Electronic Supplementary Information for:

Indoxyl-Glucosides Bearing Tethers for Enzymatically Triggered Cross-linking

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[a] Equal contribution by each author

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(1) HRMS spectra of compound 27 and 27-I

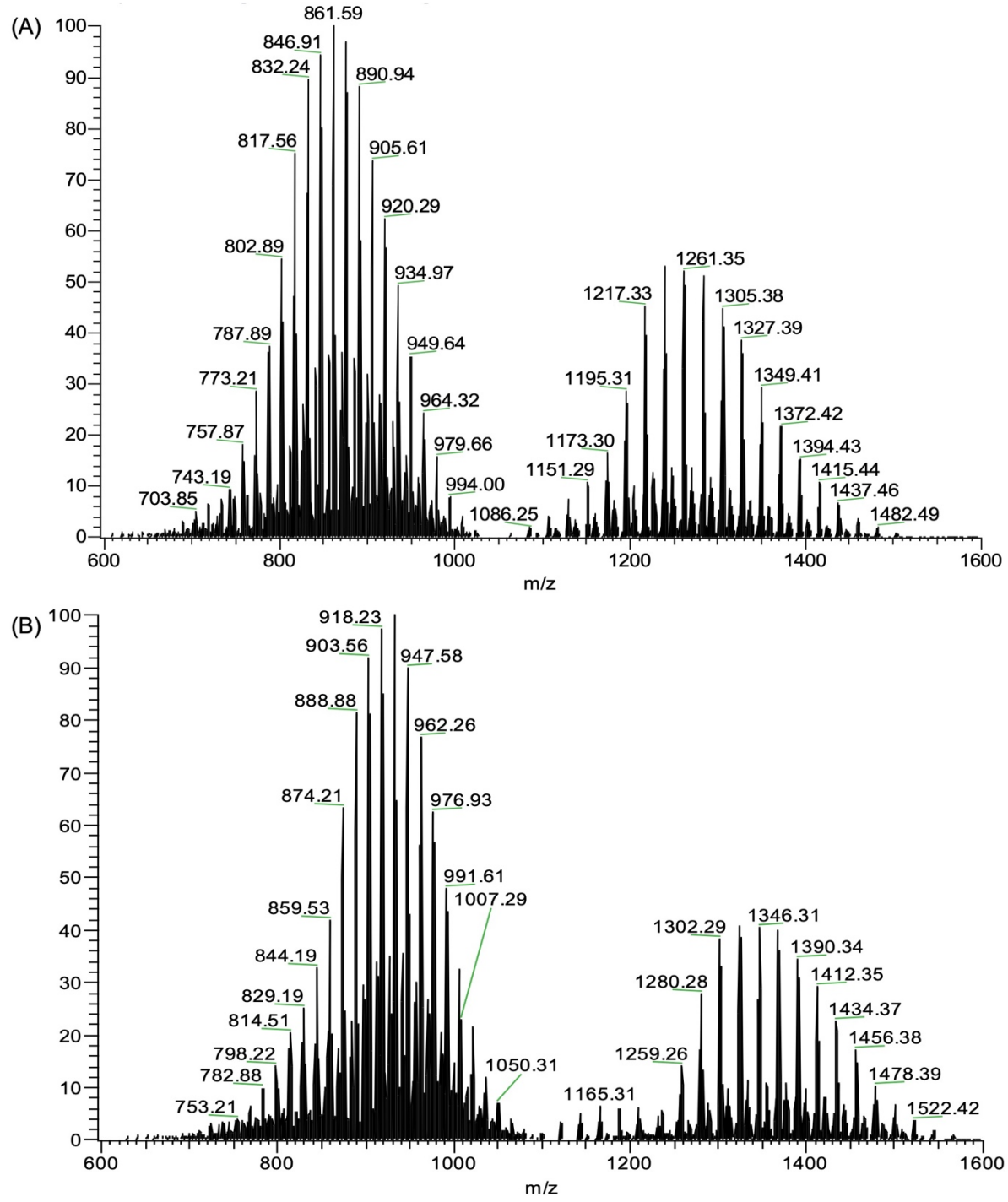
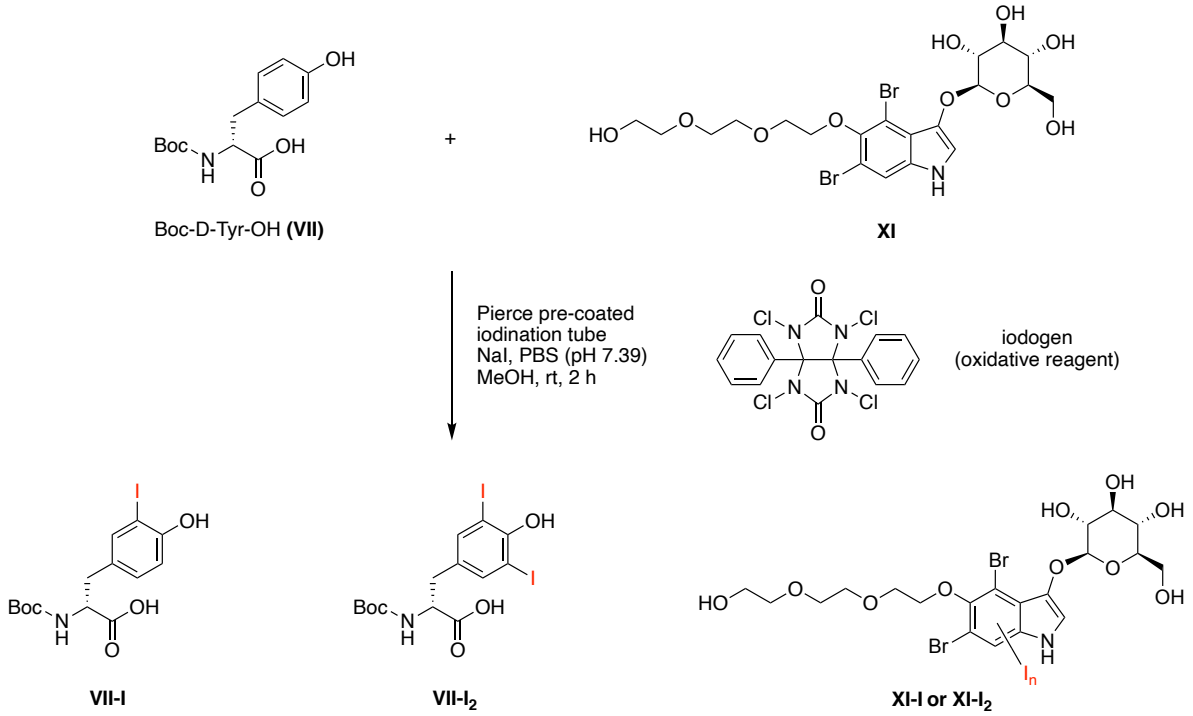


Figure S1. HRMS spectra in the positive-ion mode. (A) Compound **27**. (B) Mass analysis corresponding to the 2.8 min band of the crude reaction sample following iodination of **27**; the data are consistent with the monoiodinated species **27-I**.

(2) Competitive iodination experiment

The phenolic unit of the tyrosine as well as the indoxyl-glucoside moiety in target compound **27** might both be iodinated. To confirm selective iodination of the phenolic unit of the tyrosine, preliminary iodination experiment was carried out by using the test compounds **VII** and **XI** (Scheme S1).



Scheme S1. Iodination test reaction.

To a Pierce pre-coated iodination tube (coated with 50 μg iodogen, 116 nmol), a solution of **VII** (300 μM), **XI** (600 μM) and NaI (46 μM) in 1x PBS (pH 7.39, containing 5% MeOH) was added. The reaction mixture (200 μL) was then agitated on a shaker at room temperature for 2 h. The reaction solvent included 5% MeOH to improve the solubility of **XI** during the reaction. Subsequently, the reaction mixture was removed from the iodination tube to stop the reaction.

The final concentration of NaI was fixed at 46.0 μM because the concentration of the commercially available hot NaI solution is 46.0 μM according to our calculation, which means that 46.0 μM is the available maximum concentration for the radioiodination reaction.

The reaction mixture was then loaded on a C_{18}-reversed phase silica pad and washed with water to remove the salts. Any products were then eluted with acetonitrile and the resulting solution was subjected to the LC-MS analysis. Three peaks were observed for the reaction mixture (Figure S2, A). Retention time for three peaks was 3.2 min, 4.0 min and 4.7 min. According to the *m/z* value for each peak, each of them can be assigned to the corresponding compound (Figure S2, B-D). Boc-D-Tyr-OH **VII** (peak at 4.0 min, Figure S2, C) was partially iodinated and monoiodinated product (**VII-I**, peak at 4.7 min, Figure S2, D) was observed. The

iodination on indoxyl-glucoside **XI** was not observed. Peak at 4.2 min was from the instrument background.

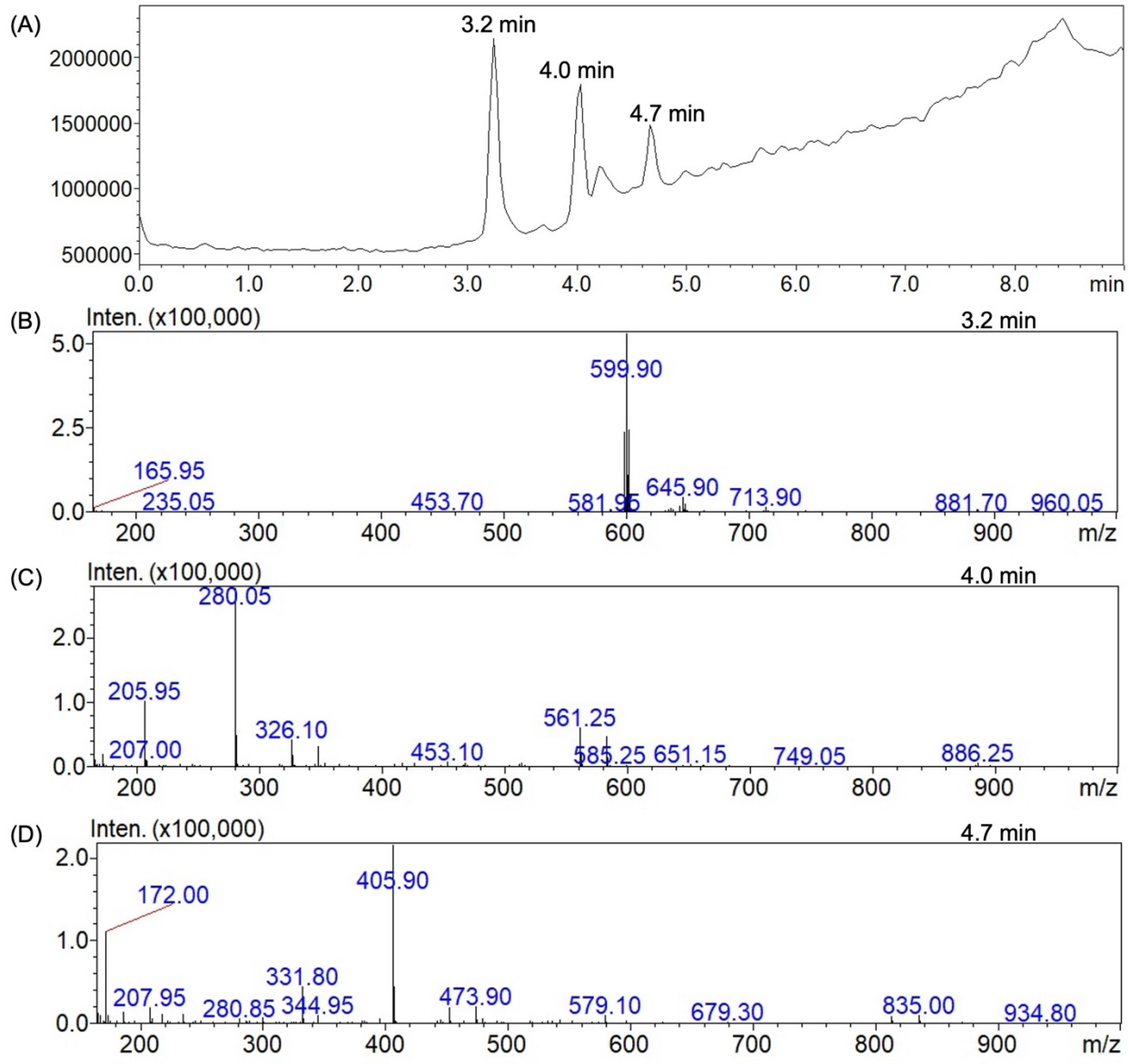


Figure S2. (A) Total ion chromatogram negative ion mode for the reaction mixture of competitive iodination experiment [Boc-D-Tyr-OH **VII** (300 μM), PEG-Br_2-Ind-Glu **XI** (600 μM) and NaI (46 μM) reacted in a Pierce pre-coated tube]. (B) Mass spectra (negative ion mode) at 3.2 min (*m/z* value = 599.90 $[M - H]^-$, corresponding to **XI**, PEG-Br_2-Ind-Glu). (C) Mass spectra (negative ion mode) at 4.0 min (*m/z* value = 280.05 $[M - H]^-$, corresponding to **VII**, Boc-D-Tyr-OH). (D) Mass spectra (negative ion mode) at 4.7 min (*m/z* value = 405.90 $[M - H]^-$, corresponding to mono-iodinated Boc-D-Tyr-OH **VII-I**).

To clarify the behavior of **XI** during the reaction, the iodination reaction was also performed between **XI** (600 μM) and NaI (46 μM), without the presence of Boc-D-Tyr-OH **VII**. The reaction solution turned yellow after 2 h treatment, while competitive reaction mixture remained colorless. The decomposition of **XI** was confirmed by LC-MS. No target mass peak for **XI** was observed after iodination reaction without the presence of compound **VII**. However, peak for **XI** remained intact in the competitive iodination reaction mixture (Figure S2, B, peak at 3.2 min).

Protocol for the competitive iodination experiment between VII and XI. A solution of **VII** (3 mM in 1x PBS, 20 μL), **XI** (12 mM in methanol, 10 μL) and NaI (0.46 mM in 1x PBS, 20 μL) were mixed with 150 μL of 1x PBS in a Pierce pre-coated tube. The total reaction volume was 200 μL. The final concentrations were 300 μM for **VII**, 600 μM for **XI** and 46 μM for NaI. The reaction solvent included 5% MeOH to improve the solubility of **XI** during the reaction. The reaction mixture was agitated on a shaker for 2 h at room temperature. The reaction was stopped by removing the solution from the tube and then loaded on a C_{18}-reversed phase silica (Silicycle, part number: R33230B) pad. The reaction mixture was washed with water (1 mL x 5) to remove the salts and then eluted with acetonitrile (1 mL x 2). The resulting solution was checked on a Shimadzu LC-MS [flow rate 0.5 mL/min, the mobile phase was changed from 95% water and 5% acetonitrile (MeCN) to 5% water and 95% MeCN (0–7 min), and stayed at 5% water and 95% MeCN (7–9 min), containing 0.1% formic acid].

(3) Indigoid formation with the iodination reaction mixture of 27

The iodination reaction mixtures of **27** (removing from the Pierce iodination tube, without further purification) were then subjected to the indigogenic reactions under acidic (pH 5.0) and neutral (pH 7.0) conditions. The results are shown in Table S1. Both iodination reaction mixtures formed indigoid in indigogenic reactions. Blue color was observed but no blue precipitate was formed after centrifugation. The yields for the indigogenic reactions were similar before and after the iodination of target compound **27**.

Table S1. Results for indigogenic reactions.

Sample	Indigogenic reactions yields[b]
27	20% at pH 7.0; 11% at pH 5.0
Reaction mixture of **27** and NaI (0.15 eq)	20% at pH 7.0; 12% at pH 5.0
Reaction mixture of **27** and NaI (0.60 eq)[a]	19% at pH 7.0; 8.1% at pH 5.0

[a] NaI was added stepwise (0.15 equivalent every 15 min).

[b] Compound **27** or reaction mixture (100 μM) and β-glucosidase (200 nM) was incubated in 50 mM sodium phosphate buffer (pH 7.0) at 37 °C for 2 h. Compound **27** or reaction mixture (100 μM) and β-glucosidase from almonds (1 U/mL) was incubated in 50 mM sodium acetate buffer (pH 5.0) at 37 °C for 8 h. The resulting solutions were analyzed by absorption spectroscopy directly after centrifugation.

(4) Indigoid formation from 26

The reaction of **26** with β-glucosidase was performed. The solubility of **26** in aqueous solution is poor, yet still indigoid was detected by absorption spectroscopy (Figure S3). Compound **26** precipitated upon addition into the buffer solution. However, the enzymatic tests were still performed with various **26** concentrations. The compound **26** was resuspended into the buffer solution and then treated with β-glucosidase. All the reactions with substrate concentration higher than 31.6 μM showed a blue color after 2 h incubation. Then the reaction solutions were further incubated overnight. After overnight incubation with β-glucosidase followed by centrifugation, all the reactions with substrate concentration higher than 10.0 μM formed blue precipitate. The blue precipitate was separated from the supernatant and dissolved in DMF (100 μL) for absorbance measurement. The absorption peak of indigoid ($\varepsilon = 2.6 \times 10^4$ $M^{-1}cm^{-1}$ in DMF/H_2O = 2:1)[7] gave the following yields as a function of concentration: 1.00 μM (<1%), 3.16 μM (12%), 10.0 μM (12%), 31.6 μM (11%), 100 μM (8.1%), 316 μM (6.6%). The low yield is probably caused by the limited solubility of **26** in aqueous buffered solution.

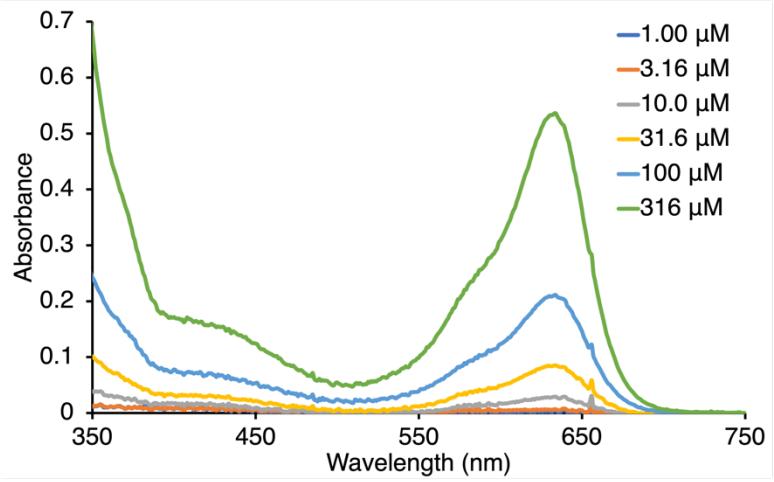


Figure S3. Absorption spectra (DMF, room temperature) of the indigoid formation by **26** with various reaction concentrations after overnight incubation with β-glucosidase.

Protocol for reactions of 26 with β-glucosidase. Samples of **26** in DMSO (0.100, 0.316, 1.00, 3.16, 10.0, 31.6 mM; 1 μL) and β-glucosidase (10 μM, 2 μL) were mixed with 97 μL of 50 mM sodium phosphate buffer (pH 7.0). The total reaction volume was 100 μL. The substrate concentration in each reaction was 1.00, 3.16, 10.0, 31.6, 100 or 316 μM. The reaction mixture was incubated overnight at 37 °C and then centrifuged for 10 min. Any precipitate was separated from the supernatant and dissolved in DMF (100 μL). The resulting solutions were analyzed by absorption spectroscopy.

(5) Indigoid formation from 27 with β-glucosidase from almonds

Given the environment in tumor is slightly acidic, a time course test was also performed by compound **27** at pH 5.0 with β-glucosidase from almonds. The yield of corresponding indigoids reached its highest value (13%) after 6 h incubation with β-glucosidase from almonds under 37 °C. The $t_{1/2}$ is ca. 3 h.

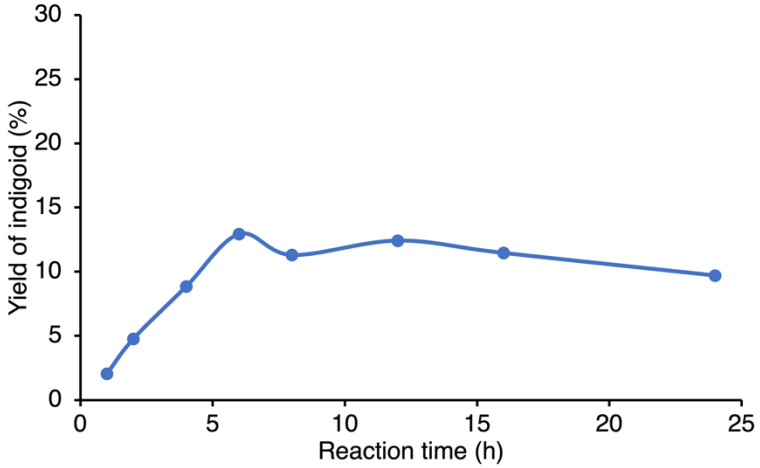


Figure S4. Yield over time of indigoid formed by **27** with β-glucosidase from almonds (pH 5.0).

Reactions of 27 with β-glucosidase from almonds over time. Samples of **27** in DMSO (10.0 mM, 1 μL) and β-glucosidase from almonds (10 U/mL, 10 μL) were mixed with 89 μL of 50 mM sodium acetate buffer (pH 5.0). The total reaction volume was 100 μL. The substrate concentration in the mixture was 100 μM. The reaction mixture was incubated at 37 °C for 1, 2, 4, 6, 8, 12, 16, 24 h and then centrifuged for 10 min. The resulting solutions were then analyzed by absorption spectroscopy.

(6) Absorption spectra of hybrid indigogenic reactions

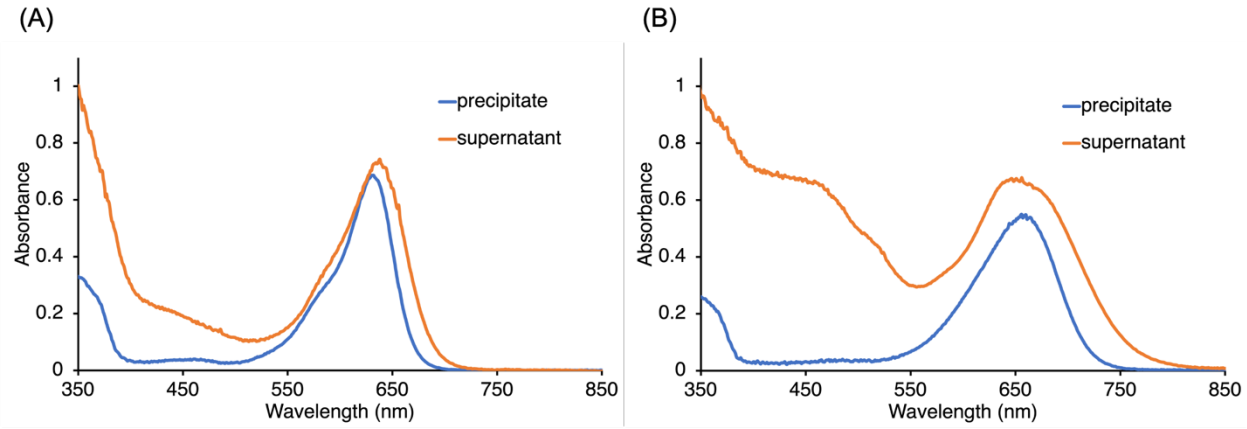


Figure S5. Absorption spectra at room temperature of indigoids formed by overnight incubation of **15** and **18** (A) or **8** and **14** (B) with β-glucosidase (precipitate: redissolved in DMF; supernatant: redissolved in DMF/H_2O = 1:1).

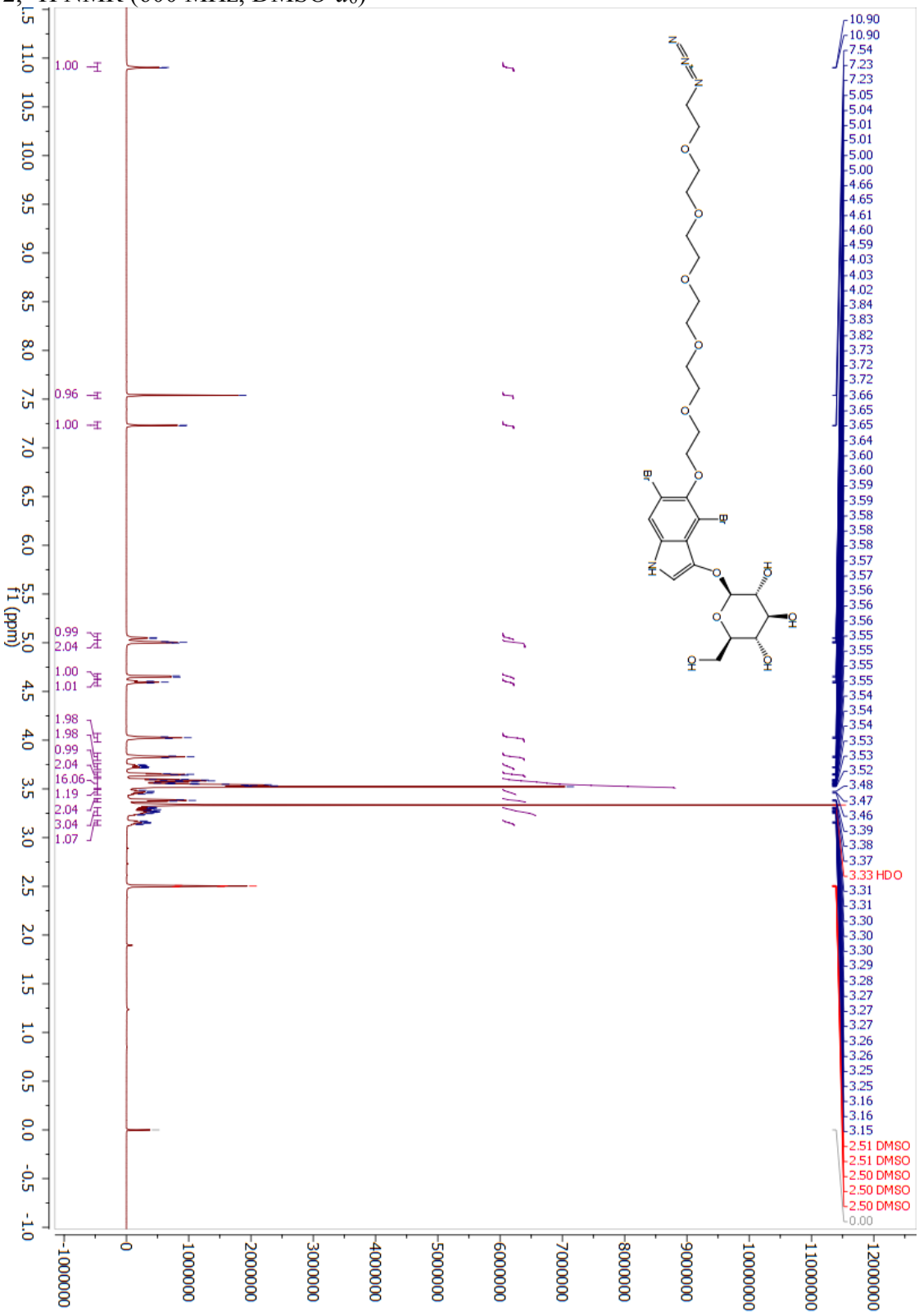
Table S2. Yields of hybrid indigogenic reactions.

Entry	Entity	Wavelength (nm)	Absorbance	Yield (%)[a]
15 + **18**	precipitate	631	0.69	122
	supernatant	638	0.74	0.65
8 + **14**	precipitate	656	0.55	63
	supernatant	656	0.68	0.78

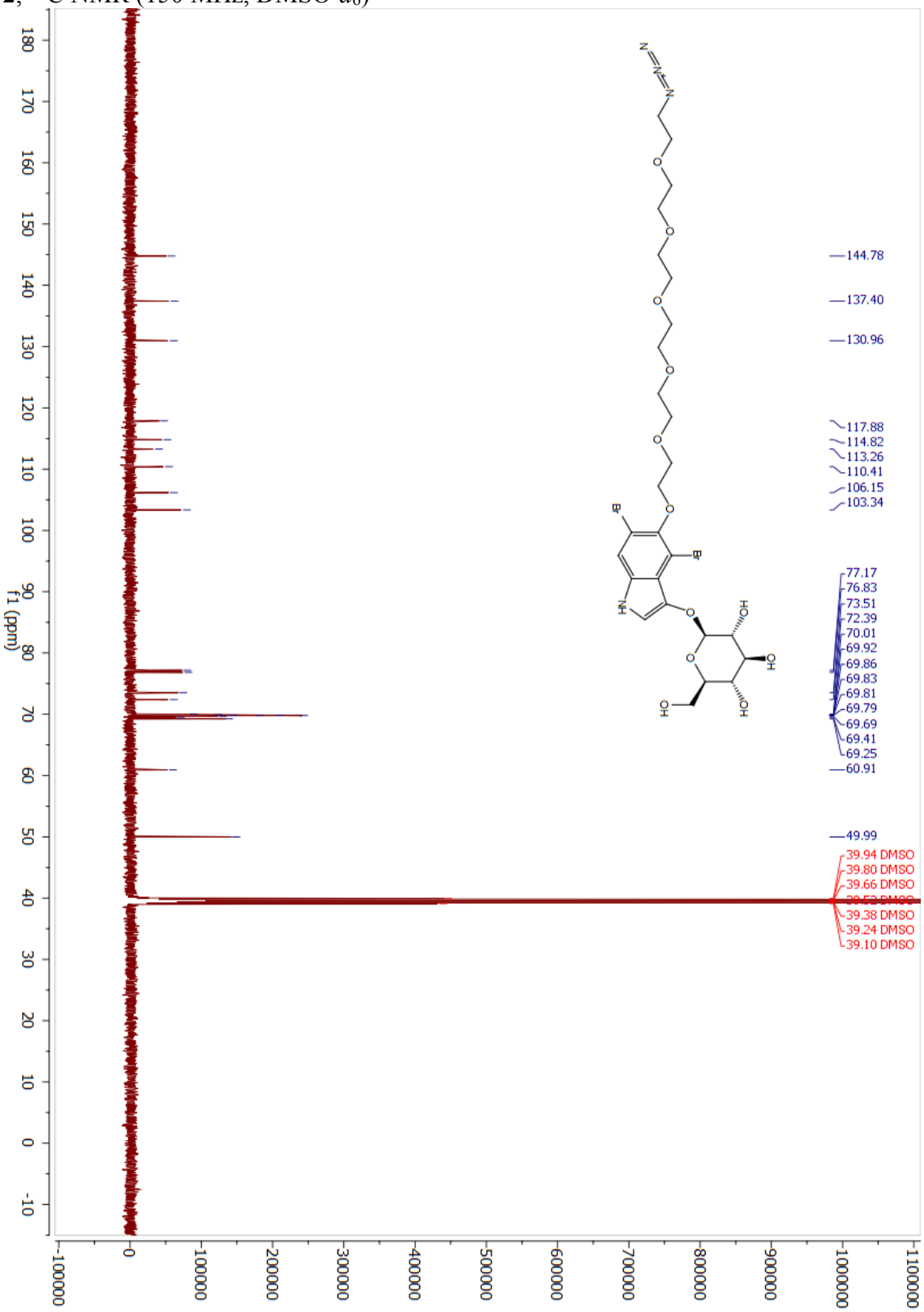
[a]The yield for the overall indigoids formation was estimated from absorption spectroscopy with ε = 2.6×10^4 $M^{-1}cm^{-1}$ (DMF/H_2O = 2:1) measured for **Ind(18)$_2$**.[7]

(7) NMR Spectral data

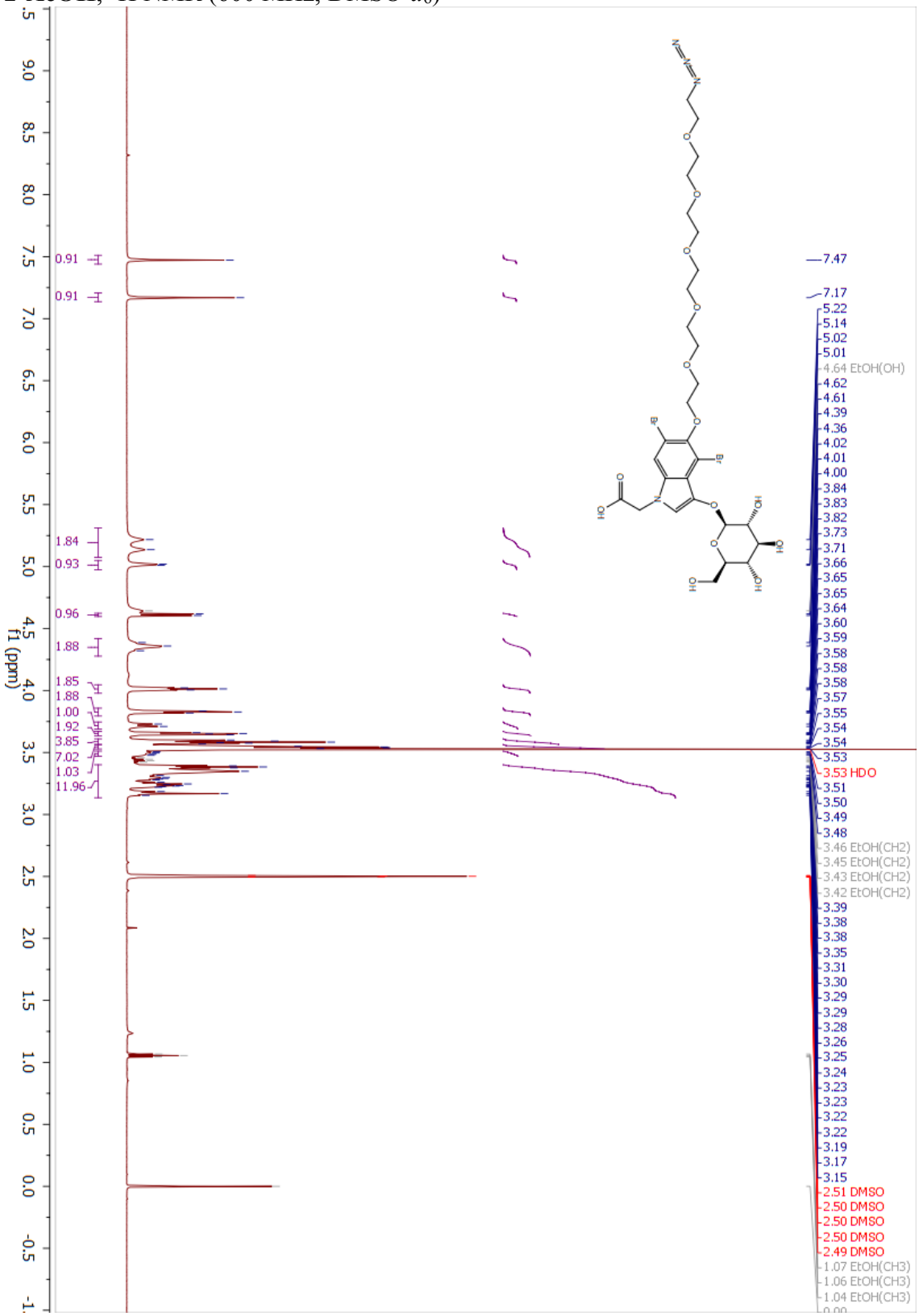
2, ^{1}H NMR (600 MHz, DMSO-d_6)



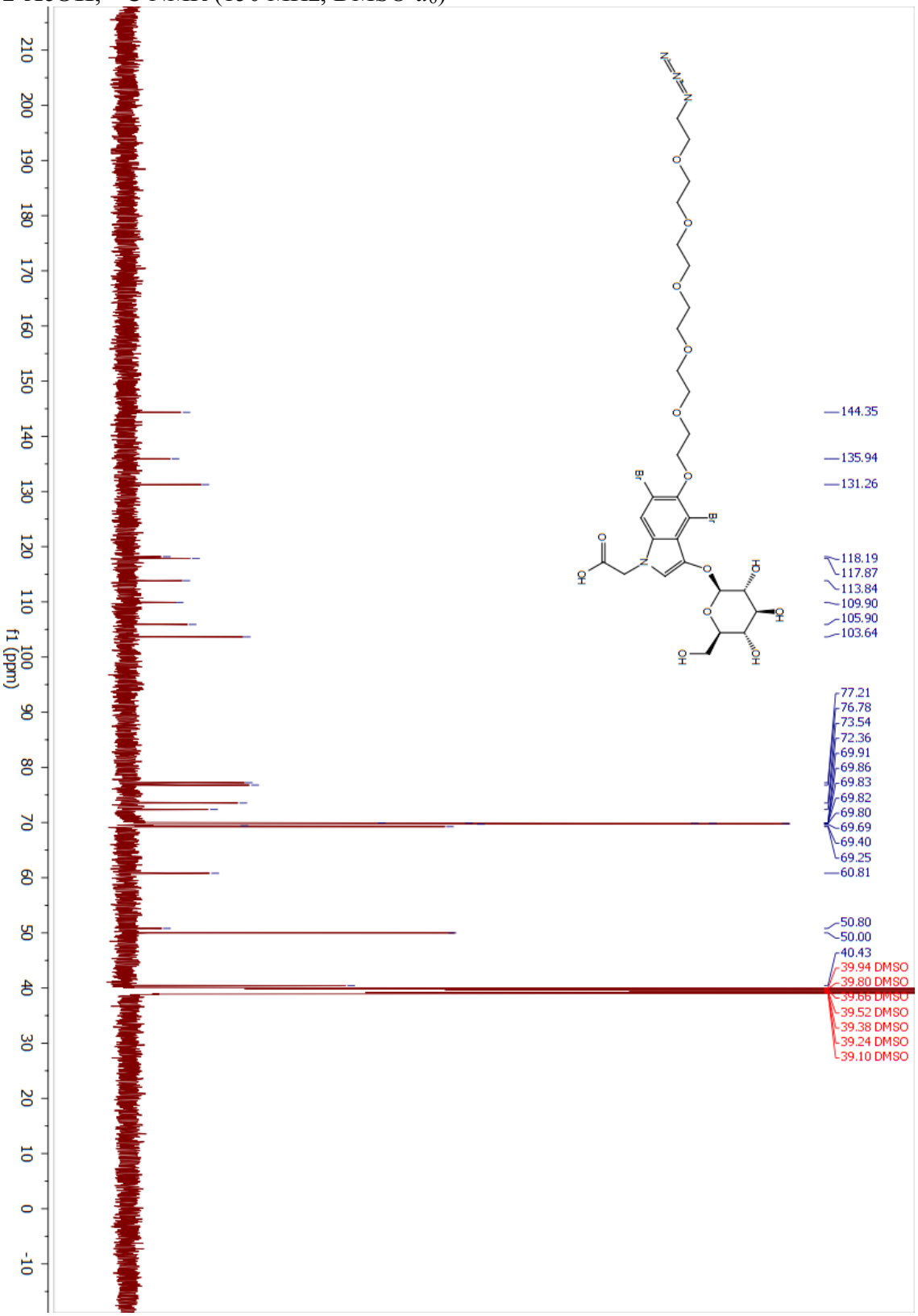
2, ^{13}C NMR (150 MHz, DMSO-d_6)



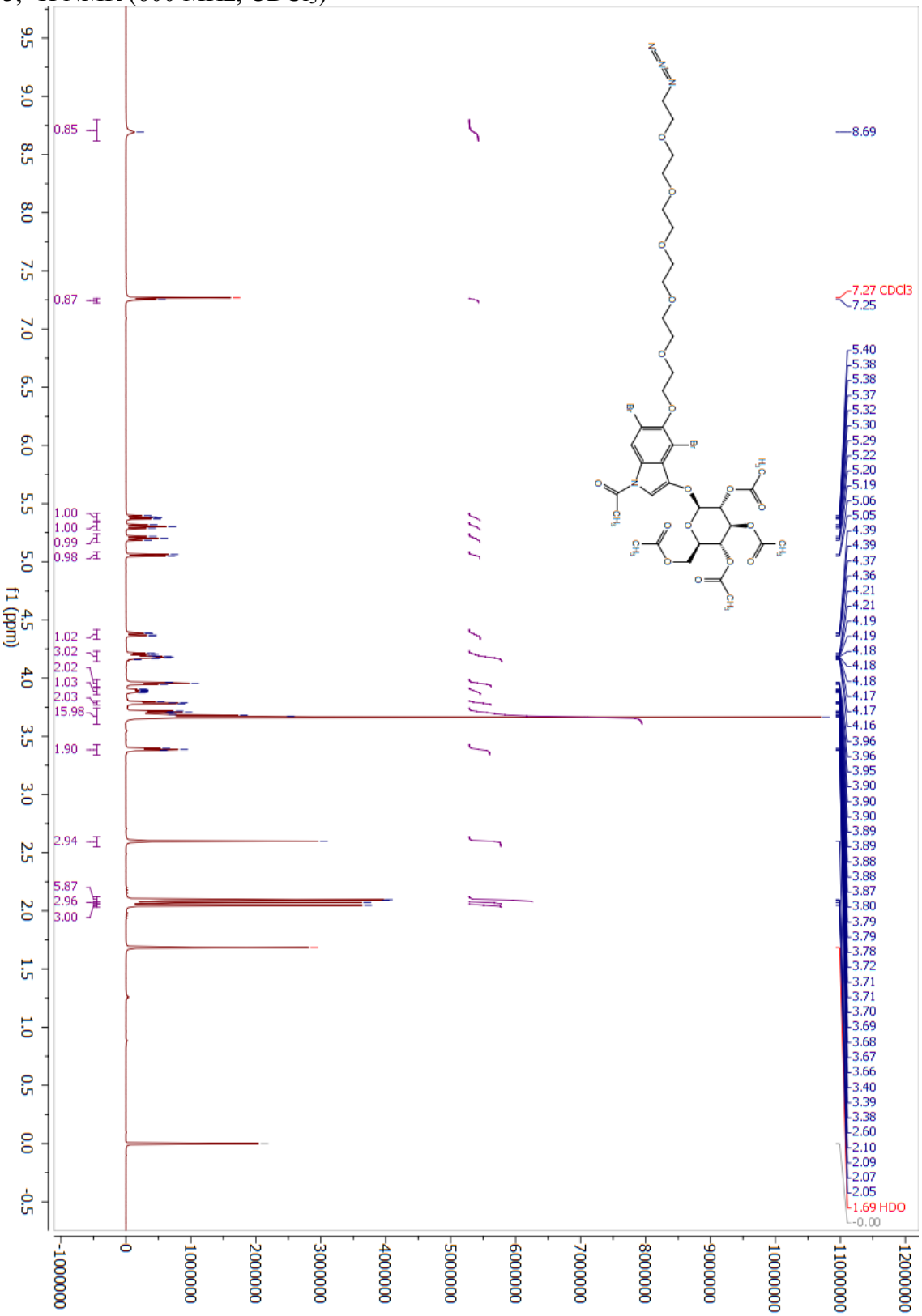
2-AcOH, ^{1}H NMR (600 MHz, DMSO-d_6)



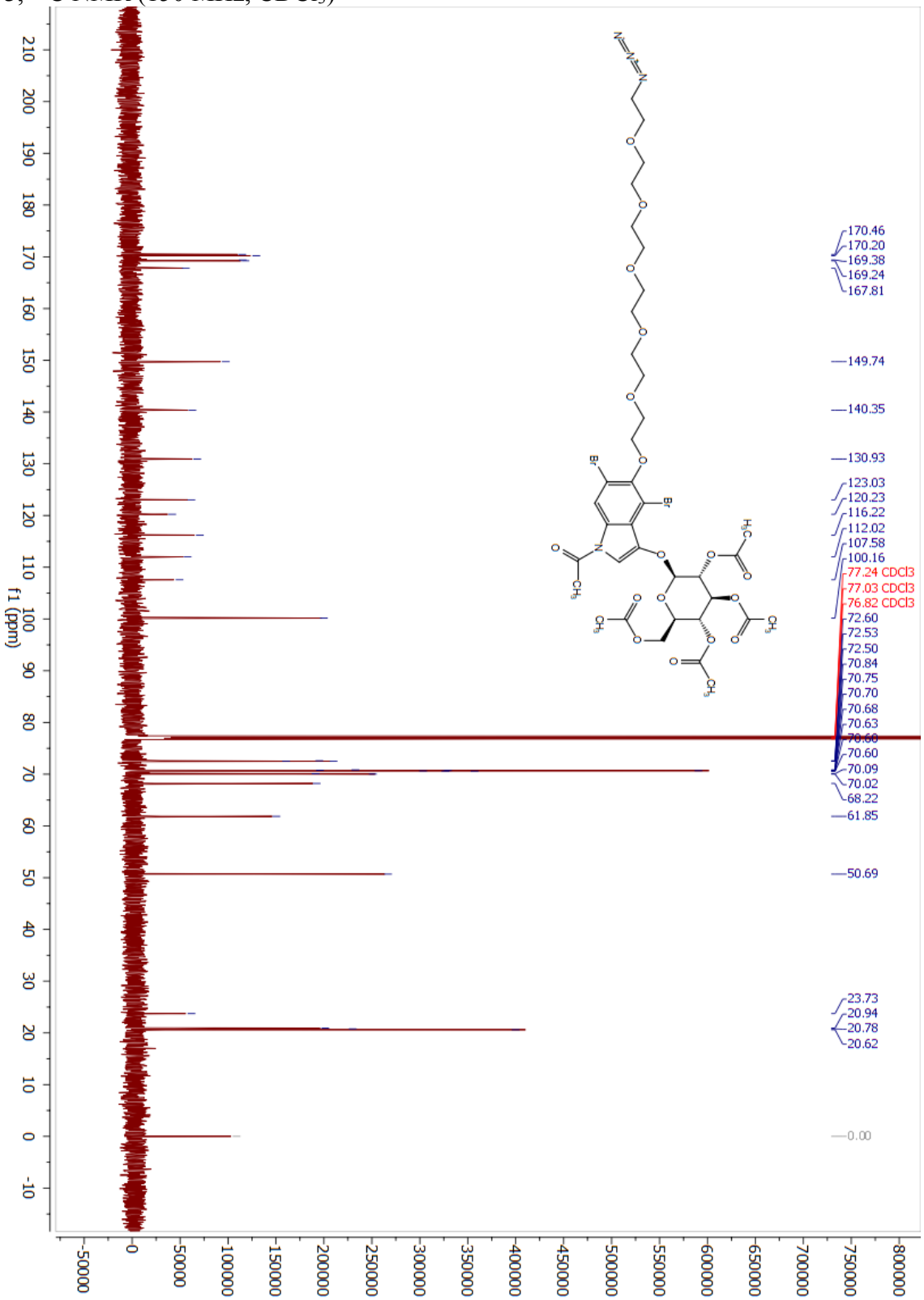
2-AcOH, ^{13}C NMR (150 MHz, DMSO-d_6)



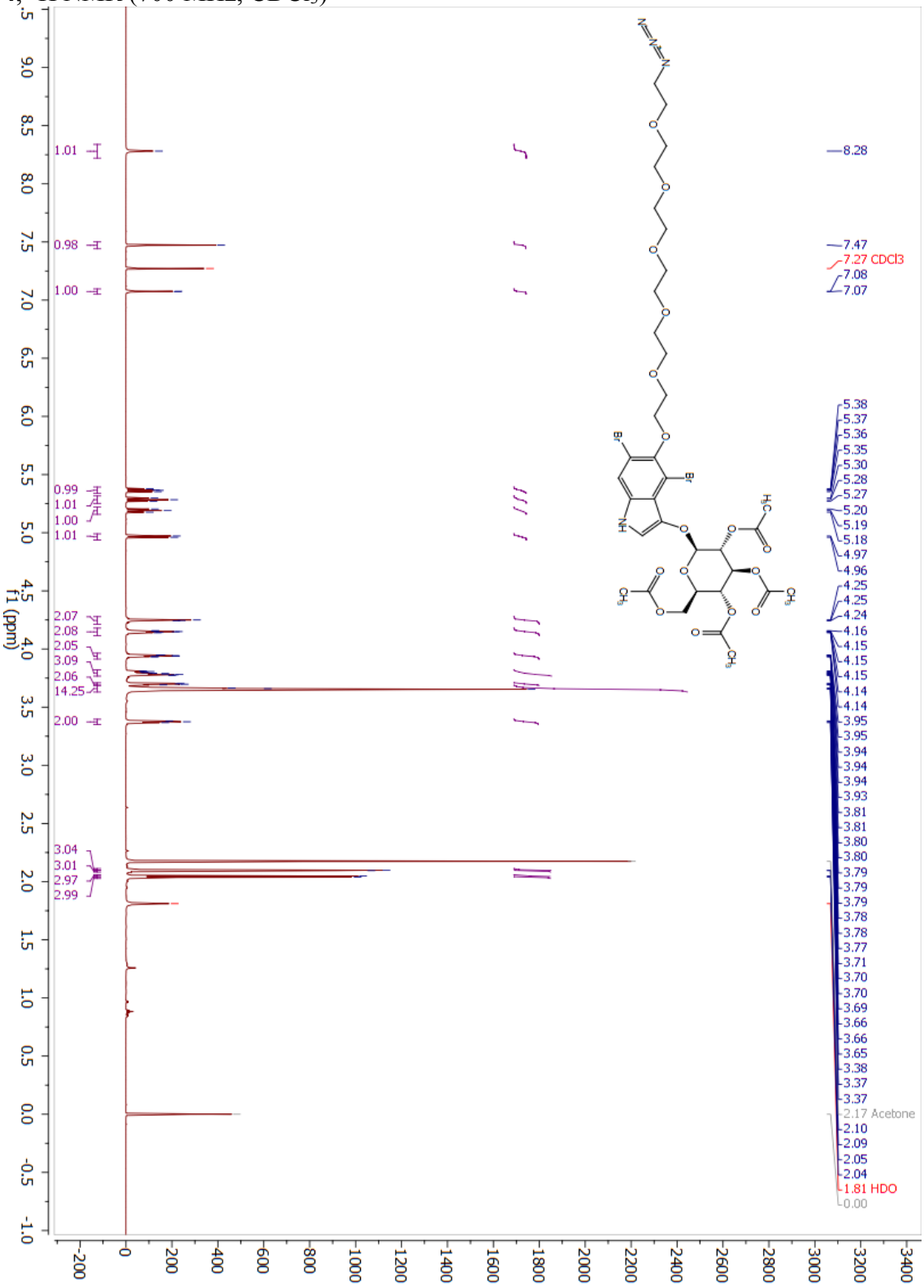
3, ^{1}H NMR (600 MHz, $CDCl_3$)



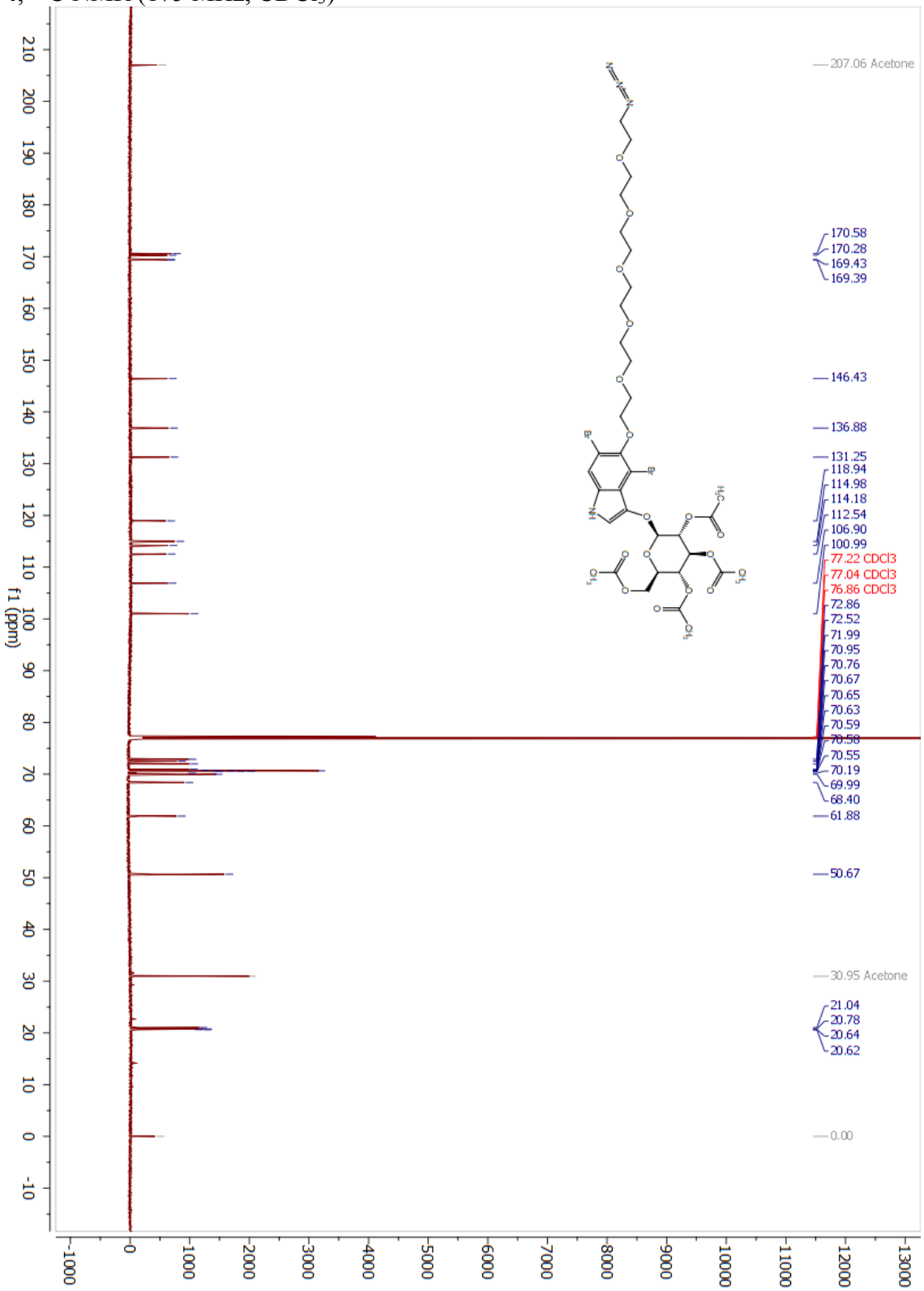
3, ^{13}C NMR (150 MHz, $CDCl_3$)



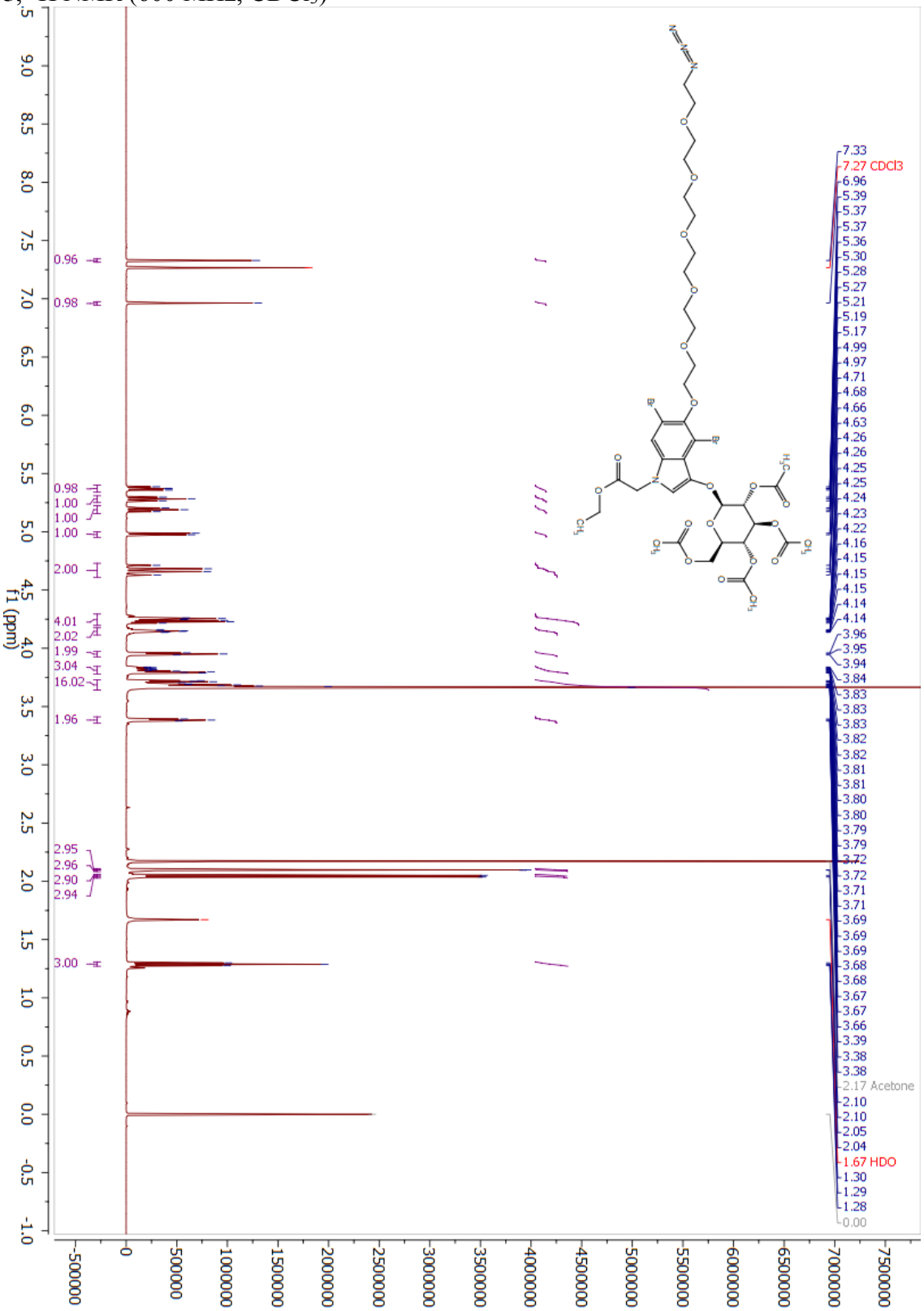
4, ^{1}H NMR (700 MHz, $CDCl_3$)



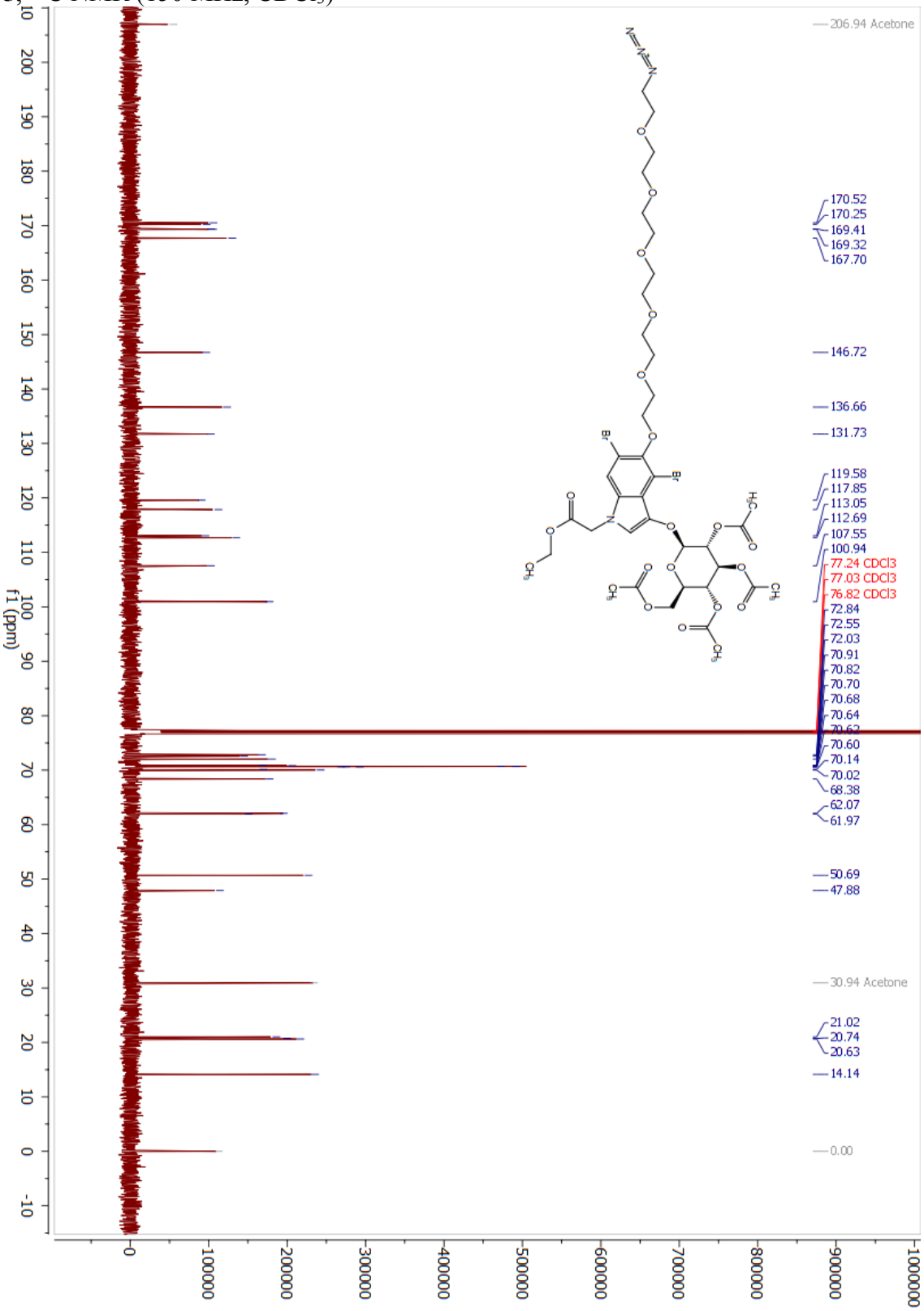
4, ^{13}C NMR (175 MHz, $CDCl_3$)



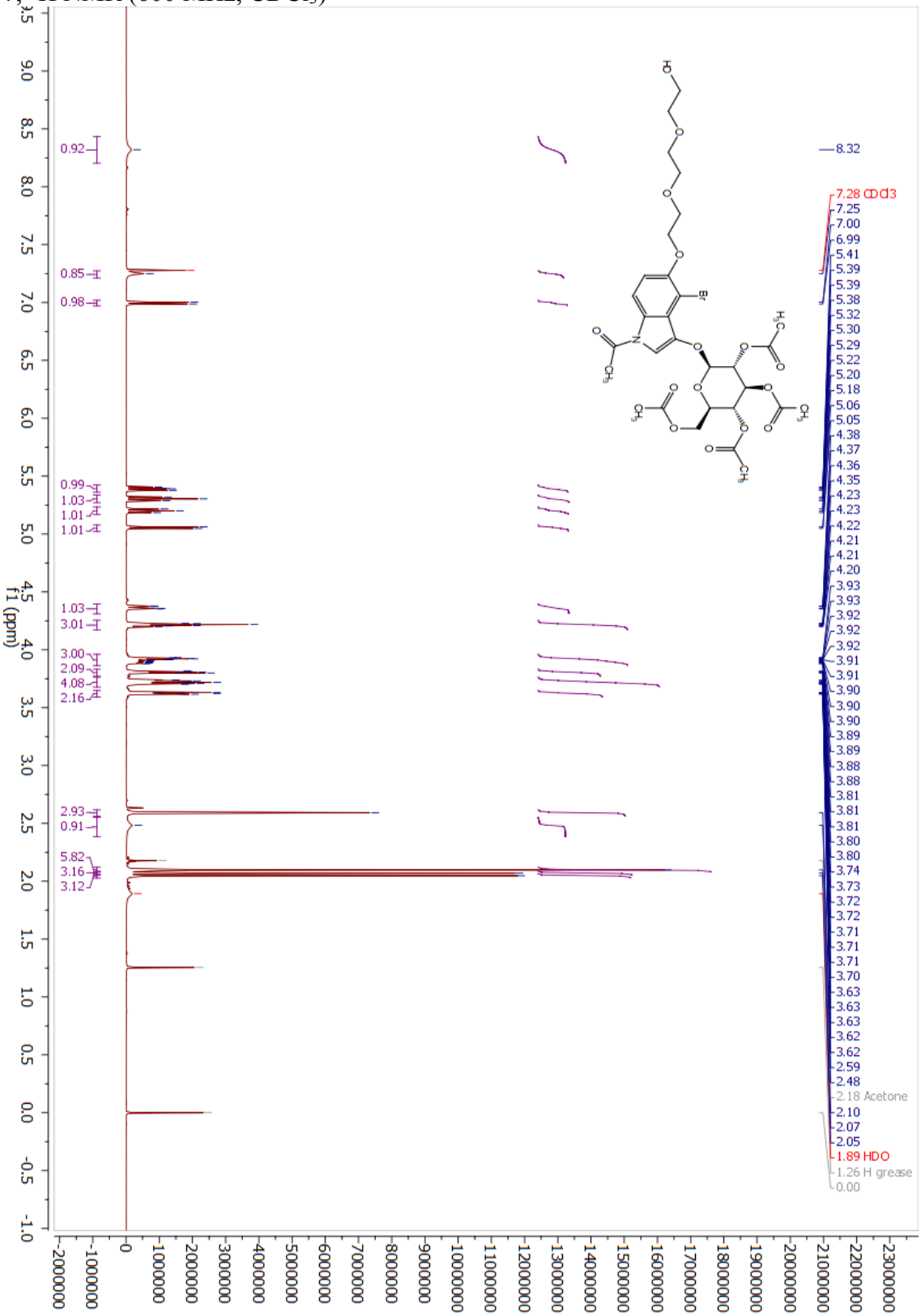
5, ^{1}H NMR (600 MHz, $CDCl_3$)



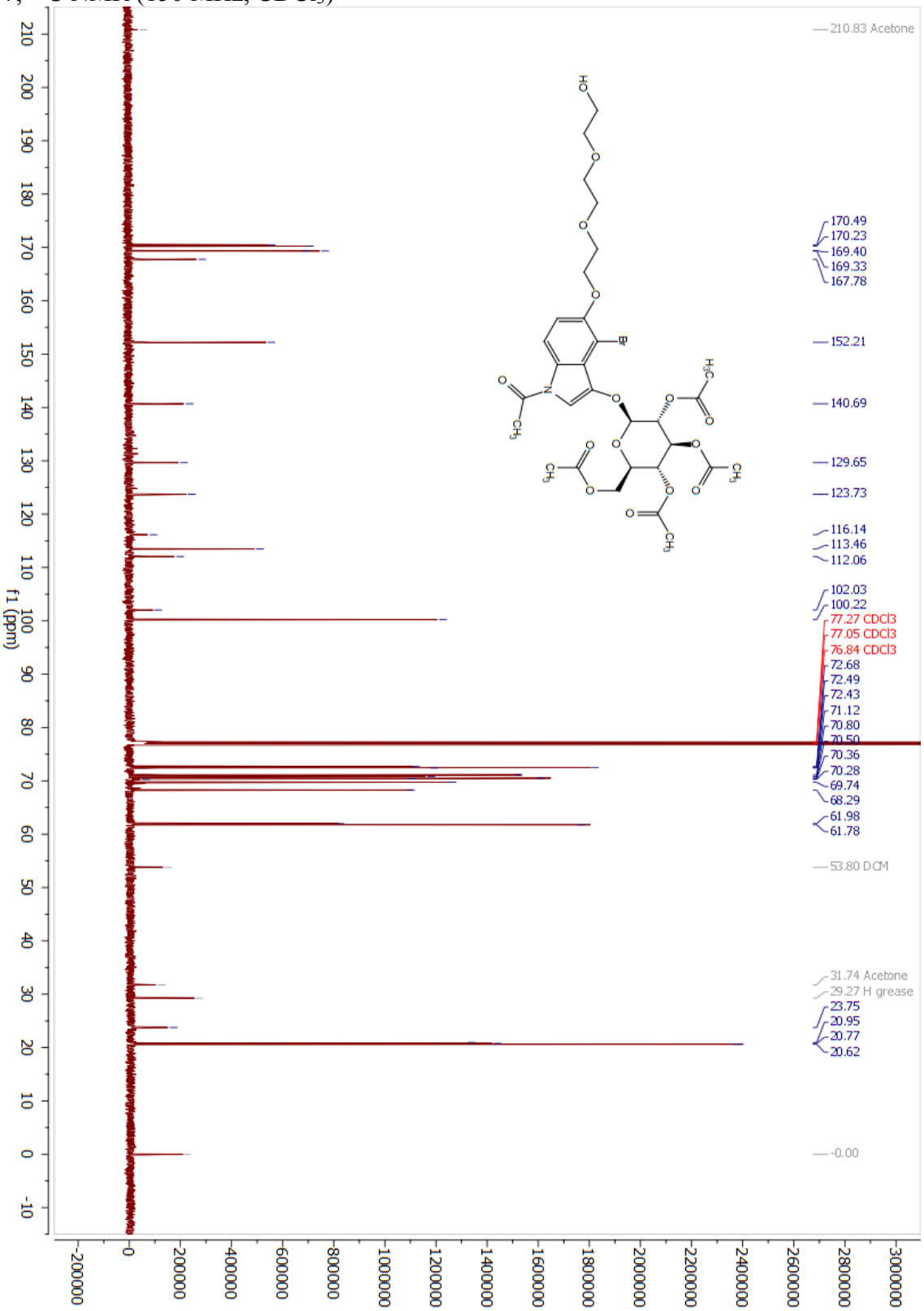
5, ^{13}C NMR (150 MHz, $CDCl_3$)



7, ^{1}H NMR (600 MHz, $CDCl_3$)



7, ^{13}C NMR (150 MHz, $CDCl_3$)



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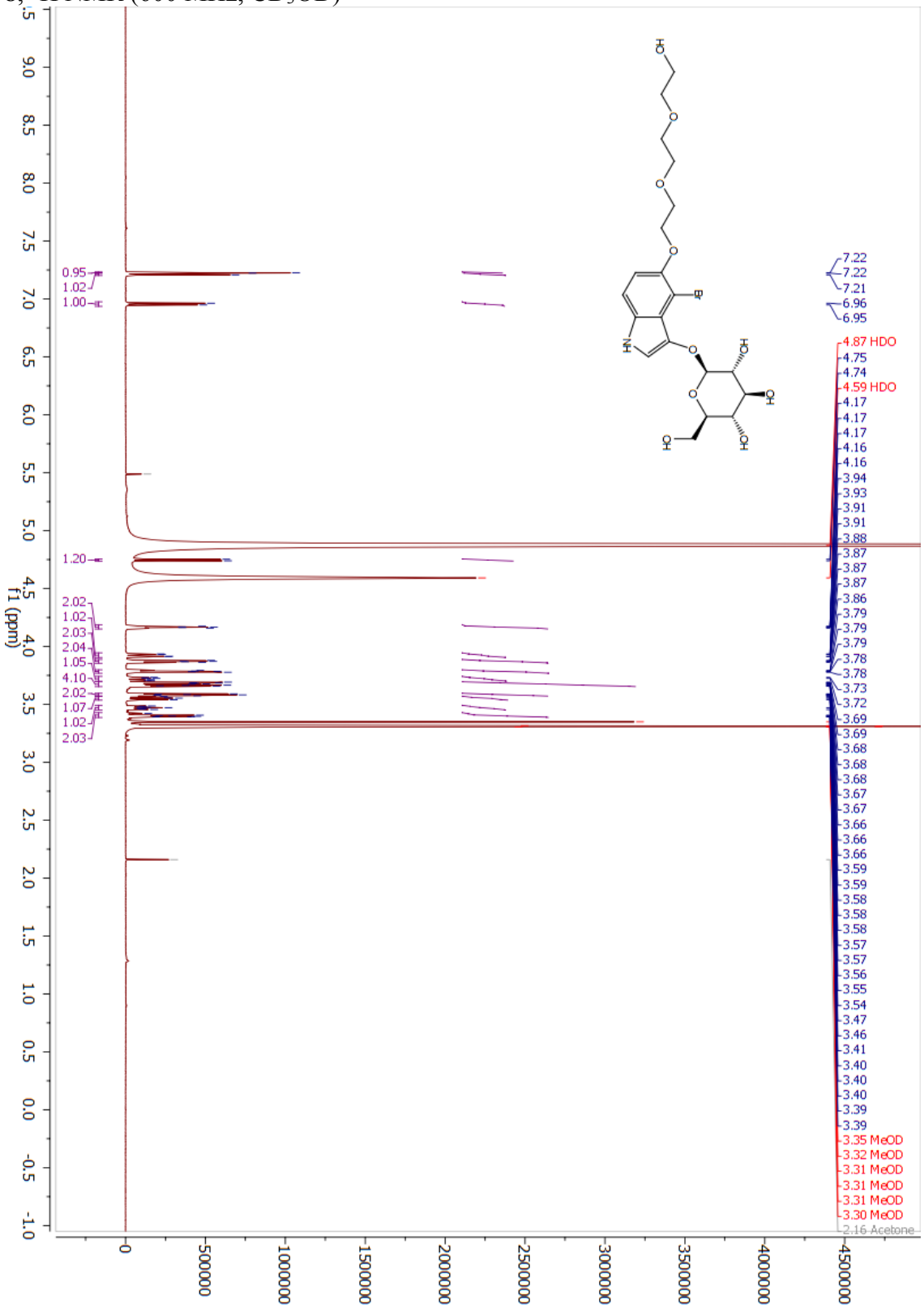

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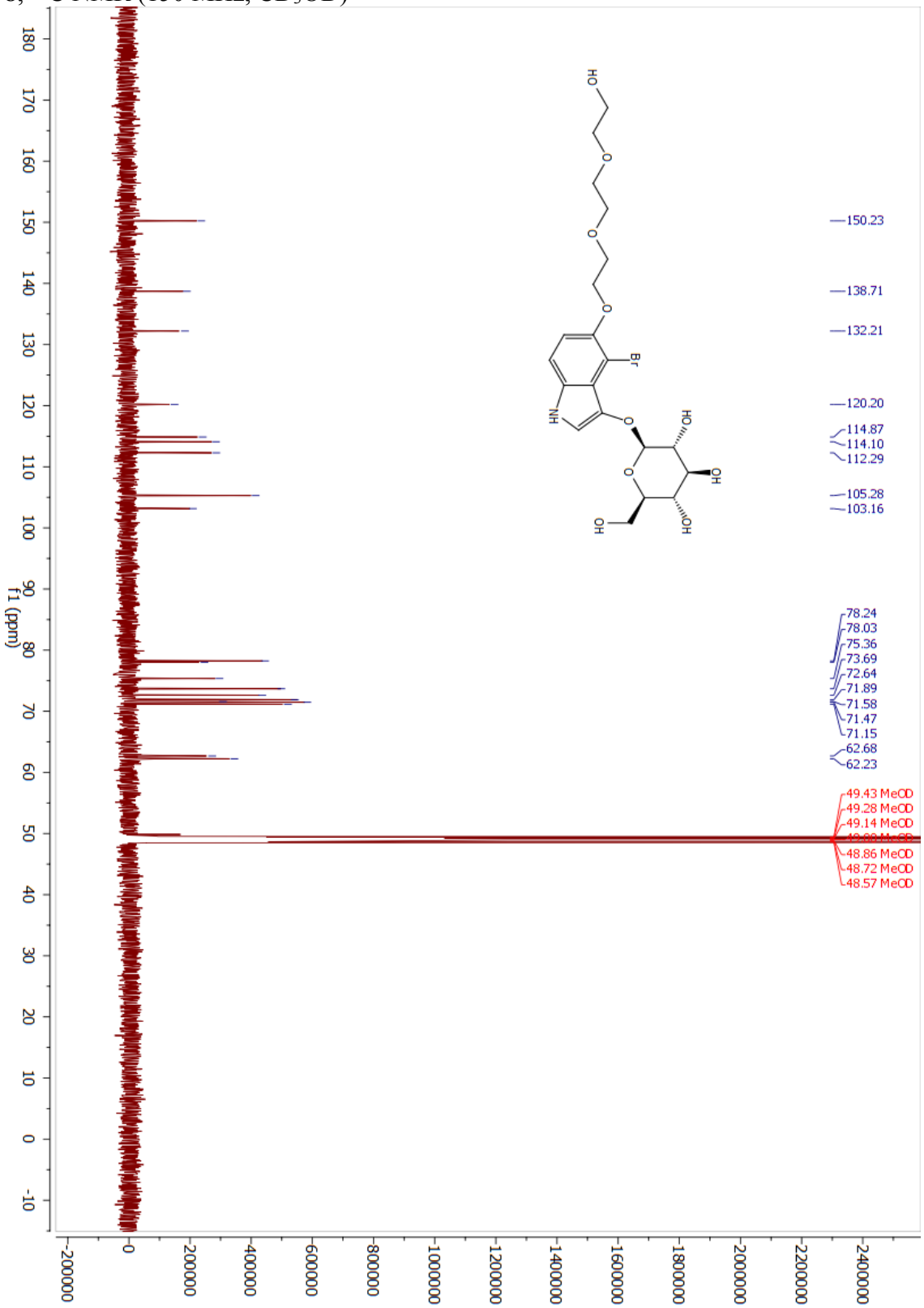
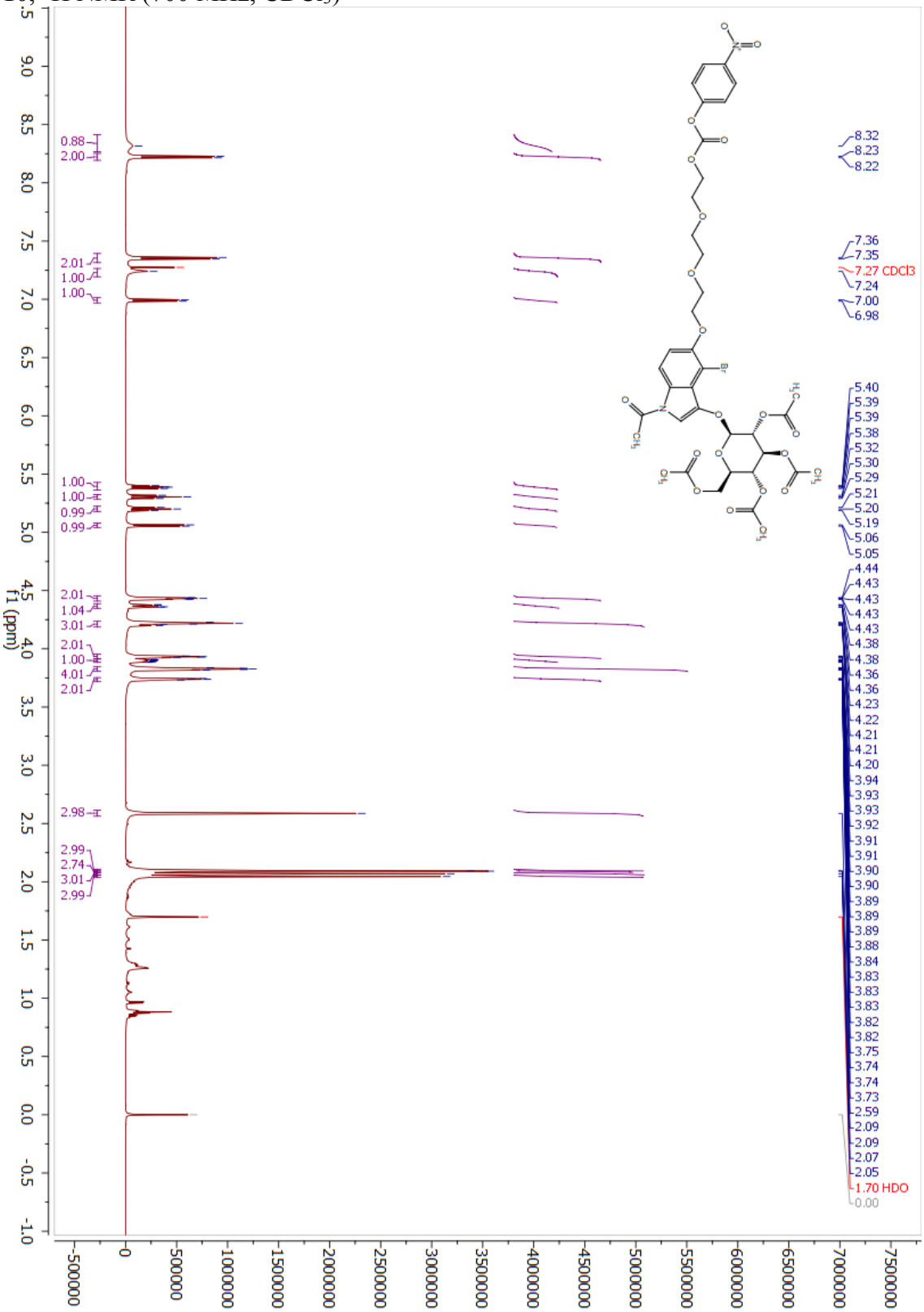
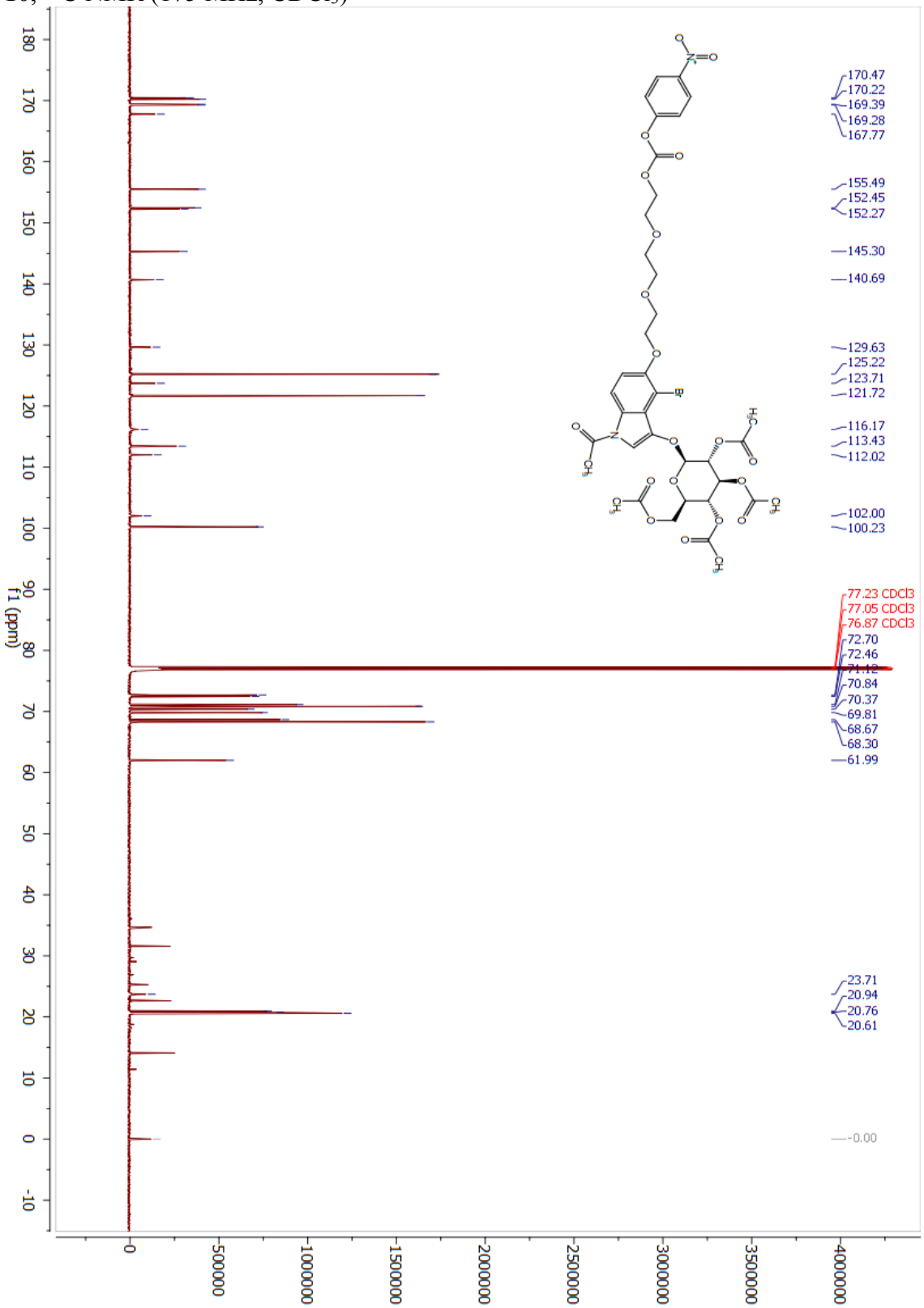


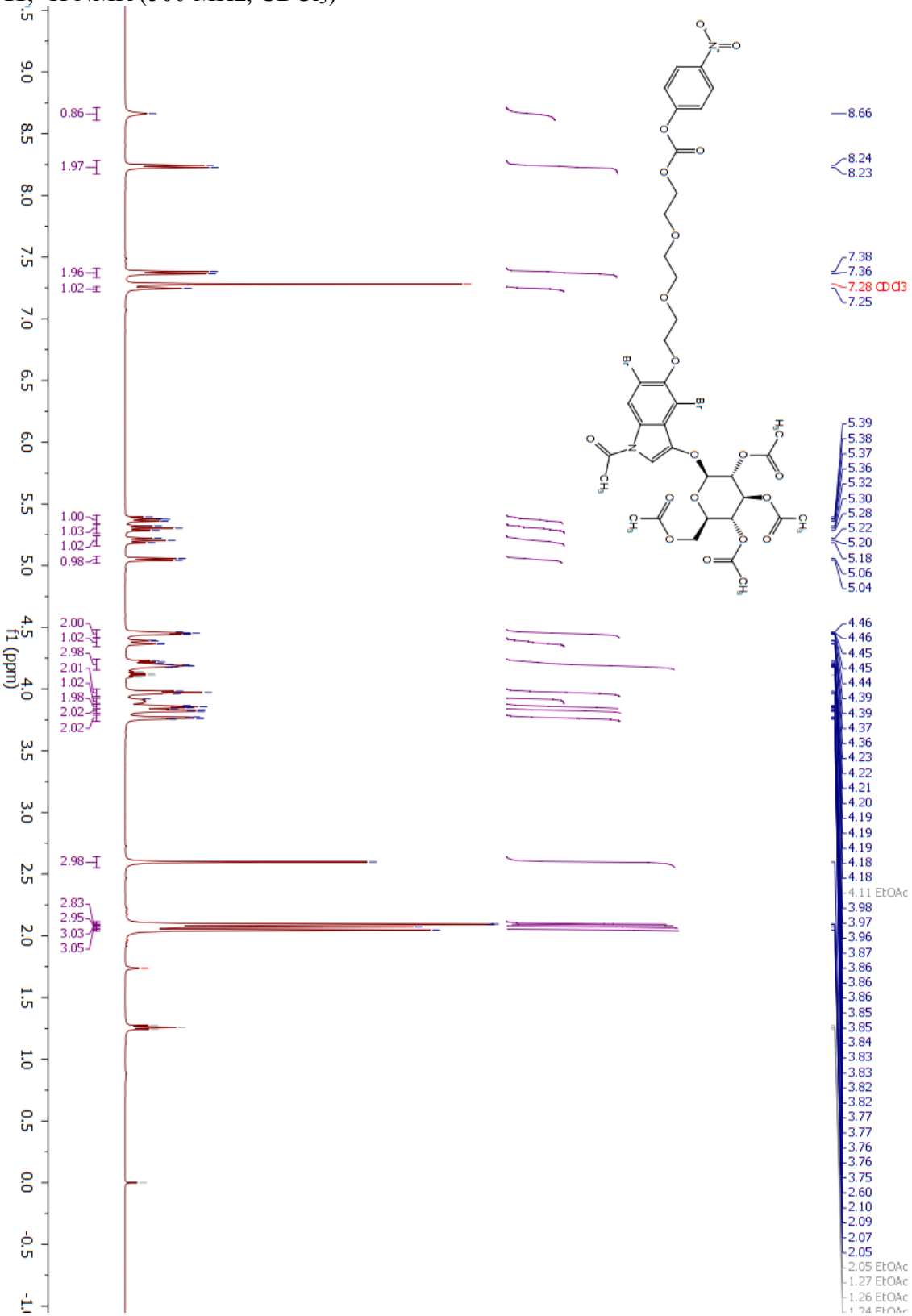
10, ^{1}H NMR (700 MHz, $CDCl_3$)



10, ^{13}C NMR (175 MHz, $CDCl_3$)



11, ^{1}H NMR (500 MHz, $CDCl_3$)



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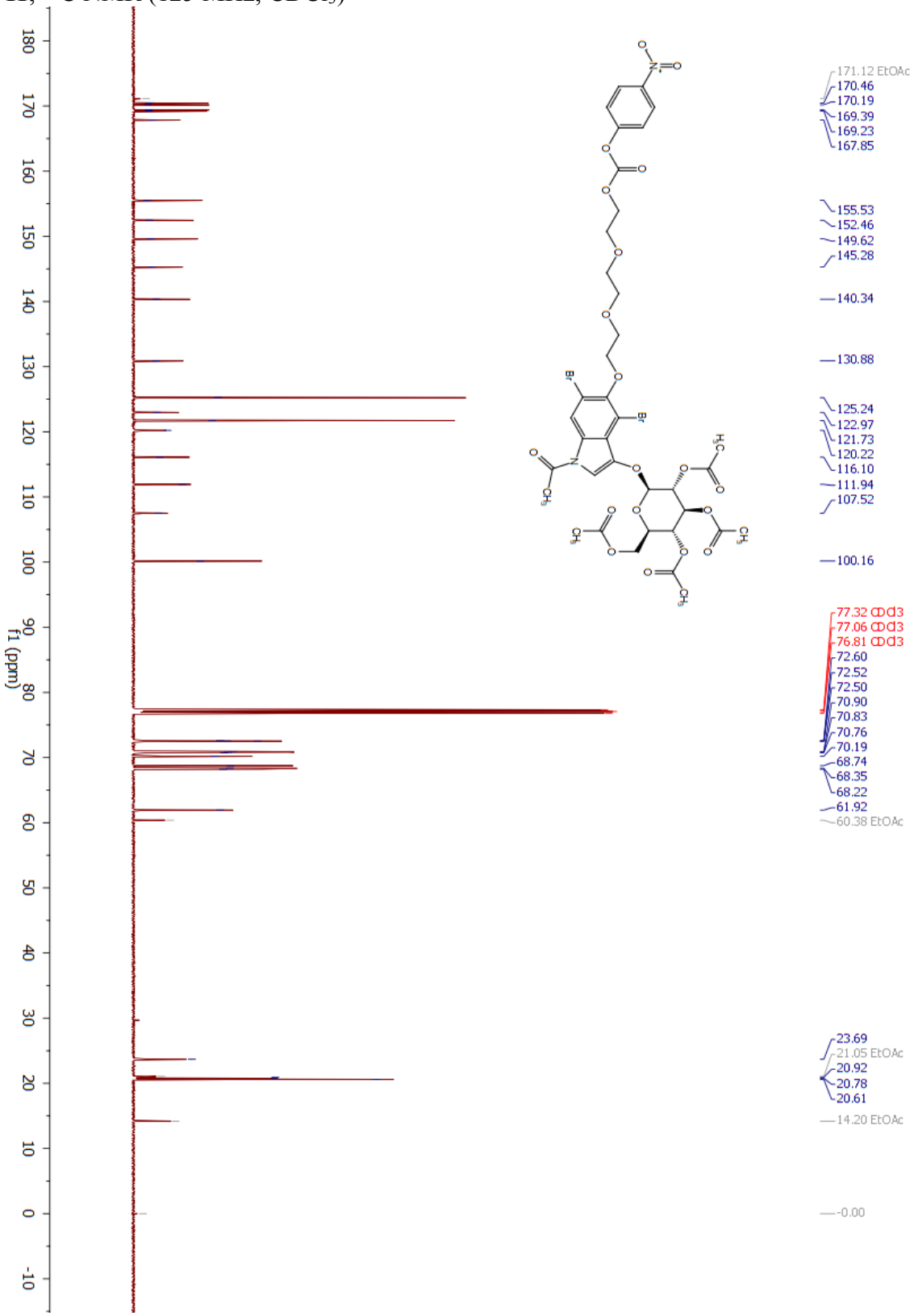

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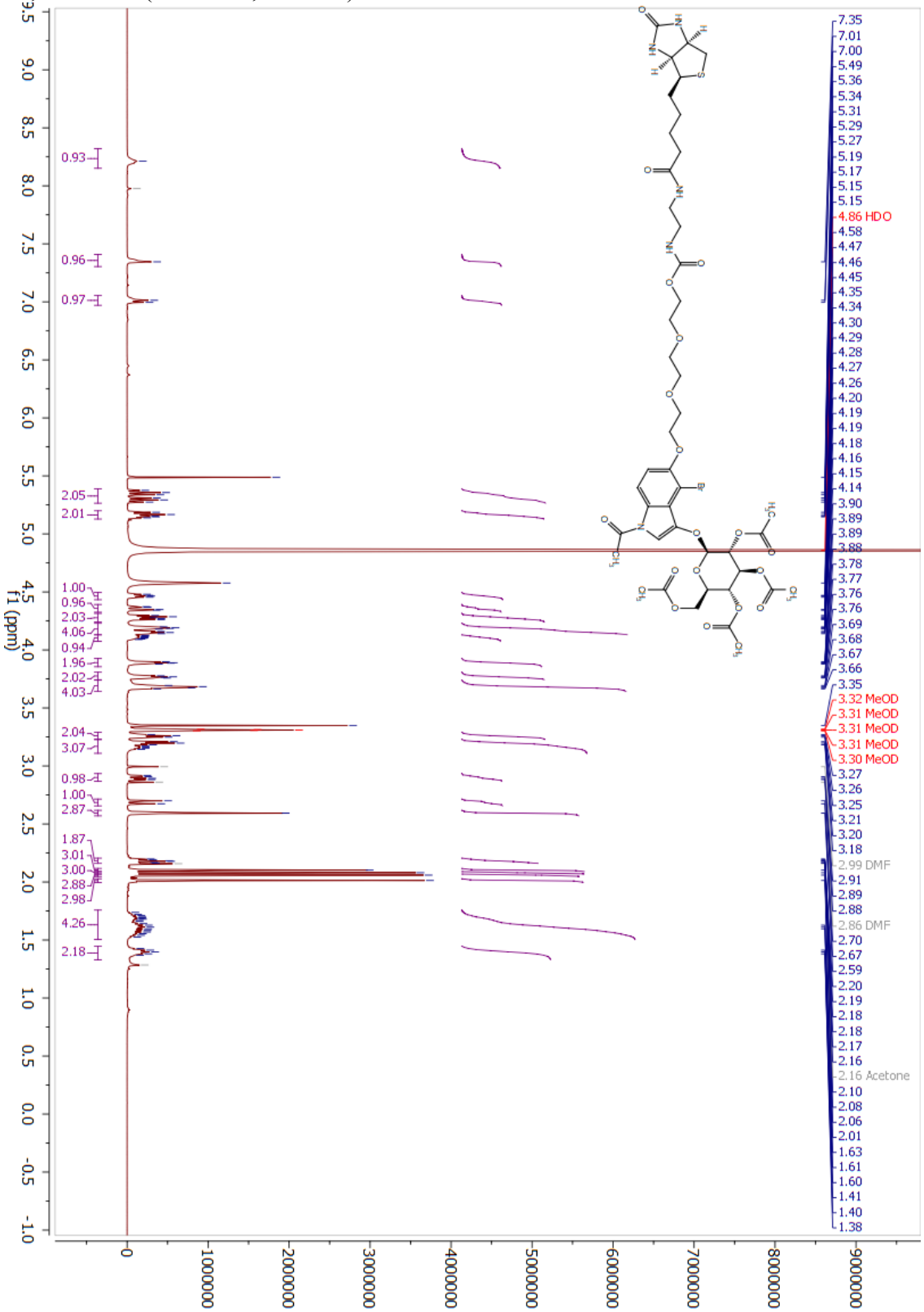

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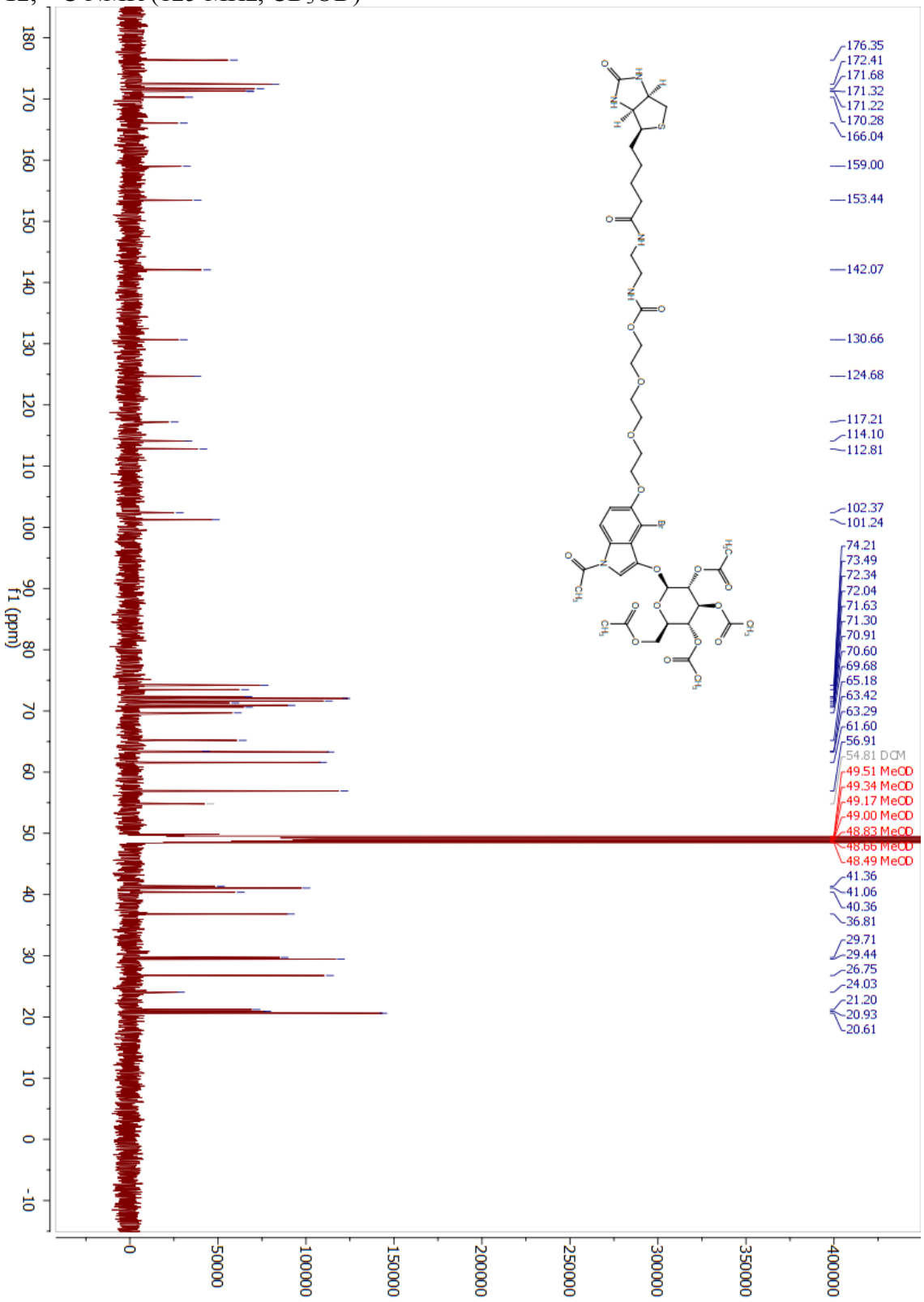

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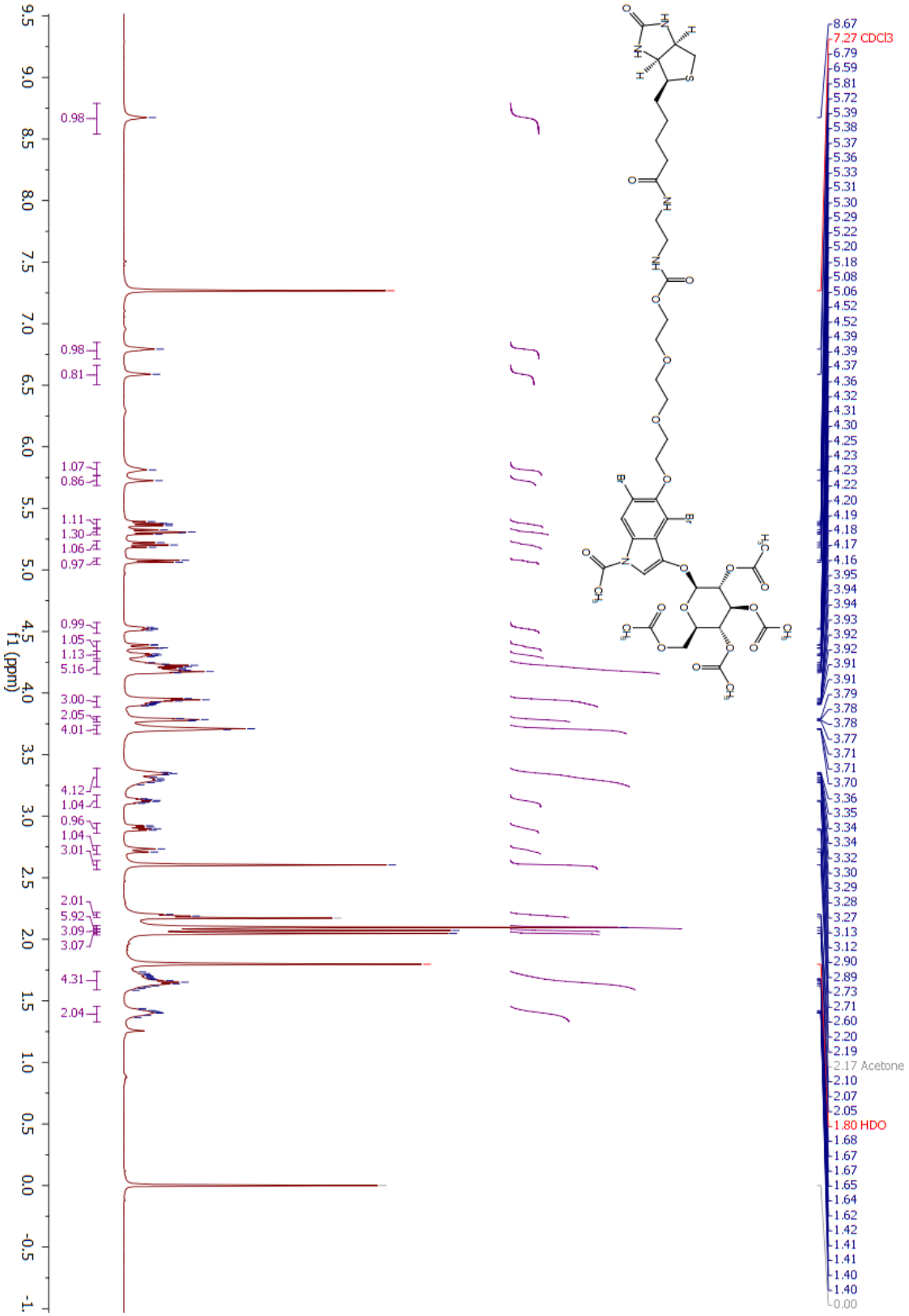

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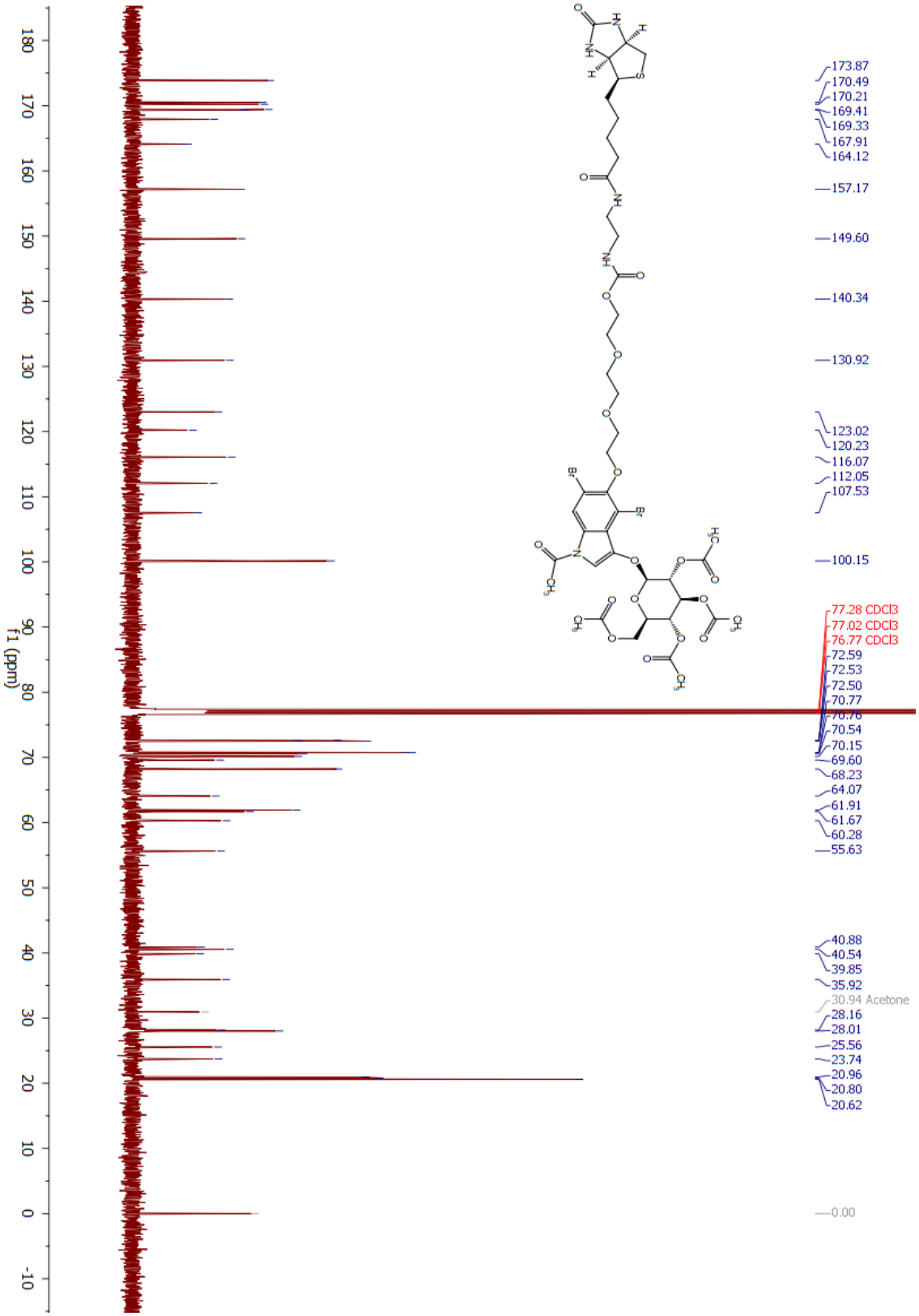
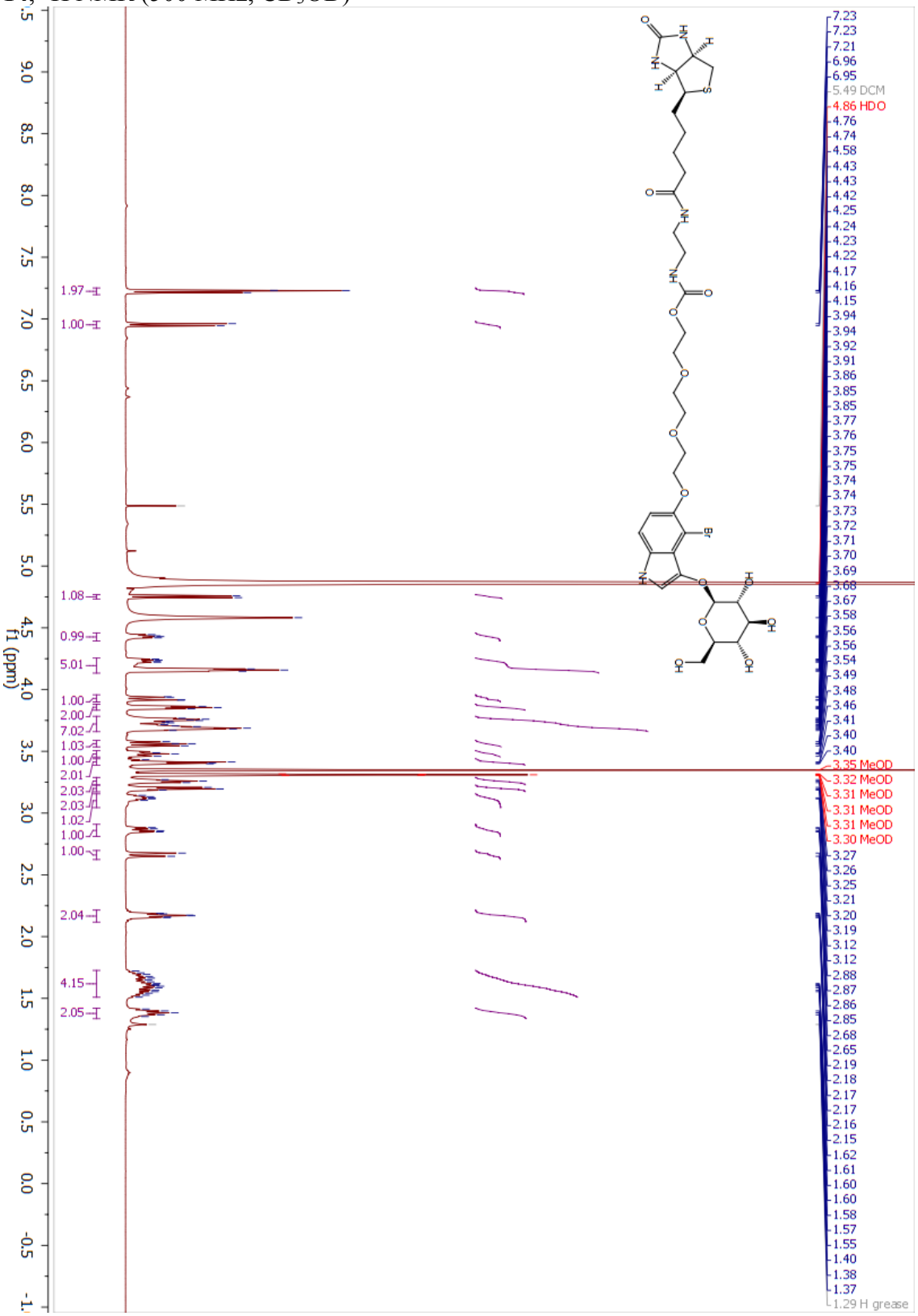


14, ^{1}H NMR (500 MHz, CD_3OD)



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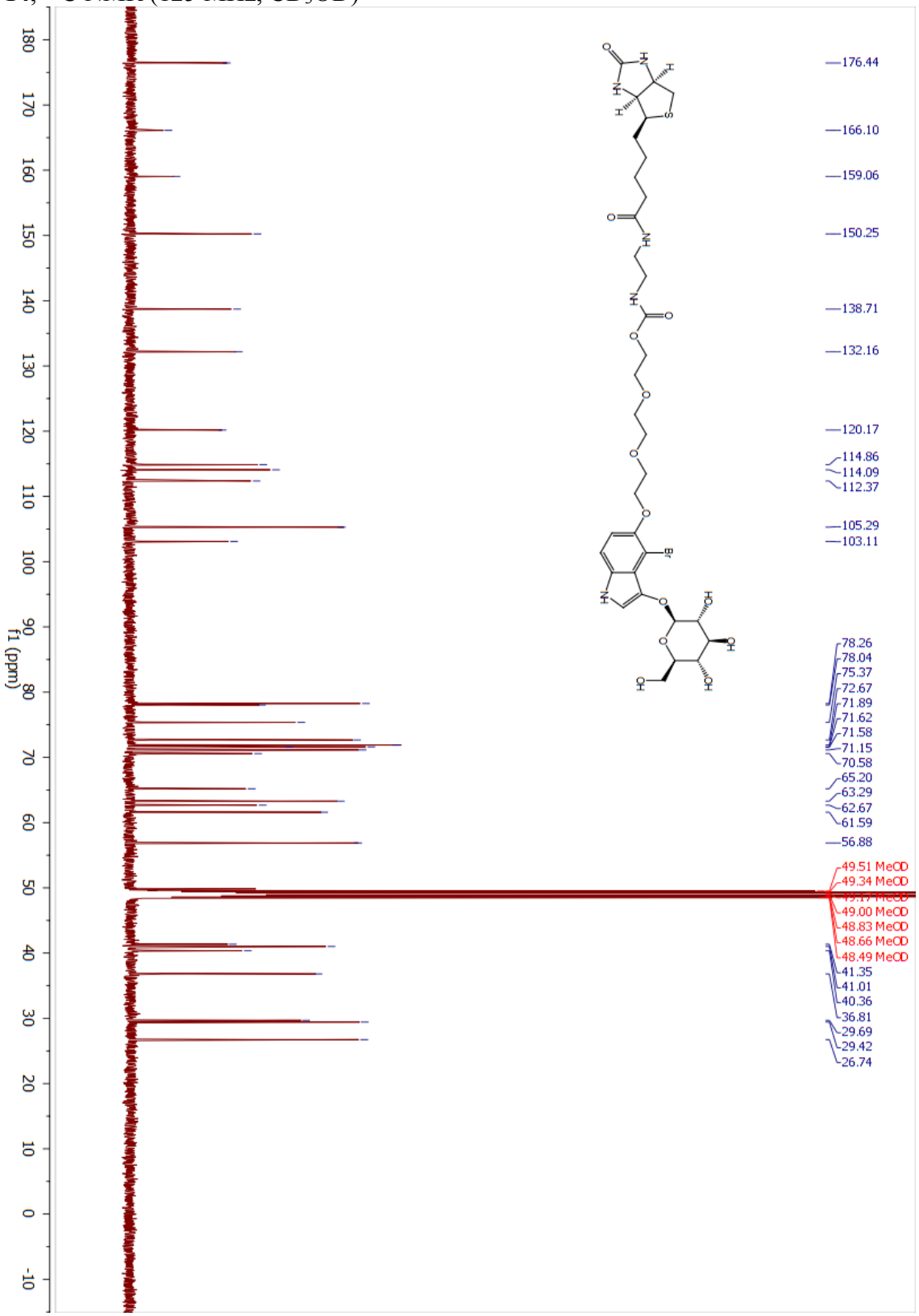

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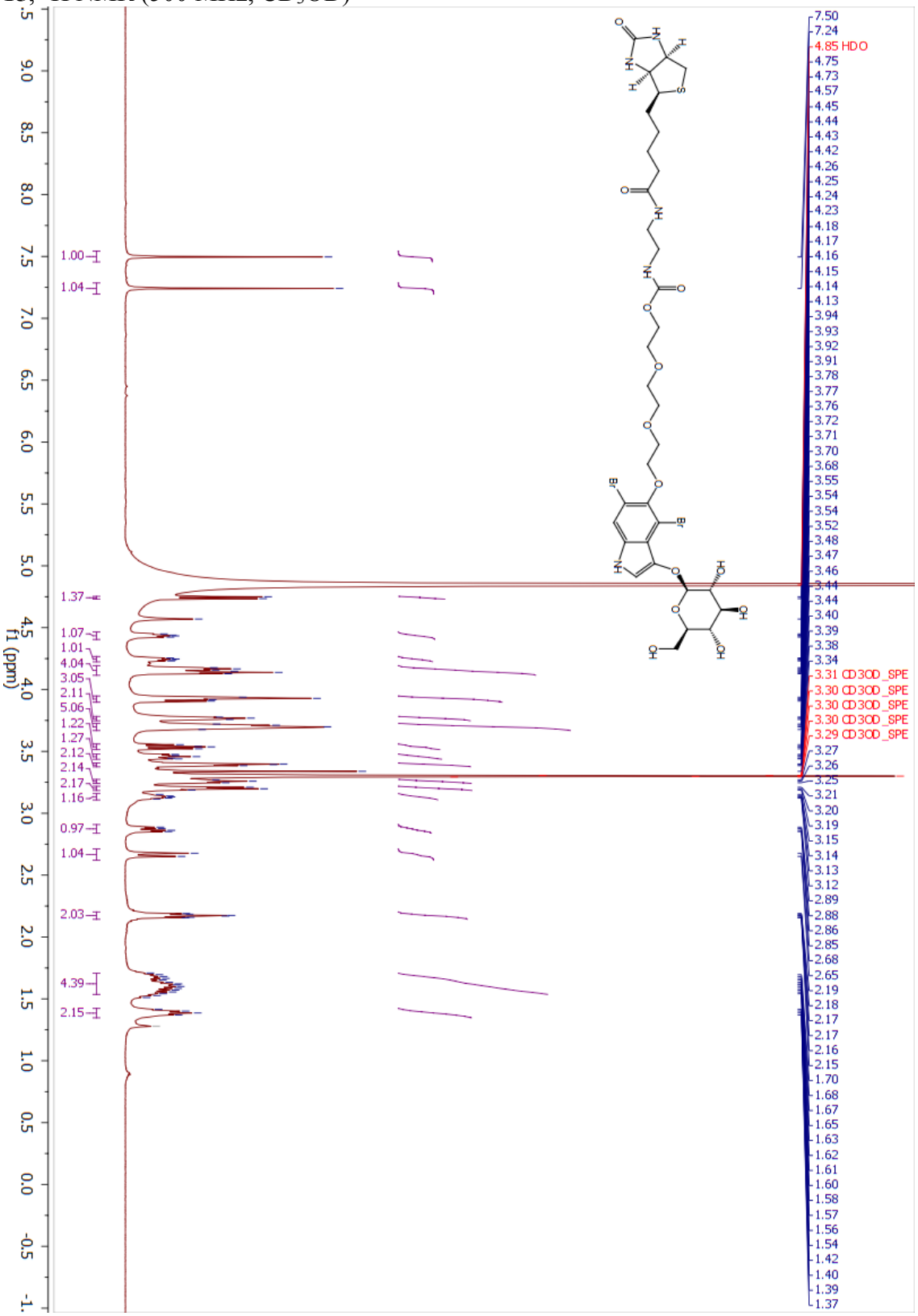

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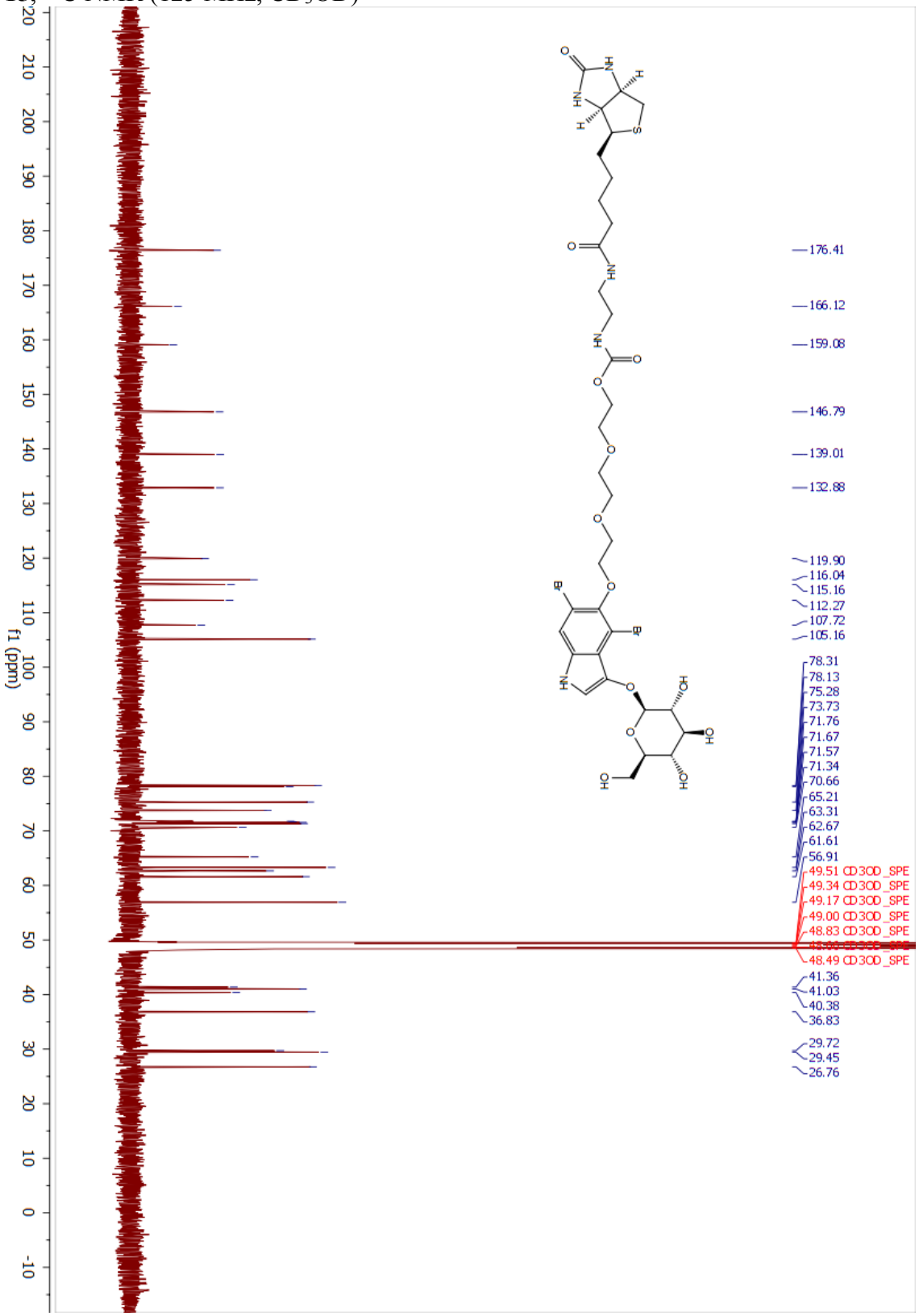

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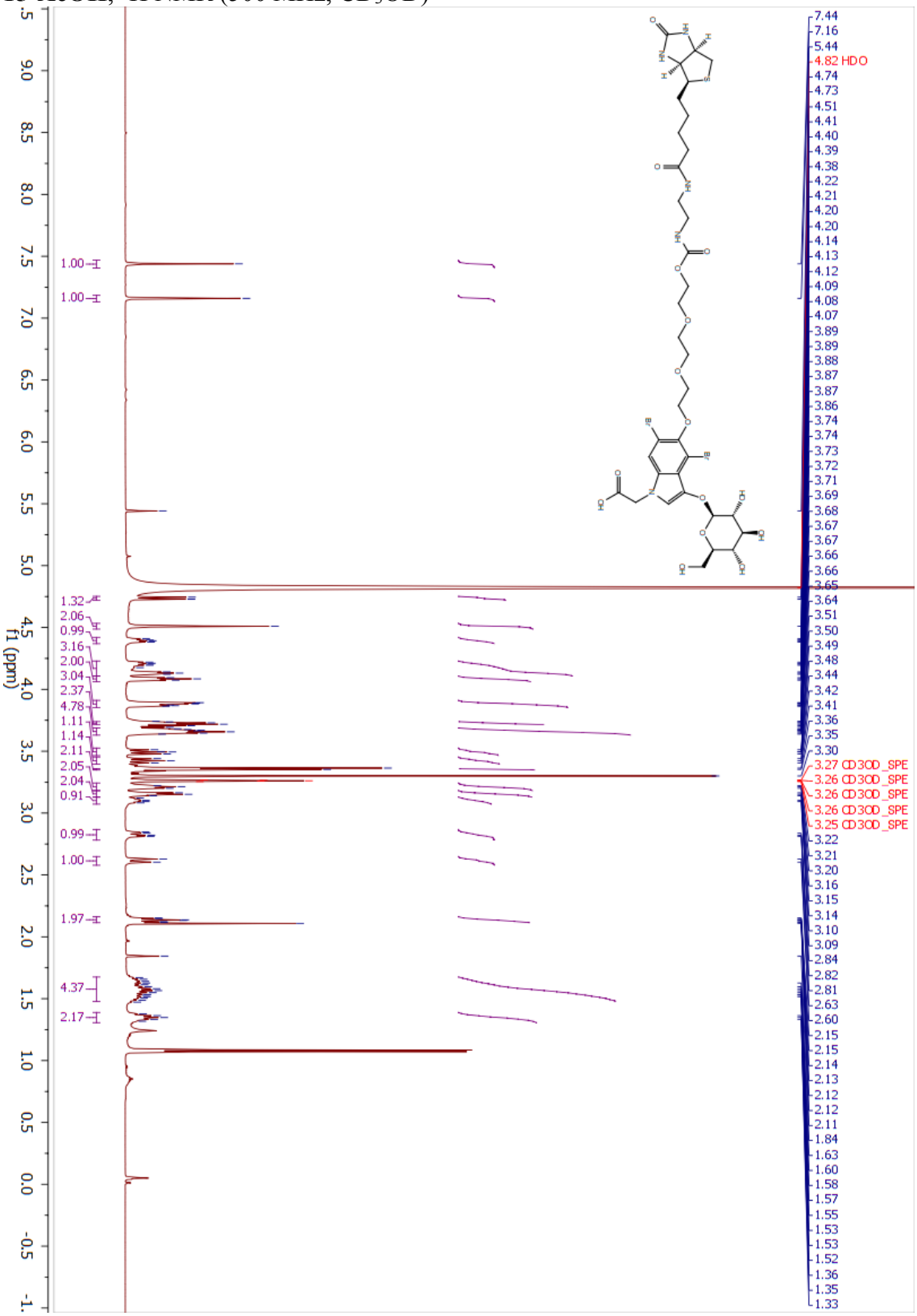

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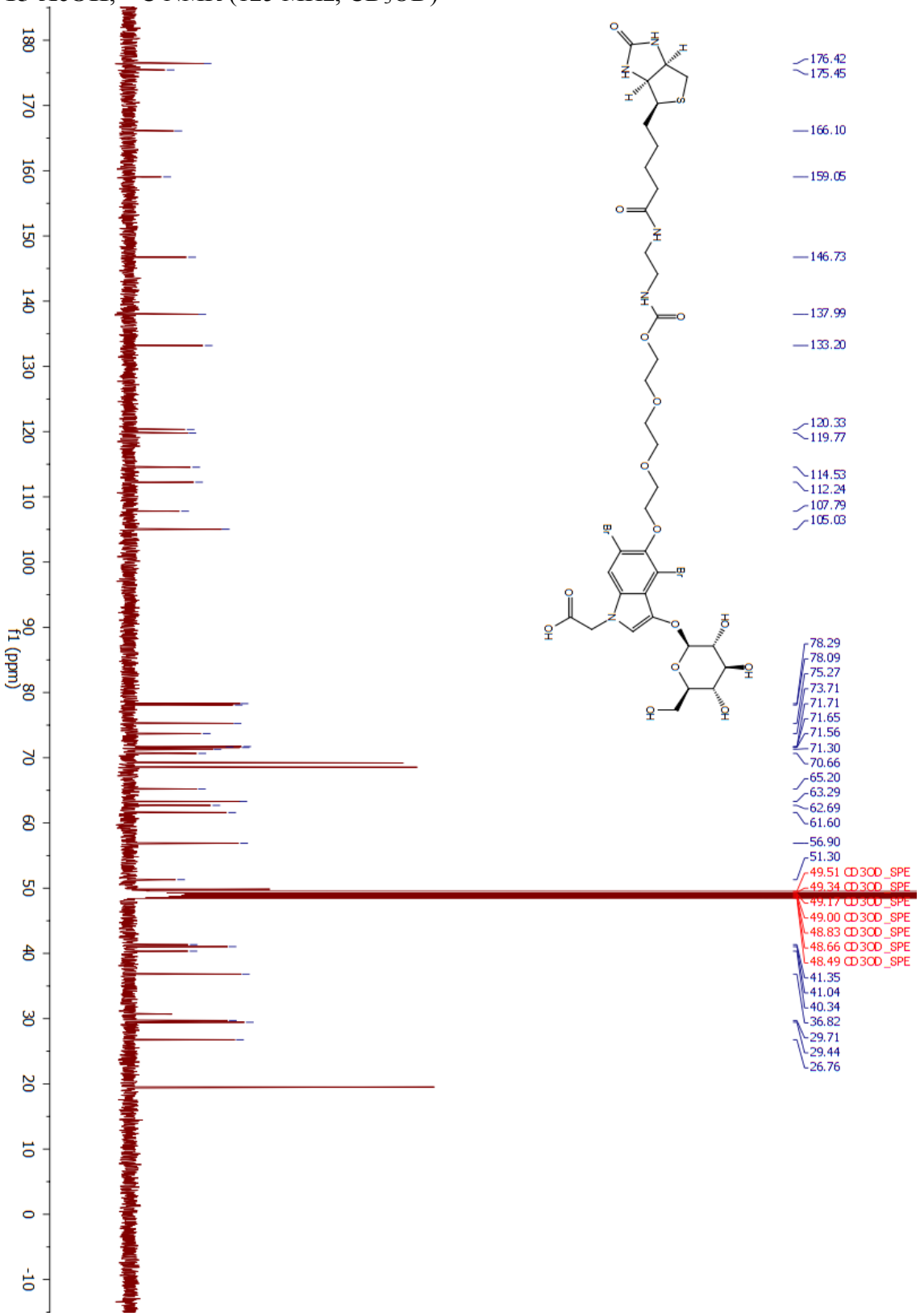

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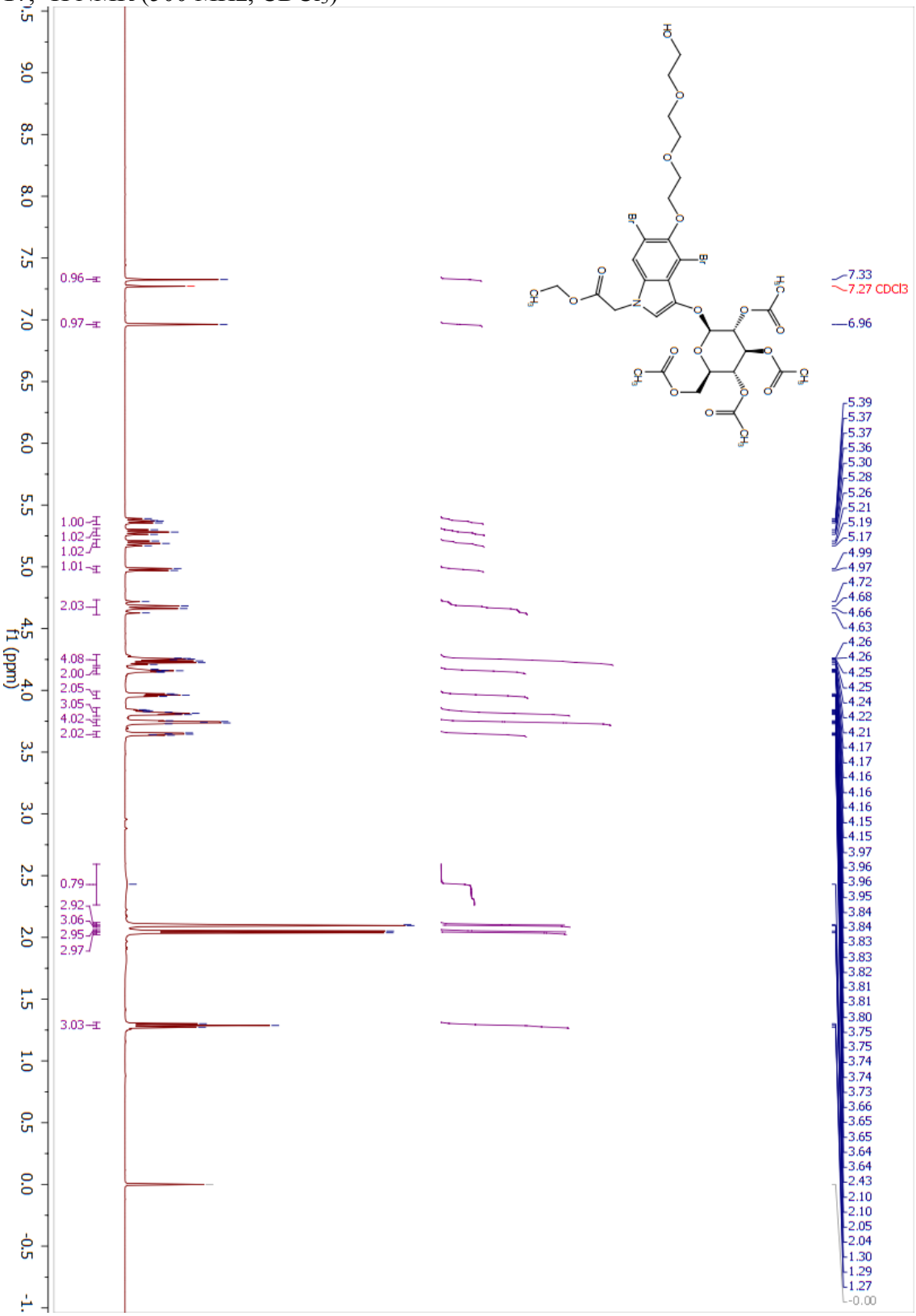
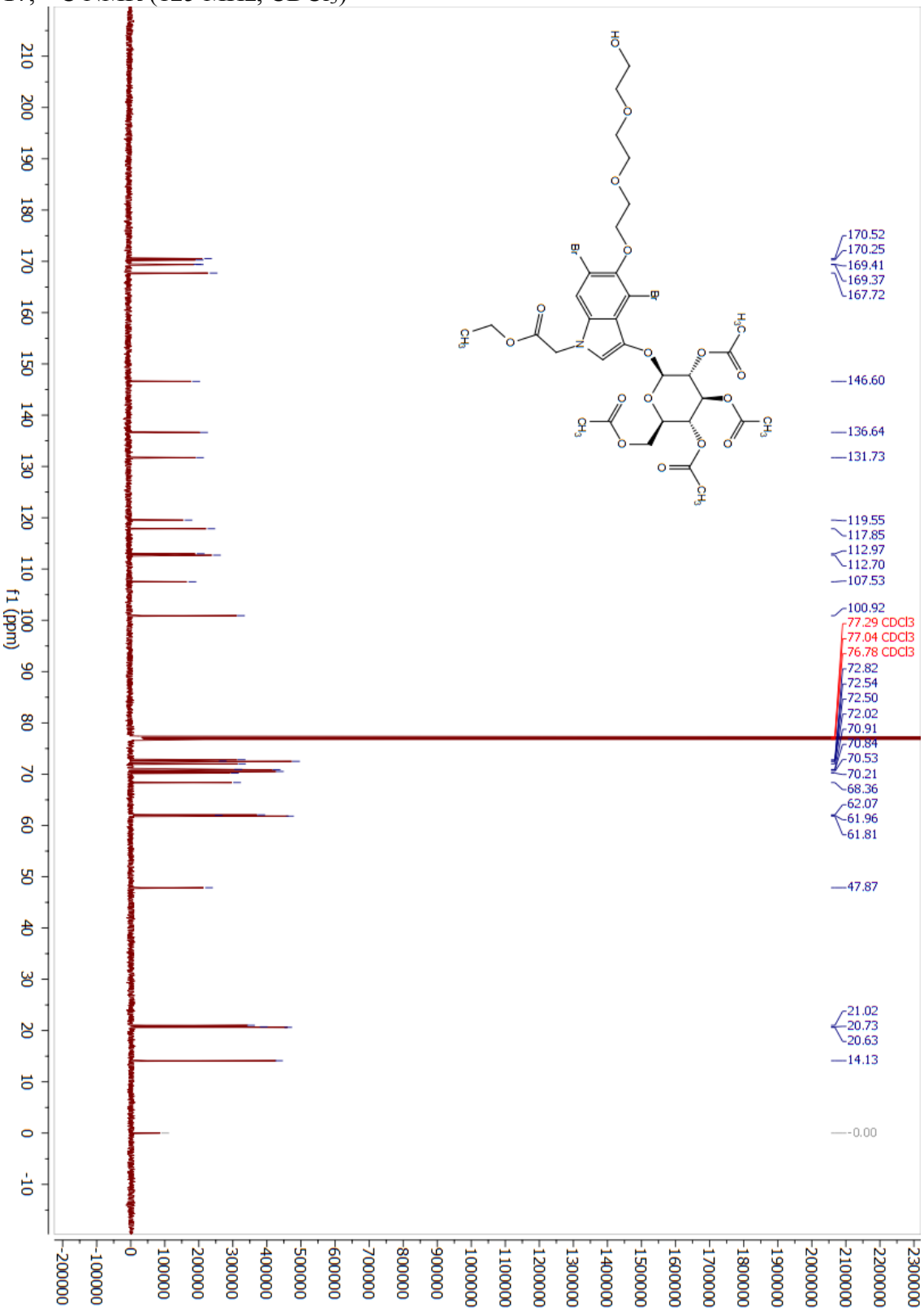
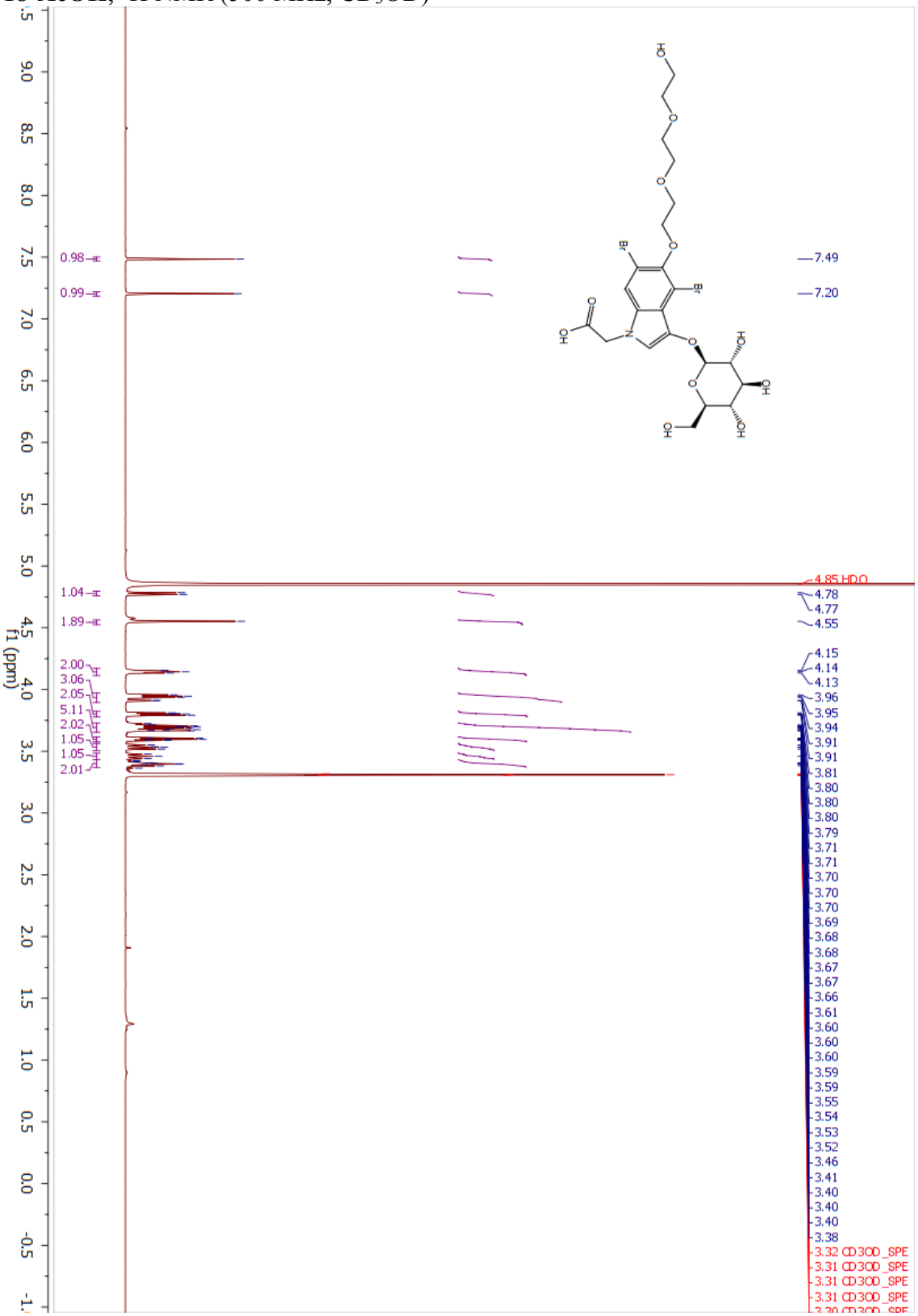


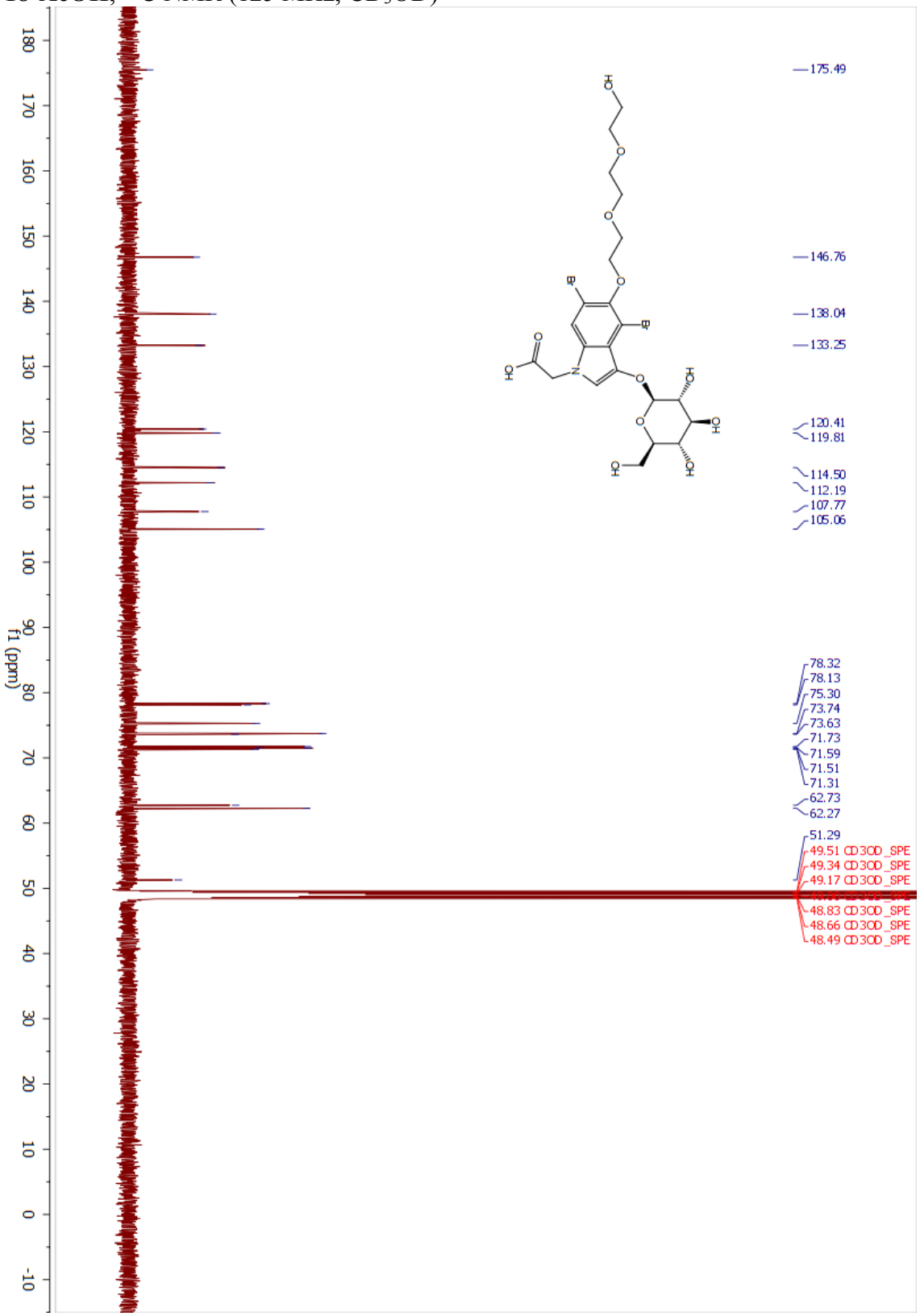
17, ^{13}C NMR (125 MHz, $CDCl_3$)



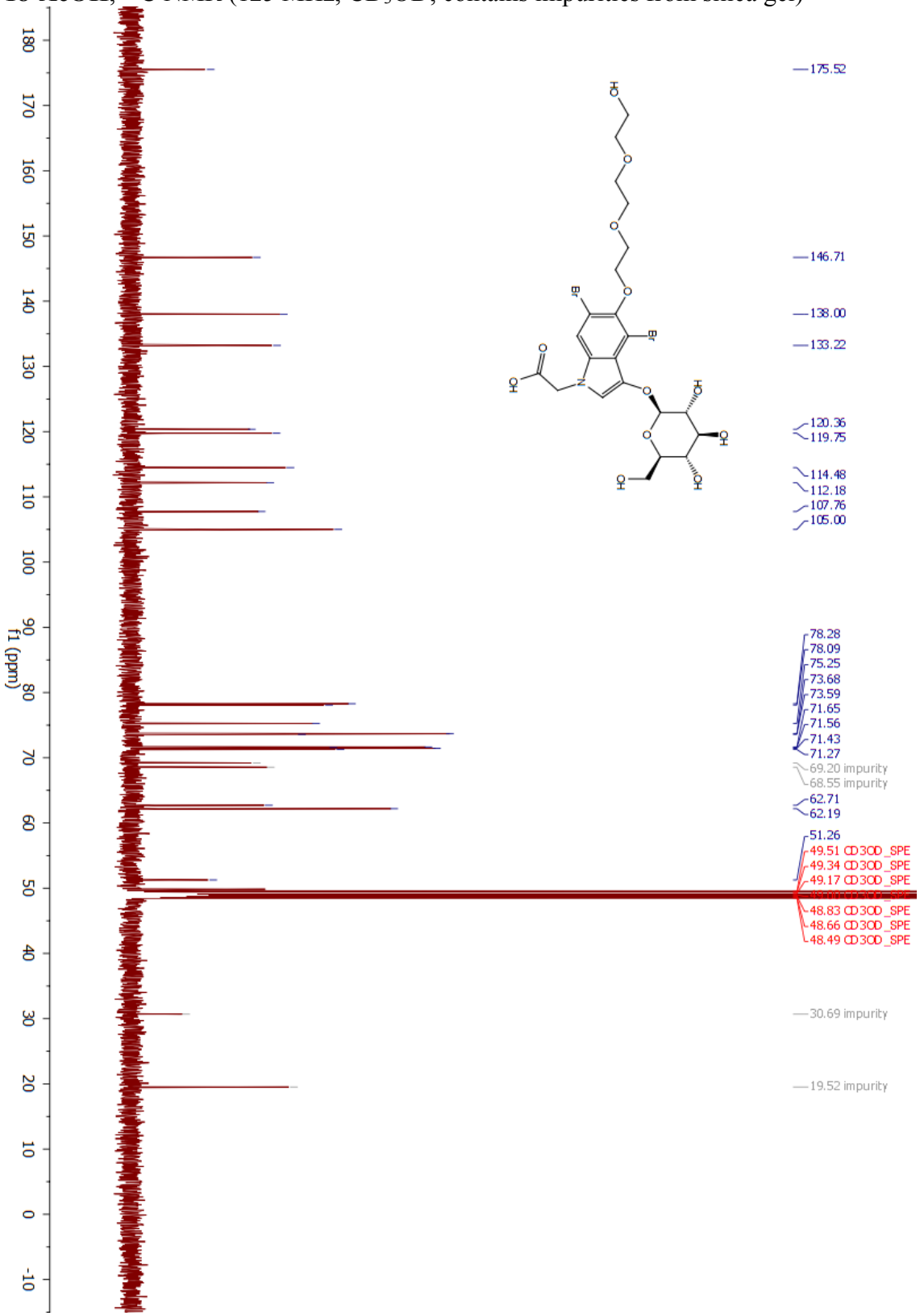
18-AcOH, ^{1}H NMR (500 MHz, CD_3OD)



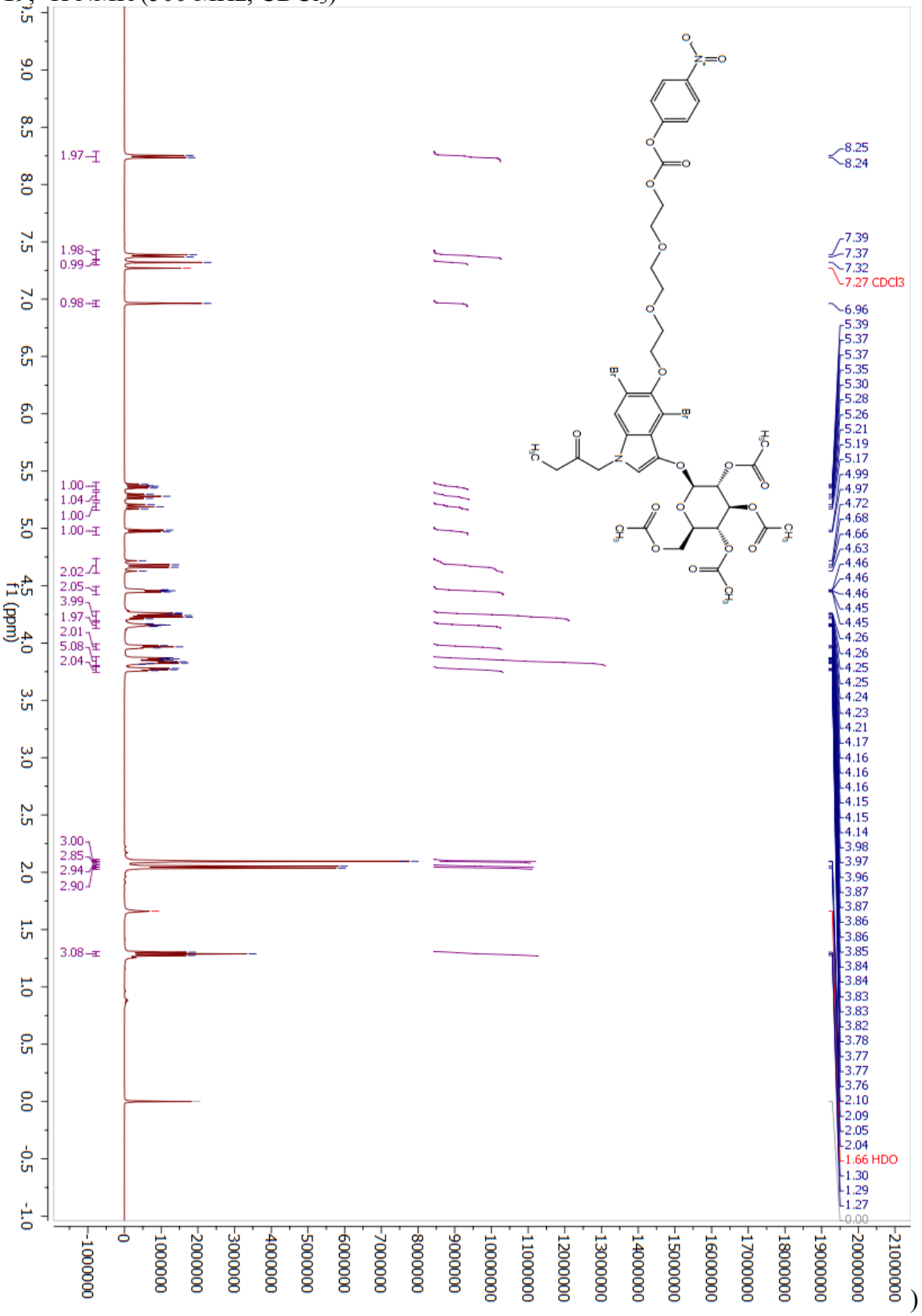
18-AcOH, ^{13}C NMR (125 MHz, CD_3OD)



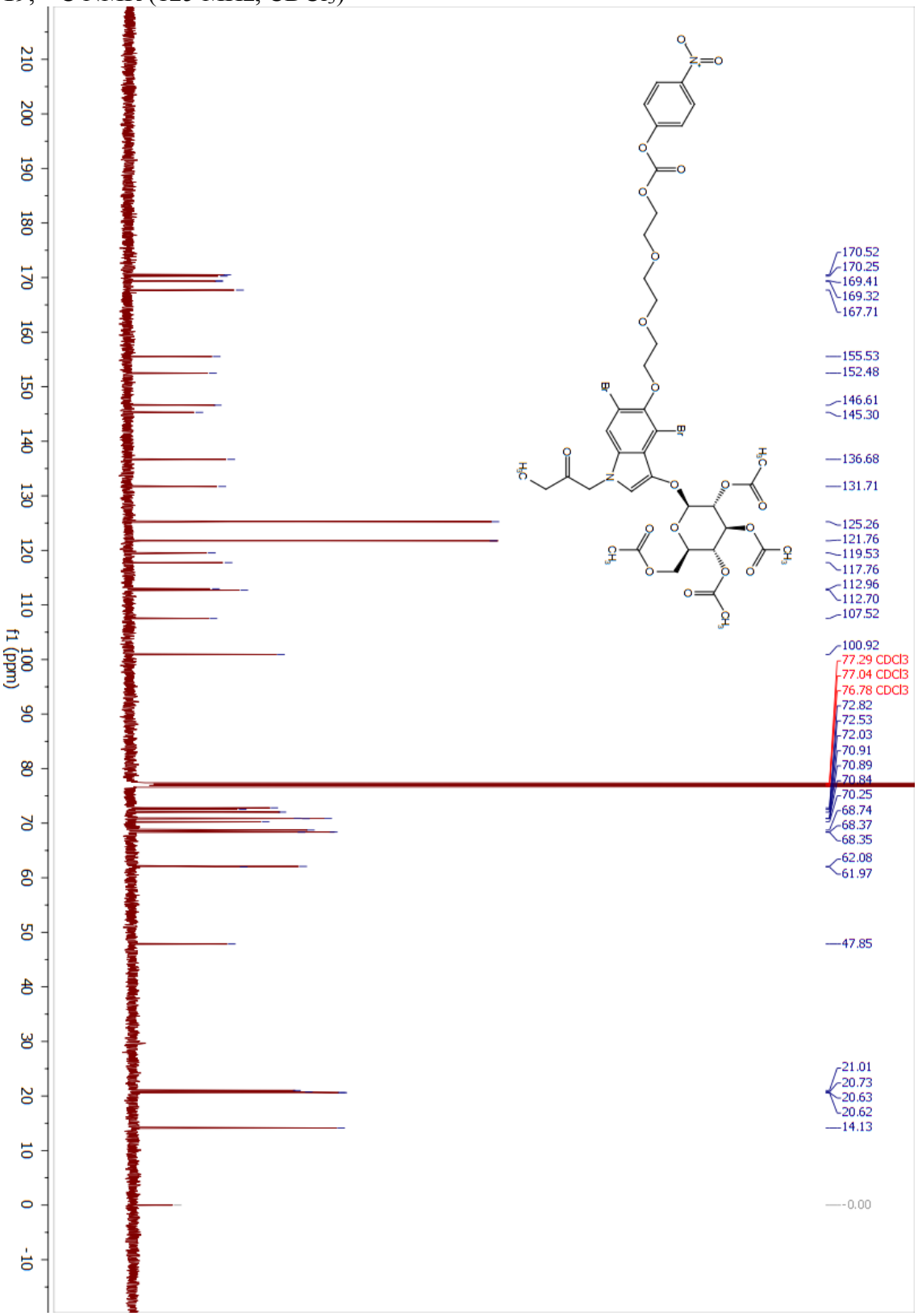
18-AcOH, ^{13}C NMR (125 MHz, CD_3OD, contains impurities from silica gel)



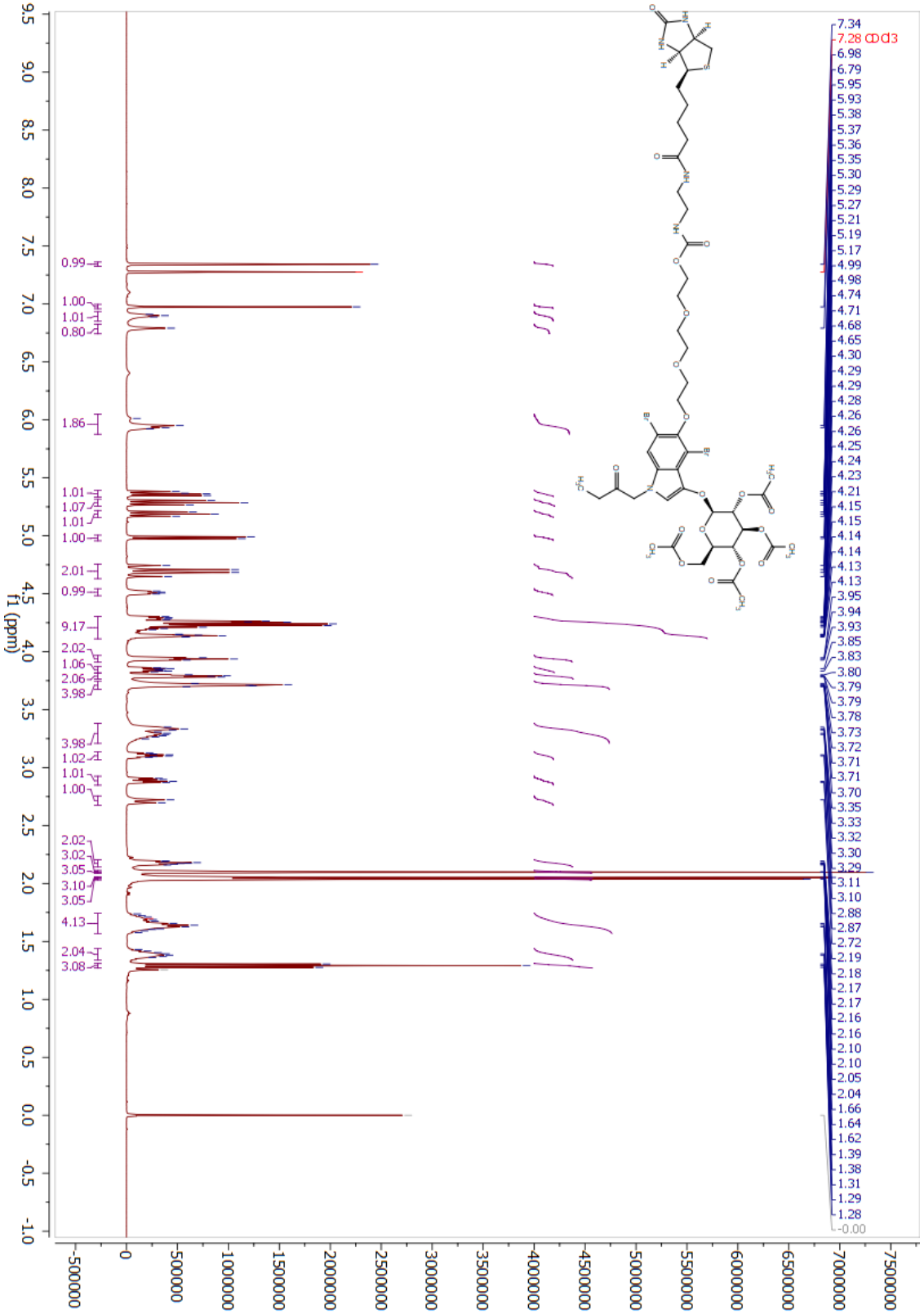
19, ^{1}H NMR (500 MHz, $CDCl_3$)



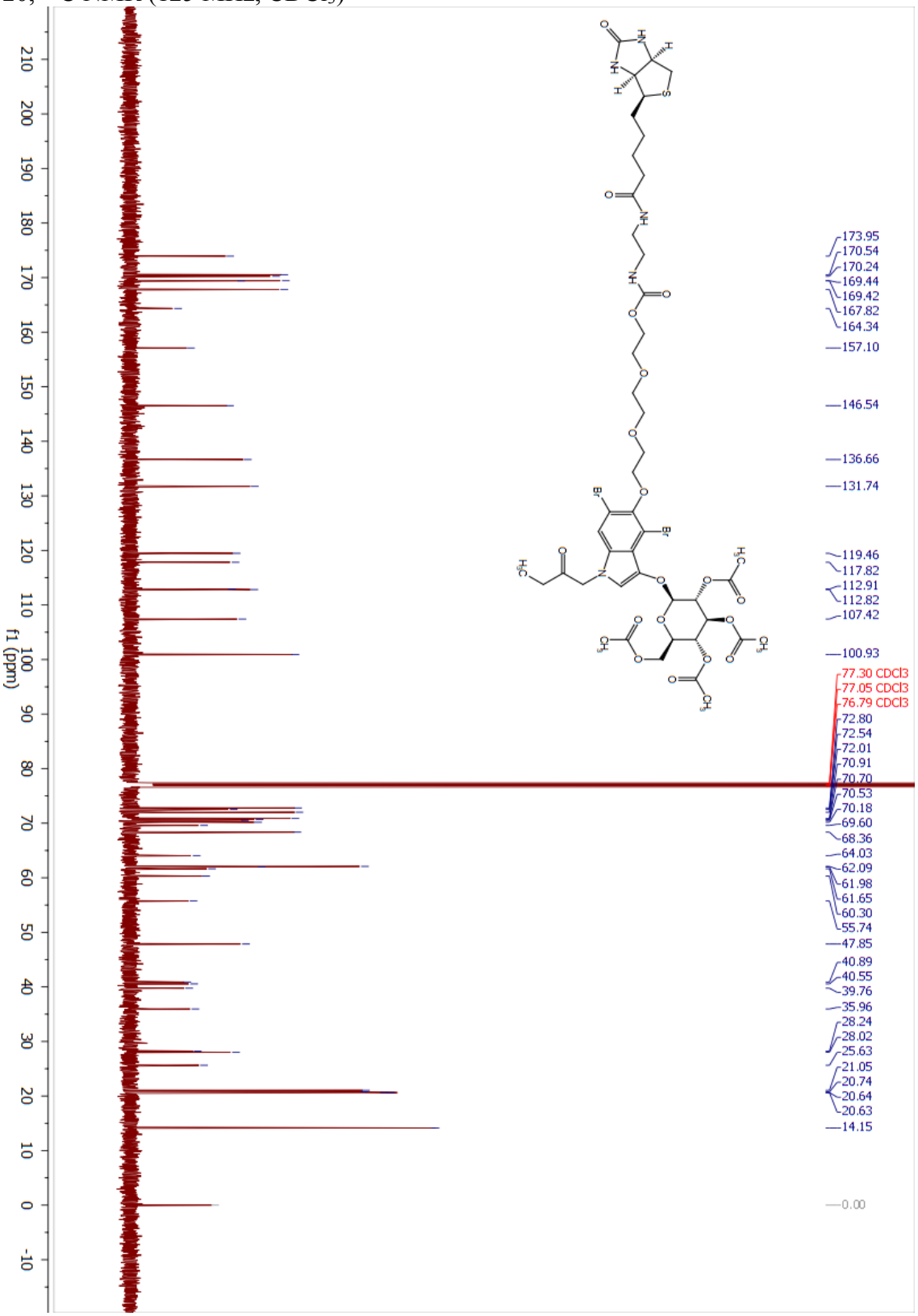
19, ^{13}C NMR (125 MHz, $CDCl_3$)



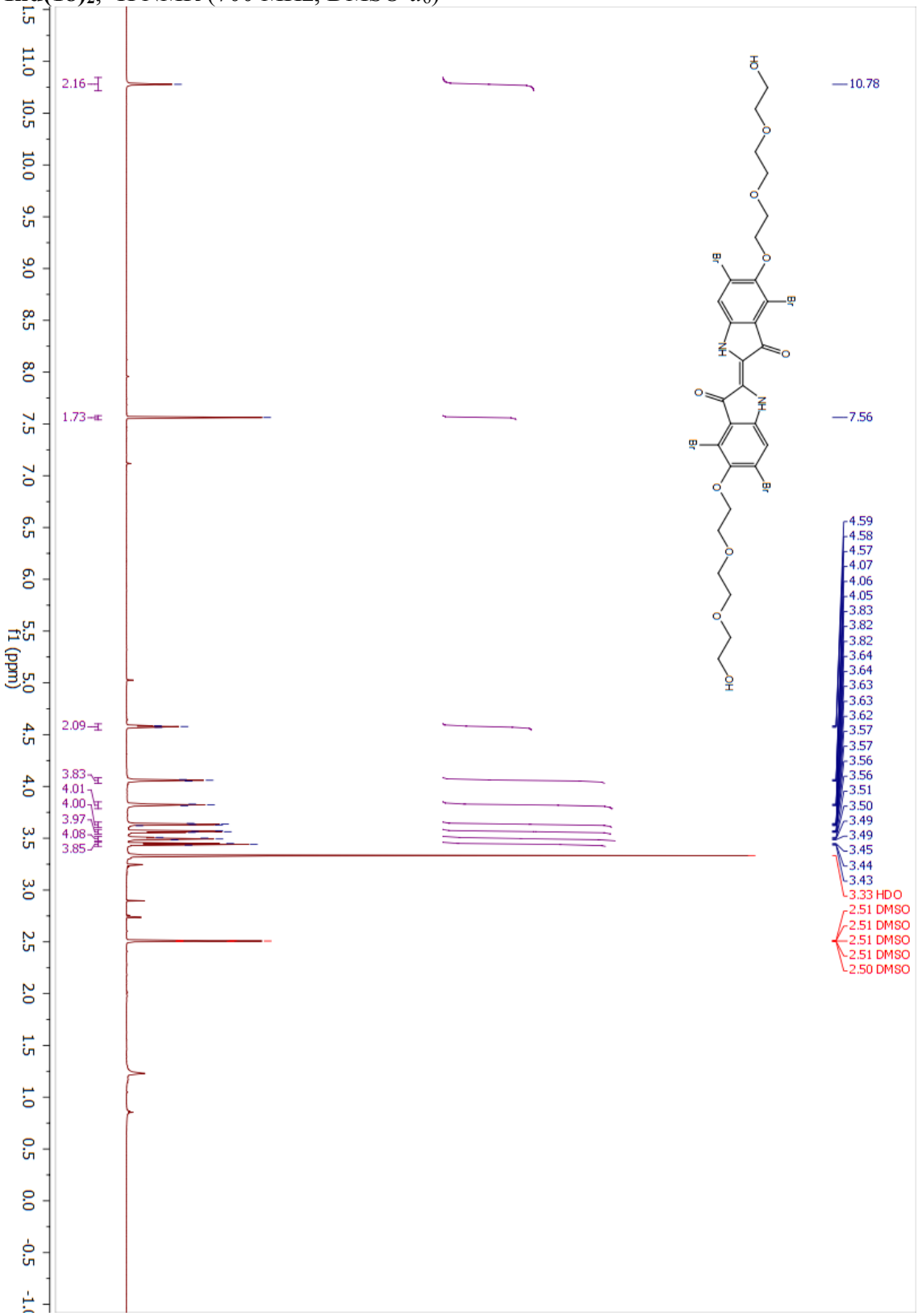
20, ^{1}H NMR (500 MHz, $CDCl_3$)



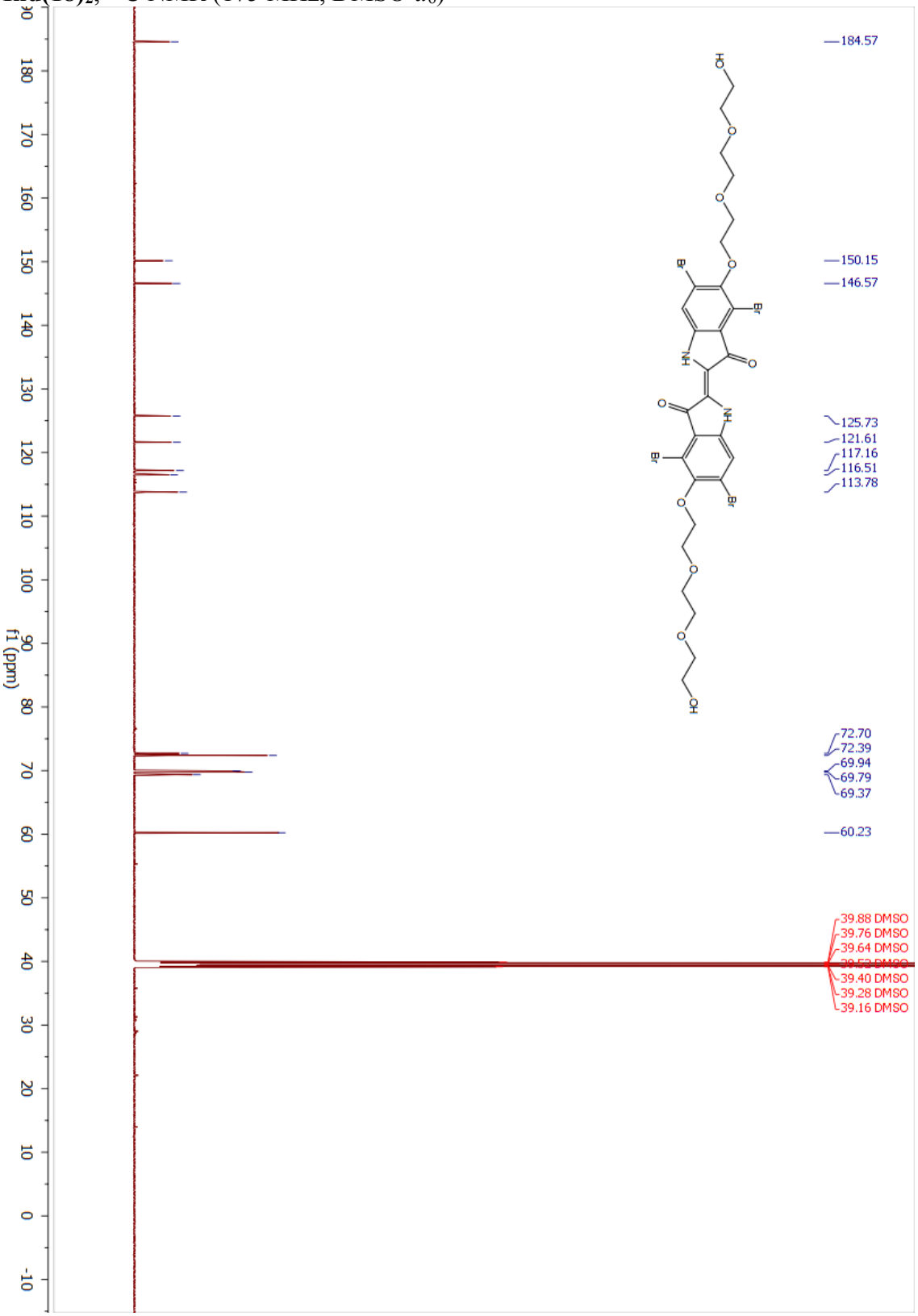
20, ^{13}C NMR (125 MHz, $CDCl_3$)



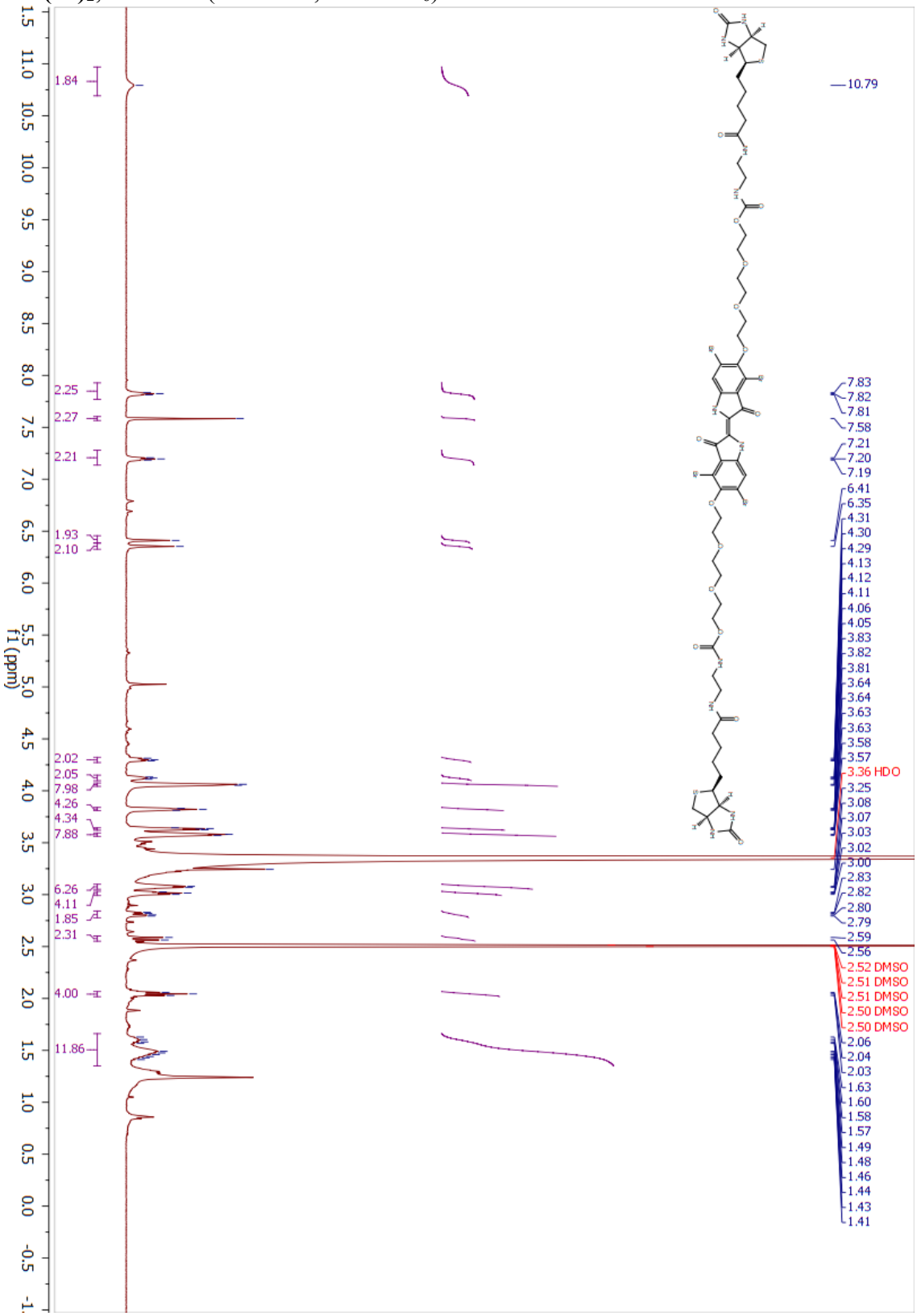
Ind(18)$_2$, ^{1}H NMR (700 MHz, DMSO-d_6)



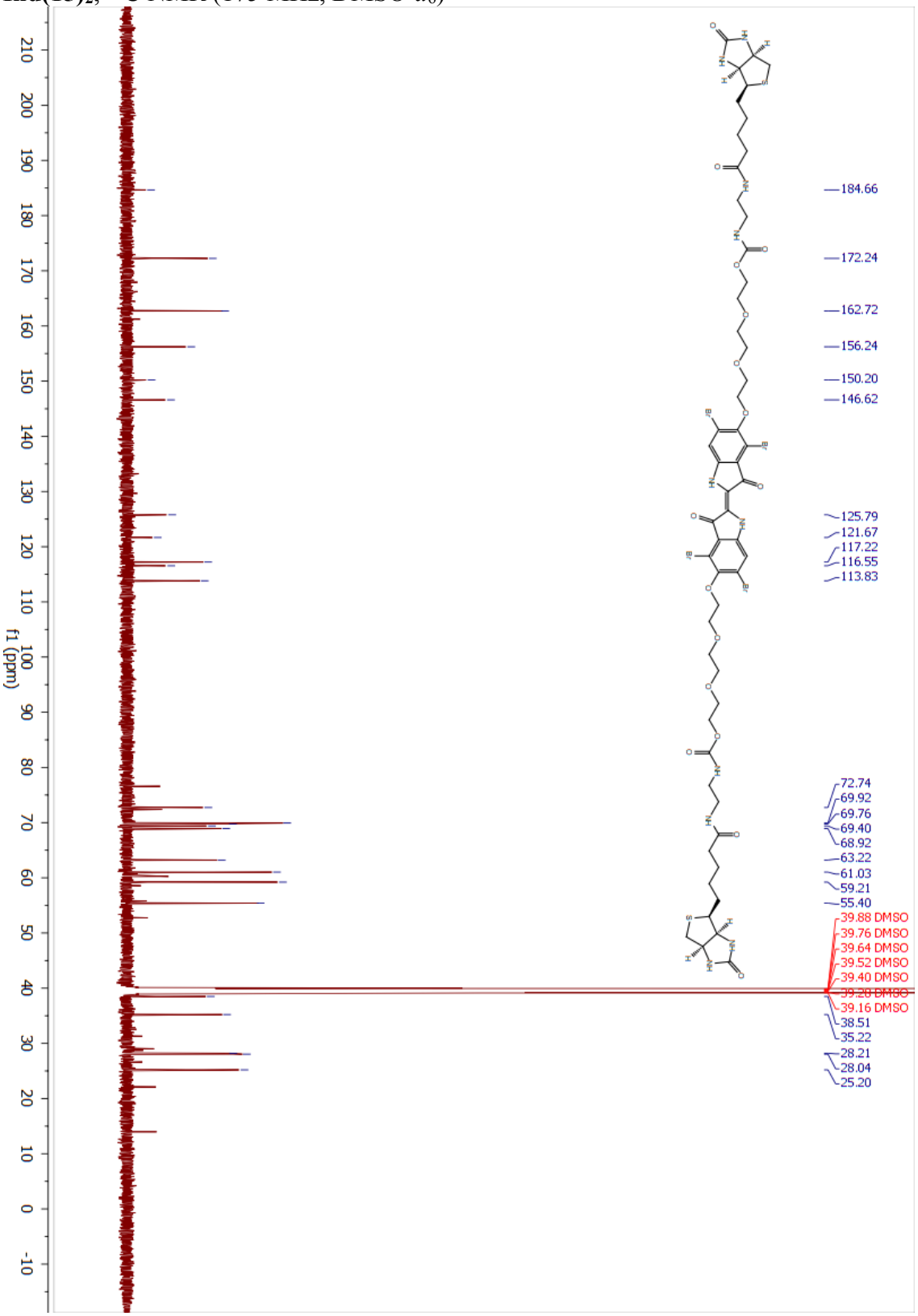
Ind(18)$_2$, ^{13}C NMR (175 MHz, DMSO-d_6)



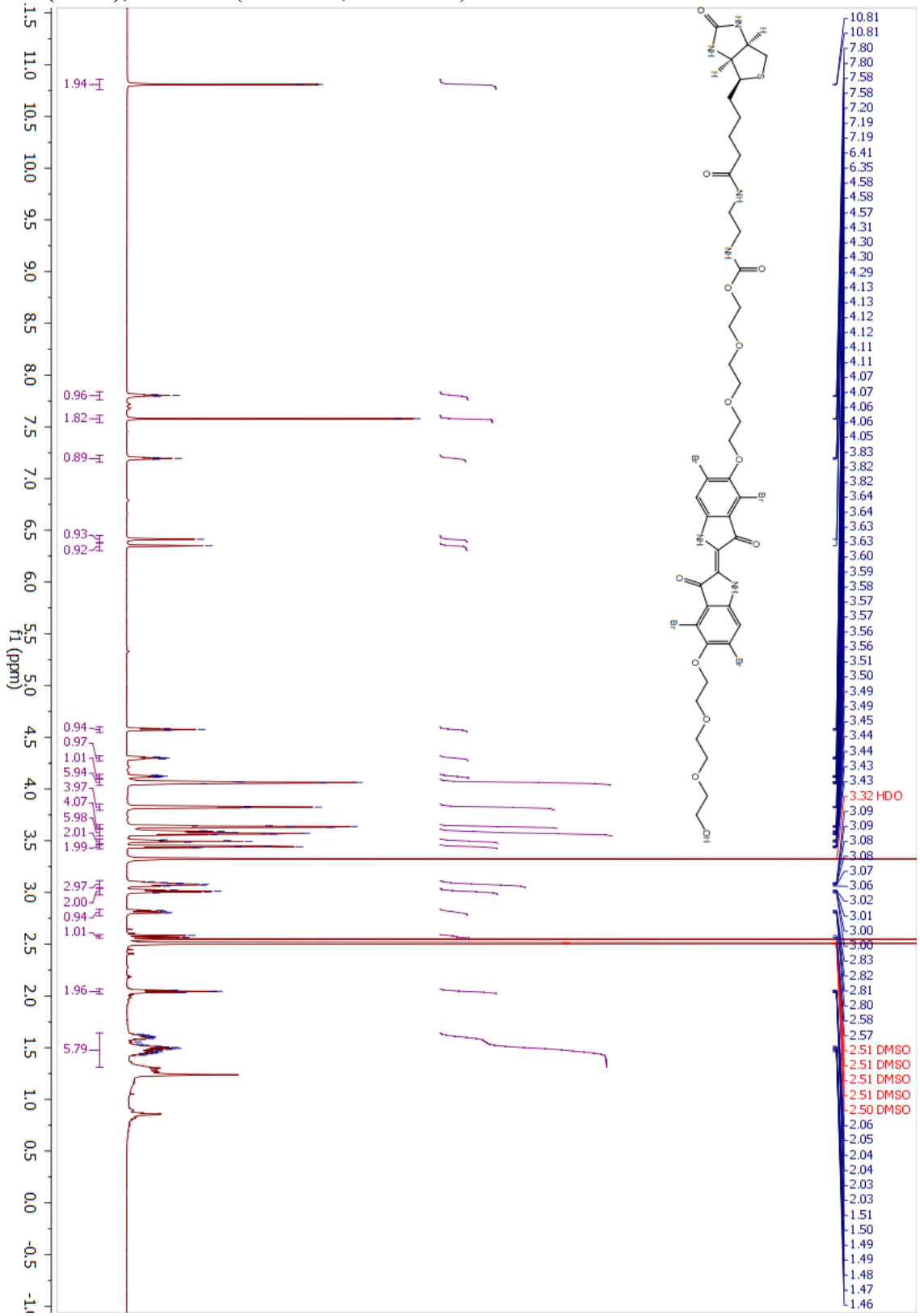
Ind(15)$_2$, ^{1}H NMR (700 MHz, DMSO-d_6)



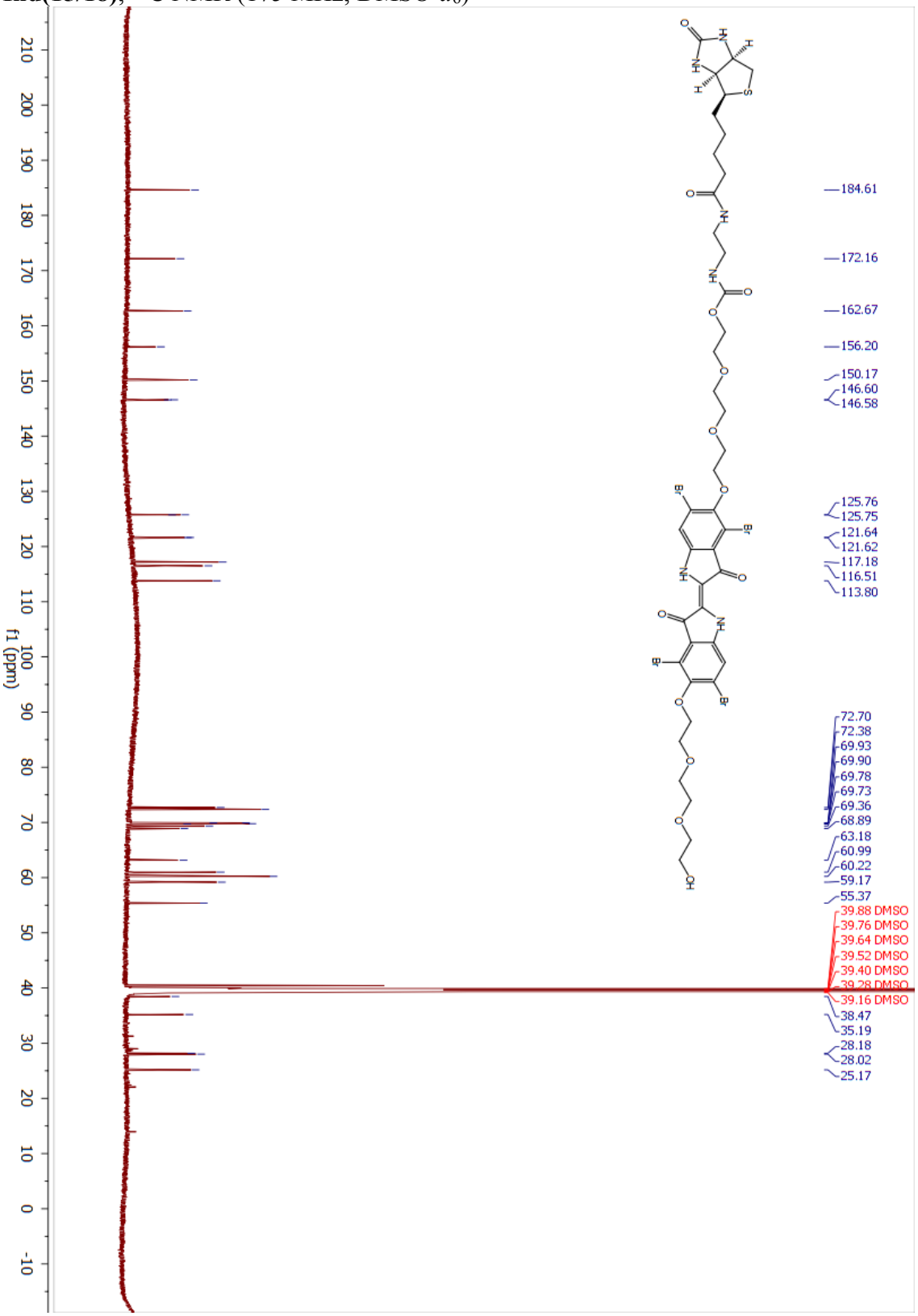
Ind(15)$_2$, ^{13}C NMR (175 MHz, DMSO-d_6)



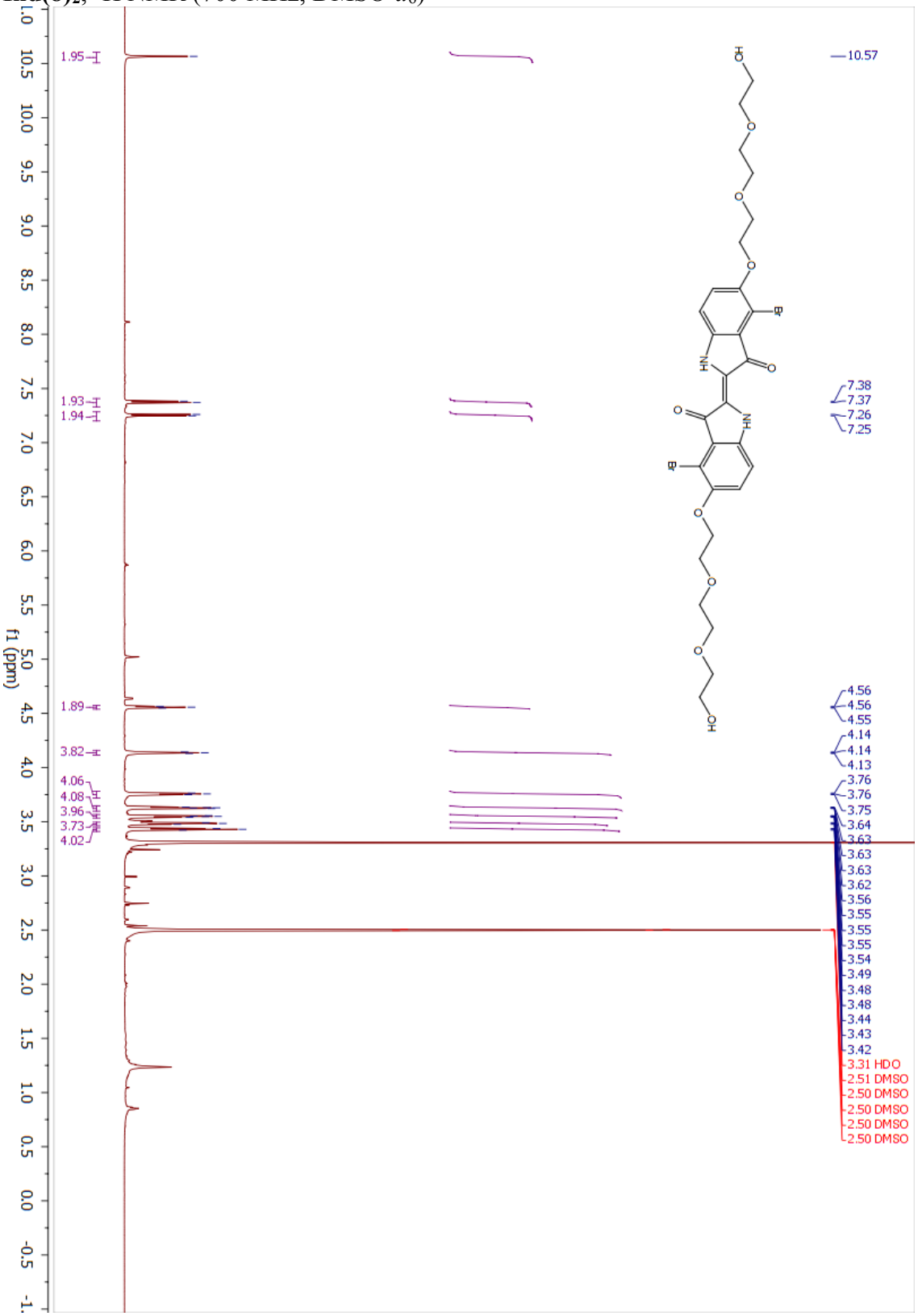
Ind(15/18), ^{1}H NMR (700 MHz, DMSO-d_6)



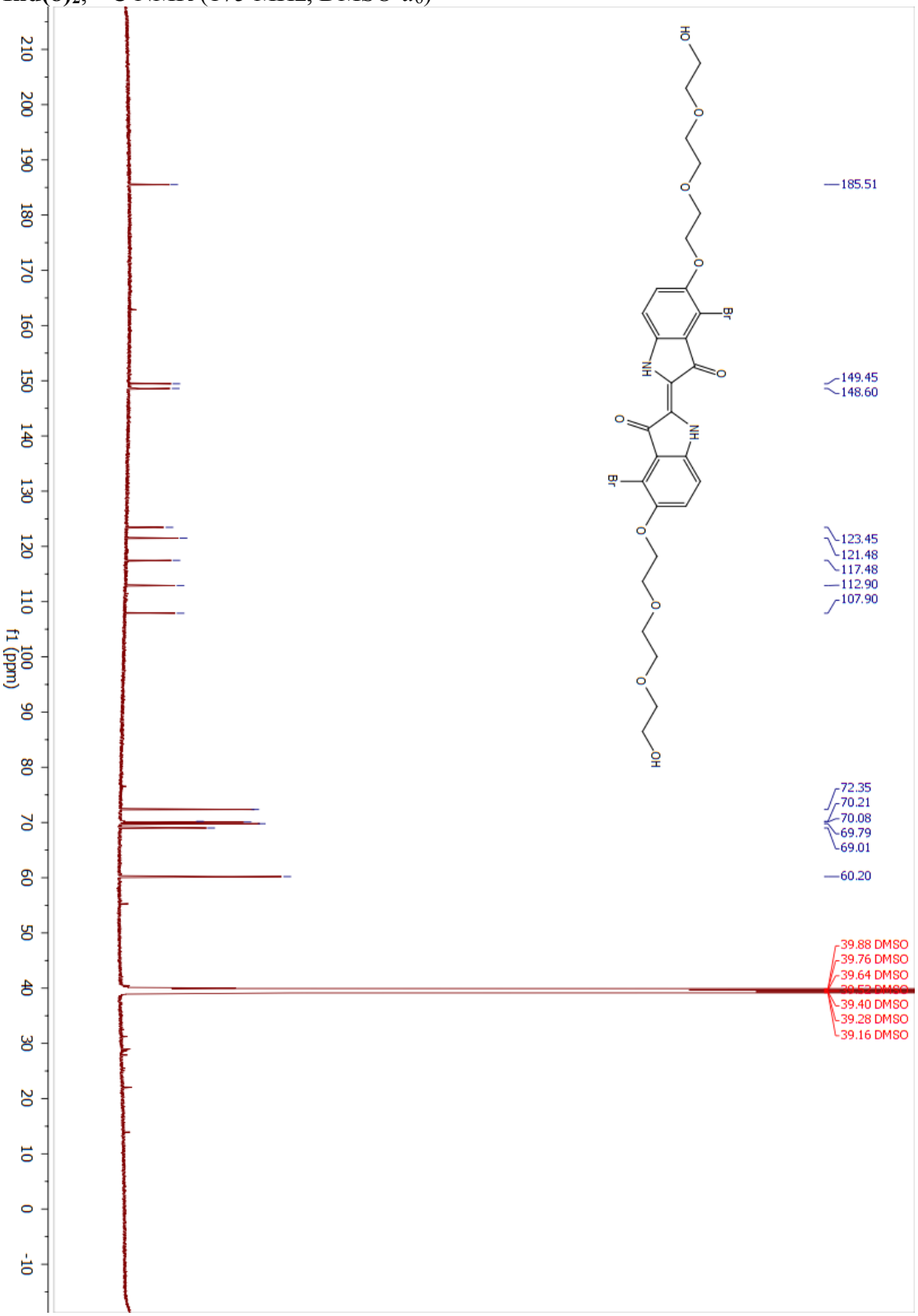
Ind(15/18), ^{13}C NMR (175 MHz, DMSO-d_6)



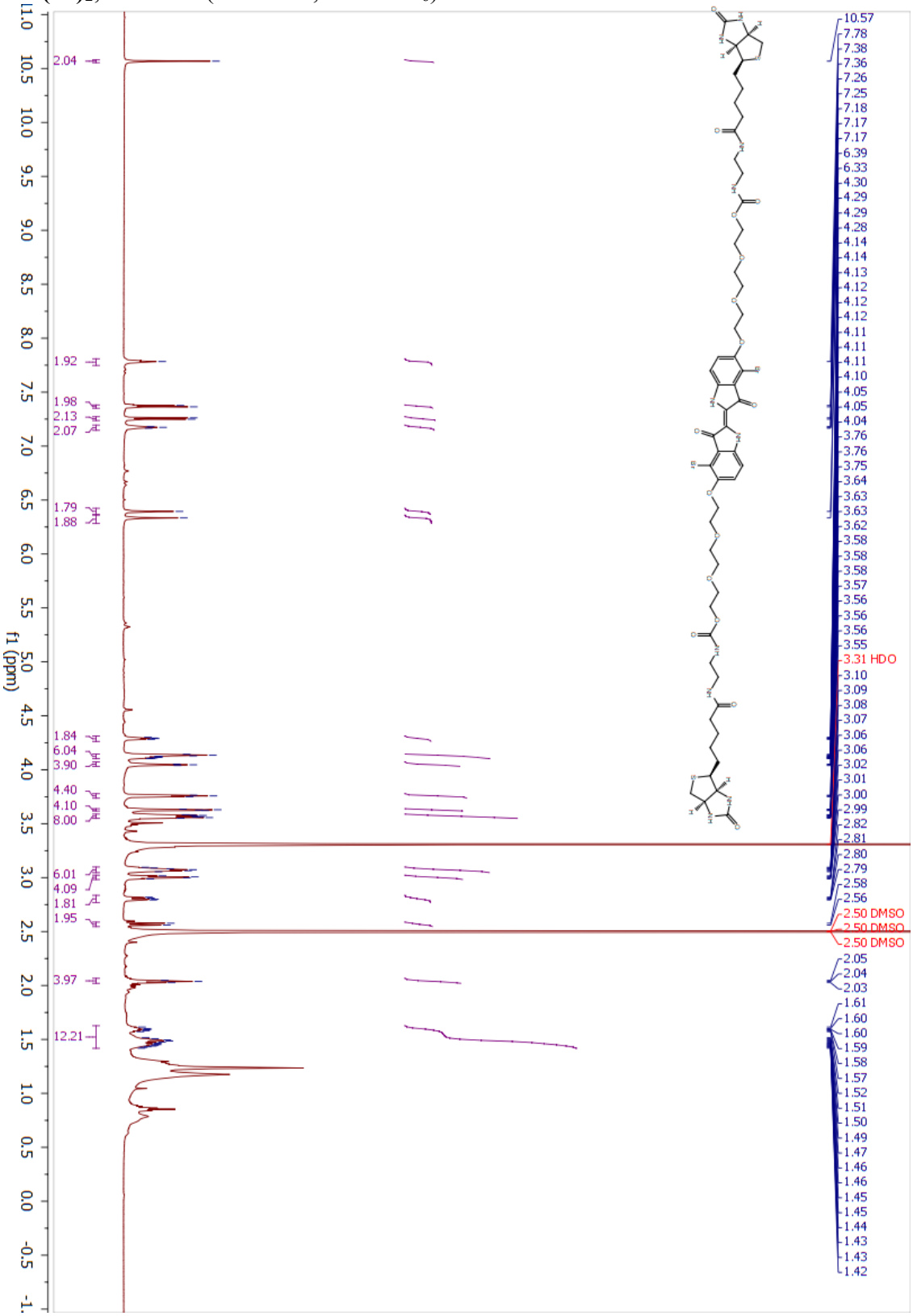
Ind(8)$_2$, ^{1}H NMR (700 MHz, DMSO-d_6)



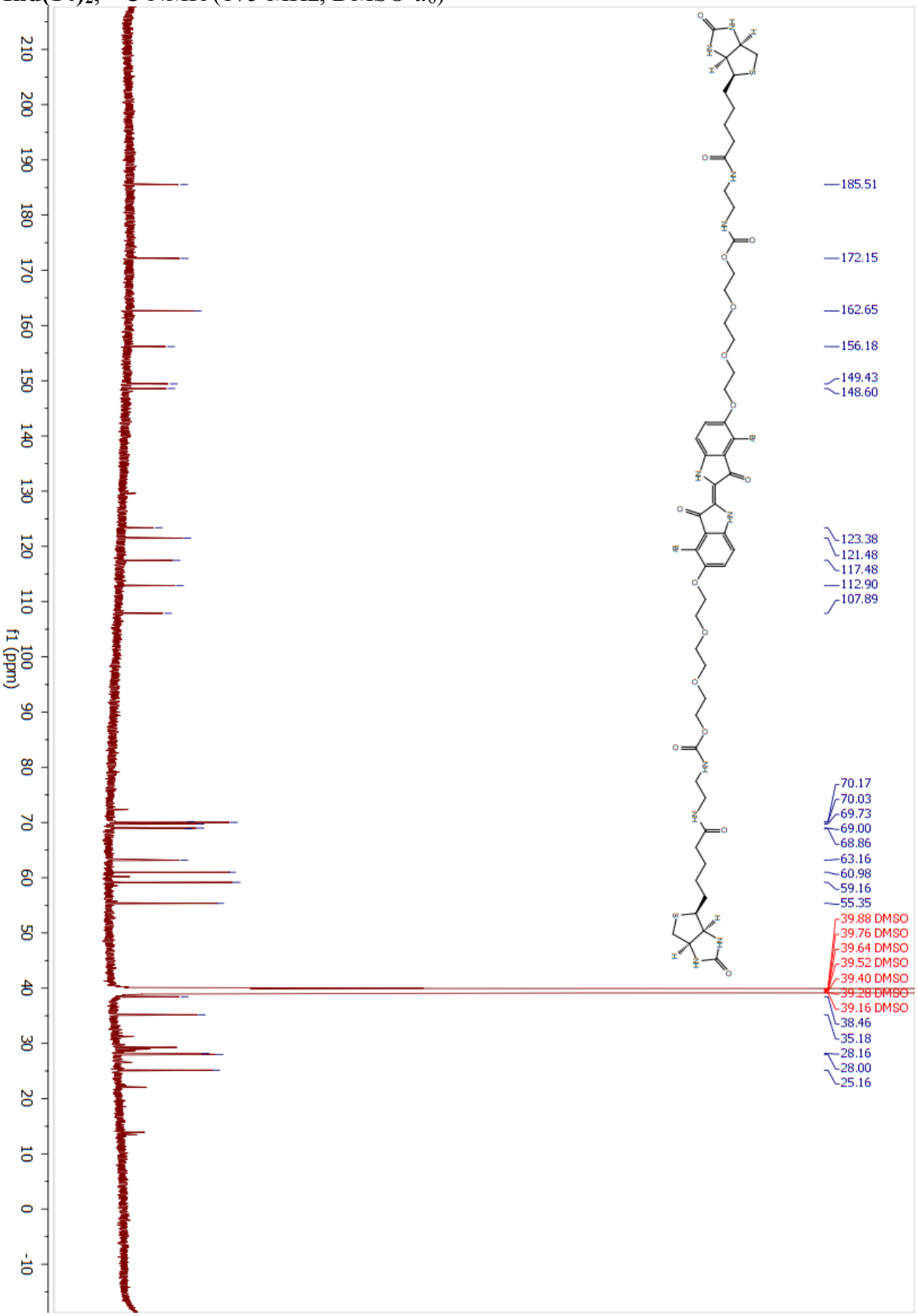
Ind(8)$_2$, ^{13}C NMR (175 MHz, DMSO-d_6)



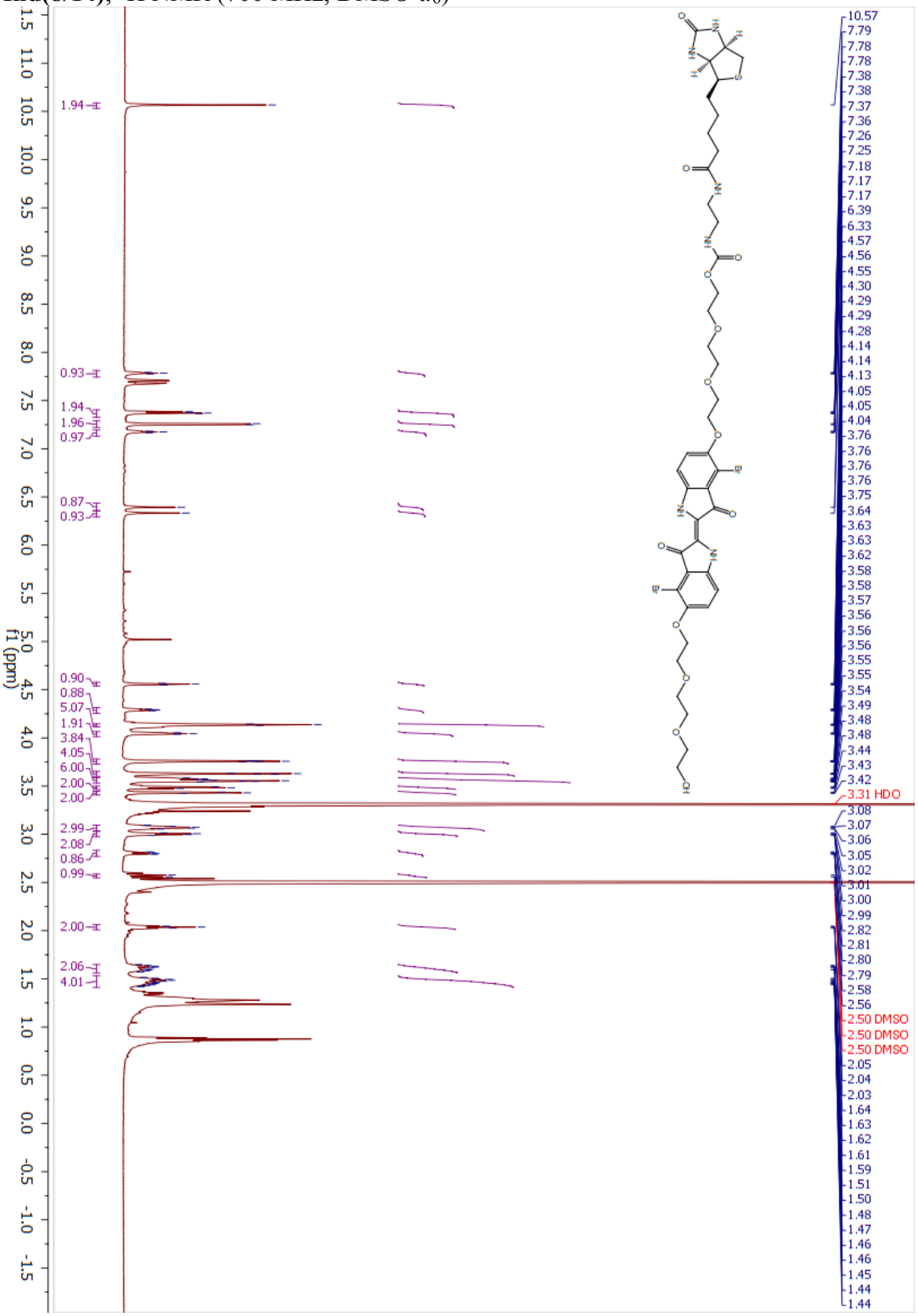
Ind(14)$_2$, ^{1}H NMR (700 MHz, DMSO-d_6)



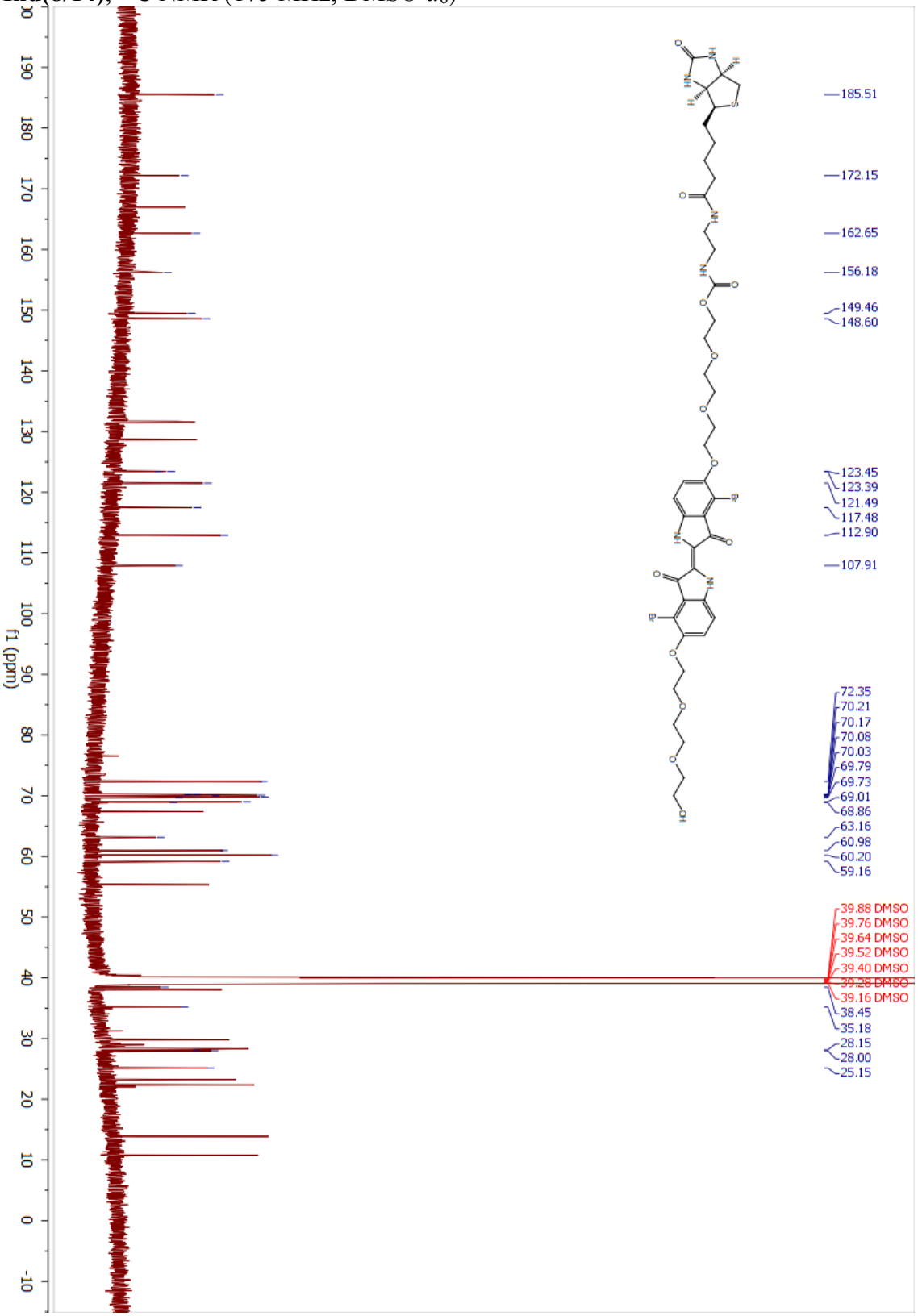
Ind(14)$_2$, ^{13}C NMR (175 MHz, DMSO-d_6)



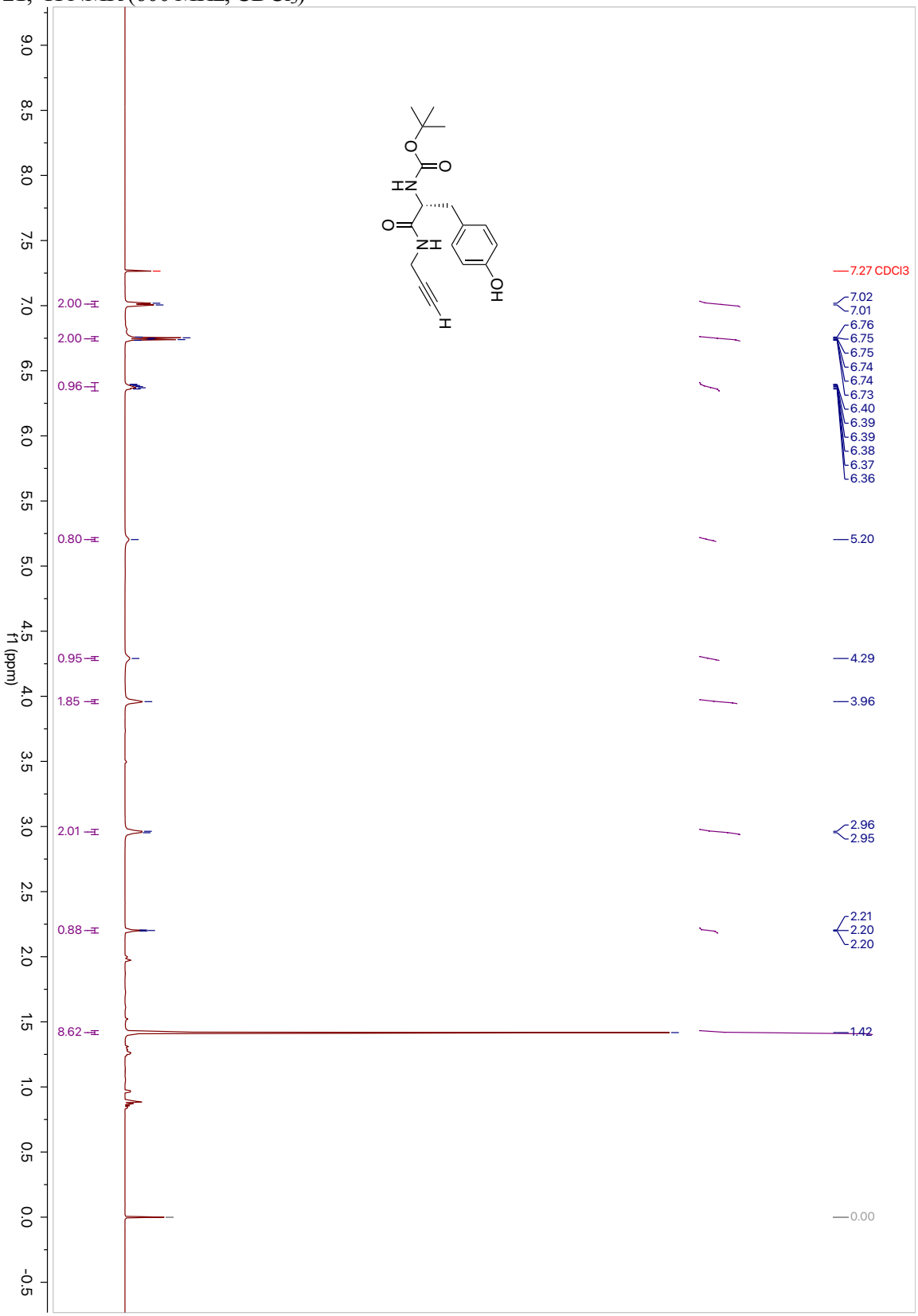
Ind(8/14), ^{1}H NMR (700 MHz, DMSO-d_6)



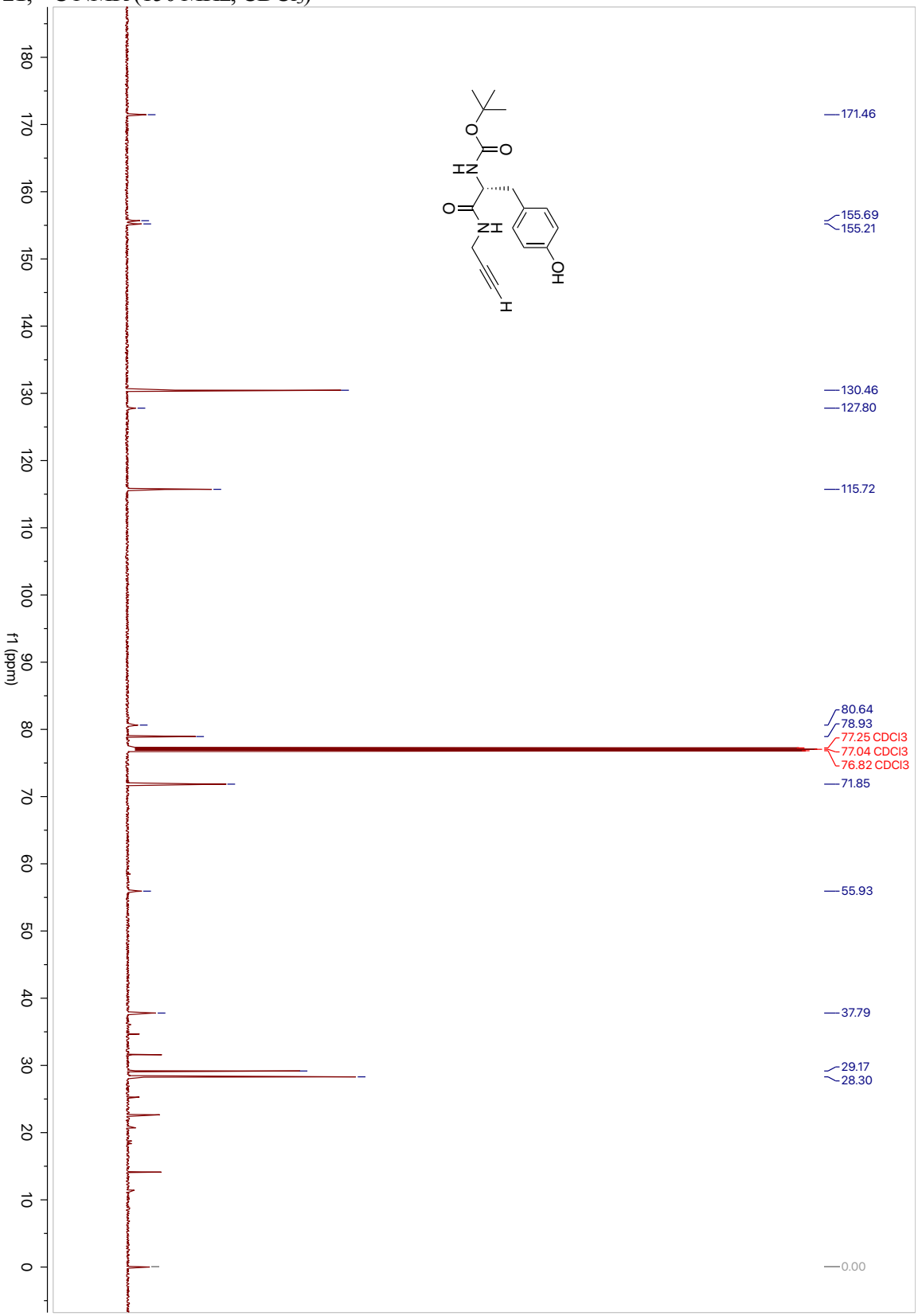
Ind(8/14), ^{13}C NMR (175 MHz, DMSO-d_6)



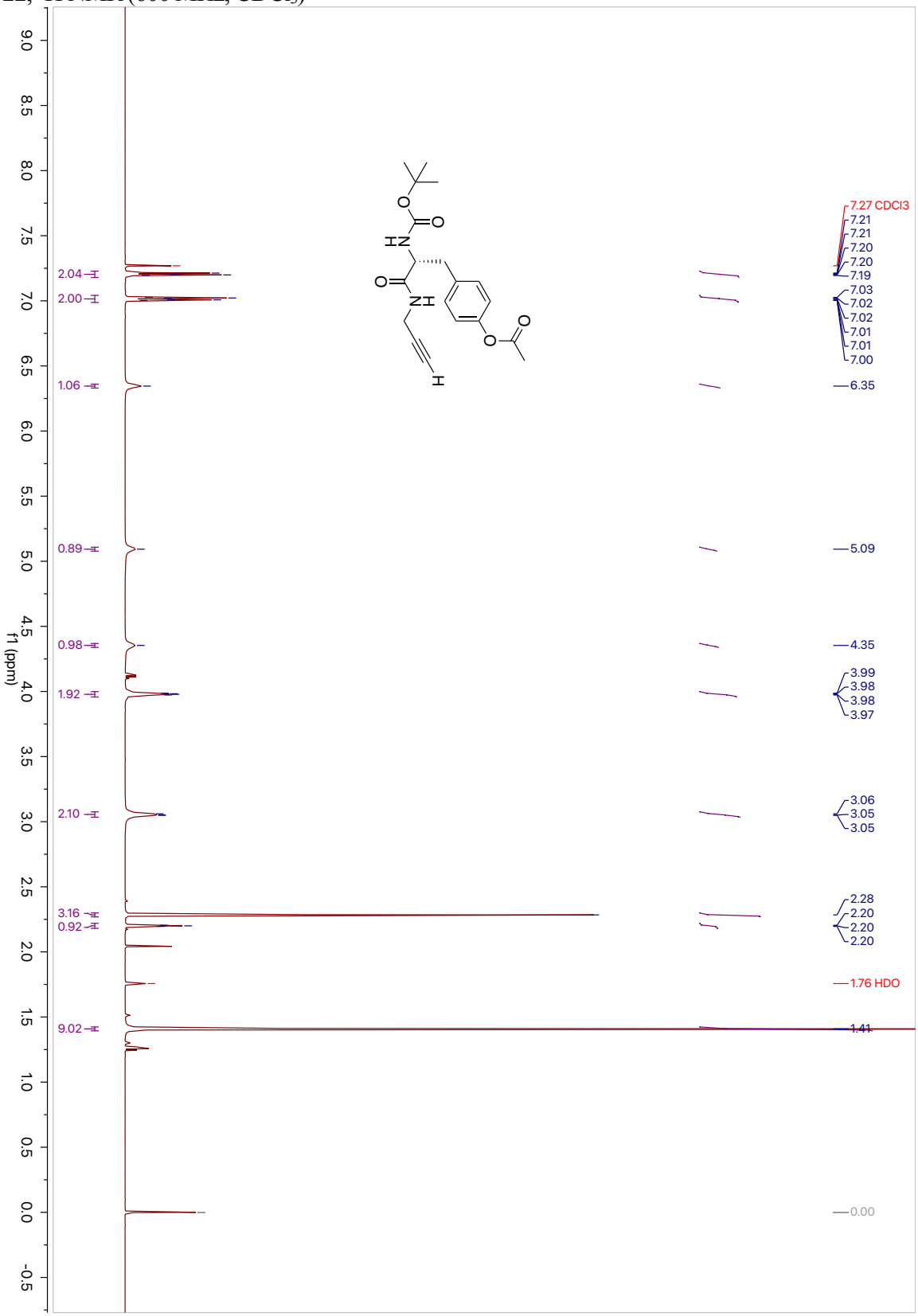
21, ^{1}H NMR (600 MHz, $CDCl_3$)



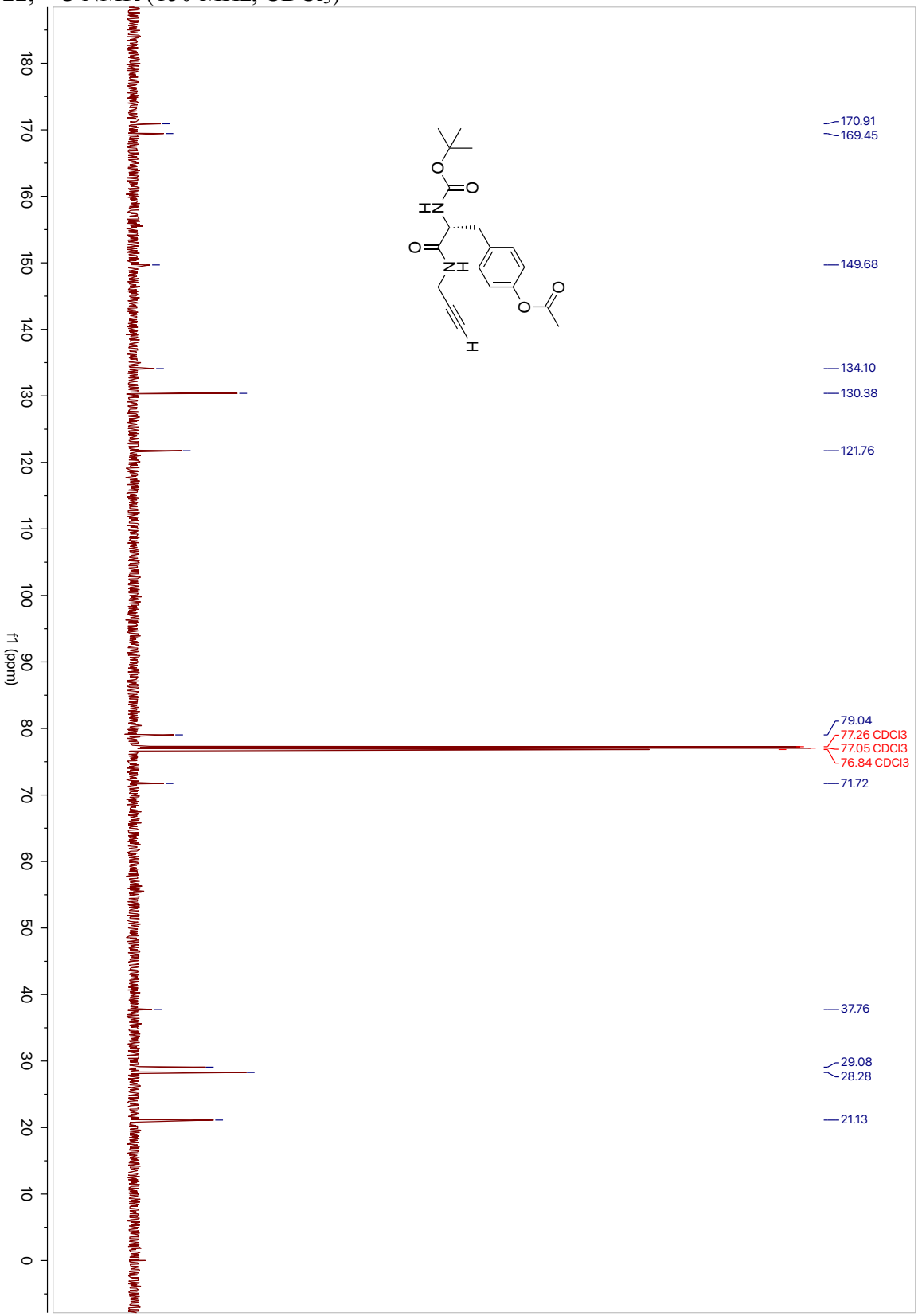
21, ^{13}C NMR (150 MHz, $CDCl_3$)



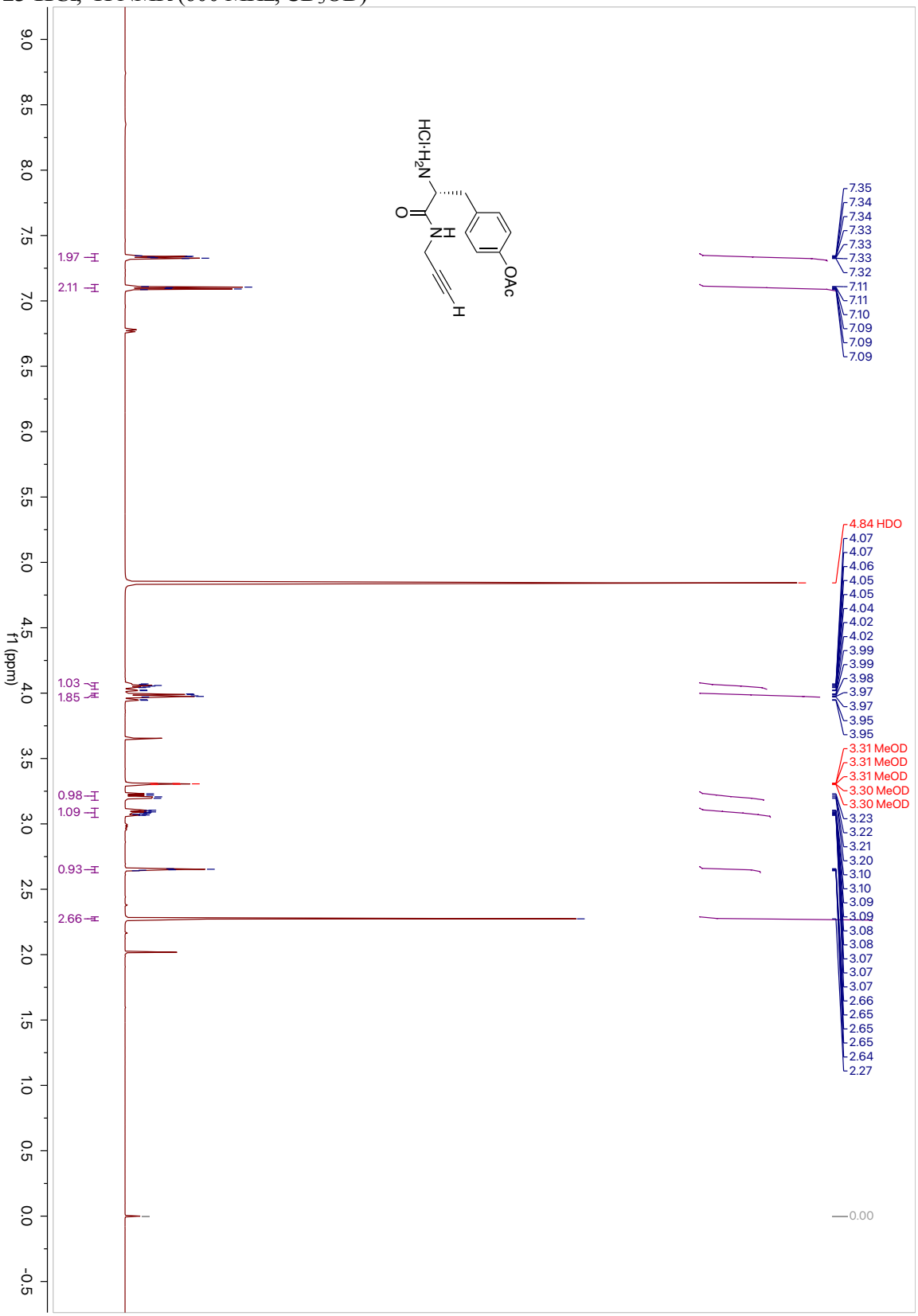
22, ^{1}H NMR (600 MHz, $CDCl_3$)



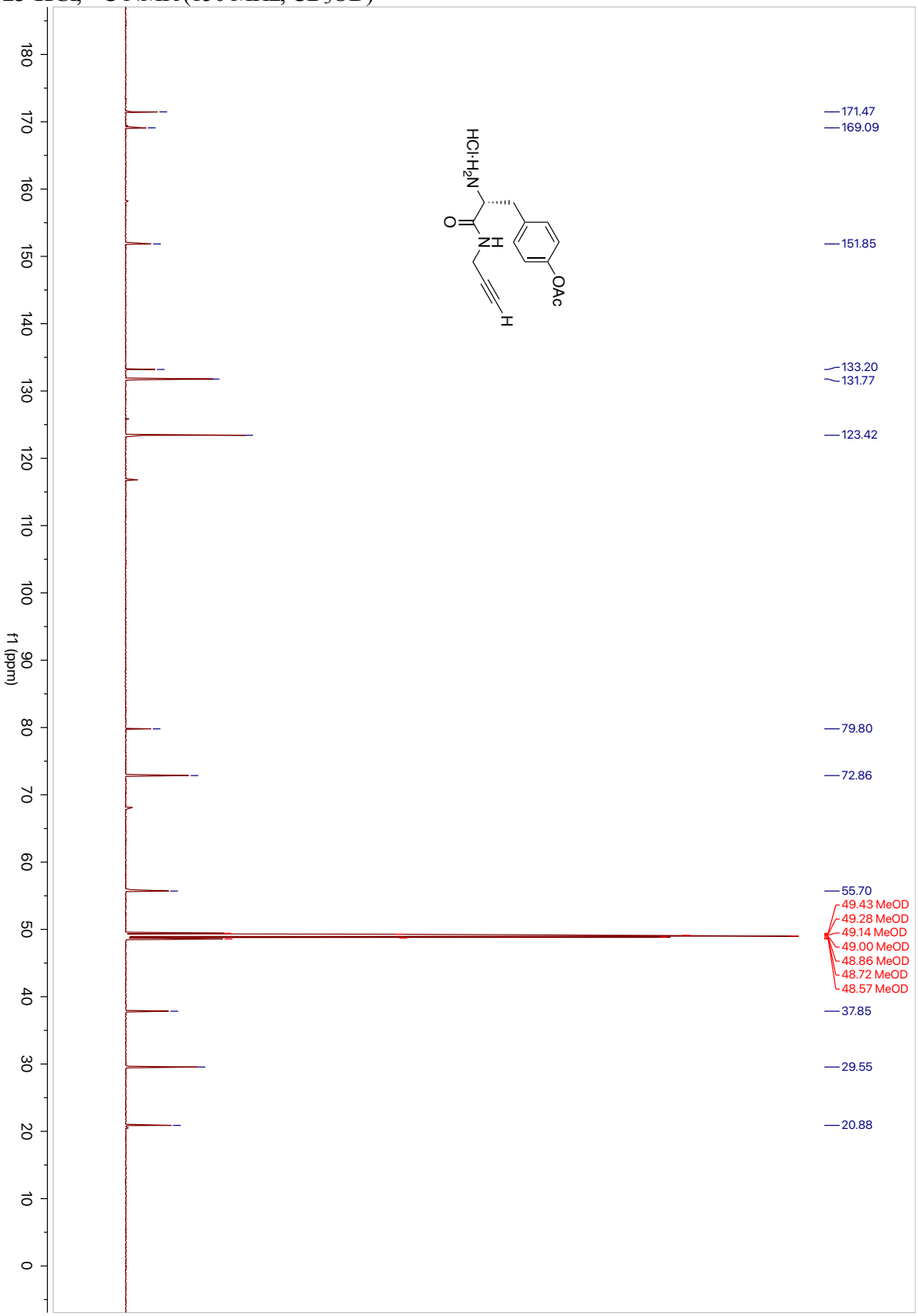
22, ^{13}C NMR (150 MHz, $CDCl_3$)



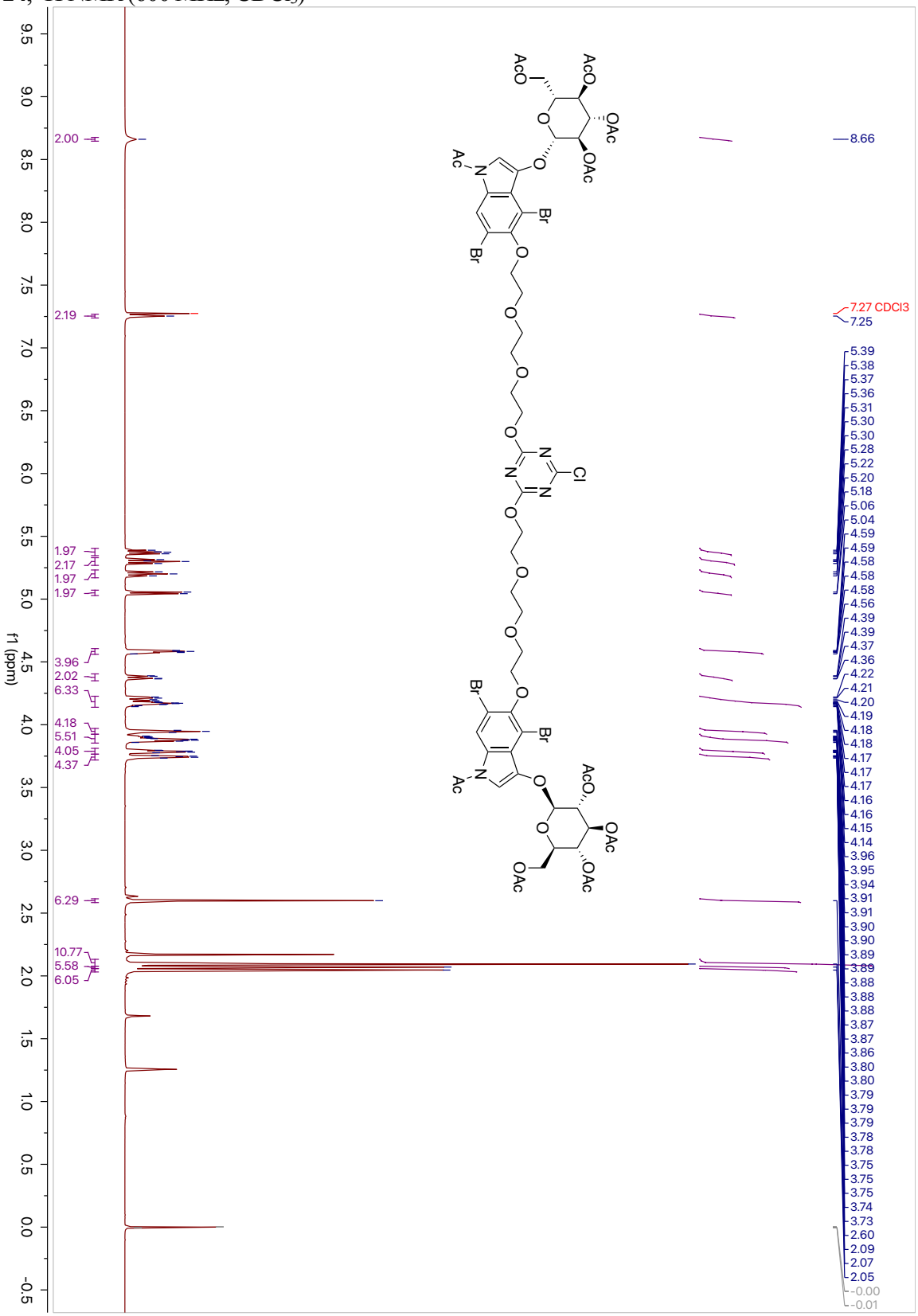
23·HCl, ^{1}H NMR (600 MHz, CD_3OD)



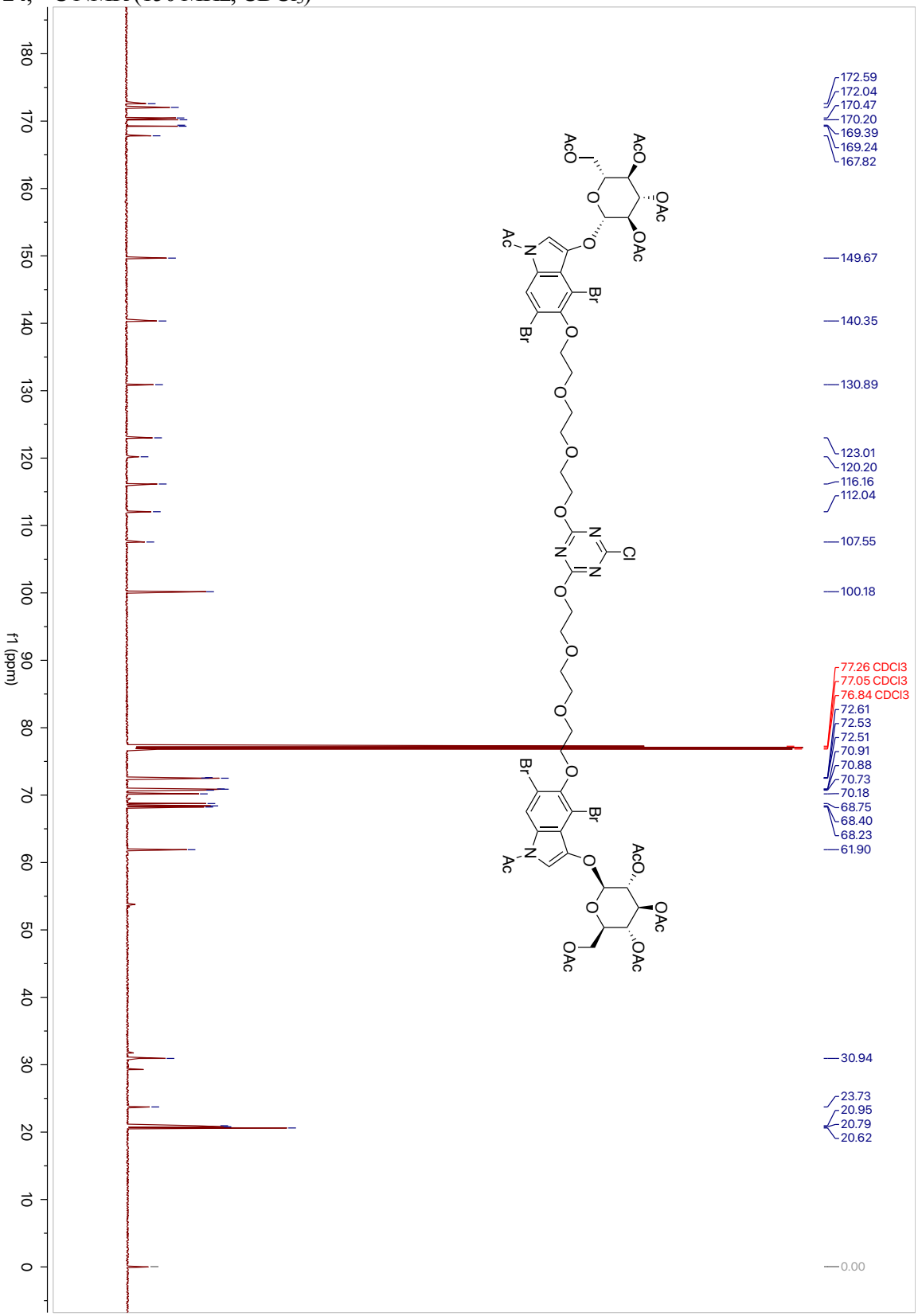
23·HCl, ^{13}C NMR (150 MHz, CD_3OD)



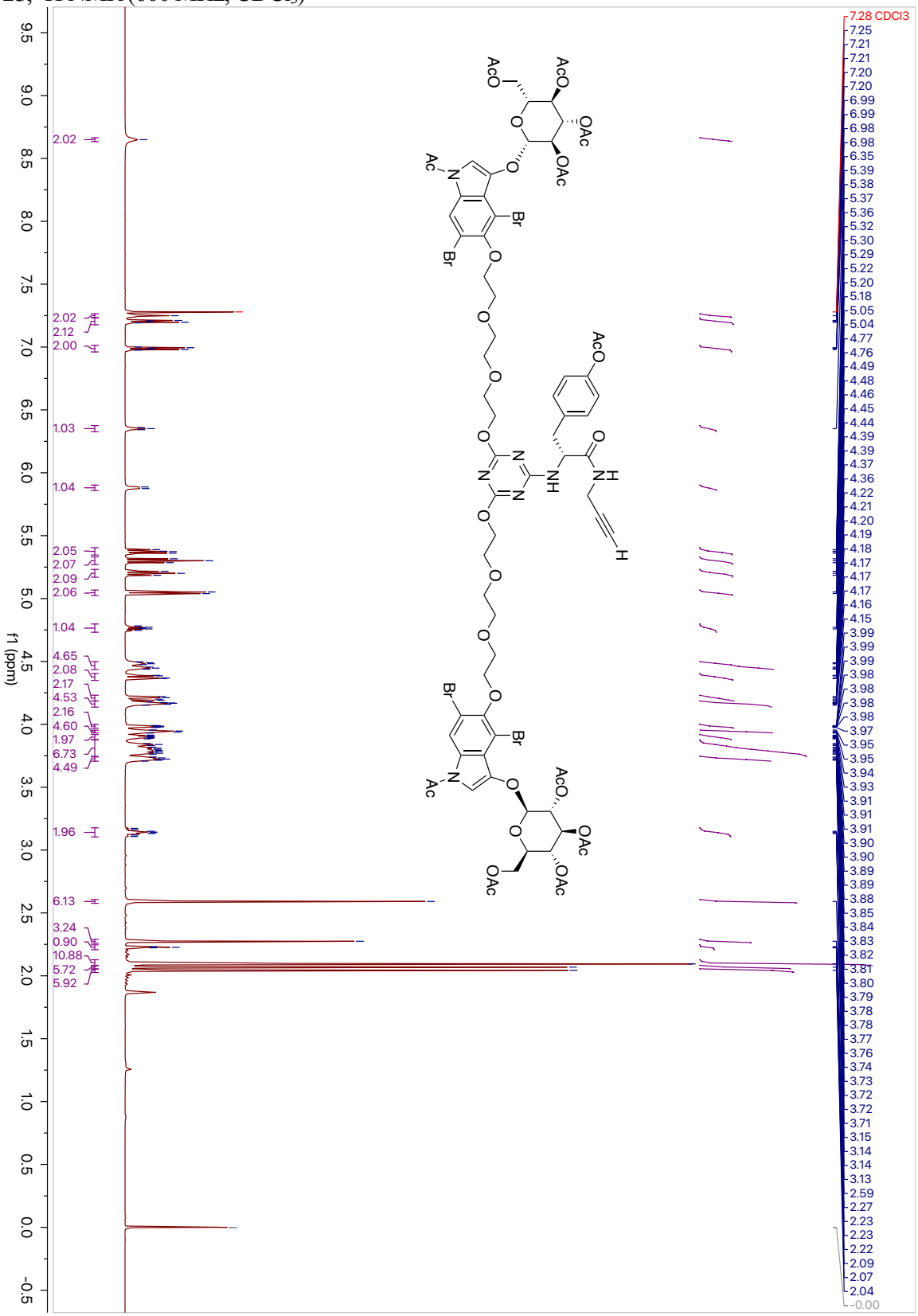
24, ^{1}H NMR (600 MHz, $CDCl_3$)



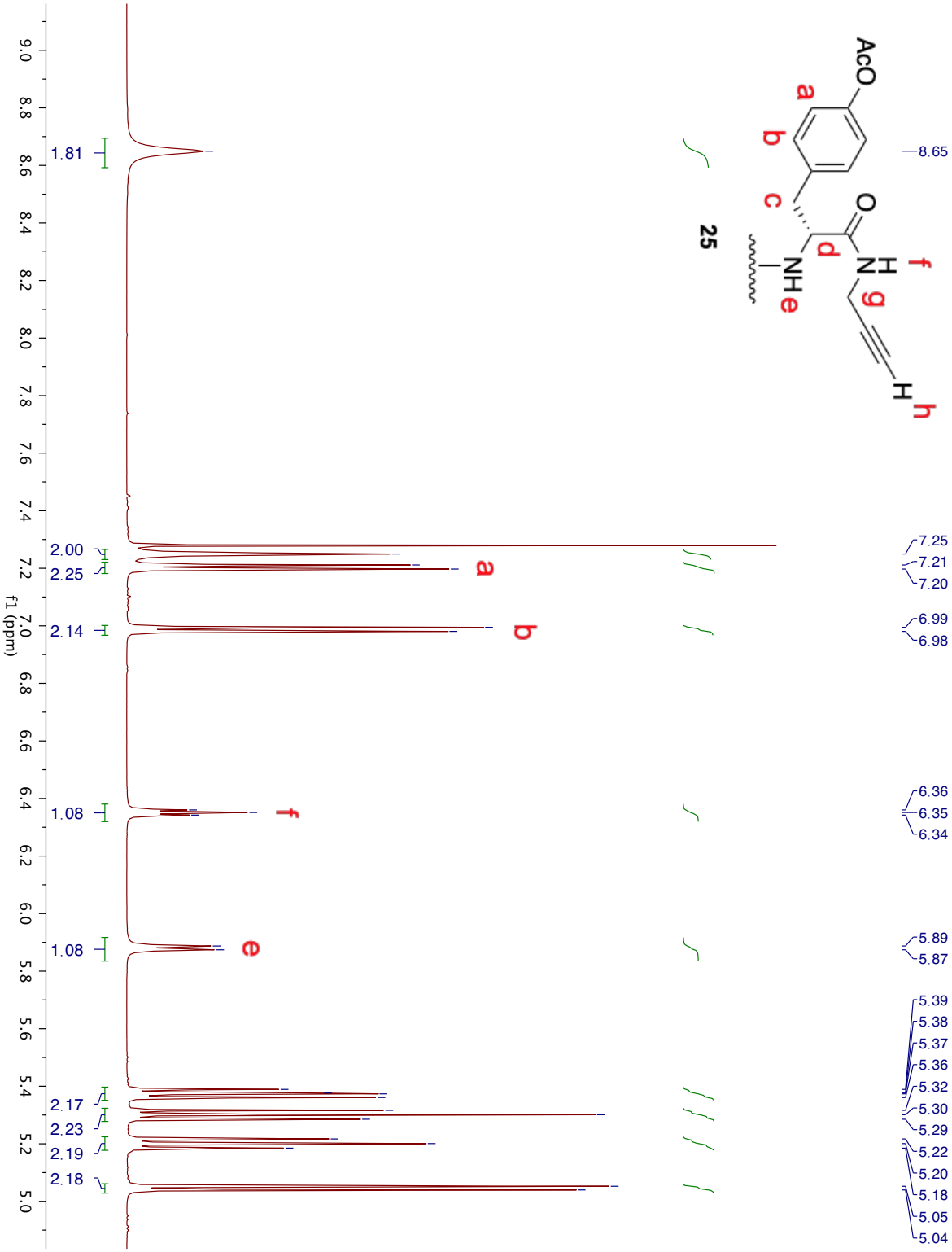
24, ^{13}C NMR (150 MHz, $CDCl_3$)



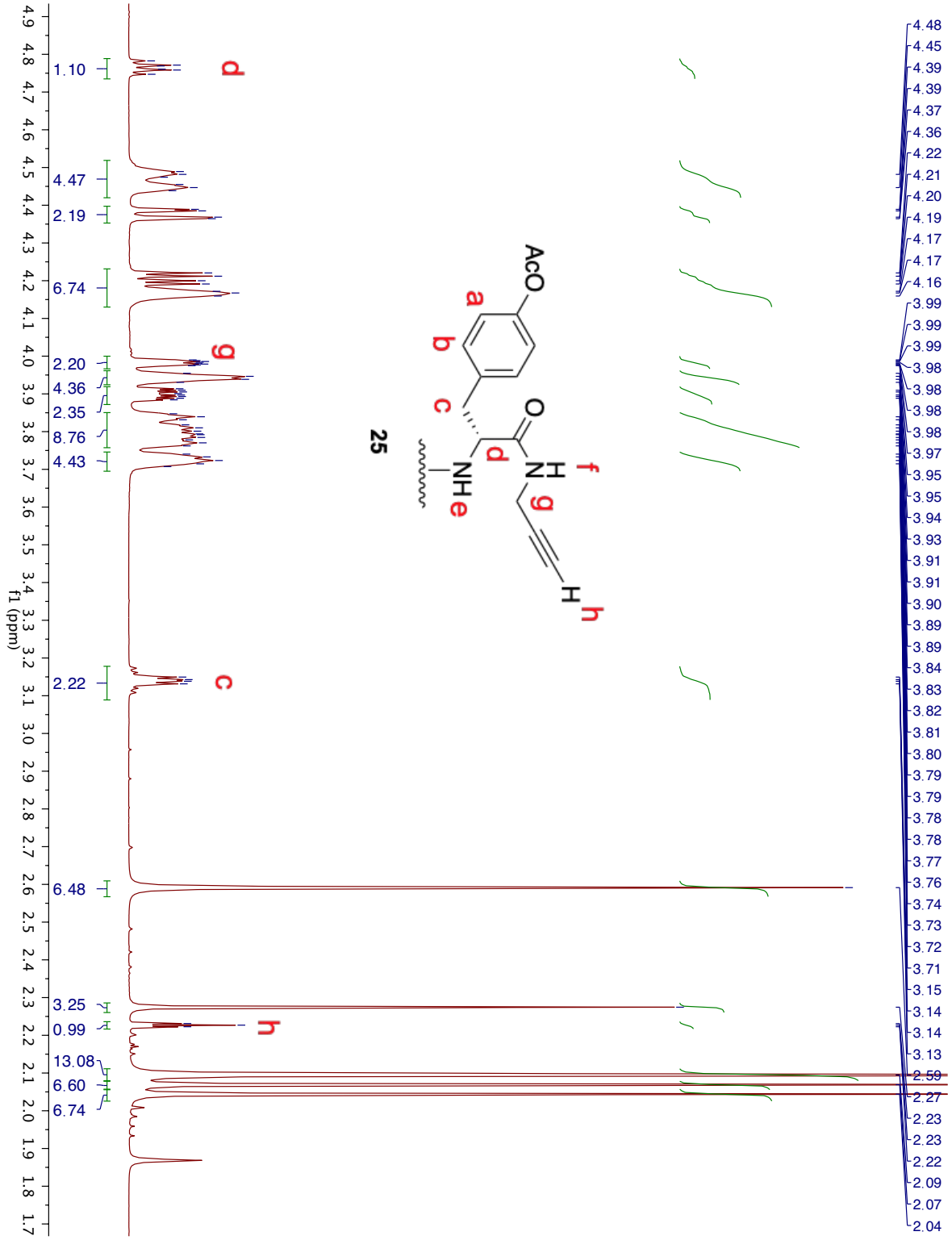
25, ^{1}H NMR (600 MHz, $CDCl_3$)



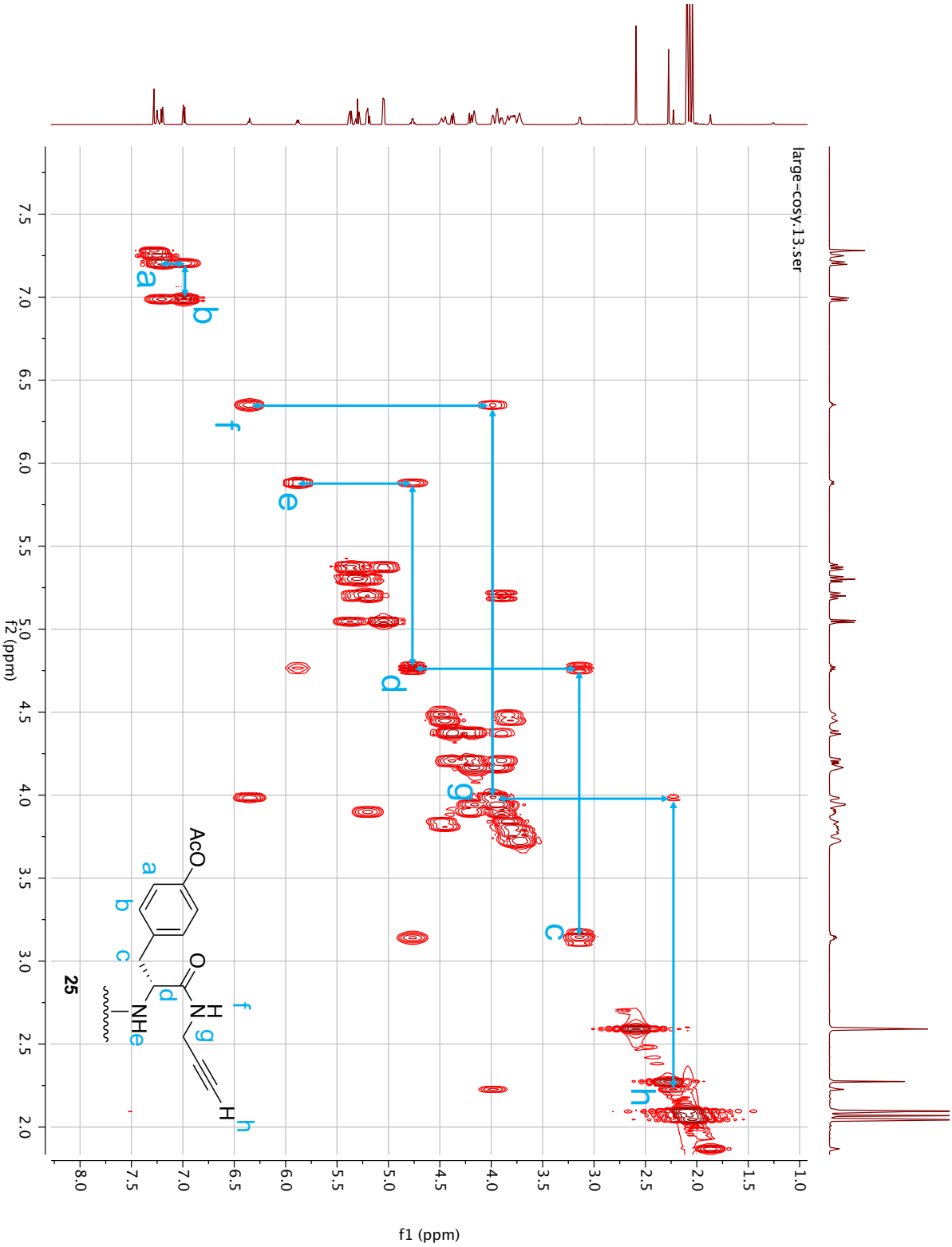
25, ^{1}H NMR (600 MHz, $CDCl_3$)



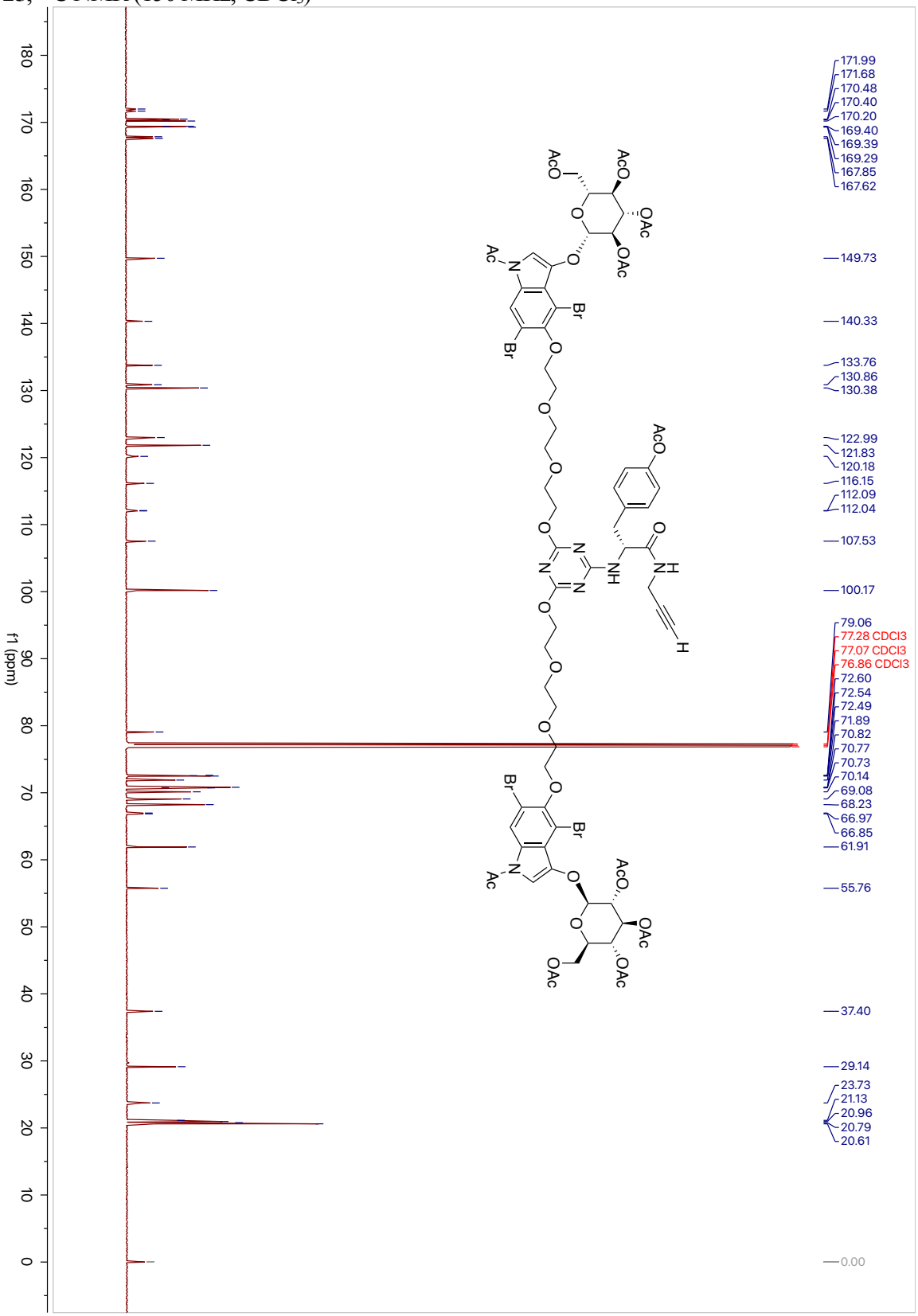
25, ^{1}H NMR (600 MHz, $CDCl_3$)



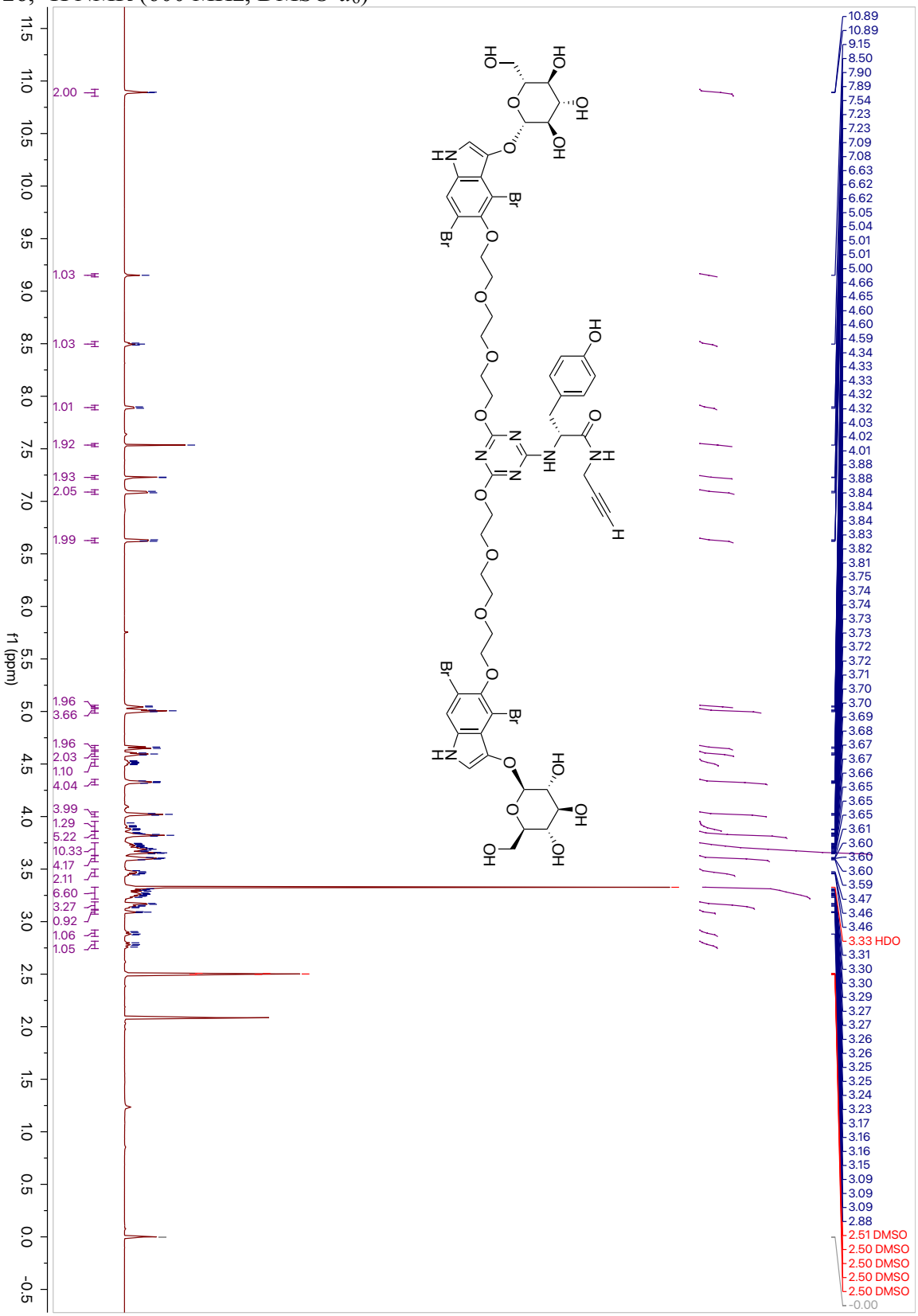
25, ^{1}H-^{1}H COSY NMR (600 MHz, $CDCl_3$)



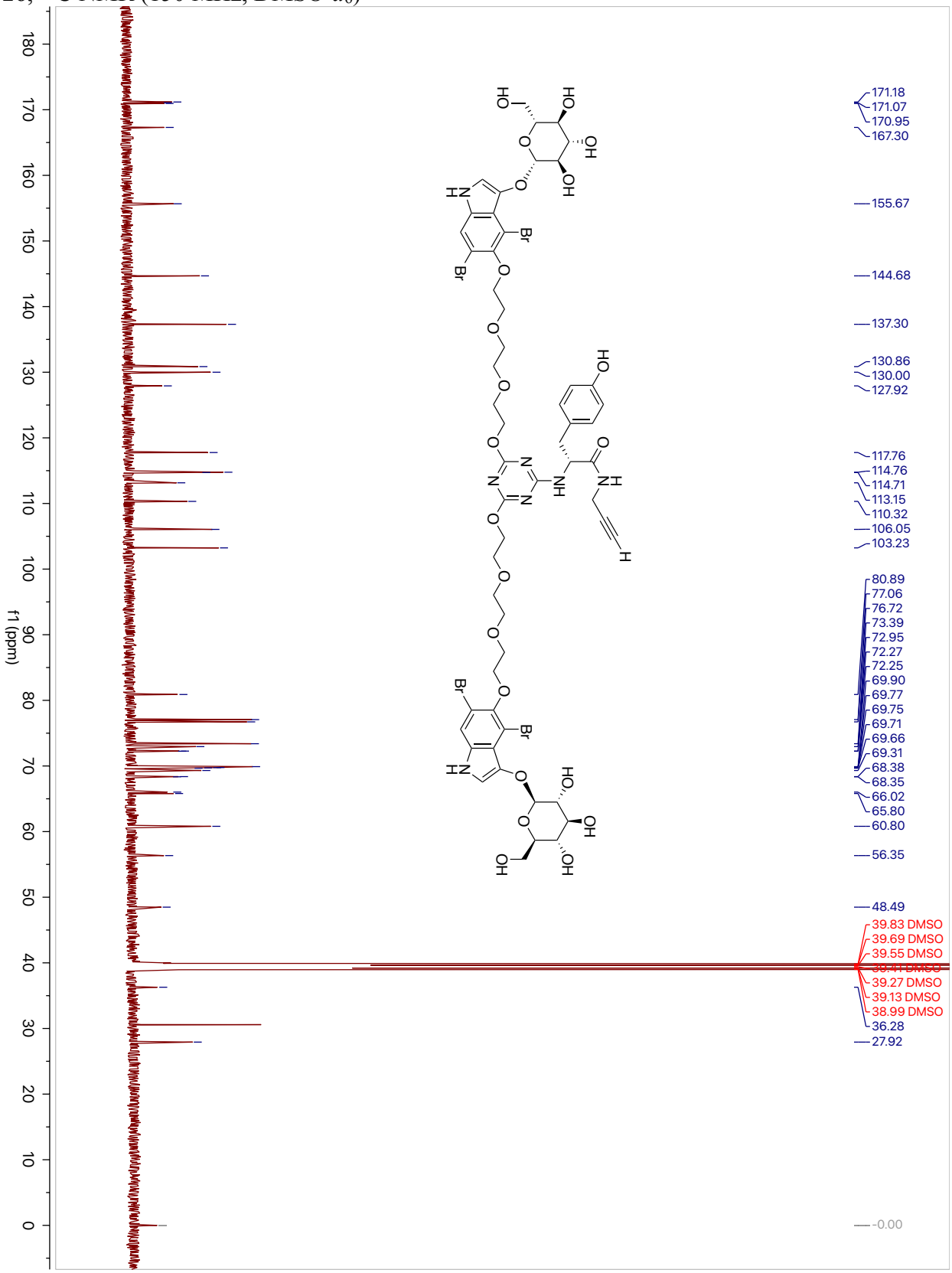
25, ^{13}C NMR (150 MHz, $CDCl_3$)



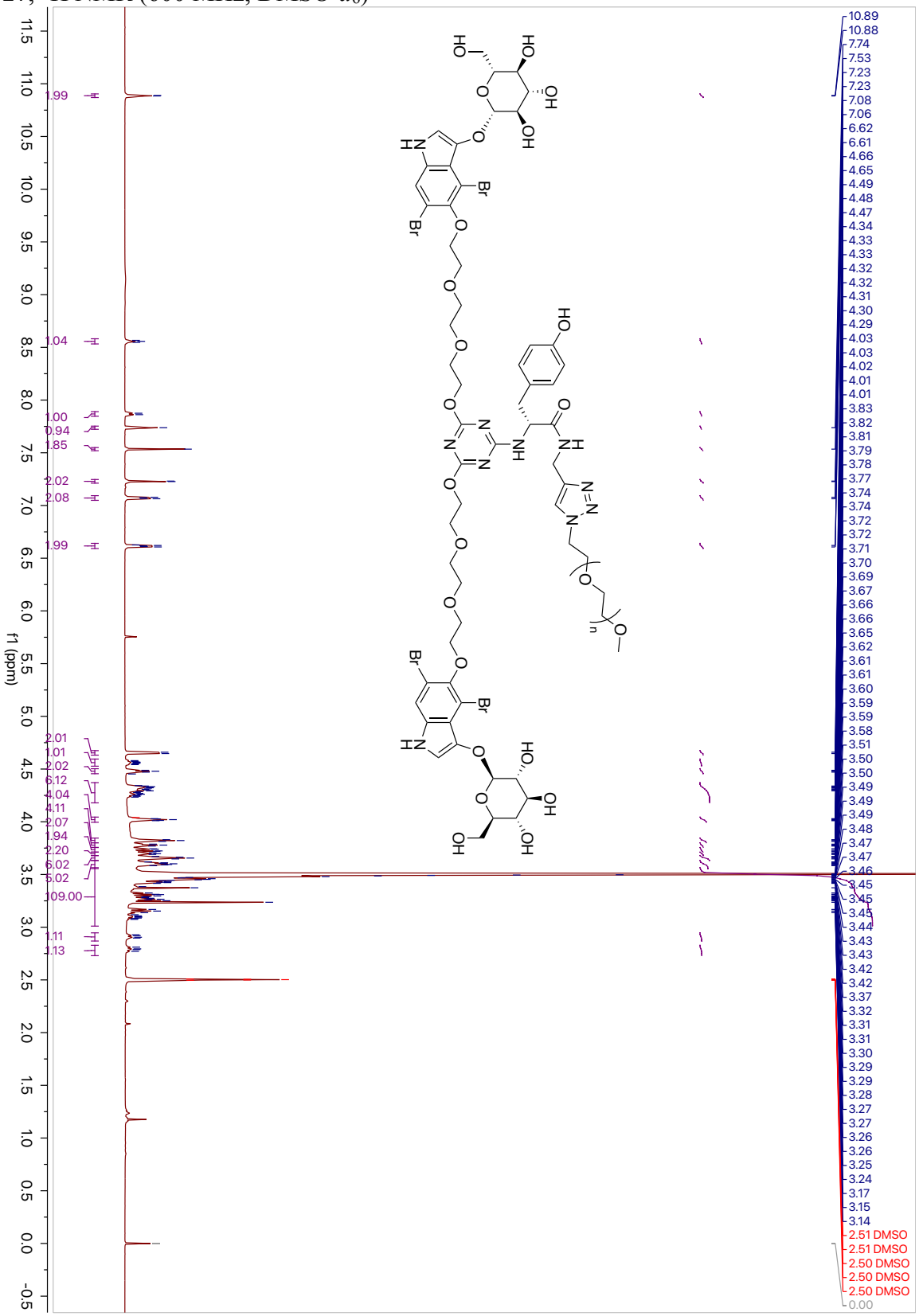
26, ^{1}H NMR (600 MHz, DMSO-d_6)



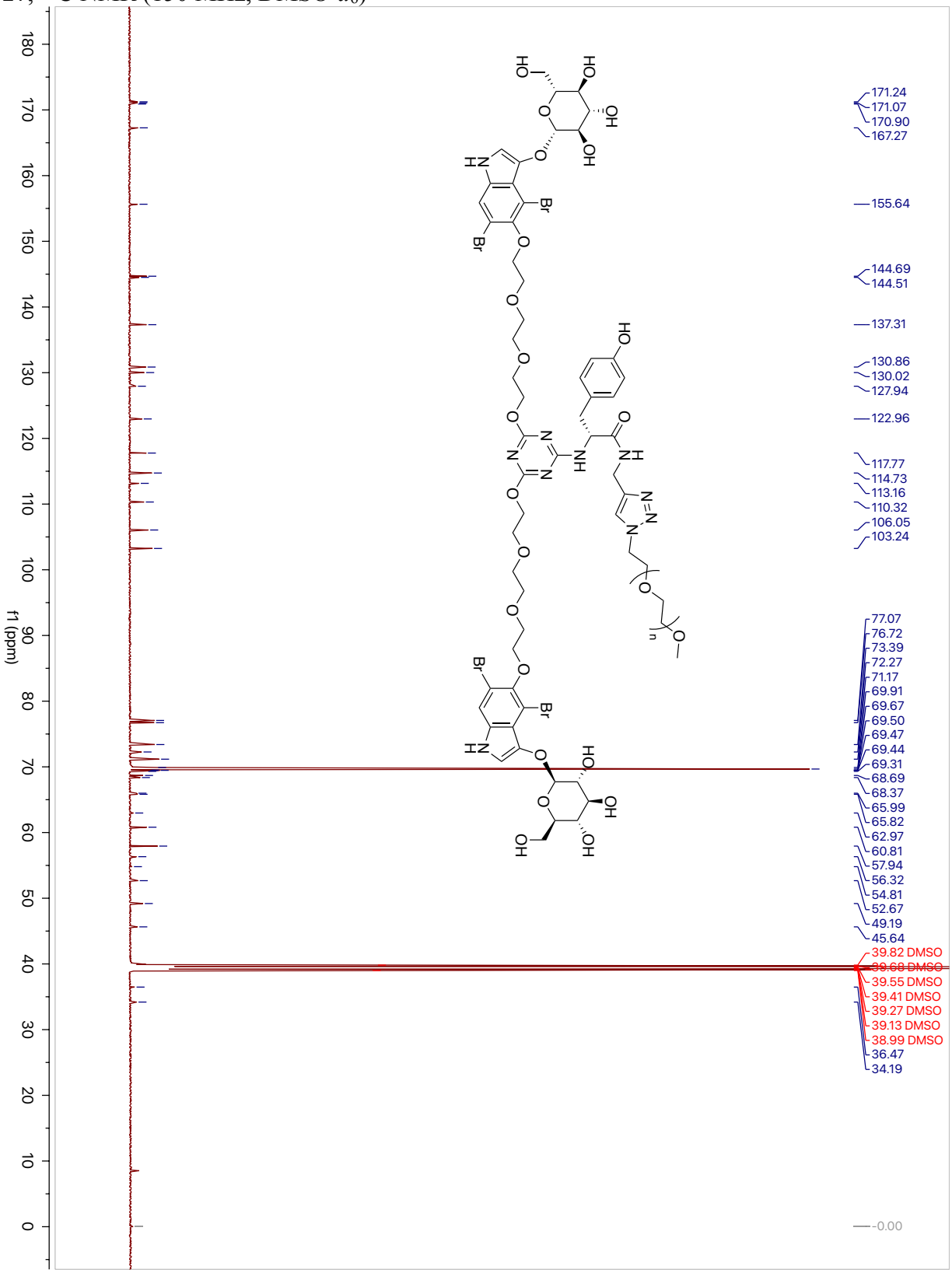
26, ^{13}C NMR (150 MHz, DMSO-d_6)



27, ^{1}H NMR (600 MHz, DMSO-d_6)



27, ^{13}C NMR (150 MHz, DMSO-d_6)



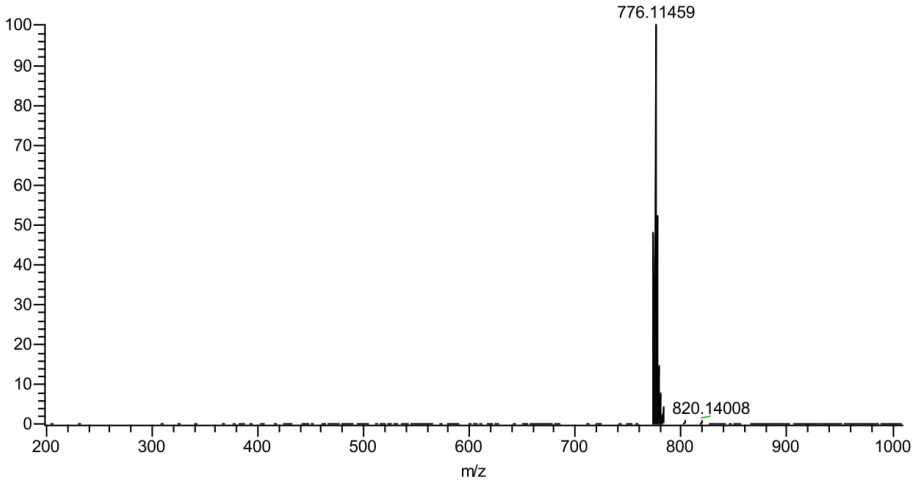
(8) Mass Spectral data

2: ESI-MS

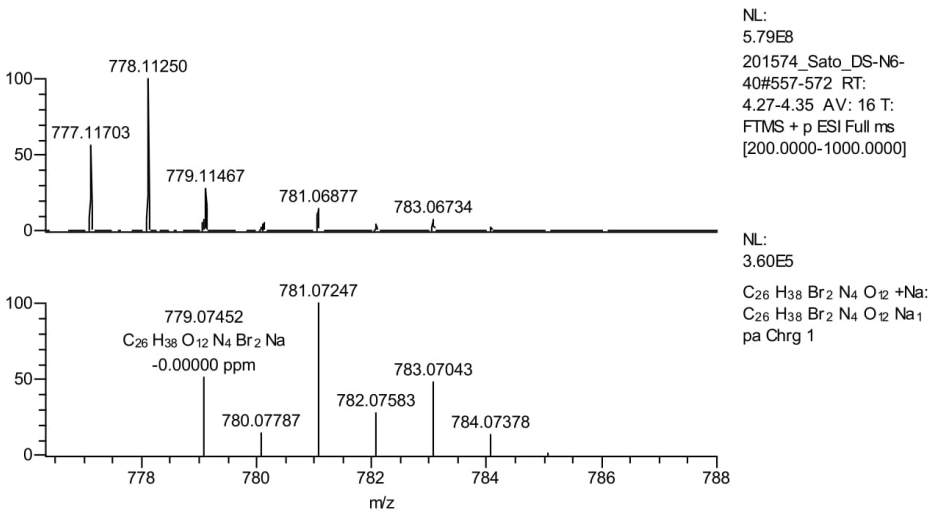
NC STATE UNIVERSITY
Molecular Education, Technology and
Research Innovation Center
Raleigh, NC 27695
https://research.ncsu.edu/metric/

Sato_DS-N6-40 Scan 4.27 – 4.35 minutes Positive Ion Mode

201574_Sato_DS-N6-40 #557-572 RT: 4.27 AV: 16 NL: 1.10E9
T: FTMS + p ESI Full ms [200.0000-1000.0000]



Sato_DS-N6-40 Experimental and Theoretical Isotopic Distribution for $C_{26}H_{38}Br_2N_4O_{12}$ $[M+Na]^+$



3: ESI-MS

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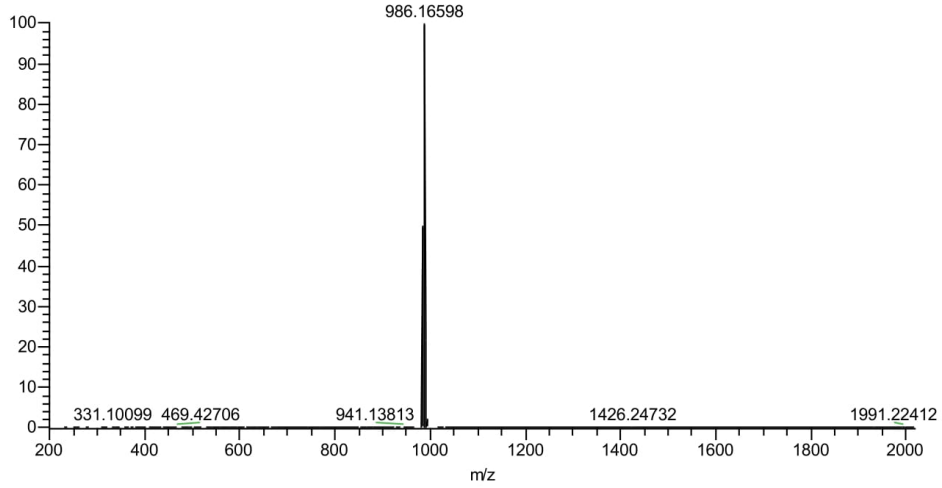
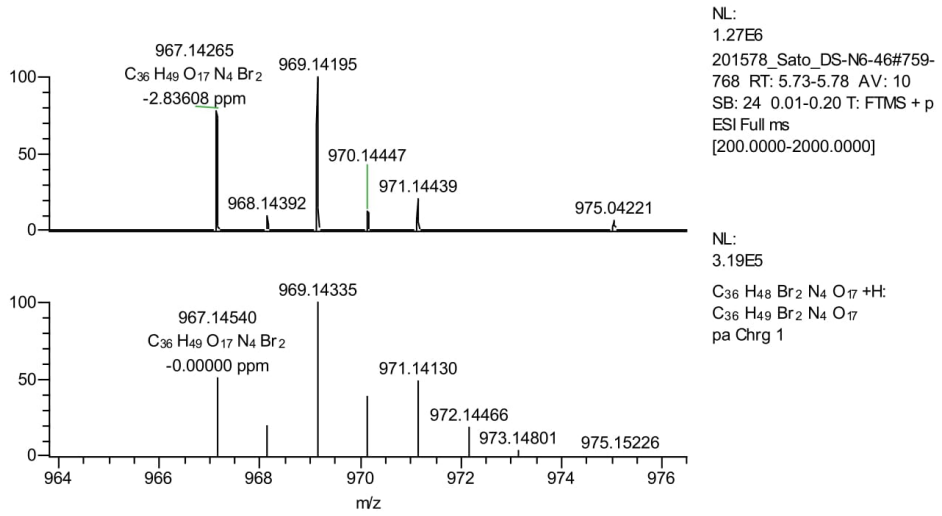
Research Innovation Center
Raleigh, NC 27695
https://research.ncsu.edu/metric/

Sato DS-N6-46 Scan 5.73 – 5.78 minutes Positive Ion Mode

201578_Sato_DS-N6-46 #759-768 RT: 5.7[illegible] AV: 10 SB: 24 0.01-0.20 NL: 2.03E9
T: FTMS + p ESI Full ms [200.0000-2000.0000]



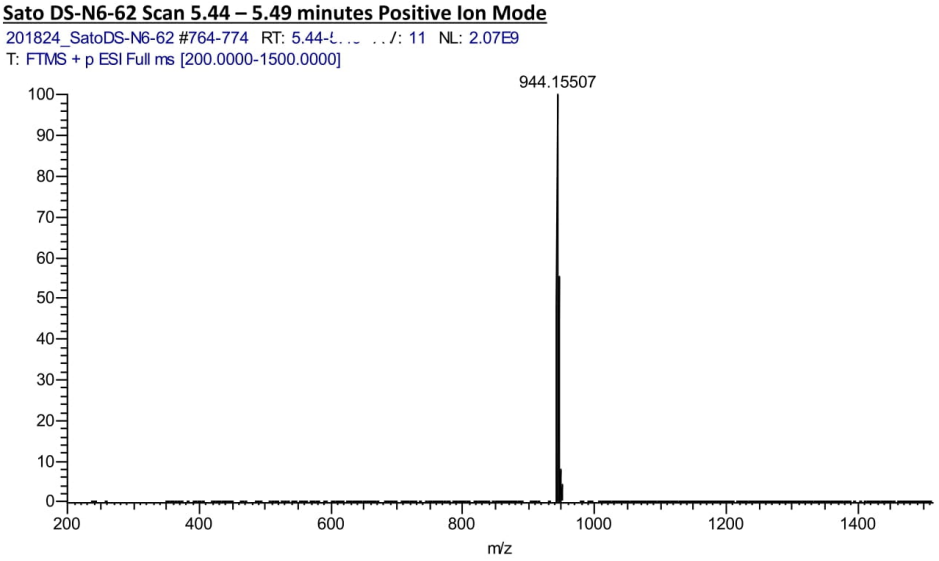
Sato DS-N6-46 Experimental and Theoretical Isotopic Distribution for $C_{36}H_{48}Br_2N_4O_{17}$ $[M+H]^+$



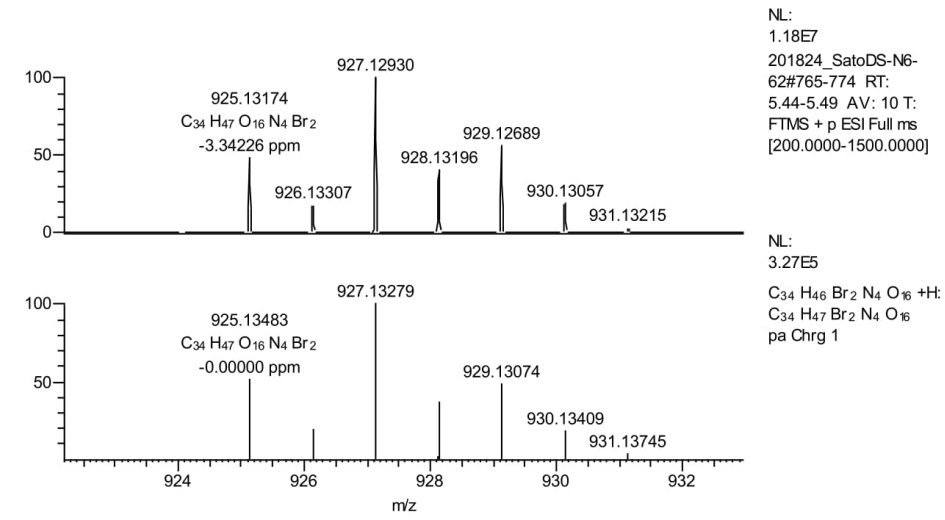
4: ESI-MS

NC STATE UNIVERSITY
Molecular Education, Technology and
Research Innovation Center
Raleigh, NC 27695
https://research.ncsu.edu/metric/

Sato DS-N6-62 Scan 5.44 – 5.49 minutes Positive Ion Mode



Sato DS-N6-62 Experimental and Theoretical Isotopic Distribution for $C_{34}H_{46}Br_2N_4O_{16}$ $[M+H]^+$



5: ESI-MS

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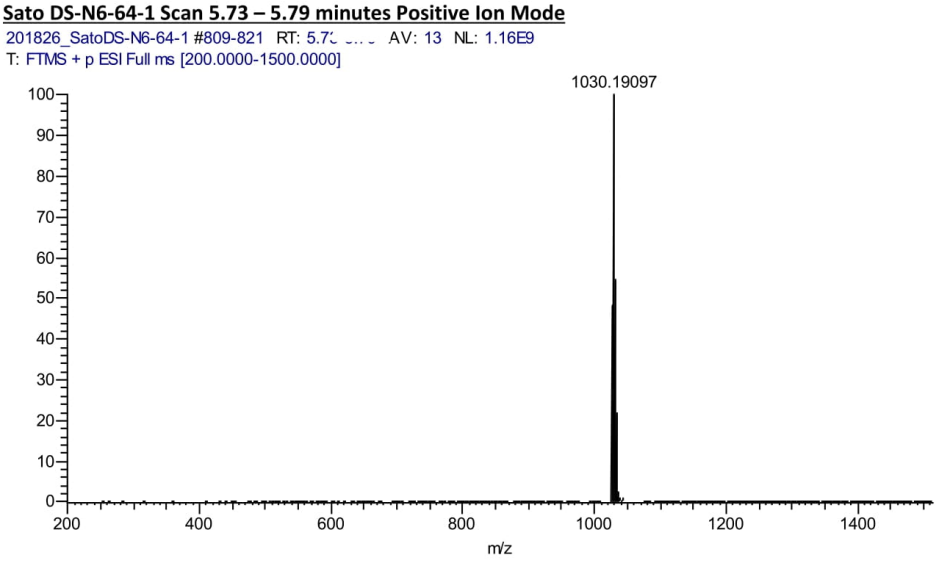
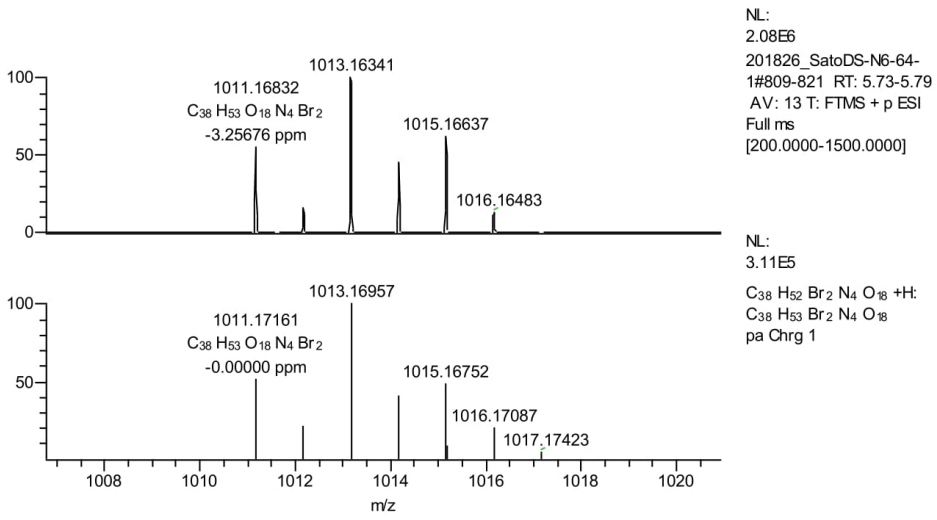
https://research.ncsu.edu/metric/

Sato DS-N6-64-1 Scan 5.73 – 5.79 minutes Positive Ion Mode



Sato DS-N6-64-1 Experimental and Theoretical Isotopic Distribution for $C_{38}H_{52}Br_2N_4O_{18}$ $[M+H]^+$



2-AcOH: ESI-MS

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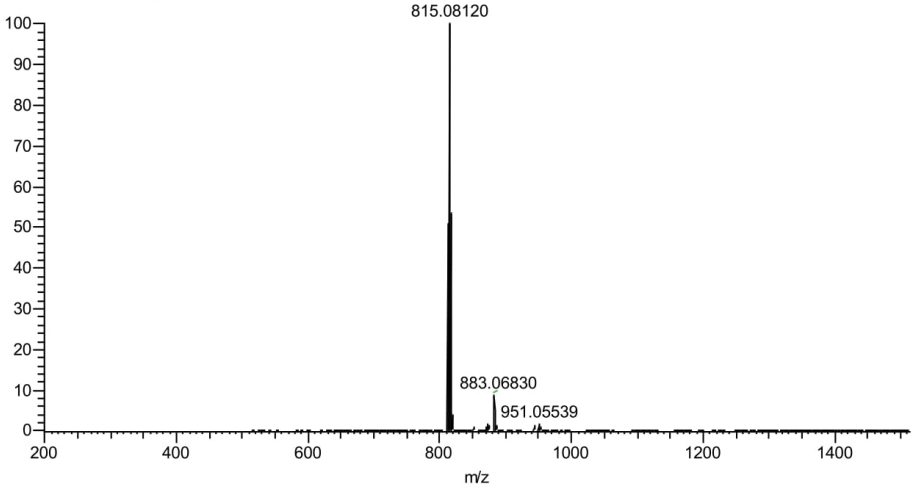
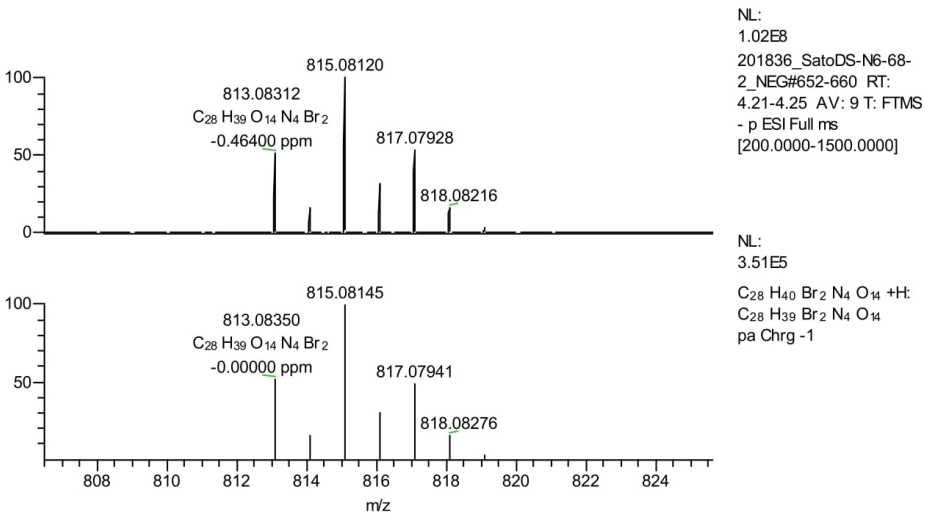
https://research.ncsu.edu/metric/

Sato DS-N6-68-2 Scan 4.20 – 4.26 minutes Negative Ion Mode

201836_SatoDS-N6-68-2_NEG #652-660 RT: ... 4.25 AV: 9 NL: 1.02E8
T: FTMS - p ESI Full ms [200.0000-1500.0000]



Sato DS-N6-68-2 Experimental and Theoretical Isotopic Distribution for $C_{28}H_{40}Br_2N_4O_{14}$ $[M-H]^-$

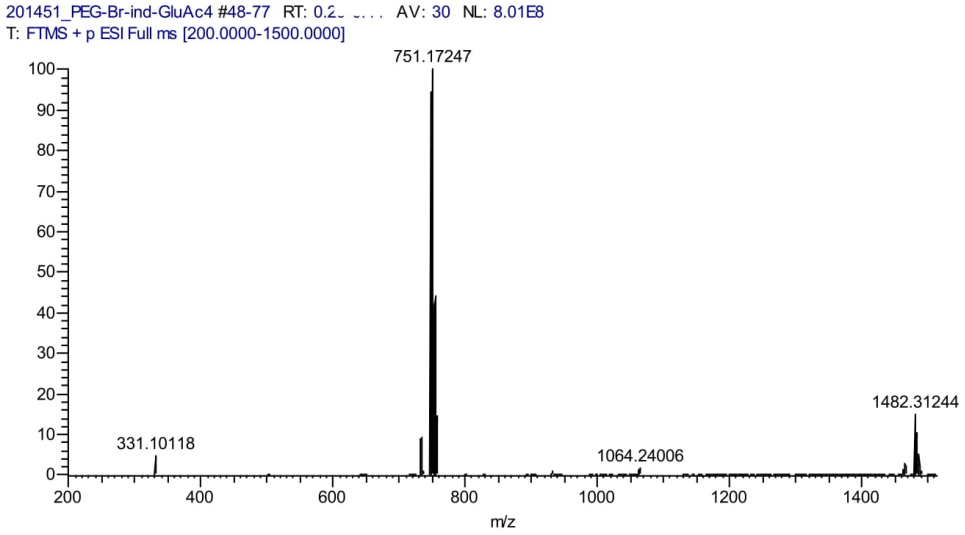


7: ESI-MS

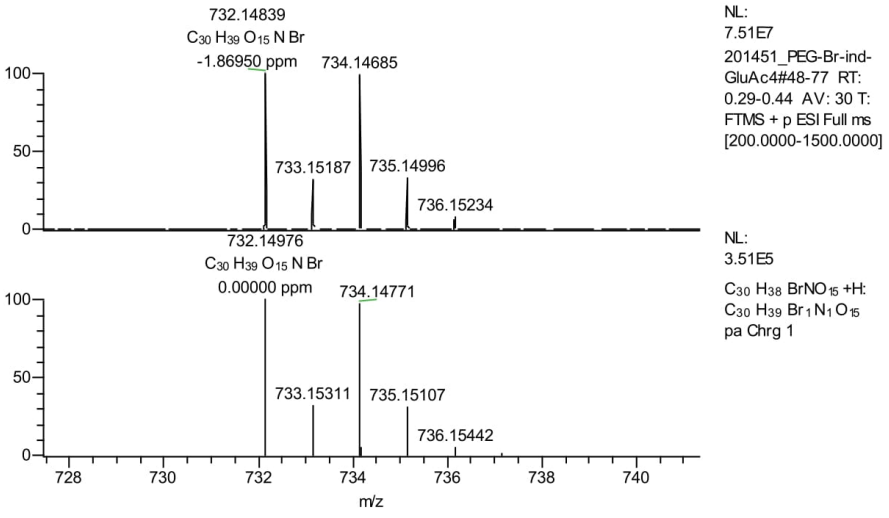
NC STATE UNIVERSITY
Molecular Education, Technology and
Research Innovation Center
Raleigh, NC 27695
https://research.ncsu.edu/metric/

MS Data

#1 PEG-Br-ind-GluAc4 Full Scan Positive Ion Mode



#1 PEG-Br-ind-GluAc4 Experimental and Theoretical Isotopic Distribution for $C_{30}H_{38}BrNO_{15}$ $[M+H]^+$

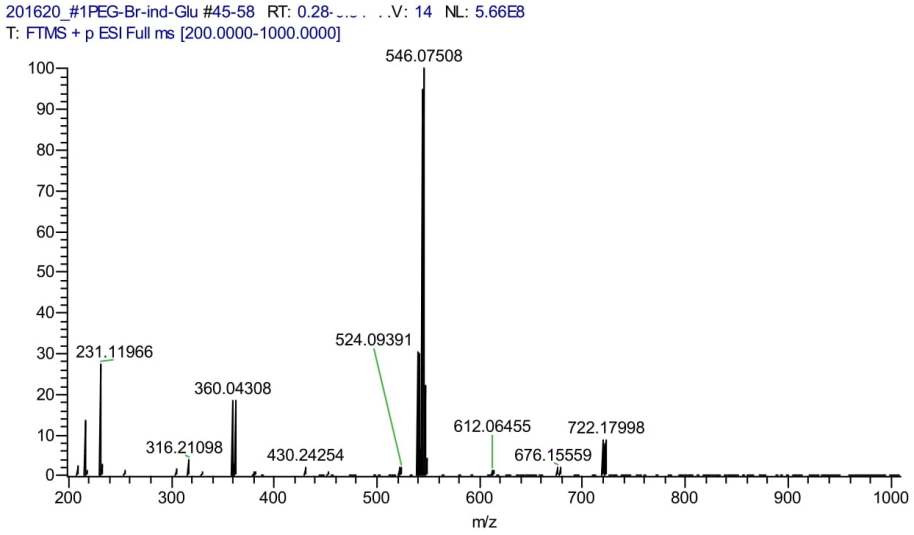


8: ESI-MS

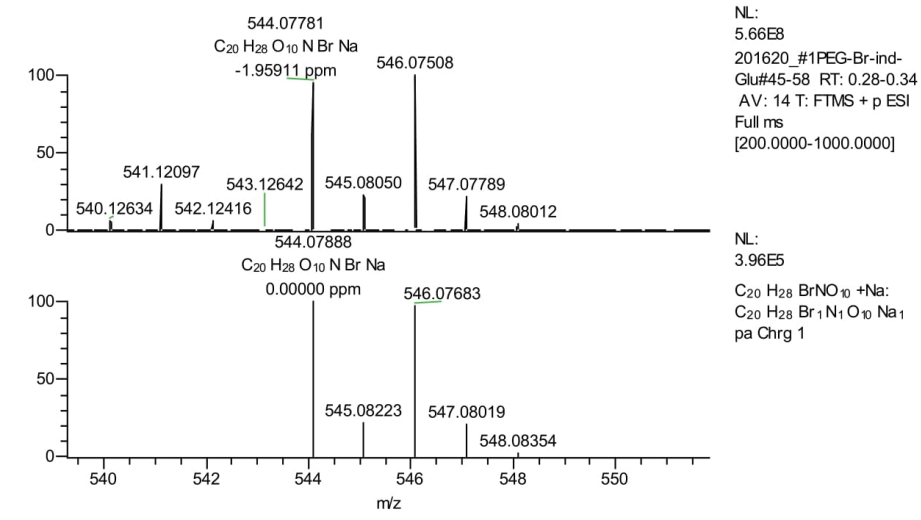
NC STATE UNIVERSITY
Molecular Education, Technology and
Research Innovation Center
Raleigh, NC 27695
https://research.ncsu.edu/metric/

MS Data

#1 PEG-Br-ind-Glu Full Scan Positive Ion Mode



#1 PEG-Br-ind-Glu Experimental and Theoretical Isotopic Distribution for $C_{20}H_{28}BrNO_{10}$ $[M+Na]^+$



10: ESI-MS

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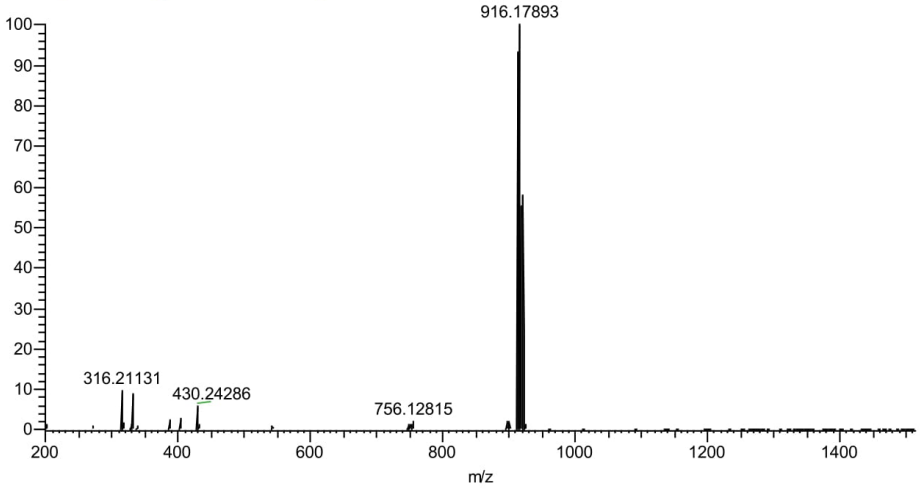
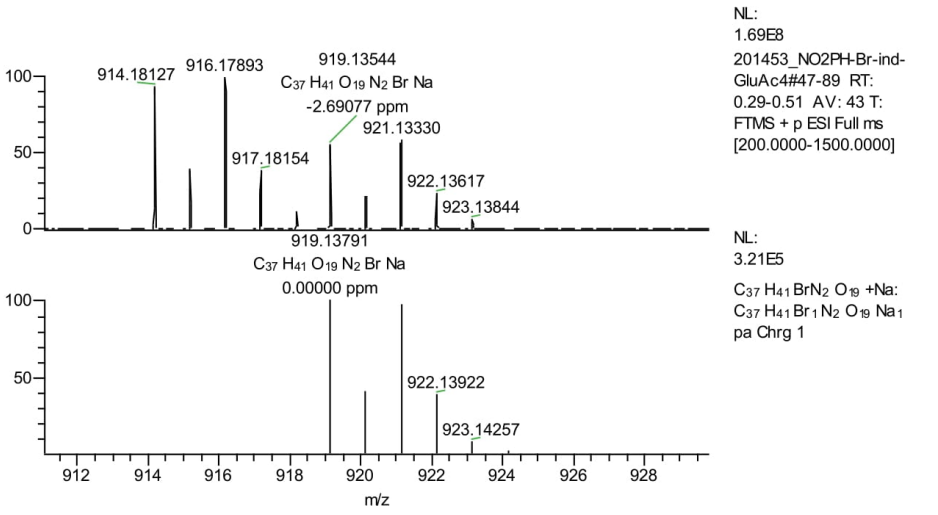
#2 NO2PH-Br-ind-GluAc4 Full Scan Positive Ion Mode

201453_NO2PH-Br-ind-GluAc4 #47-89 RT: [illegible] AV: 43 NL: 1.69E8
T: FTMS + p ESI Full ms [200.0000-1500.0000]



#2 NO2PH-Br-ind-GluAc4 Experimental and Theoretical Isotopic Distribution for $C_{37}H_{41}BrN_2O_{19}$ $[M+Na]^+$



11: ESI-MS

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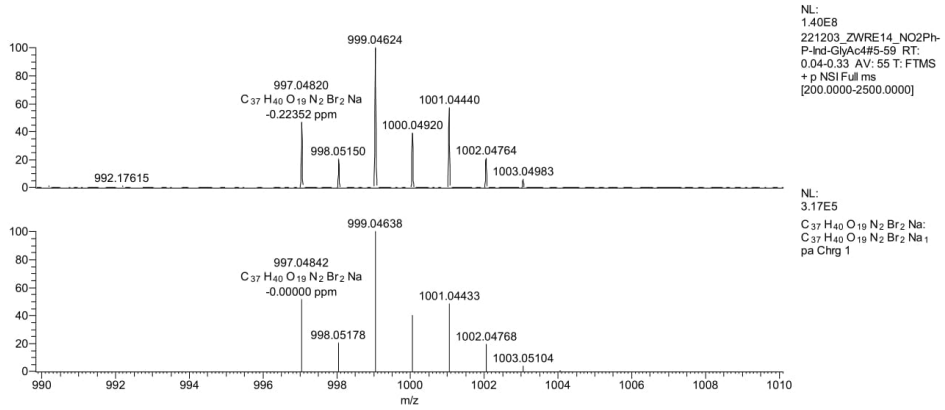
ZWRE14 6/6/22 [M+Na]$^+$



12: ESI-MS

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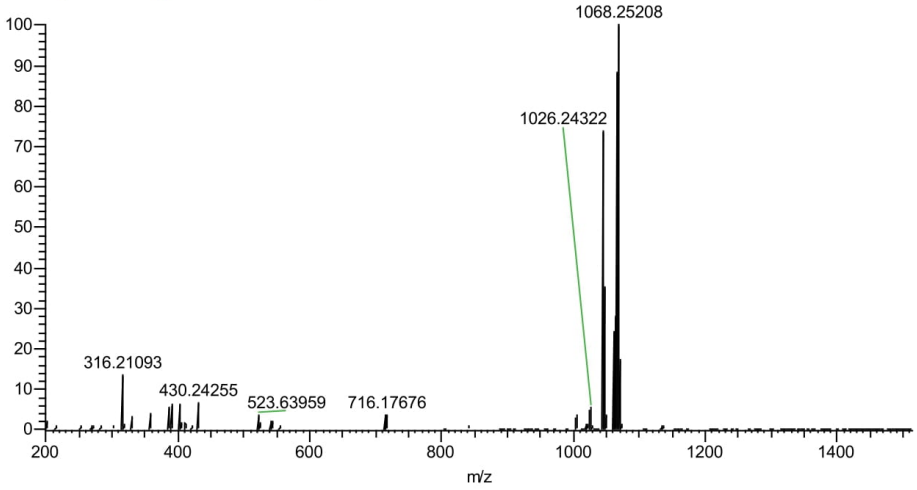
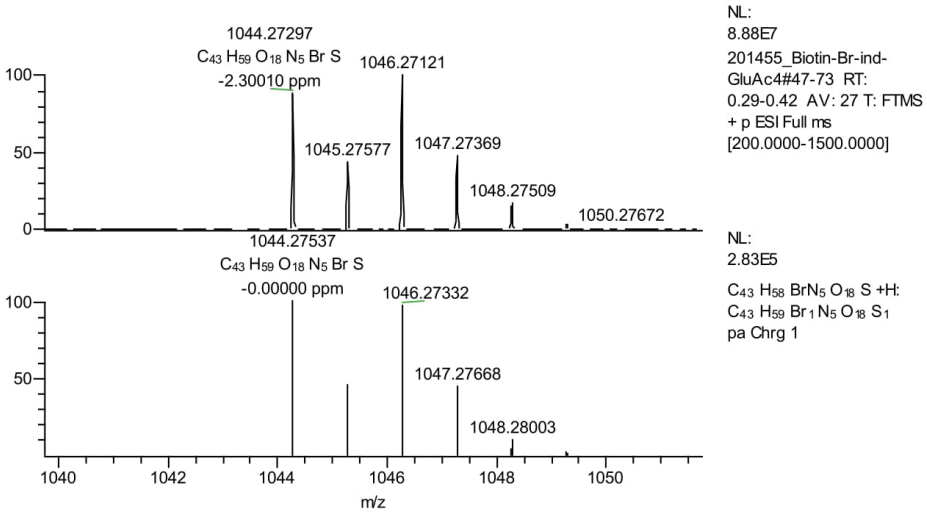
#3 Biotin-Br-ind-GluAc4 Full Scan Positive Ion Mode

201455_Biotin-Br-ind-GluAc4 #47-73 RT: 0.[illegible] AV: 27 NL: 1.20E8
T: FTMS + p ESI Full ms [200.0000-1500.0000]



#3 Biotin-Br-ind-GluAc4 Experimental and Theoretical Isotopic Distribution for $C_{43}H_{58}BrN_5O_{18}S$ $[M+H]^+$



14: ESI-MS

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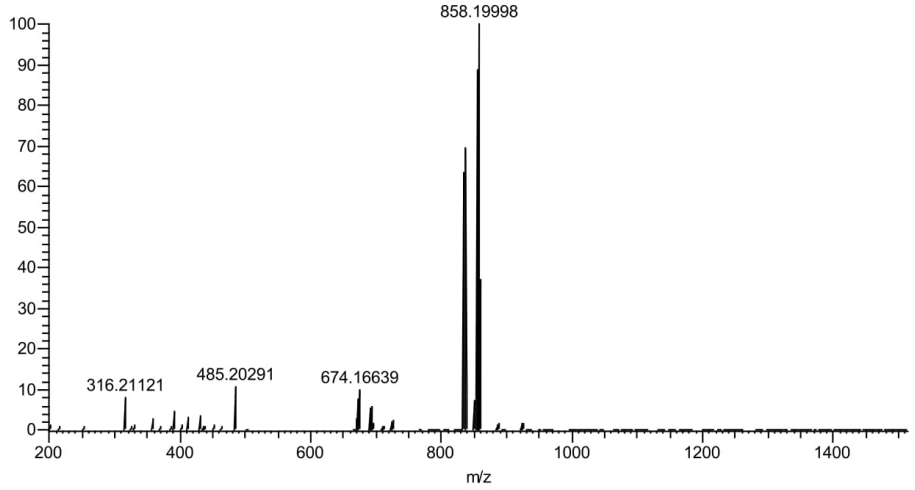
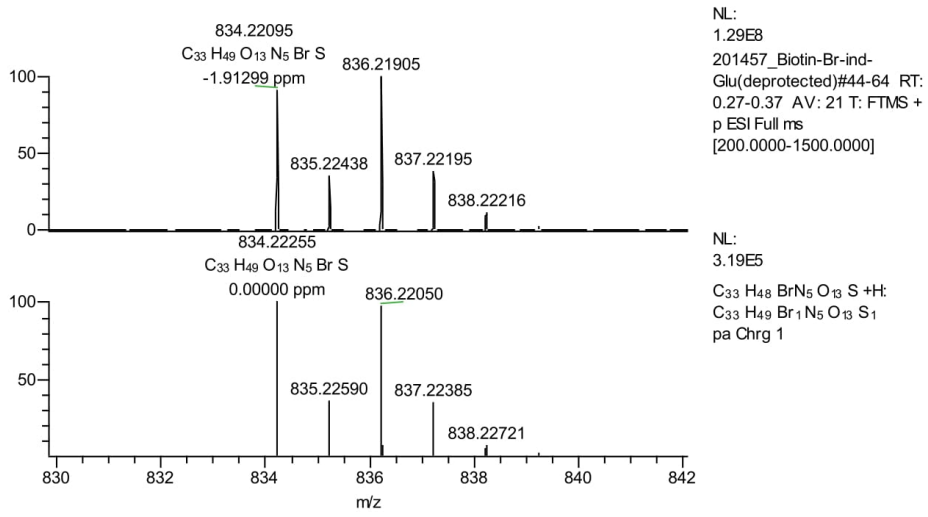
#4 Biotin-Br-ind-Glu (deprotected) Full Scan Positive Ion Mode

201457_Biotin-Br-ind-Glu(deprotected) #44-[illegible] .... 0.27-0.37 AV: 21 NL: 1.85E8
T: FTMS + p ESI Full ms [200.0000-1500.0000]



#4 Biotin-Br-ind-Glu (deprotected) Experimental and Theoretical Isotopic Distribution for $C_{33}H_{48}BrN_5O_{13}S$ $[M+H]^+$



15: MALDI-MS

20221207_RE90_Biotin-Peg-IndBr2-Gly
20221207_RE90_Biotin-Peg-IndBr2-Gly
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
915
920
925
930
935
940
945
950
955
960
m/z
936.634
934.620
938.651
950.655
952.651
954.685
Target
Target type 0280781
Target serial number 1002424
Position G11
Laser
Laser beam attenuation 37
Laser beam focus 36
Laser repetition rate 2000 Hz
Number of shots 500
Spectrometer
positive voltage polarity POS
PIE delay 130 ns
Ion source voltage 1 19 kV
Ion source voltage 2 16.85 kV
Lens voltage 8.3 kV
Linear detector voltage 2.717 kV
Deflection on
Deflection mass
MSMS parent mass
LIFT voltage 1
LIFT voltage 2
LIFT 1 Pulser time
depending on the parent
mass
LIFT 2 Pulser time
Reflector voltage 1 21 kV
Reflector voltage 2 9.6 kV
Reflector detector volt. 1.662 kV
Instrument
Instrument type autoflex
Instrument serial 1857351.00828
Name of computer FLEX-PC
Operator ID or name flex-user
flexControl version flexControl 3.4.168.0
flexAnalysis version
Date of Acquisition 2022-12-07T16:05:39.020-05:00 printed: 12/7/2022 4:08:16 PM
Acquisition method D:\Methods\flexControlMethods\LindseyLindsey_ZhiyuanRP_0-1500_Da.par
Processing method
File Name D:\Data\LindseyZhiyuanW\20221207_RE90_Biotin-Peg-IndBr2-Gly\0_G11\1
Performed by
Date / Sign
Viewed by
Date / Sign
Bruker Daltonics

15-AcOH: ESI-MS

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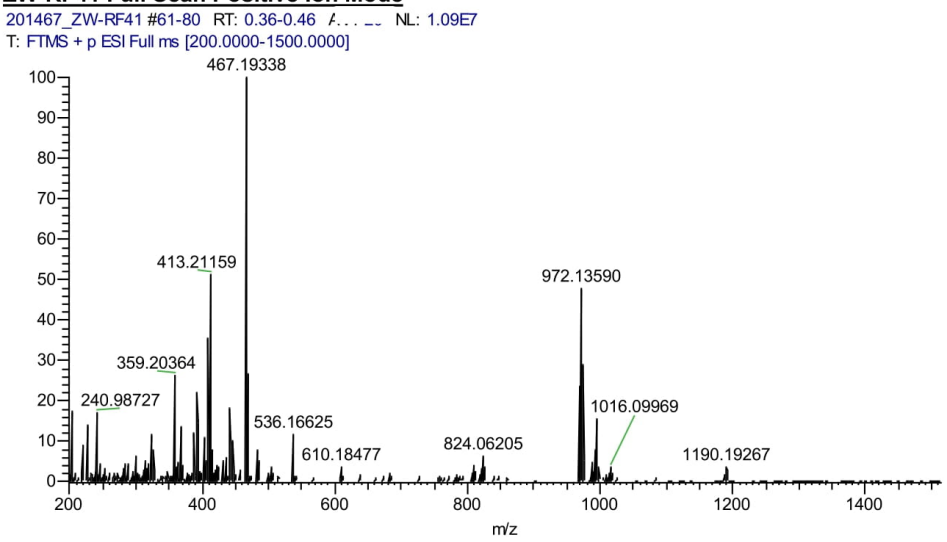
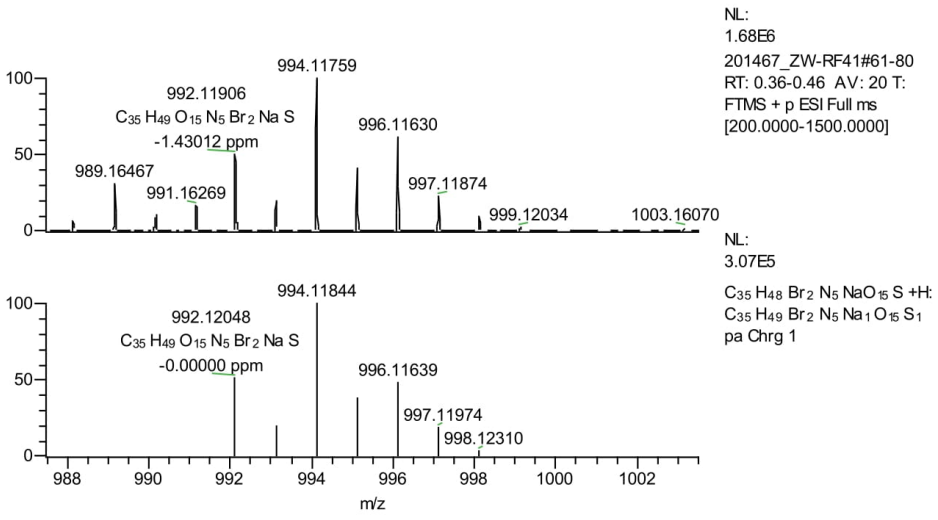
ZW-RF41 Full Scan Positive Ion Mode



ZW-RF41 Experimental and Theoretical Isotopic Distribution for $C_{35}H_{48}Br_2N_5NaO_{15}S$ $[M+H]^+$



17: ESI-MS

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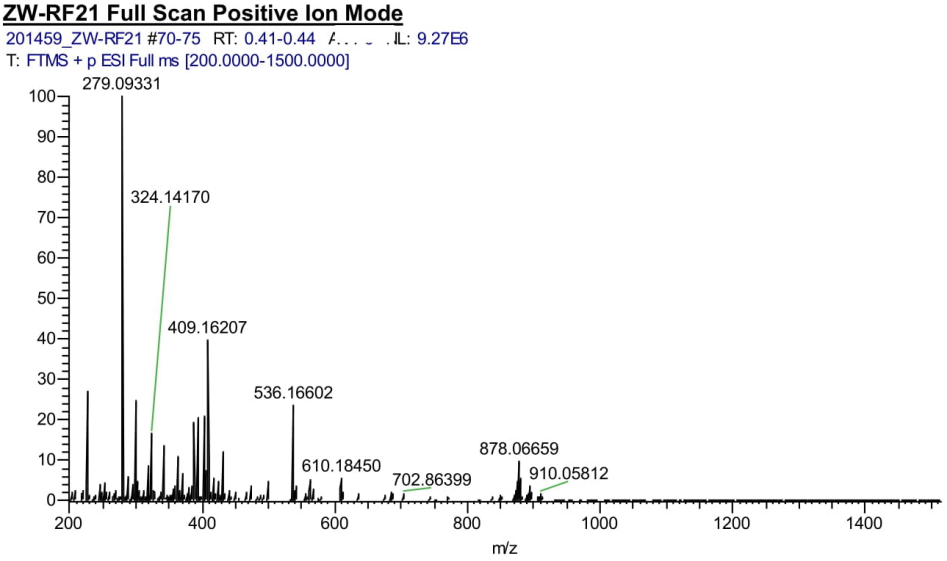
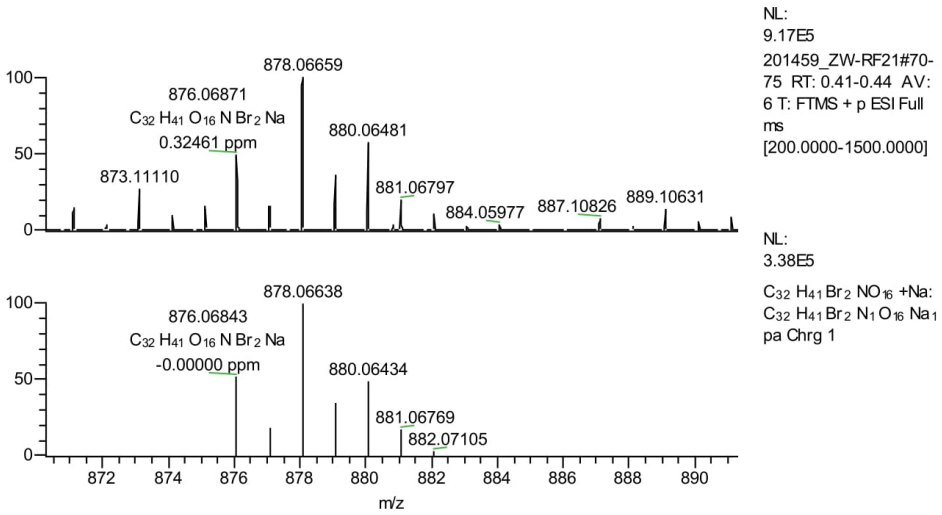
ZW-RF21 Full Scan Positive Ion Mode



ZW-RF21 Experimental and Theoretical Isotopic Distribution for $C_{32}H_{41}Br_2NO_{16}$ $[M+Na]^+$



18-AcOH: ESI-MS

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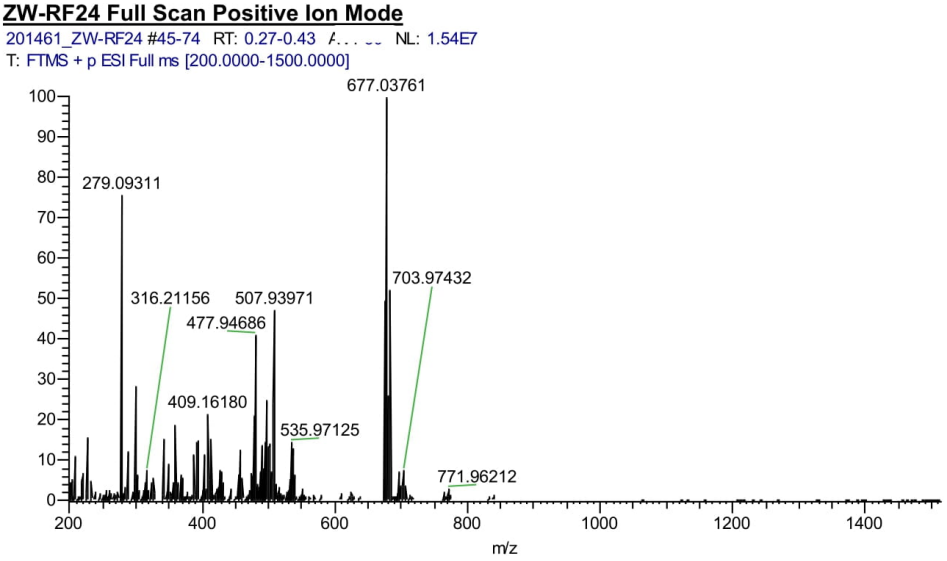
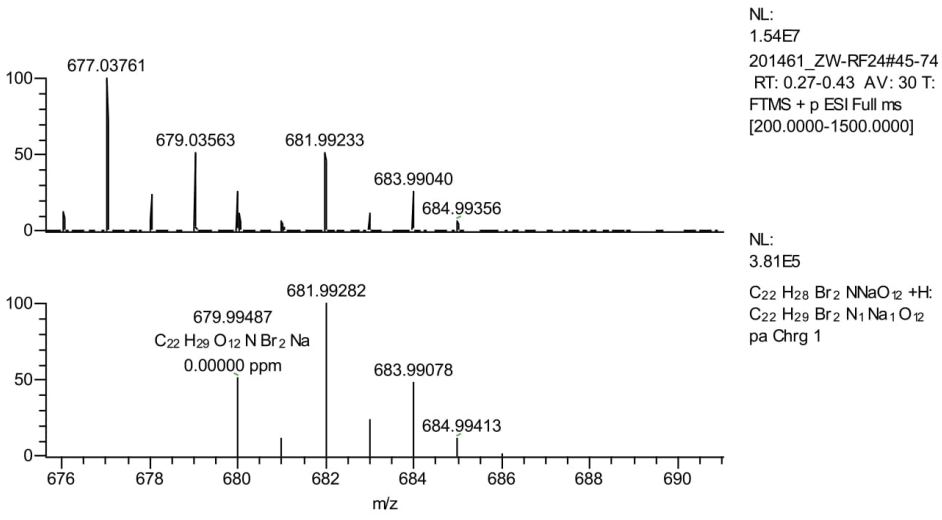
ZW-RF24 Full Scan Positive Ion Mode



ZW-RF24 Experimental and Theoretical Isotopic Distribution for $C_{22}H_{28}Br_2NNaO_{12}$ $[M+H]^+$



19: ESI-MS

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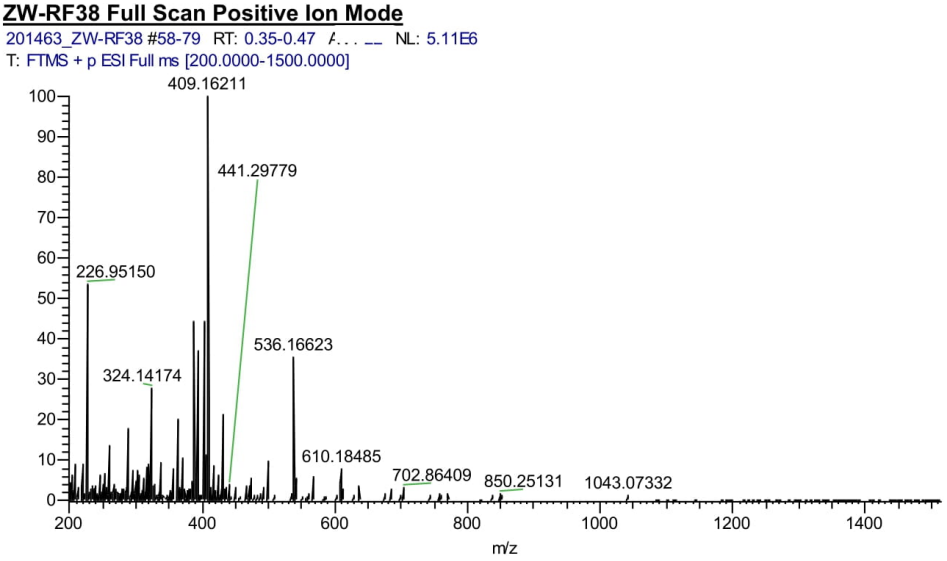
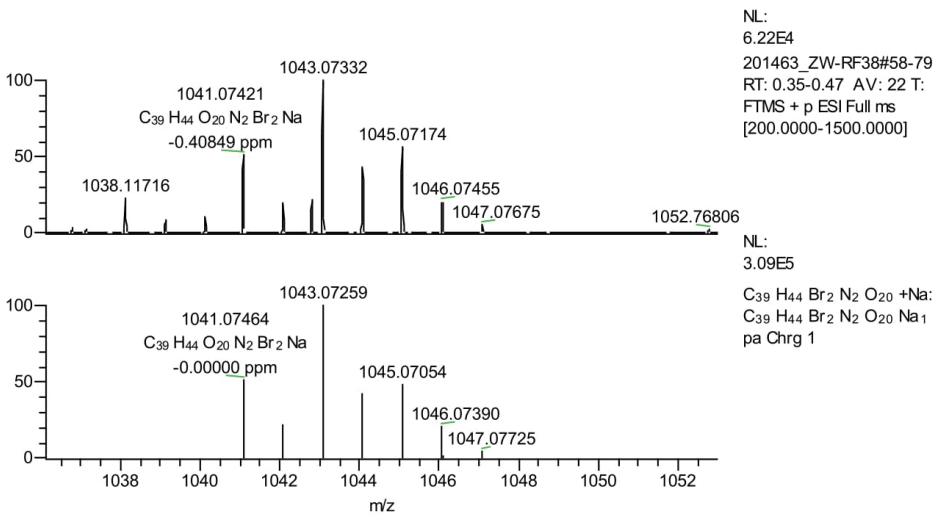
ZW-RF38 Full Scan Positive Ion Mode



ZW-RF38 Experimental and Theoretical Isotopic Distribution for $C_{39}H_{44}Br_2N_2O_{20}$ $[M+Na]^+$



20: ESI-MS

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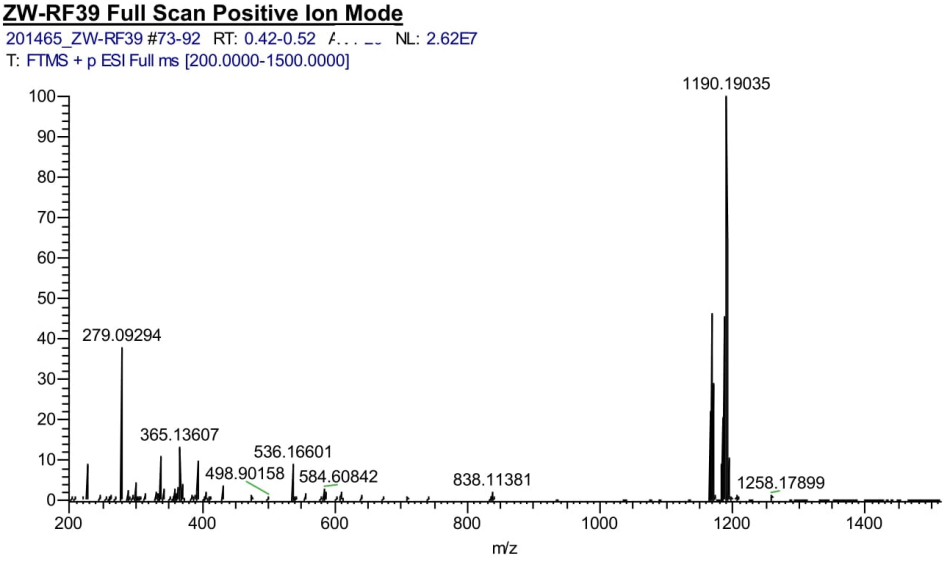
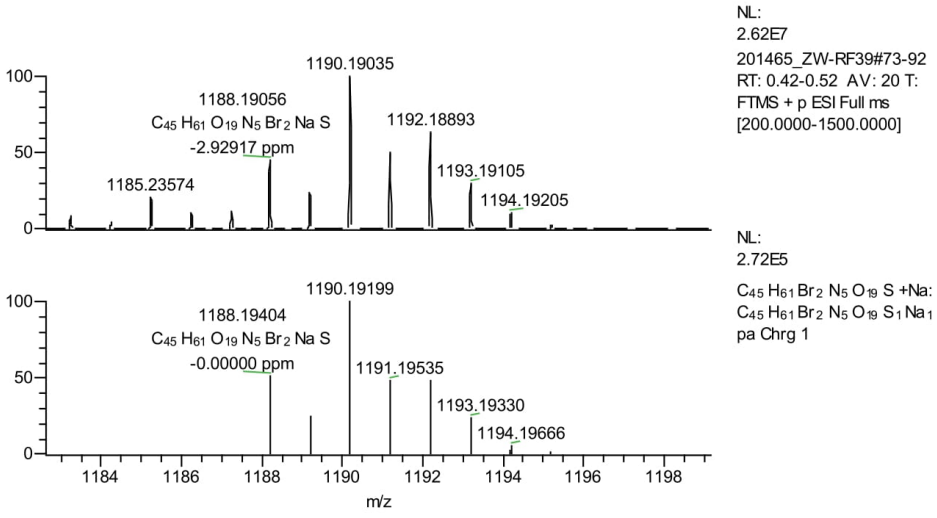
ZW-RF39 Full Scan Positive Ion Mode



ZW-RF39 Experimental and Theoretical Isotopic Distribution for $C_{45}H_{61}Br_2N_5O_{19}S$ [M+Na]$^+$



21: ESI-MS

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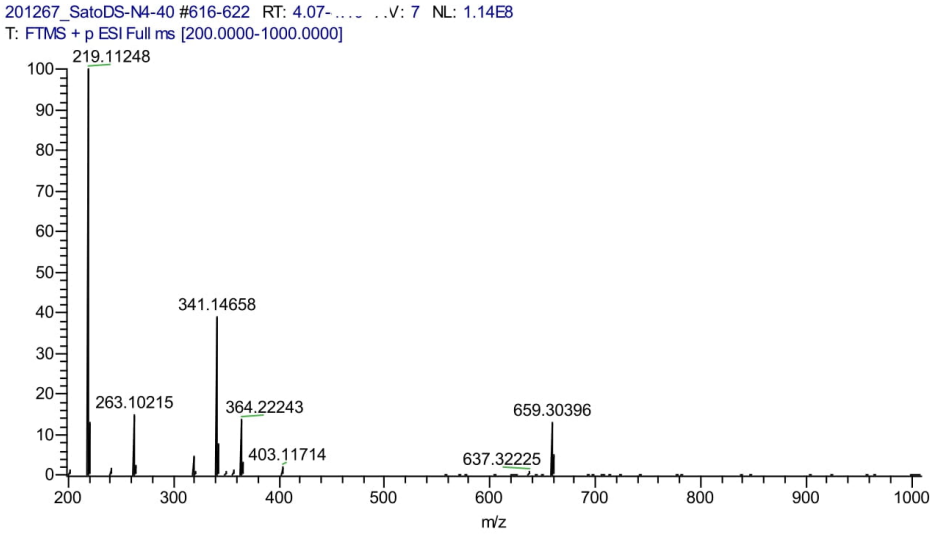
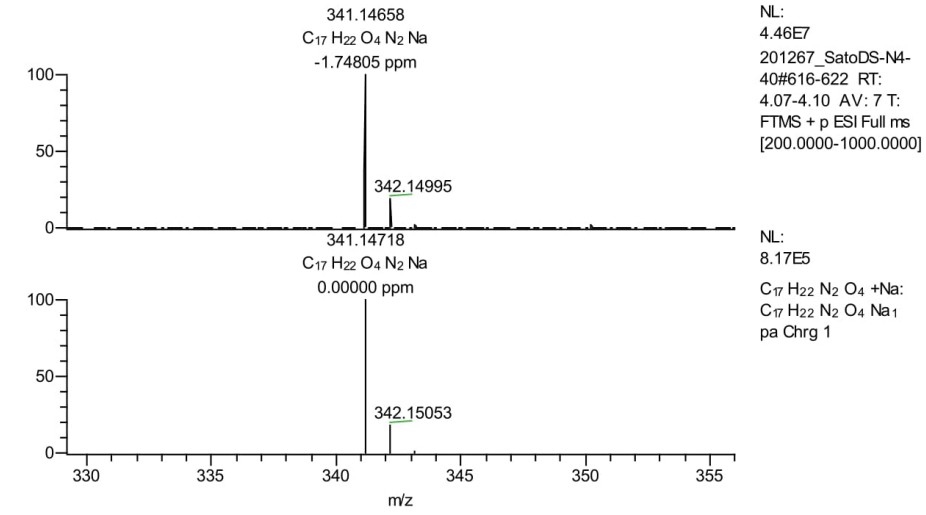
Sato DS-N4-40 Scan 4.04 – 4.09 minutes Positive Ion Mode



Sato DS-N4-40 Experimental and Theoretical Isotopic Distribution for $C_{17}H_{22}N_2O_4$ [M+Na]$^+$



22: ESI-MS

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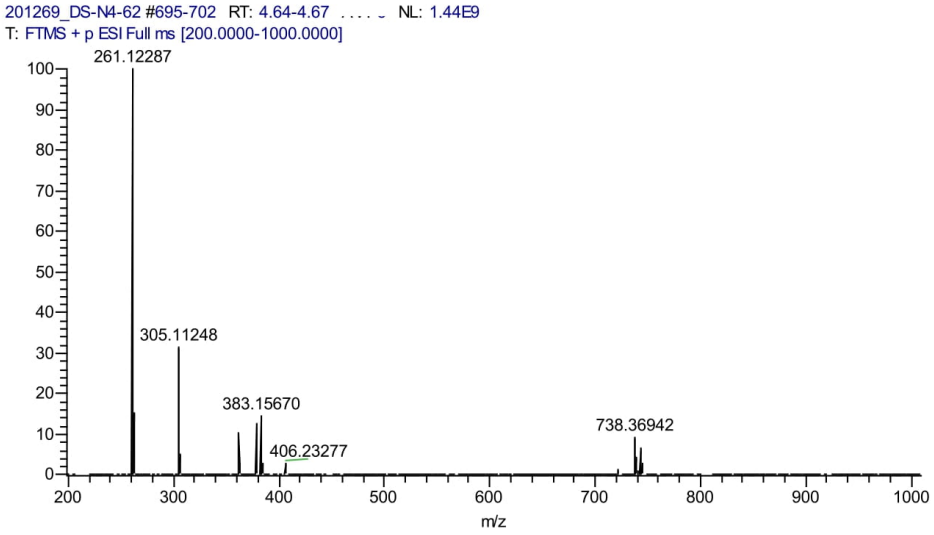
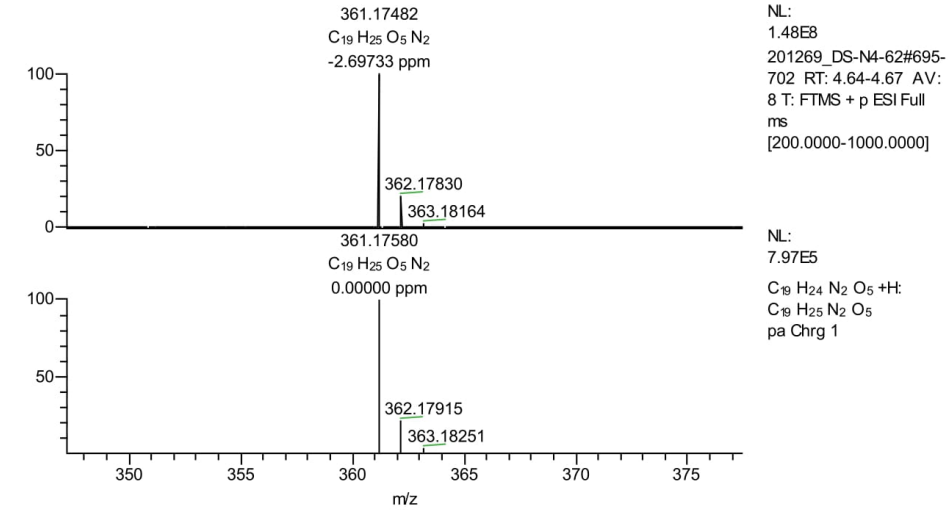
Sato DS-N4-62 Scan 4.64 – 4.67 minutes Positive Ion Mode



Sato DS-N4-62 Experimental and Theoretical Isotopic Distribution for $C_{19}H_{24}N_2O_5$ [M+H]$^+$



23·HCl: ESI-MS

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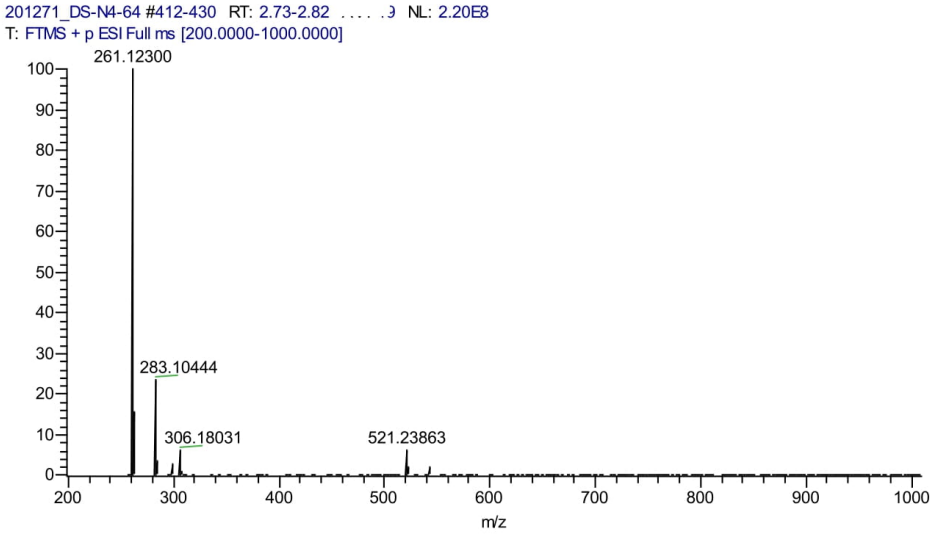
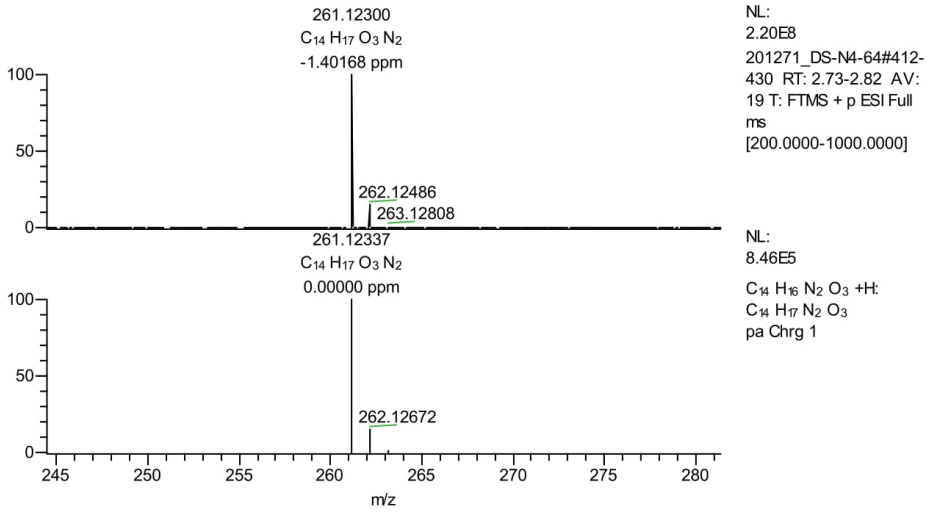
Sato DS-N4-64 Scan 2.73 – 2.82 minutes Positive Ion Mode



Sato DS-N4-64 Experimental and Theoretical Isotopic Distribution for $C_{14}H_{16}N_2O_3$ [M+H]$^+$



24: ESI-MS

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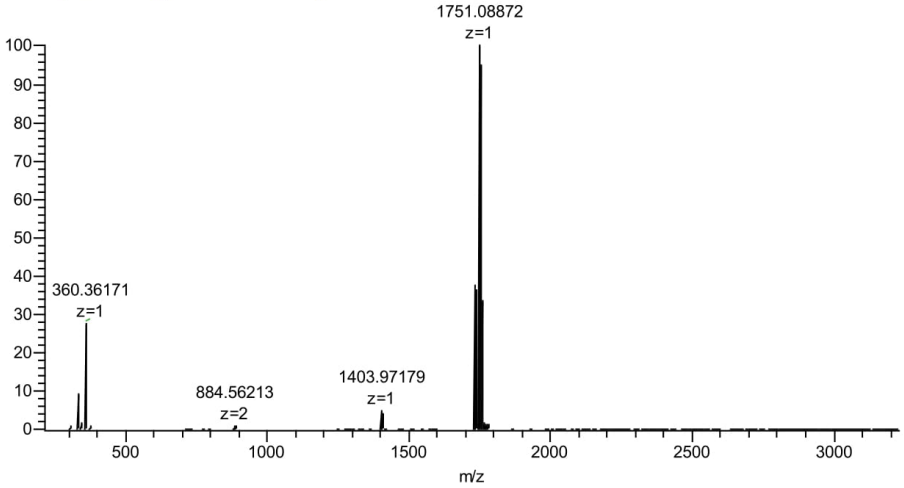
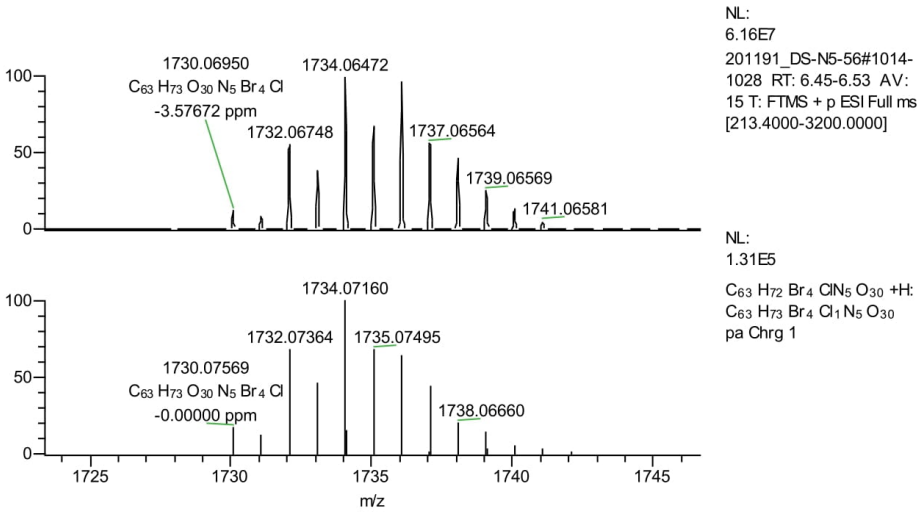
Sato DS-N5-56 Scan 6.45 – 6.53 minutes Positive Ion Mode

201191_DS-N5-56 #1014-1028 RT: 6.45-6.5[illegible] ... I5 NL: 1.64E8
T: FTMS + p ESI Full ms [213.4000-3200.0000]



Sato DS-N5-56 Experimental and Theoretical Isotopic Distribution for $C_{63}H_{72}Br_4ClN_5O_{30}$ $[M+H]^+$



25: ESI-MS

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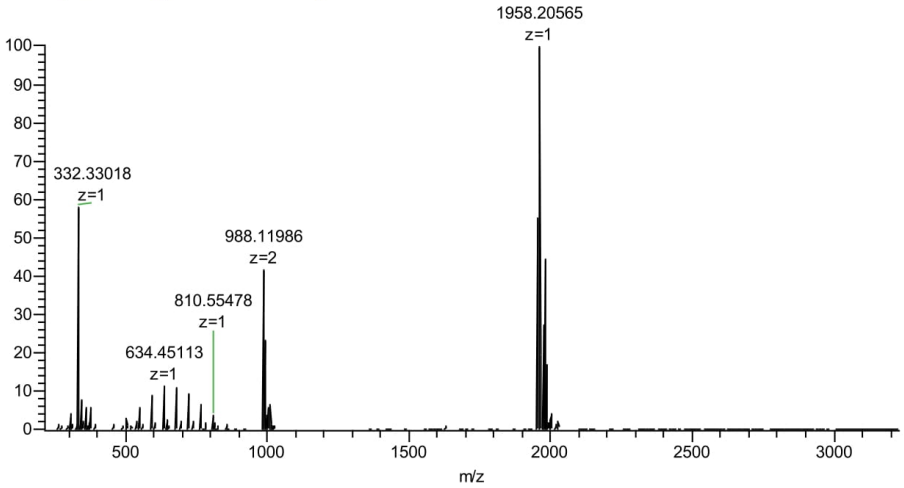
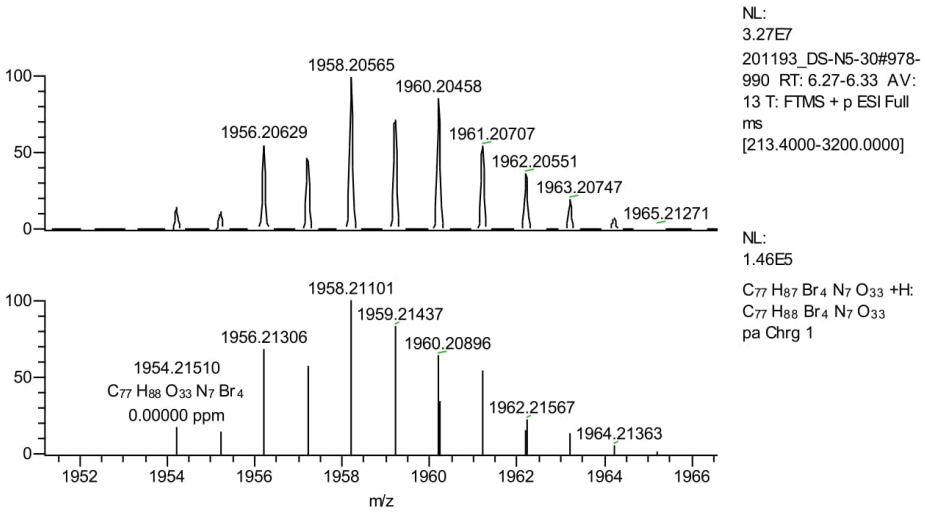
Sato DS-N5-30 Scan 6.27 – 6.33 minutes Positive Ion Mode

201193_DS-N5-30 #978-990 RT: 6.27-6.33 . . . . . NL: 3.27E7
T: FTMS + p ESI Full ms [213.4000-3200.0000]



Sato DS-N5-30 Experimental and Theoretical Isotopic Distribution for $C_{77}H_{87}Br_4N_7O_{33}$ [M+H]$^+$



26: ESI-MS

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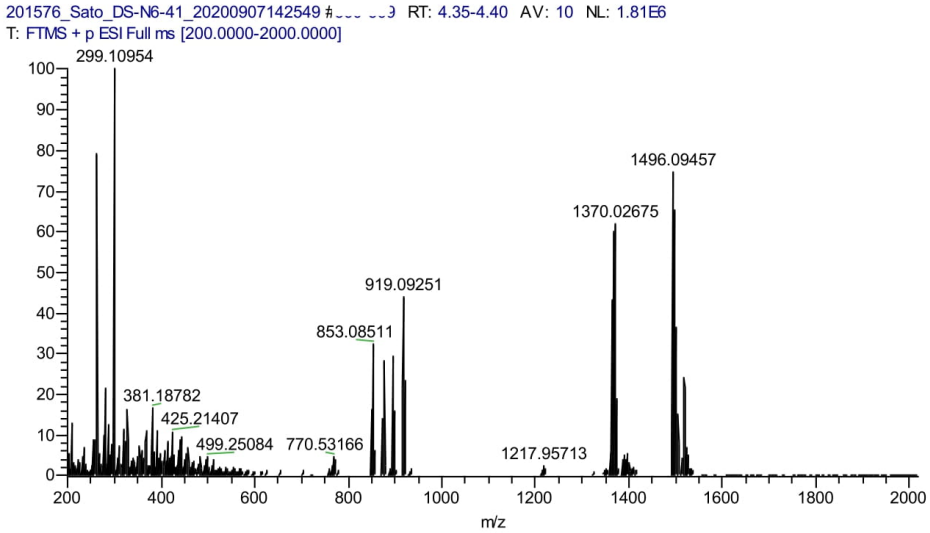
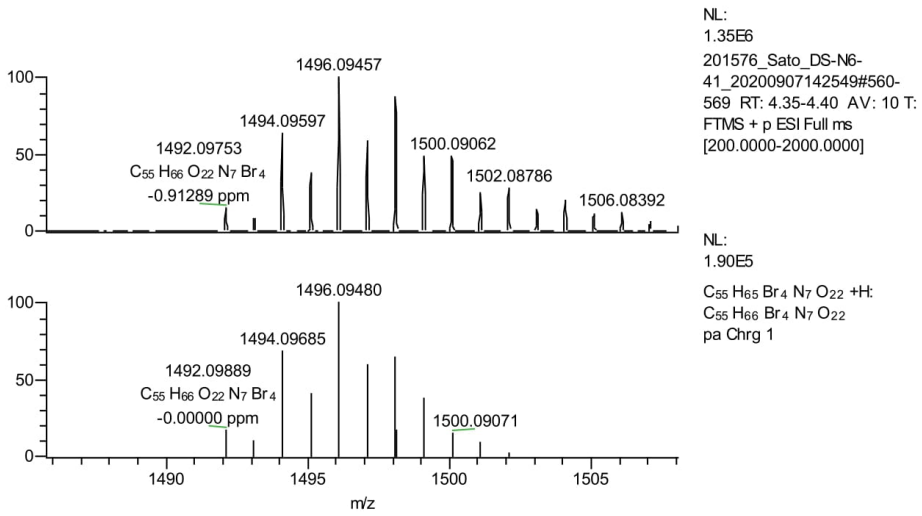
Sato DS-N5-41 Scan 4.27 – 4.35 minutes Positive Ion Mode



Sato DS-N5-41 Experimental and Theoretical Isotopic Distribution for $C_{55}H_{65}Br_4N_7O_{22}$ $[M+H]^+$



27: ESI-MS (S95–S97)

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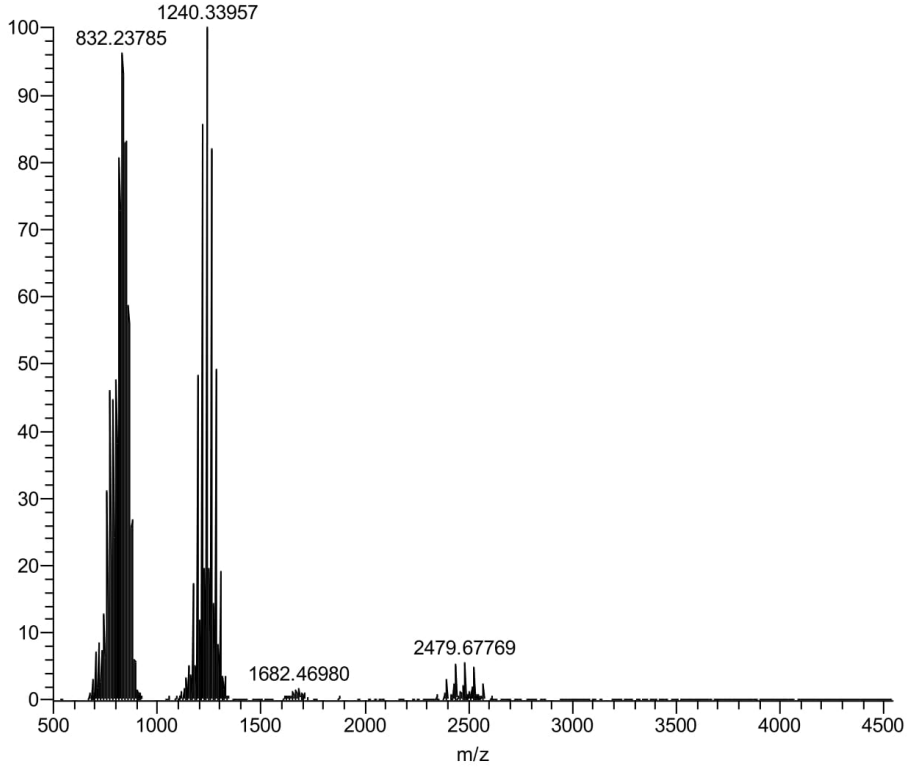
MS Data

JD-6-13-1 Full Scan Positive Ion Mode:
230027_JD-6-13-1 #588-594 RT: 4.43-4.46 AV: 7 NL: 1.73E6
T: FTMS + p ESI Full ms [500.0000-4500.0000]



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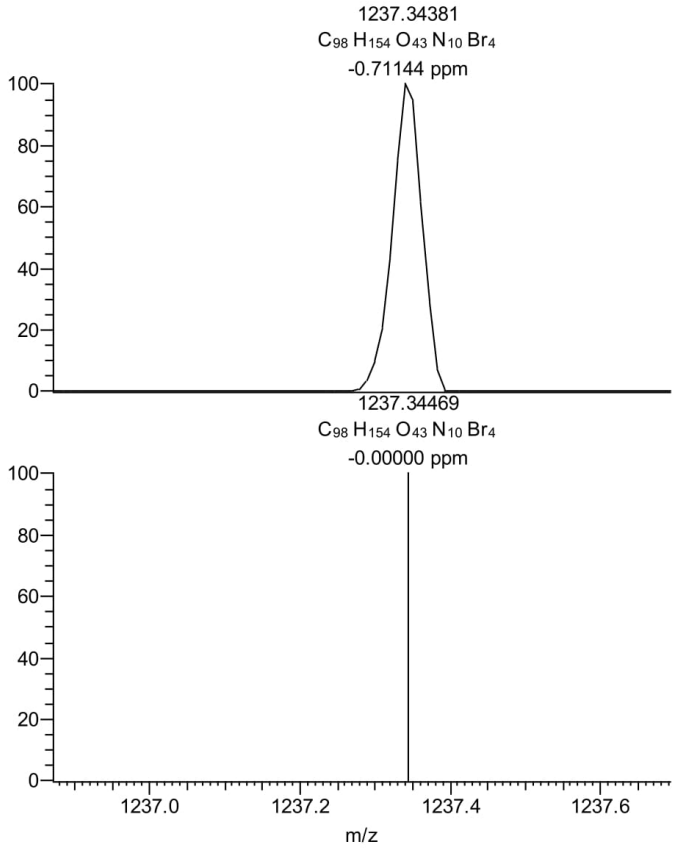
JD-6-13-1 Experimental and Theoretical Isotopic Distribution $[M+2H]^{2+}$



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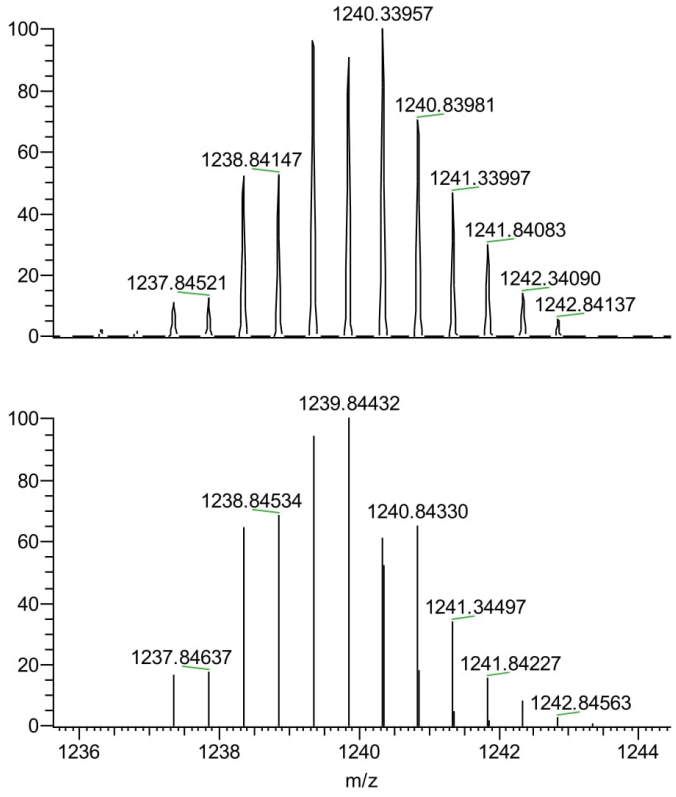

Ind(18)$_2$: ESI-MS

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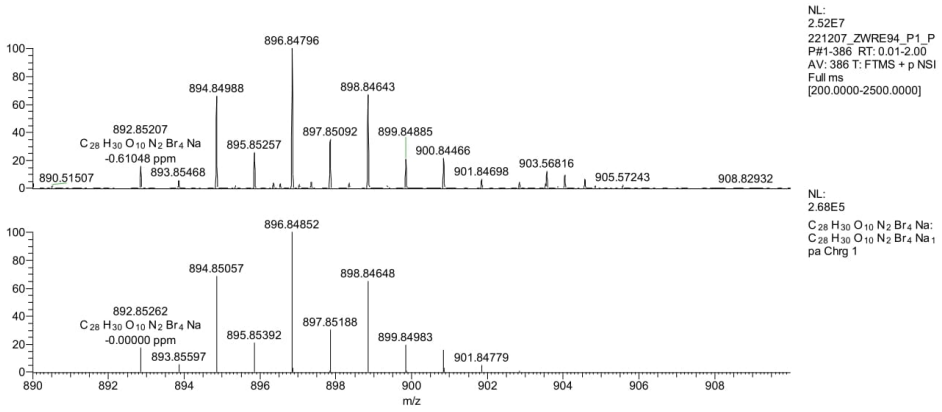
ZWRE94_P1_PP 6/6/2022 [M+Na]$^+$



Ind(15)$_2$: ESI-MS

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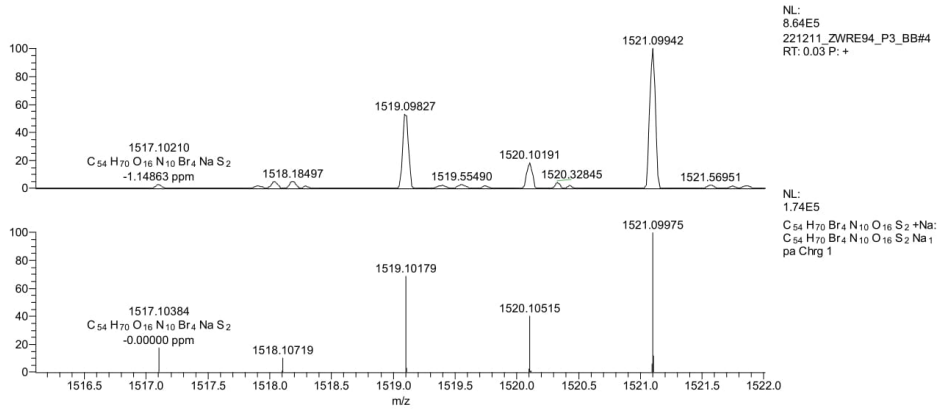
ZWRE94_P3 6/6/2022 [M+Na]$^+$



Ind(15/18): ESI-MS

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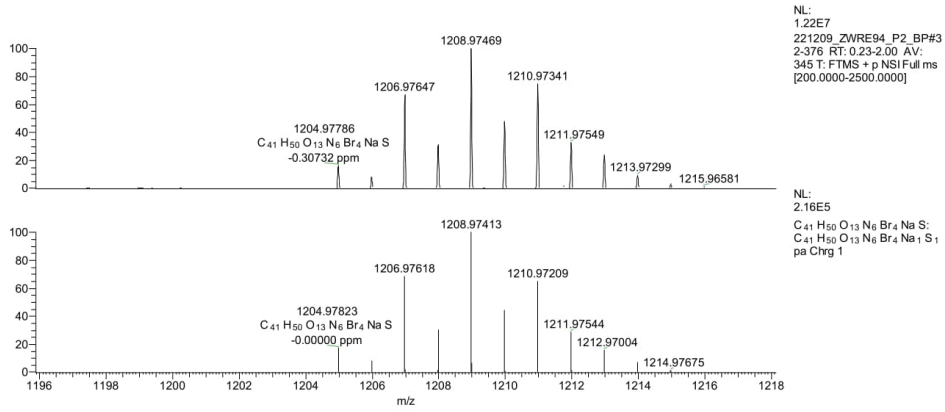
ZWRE94_P2 6/6/2022 $[M+Na]^+$



Ind(8)$_2$: ESI-MS

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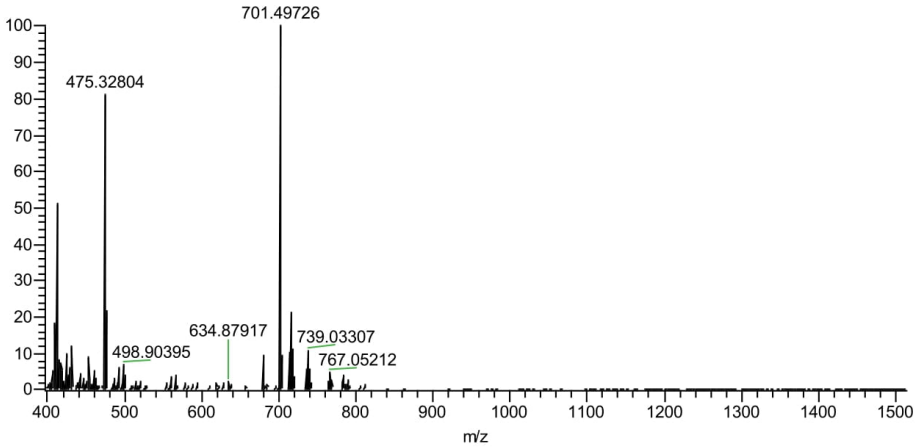
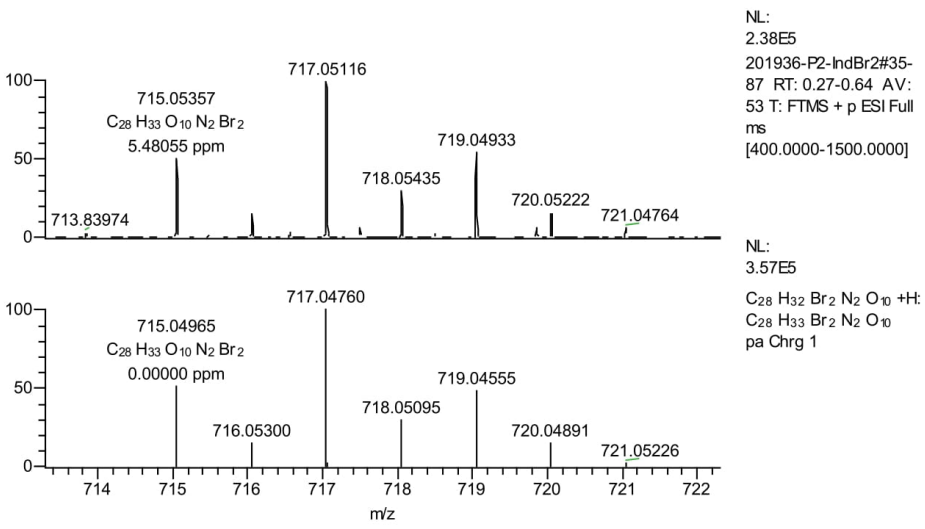
MS Data

#1 P2-IndBr2 Full Scan Positive Ion Mode

201936-P2-IndBr2 #44-55 RT: 0.33-0.39 AV: 3.72E6
T: FTMS + p ESI Full ms [400.0000-1500.0000]



#1 P2-IndBr2 Experimental and Theoretical Isotopic Distribution for $C_{28}H_{32}Br_2N_2O_{10}$ $[M+H]^+$



Ind(14)$_2$: ESI-MS

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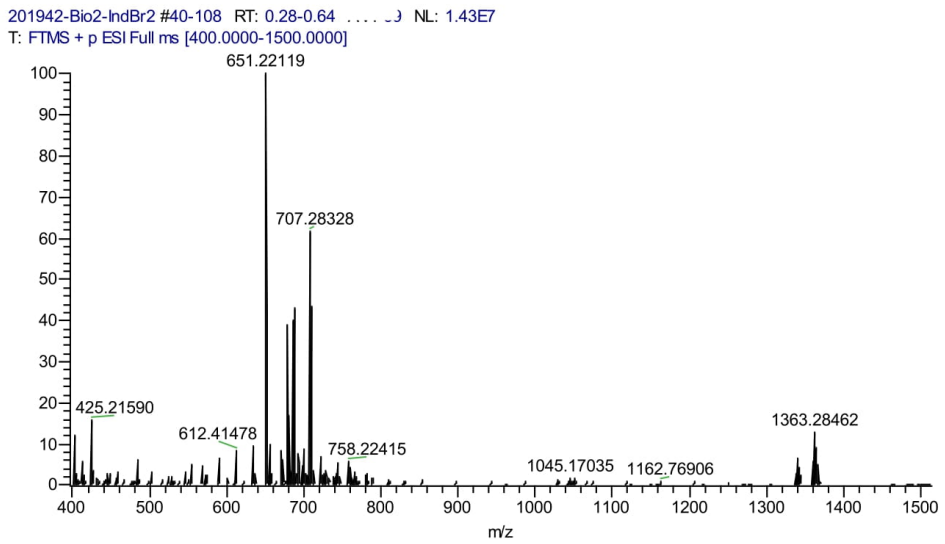
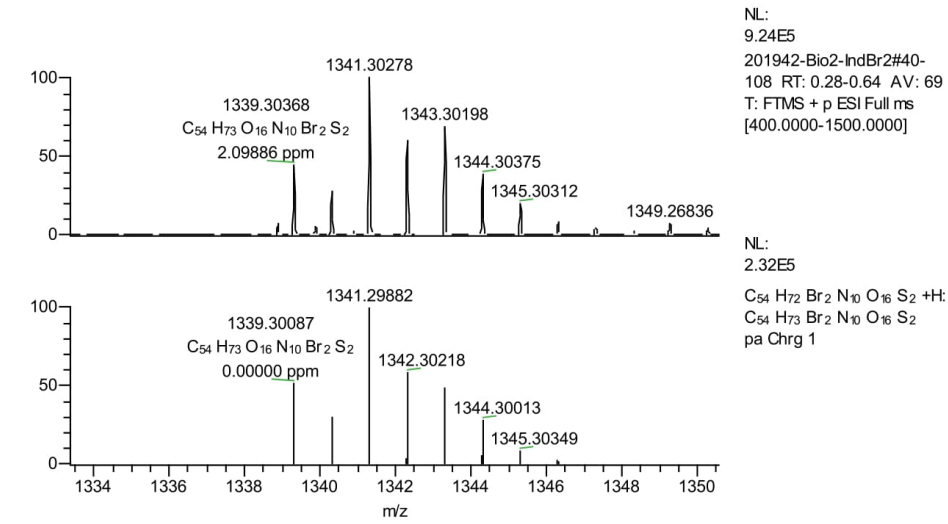
#3 Bio2-IndBr2 Full Scan Positive Ion Mode



#3 Bio2-IndBr2 Experimental and Theoretical Isotopic Distribution for $C_{54}H_{72}Br_2N_{10}O_{16}S_2$ $[M+H]^+$



Ind(8/14): ESI-MS

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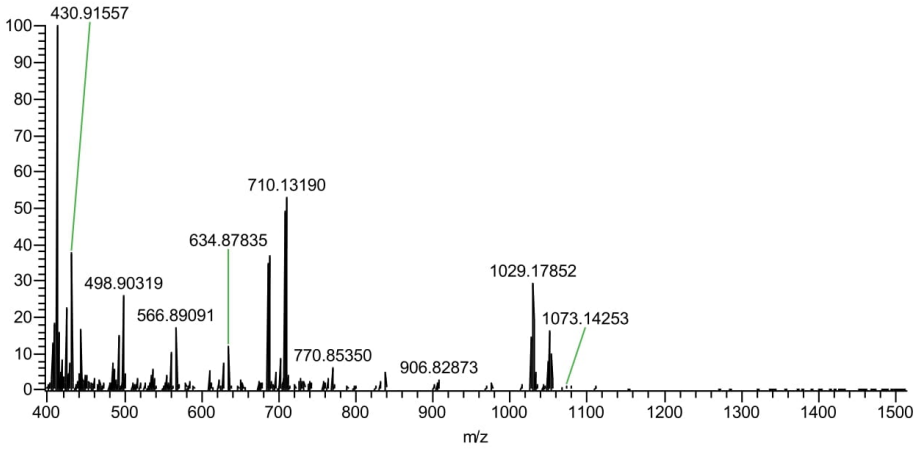
#2 Bio-IndBr2-P Full Scan Positive Ion Mode

201939-Bio-IndBr2-P #31-61 RT: 0.25-0.44 A\ . . . IL: 2.24E6
T: FTMS + p ESI Full ms [400.0000-1500.0000]



#2 Bio-IndBr2-P Experimental and Theoretical Isotopic Distribution for $C_{41}H_{52}Br_2N_6O_{13}S$ [M+H]$^+$