

Supporting Information

Mechanochemical synthesis of β -cyclodextrin urea derivatives under reactive CO₂ atmosphere by Staudinger aza-Wittig reaction

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Reactants:

β -cyclodextrin was purchased from Roquette Frères (Lestrem, France). All reactants were purchased from Sigma-Aldrich. All chemicals were used without further purification. Compounds **1A** and **1B** were synthesized according to the protocol established by Molina and co¹.

Milling protocol:

Solids are ground using a Frisch PULVERISETTE 7 premium line planetary microgrinder equipped with 20mL zirconium oxide bowls lined associate to gassing lids with valves with 10 x 10mm zirconium oxide balls (average mass 2.8g) rotating at 850 rpm.

Purification methods:

The 7Ax products are purified by flash chromatography on a silica column starting from a solid deposit (reactive crude powder dispersed in three times its mass of silica), and then eluted with a chloroform / acetonitrile mixture ranging from 9:1 to 6:4.

The 7Bx products are purified by flash chromatography on a silica column starting from a solid deposit (reactive crude powder dispersed in three times its mass of silica), and then eluted with a chloroform / methanol mixture ranging from 9:1 to 8:2.

Characterization methods:

NMR spectra were recorded at 298 K on a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm broadband BBFO probe with Z gradients, operating at 7.05 T field strength (300 MHz for ¹H nuclei, 121 MHz for ³¹P nuclei and 75 MHz for ¹³C nuclei). Mass spectra were recorded using a MALDI-TOF/TOF UltraFlex II (Bruker Daltonics) spectrometer in positive reflectron mode with 2,5-DHB as the matrix.

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¹ A.G. Molina, V. Kungurtsev, P. Virta, H. Lönnberg, *molecules*, **2012**, (17), 12102-12120

Green Chemistry Metrics calculations for **7Ak**

Mol wt of **1A** : 2000.7 g/mol

Mol wt of TPP : 262.3 g/mol

Mol wt of TPPO : 278.3 g/mol

Mol wt of CO₂ : 44.0 g/mol

Mol wt of N₂ : 28.0 g/mol

Mol wt of 2-iodoaniline : 219.0 g/mol

Mol wt of **7Ak** : 2219.8 g/mol

Density of CHCl₃ : 1.489 g/cm³ (25 °C)

Atom Economy (AE) = ((Mol wt of product) / (Sum of mol wts of reactants)) x 100

Reaction Masse Efficiently (RME) = ((Mass of product)/ (Total mass of reactants)) x 100

Process Mass Intensity (PMI) = Total mass in process / Mass of product

E-Factor = (Total mass in process – Mass of product) / Mass of product

example in solution:

For **1A** (1000 mg, 0.5 mmol, 1 equiv.), TPP (157 mg, 0.60 mmol, 1.2 equiv.), 2-iodoaniline (131 mg, 0.60mmol, 1.2 equiv.), CHCl₃ (15 mL), CO₂ (10 bars), R.T.

Atom Economy (AE) = ((2219.8)/(2000.7+262.3+44+219))*100 ≈ 87.9

Reaction Masse Efficiently (RME) = (533/(1000+157+131+22))* 100 ≈ 40.7 (Please note : In solution, the amount of CO₂ introduced depends on the free volume and the solubility of CO₂ in the solvent. We do not have access to this experimental data, but only to the CO₂ pressure in the reactor at t0. Therefore, we arbitrarily chose to consider the amount of CO₂ corresponding to the stoichiometry relative to the cyclodextrins, which is 22 mg of CO₂.)

Process Mass Intensity (PMI) = (1000+157+131+22+22500)/533 ≈ 45 (Please note: We have chosen to exclude the purification steps from the calculation of the process mass intensity to allow for a more direct and fair comparison of the synthesis steps themselves. Furthermore, since the purification methods are the same in both processes, their inclusion is less relevant for this comparative analysis.)

E-Factor = ((1000+157+131+22+22500)-533)/533 ≈ 44

example by ball-milling:

For **1A** (1000 mg, 0.5 mmol, 1 equiv.), TPP (157 mg, 0.60 mmol, 1.2 equiv.), 2-iodoaniline (131 mg, 0.60mmol, 1.2 equiv.), CO₂ (10 bars), 850 rpm. R.T.

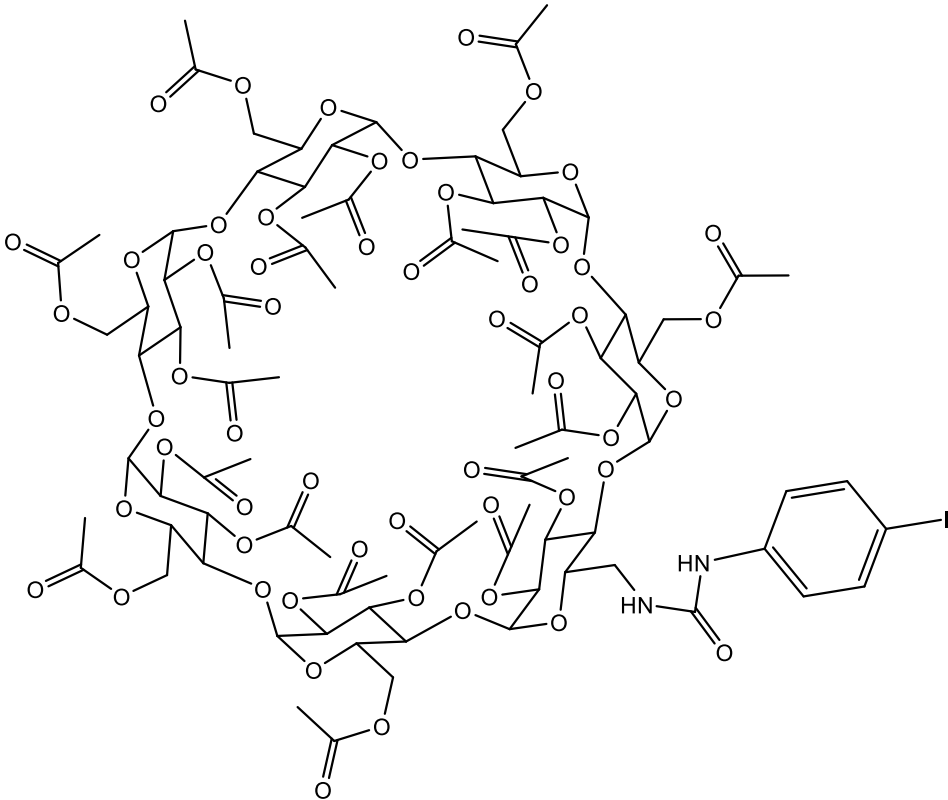
Atom Economy (AE) = $((2219.8)/(2000.7+262.3+44+219))*100 \approx 87.9$

Reaction Masse Efficiently (RME) = $(523/(1000+157+131+22))* 100 \approx 39.9$ ((Please note The determination of the introduced CO₂ mass depends on the free volume of the jar (total volume minus the volume of the reactants and balls) and the pressure. We do not have access to the actual available volume without precisely knowing the volume of the reactants, as we introduce masses without knowing their densities and porosities. Therefore, we arbitrarily chose to consider the CO₂ mass corresponding to the stoichiometry with respect to the cyclodextrins, which is 22 mg of CO₂.)

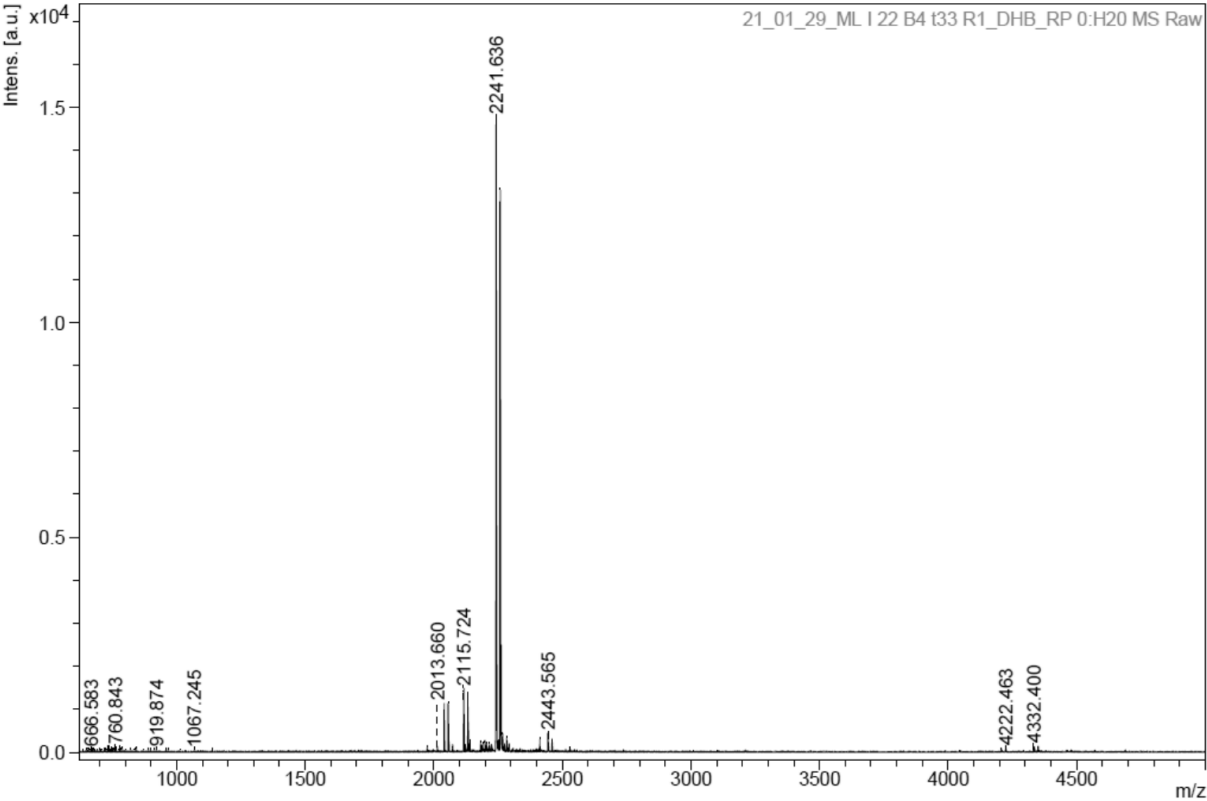
Process Mass Intensity (PMI) = $(1000+157+131+22)/523 \approx 2.5$ (Please note: We have chosen to exclude the purification steps from the calculation of the process mass intensity to allow for a more direct and fair comparison of the synthesis steps themselves. Furthermore, since the purification methods are the same in both processes, their inclusion is less relevant for this comparative analysis.)

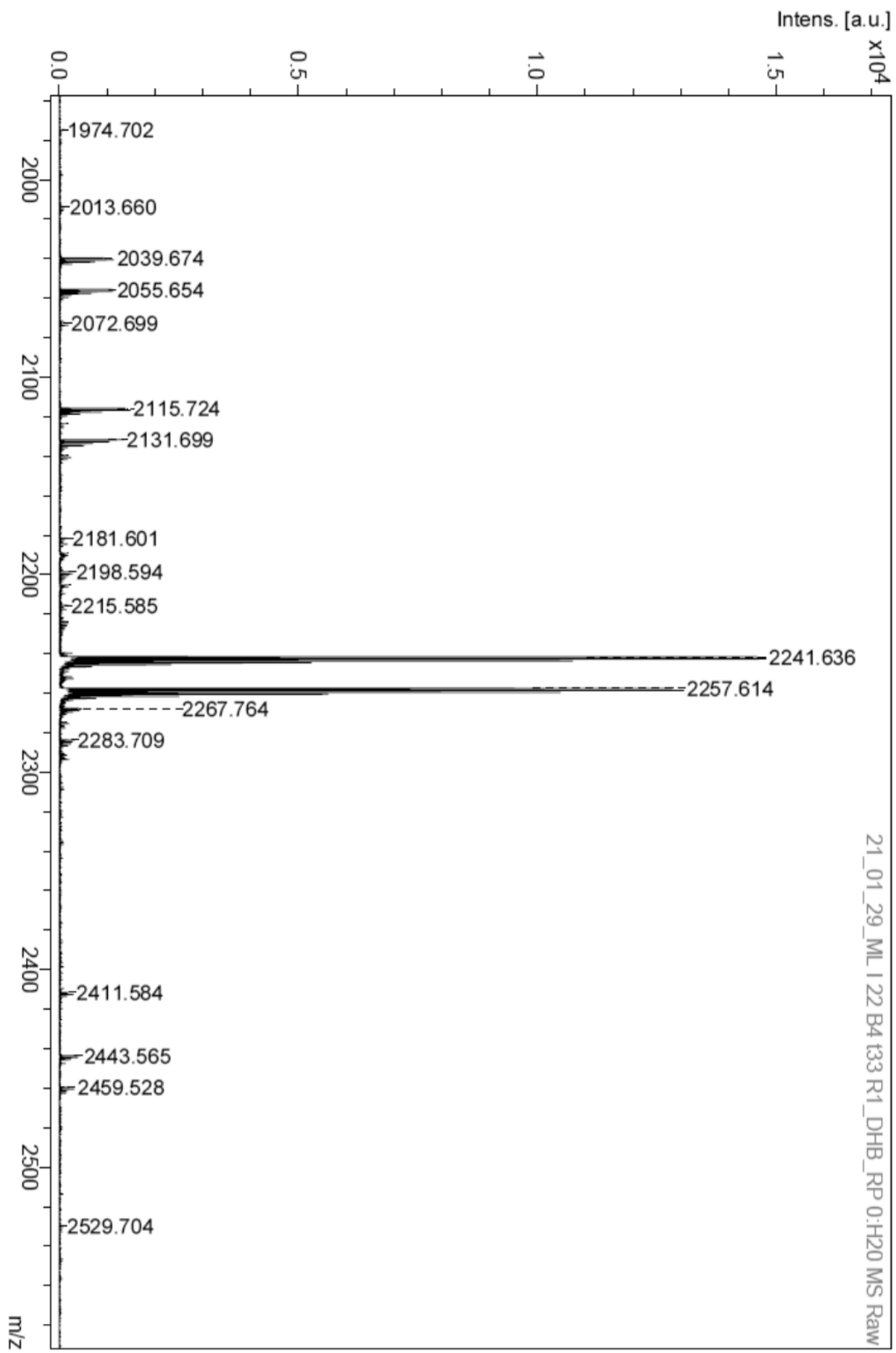
E-Factor = $((1000+157+131+22)-523)/523 \approx 1.5$

Characterisation of 7Aa (C₈₉H₁₁₅N₂O₅₅)



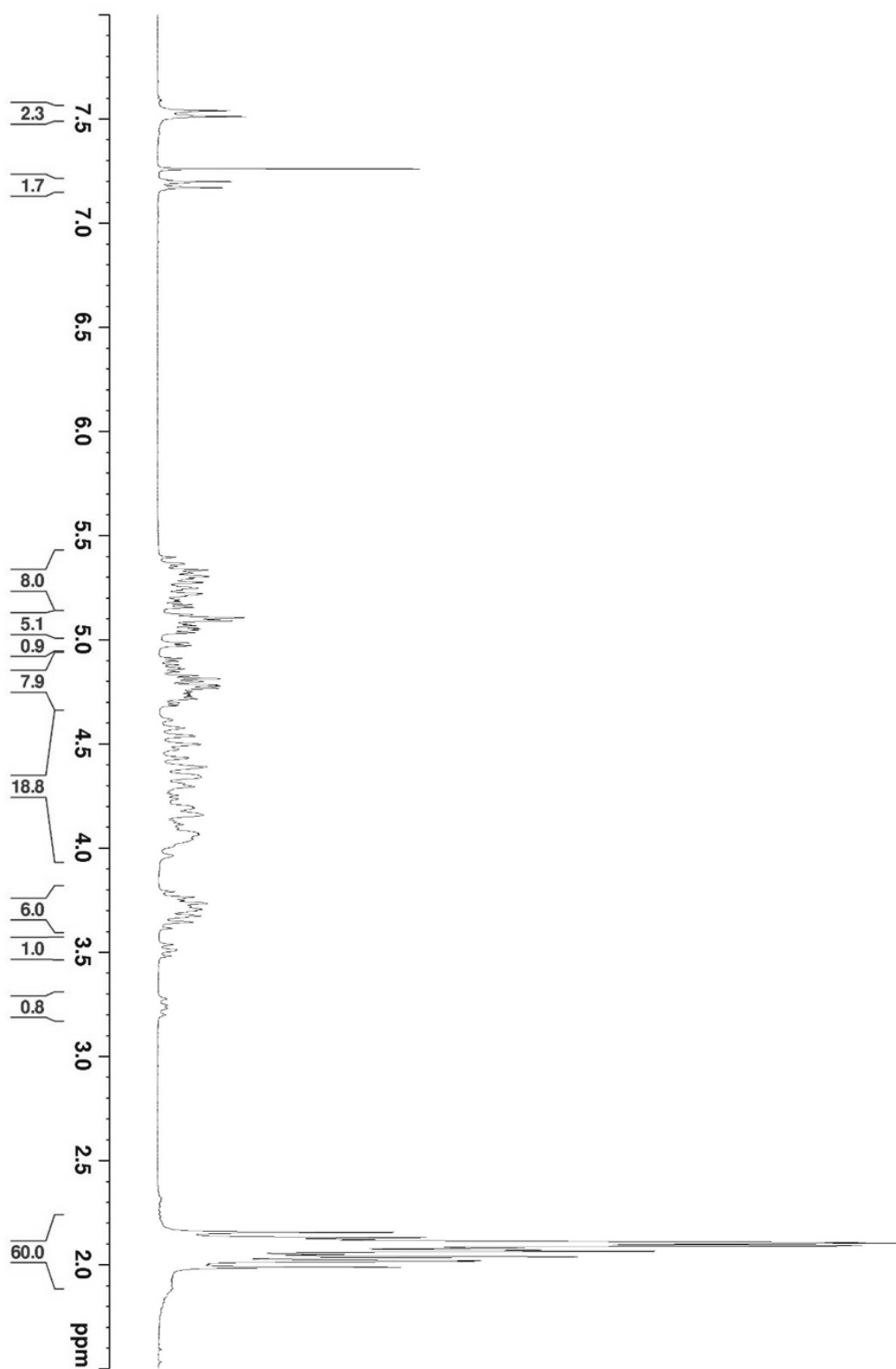
MALDI TOF of 7Aa



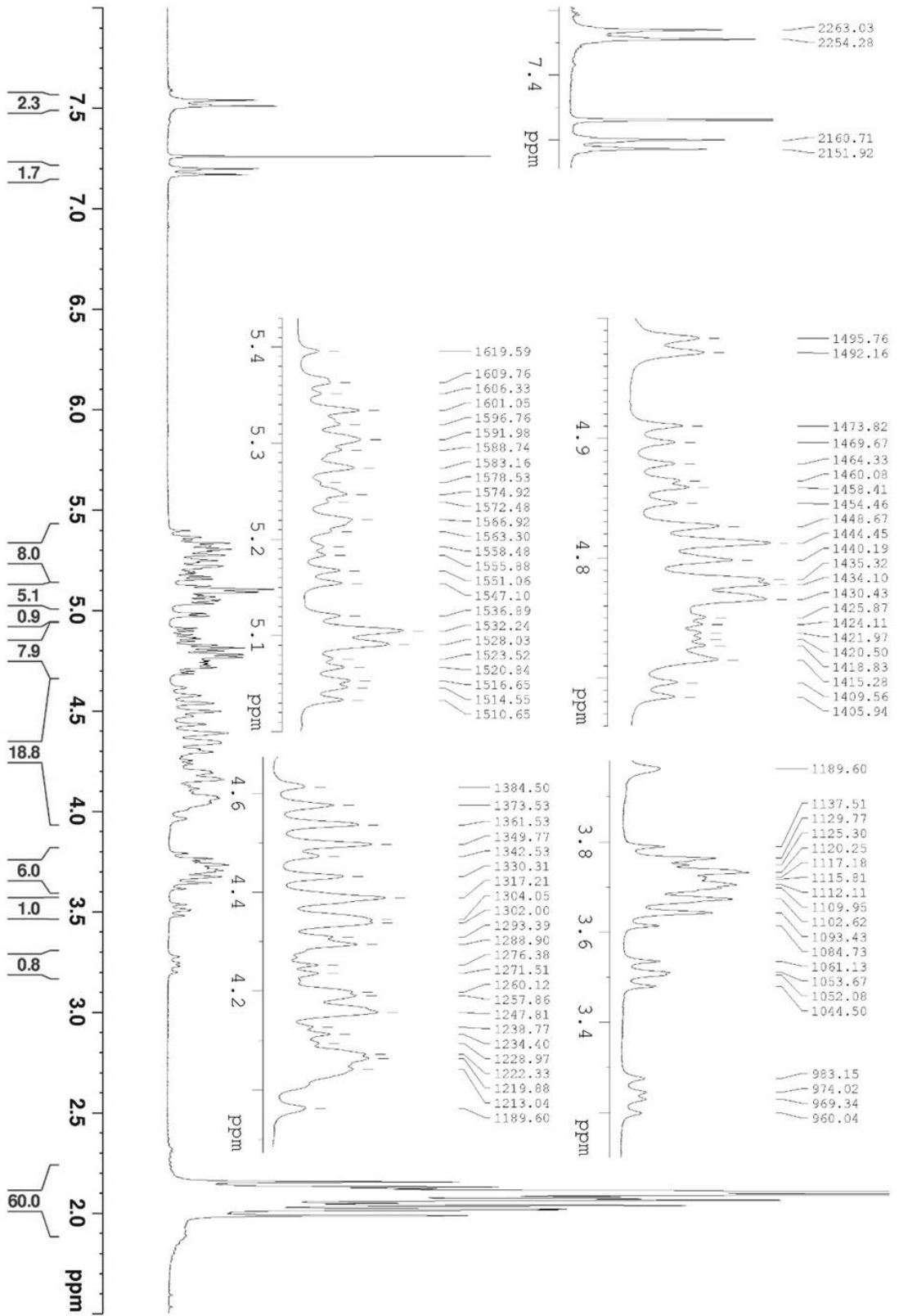


RMN¹H(CDCl₃) of 7Aa

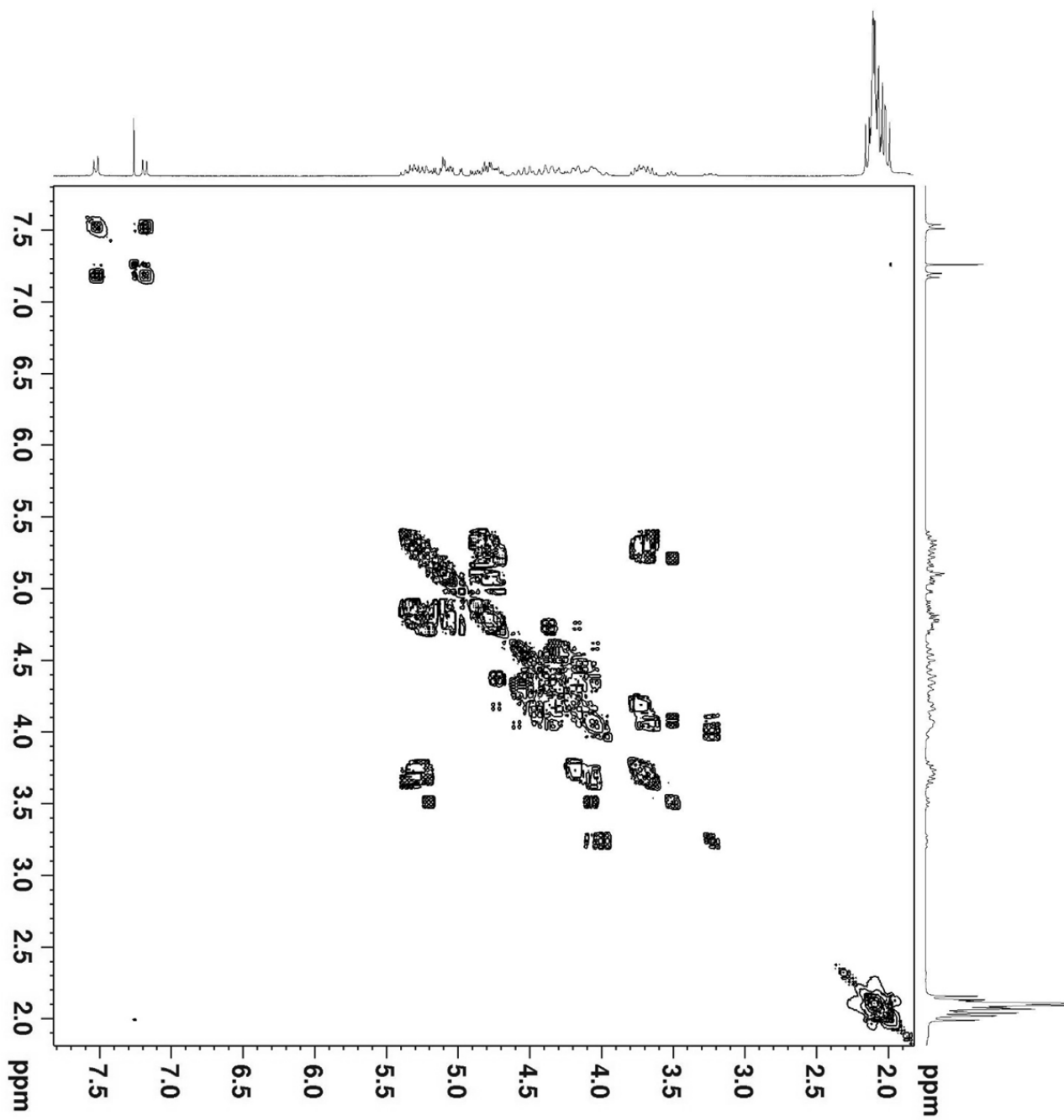
ML I 22 t33 R1



ML I 22 t33 R1

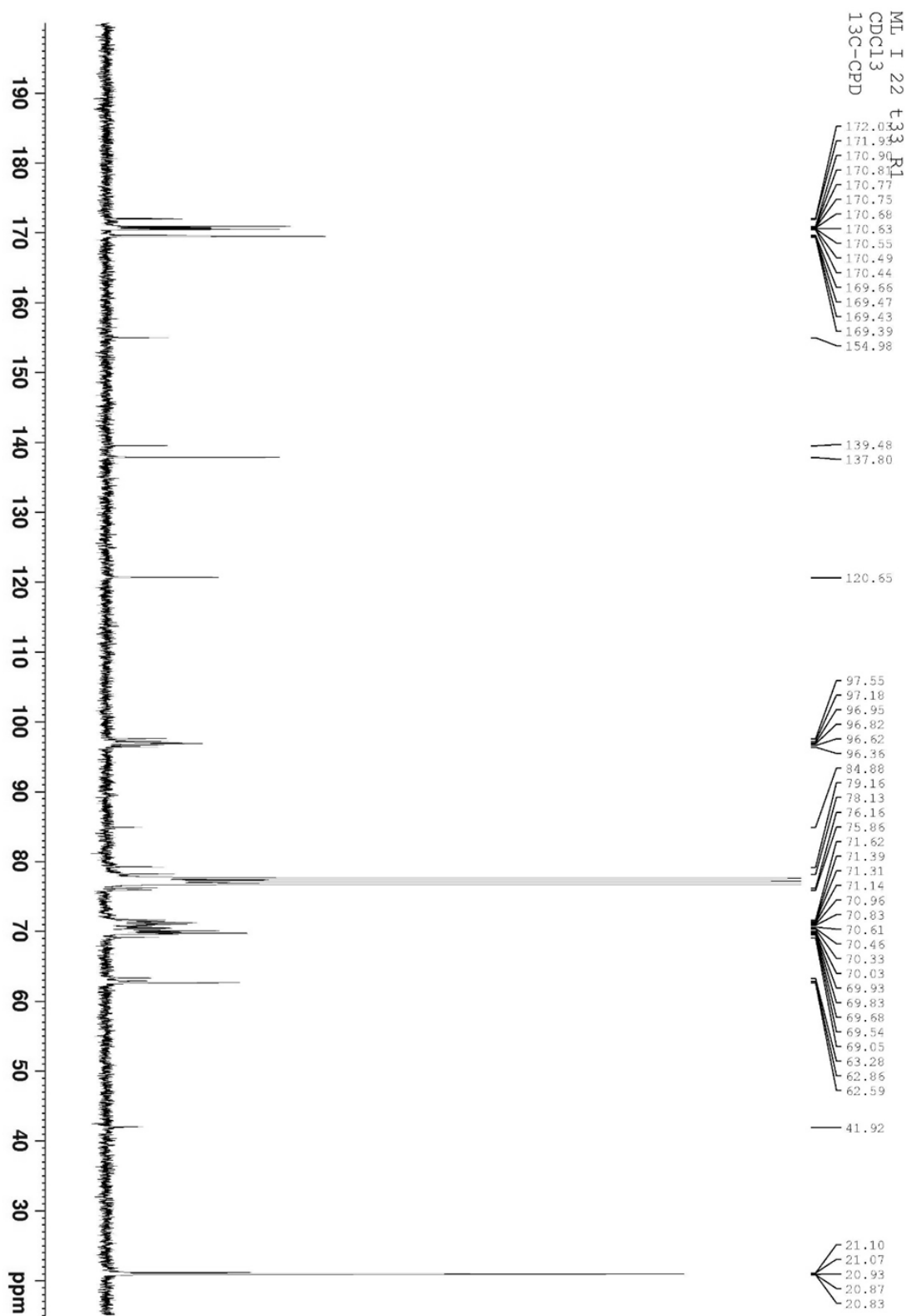


ML I 22 t33 R1
CDCl3
COSY45

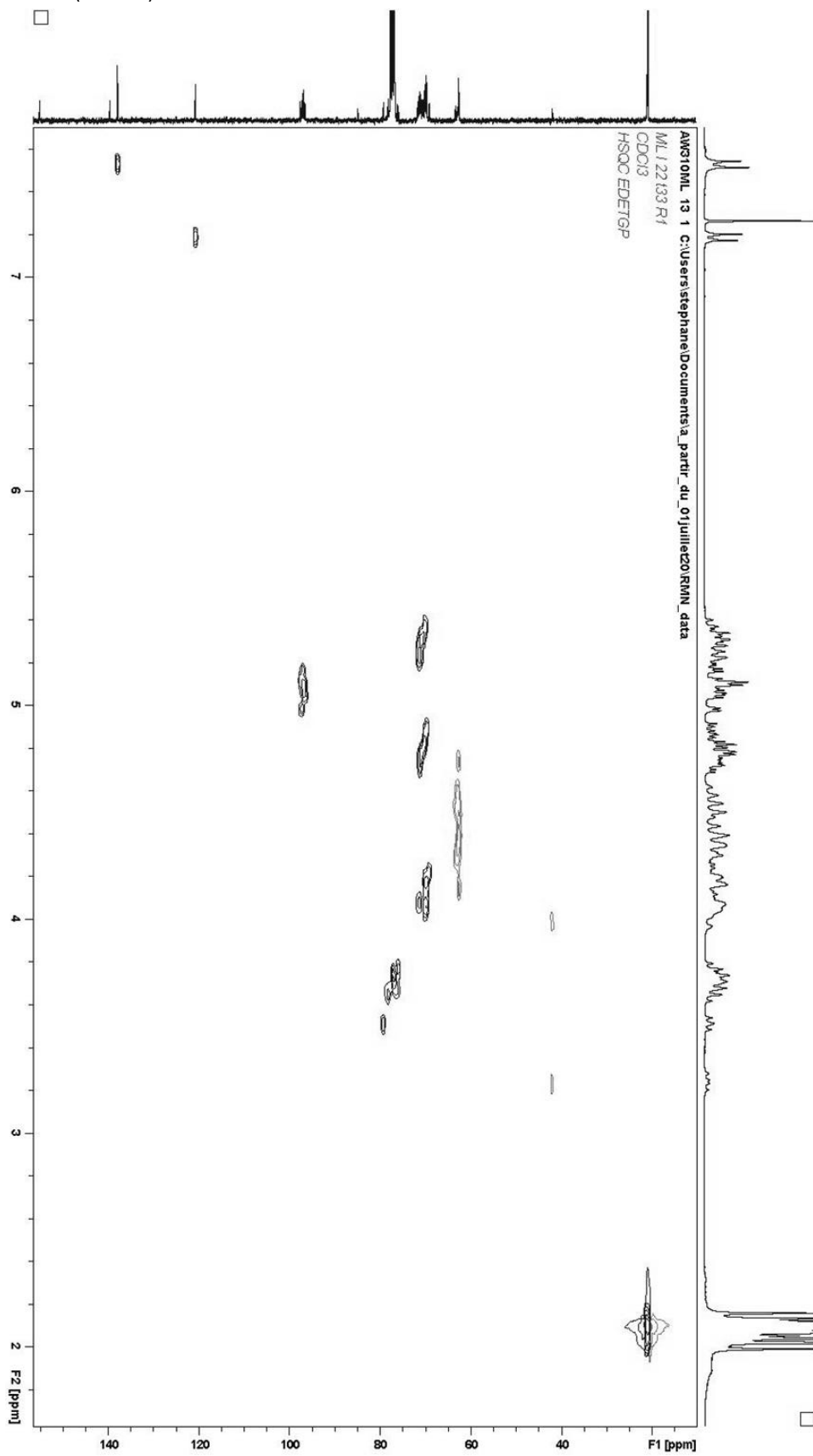


COSY (CDCl₃) of 7Aa

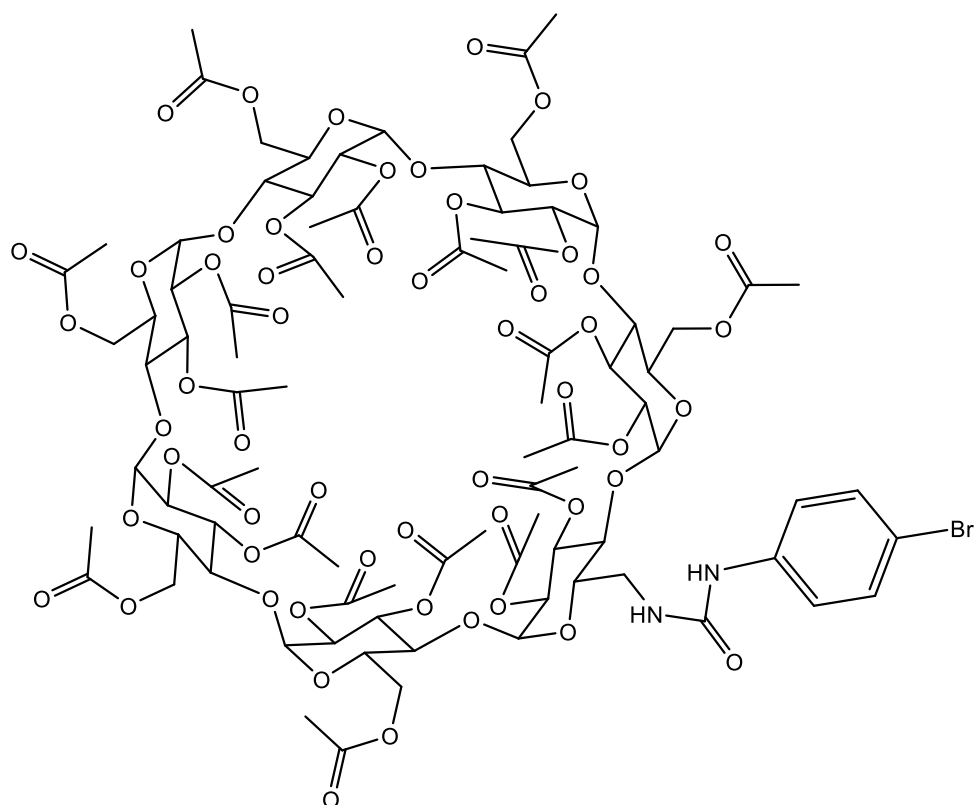
RMN¹³C(CDCl₃) of 7Aa



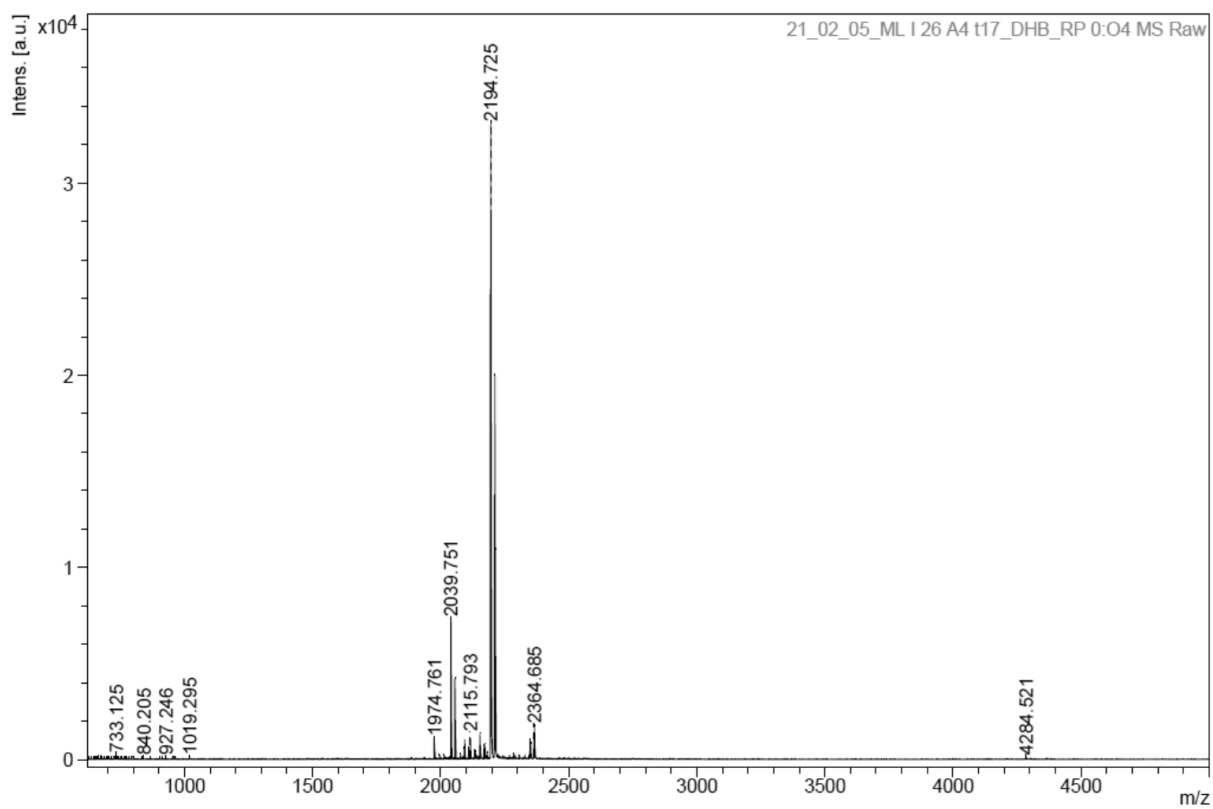
HSQC(CDC₃) of 7Aa

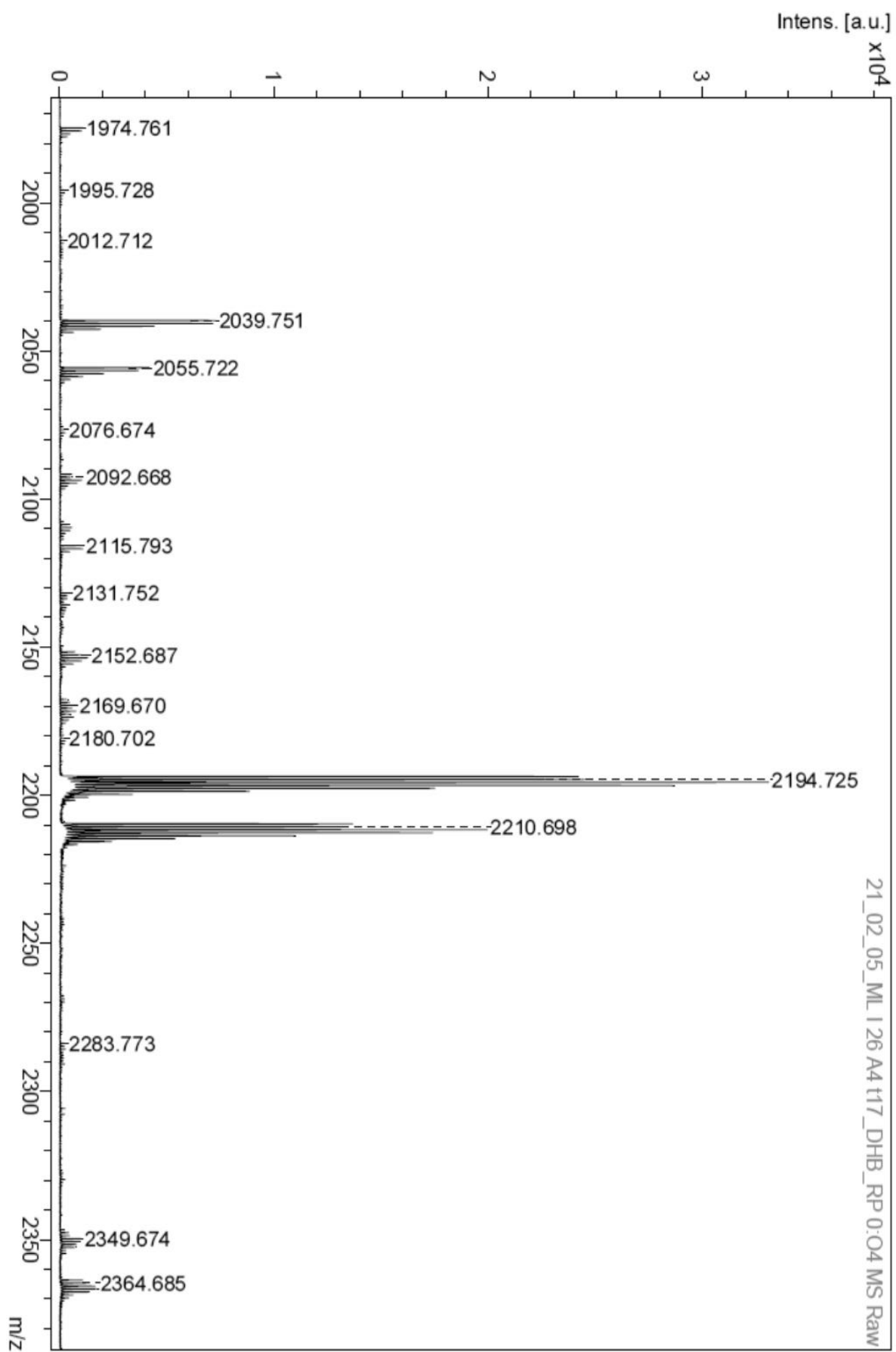


Characterisation of 7Ab ($C_{89}H_{115}N_2O_{55}Br$)



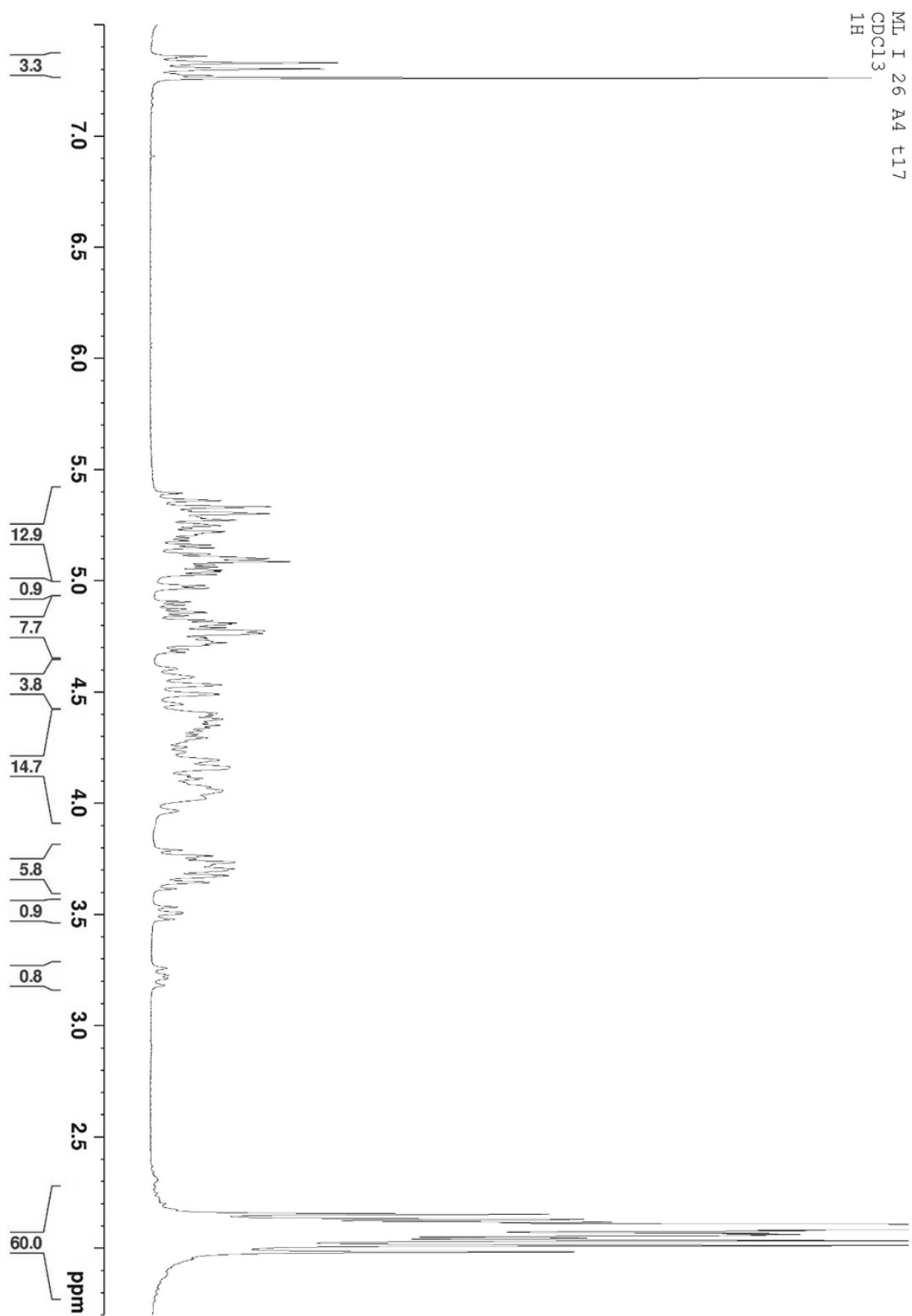
MALDI TOF of 7Ab



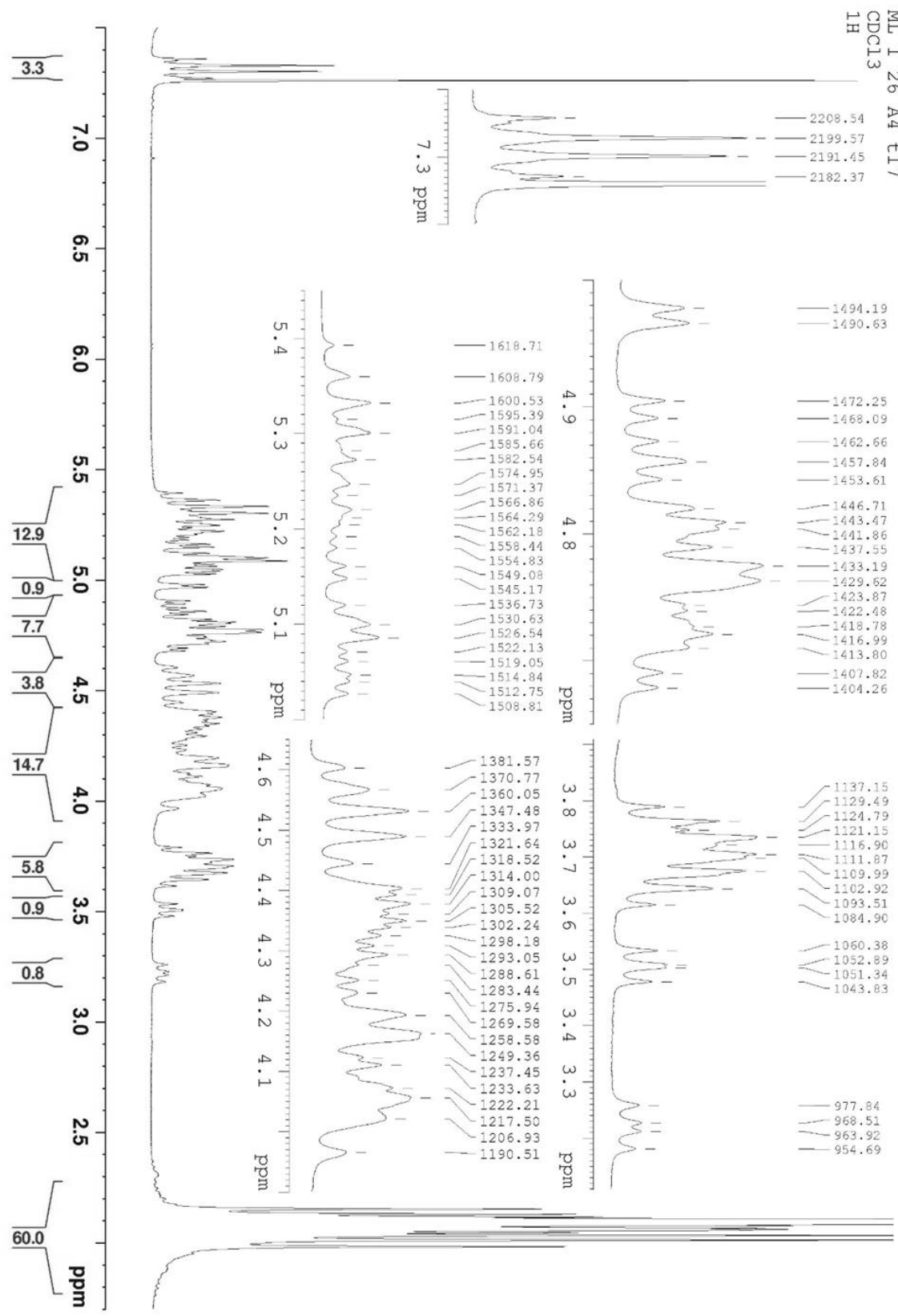


21_02_05_ML I 26 A4 t17_DHB_RP 0:04 MS Raw

RMN¹H(CDCl₃) of 7Ab

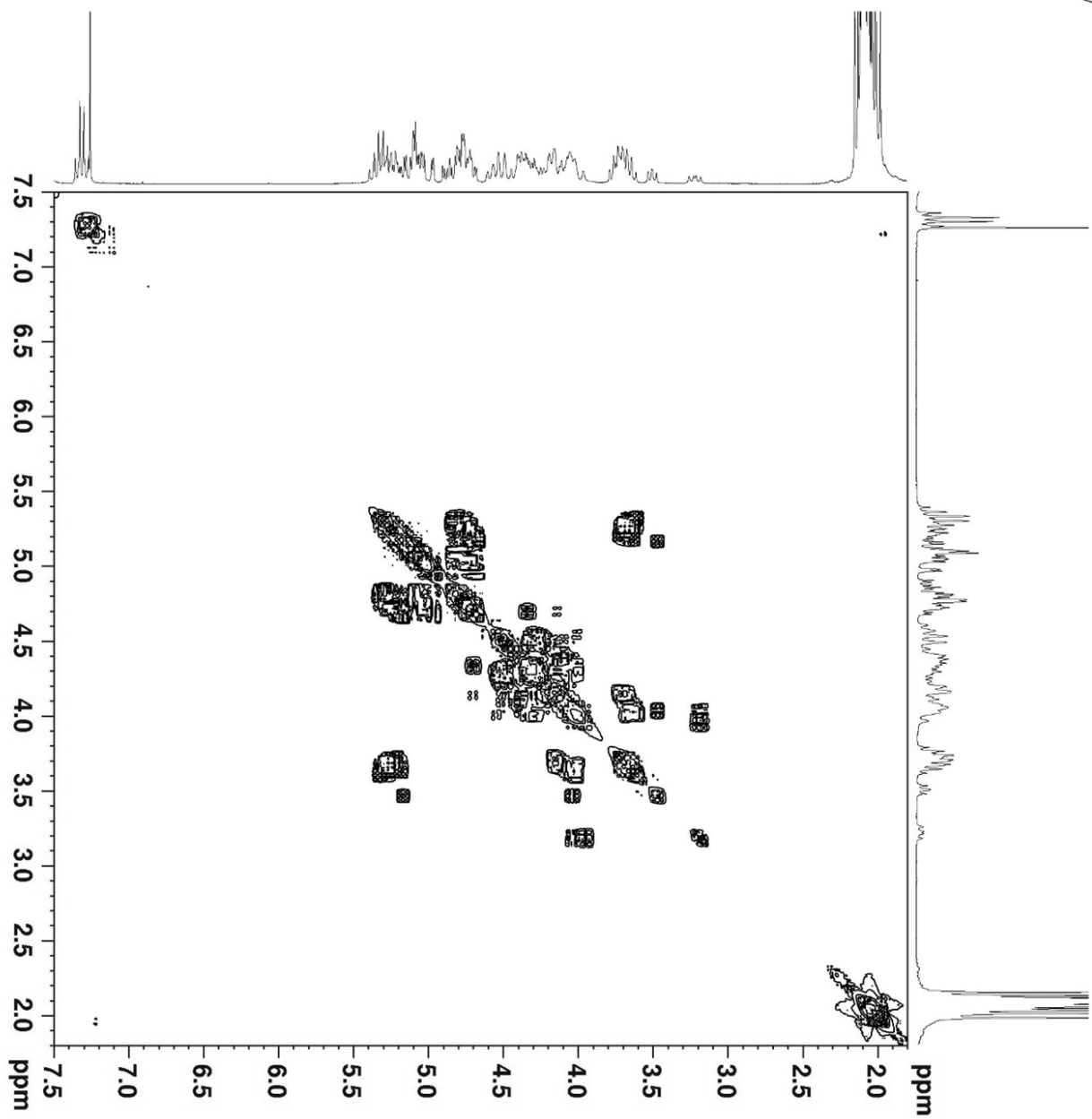


ML I 26 A4 t17
 CDCl3
 1H

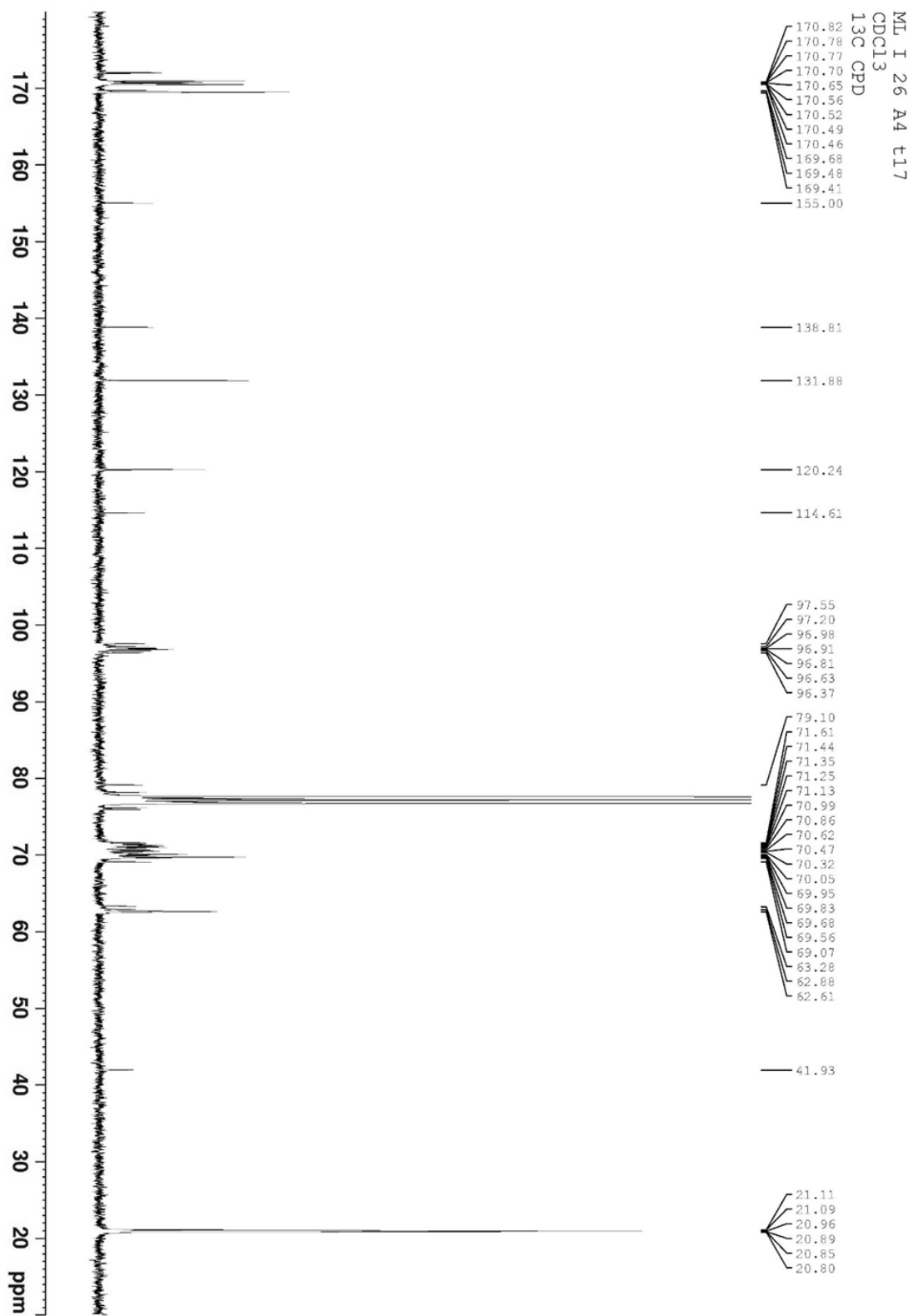


COSY (CDCl₃) of 7Ab

ML I 26 A4 t17
CDCl₃
COSY

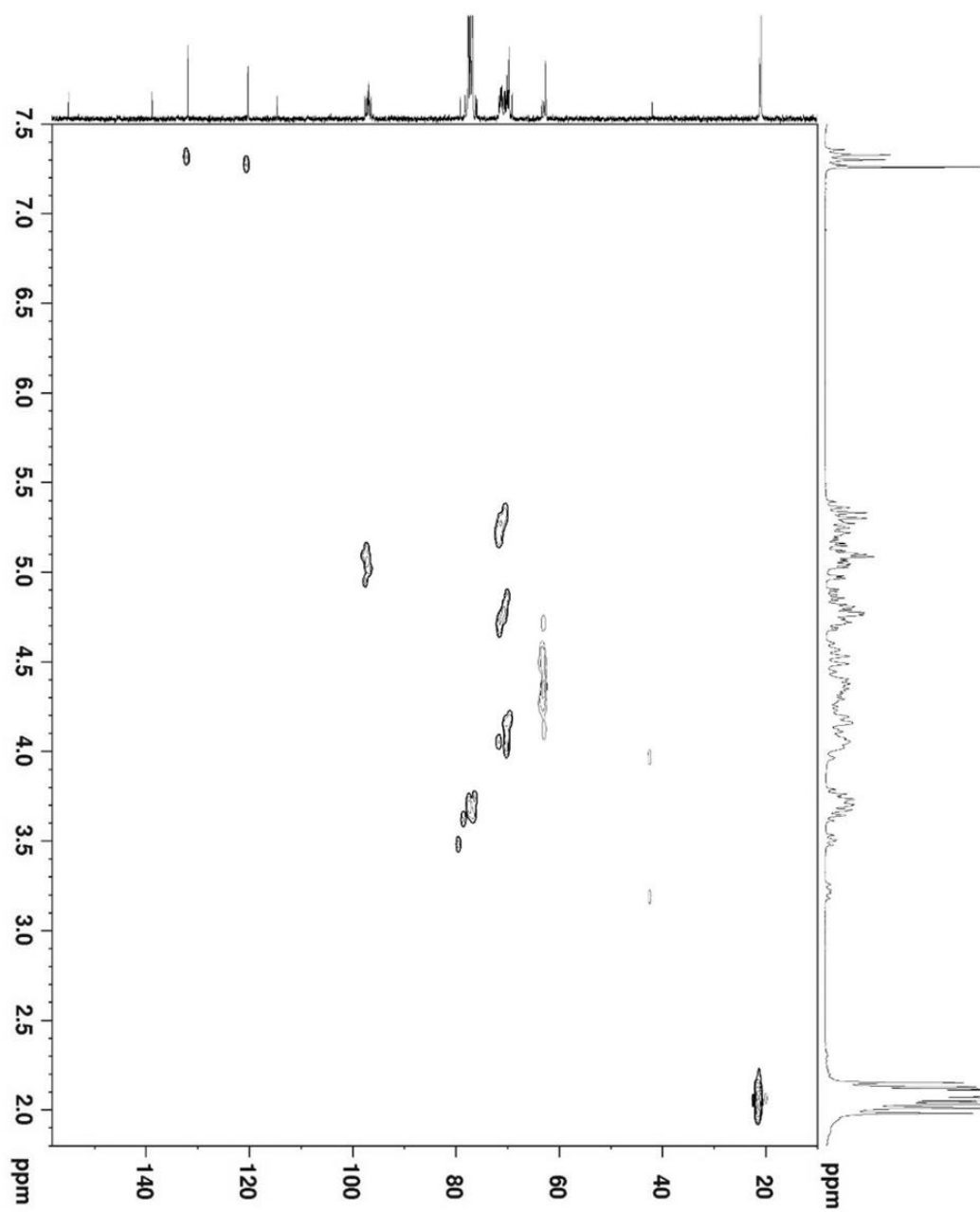


RMN¹³C(CDCI₃) of 7Ab

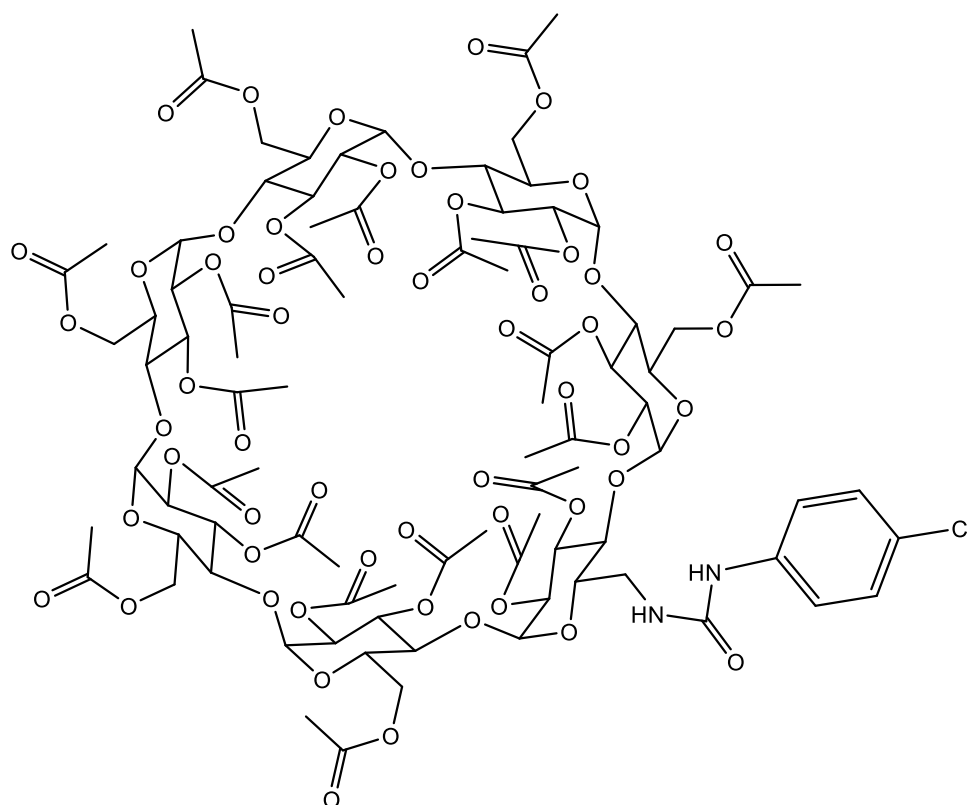


HSQC(CDCl₃) of 7Ab

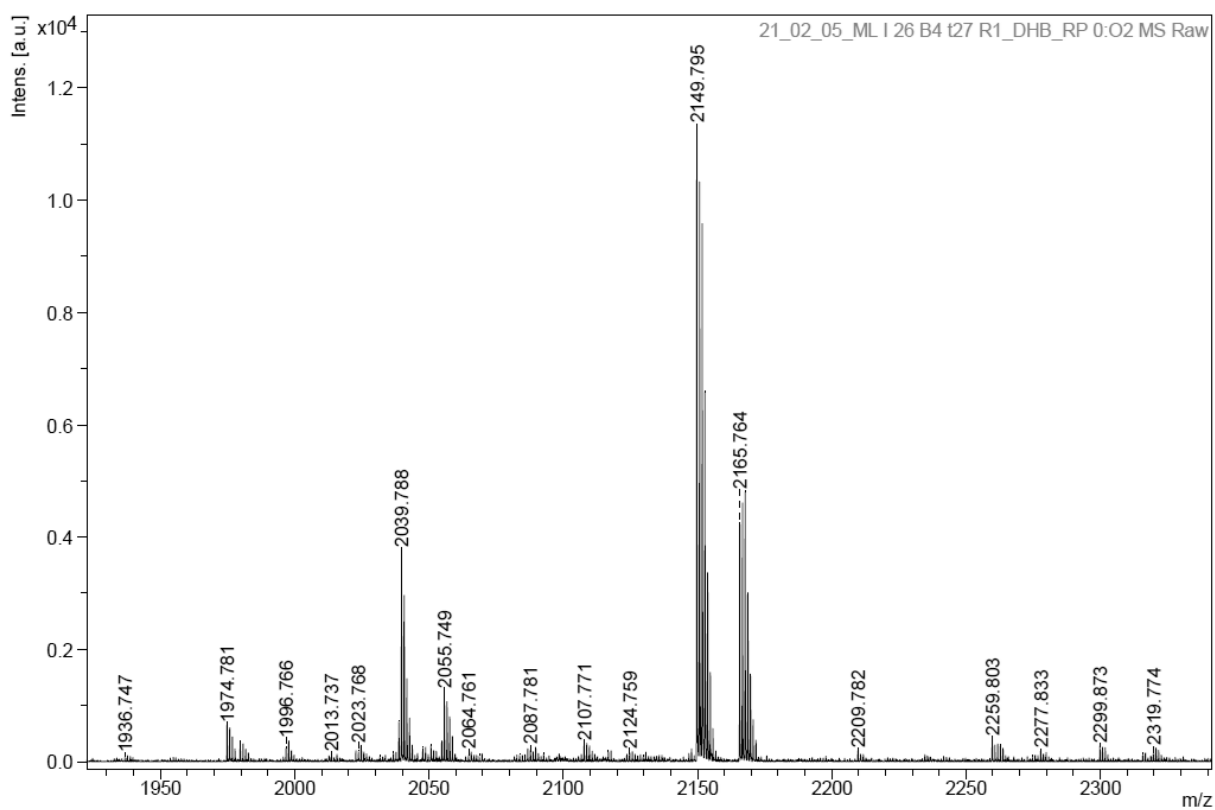
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CDCl₃
HSQC



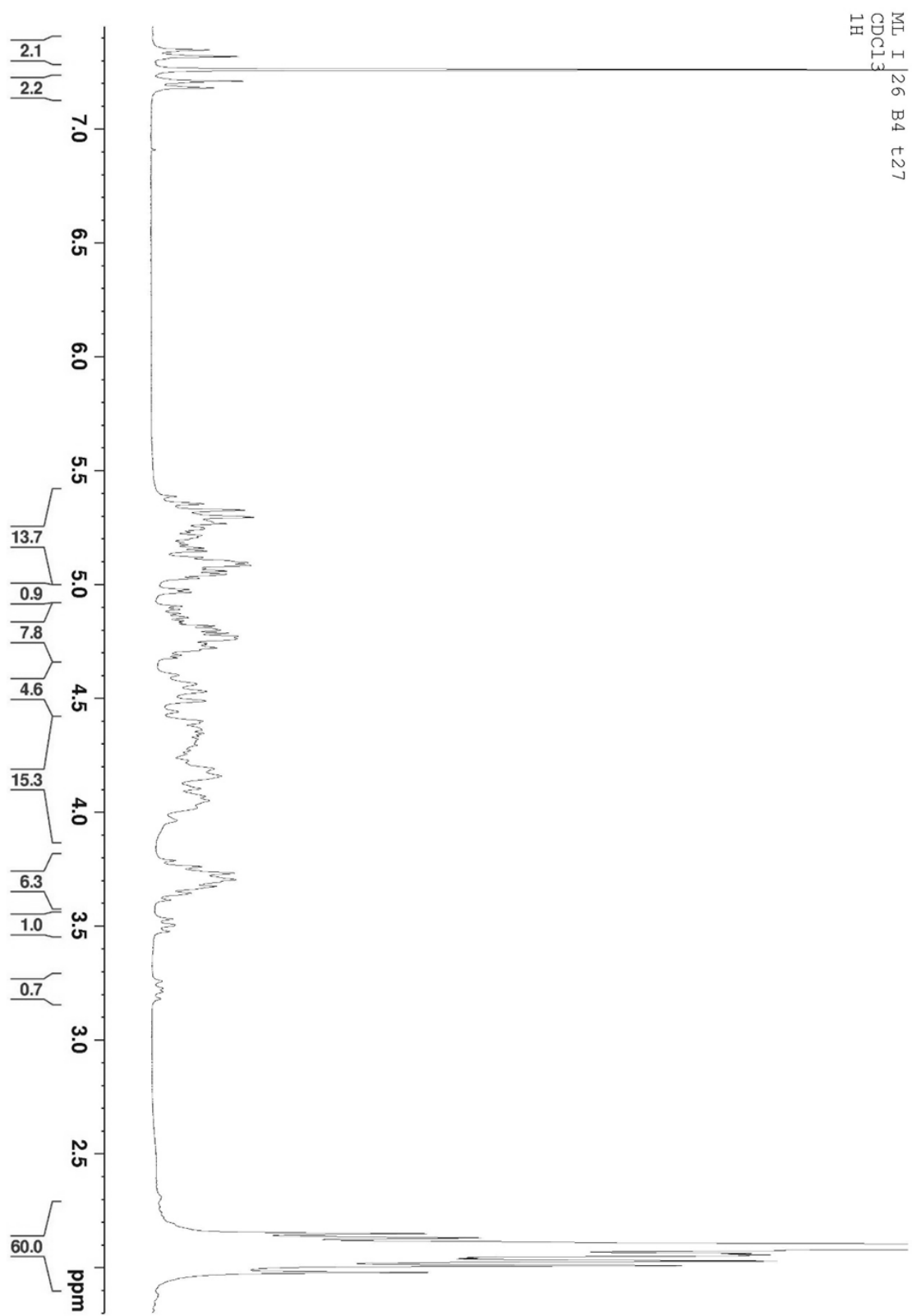
Characterisation of 7Ac ($C_{89}H_{115}N_2O_{55}Cl$)



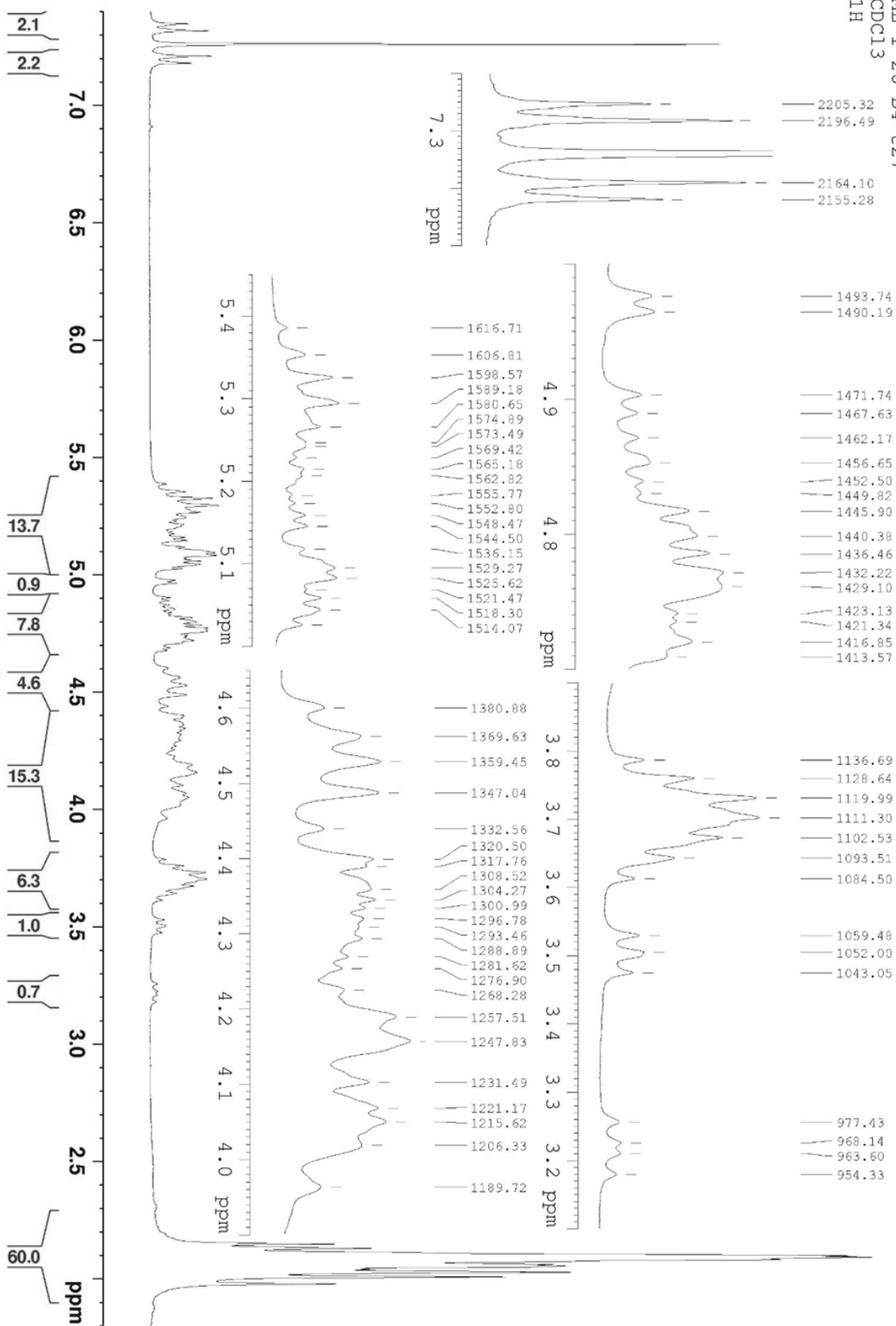
MALDI TOF of 7Ac



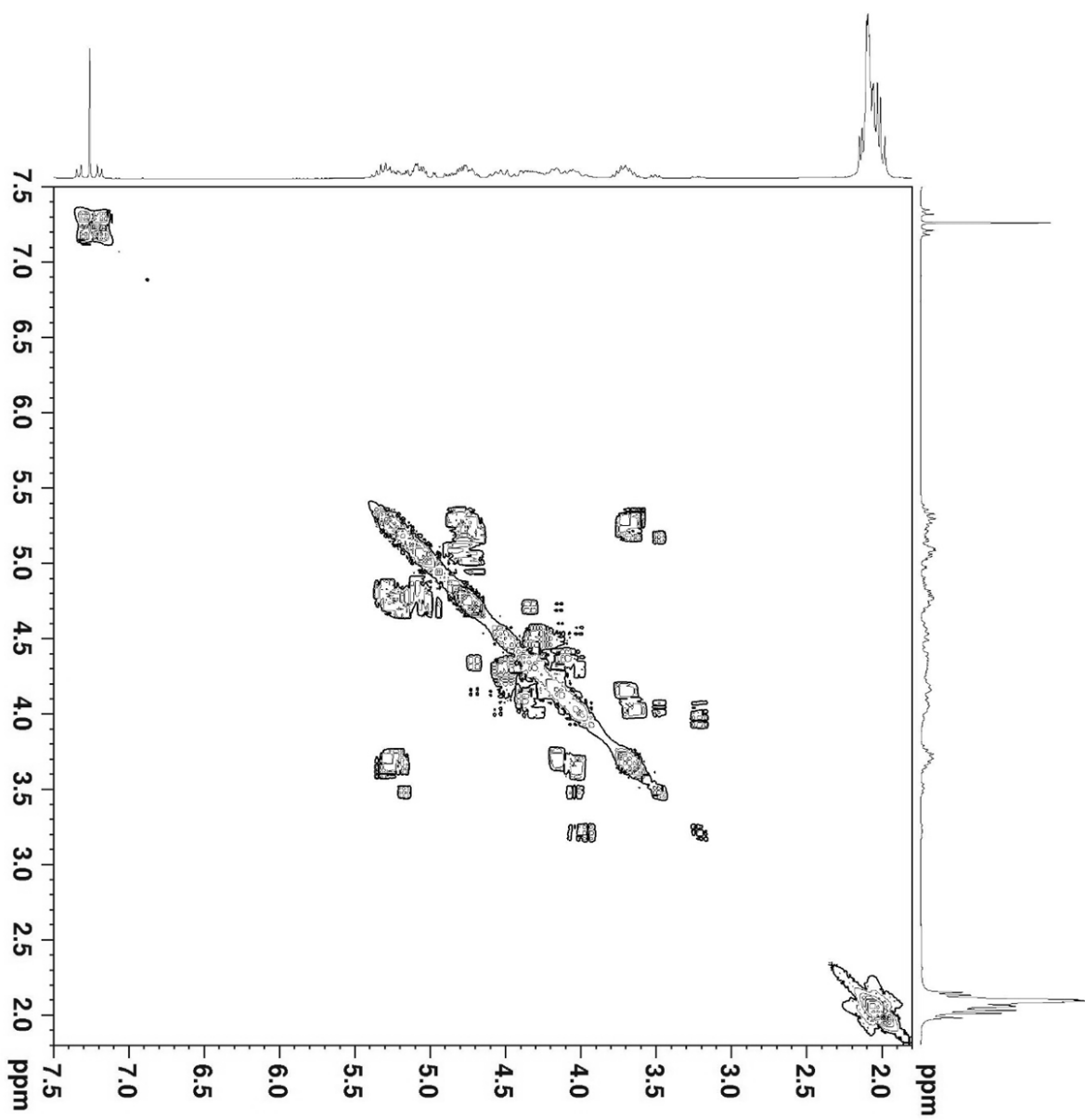
RMN¹H(CDCl₃) of 7Ac



ML I 26 B4 t27
 CDCl3
 1H

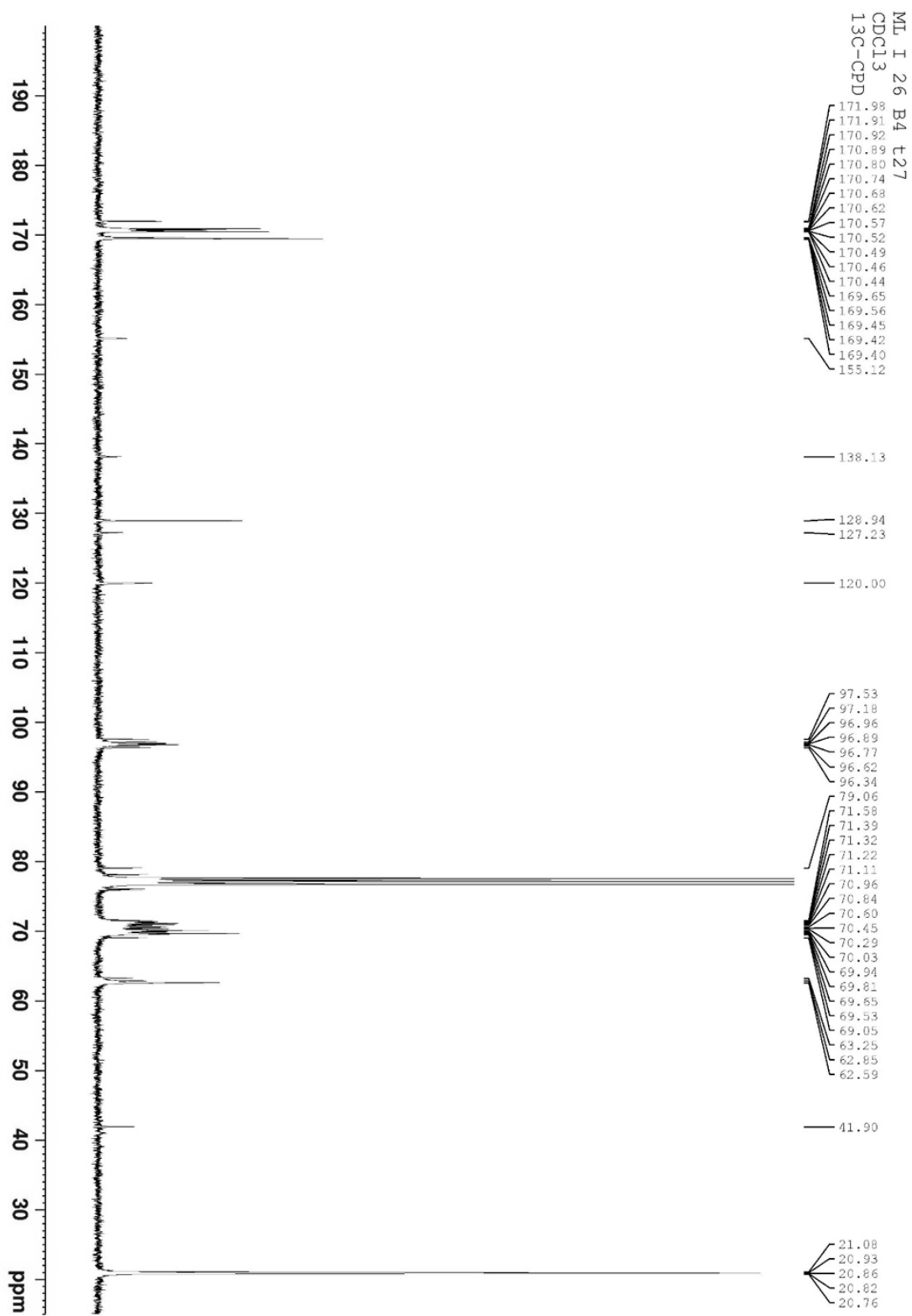


ML I 26 B4 t27
CDCl3
COSY45

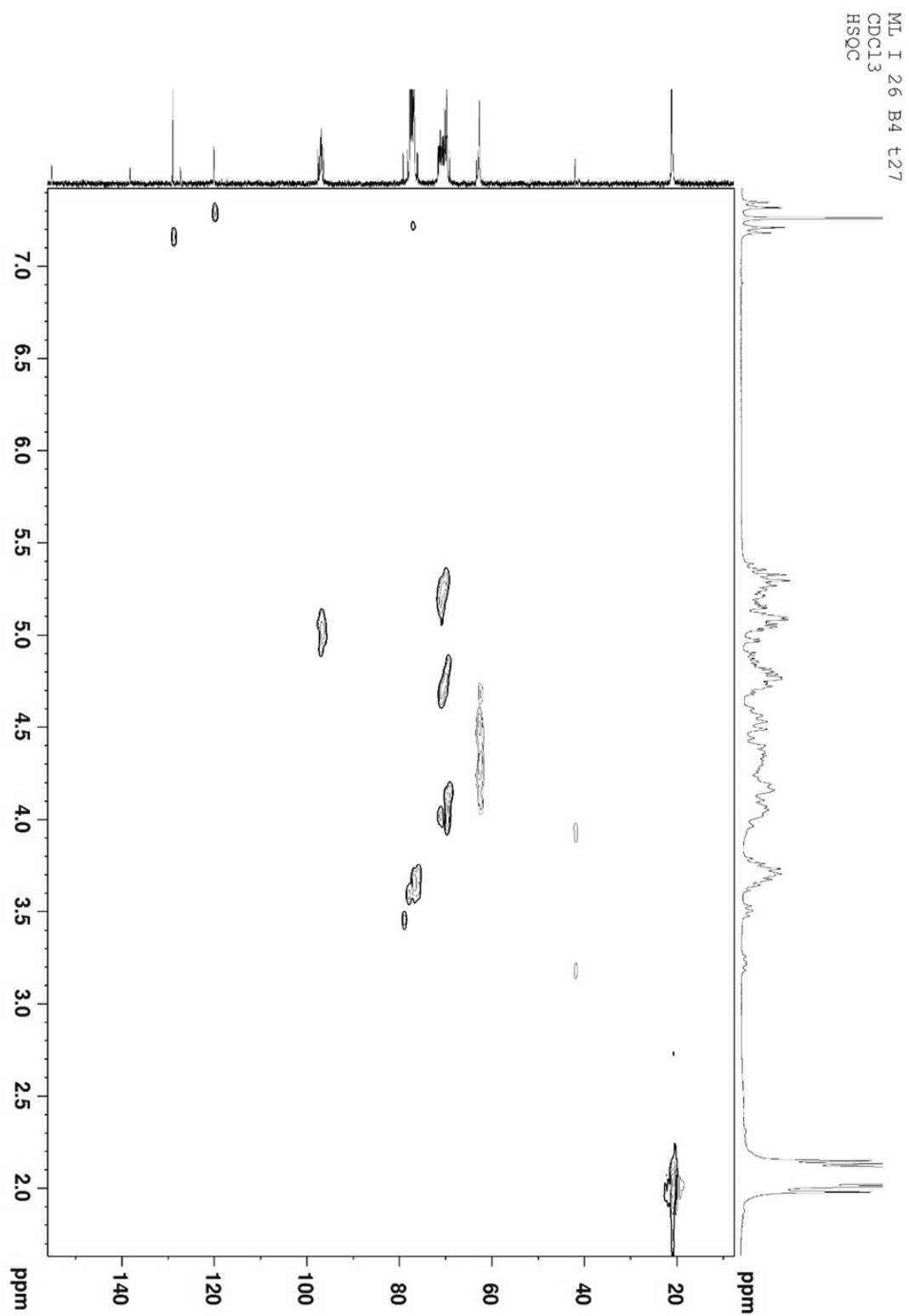


COSY (CDCl₃) of 7Ac

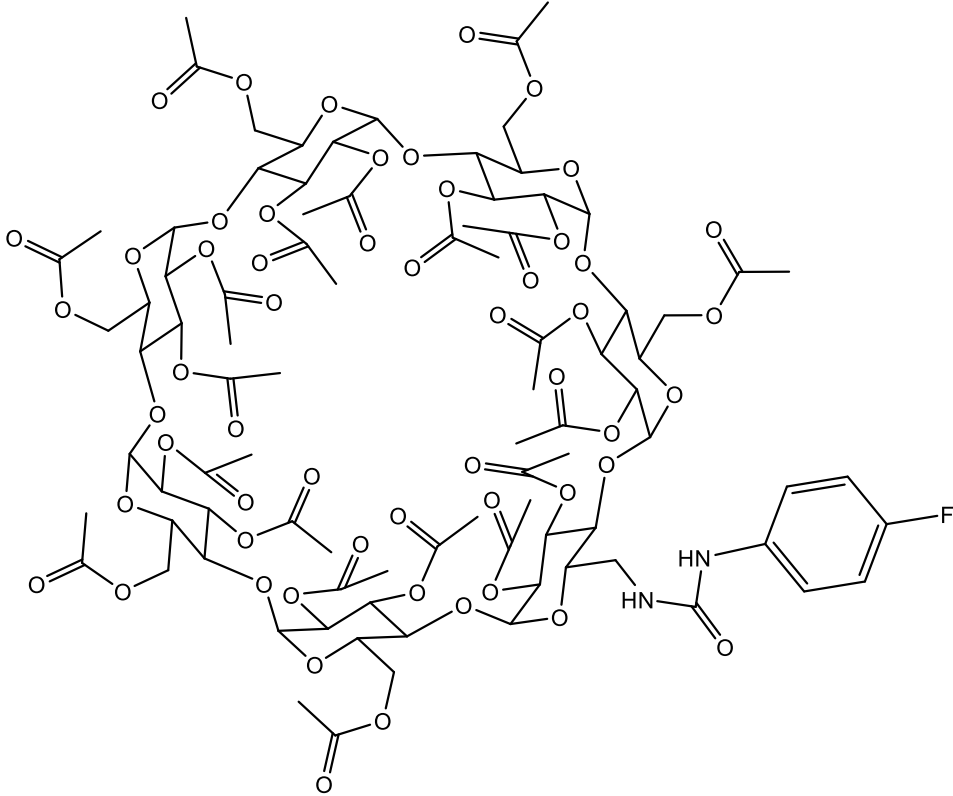
RMN¹³C(CDCl₃) of 7Ac



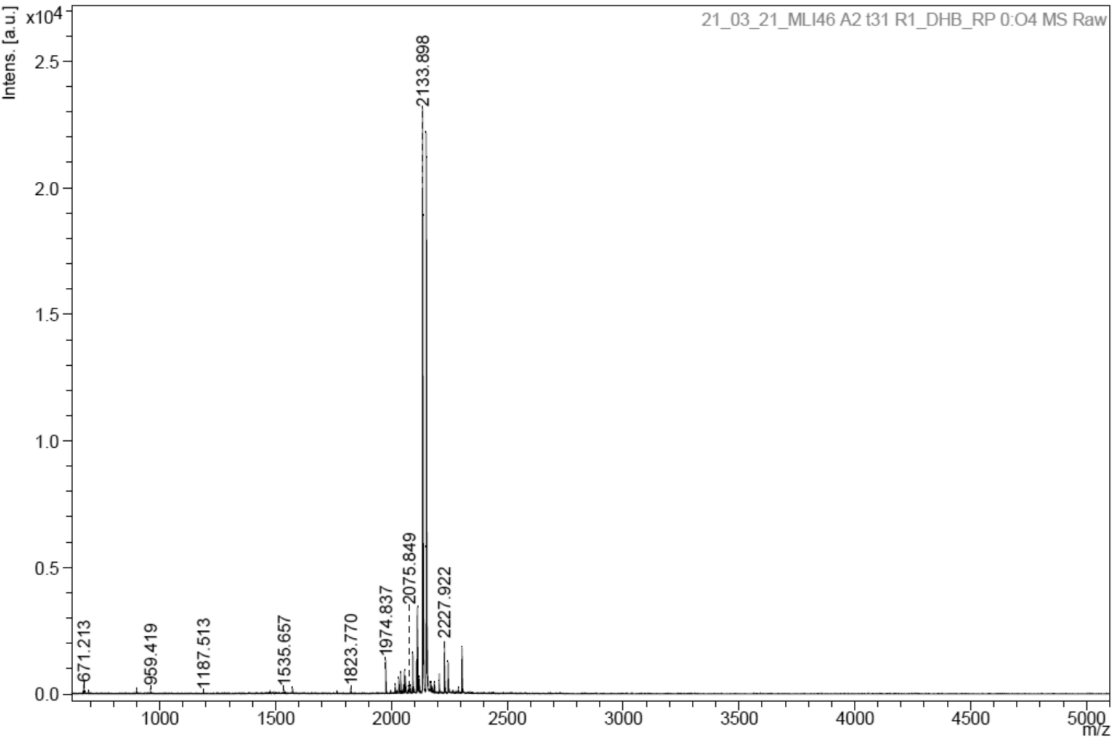
HSQC(CDCl₃) of 7Ac

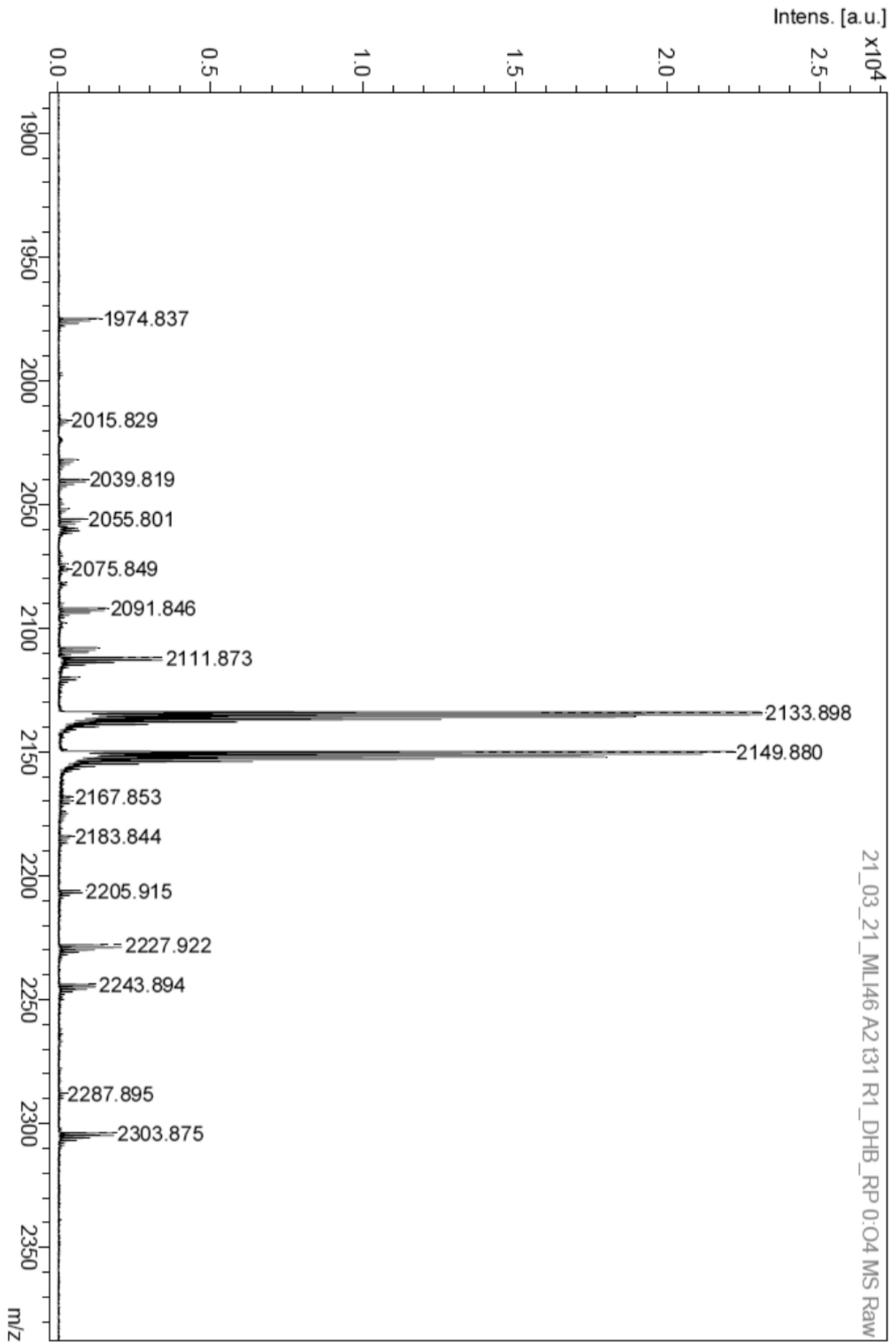


Characterisation of 7Ad (C₈₉H₁₁₅N₂O₅₅F)



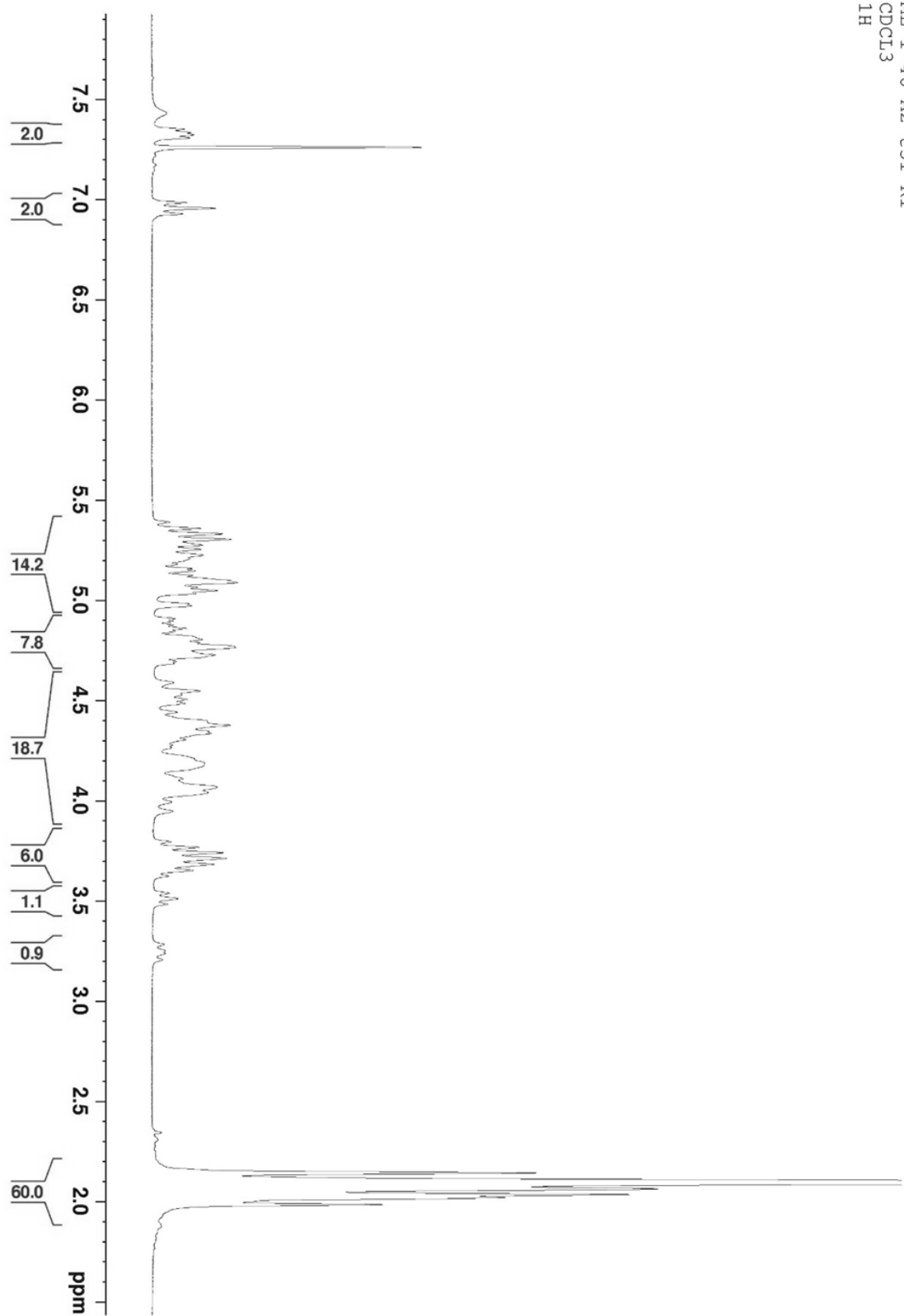
MALDI TOF of 7Ad



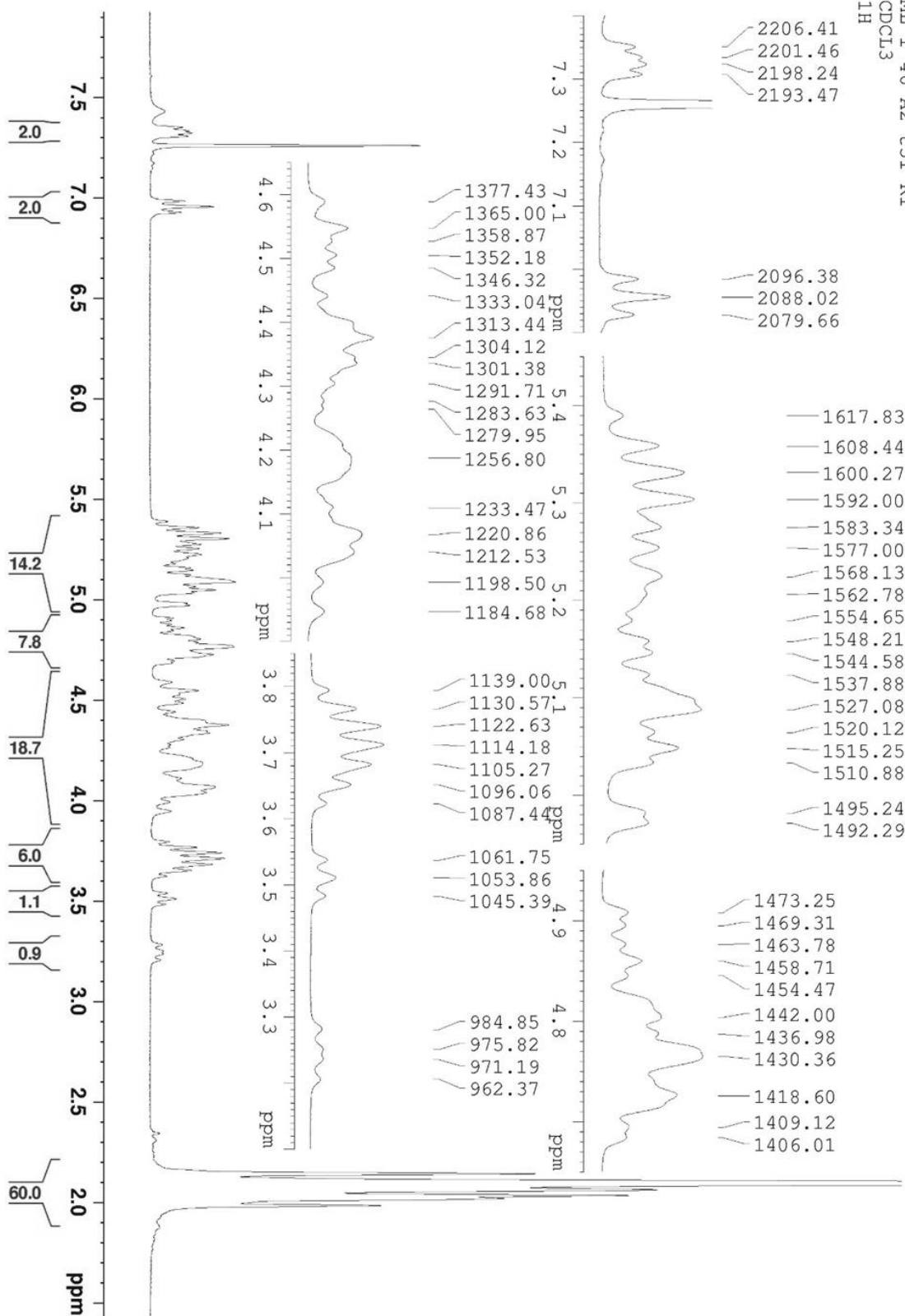


21_03_21_ML146 A2 t31 R1_DHB_RP 0:04 MS Raw

RMN¹H(CDCl₃) of 7Ad

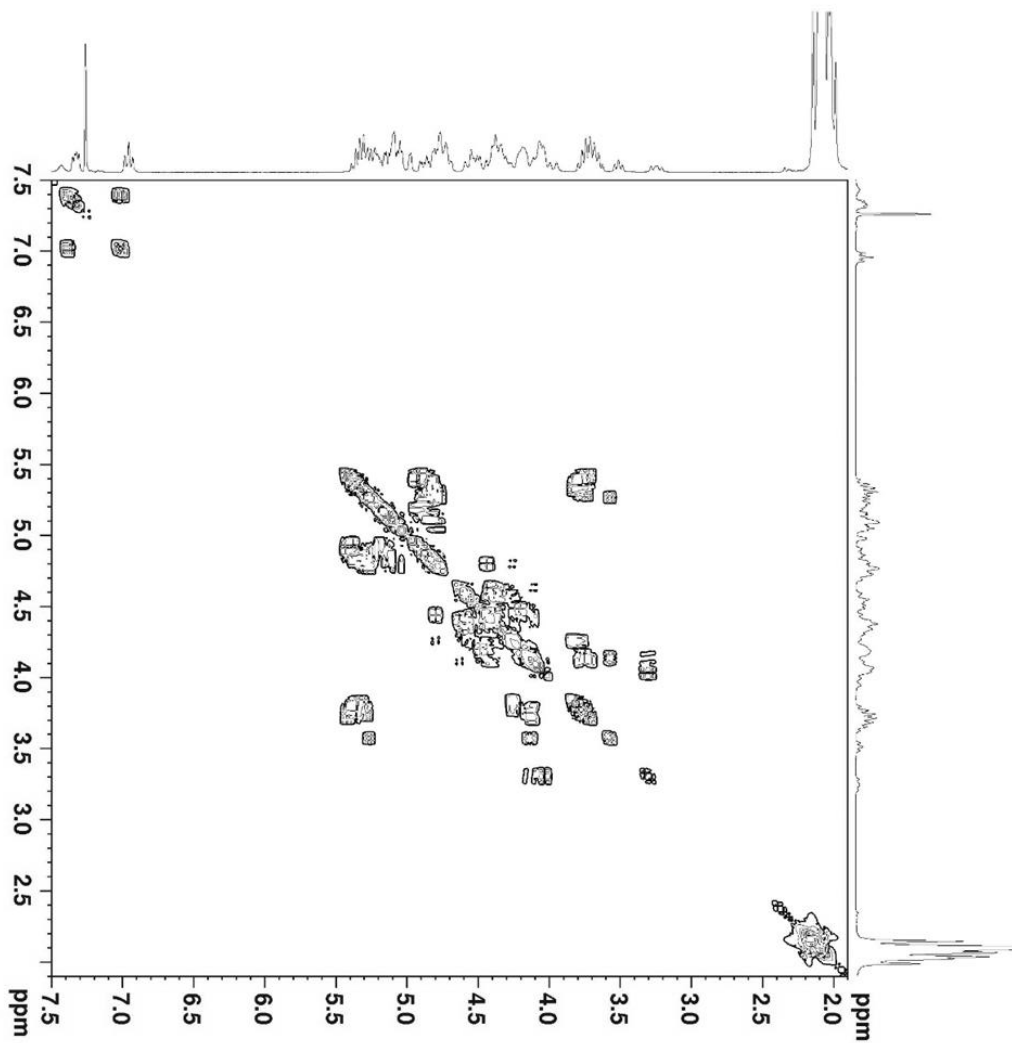


ML I 46 A2 t31 R1
 CDCL3
 1H

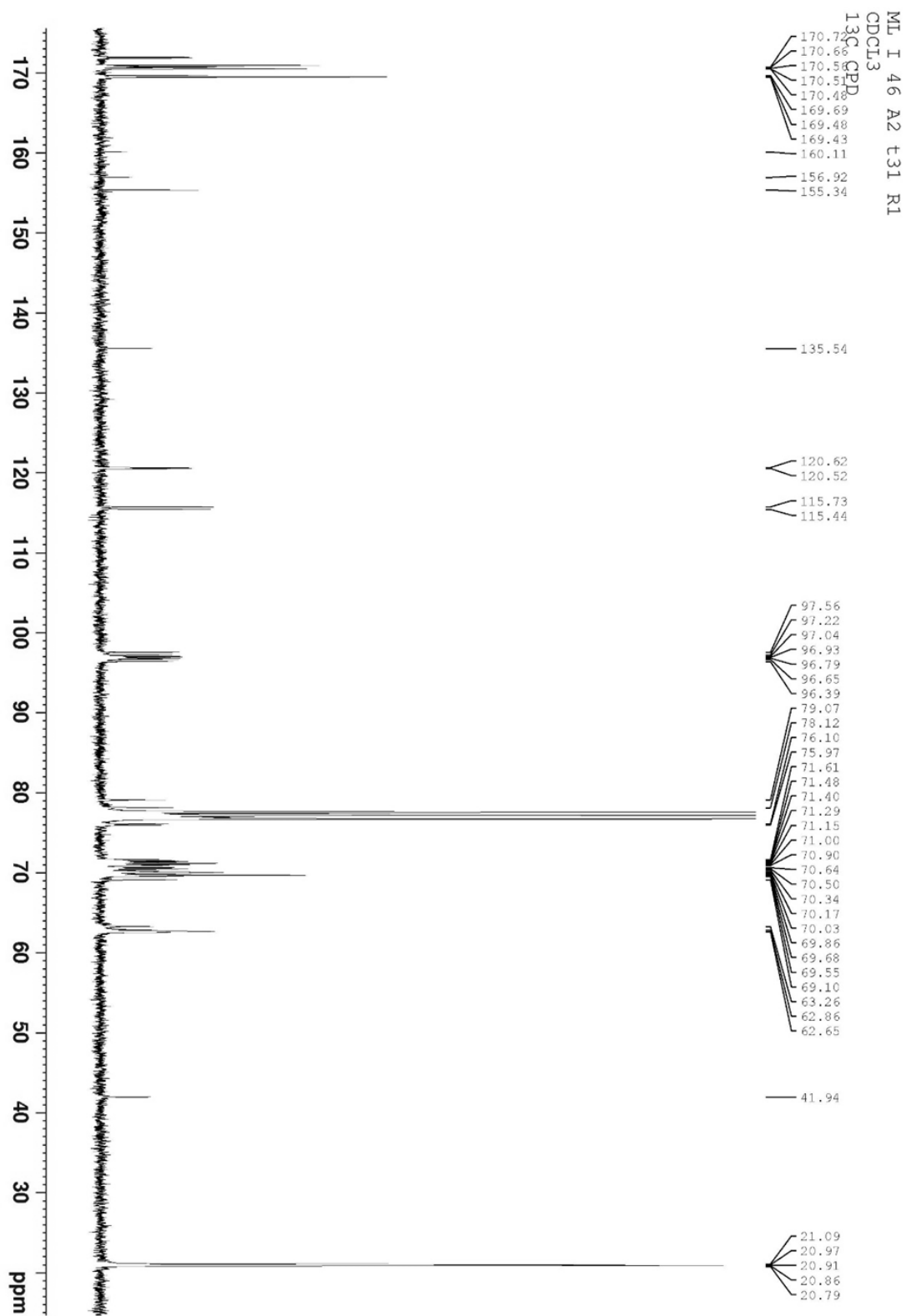


COSY (CDCl₃) of 7Ad

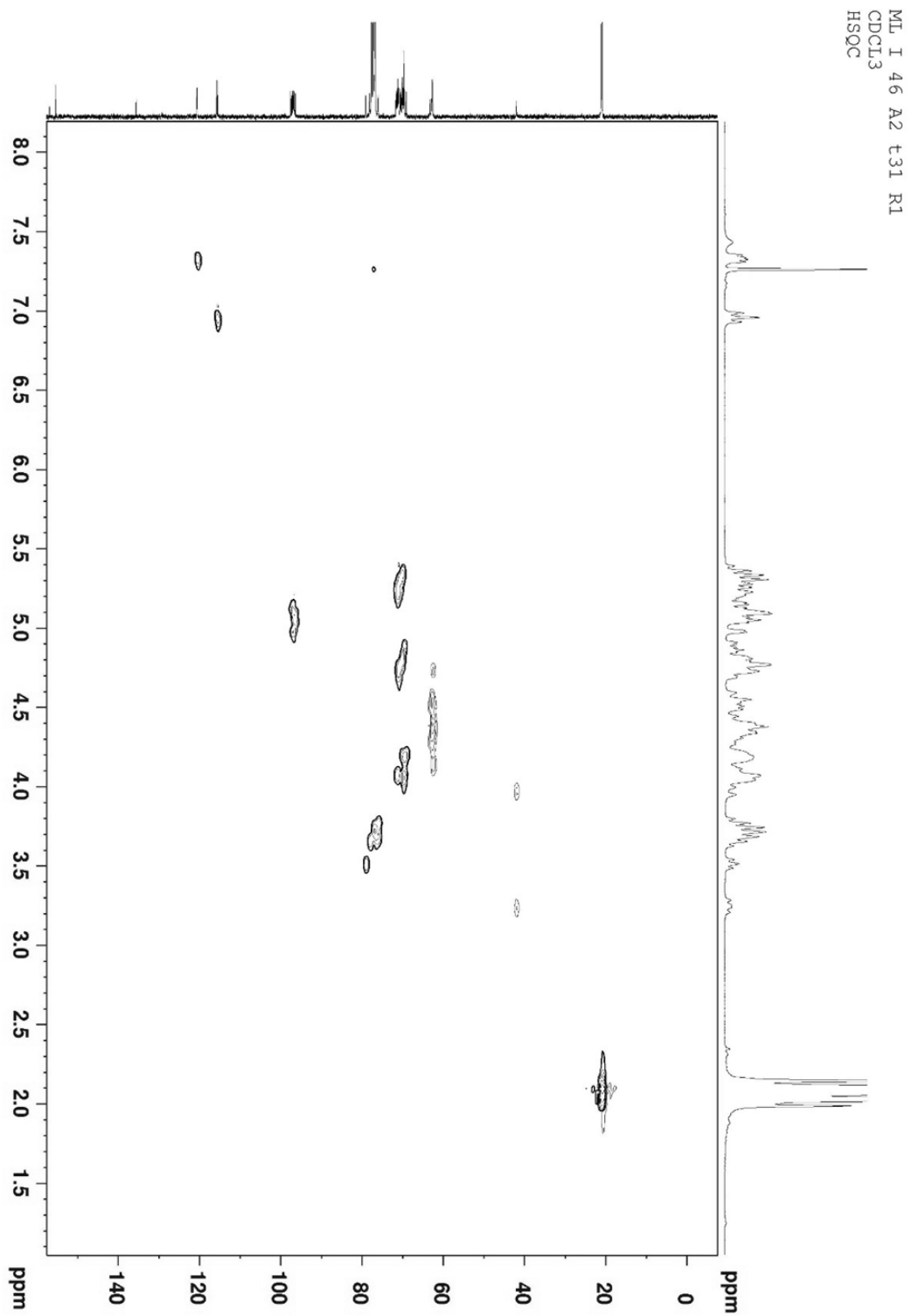
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CDCl₃
COSY45

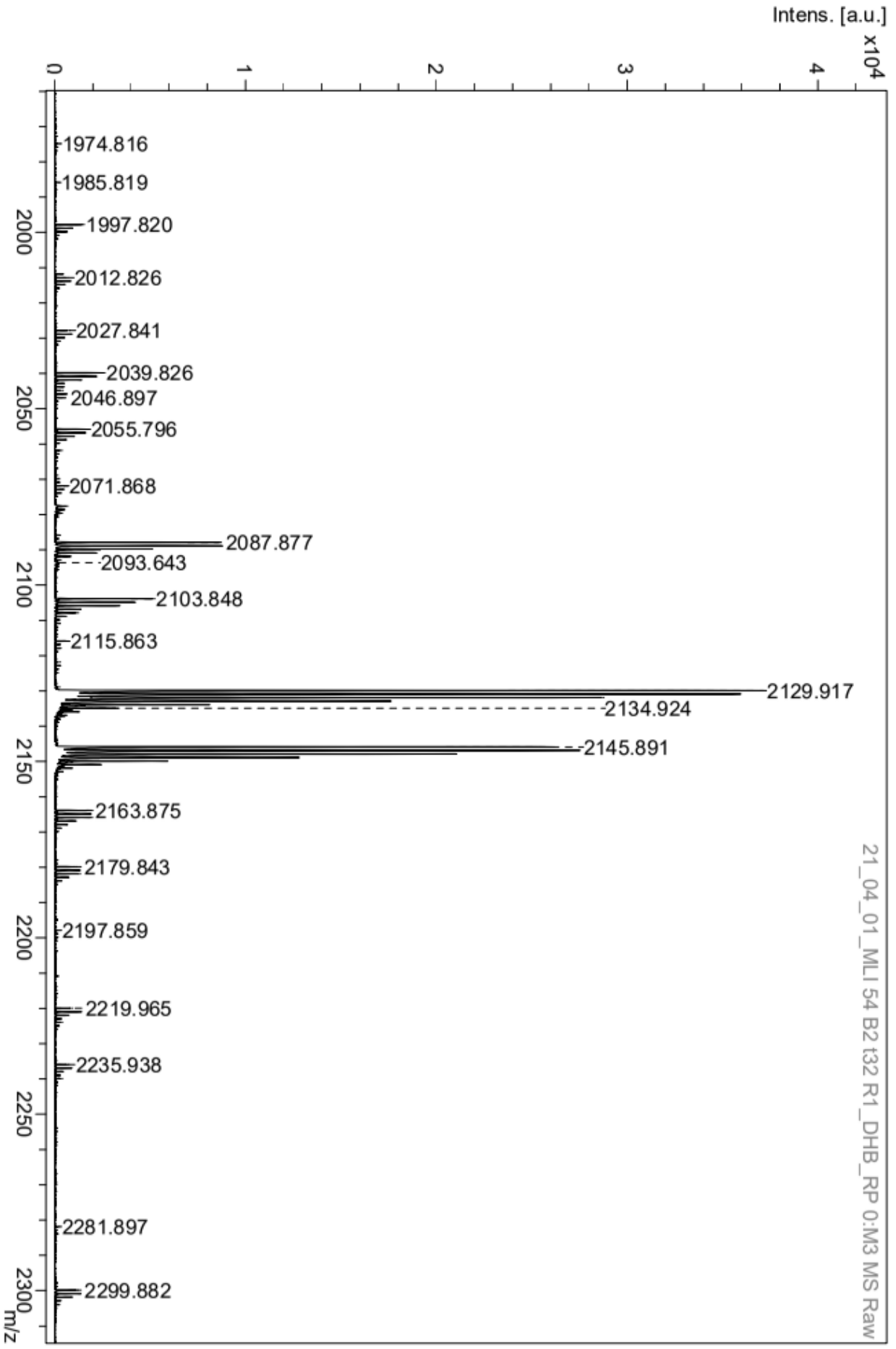


RMN¹³C(CDCl₃) of 7Ad



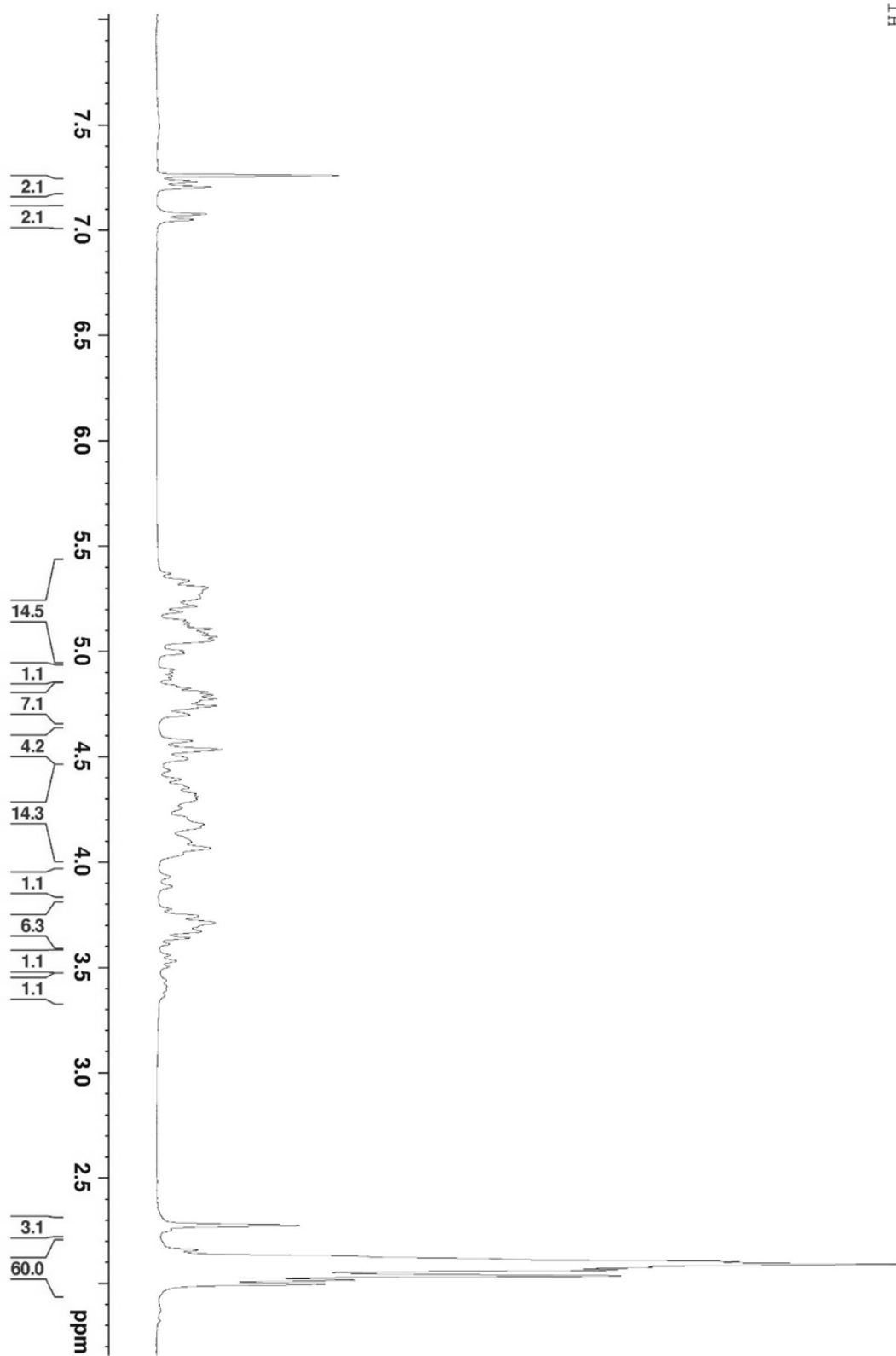
HSQC(CDCl₃) of 7Ad



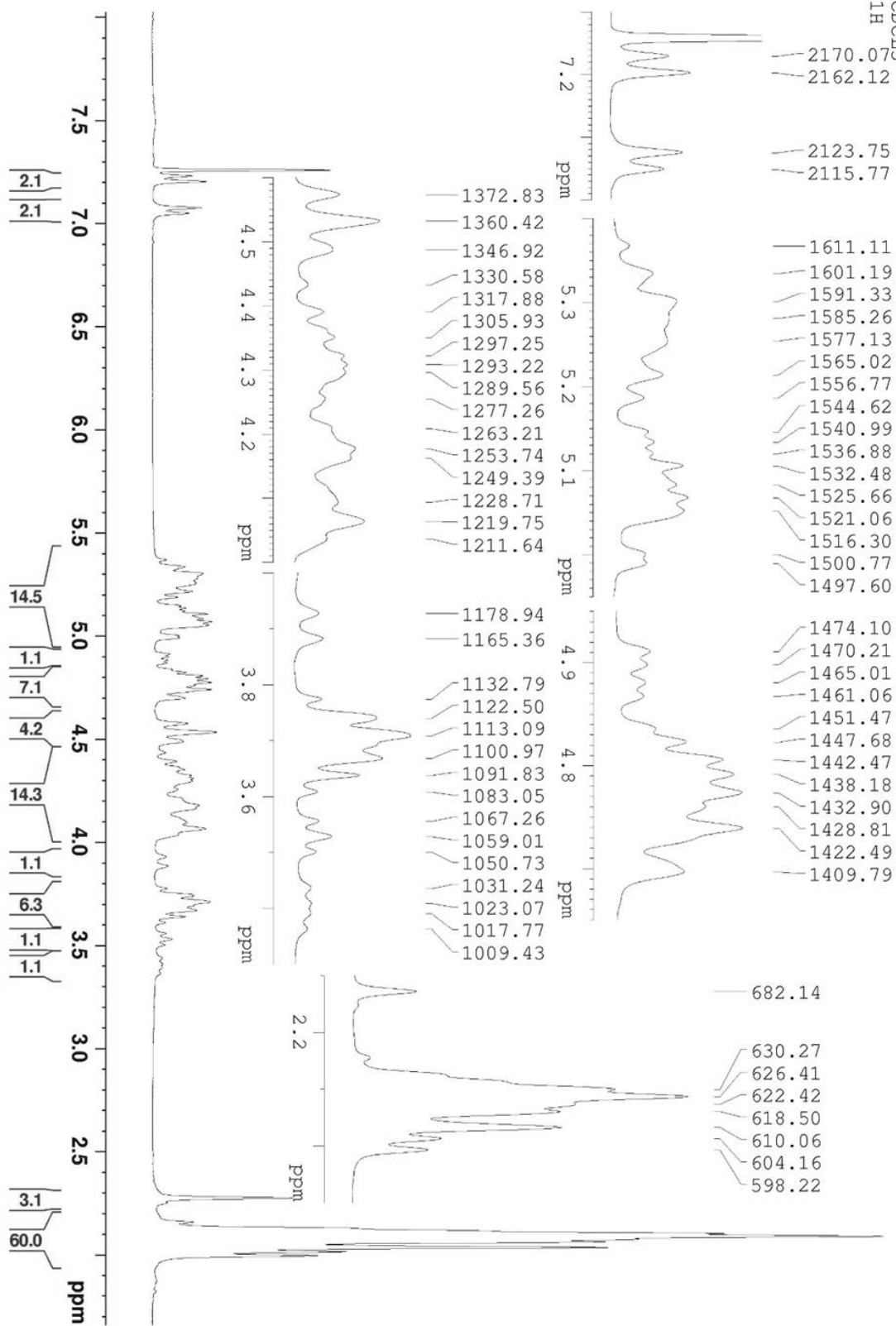


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RMN¹H(CDCl₃) of 7Ae

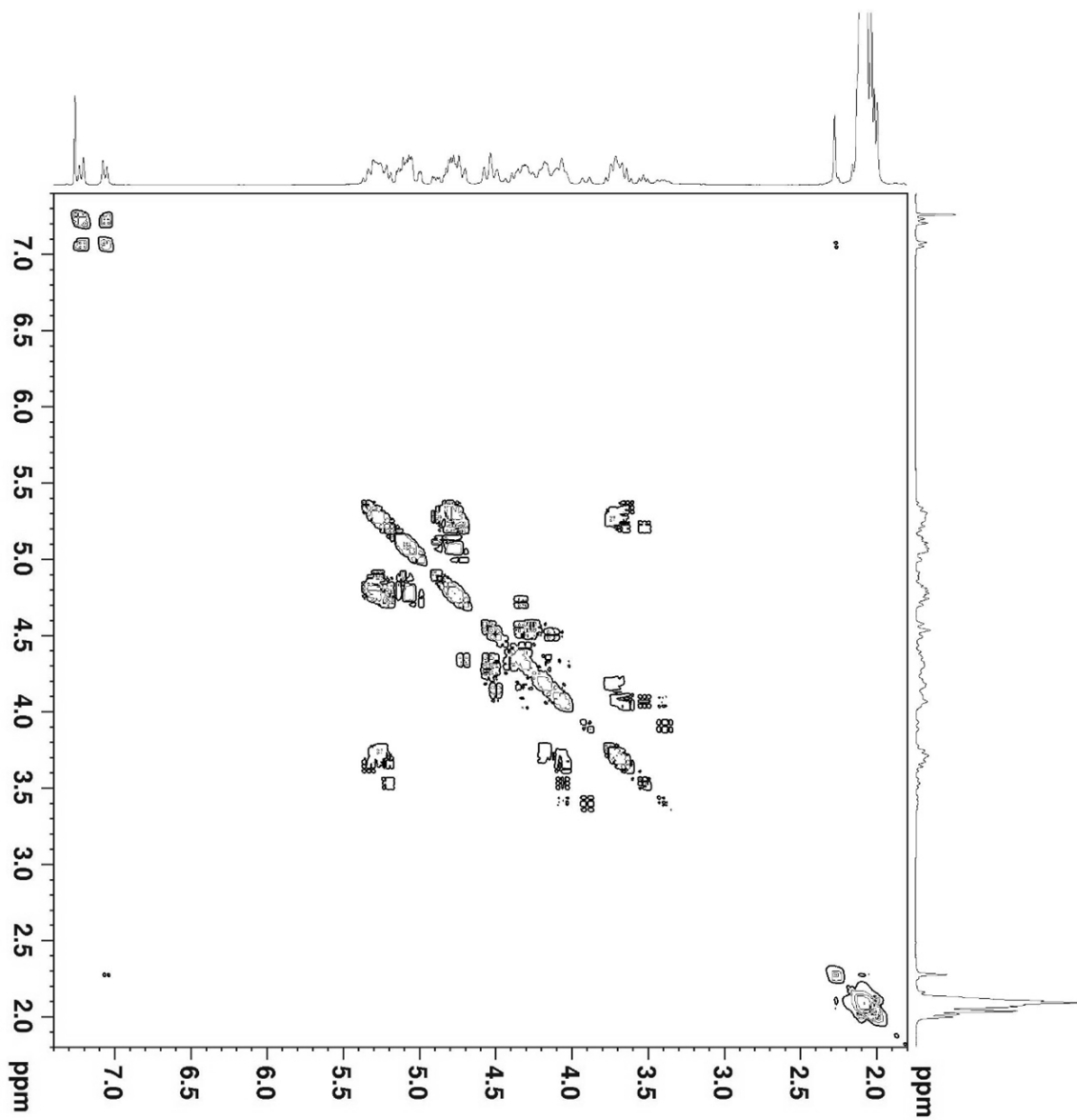


ML I 54 B2 t32 R1
 CDCL₃
 1H

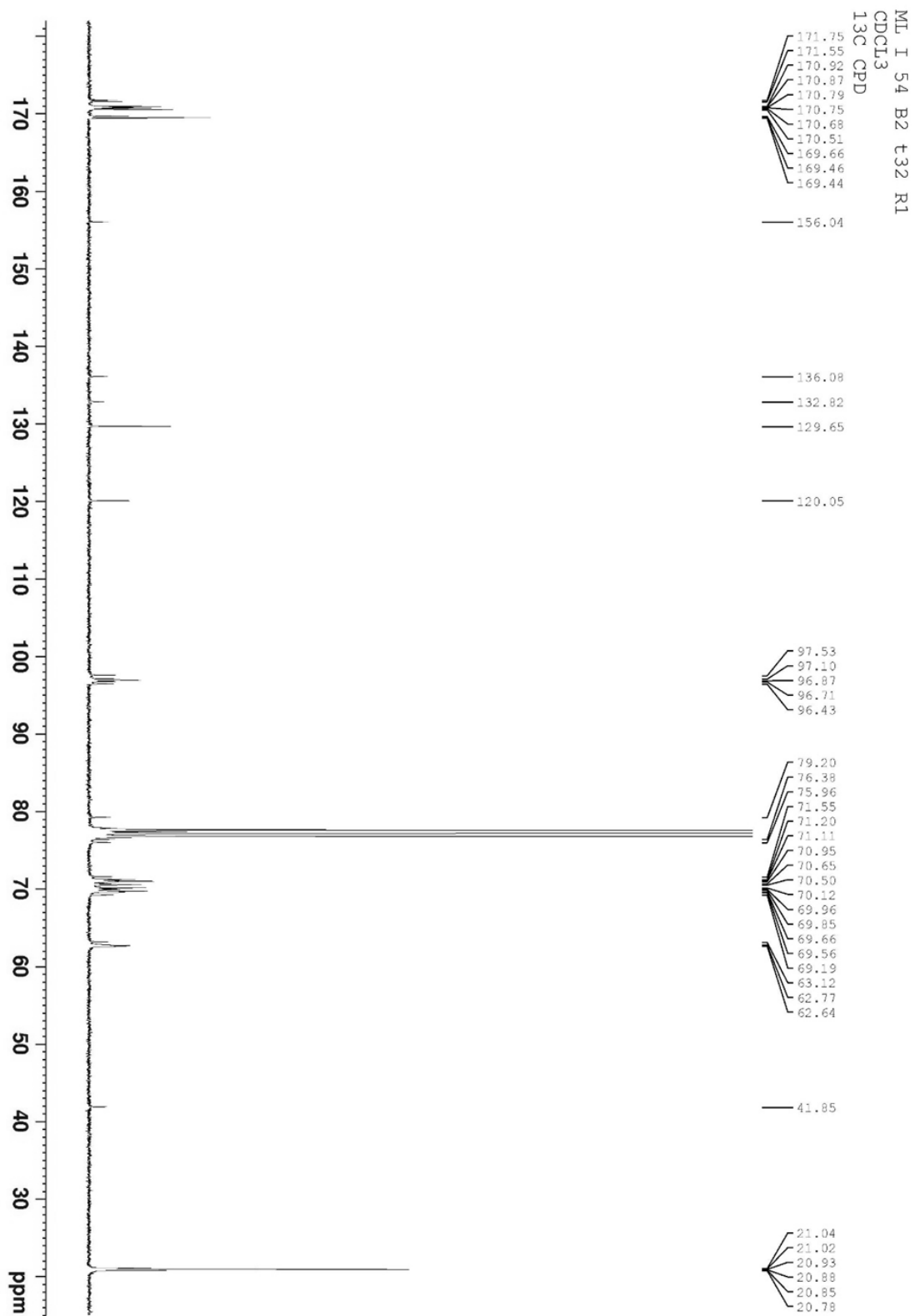


COSY (CDCl₃) of 7Ae

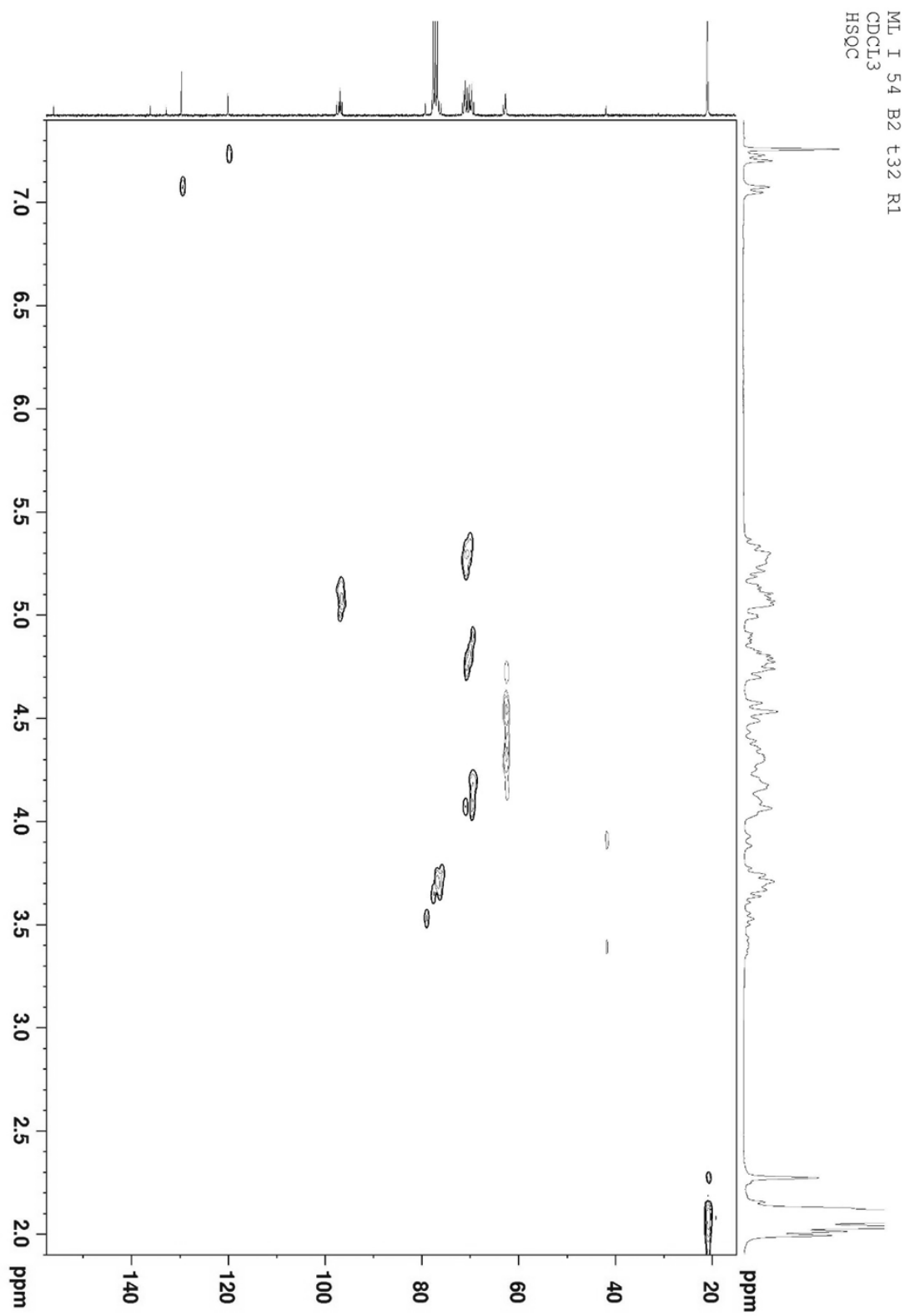
ML I 54 B2 t32 R1
CDCl₃
COSY45



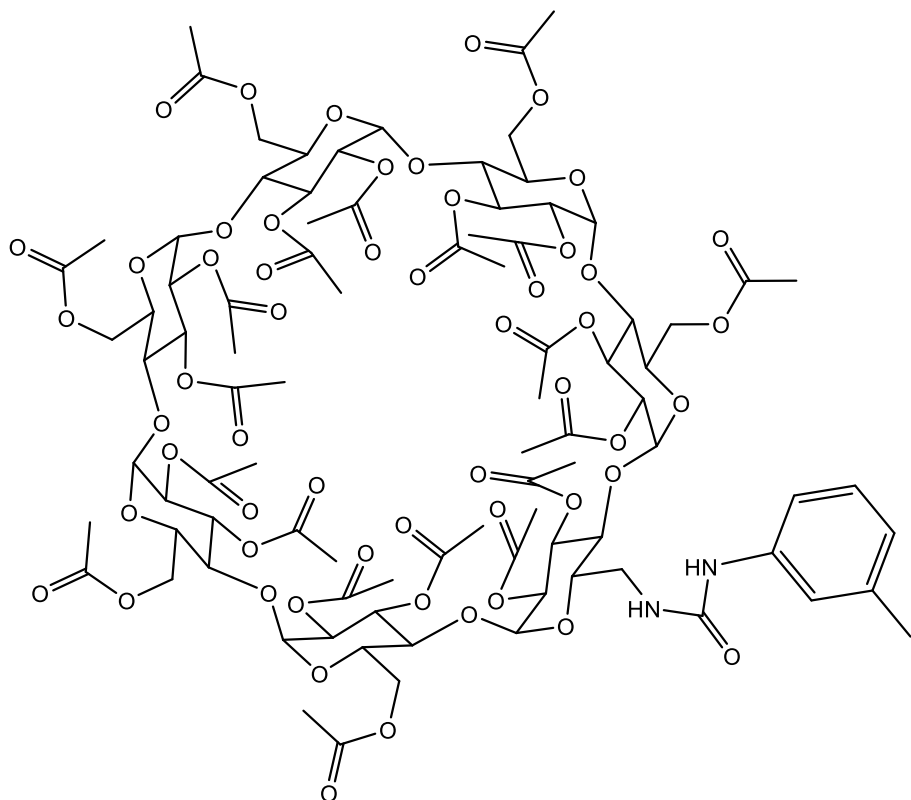
RMN¹³C(CDCl₃) of 7Ae



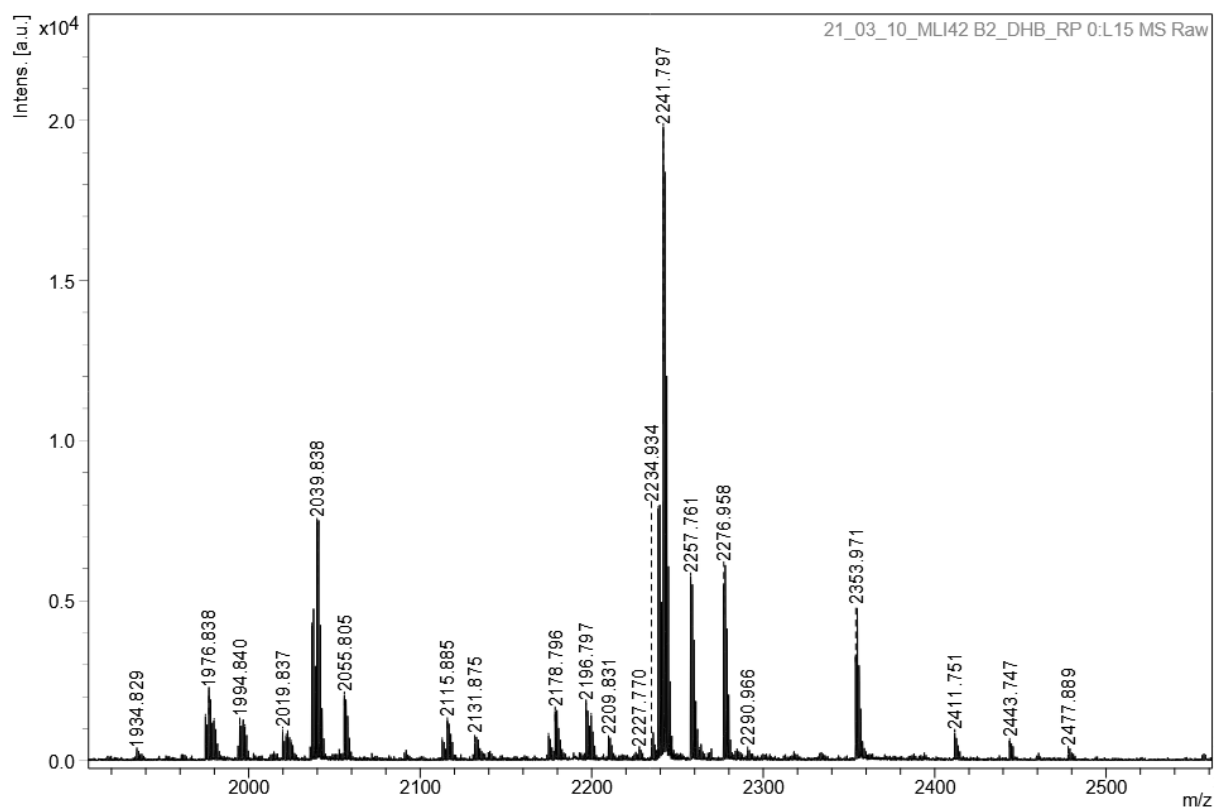
HSQC(CDCl₃) of 7Ae



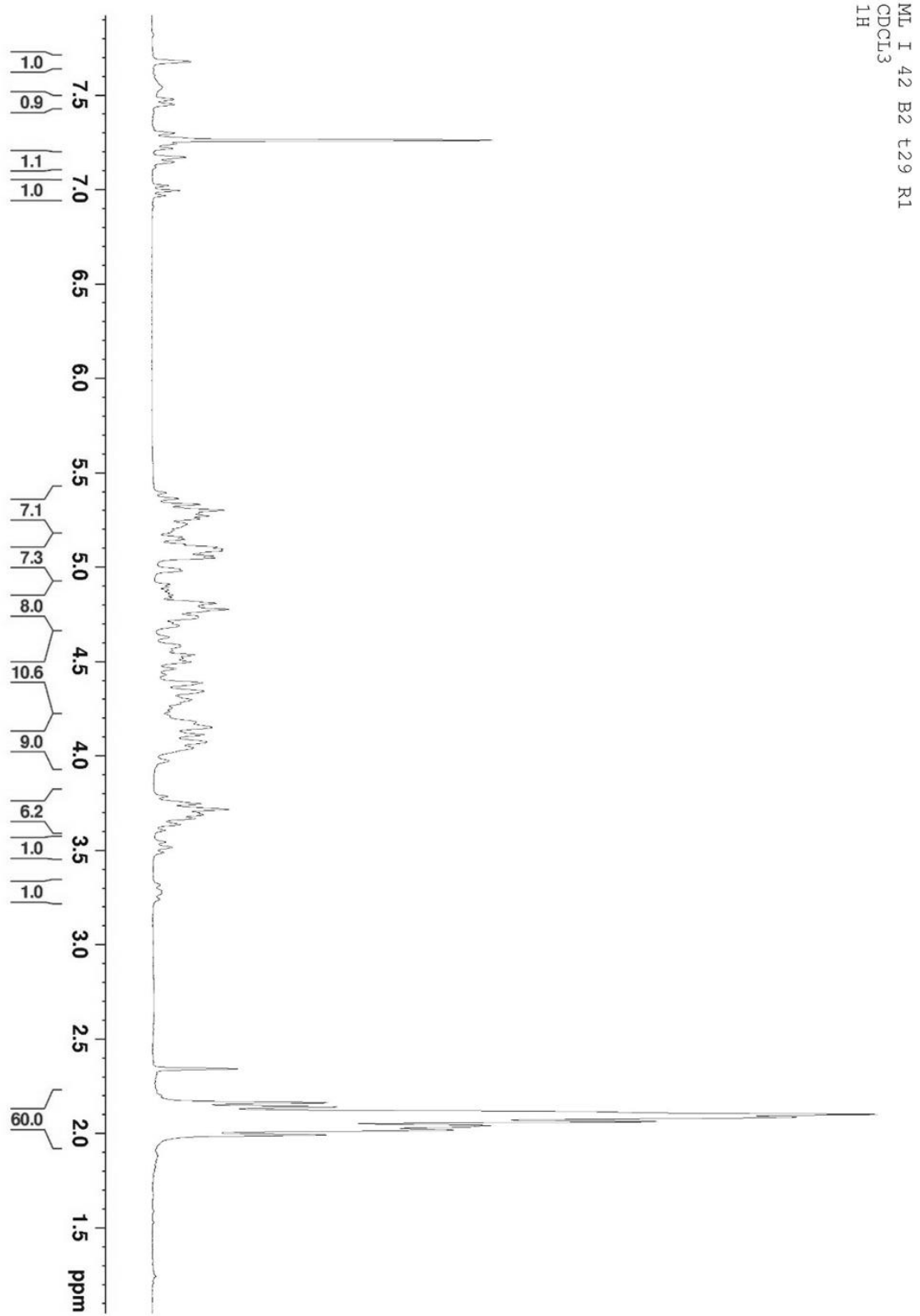
Characterisation of 7Af (C₈₉H₁₁₅N₂O₅₅)



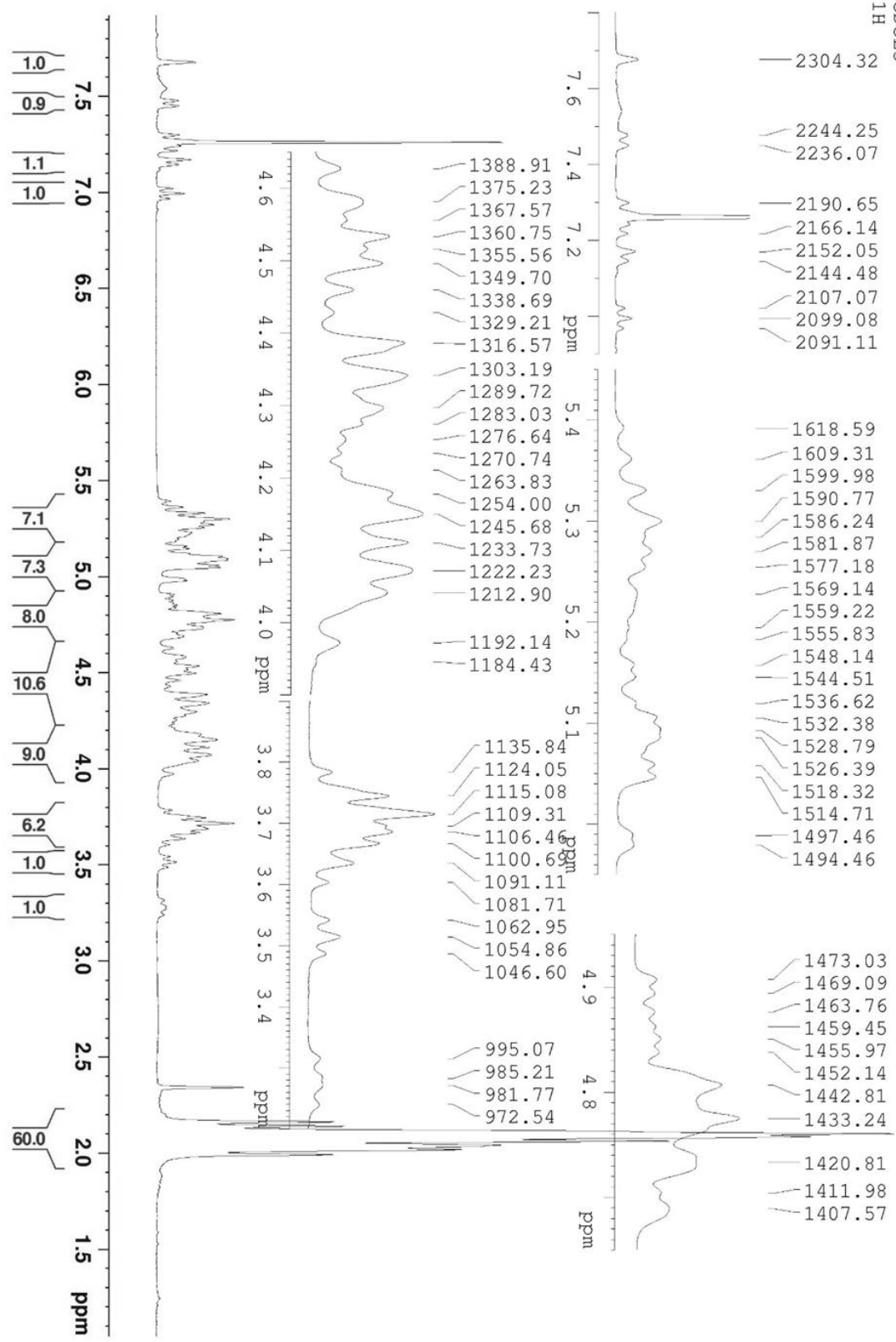
MALDI TOF of 7Af



RMN¹H(CDCl₃) of 7Af

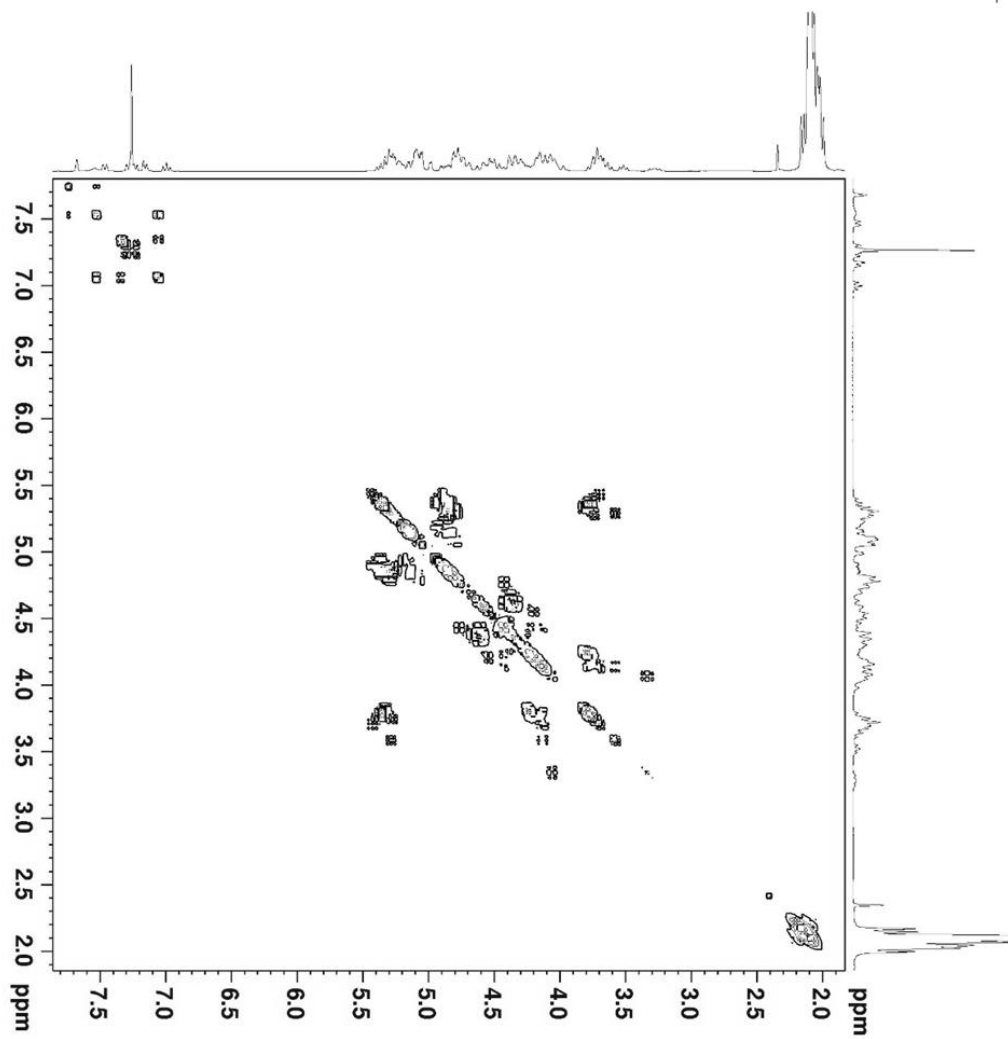


ML I 42 B2 t29 R1
 CDCL3
 1H

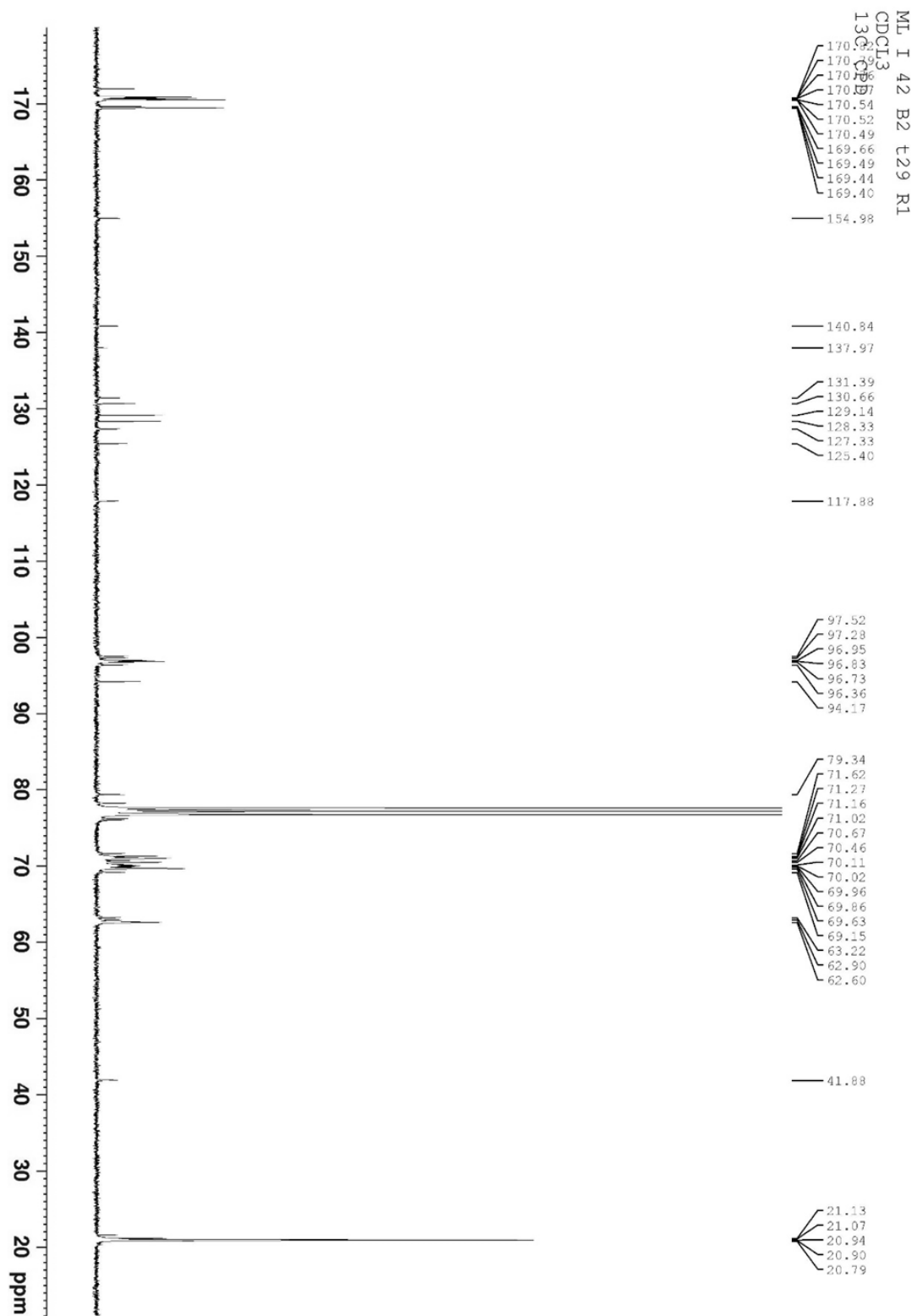


COSY (CDCl₃) of 7Af

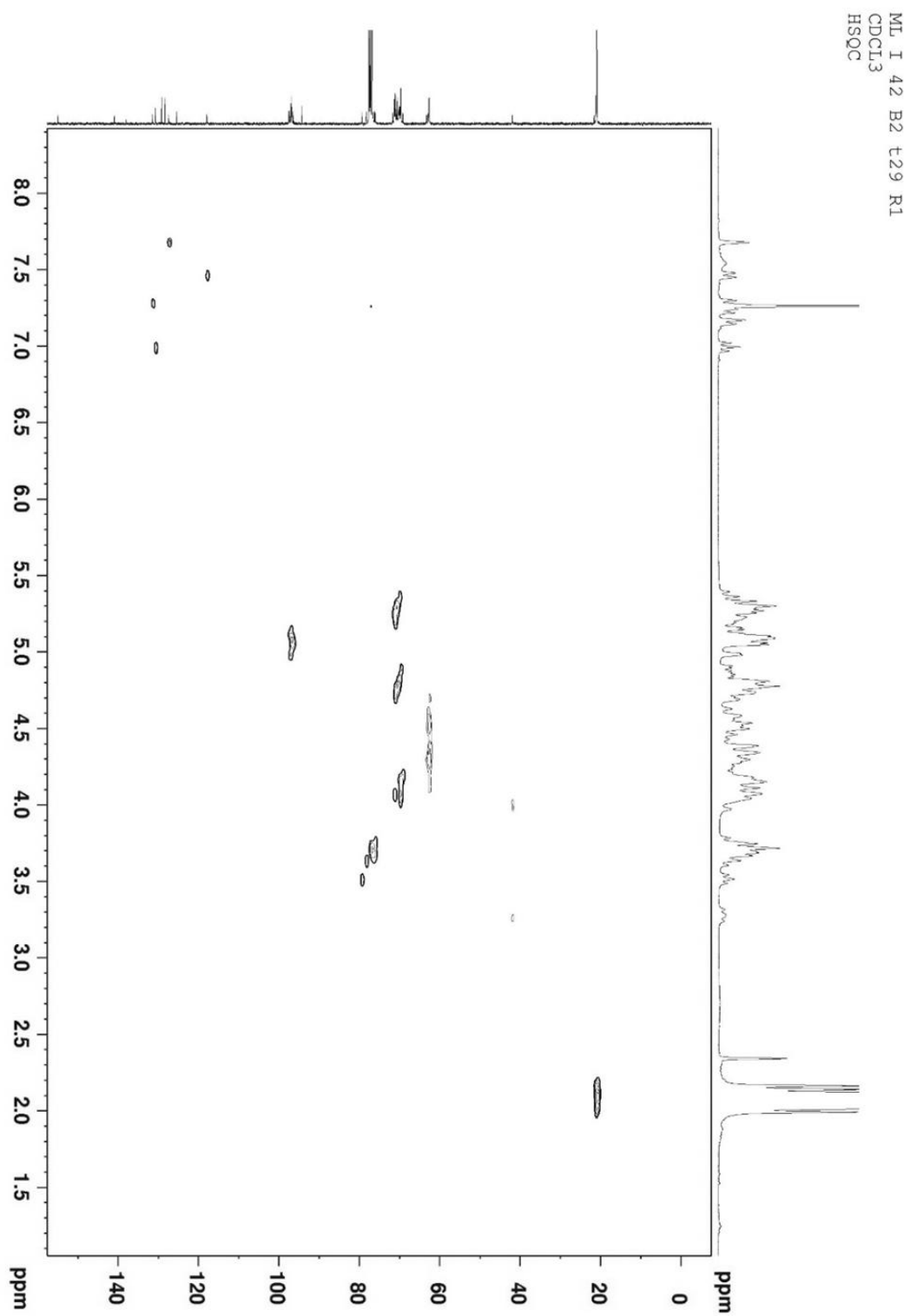
ML I 42 B2 t29 R1
CDCl₃
COSY45



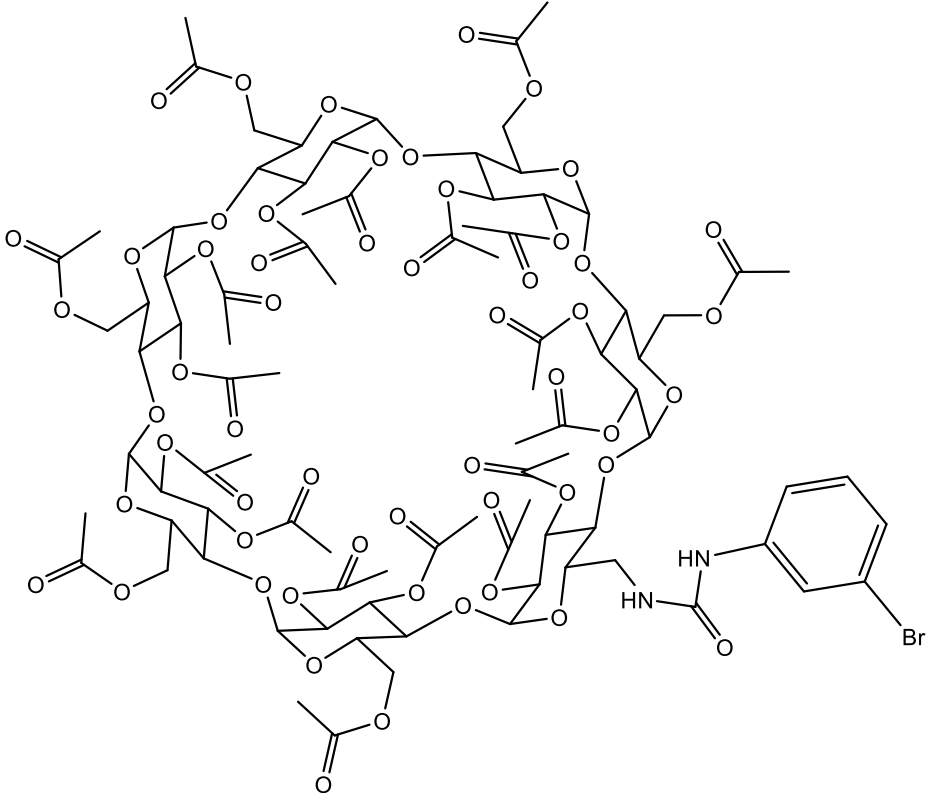
RMN¹³C(CDCl₃) of 7Af



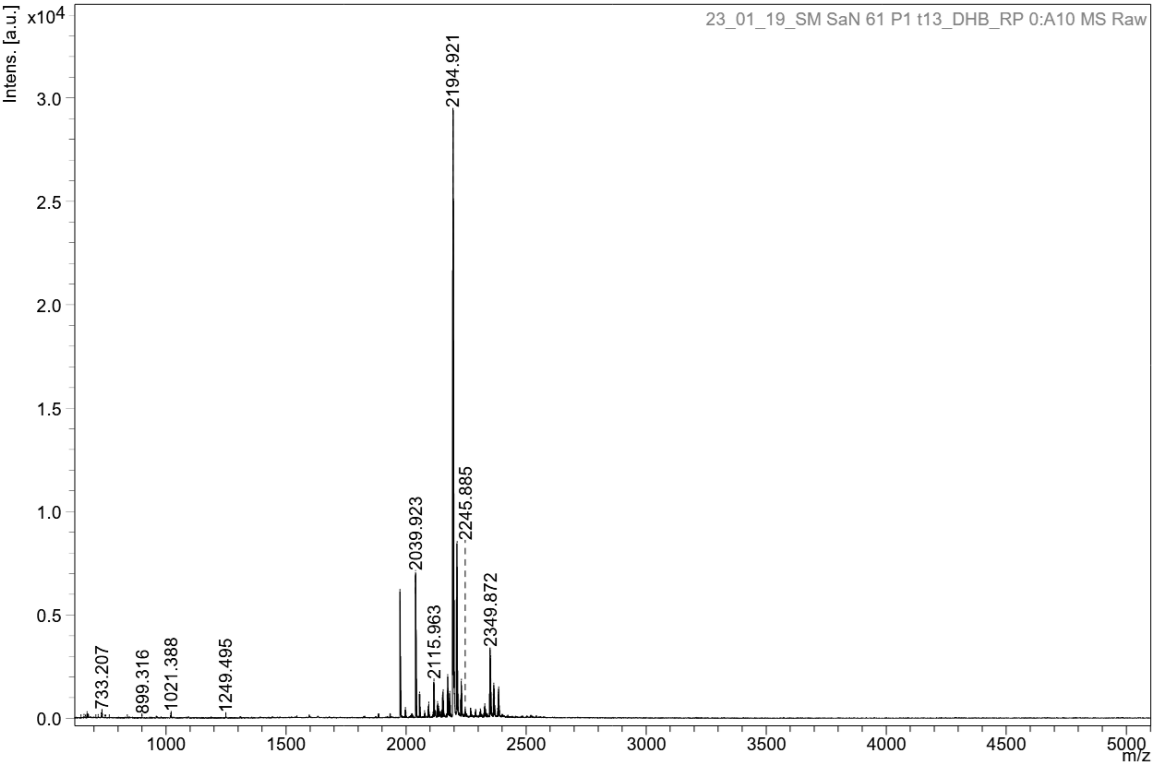
HSQC(CDCl₃) of 7Af



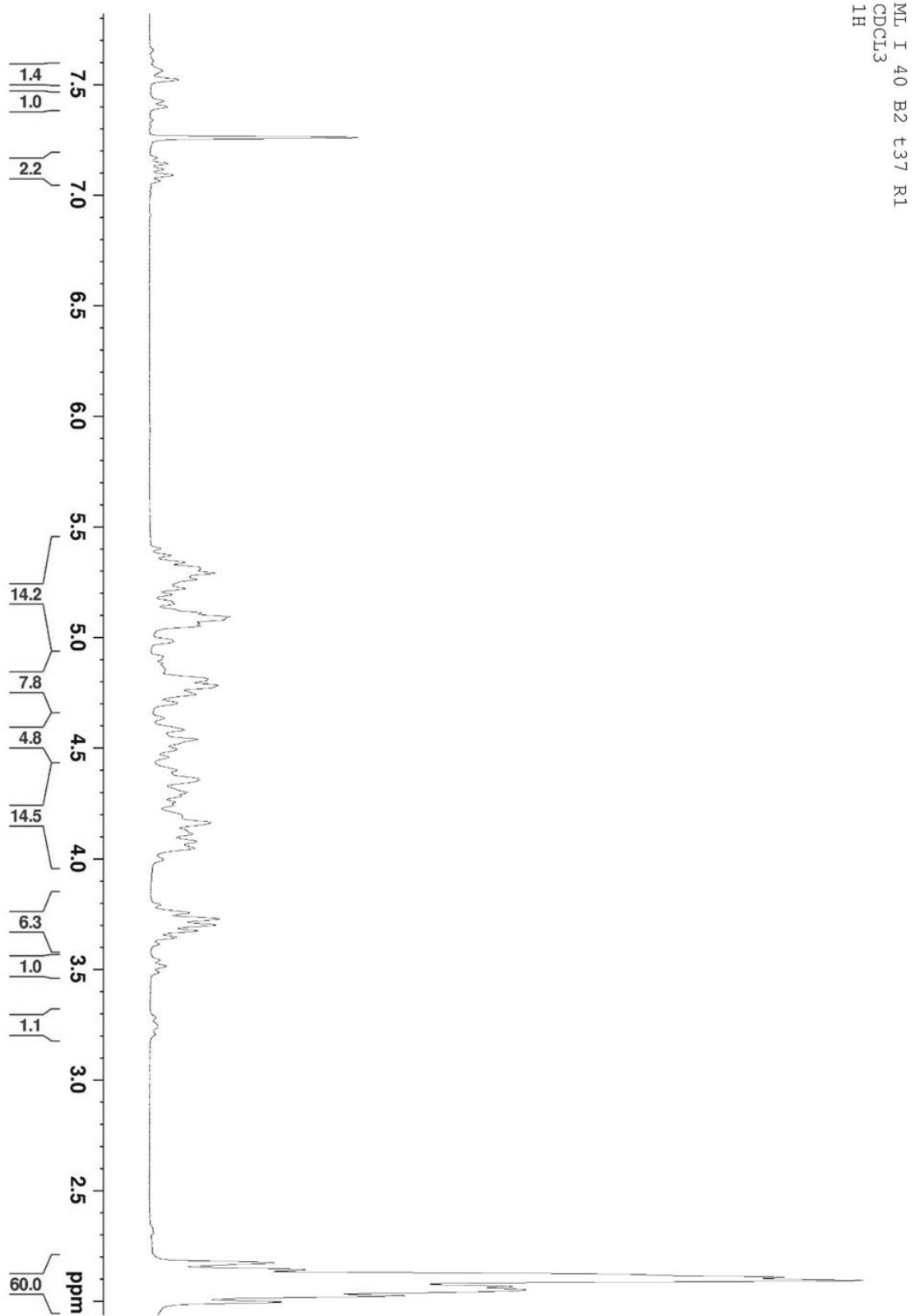
Characterisation of 7Ag (C₈₉H₁₁₅N₂O₅₅Br)



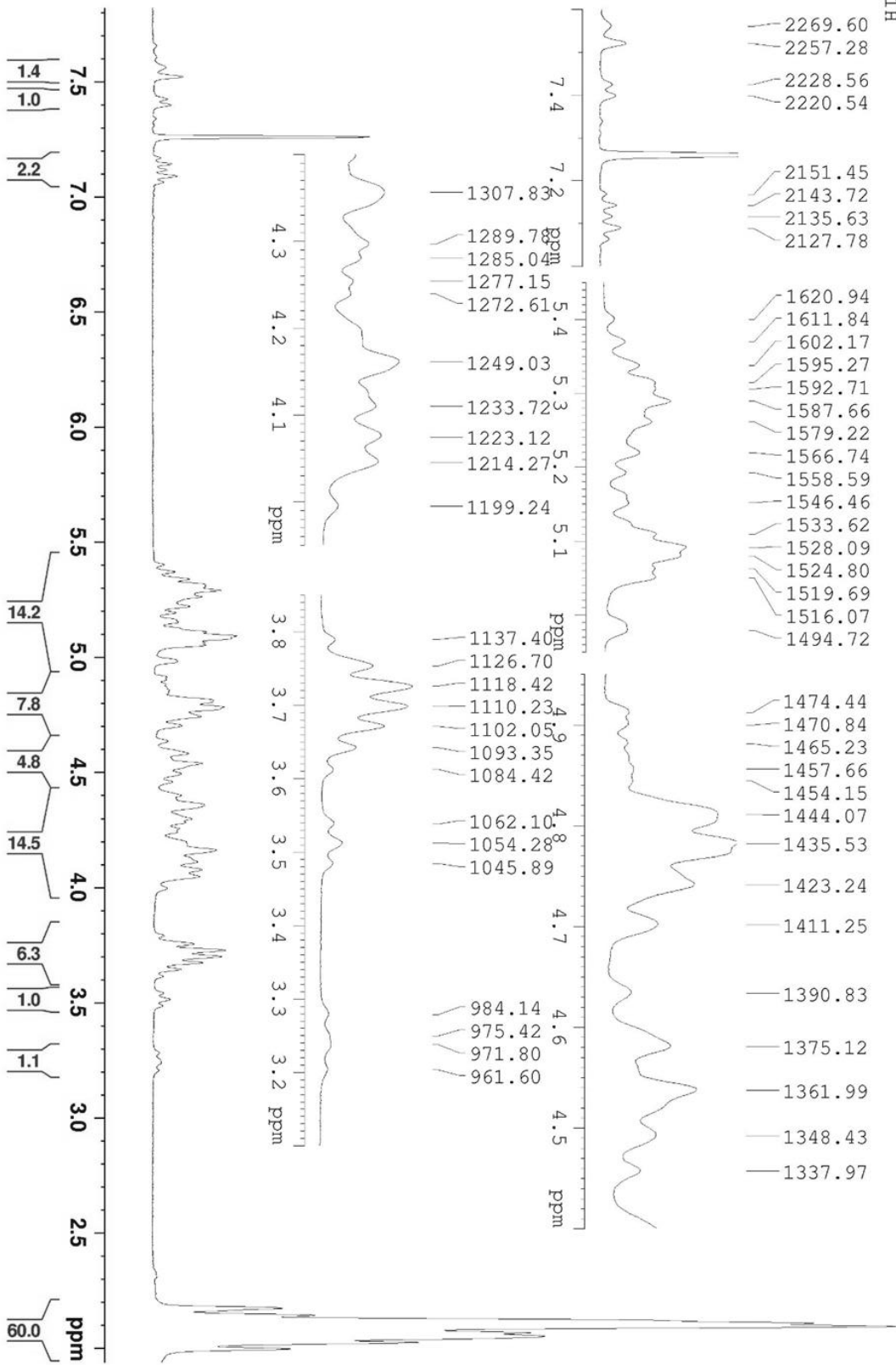
MALDI TOF of 7Ag



RMN¹H(CDCl₃) of 7Ag

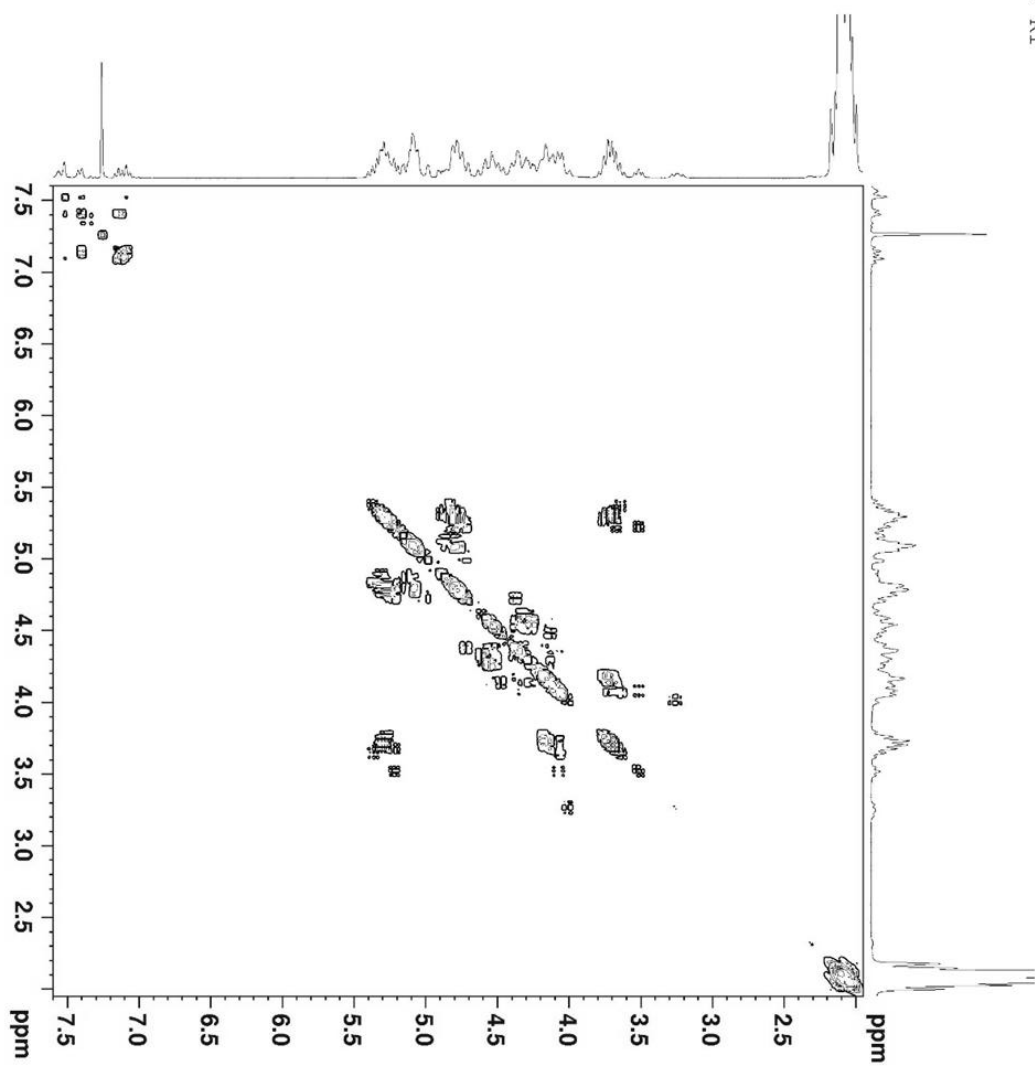


ML I 40 B2 t37 R1
 CDCL3
 1H

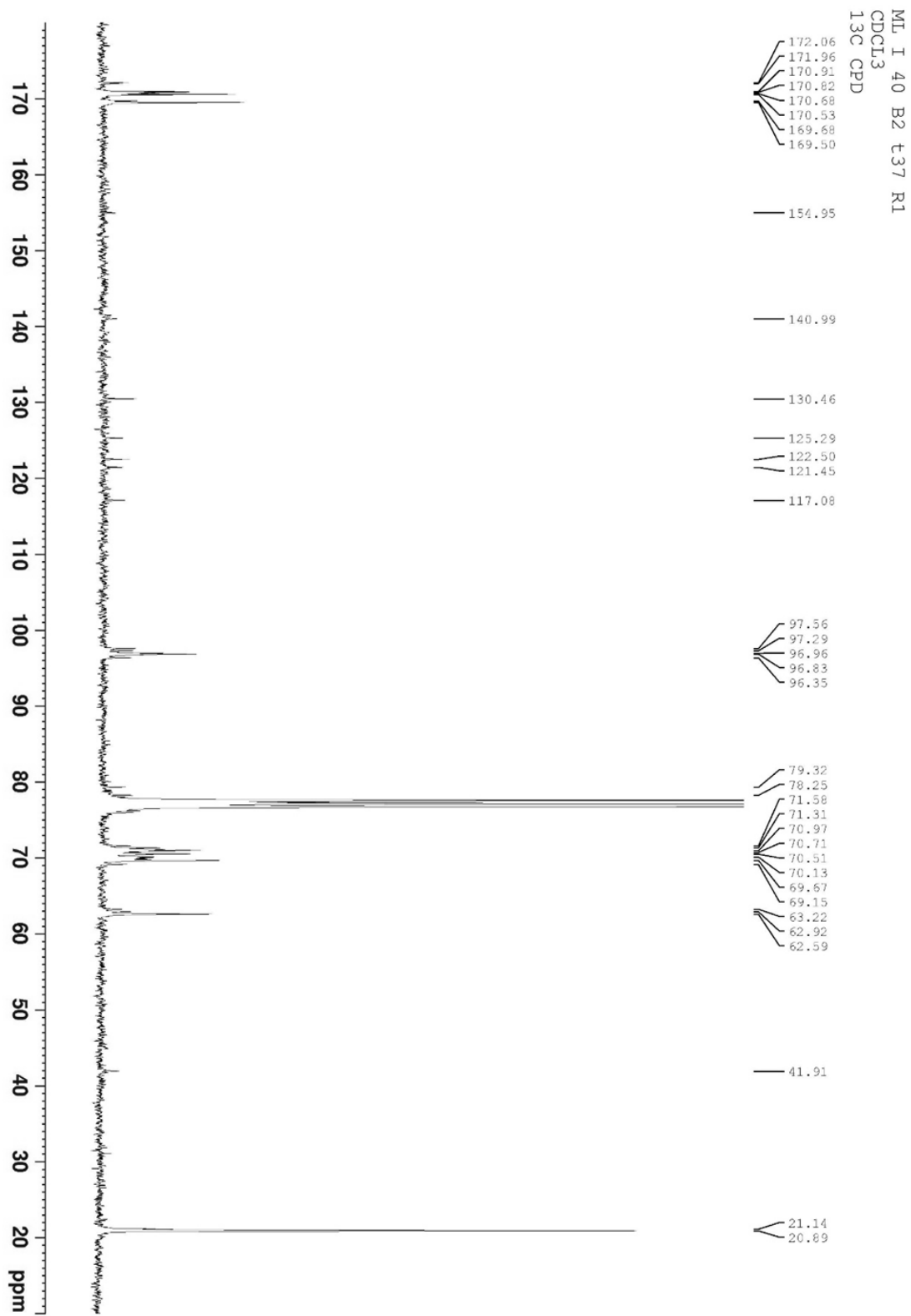


COSY (CDCl₃) of 7Ag

ML I 40 B2 t37 R1
CDCl₃
COSY45

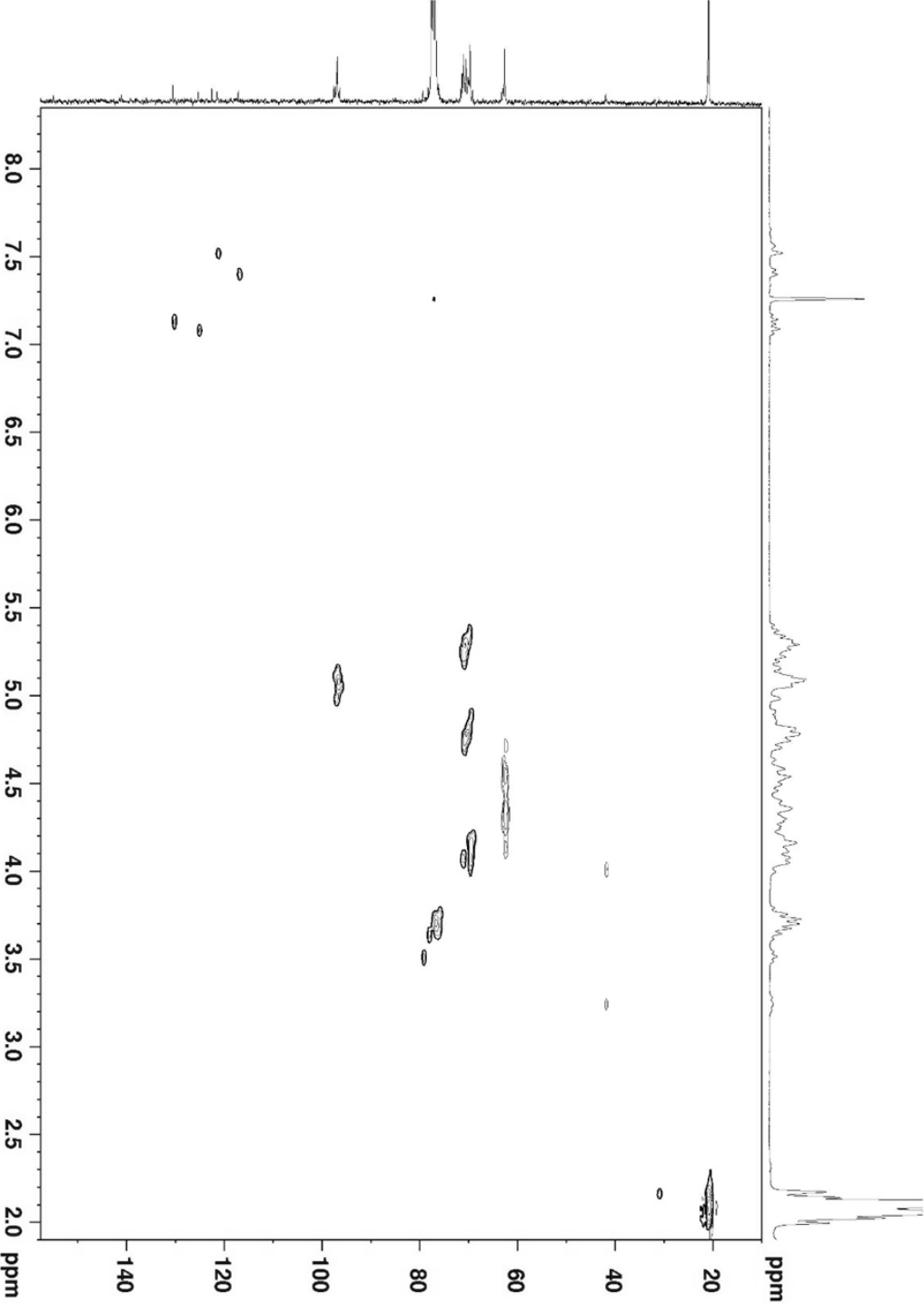


RMN¹³C(CDCI₃) of 7Ag

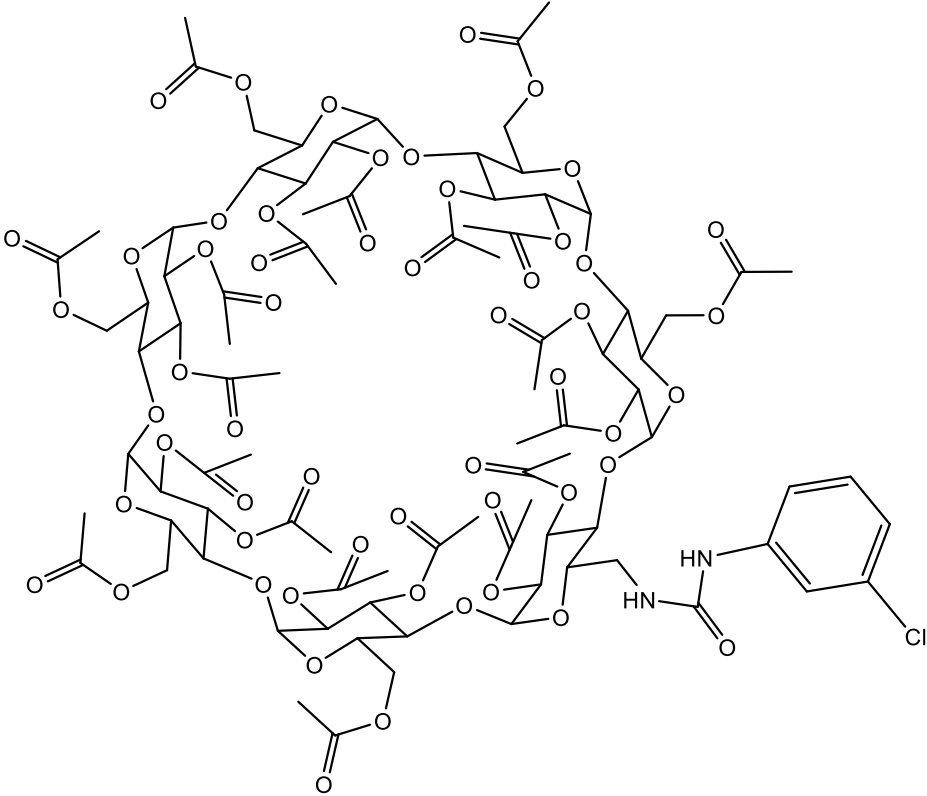


HSQC(CDCl₃) of 7Ag

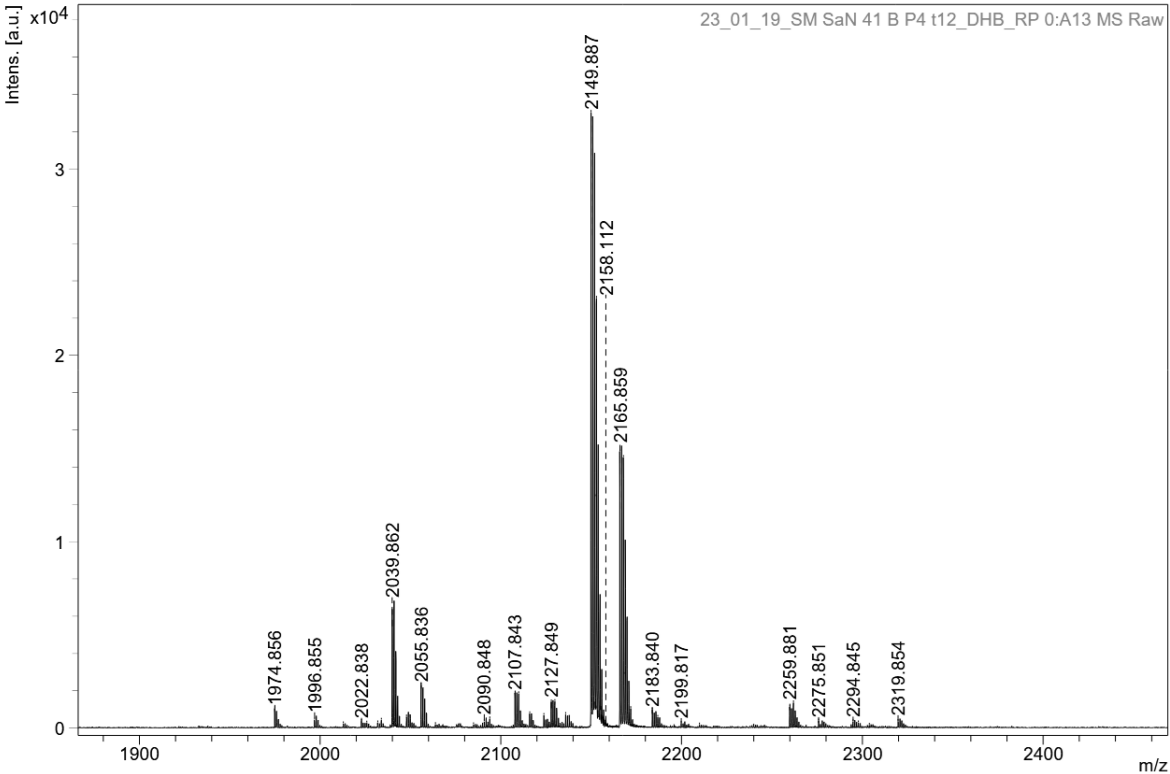
ML I 40 B2 t37 R1
CDCl₃
HSQC



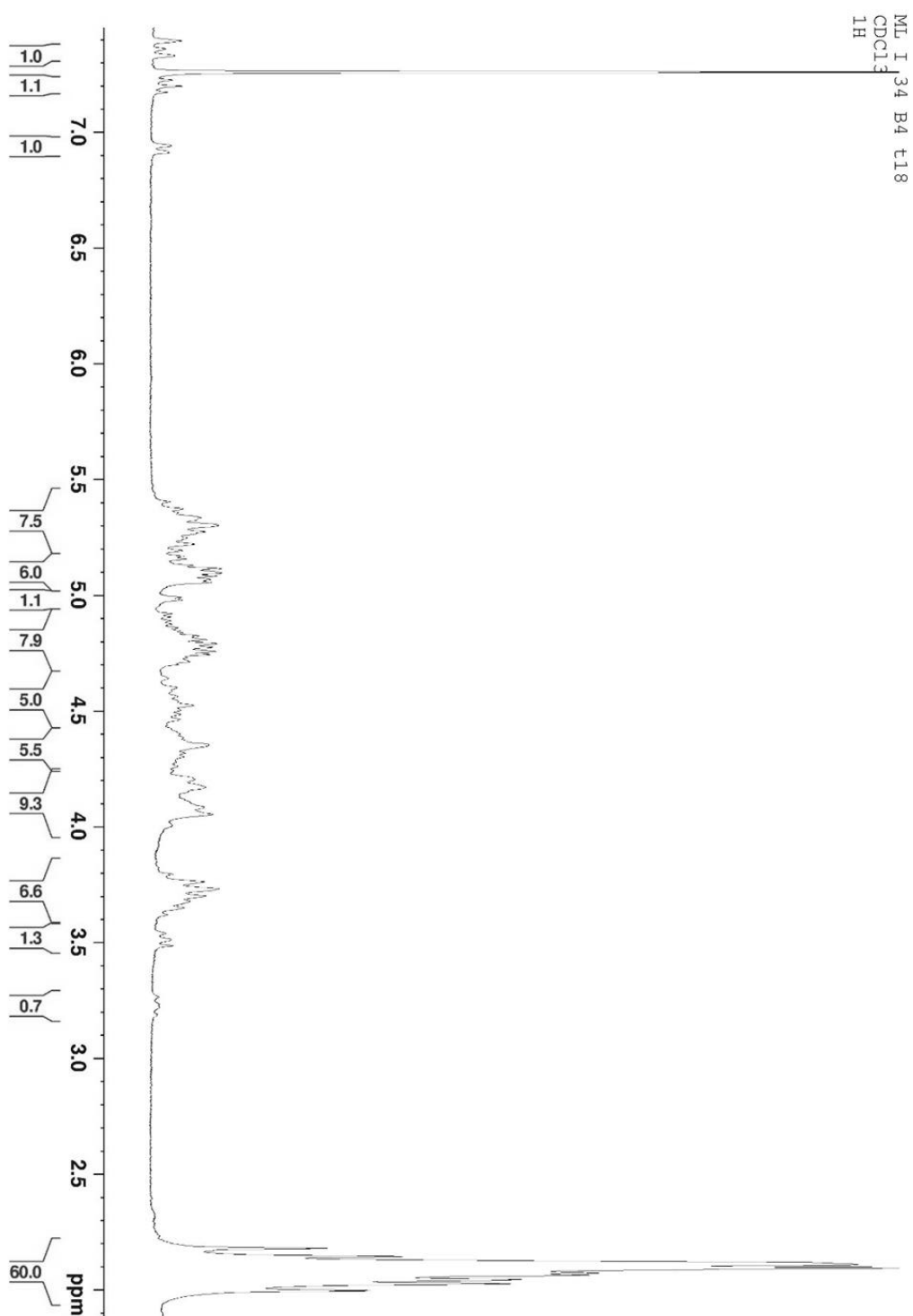
Characterisation of 7Ah (C₈₉H₁₁₅N₂O₅₅Cl)

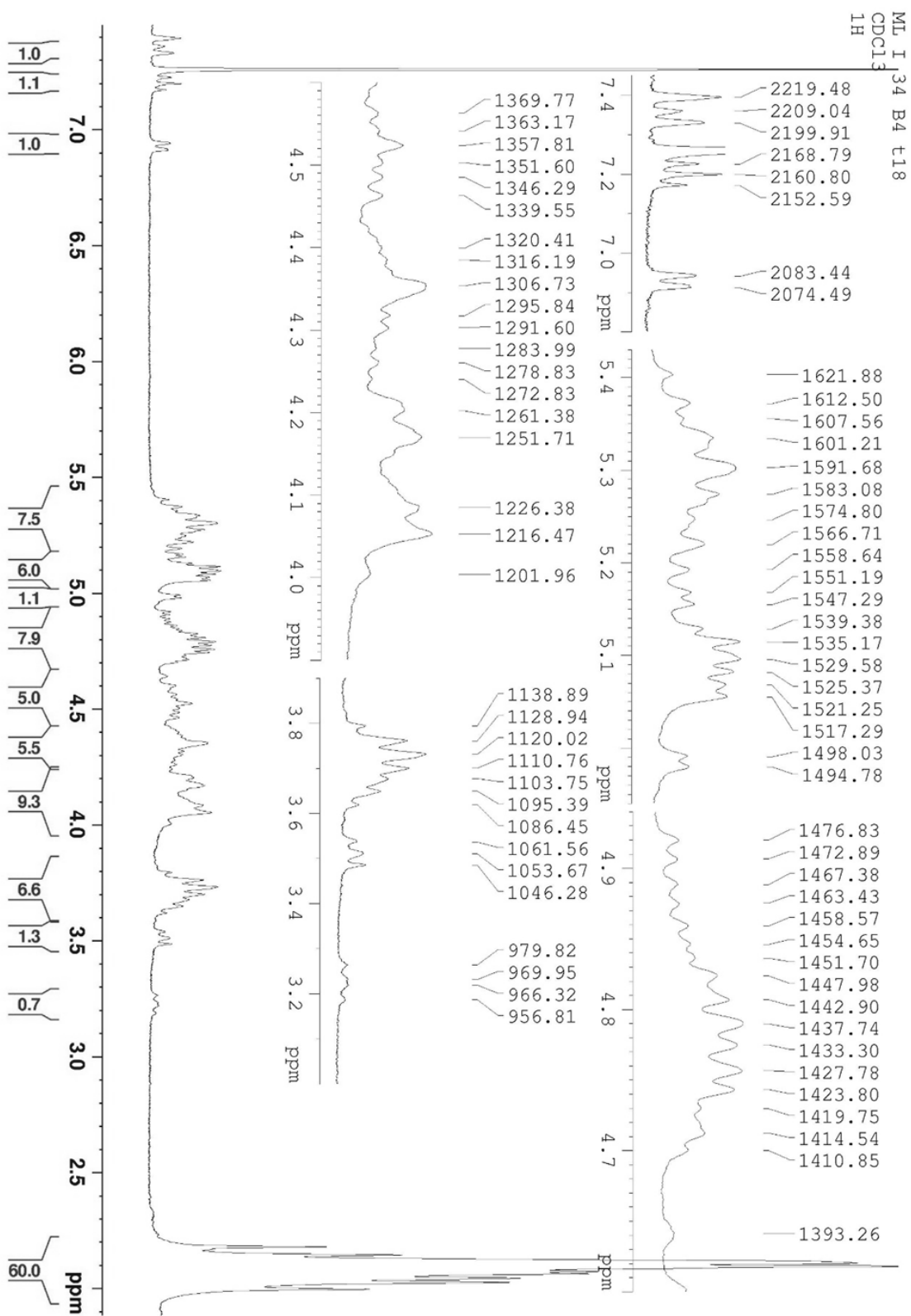


MALDI TOF of 7Ah



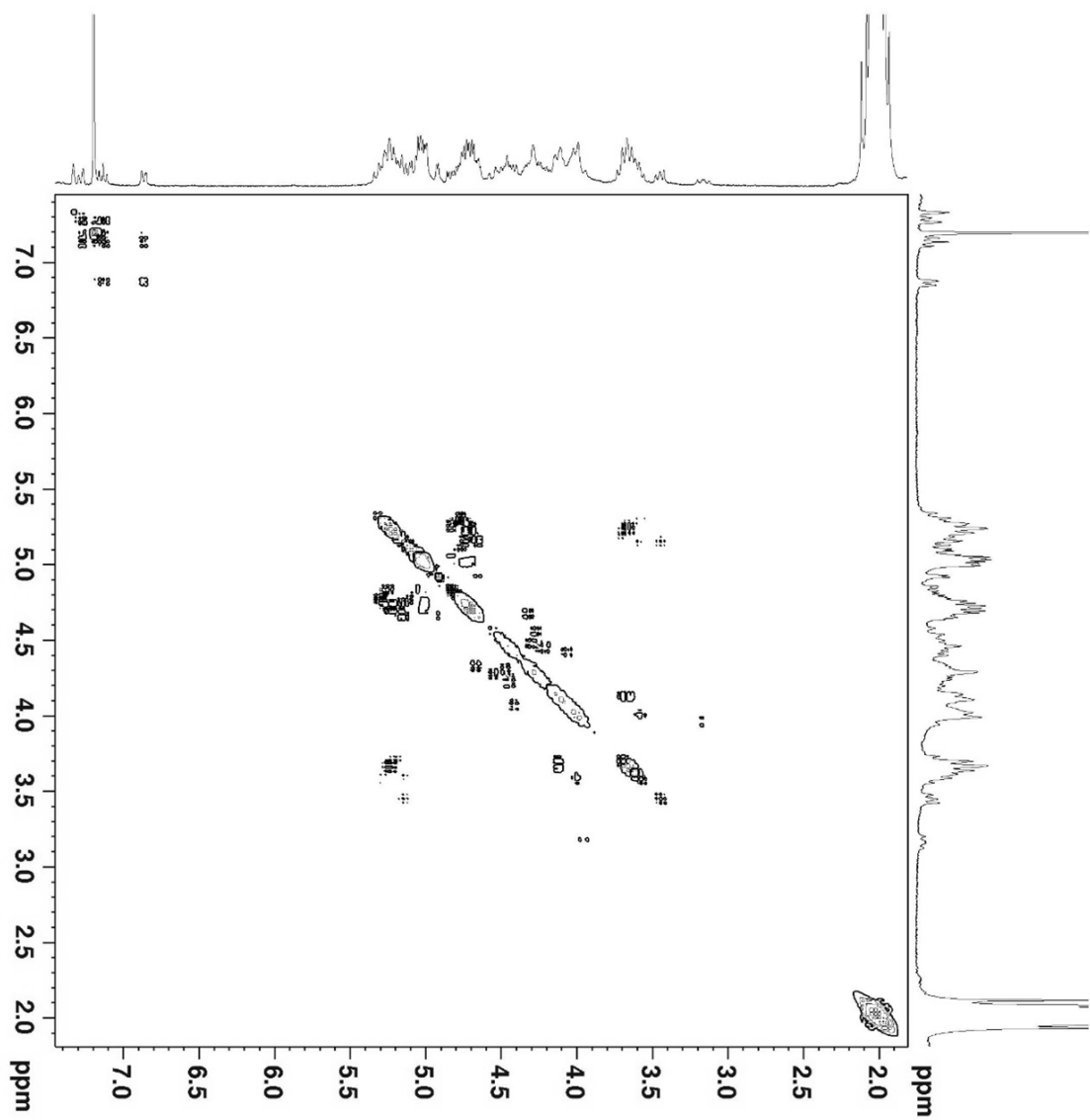
RMN¹H(CDCl₃) of 7Ah



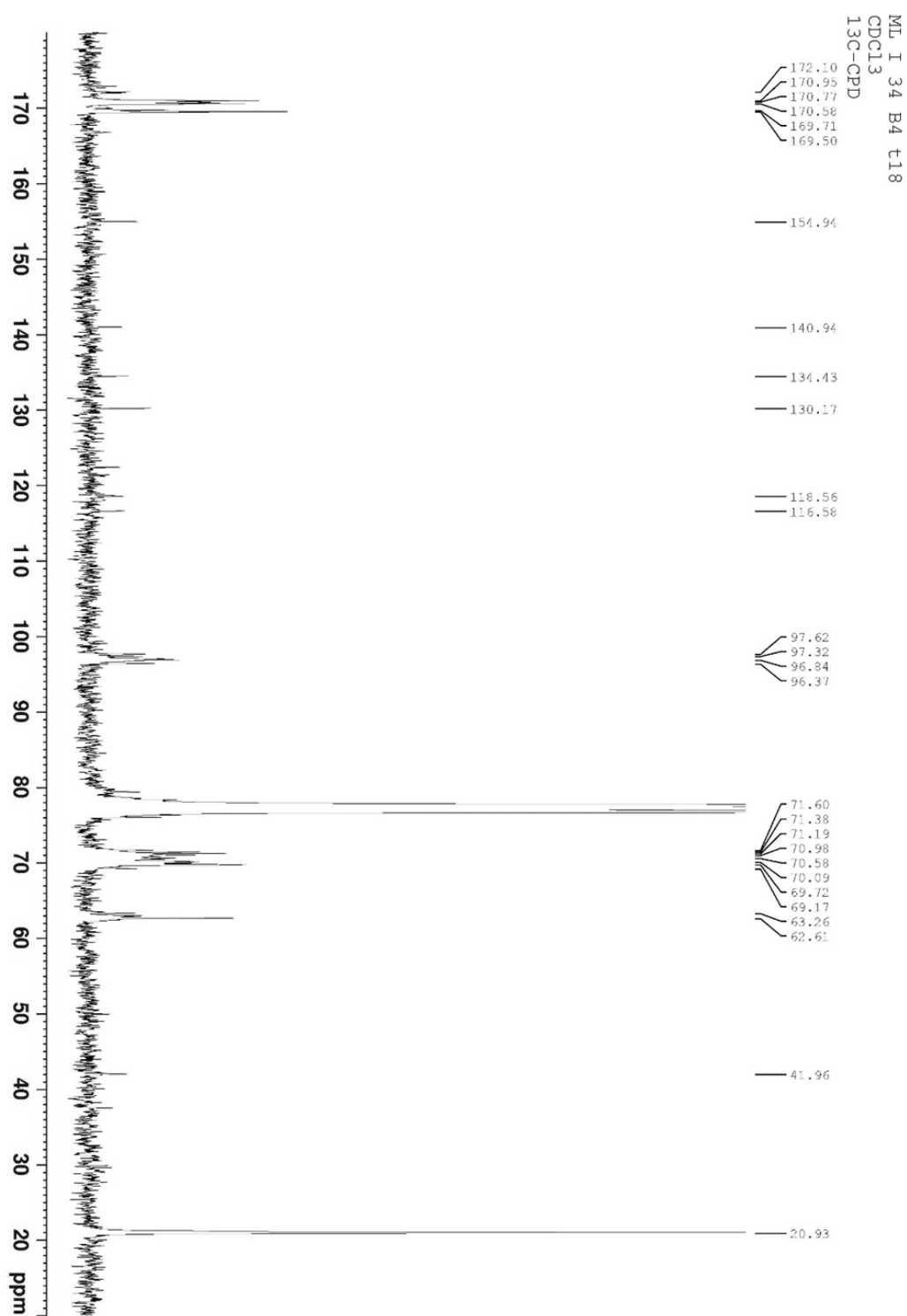


COSY (CDCl₃) of 7Ah

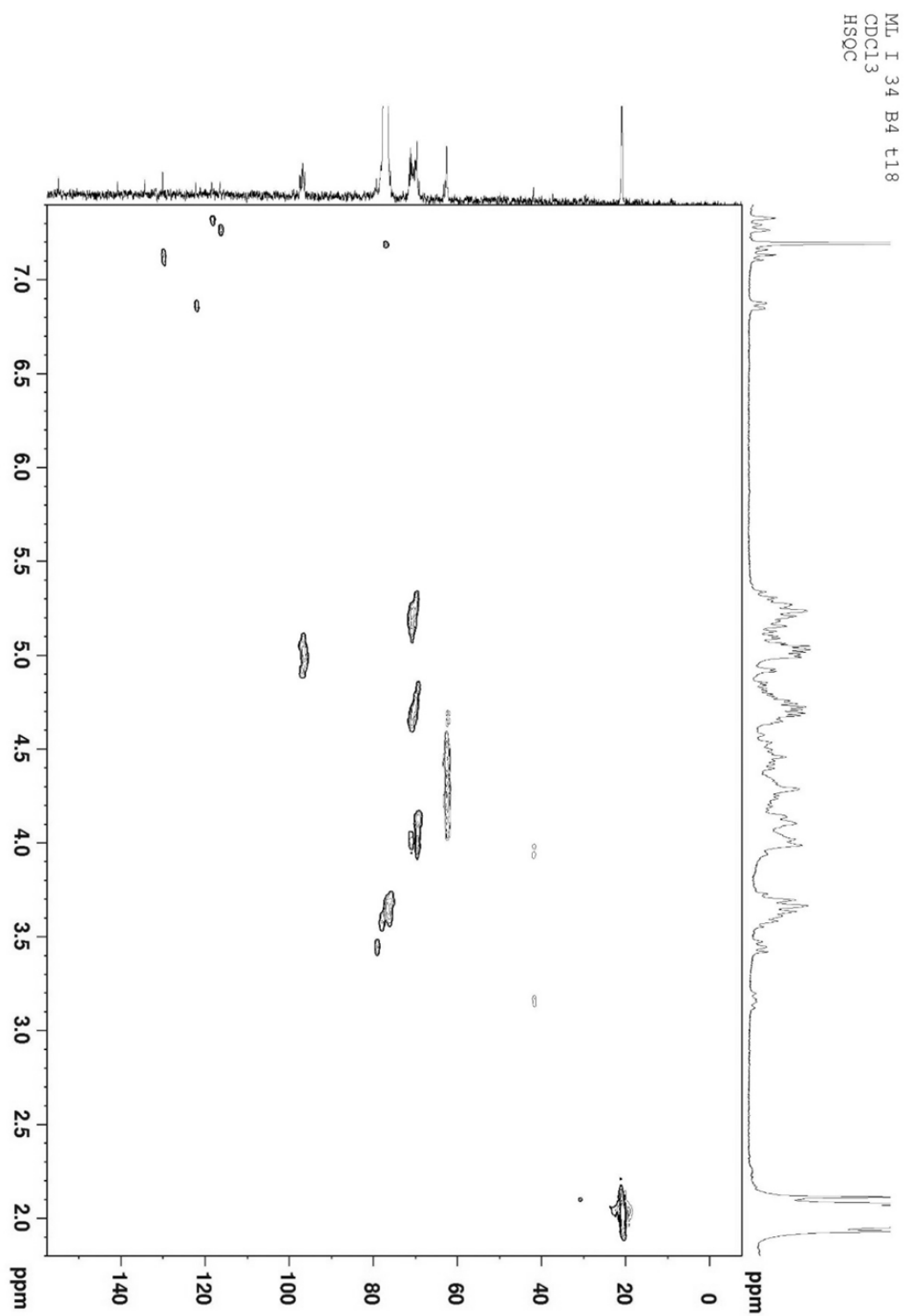
ML I 34 B4 t18
CDCl₃
COSY45



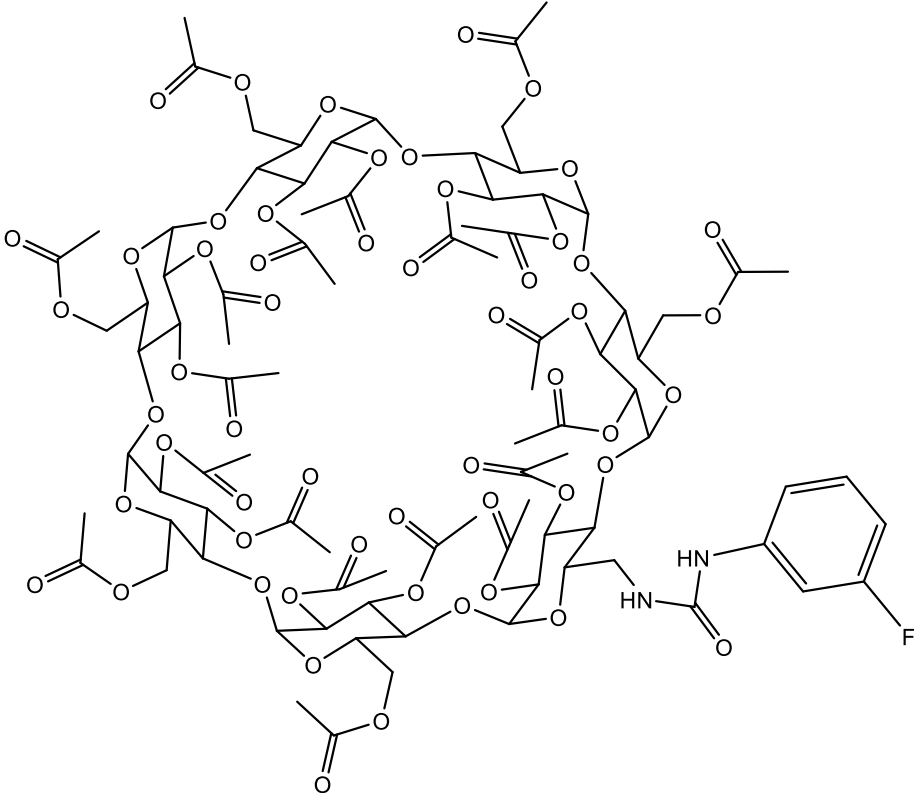
RMN¹³C(CDCl₃) of 7Ah



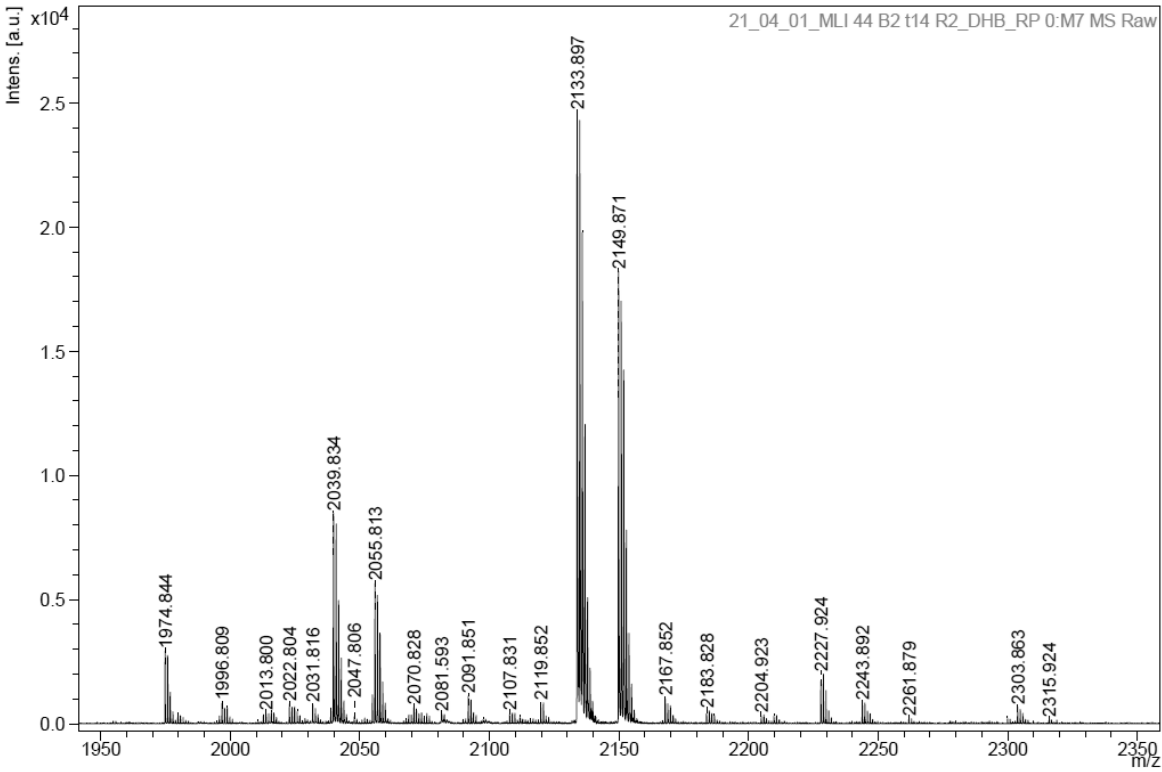
HSQC(CDCl₃) of 7Ah



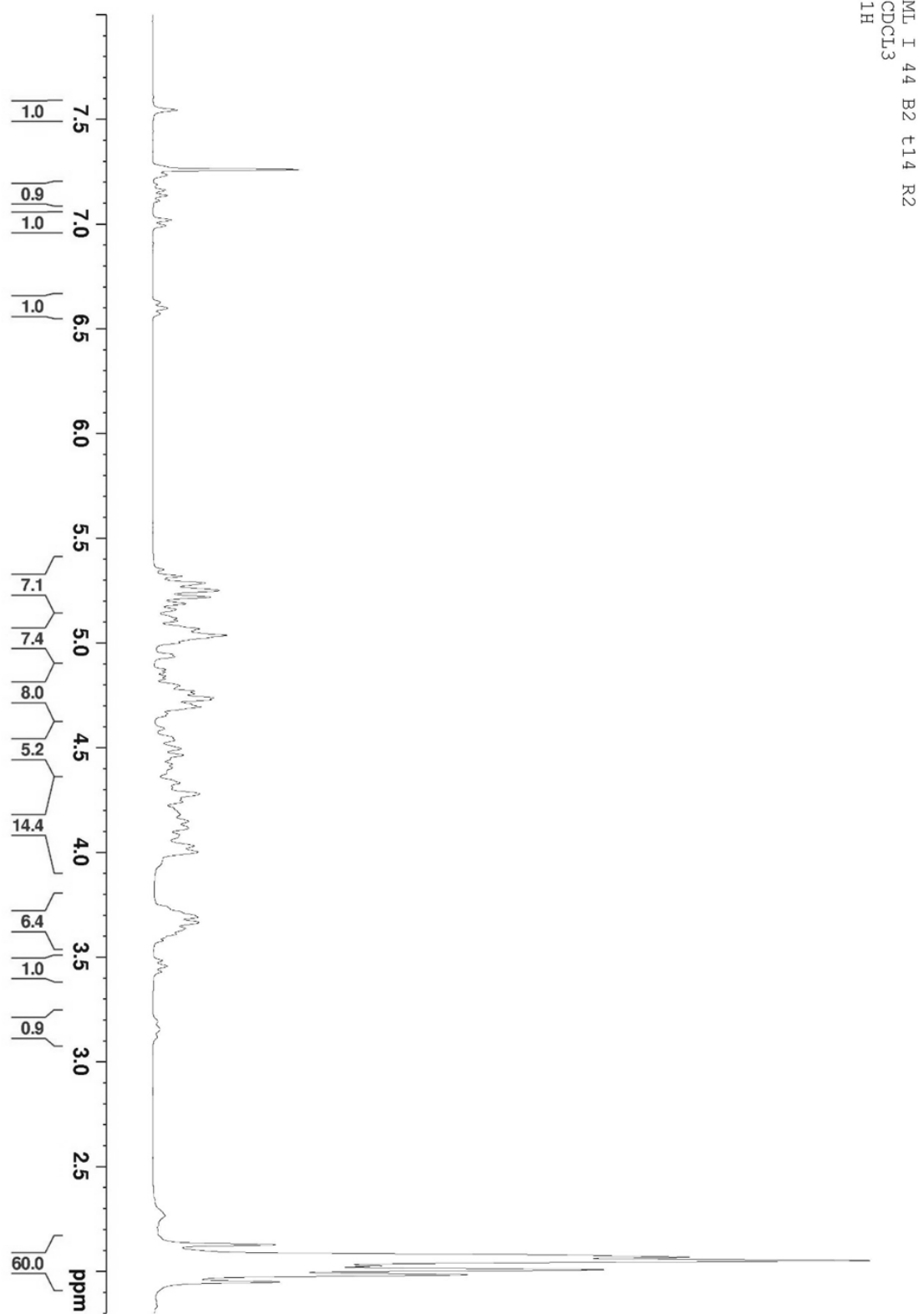
Characterisation of 7Ai (C₈₉H₁₁₅N₂O₅₅F)



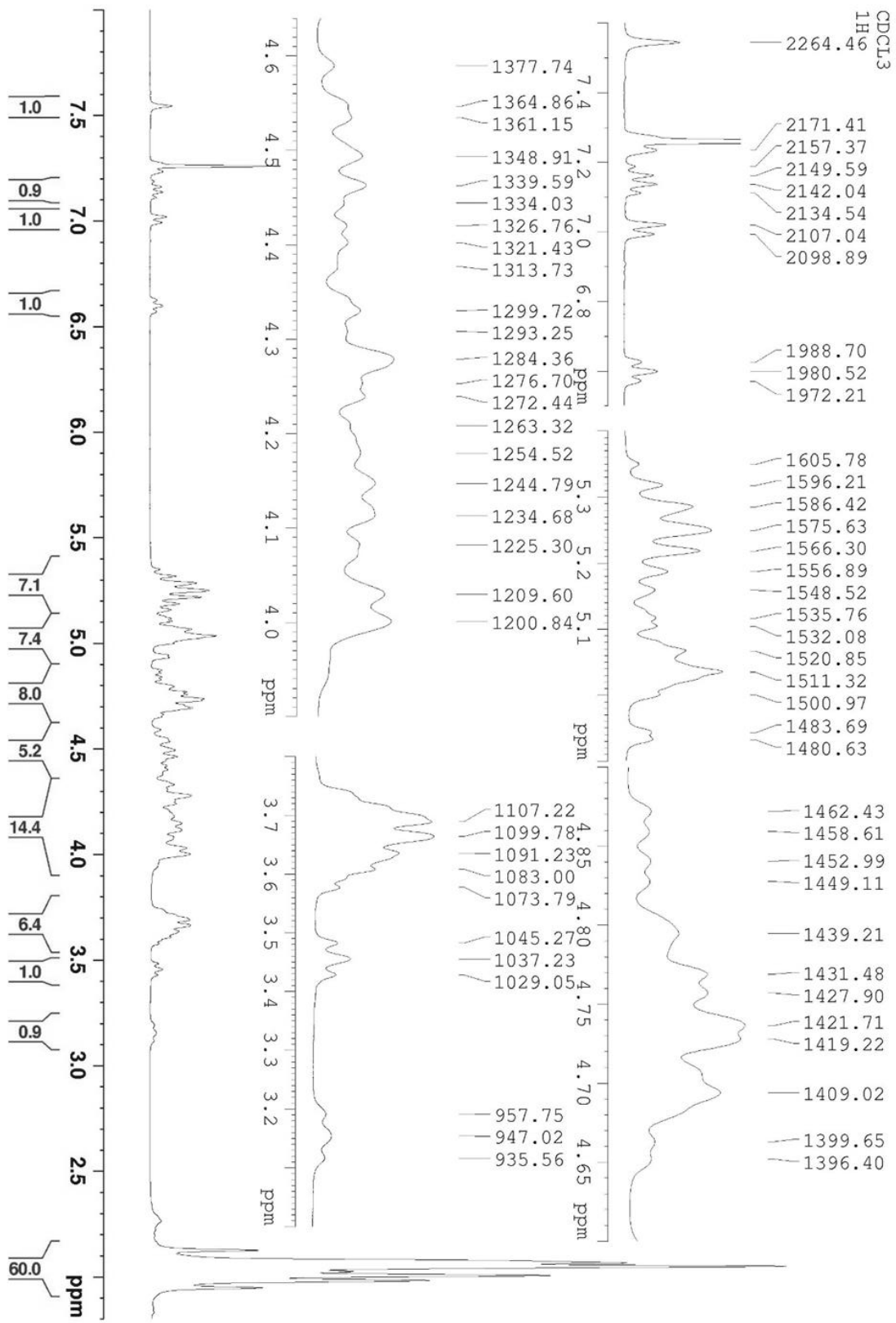
MALDI TOF of 7Ai



RMN¹H(CDCl₃) of 7Ai

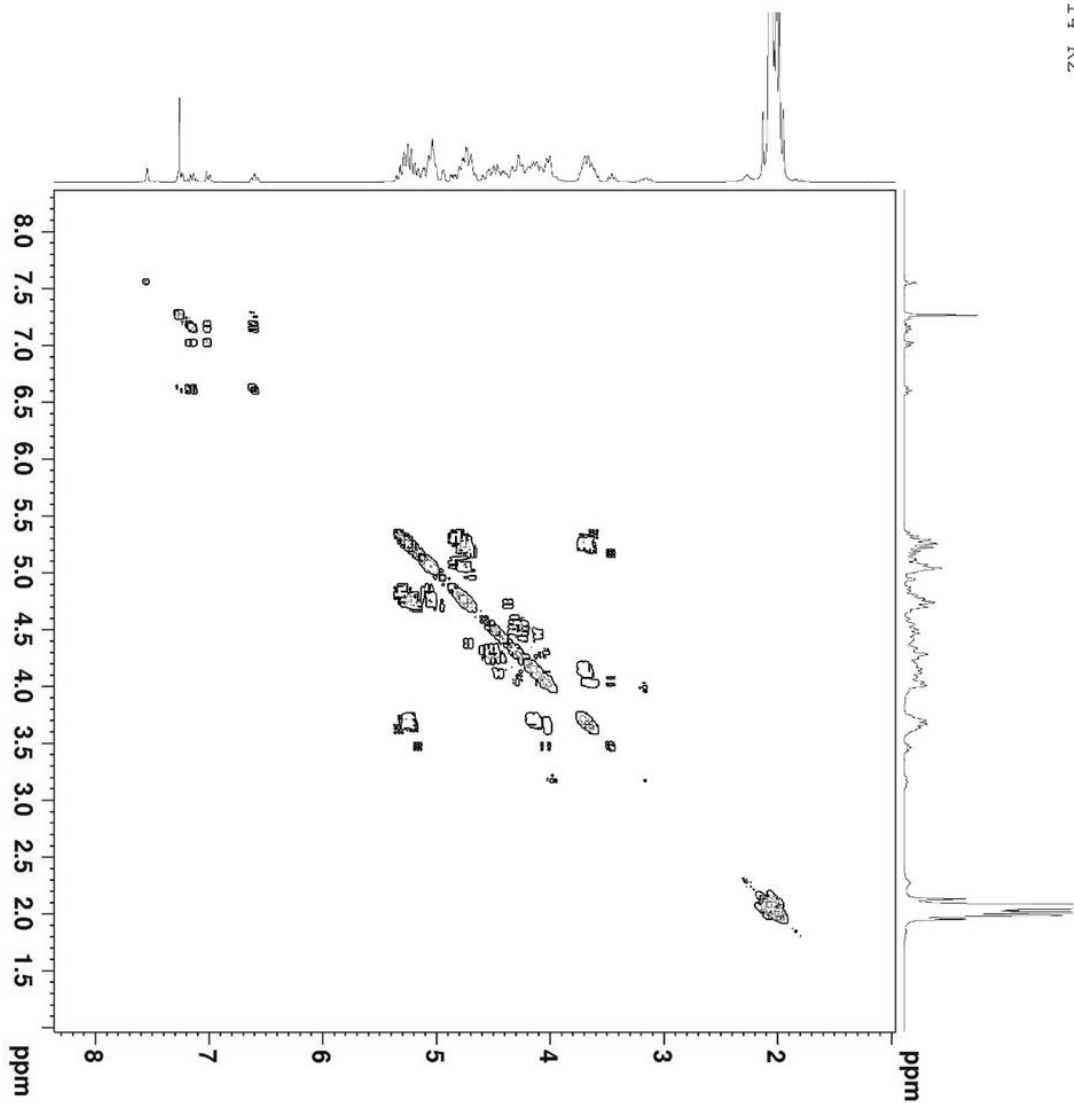


ML I 44 B2 t14 R2
 CDCL3
 1H

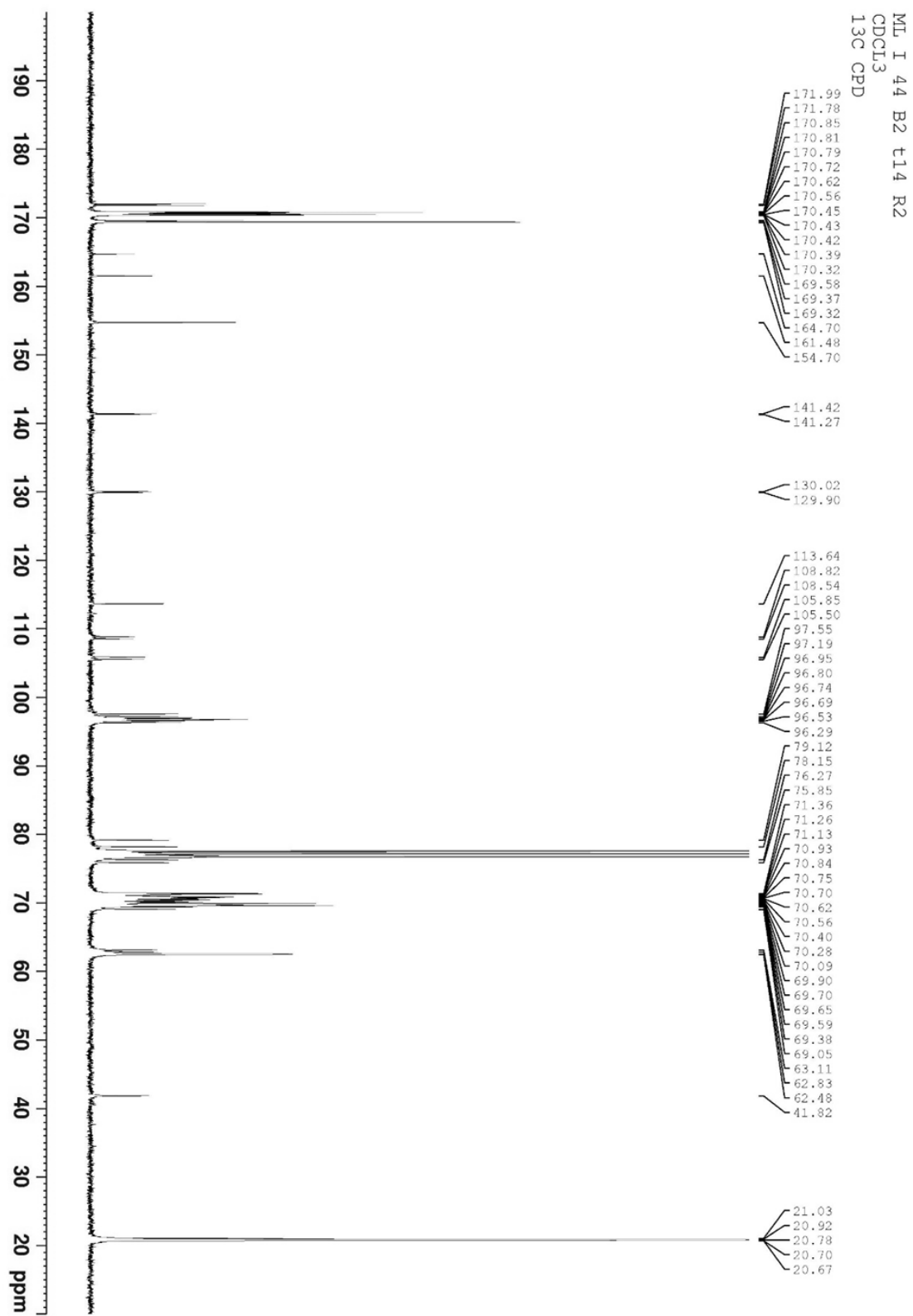


COSY (CDCl₃) of 7Ai

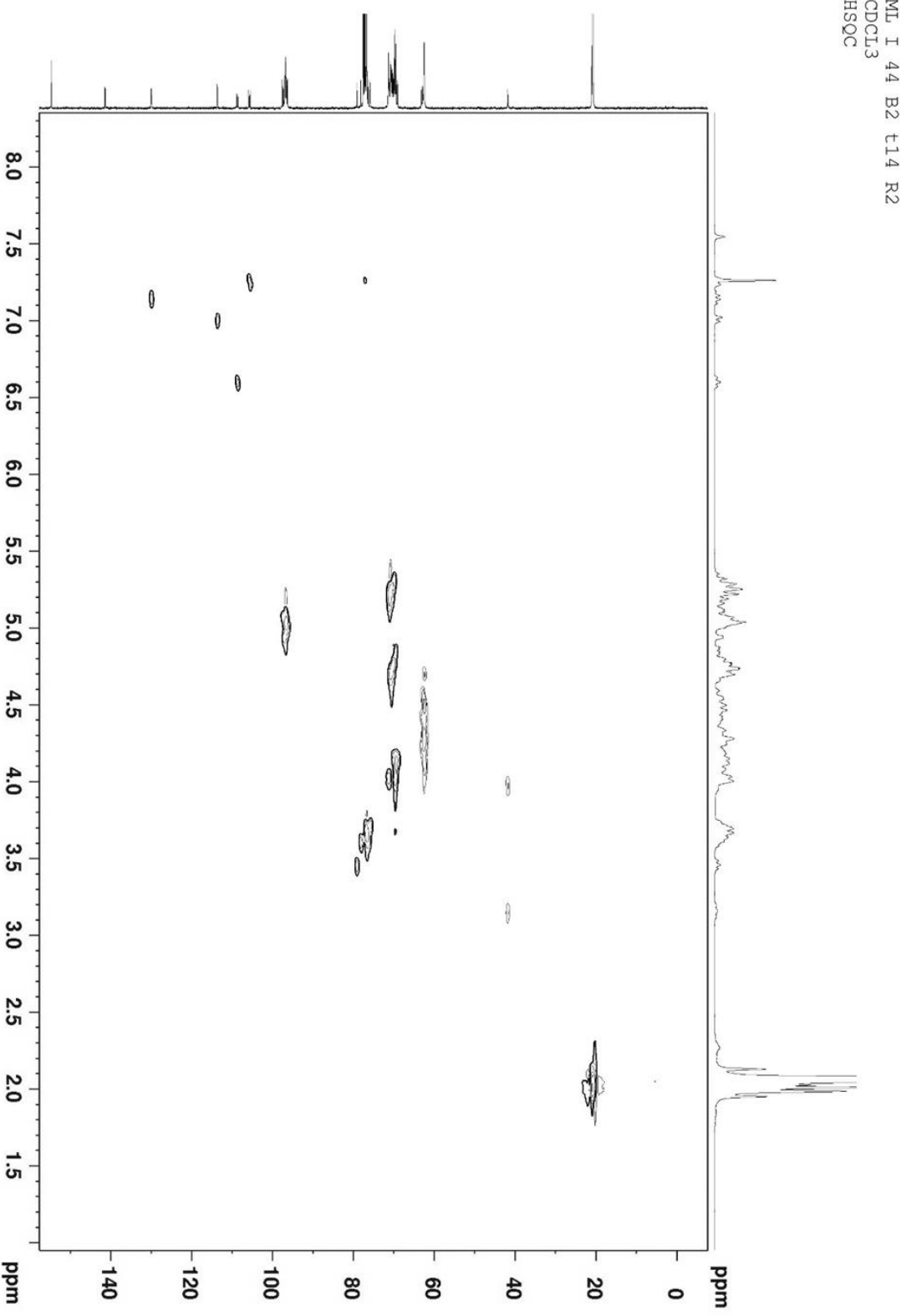
ML I 44 B2 t14 R2
CDCl₃
COSY45



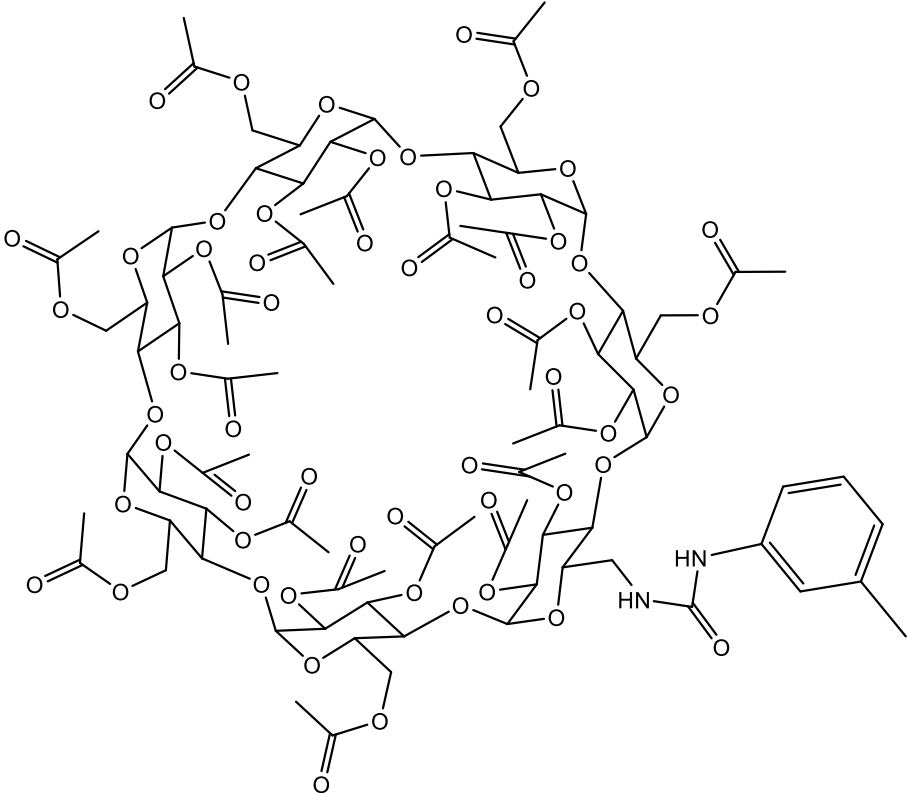
RMN¹³C(CDCl₃) of 7Ai



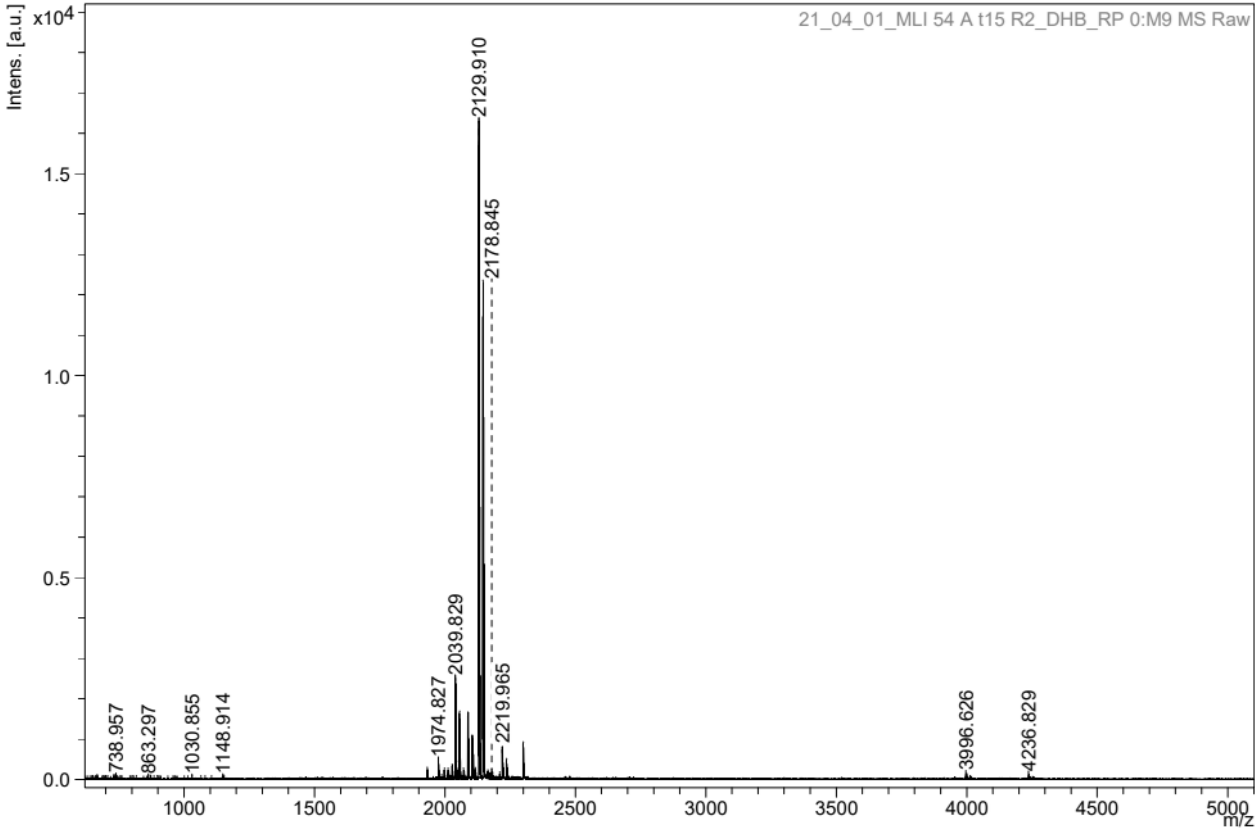
HSQC(CDCl₃) of 7Ai

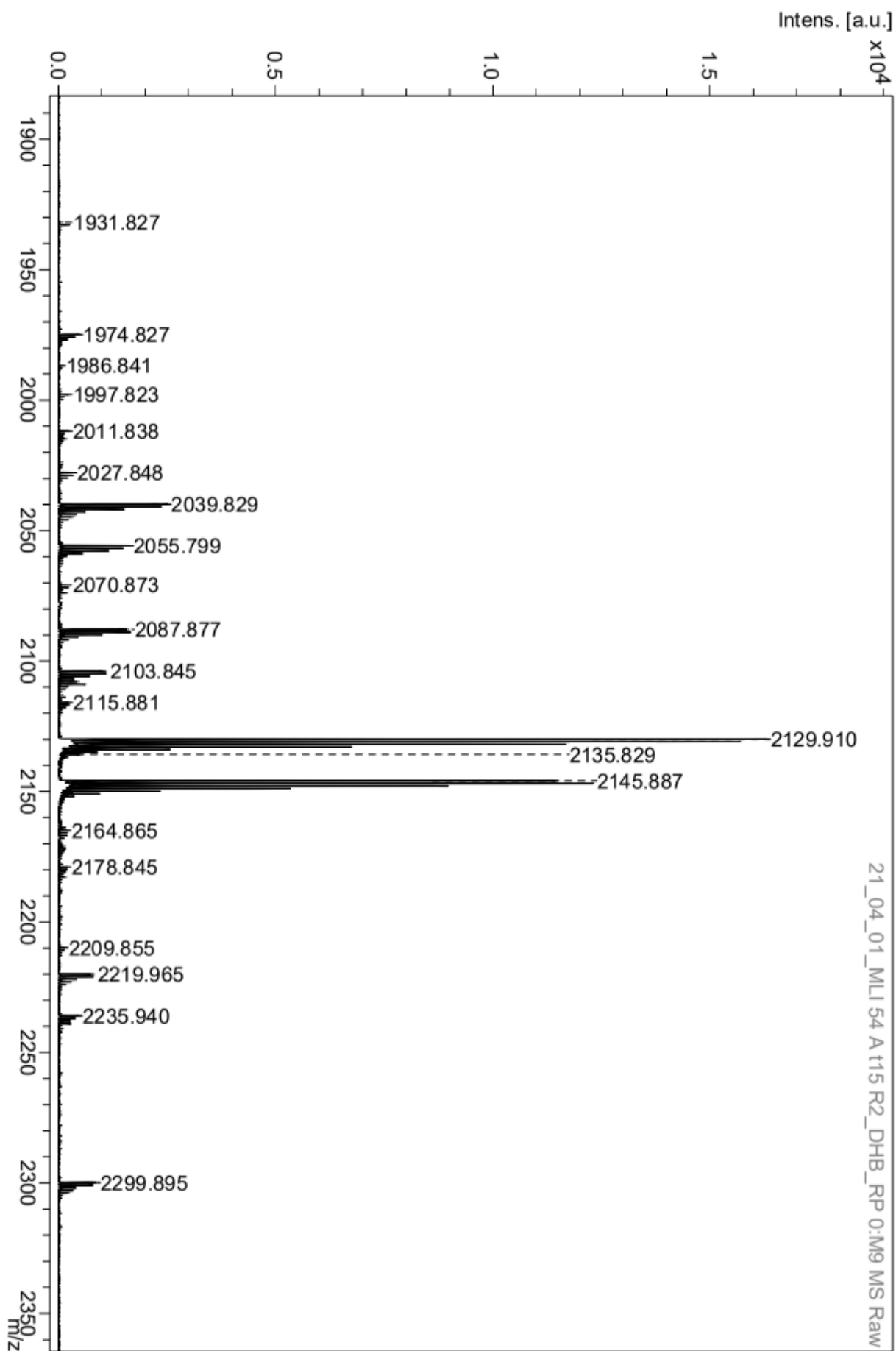


Characterisation of 7Aj (C₉₀H₁₁₈N₂O₅₅)



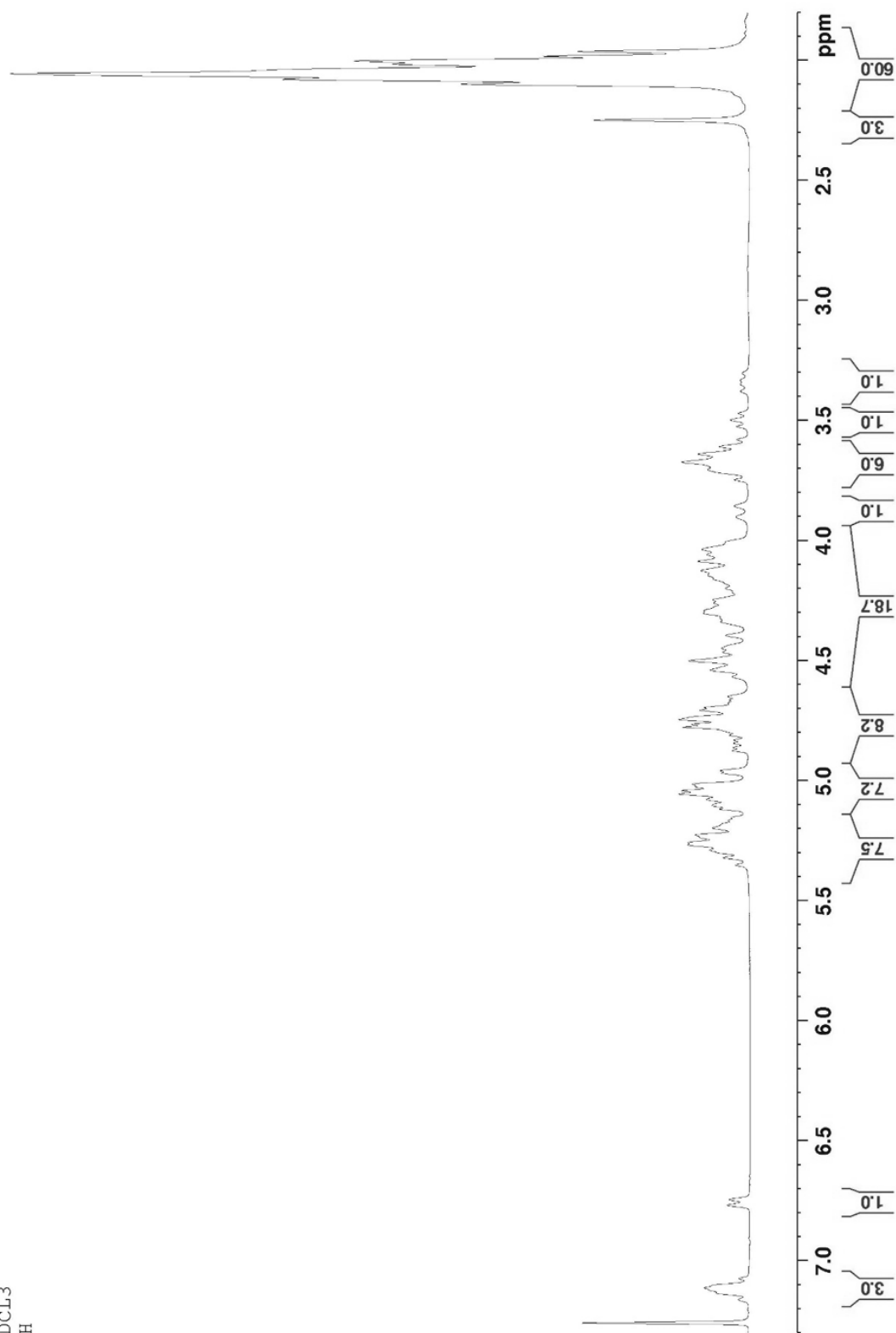
MALDI TOF of 7Aj





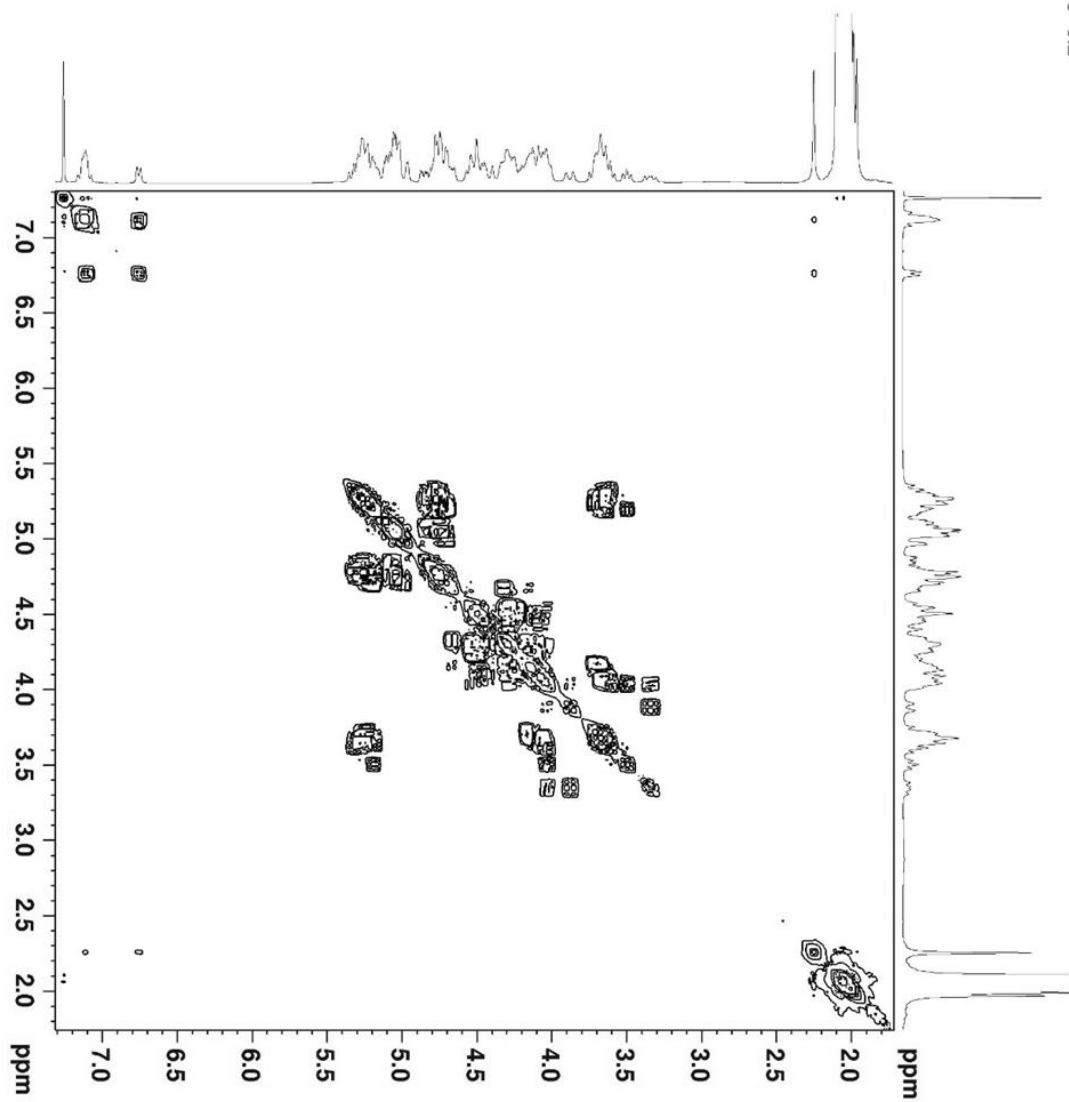
RMN¹H(CDCl₃) of 7Aj

ML I 54 A2 t15 R2
CDCl₃
1H

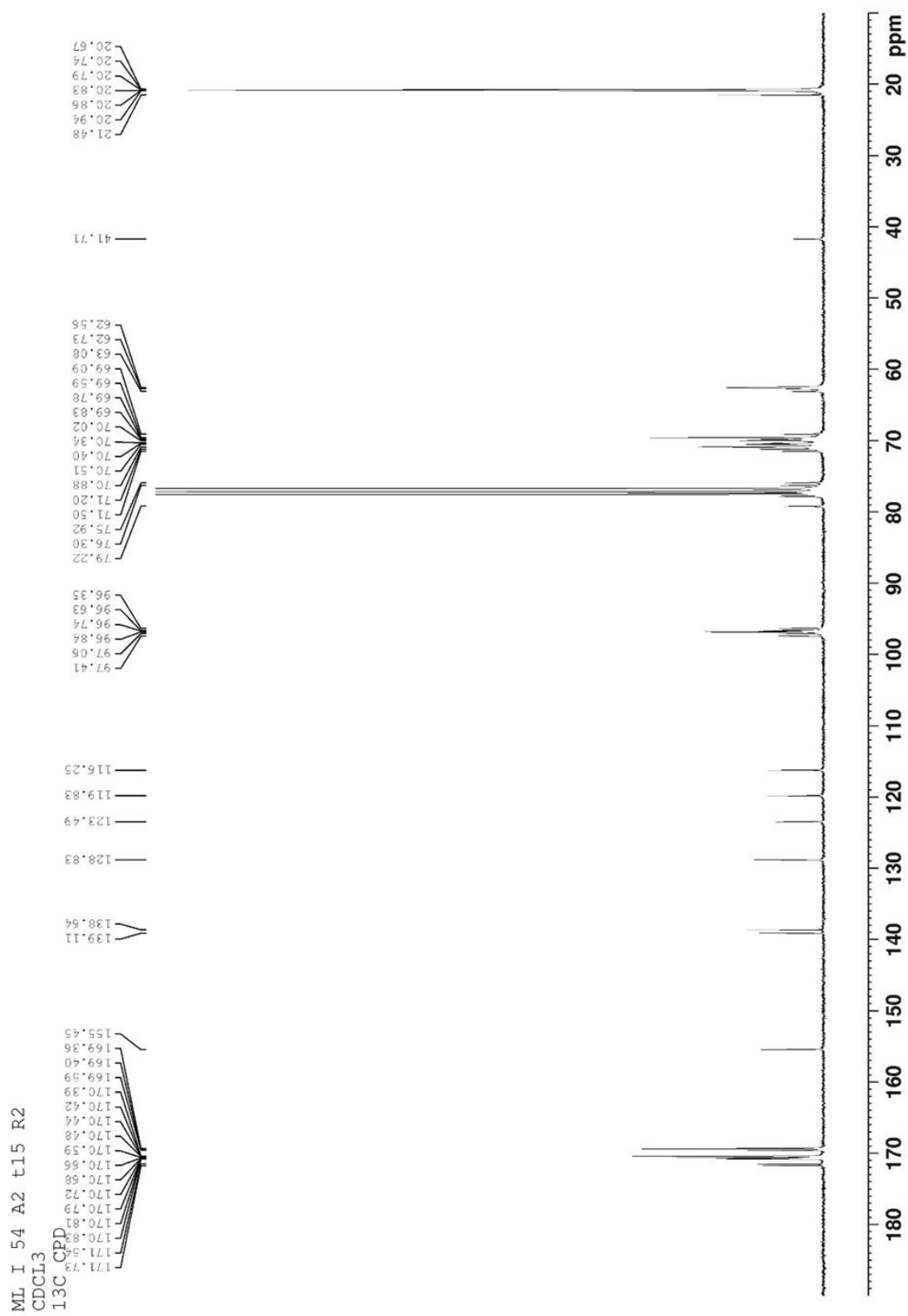


COSY (CDCl₃) of 7Aj

ML I 54 A2 f15 R2
CDCl₃
COSY45

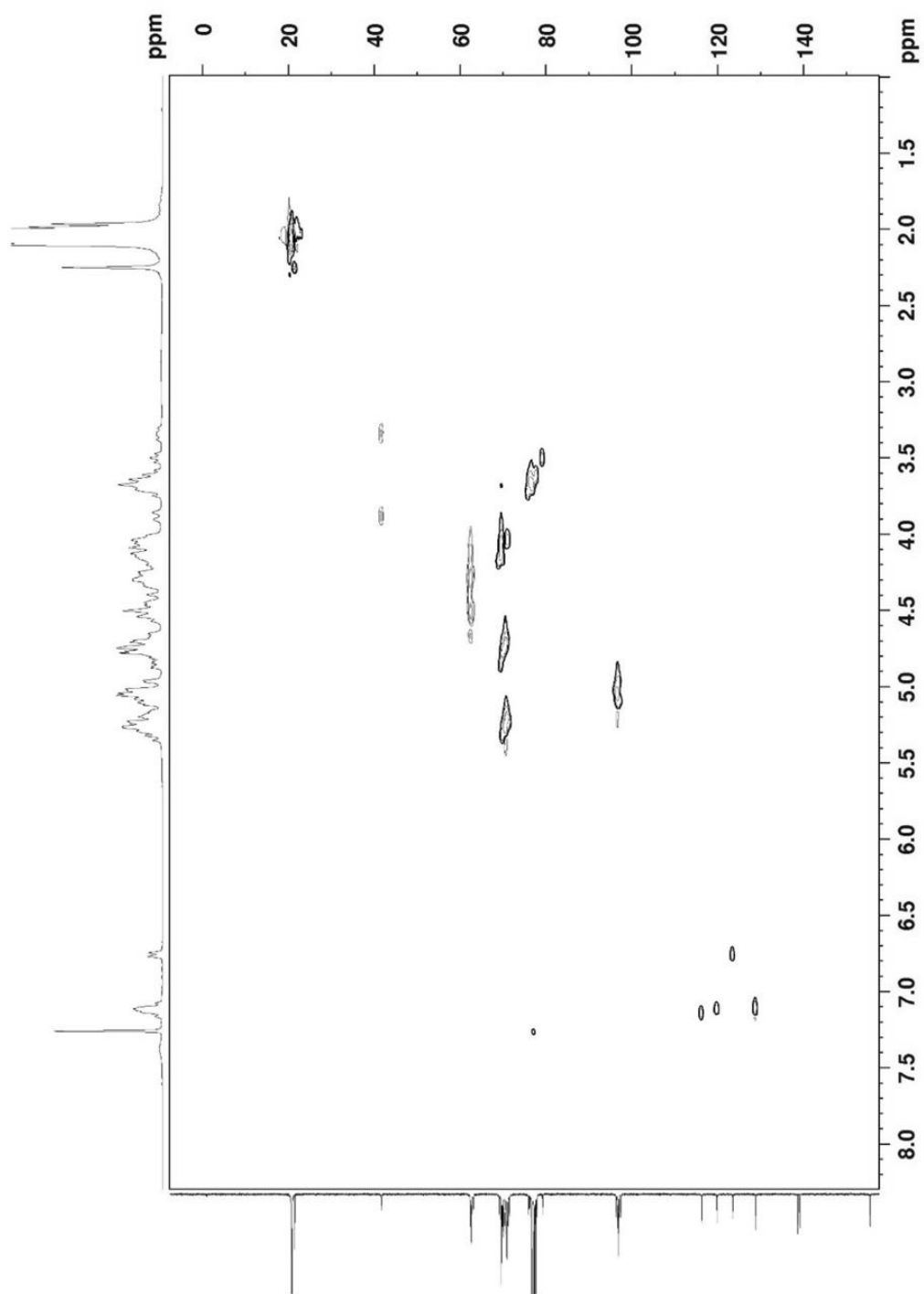


RMN¹³C(CDCl₃) of 7Aj

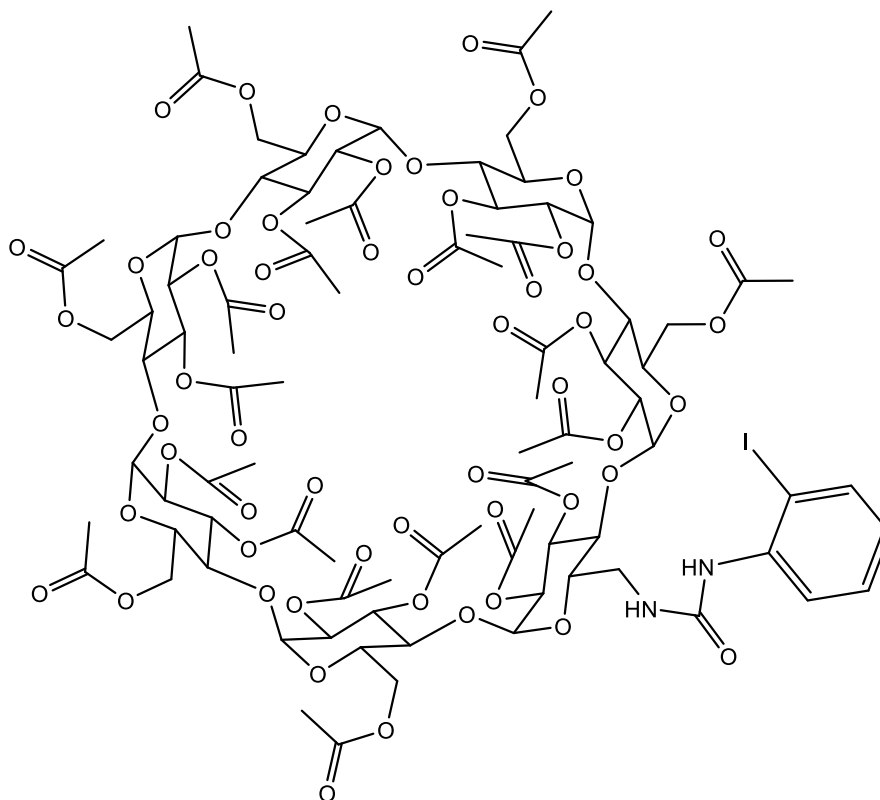


HSQC(CDCl₃) of 7Aj

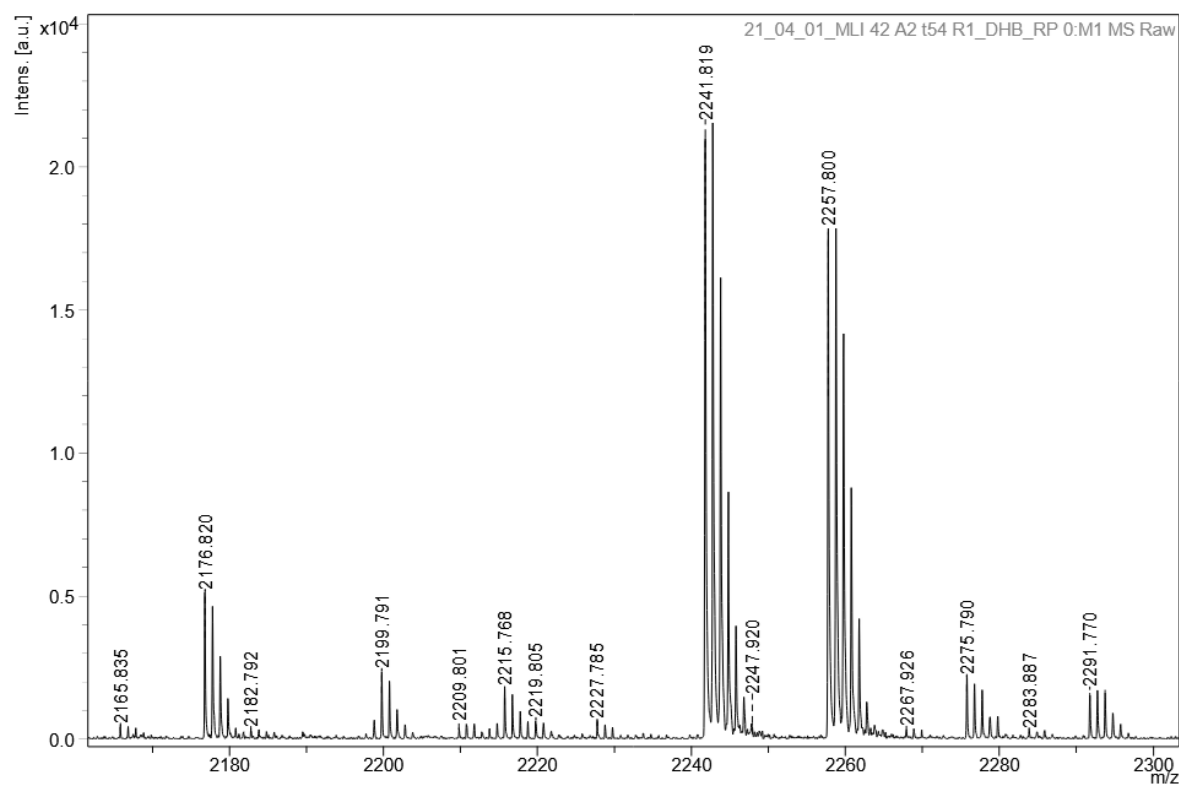
ML I 54 A2 t15 R2
CDCL₃
HSQC



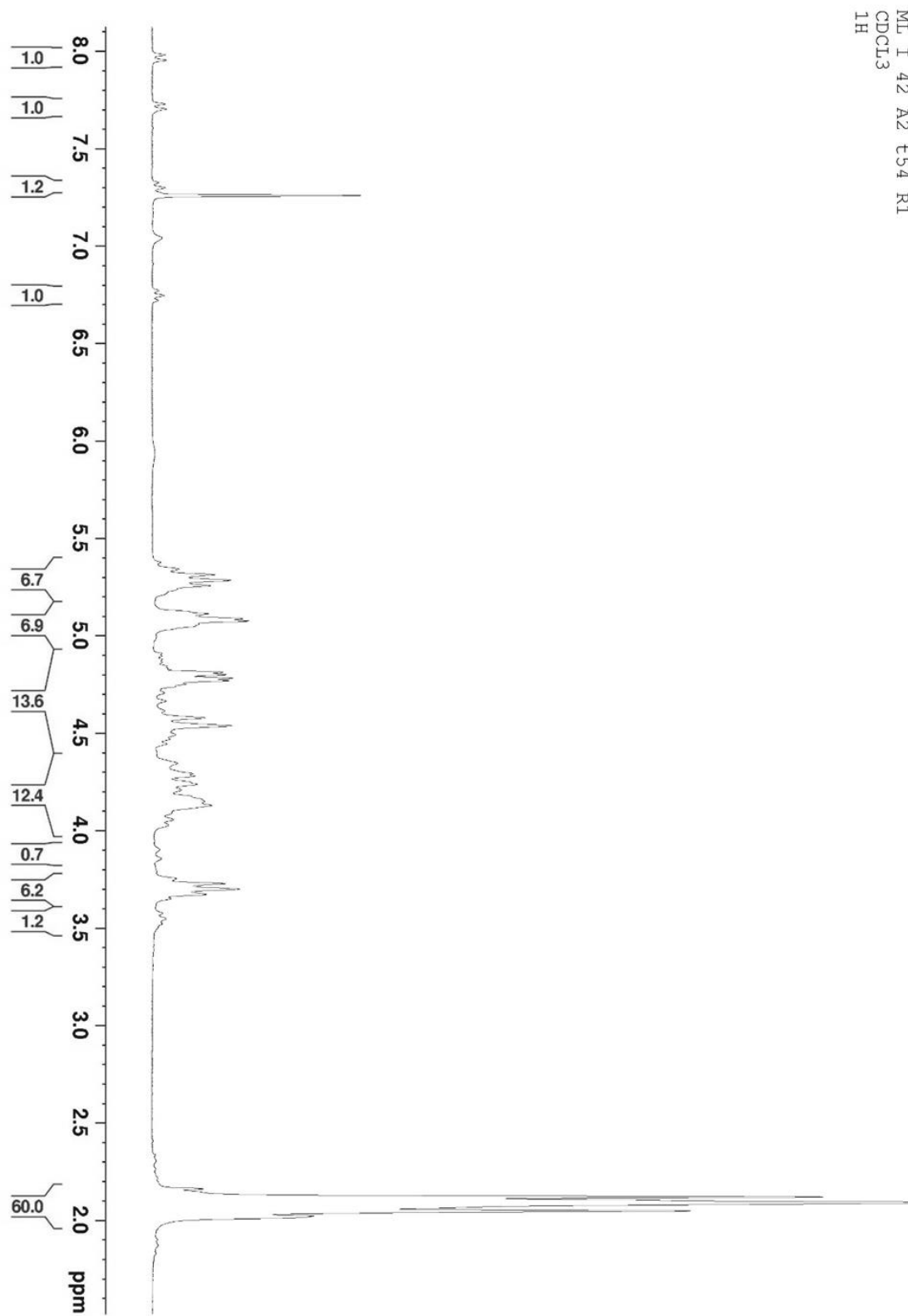
Characterisation of 7Ak (C₈₉H₁₁₅N₂O₅₅)

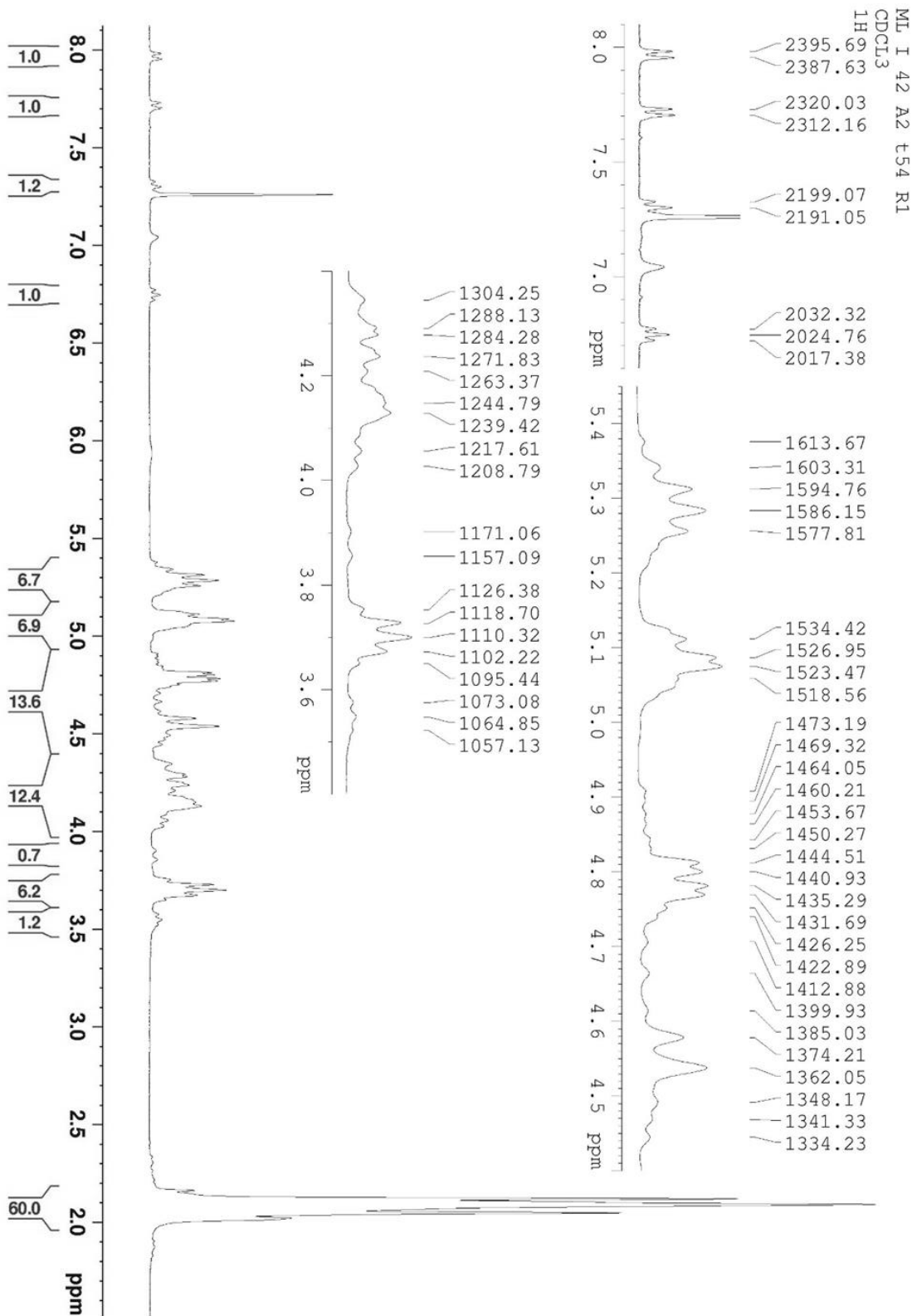


MALDI TOF of 7Ak



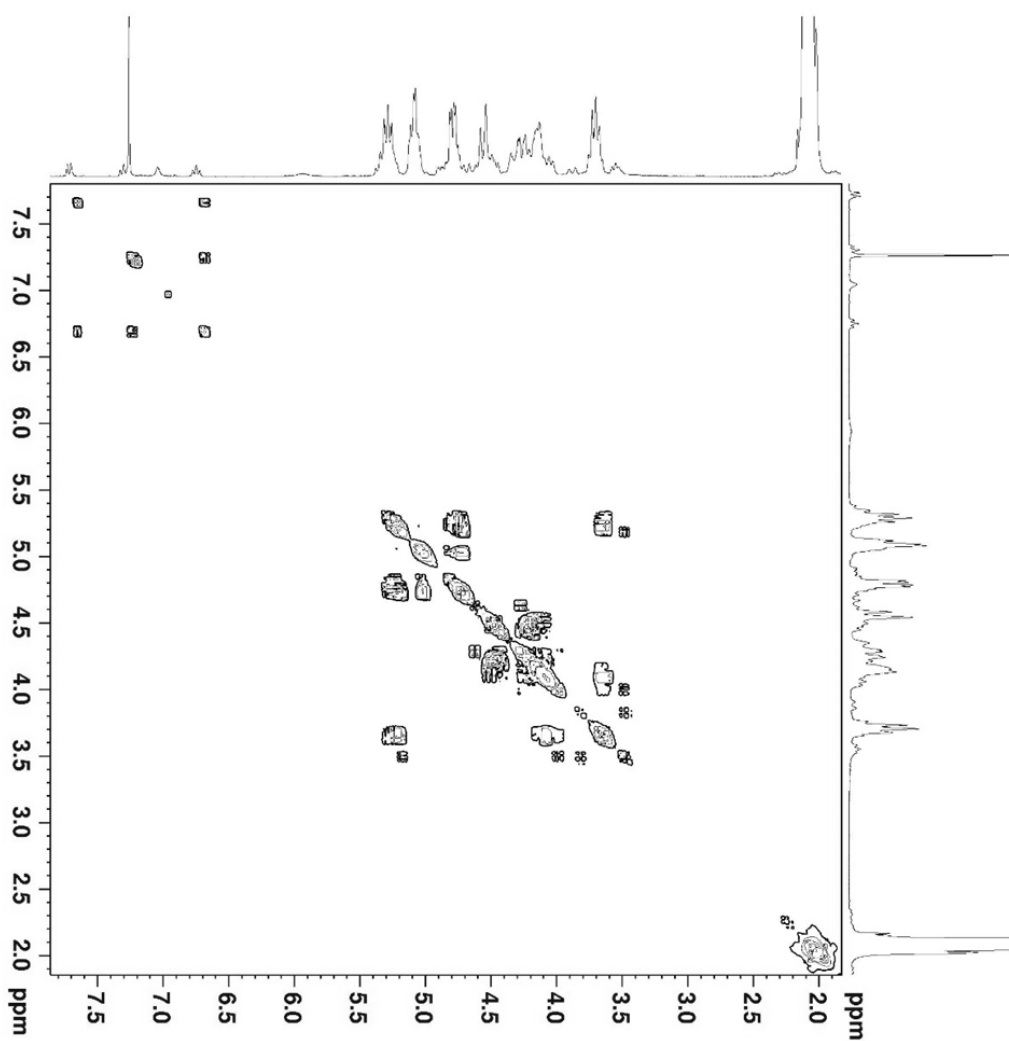
RMN¹H(CDCl₃) of 7Ak



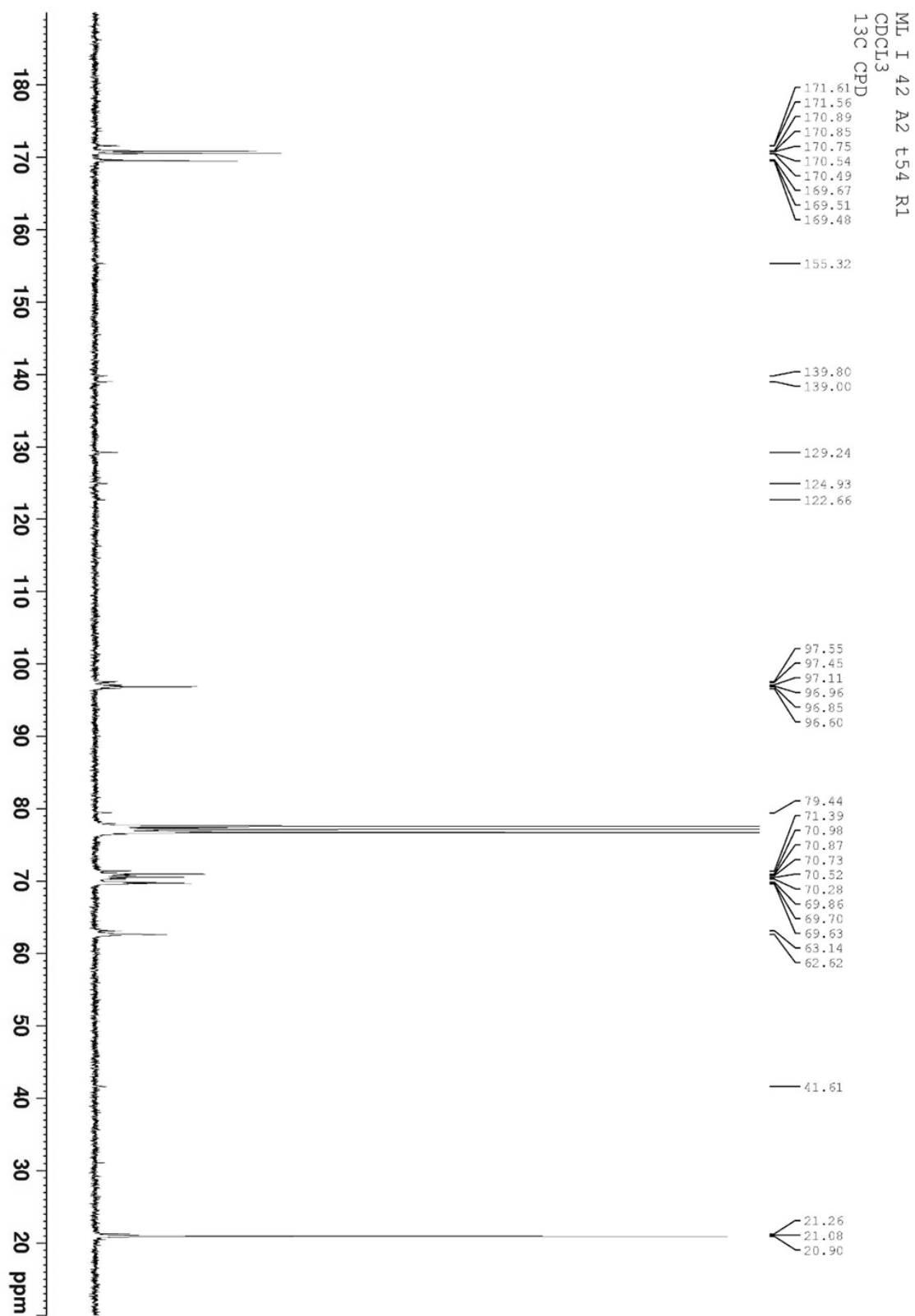


COSY (CDCl₃) of 7Ak

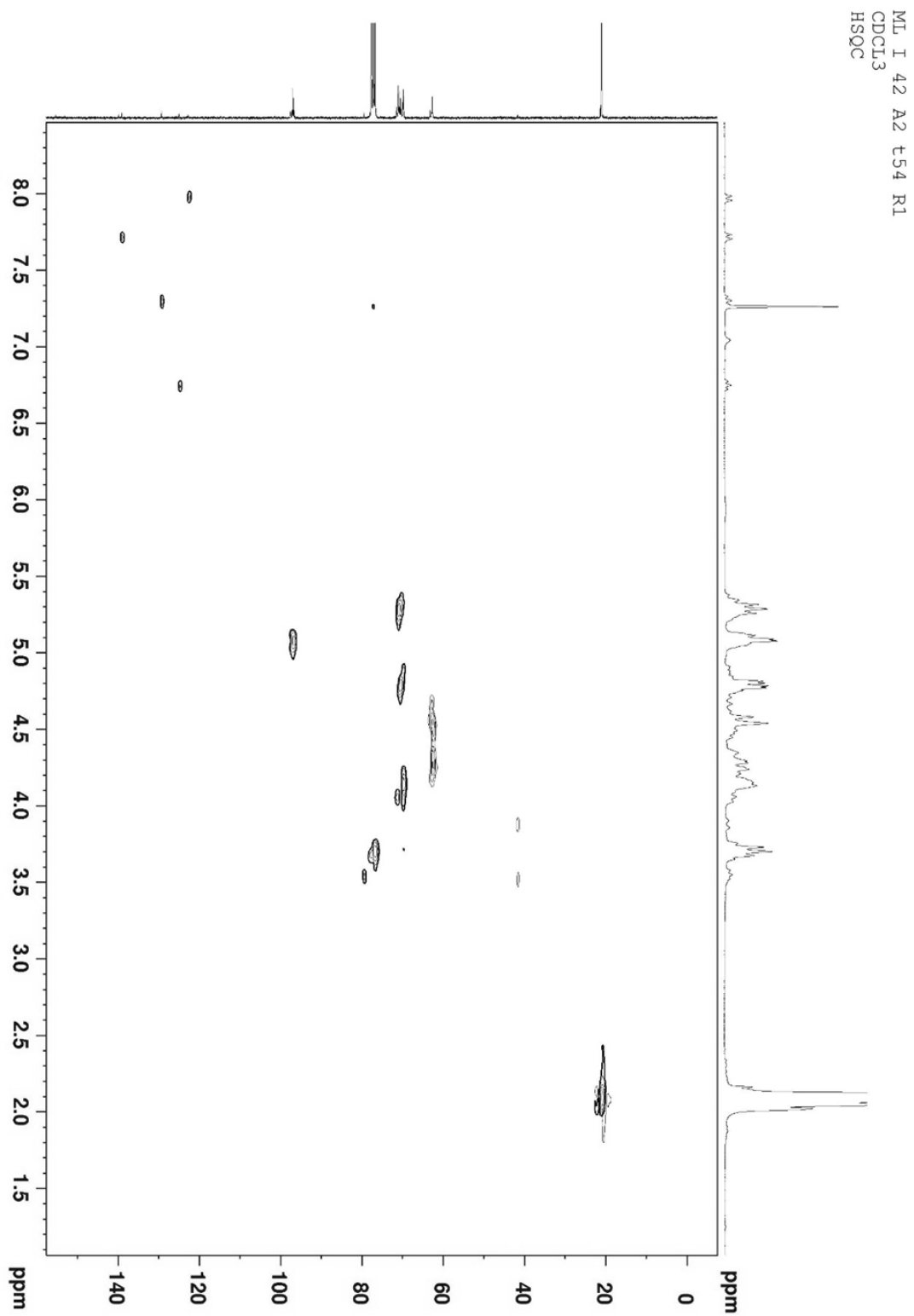
ML I 42 A2 t54 R1
CDCl₃
COSY45



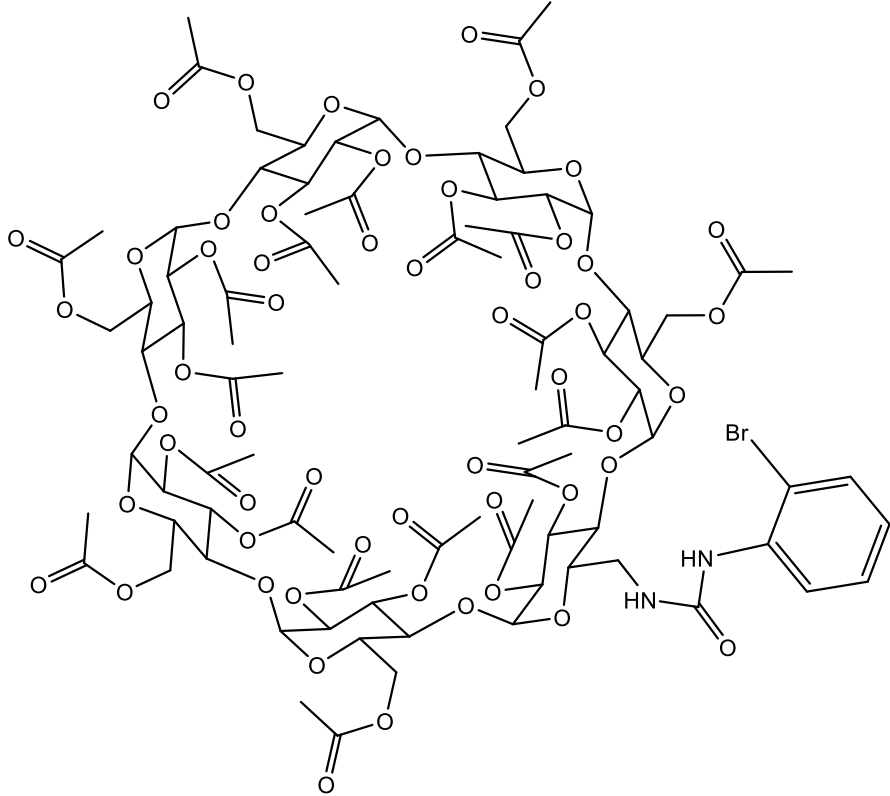
RMN¹³C(CDCl₃) of 7Ak



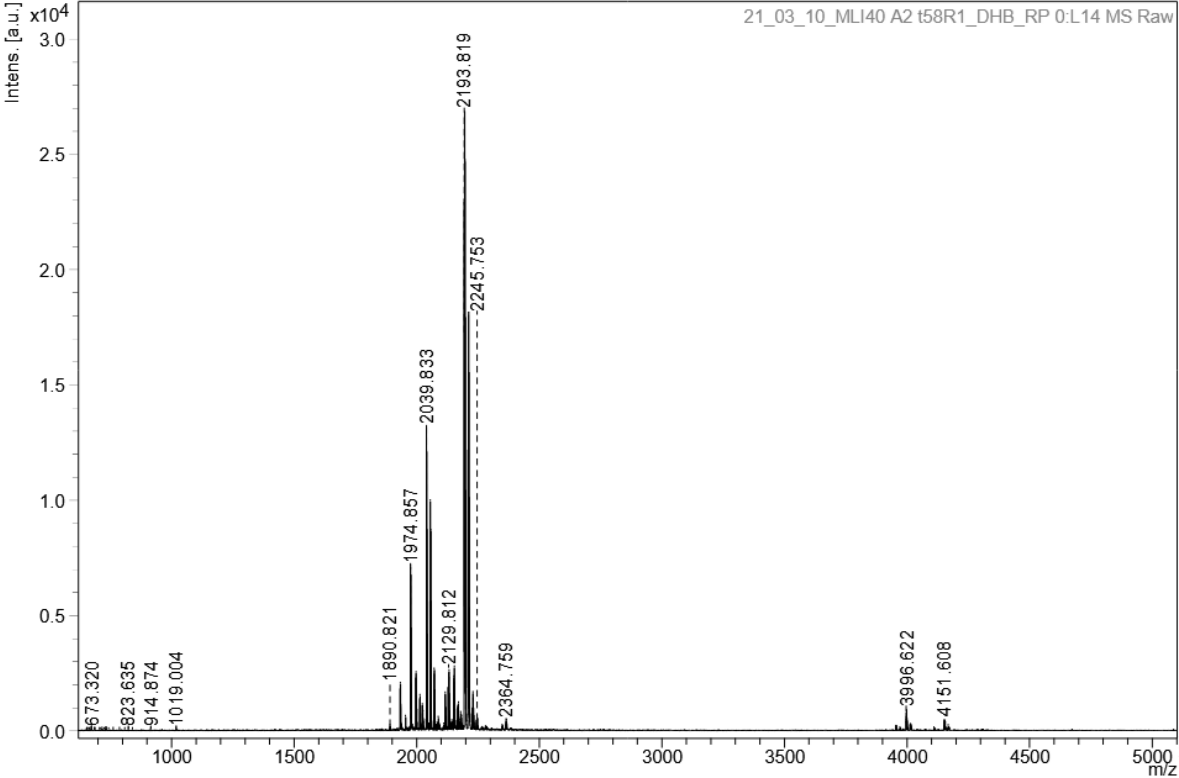
HSQC(CDCl₃) of 7Ak



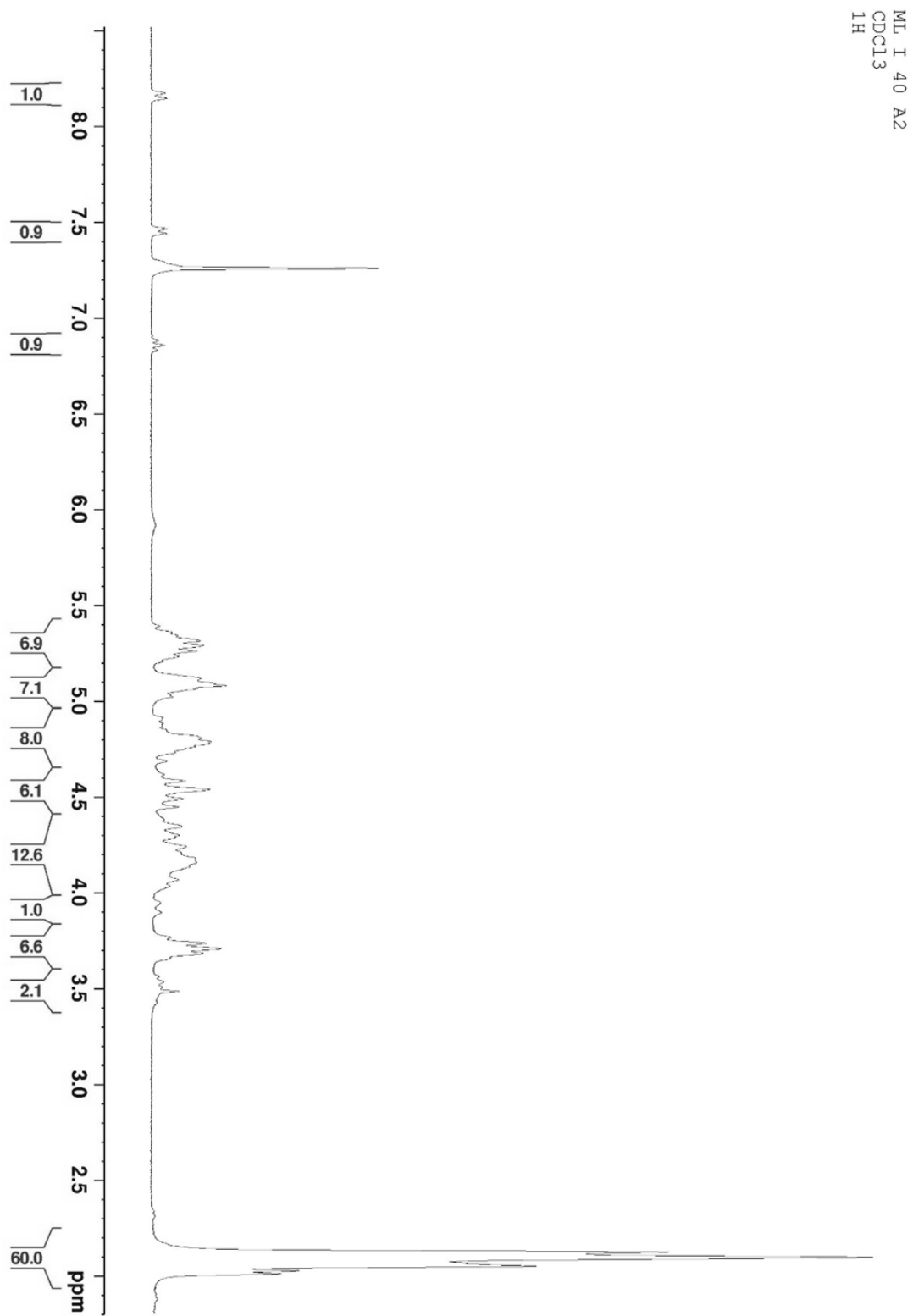
Characterisation of 7AI (C₈₉H₁₁₅N₂O₅₅Br)

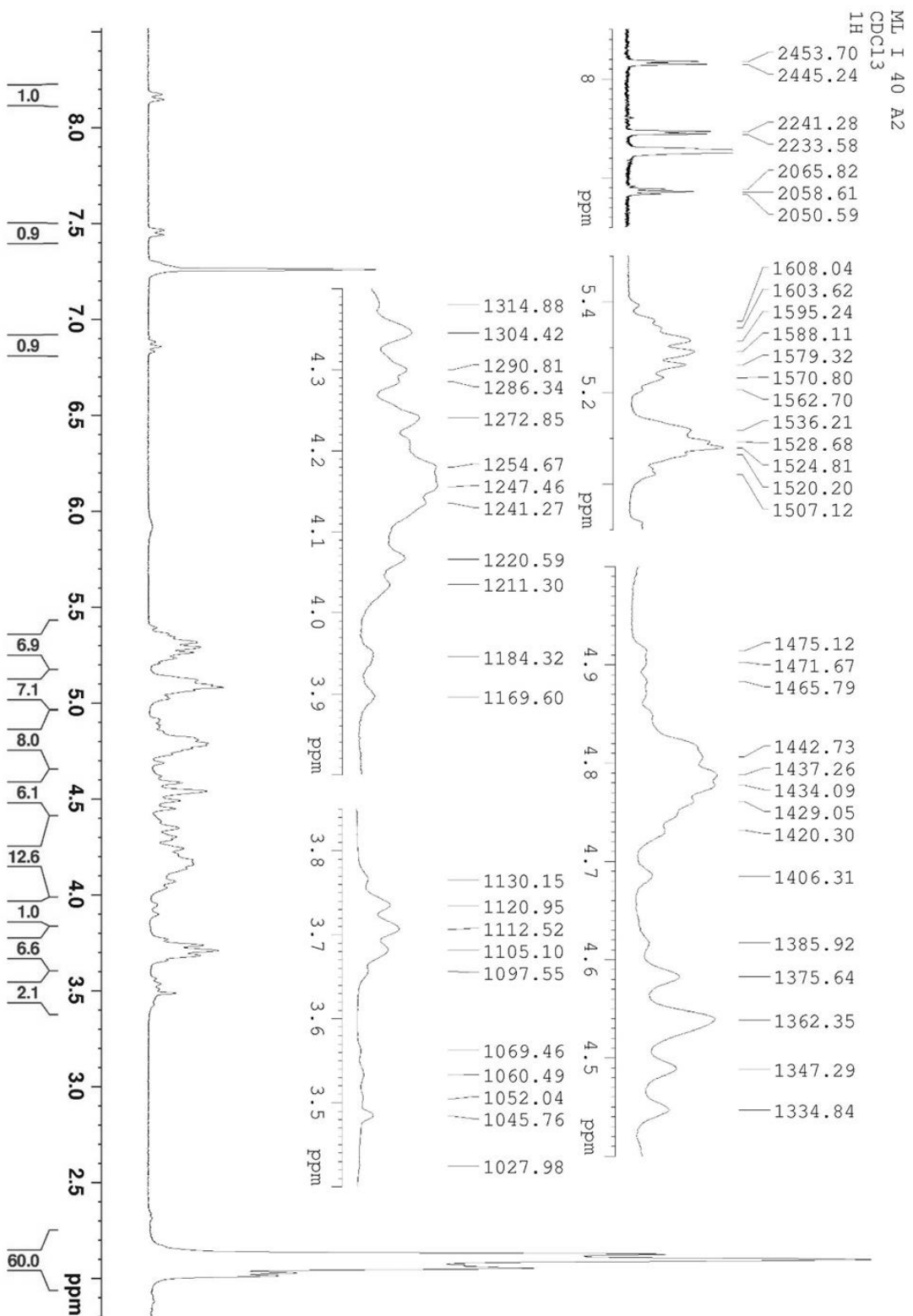


MALDI TOF of 7AI

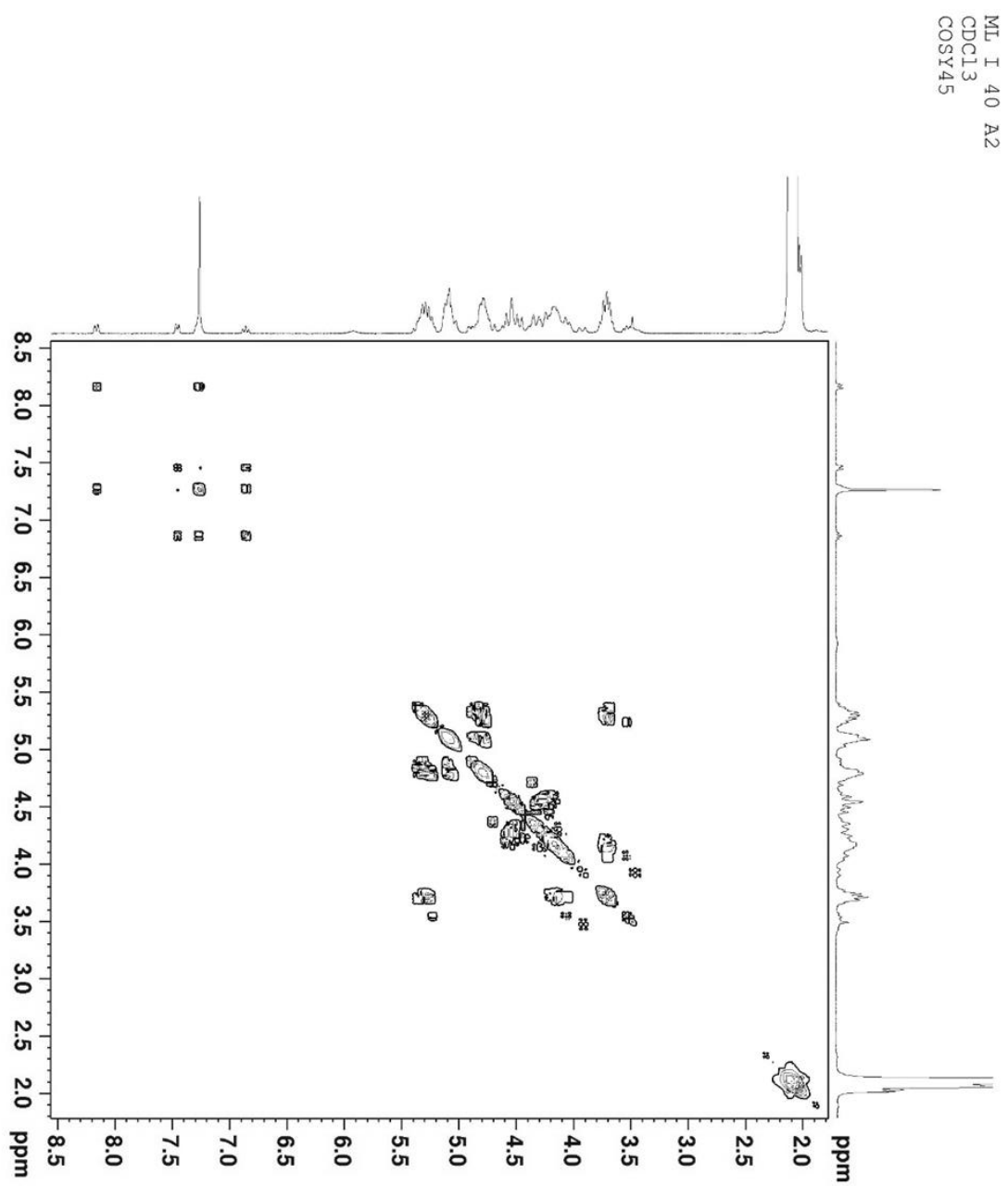


RMN¹H(CDCl₃) of 7AI

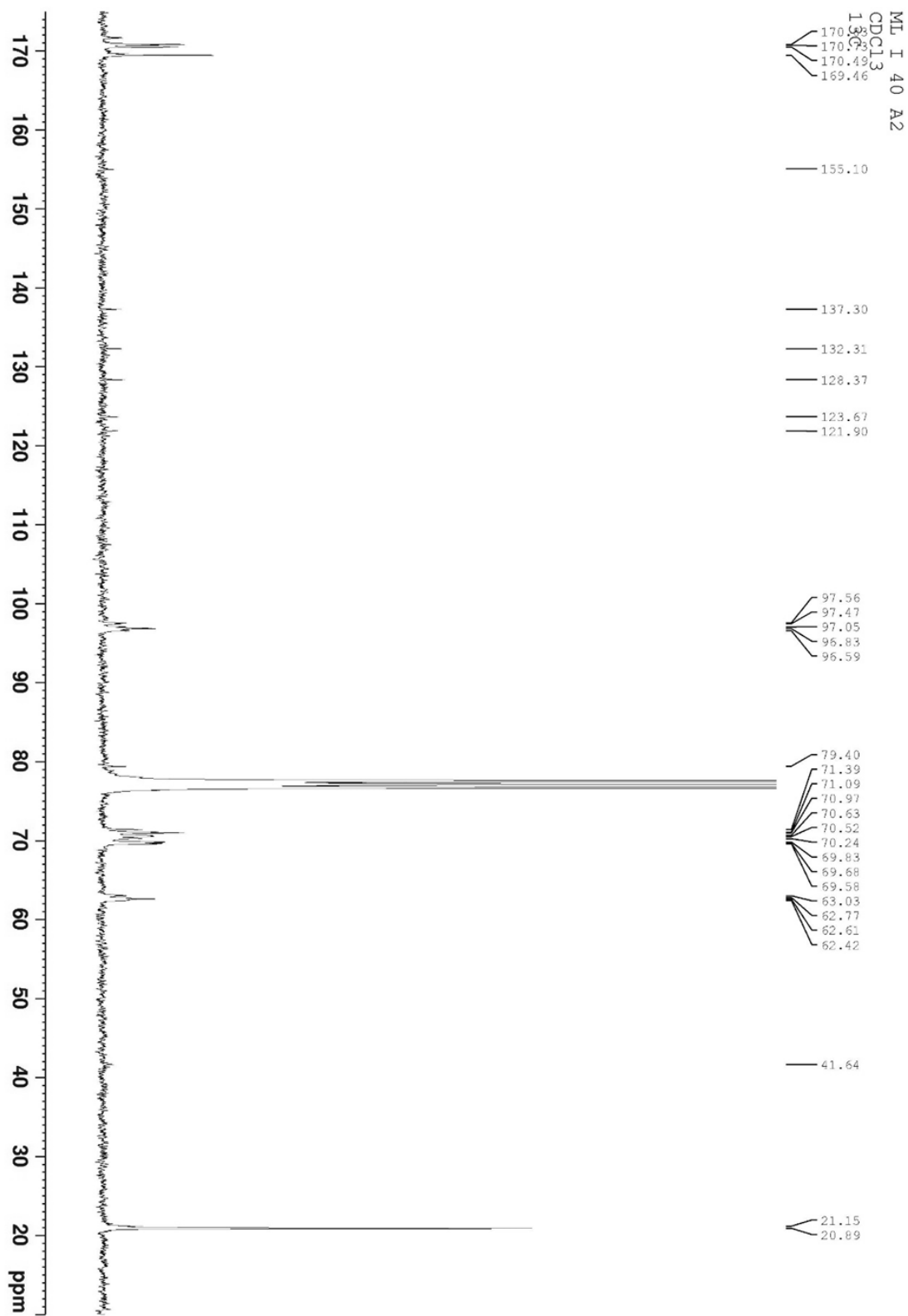




COSY (CDCl₃) of 7AI

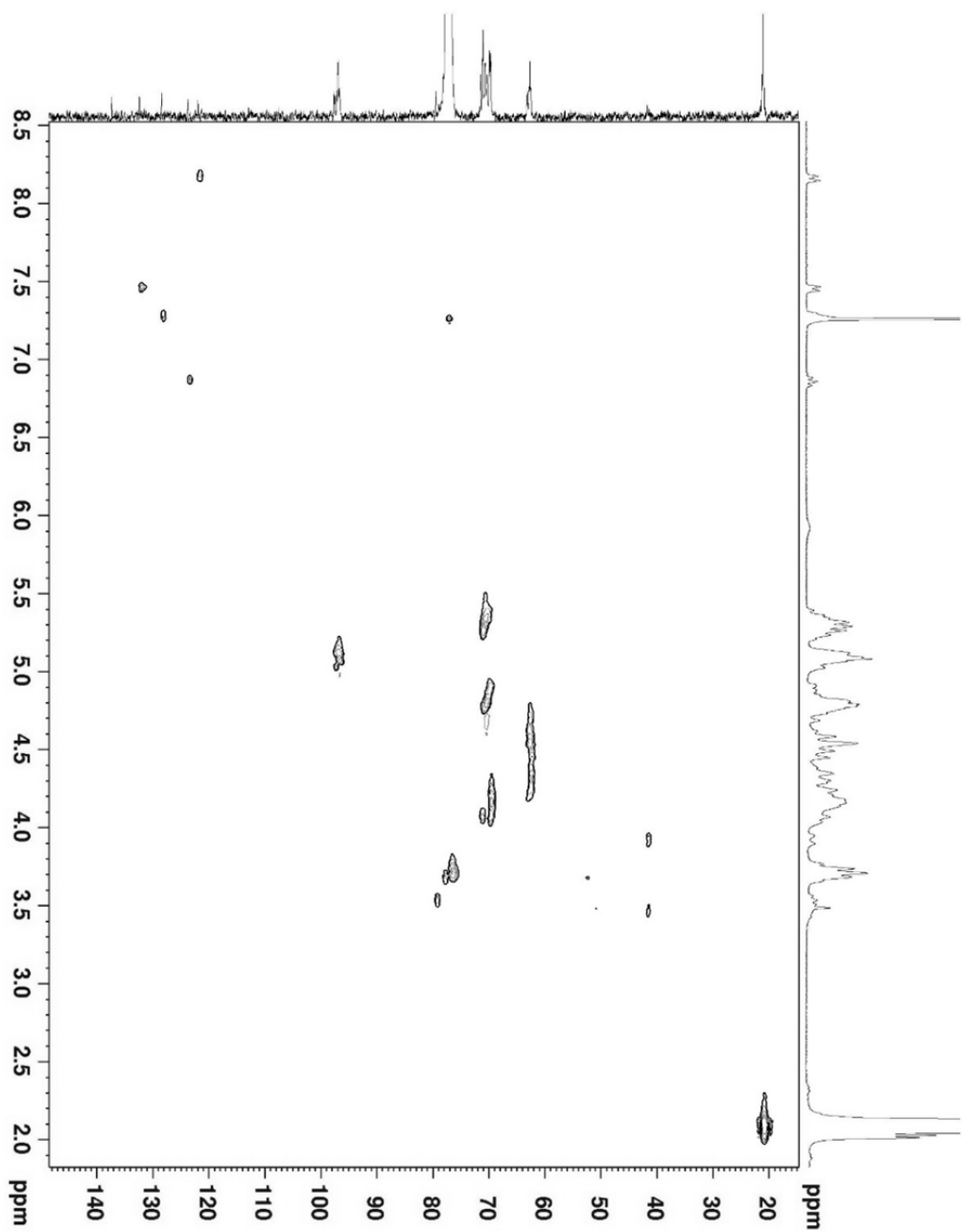


RMN¹³C(CDCl₃) of 7AI

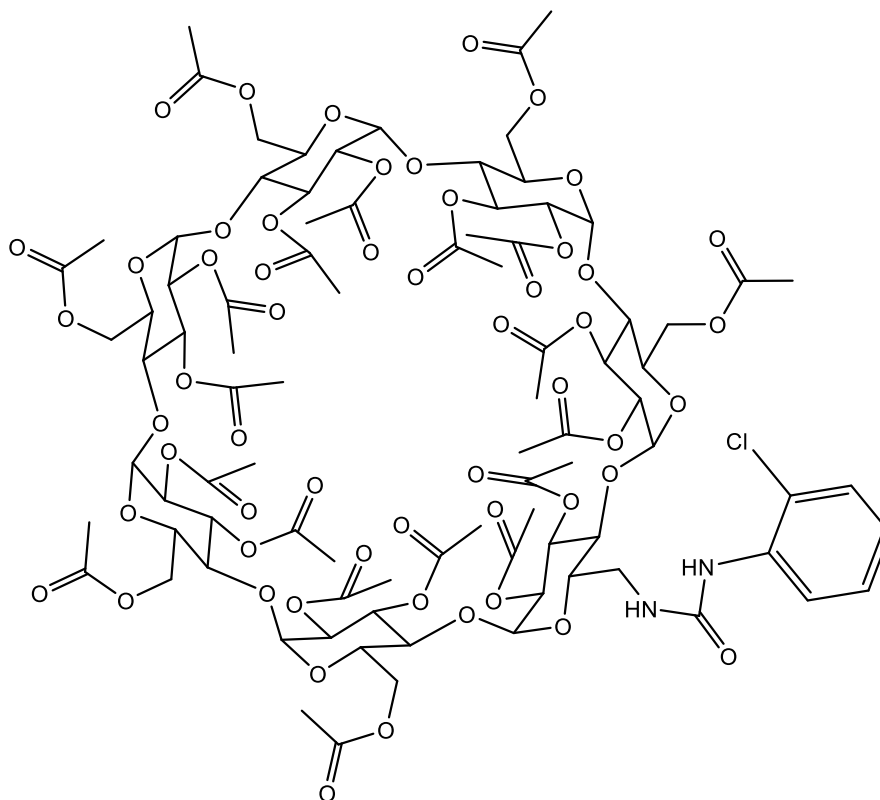


HSQC(CDCl₃) of 7Al

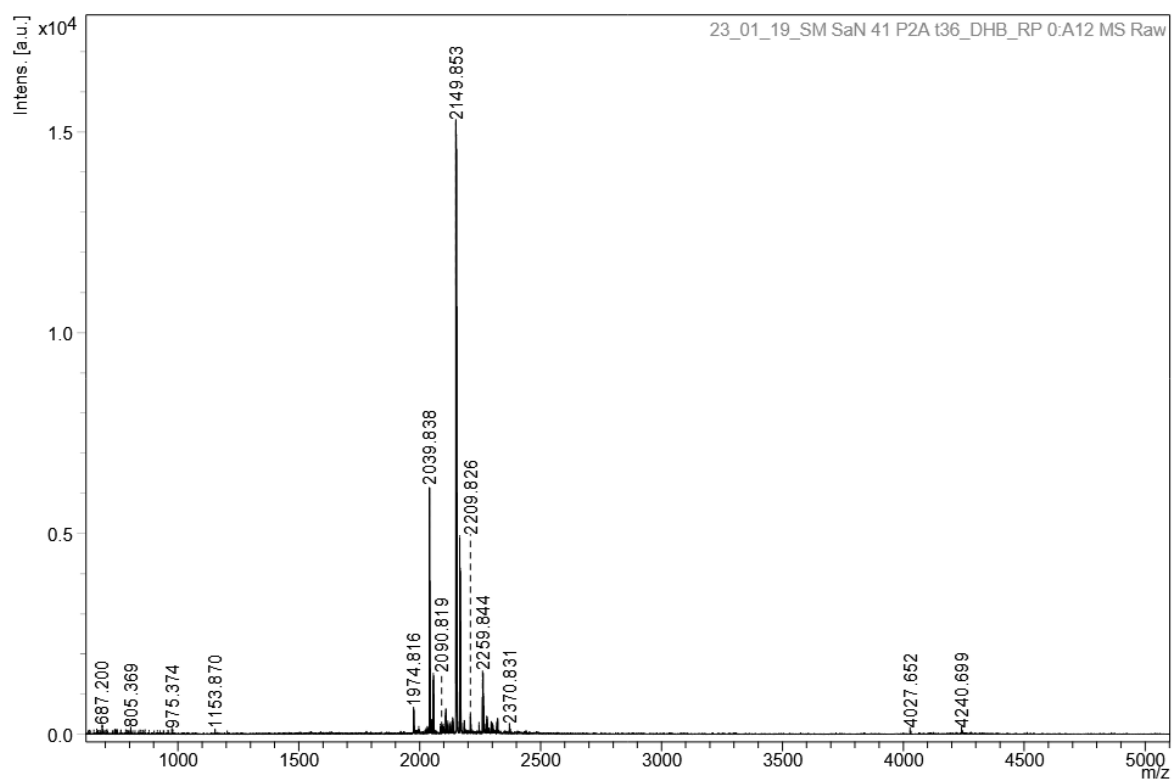
ML I 40 A2
CDCl₃
HSQC



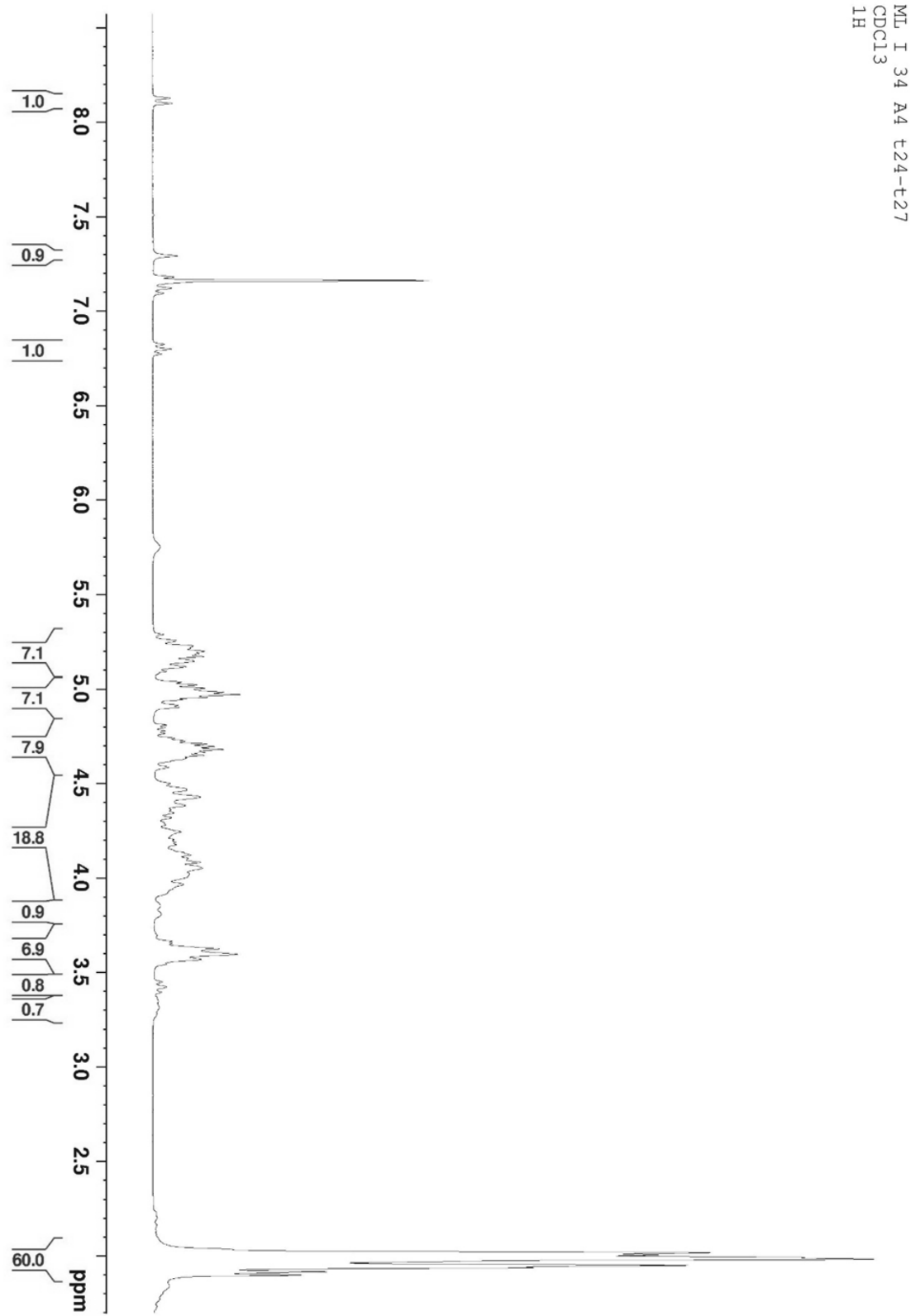
Characterisation of 7Am (C₈₉H₁₁₅N₂O₅₅Cl)

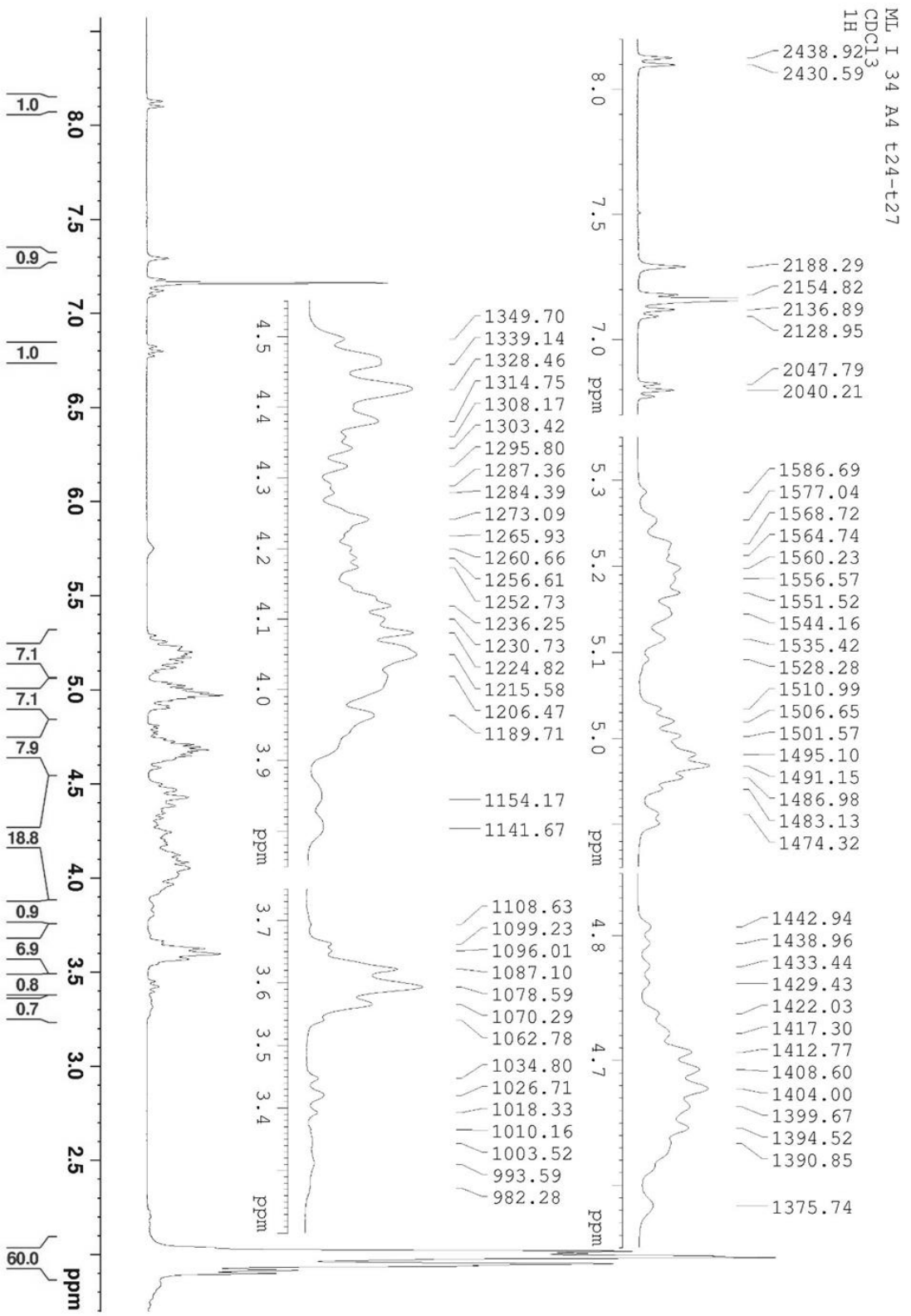


MALDI TOF of 7Am



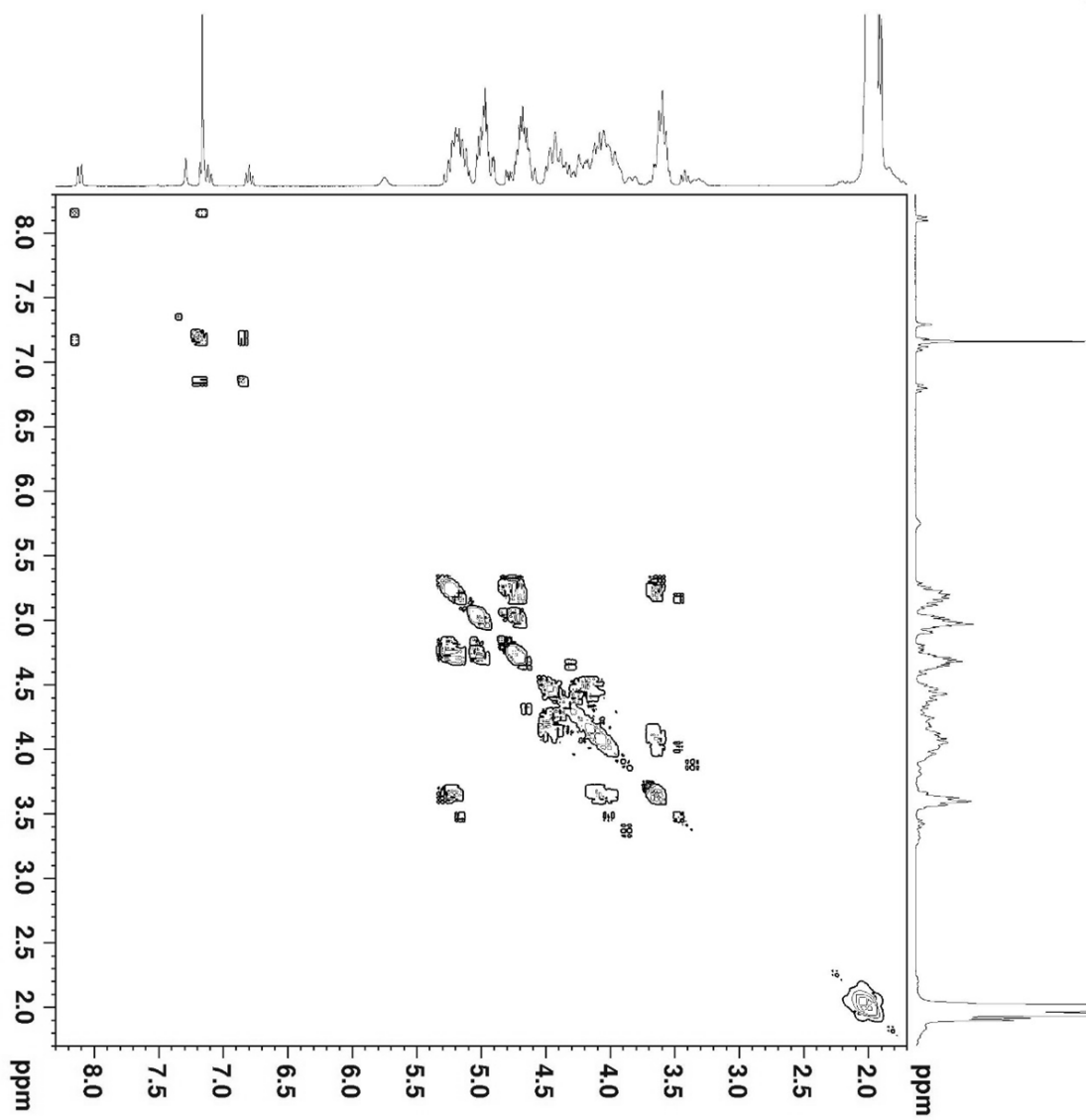
RMN¹H(CDCl₃) of 7Am



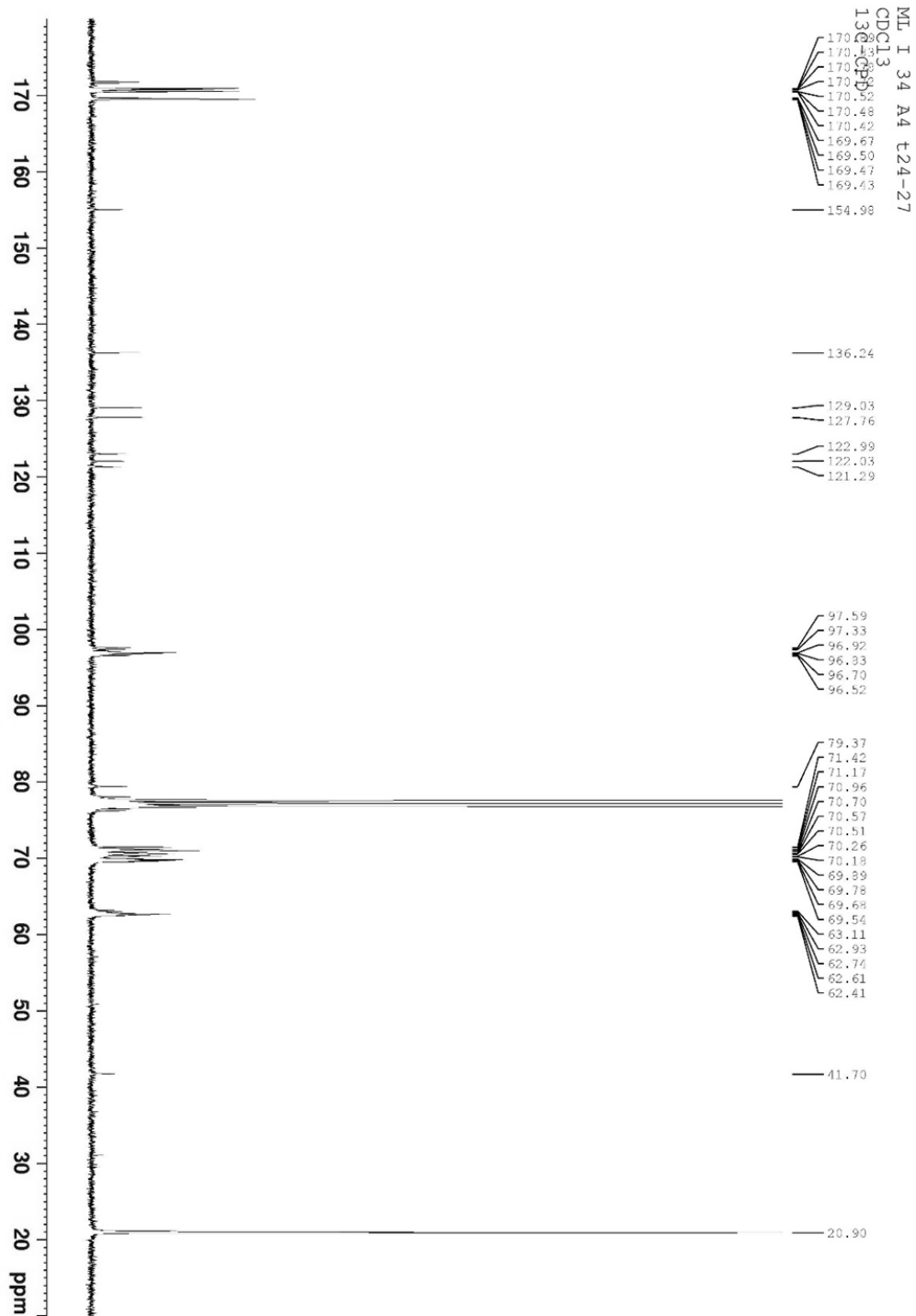


COSY (CDCl₃) of 7Am

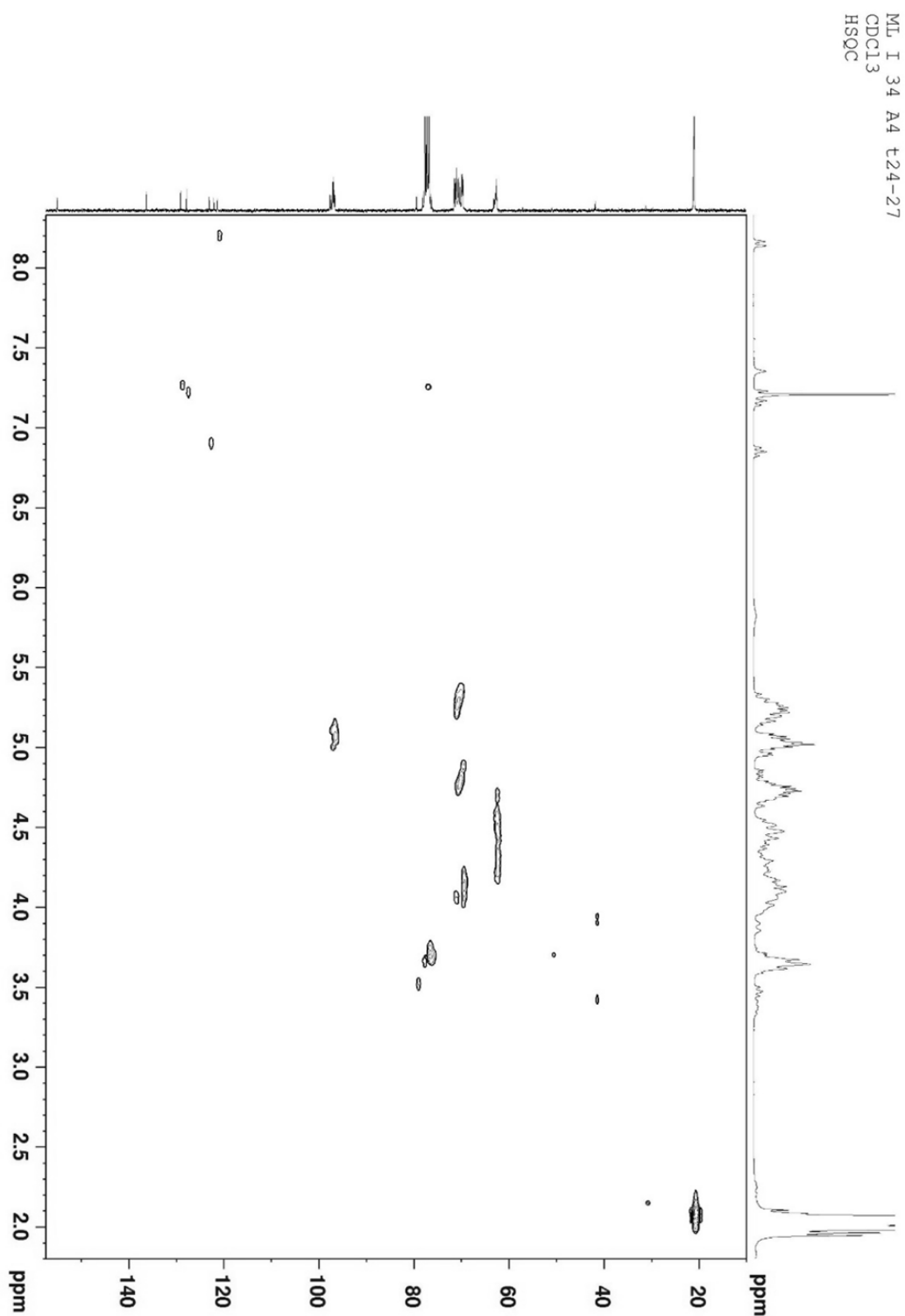
ML I 34 A4 t24-t27
CDCl₃
cosy45



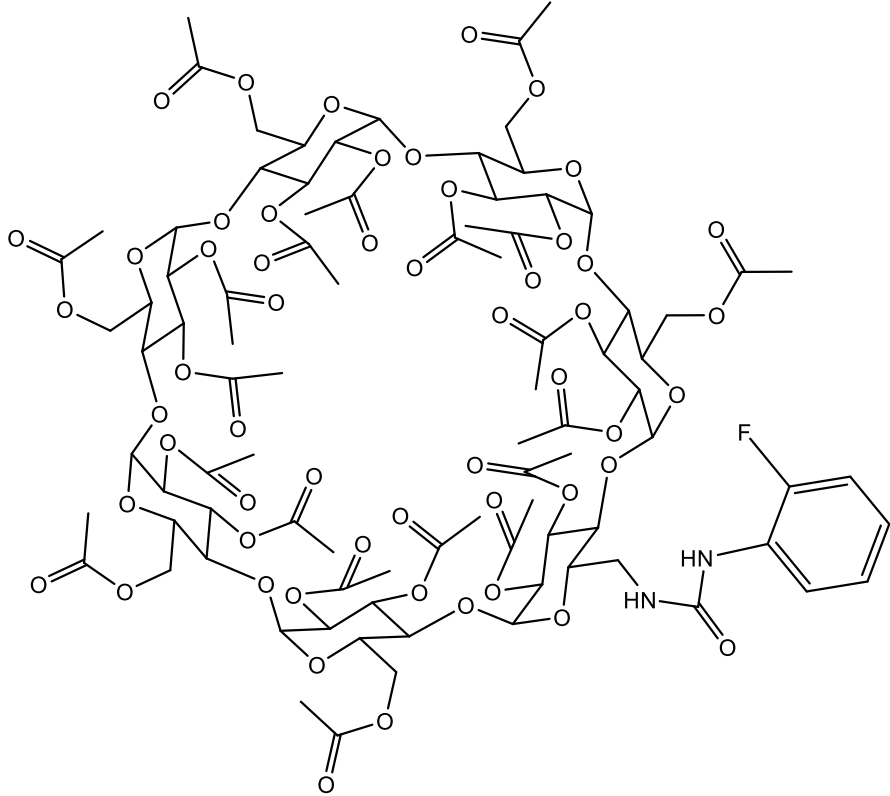
RMN¹³C(CDCl₃) of 7Am



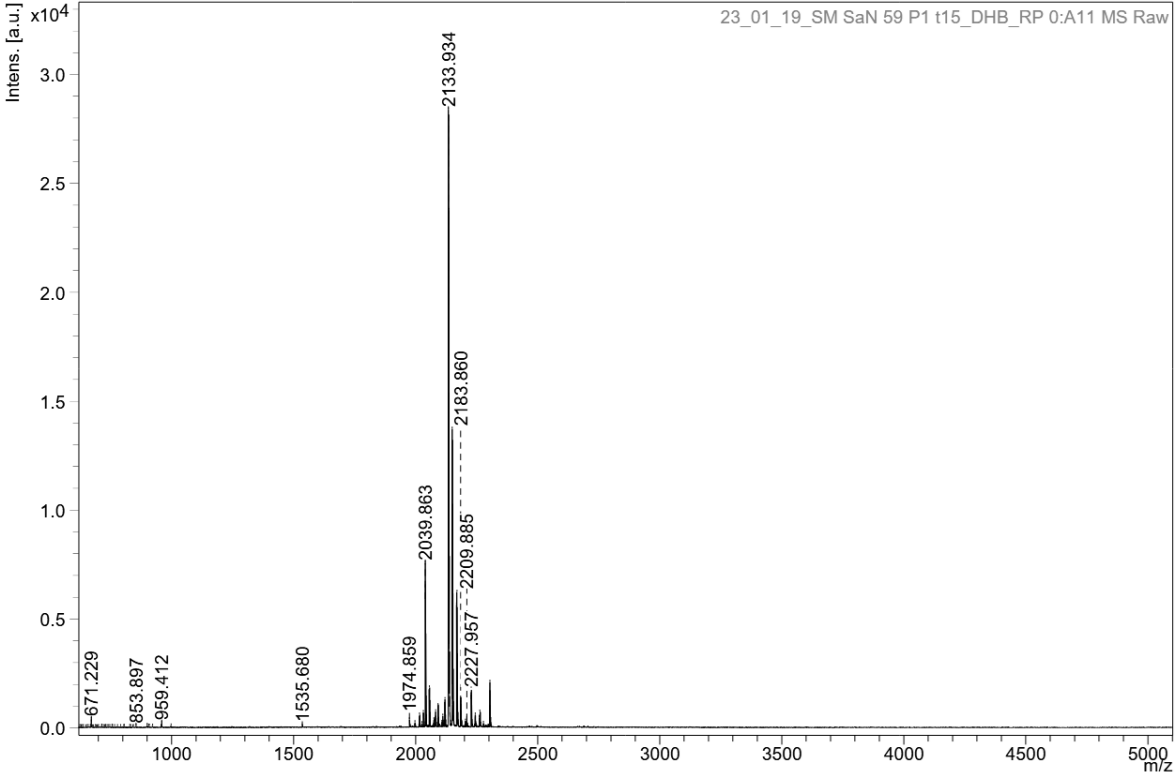
HSQC(CDCl₃) of 7Am



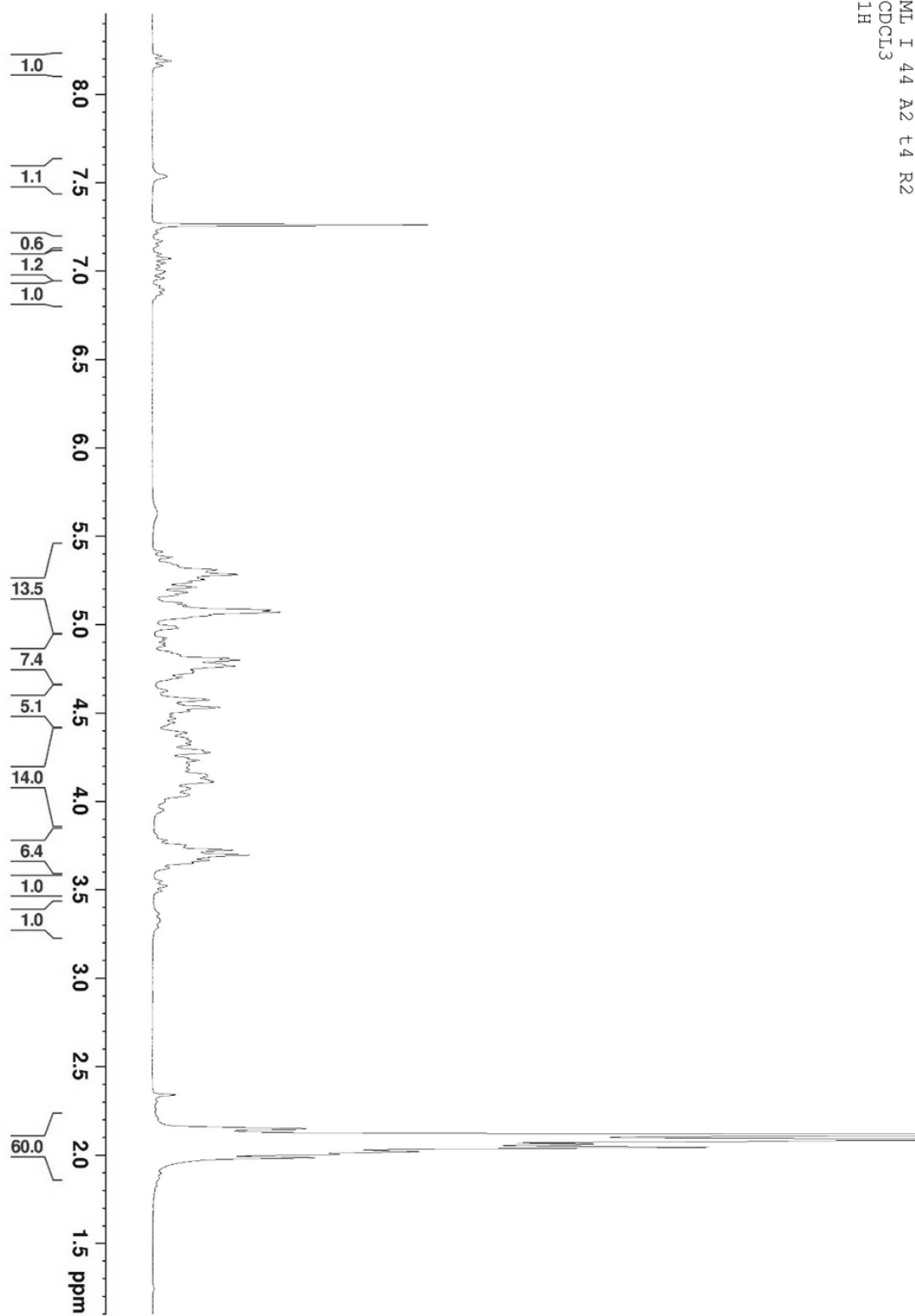
Characterisation of 7An (C₈₉H₁₁₅N₂O₅₅F)



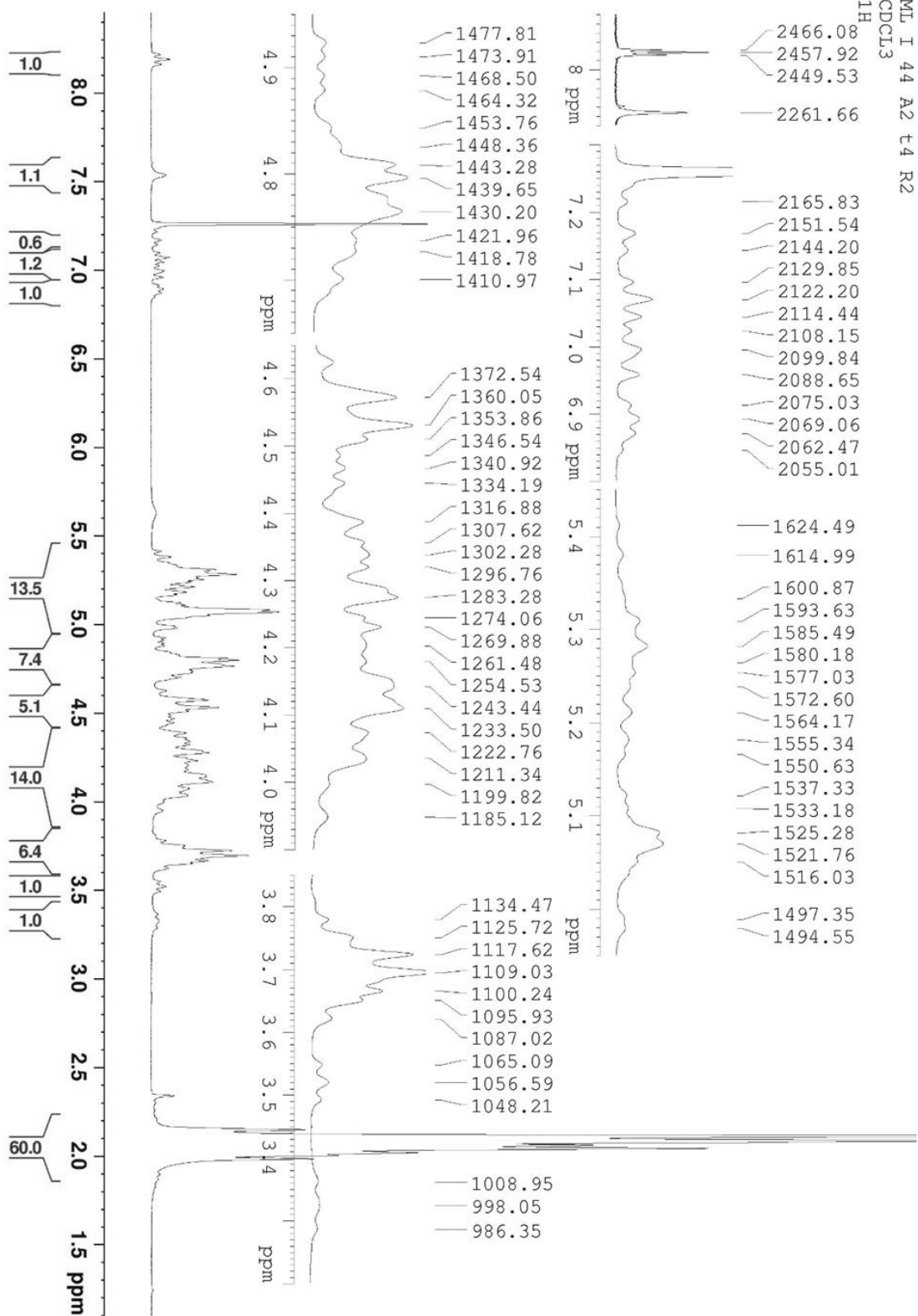
MALDI TOF of 7An



RMN¹H(CDCl₃) of 7An

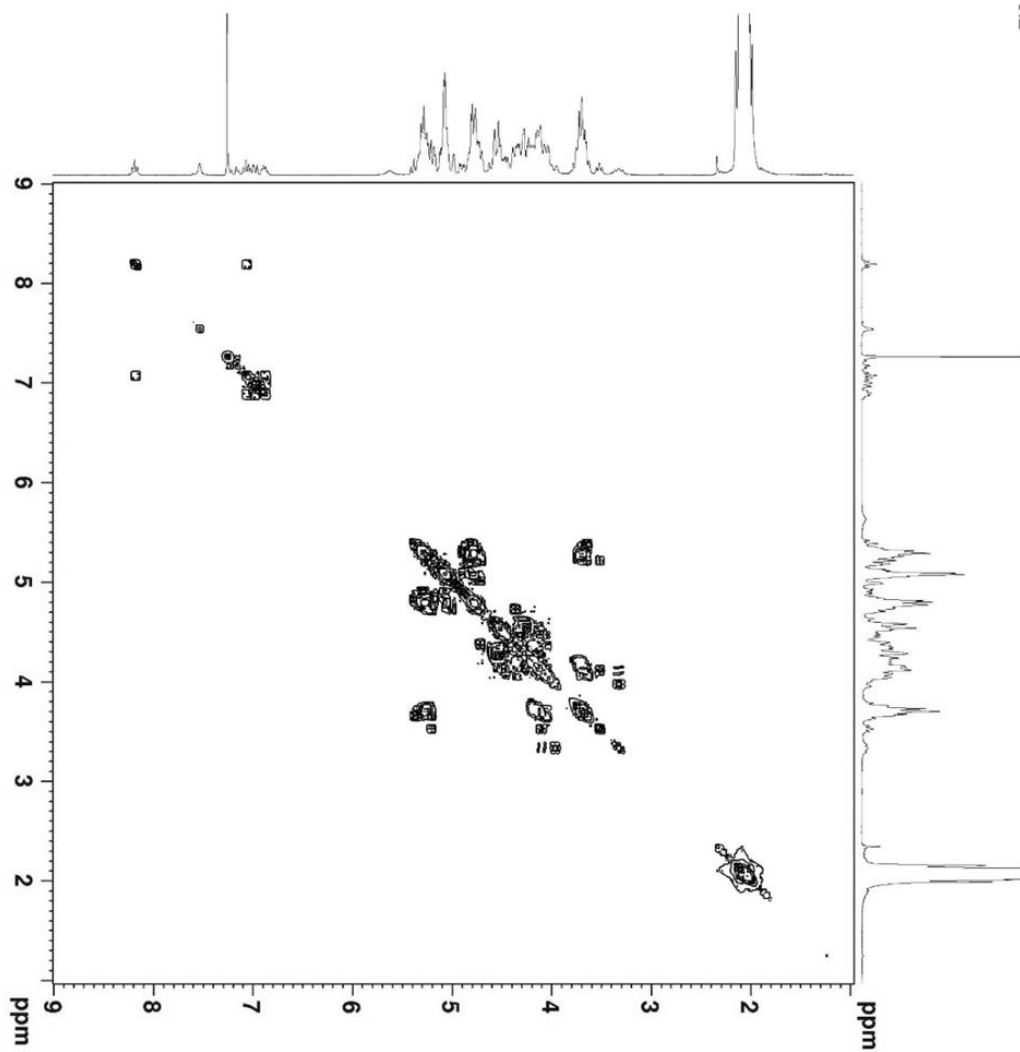


ML I 44 A2 t4 R2
 CDCL3
 1H

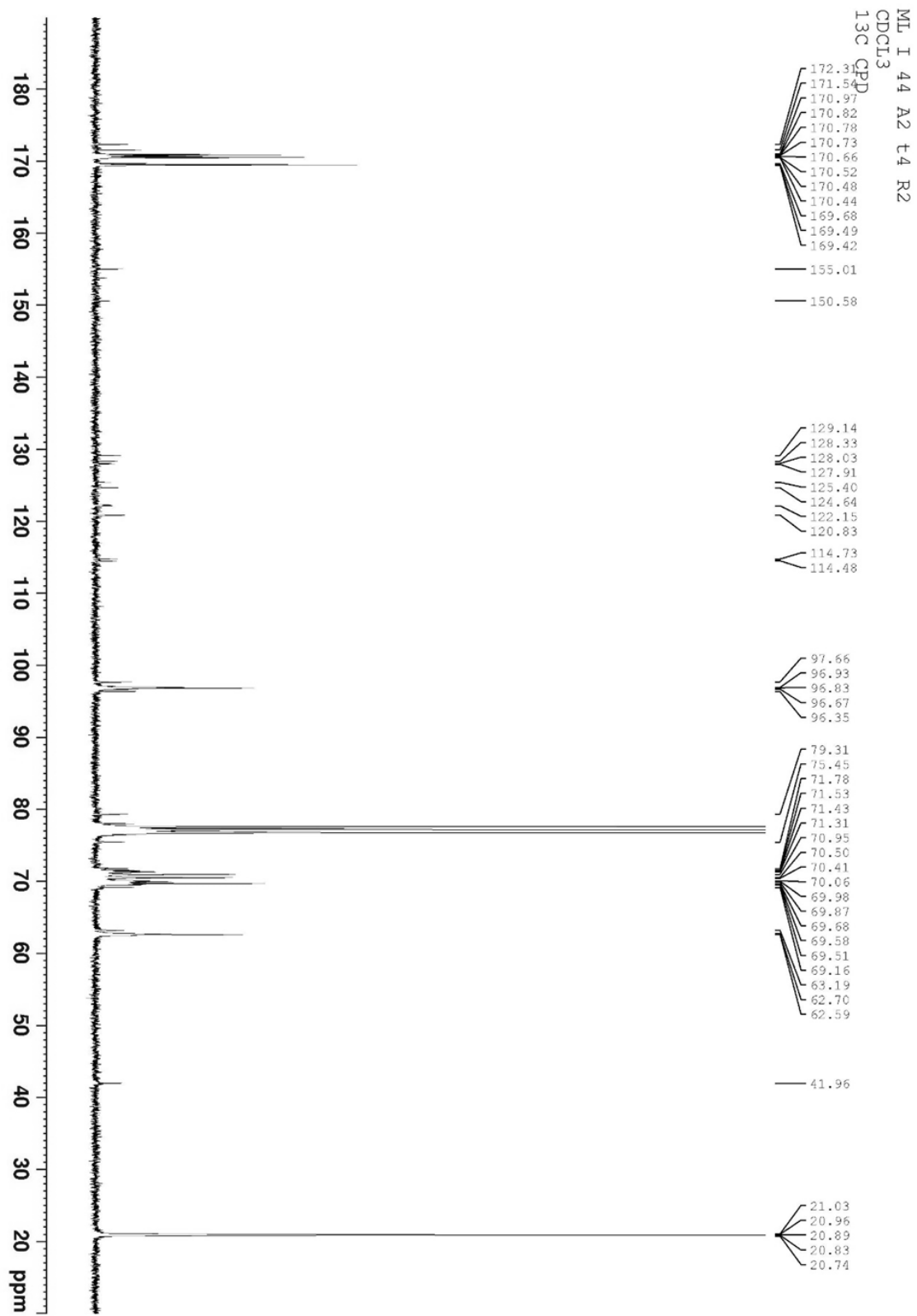


COSY (CDCl₃) of 7An

ML I 44 A2 t4 R2
CDCl₃
COSY45

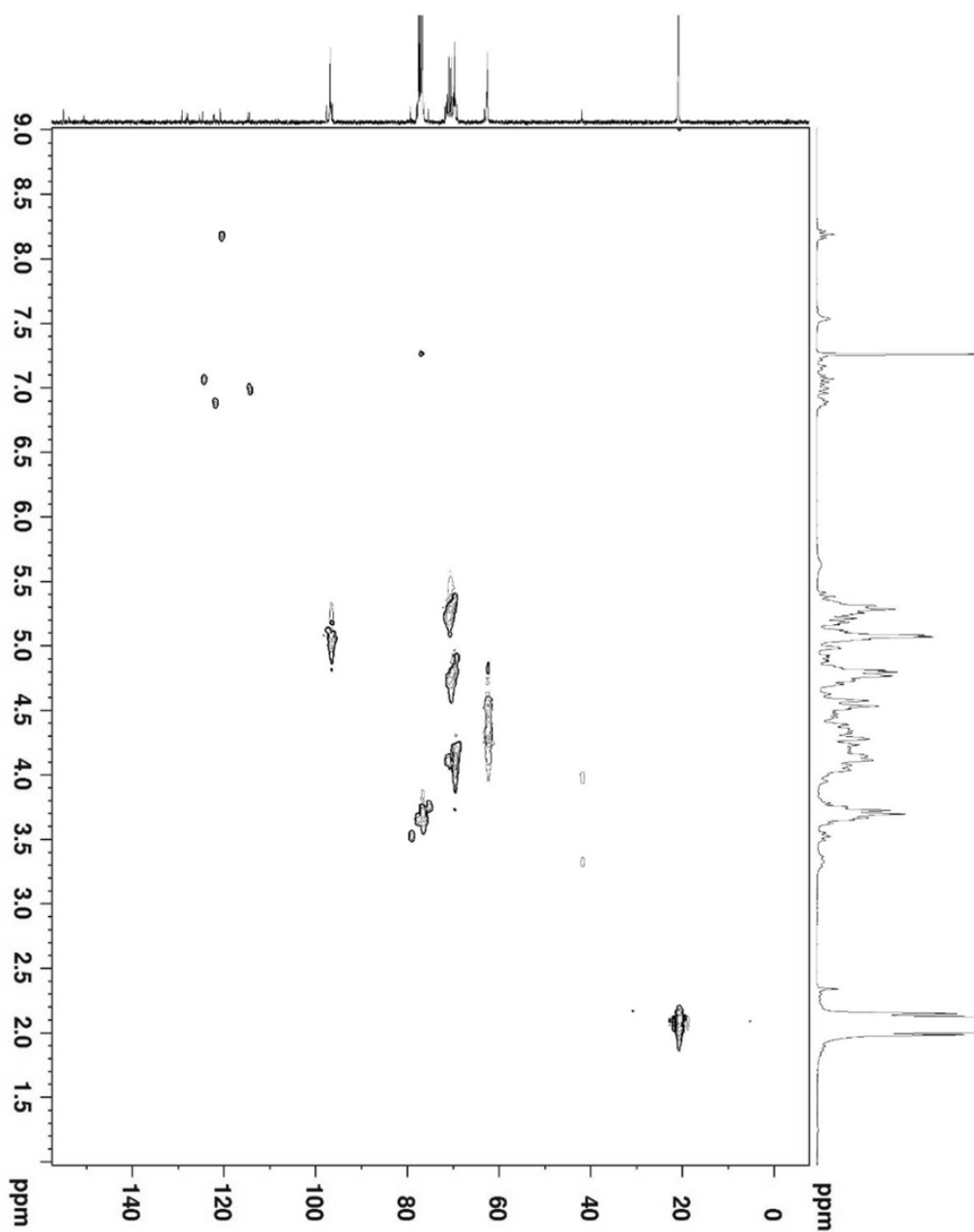


RMN¹³C(CDCl₃) of 7An

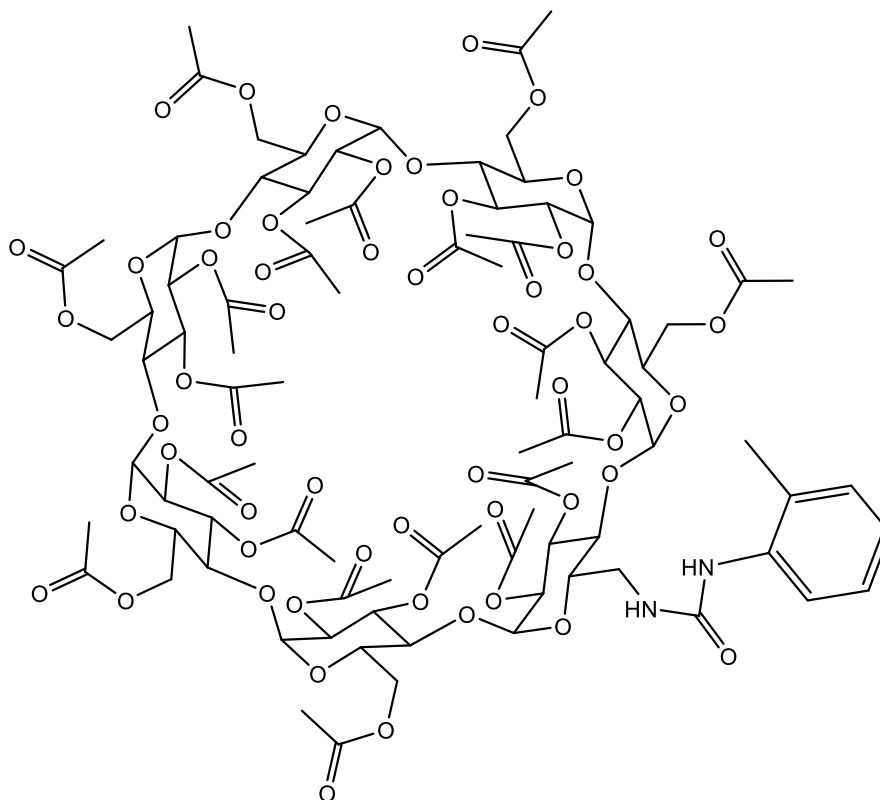


HSQC(CDCl₃) of 7An

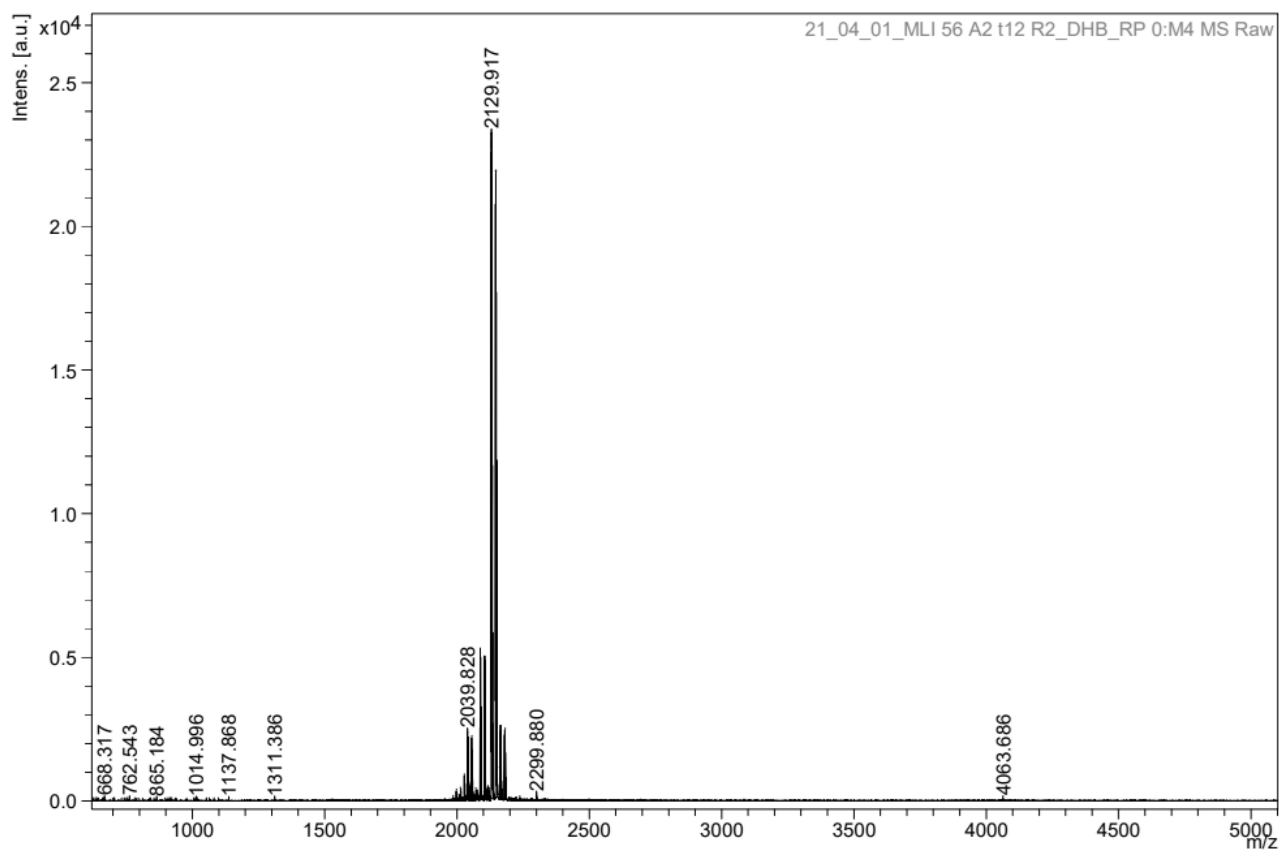
ML I 44 A2 t4 R2
CDCl₃
HSQC

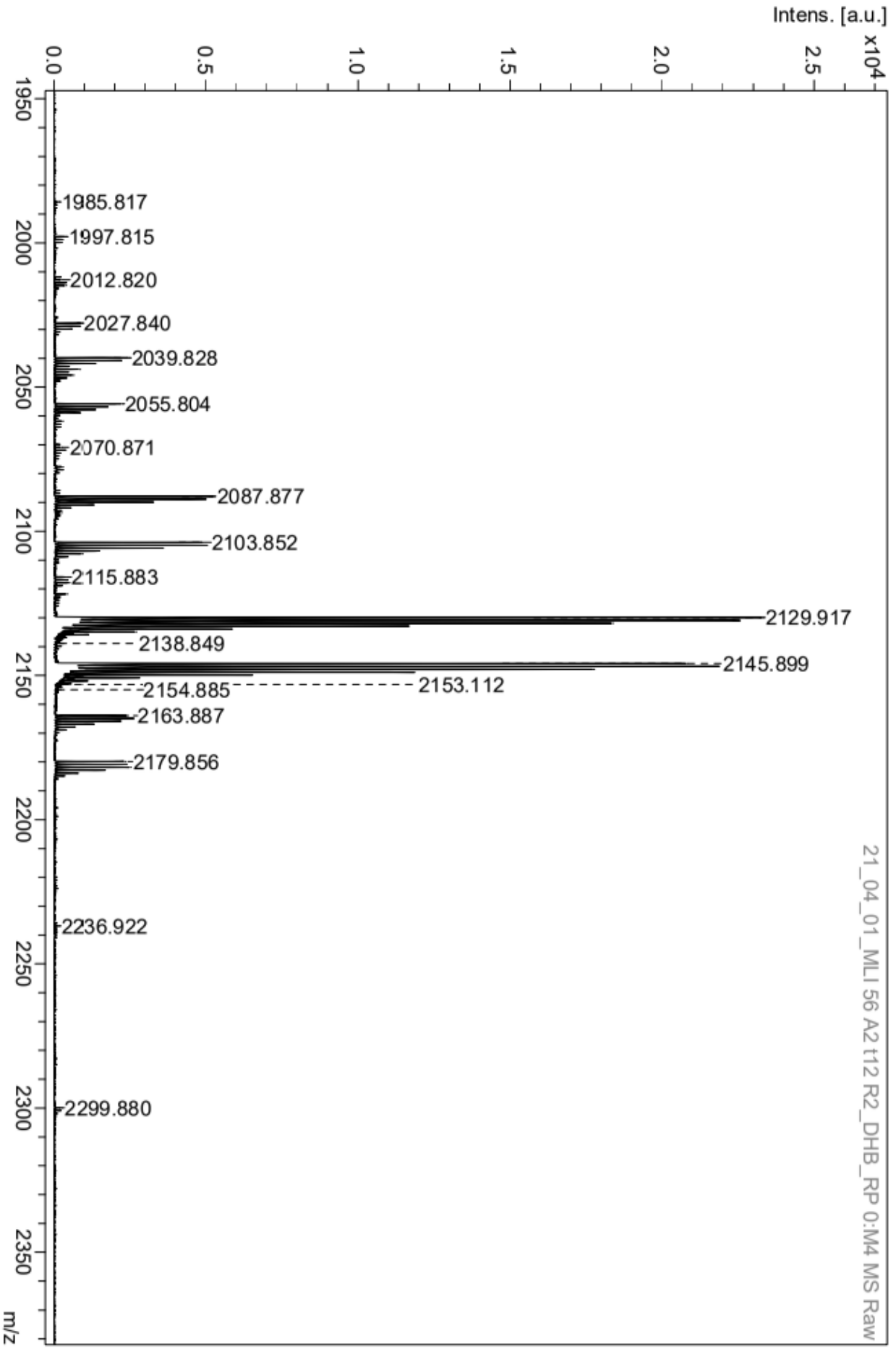


Characterisation of 7Ao ($C_{90}H_{118}N_2O_{55}$)

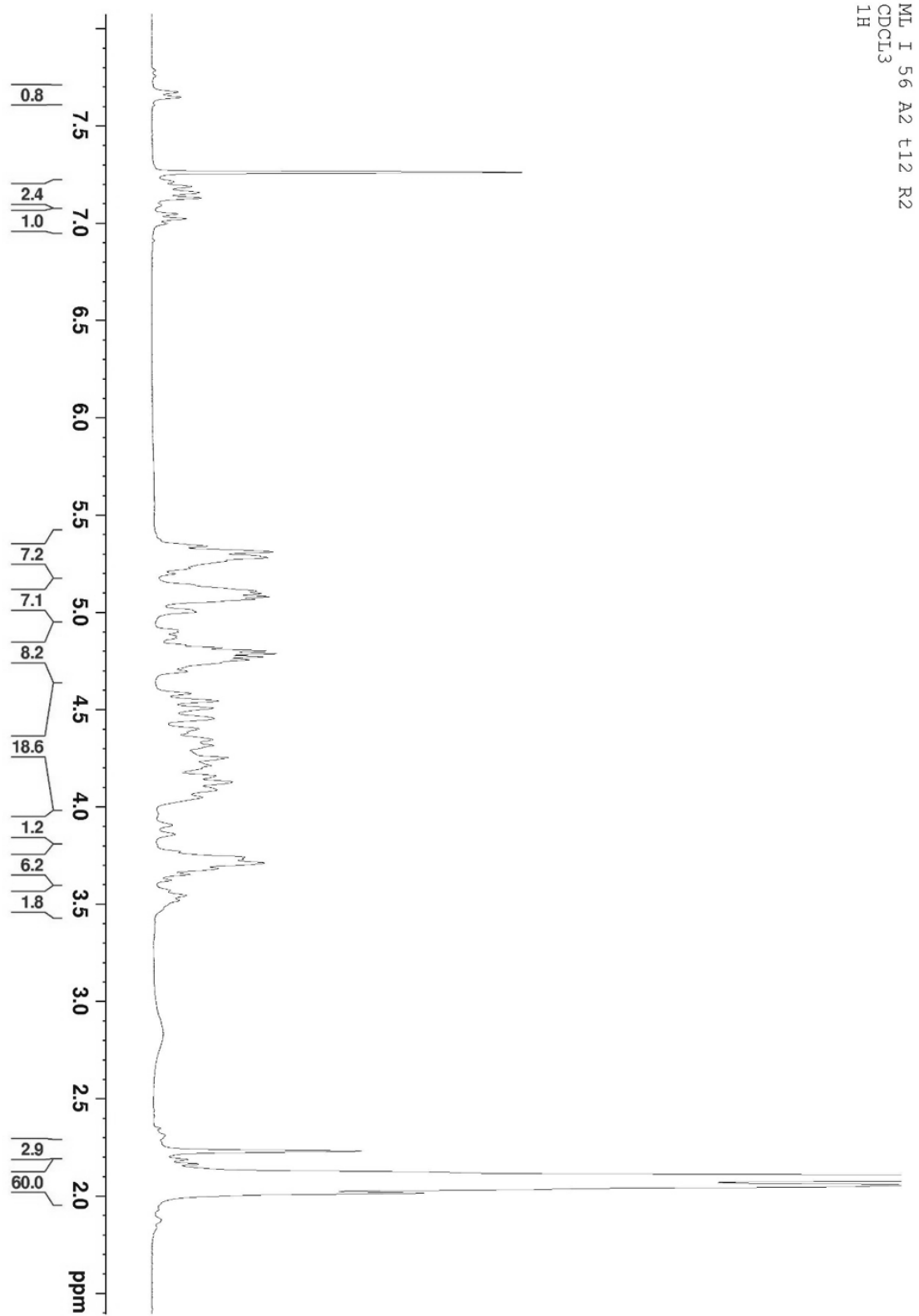


MALDI TOF of 7Ao

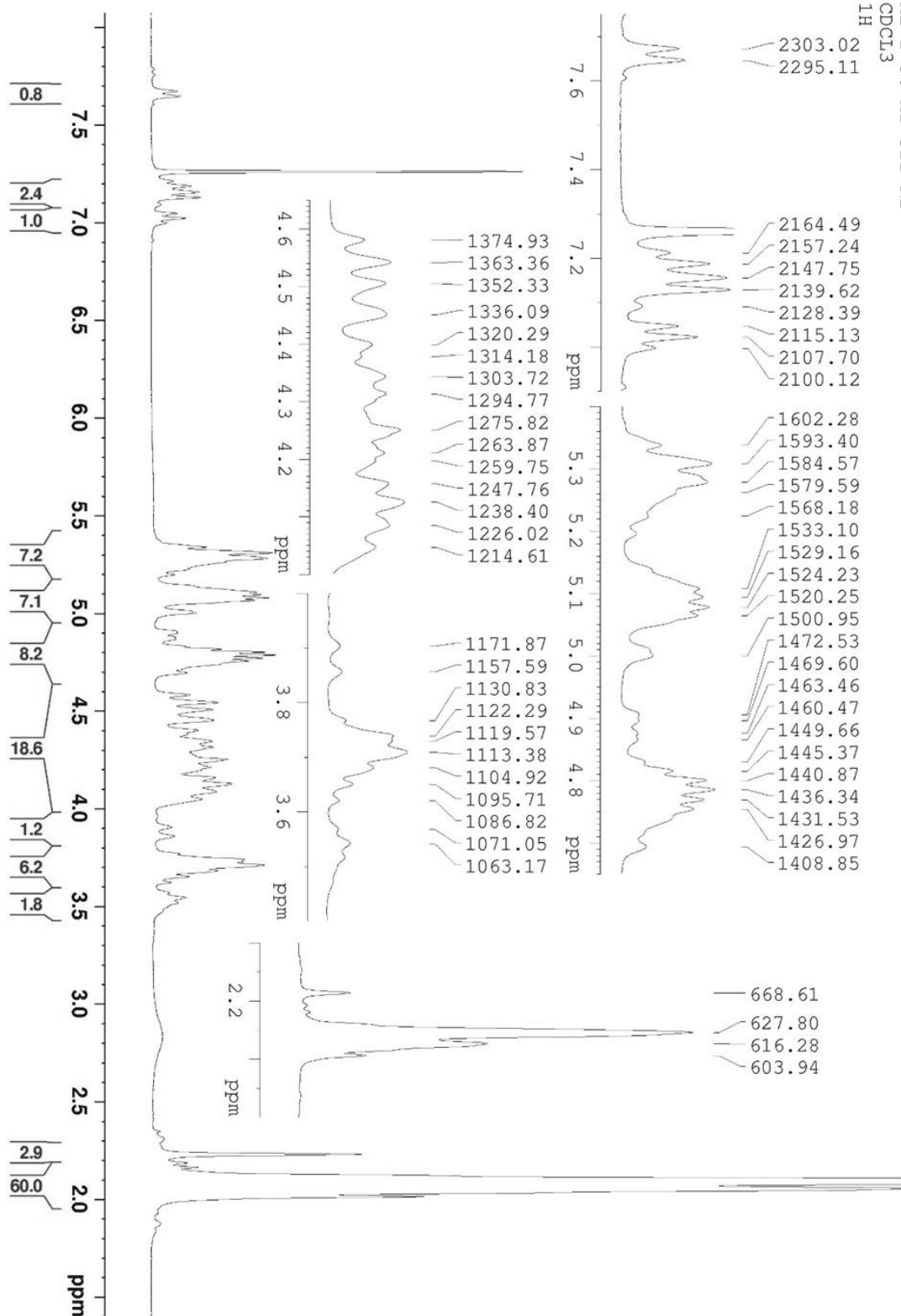




RMN¹H(CDCl₃) of 7A_o

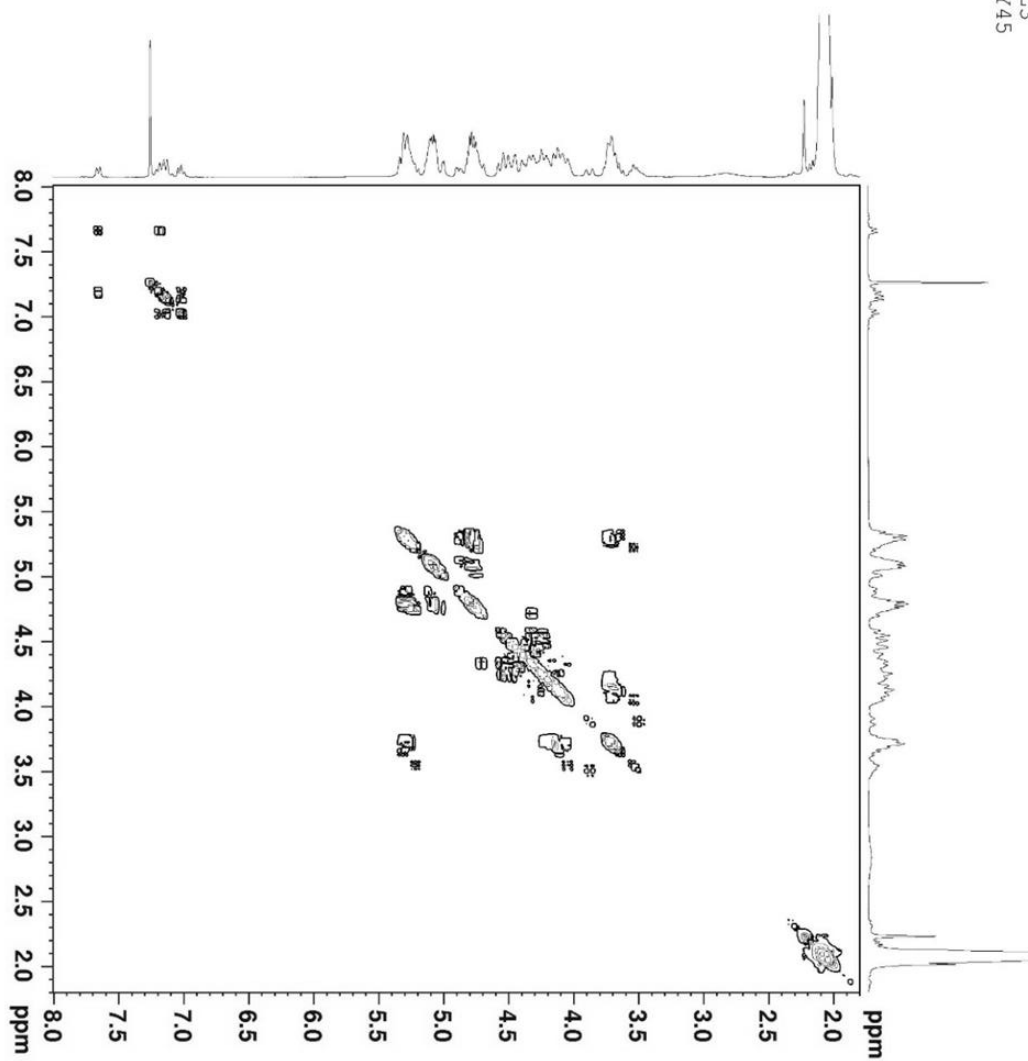


ML I 56 A2 t12 R2
CDCL3
1H

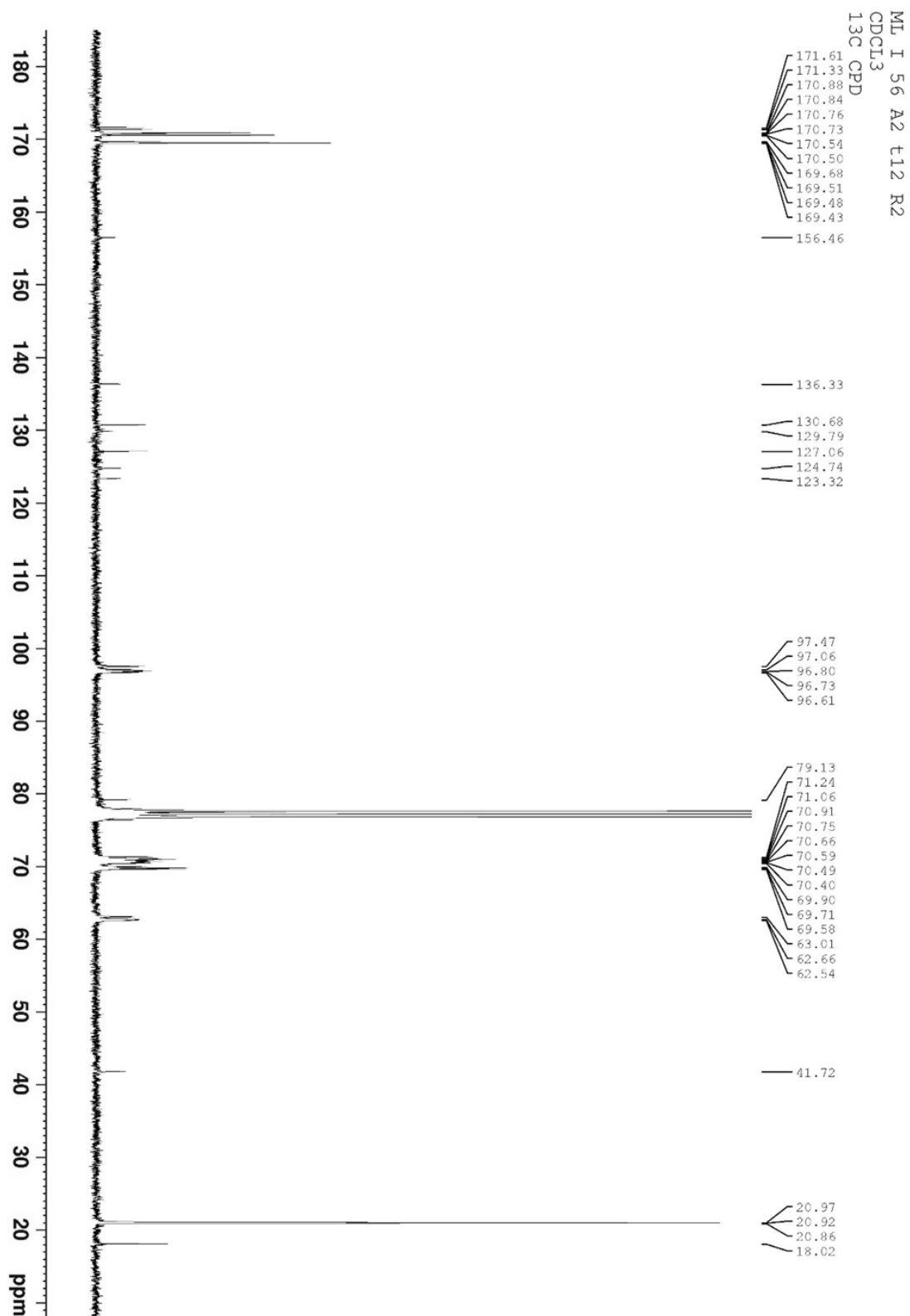


COSY (CDCl₃) of 7Ao

ML I 56 A2 t12 R2
CDCl₃
COSY45

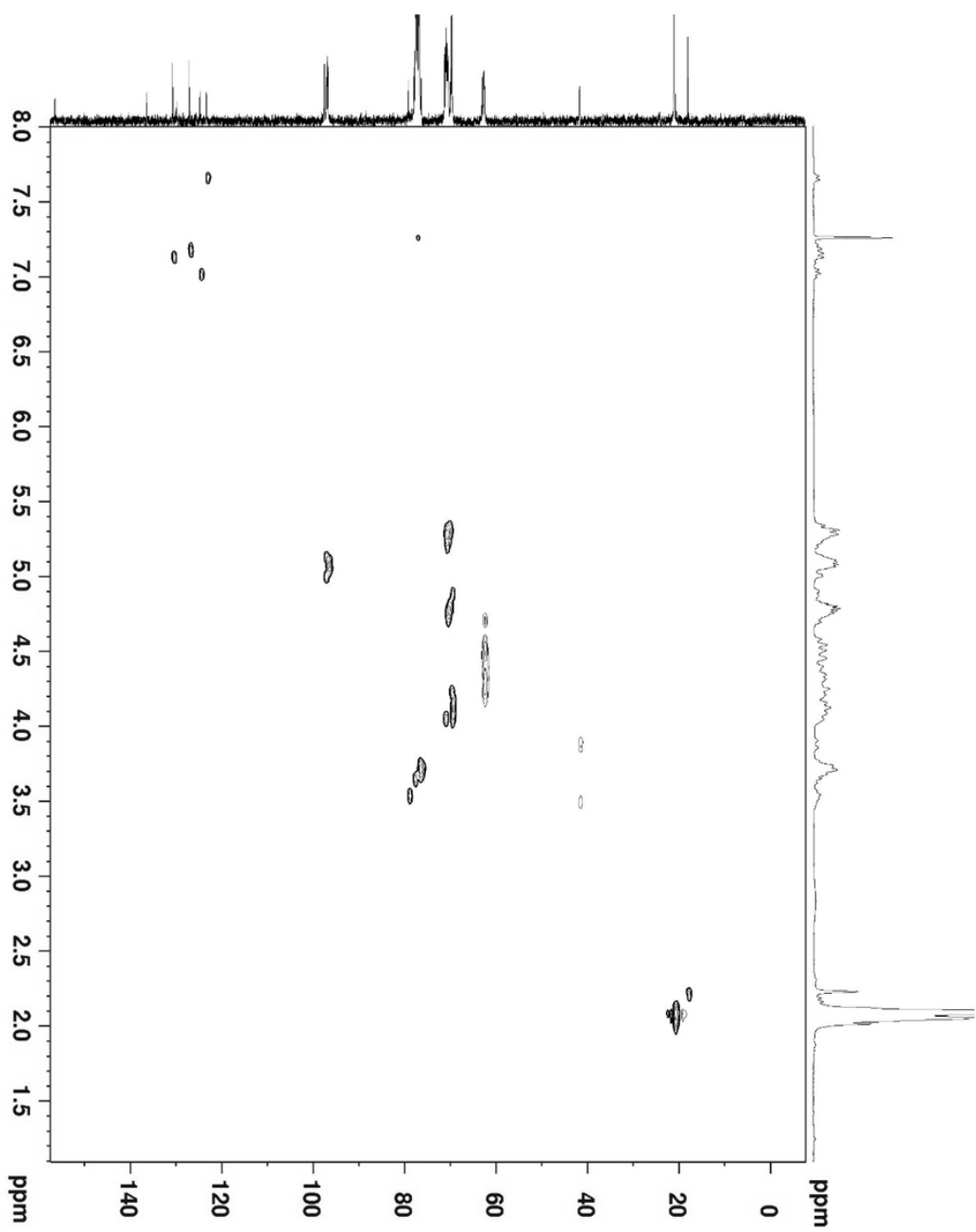


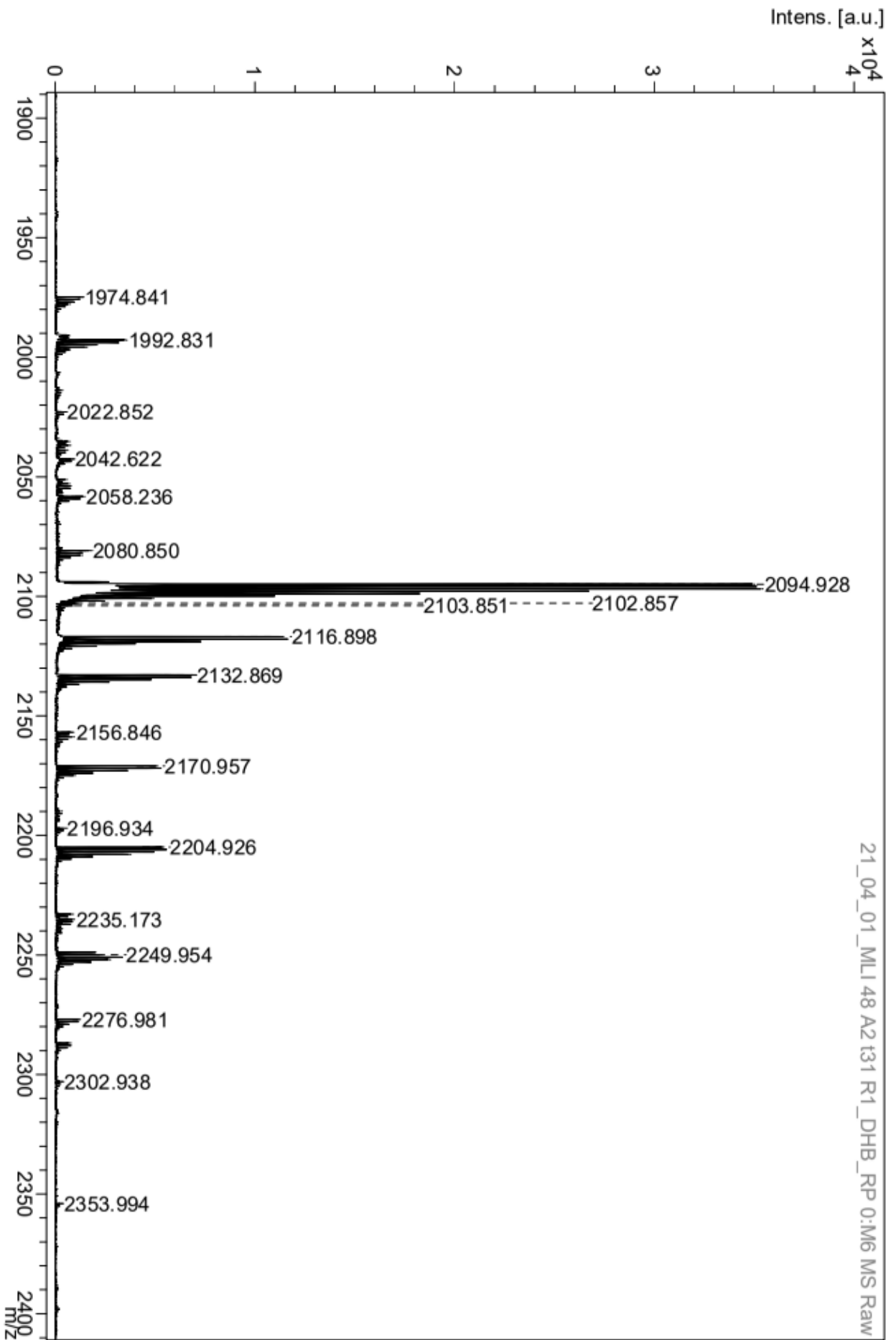
RMN¹³C(CDCl₃) of 7Ao



HSQC(CDCl₃) of 7Ao

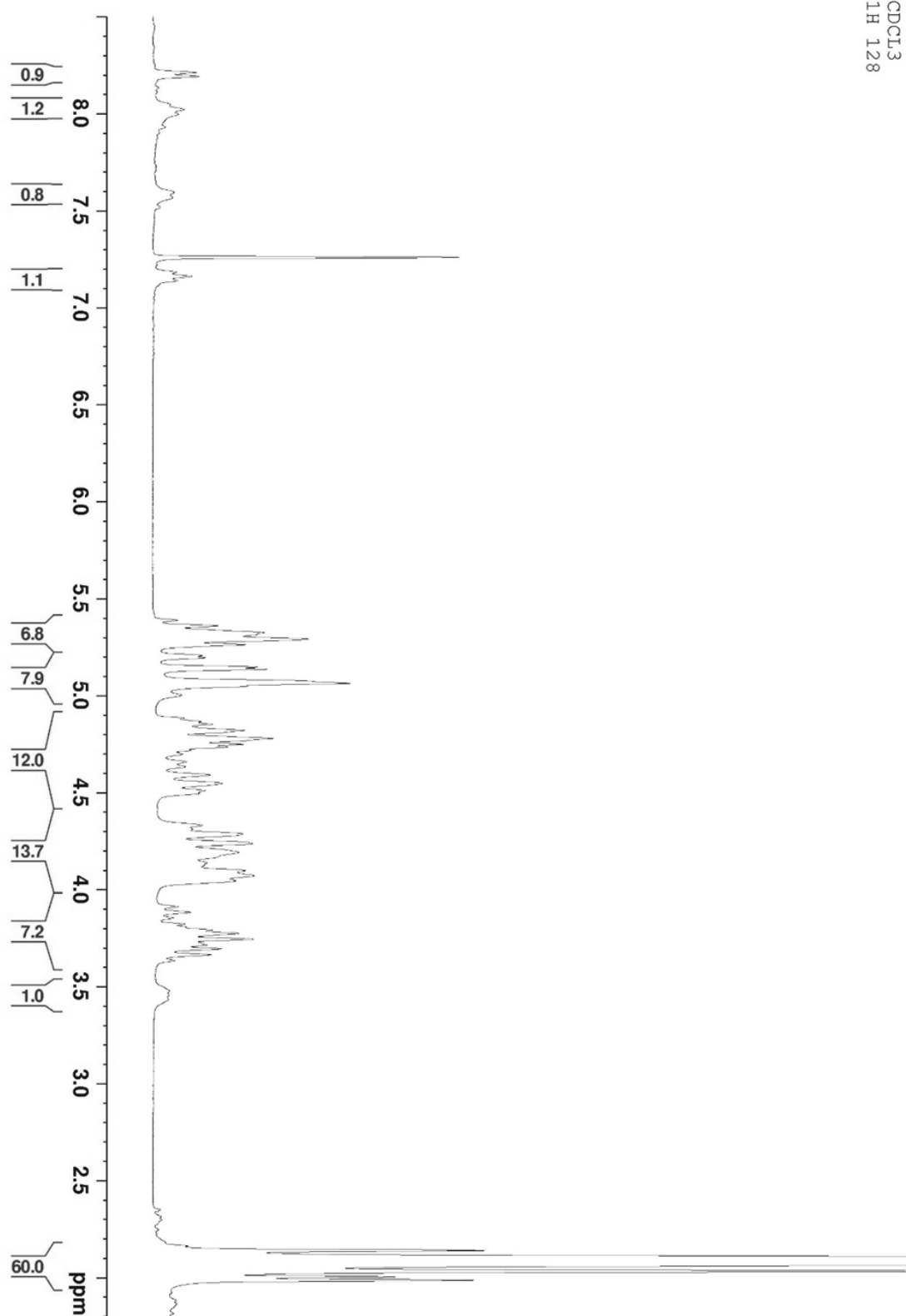
ML I 56 A2 t12 R2
CDCl₃
HSQC



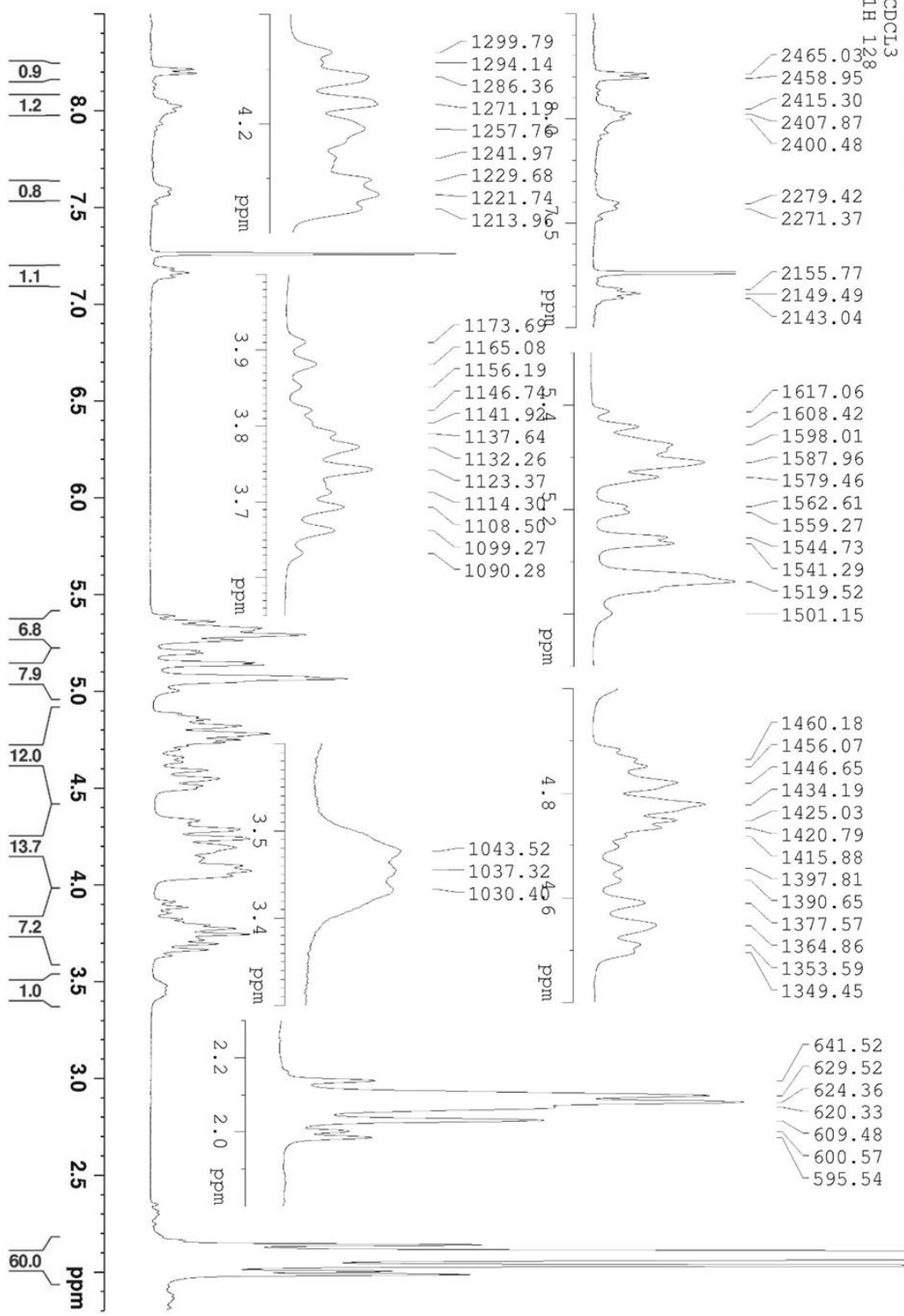


21_04_01_MLI 48 A2 t31 R1_DHB_RP 0:06 MS Raw

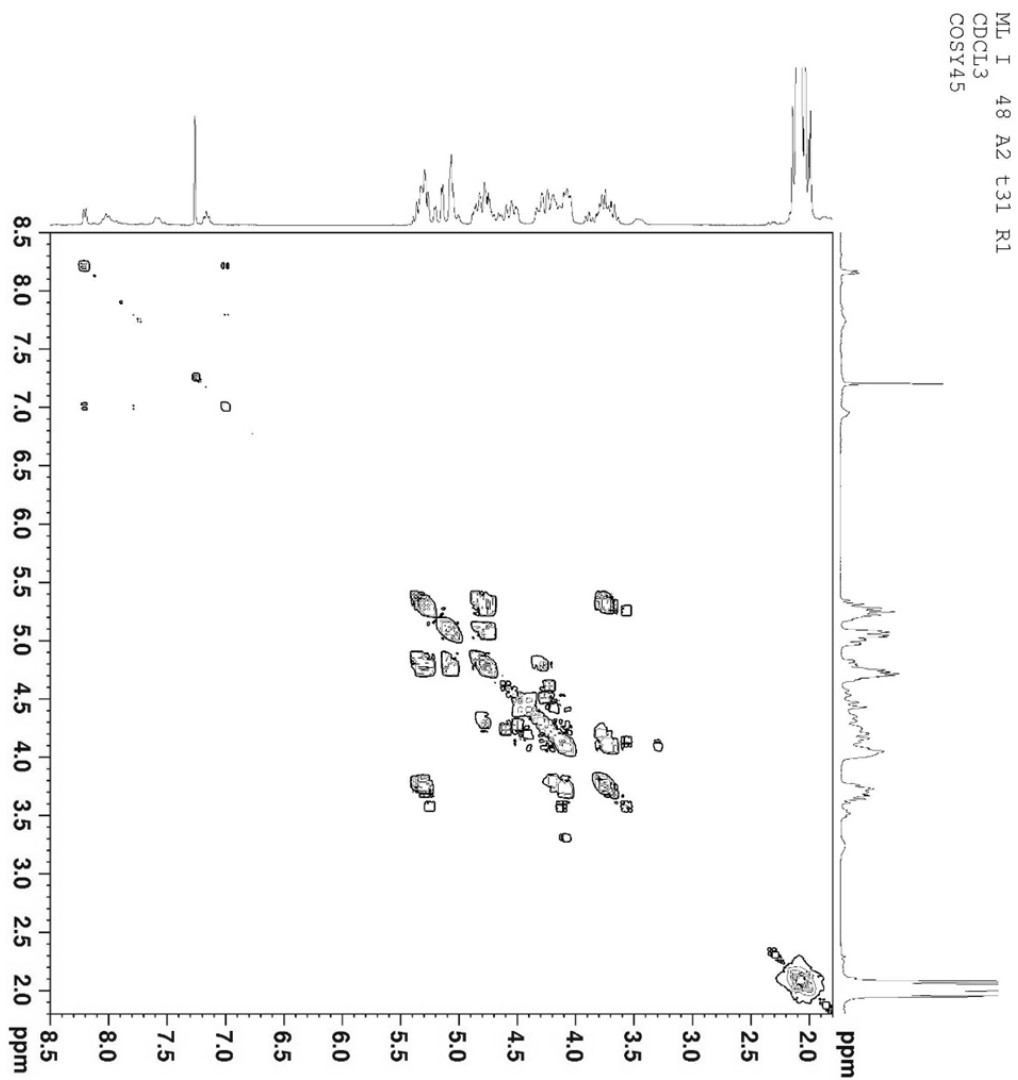
RMN¹H(CDCl₃) of 7Ap



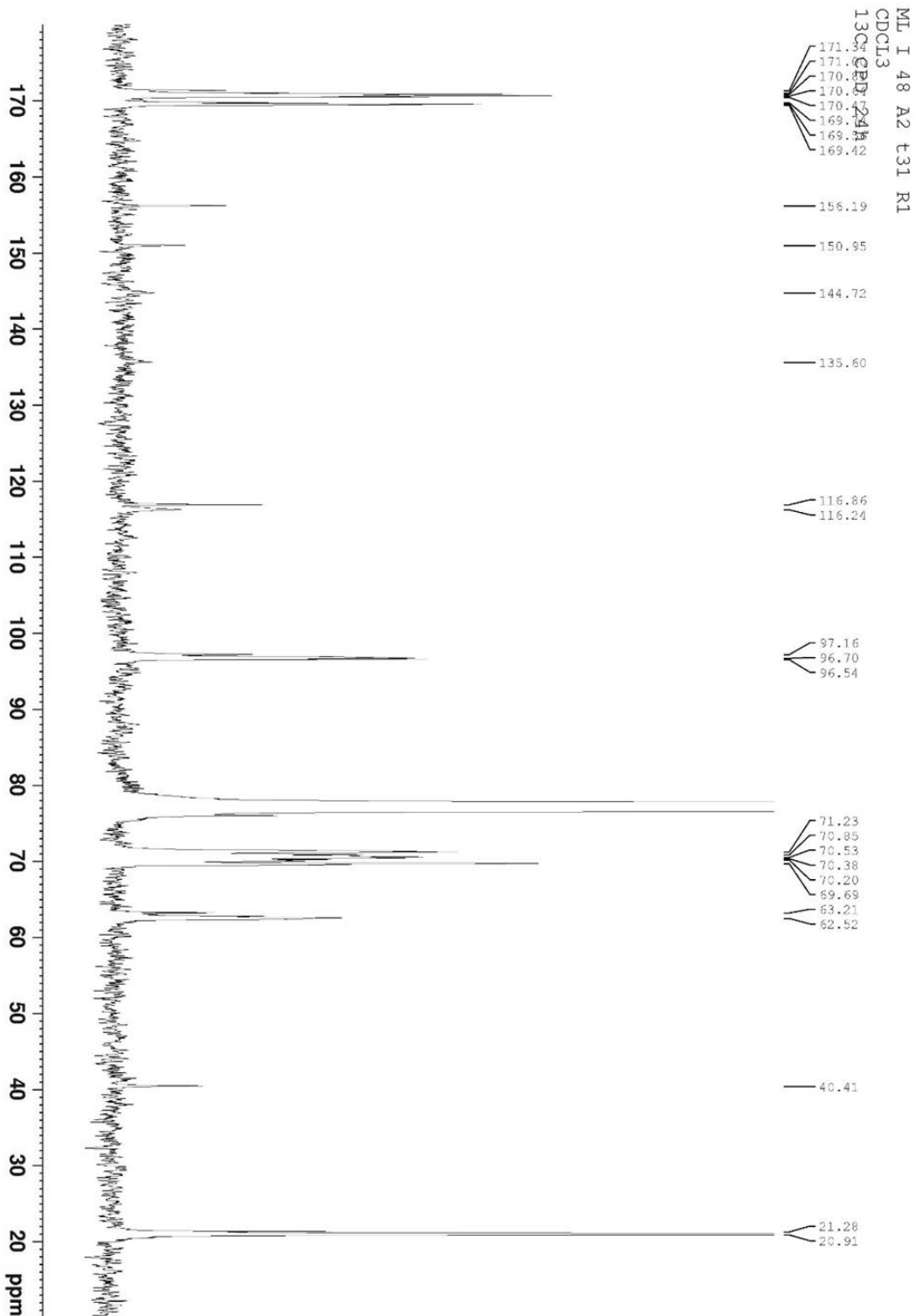
ML I 48 A2 t31 R1
 CDCL3
 1H 128



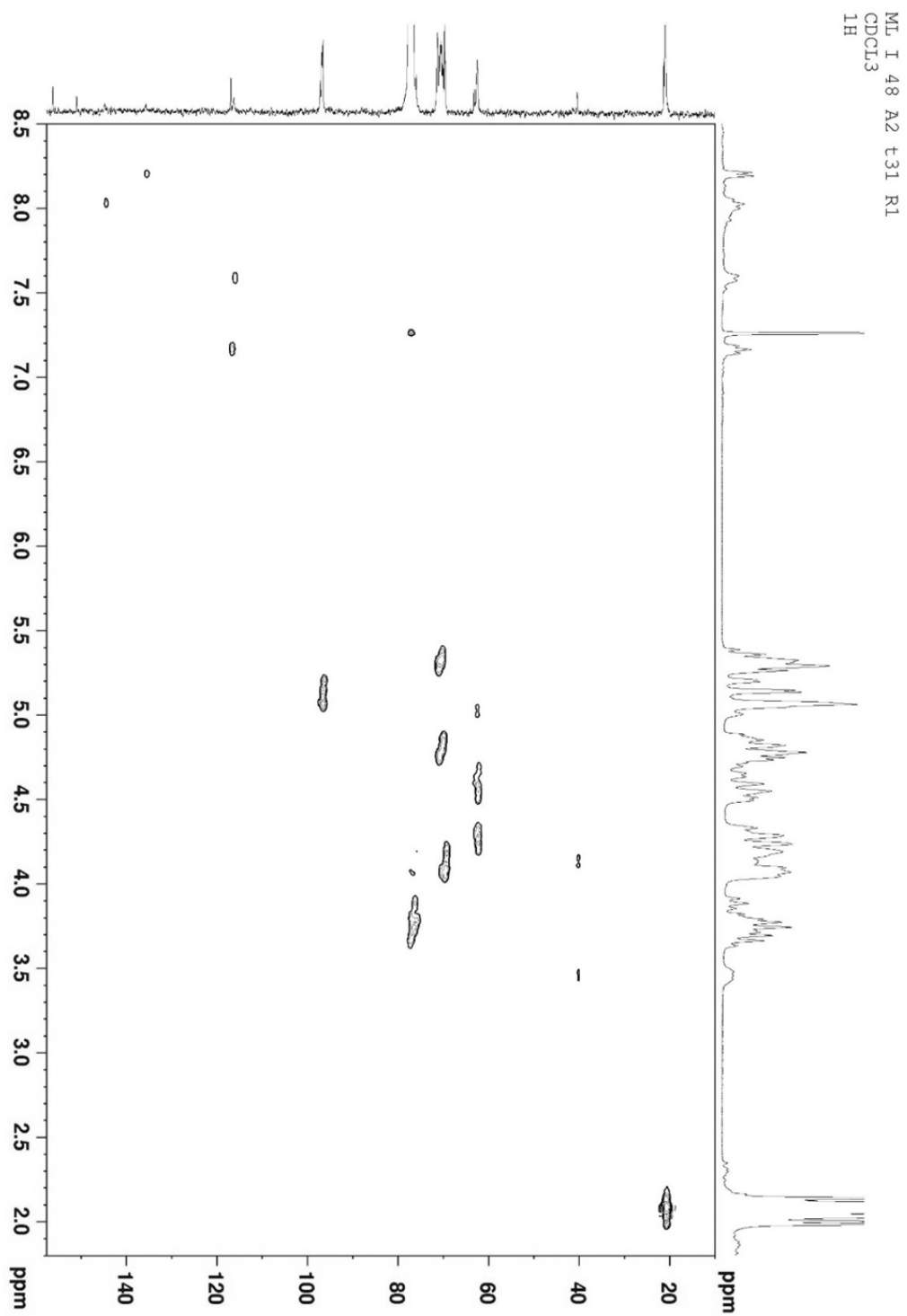
COSY (CDCl₃) of 7Ap

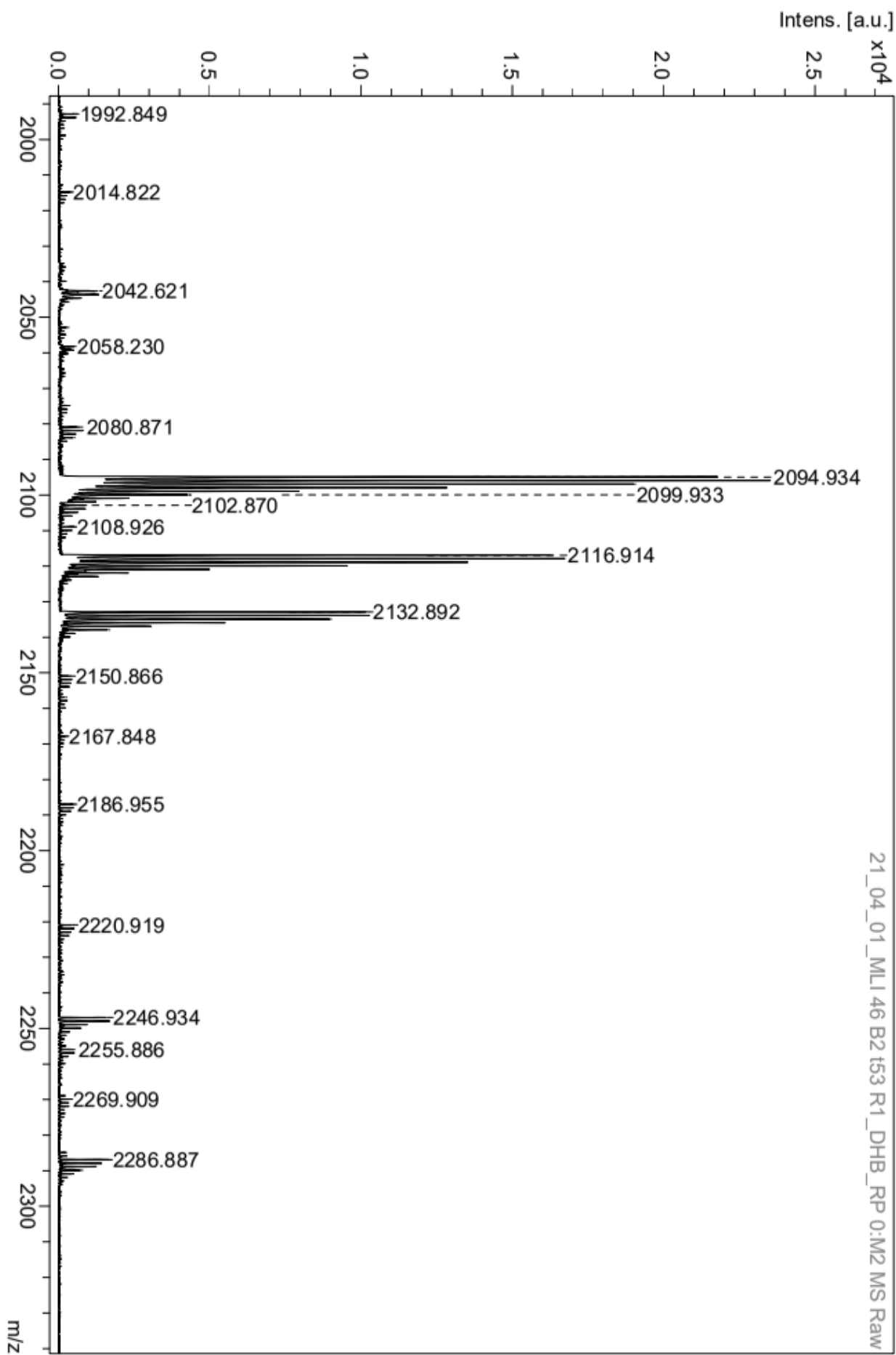


RMN¹³C(CDCl₃) of 7Ap

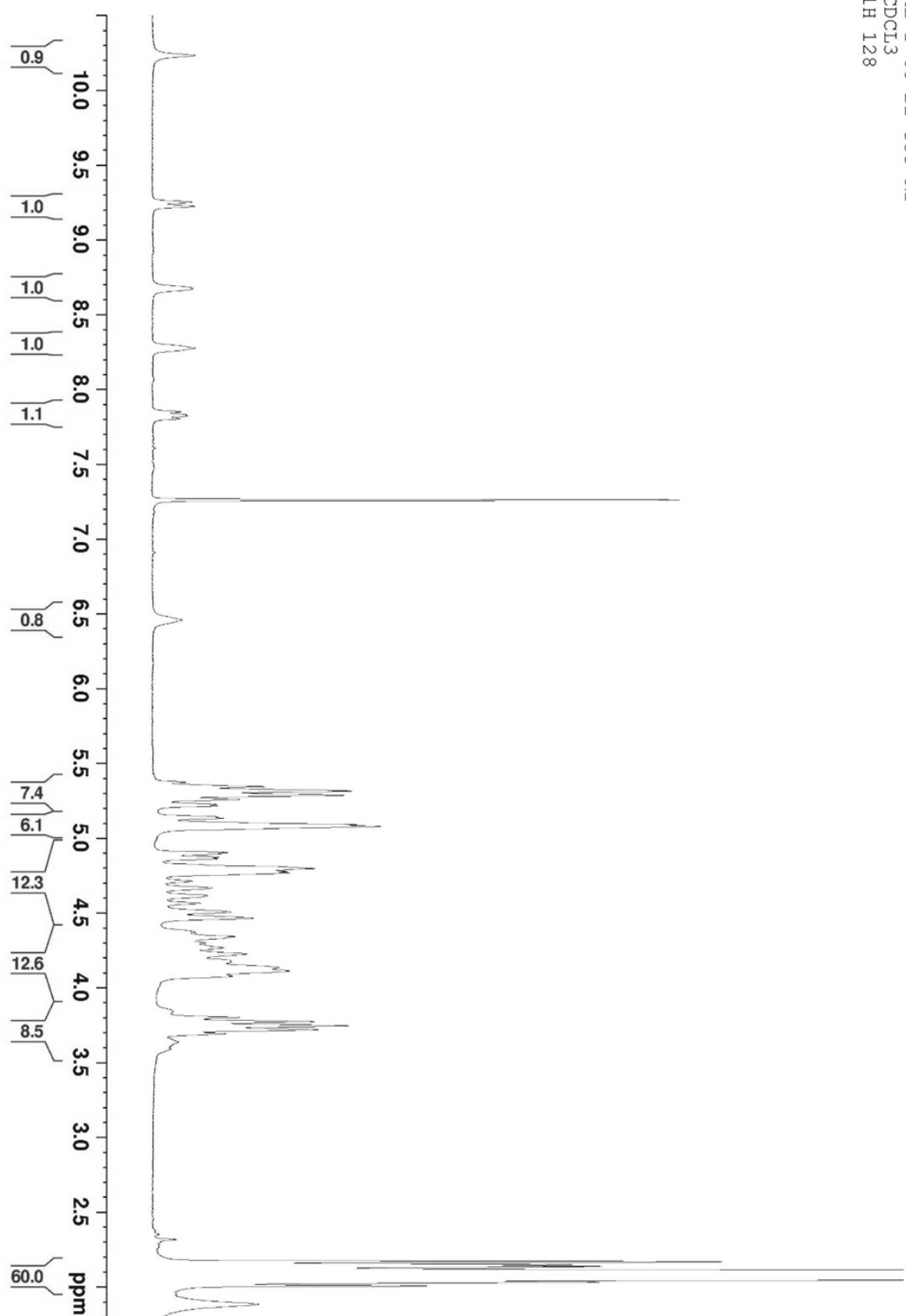


HSQC(CDCl₃) of 7Ap

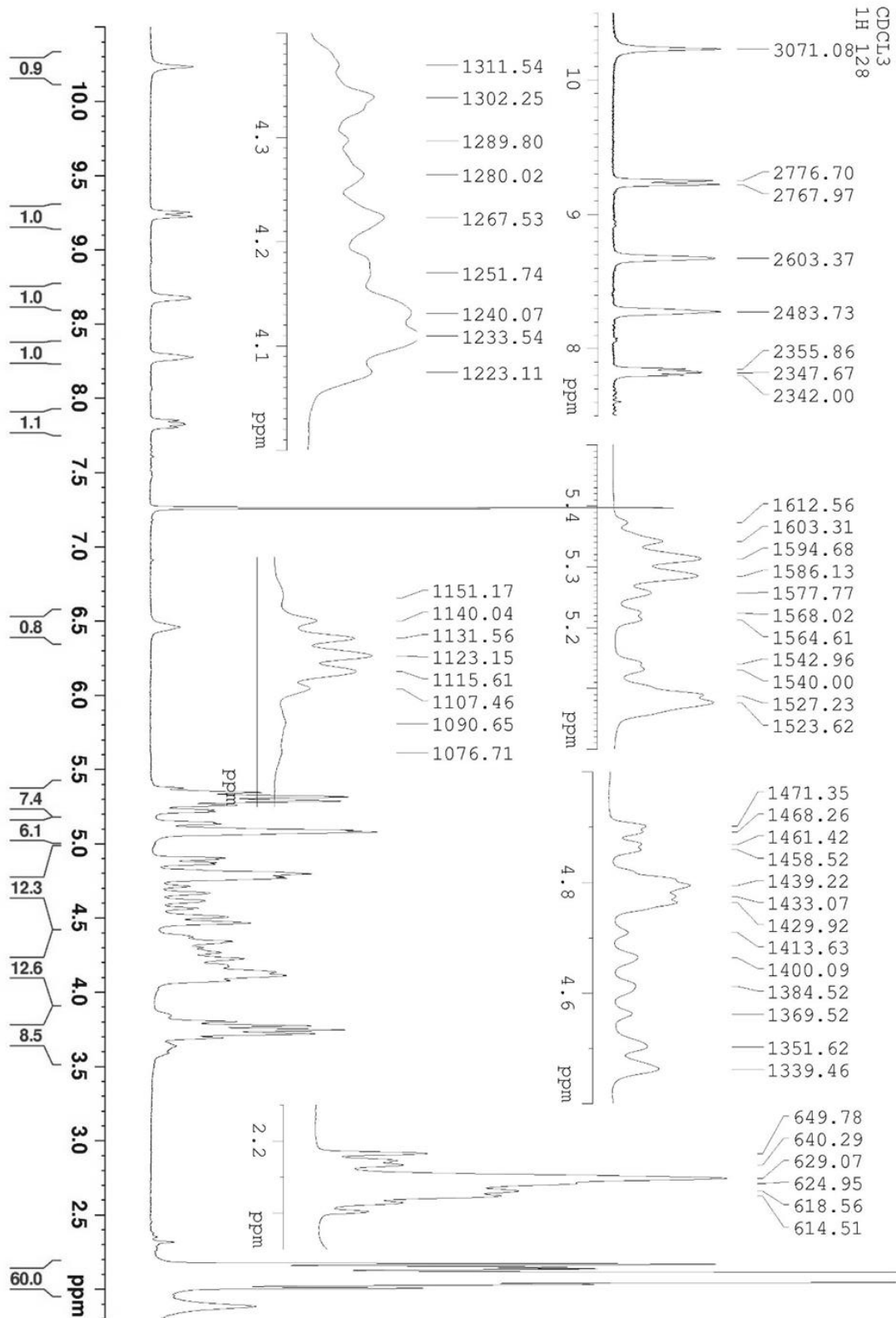




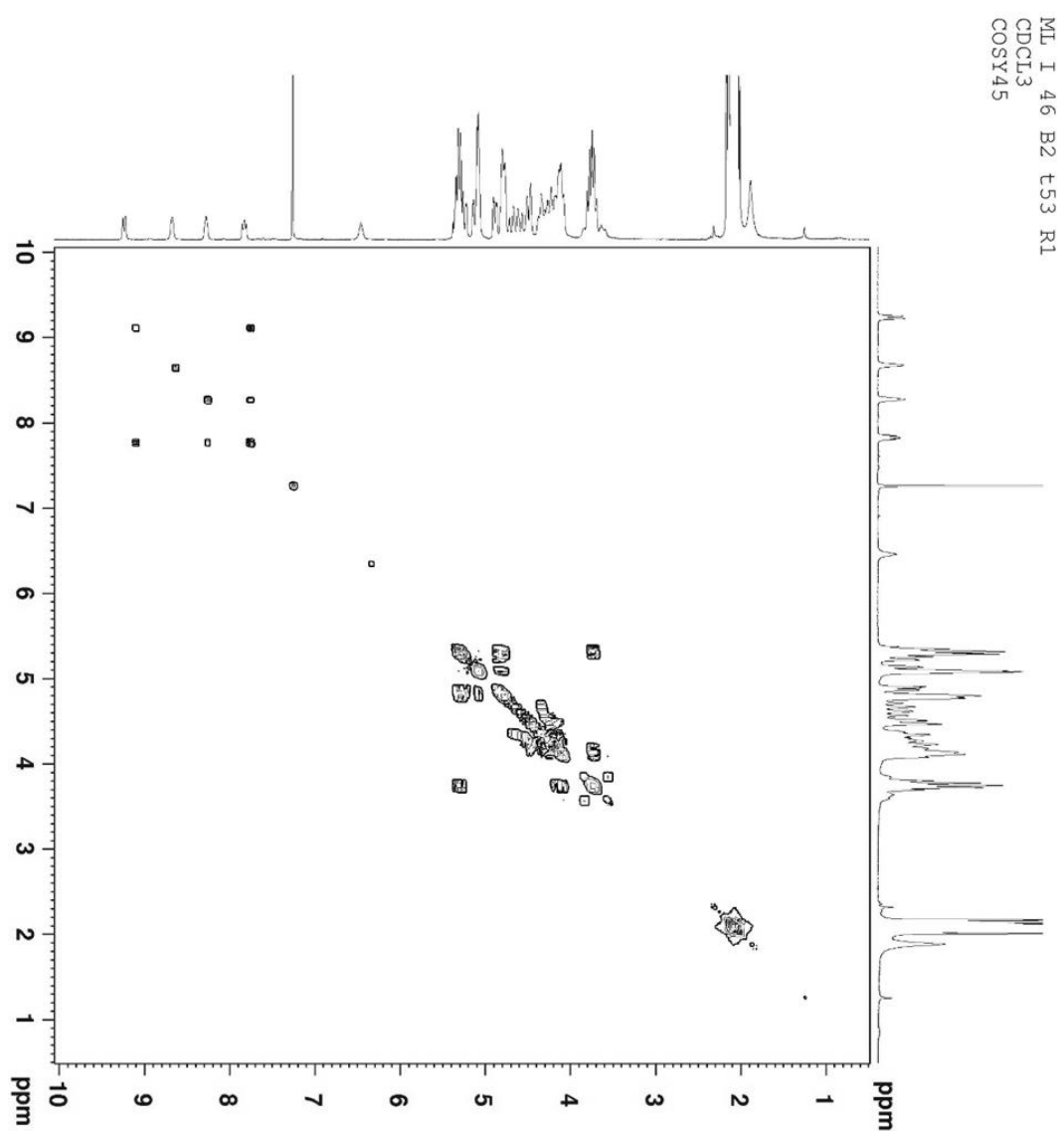
RMN¹H(CDCl₃) of 7Aq



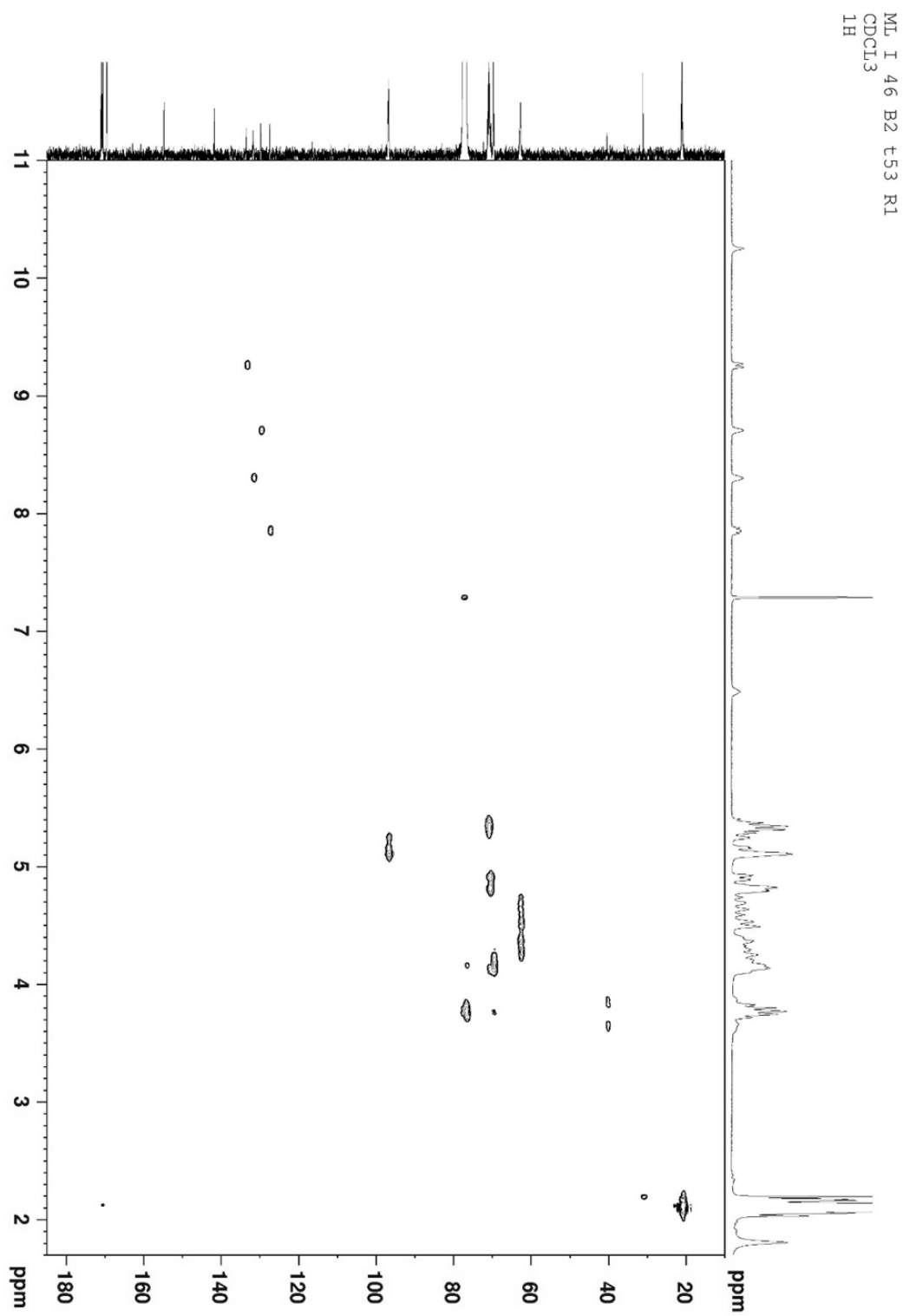
ML I 46 B2 t53 R1
 CDCL3
 1H 128



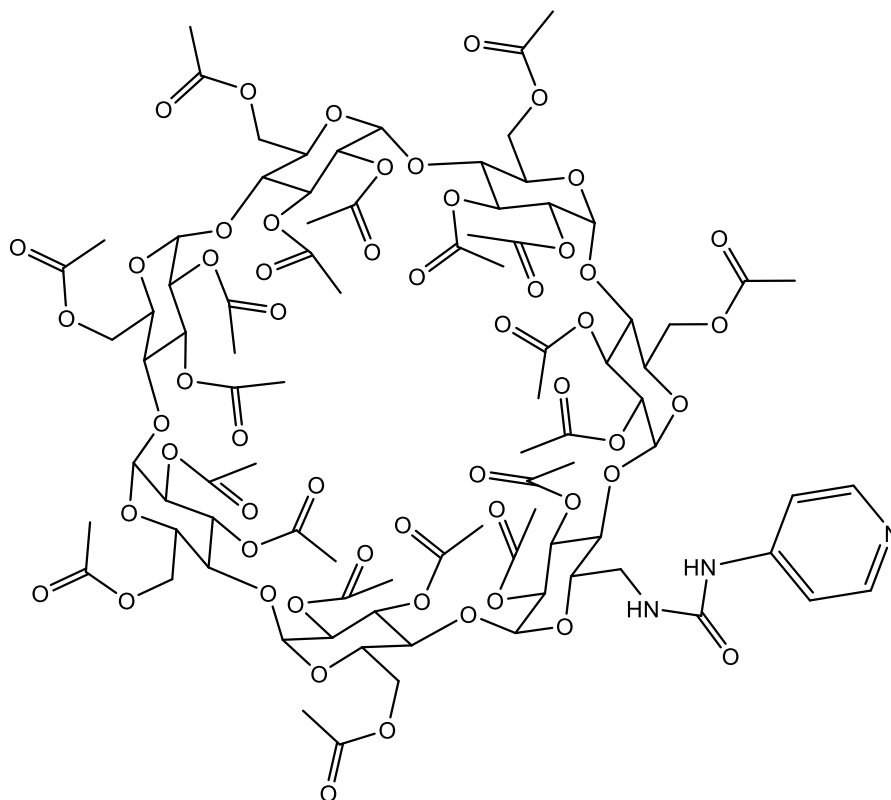
COSY (CDCl₃) of 7Aq



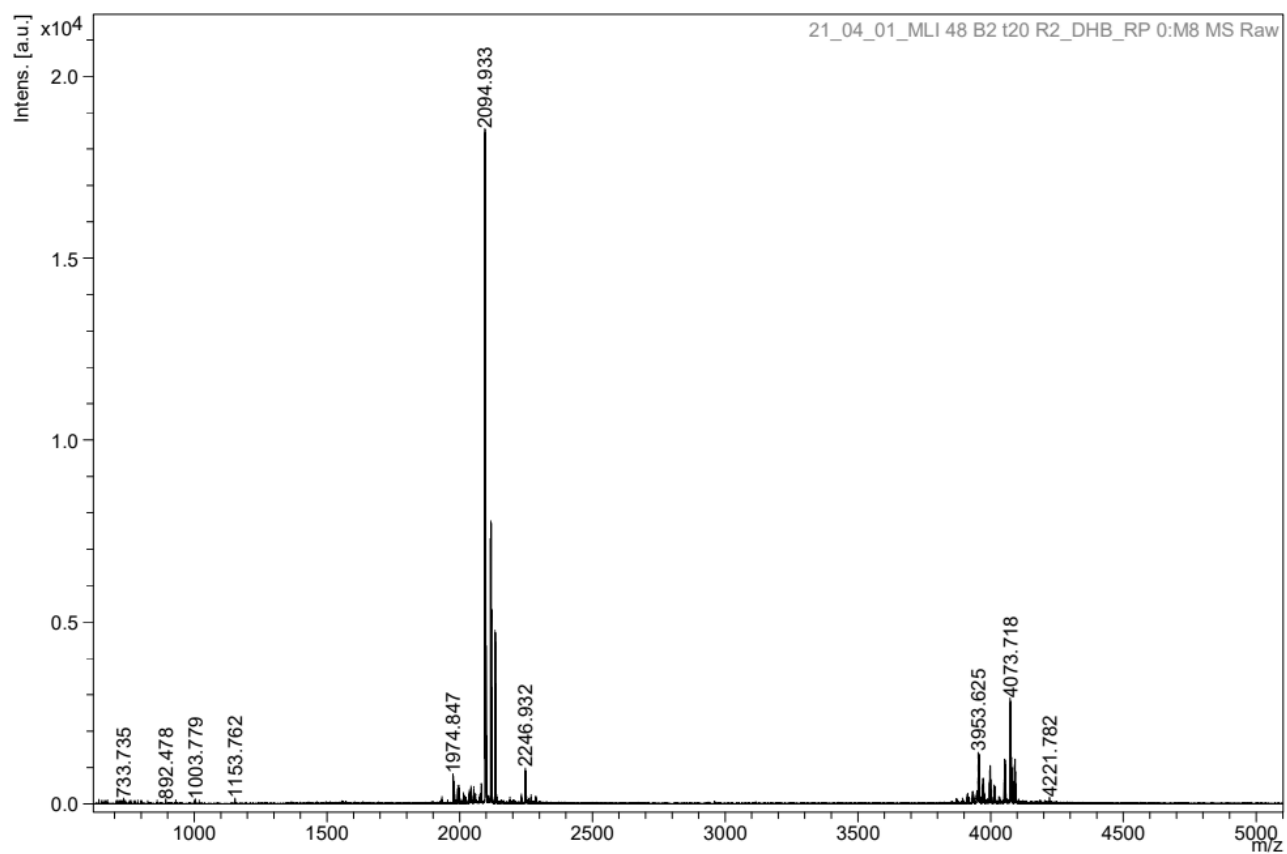
HSQC(CDCl₃) of 7Aq

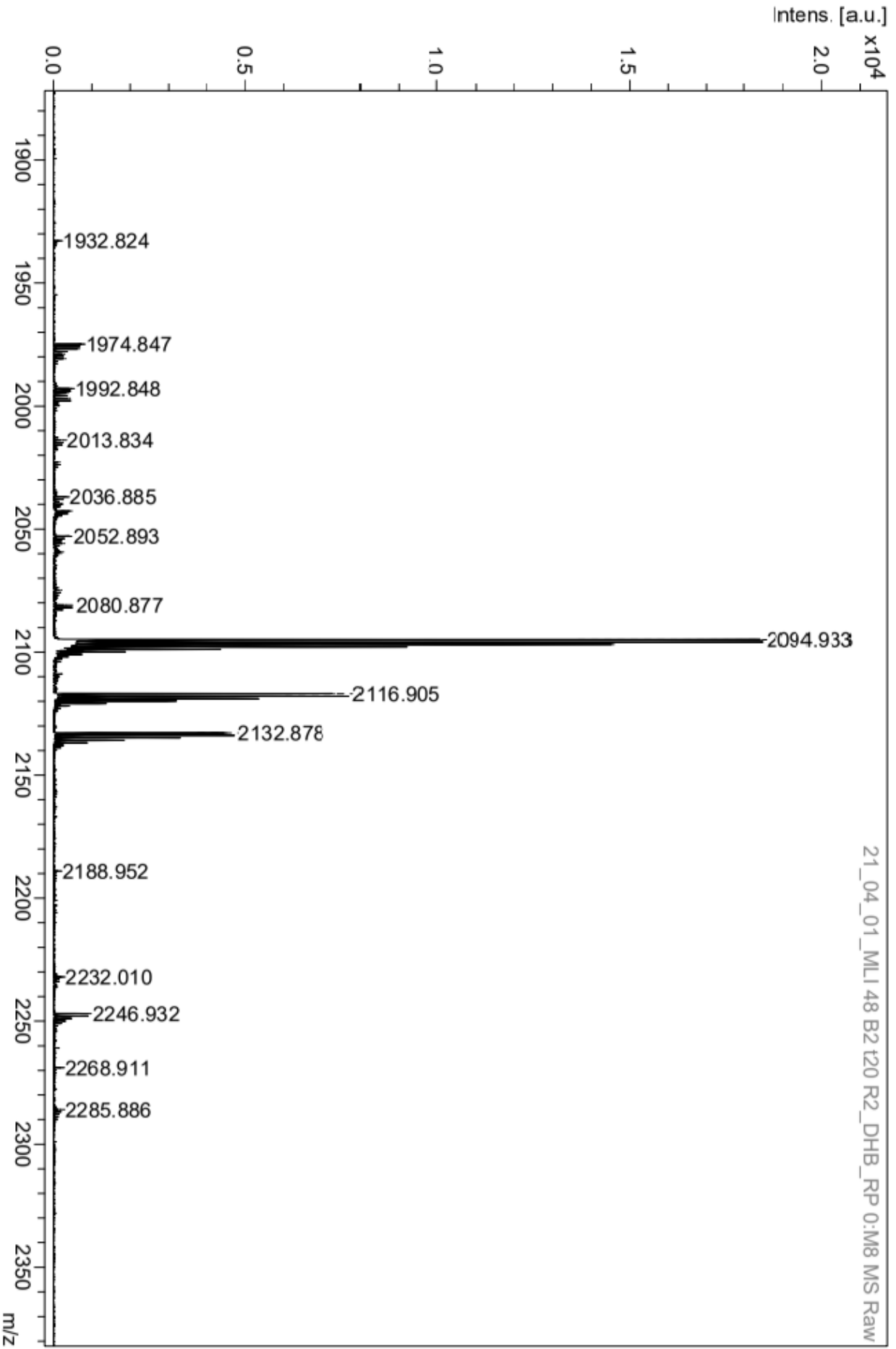


Characterisation of 7Ar (C₈₈H₁₁₅N₃O₅₅)



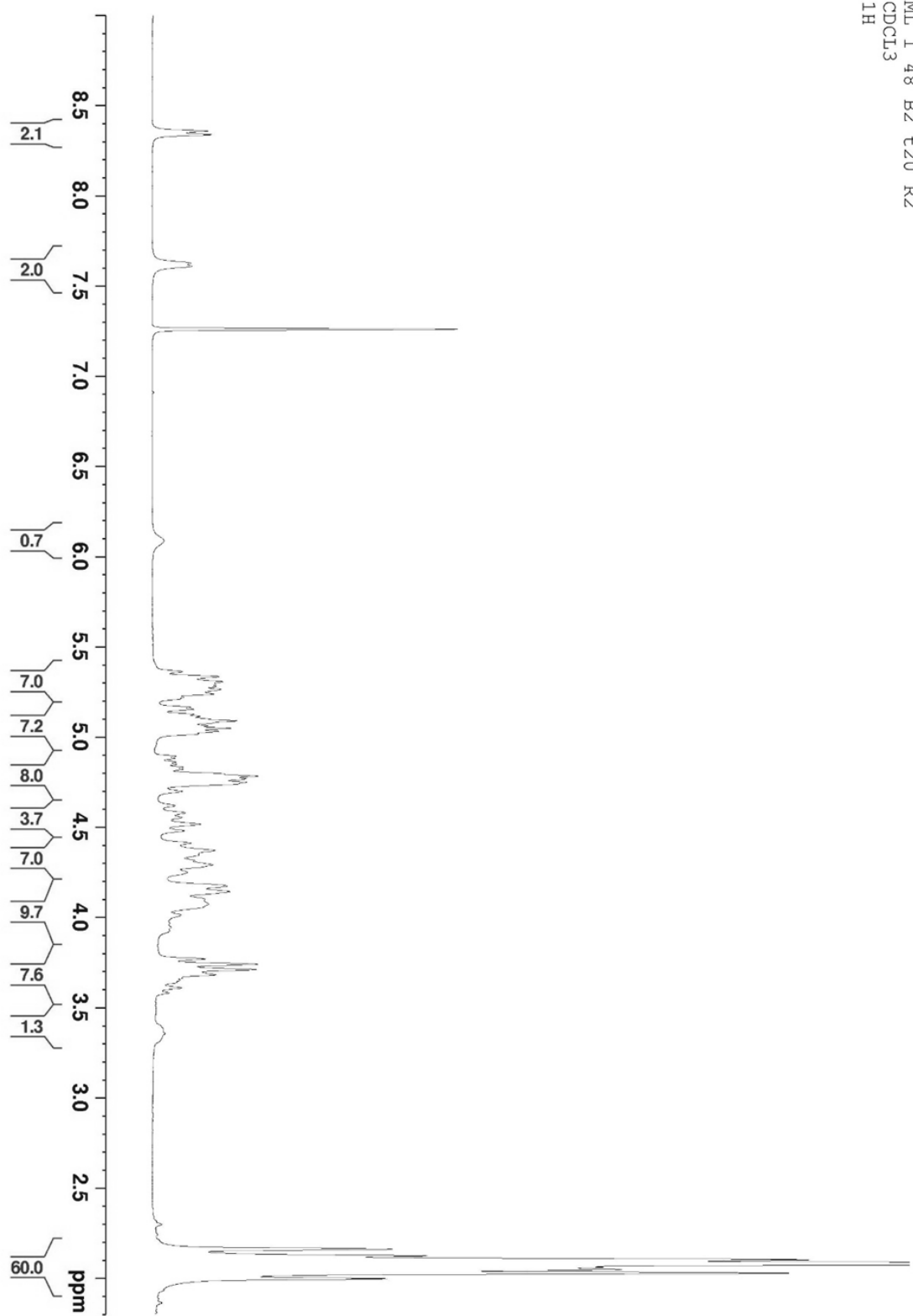
MALDI TOF of 7Ar

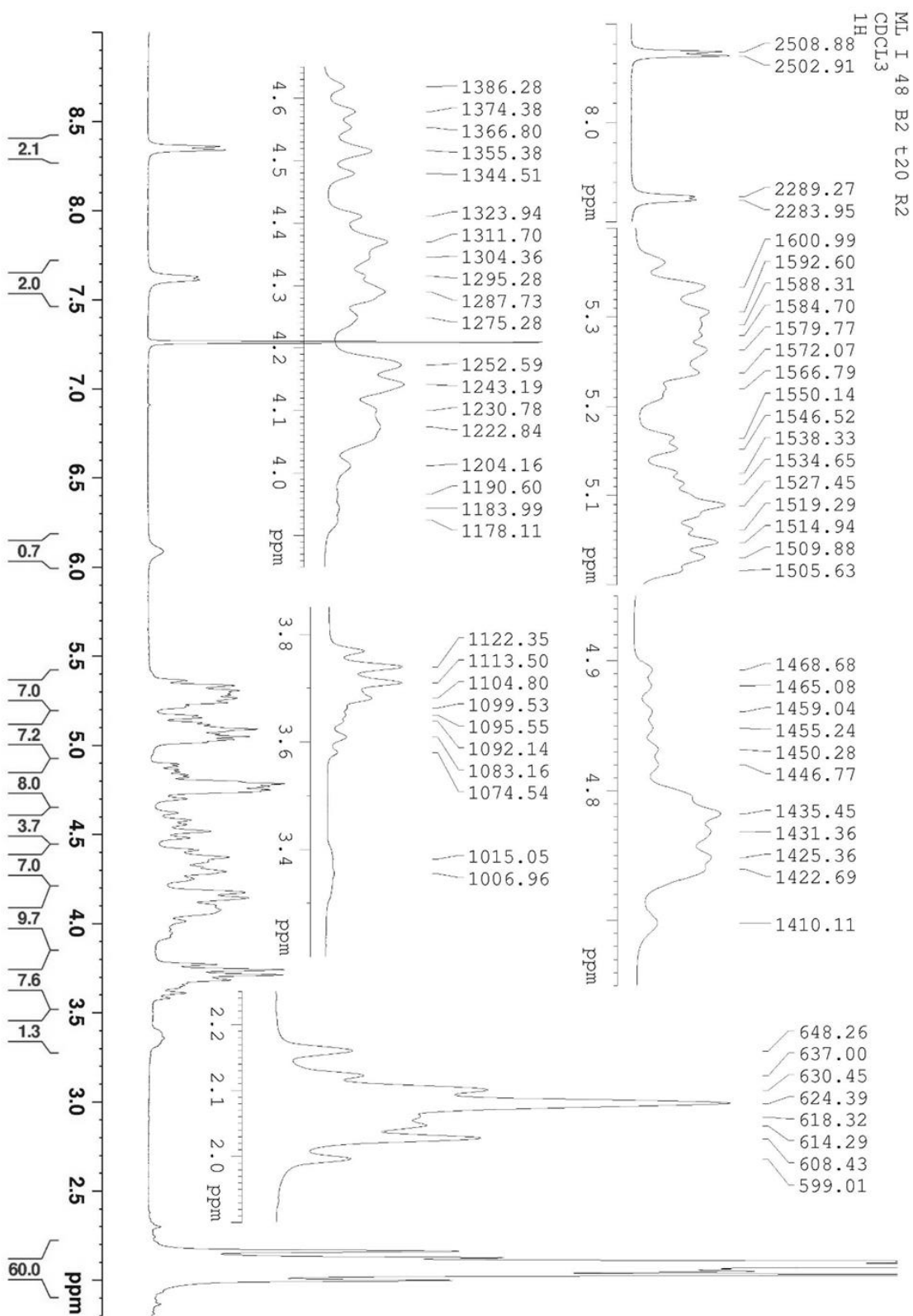




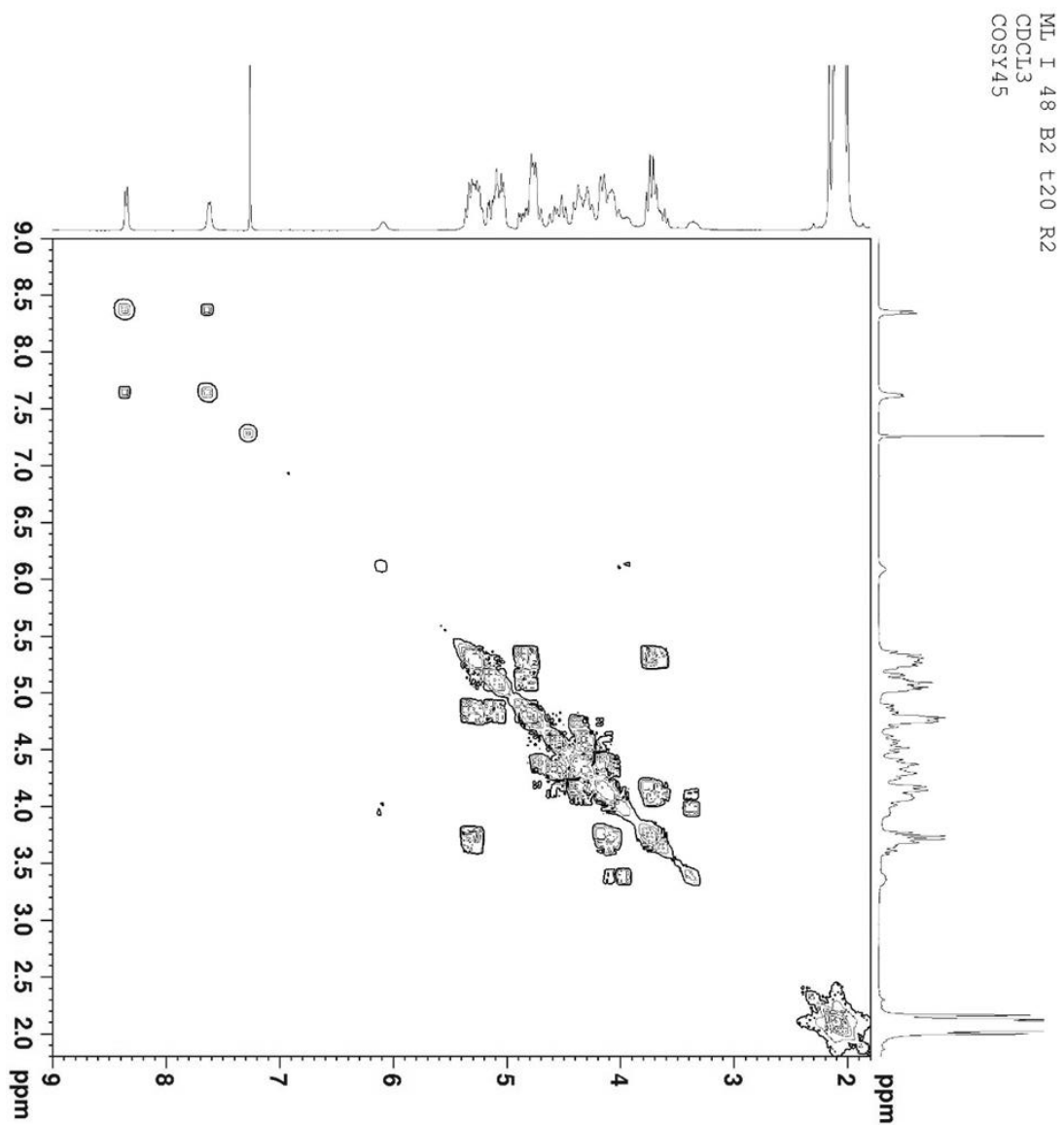
21_04_01_MLI 48 B2 t20 R2_DHB_RP 0:08 MS Raw

RMN¹H(CDCl₃) of 7Ar

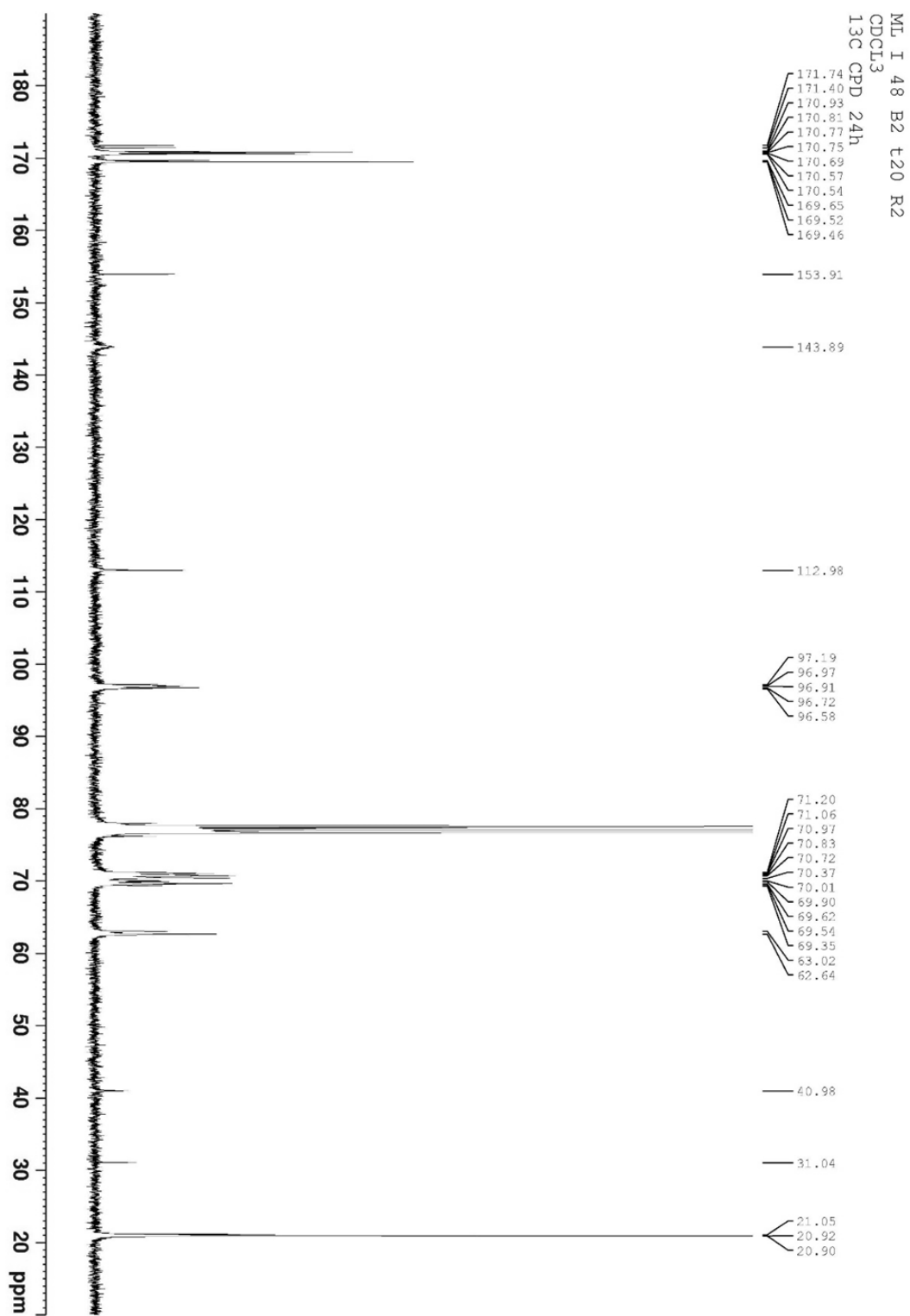




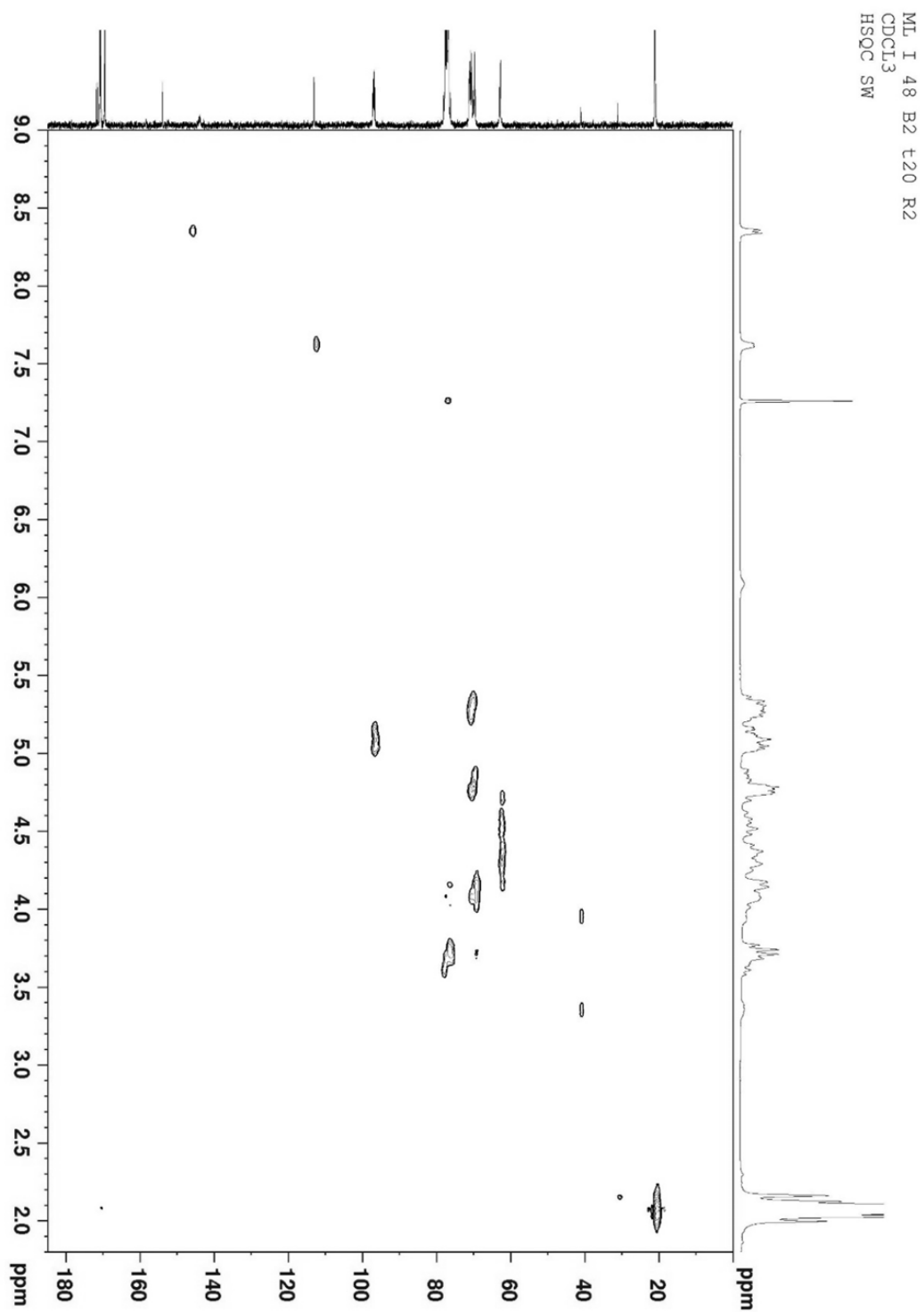
COSY (CDCl₃) of 7Ar



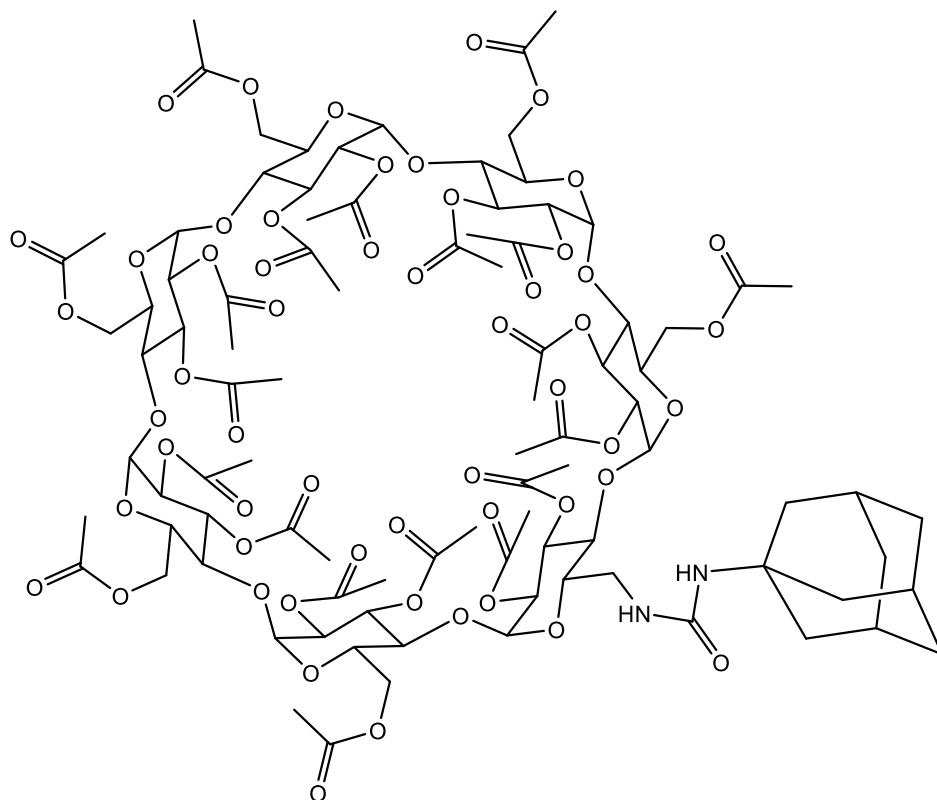
RMN¹³C(CDCl₃) of 7Ar



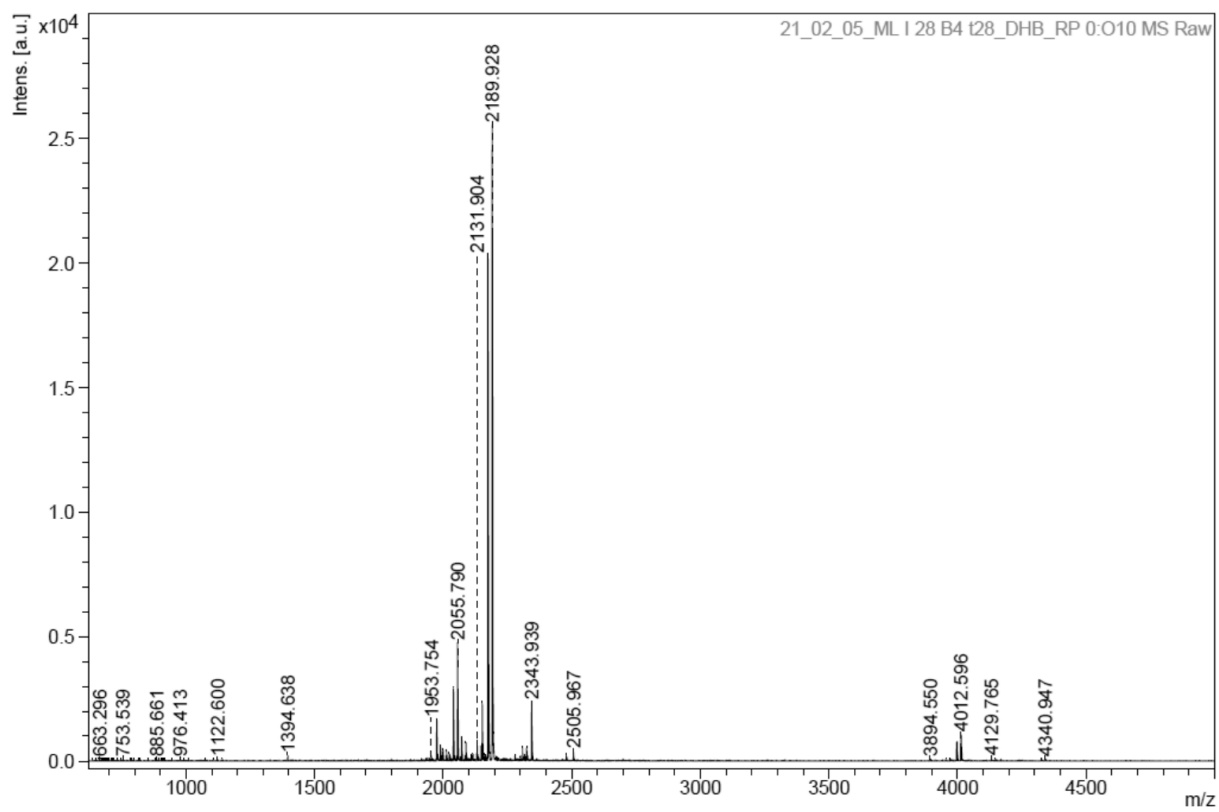
HSQC(CDCl₃) of 7Ar

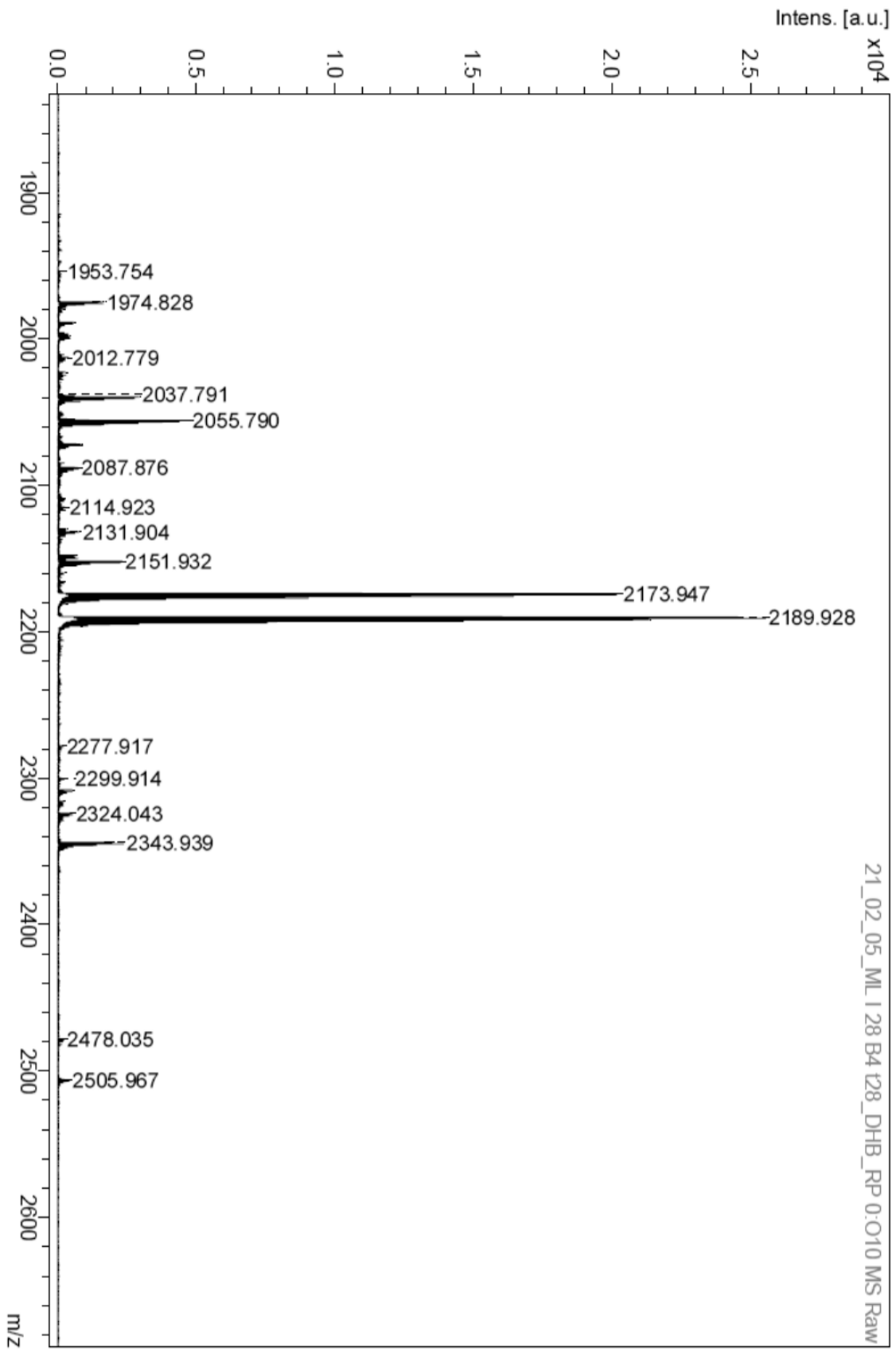


Characterisation of 7As (C₉₃H₁₂₆N₂O₅₅)

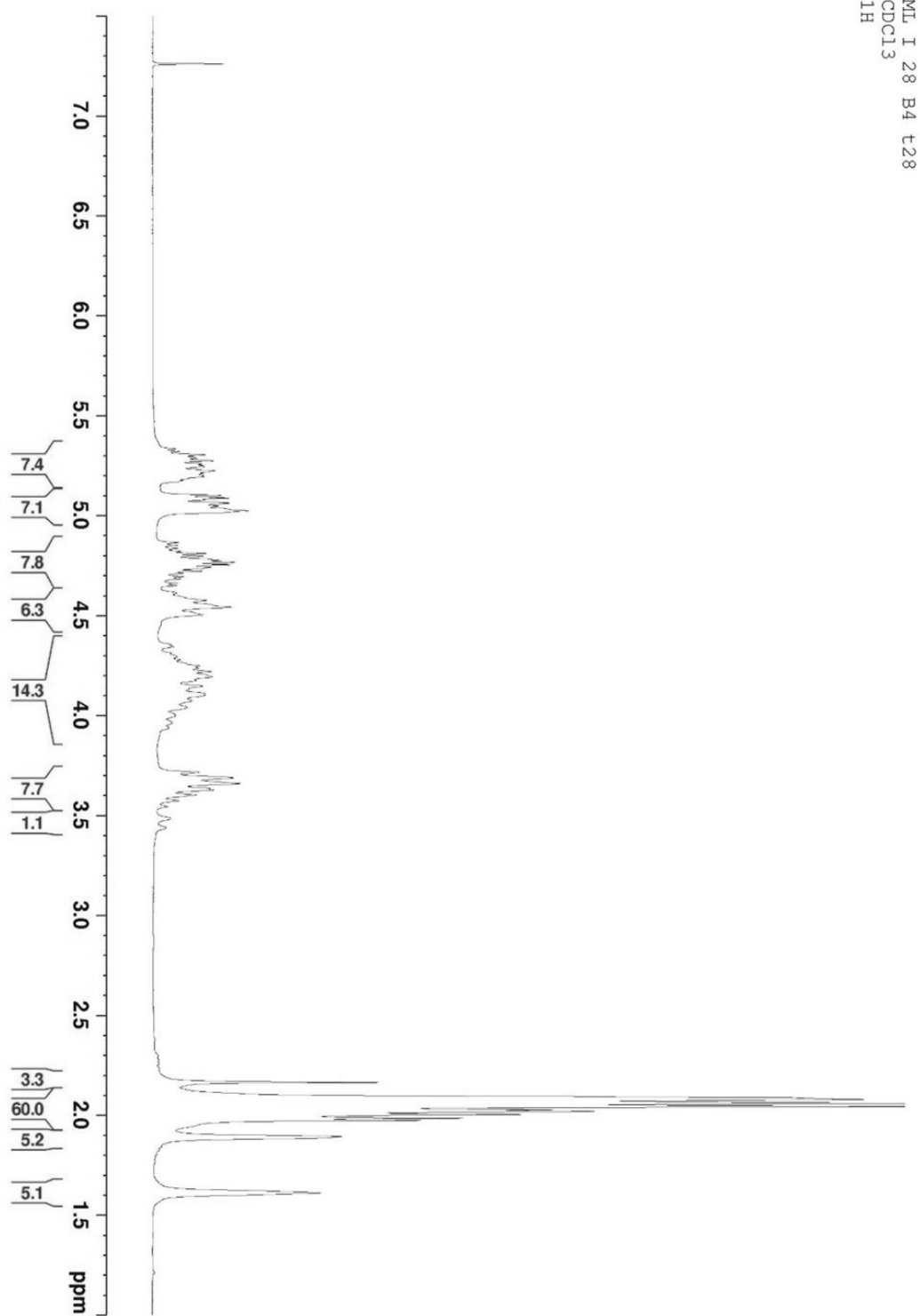


MALDI TOF of 7As

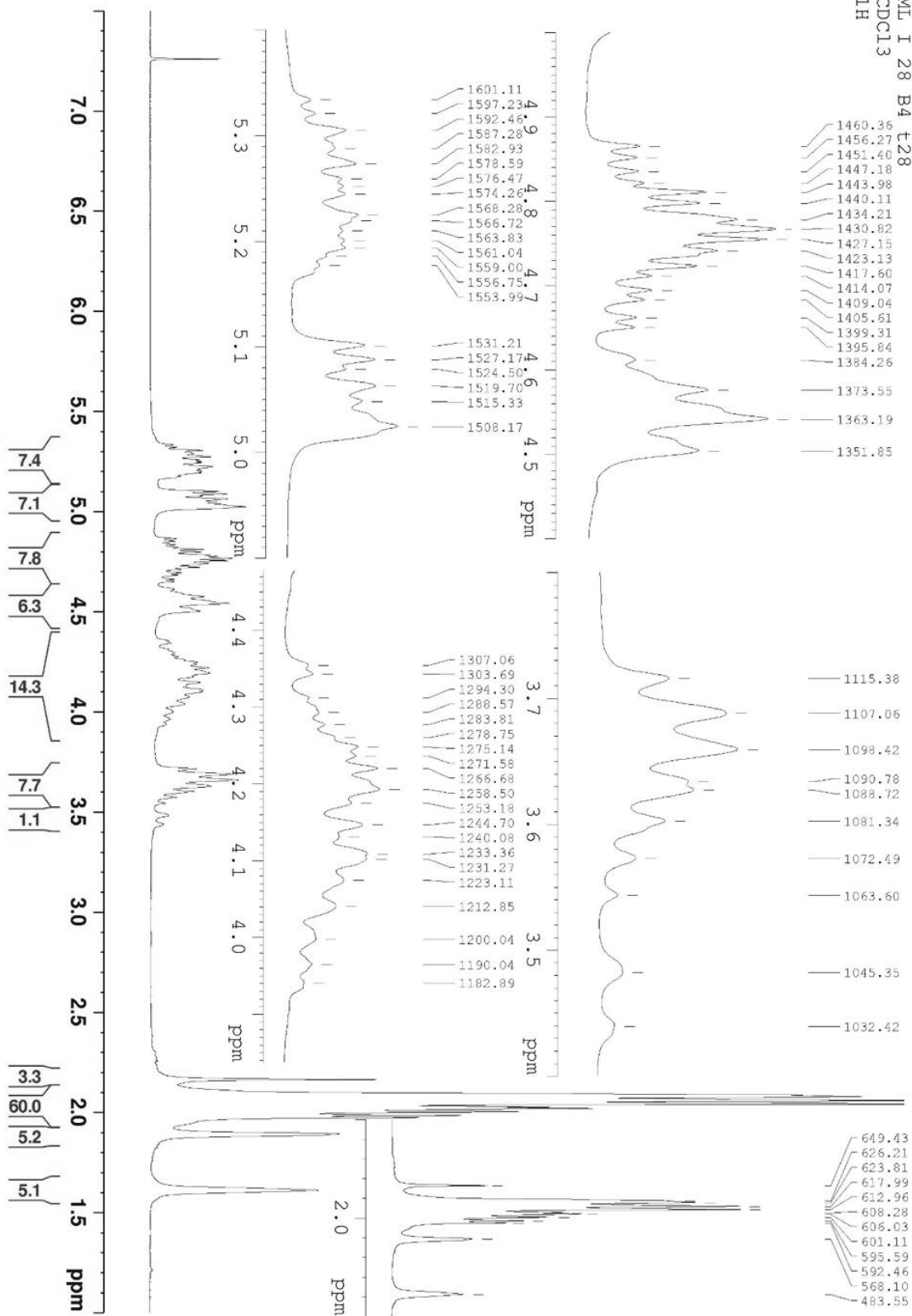




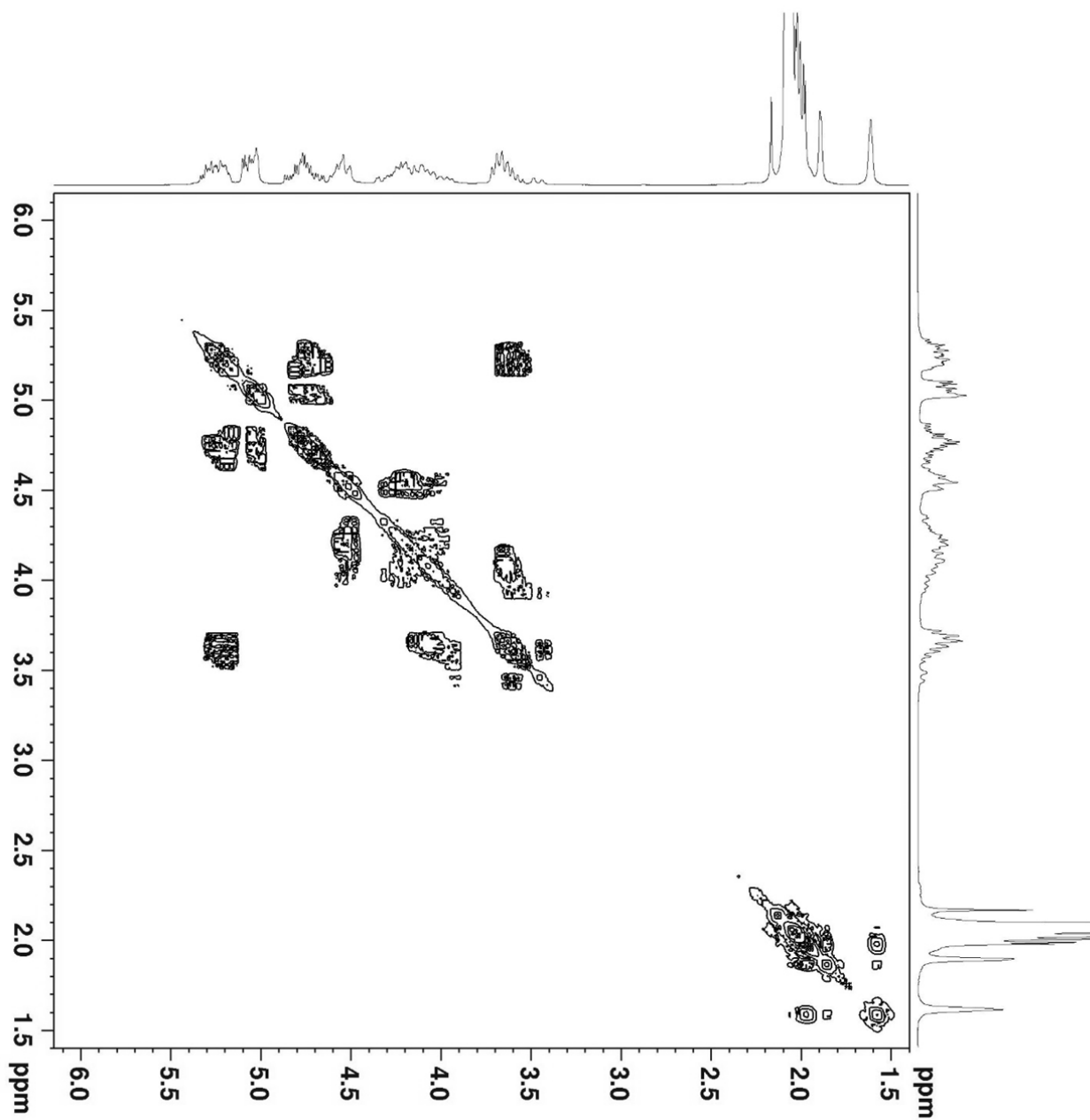
RMN¹H(CDCl₃) of 7As



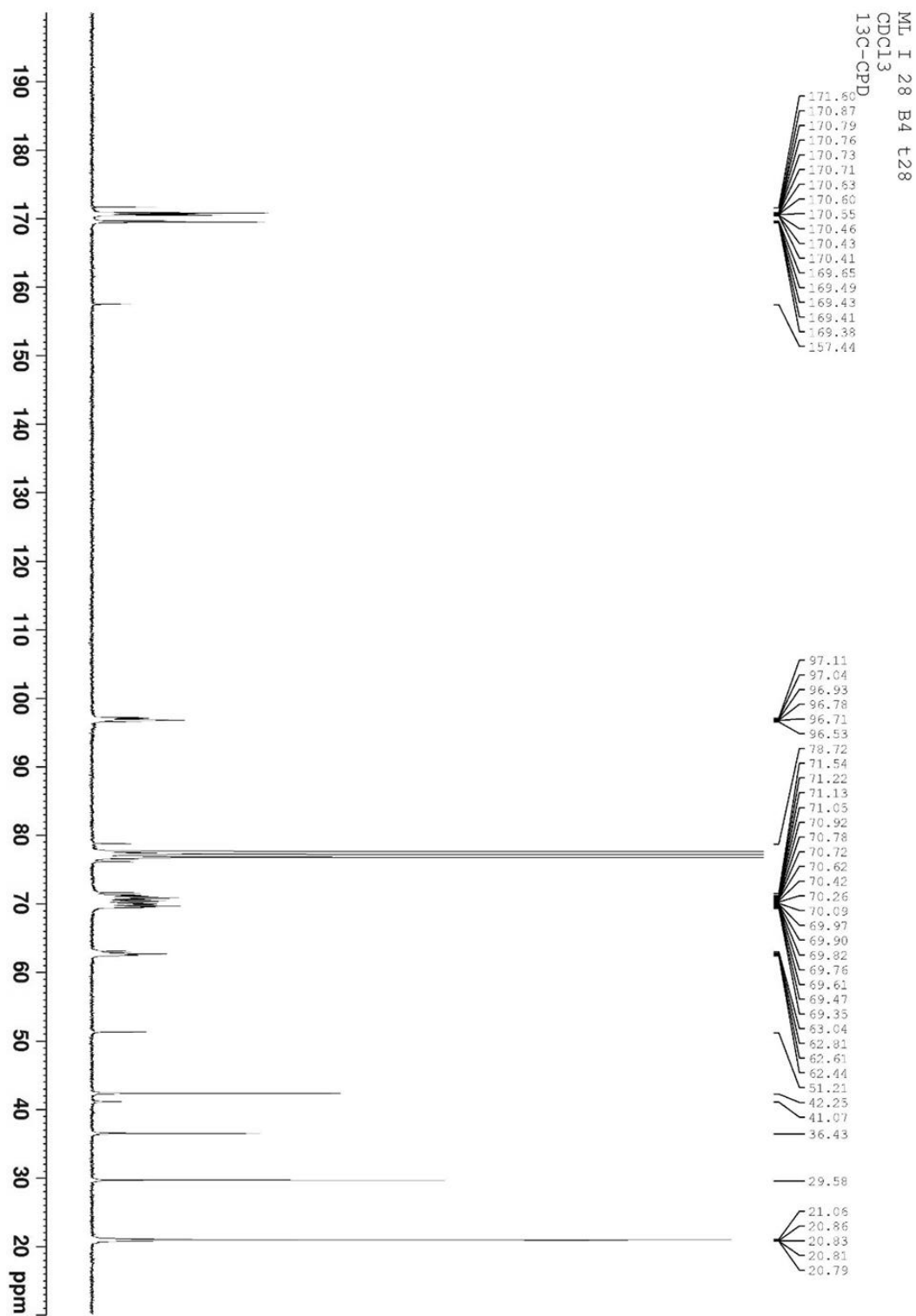
ML I 28 B4 t28
CDCl3
1H



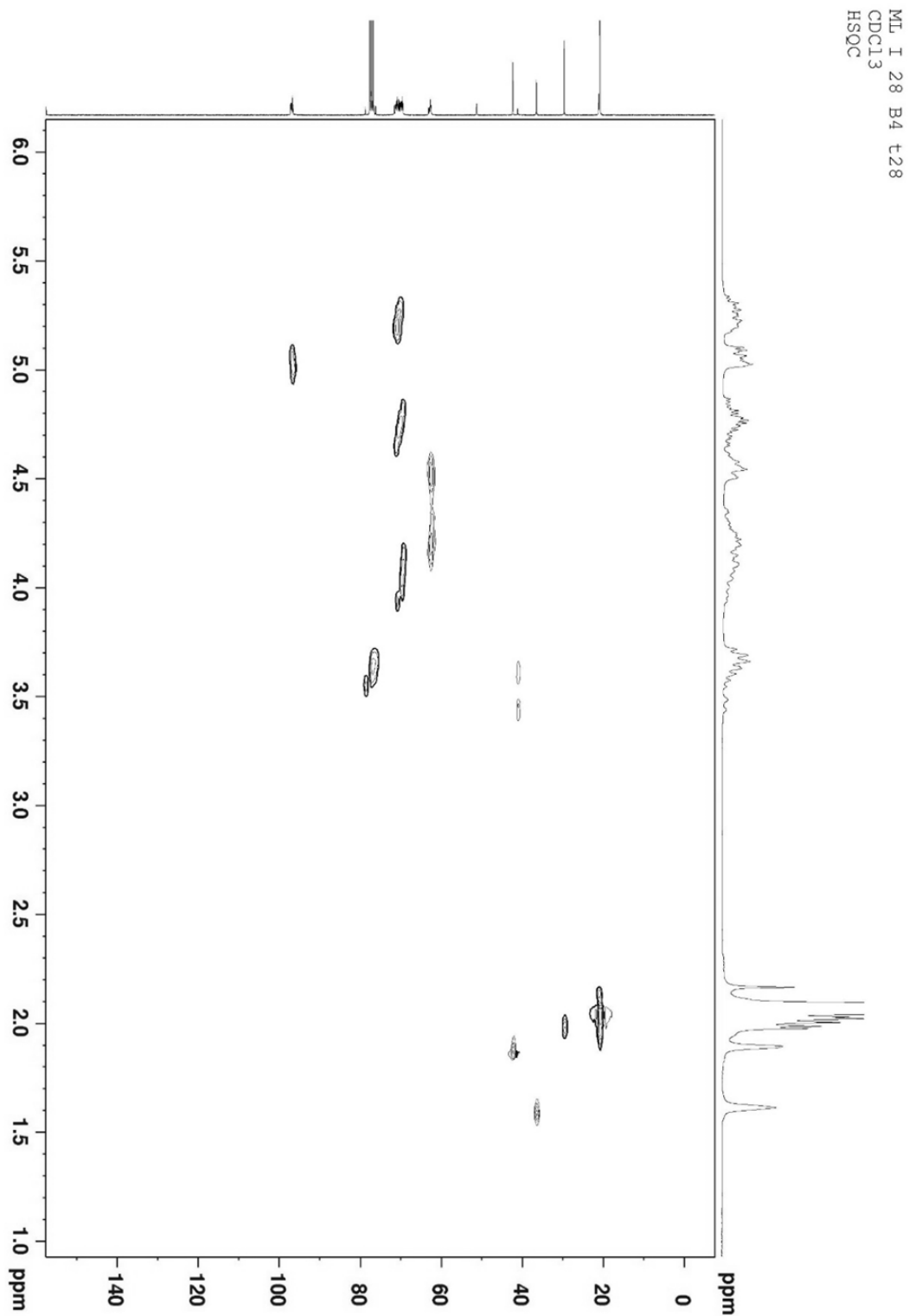
ML I 28 B4 t28
CDCl3
COSY45



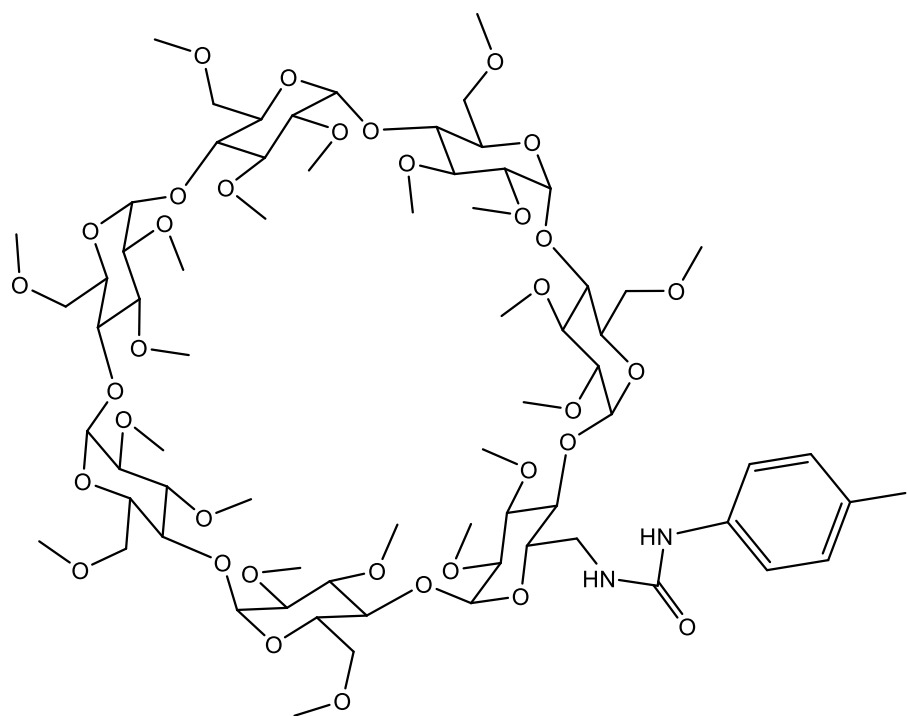
RMN¹³C(CDCl₃) of 7As



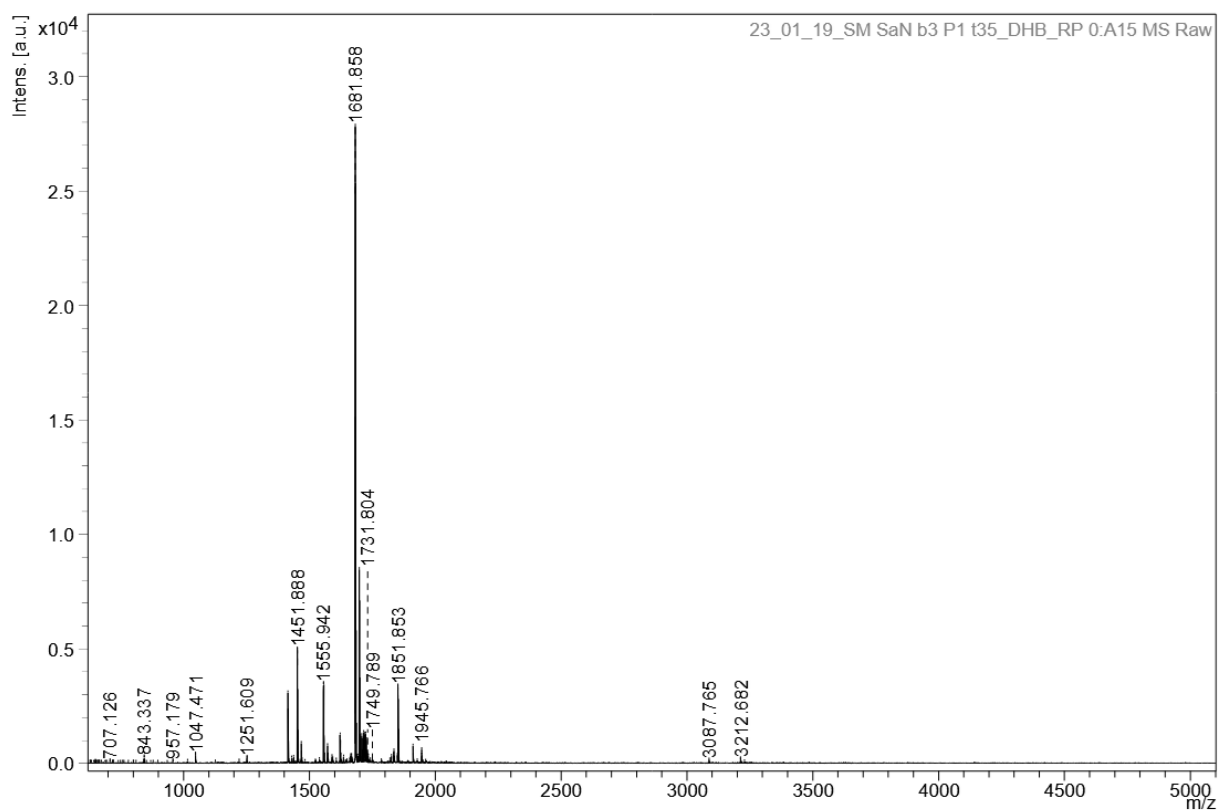
HSQC(CDCl₃) of 7As

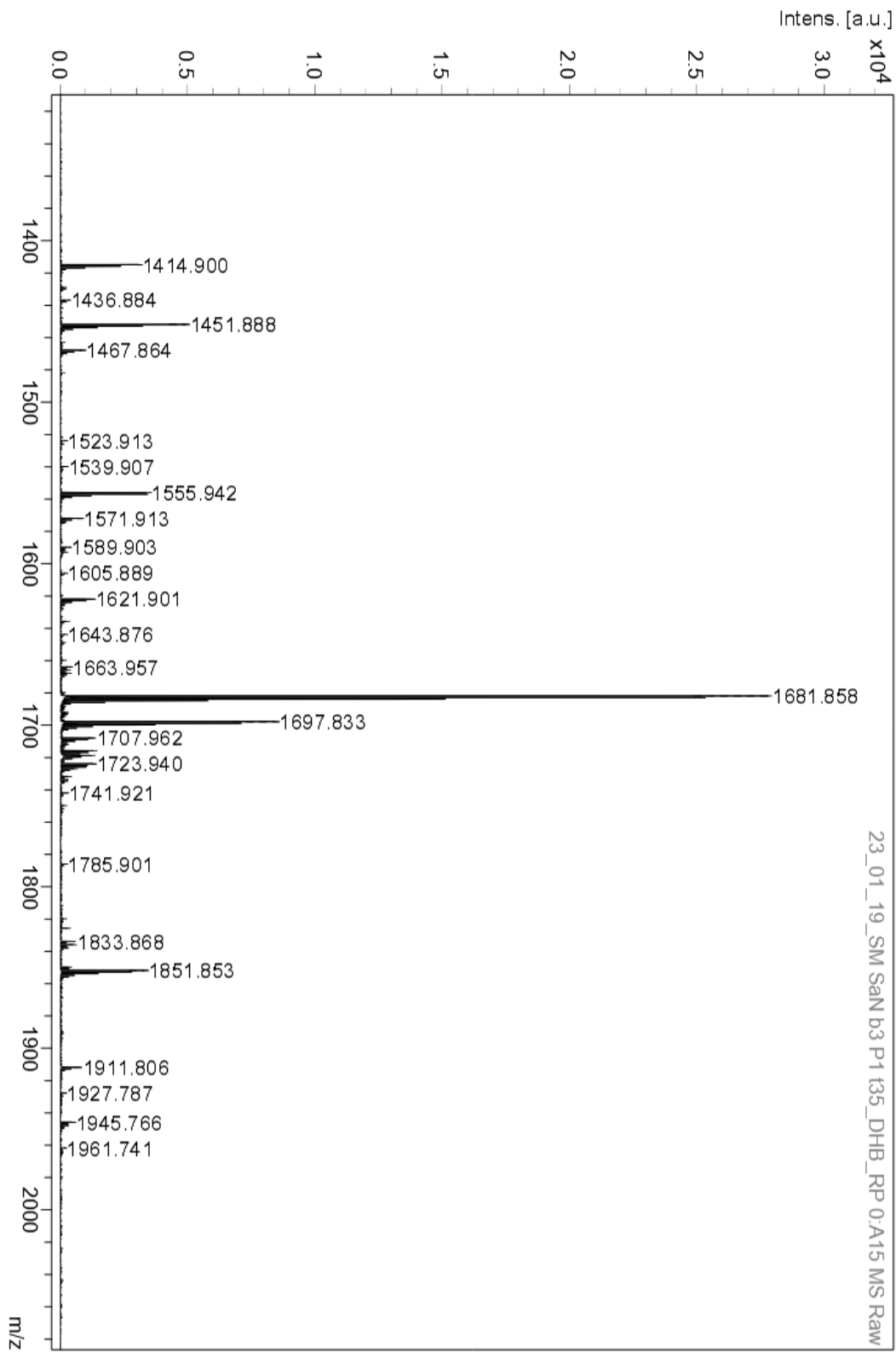


Characterisation of 7Ba (C₆₉H₁₁₅N₂O₃₅I)

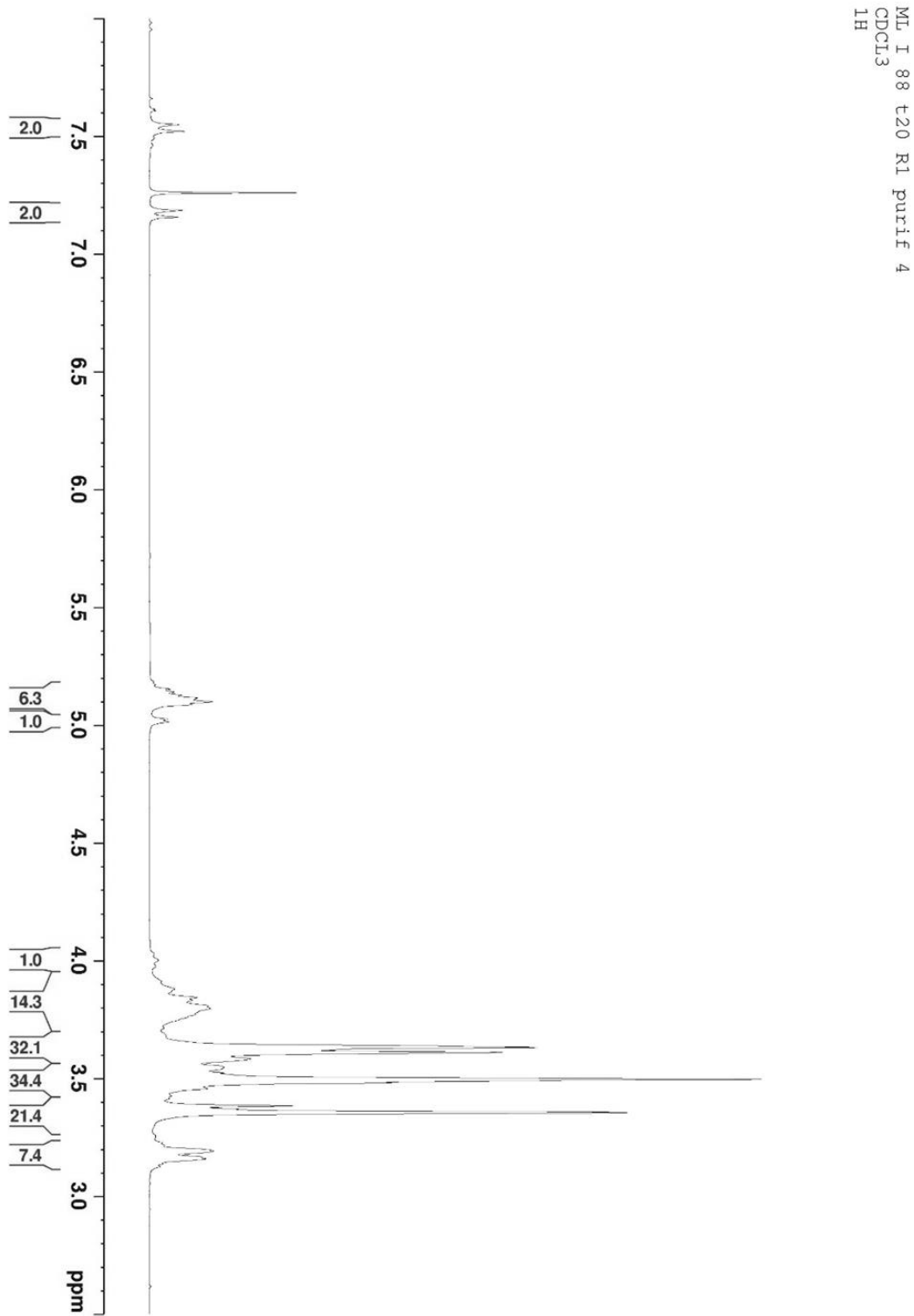


MALDI TOF of 7Ba

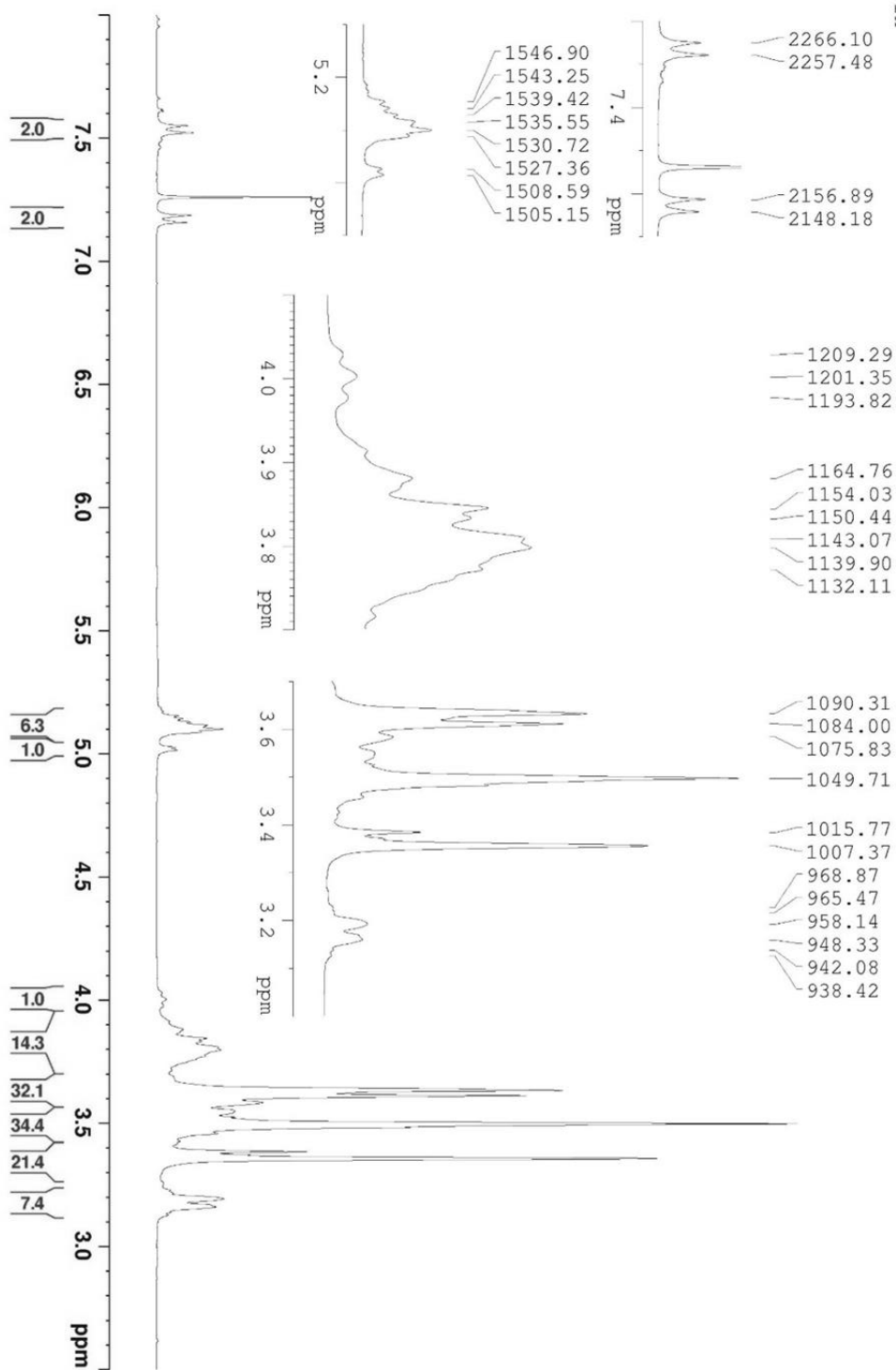




RMN¹H(CDCl₃) of 7Ba

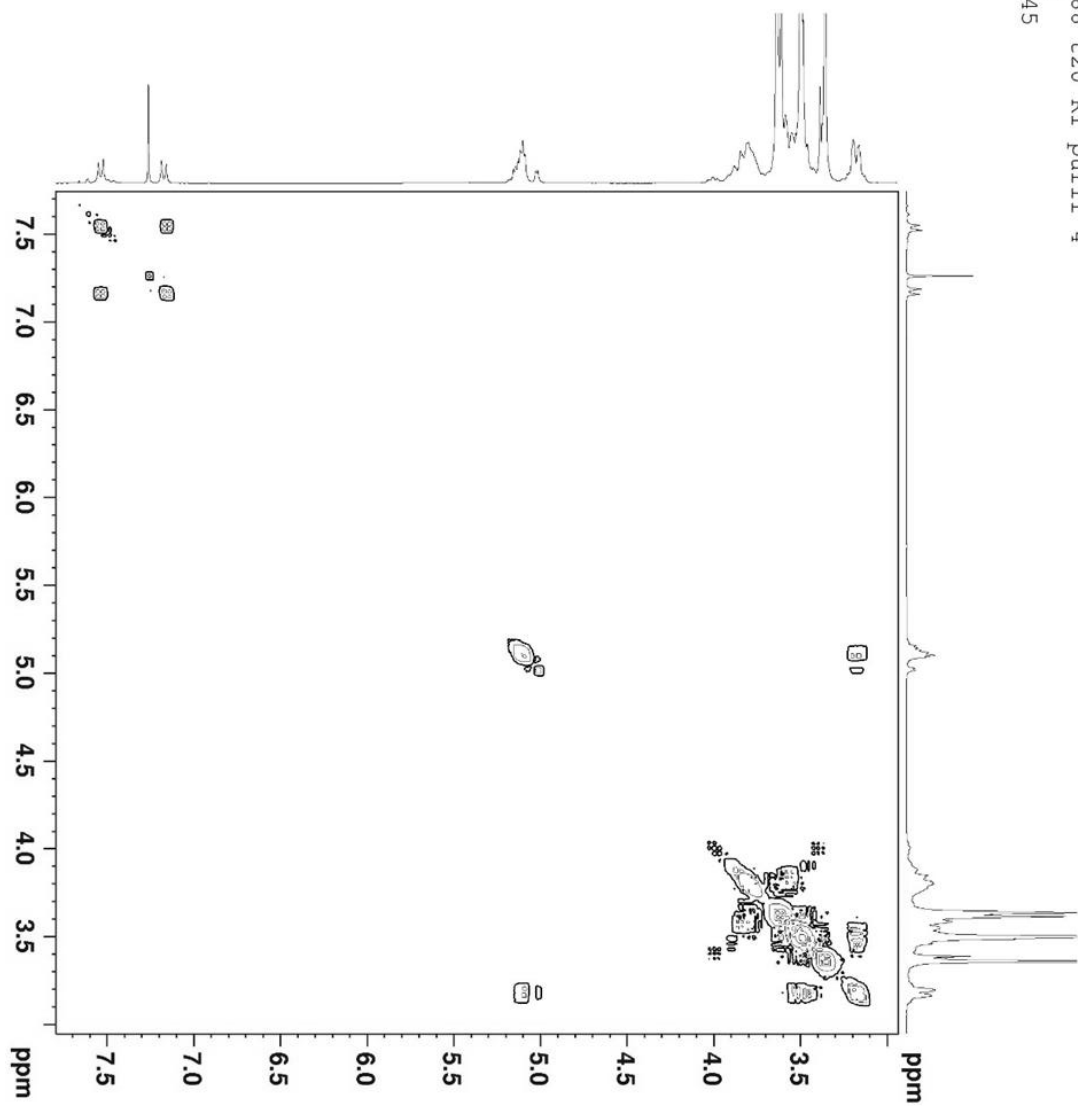


ML I 88 t20 R1 purif 4
CDCl3
1H

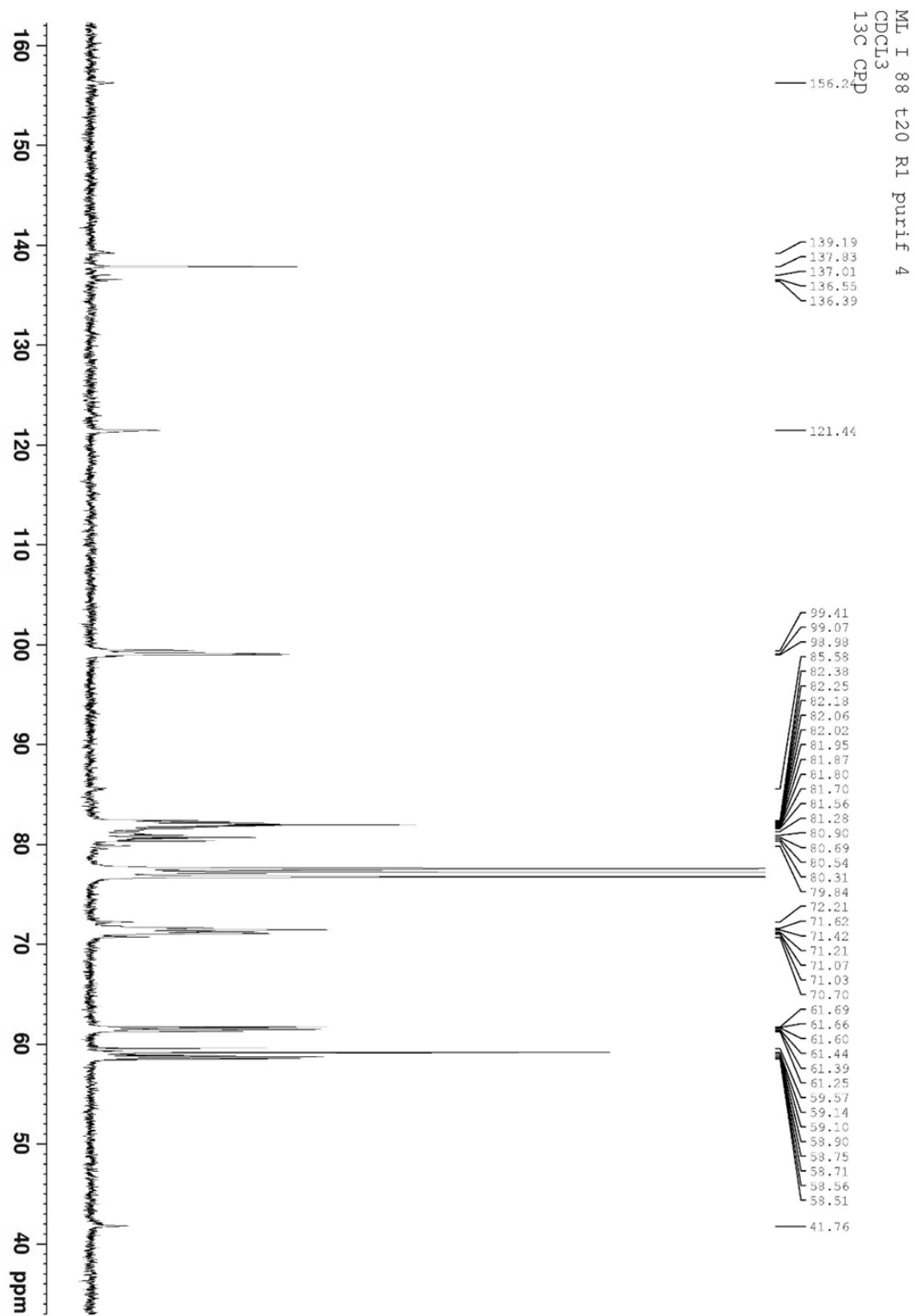


COSY (CDCl₃) of 7Ba

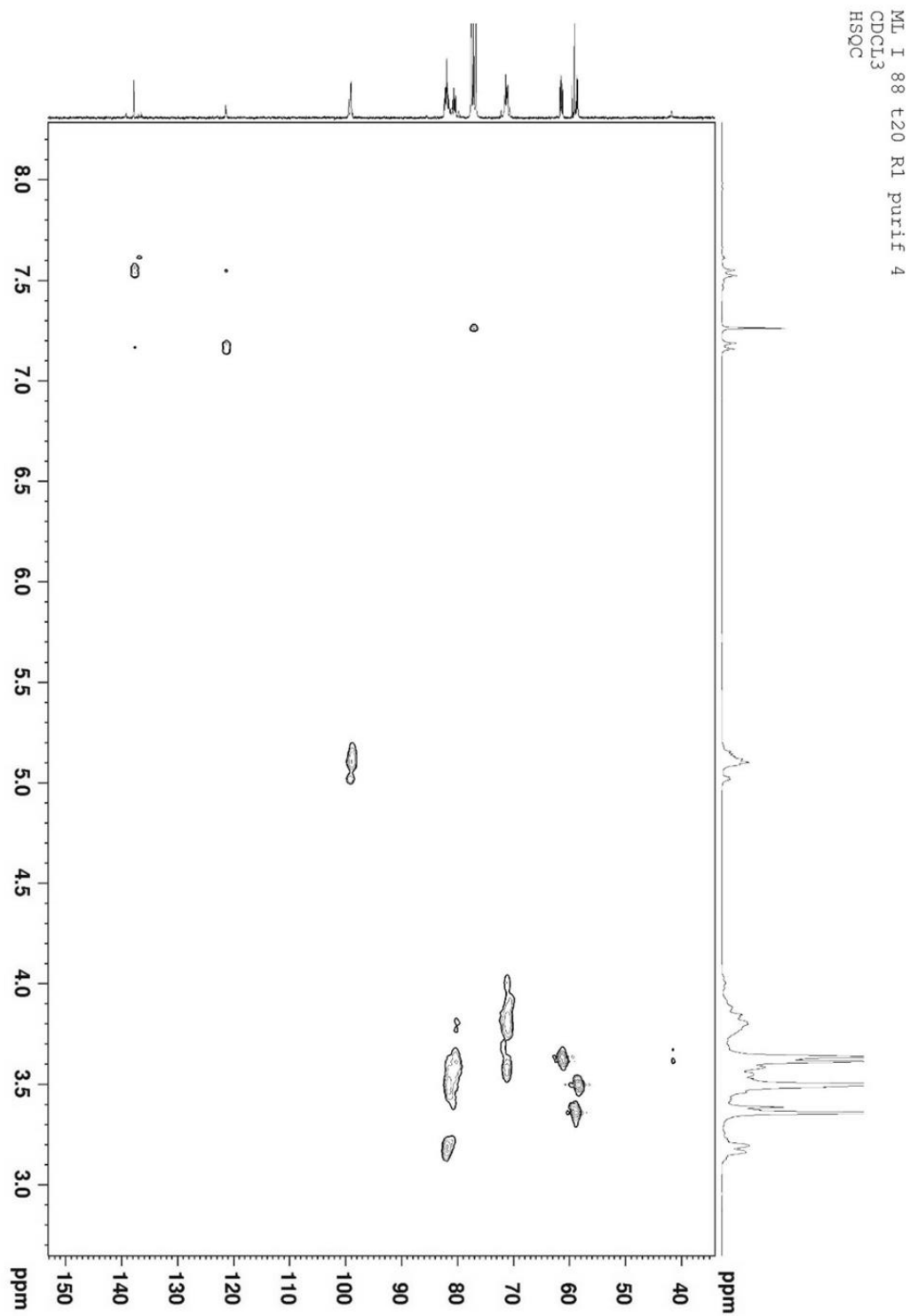
ML I 88 t20 R1 purif 4
CDCl₃
COSY 45



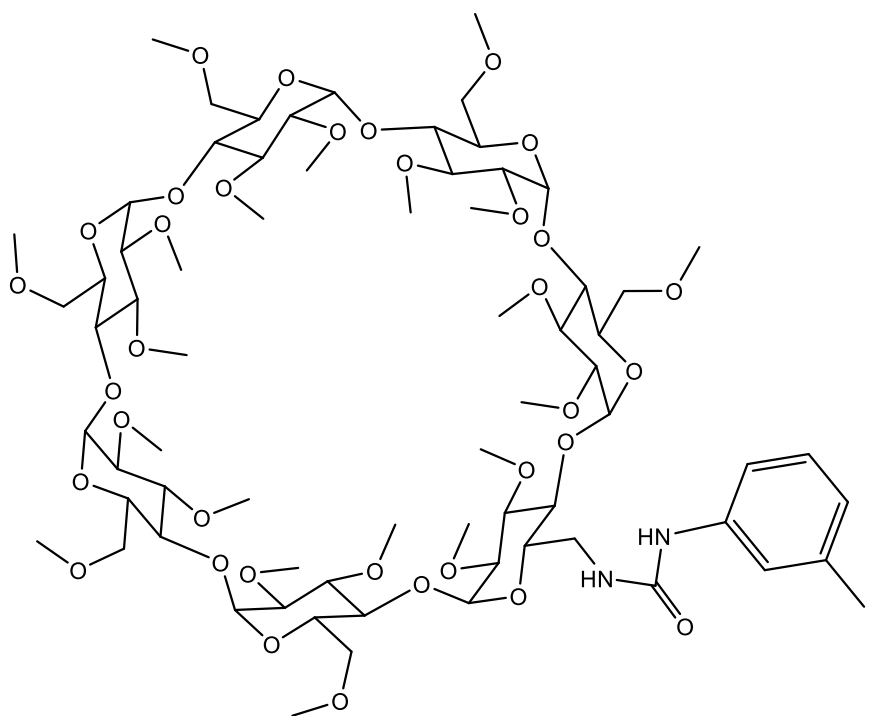
RMN¹³C(CDCl₃) of 7Ba



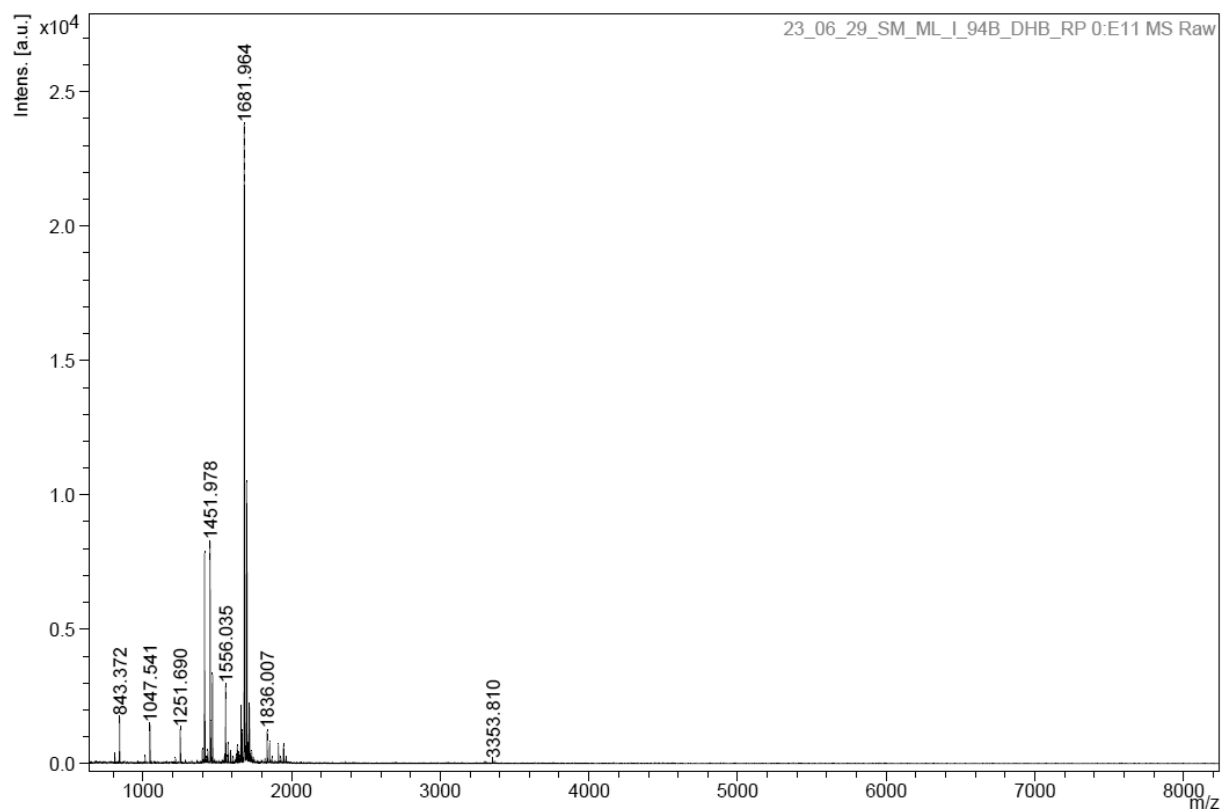
HSQC(CDCl₃) of 7Ba

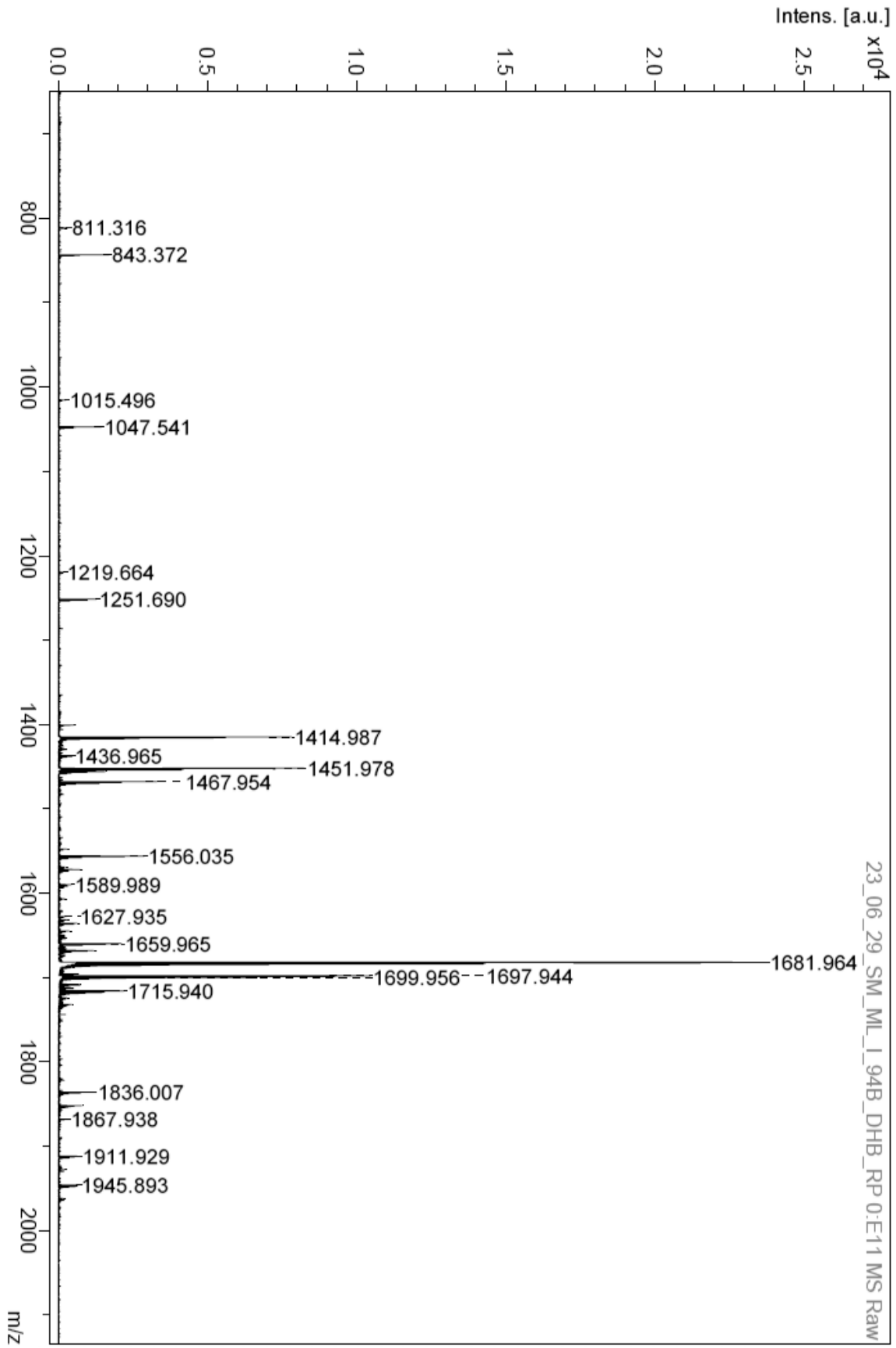


Characterisation of 7Bf (C₆₉H₁₁₅N₂O₃₅I)

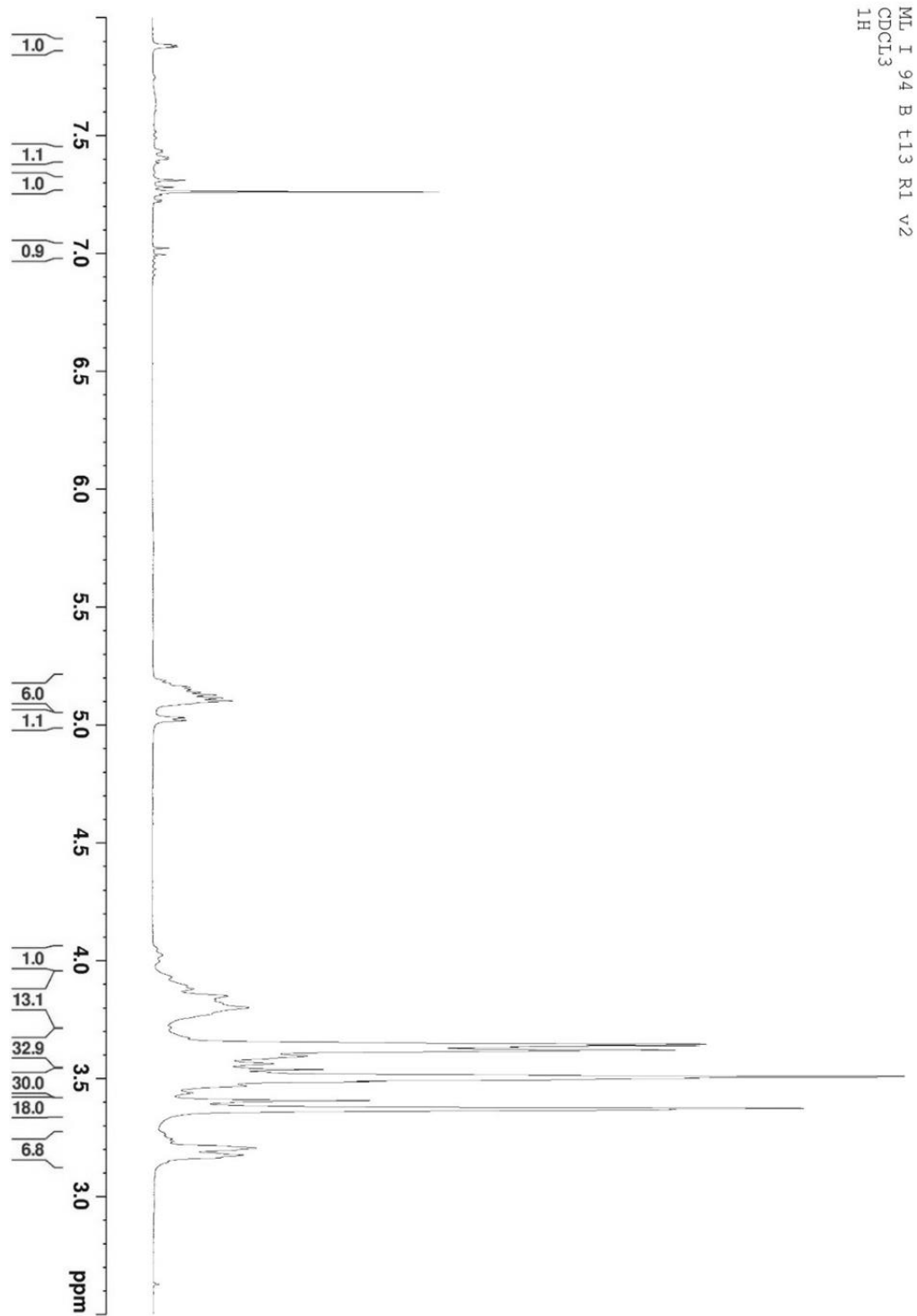


MALDI TOF of 7Bf

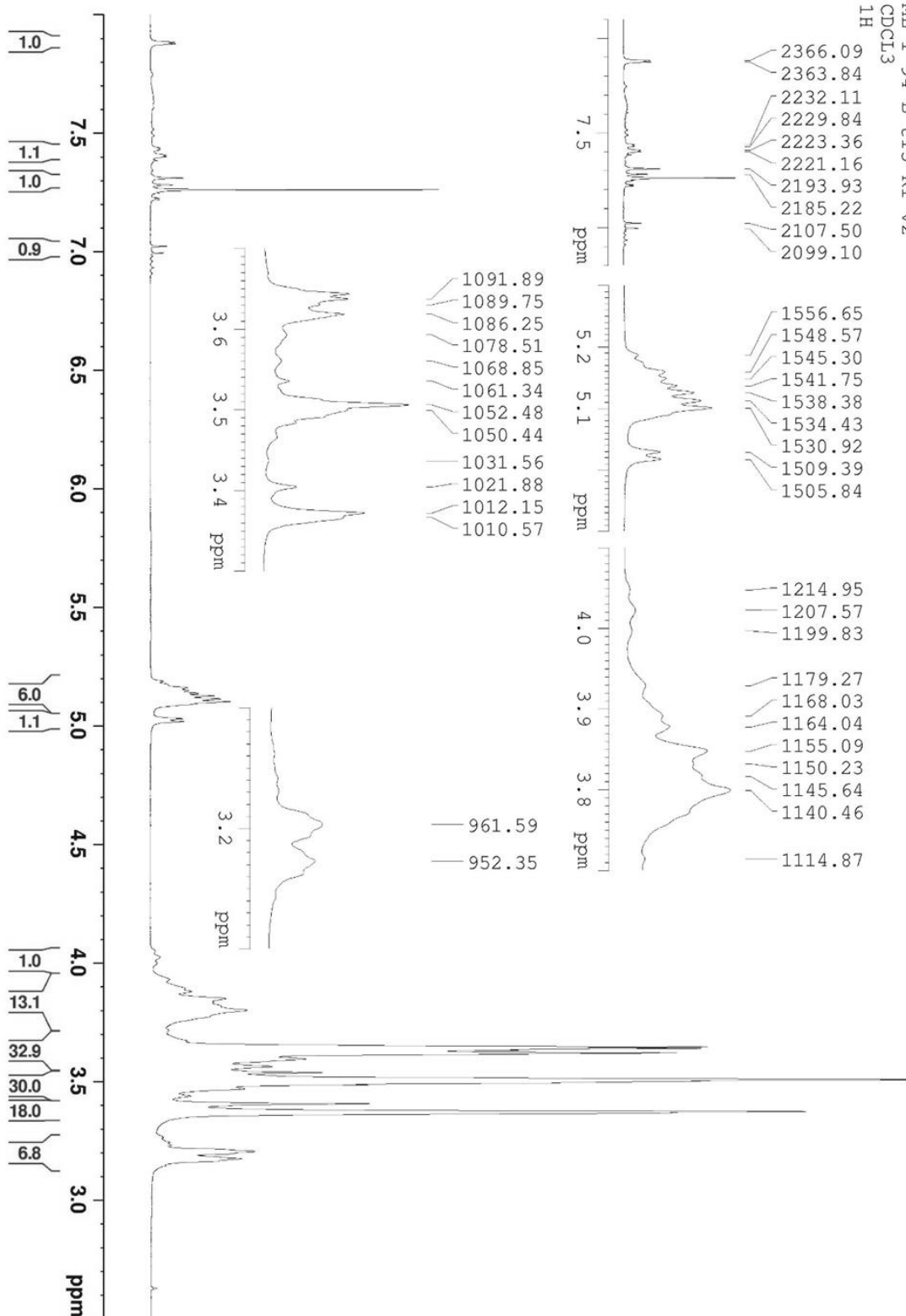




RMN¹H(CDCl₃) of 7Bf

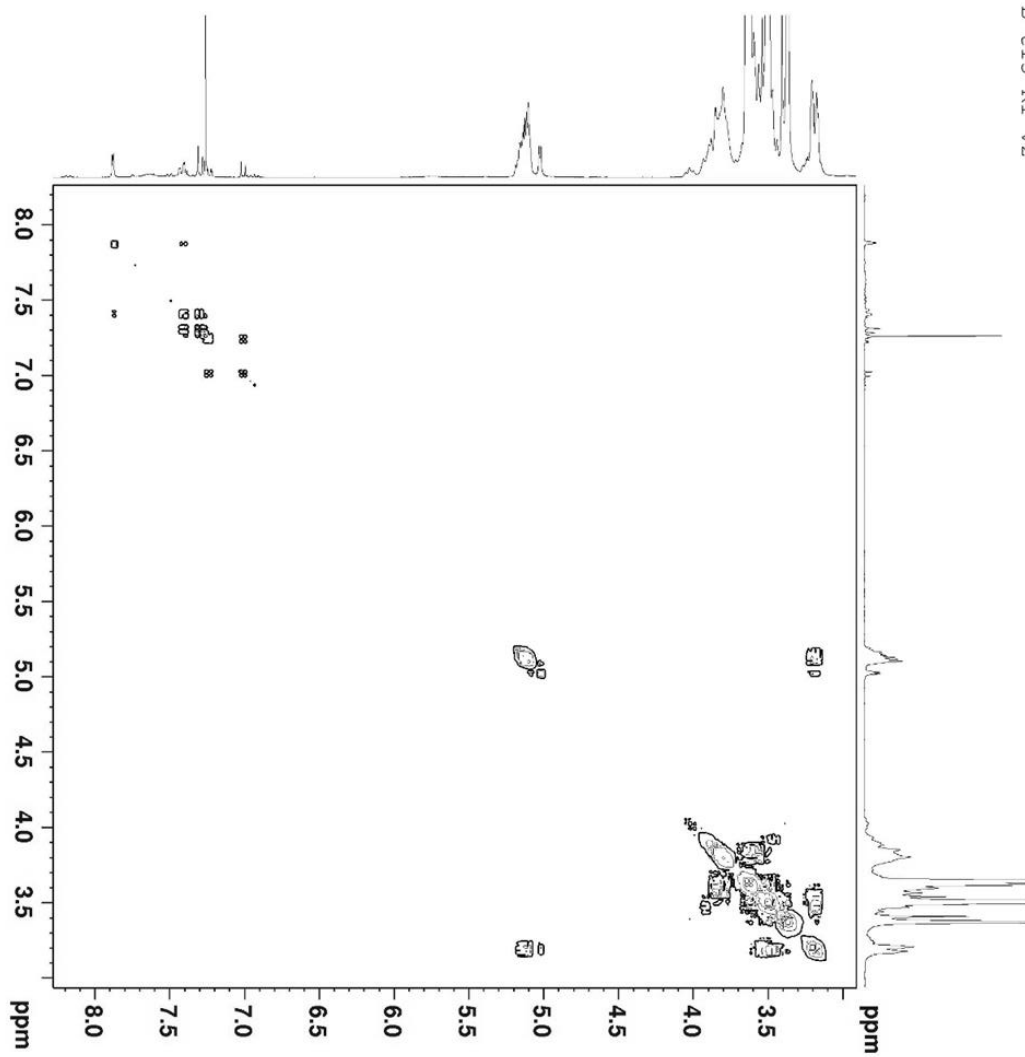


ML I 94 B t13 R1 v2
 CDCL3
 1H

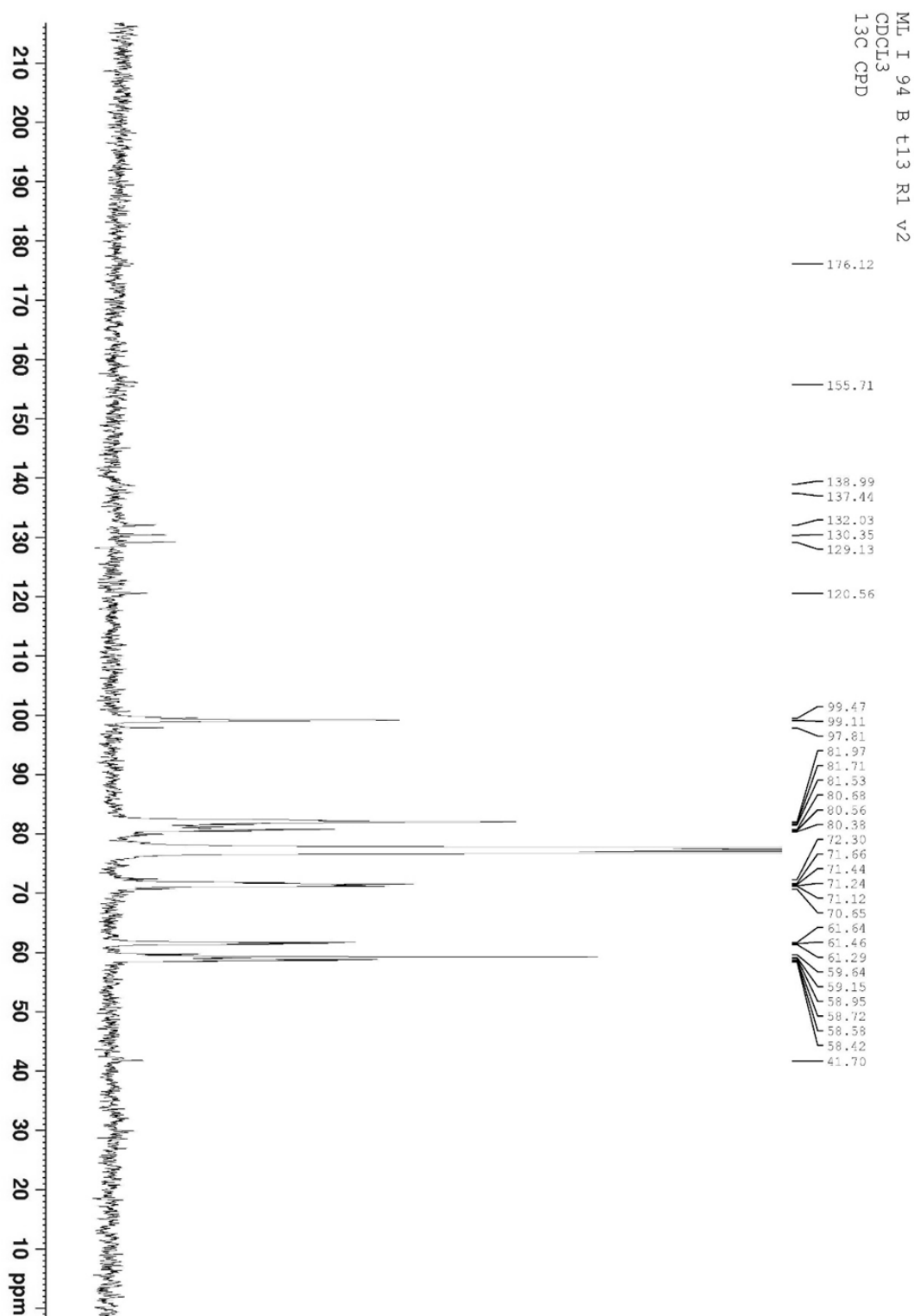


COSY (CDCl₃) of 7Bf

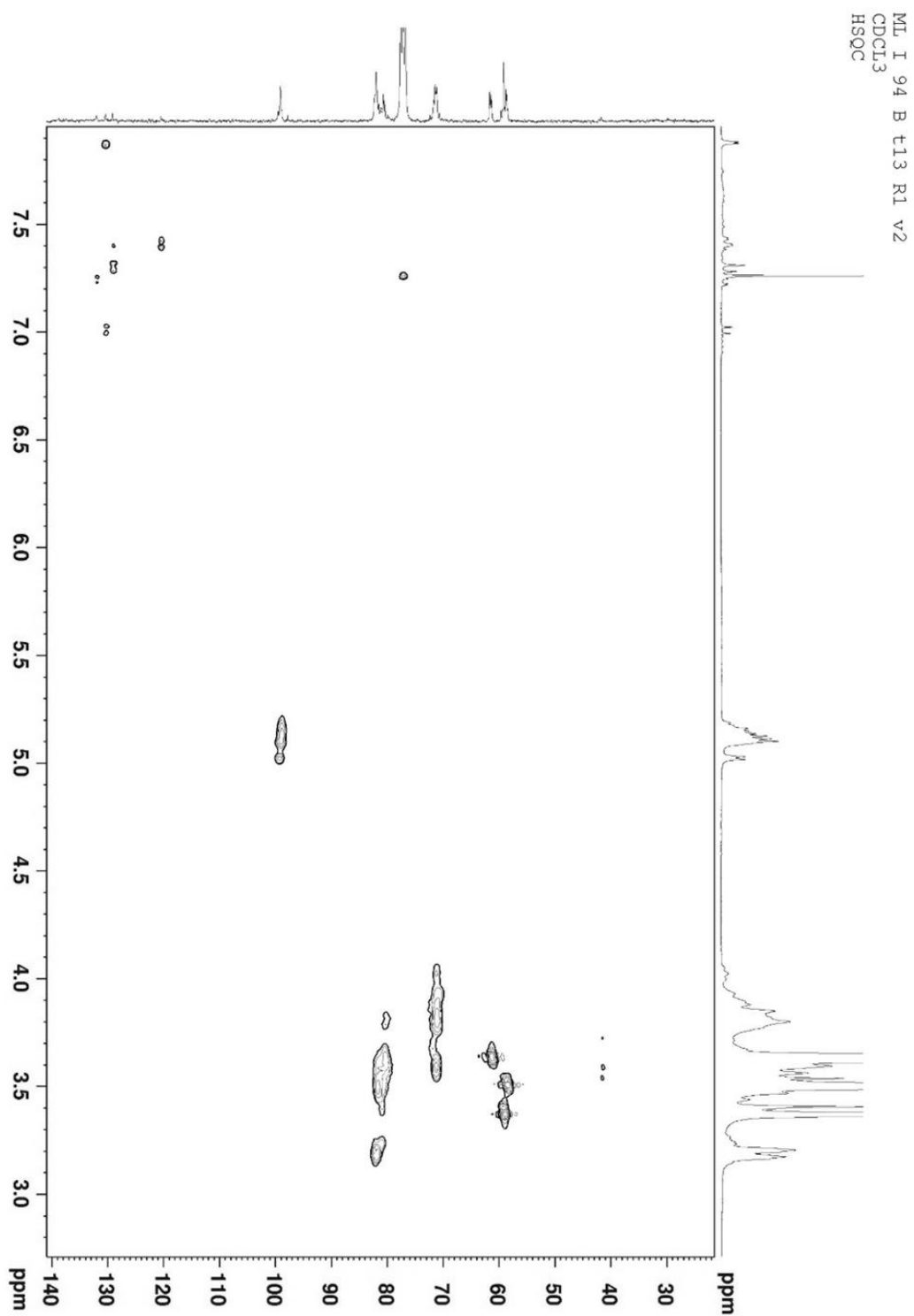
ML I 94 B t13 R1 v2
CDCl₃
COSY45



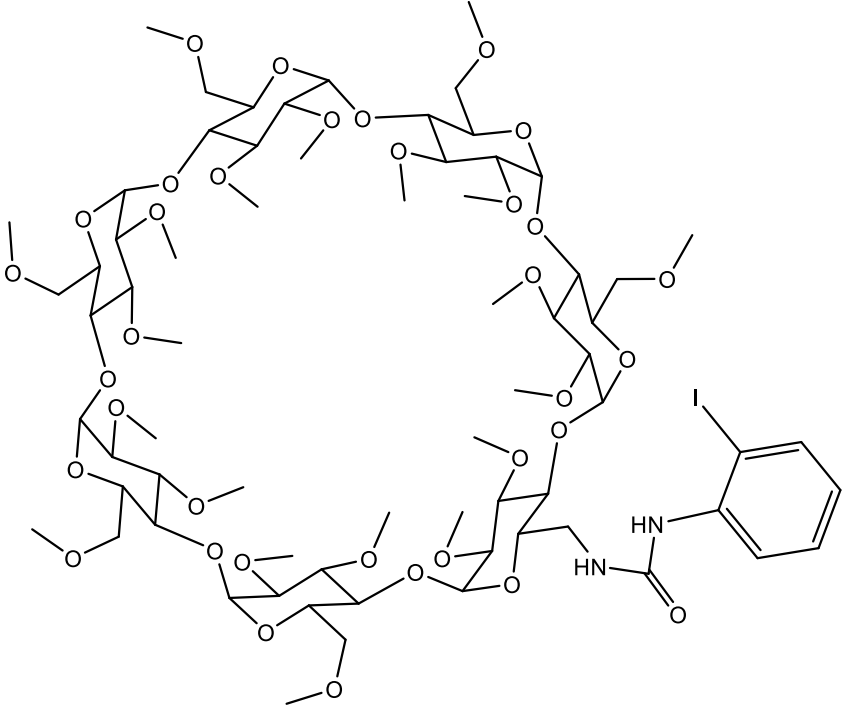
RMN¹³C(CDCl₃) of 7Bf



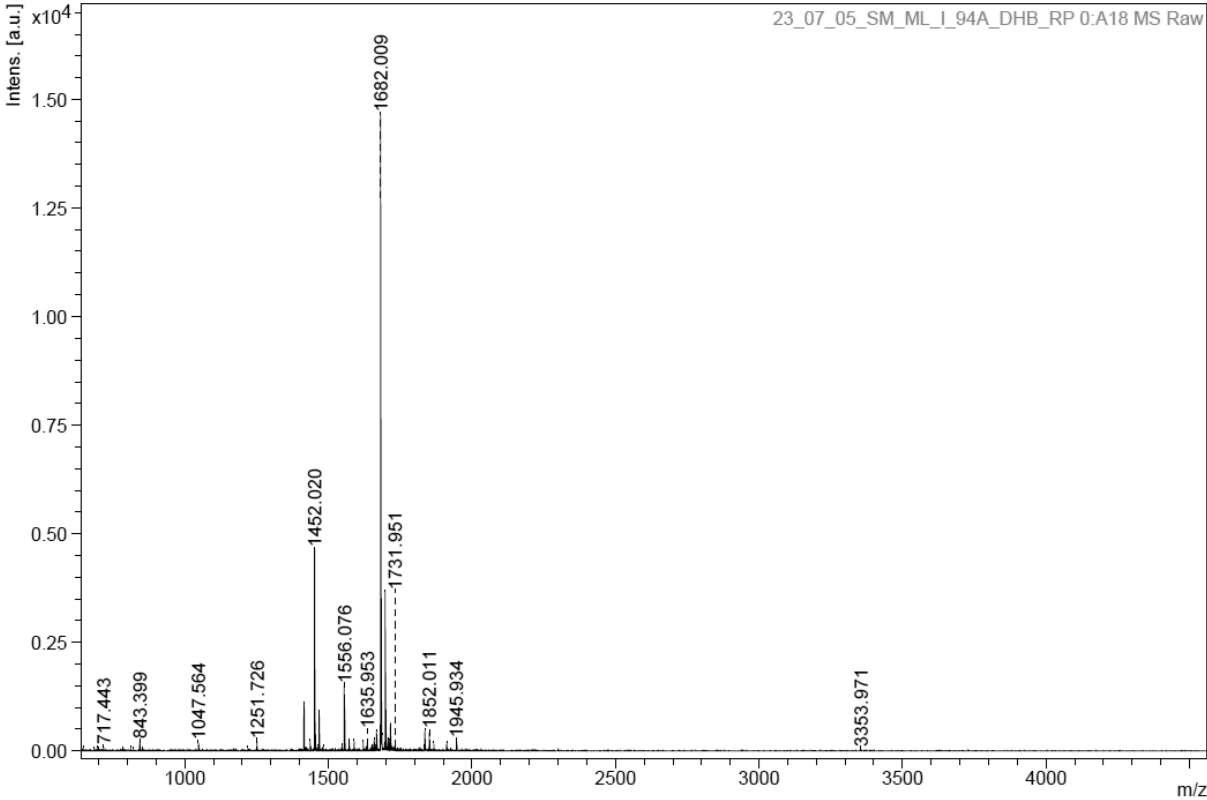
HSQC(CDCl₃) of 7Bf

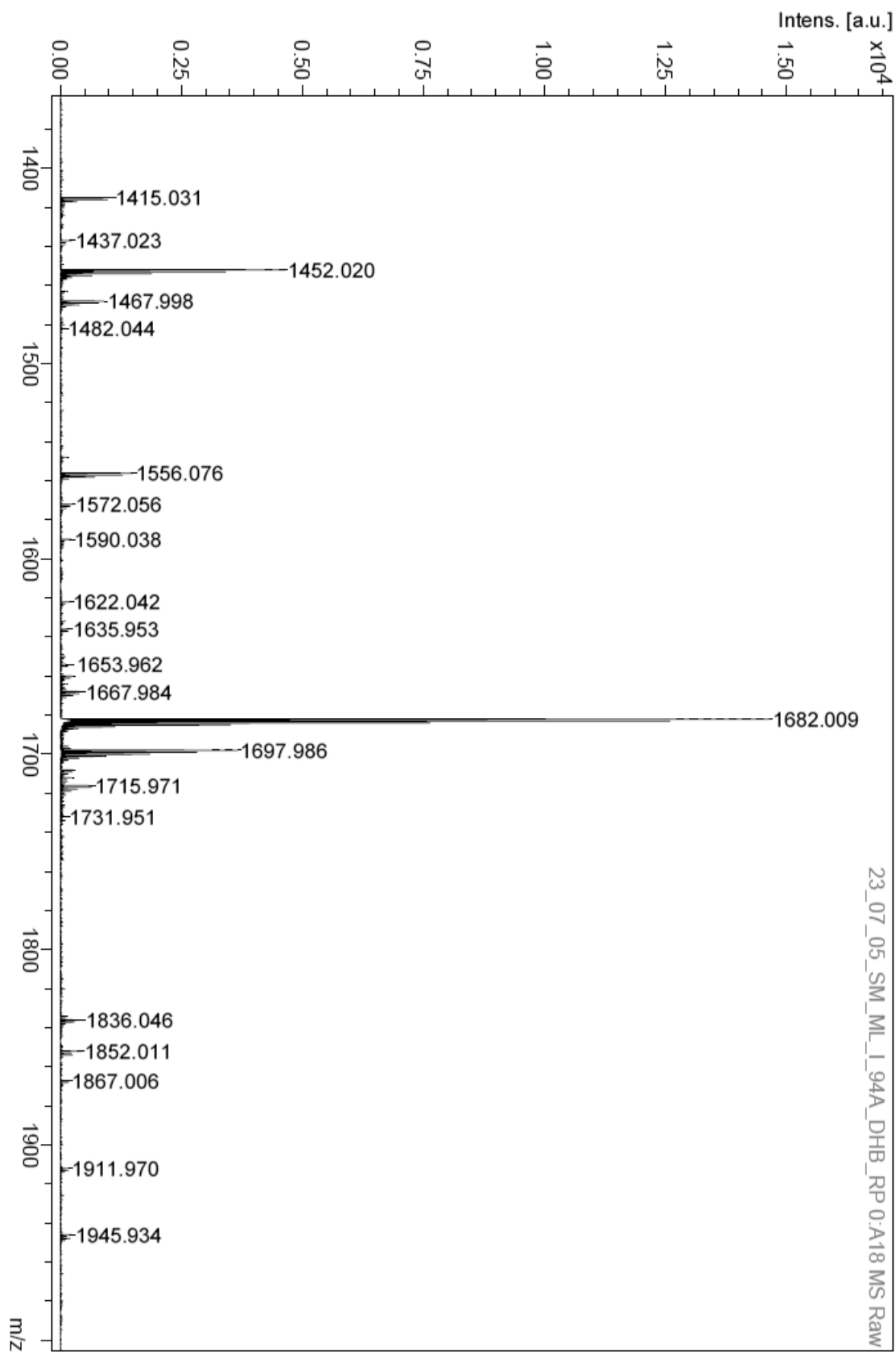


Characterisation of 7Bk (C₆₉H₁₁₅N₂O₃₅I)

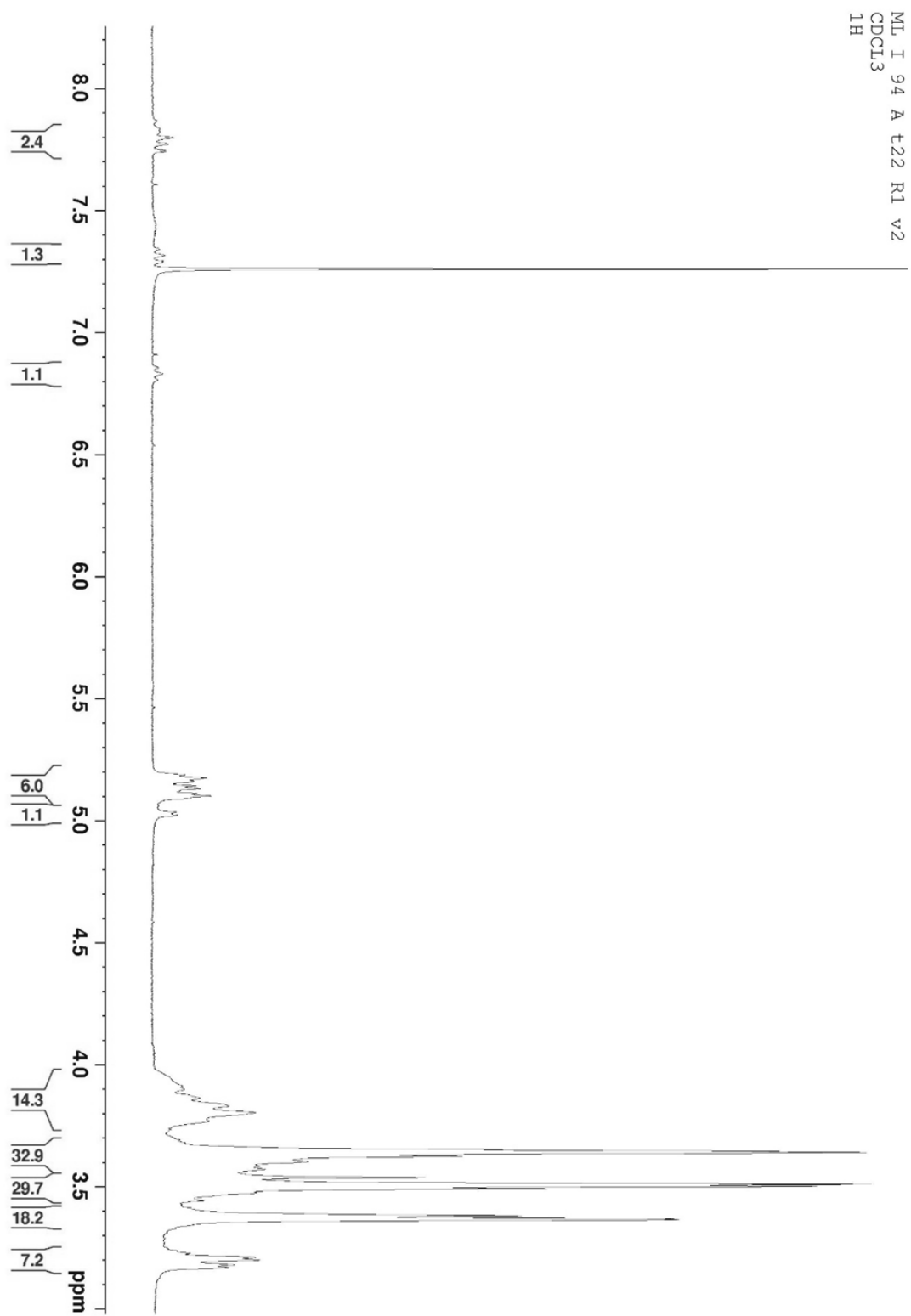


MALDI TOF of 7Bk

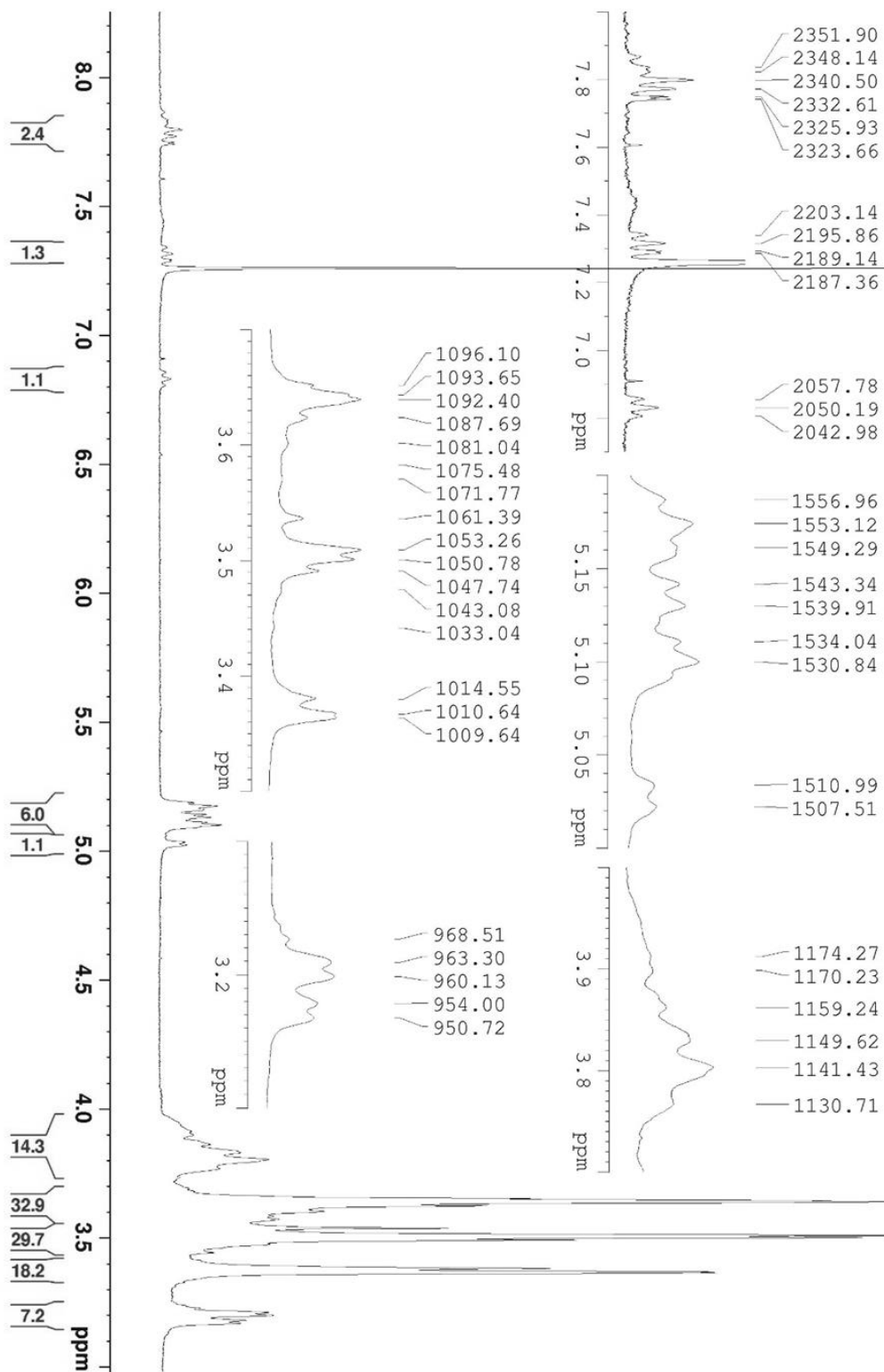




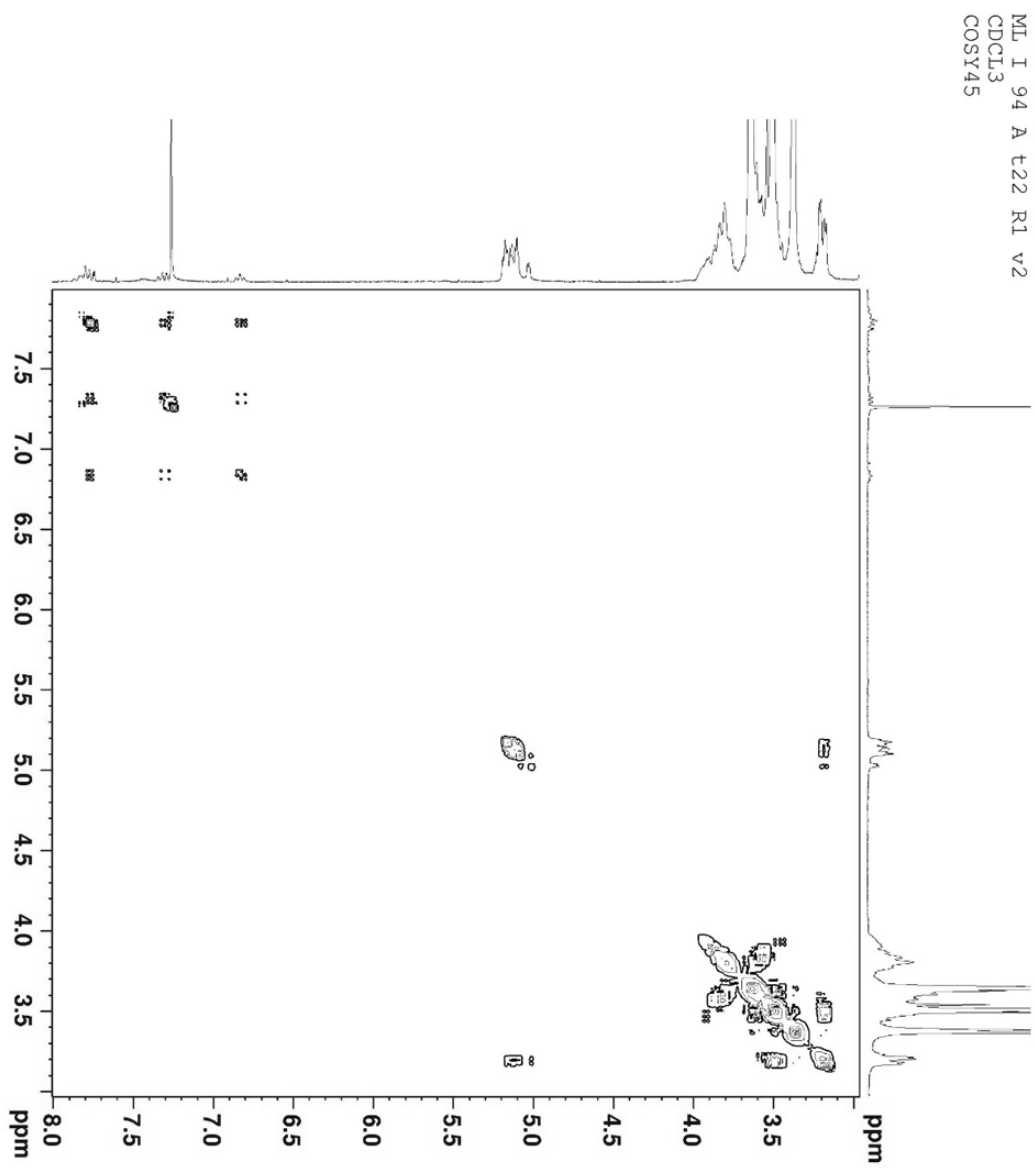
RMN¹H(CDCl₃) of 7Bk



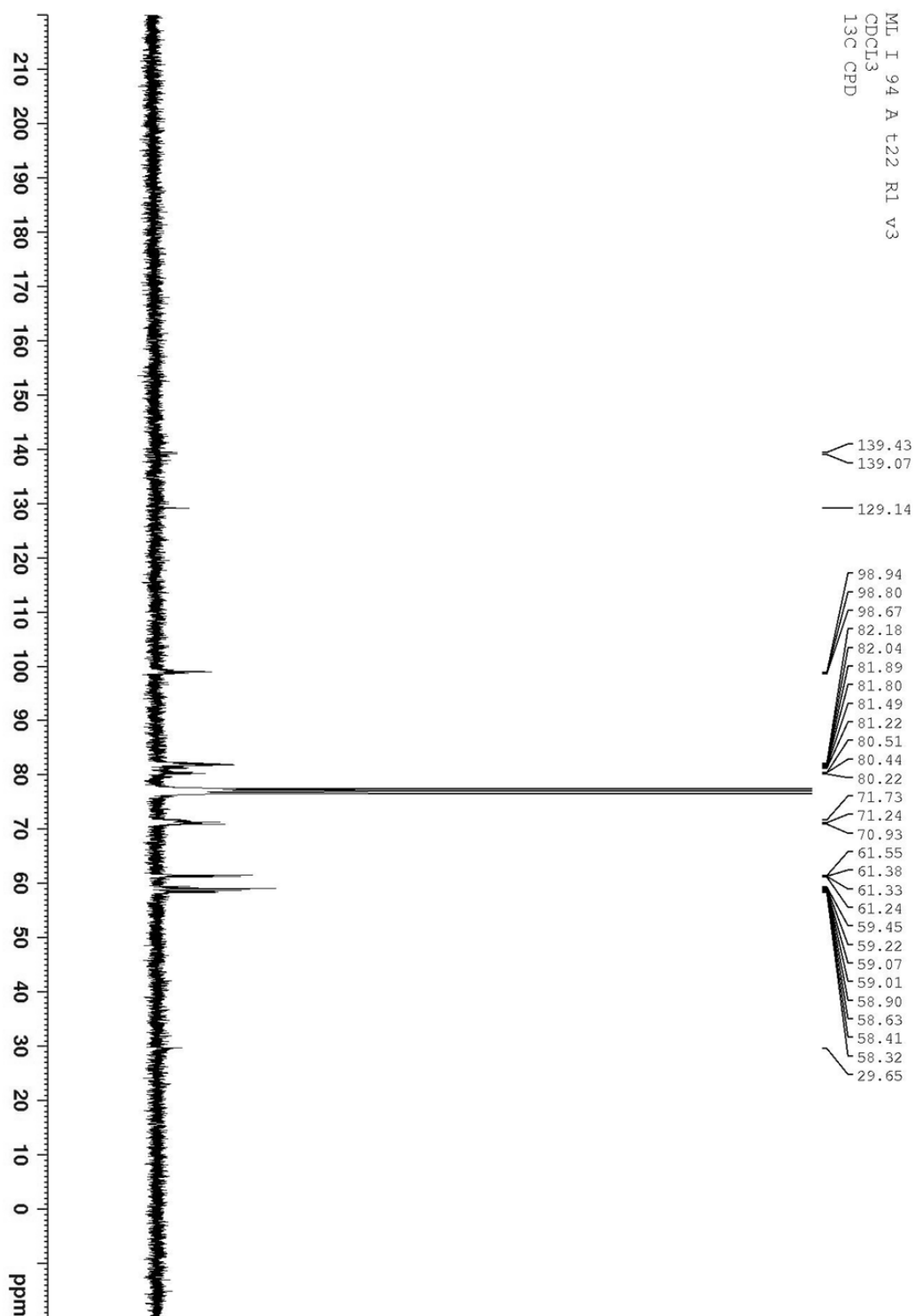
ML I 94 A t22 R1 v2
CDCL3
1H



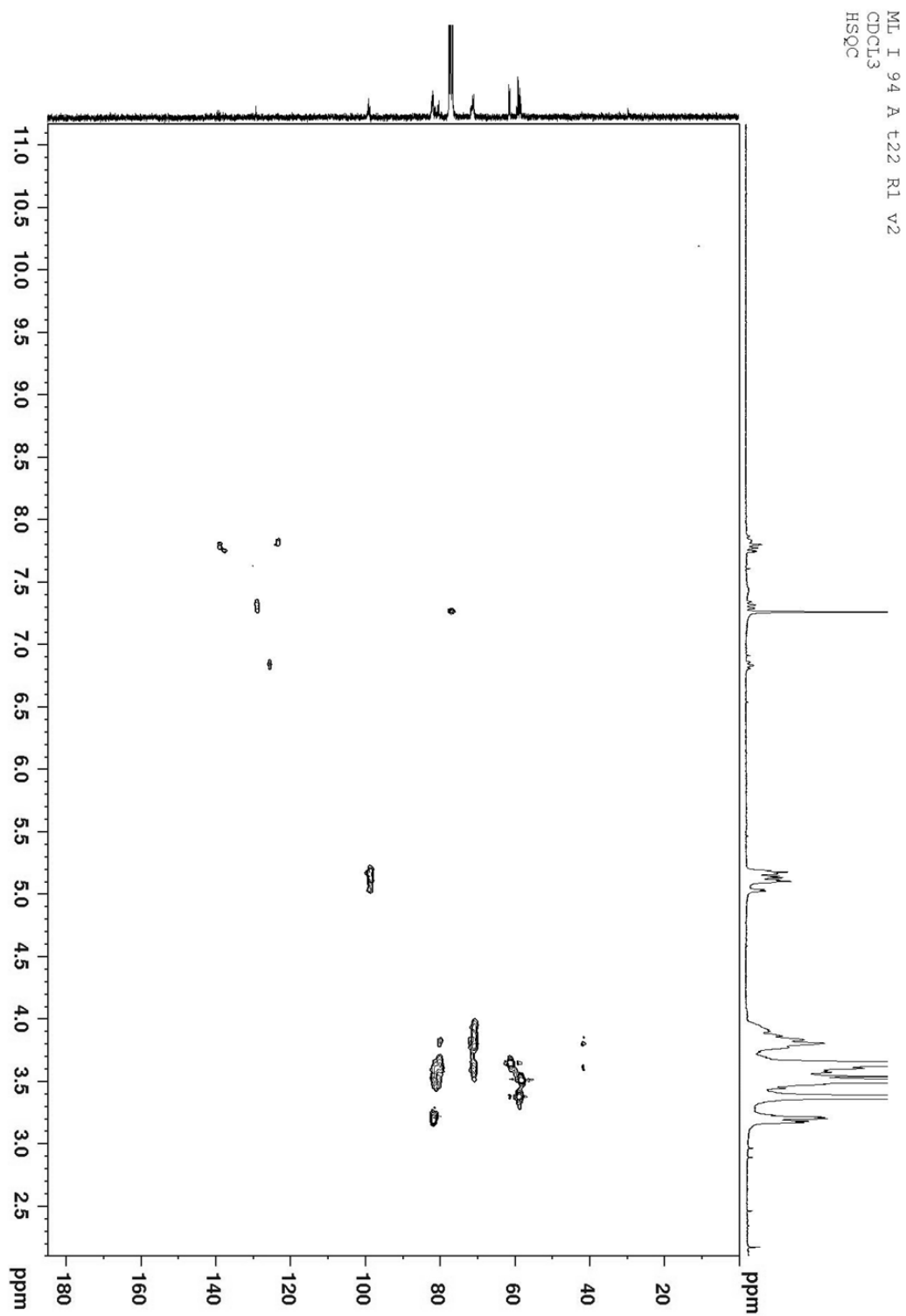
COSY (CDCl₃) of 7Bk



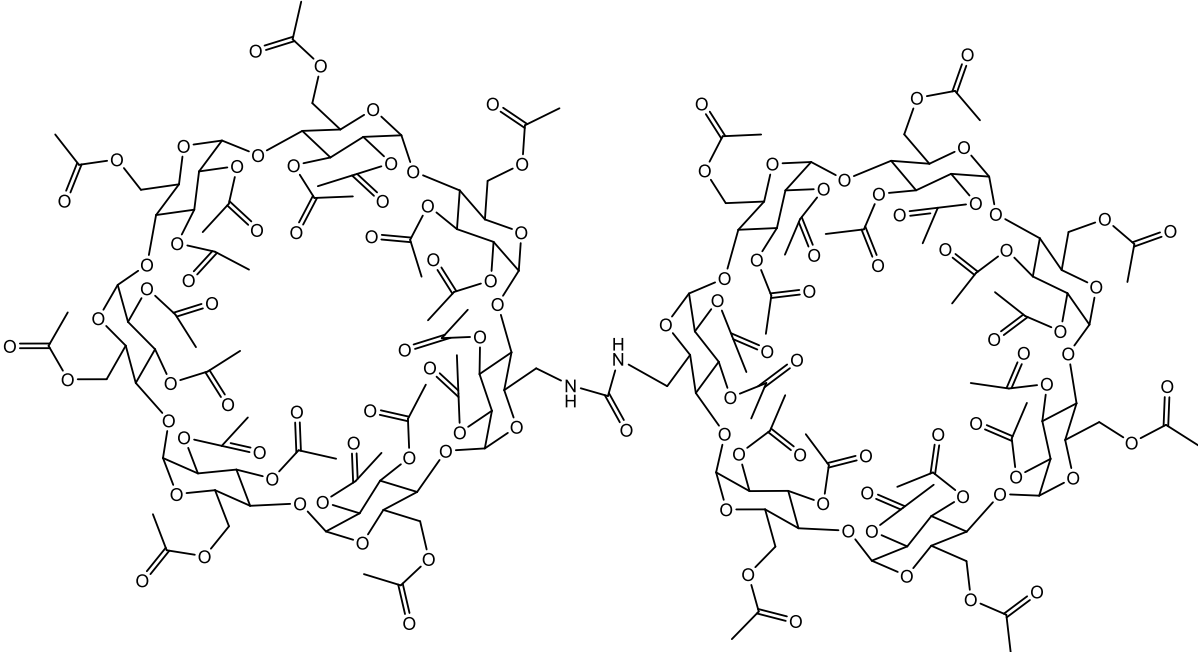
RMN¹³C(CDCl₃) of 7Bk



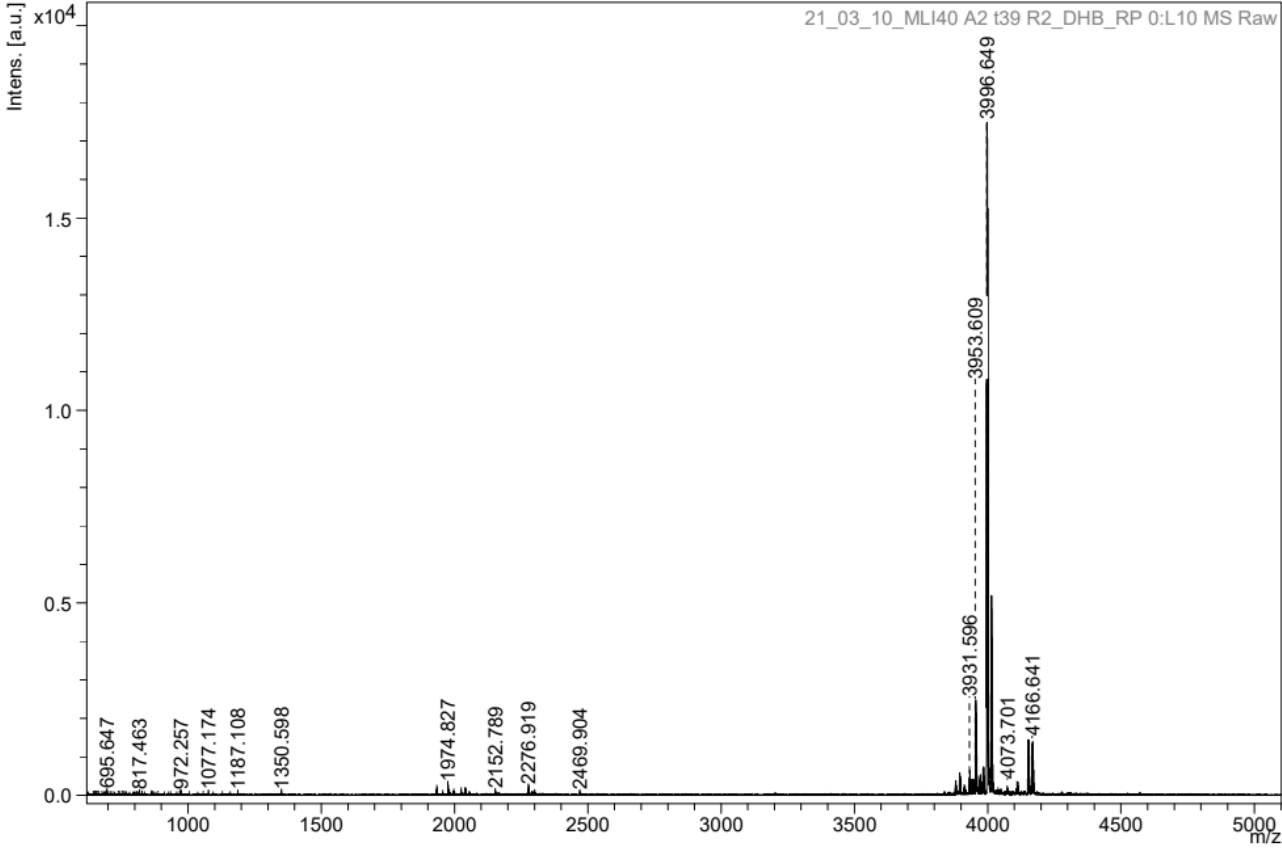
HSQC(CDCl₃) of 7Bk

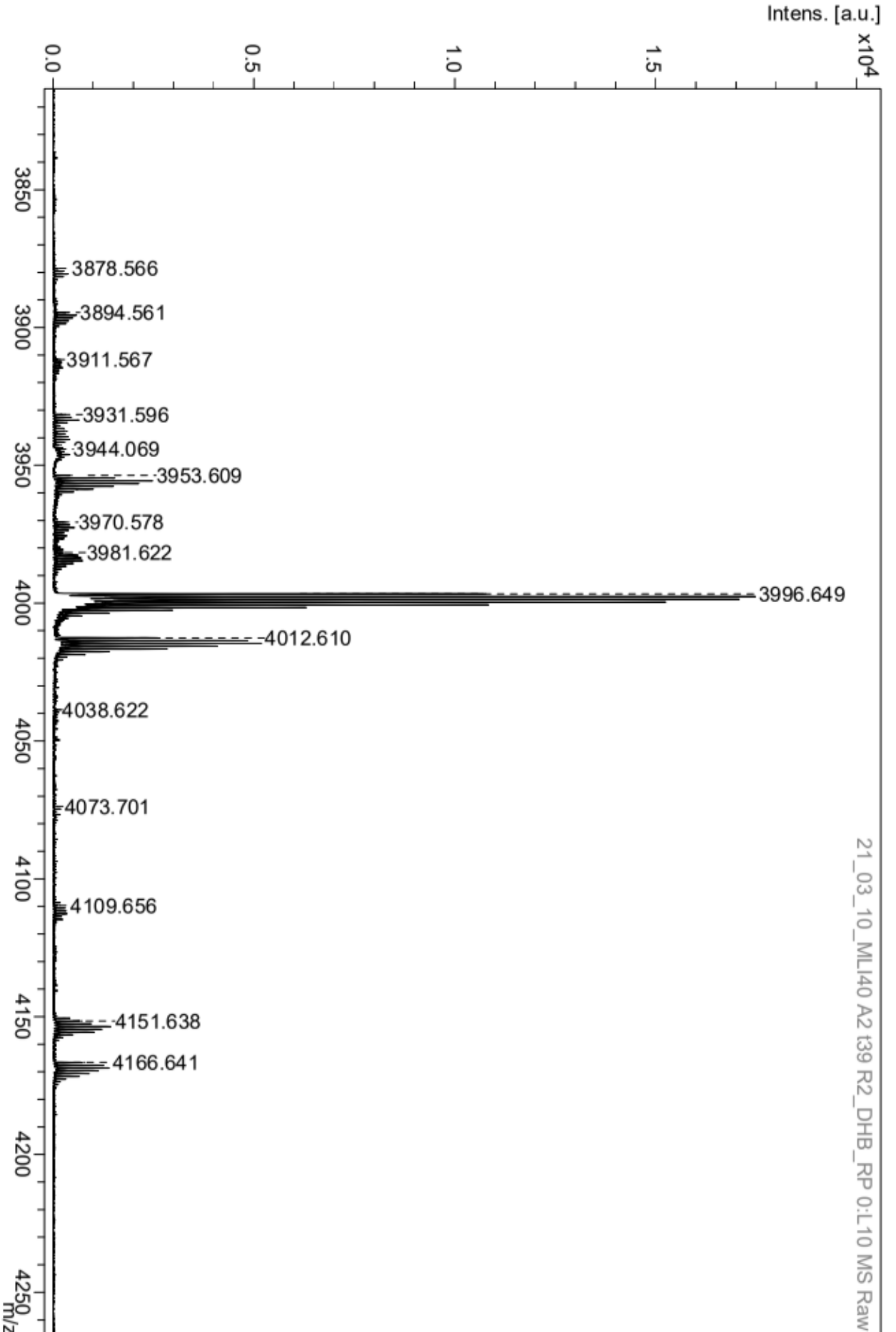


Characterisation of 9A (C₁₆₅H₂₂₀N₂O₁₀₉)



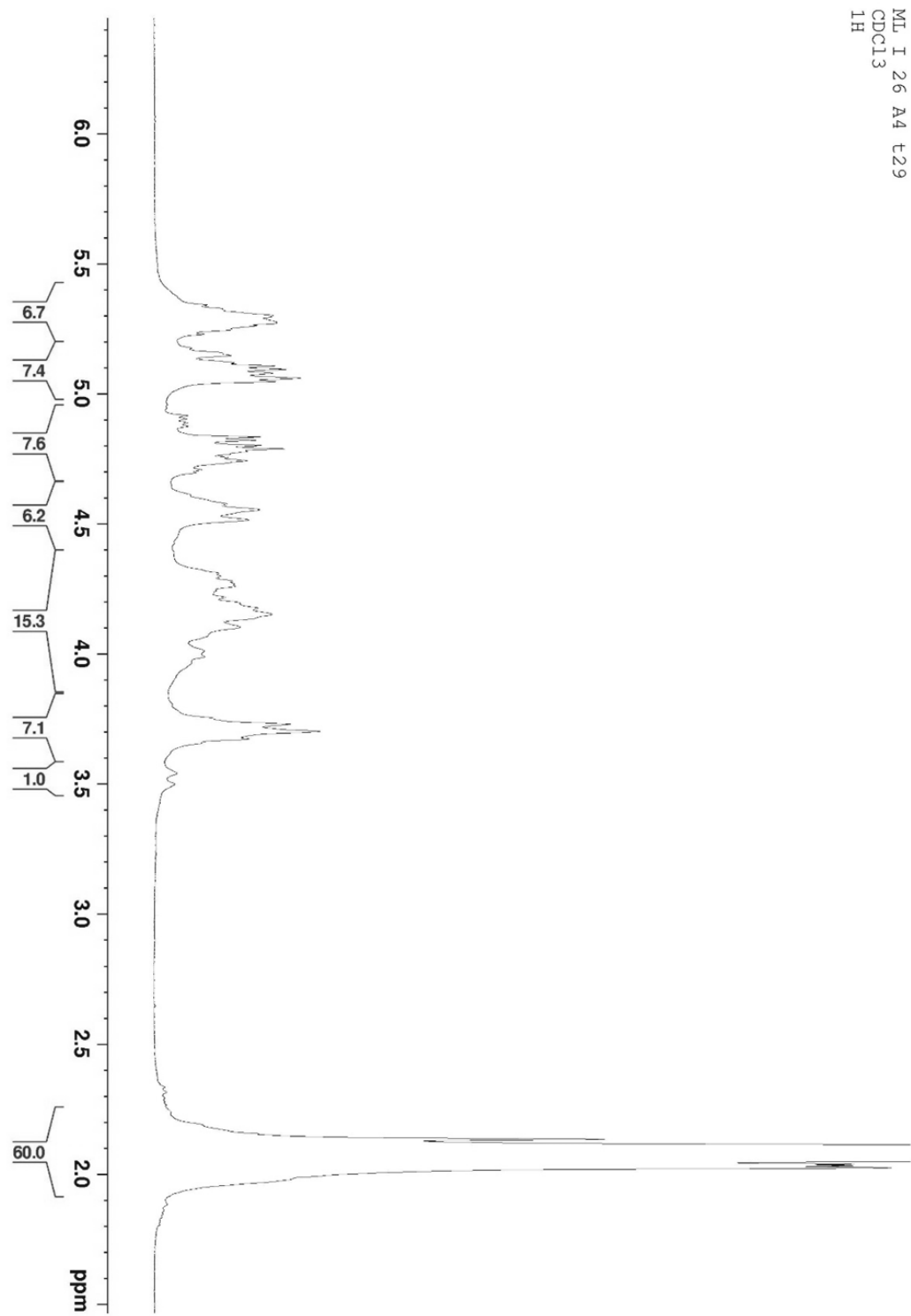
MALDI TOF of 9A



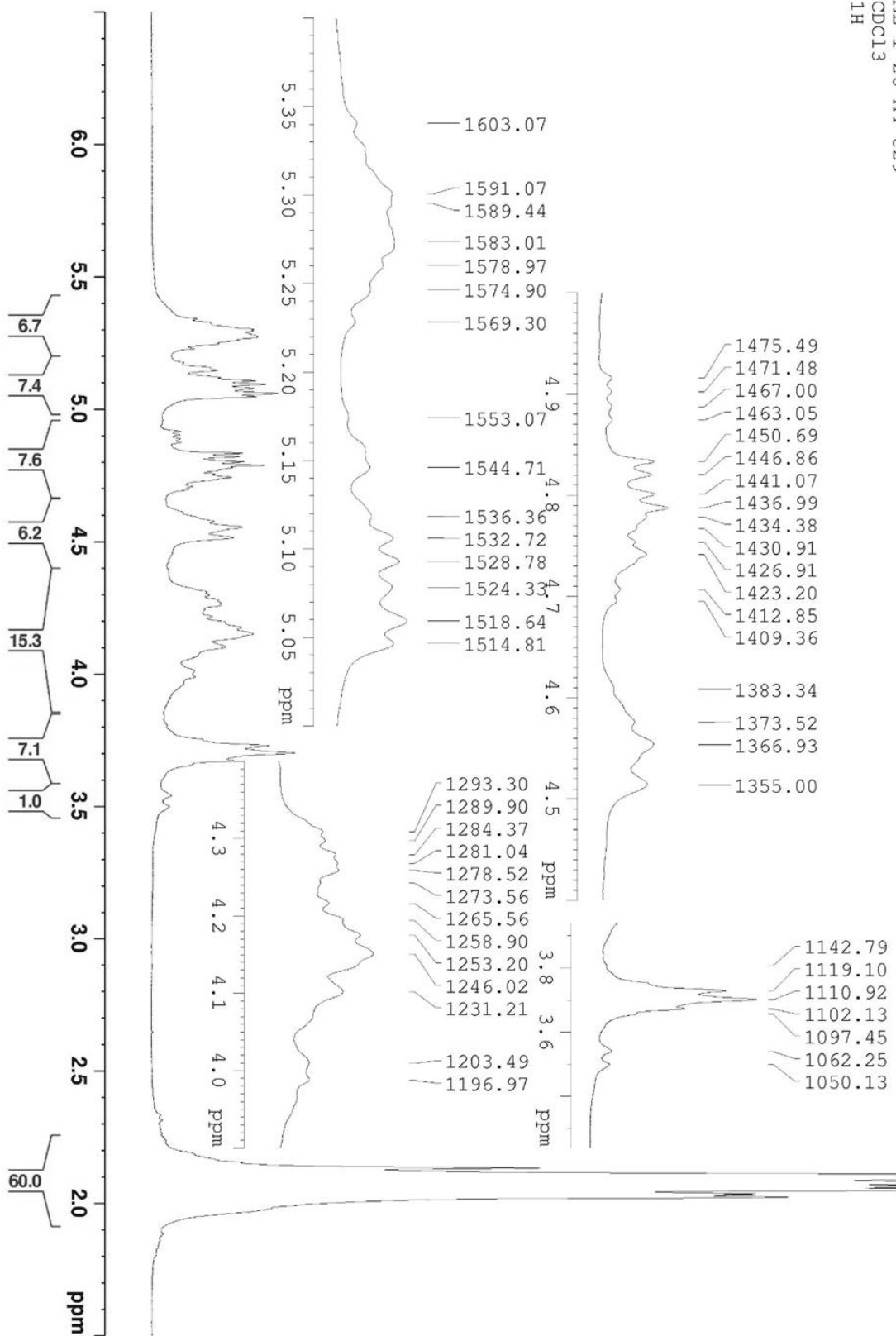


21_03_10_MLI40 A2 I39 R2_DHB_RP 0:1:10 MS Raw

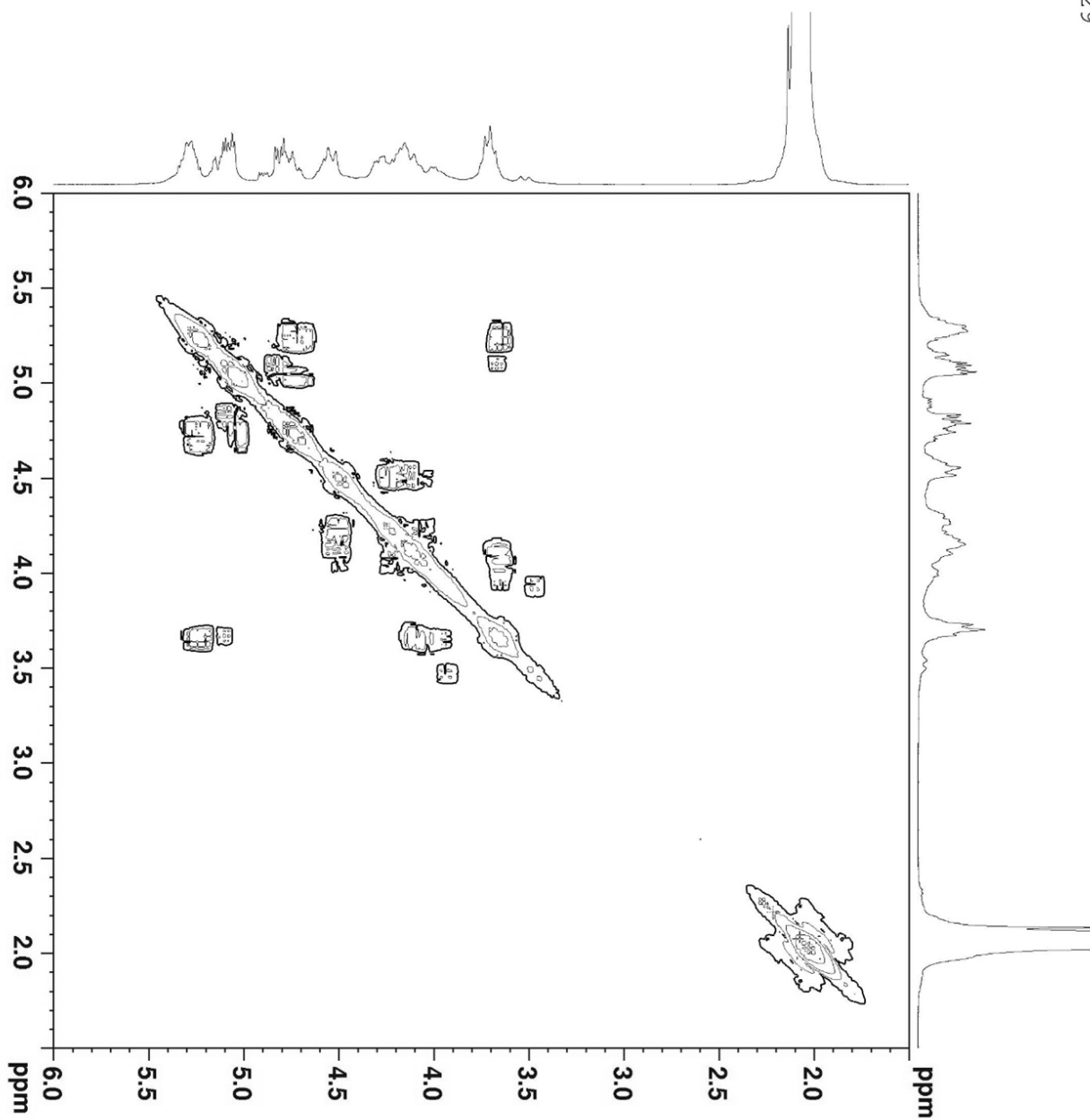
RMN¹H(CDCl₃) of 9A



ML I 26 A4 t29
 CDCl3
 1H

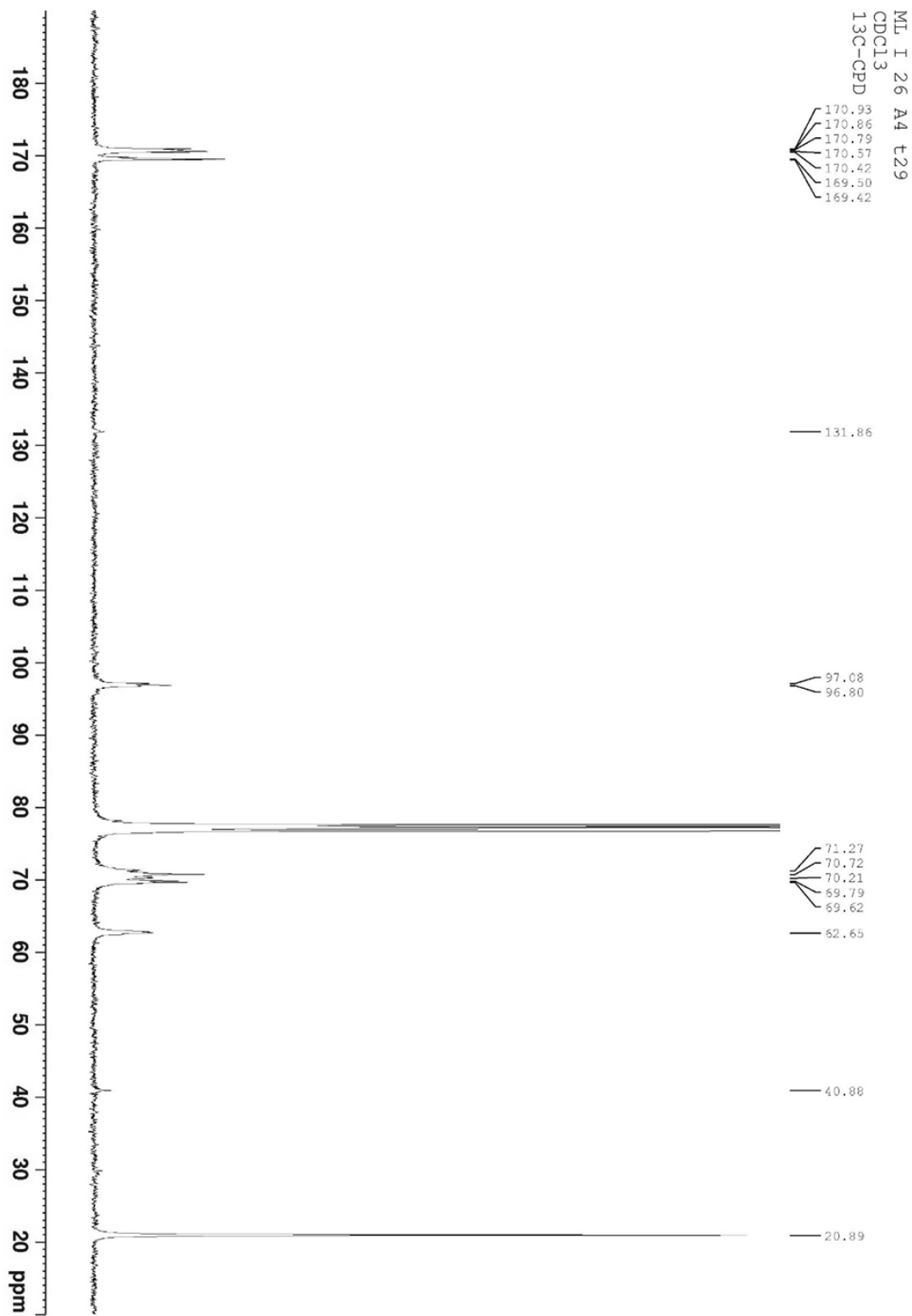


ML I 26 A4 t29
CDCl3
COSY45

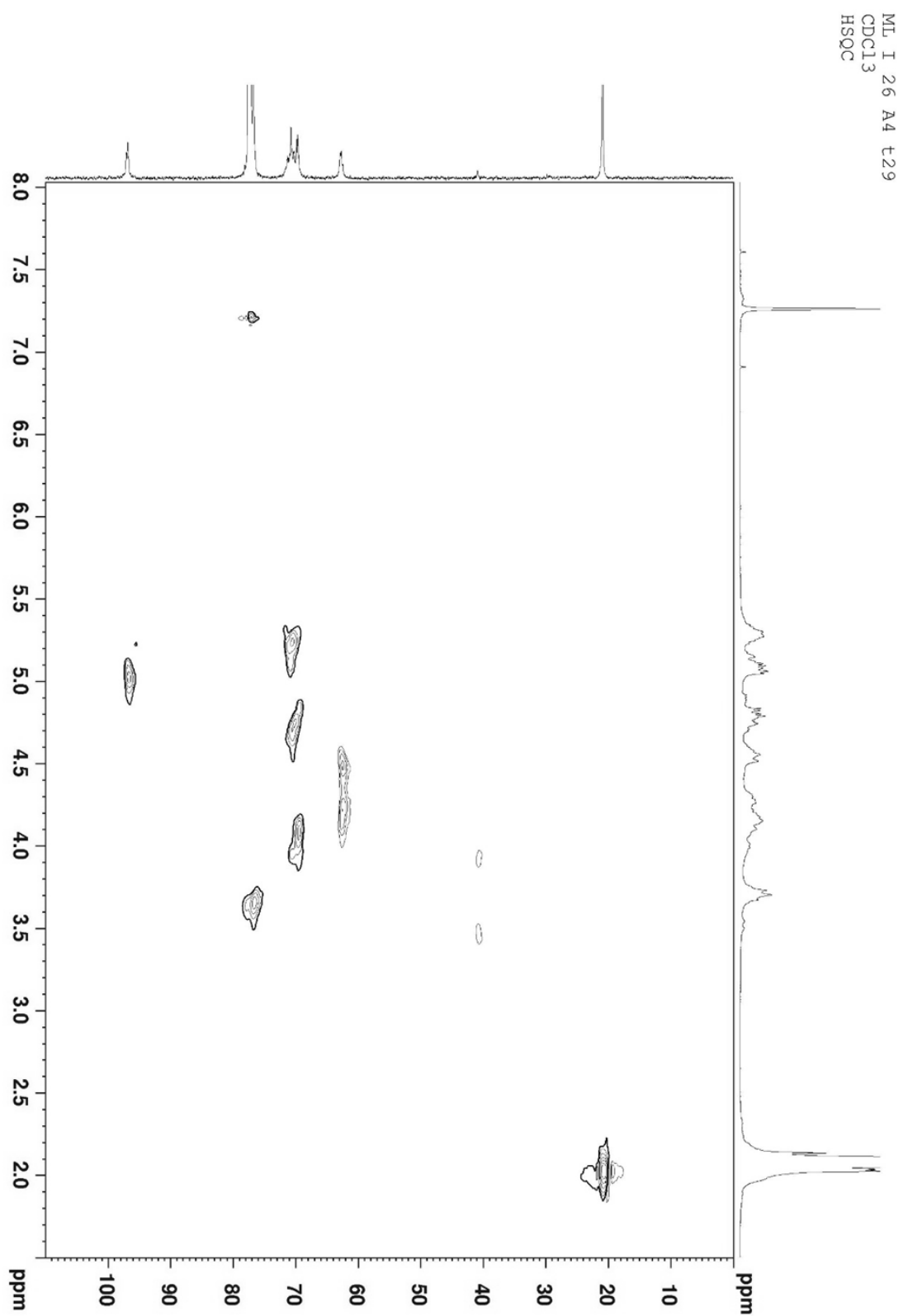


COSY (CDCl₃) of 9A

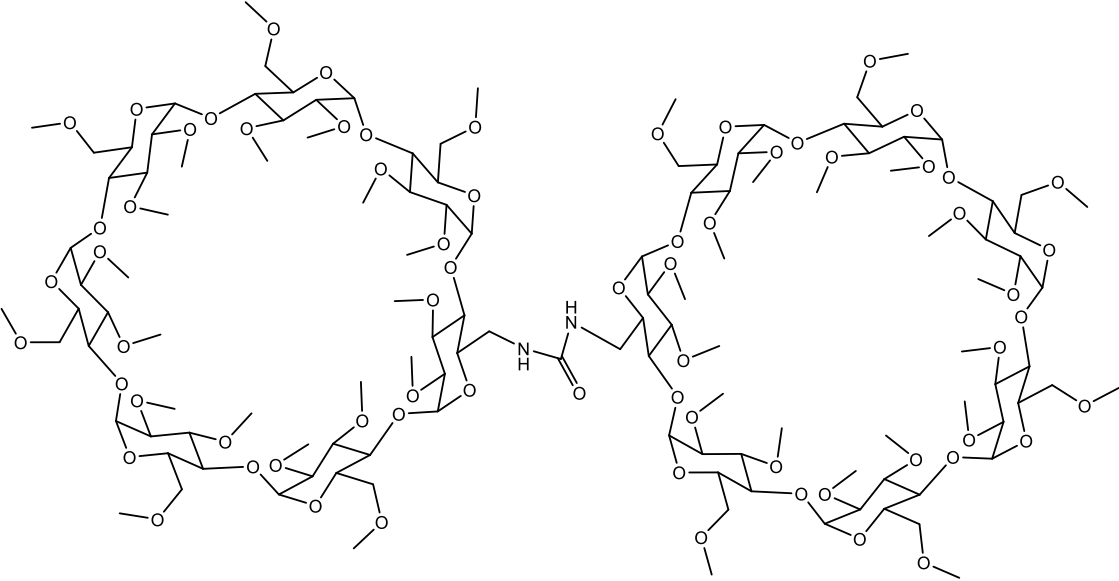
RMN¹³C(CDCl₃) of 9A



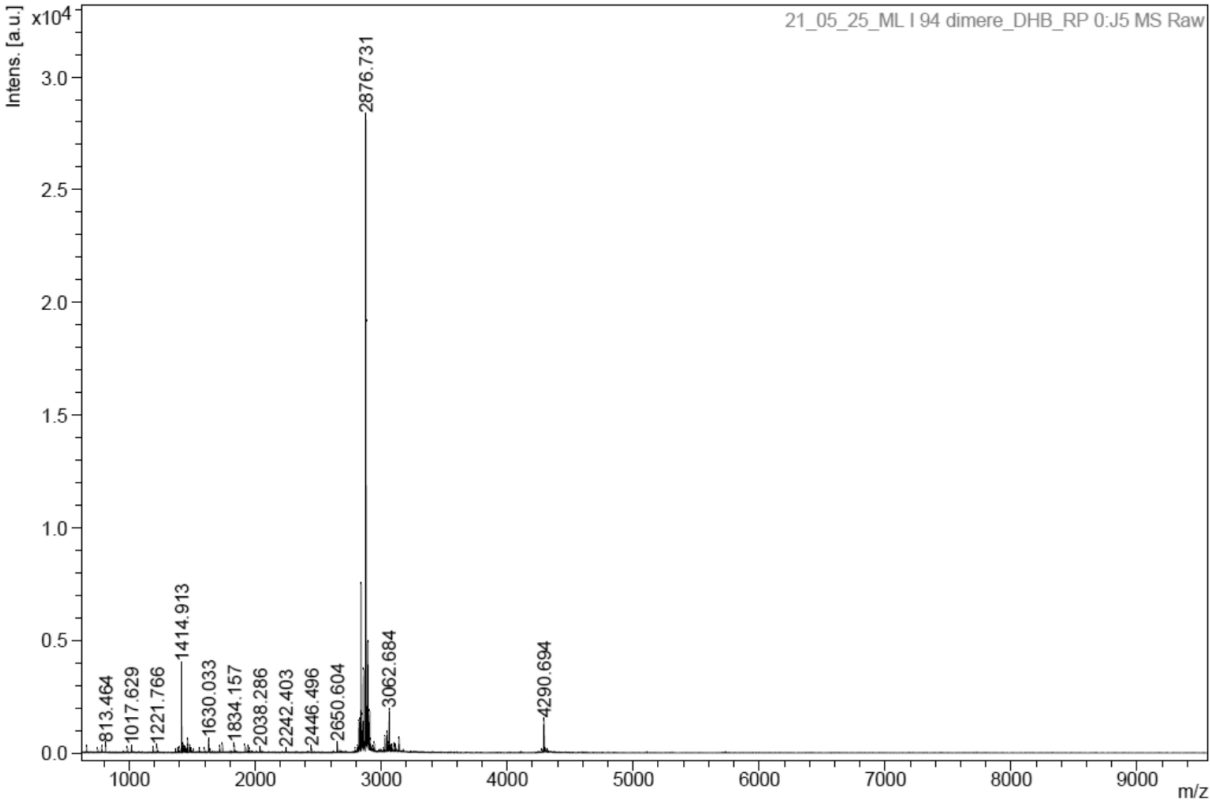
HSQC(CDCl₃) of 9A



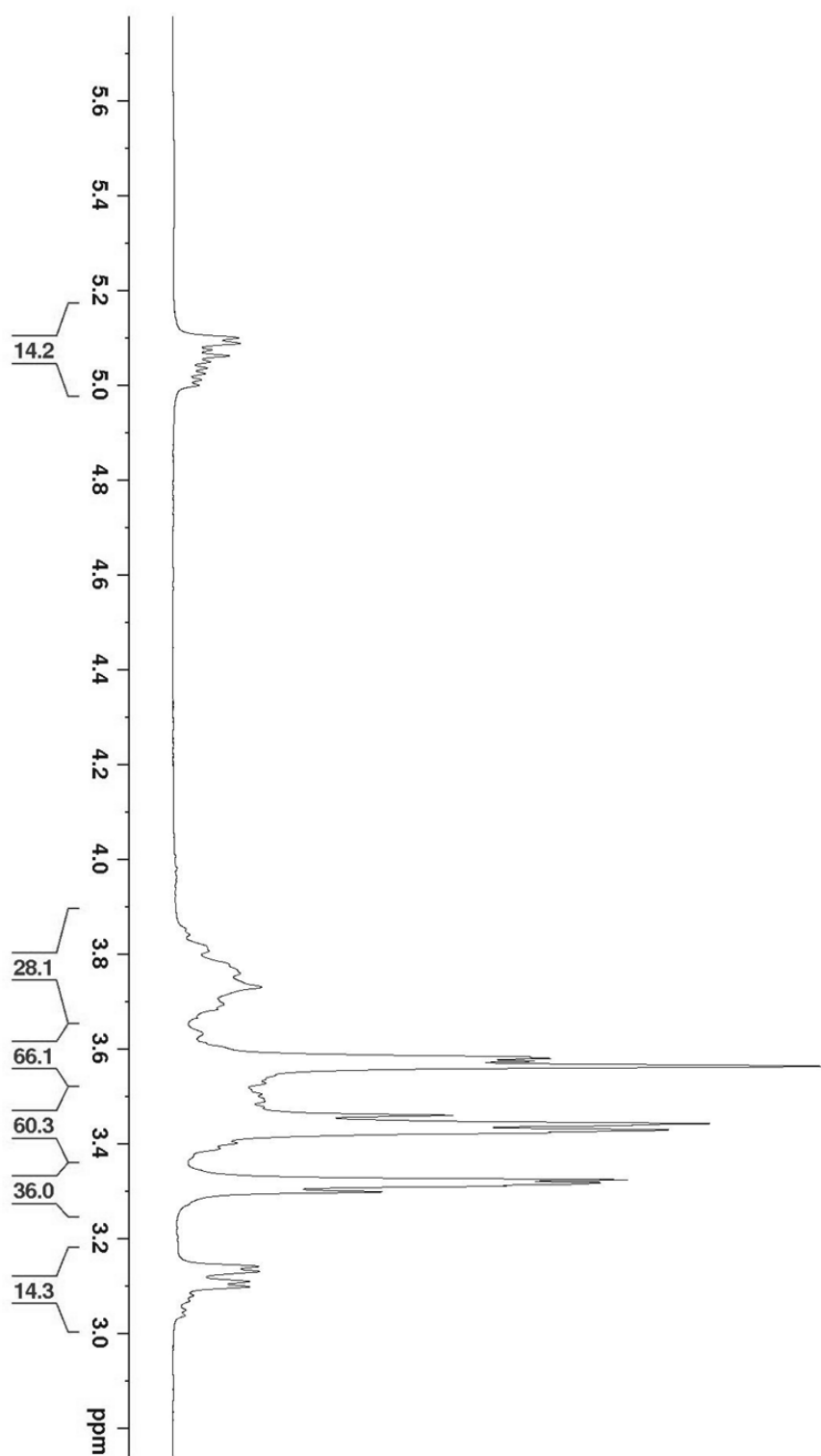
Characterisation of 9B (C₁₂₅H₂₂₀N₂O₆₉)



MALDI TOF of 9B

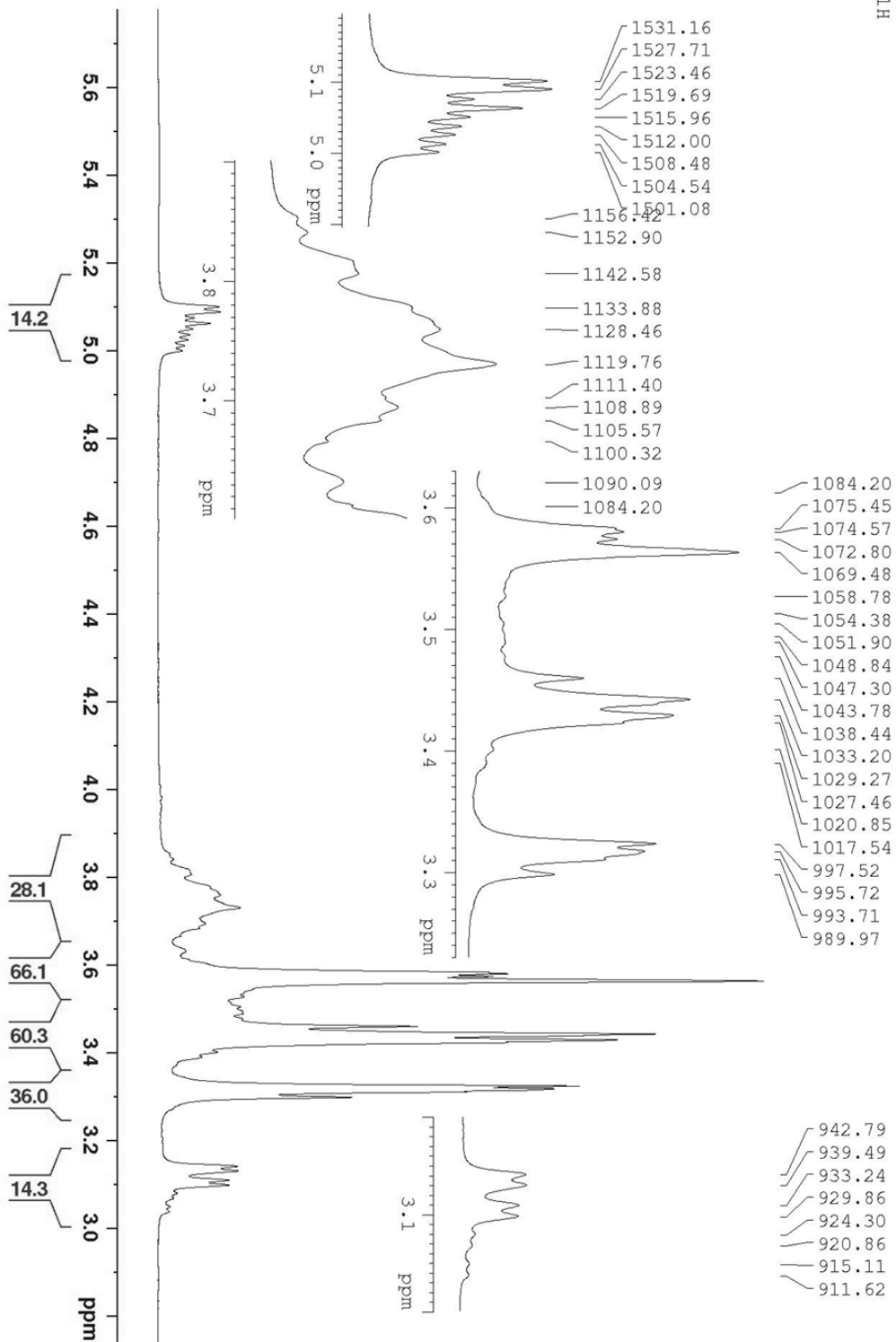


RMN¹H(CDCl₃) of 9B

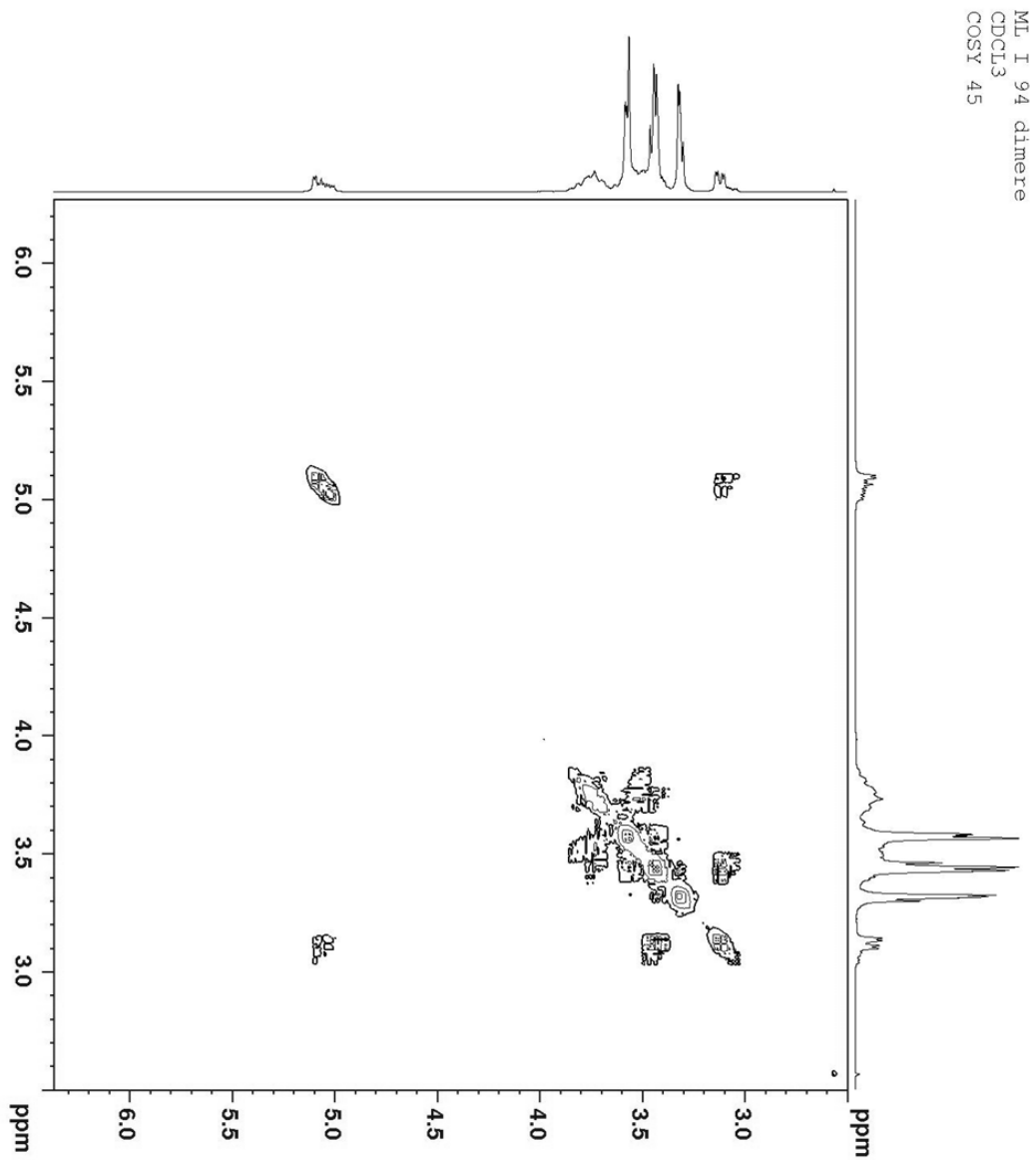


ML I 94 dimere
CDCl₃
1H

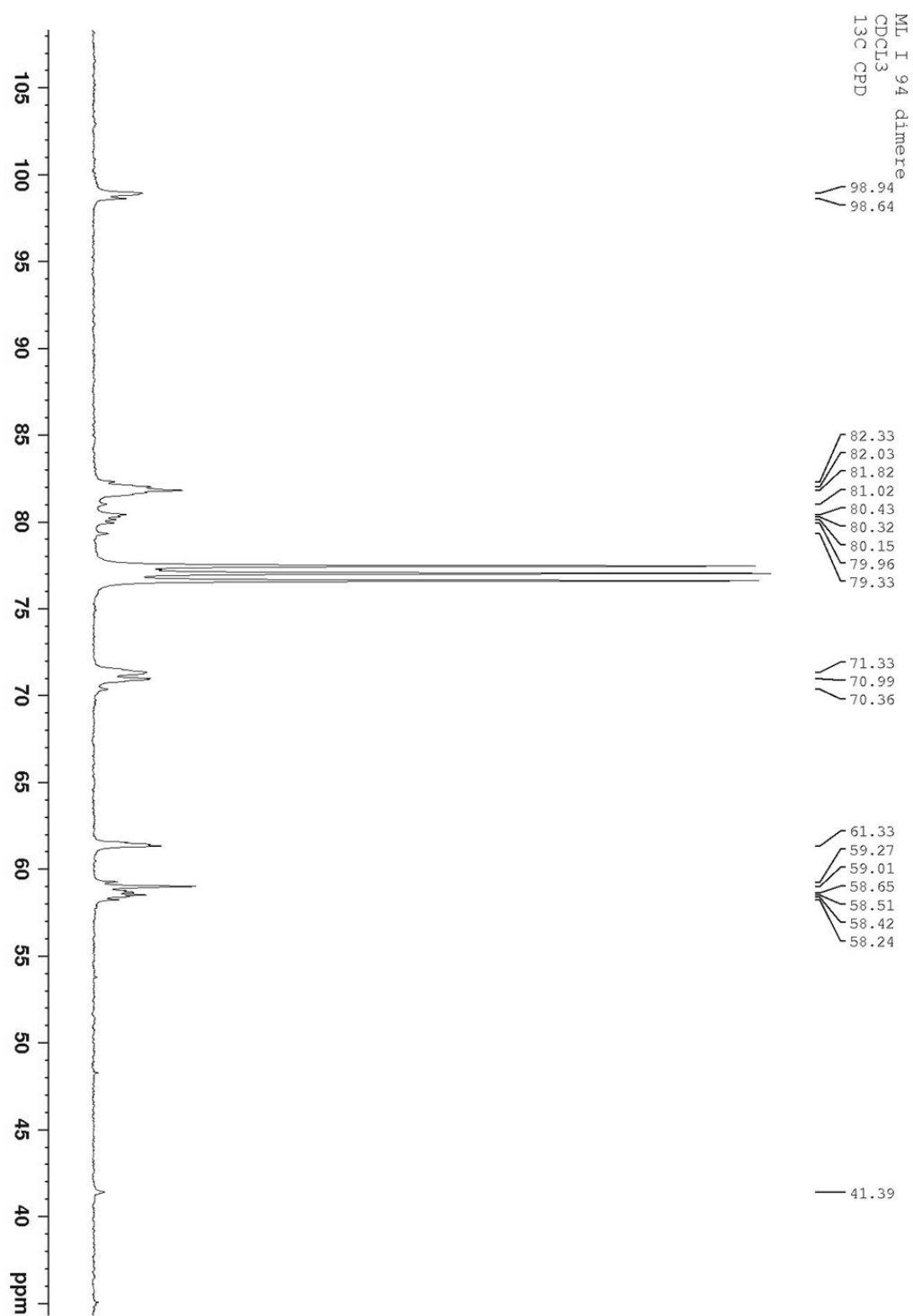
ML I 94 dimere
 CDCl3
 1H



COSY (CDCl₃) of 9B



RMN¹³C(CDCl₃) of 9B



HSQC(CDCl₃) of 9B

ML I 94 dimere
CDCl₃
HSQC

