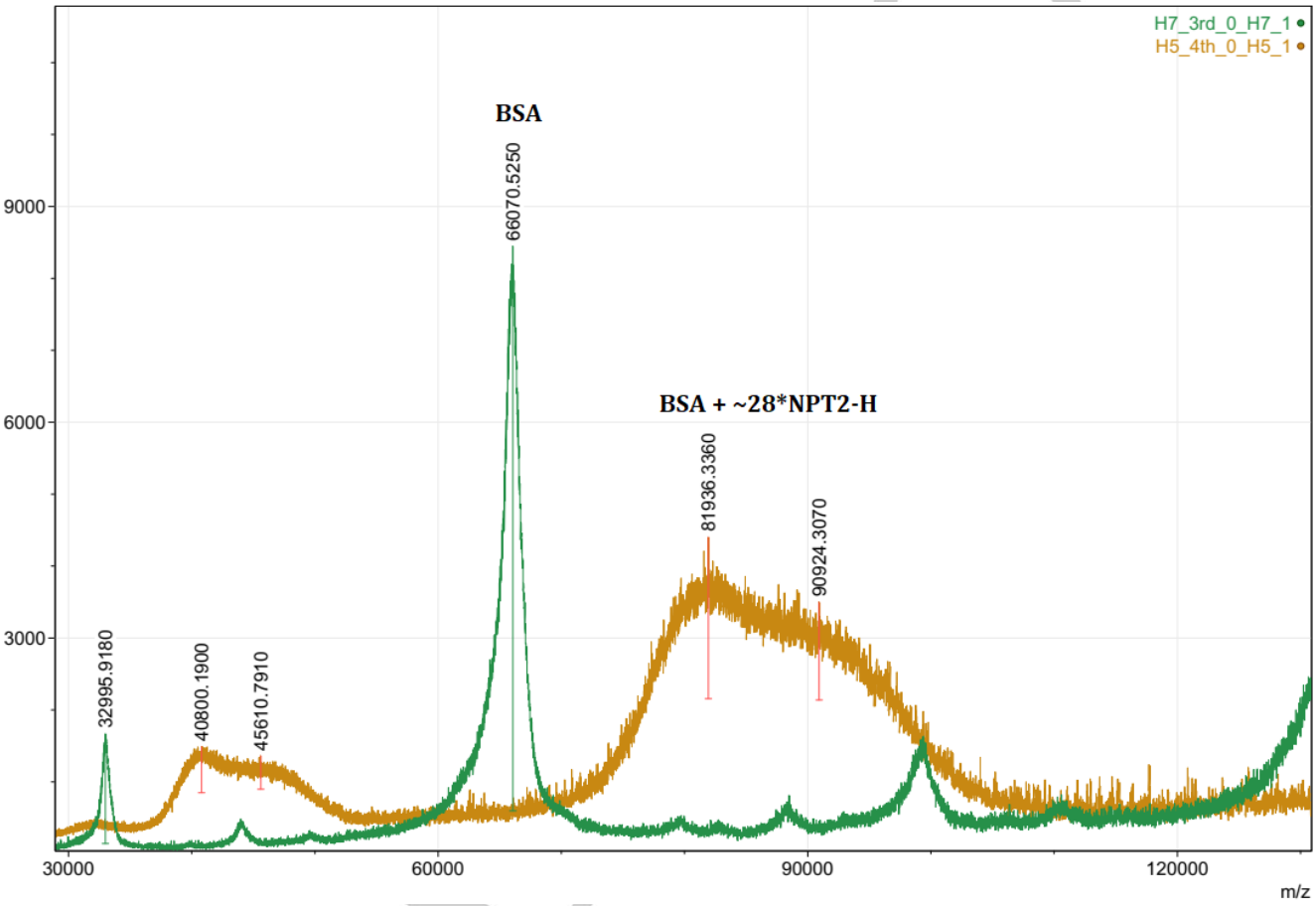
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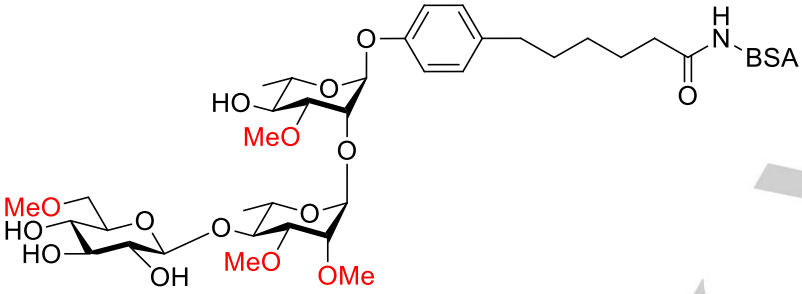
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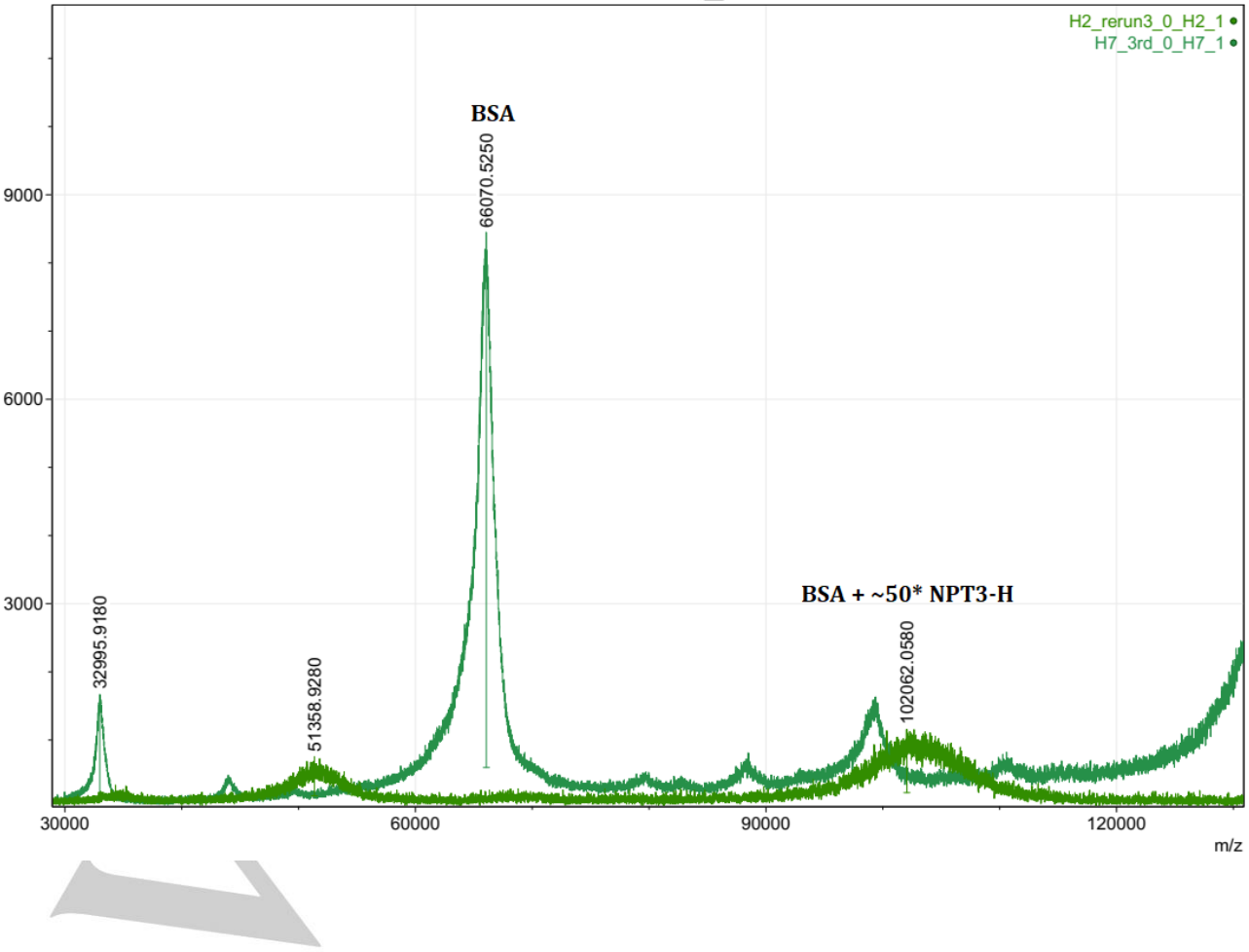
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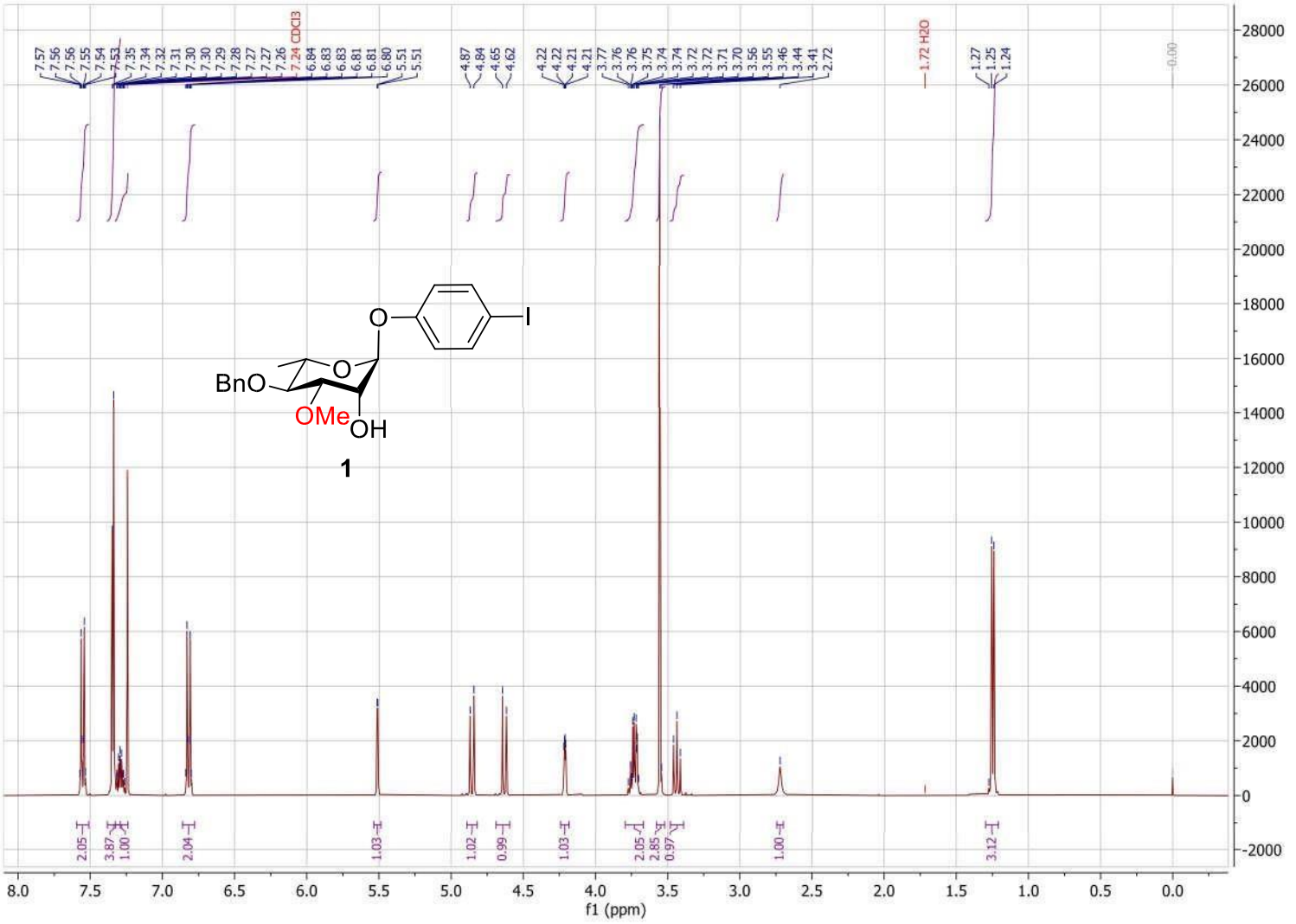
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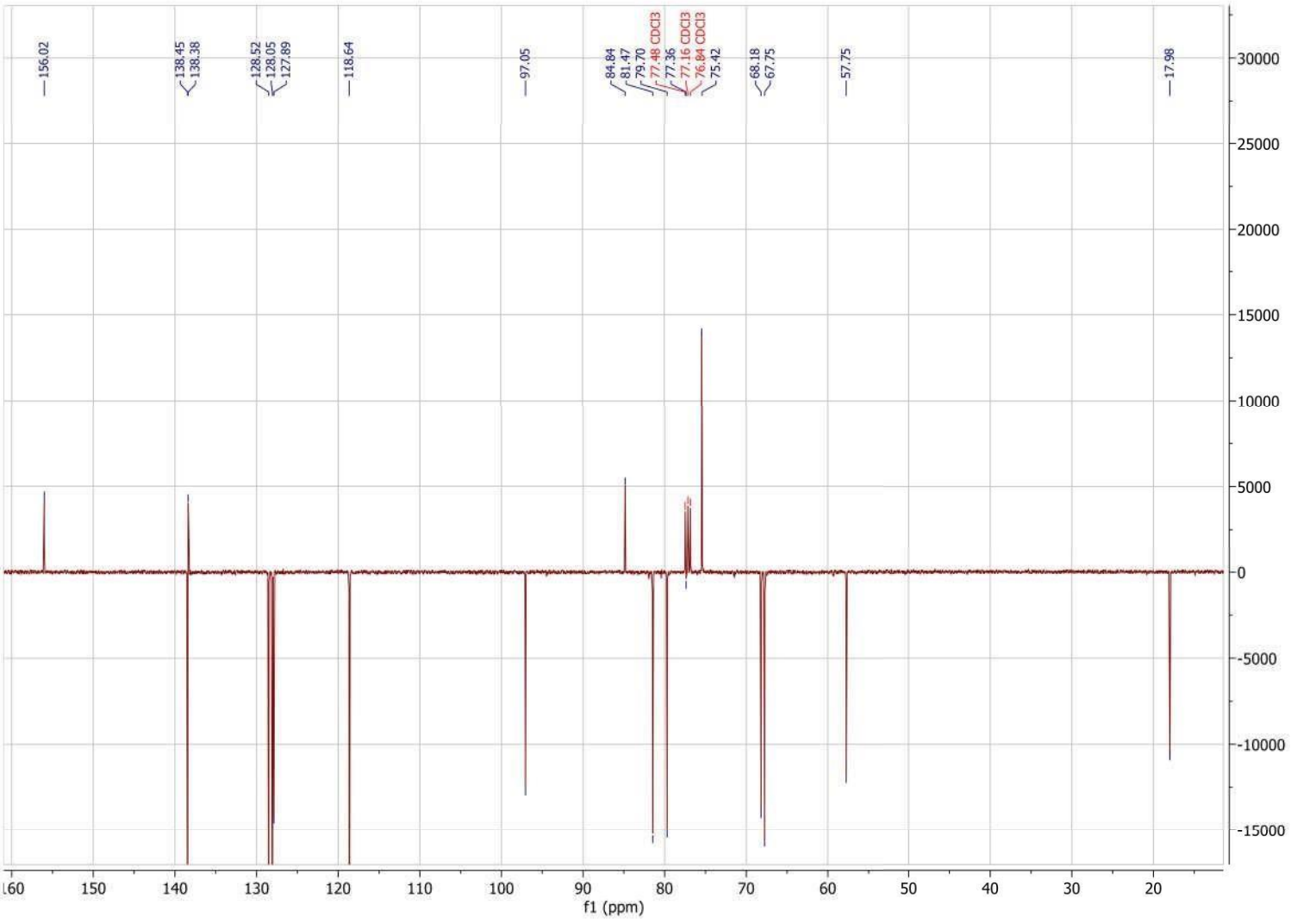
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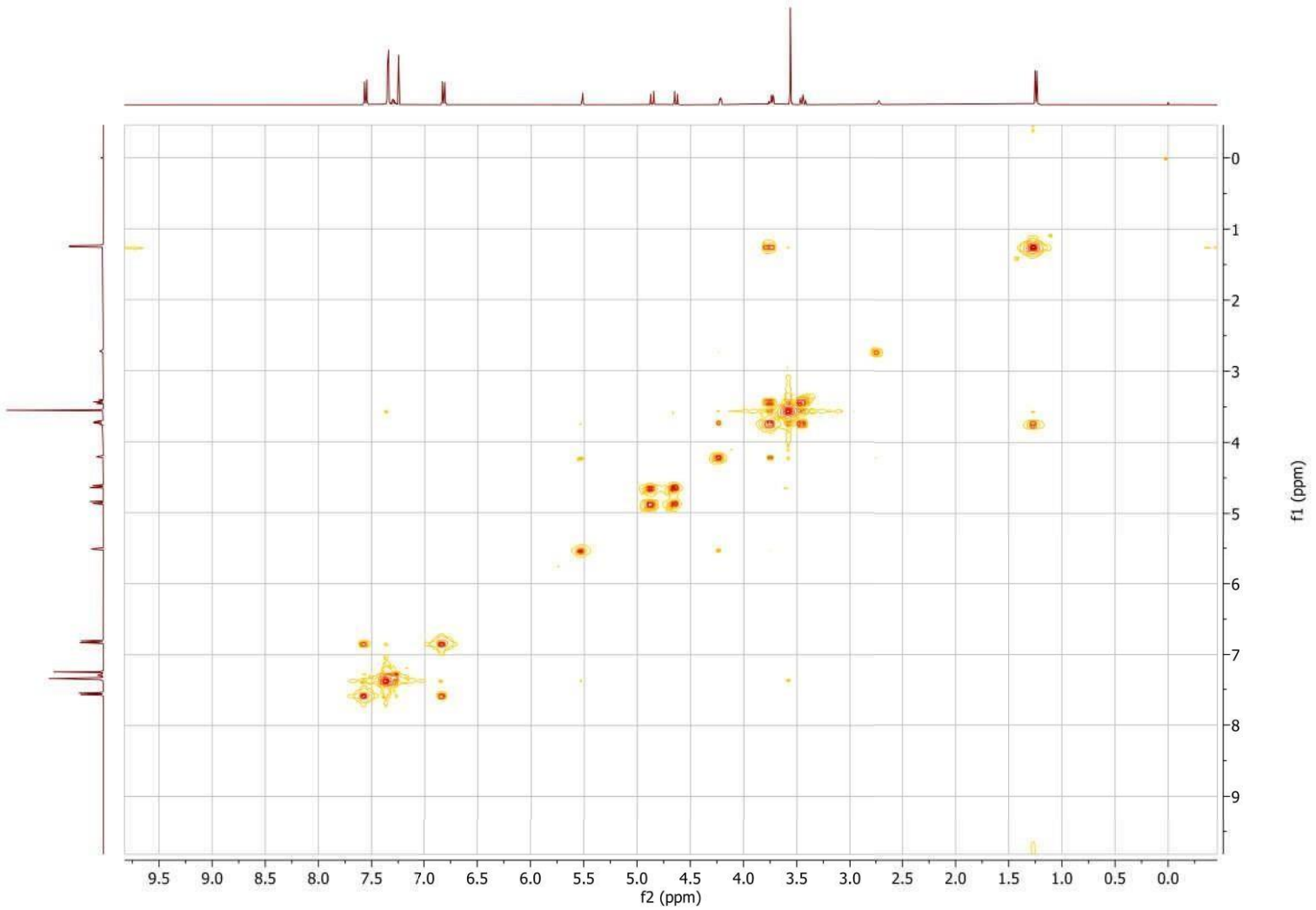
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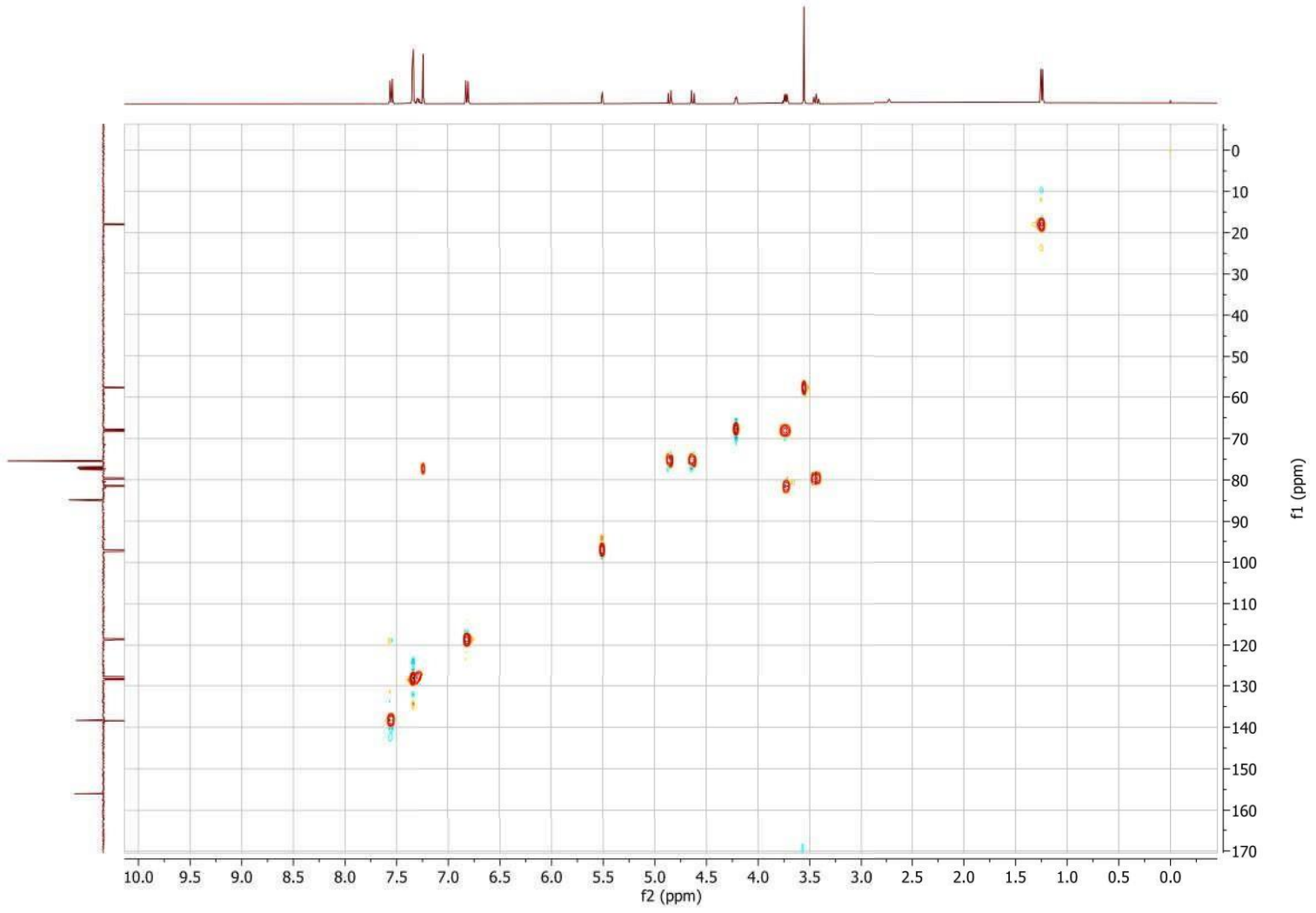
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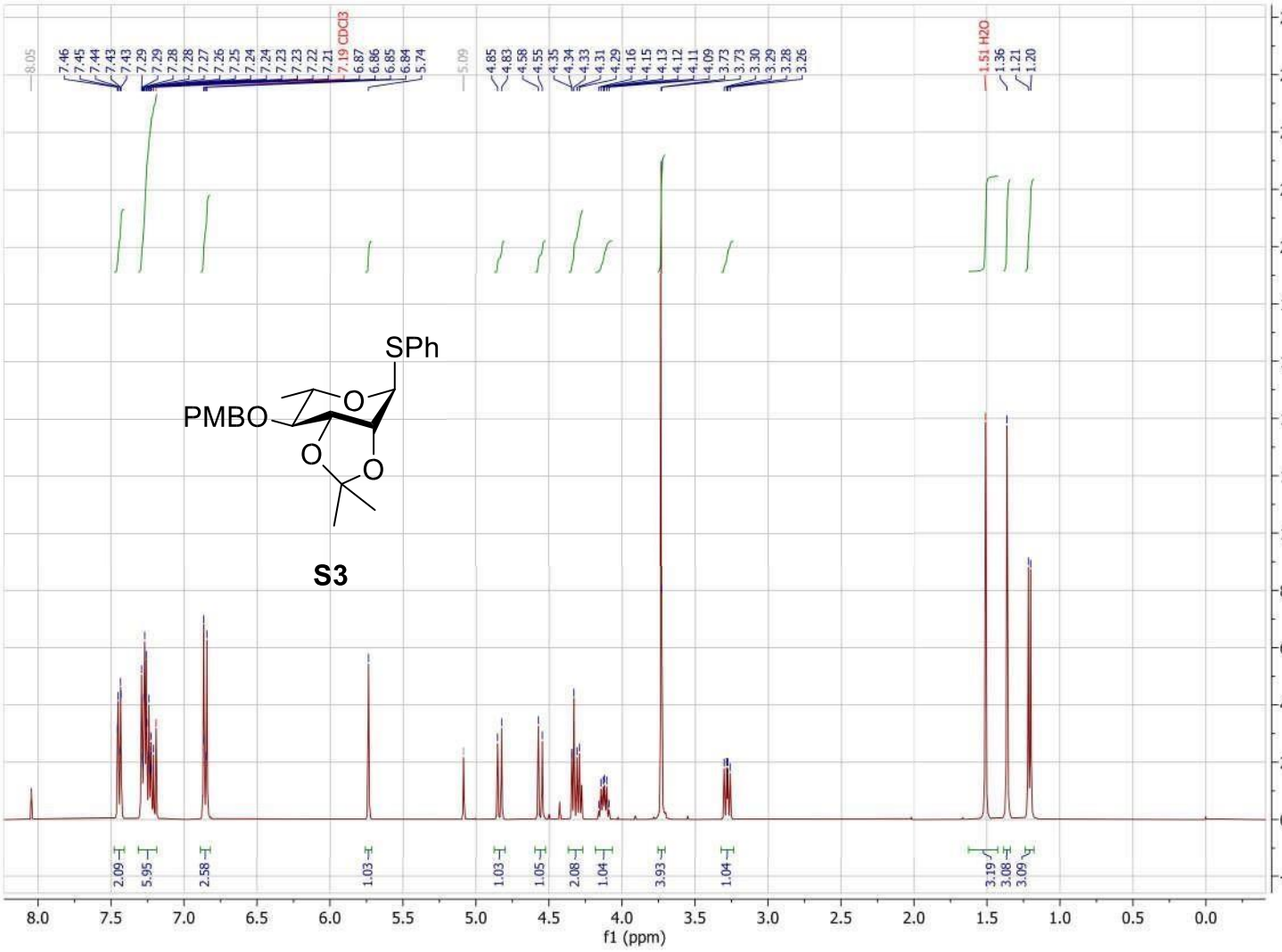
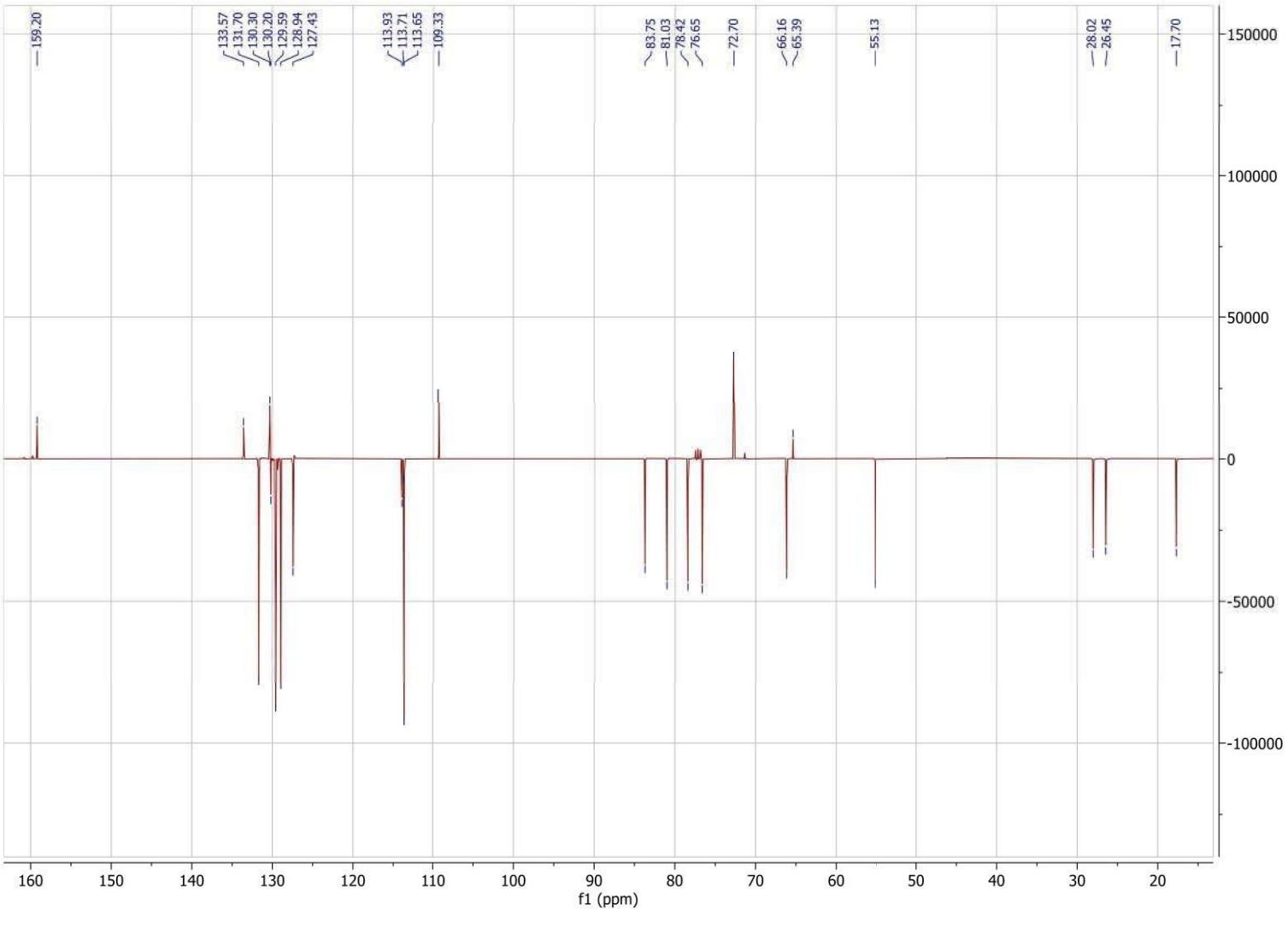
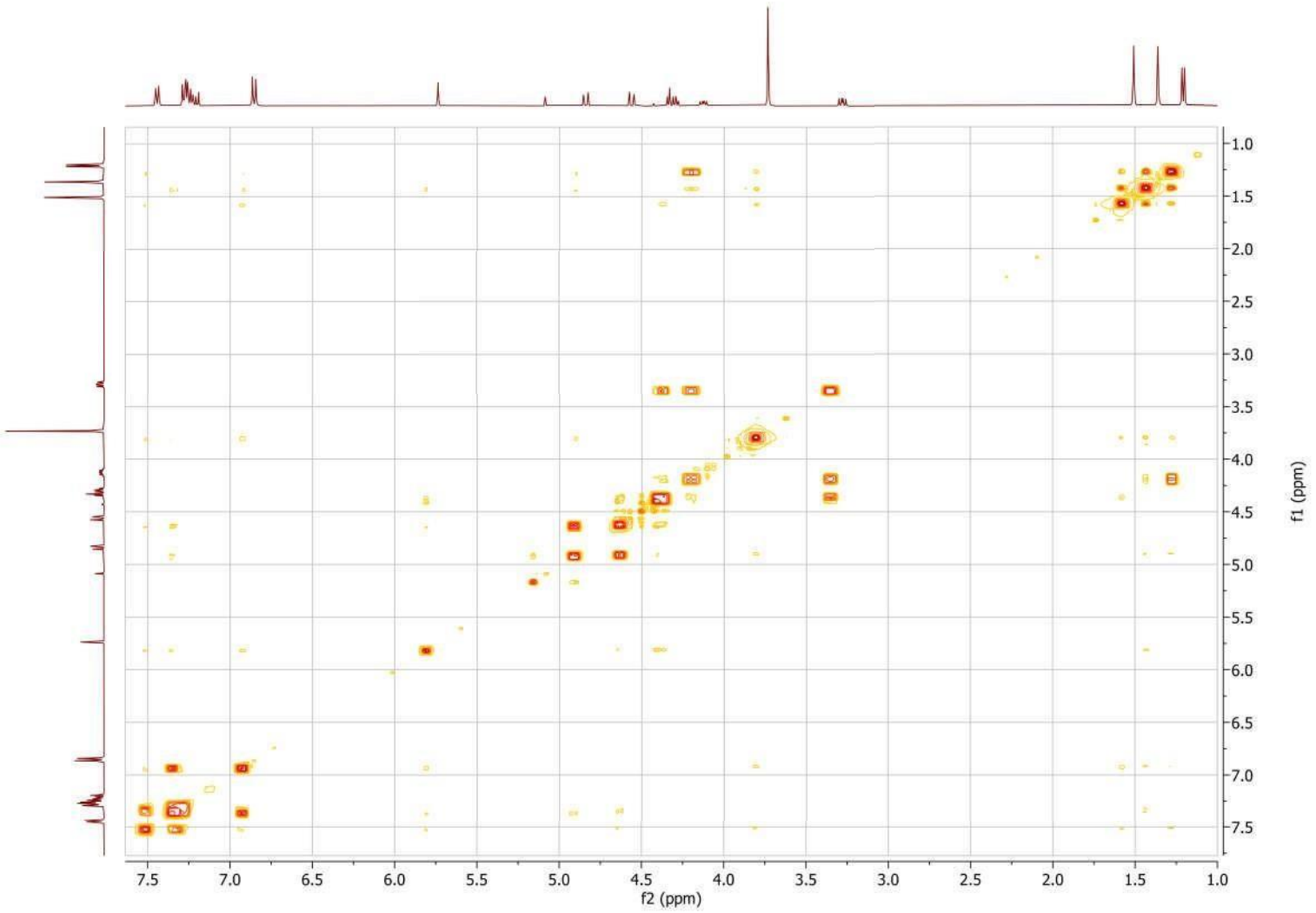
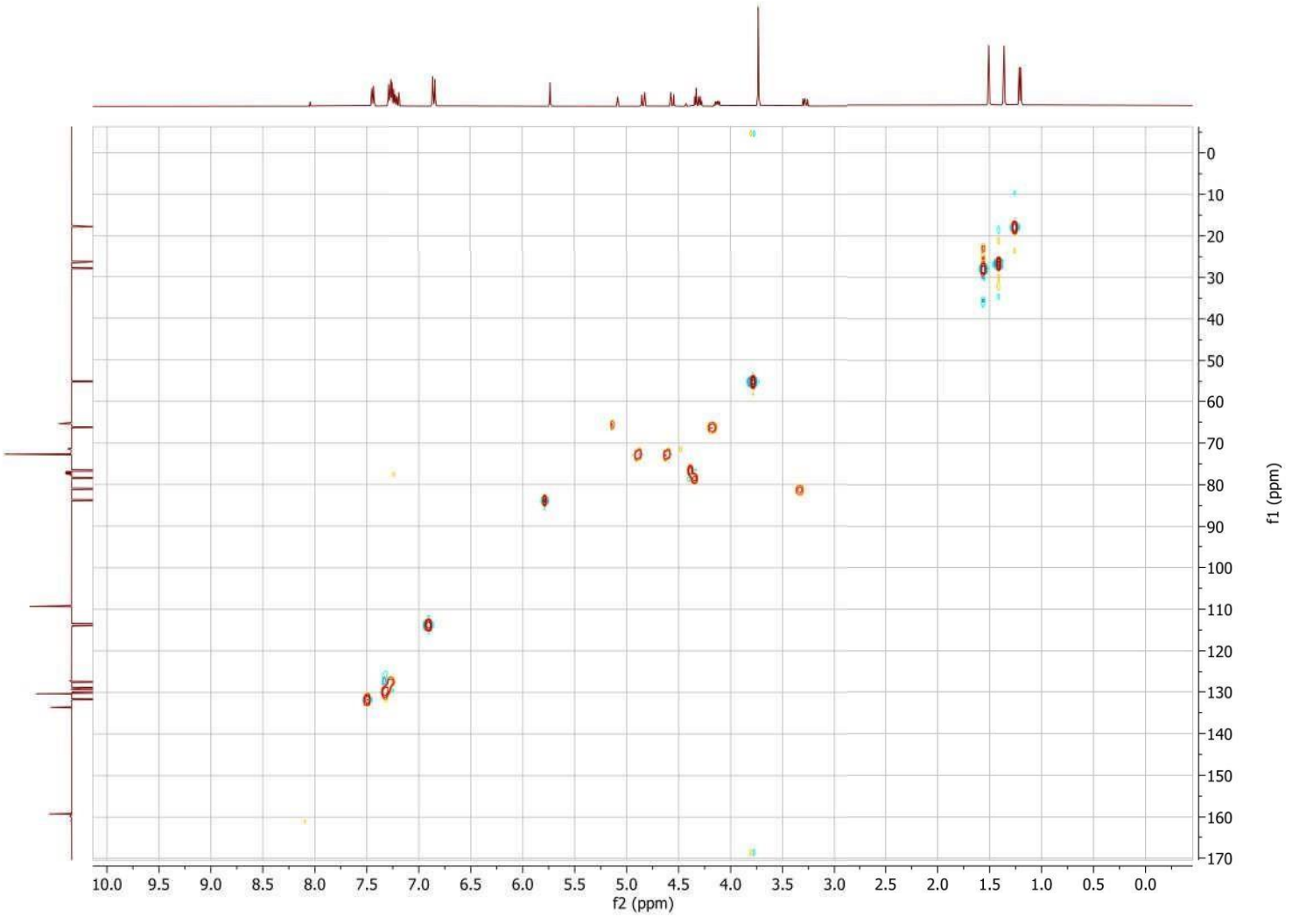
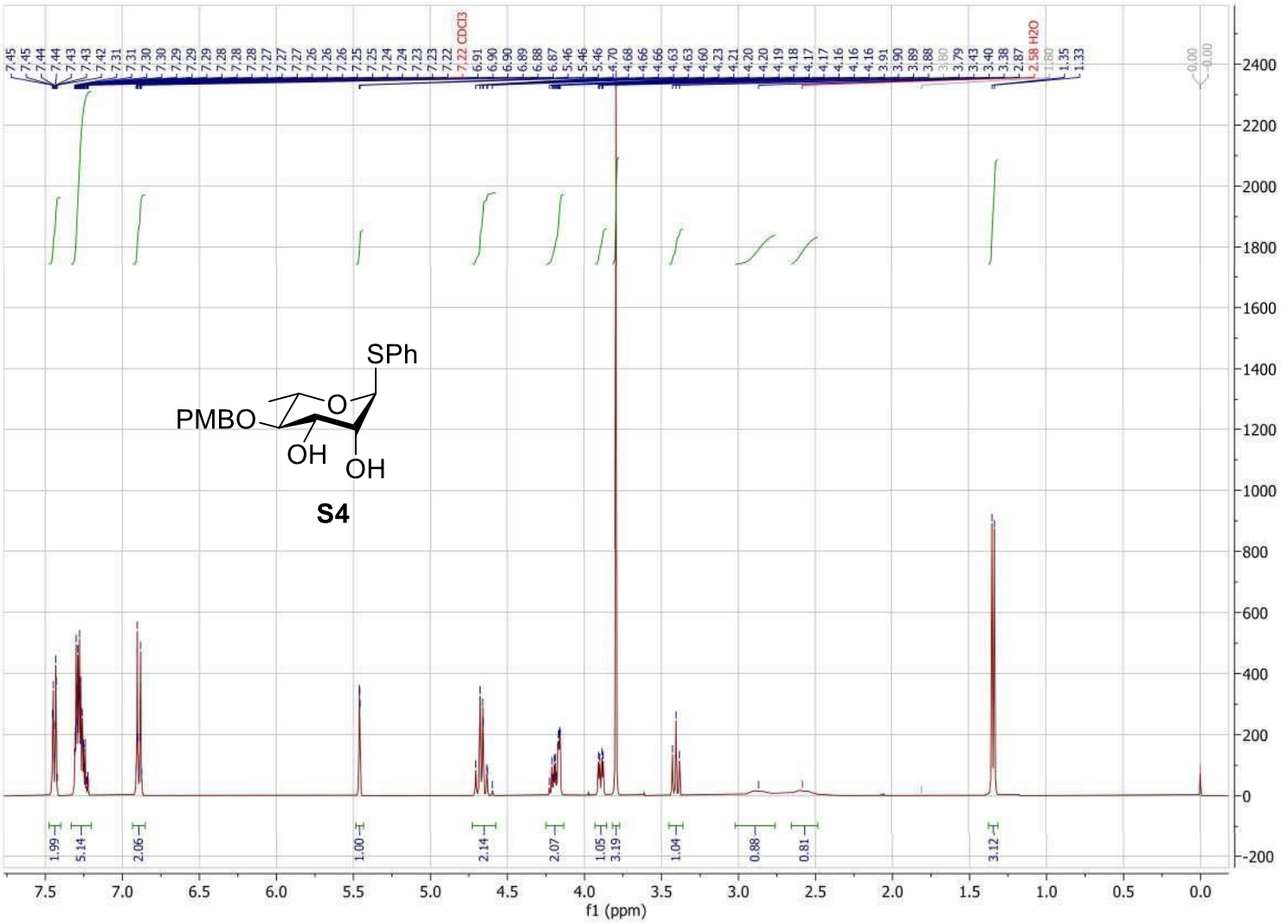


S3

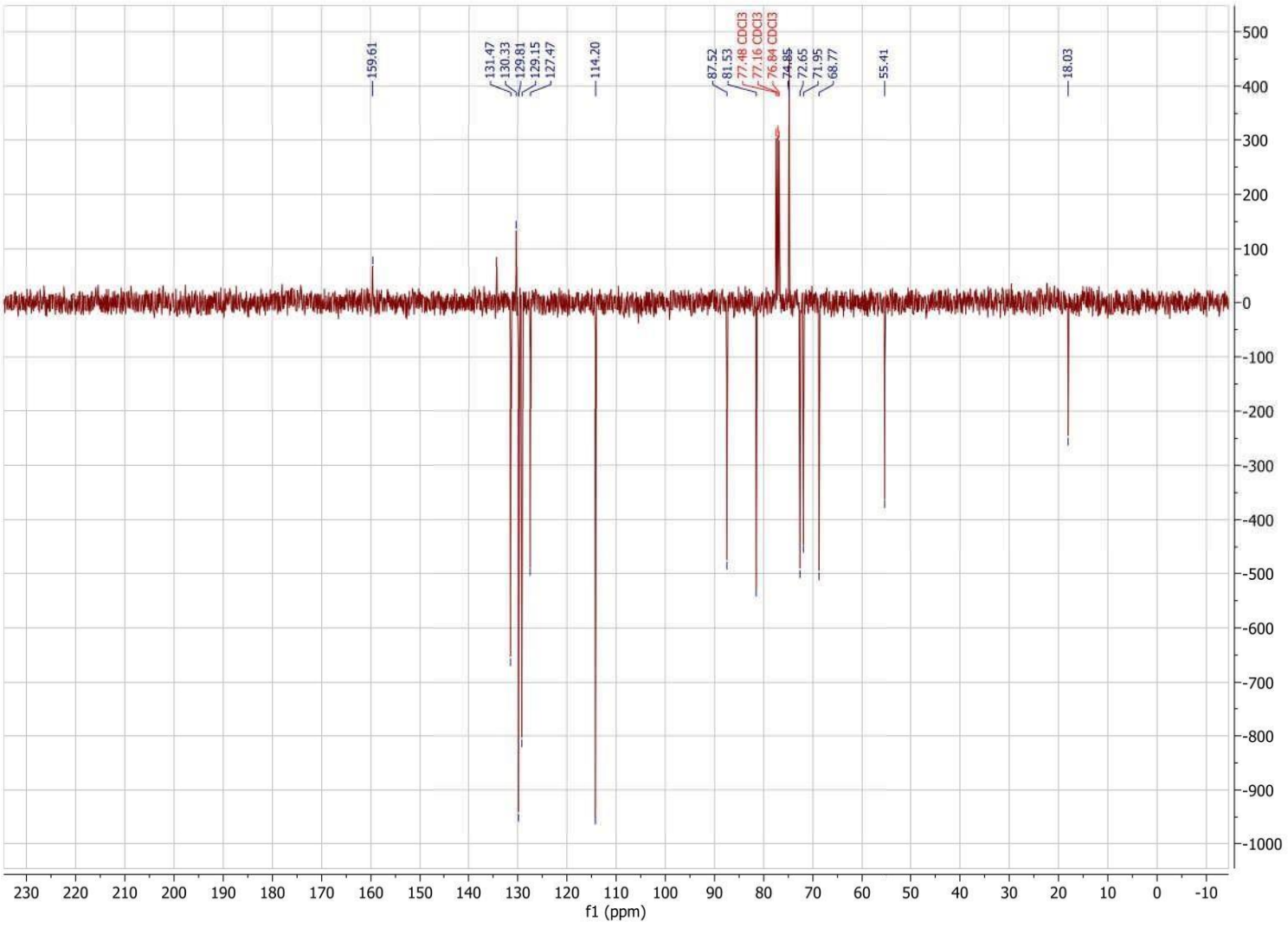


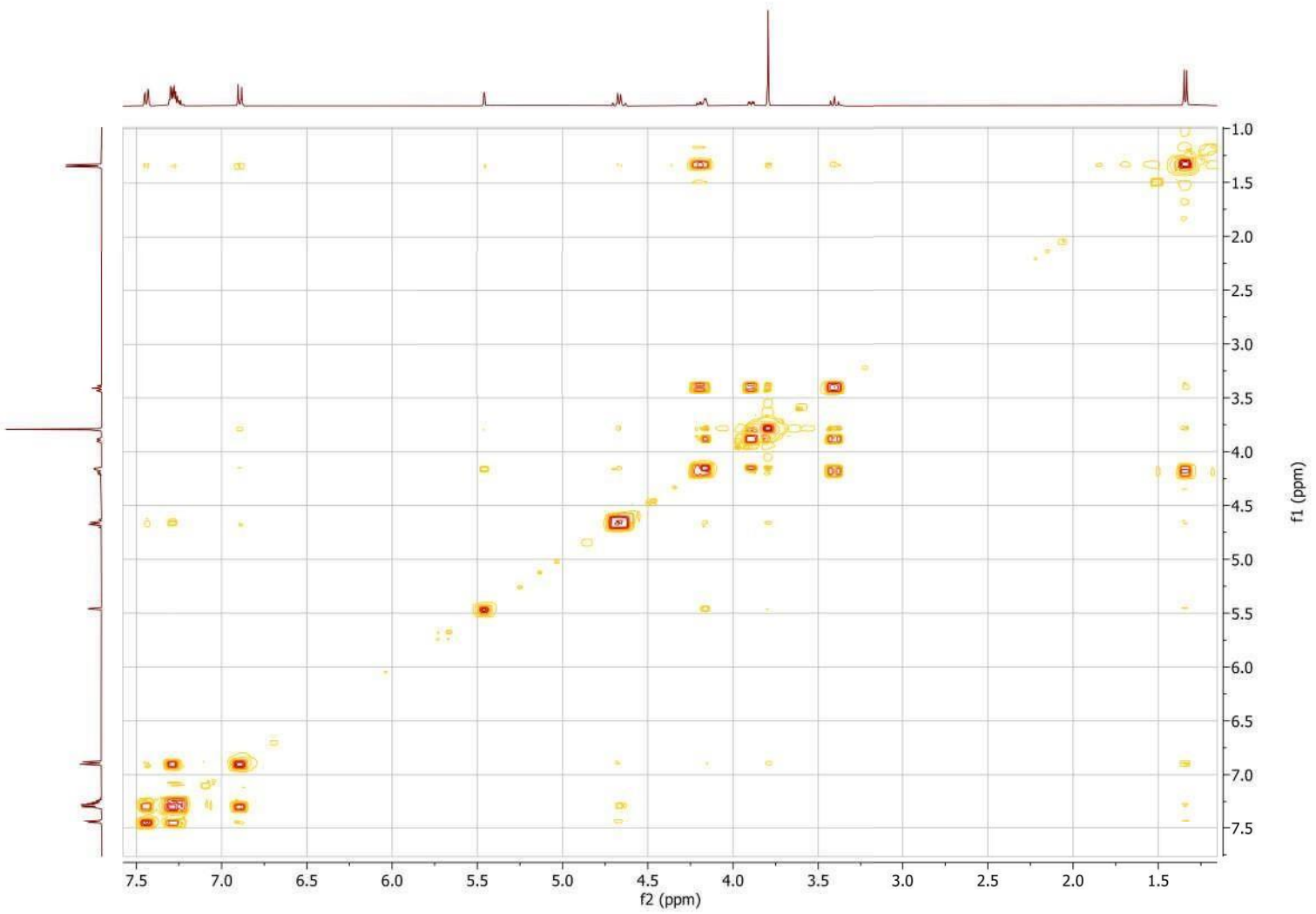

f1 (ppm)
f2 (ppm)

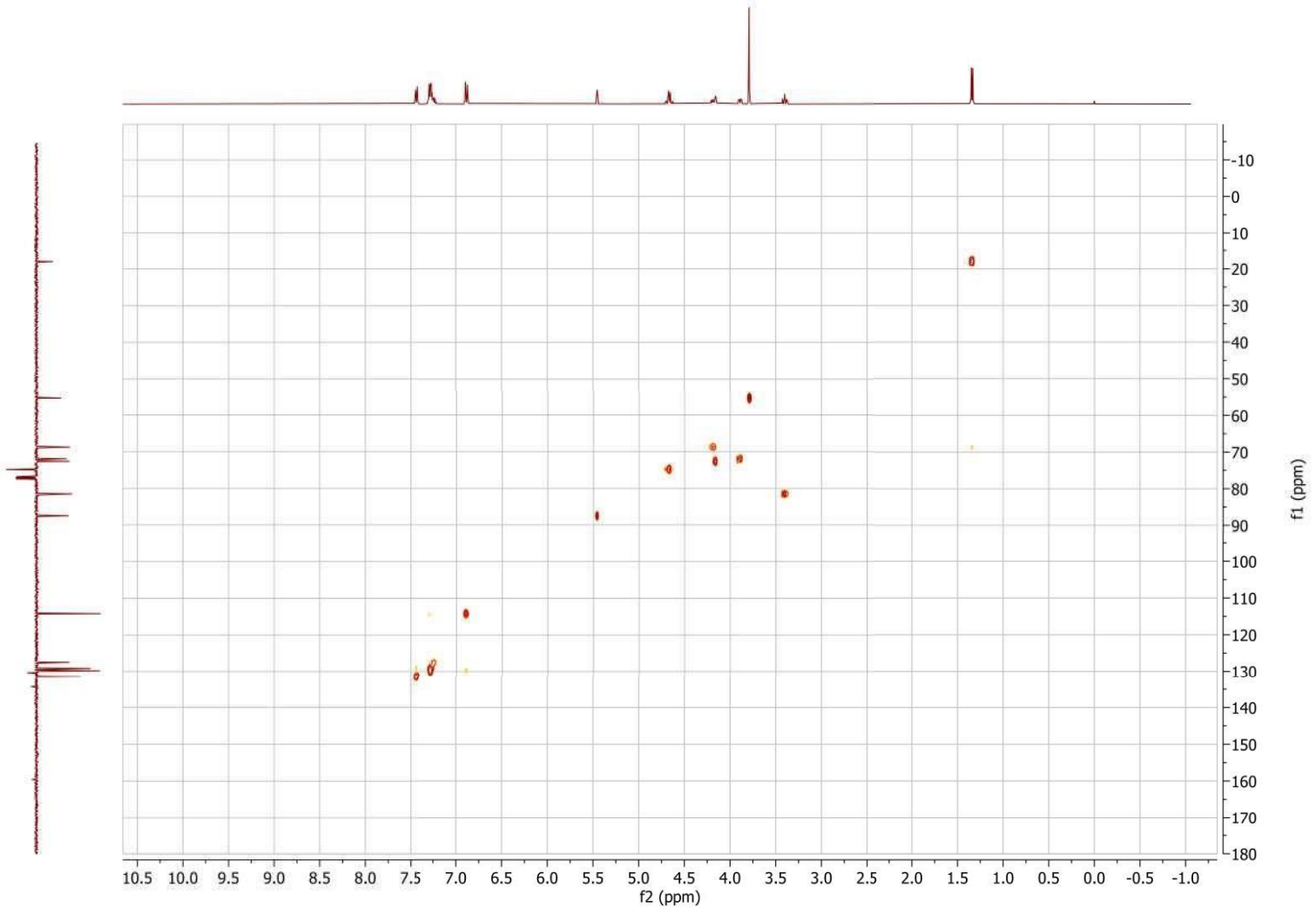

f1 (ppm)
f2 (ppm)

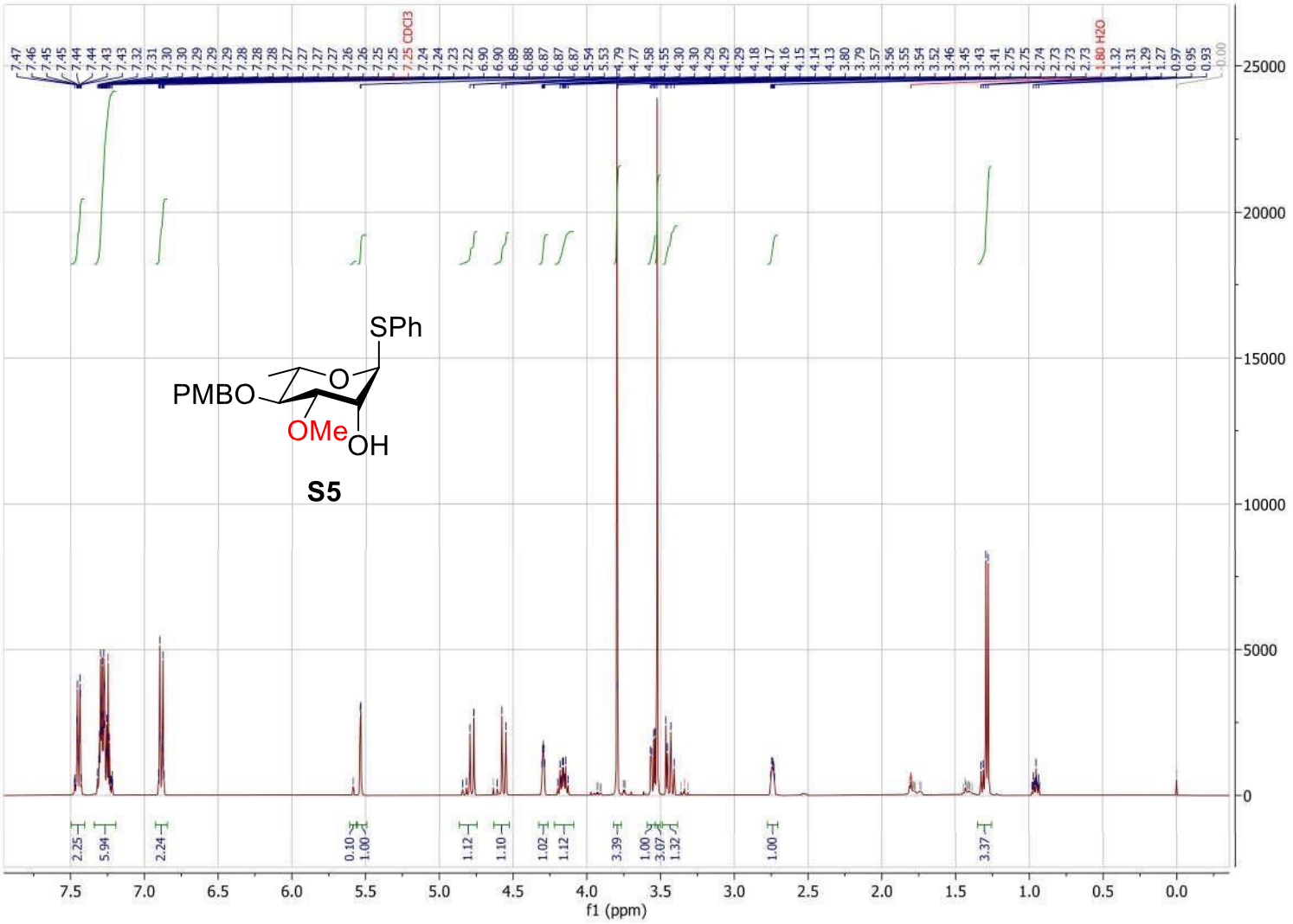


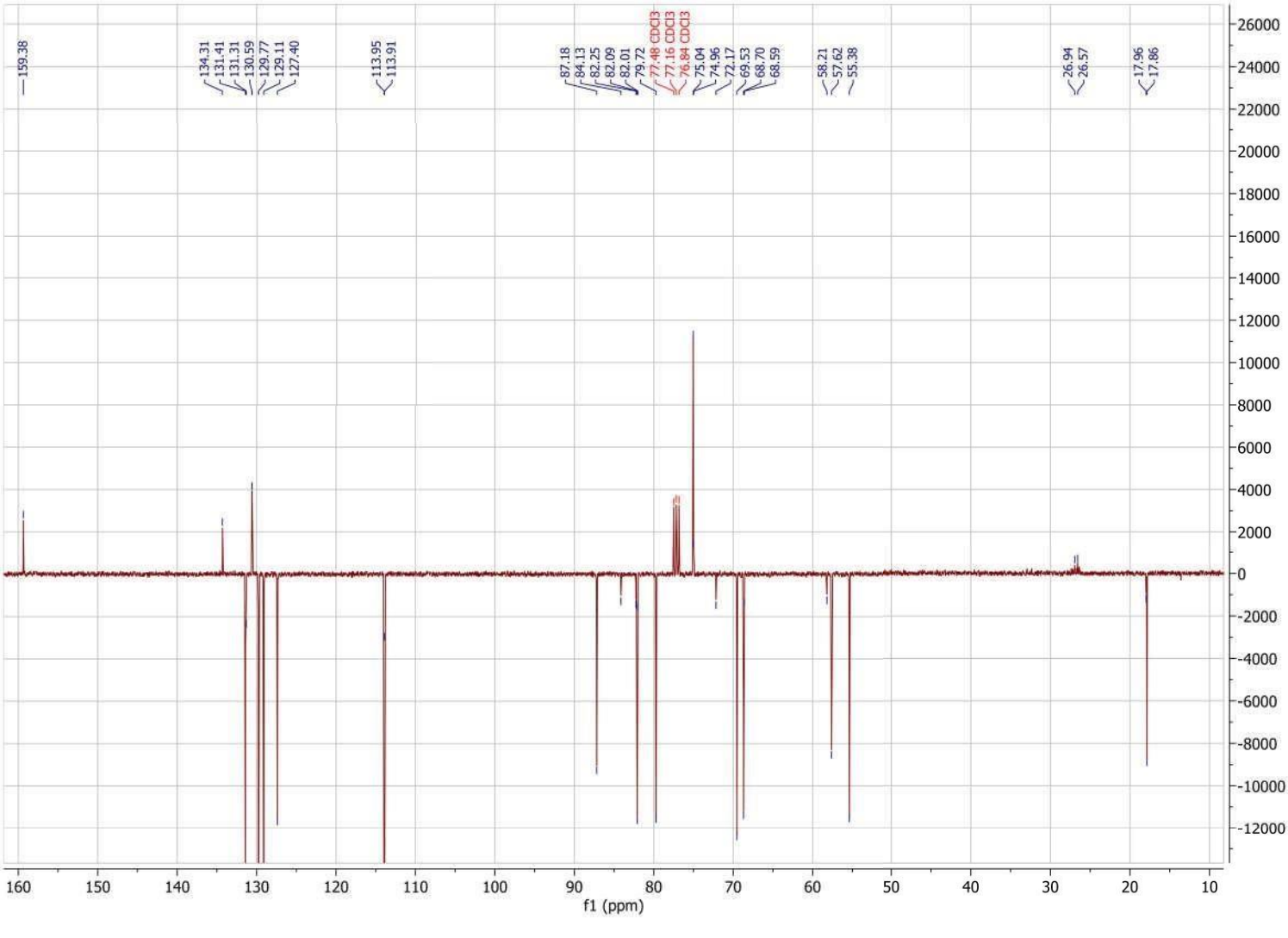
S4

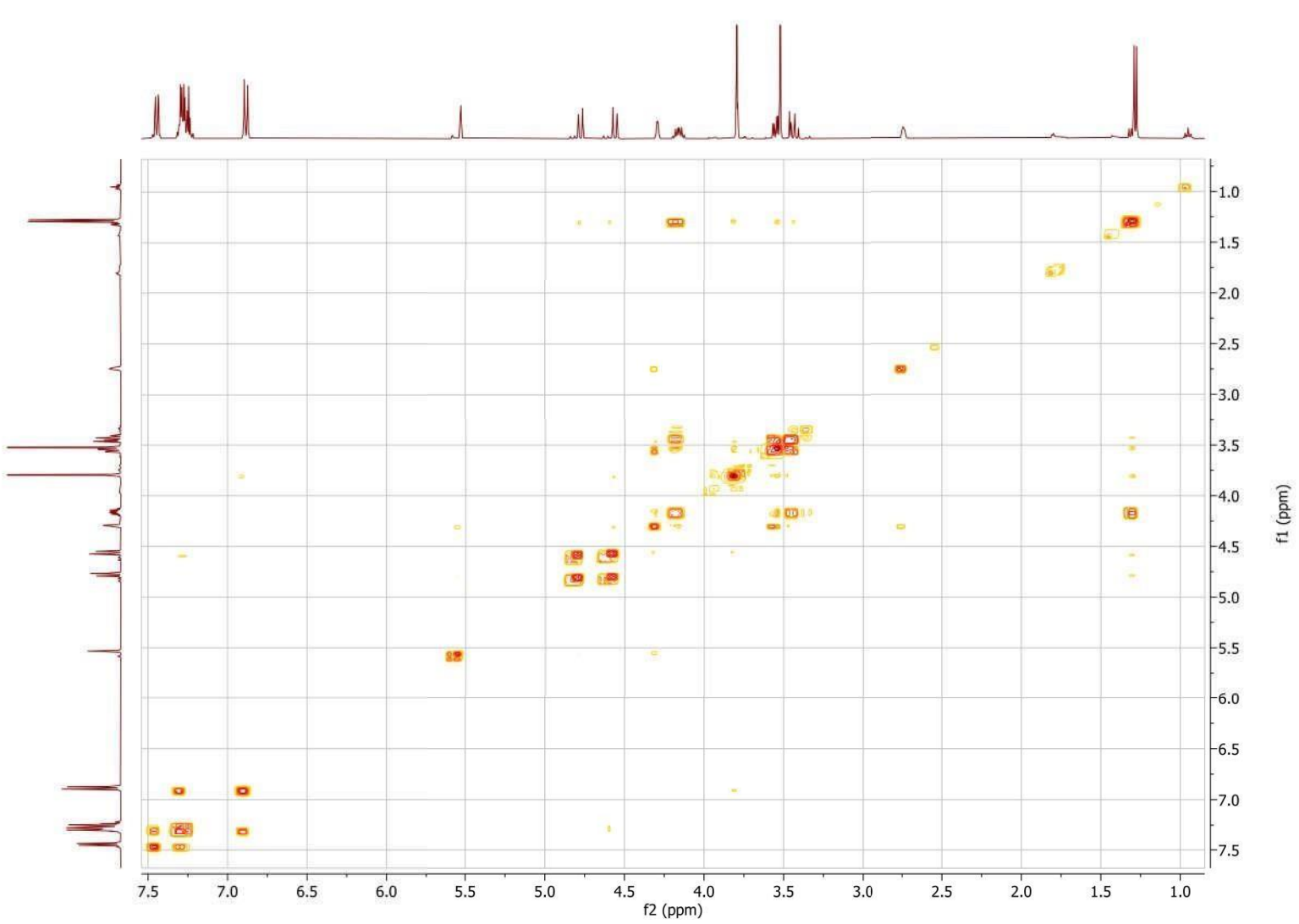


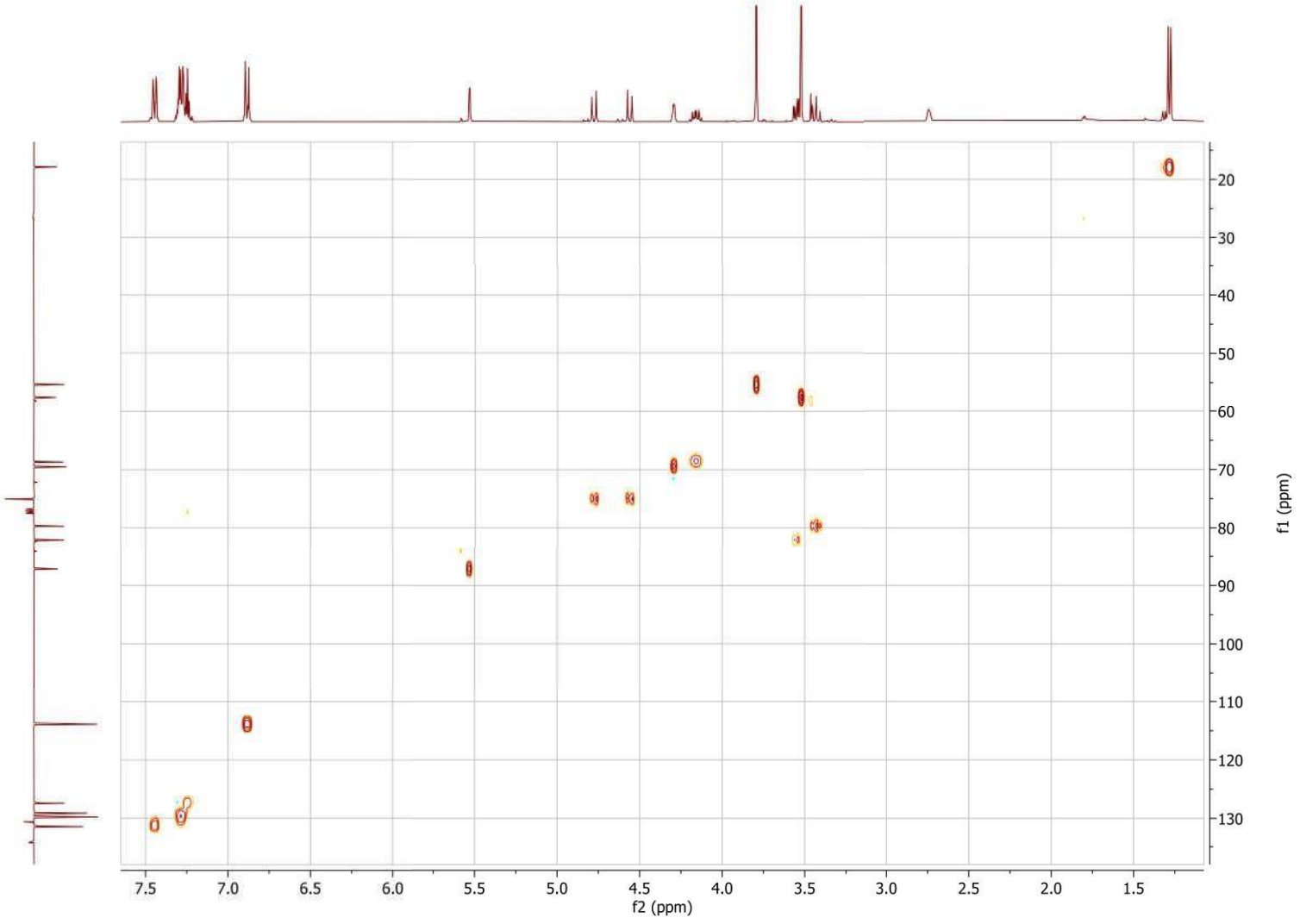

f2 (ppm)
f1 (ppm)

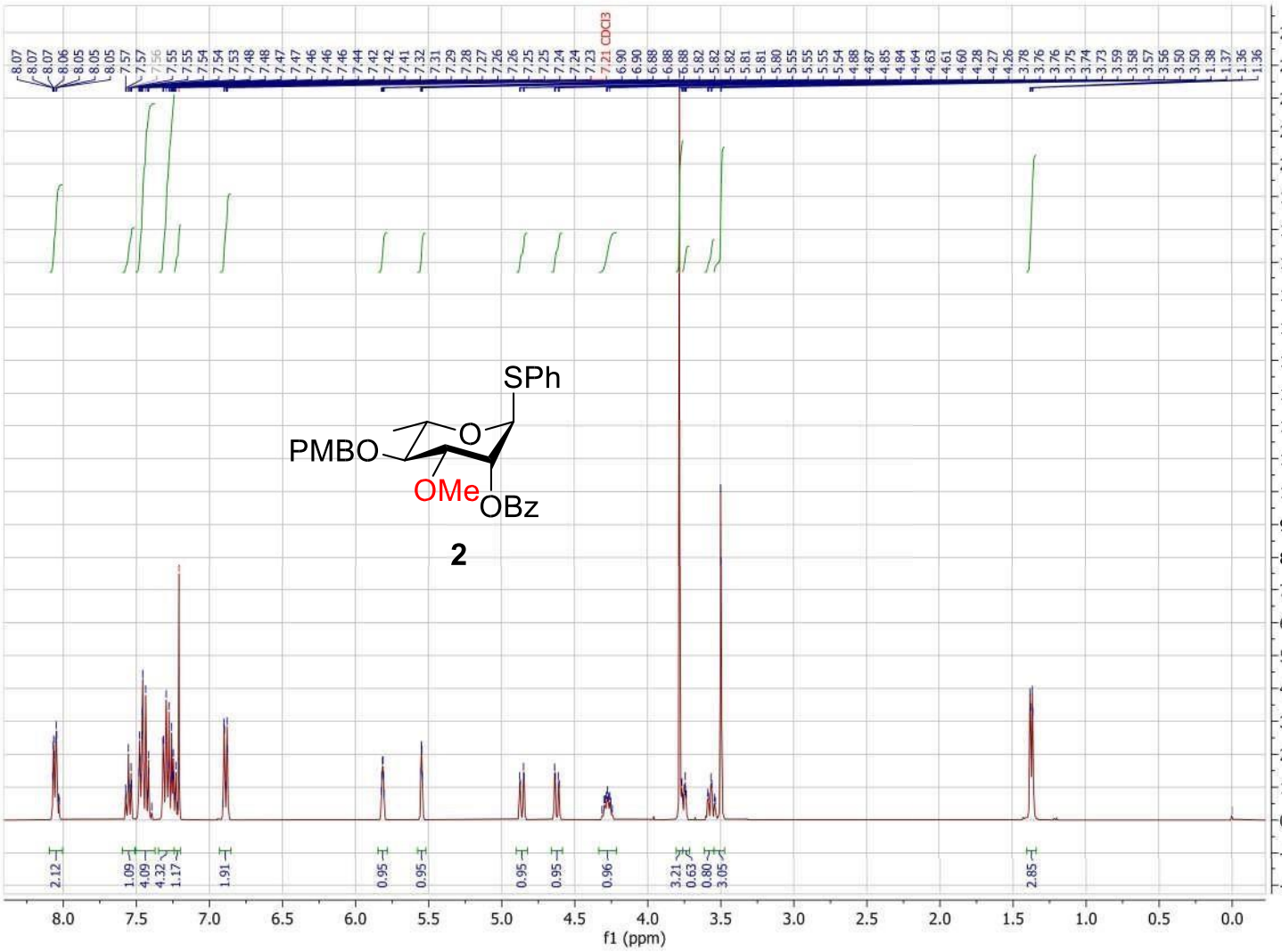

f2 (ppm)
f1 (ppm)


SPh
PMBO
O
OMe
OH
S5
f1 (ppm)

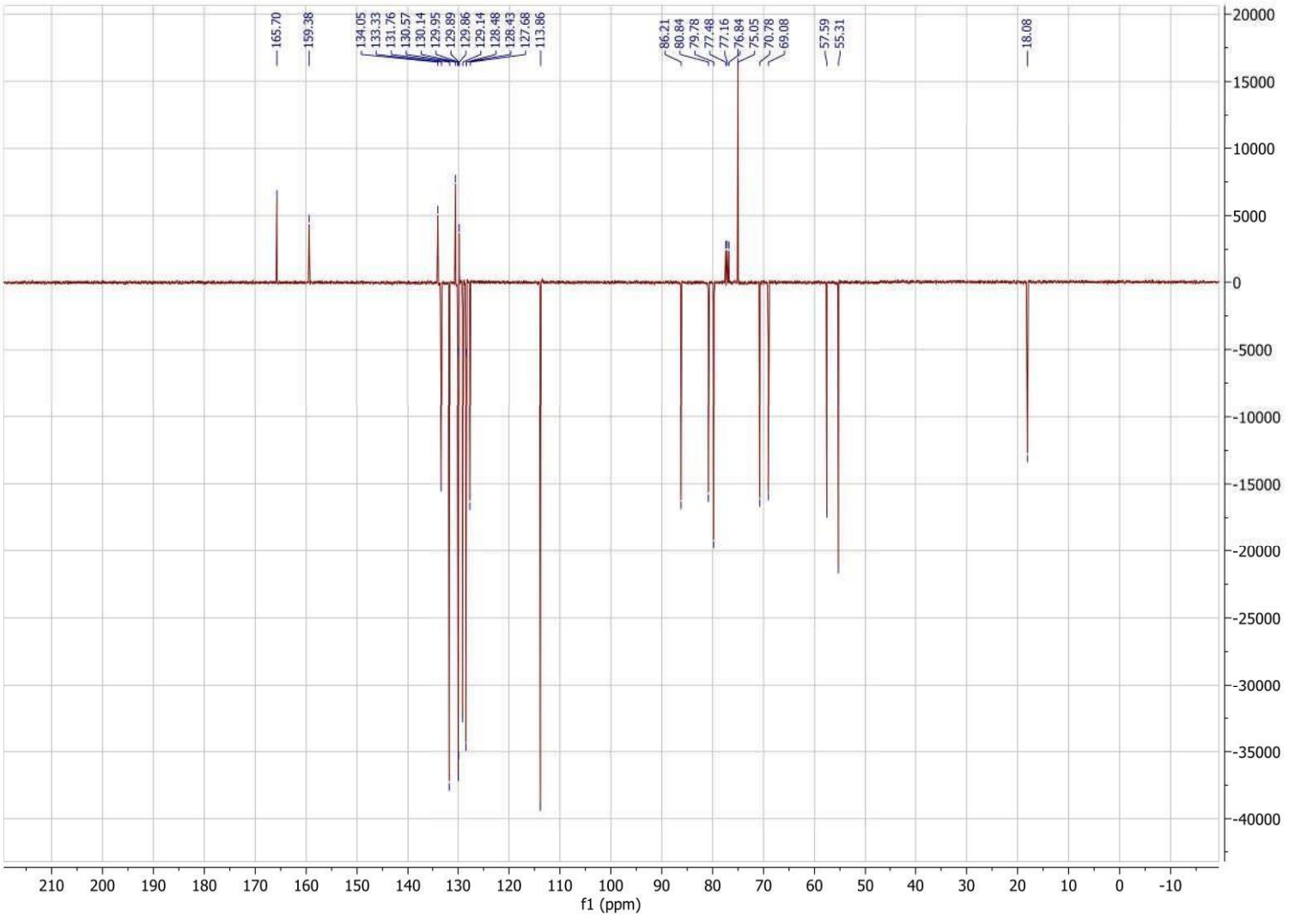

f1 (ppm)

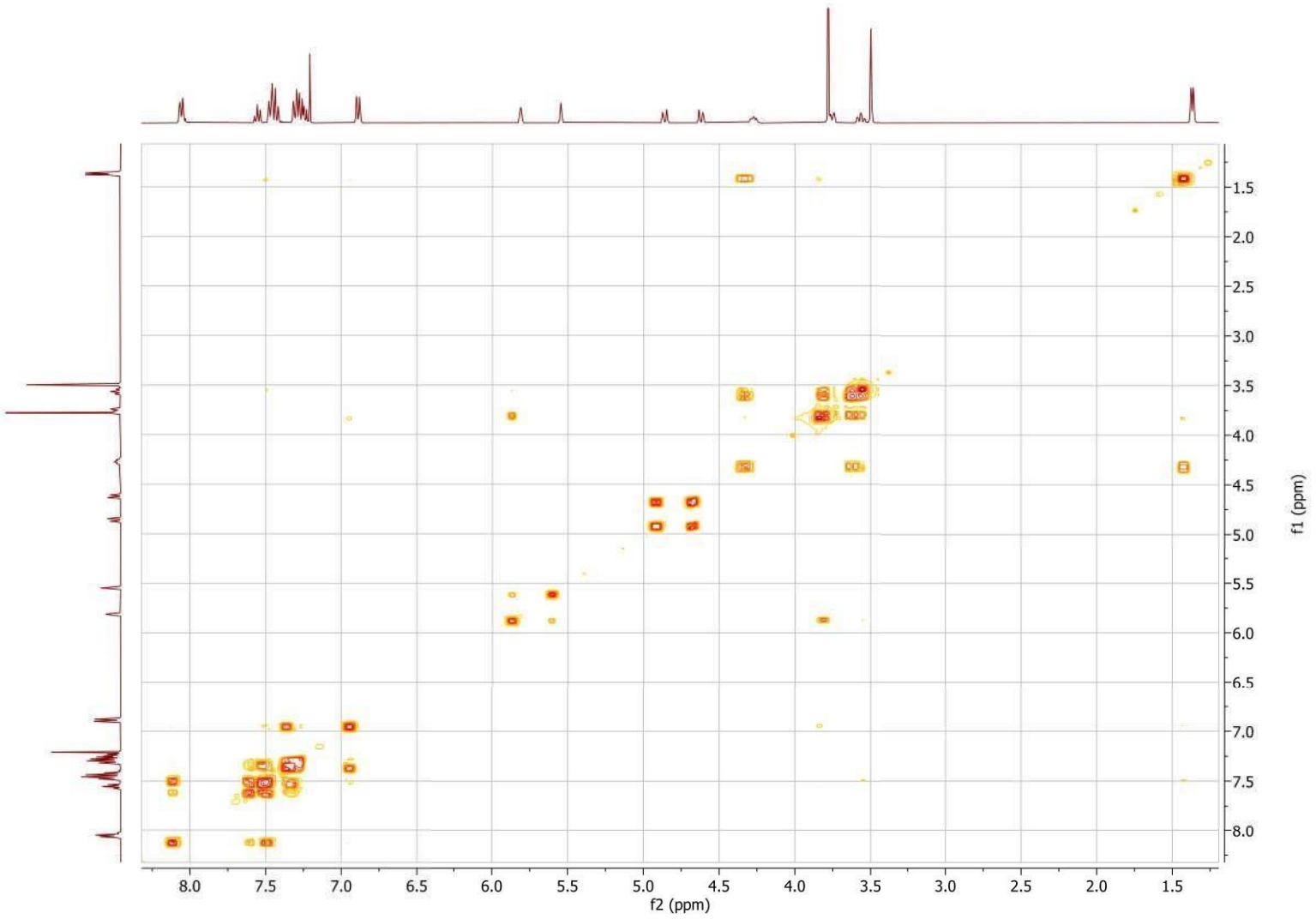

f1 (ppm)
f2 (ppm)

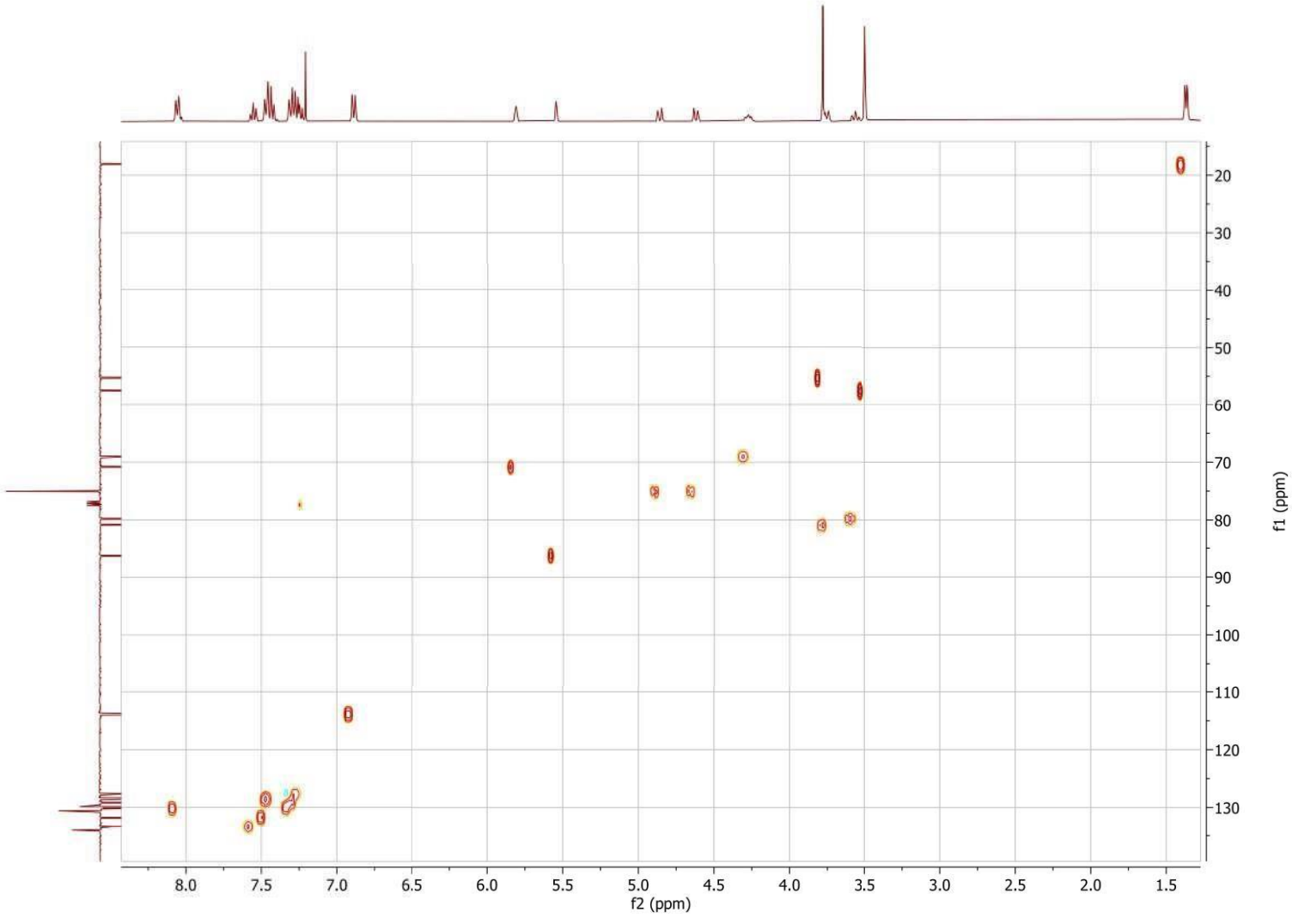

f1 (ppm)
f2 (ppm)

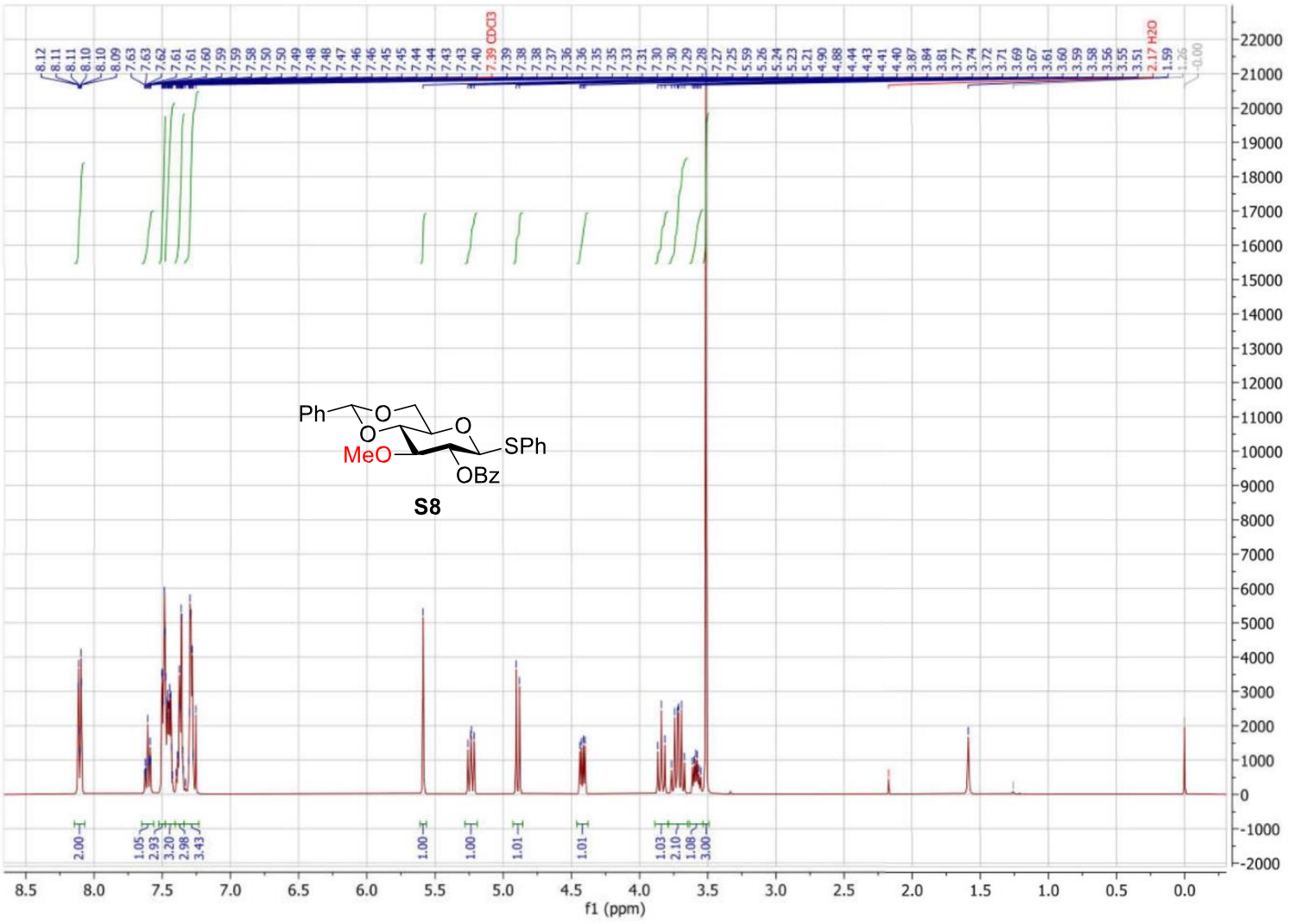


2

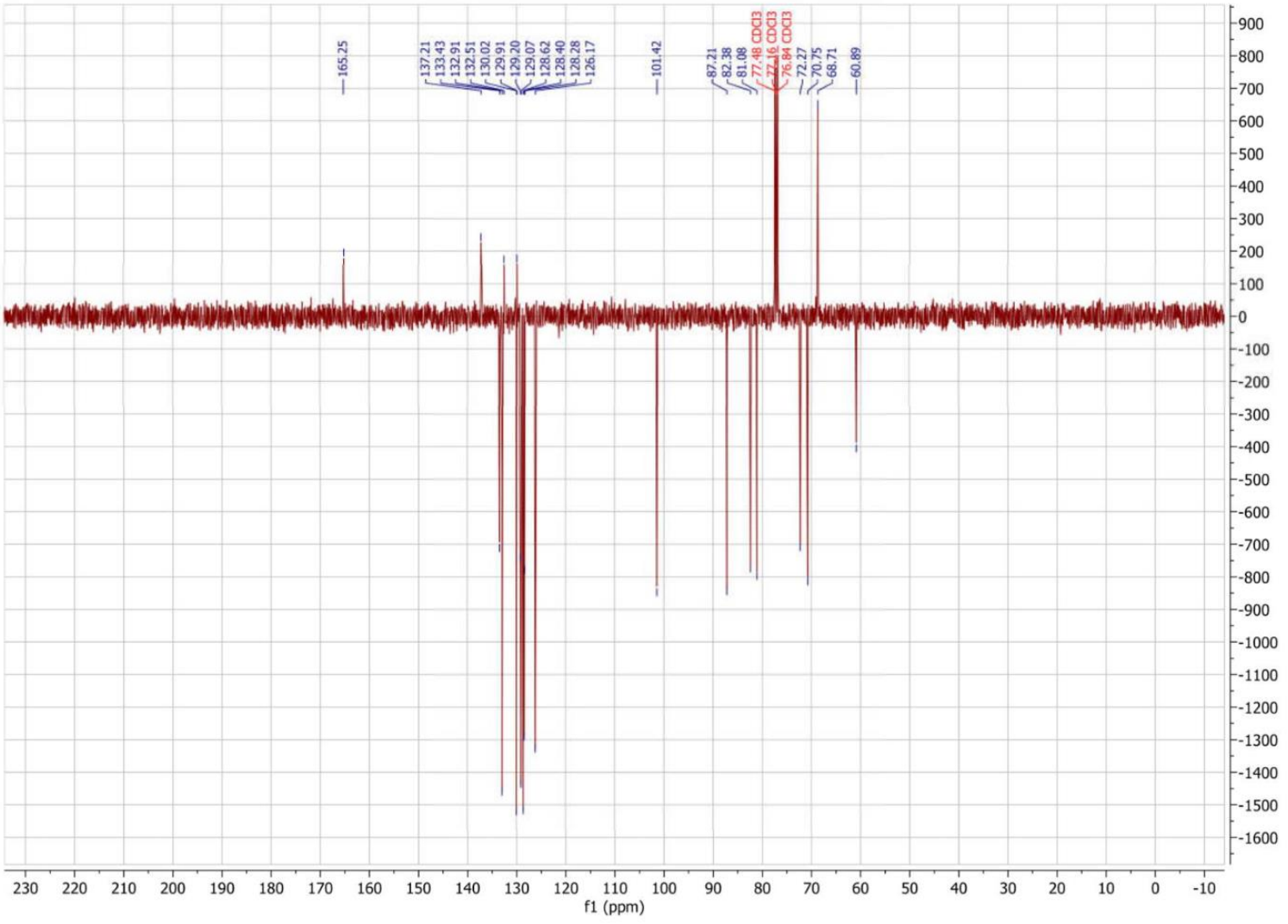


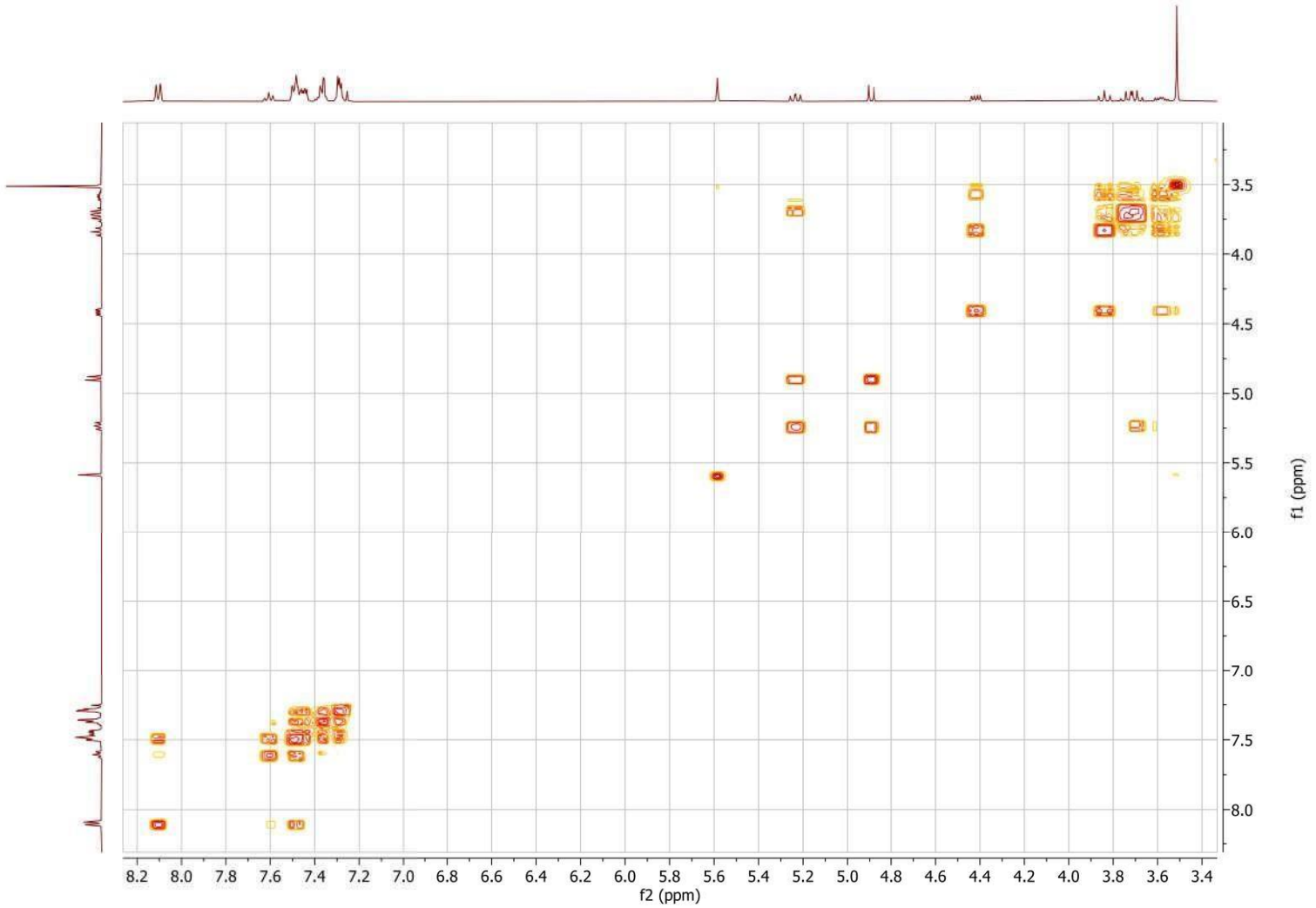

f1 (ppm)
f2 (ppm)

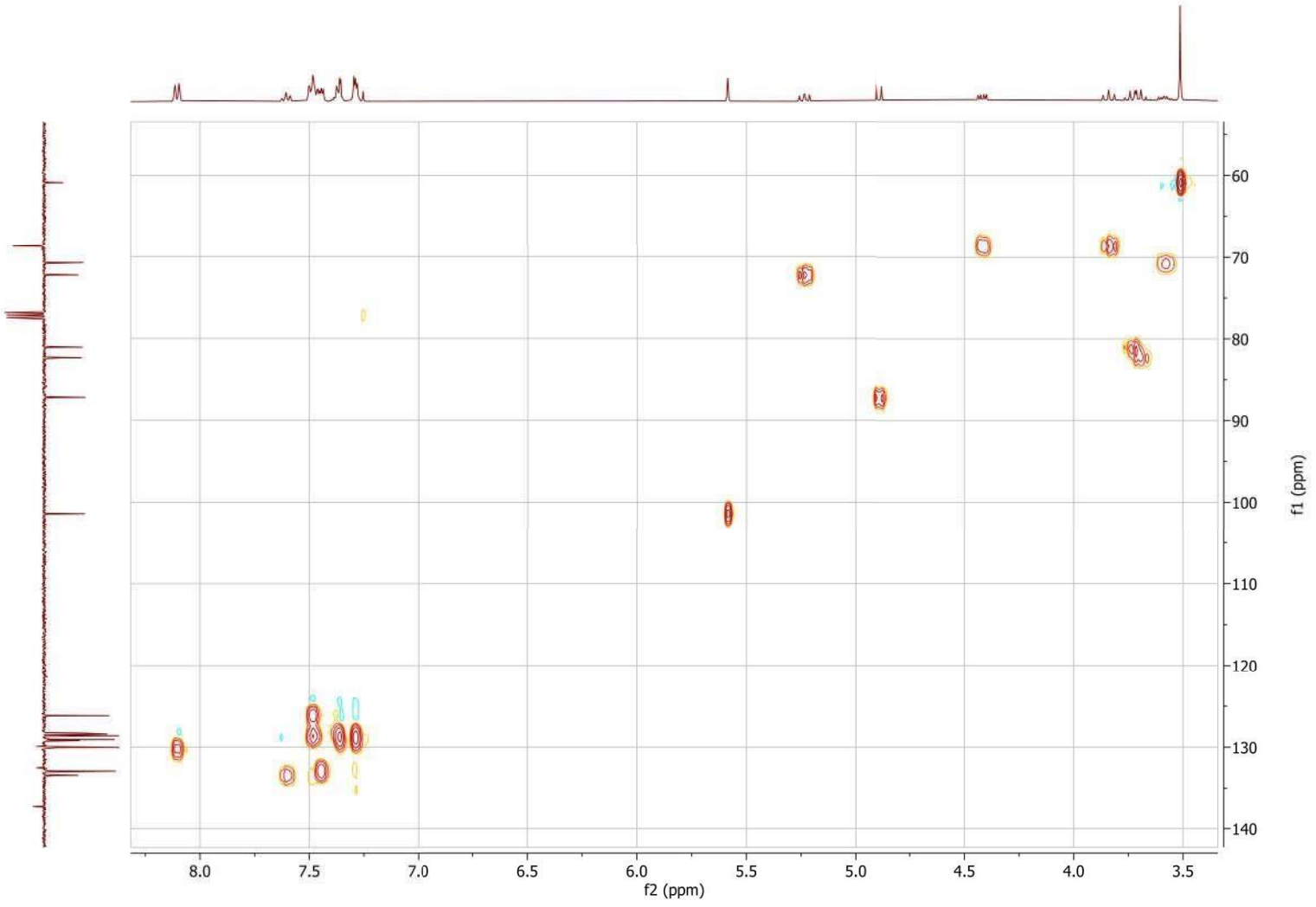

f1 (ppm)
f2 (ppm)

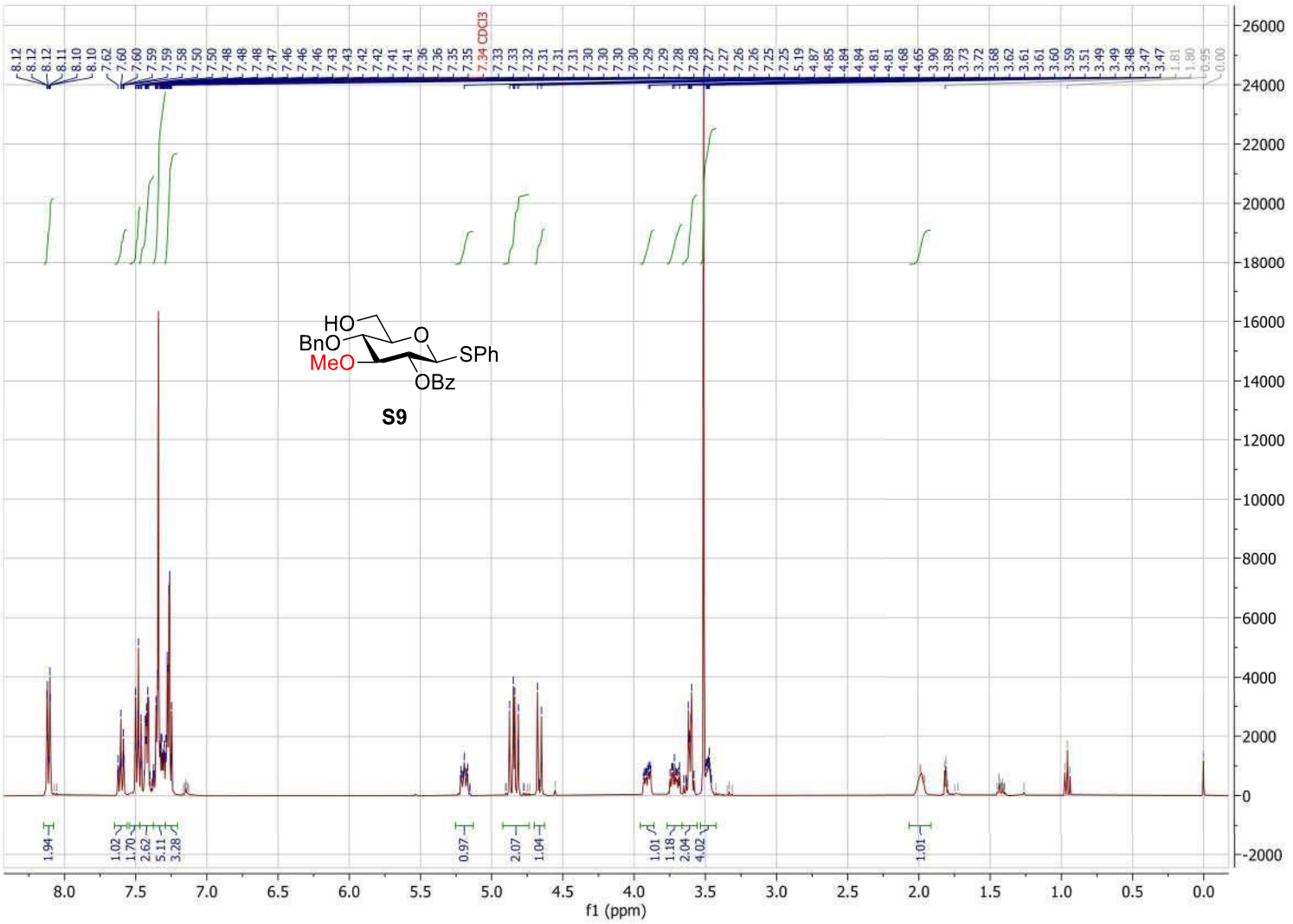


S8

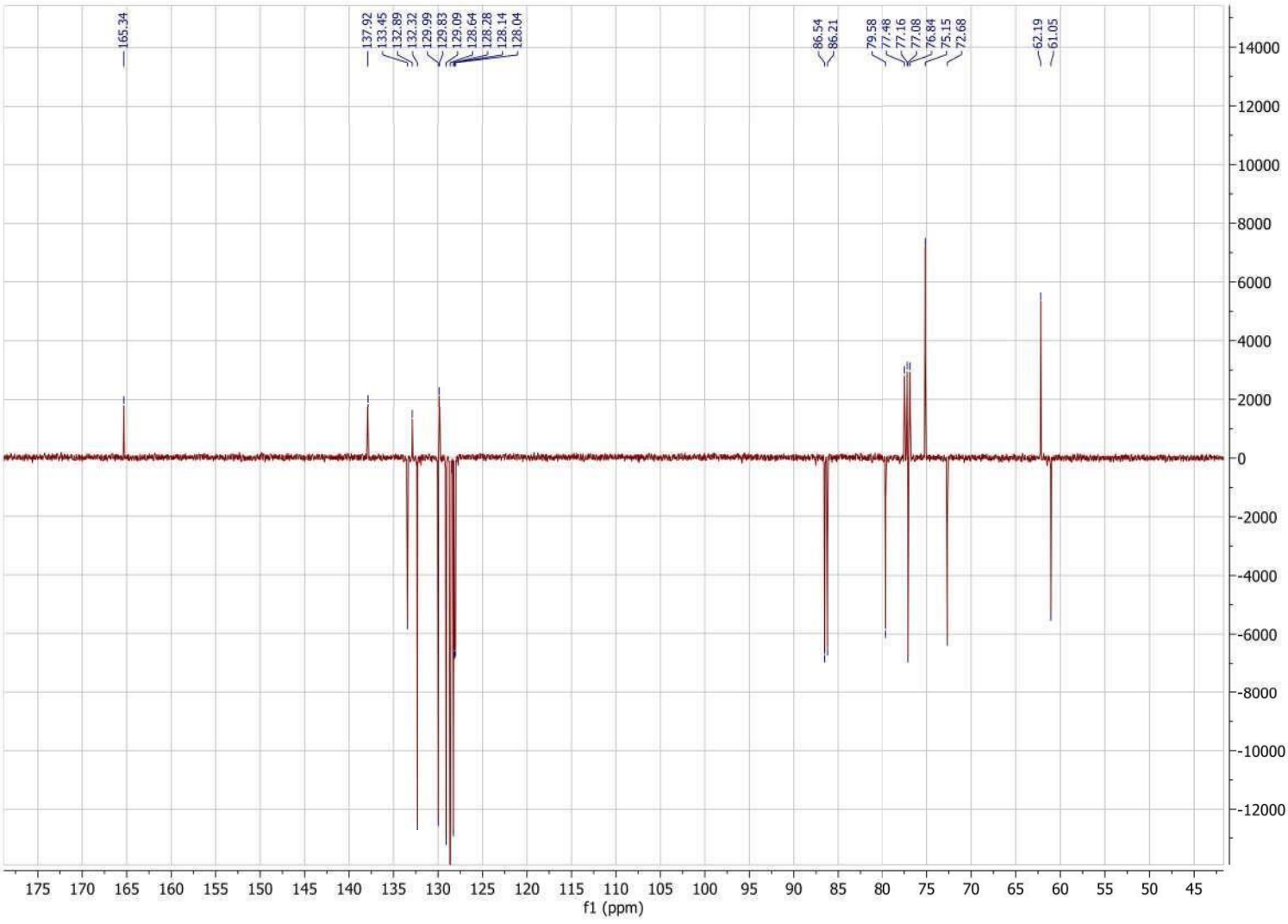


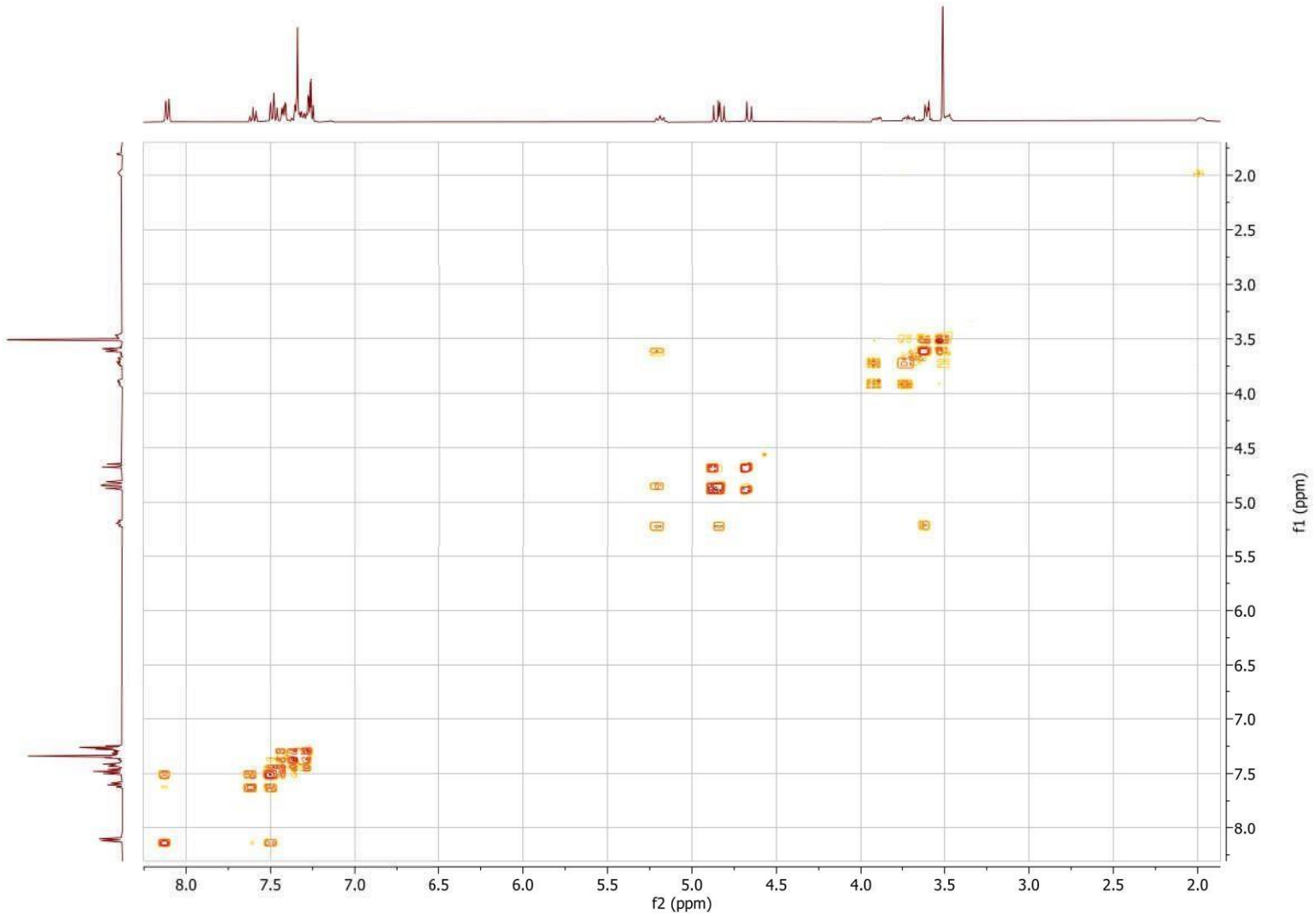

8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
f2 (ppm)
3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
f1 (ppm)

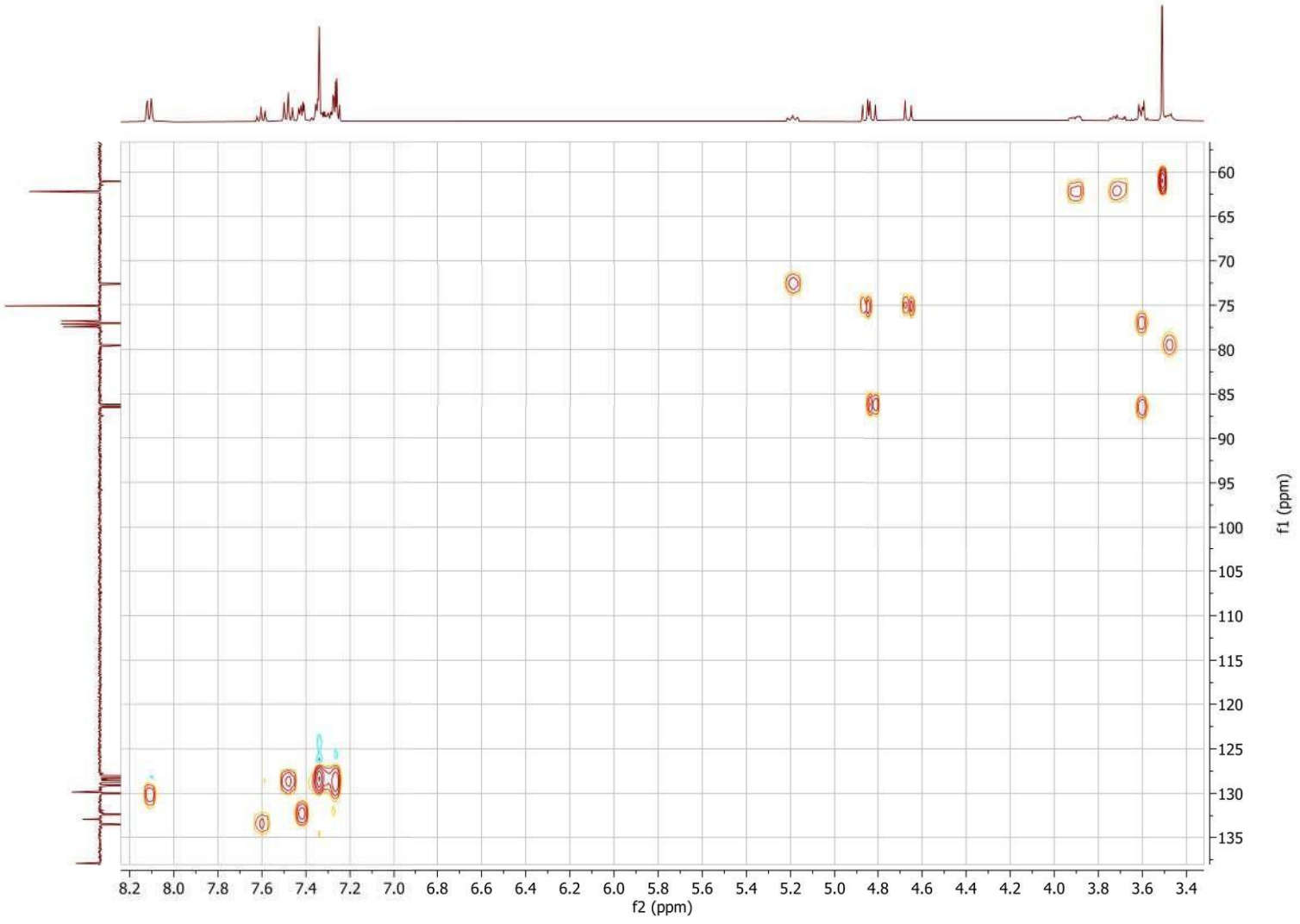

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
f2 (ppm)
60 70 80 90 100 110 120 130 140
f1 (ppm)

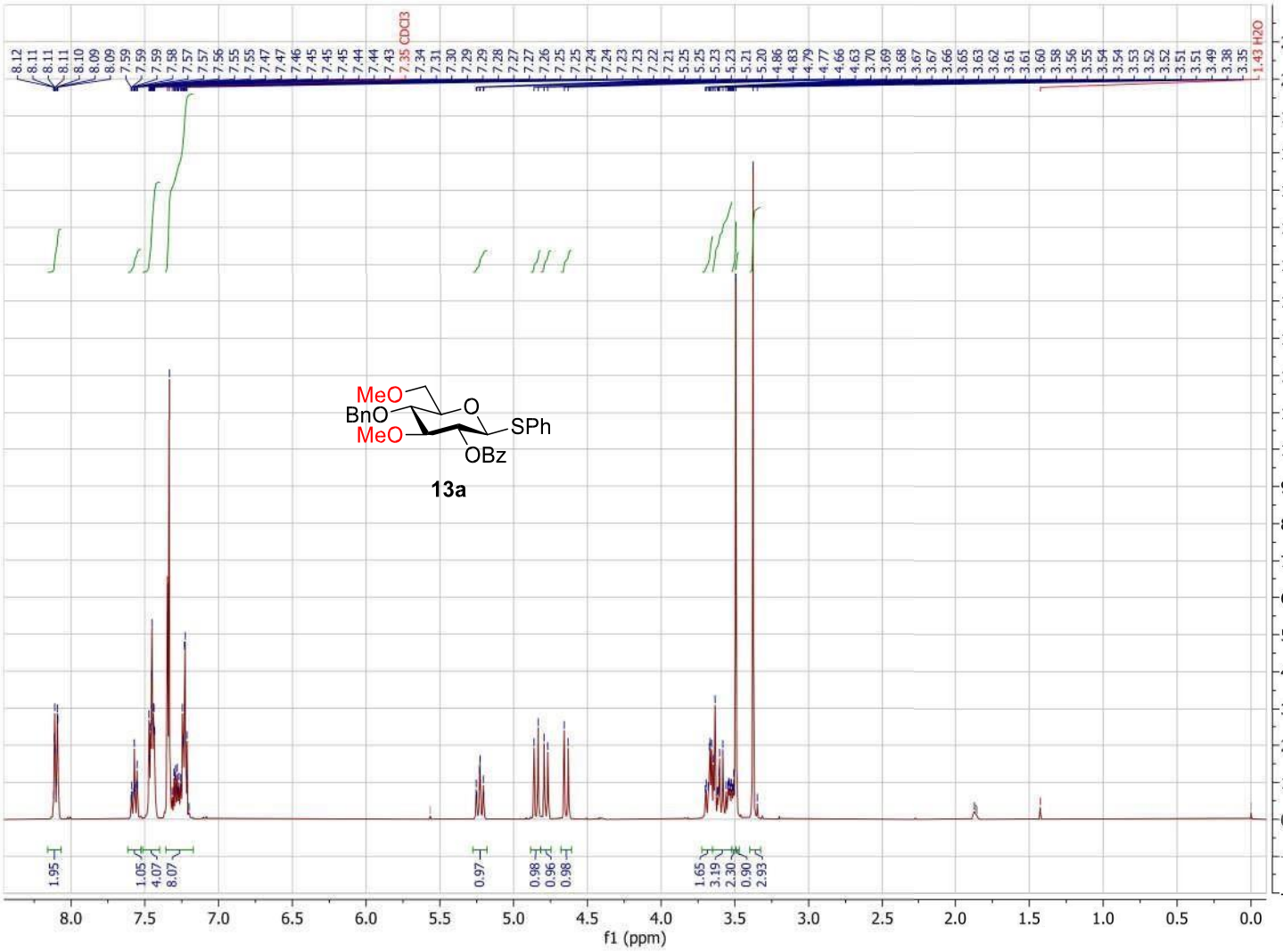


S9

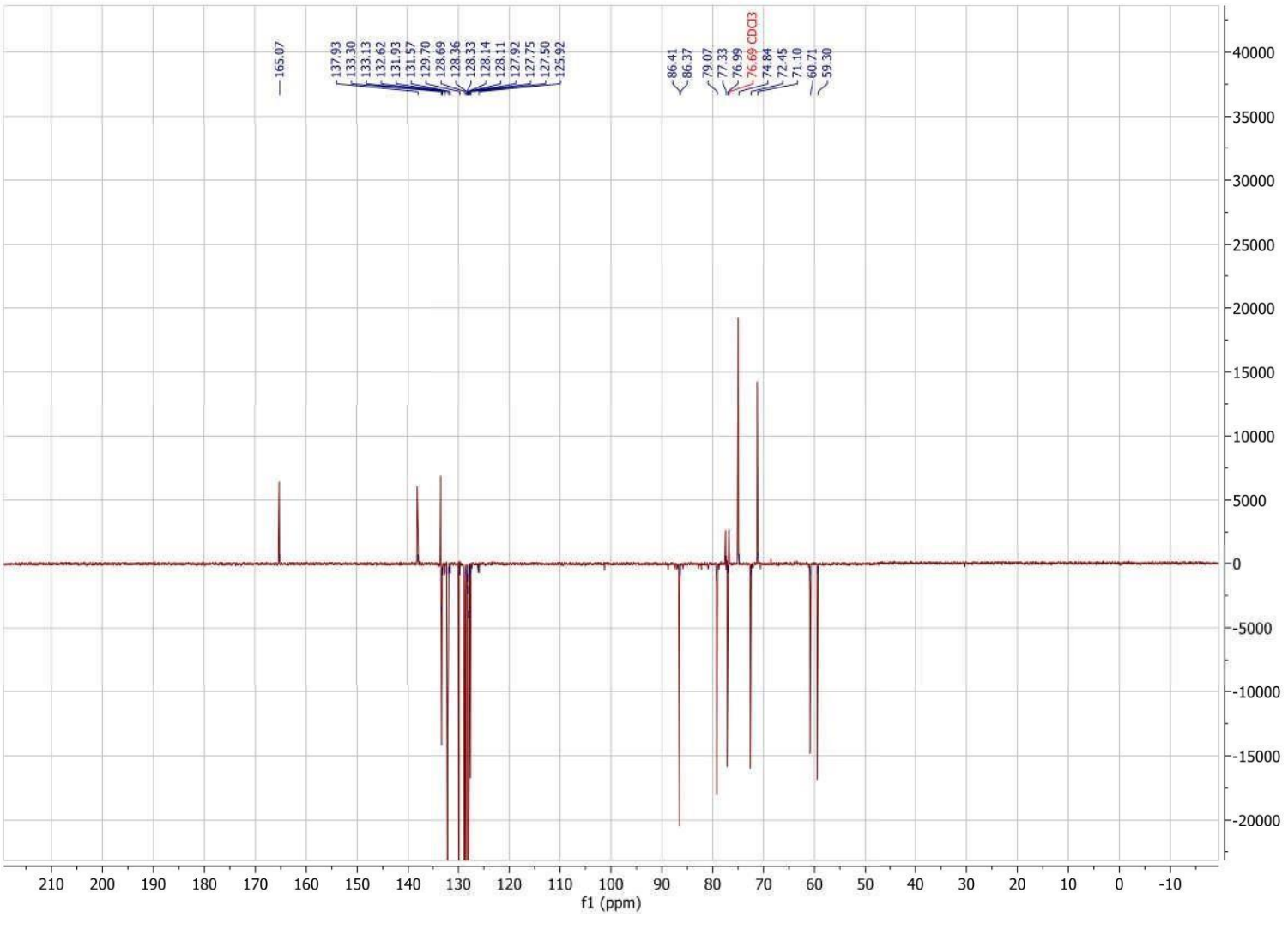


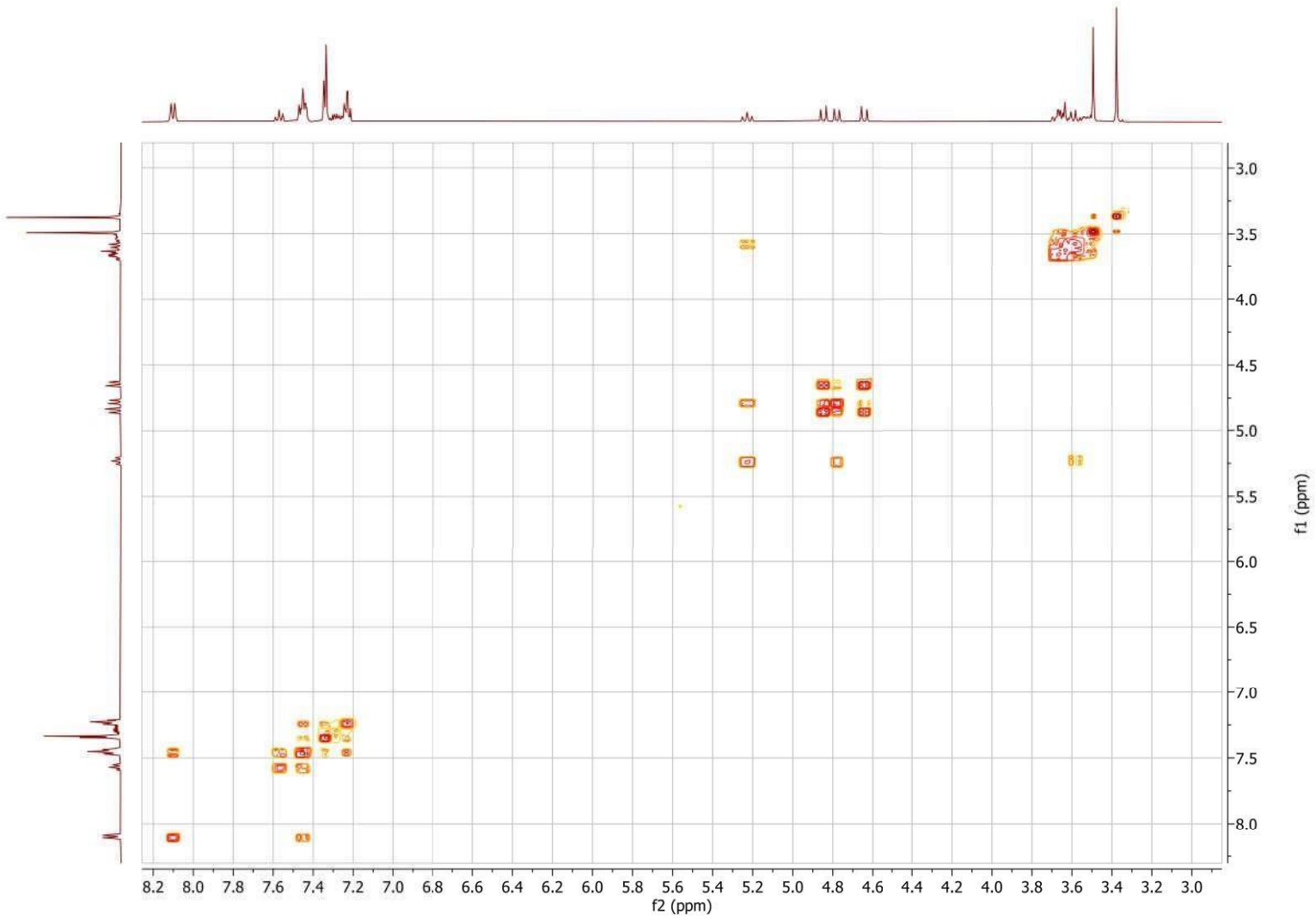

f2 (ppm)
f1 (ppm)

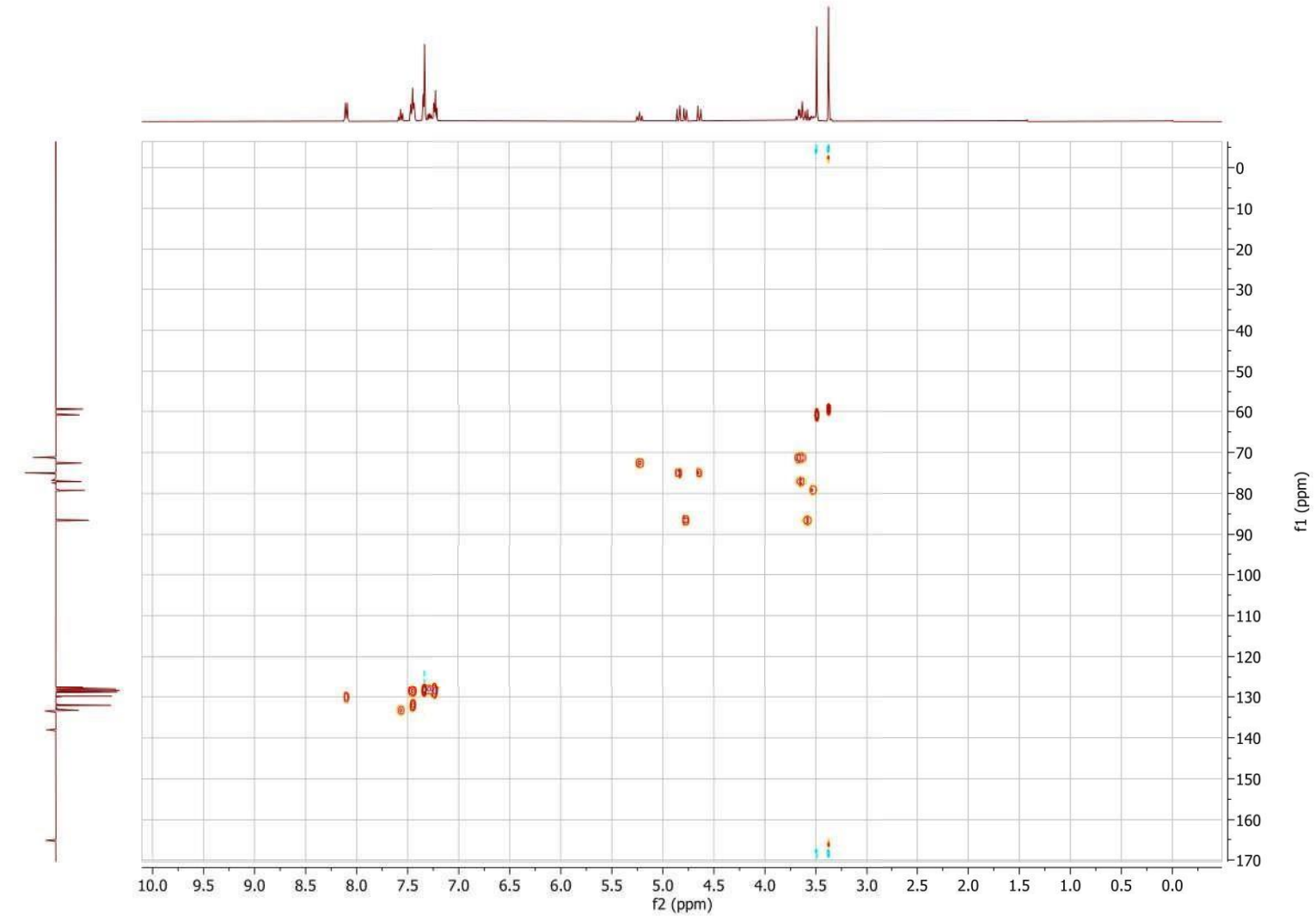

f2 (ppm)
f1 (ppm)

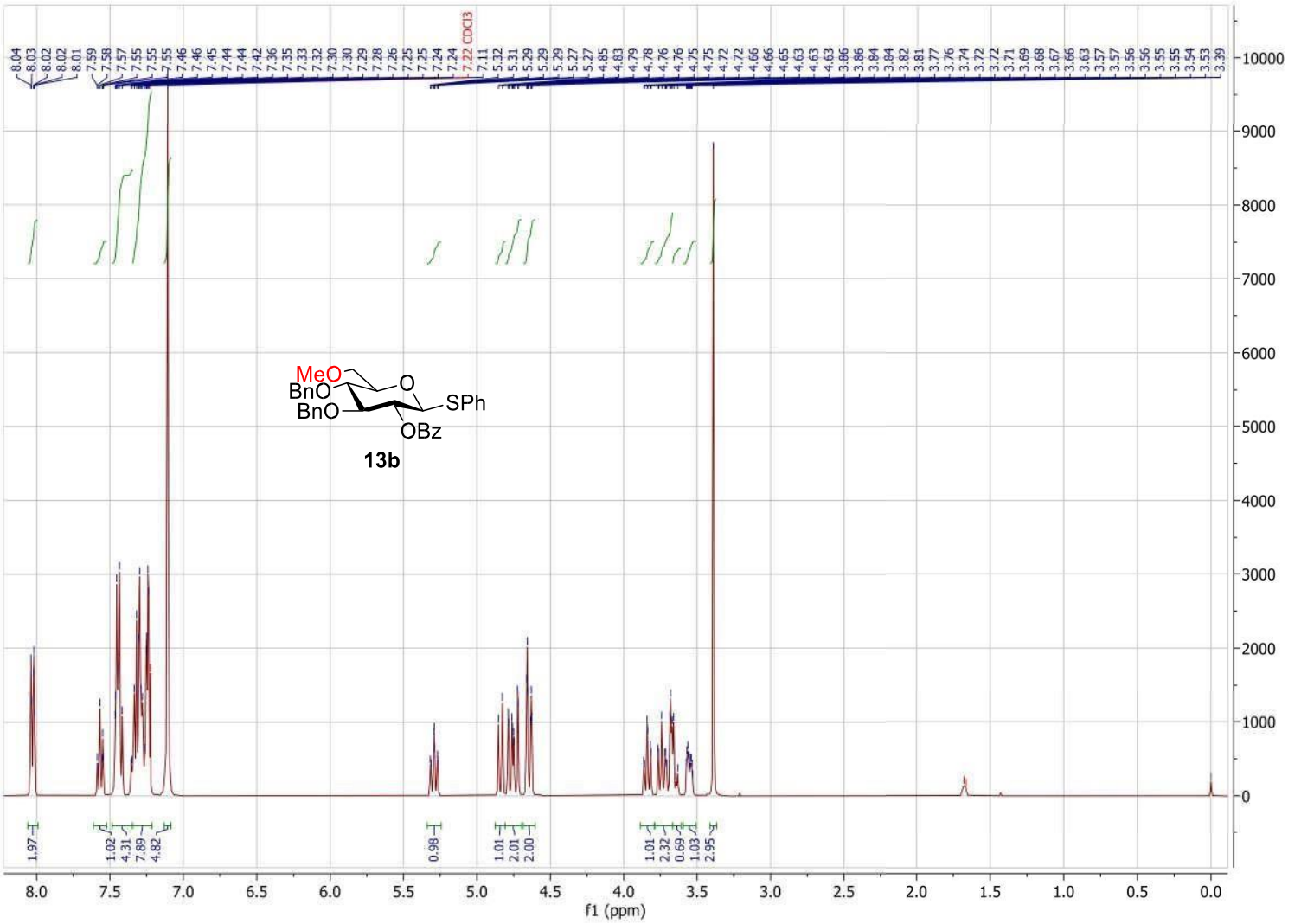


13a

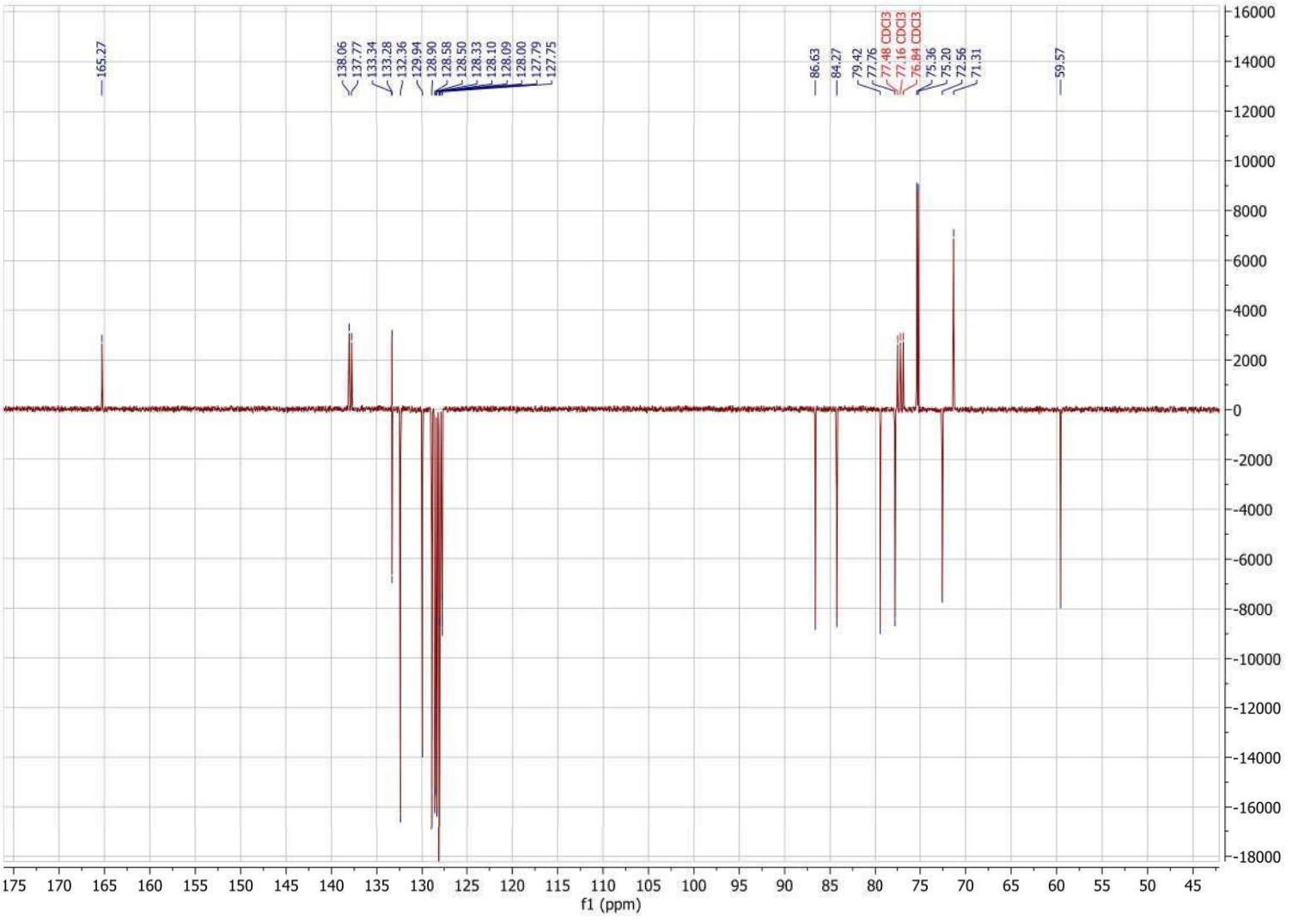


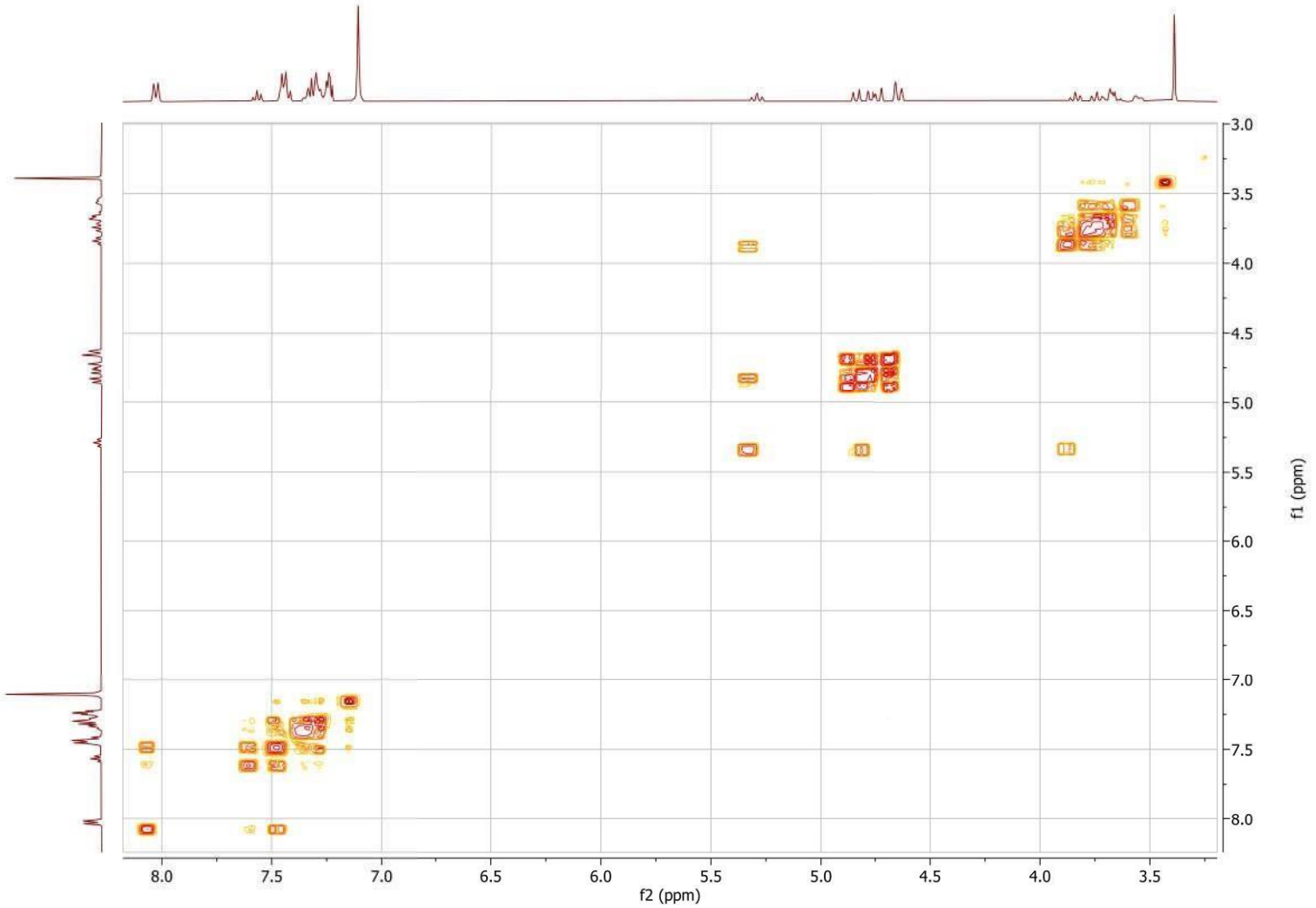

f2 (ppm)
f1 (ppm)

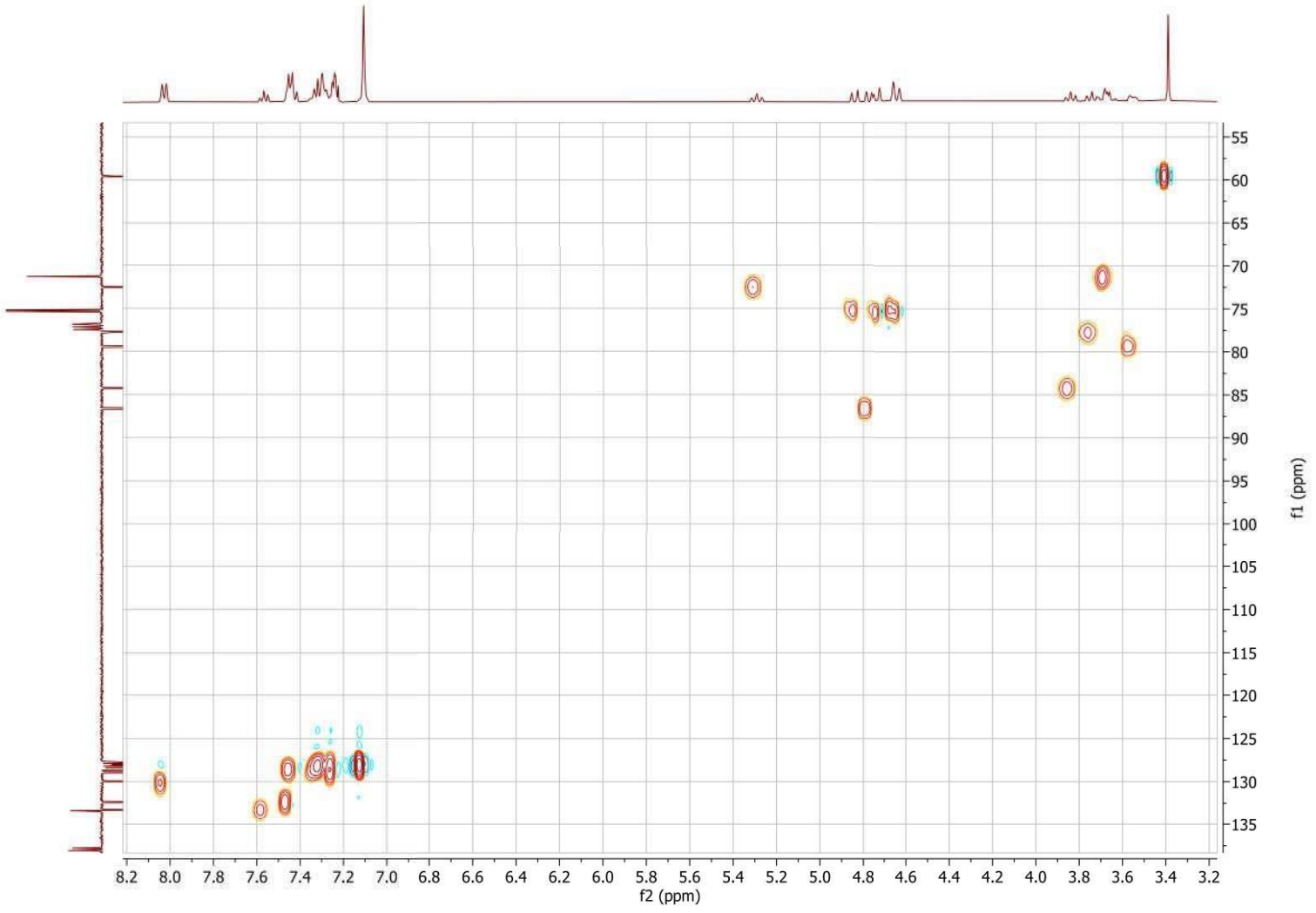

f2 (ppm)
f1 (ppm)

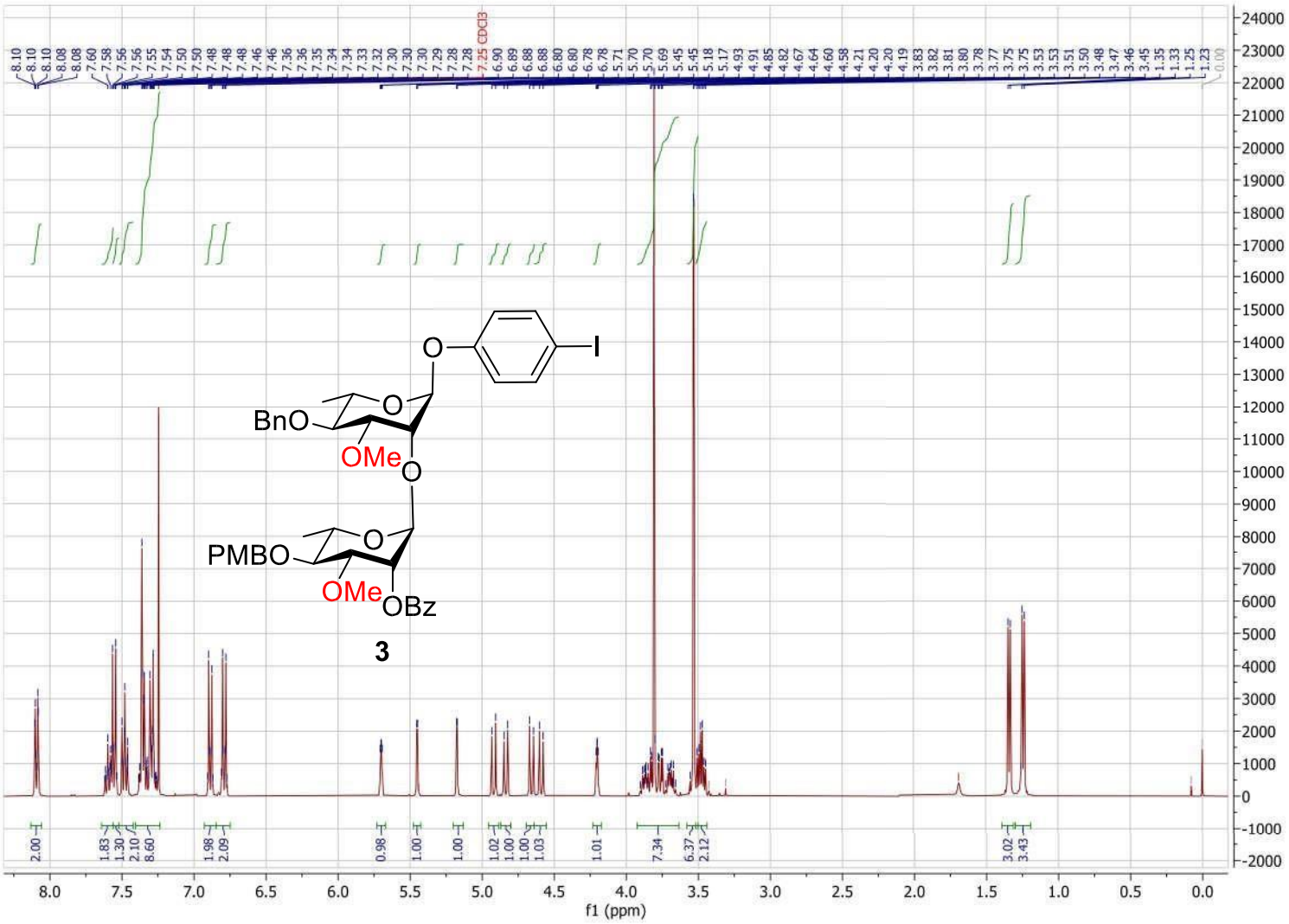


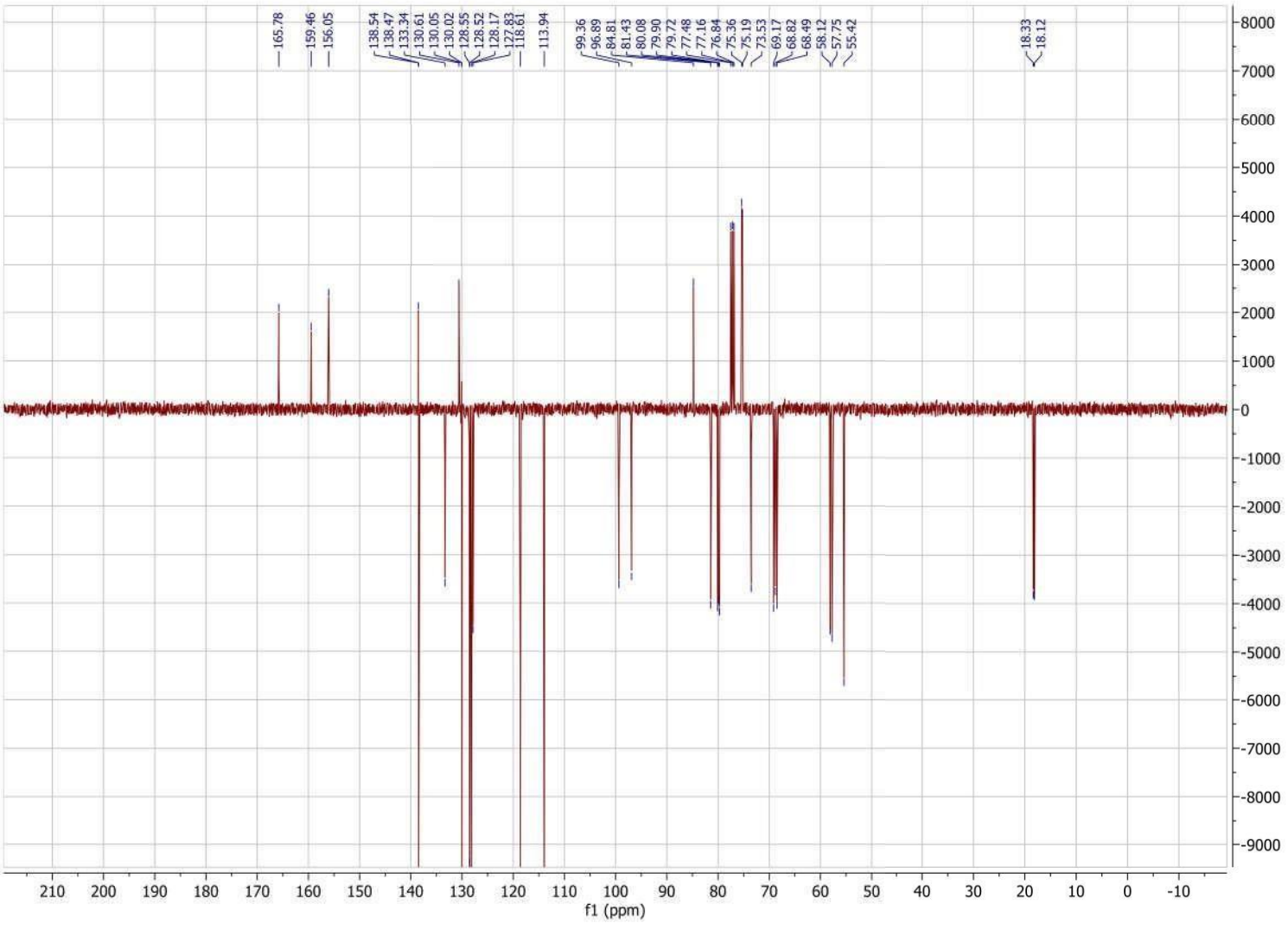
13b

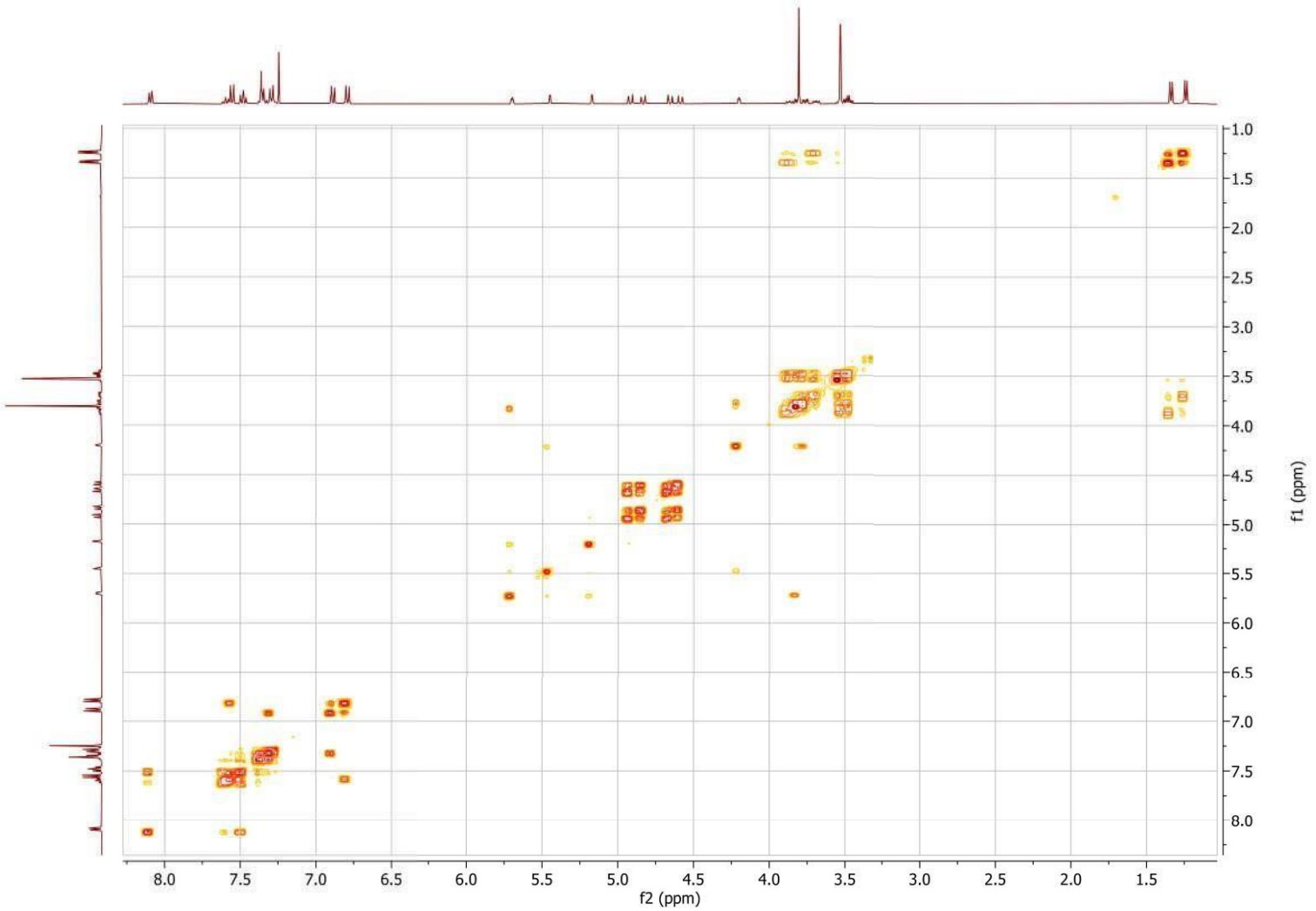


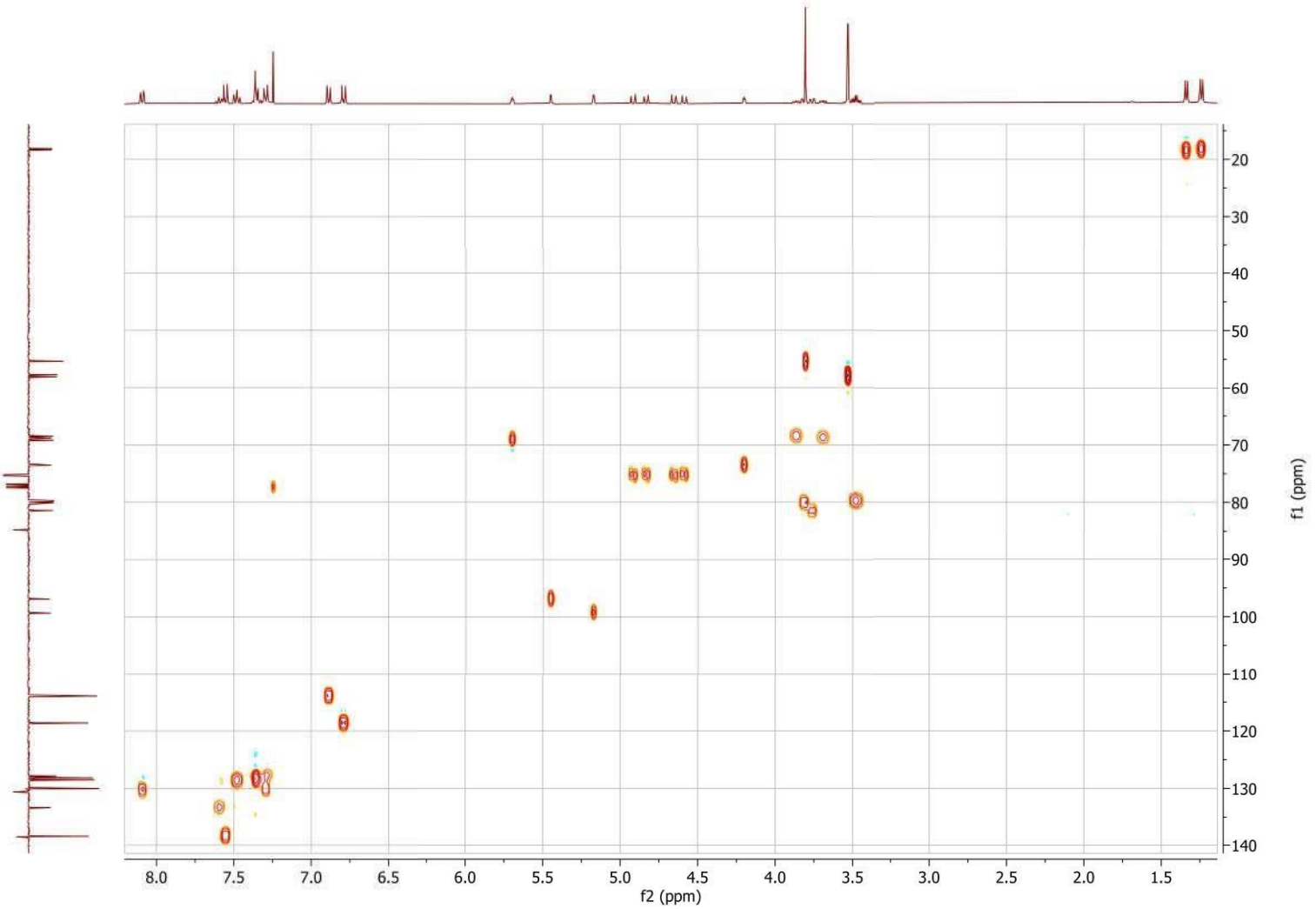

f2 (ppm)
f1 (ppm)

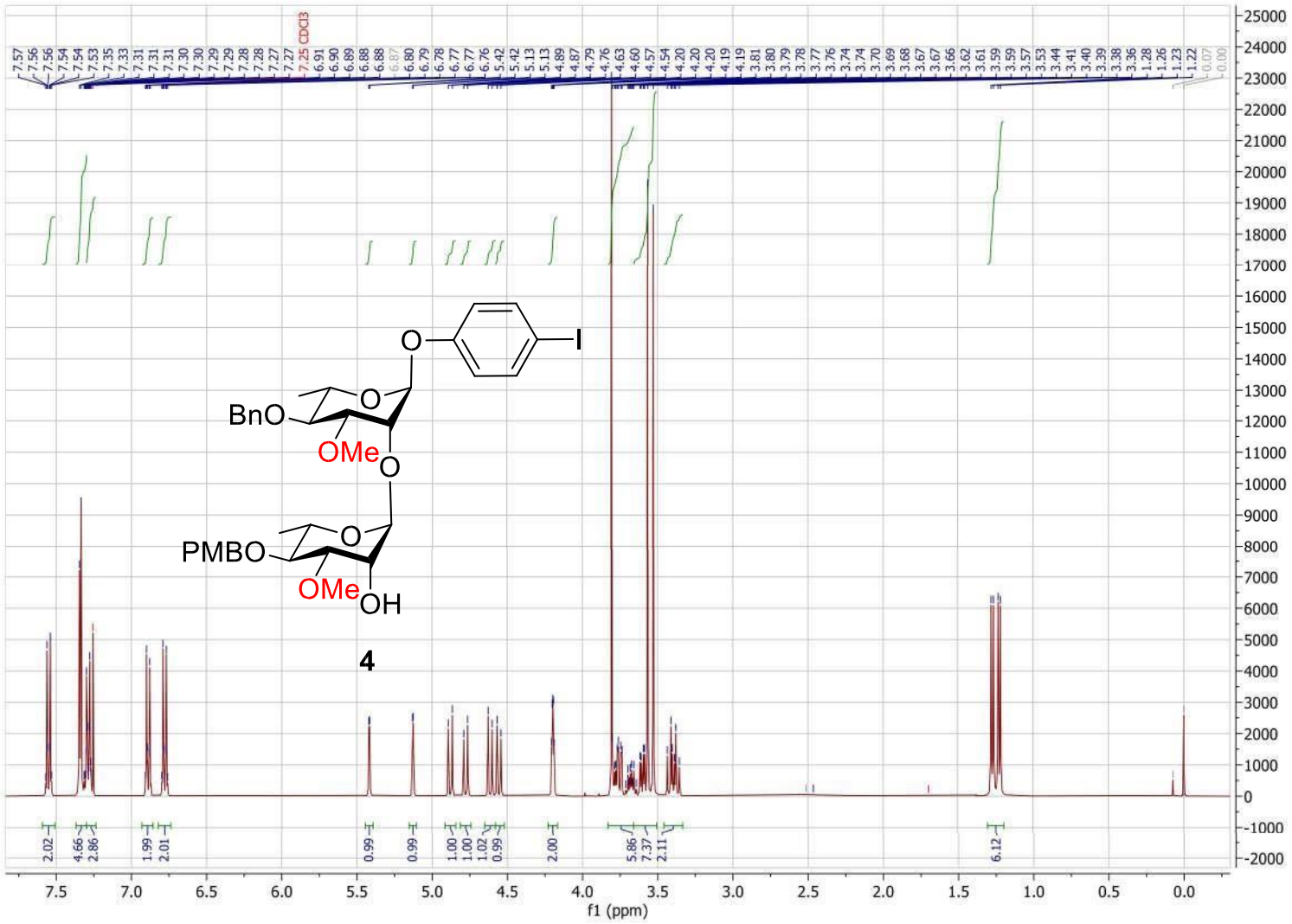

f2 (ppm)
f1 (ppm)

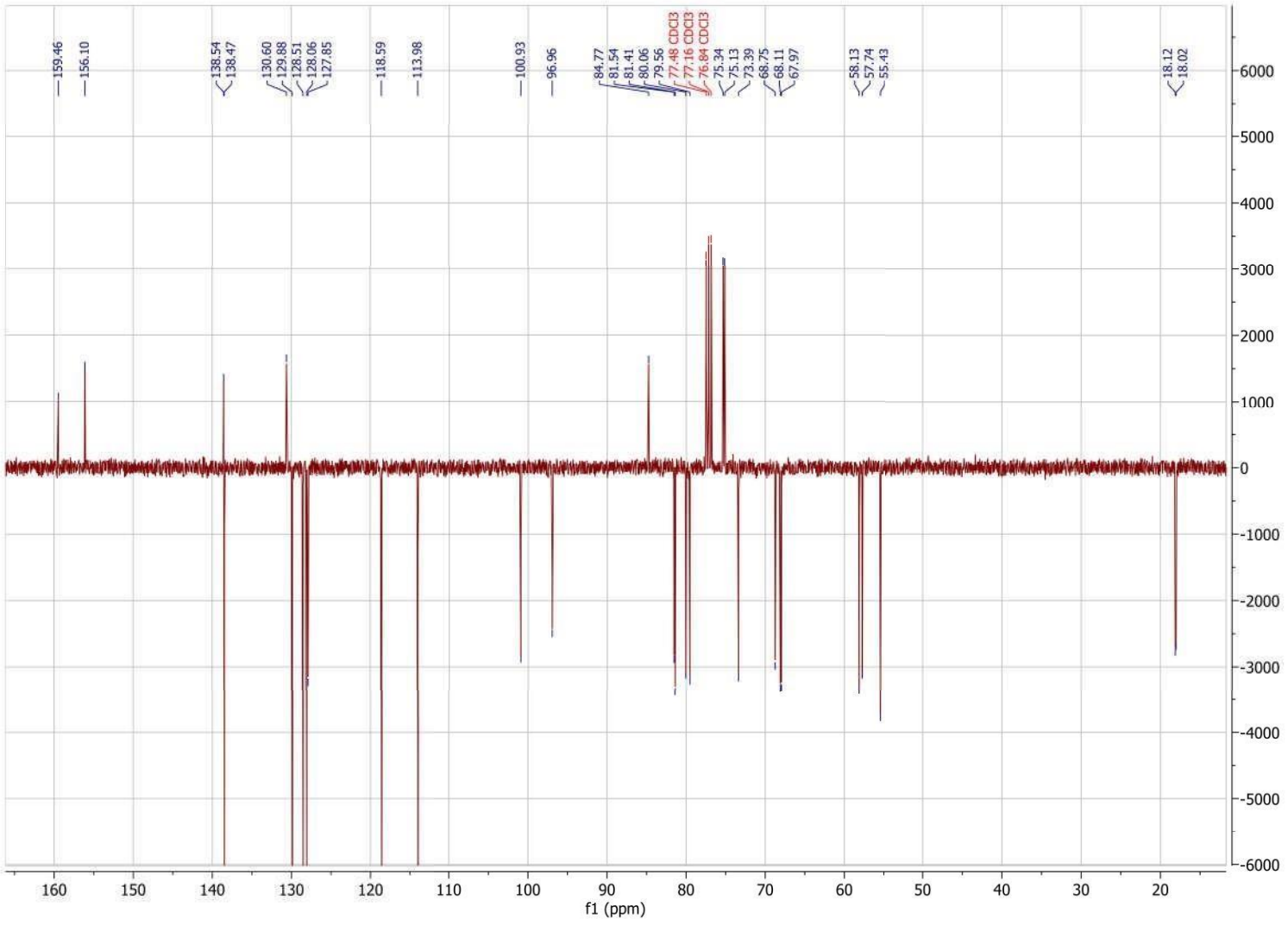

O
I
BnO
O
OMe
O
PMBO
O
OMe
OBz
3
f1 (ppm)

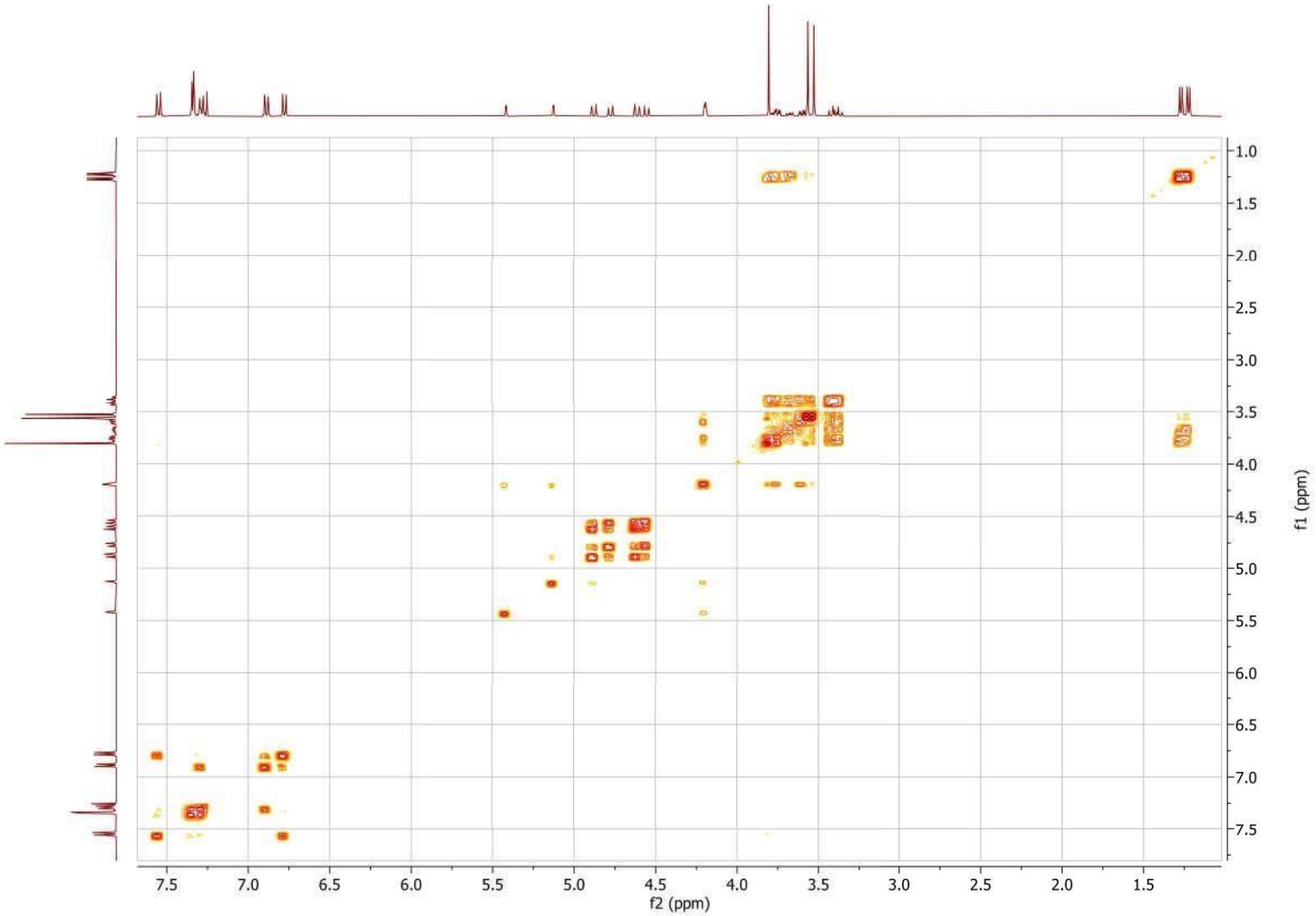

f1 (ppm)

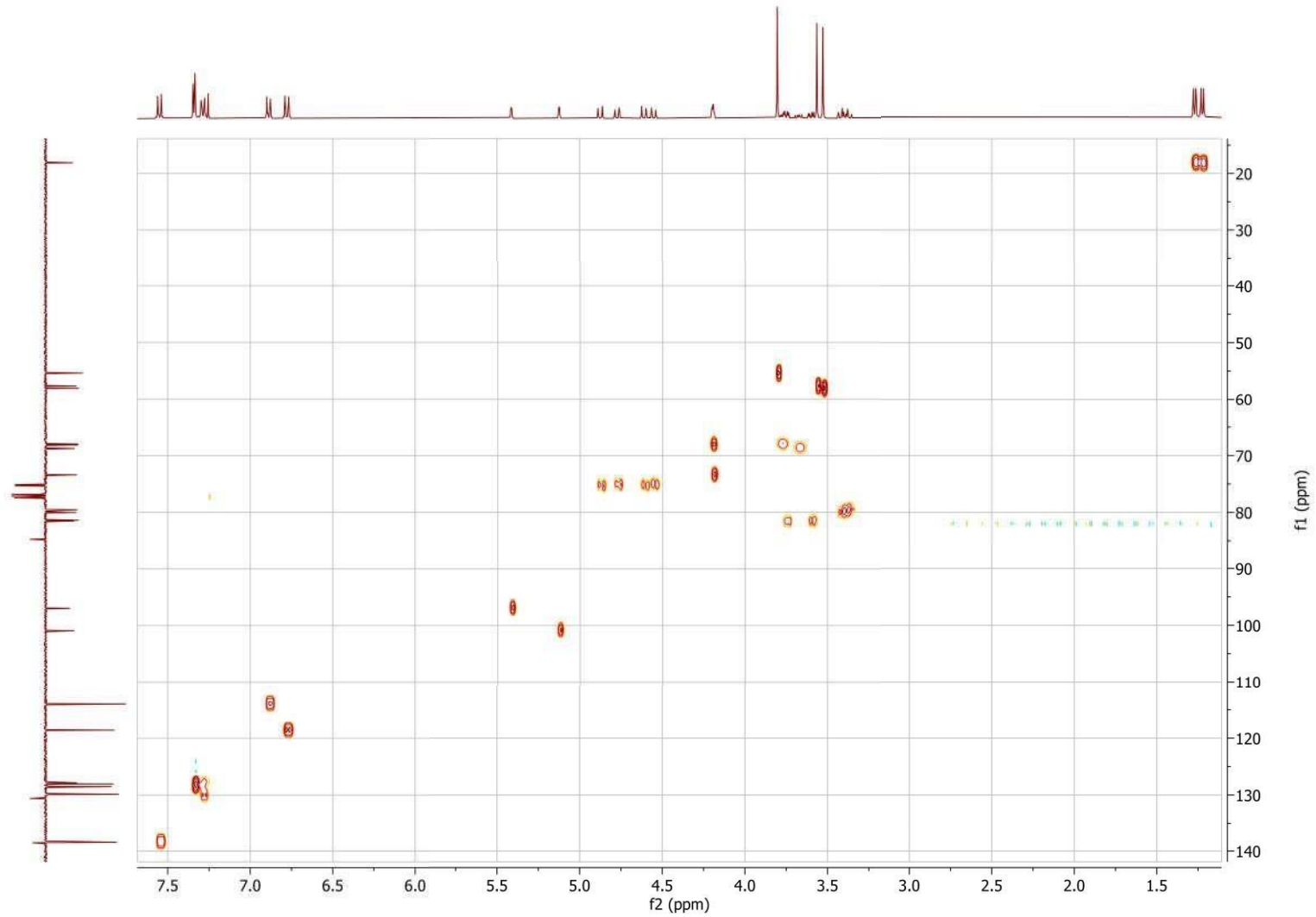

f2 (ppm)
f1 (ppm)

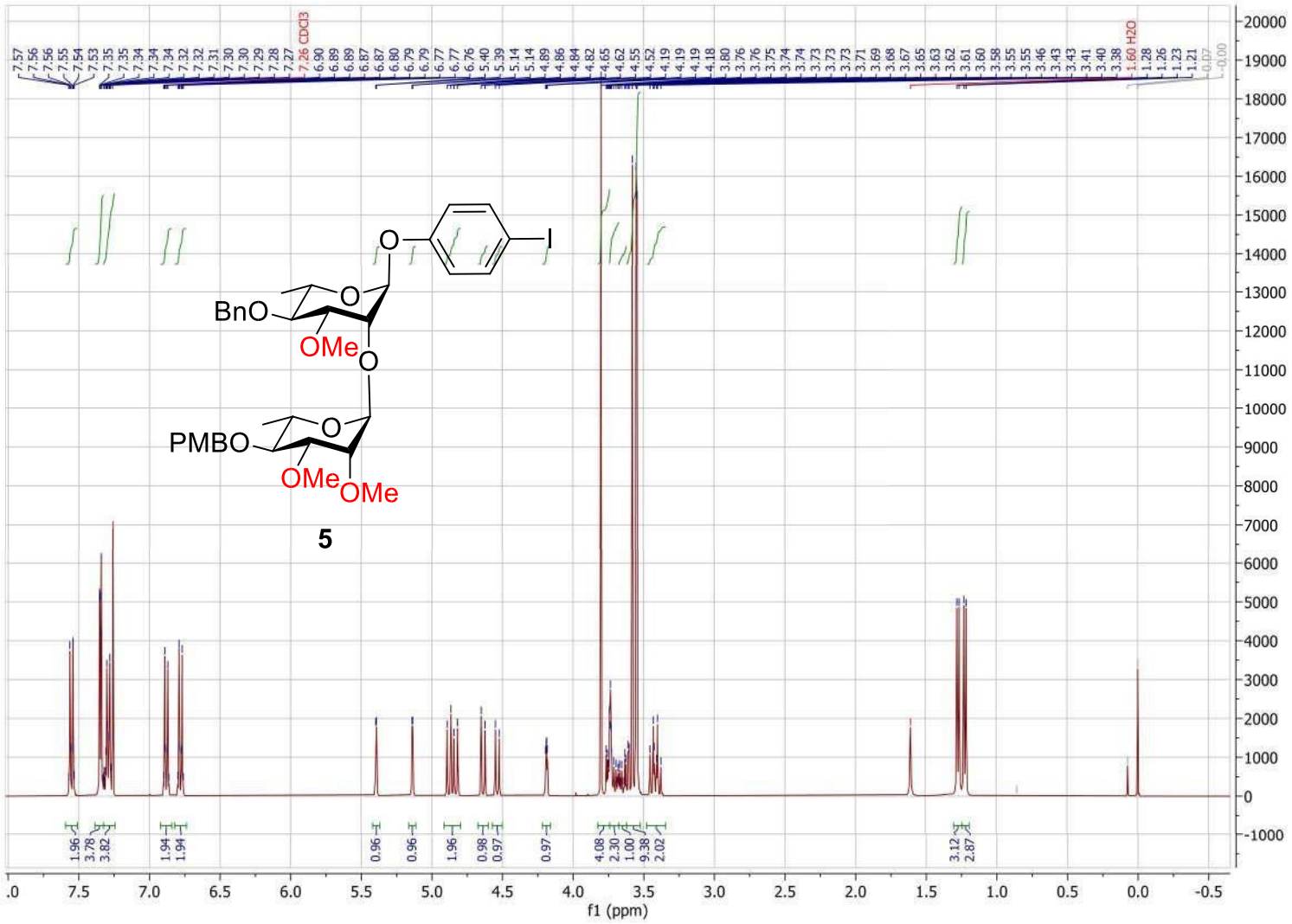

f2 (ppm)
f1 (ppm)

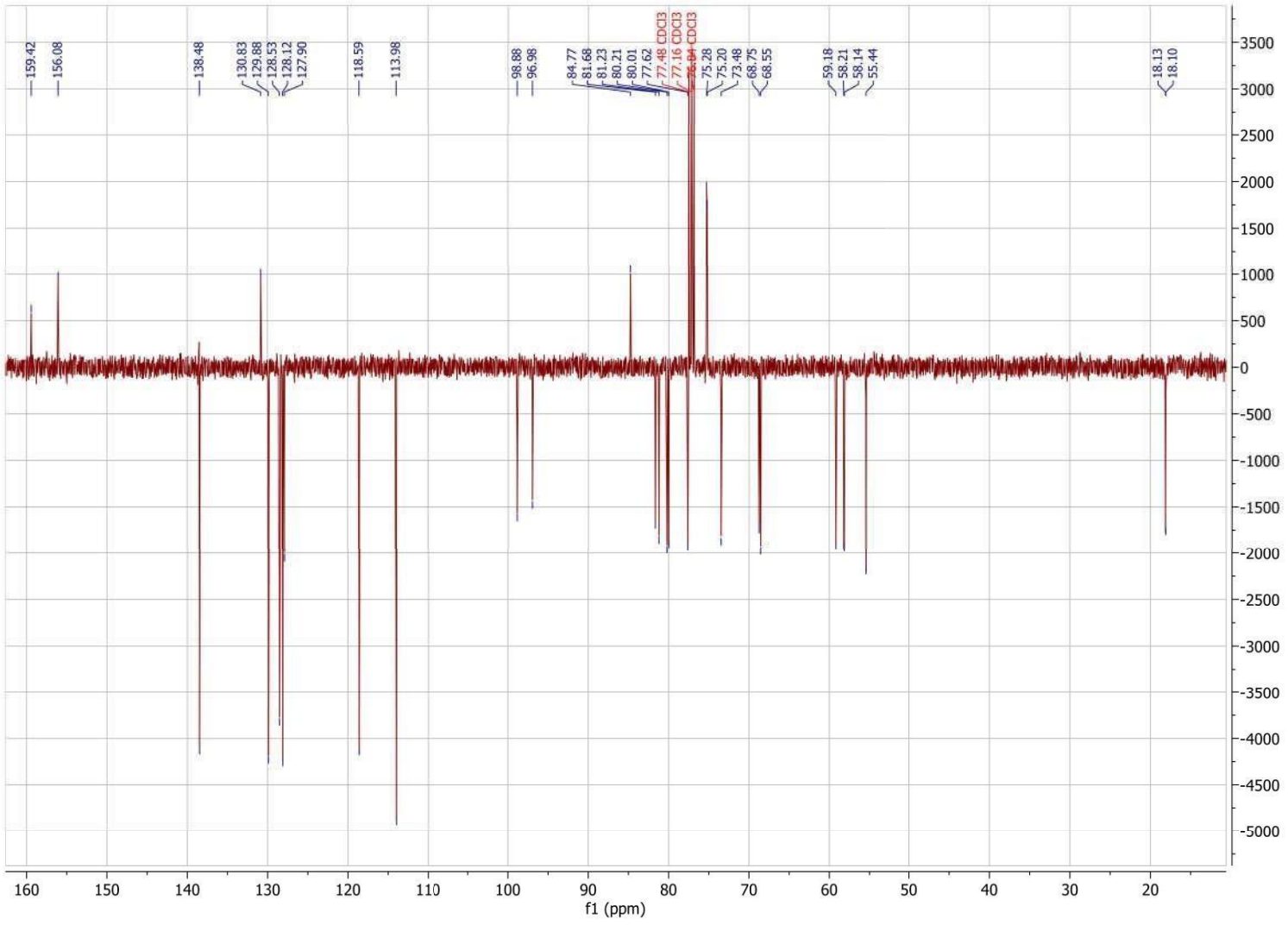

BnO
OMe
PMBO
OMe
OH
I
4
f1 (ppm)

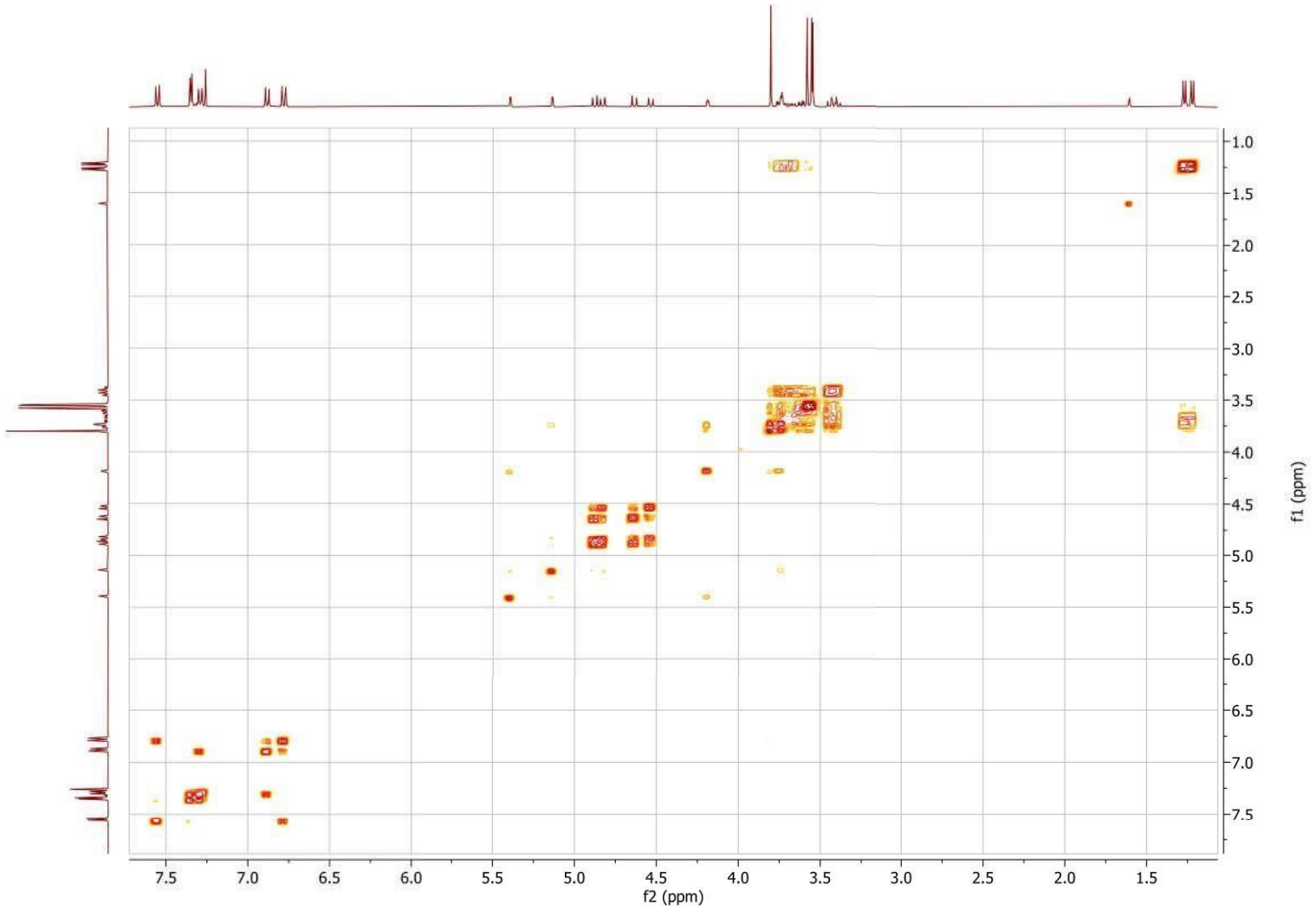

f1 (ppm)

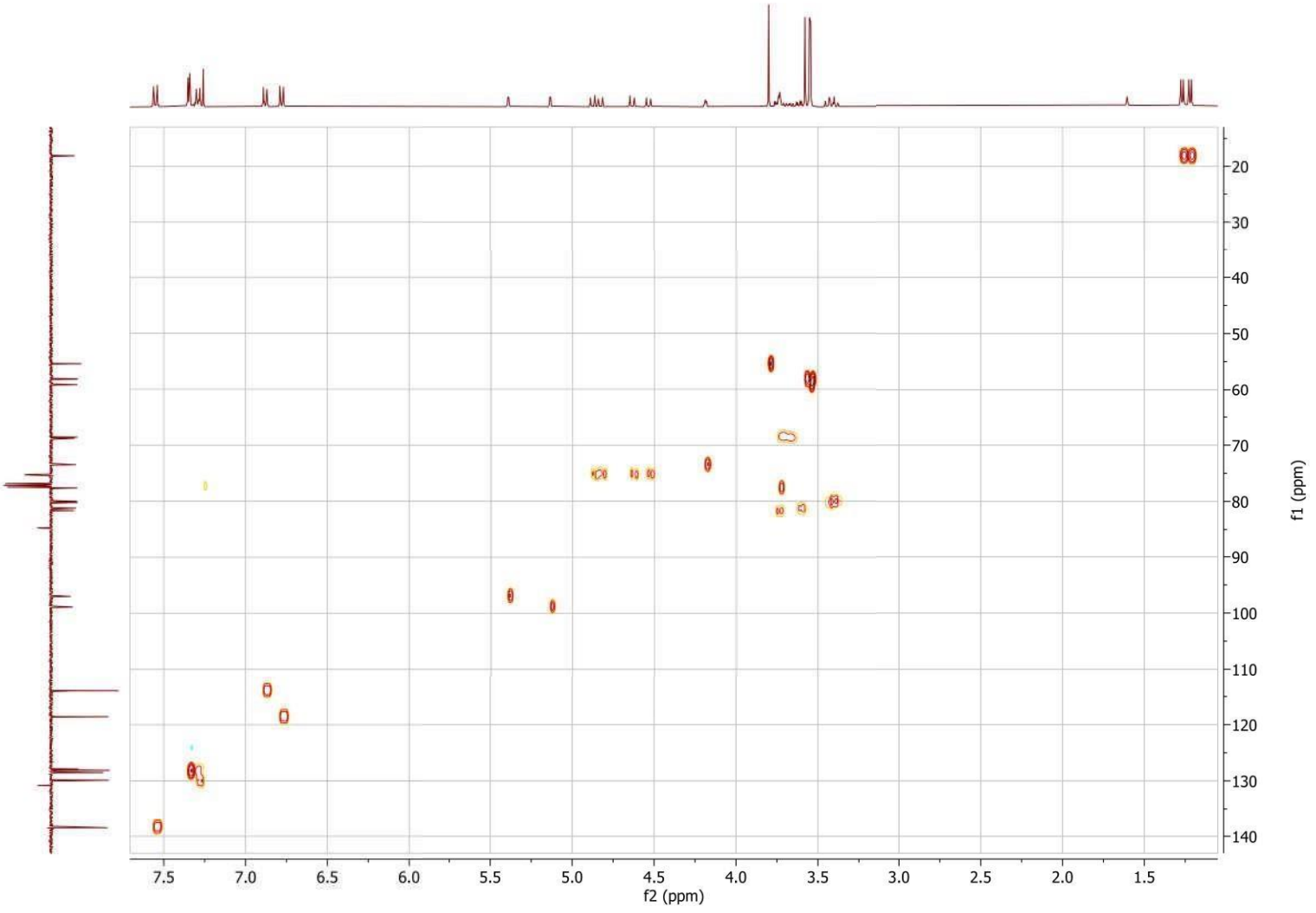

f1 (ppm)
f2 (ppm)

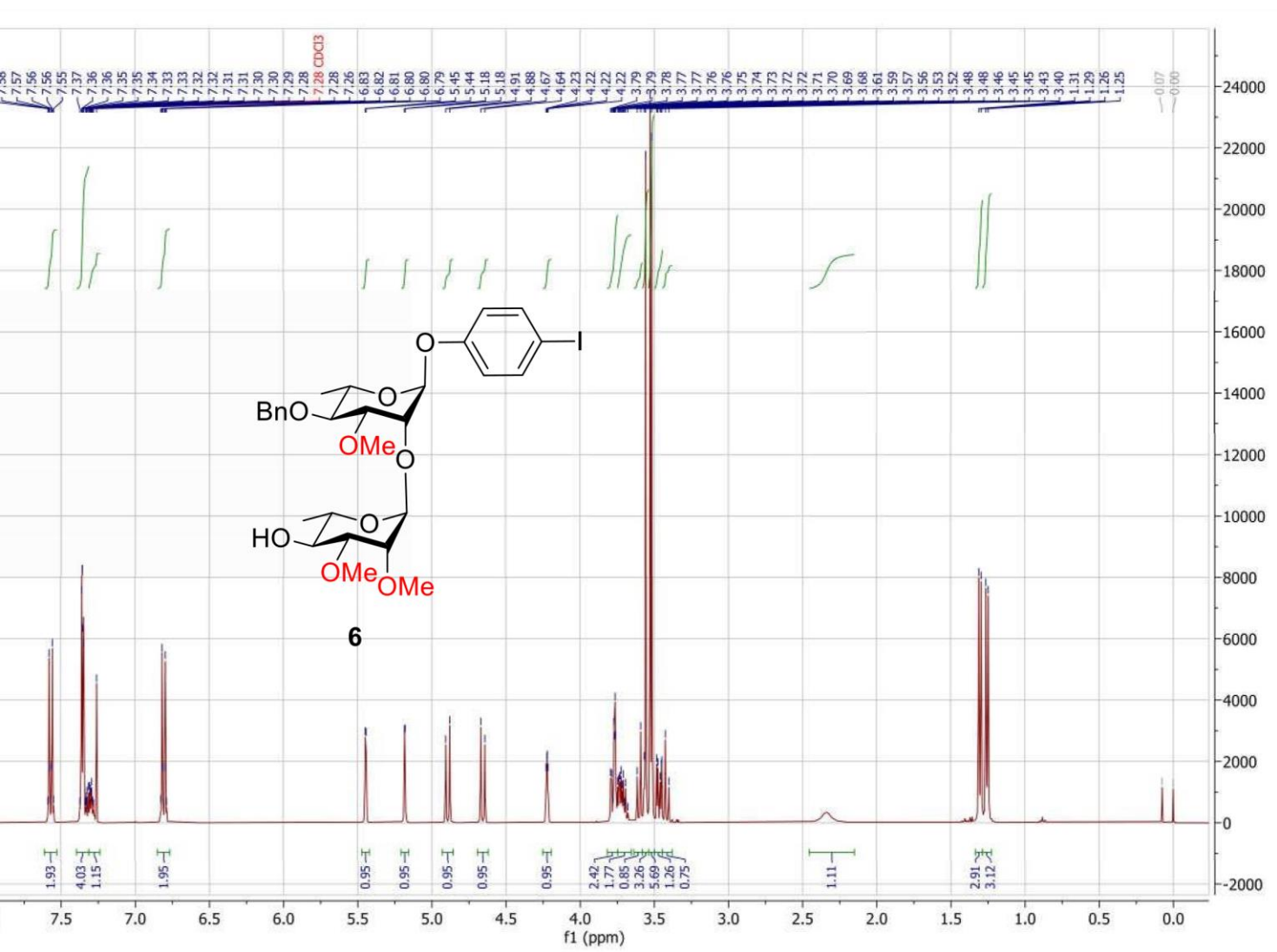

f1 (ppm)
f2 (ppm)

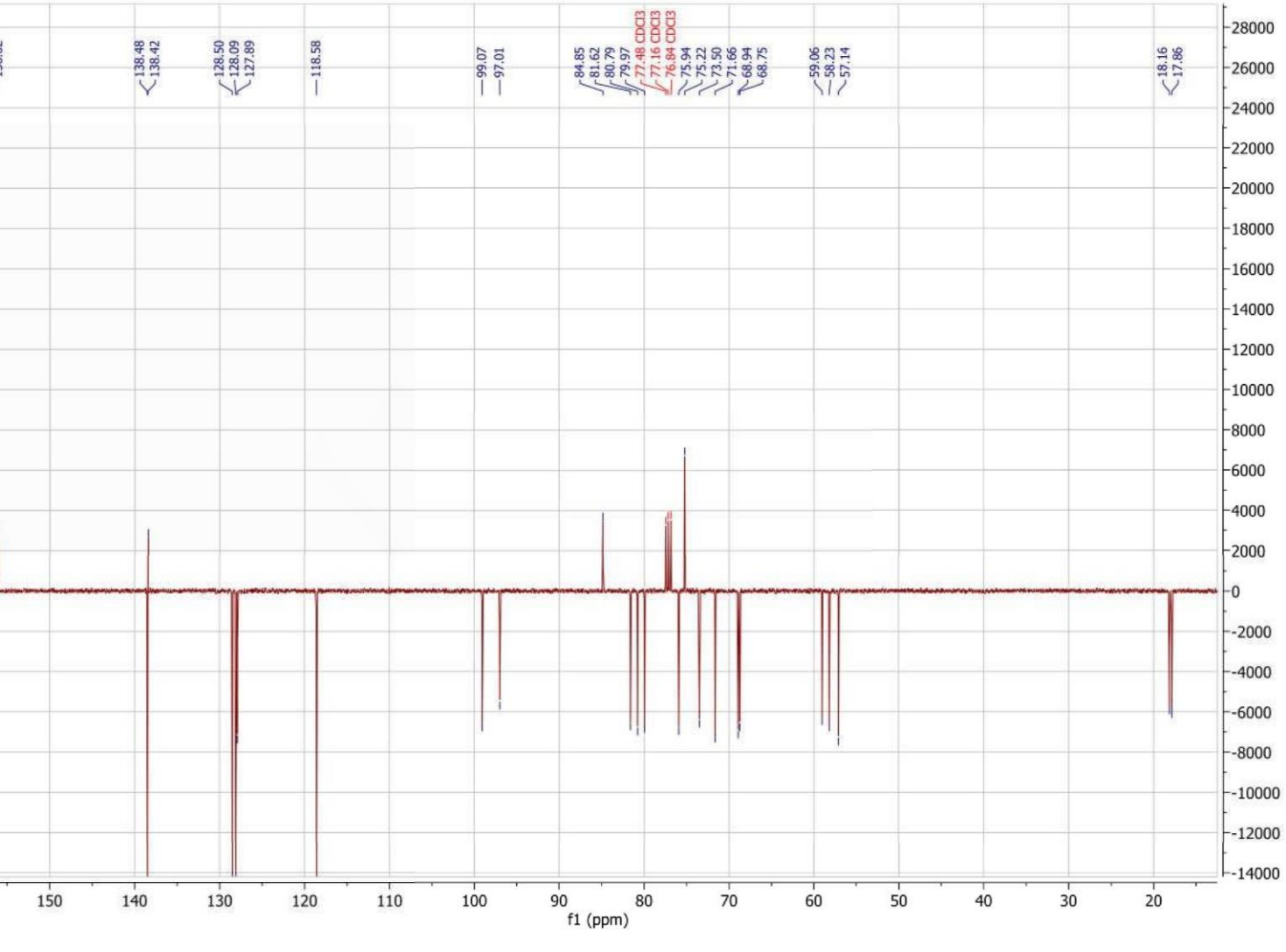

BnO
OMe
O
PMBO
OMe
OMe
I
5
f1 (ppm)

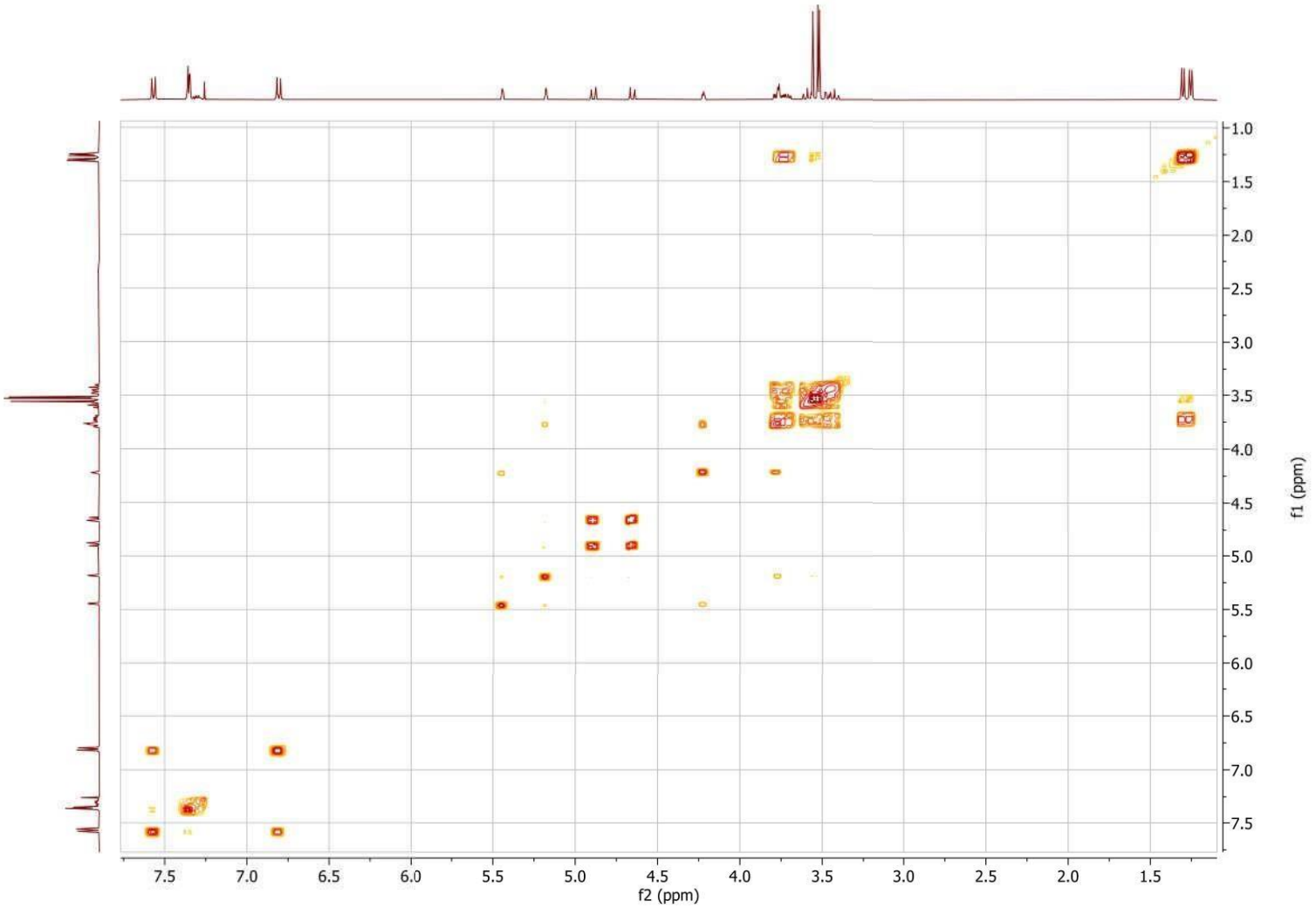

f1 (ppm)

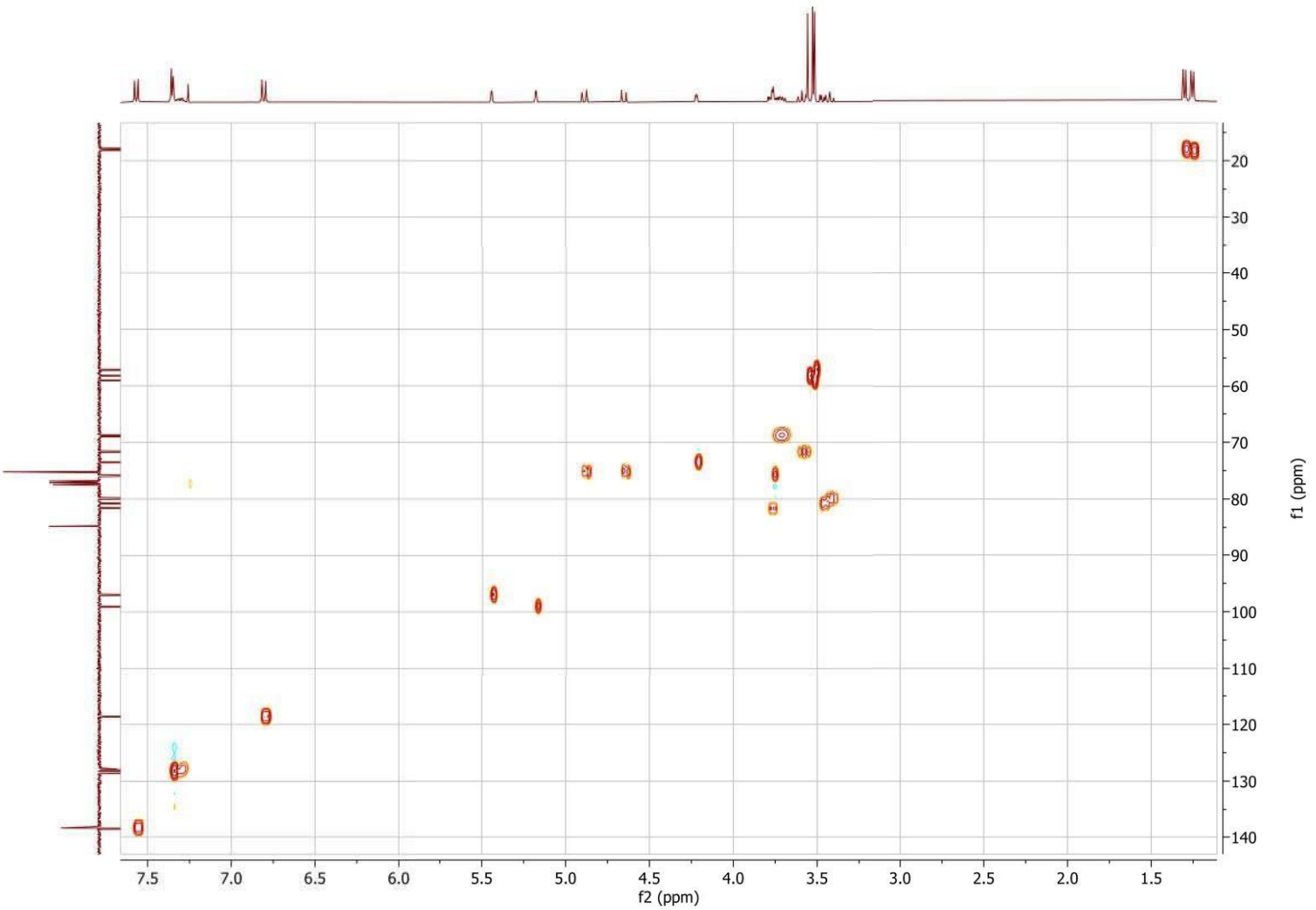

f1 (ppm)
f2 (ppm)

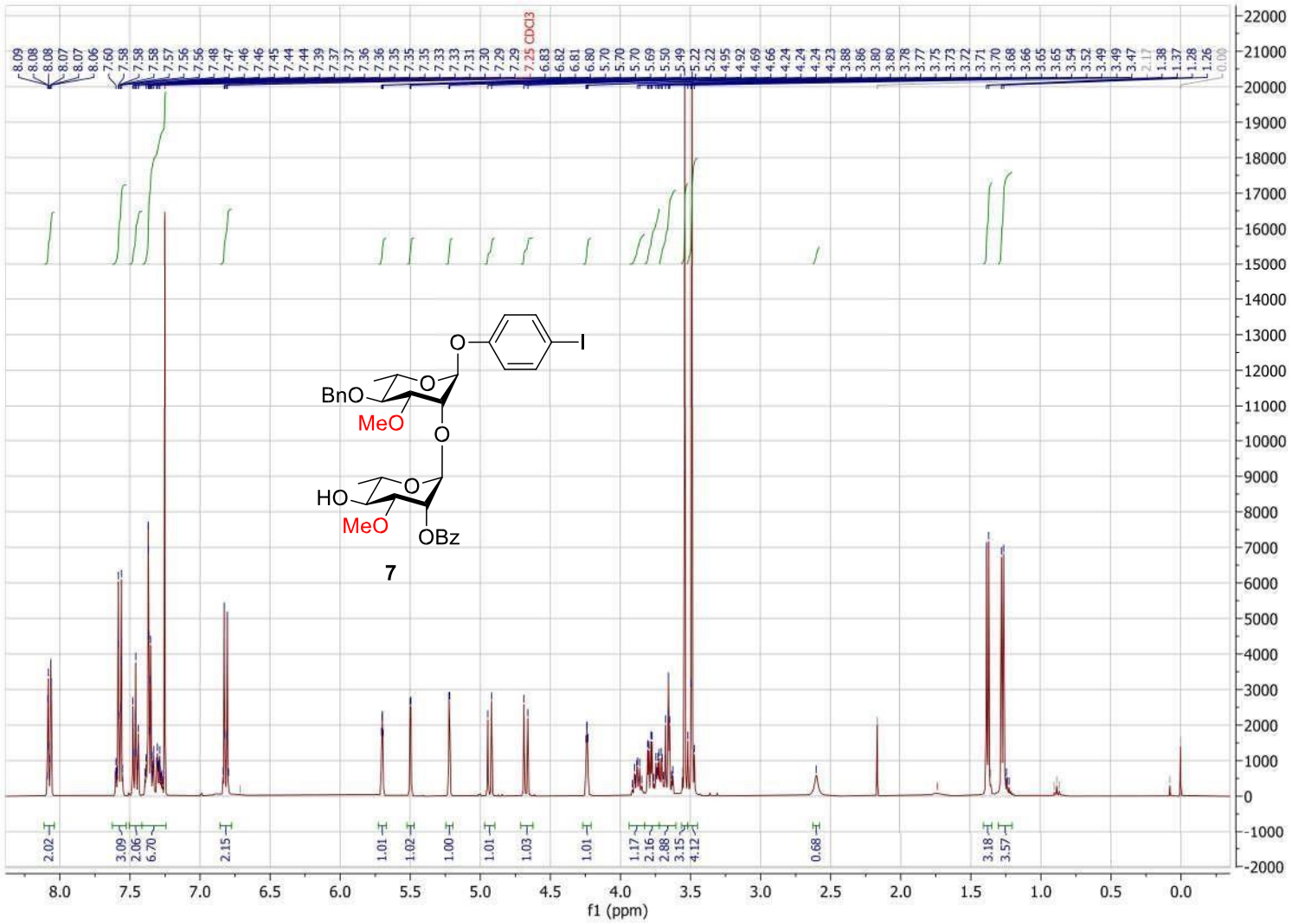

f1 (ppm)
f2 (ppm)

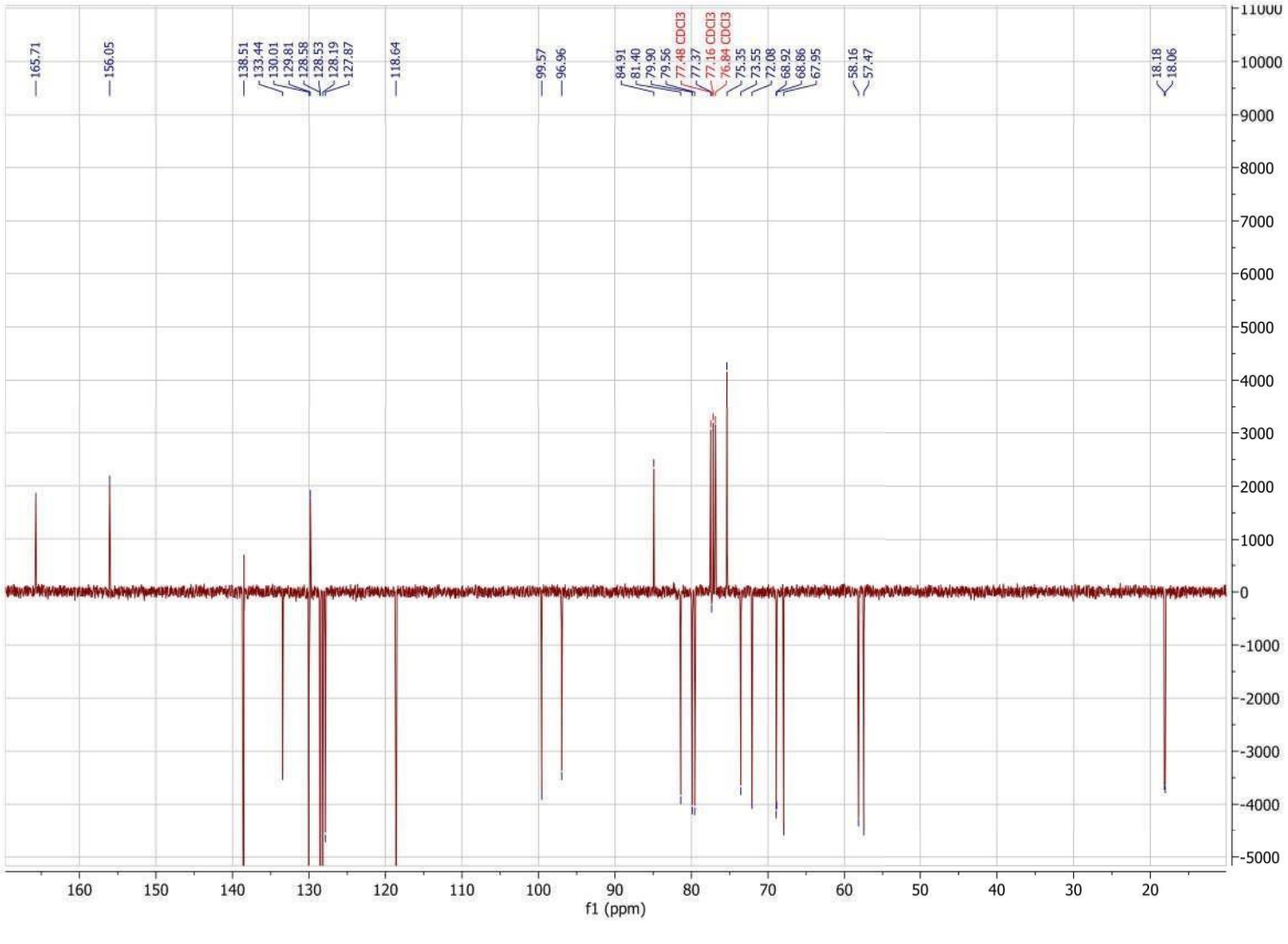

BnO
OMe
O
HO
OMe
OMe
I
6
f1 (ppm)

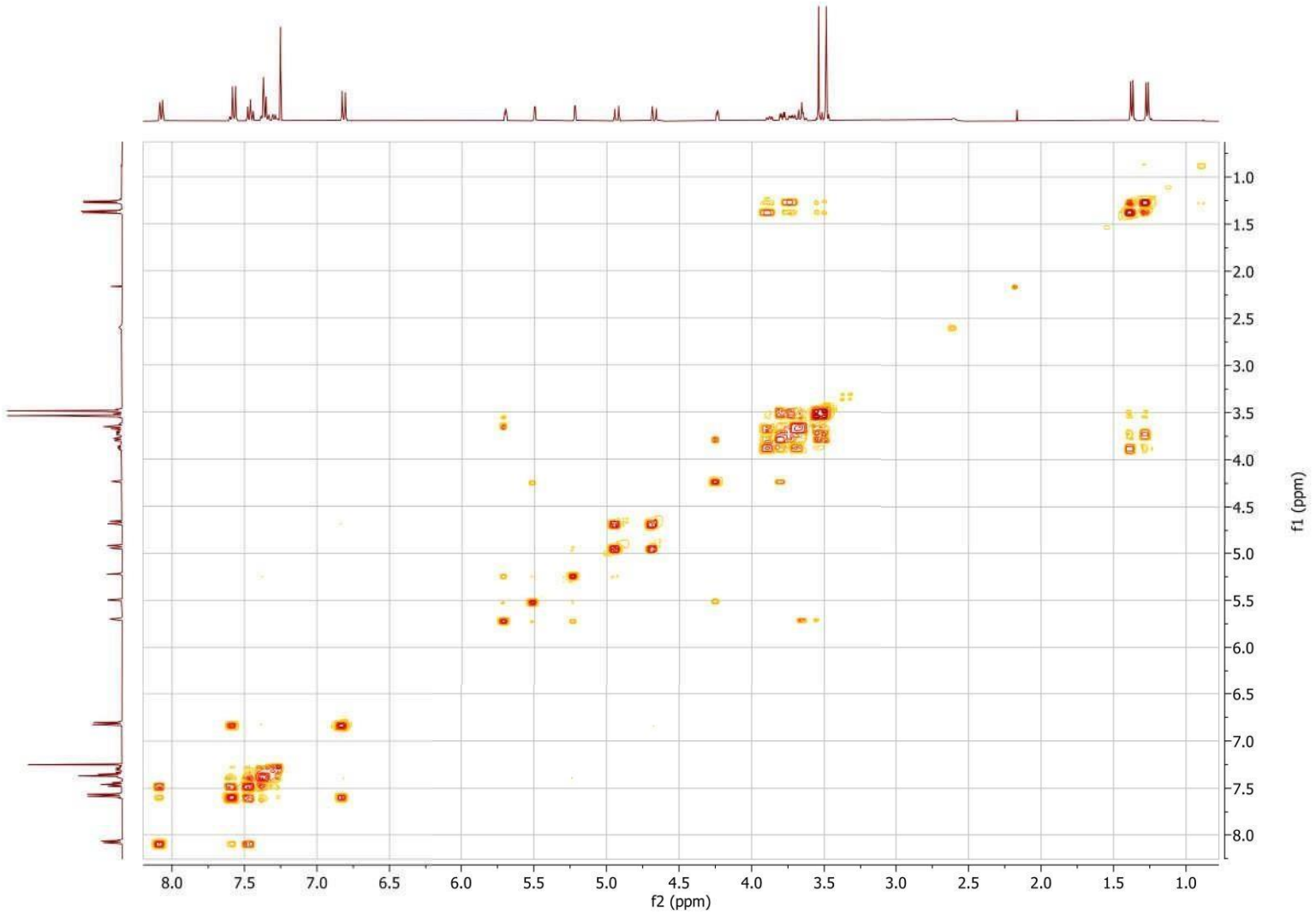

f1 (ppm)

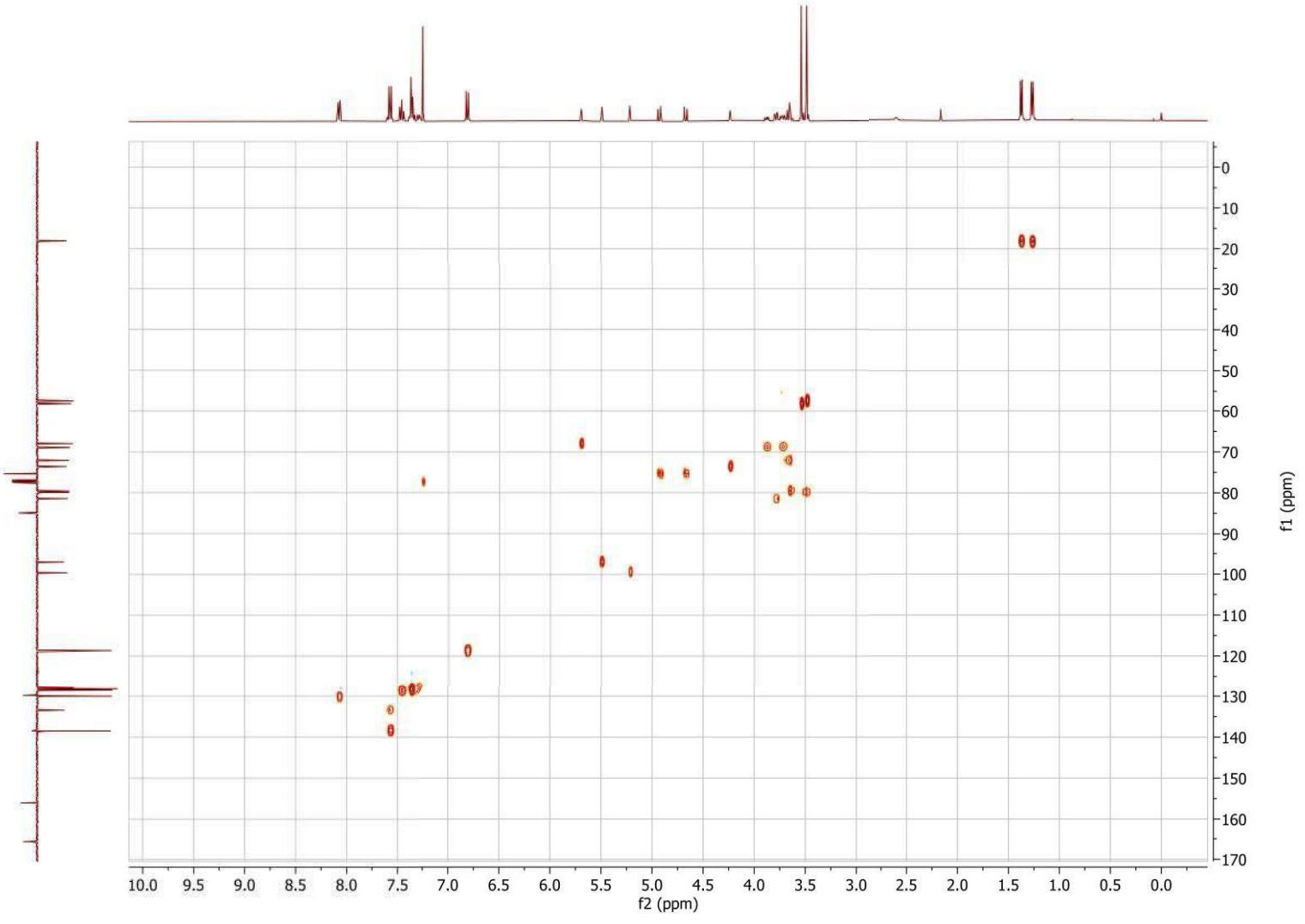

f1 (ppm)
f2 (ppm)

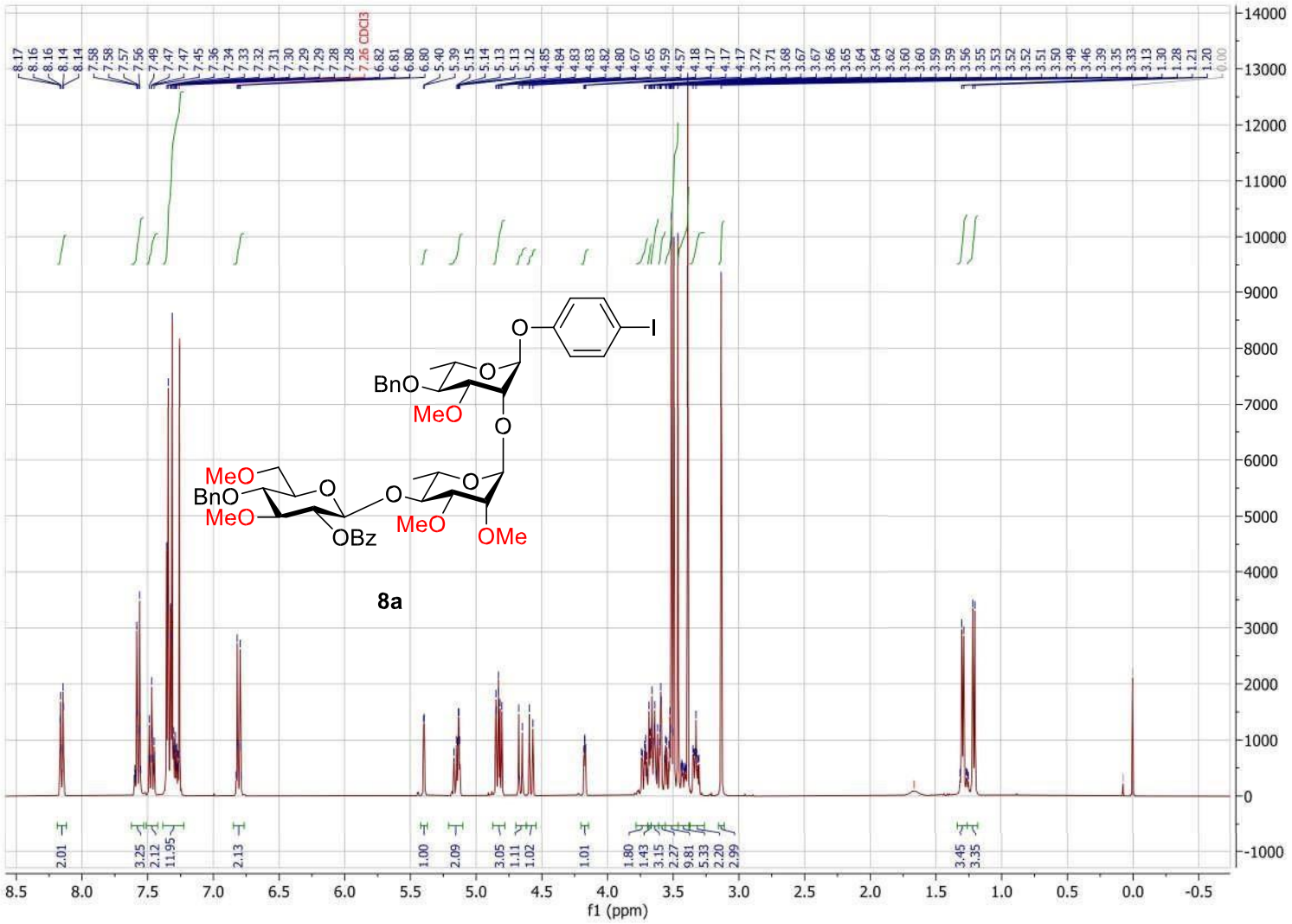

f1 (ppm)
f2 (ppm)

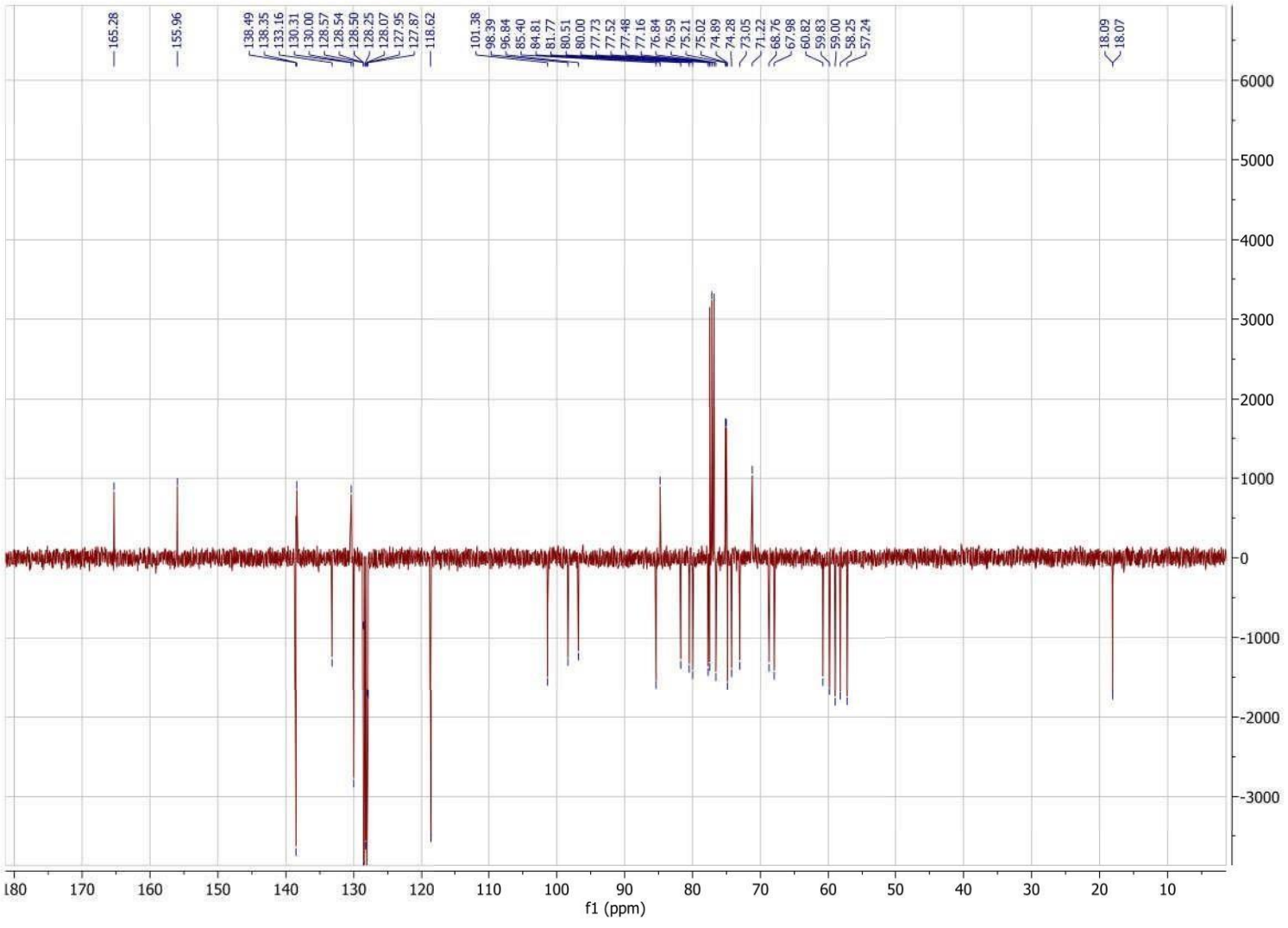

BnO
MeO
O
HO
MeO
OBz
I
7
f1 (ppm)

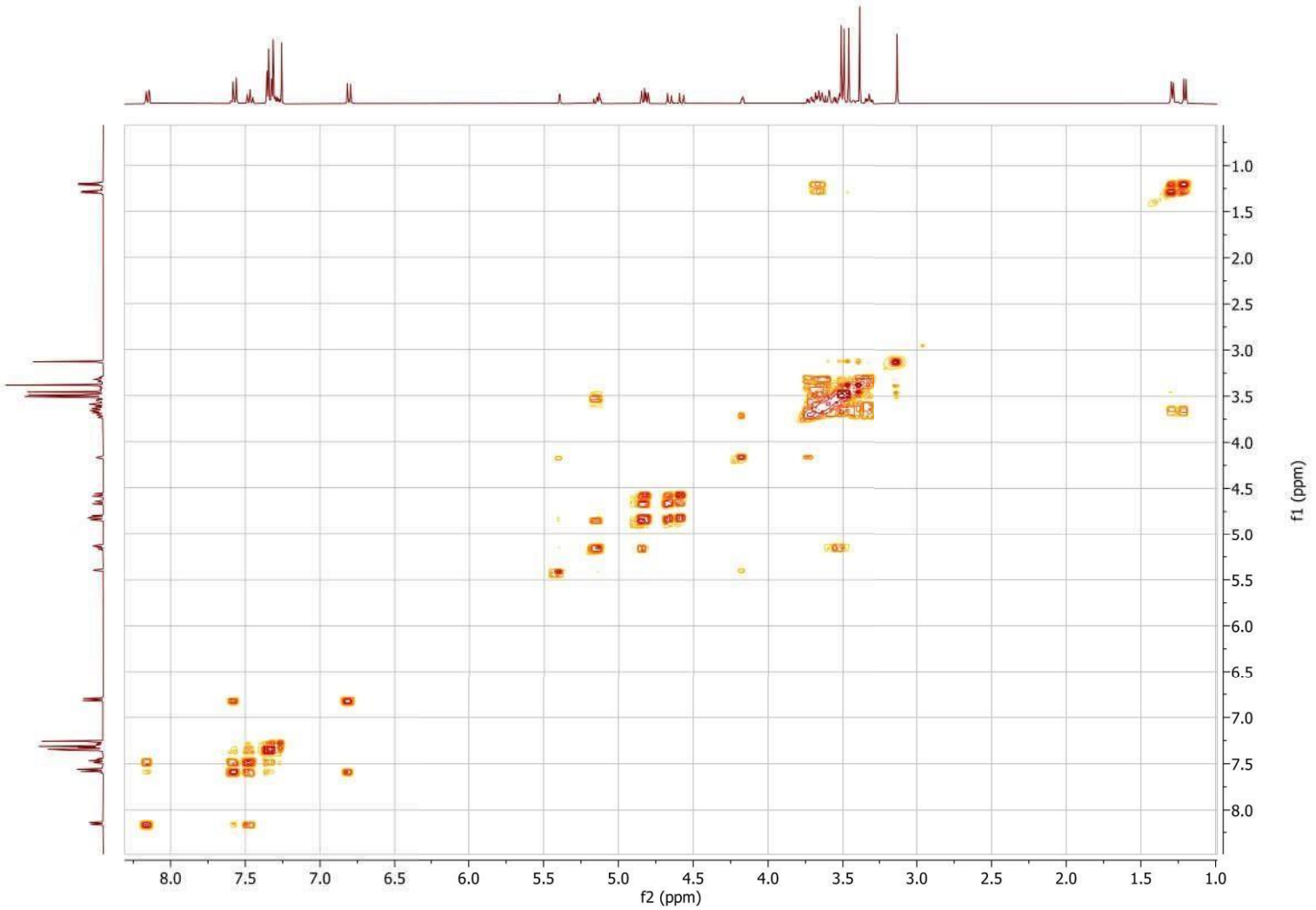

f1 (ppm)

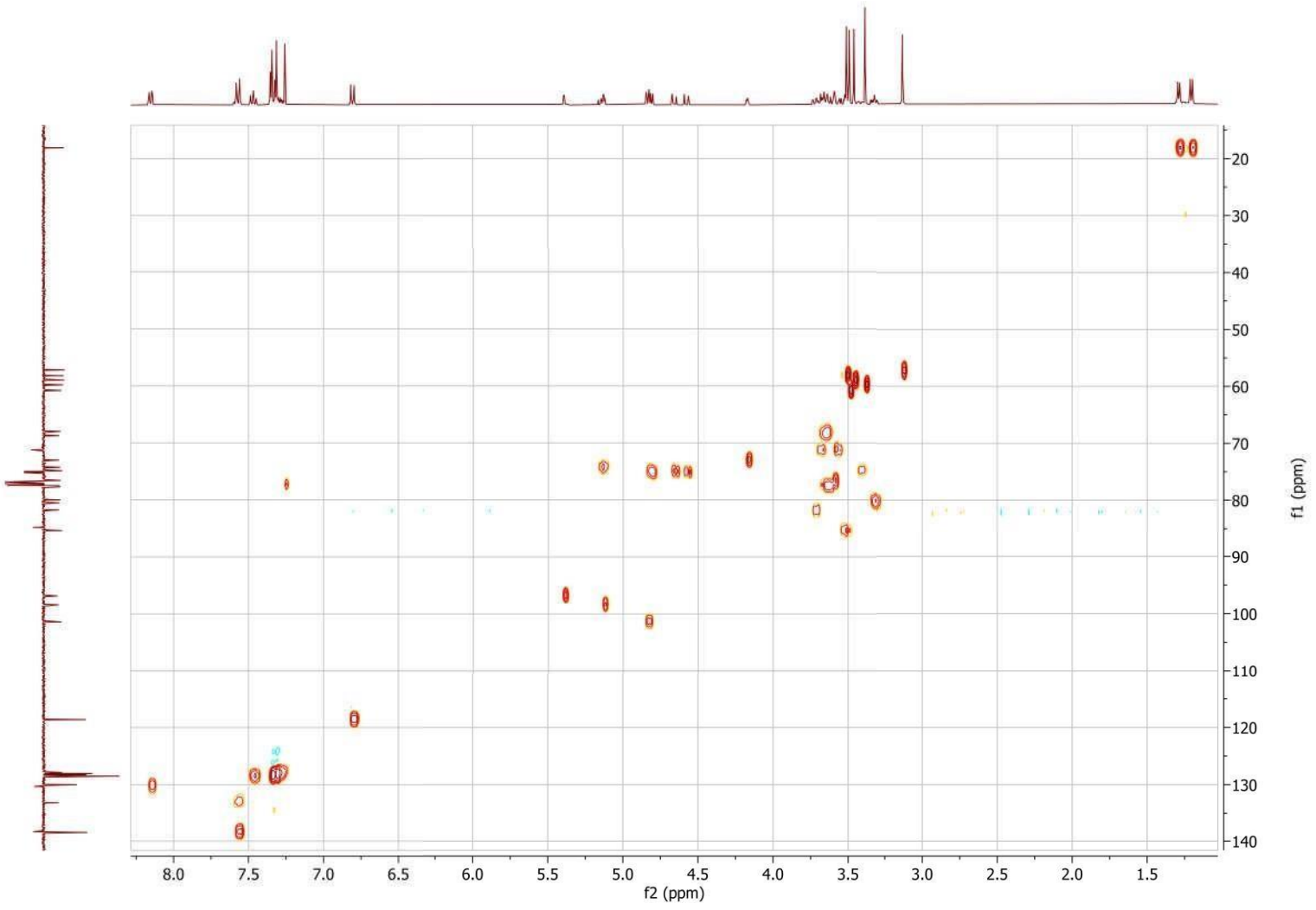

f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


BnO
MeO
O
I
MeO
BnO
MeO
OBz
MeO
MeO
OMe
8a
f1 (ppm)


f1 (ppm)


f2 (ppm)
f1 (ppm)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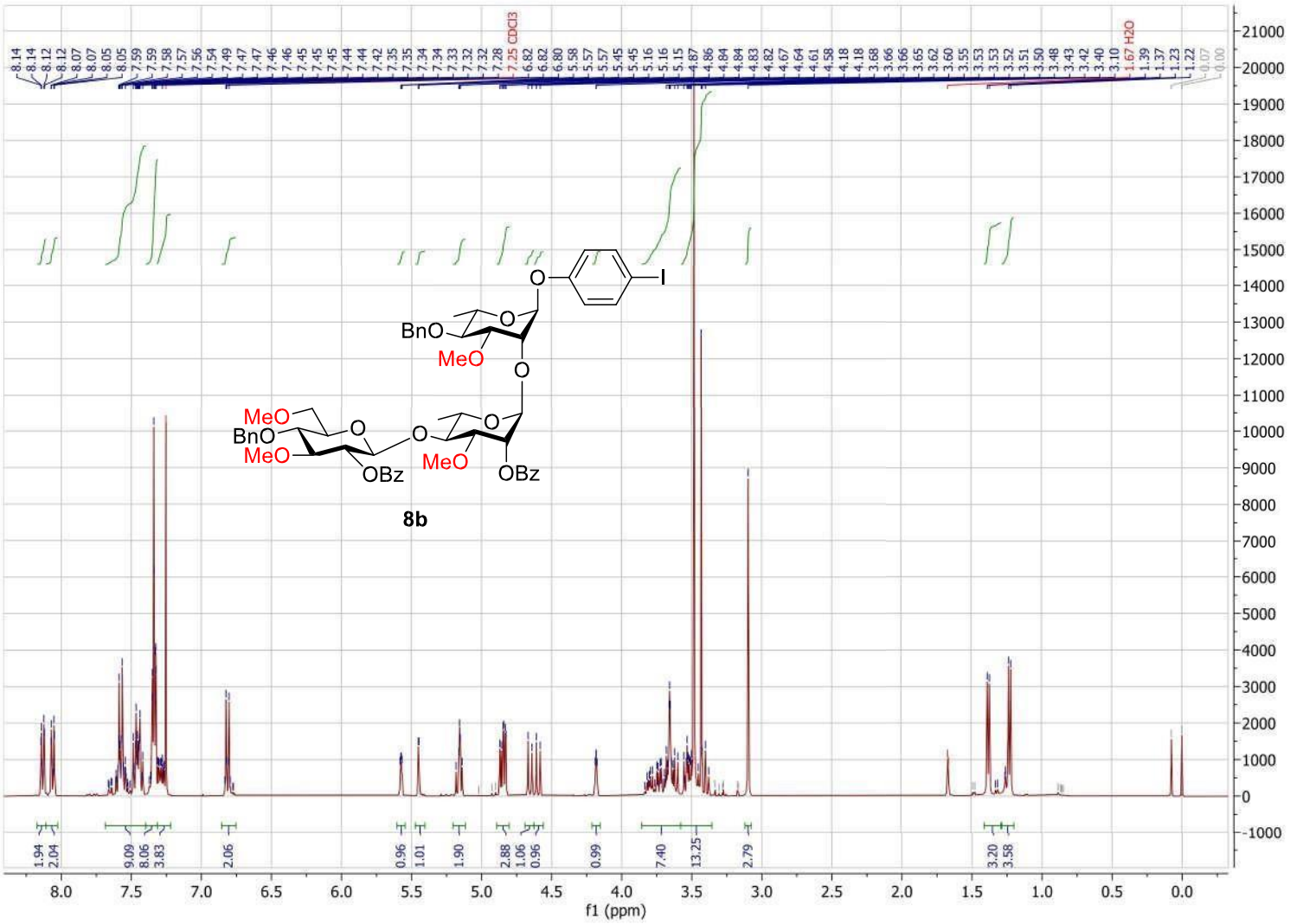

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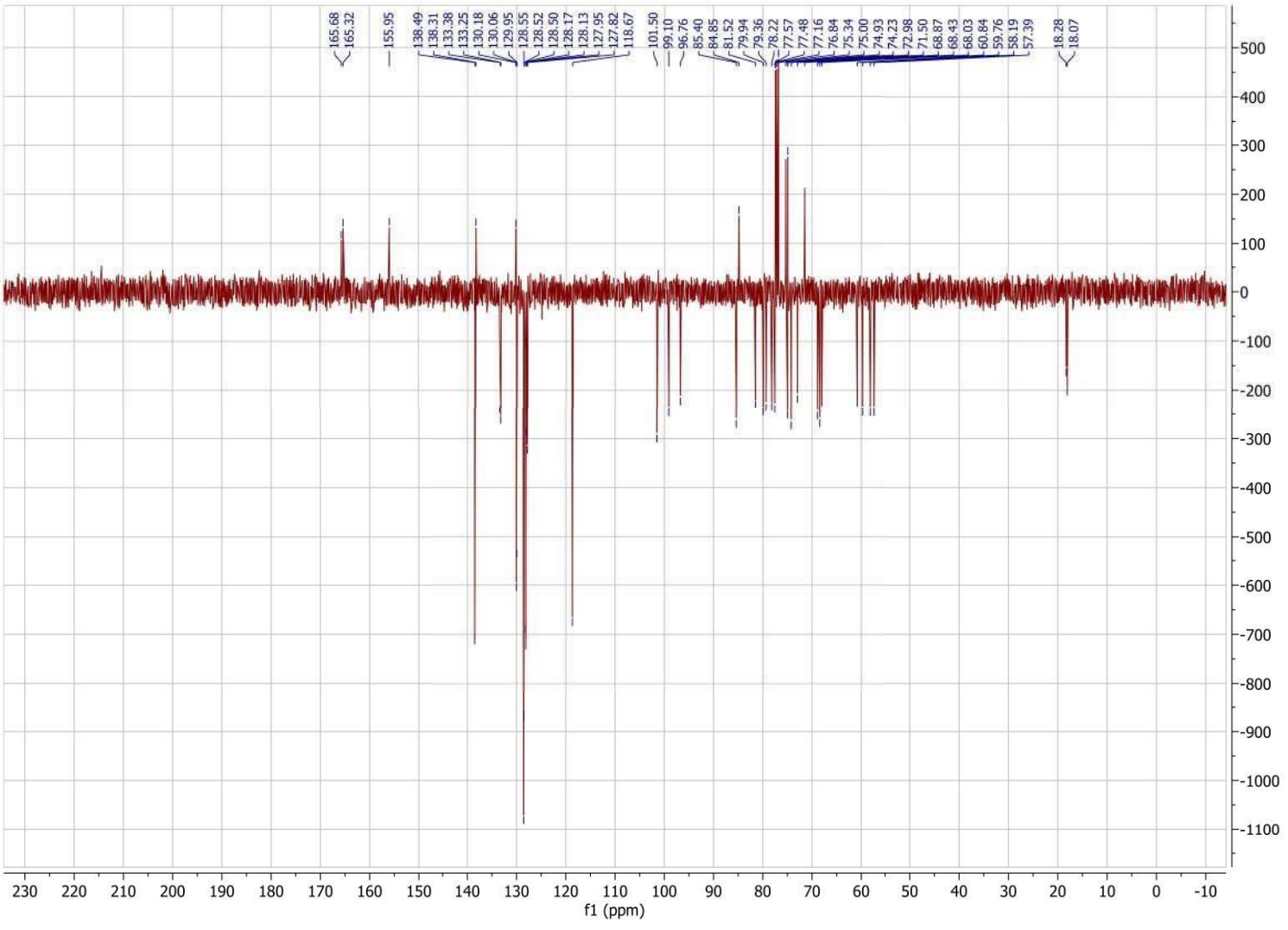

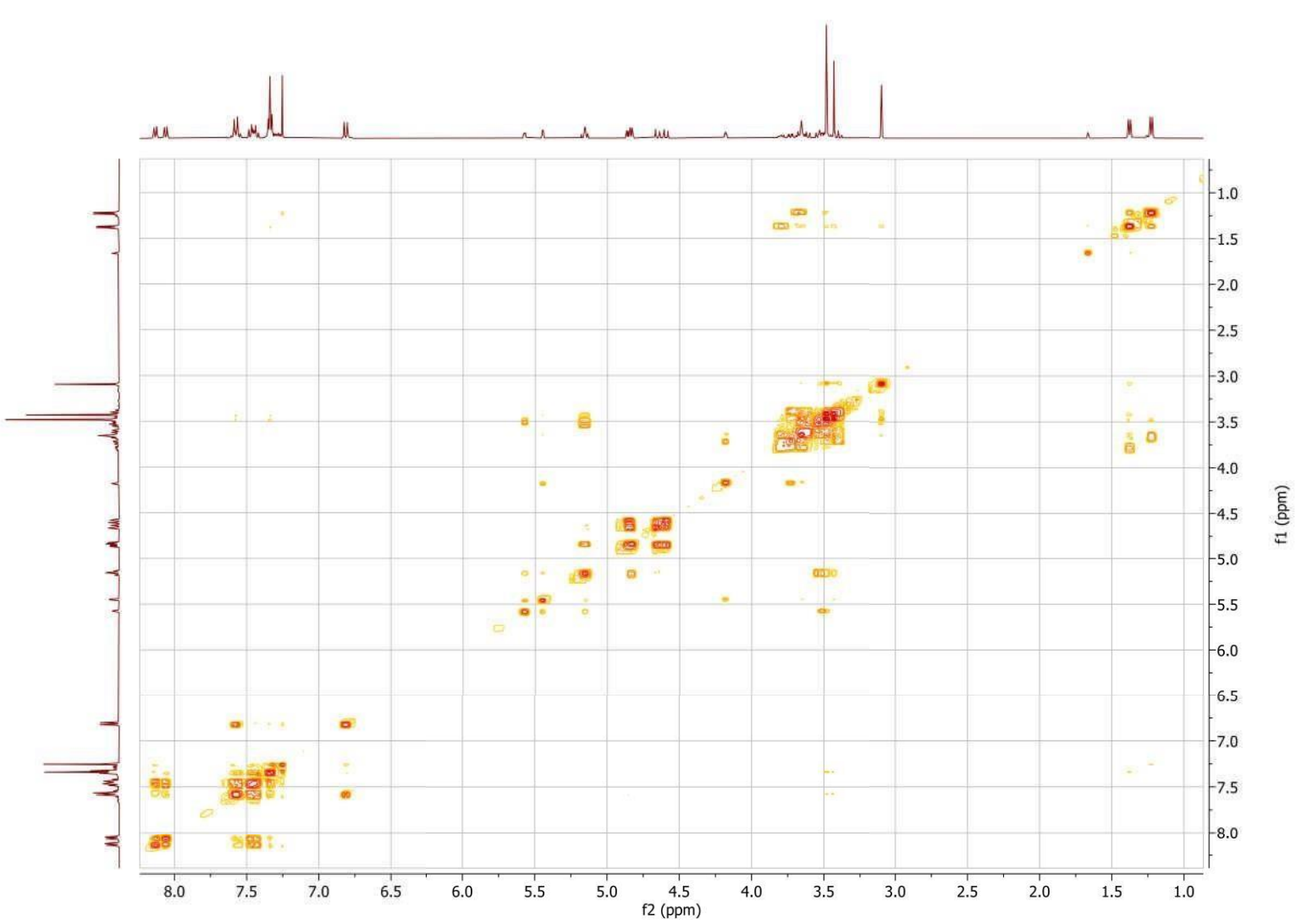
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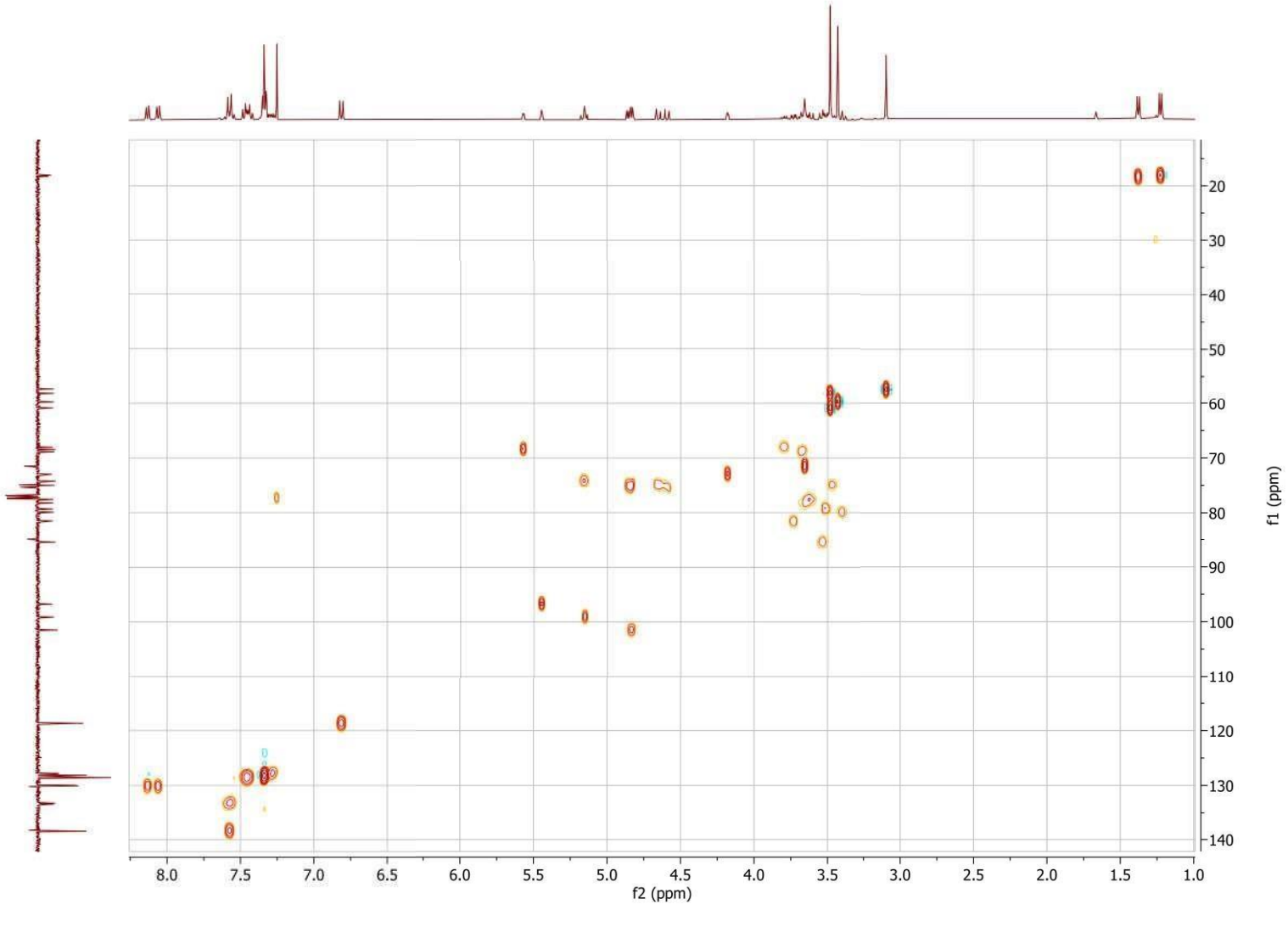
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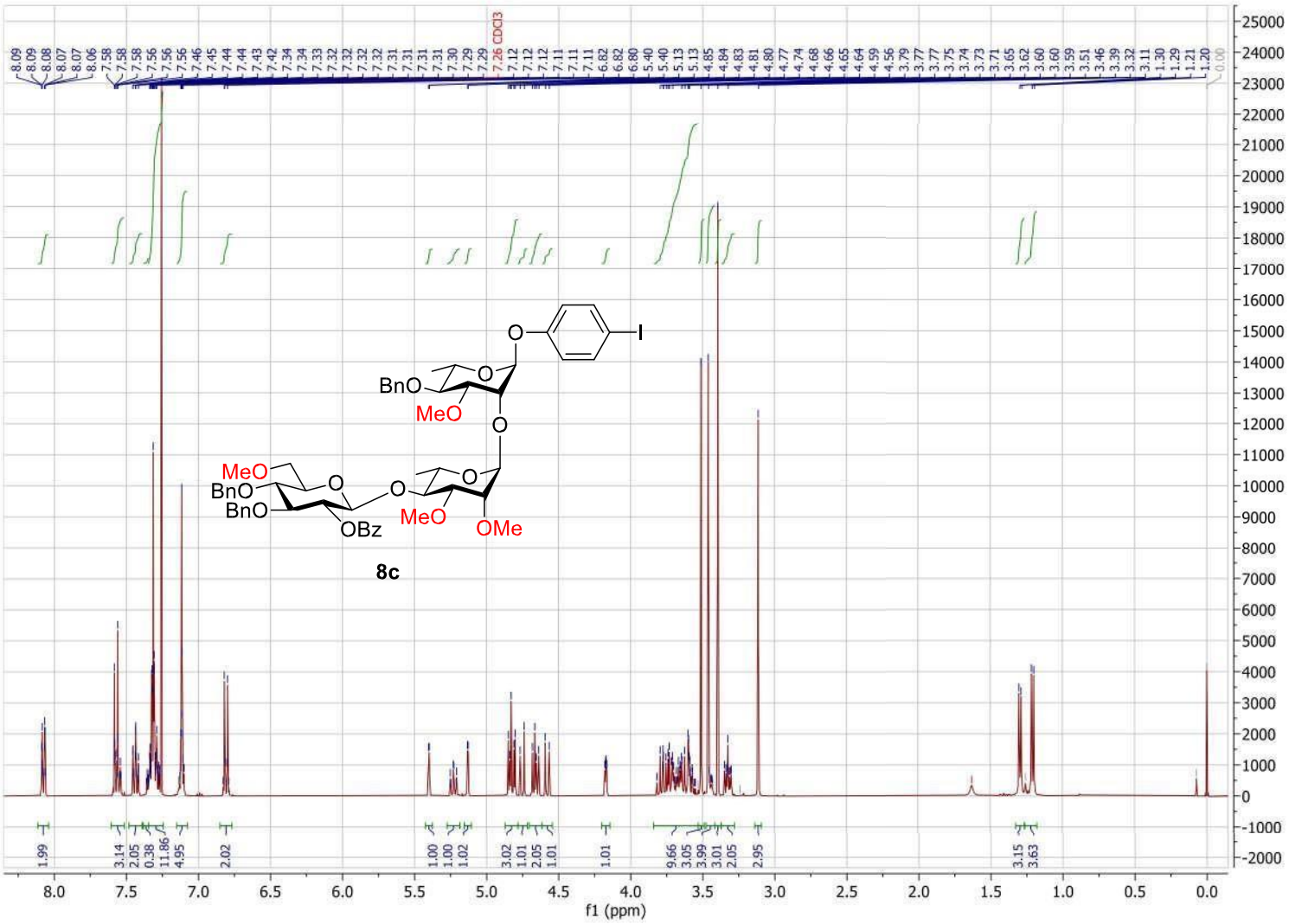

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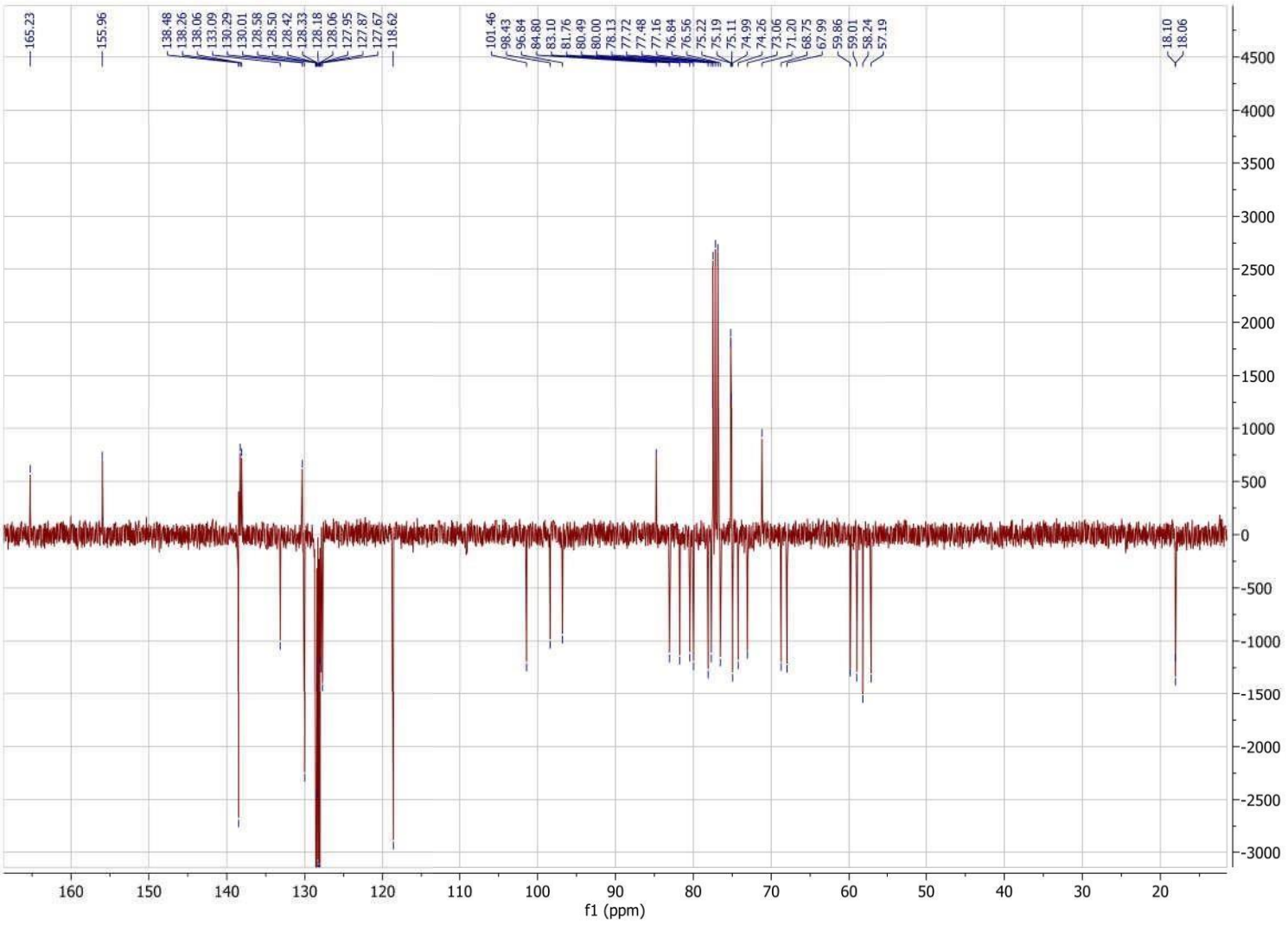

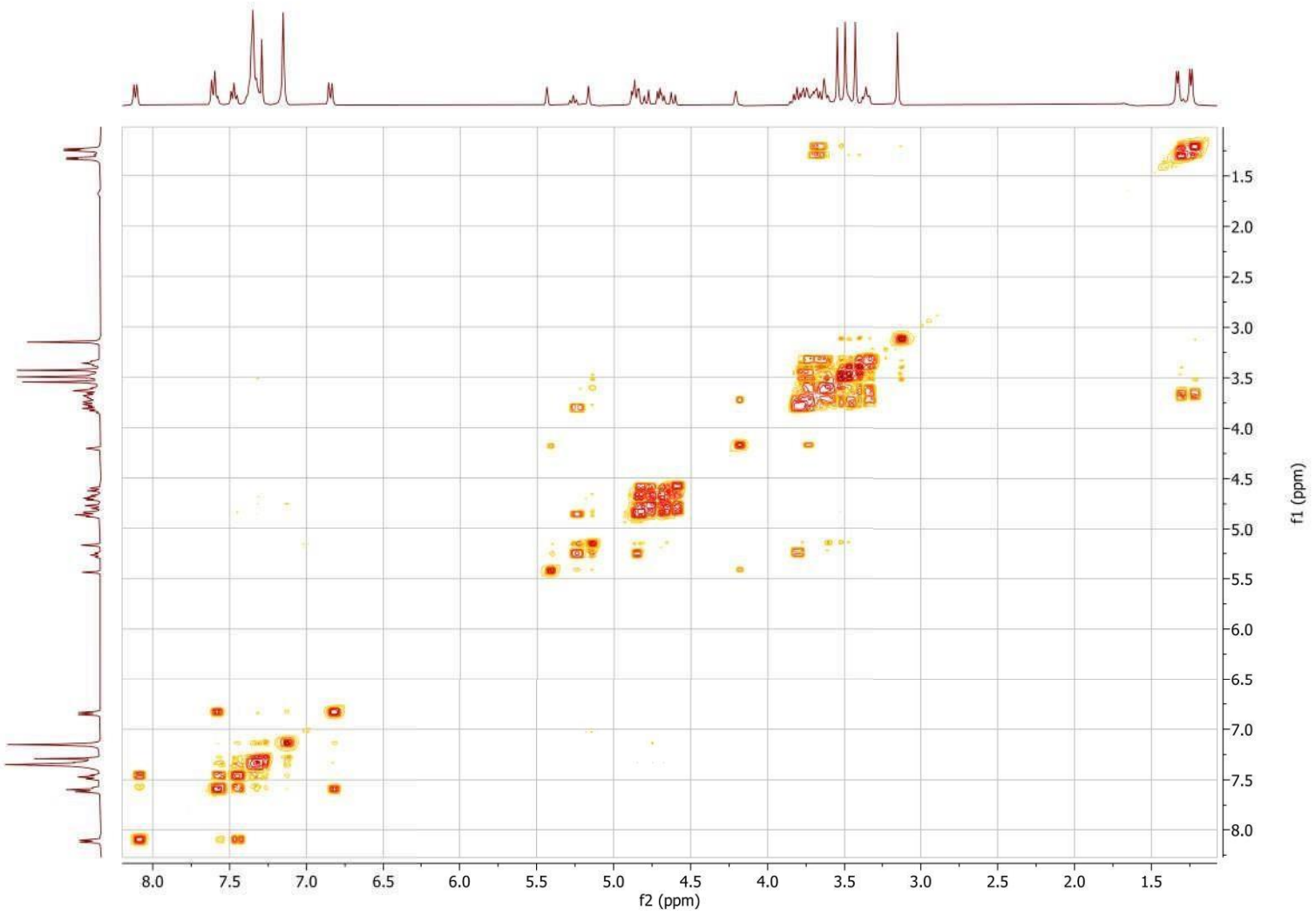
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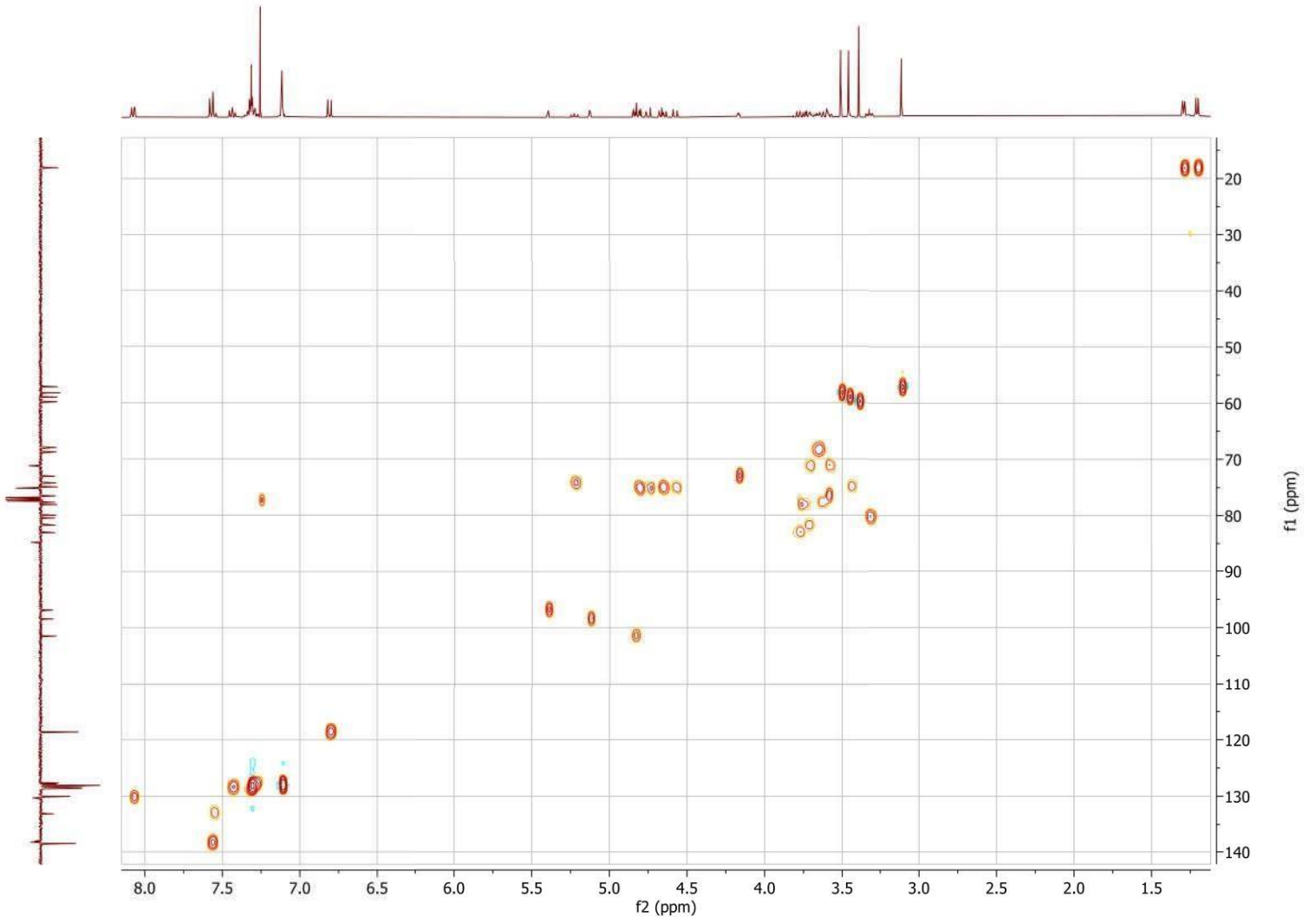
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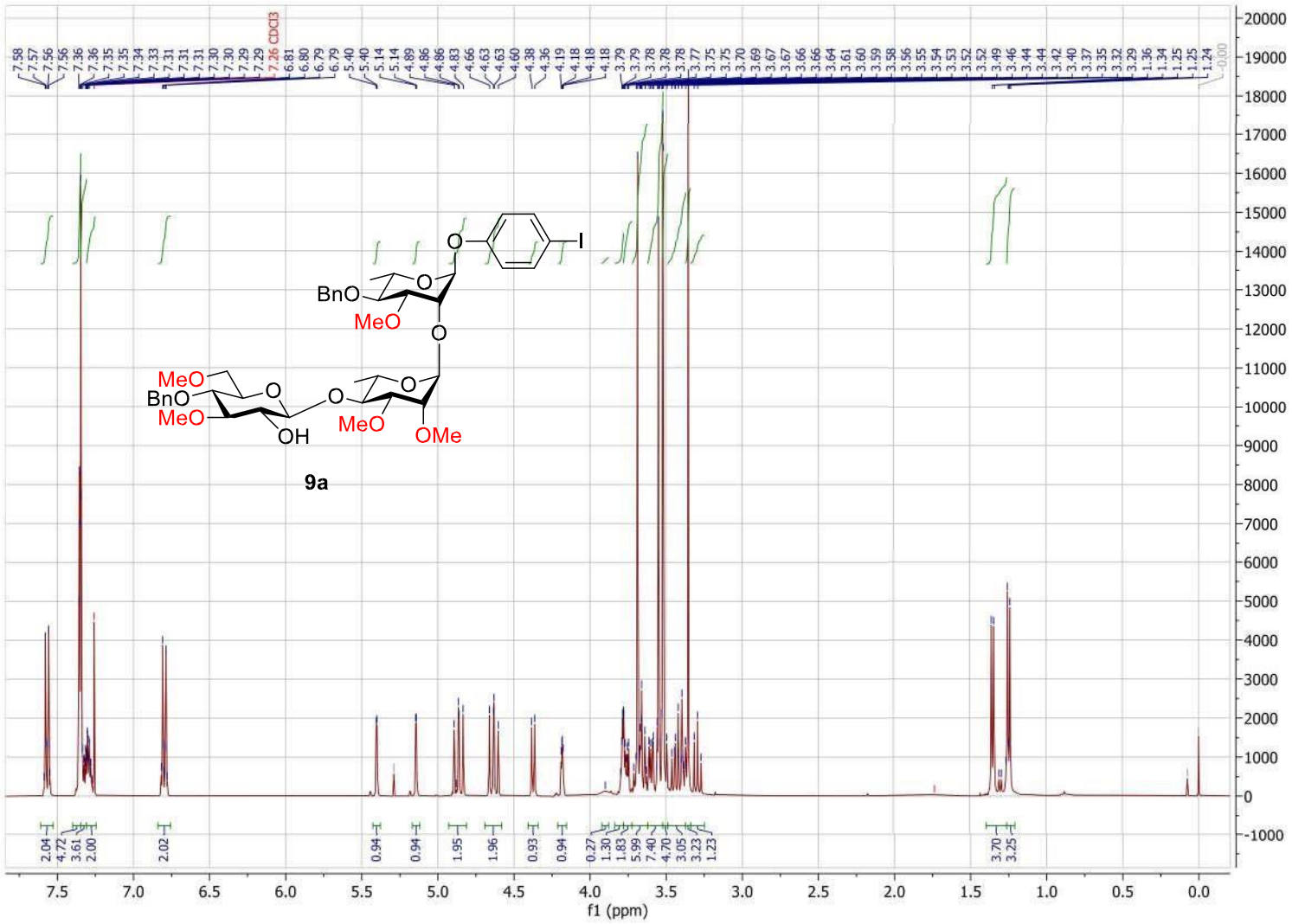
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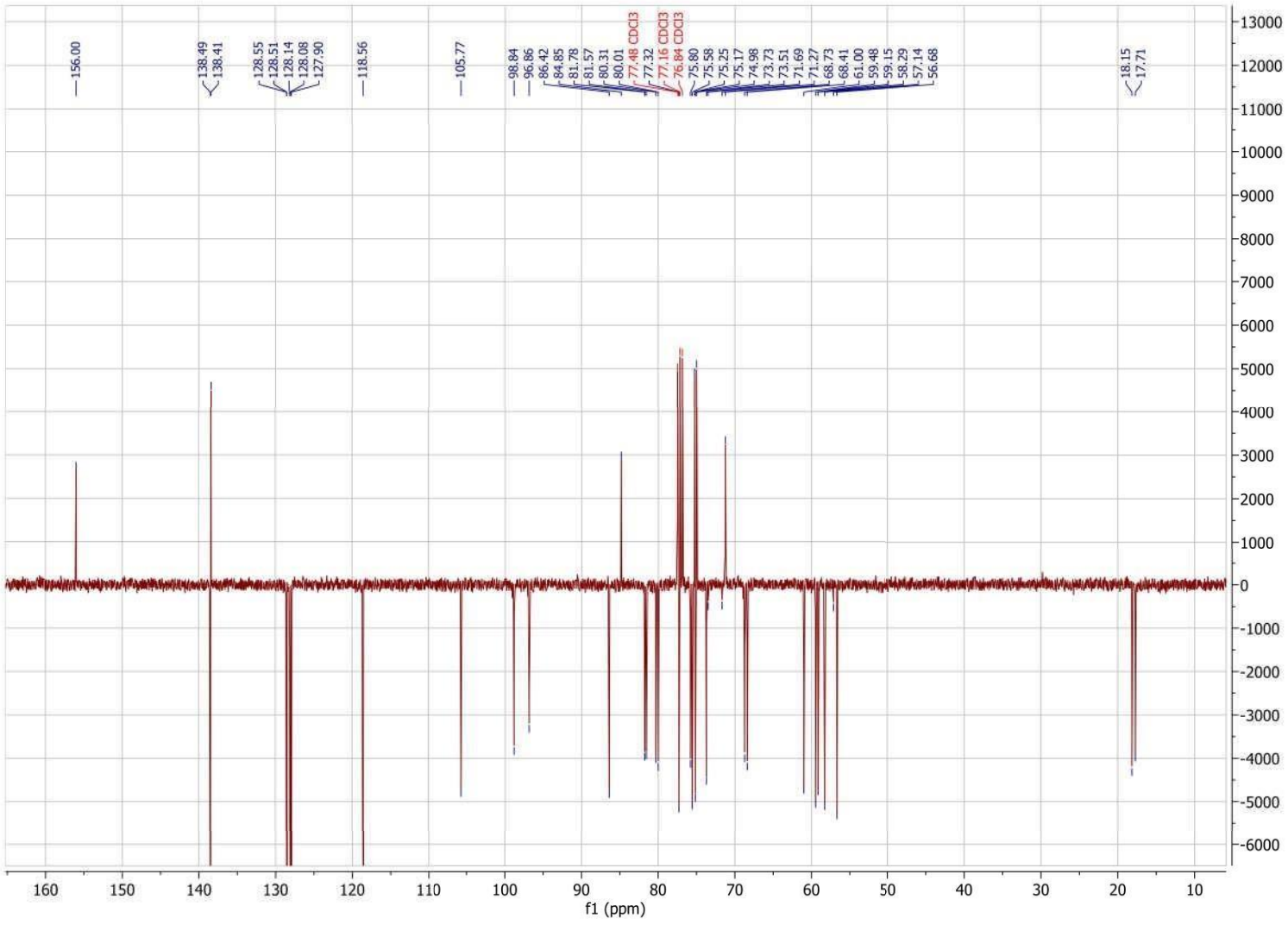
9a
f1 (ppm)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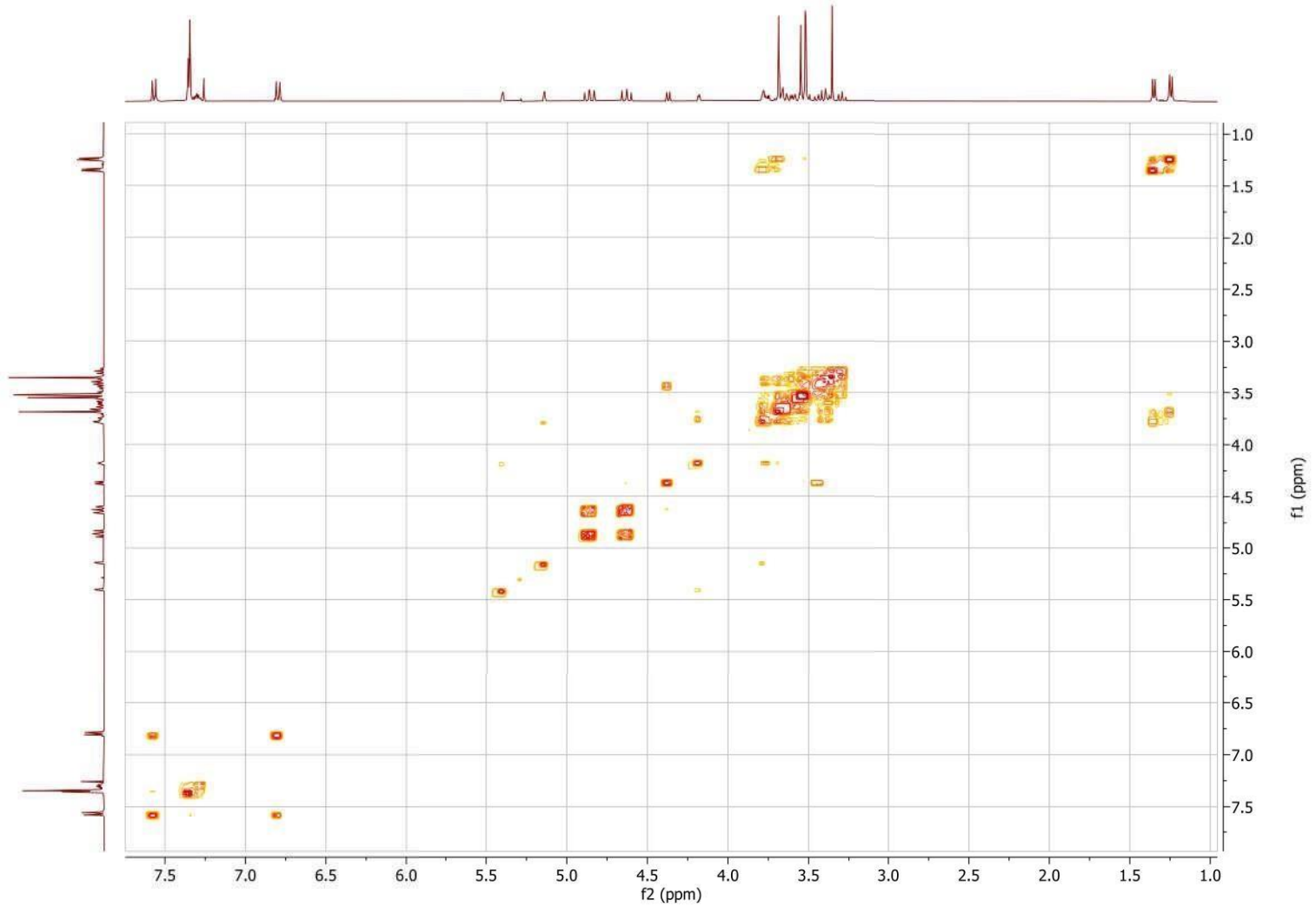
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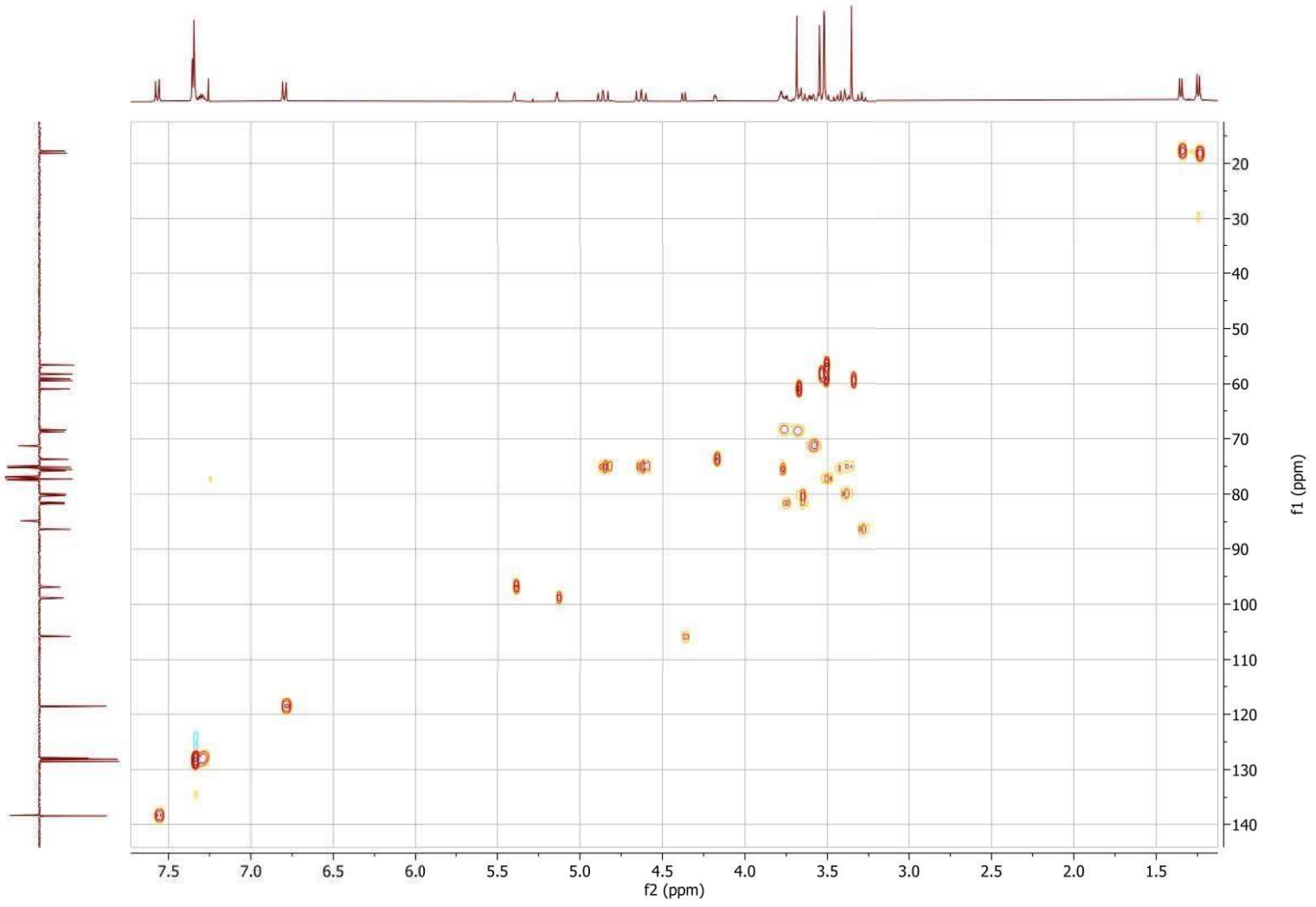
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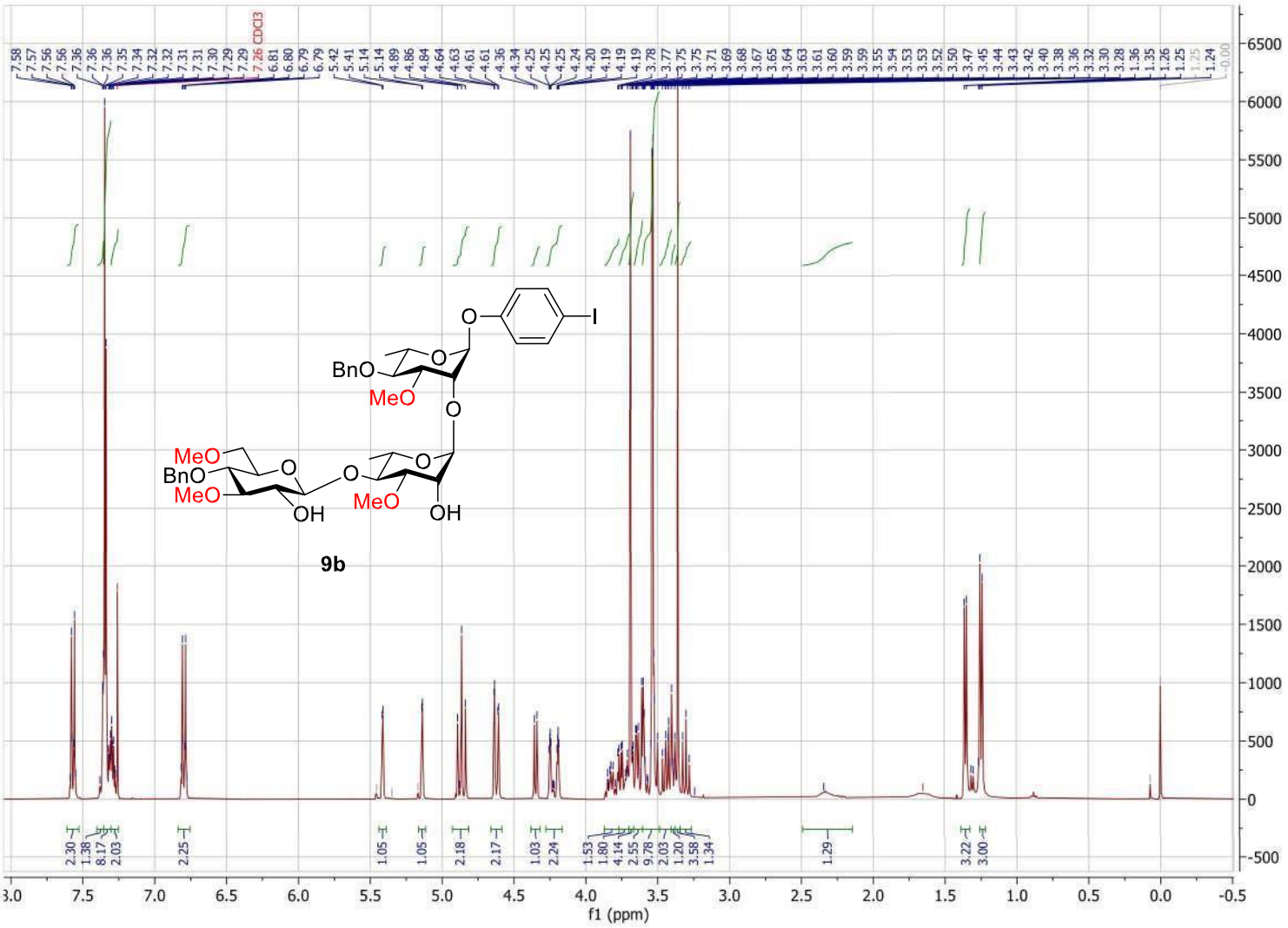

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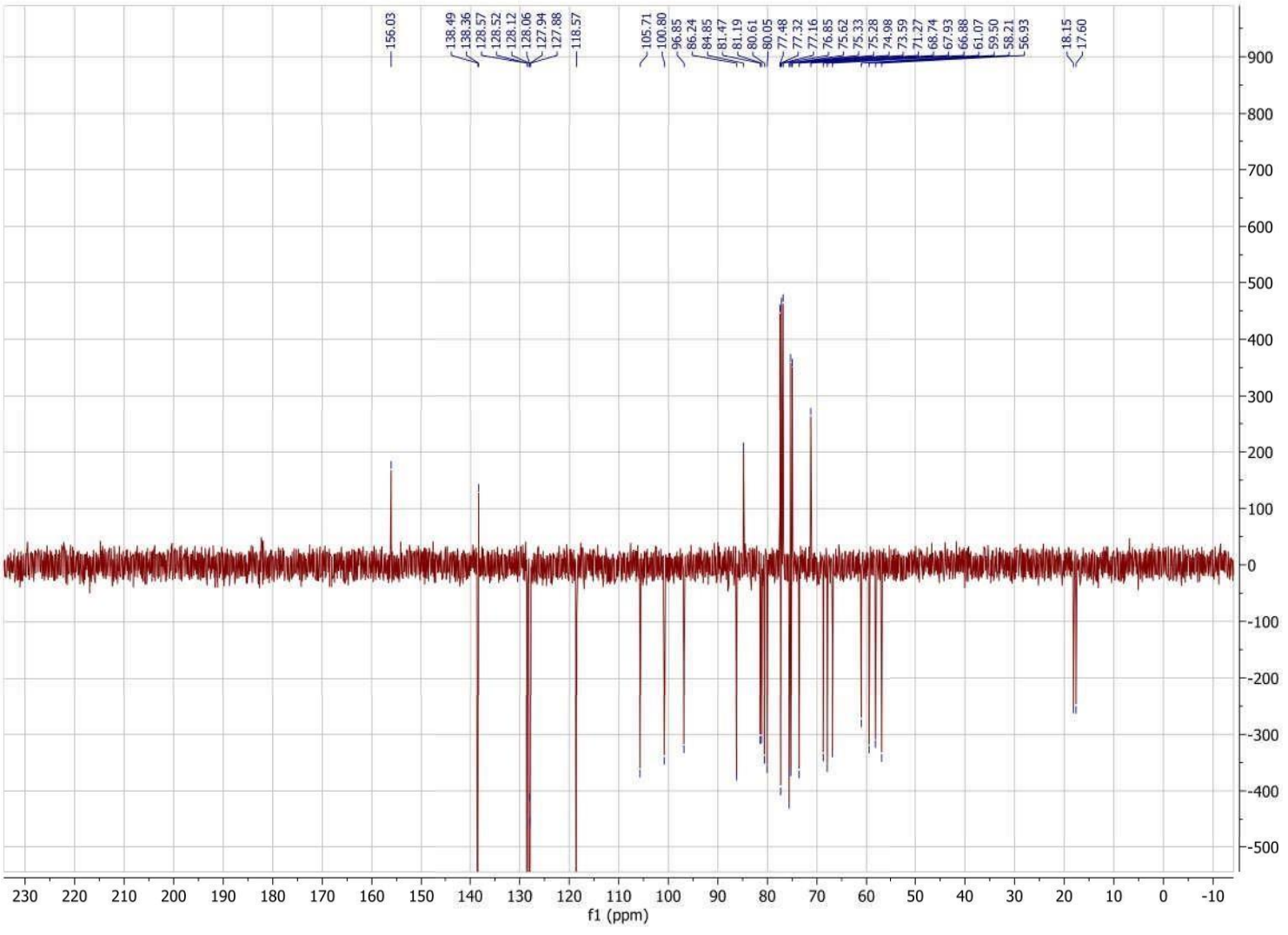

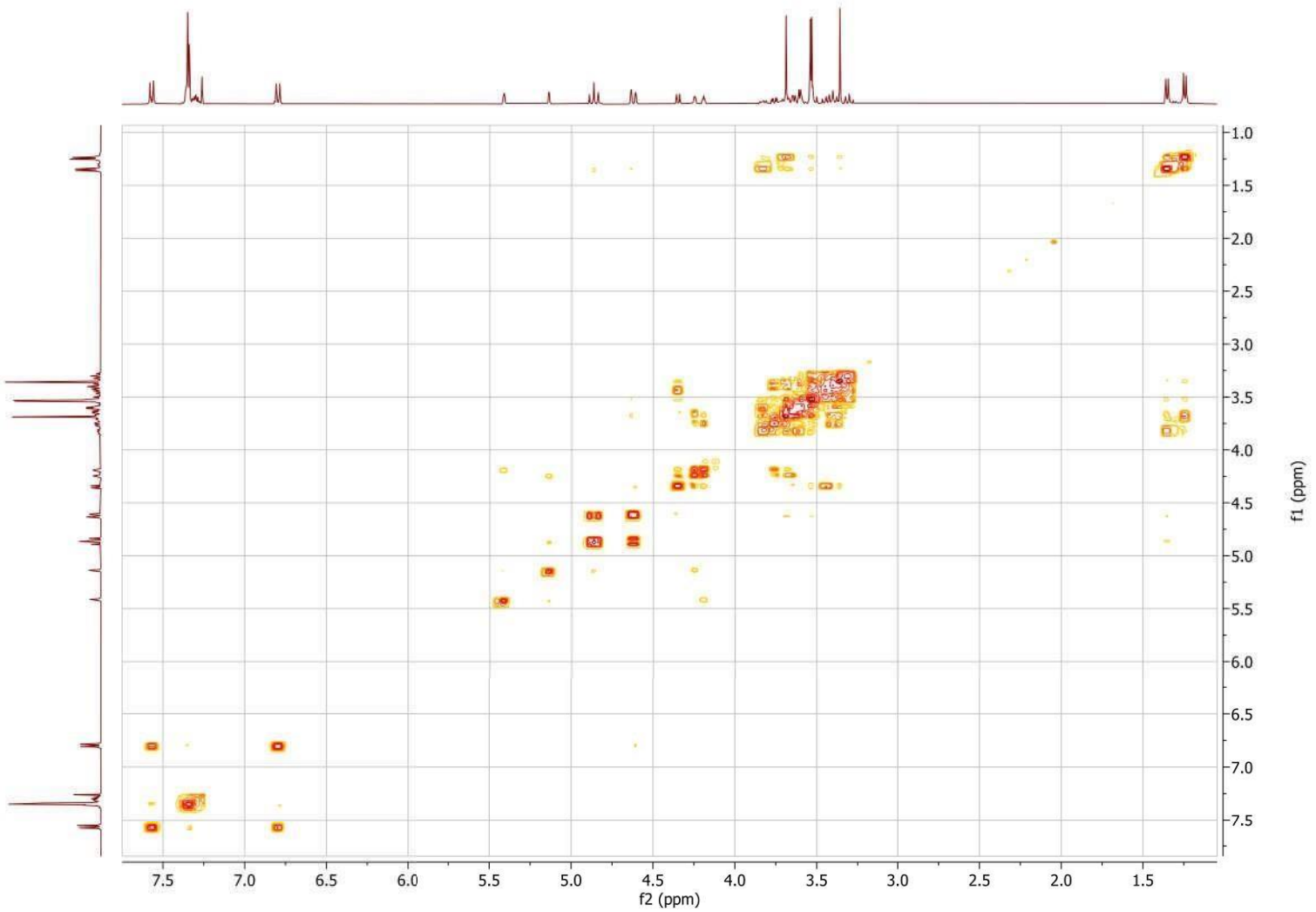
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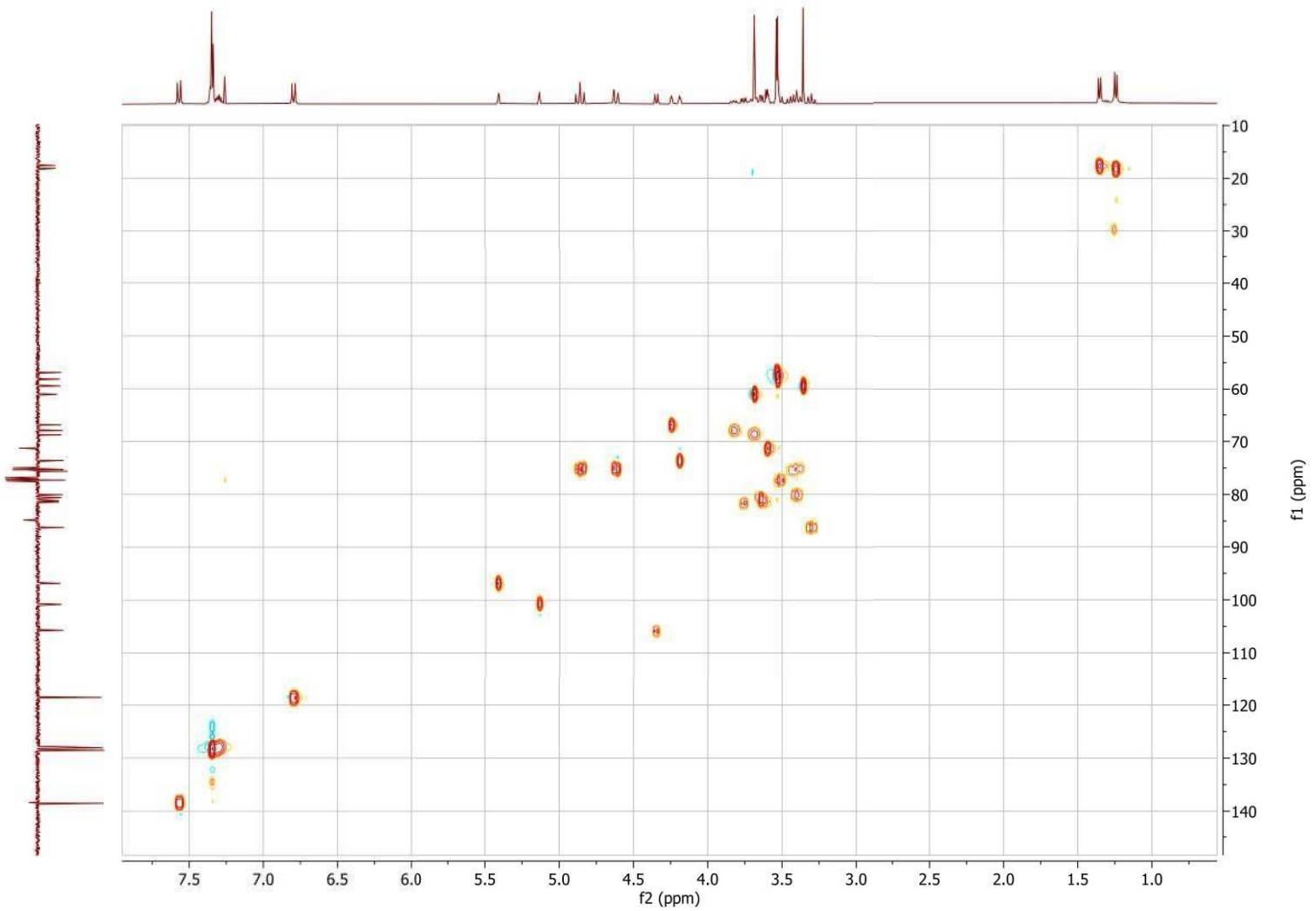
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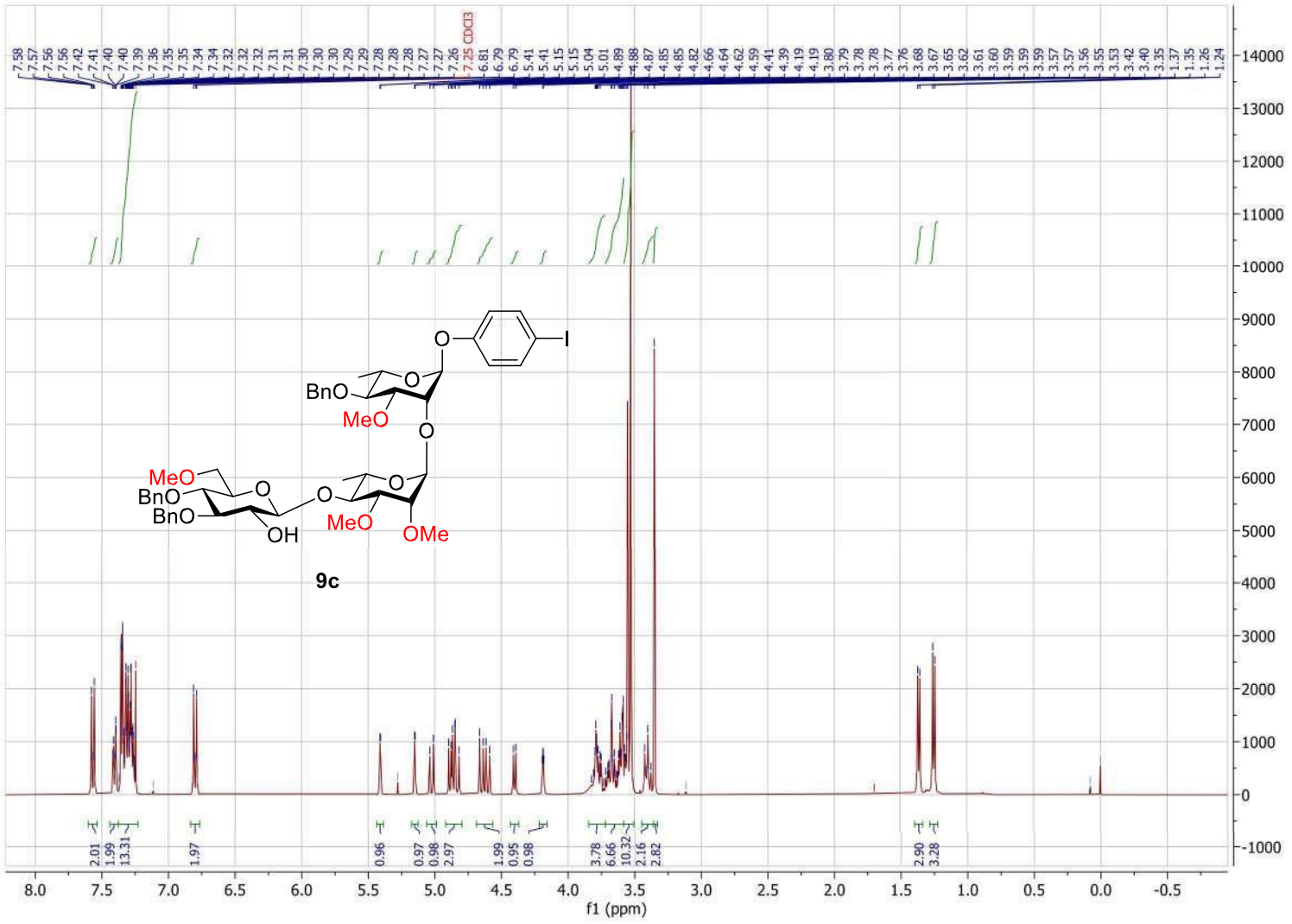

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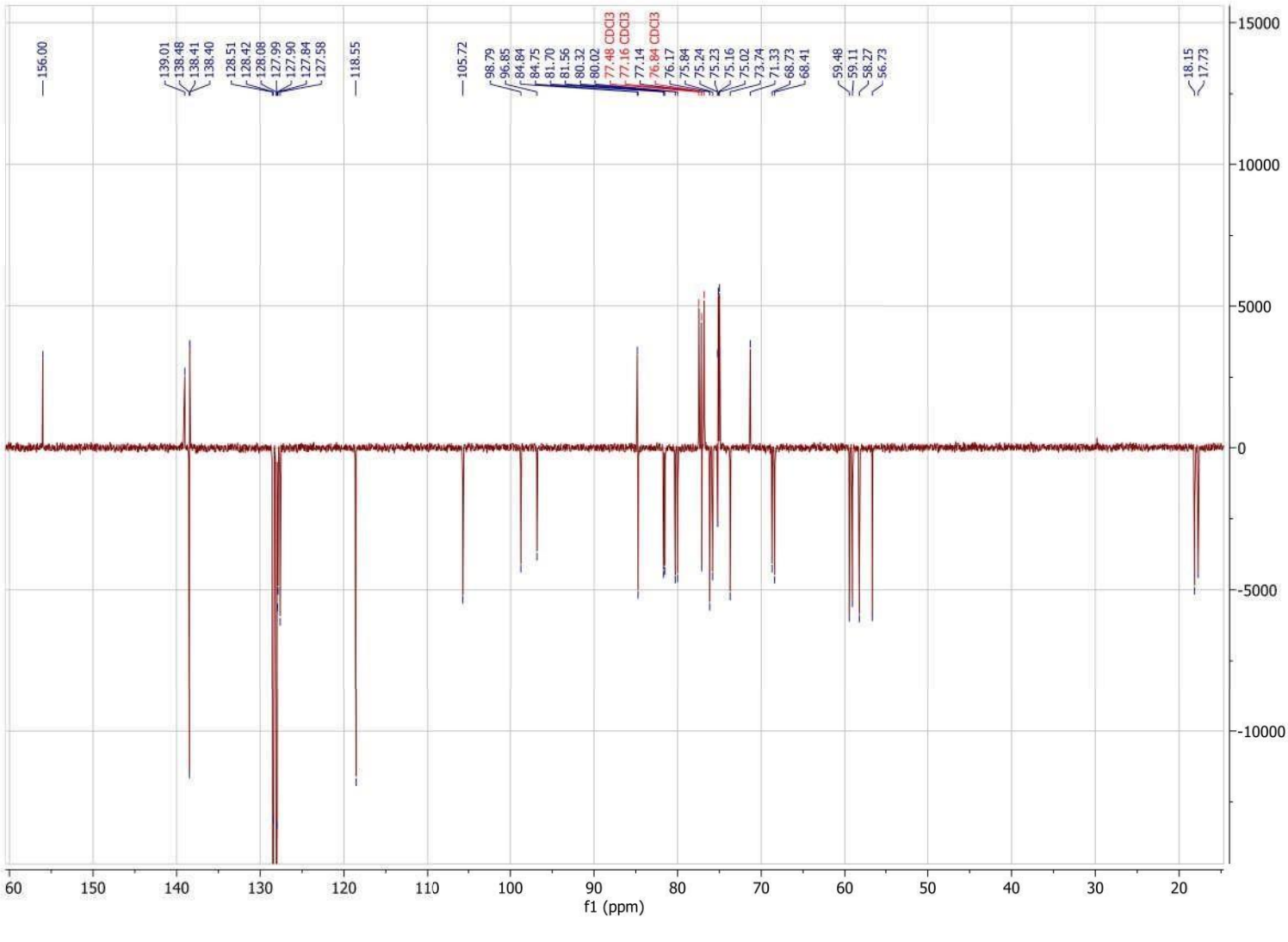

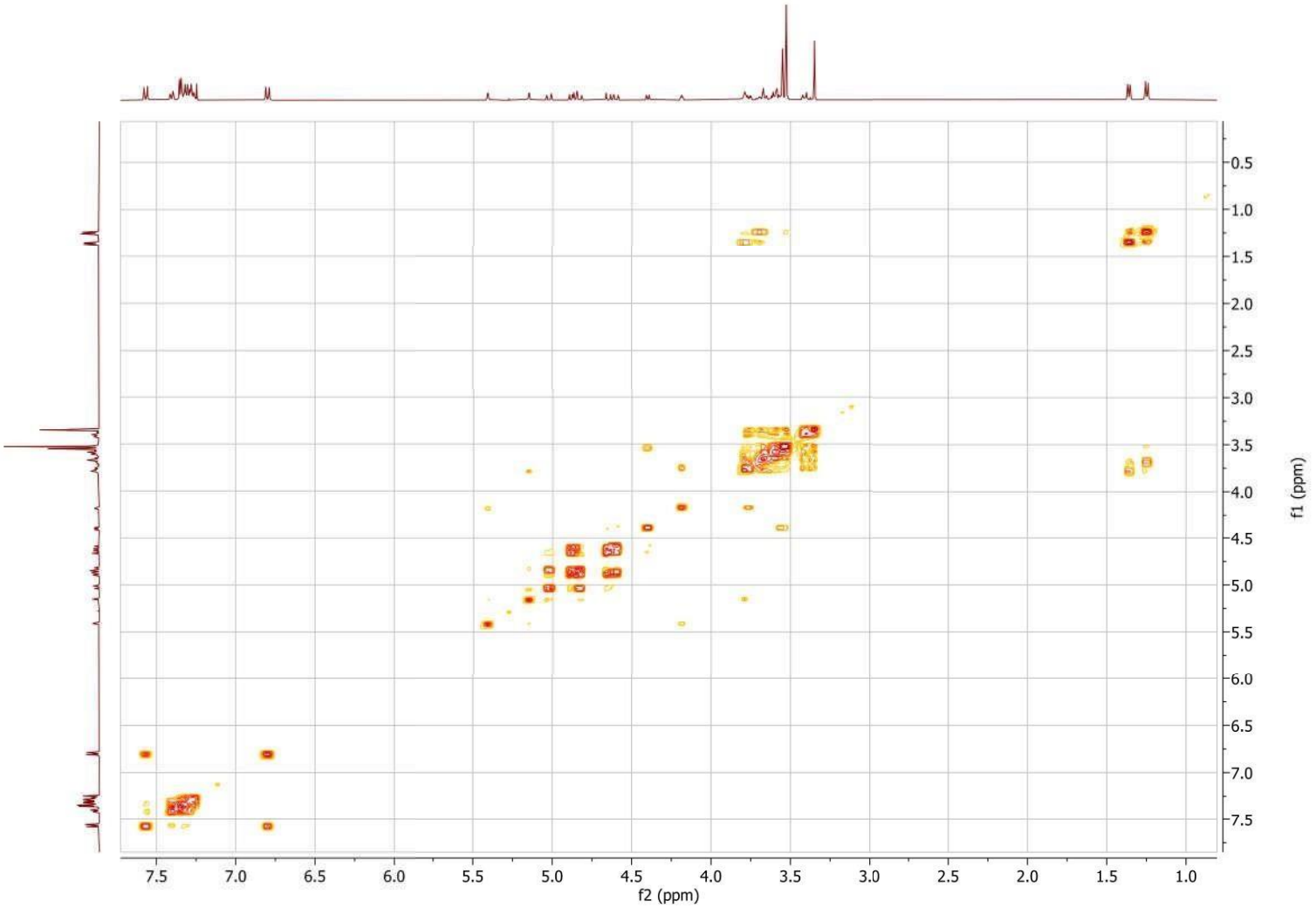
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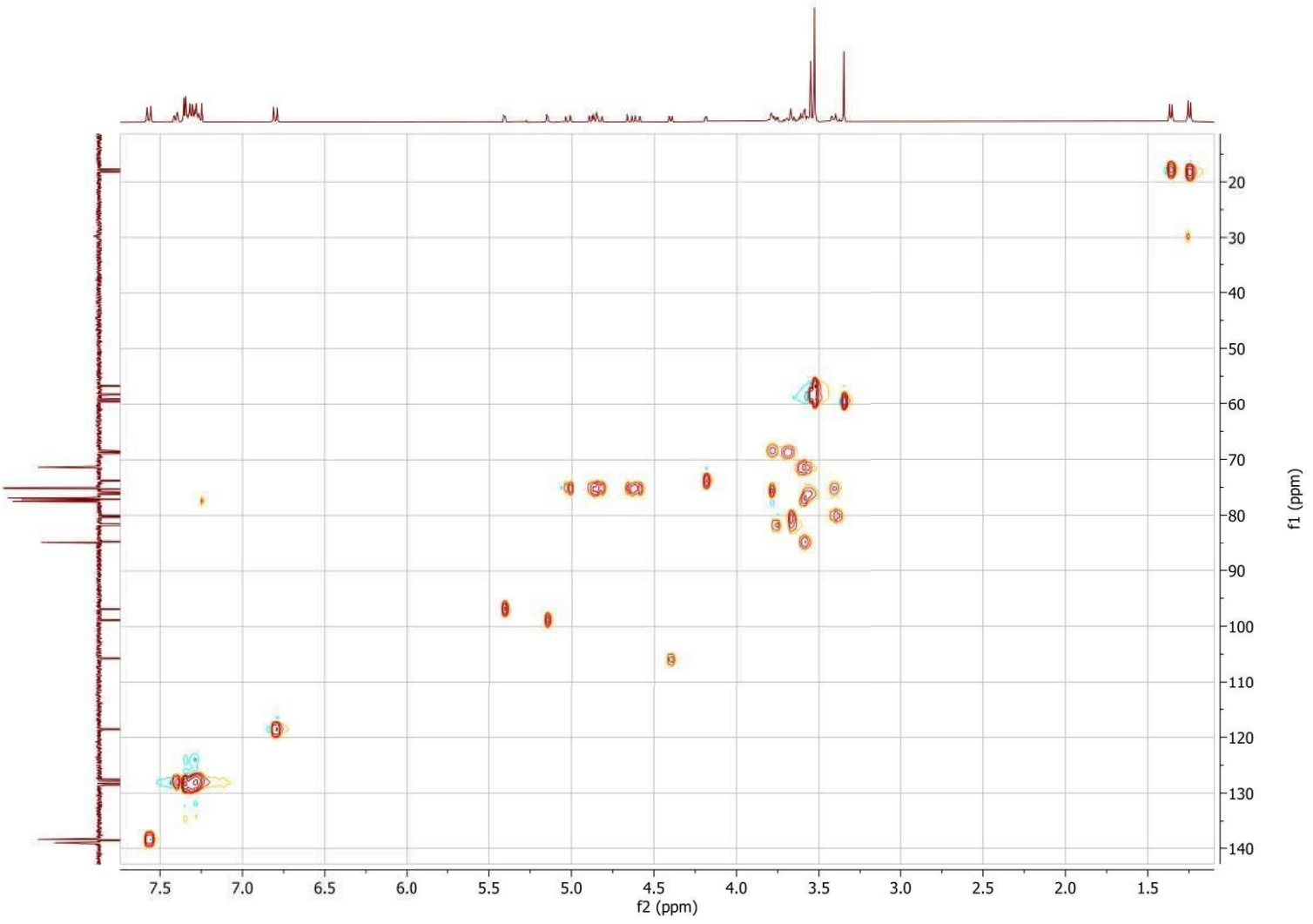
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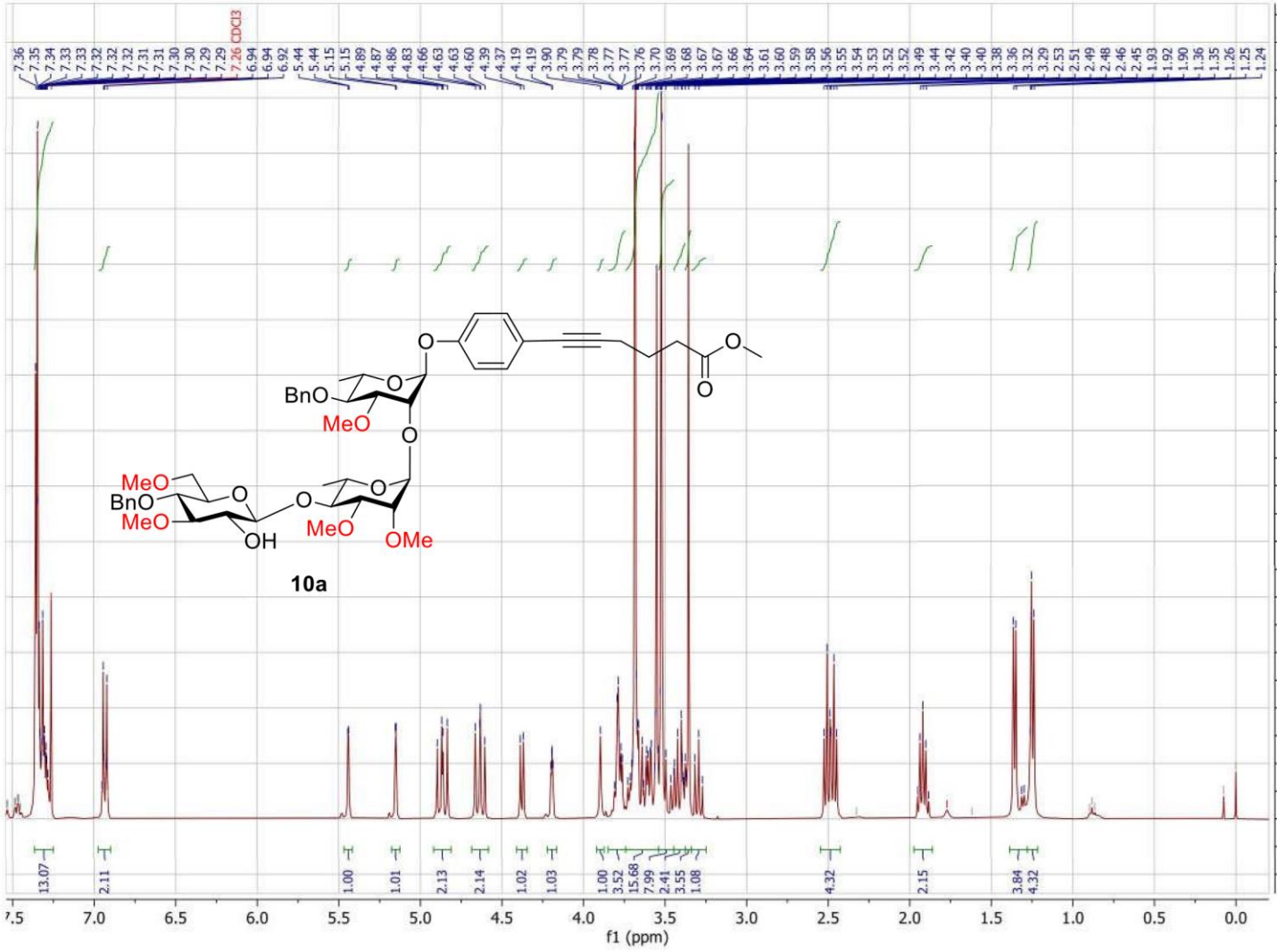
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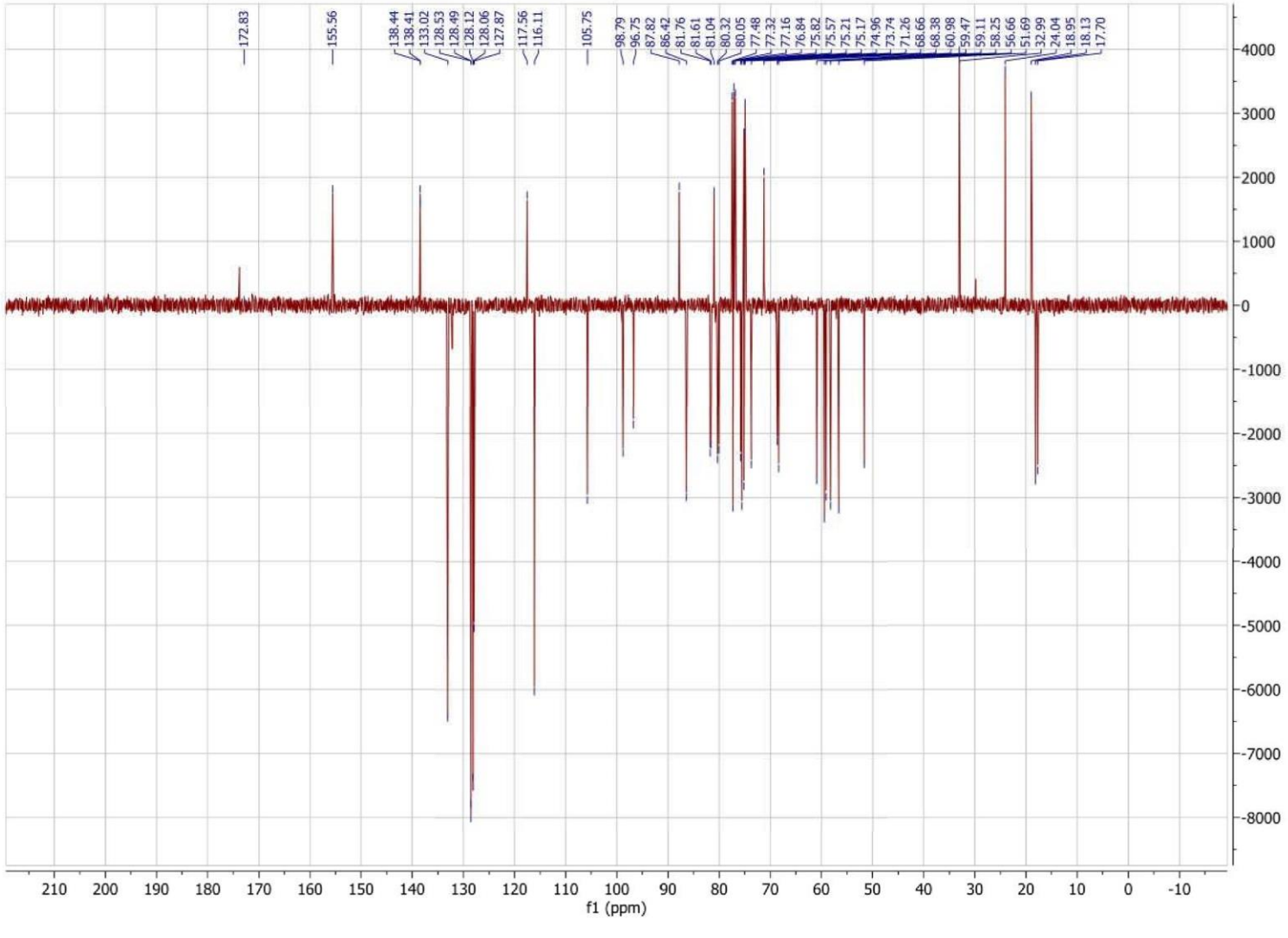
MeO
BnO
MeO
OH
MeO
OMe
O
O
O
10a
f1 (ppm)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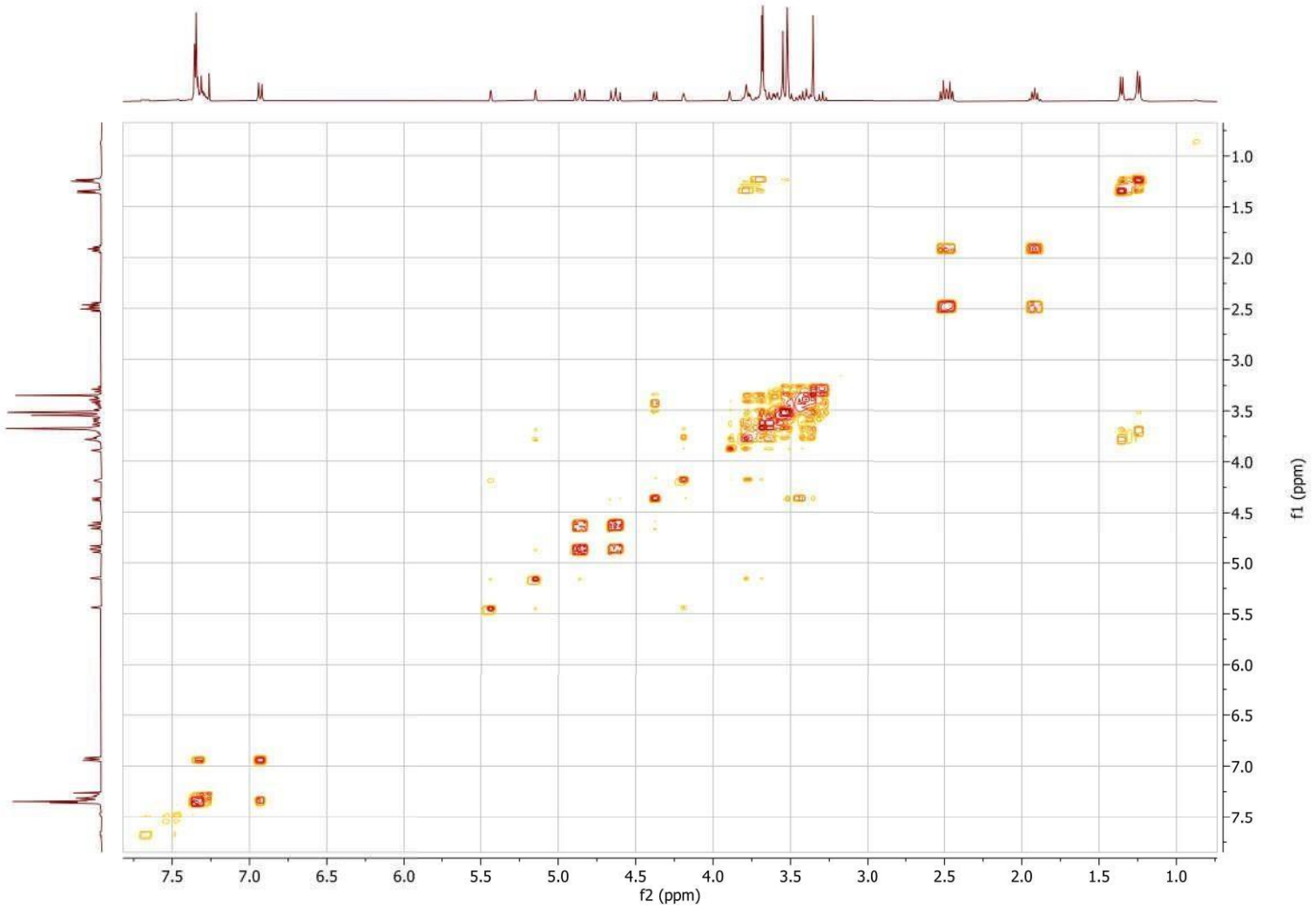
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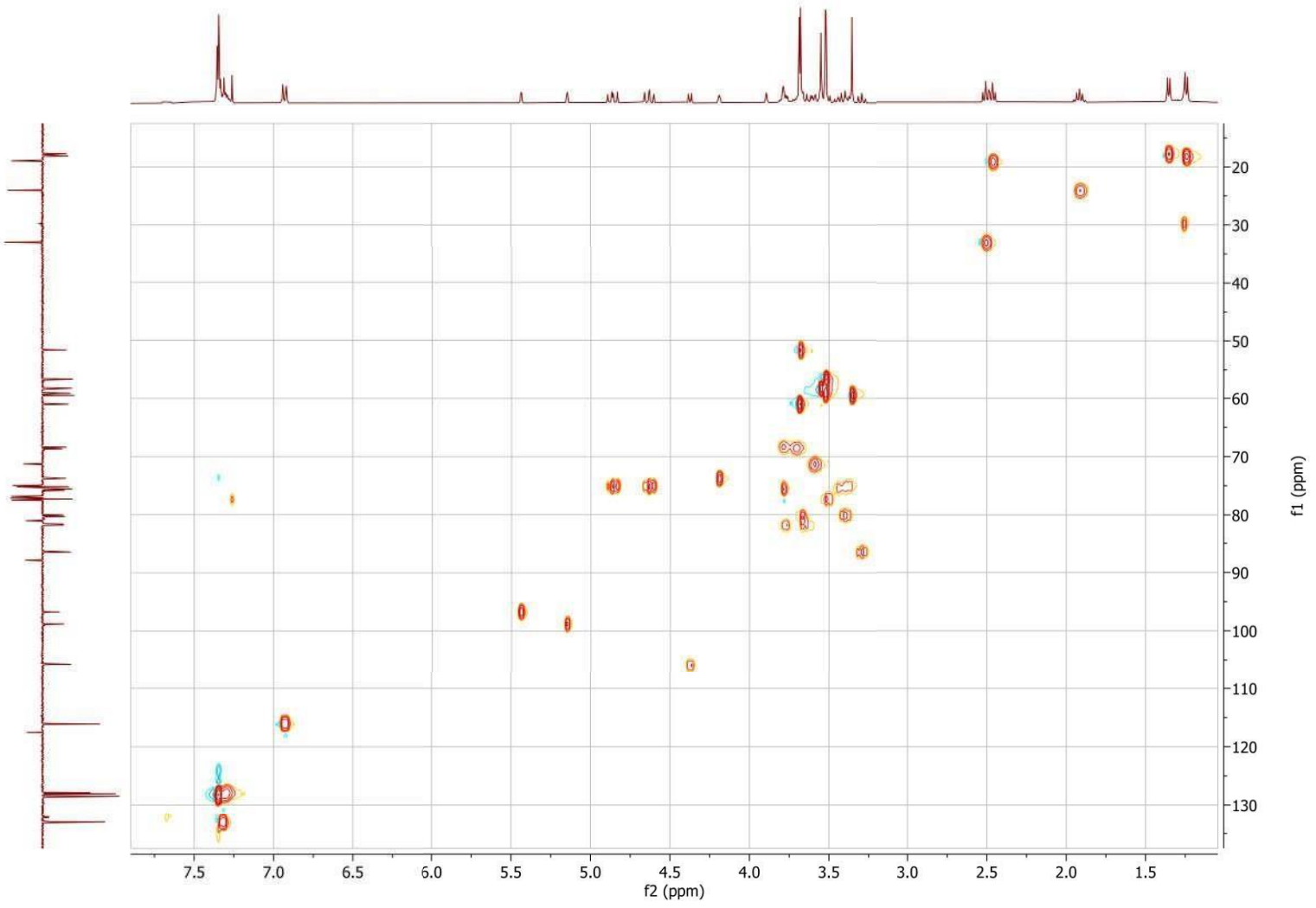
f1 (ppm)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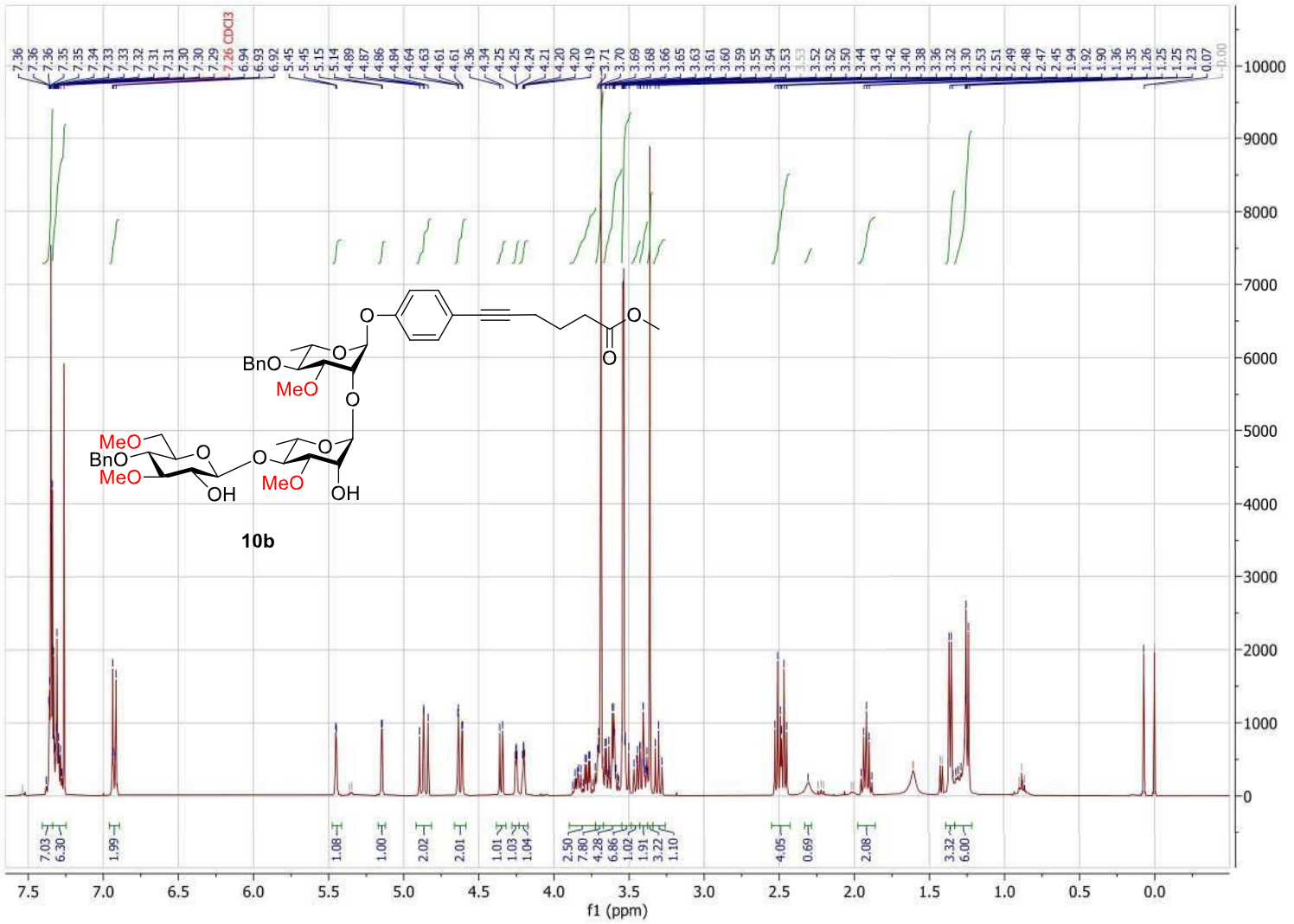
f1 (ppm)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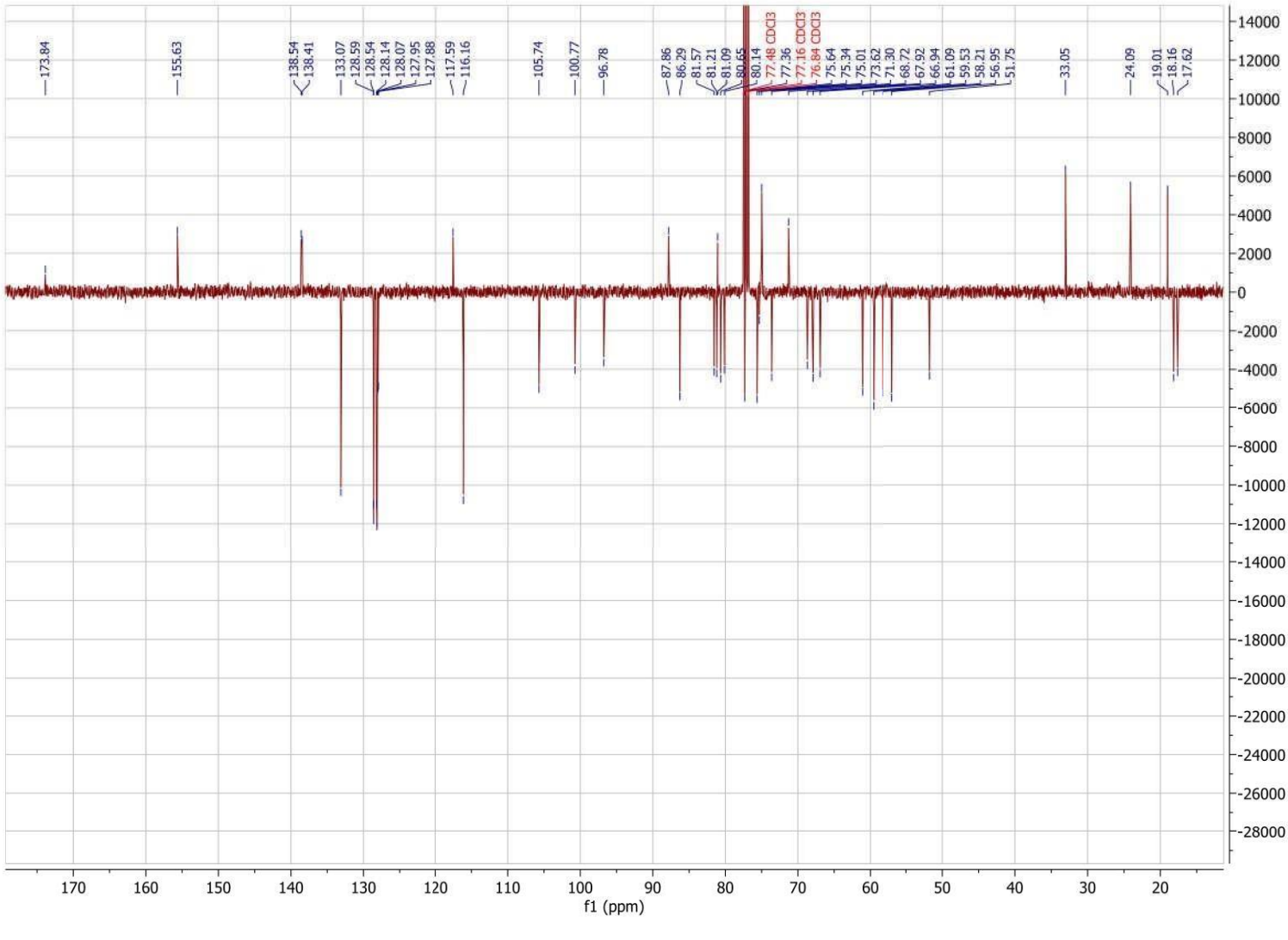
MeO
MeO
BnO
MeO
OH
MeO
OH
10b
f1 (ppm)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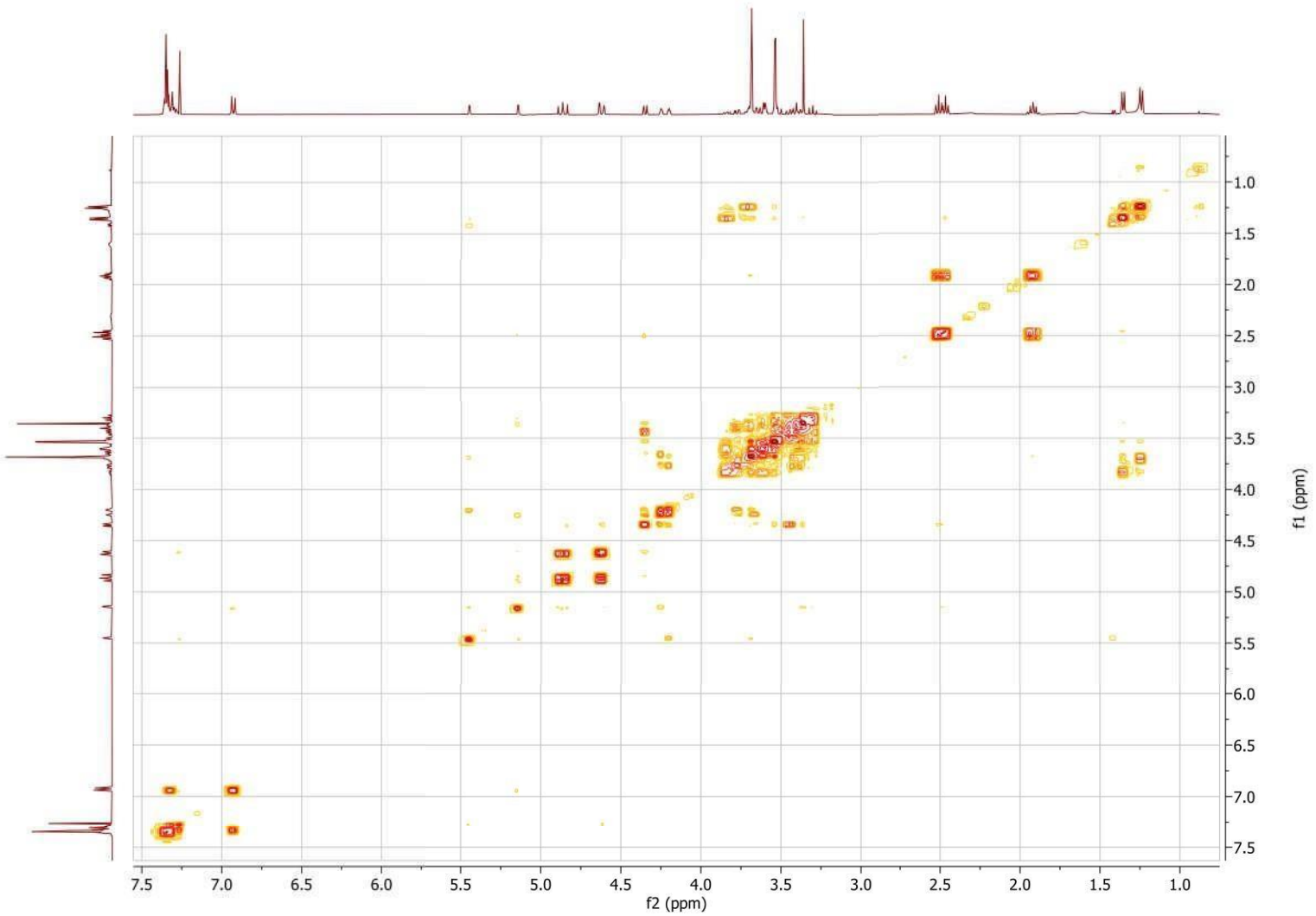
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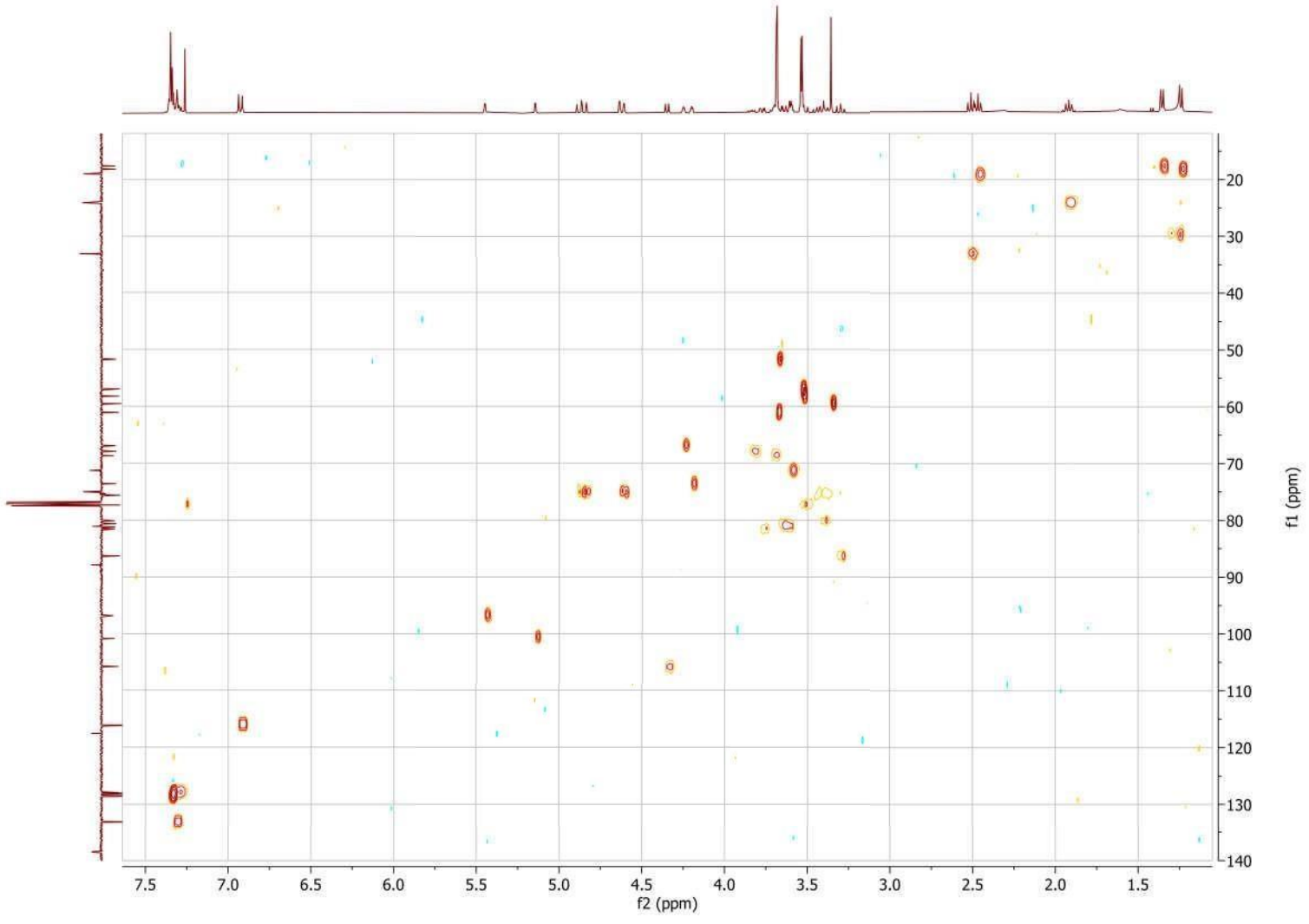
f1 (ppm)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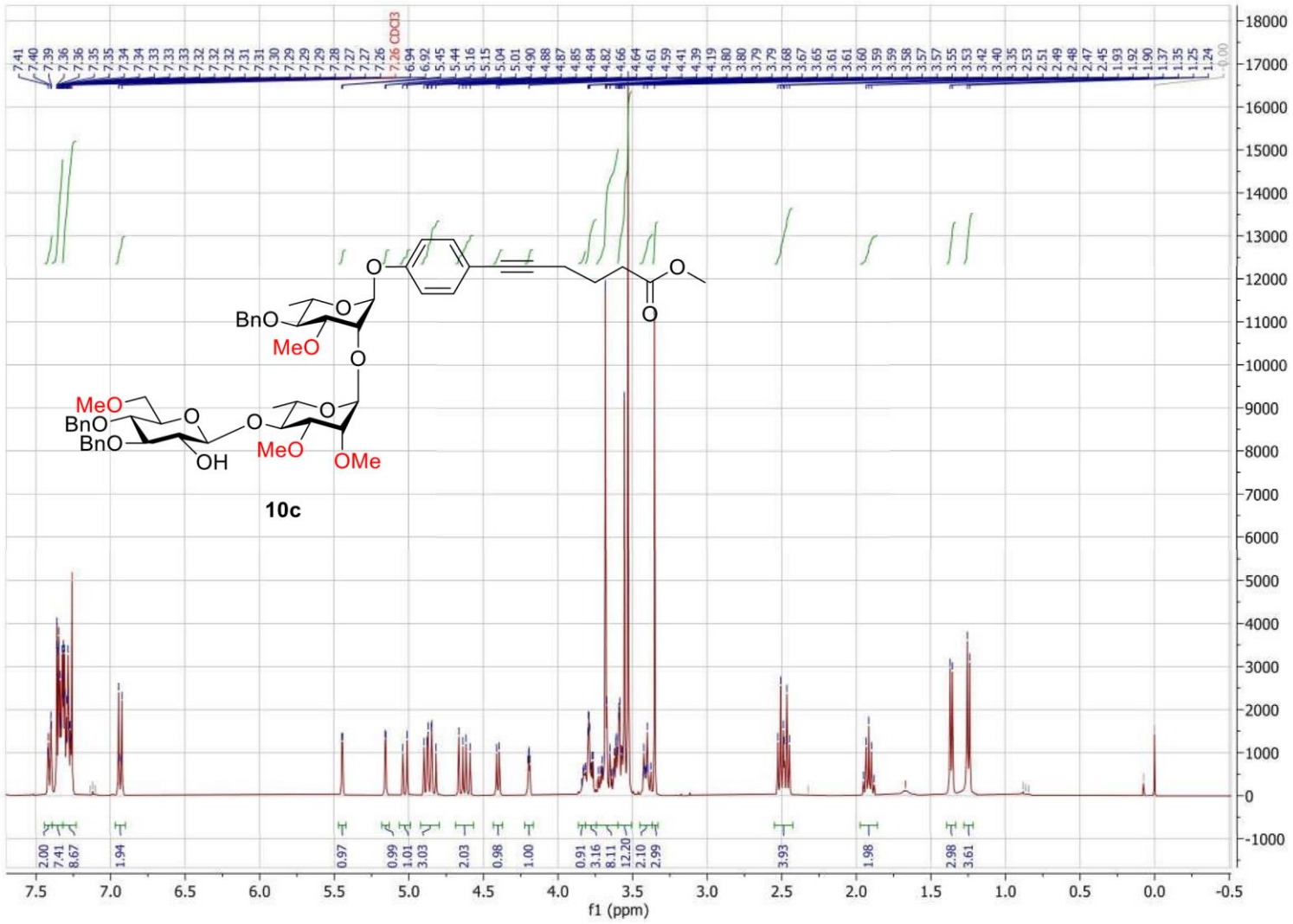
f1 (ppm)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MeO
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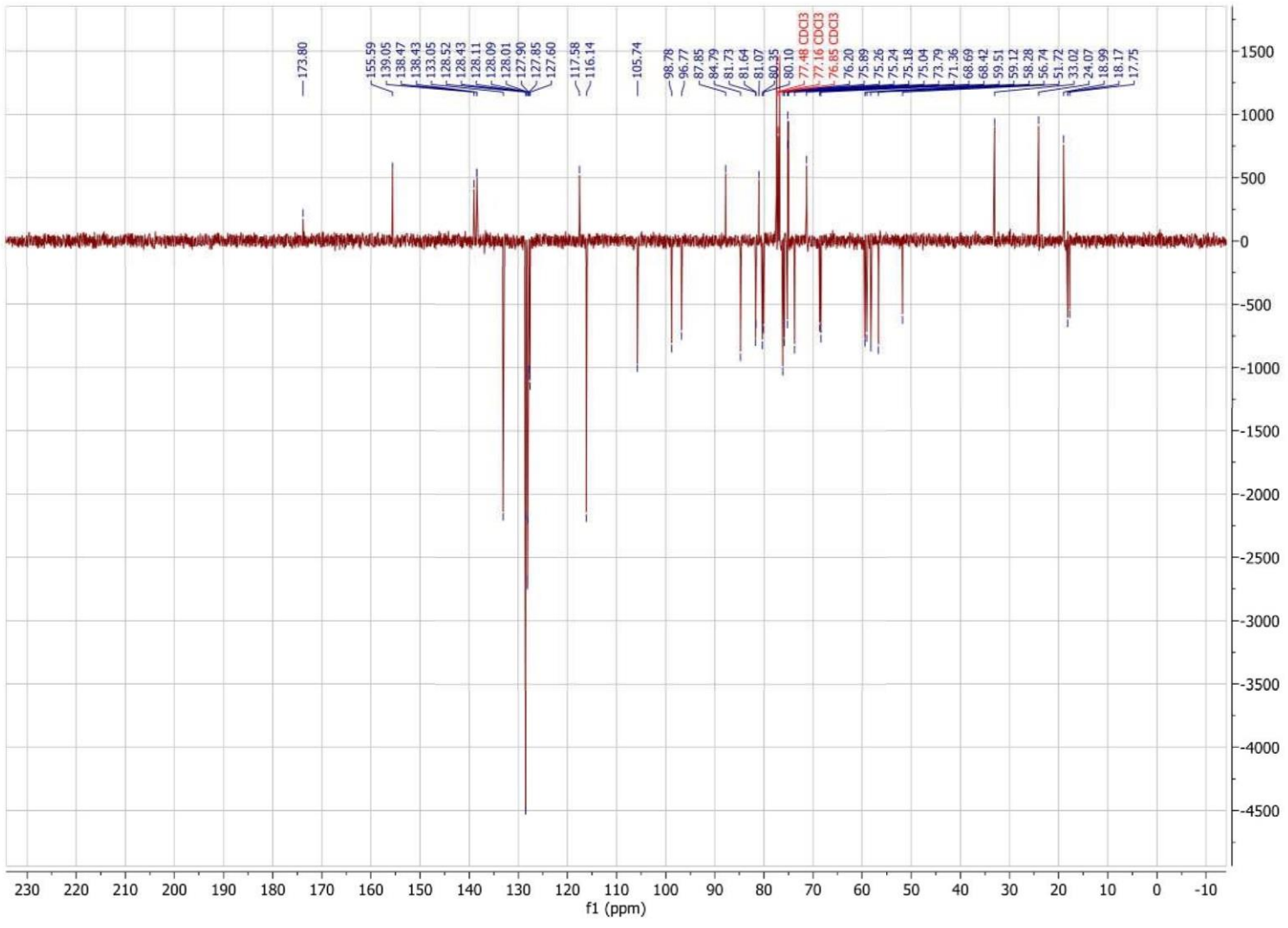
MeO
BnO
BnO
OH
MeO
OMe
10c
f1 (ppm)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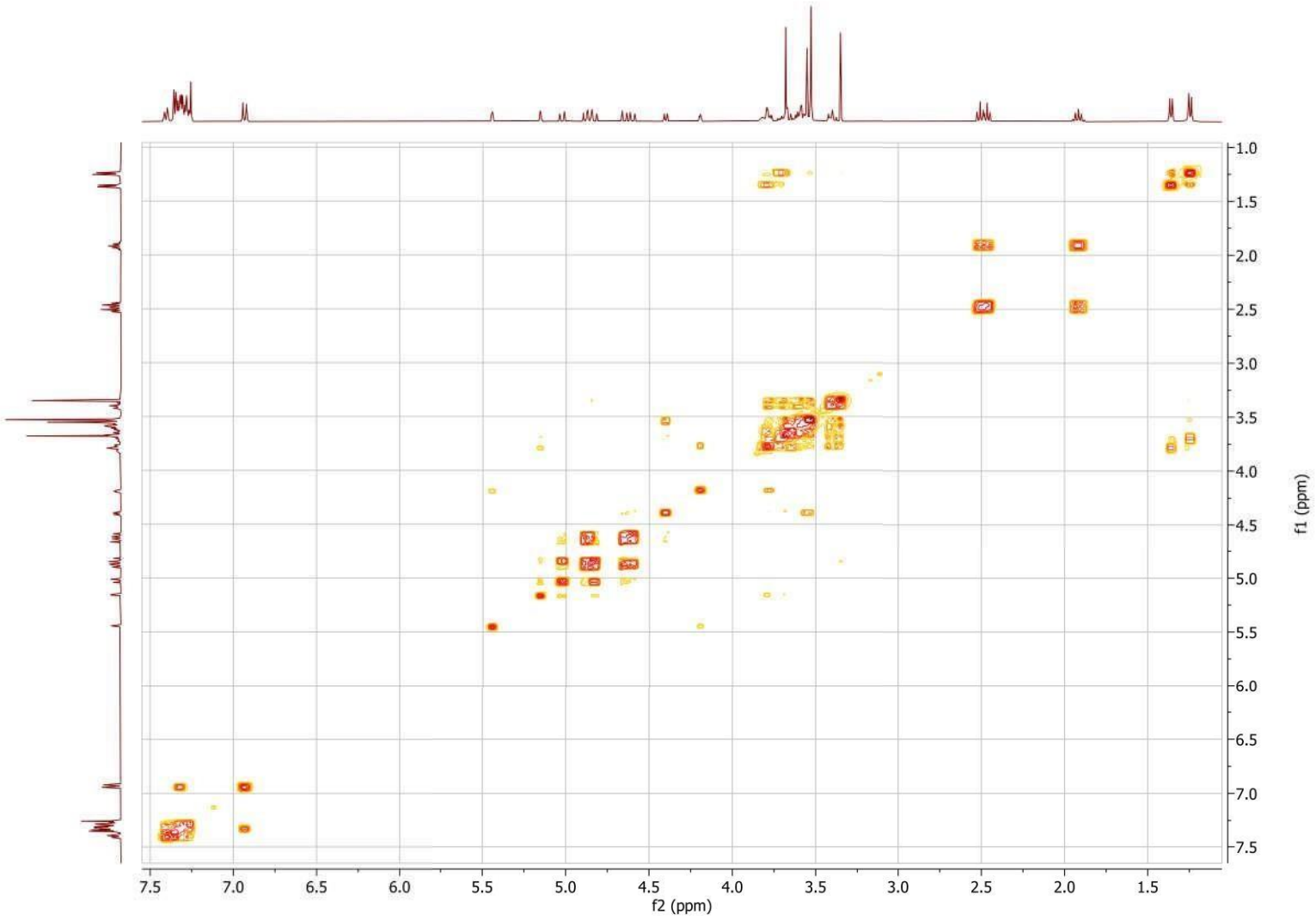
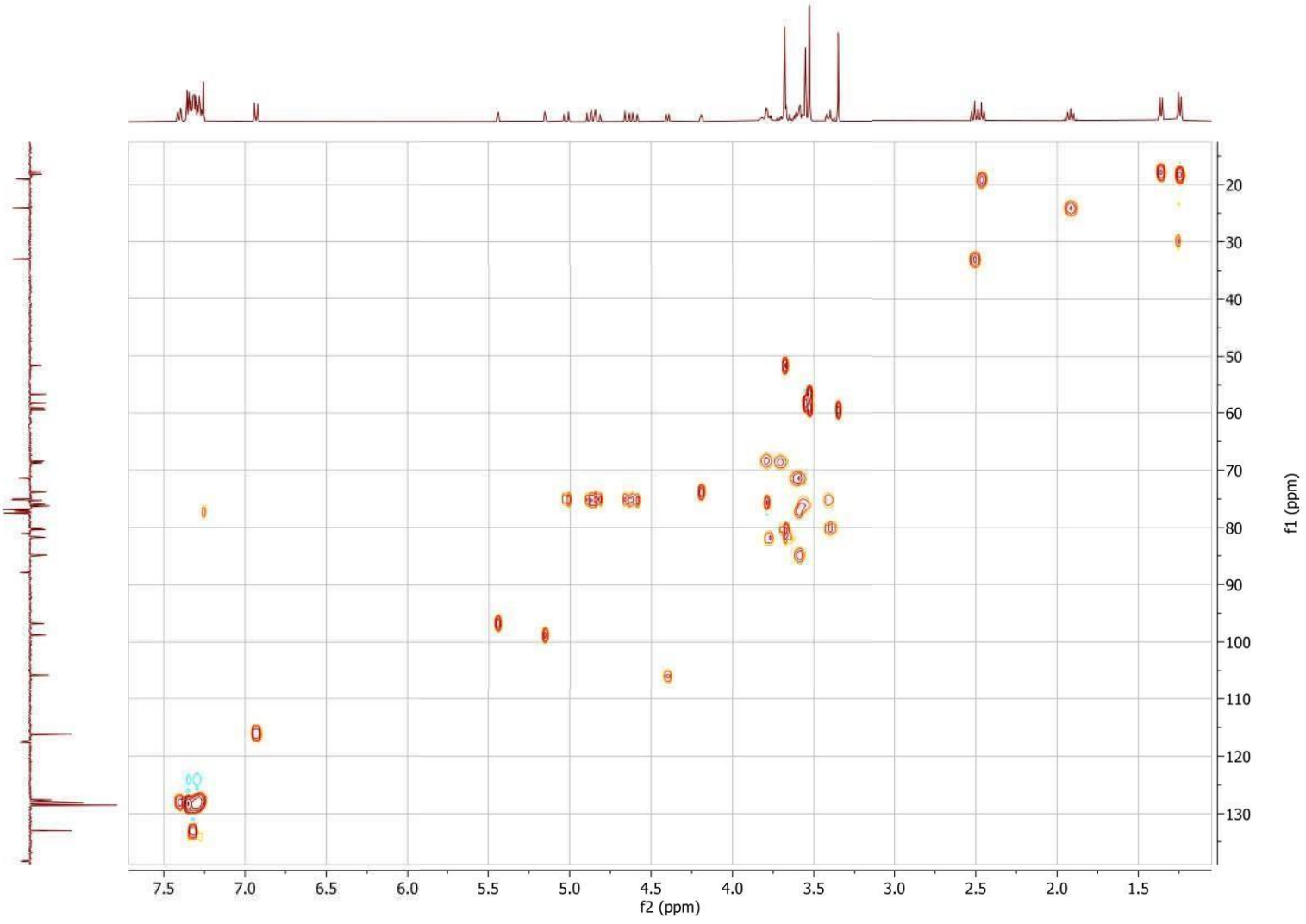
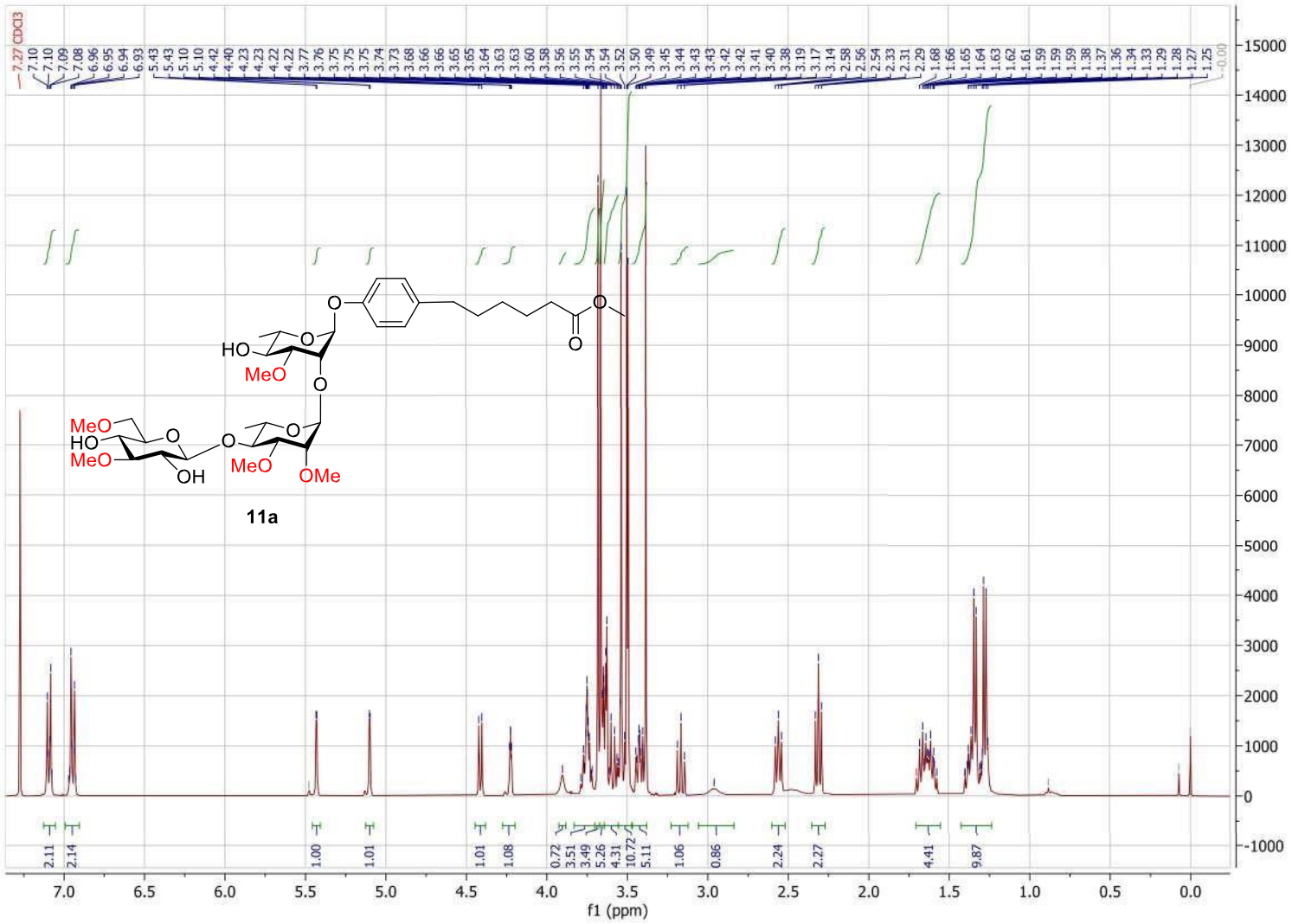
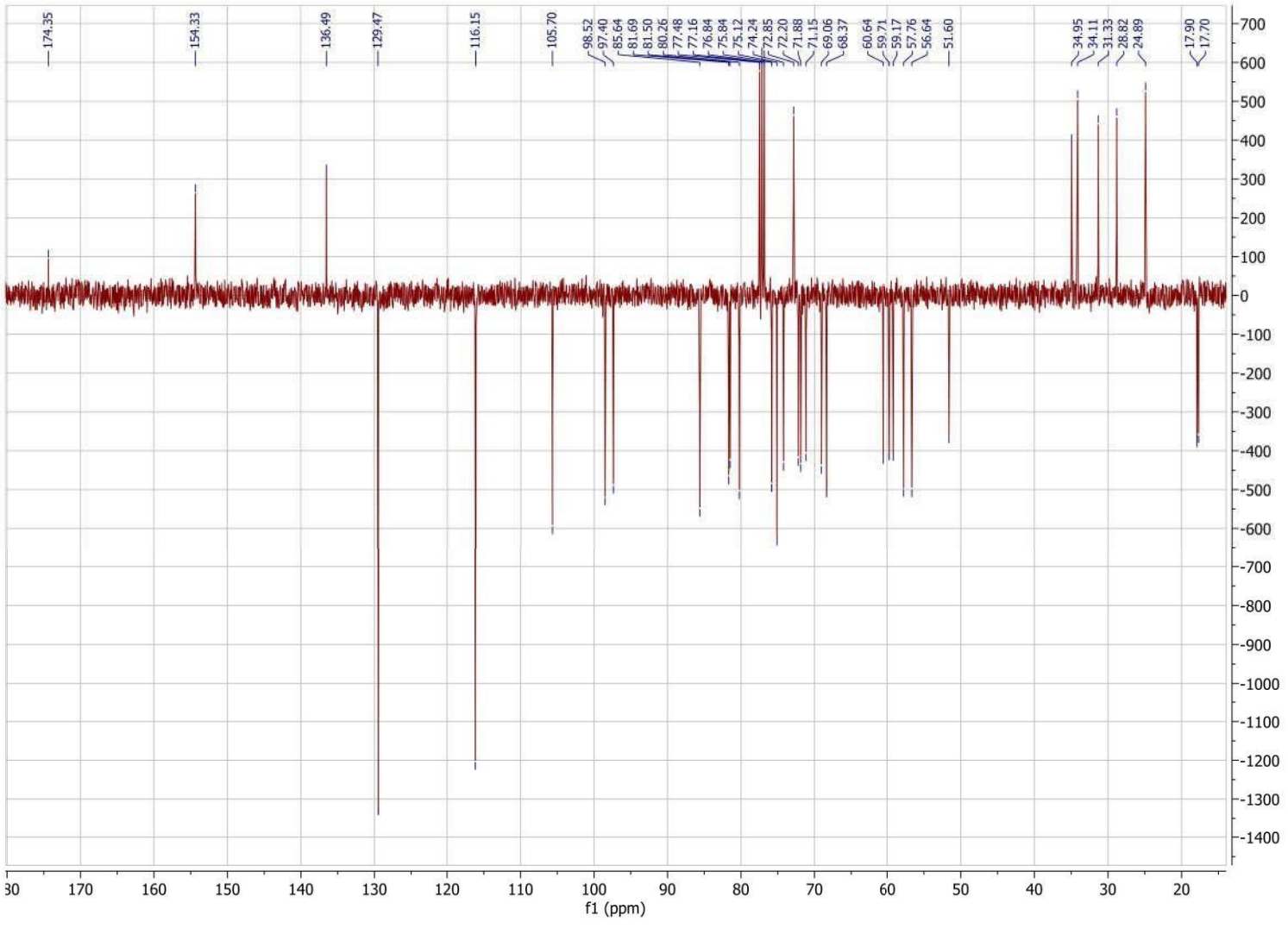

f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


HO
MeO
O
MeO
HO
MeO
OH
MeO
OMe
11a
f1 (ppm)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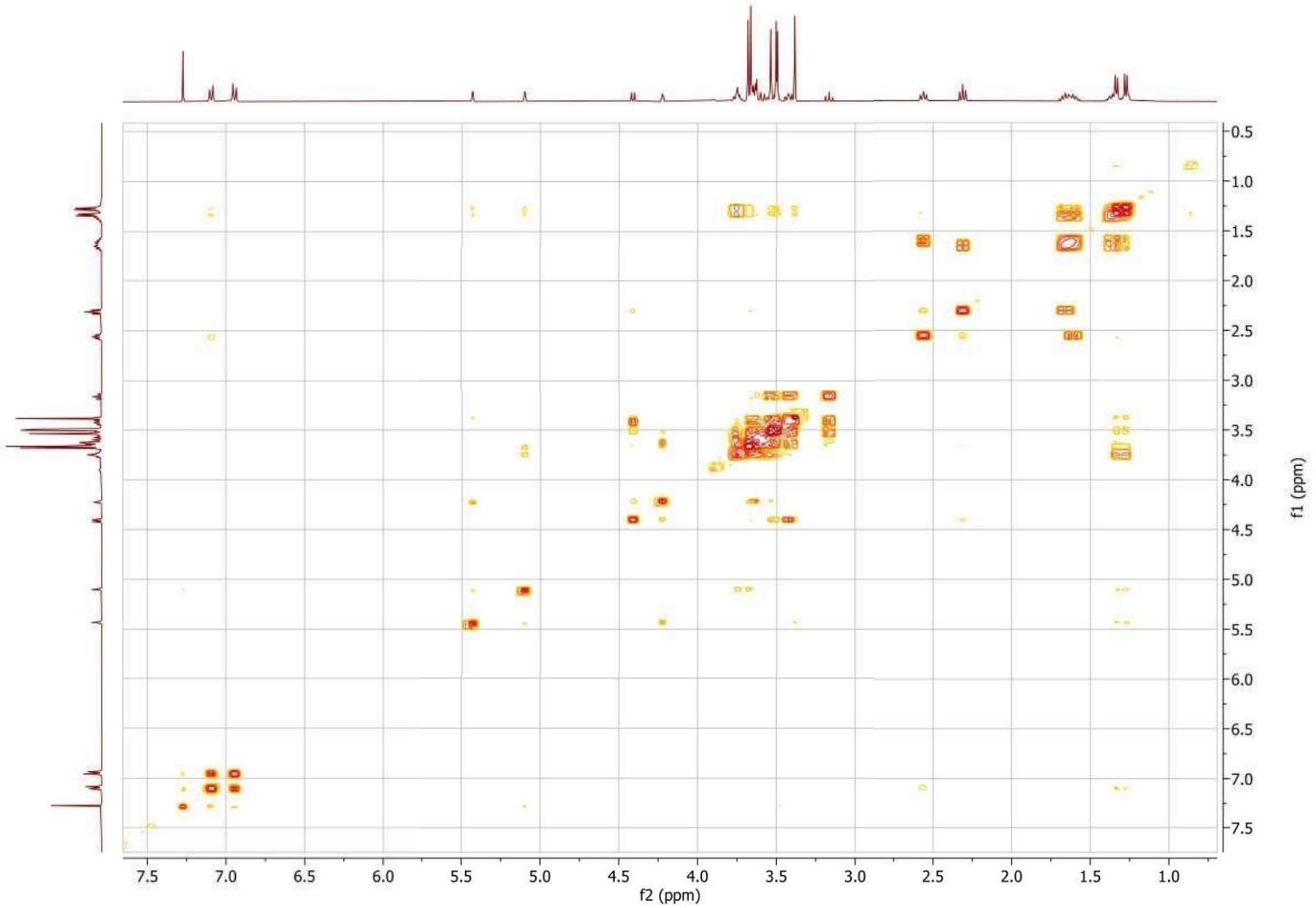
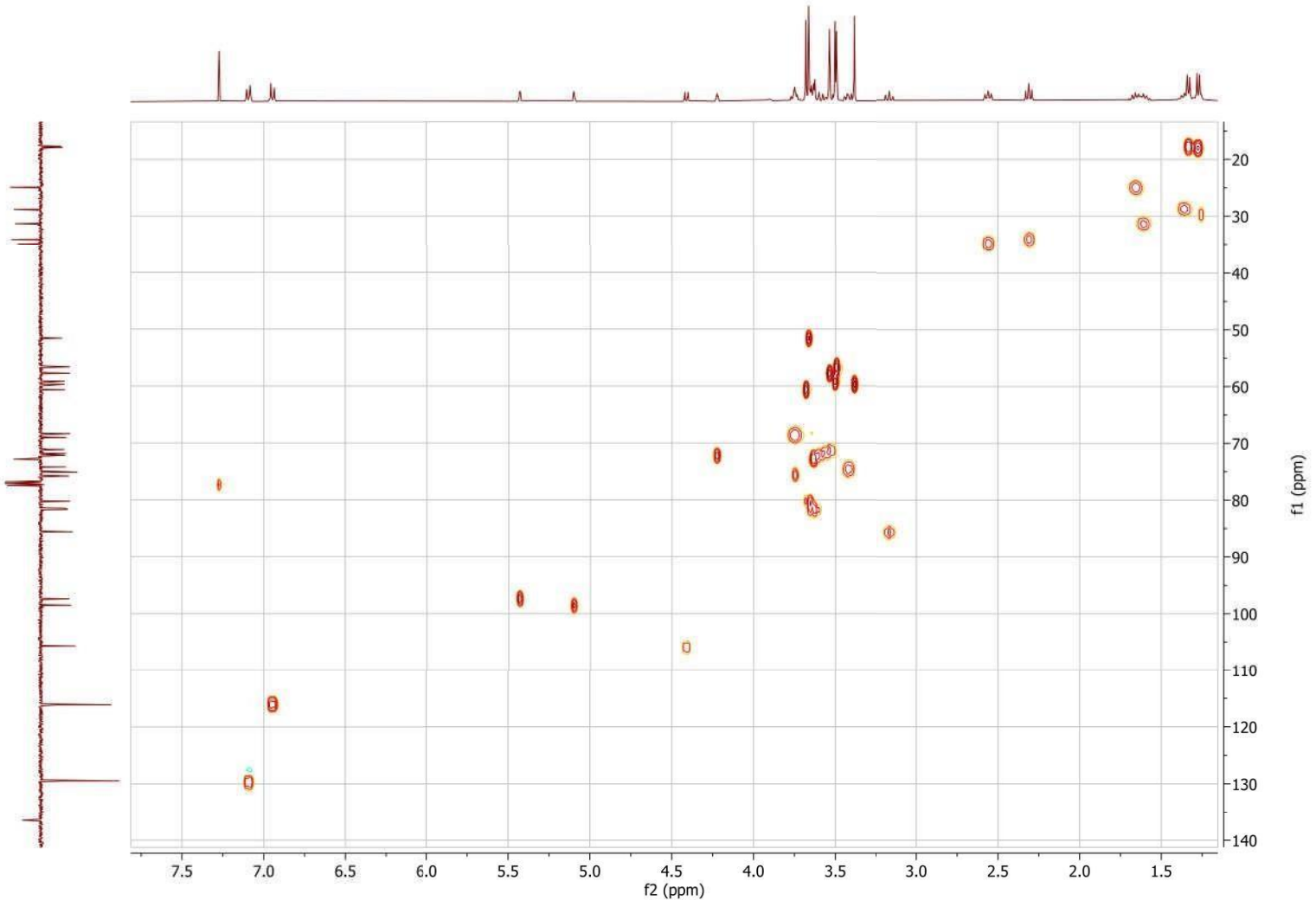

f2 (ppm)
f1 (ppm)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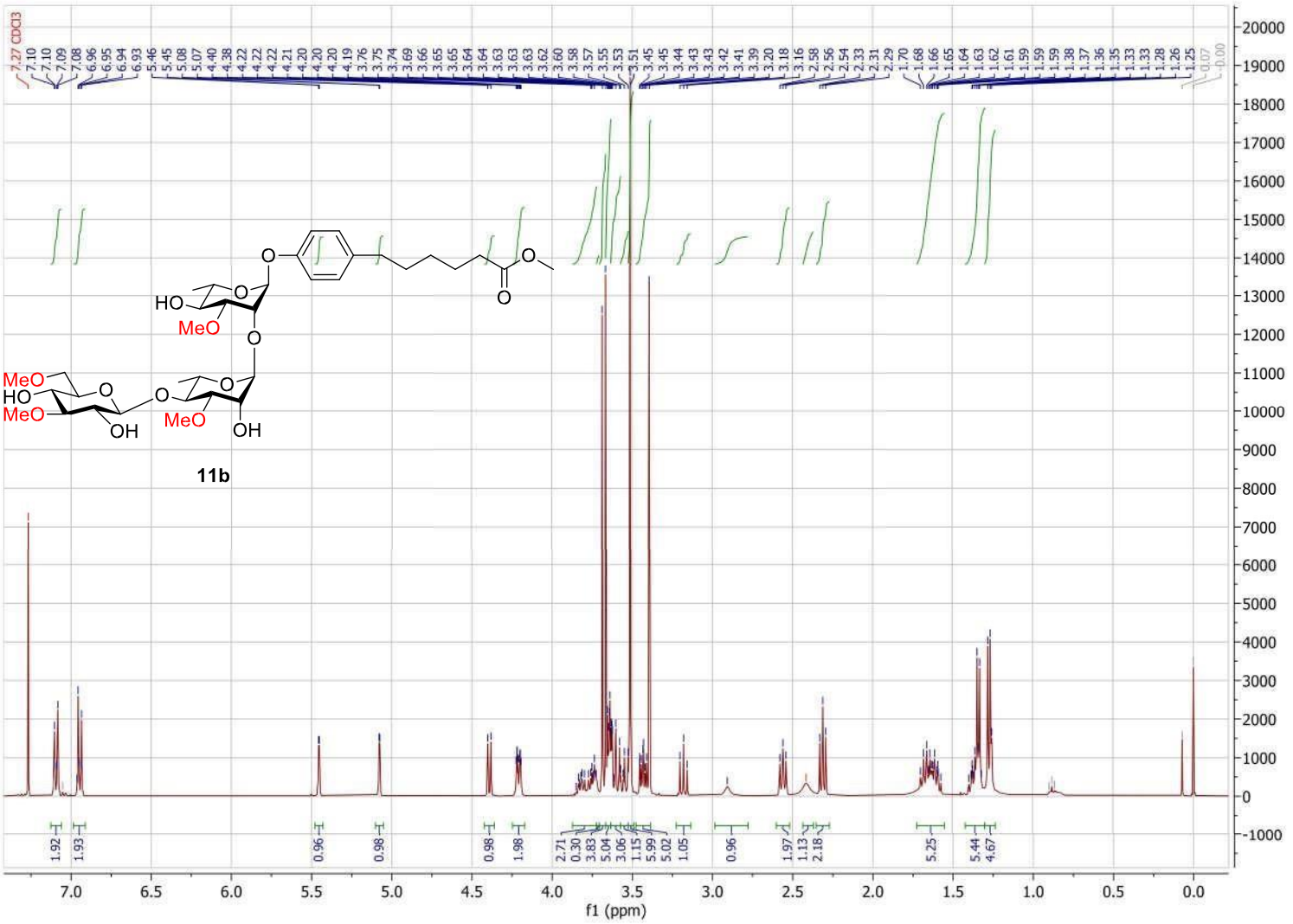
f1 (ppm)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MeO
MeO
OH
OH
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O
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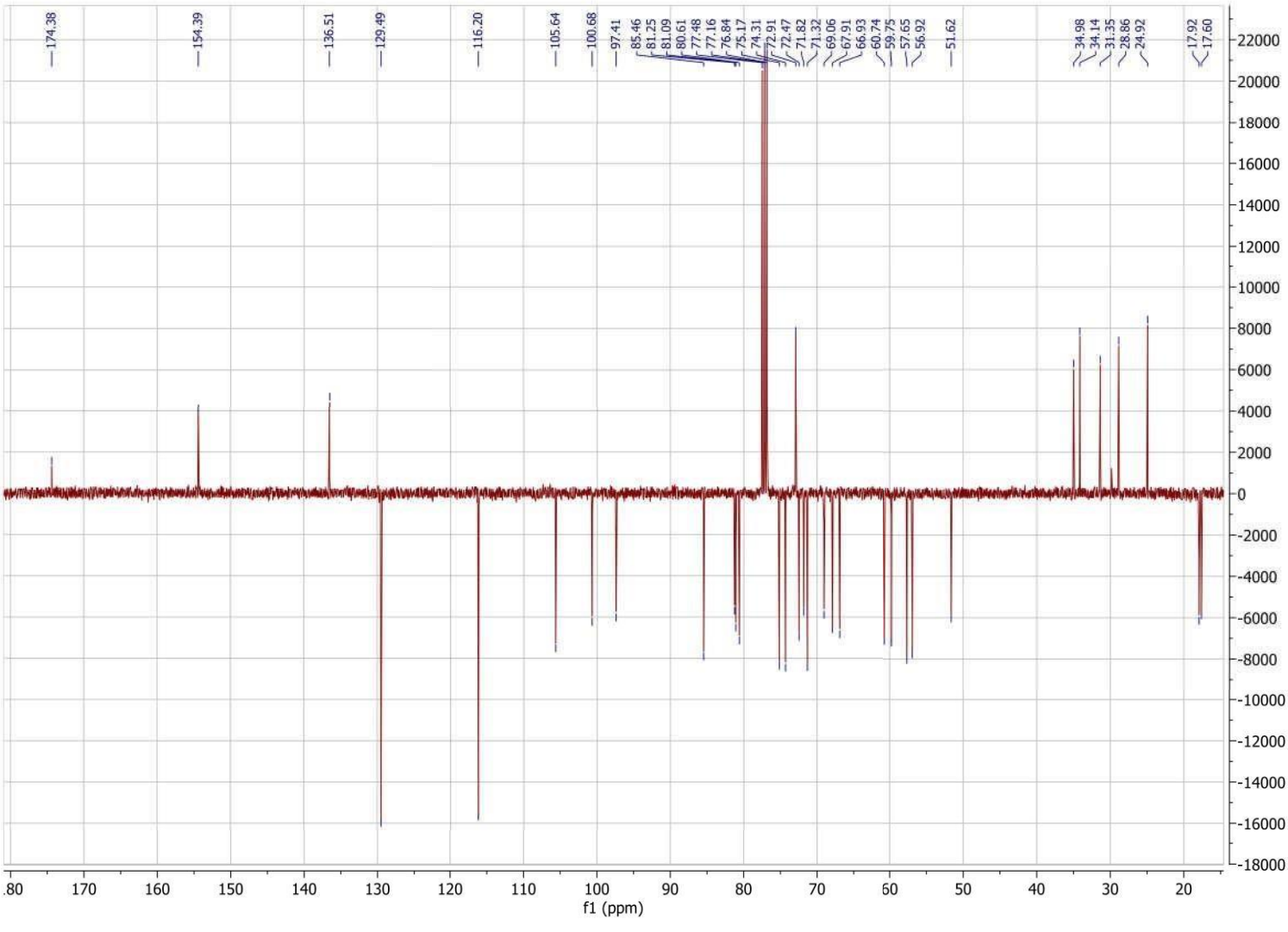
O
O
O
O
O
11b
f1 (ppm)


174.38
154.39
136.51
129.49
116.20
105.64
100.68
97.41
85.46
81.25
81.09
80.61
77.48
77.16
76.84
75.17
74.31
72.91
72.47
71.82
71.32
69.06
67.91
66.93
60.74
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57.65
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51.62
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34.14
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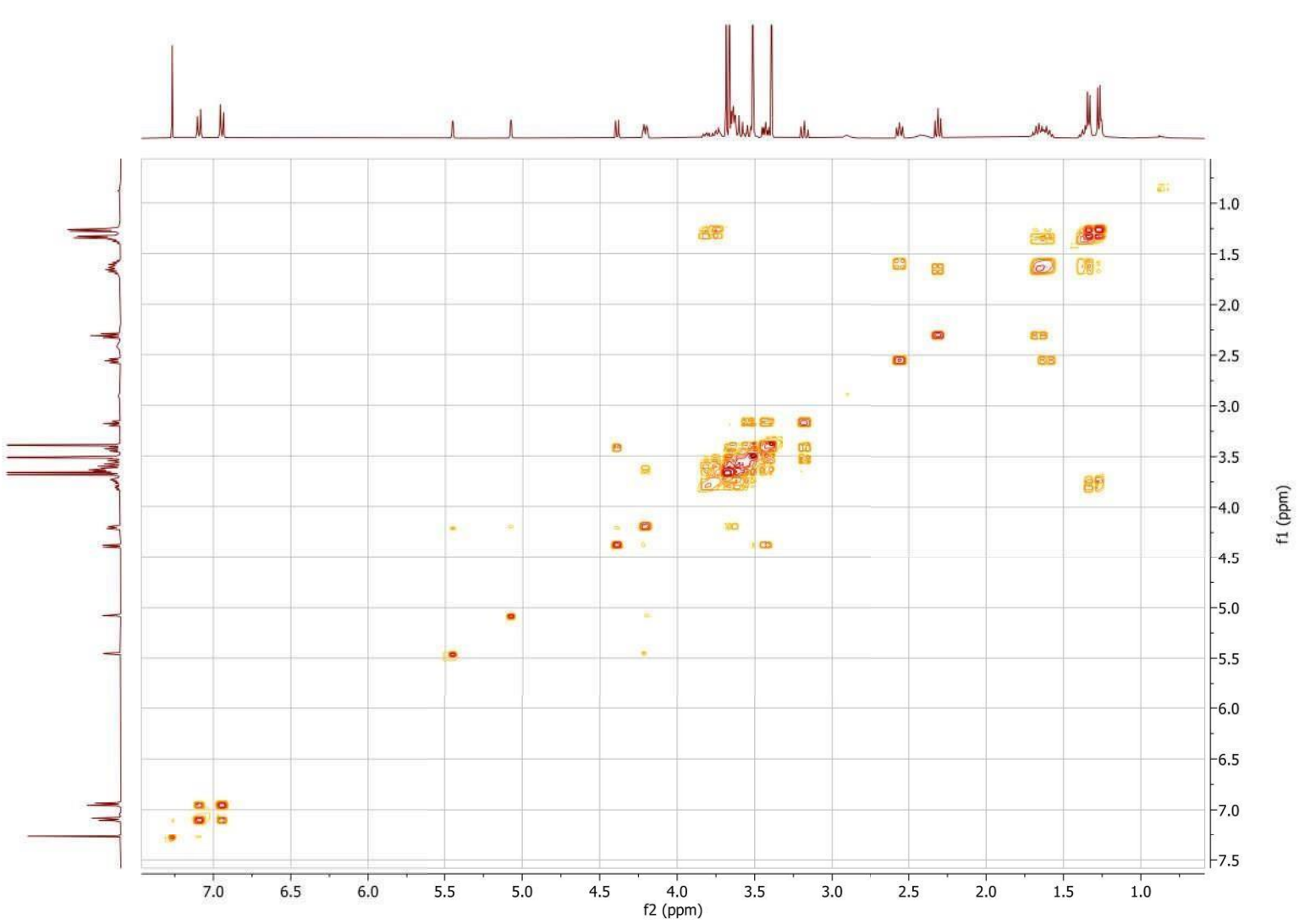
24.92
17.92
17.60
f1 (ppm)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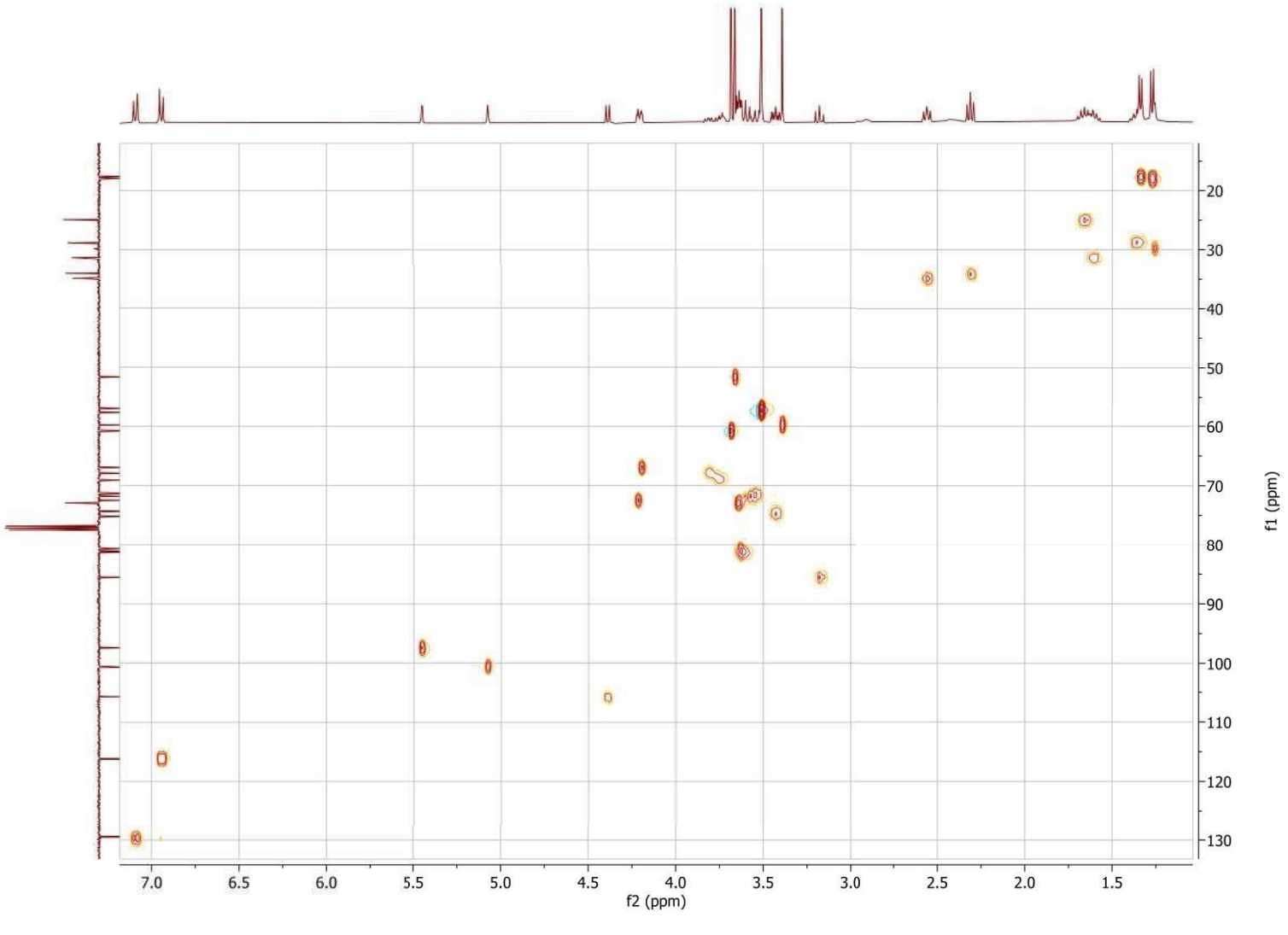
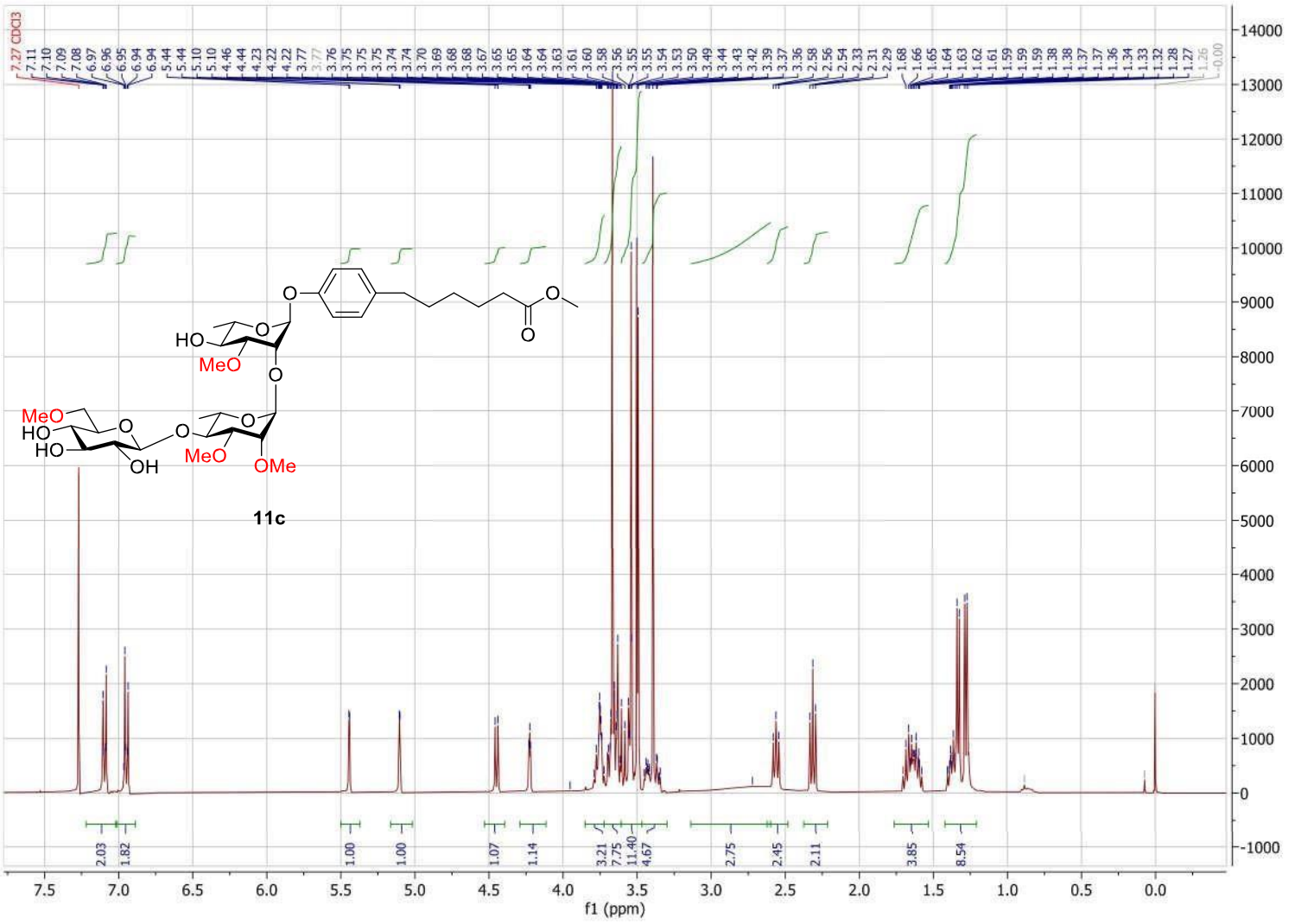
f1 (ppm)


f2 (ppm)
f1 (ppm)


HO
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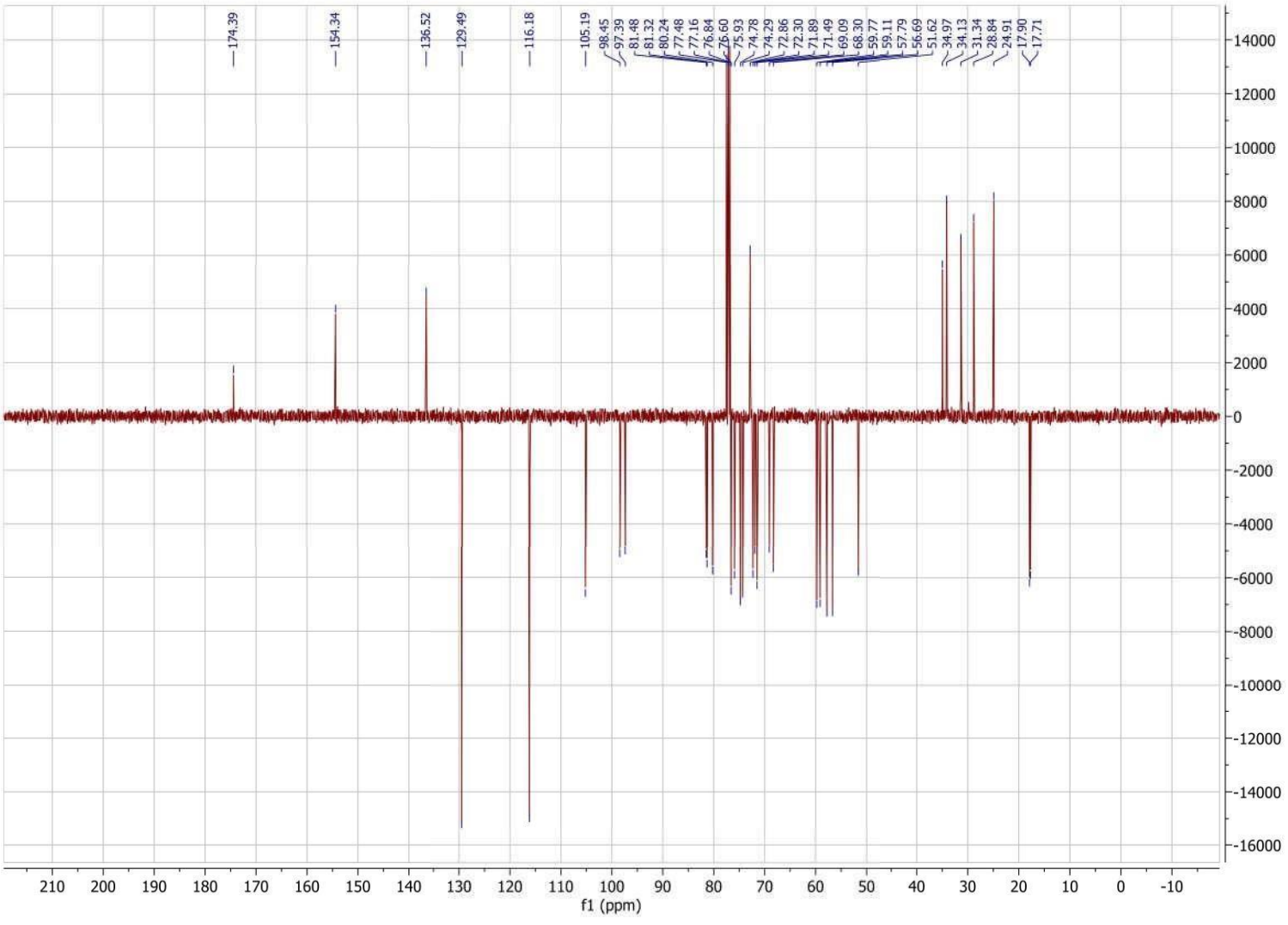
HO
OH
MeO
OMe
O
O
O
O
O
O
O
O
11c
f1 (ppm)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72.30
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71.49
69.09
68.30
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17.71
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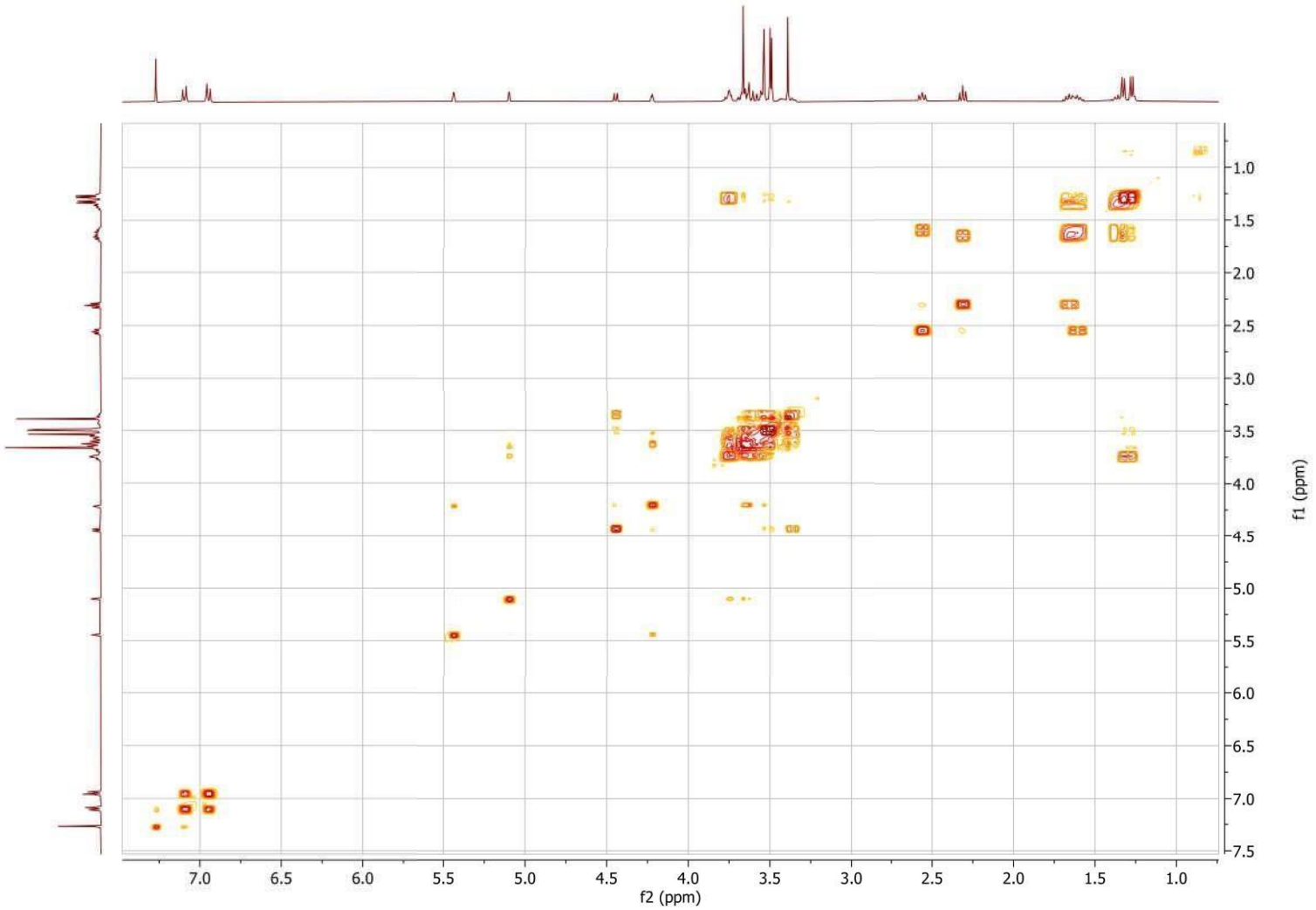
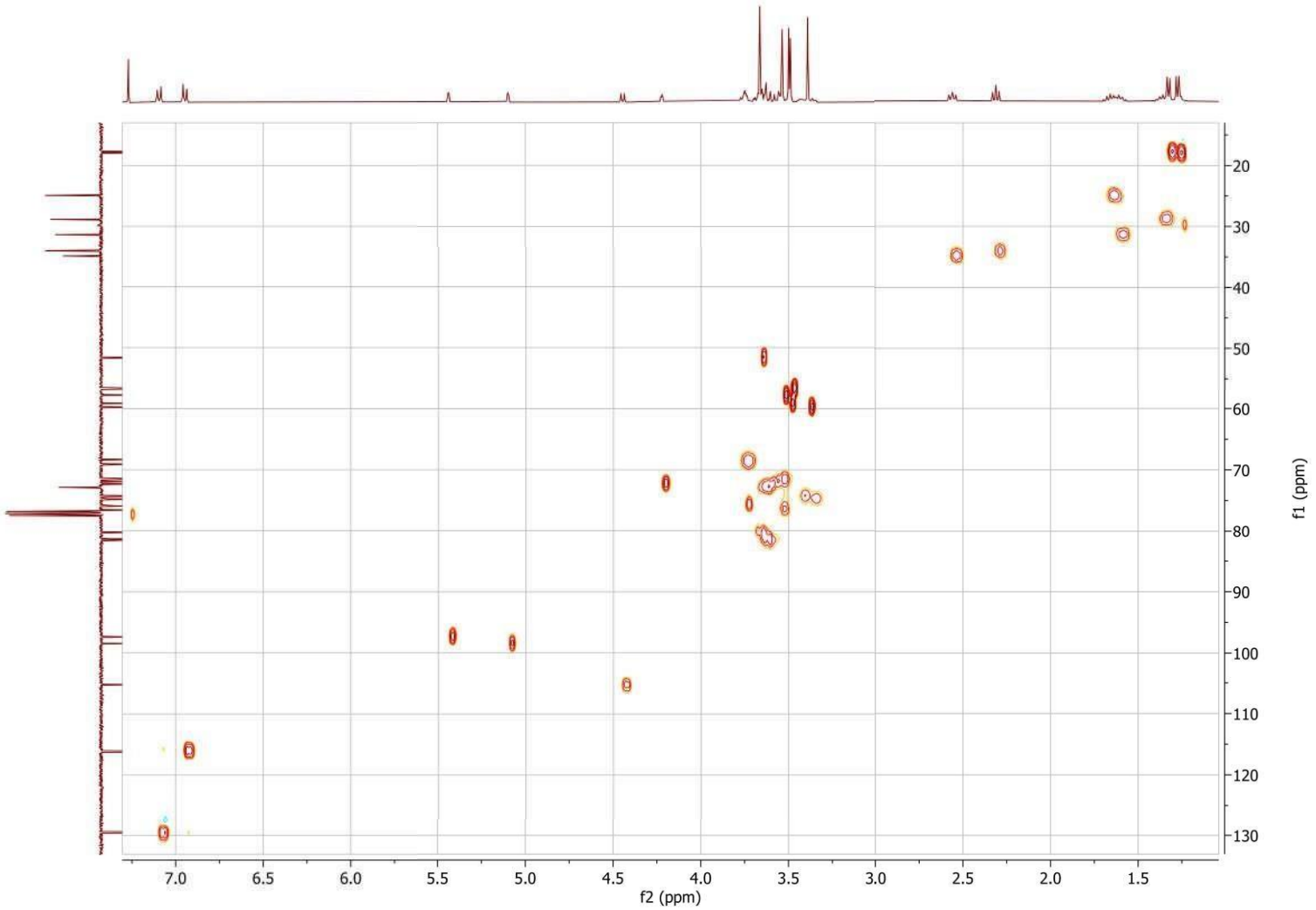
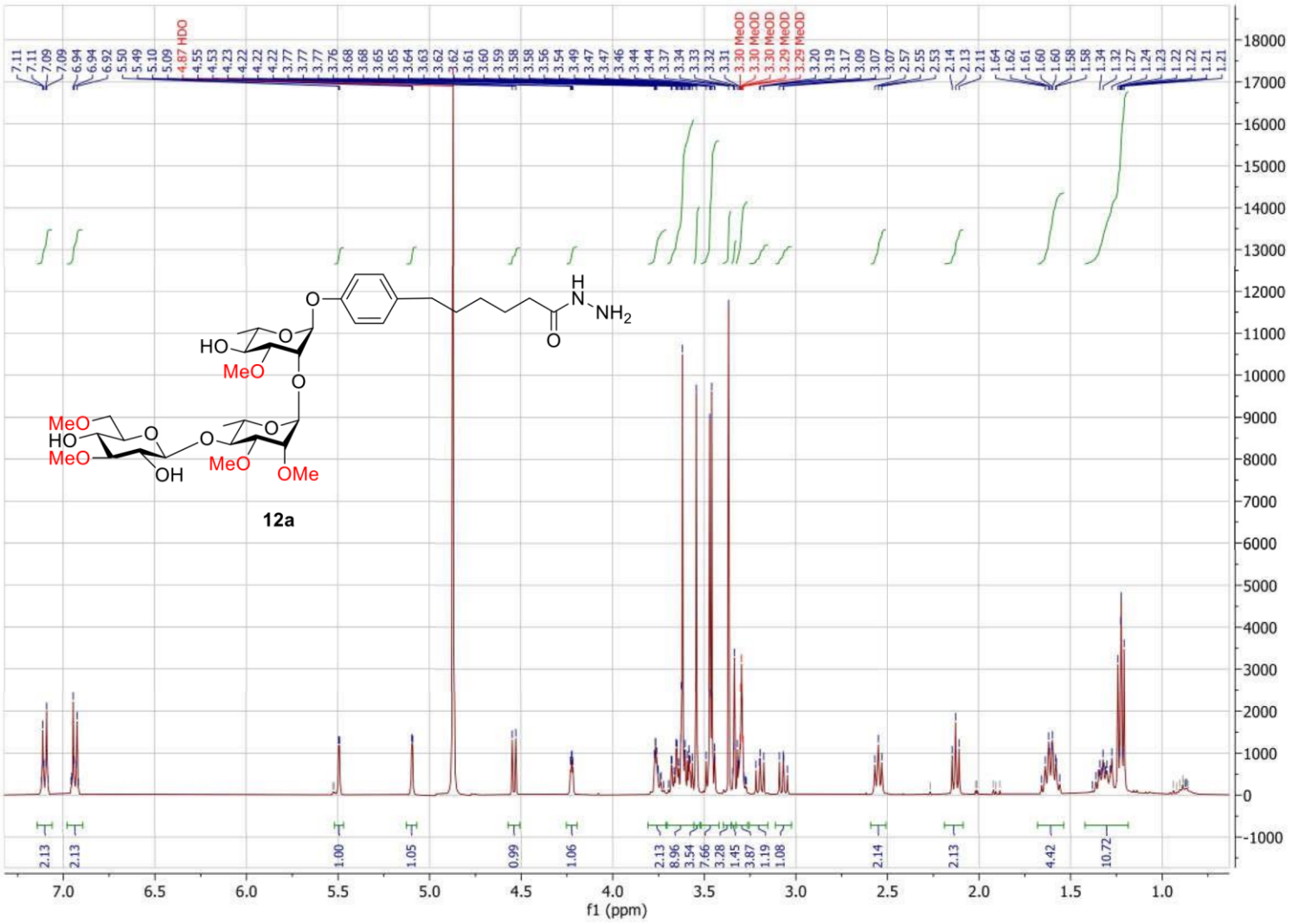

f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


HO
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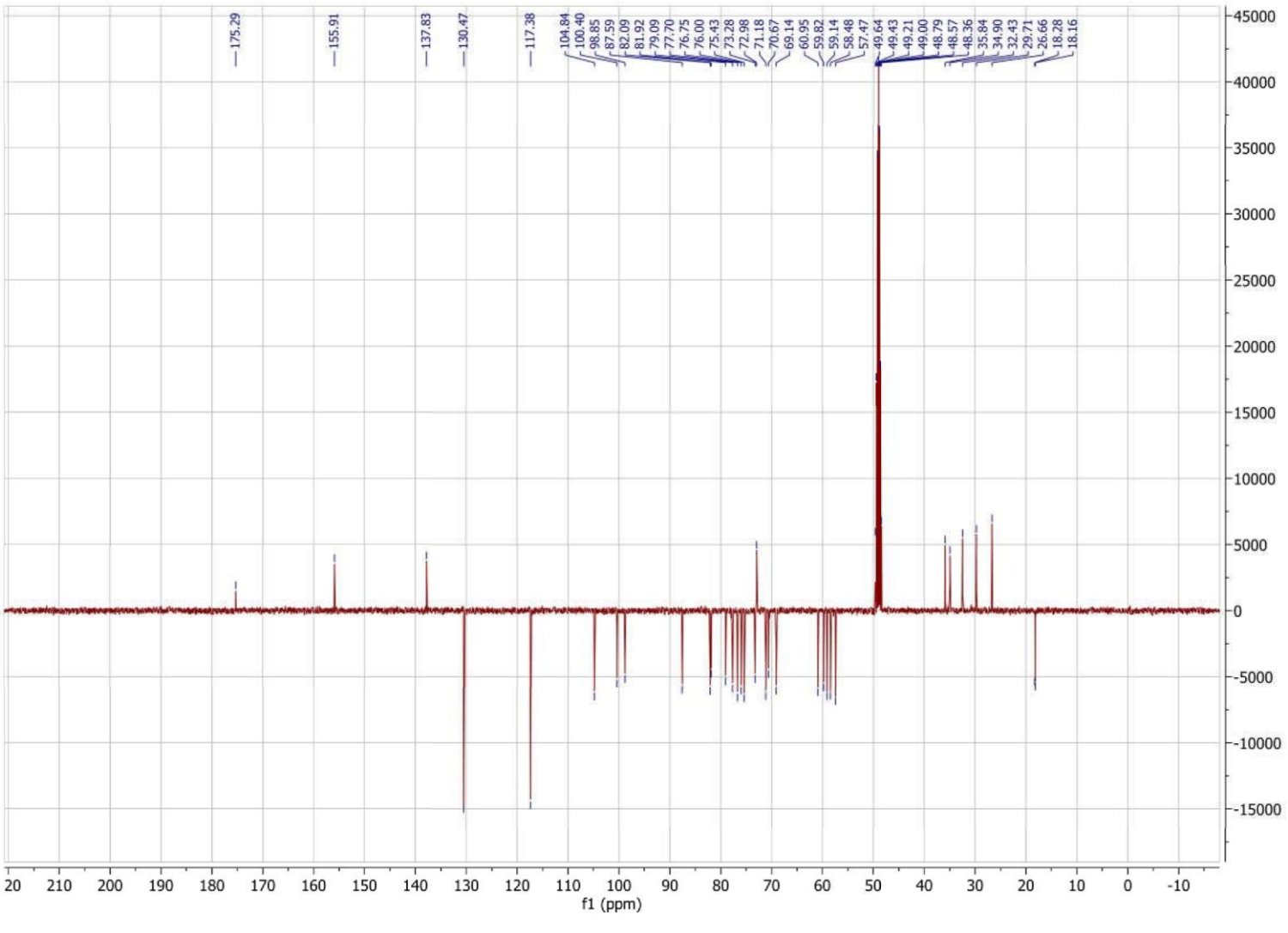
HO
MeO
OH
MeO
MeO
OMe
H
N
NH2
O
12a
f1 (ppm)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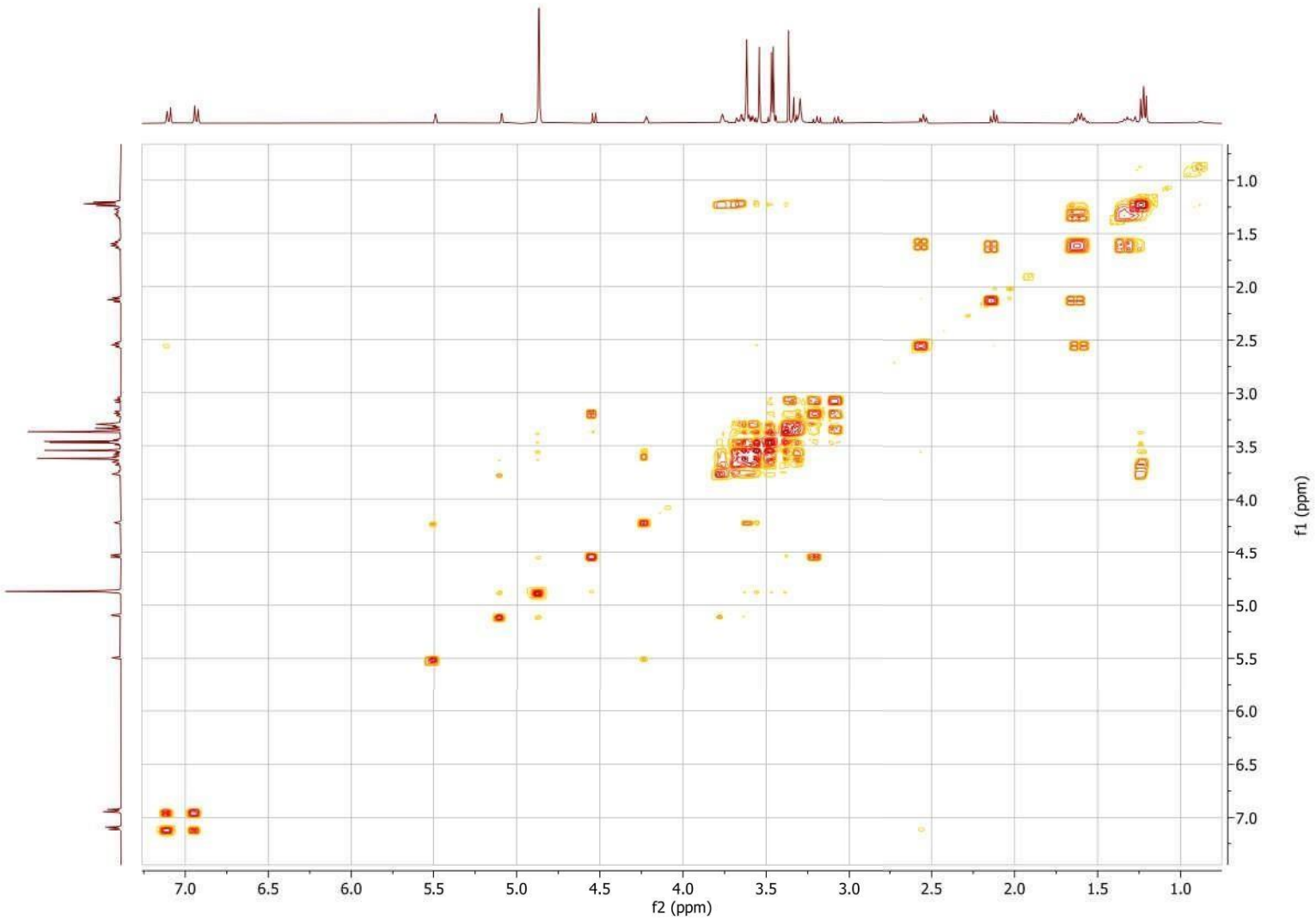
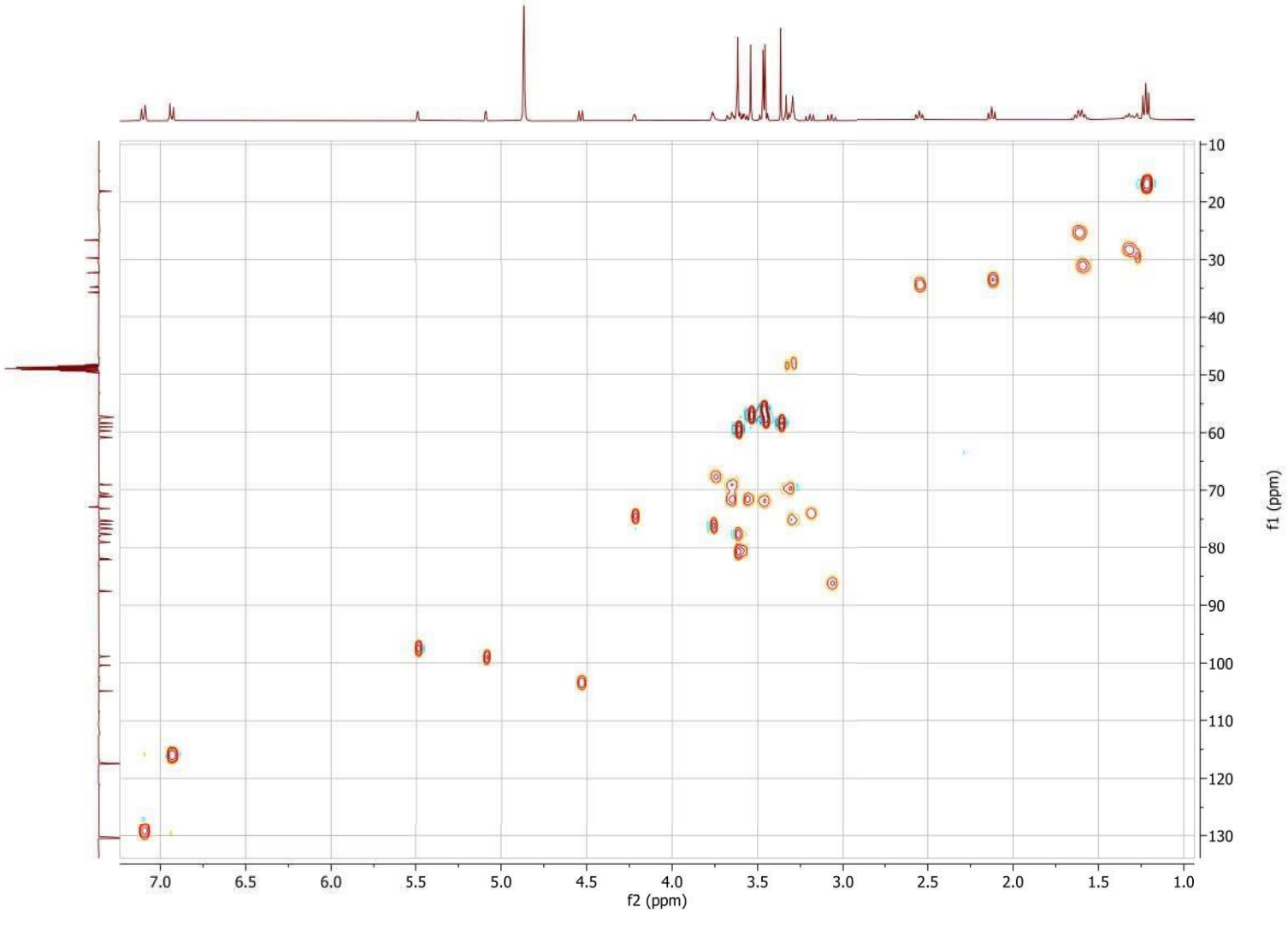
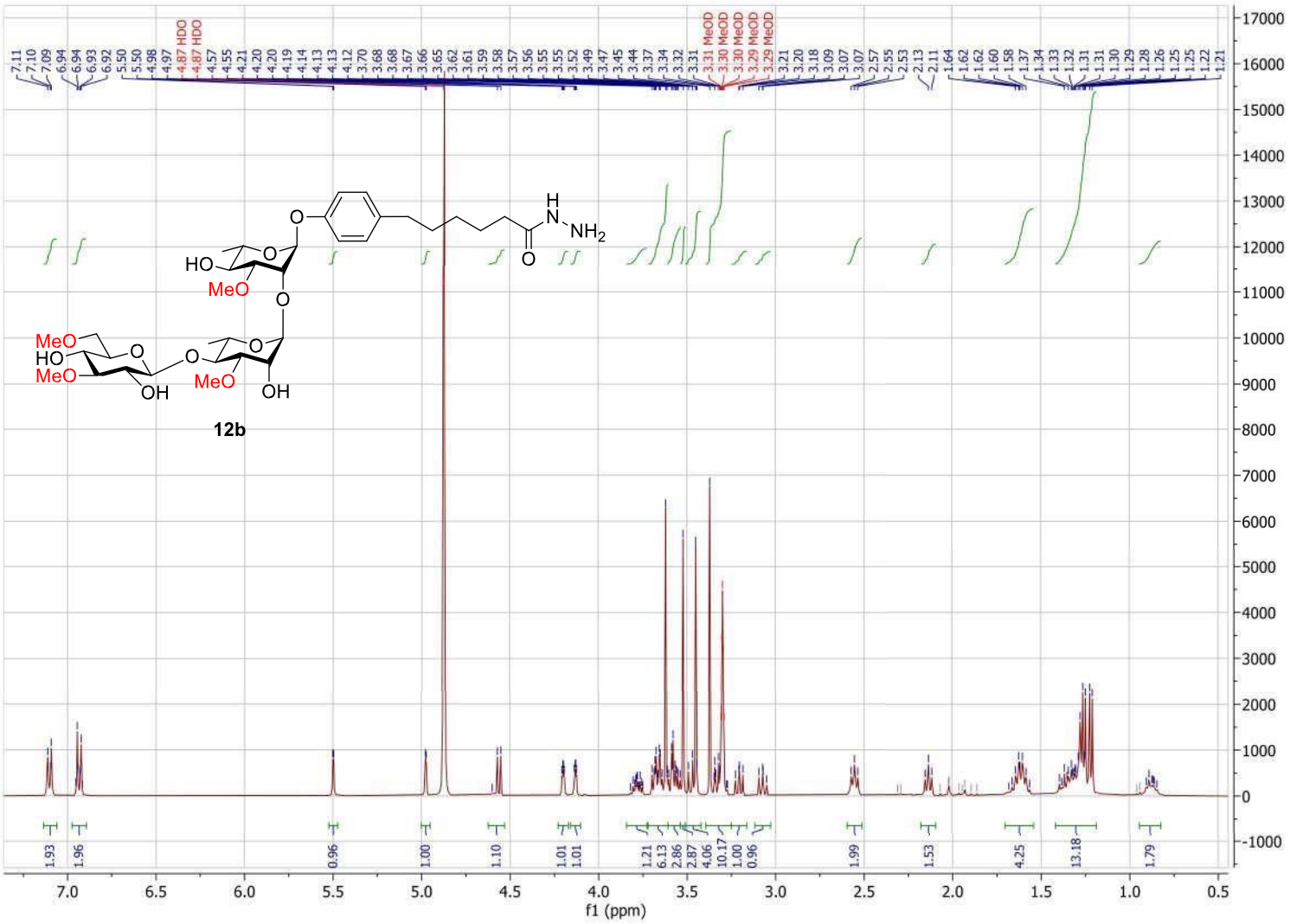

f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)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MeO
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OH
O
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O
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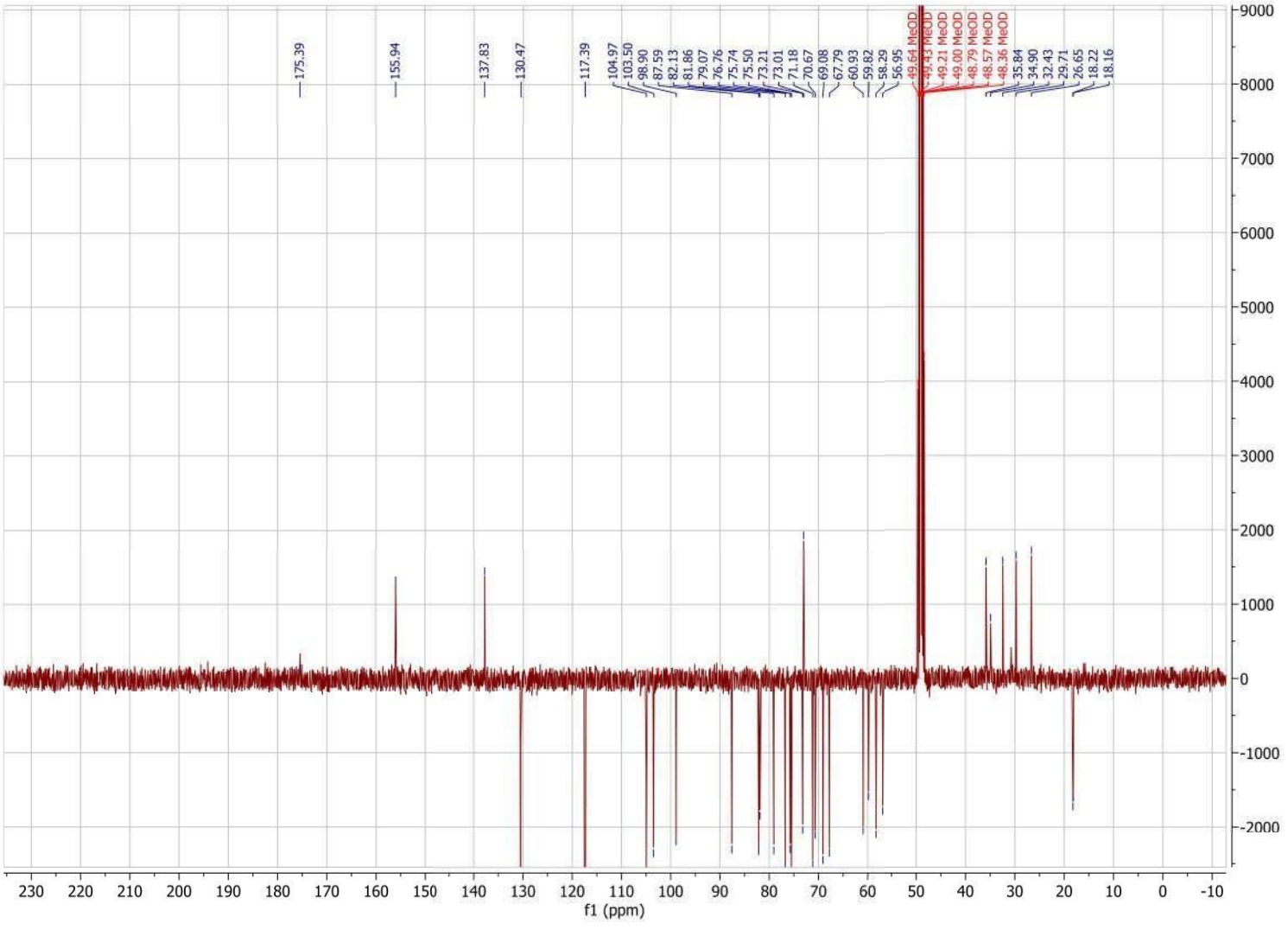
H
N
NH2
O
12b
f1 (ppm)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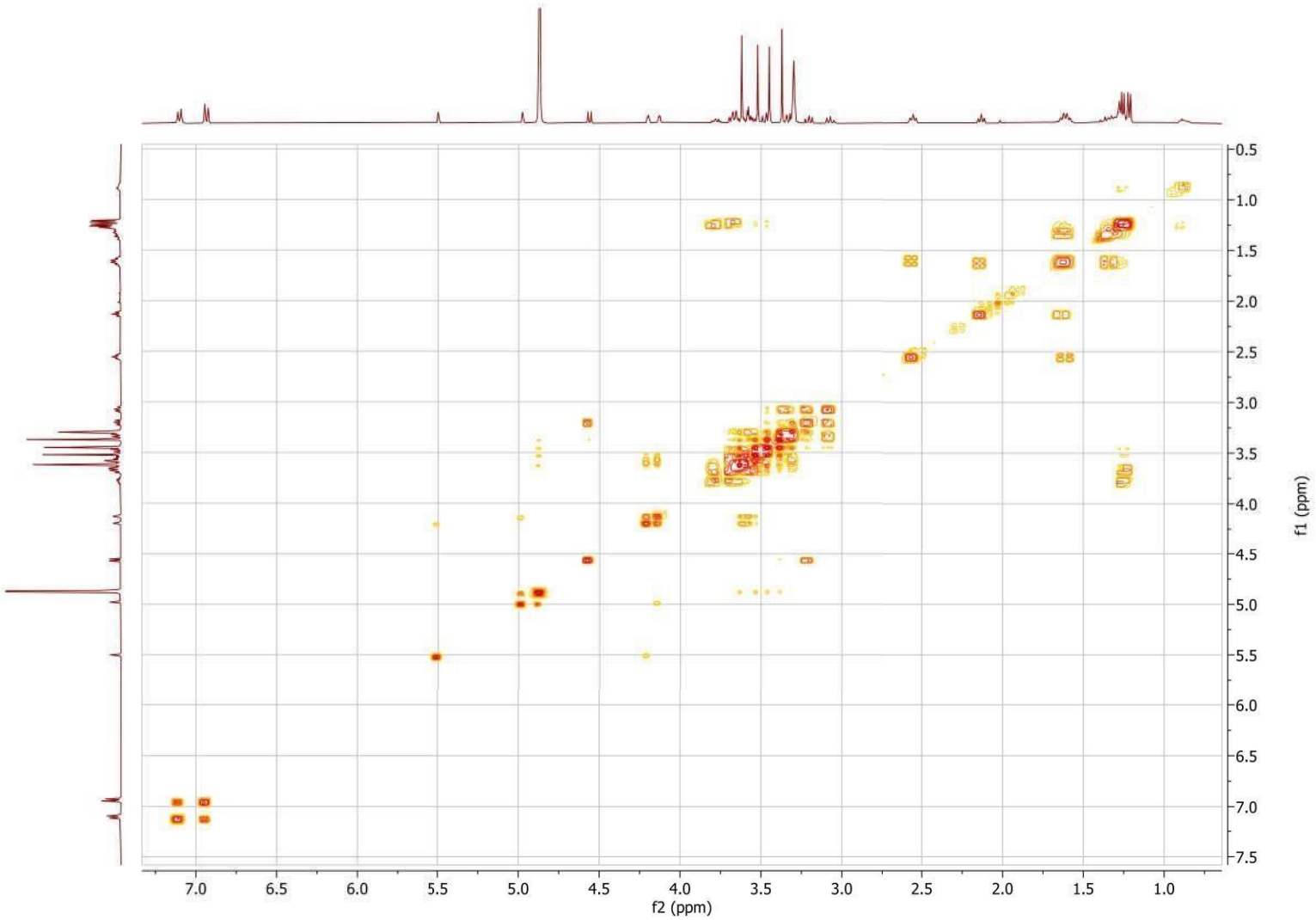
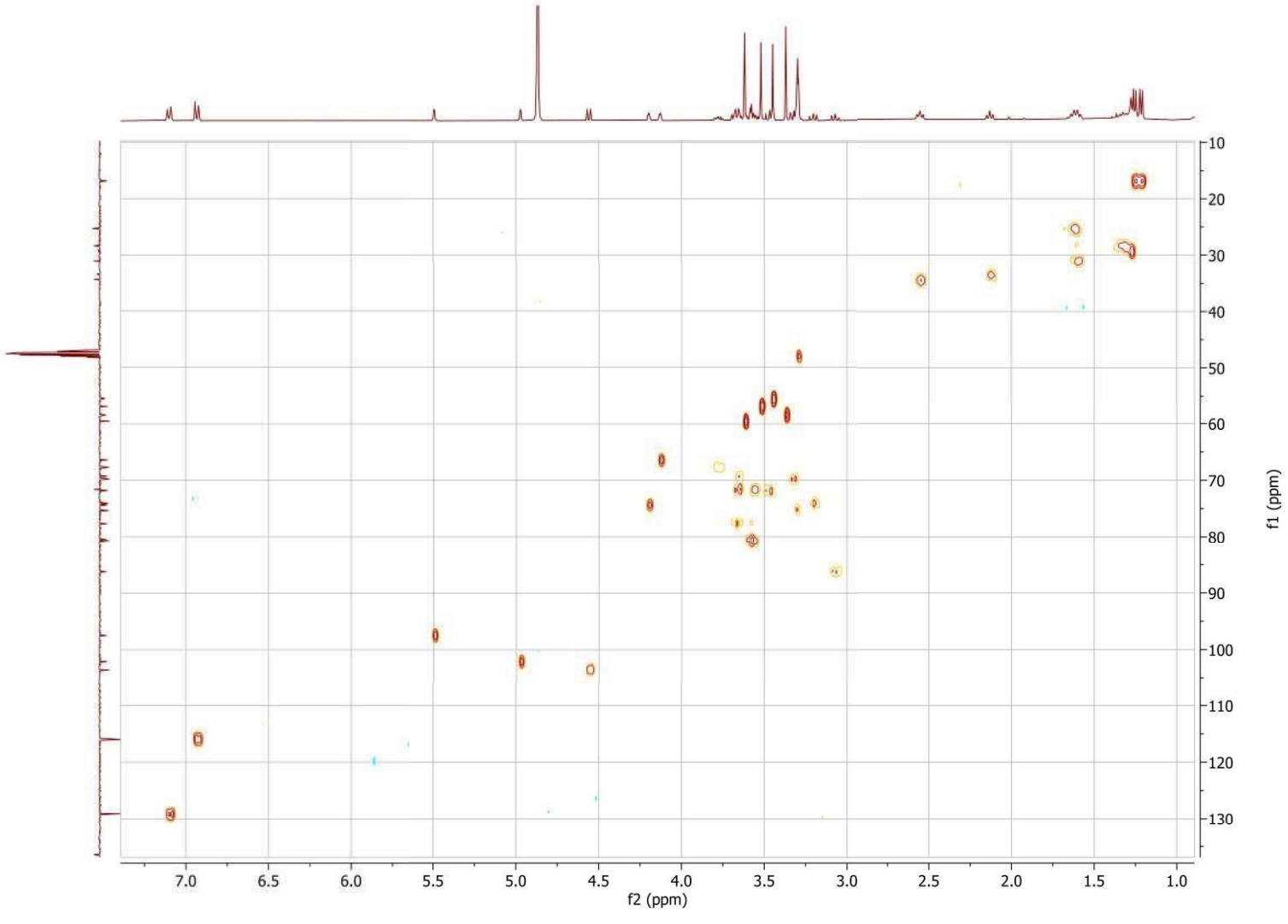
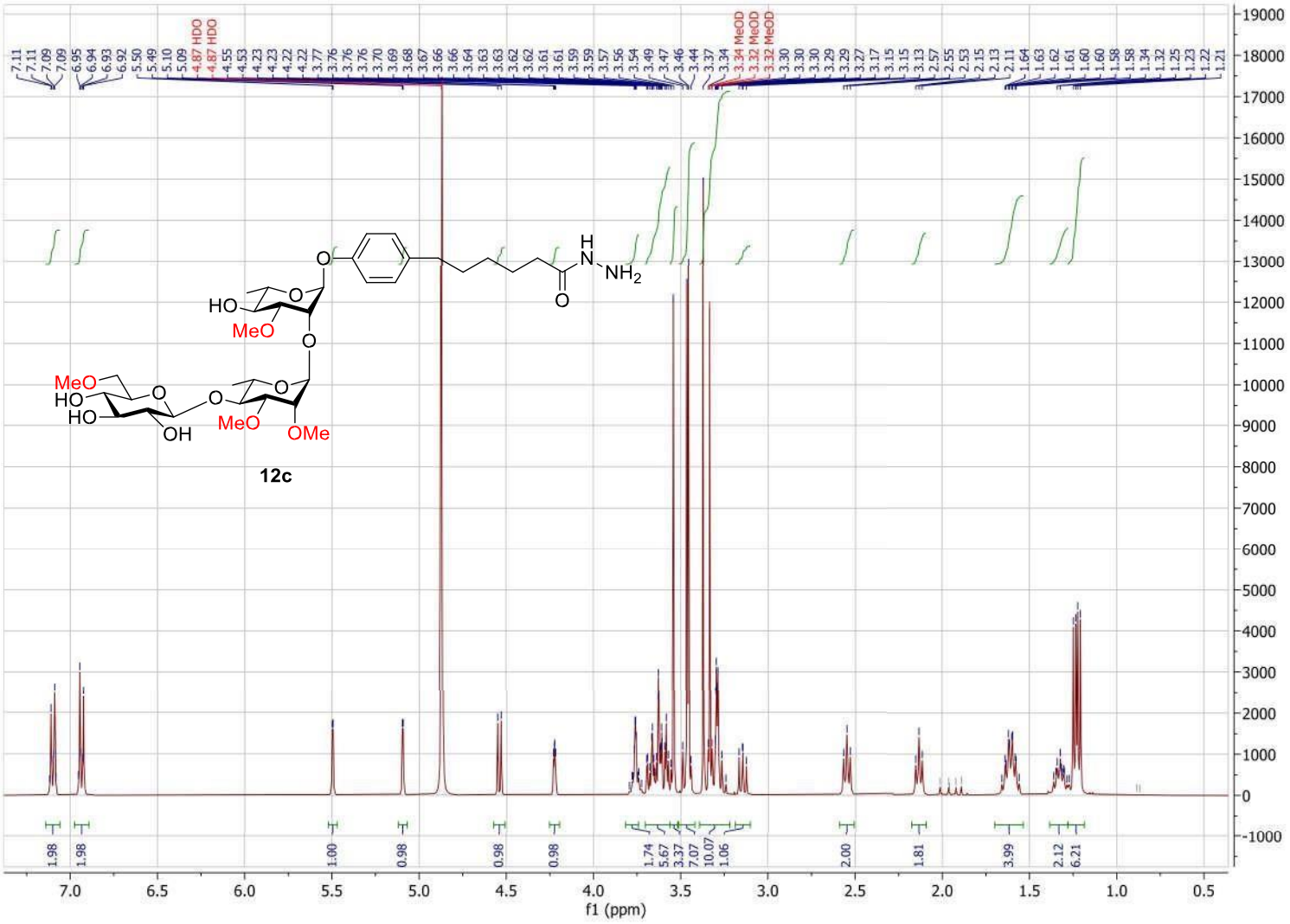
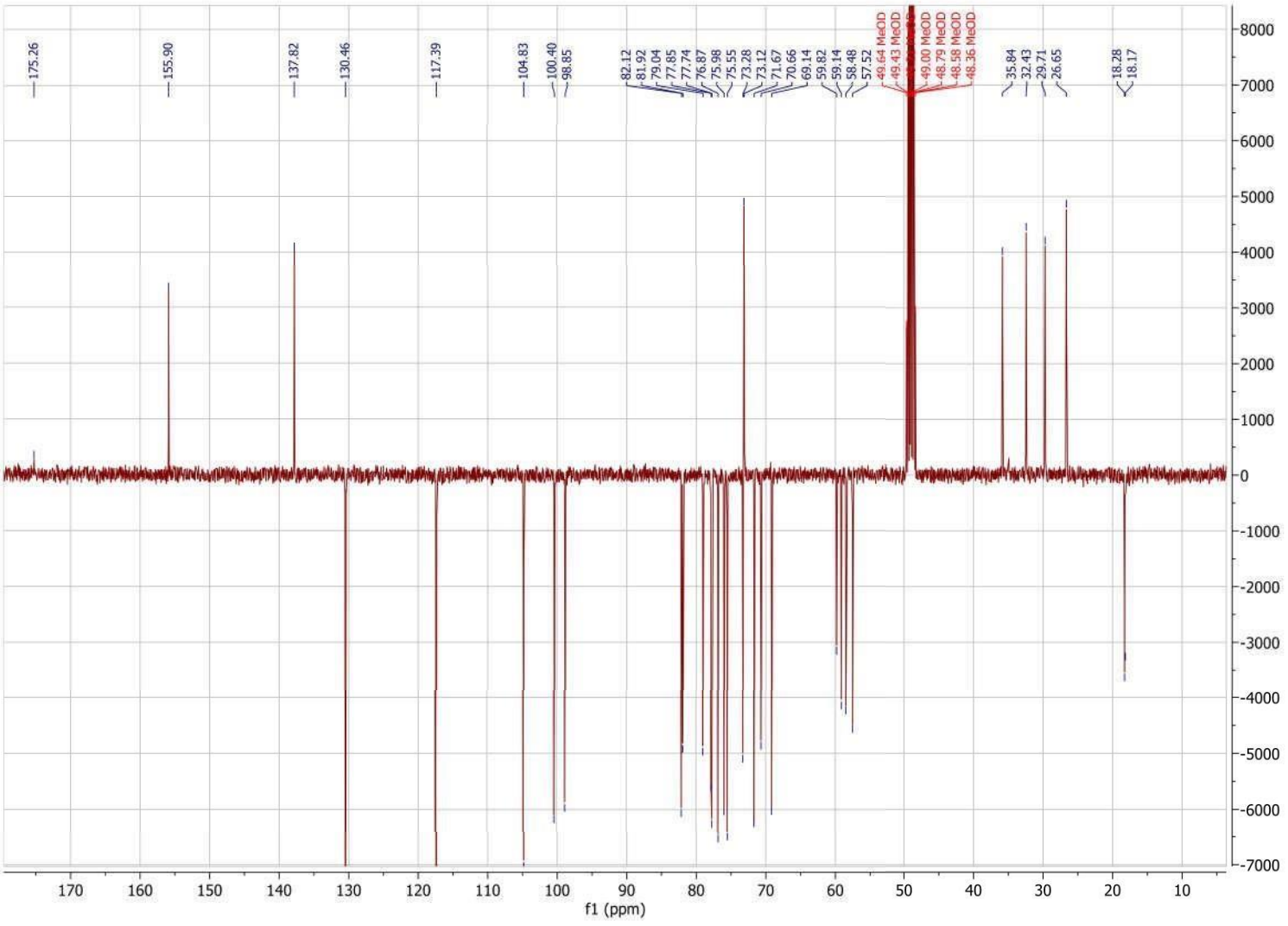
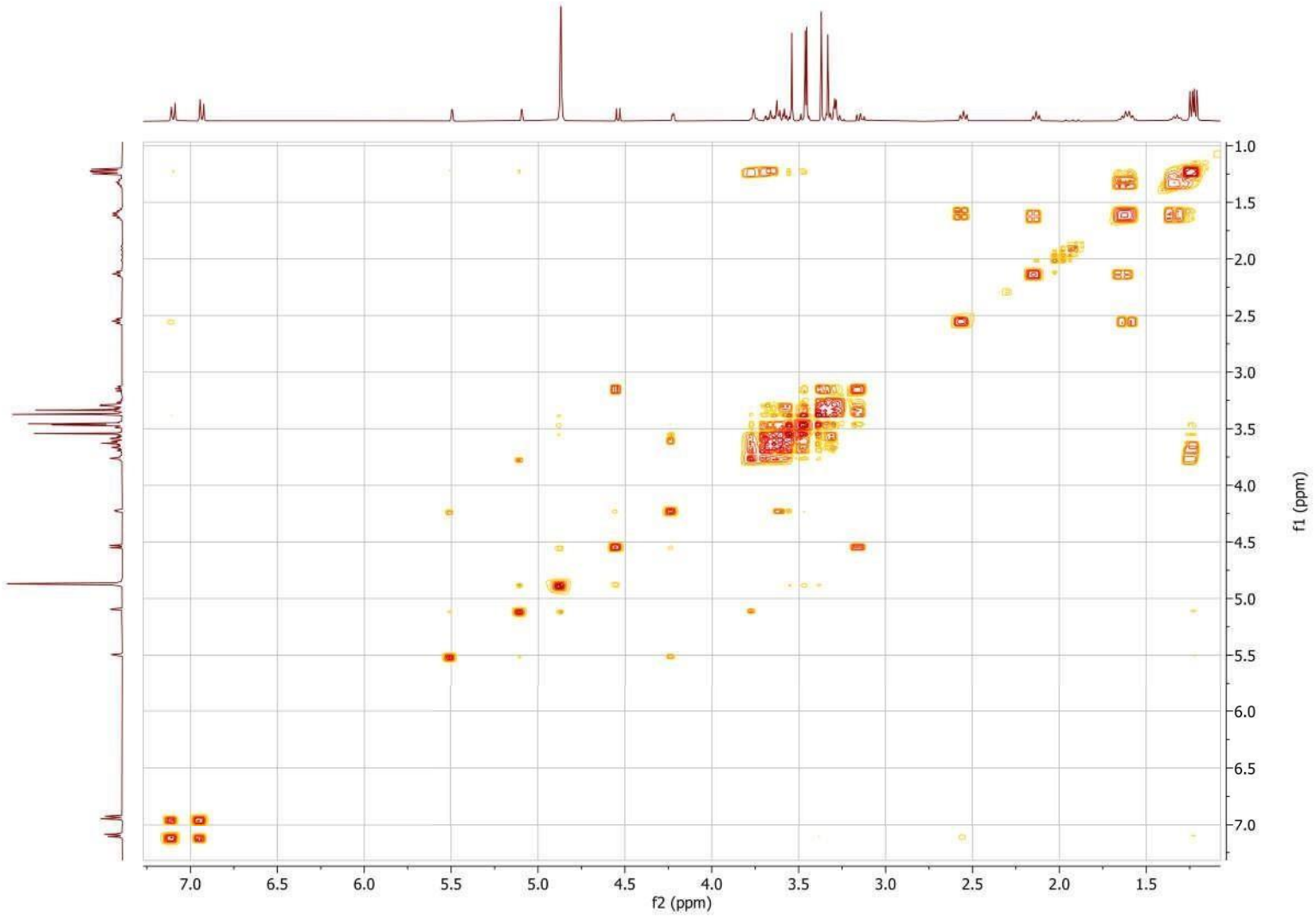
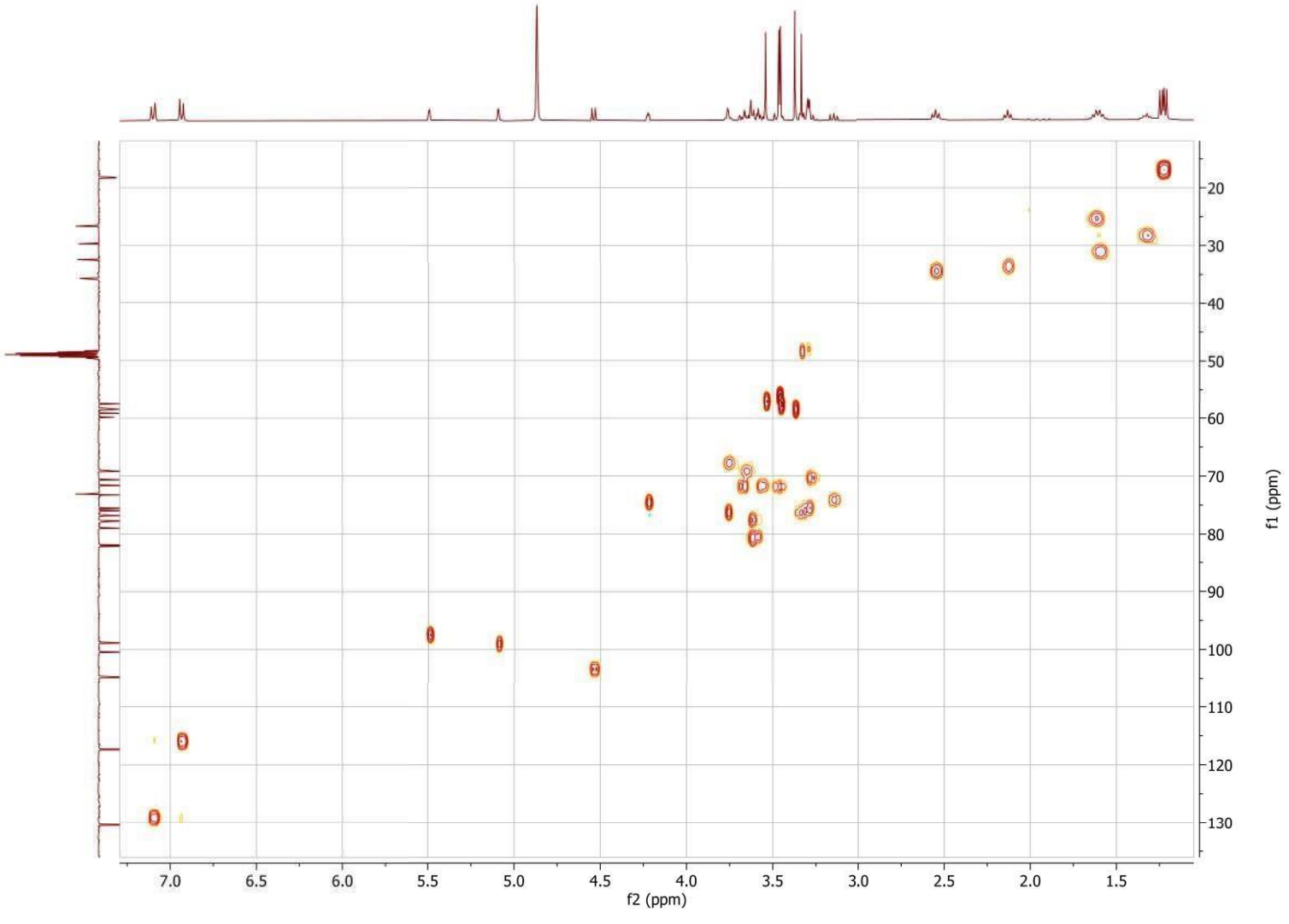

f2 (ppm)
f1 (ppm)

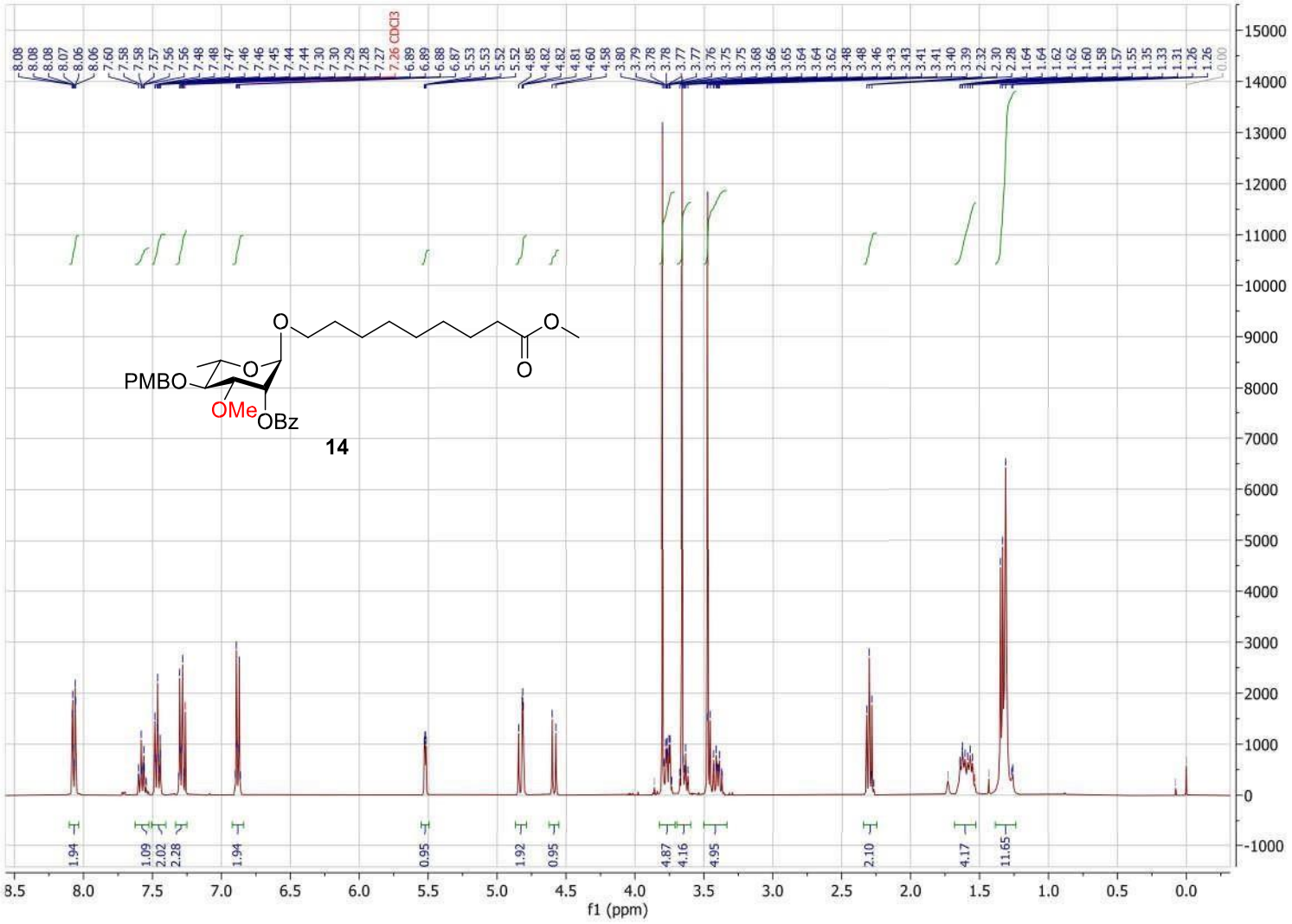

f2 (ppm)
f1 (ppm)

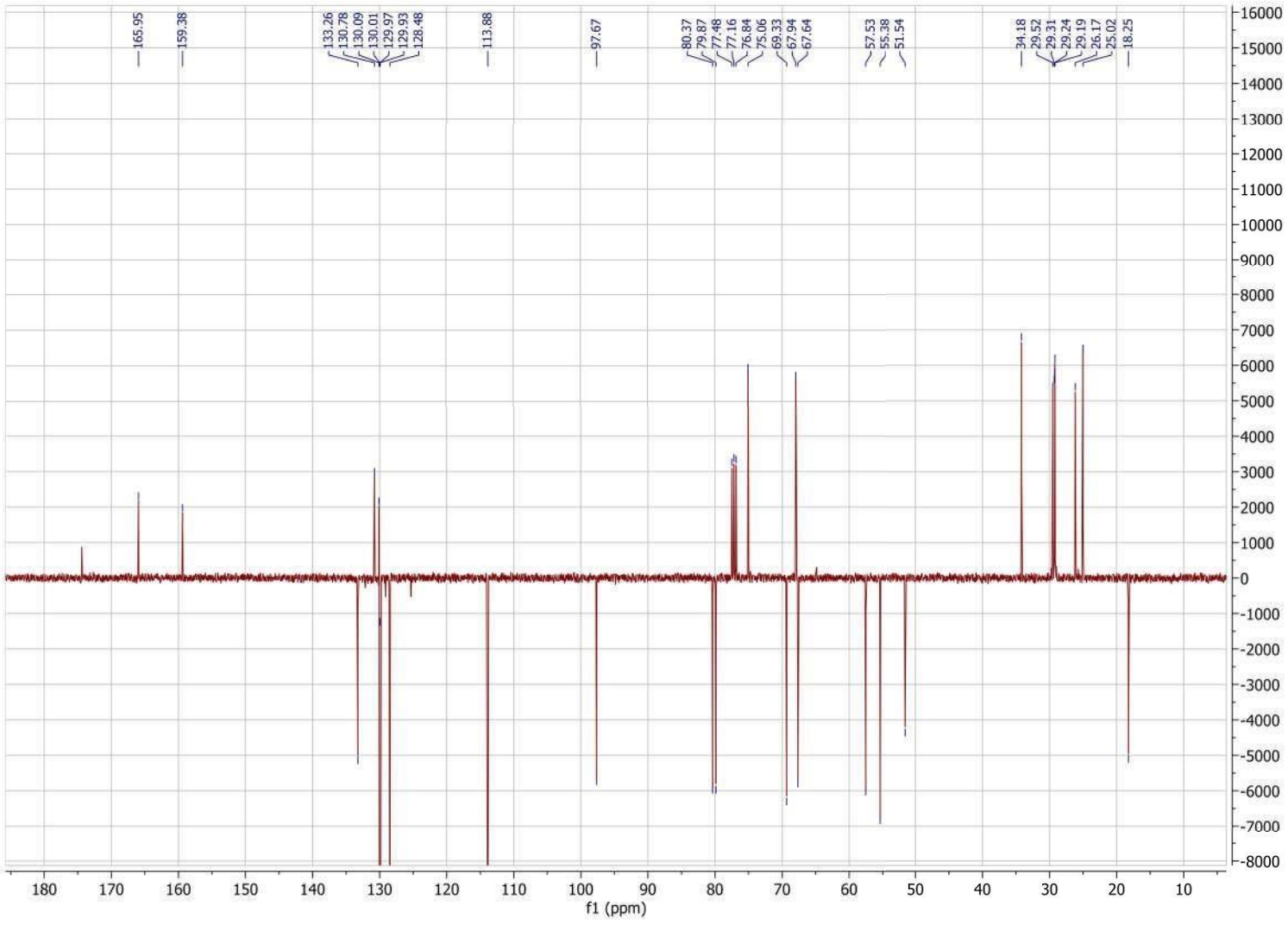

HO
MeO
MeO
HO
HO
OH
MeO
OMe
H
N
NH2
O
12c
f1 (ppm)

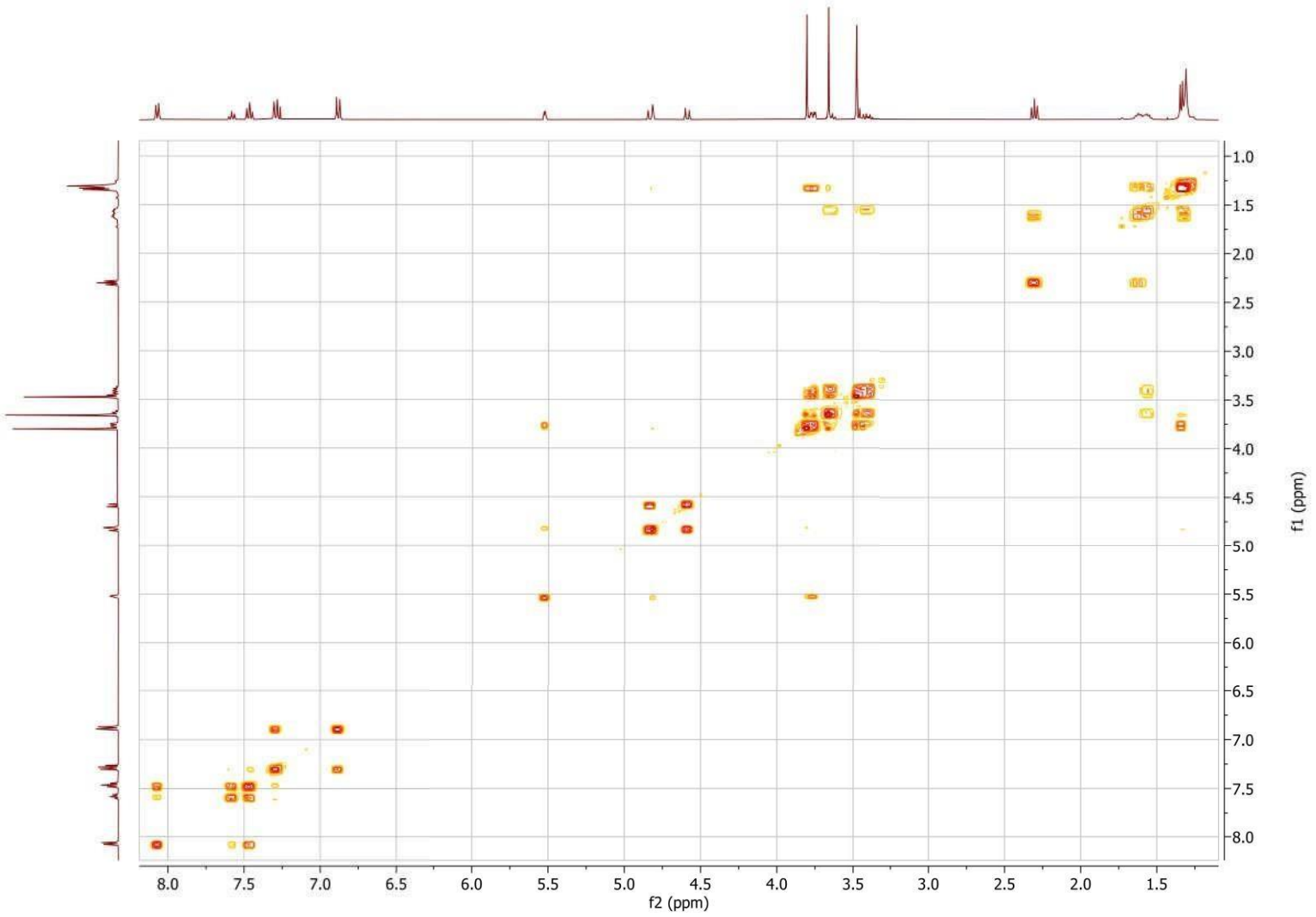

f1 (ppm)

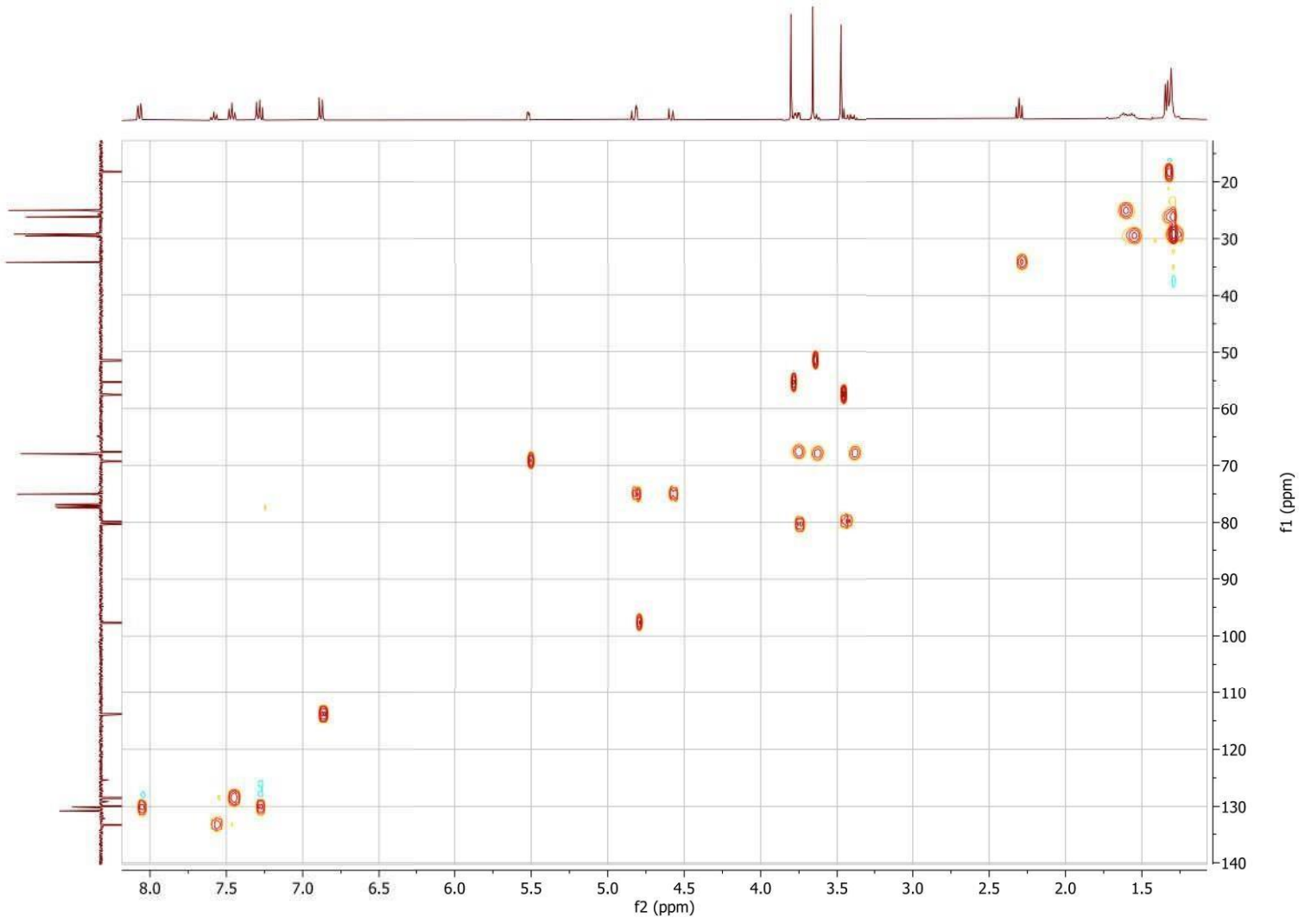

f2 (ppm)
f1 (ppm)

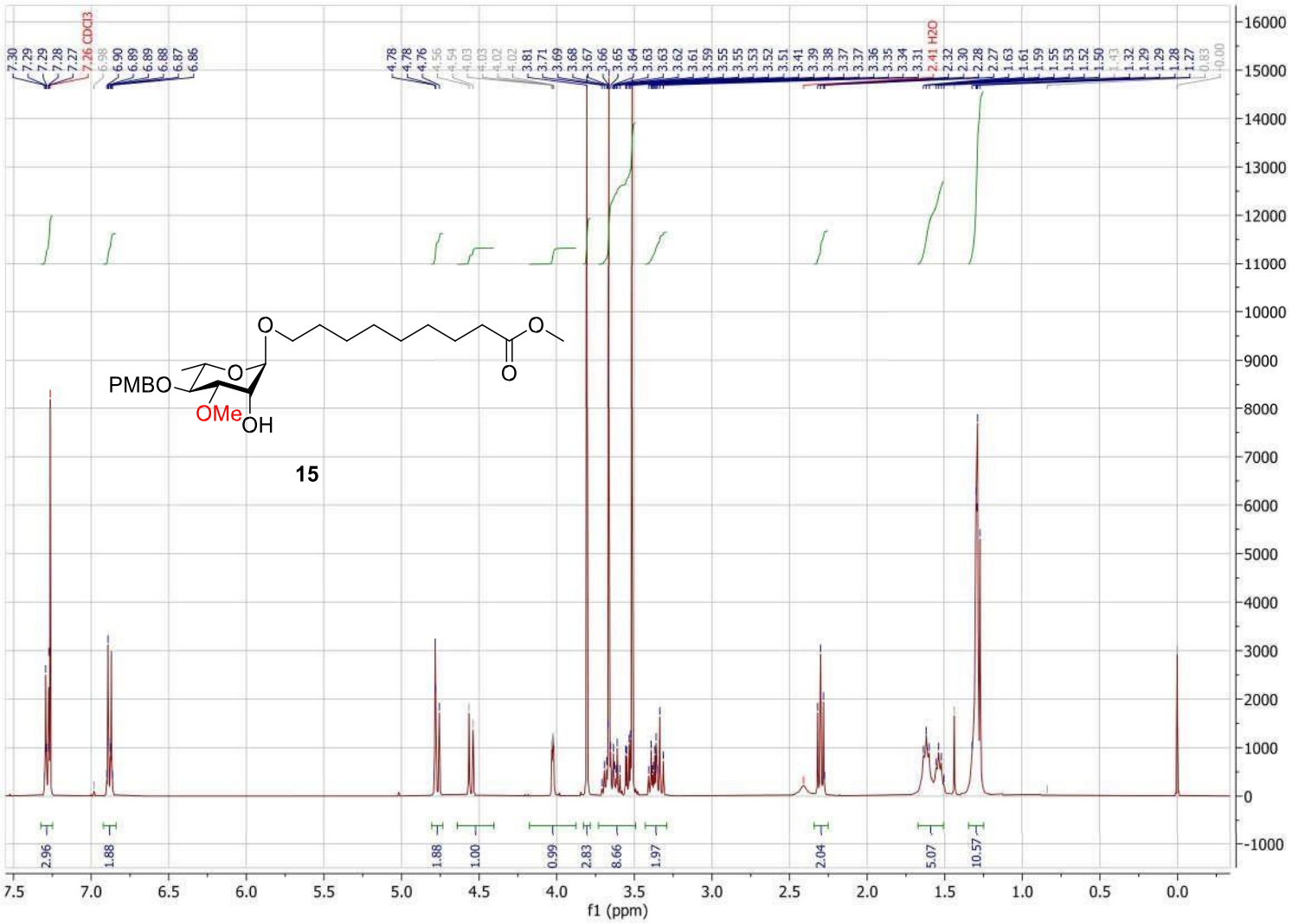

f2 (ppm)
f1 (ppm)

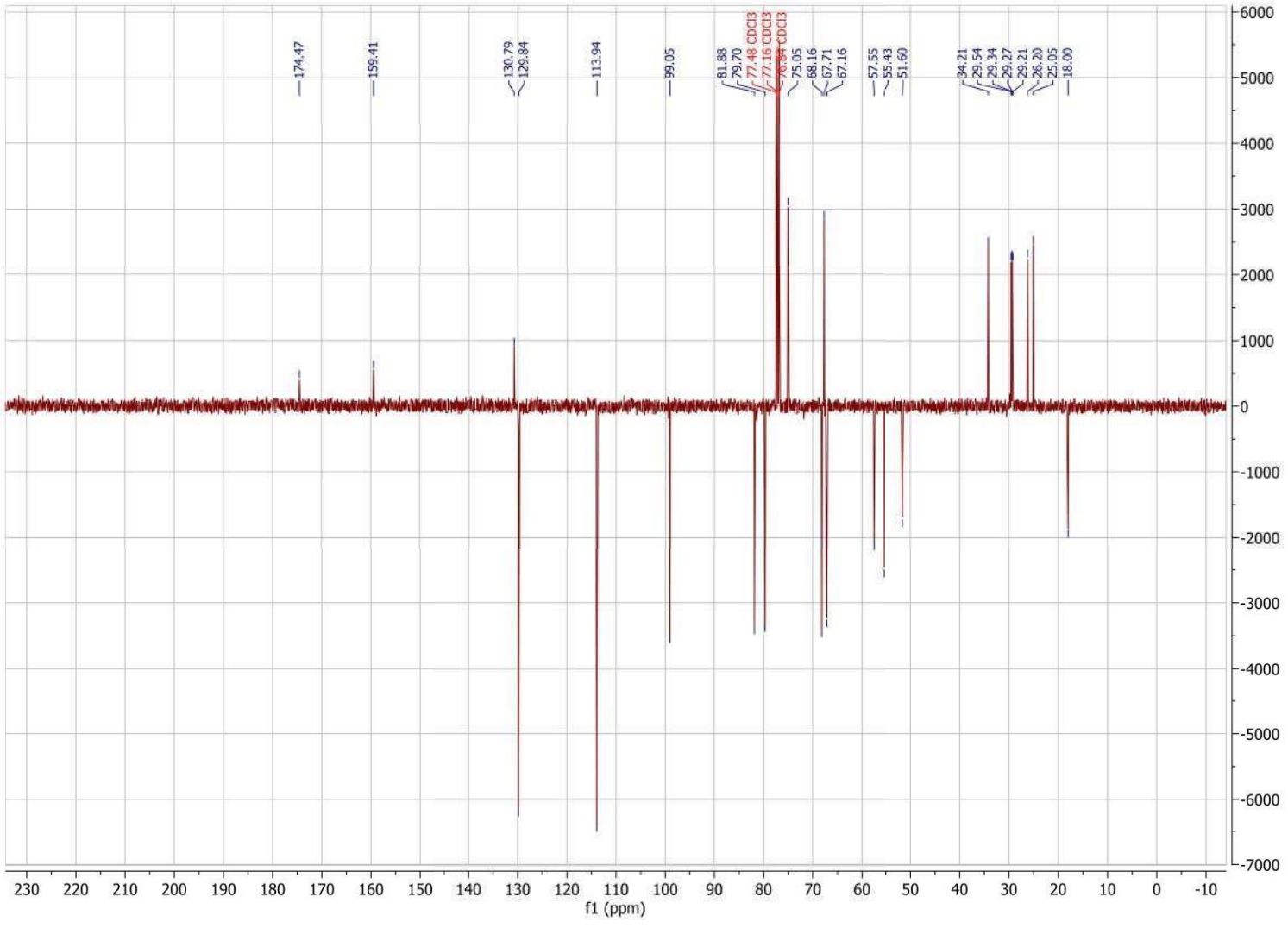

PMBO
OMe
OBz
O
O
O
O
14
f1 (ppm)

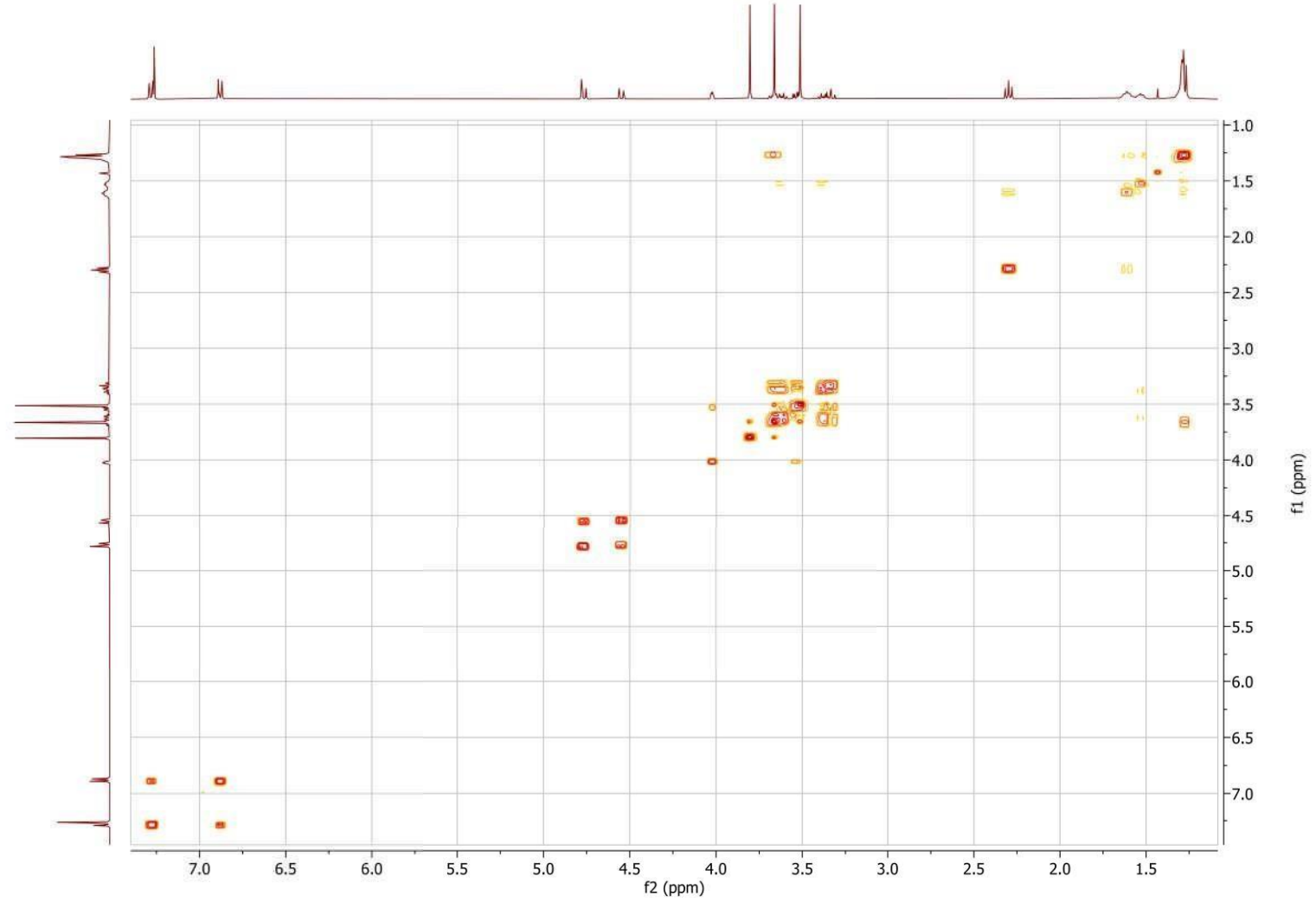

165.95
159.38
133.26
130.78
130.09
130.01
129.97
129.93
128.48
113.88
97.67
80.37
79.87
77.48
77.16
76.84
75.06
69.33
67.94
67.64
57.53
55.38
51.54
34.18
29.52
29.31
29.24
29.19
26.17
25.02
18.25
f1 (ppm)

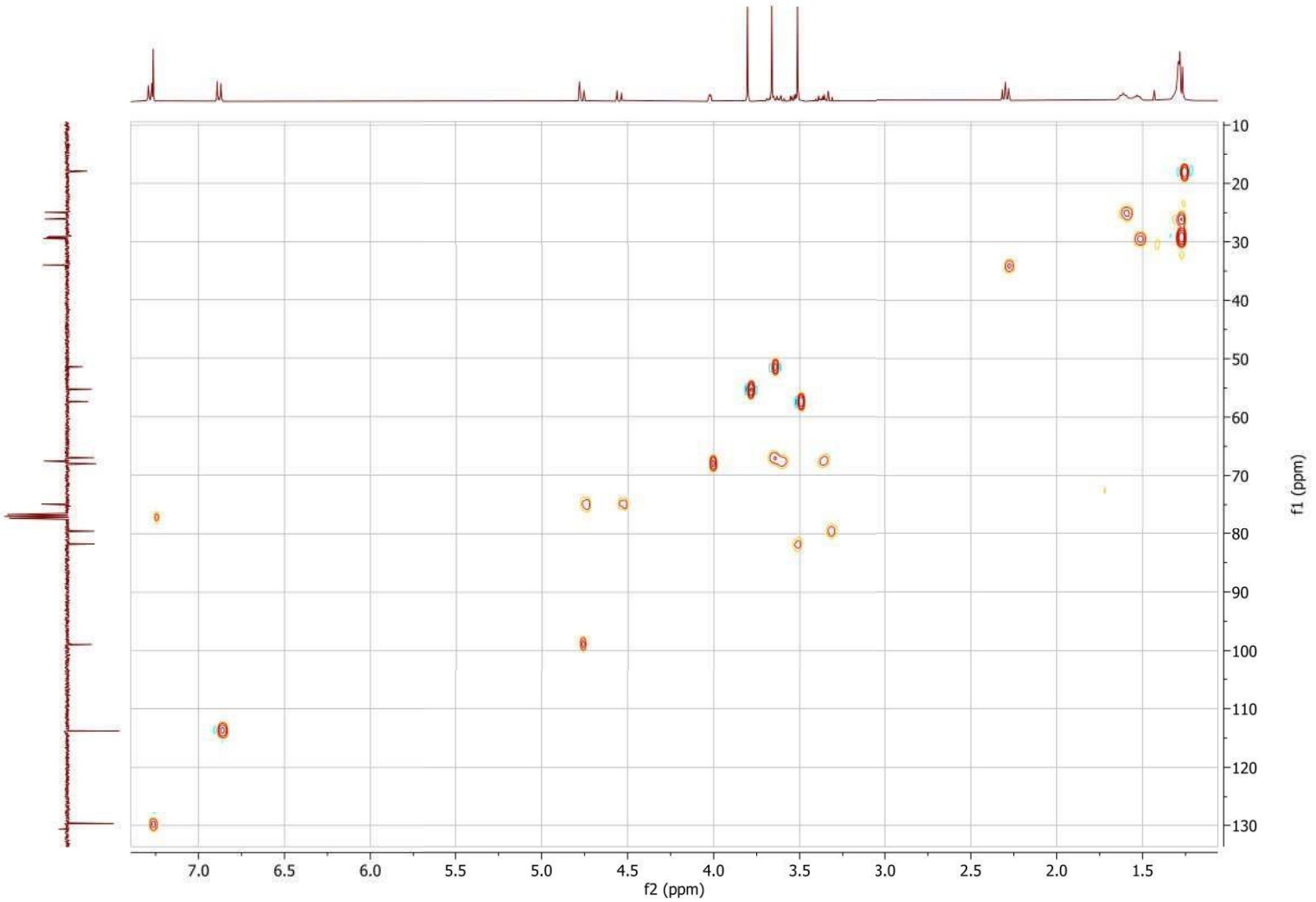

f2 (ppm)
f1 (ppm)

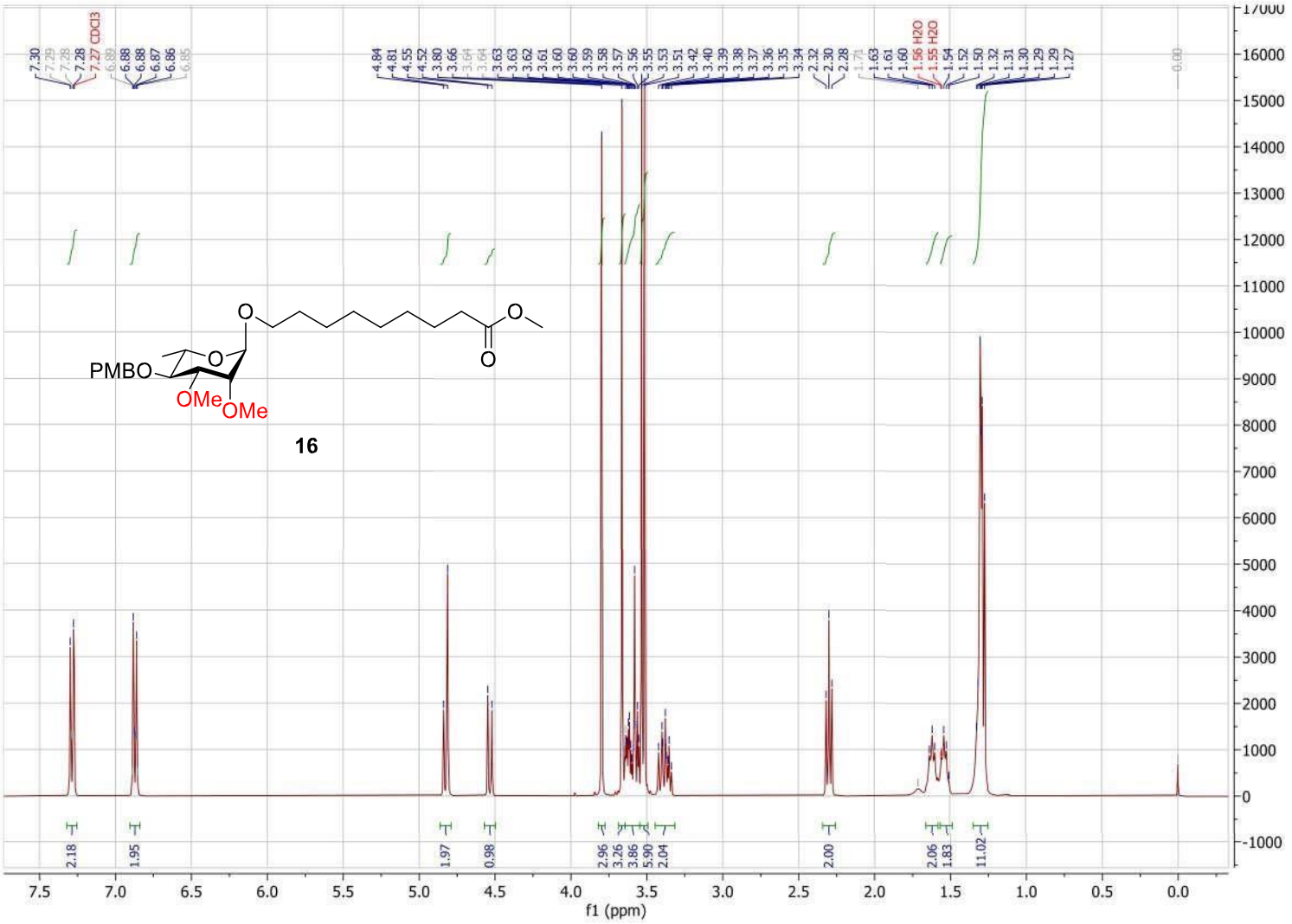

f2 (ppm)
f1 (ppm)

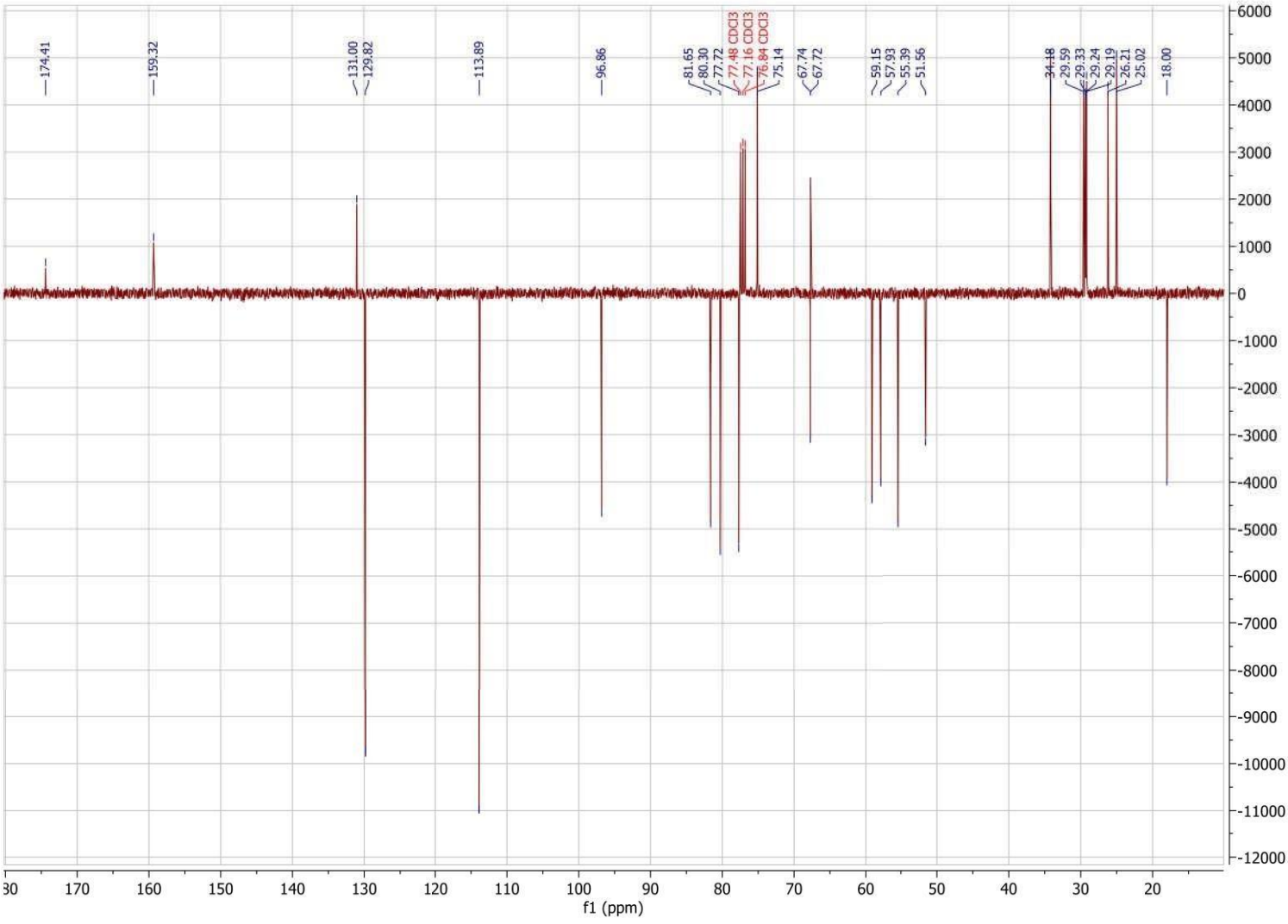

PMBO
OMe
OH
O
O
O
O
15
f1 (ppm)

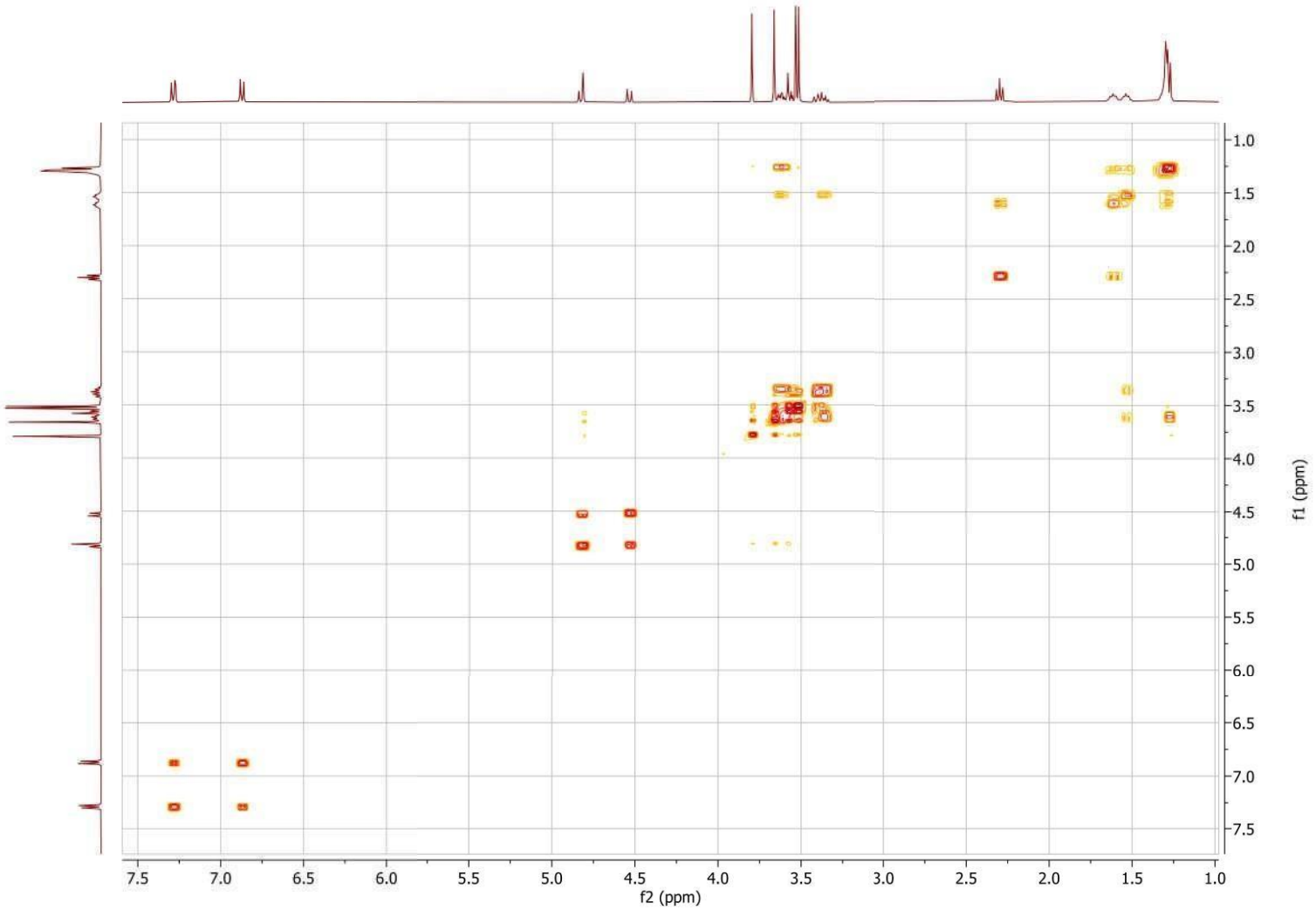

174.47
159.41
130.79
129.84
113.94
99.05
81.88
79.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.05
68.16
67.71
67.16
57.55
55.43
51.60
34.21
29.54
29.34
29.27
29.21
26.20
25.05
18.00
f1 (ppm)

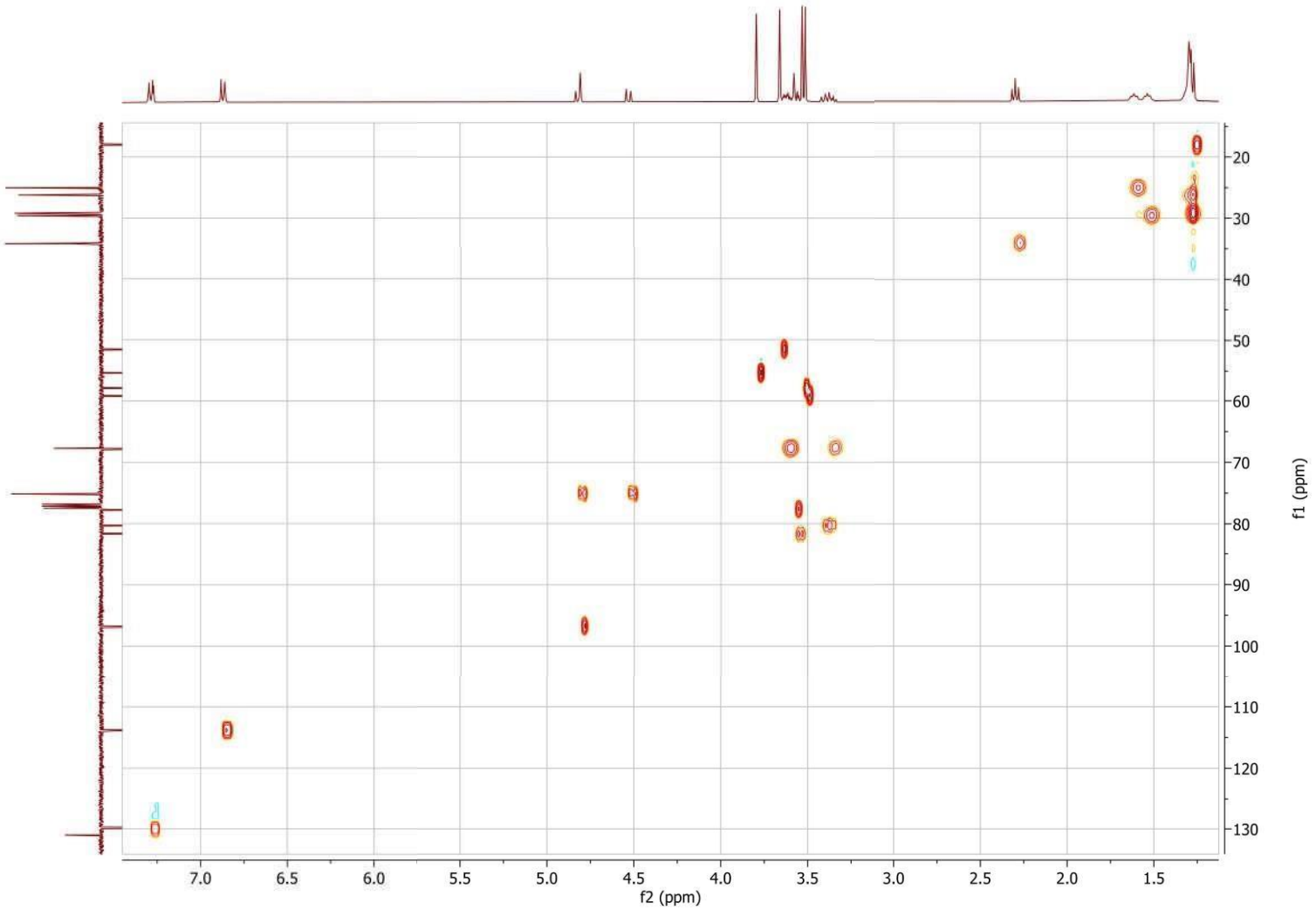

f2 (ppm)
f1 (ppm)

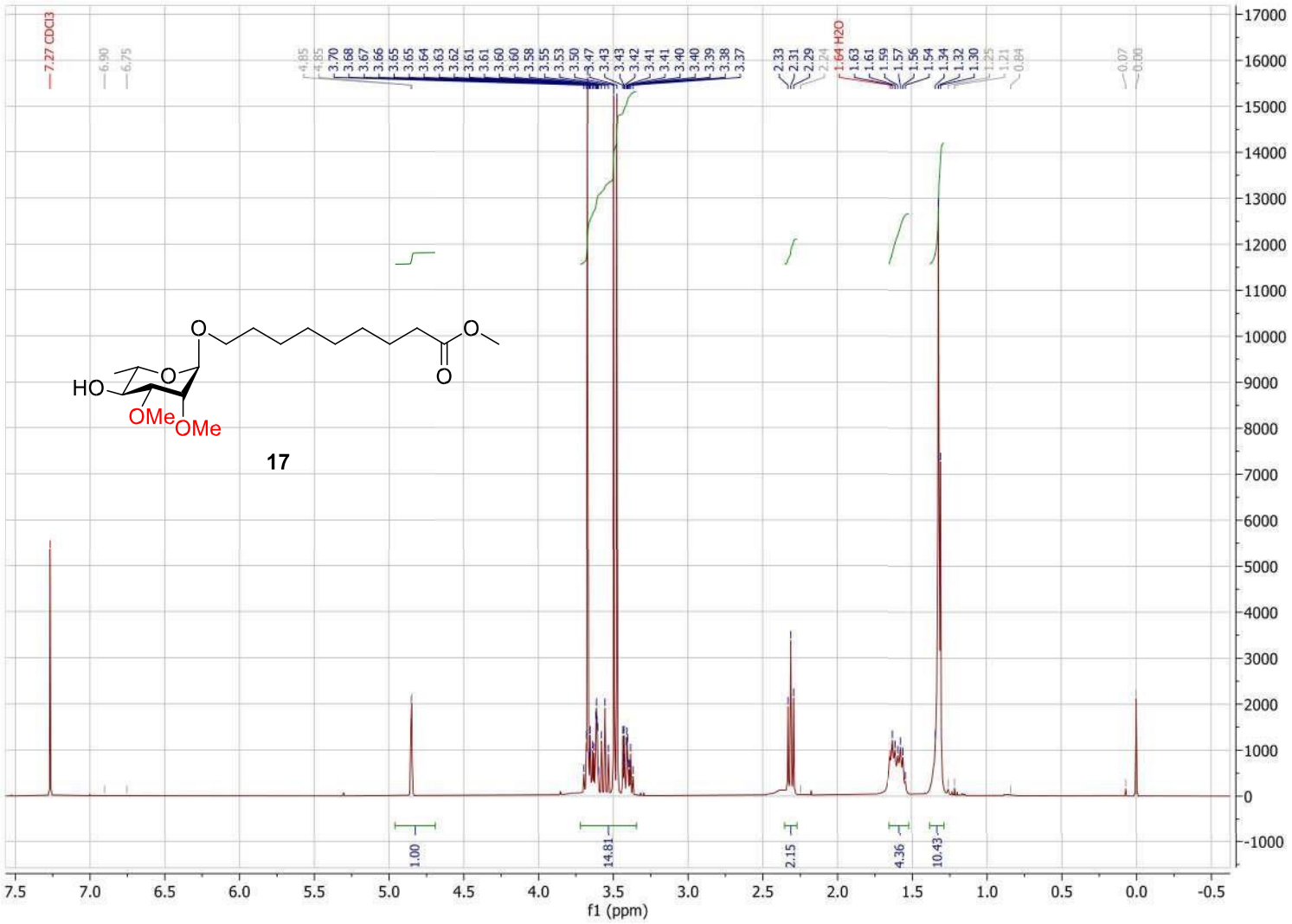

f2 (ppm)
f1 (ppm)


PMBO
OMe
OMe
16
f1 (ppm)


f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


7.27 CDCl3
6.90
6.75
4.85
3.70
3.68
3.67
3.66
3.65
3.65
3.64
3.63
3.62
3.61
3.61
3.60
3.60
3.58
3.55
3.53
3.50
3.47
3.43
3.43
3.42
3.41
3.41
3.40
3.40
3.39
3.38
3.37
2.33
2.31
2.29
2.24
1.64 H2O
1.63
1.61
1.59
1.57
1.56
1.54
1.34
1.32
1.30
1.25
1.21
0.84
0.07
0.00
HO
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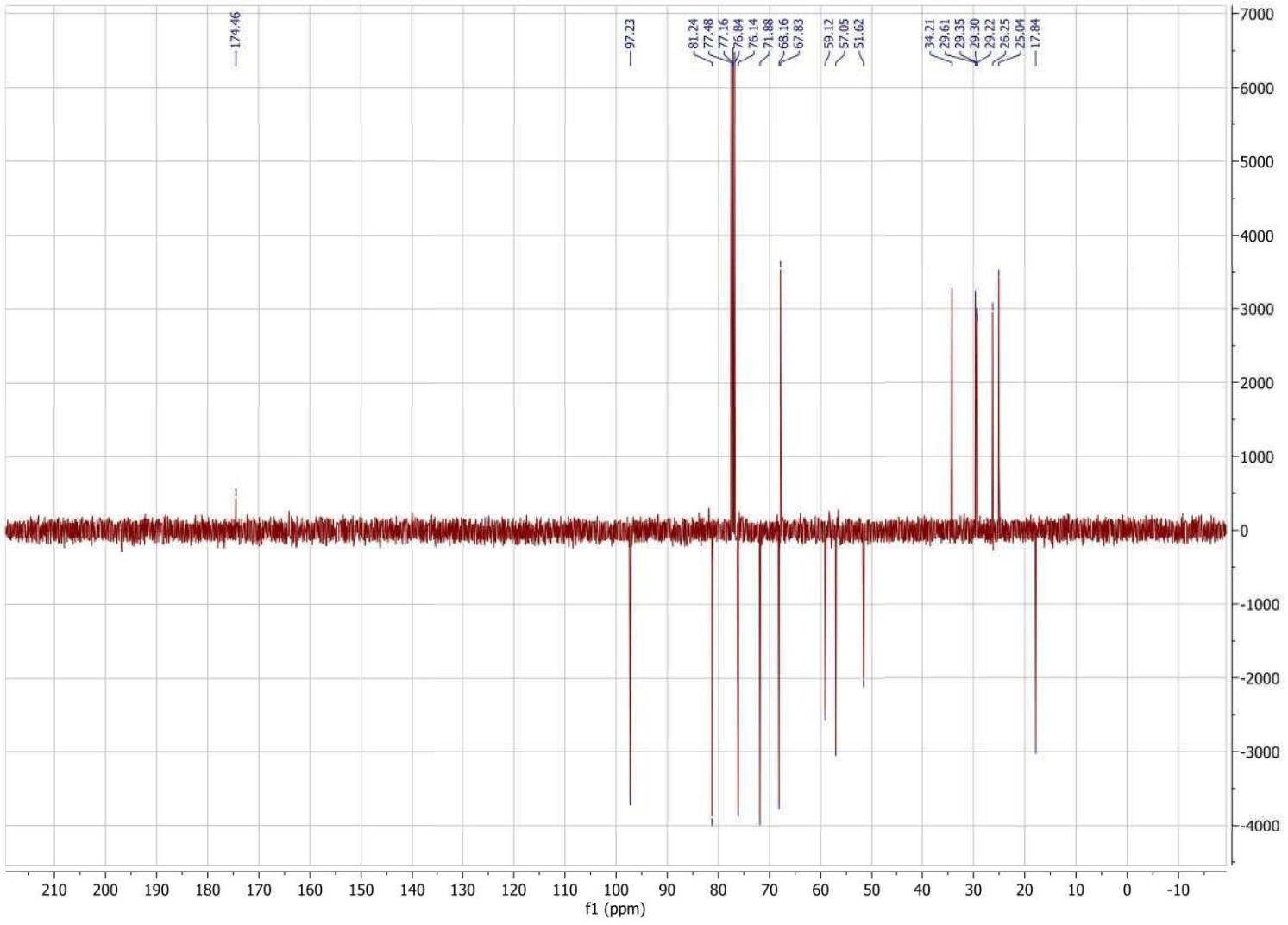
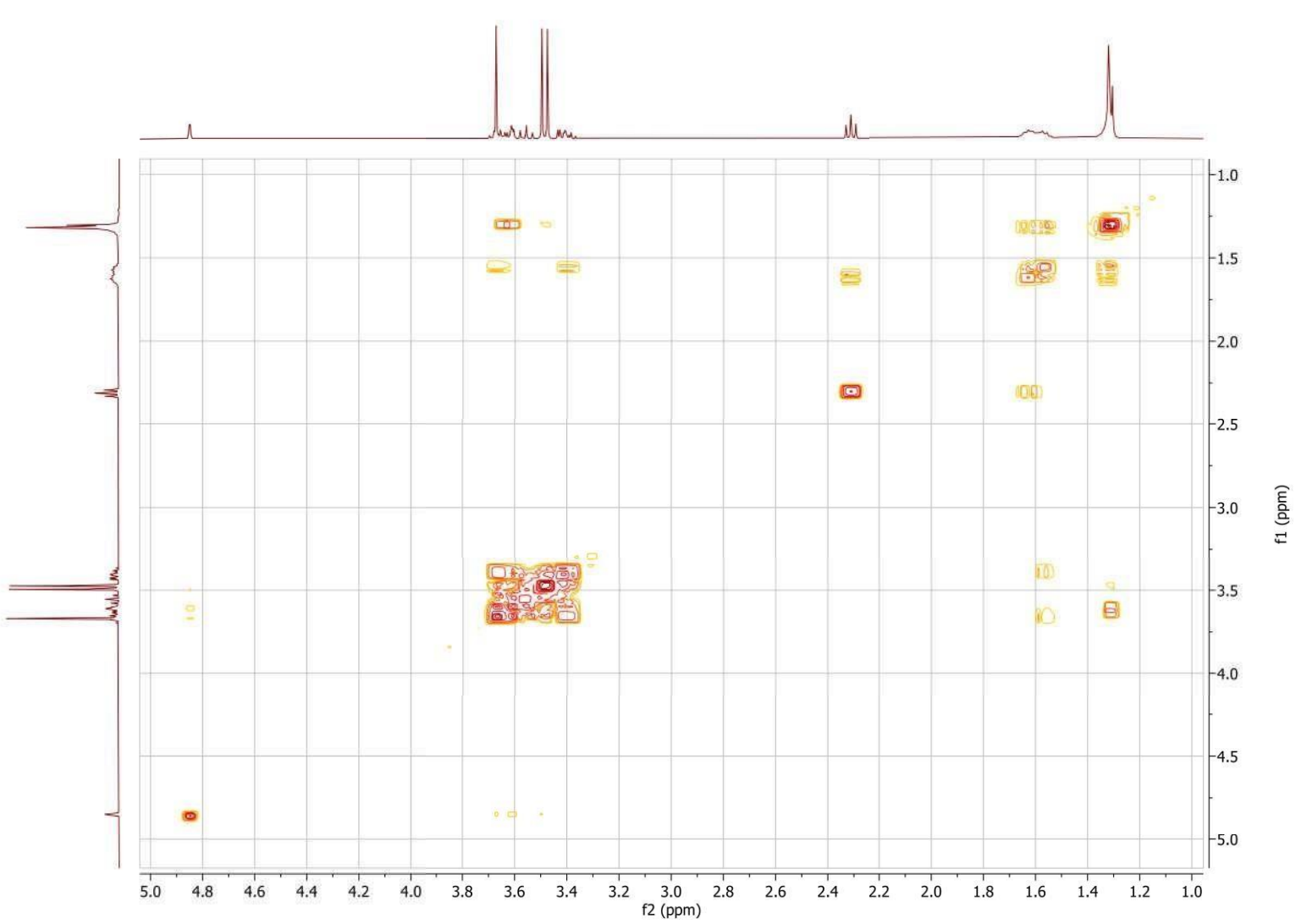
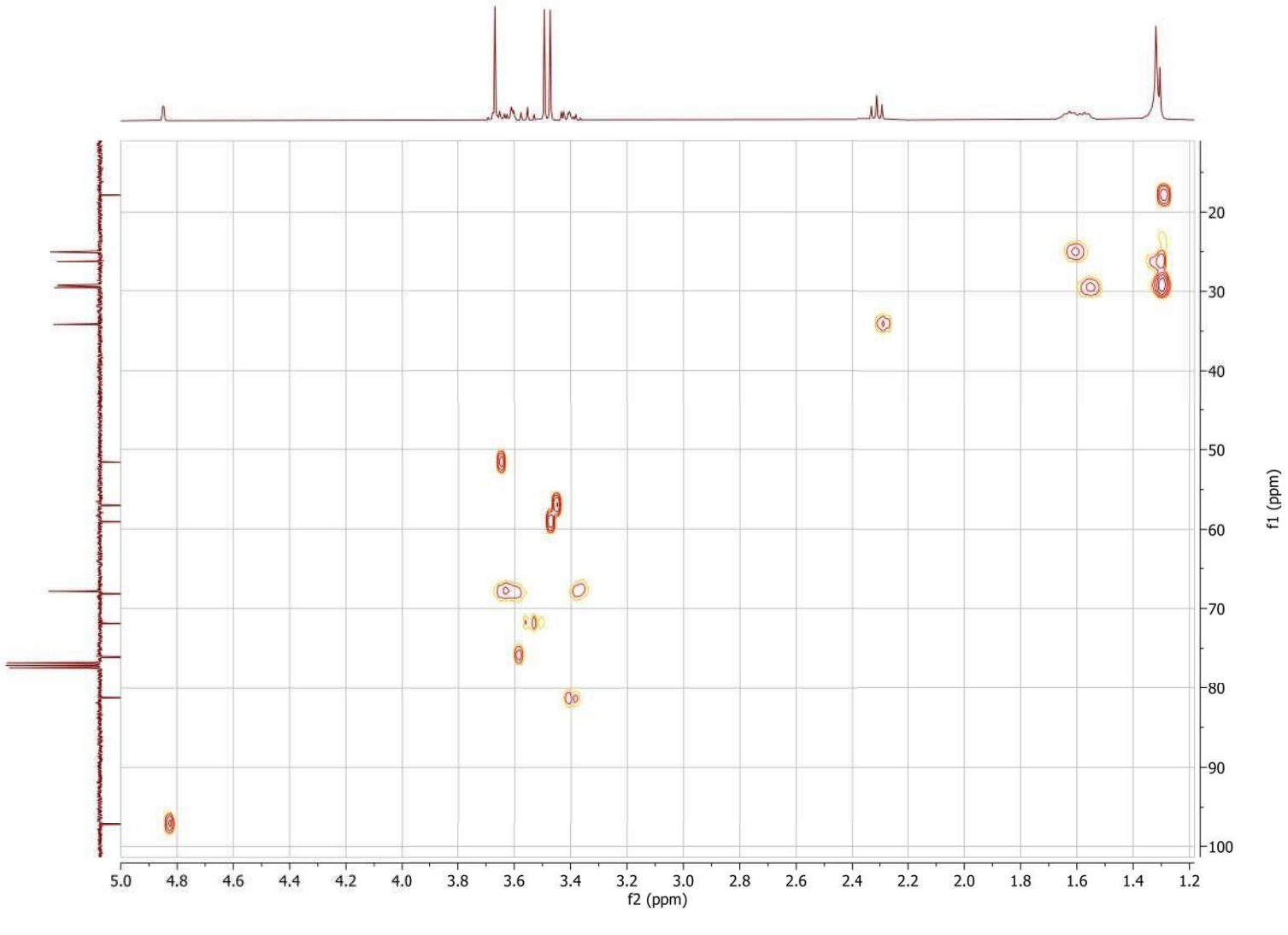
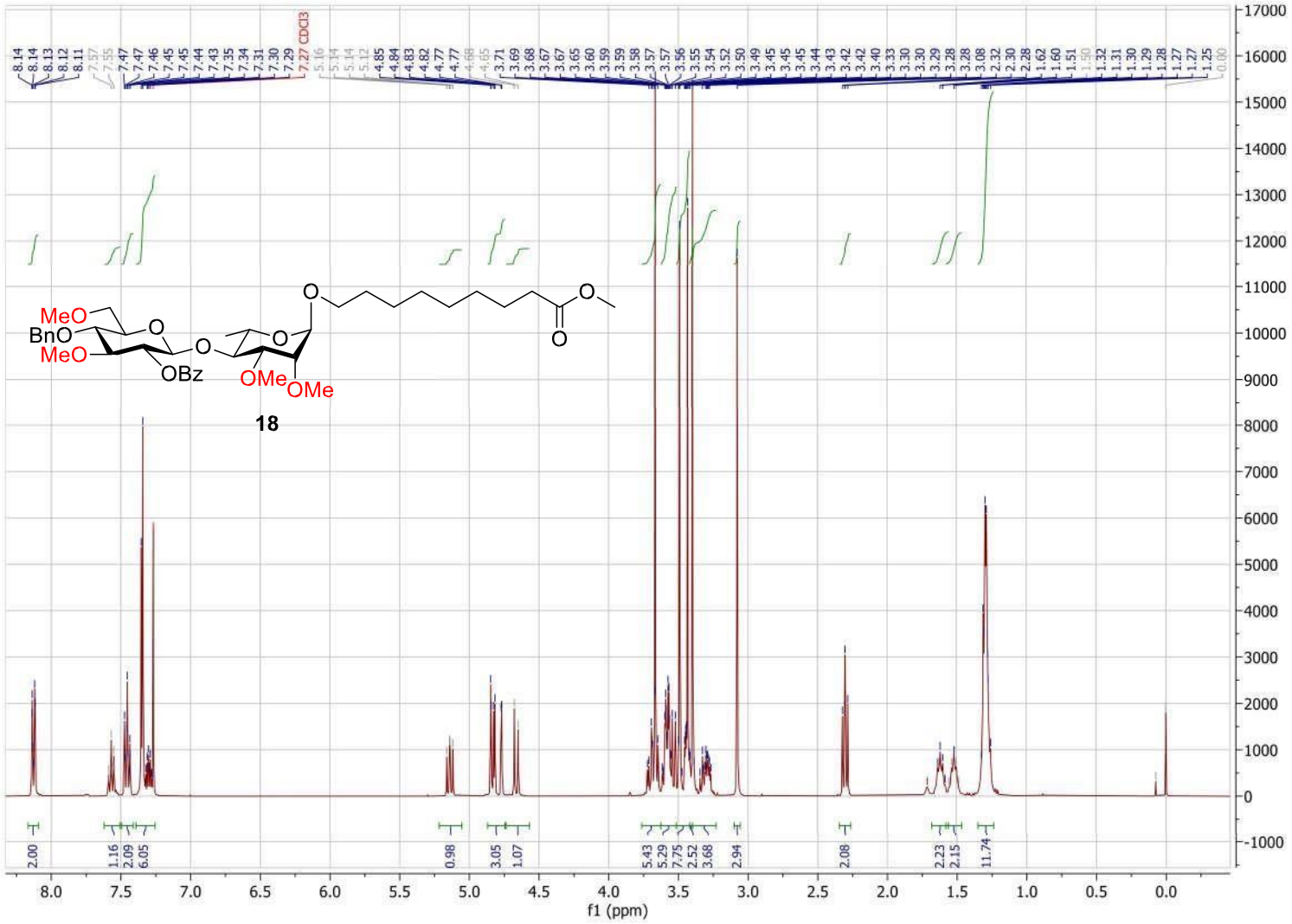
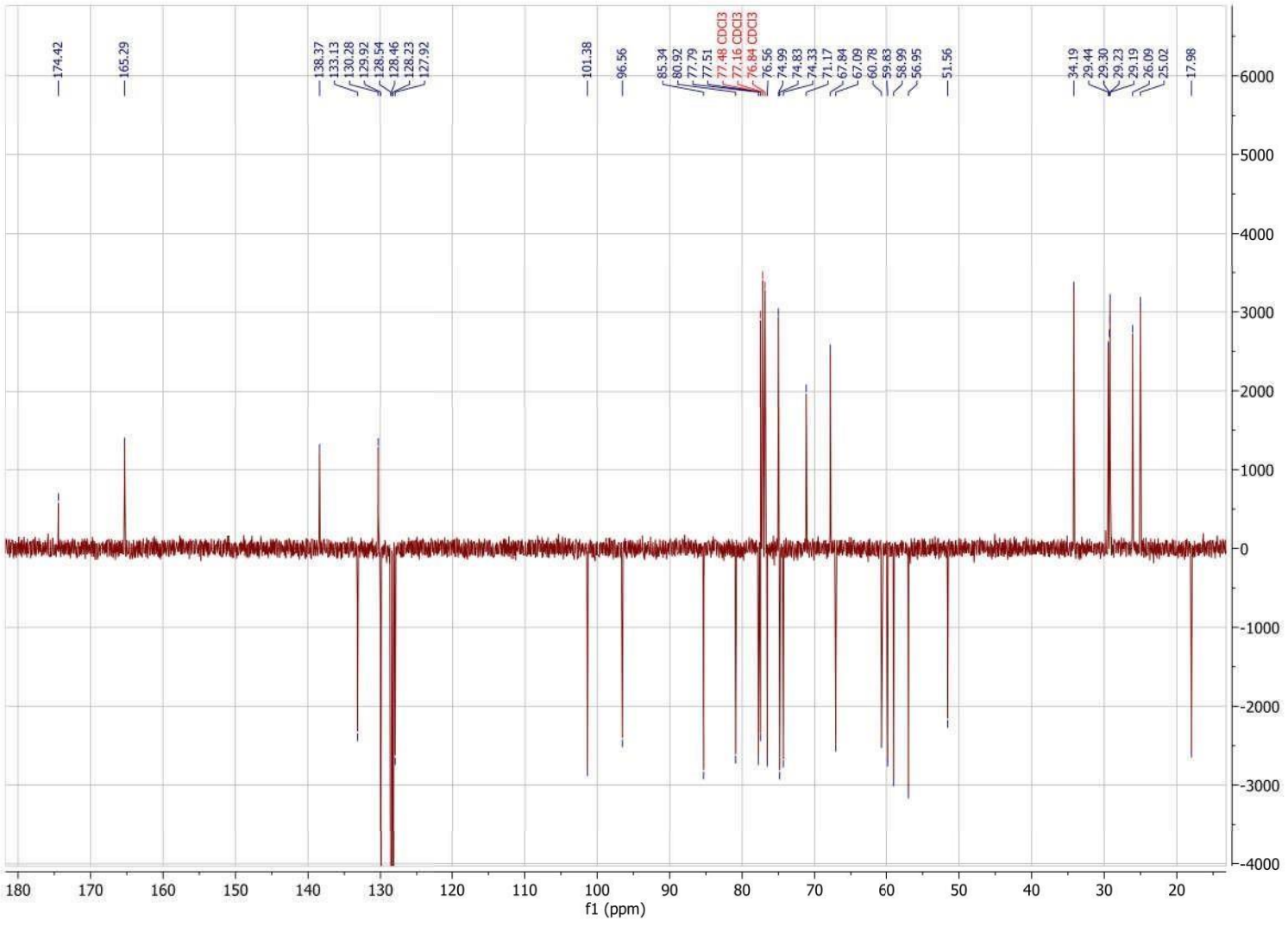
O
O
O
OMe
OMe
17
1.00
14.81
2.15
4.36
10.43
f1 (ppm)

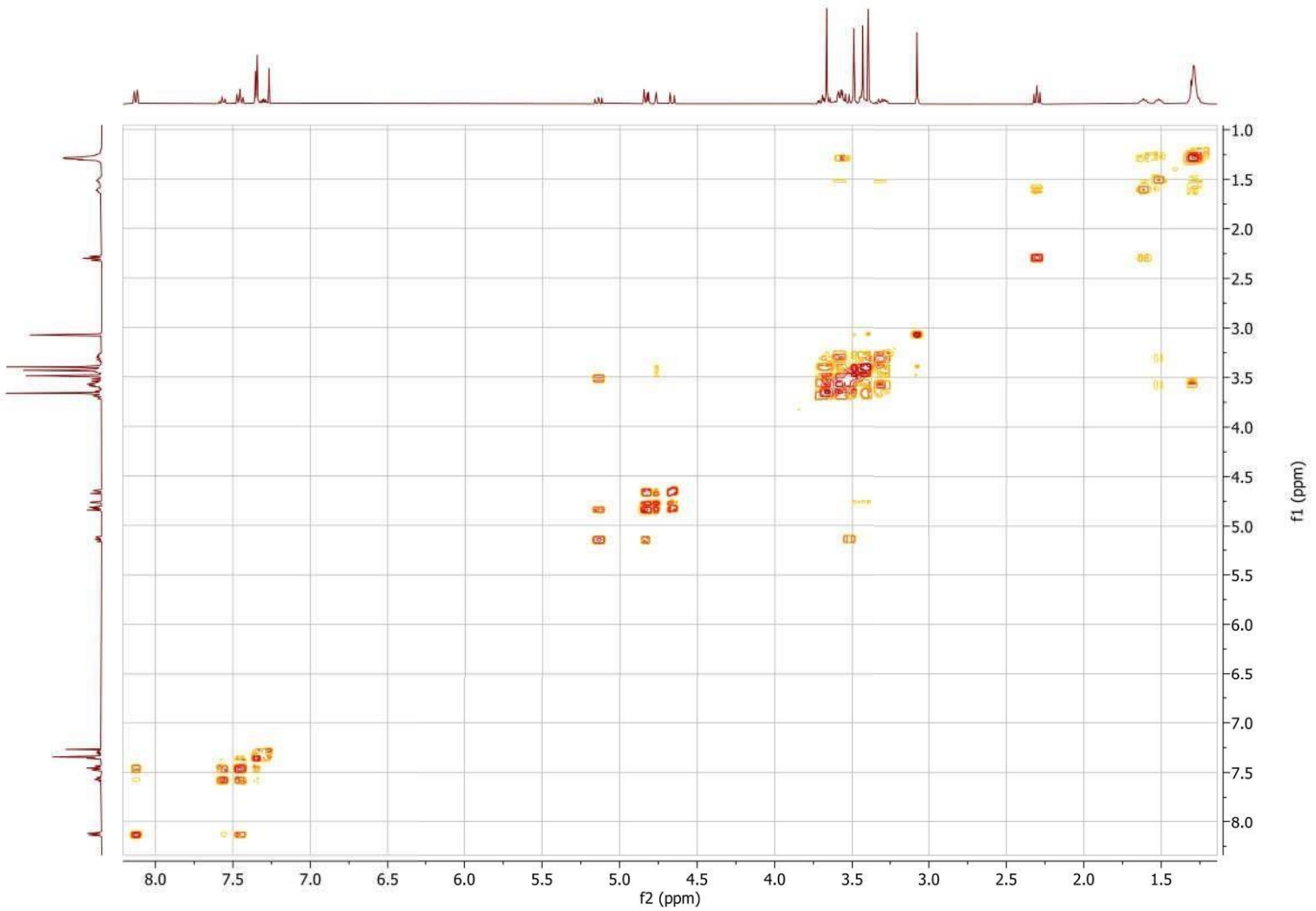

174.46
97.23
81.24
77.48
77.16
76.84
76.14
71.88
68.16
67.83
59.12
57.05
51.62
34.21
29.61
29.35
29.30
29.22
26.25
25.04
17.84
f1 (ppm)

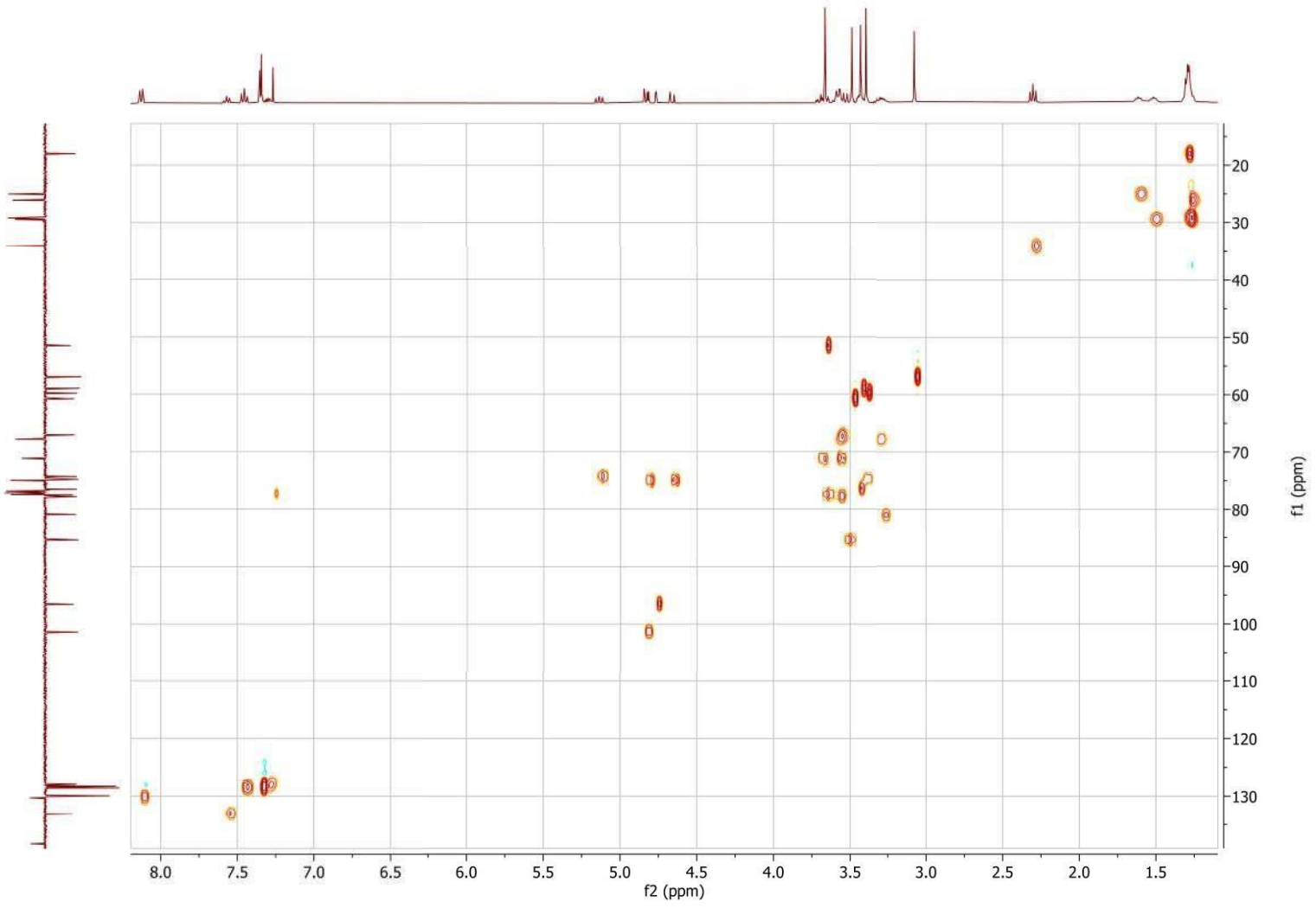

f2 (ppm)
f1 (ppm)

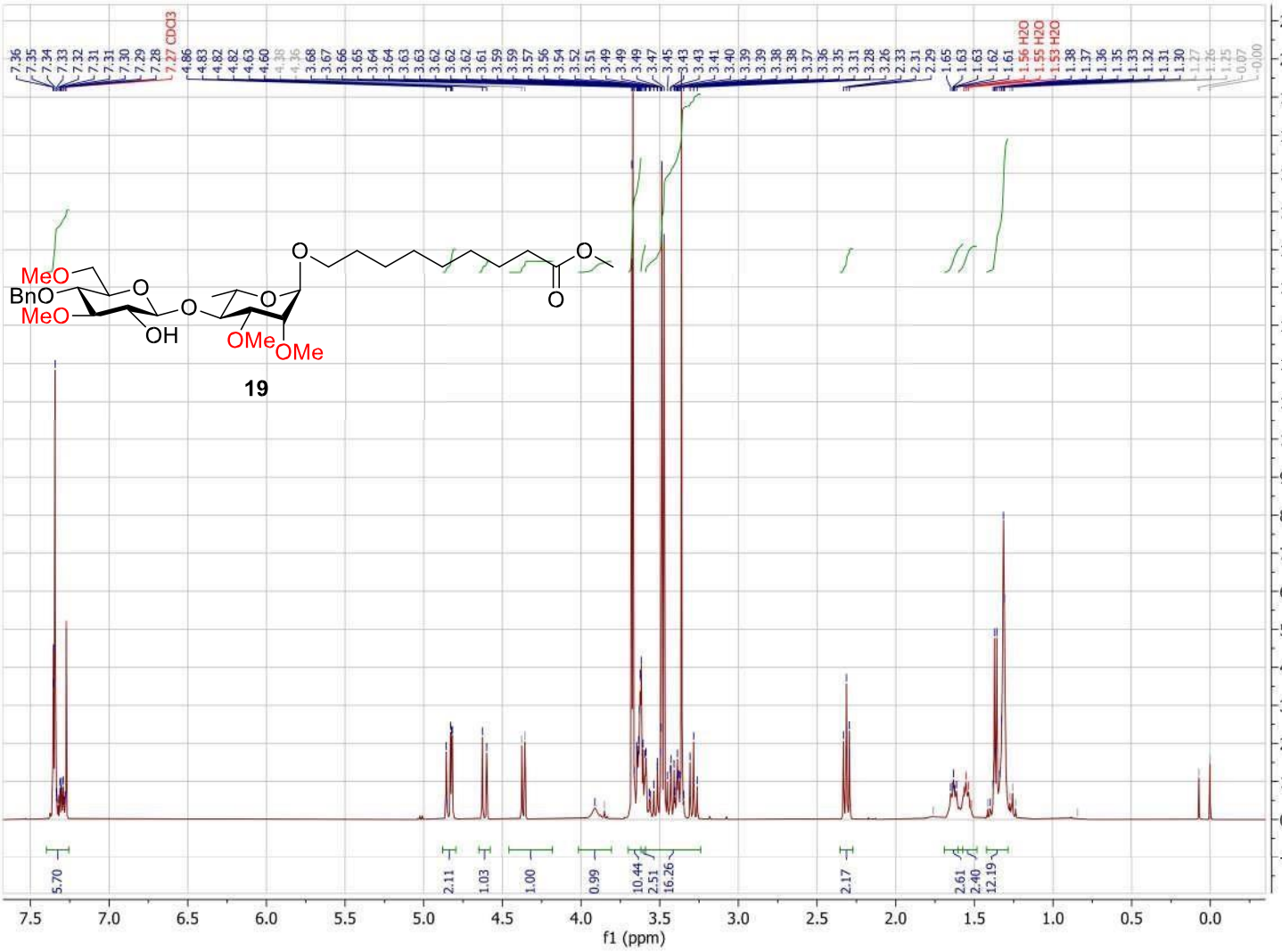

f2 (ppm)
f1 (ppm)

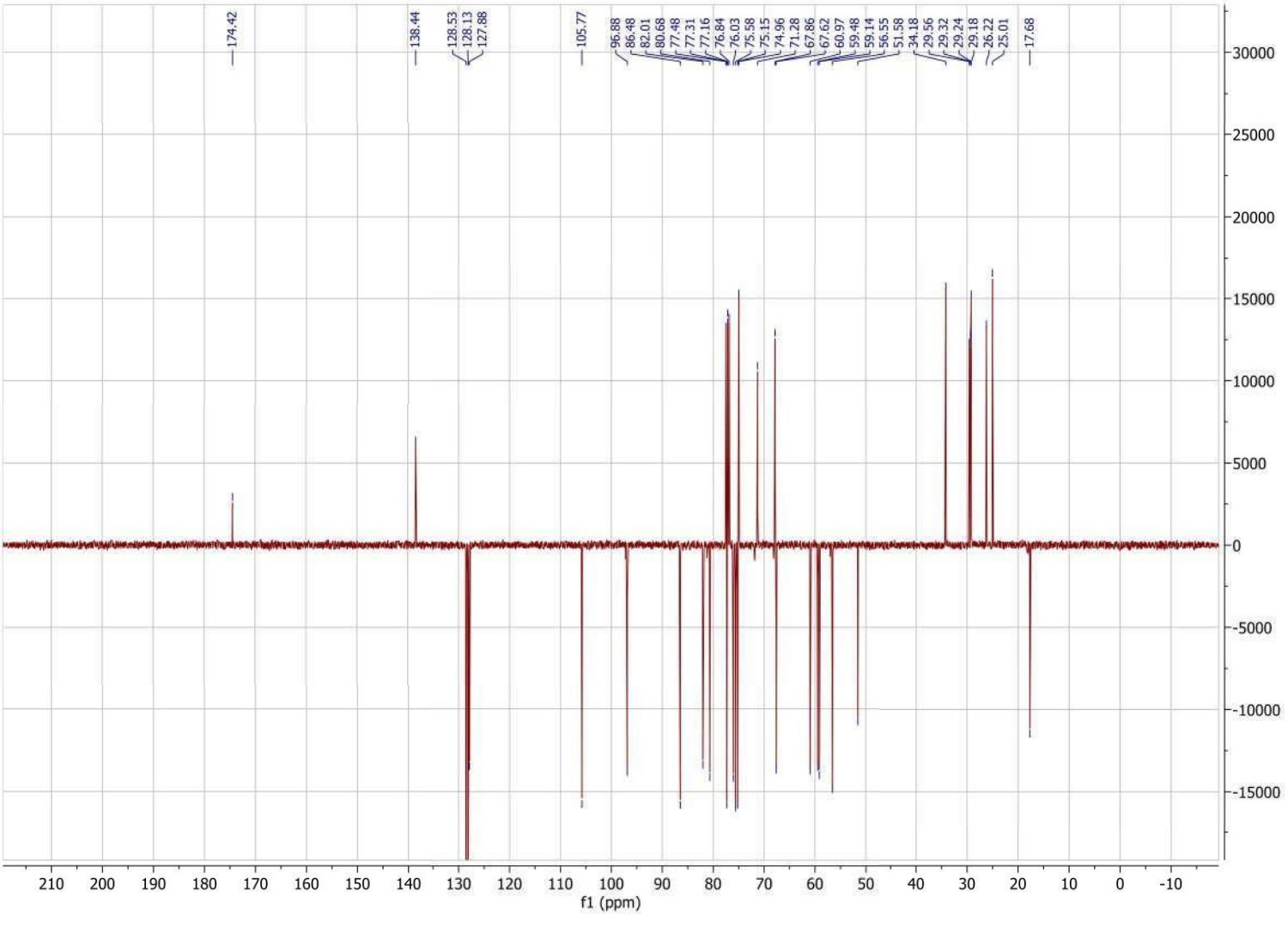

MeO
BnO
MeO
OBz
OMe
OMe
O
O
O
O
O
O
18
f1 (ppm)

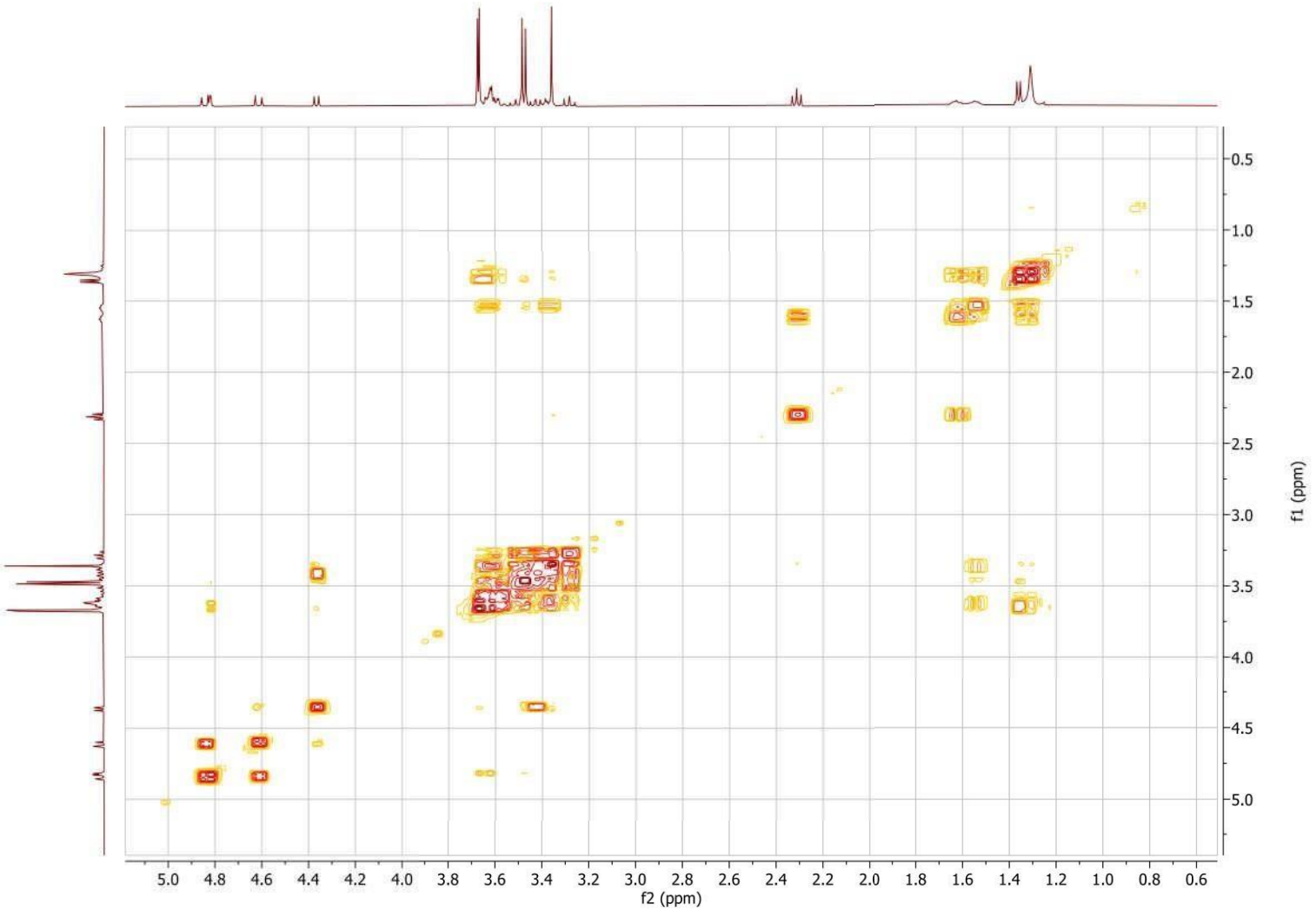

f1 (ppm)

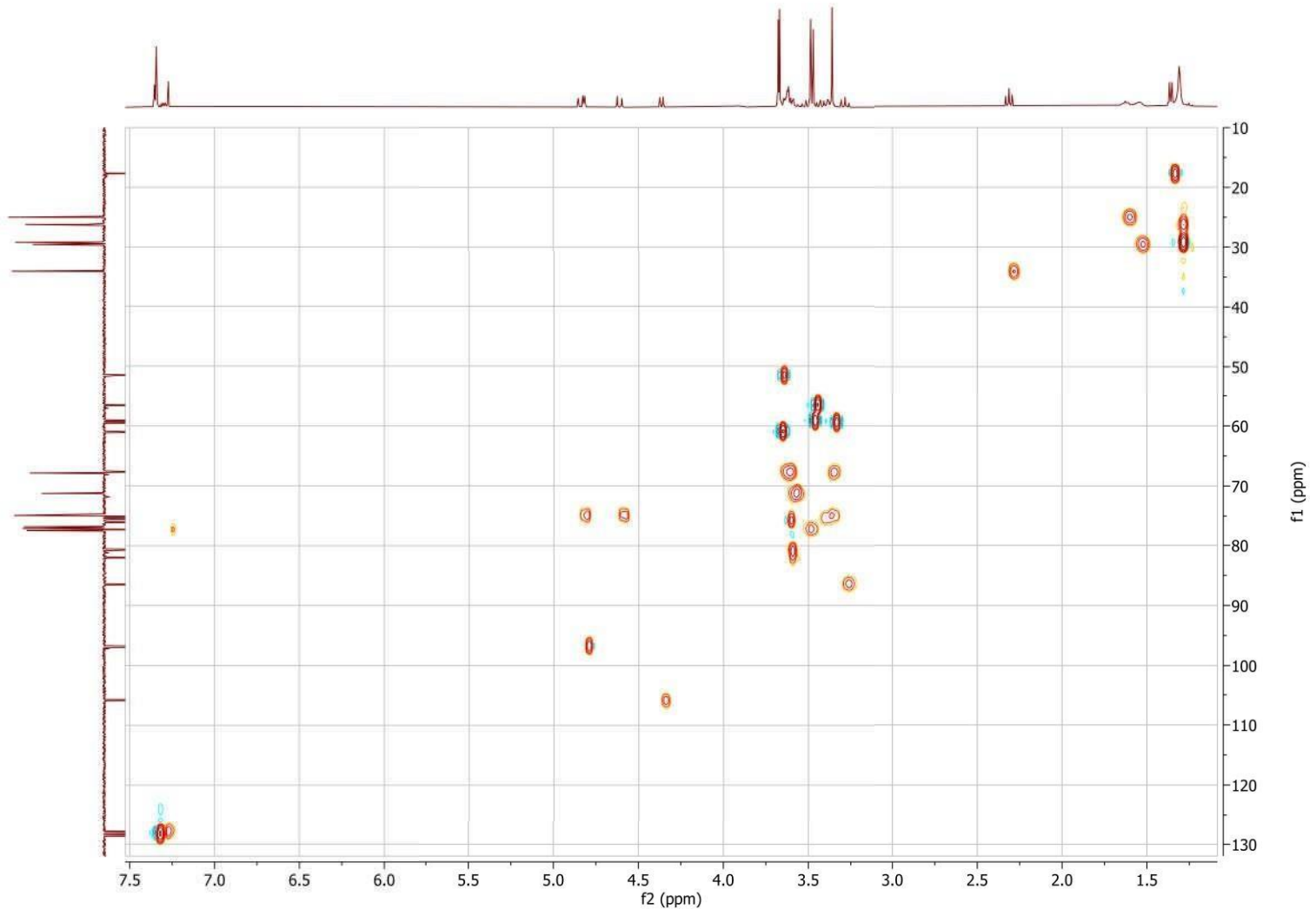

f2 (ppm)
f1 (ppm)

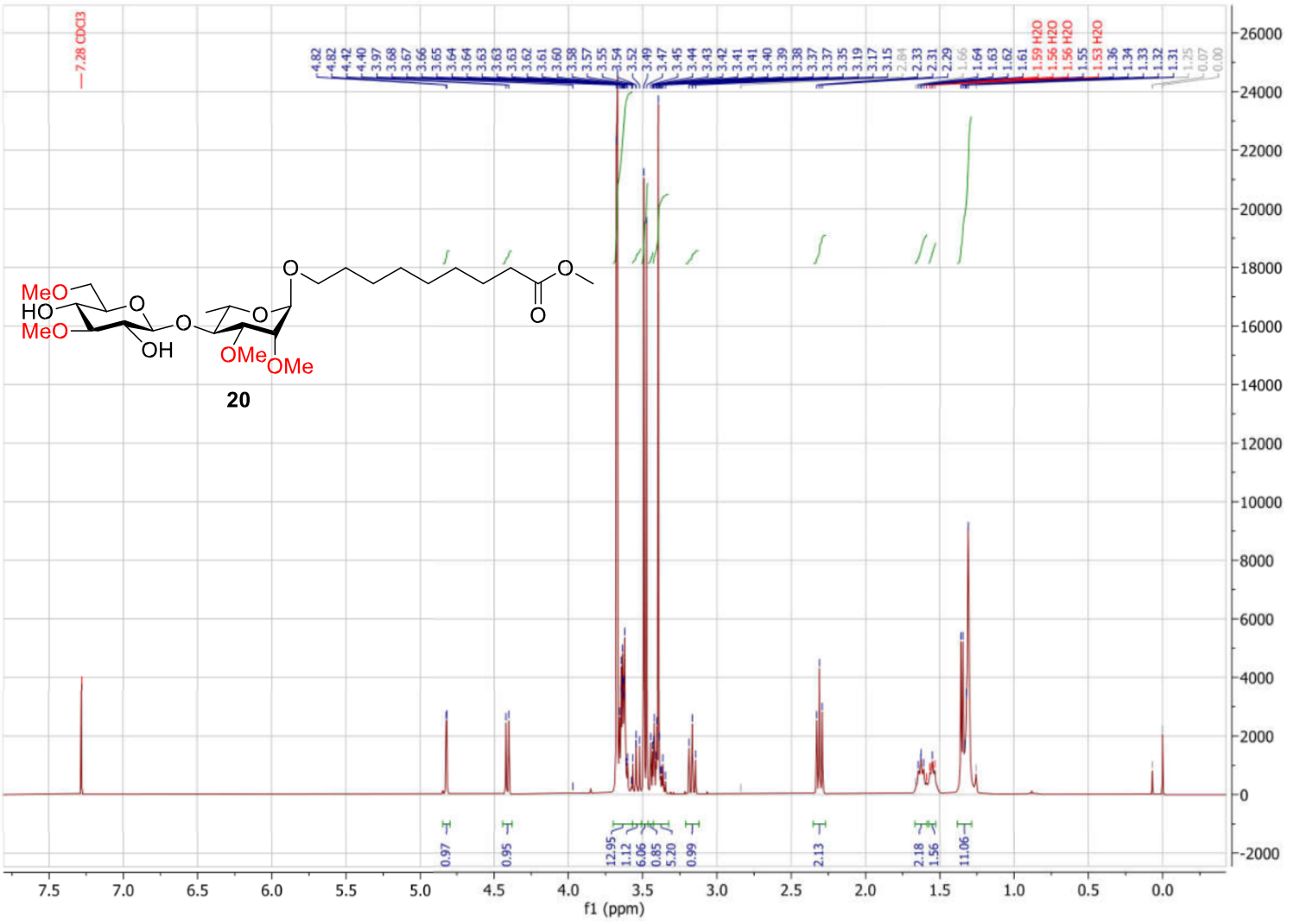

f2 (ppm)
f1 (ppm)

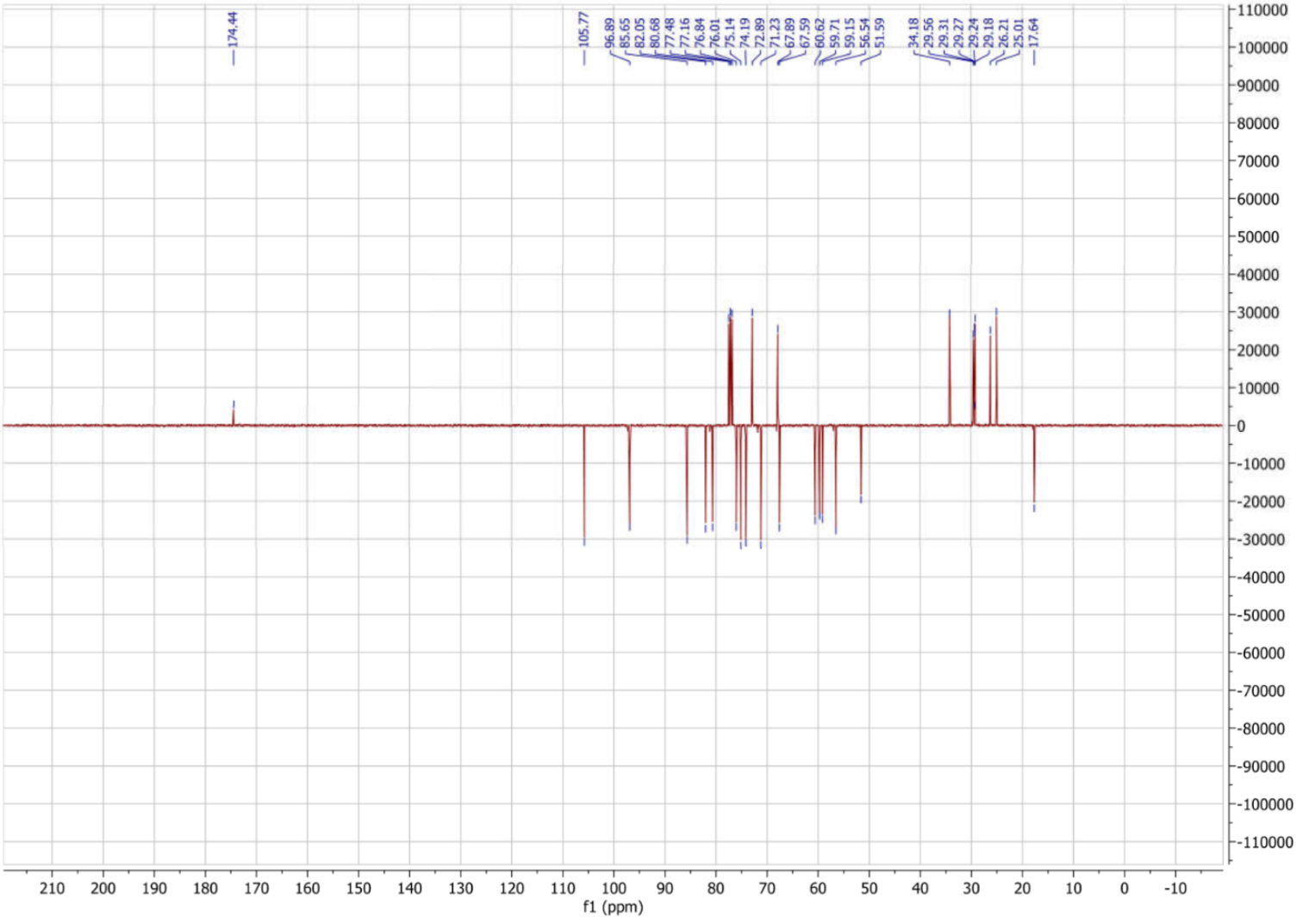

MeO
BnO
MeO
OH
OMe
OMe
O
O
O
O
O
O
19
f1 (ppm)

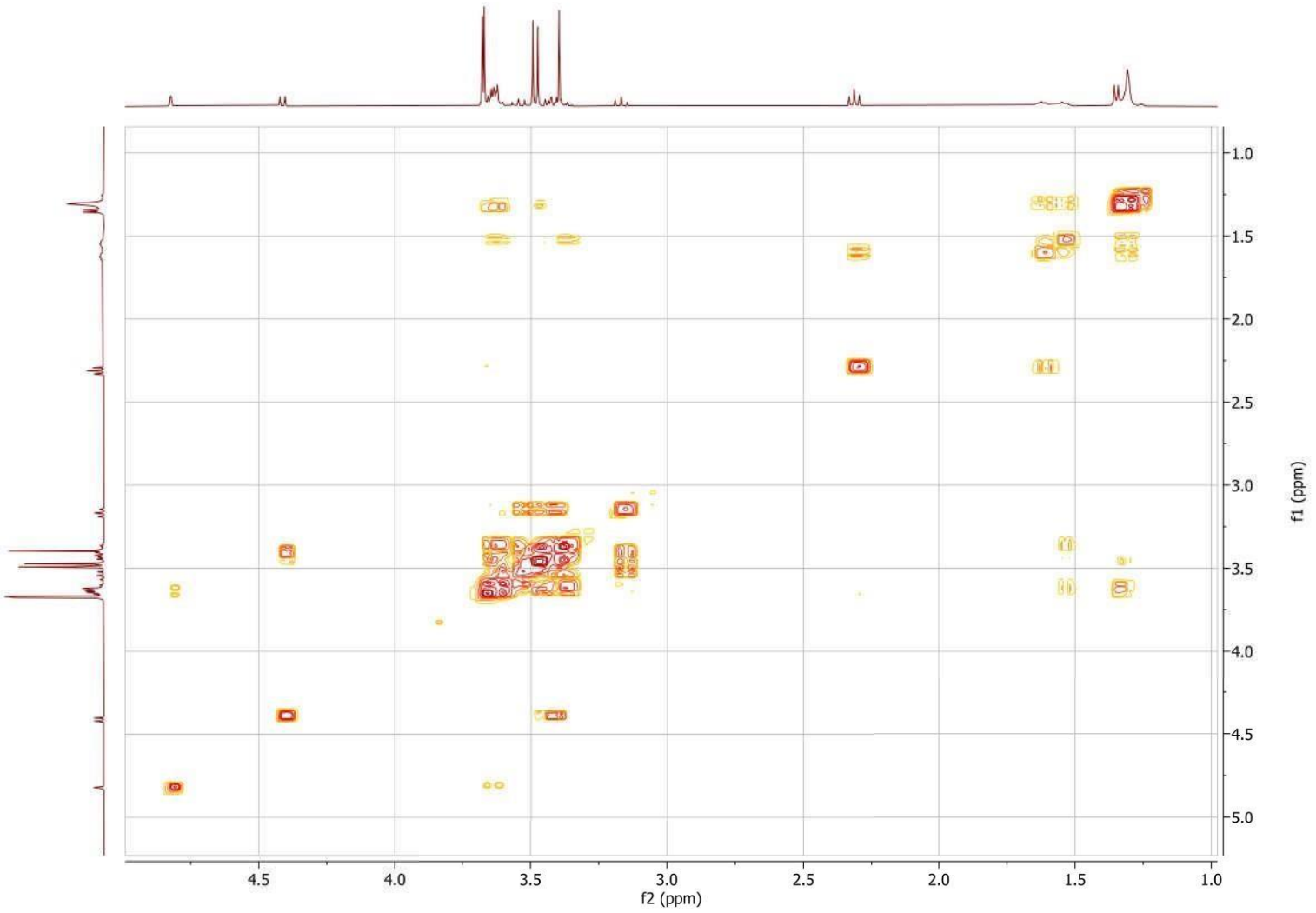

f1 (ppm)

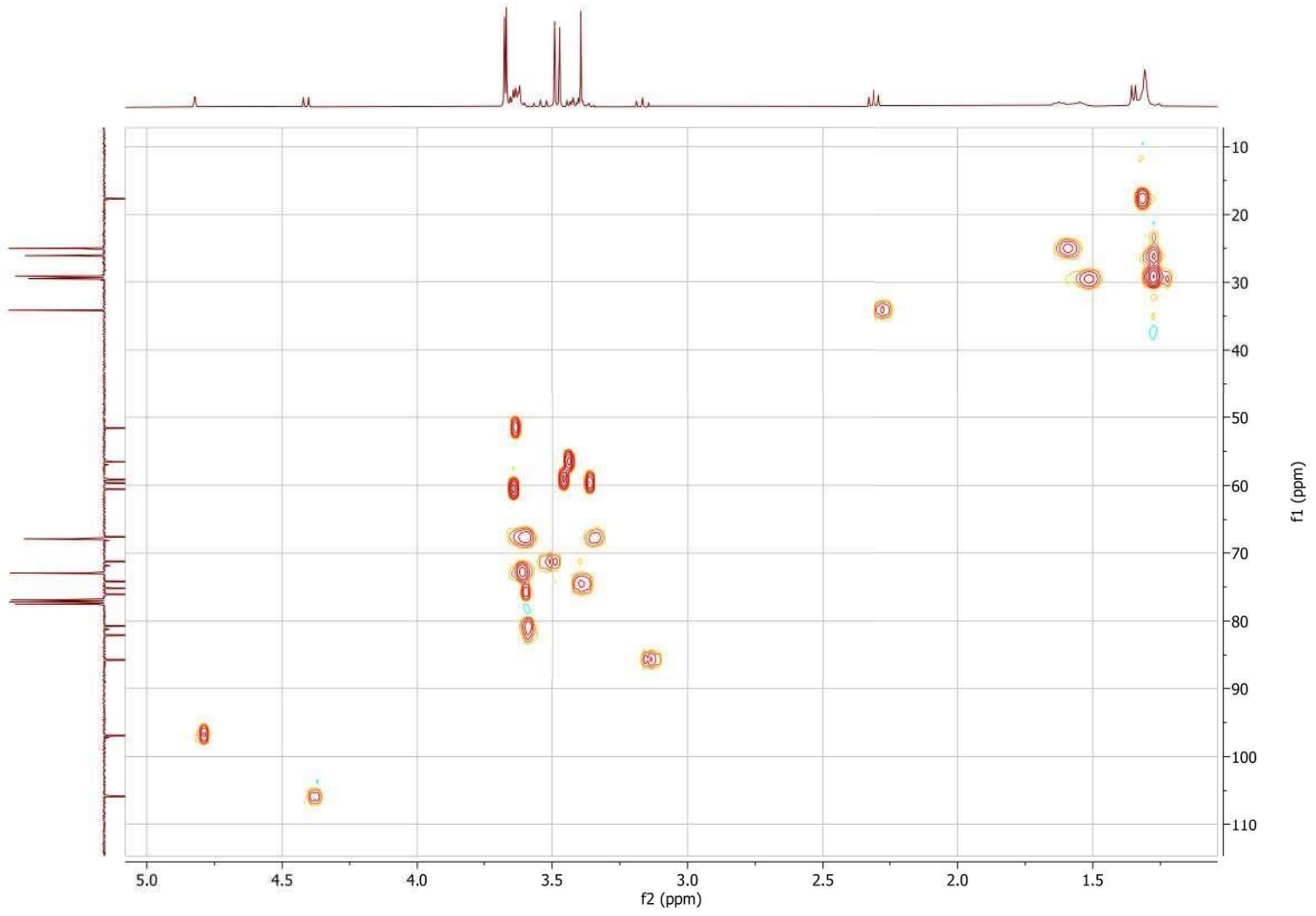

f2 (ppm)
f1 (ppm)

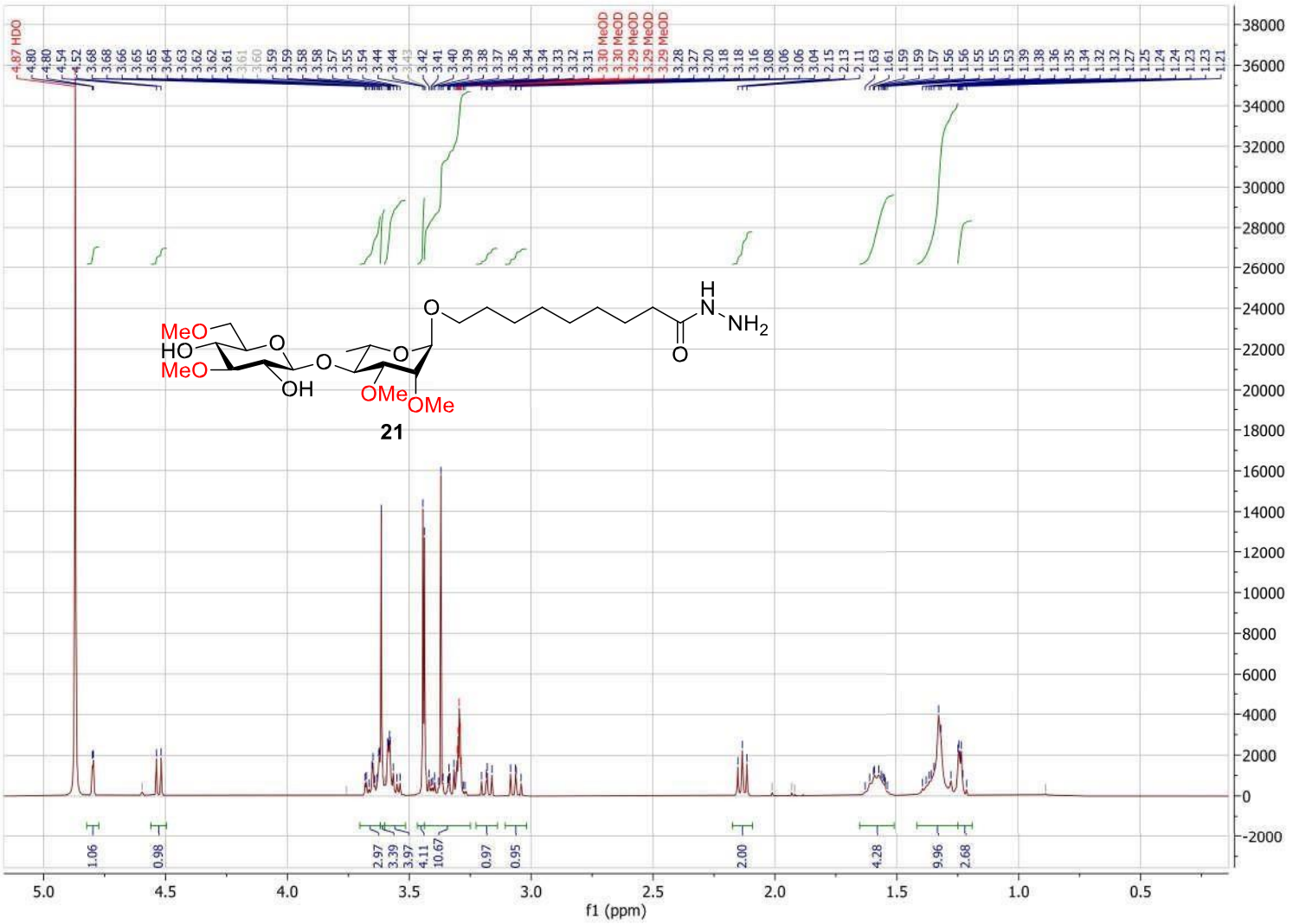

f2 (ppm)
f1 (ppm)

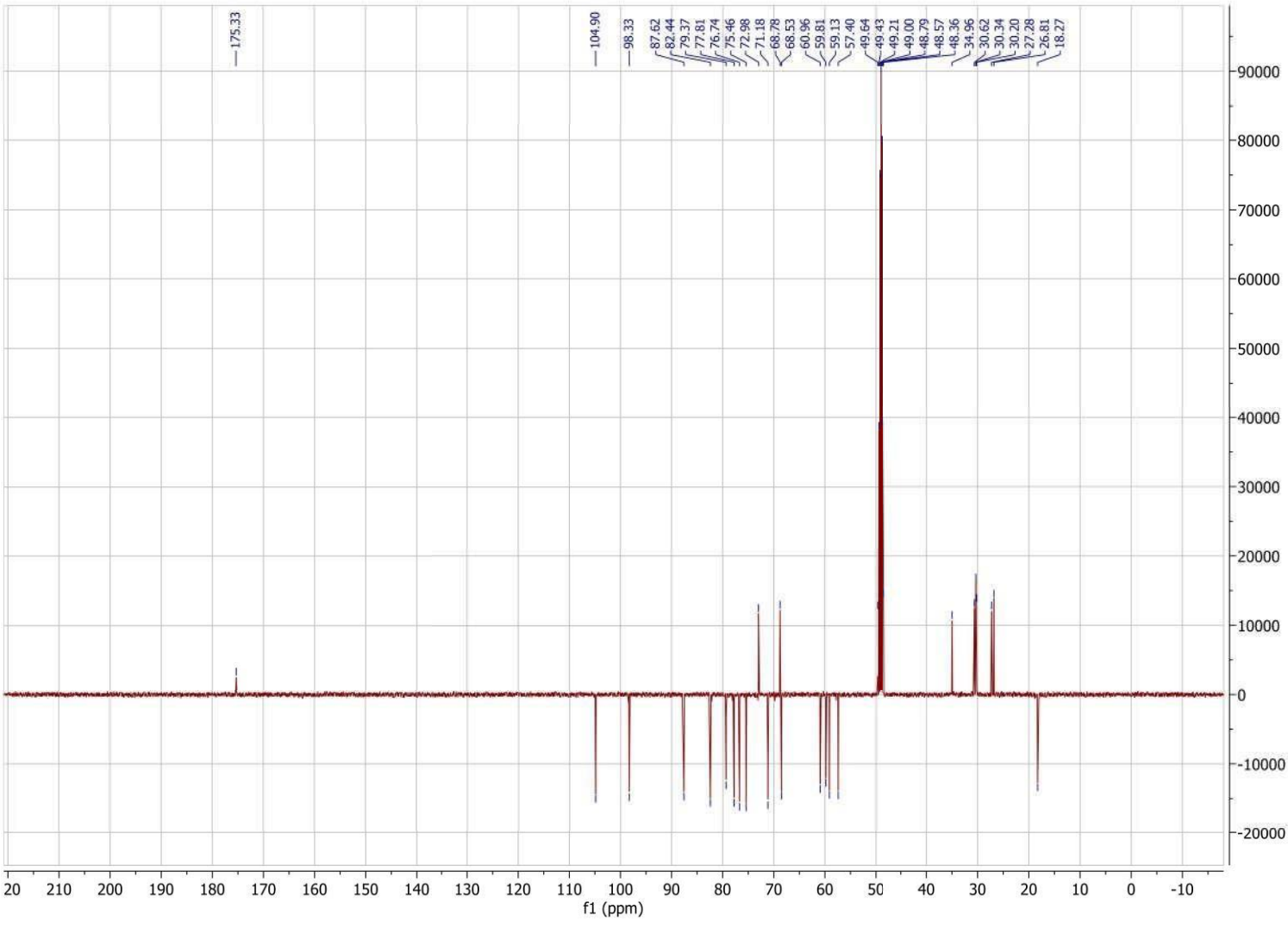

MeO
HO
MeO
OH
OMe
OMe
O
O
O
O
O
O
20
f1 (ppm)

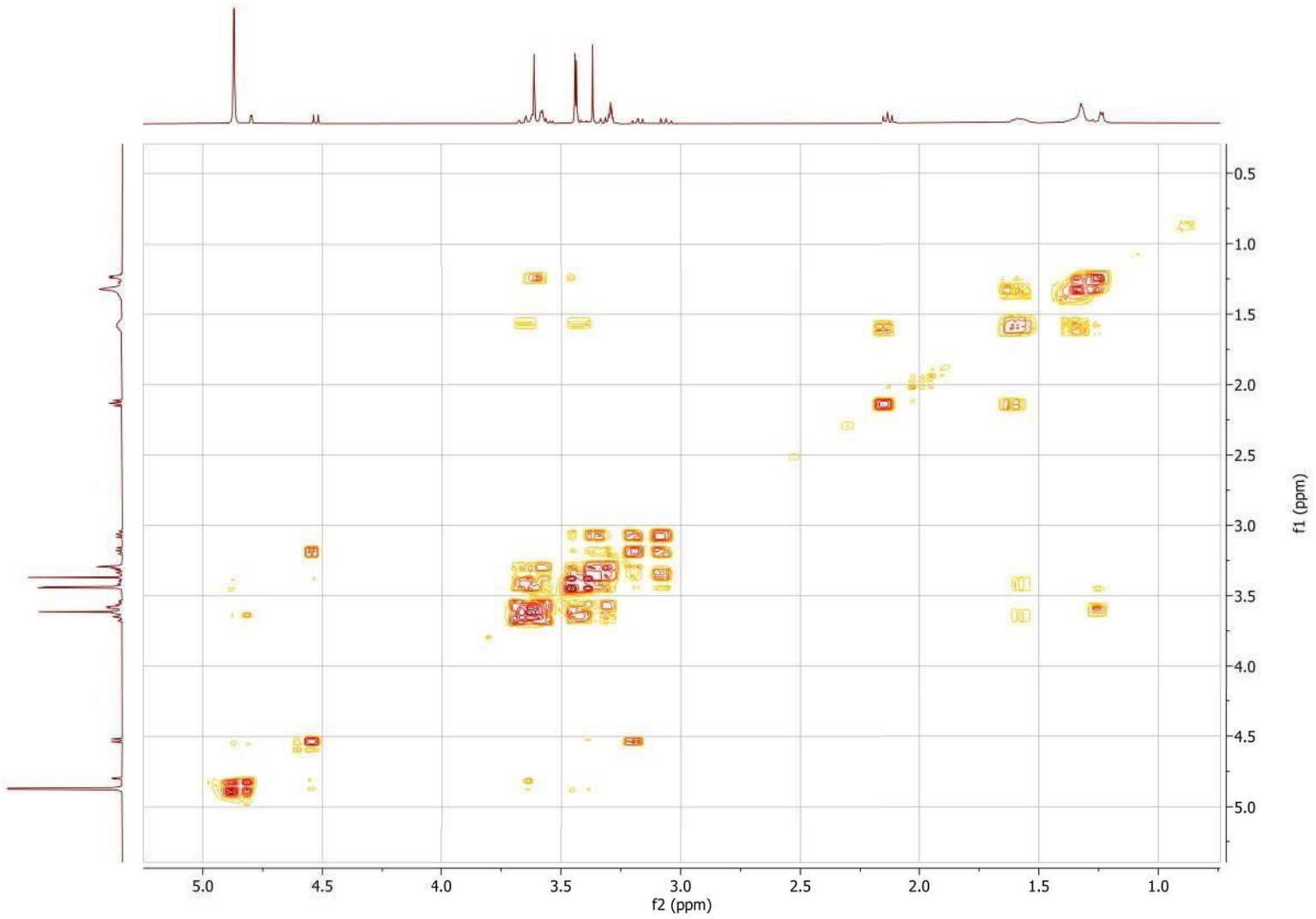

f1 (ppm)

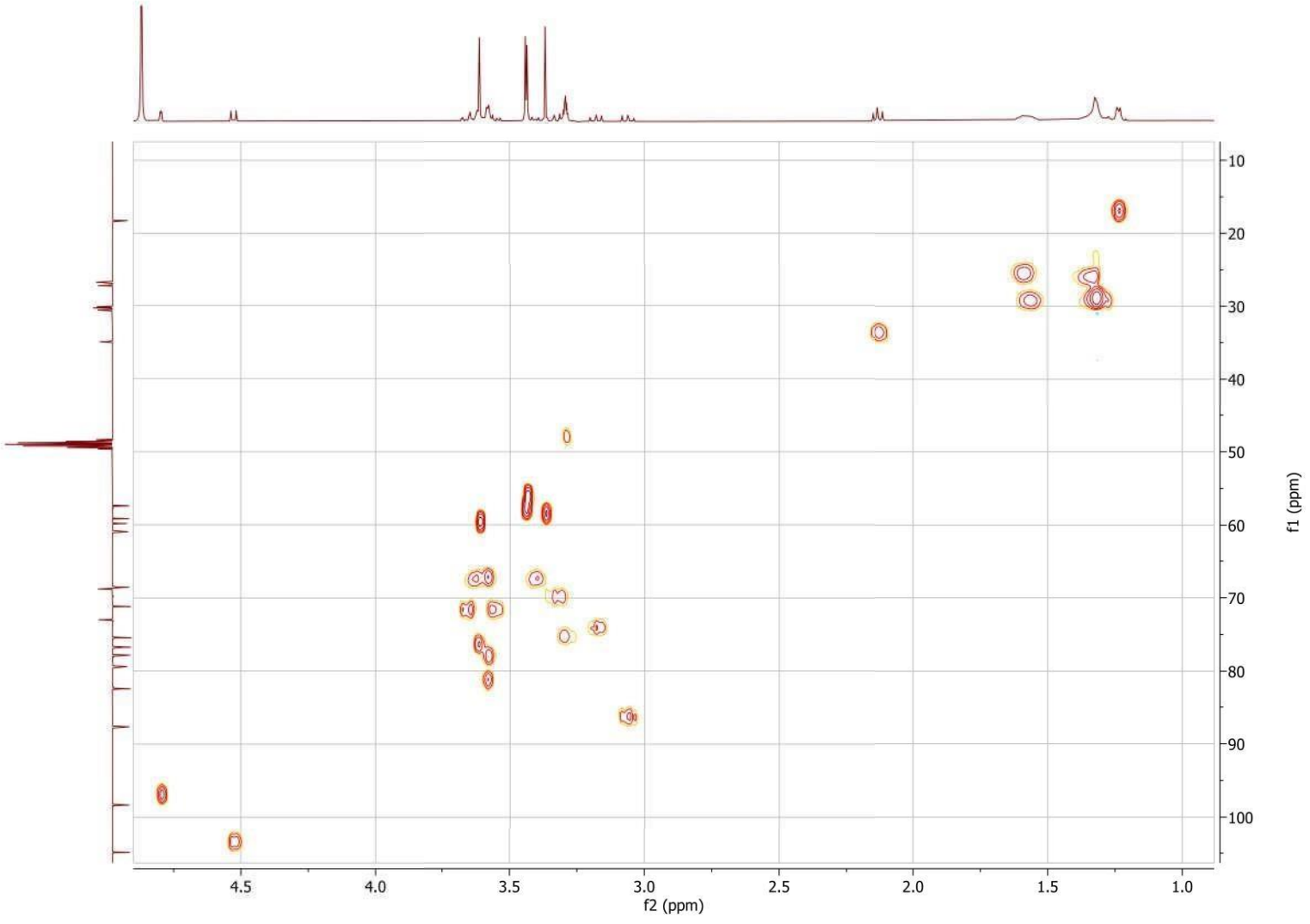

1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)


10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)


MeO
HO
MeO
OH
OMe
OMe
O
N
H
NH2
O
21
f1 (ppm)


f1 (ppm)


0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)


10
20
30
40
50
60
70
80
90
100
f1 (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)