Chemistry of Heterocyclic Compounds **2024**, *60*(3/4), 190–195

3-Spiroandrostene-substituted 1,3,4-thiadiazolines

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SUPPLEMENTARY INFORMATION

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1. Experimental Section

^{1}H, ^{13}C NMR, 2D NMR HSQC, HMBC and COSY experiments were recorded on Bruker AV-600 (600 and 151 MHz, respectively). The chemical shifts (δ) were expressed in ppm and referenced to DMSO-d_6 (39.5 ppm) for ^{1}H and ^{13}C NMR, respectively. The coupling constants (*J*) are in Hertz. The assignment of the signals in the NMR spectra was based on the 2D NMR data. High-resolution mass spectra were obtained on a Bruker MicroTOF mass spectrometer by electrospray ionization (ESI) using Q-TOF detection. IR spectra were recorded on a Bruker Alpha spectrometer as KBr pellets, significant band (ν) reported in cm^{-1}. The melting points were determined on a Kofler hot stage apparatus and are uncorrected. TLC was performed using Silicagel 60 F254 plates. The chromatograms were visualized with an UV lamp (254 and 365 nm) and [$Ce(SO_4)_2/H_2SO_4$] developing solution. Column chromatography was carried out on silica gel 60 (0.063–0.200 mm, Merck). Commercial reagents were used without further purification. All reactions were carried out using freshly distilled and dry solvents. 16α,17α-epoxypregn-5-en-20-one was prepared according to published procedure.[1]

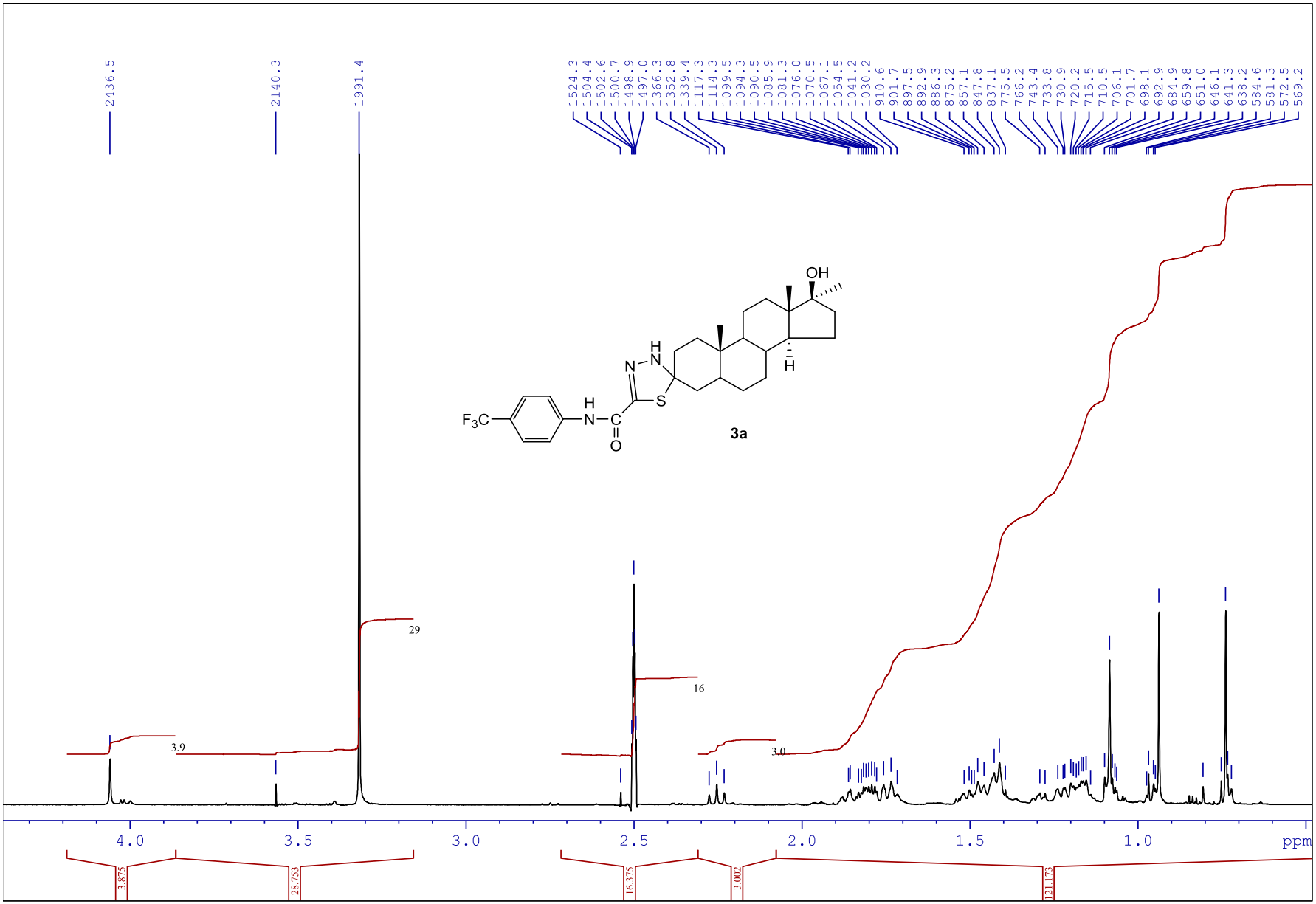
For the nomenclature of steroid derivatives, we use the definitive rules for the nomenclature of steroid published by the Joint Commission on the Biochemical Nomenclature IUPAC.[2]

[1] A. V. Komkov, L. G. Menchikov, A. S. Dmitrenok, A. M. Scherbakov, D. I. Salnikova, I. S. Levina, and I. V. Zavarzin. A new approach to the synthesis of 17-pyrazolylandrostane. *Chemistry of Heterocyclic Compounds,* 2023, **59**, 554. DOI: 10.1007/s10593-023-03233-8

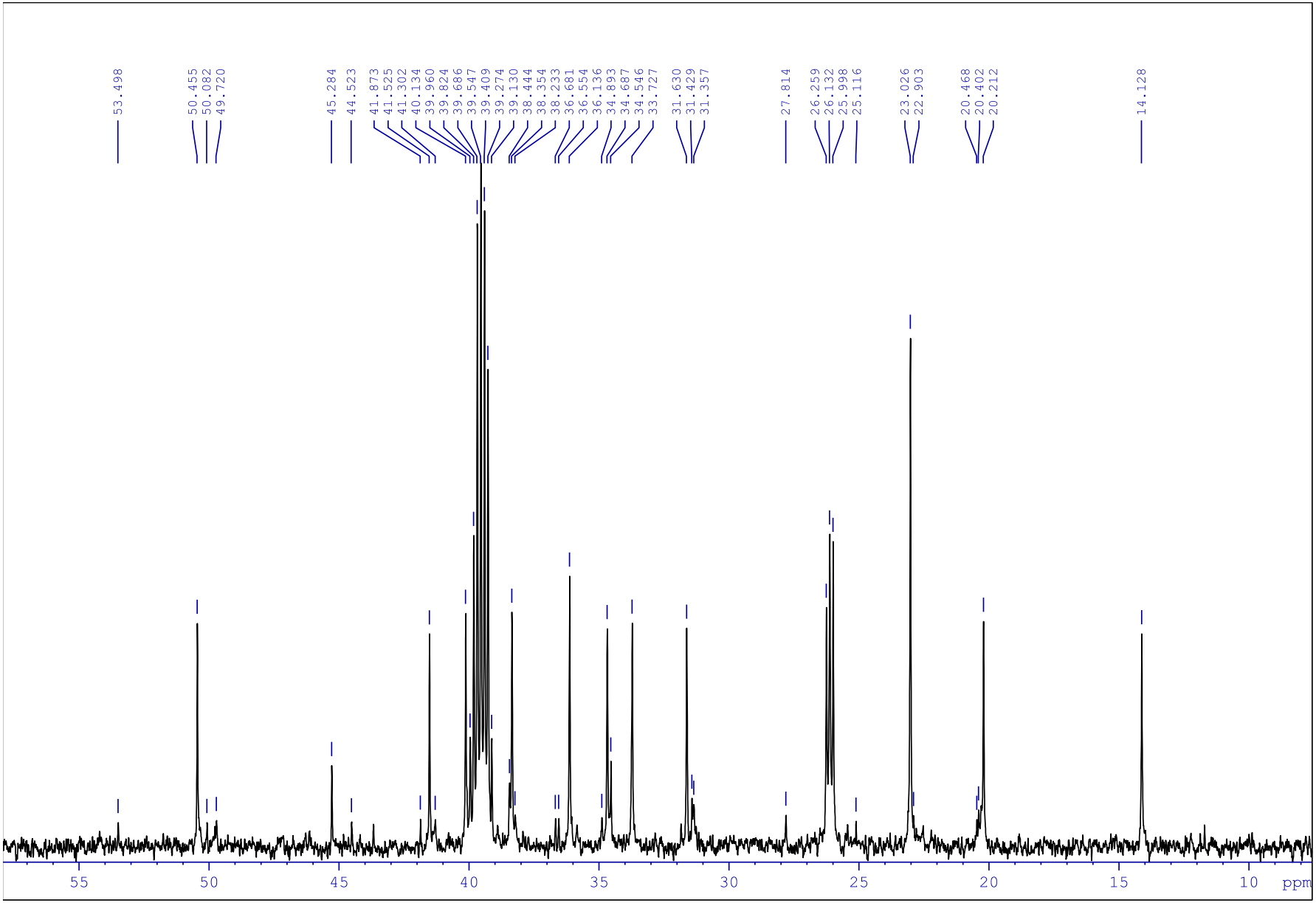
A. V. Komkov, A. O. Chizhov, A. S. Shashkov, and I. V. Zavarzin. Synthesis of androsteno[17,16-d]pyrazoles and androsteno[17,16-d]-2′-pyrazolines with pyrazolo[3,4-d]pyrimidine fragments. *Russian Chemical Bulletin,* 2018, **67**, 1088. DOI: 10.1007/s11172-018-2185-5

[2] Moss, G. P., *Pure Appl. Chem.*, **1989**, *61*, 1783. DOI: 10.1351/pac198961101783. IUPAC-IUB Joint Commission on Biochemical Nomenclature (JCBN), *Eur. J. Biochem.*, **1989**, *186*, 429. DOI: 10.1111/j.1432-1033.1989.tb15228.x

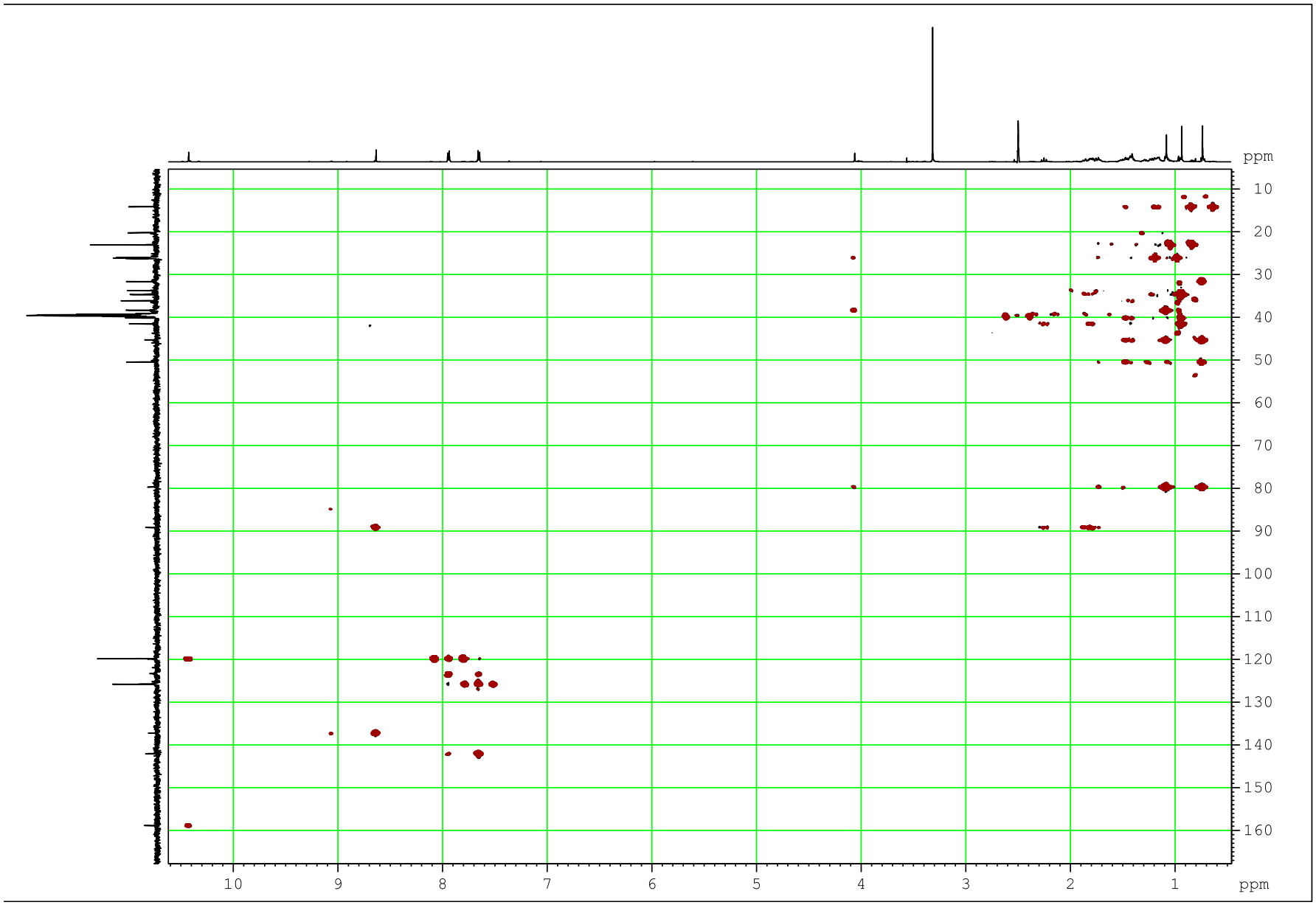
1. NMR spectra (Bruker AV-600)



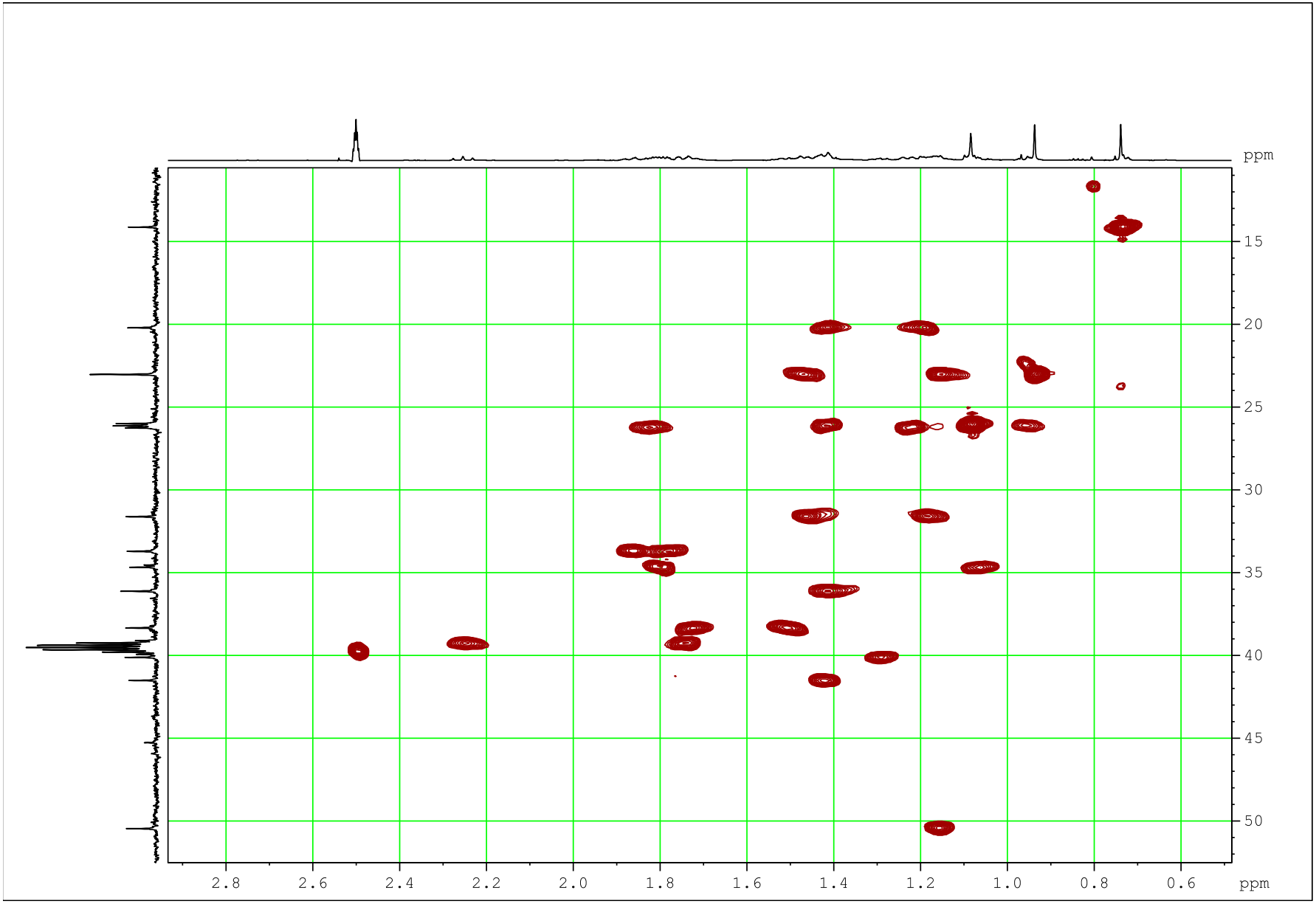
^{1}H NMR spectrum of **3a** (DMSO-d_6).



^{13}C NMR spectrum of **3a** (DMSO-d_6).



2D ^{1}H-^{13}C HMBC NMR spectrum of **3a** (DMSO-d_6).



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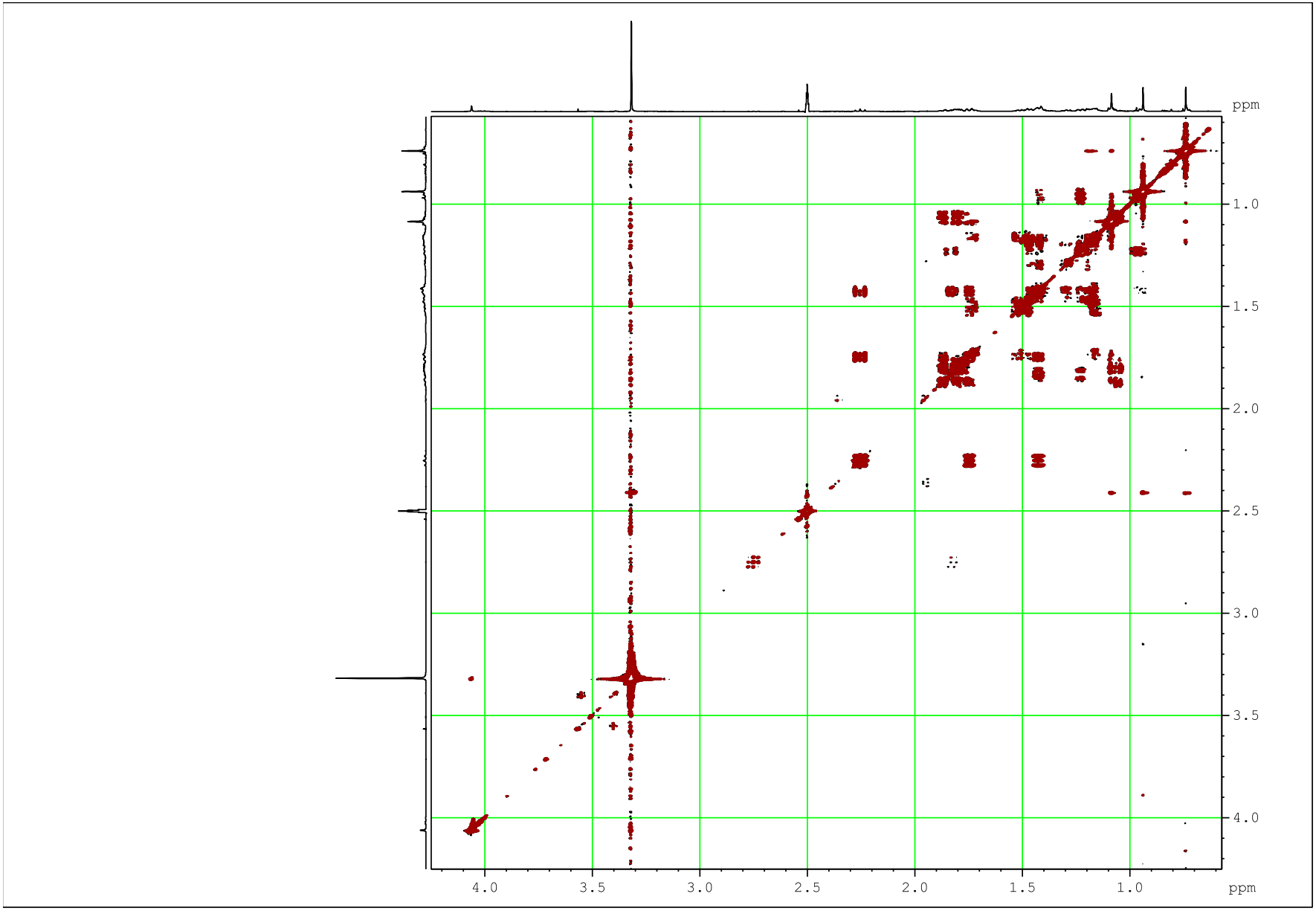
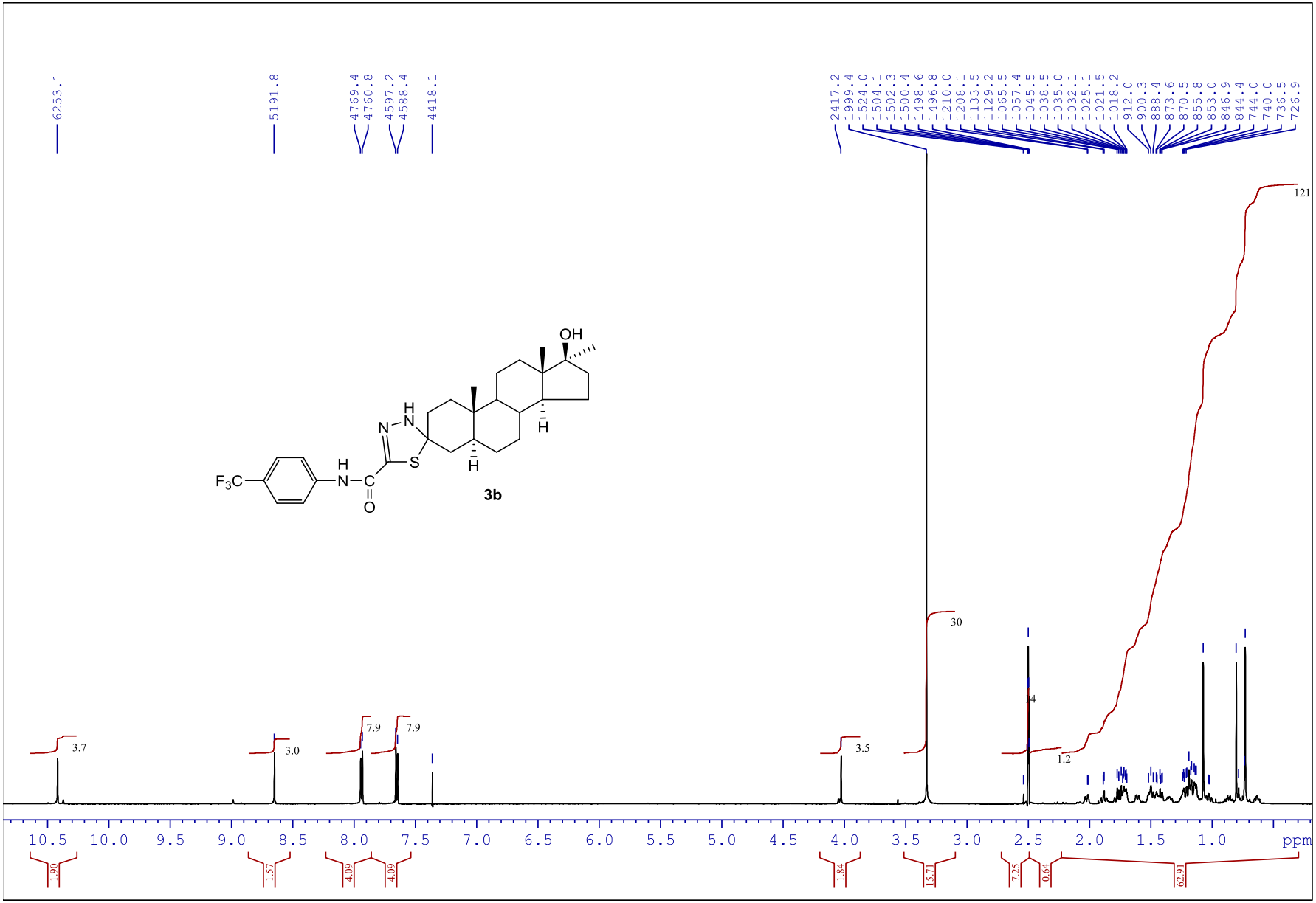
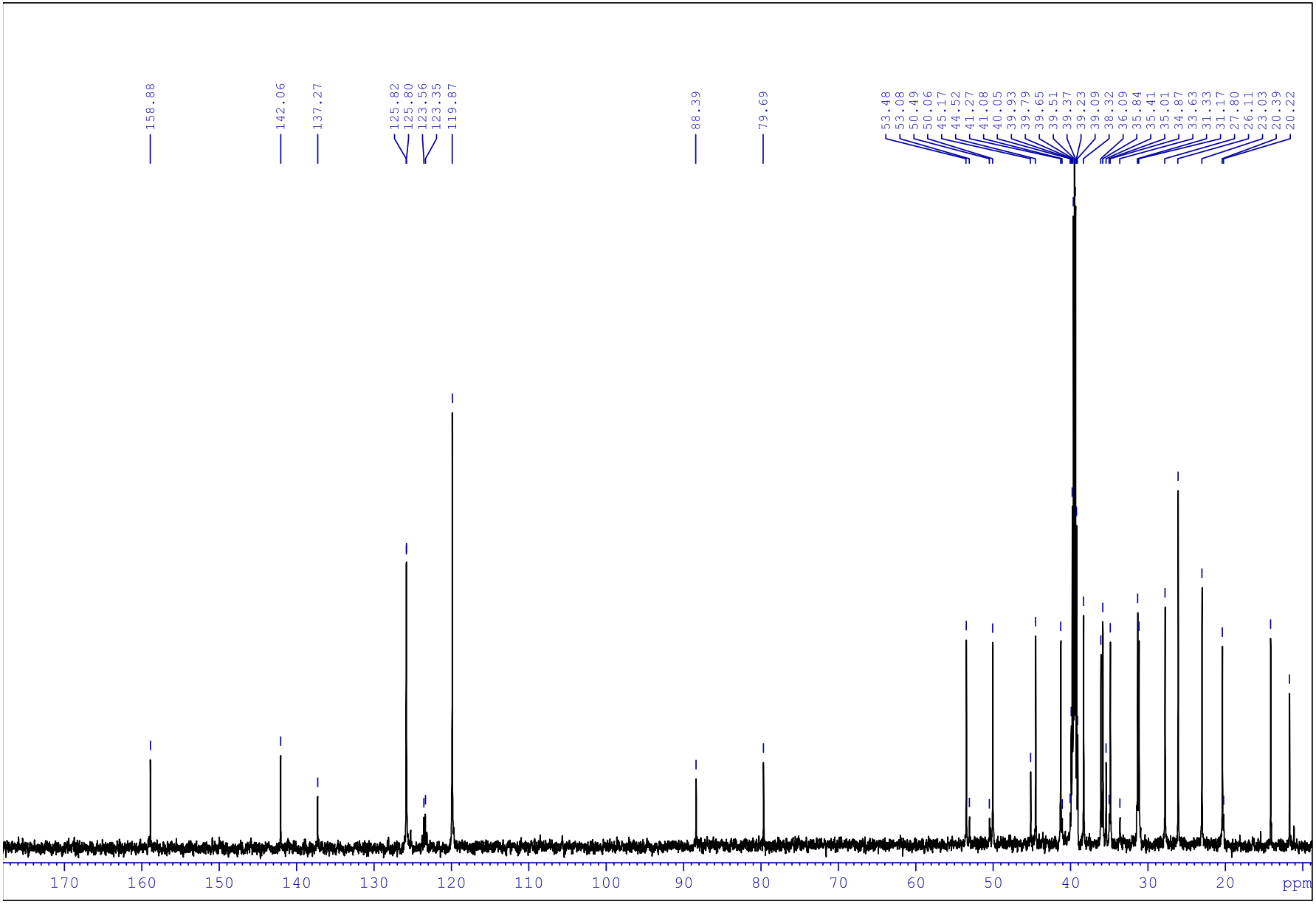


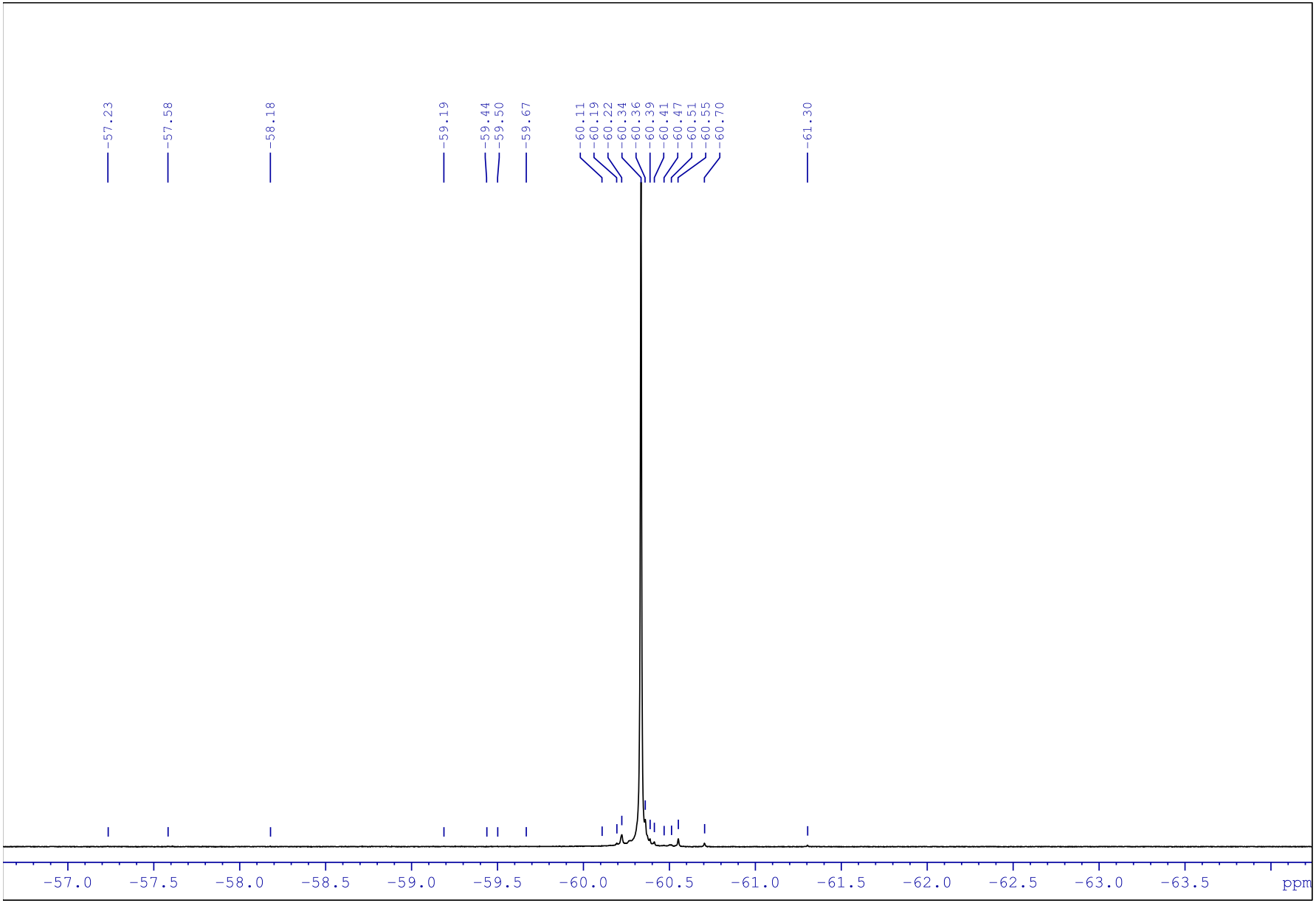
2D ^{1}H-^{1}H COSY NMR spectrum of **3a** (DMSO-d_6).



^{1}H NMR spectrum of **3b** (DMSO-d_6).



^{13}C NMR spectrum of **3b** (DMSO-d_6).



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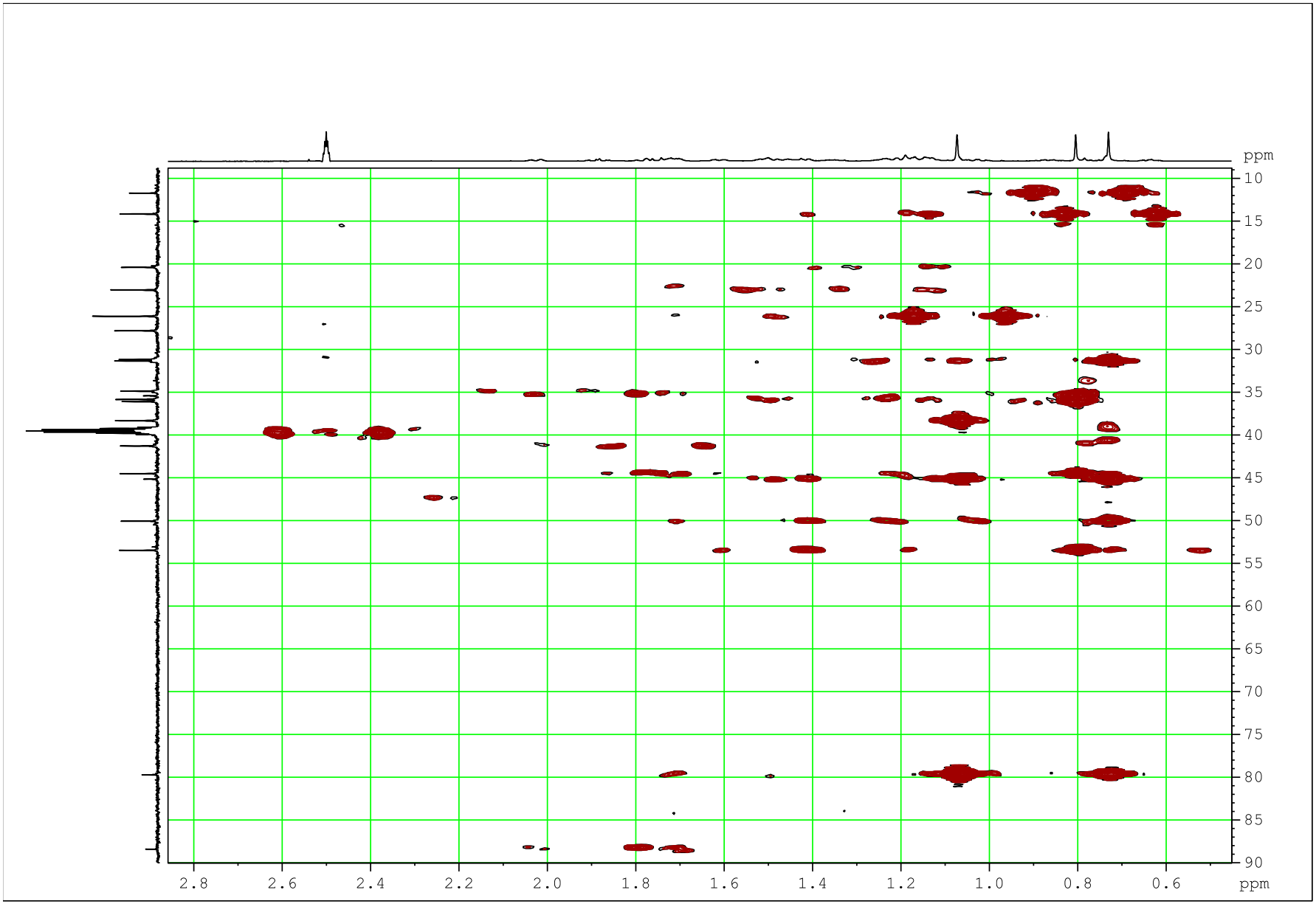
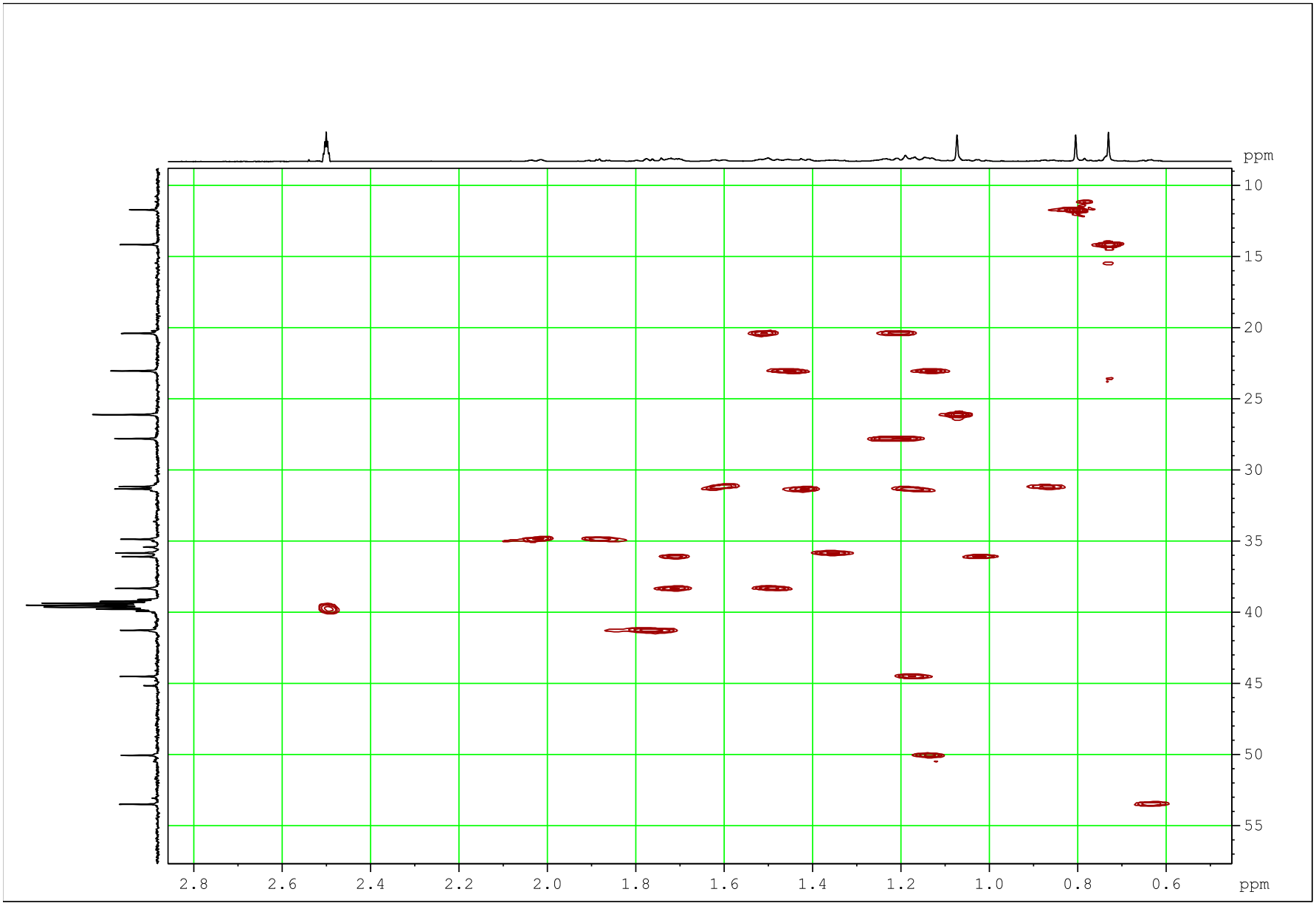


2D ^{1}H-^{13}C HMBC NMR spectrum of **3b** (DMSO-d_6).



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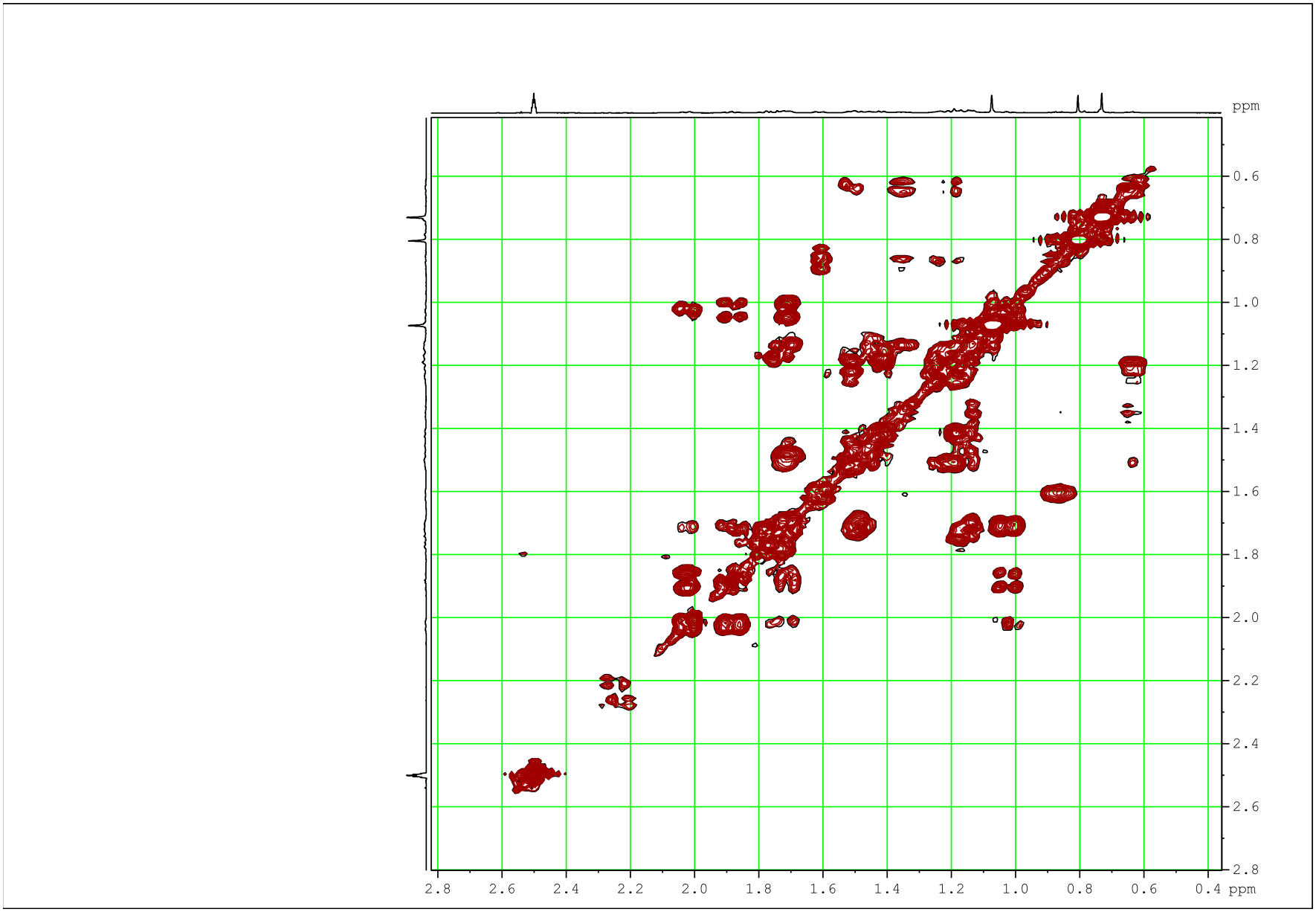

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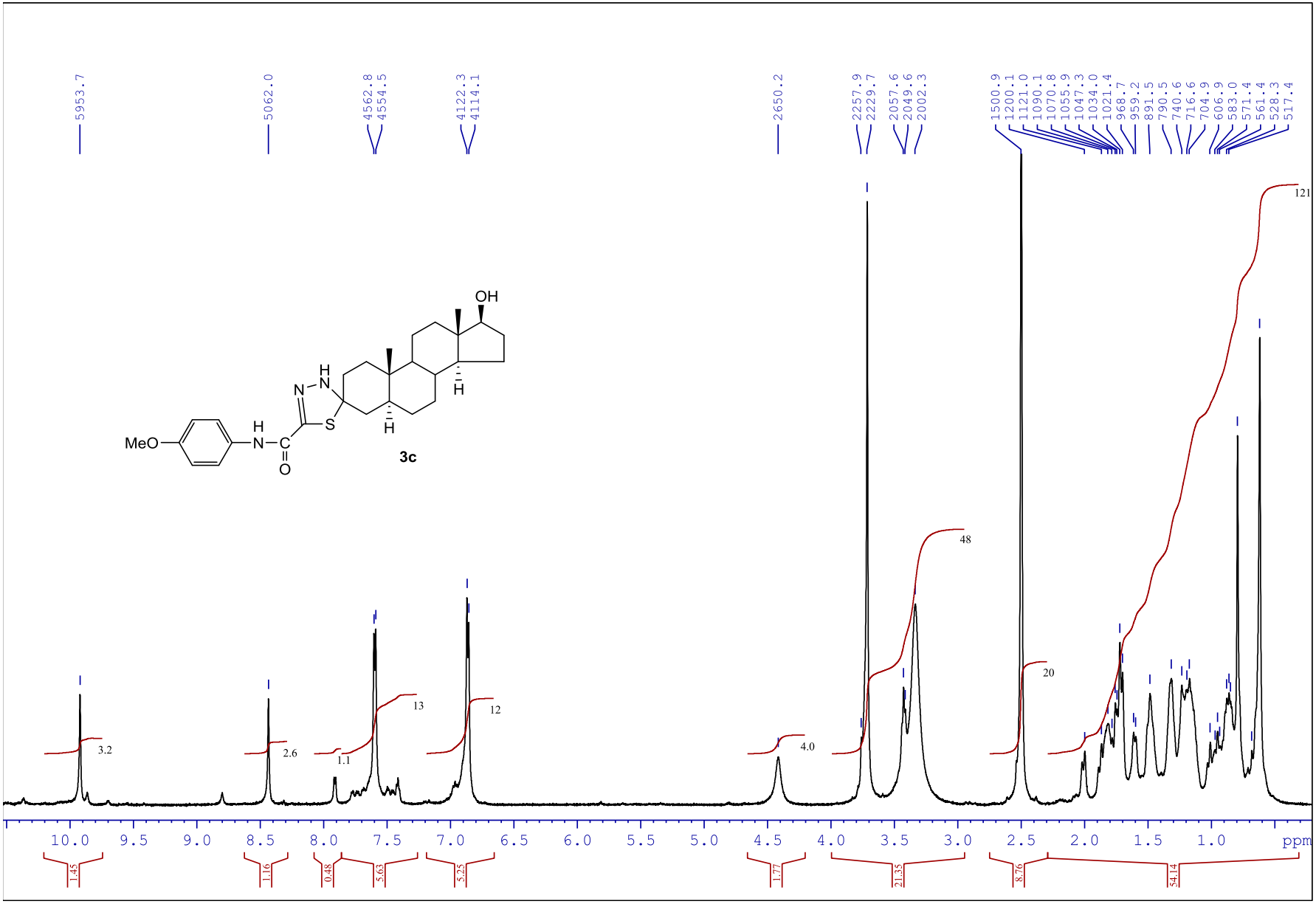
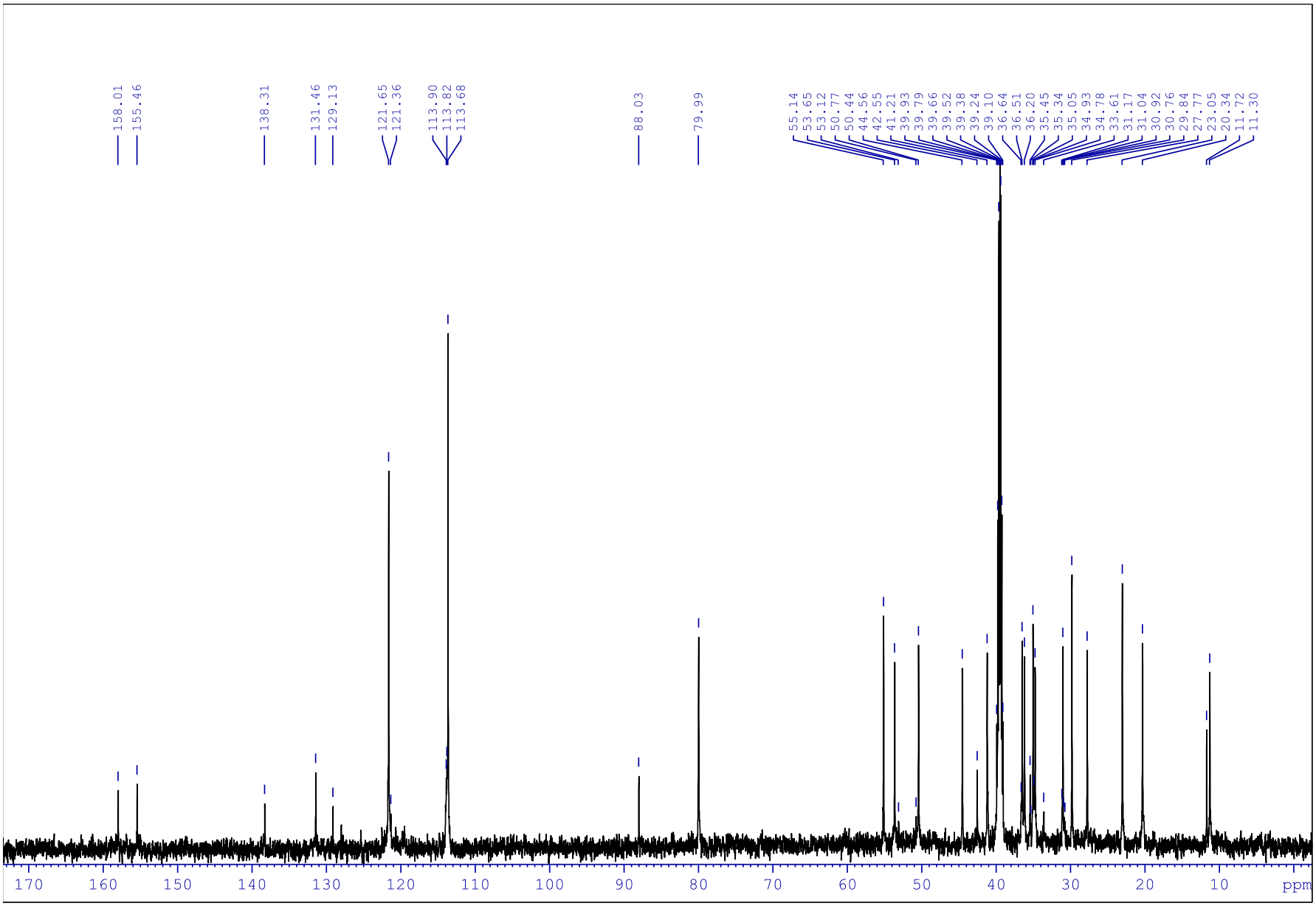
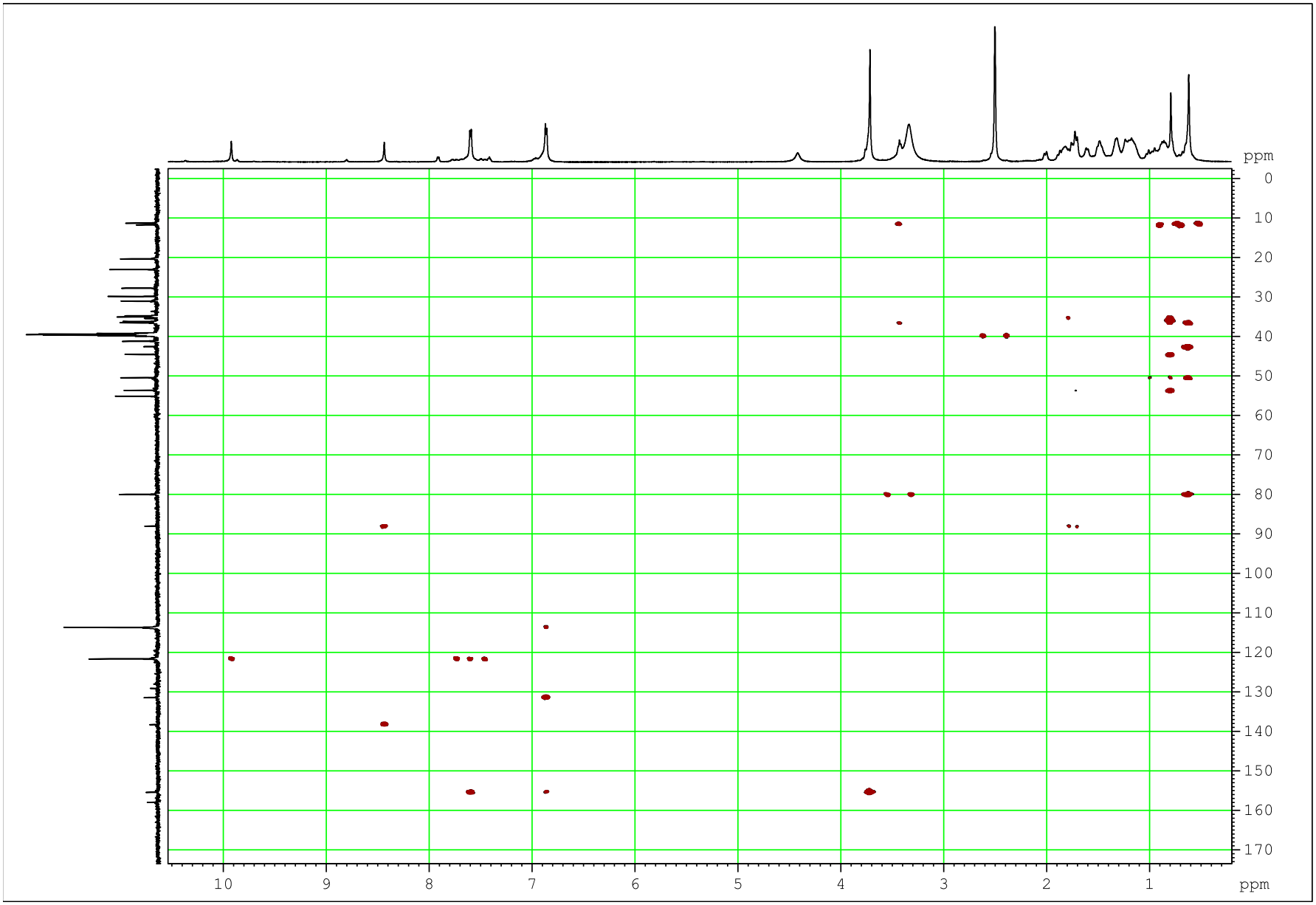


^{1}H NMR spectrum of **3c** (DMSO-d_6).



^{13}C NMR spectrum of **3c** (DMSO-d_6).



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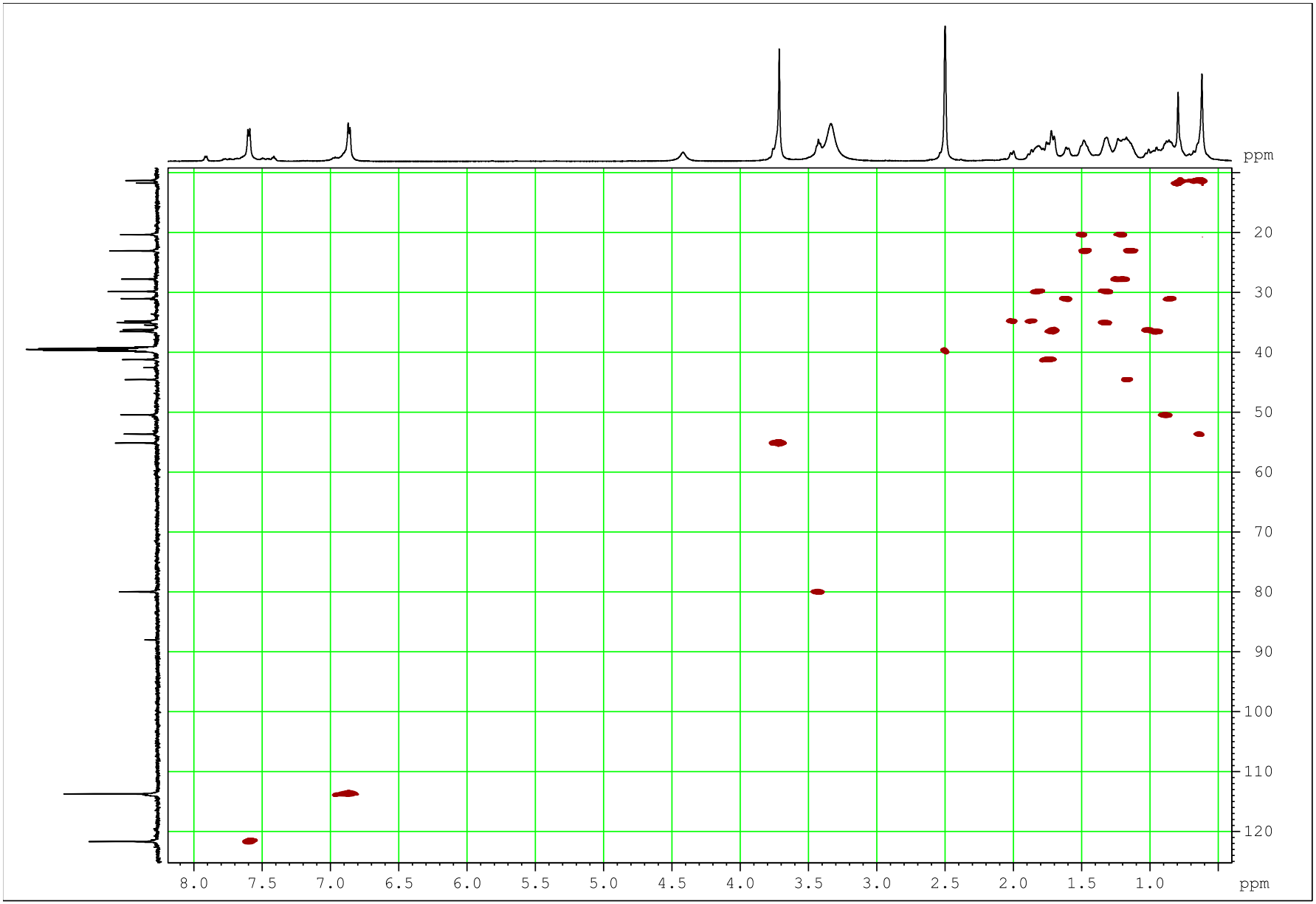

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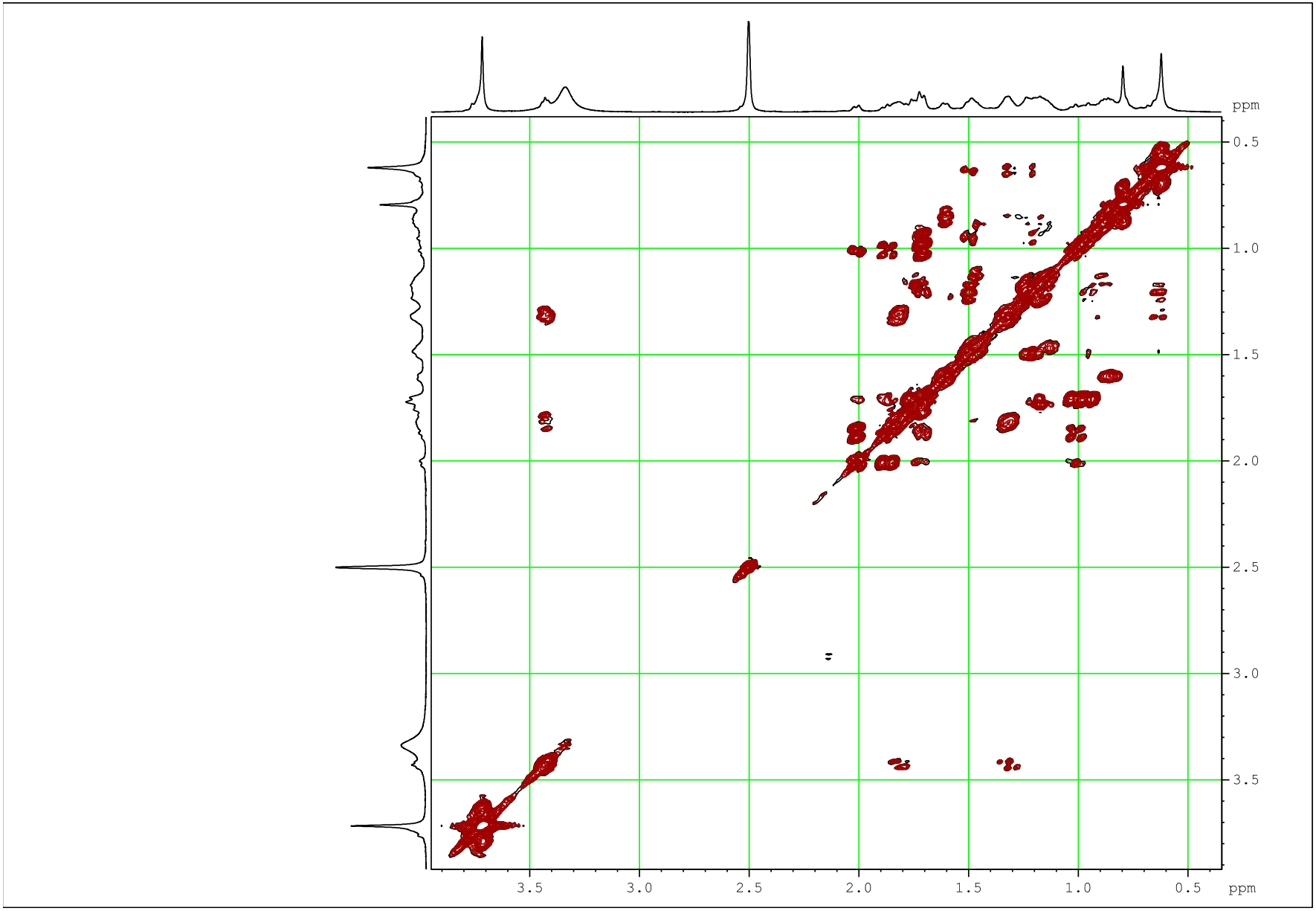

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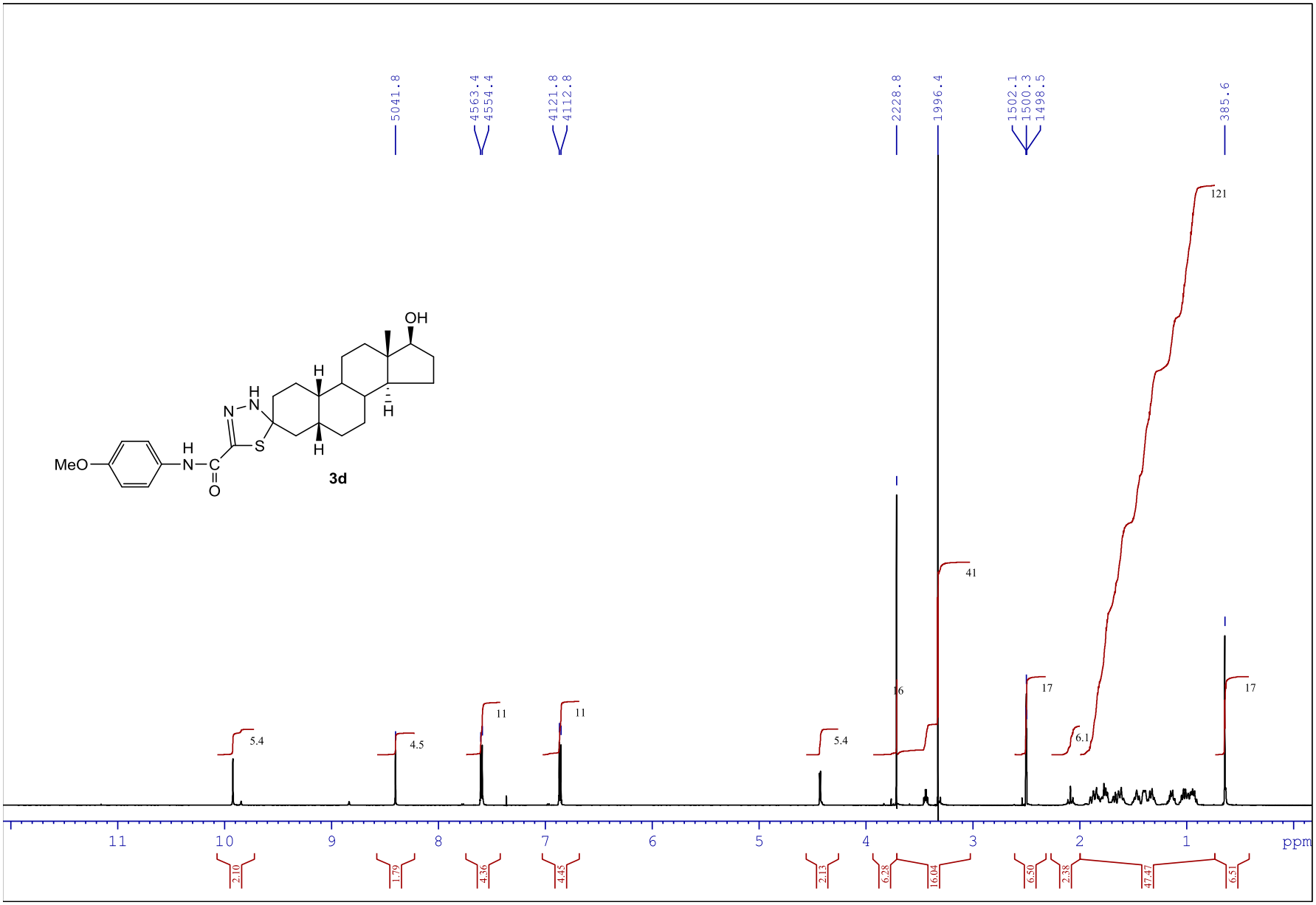

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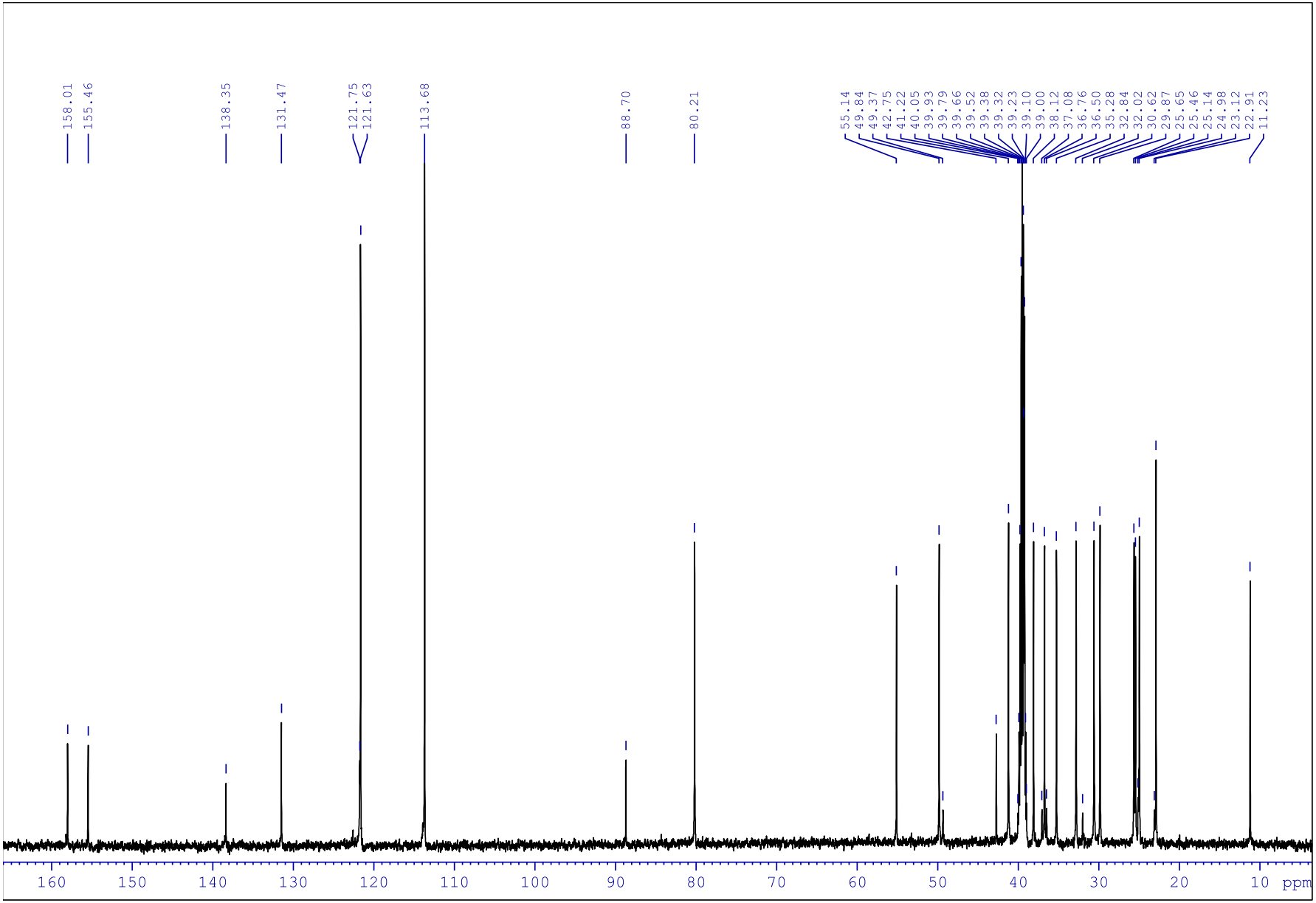

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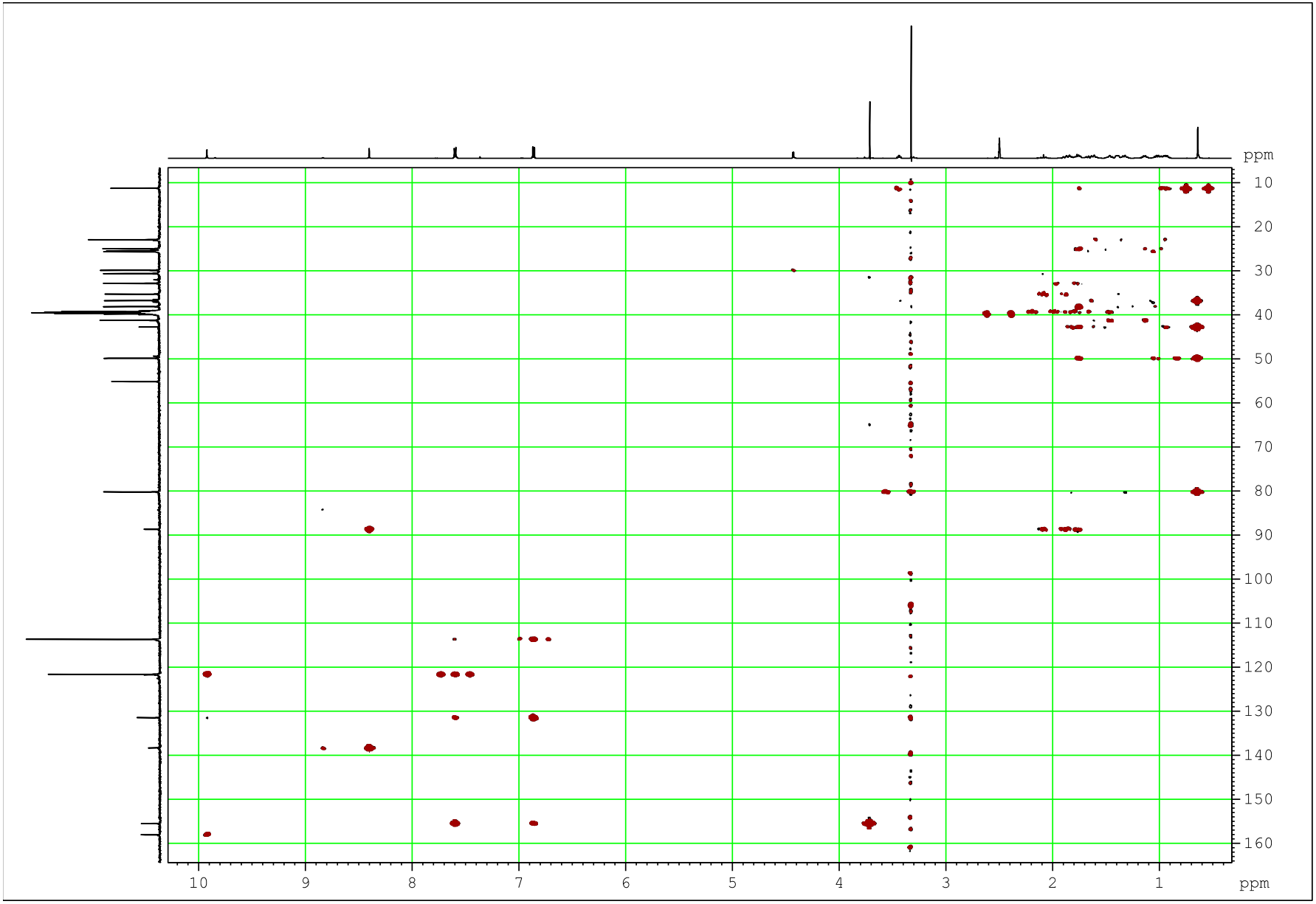

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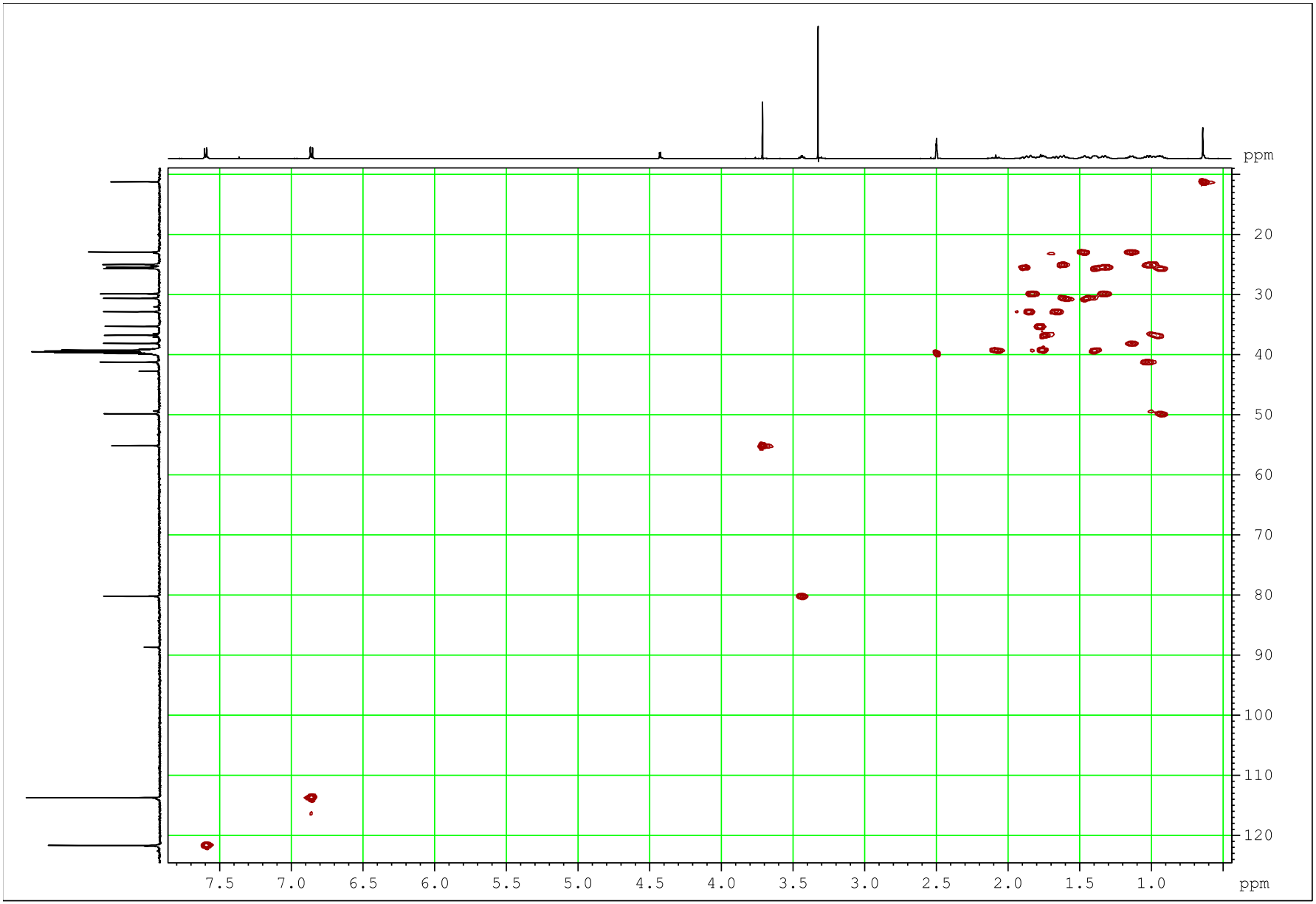

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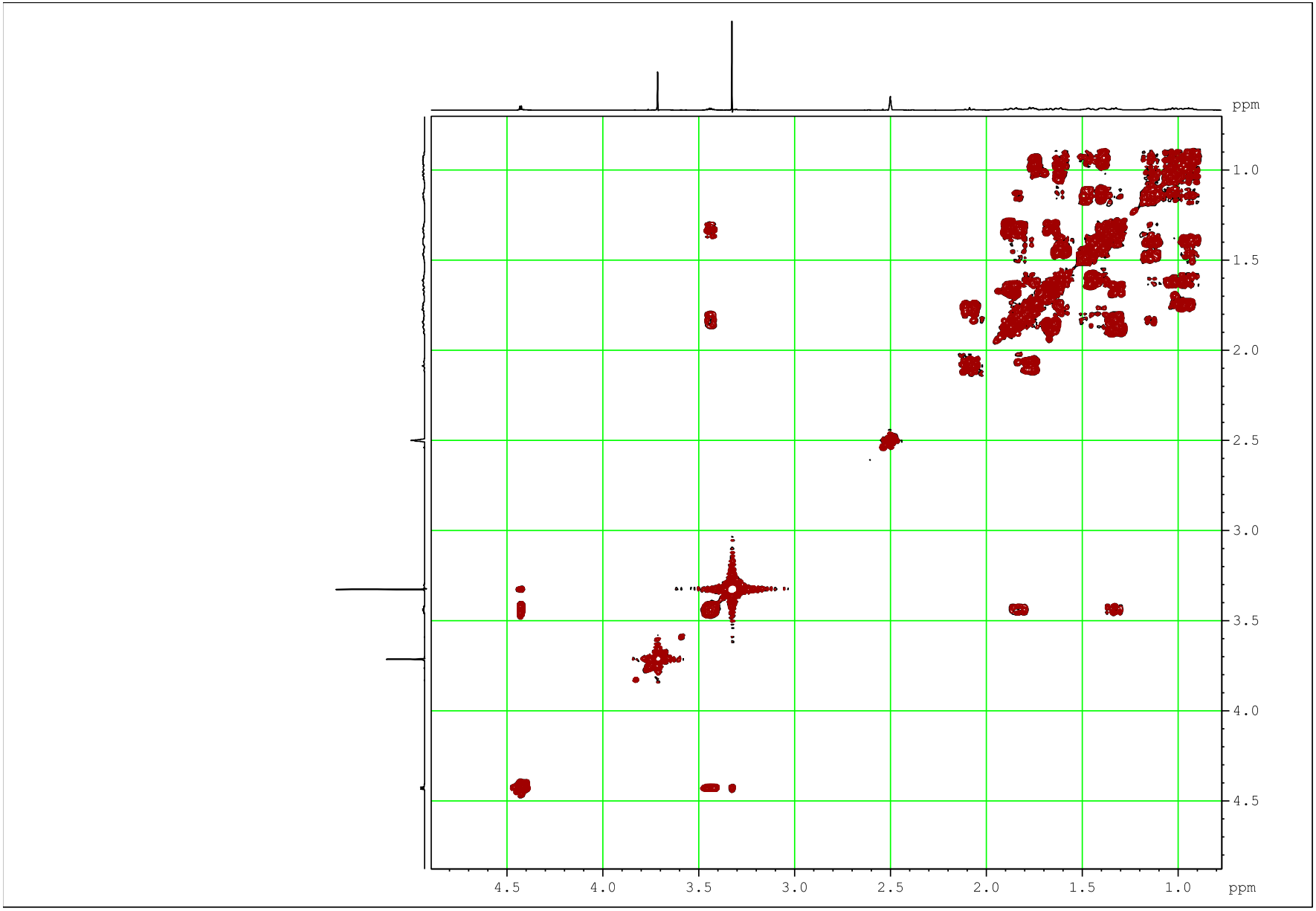

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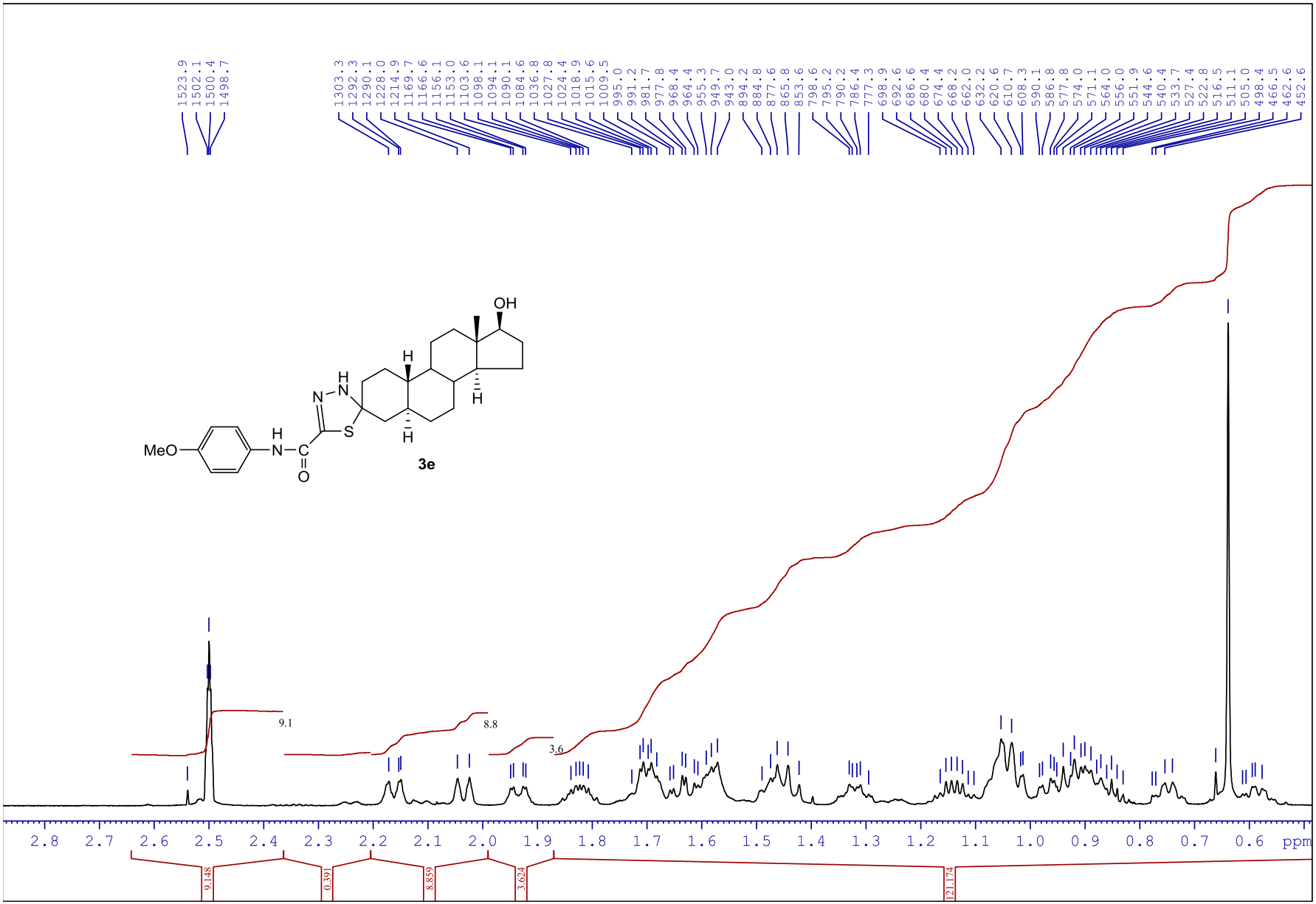

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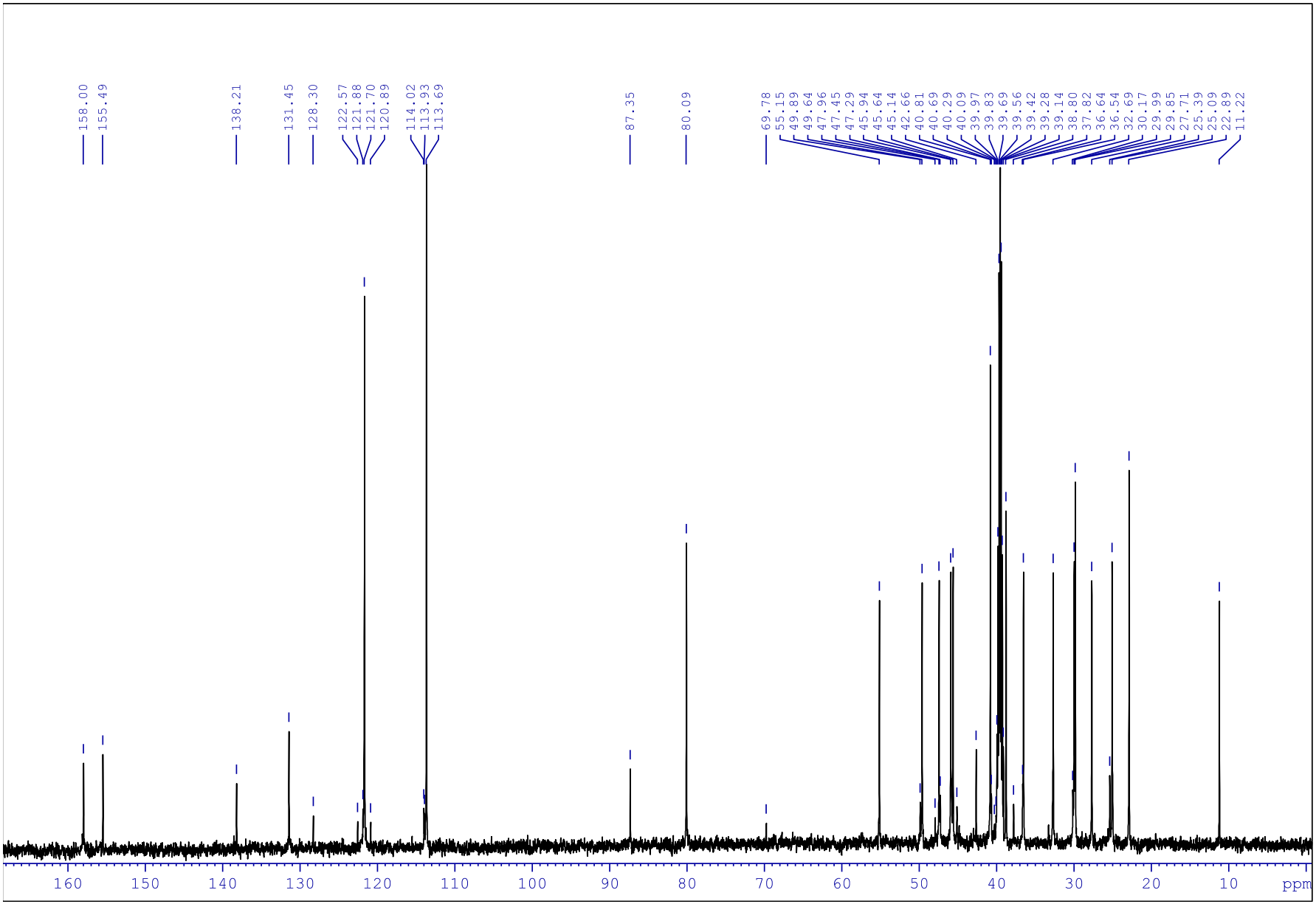

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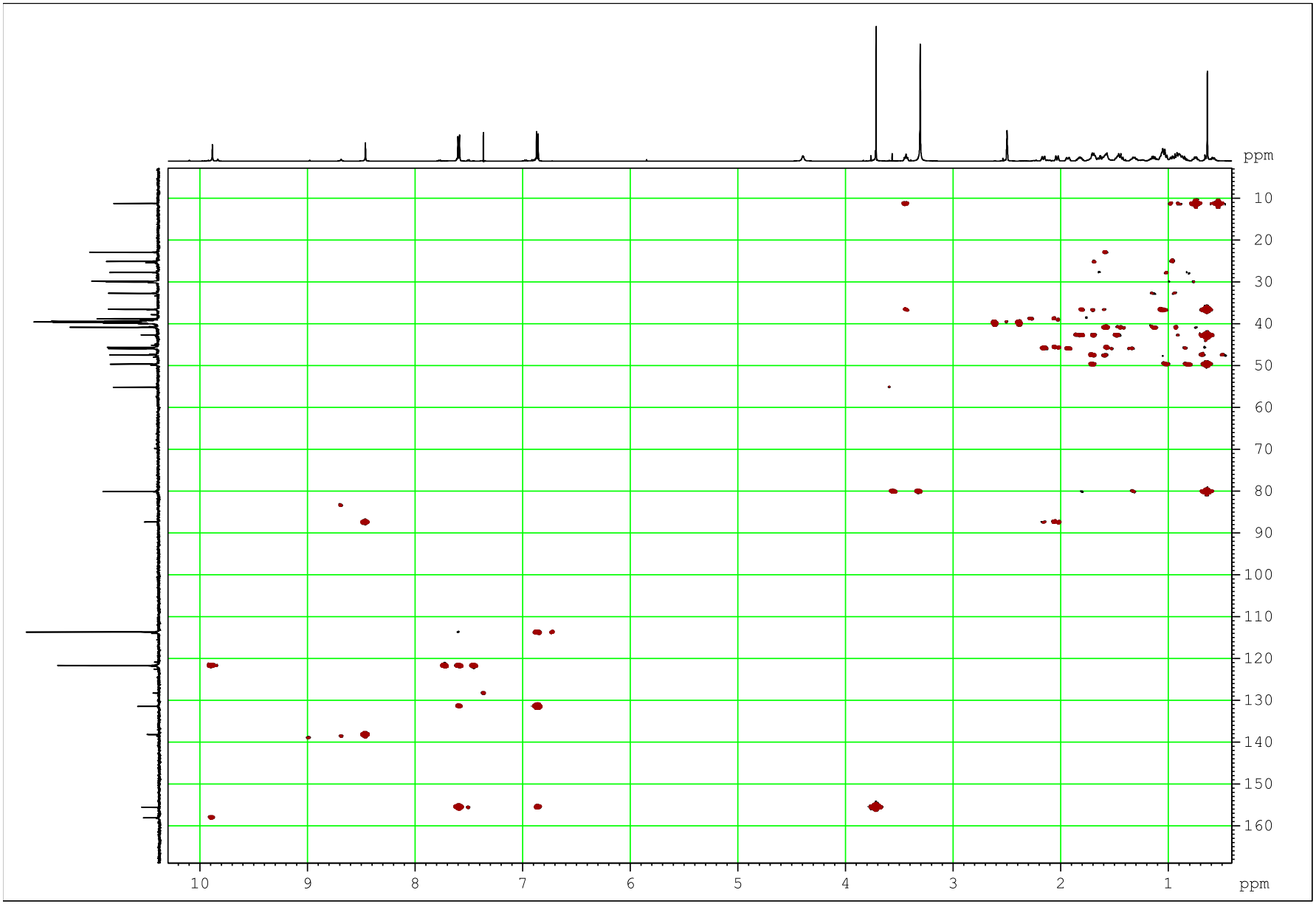

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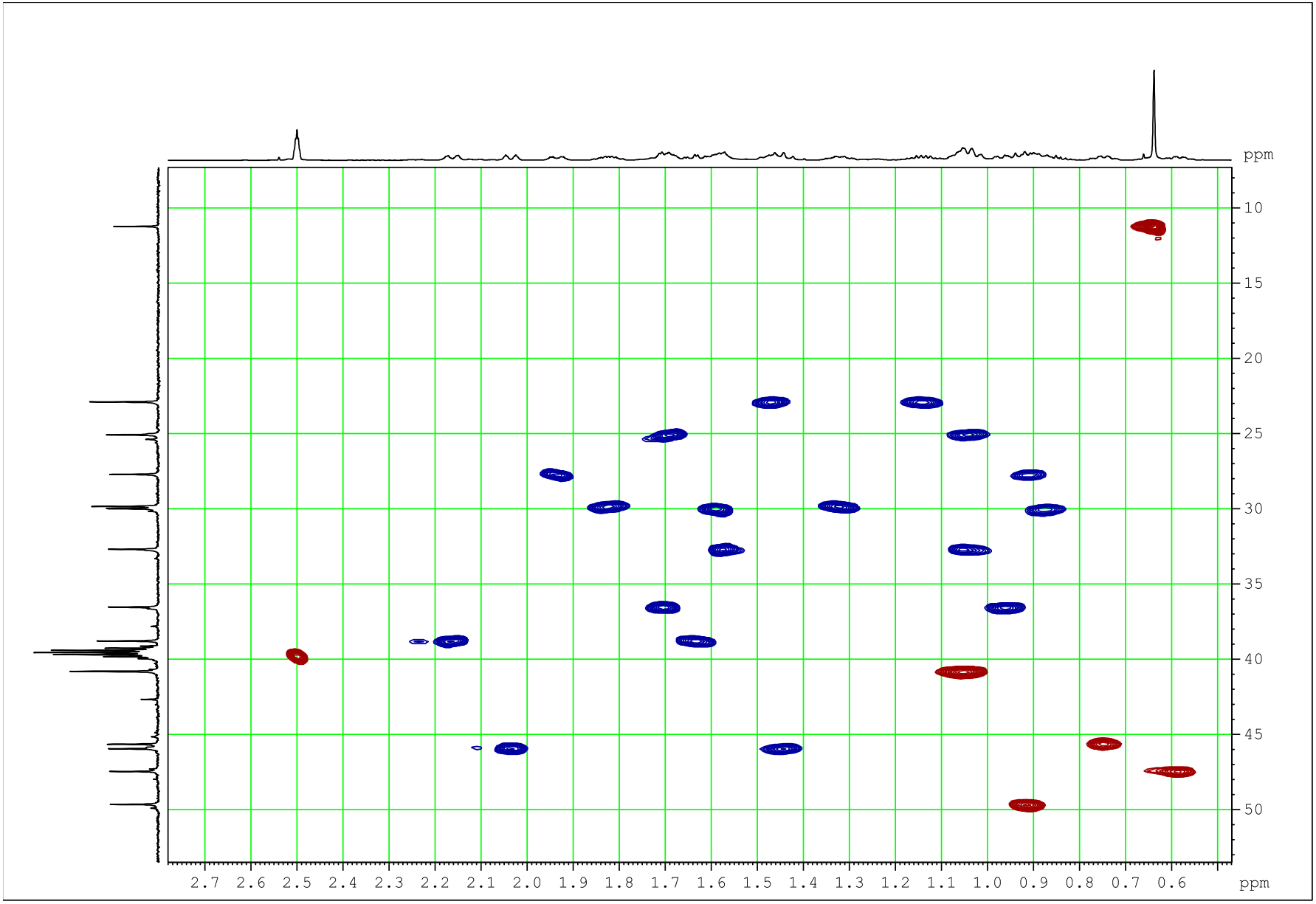

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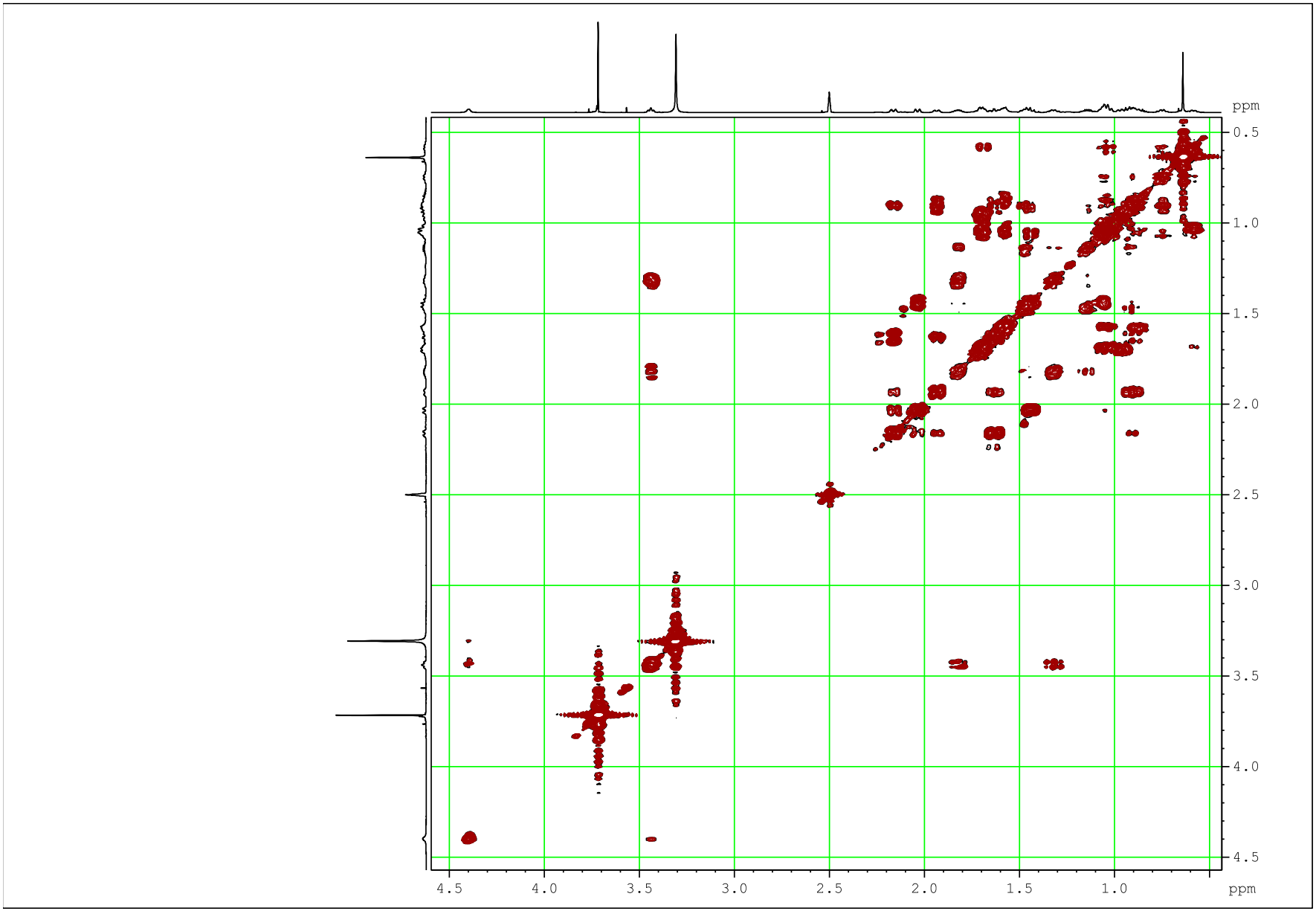

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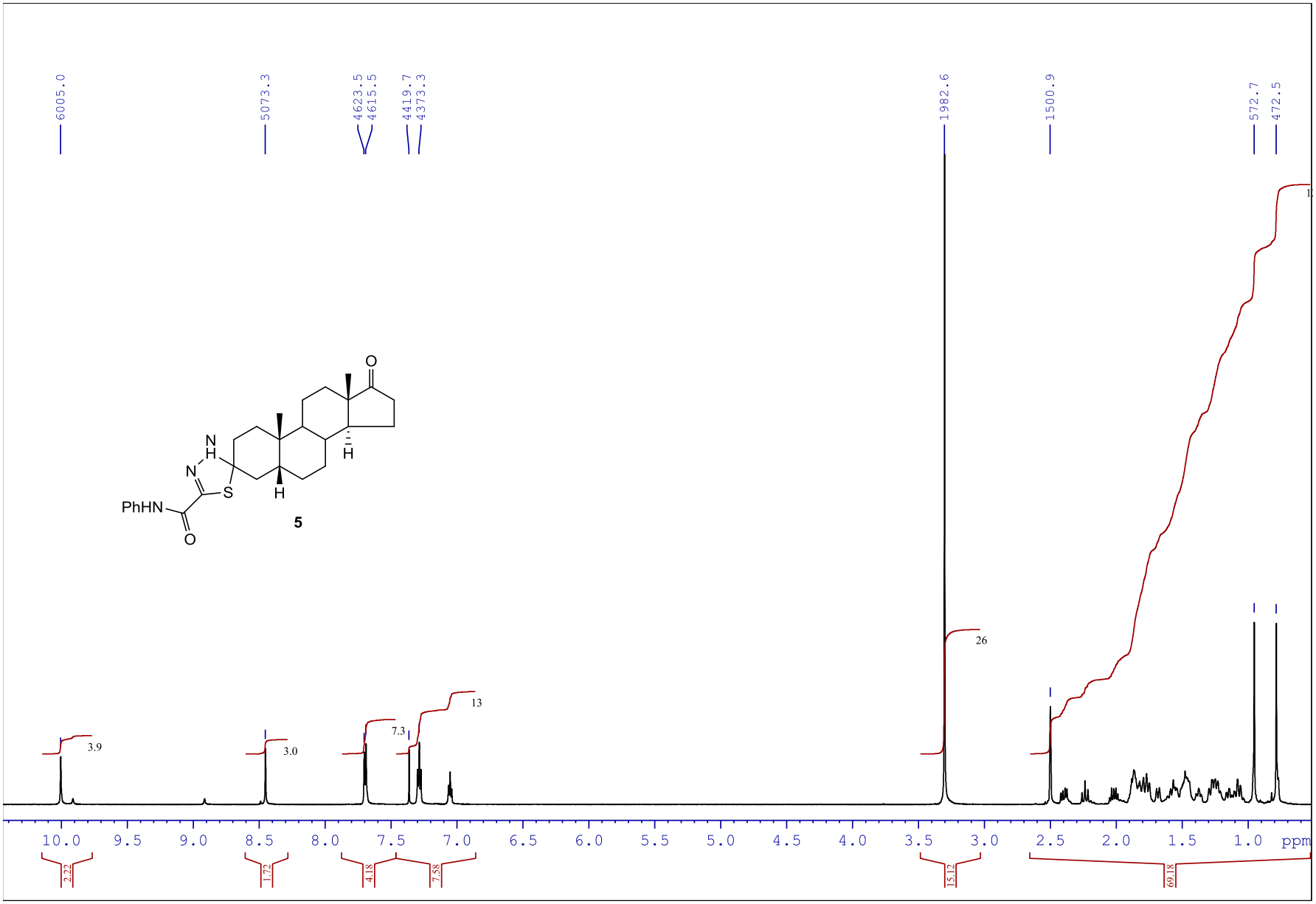

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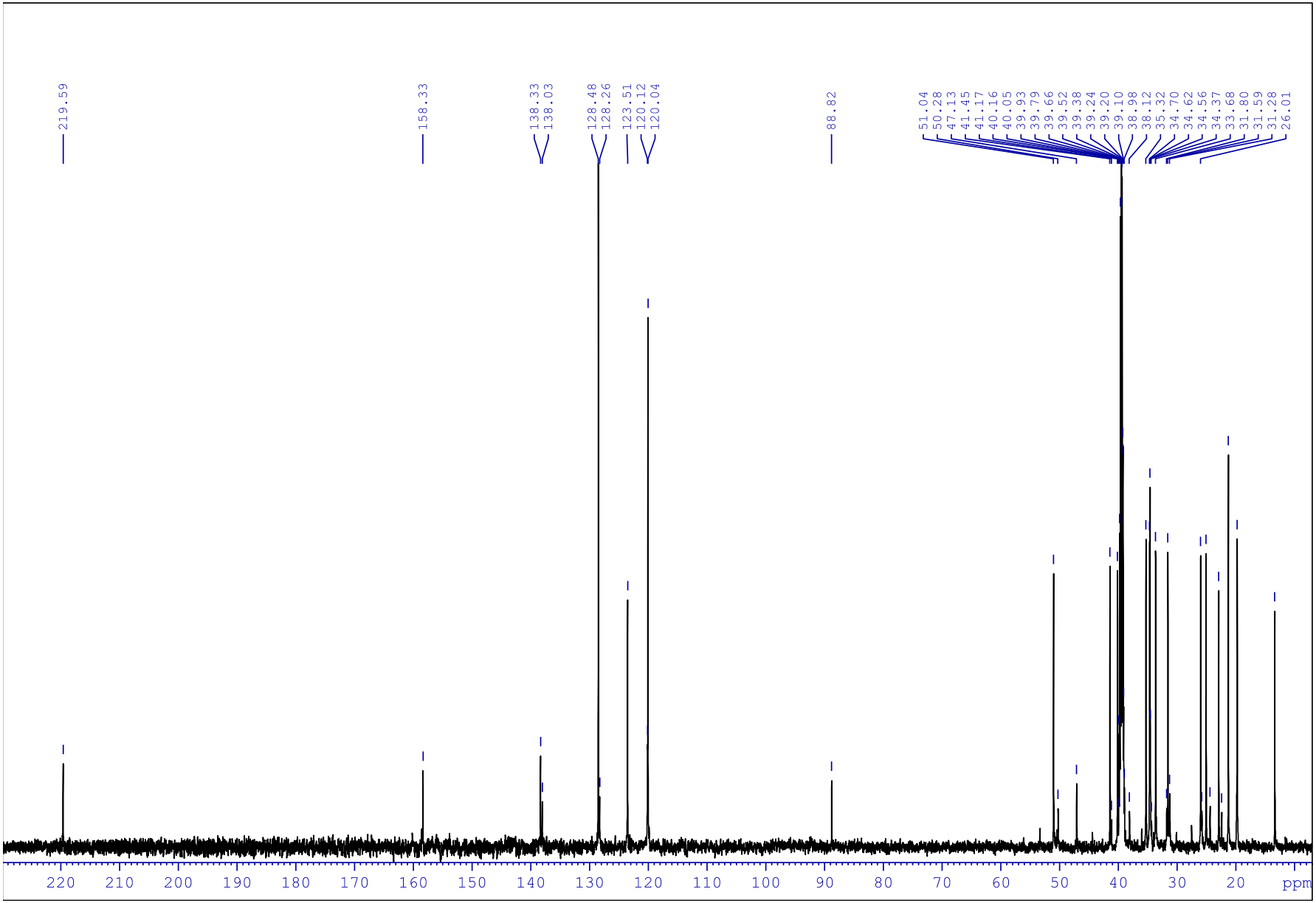
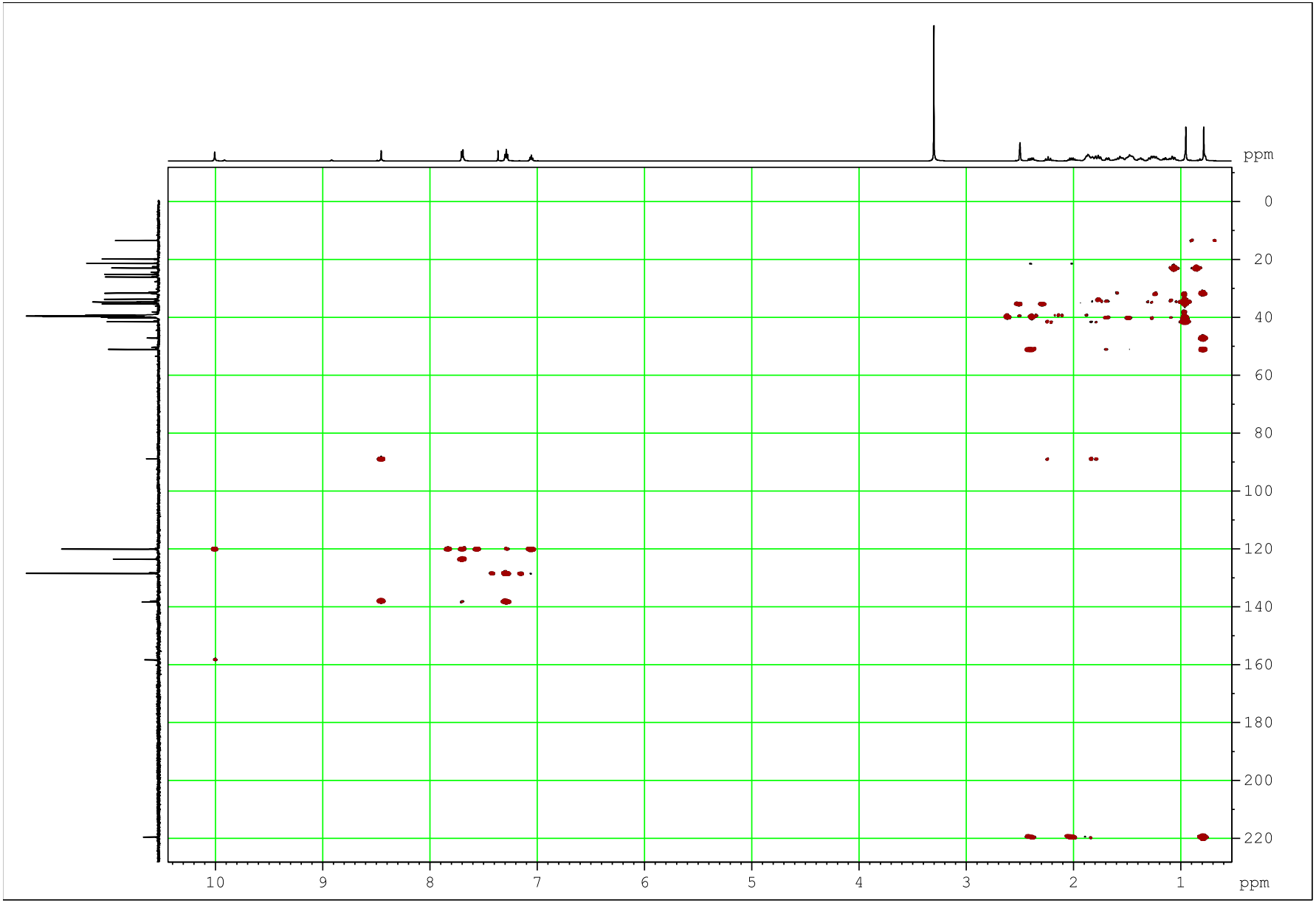


^{13}C NMR spectrum of **5** (DMSO-d_6).



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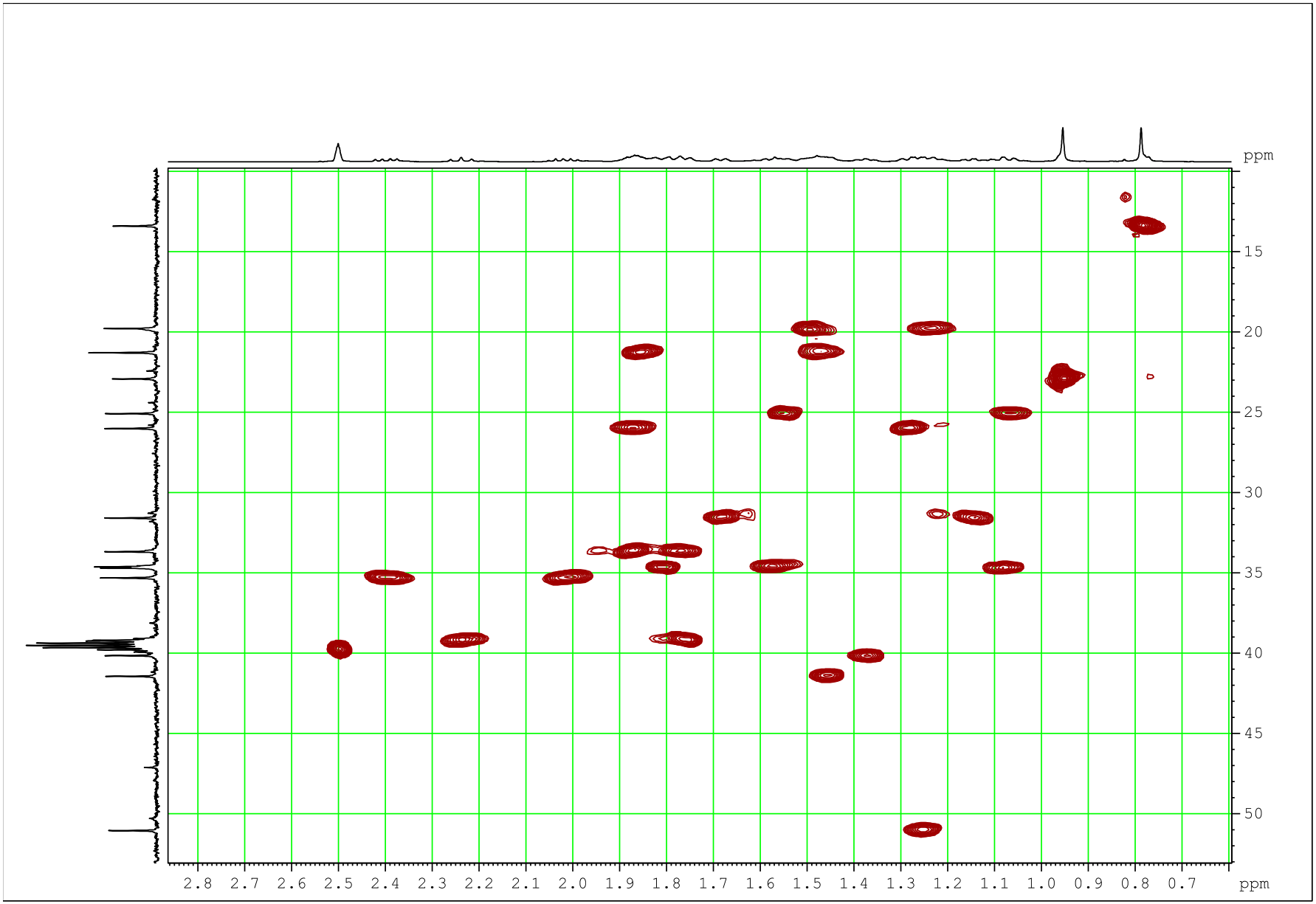
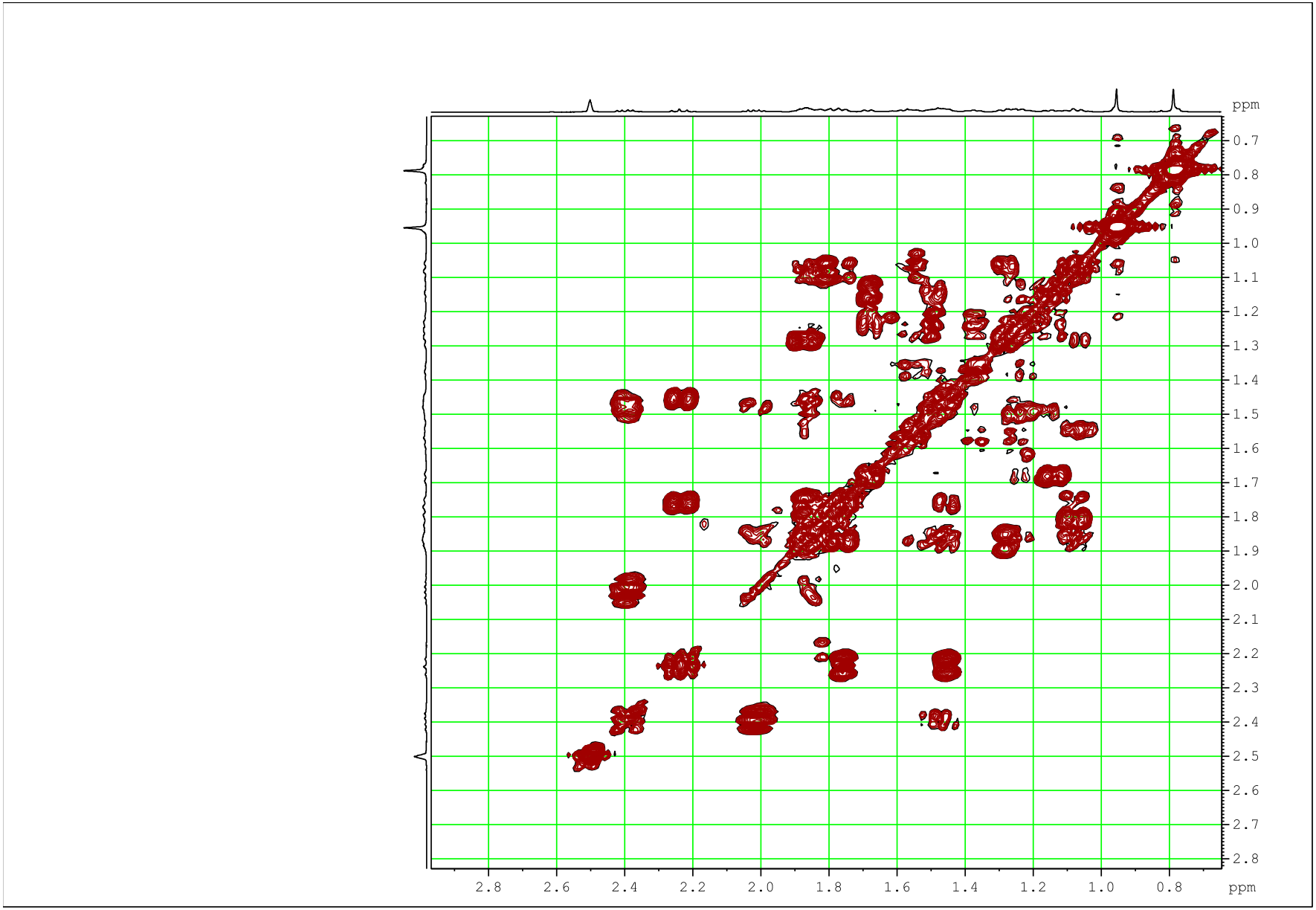


2D ^{1}H-^{13}C HSQC NMR spectrum of **5** (DMSO-d_6).



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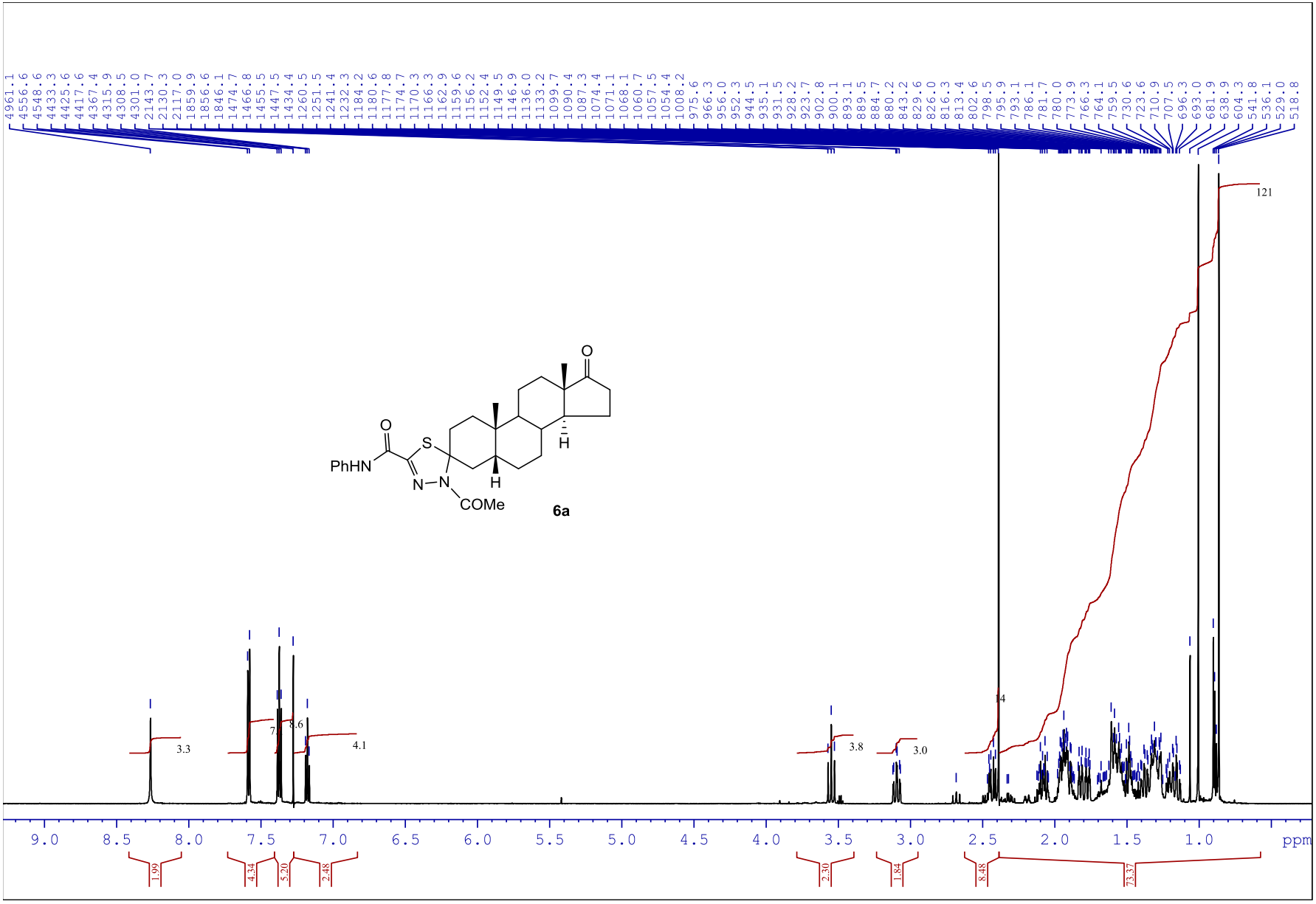
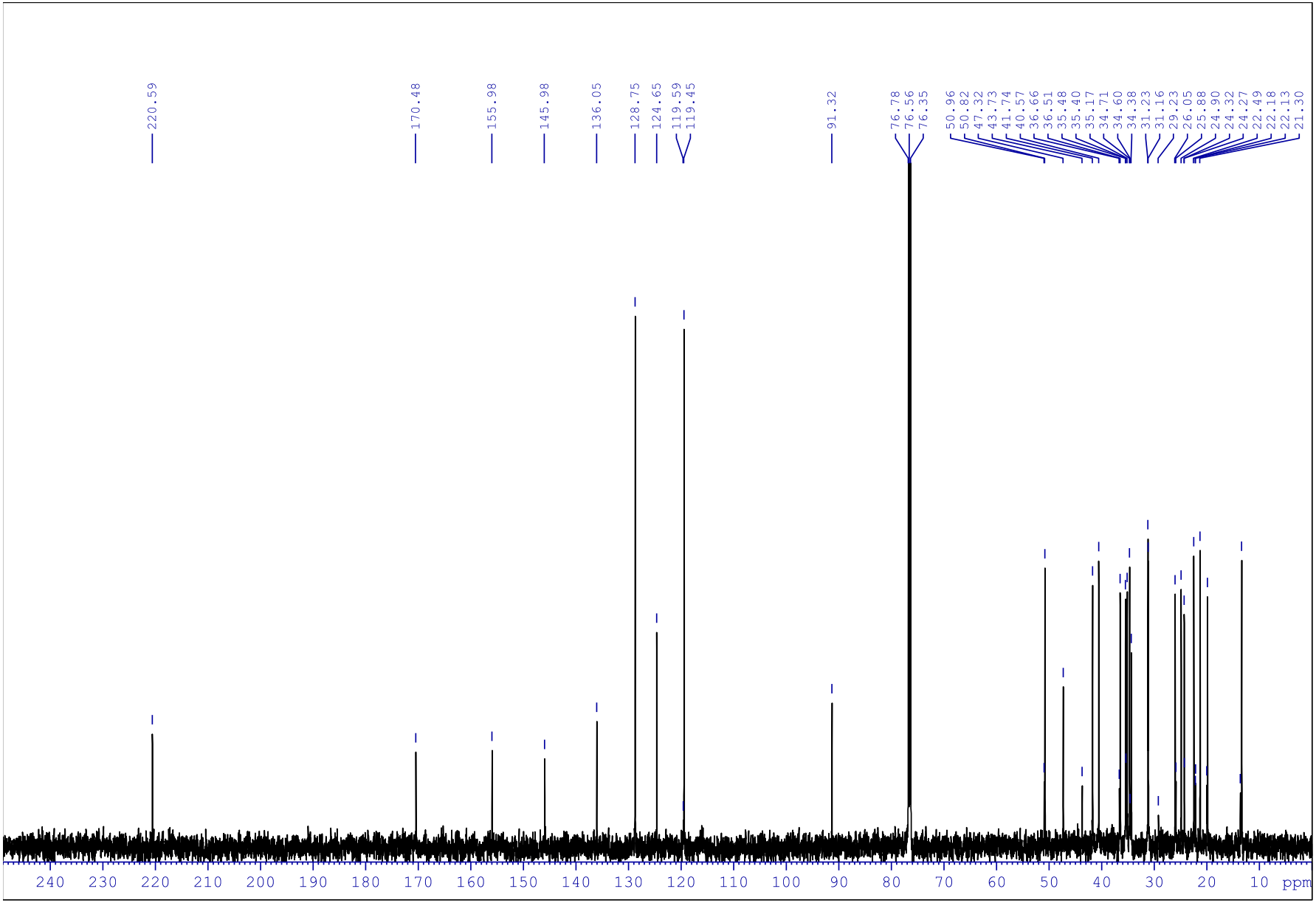


^{1}H NMR spectrum of **6a** ($CDCl_3$).



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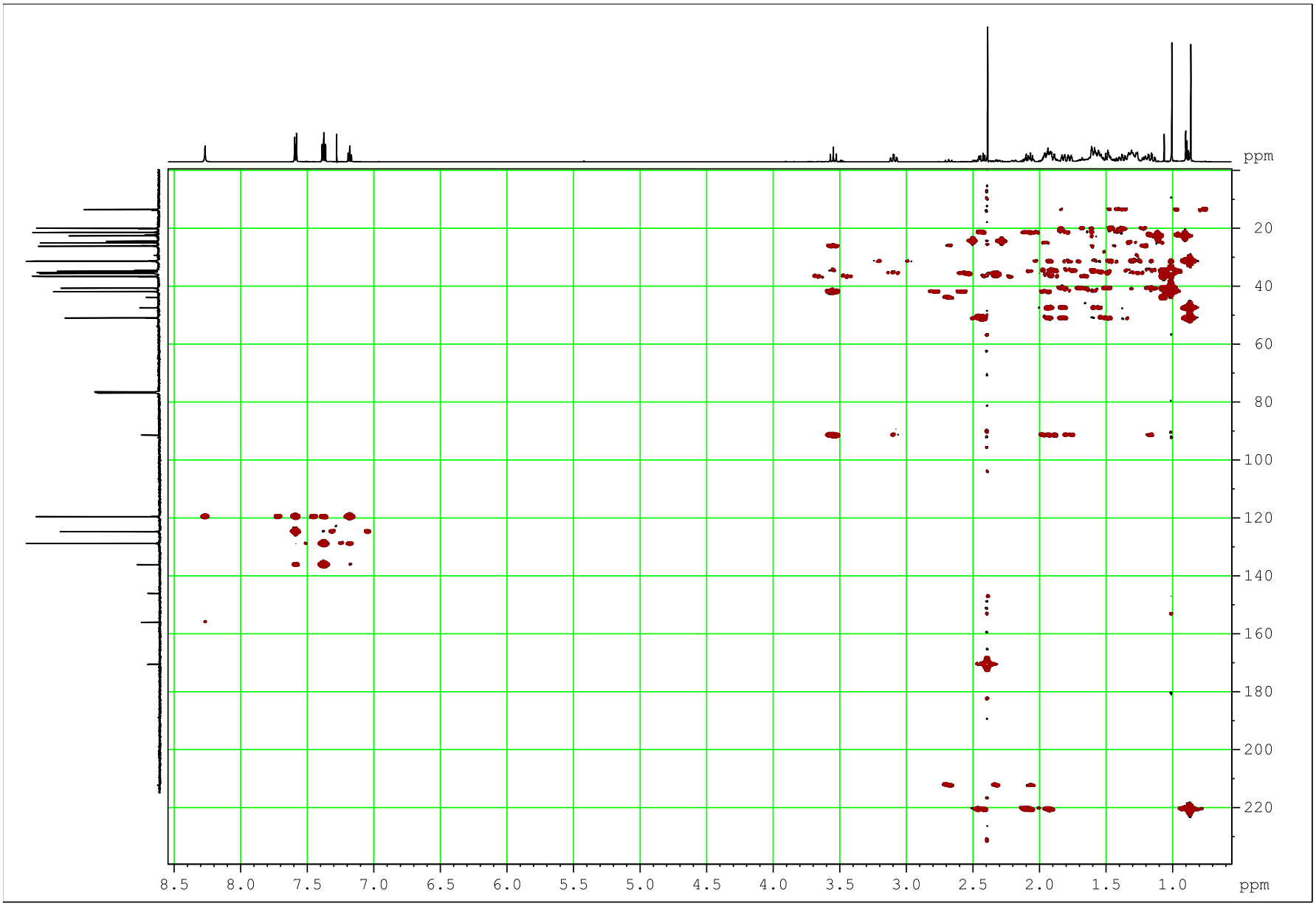

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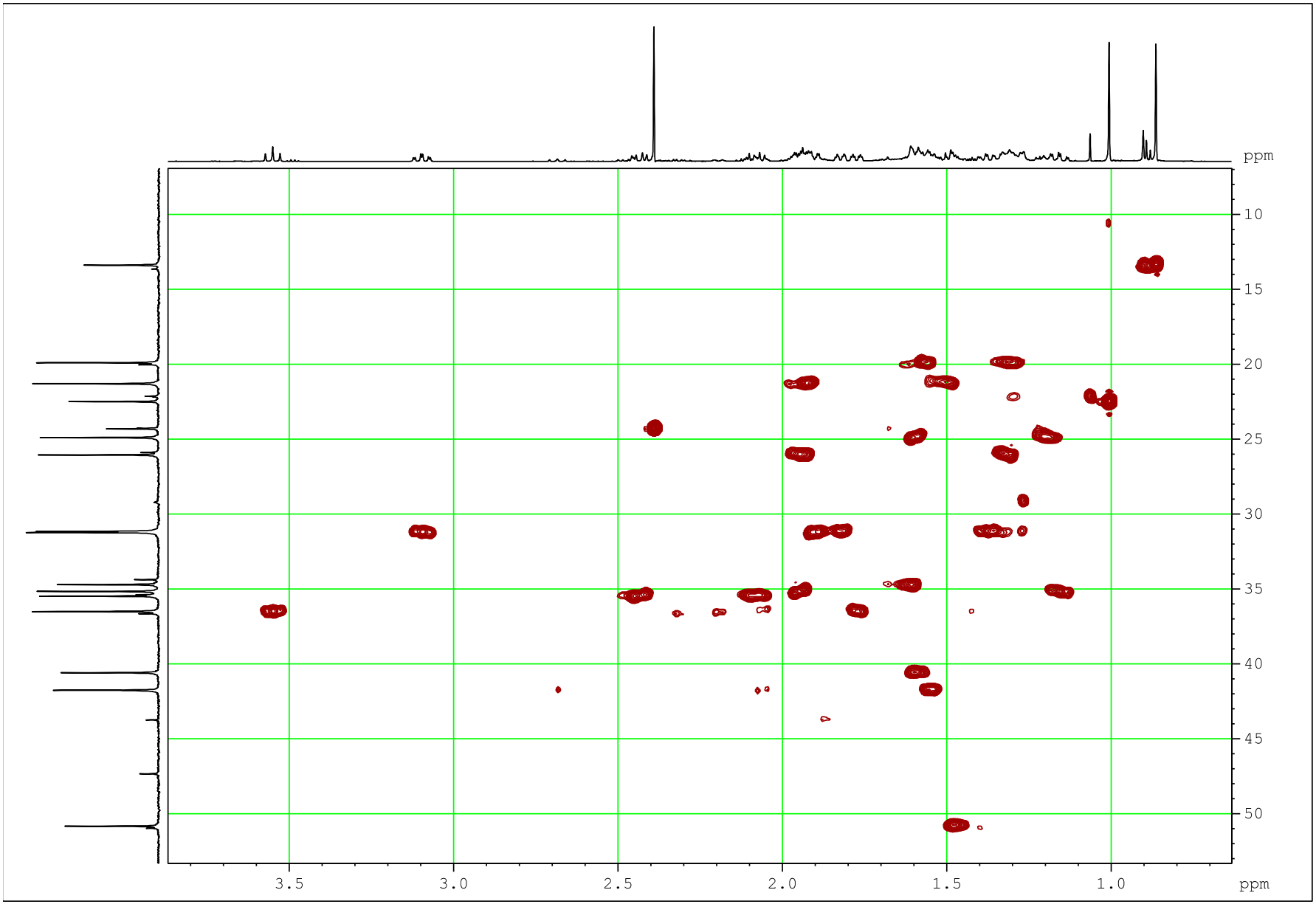

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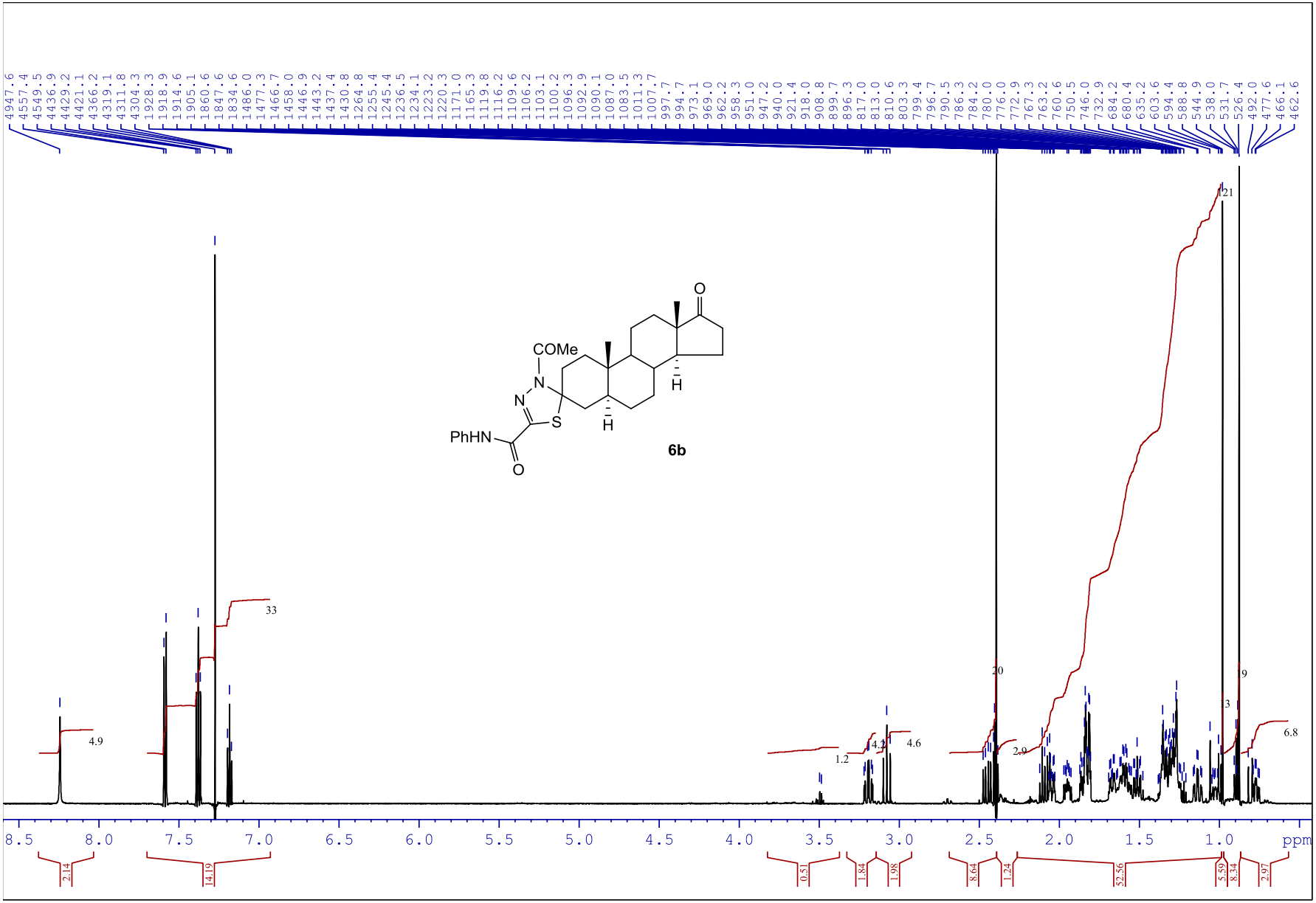

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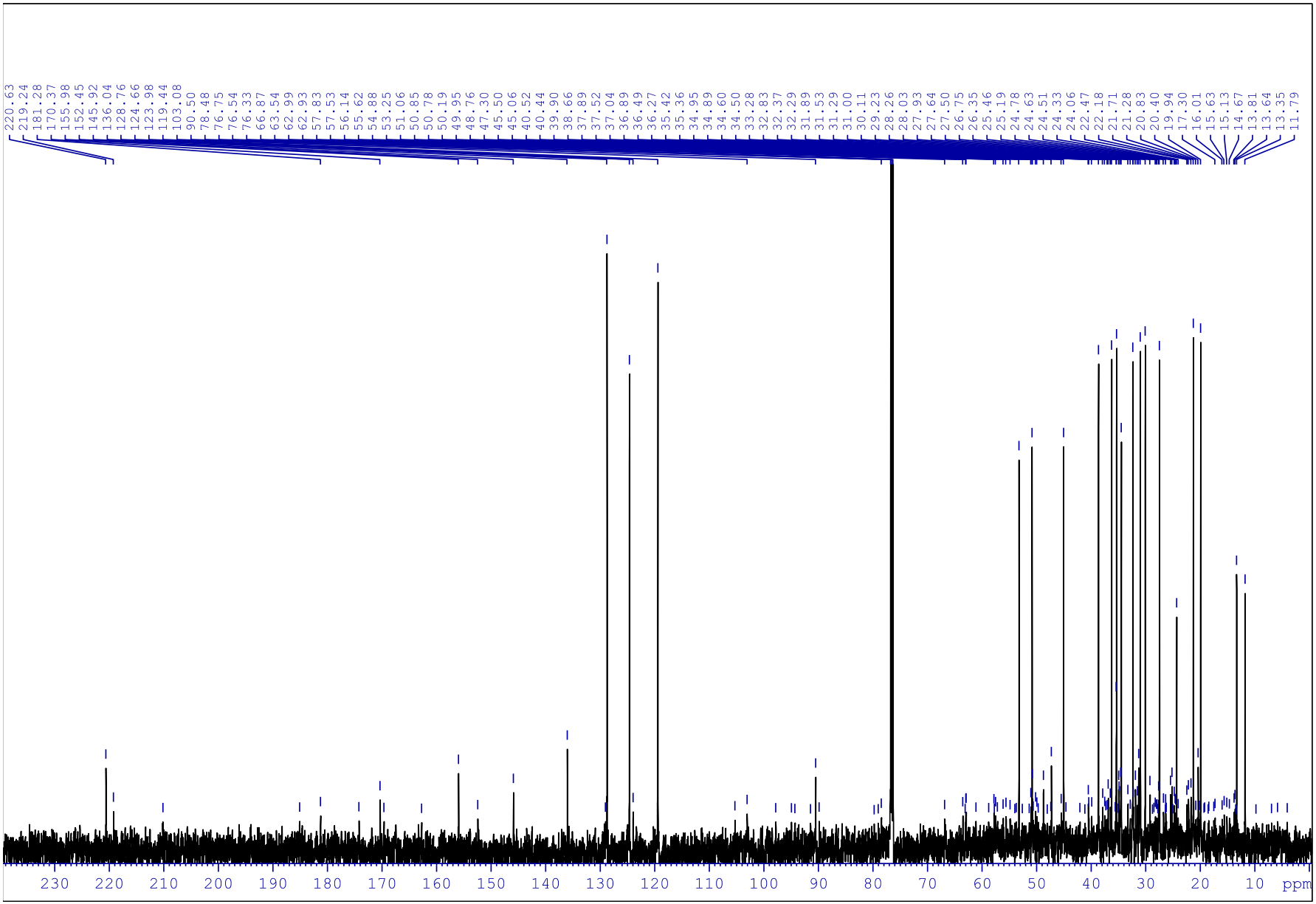

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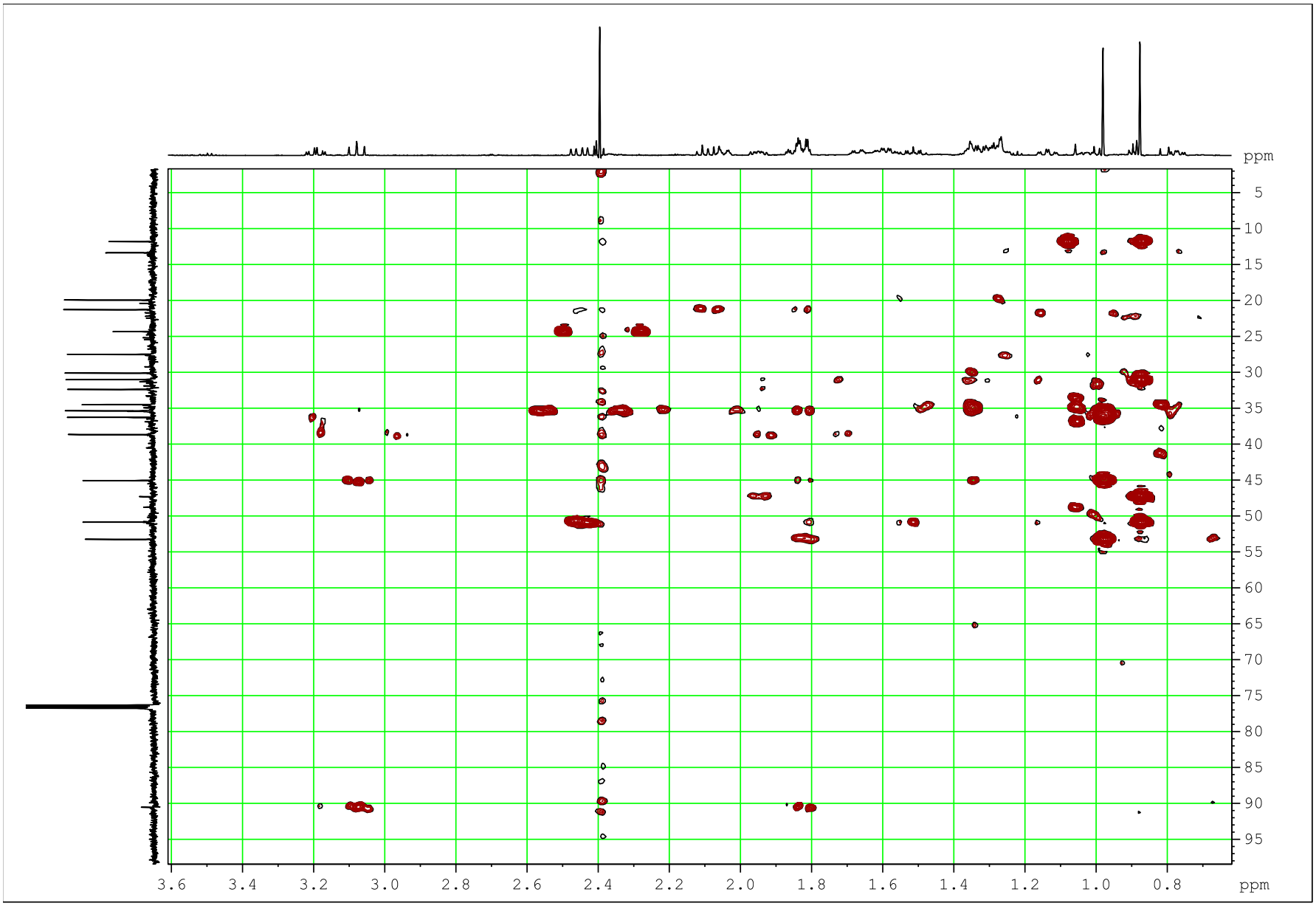

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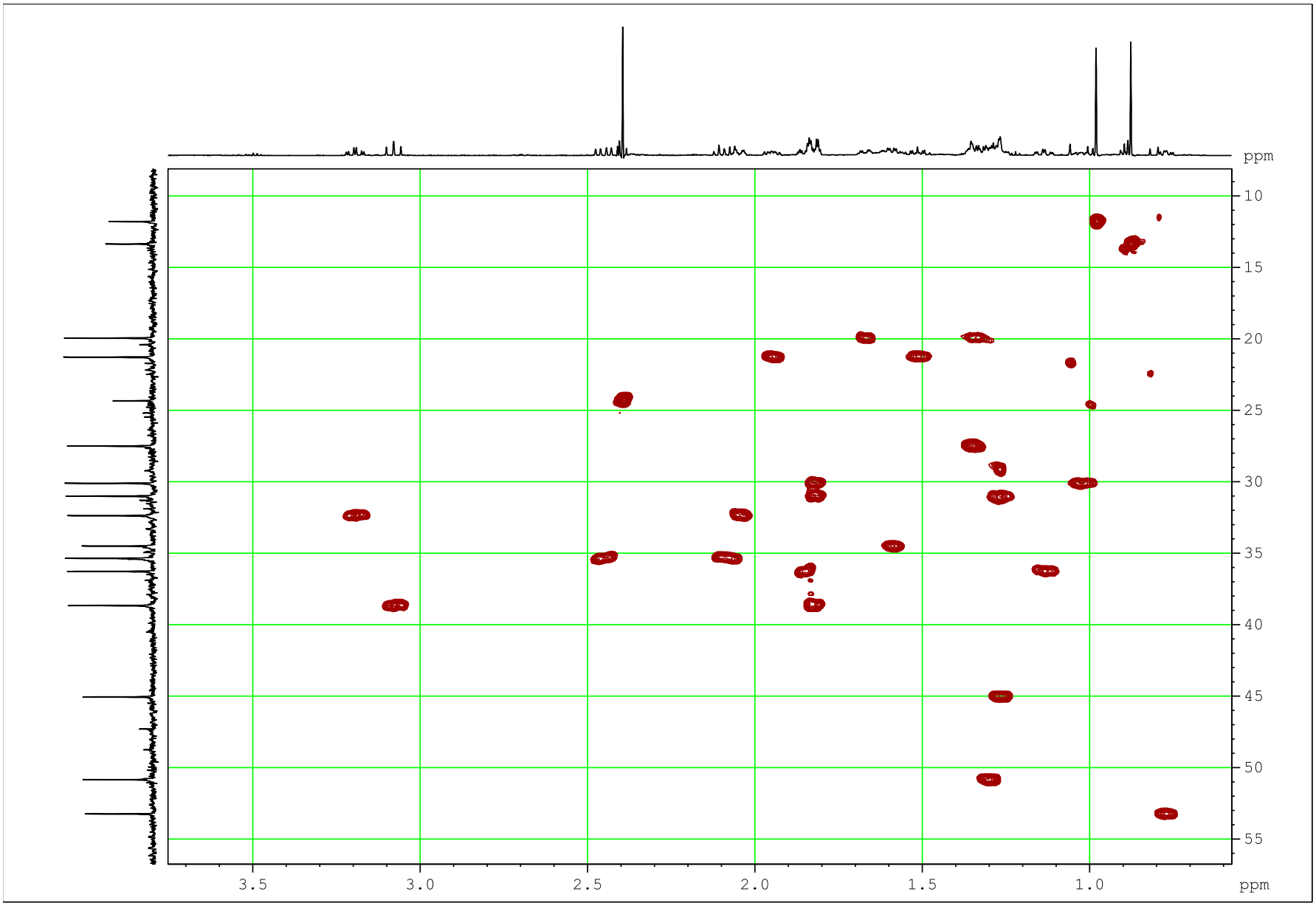

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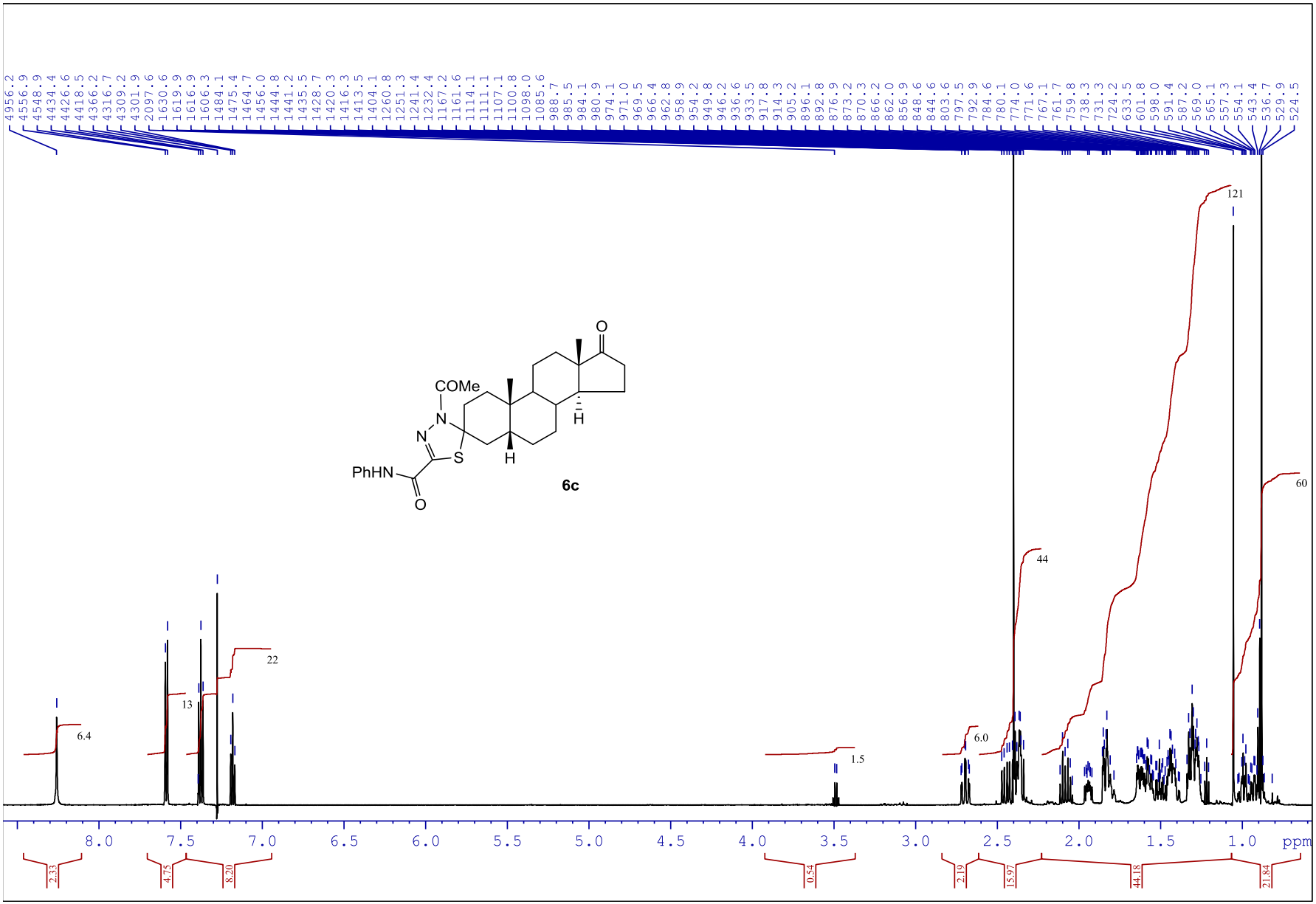

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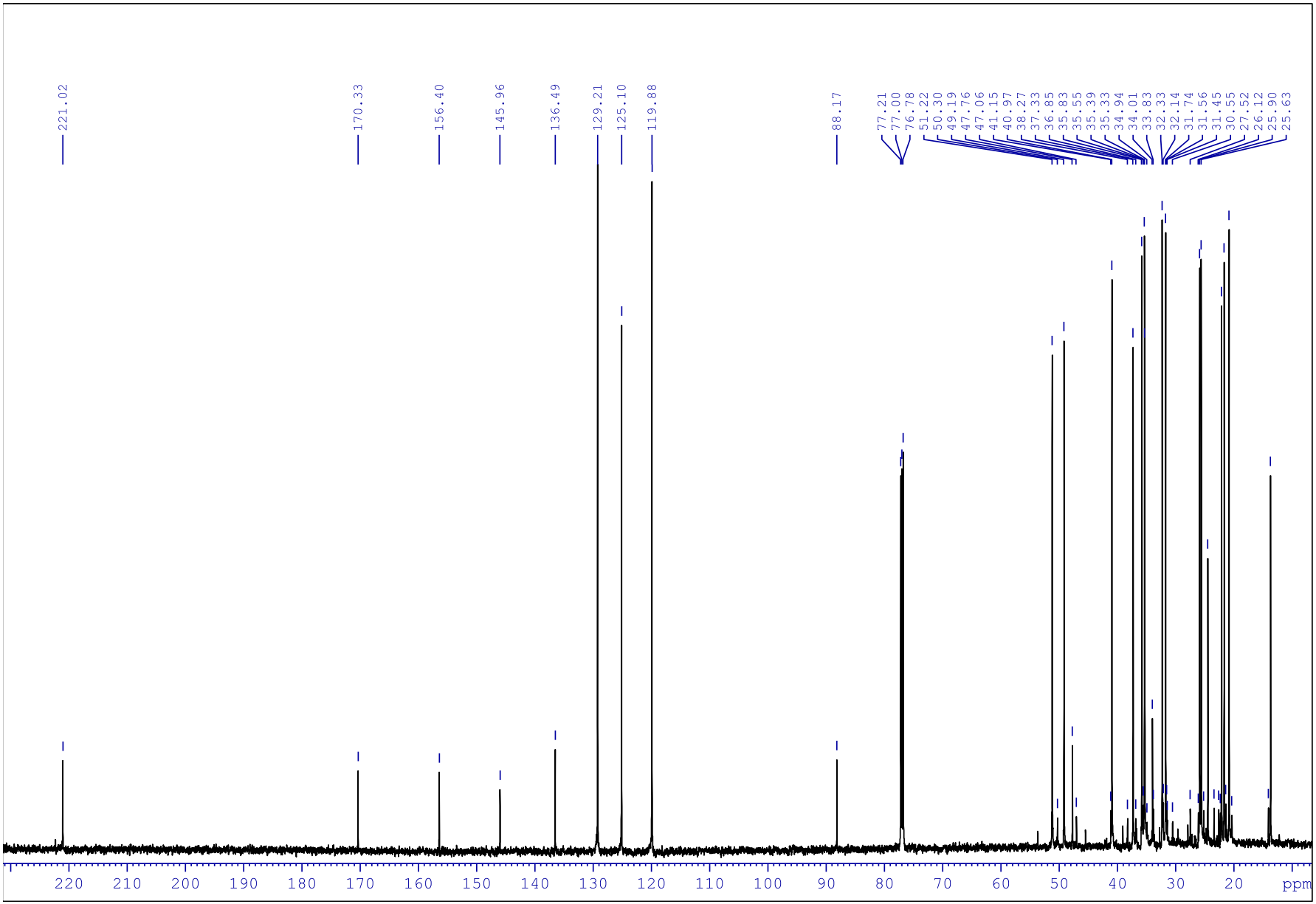

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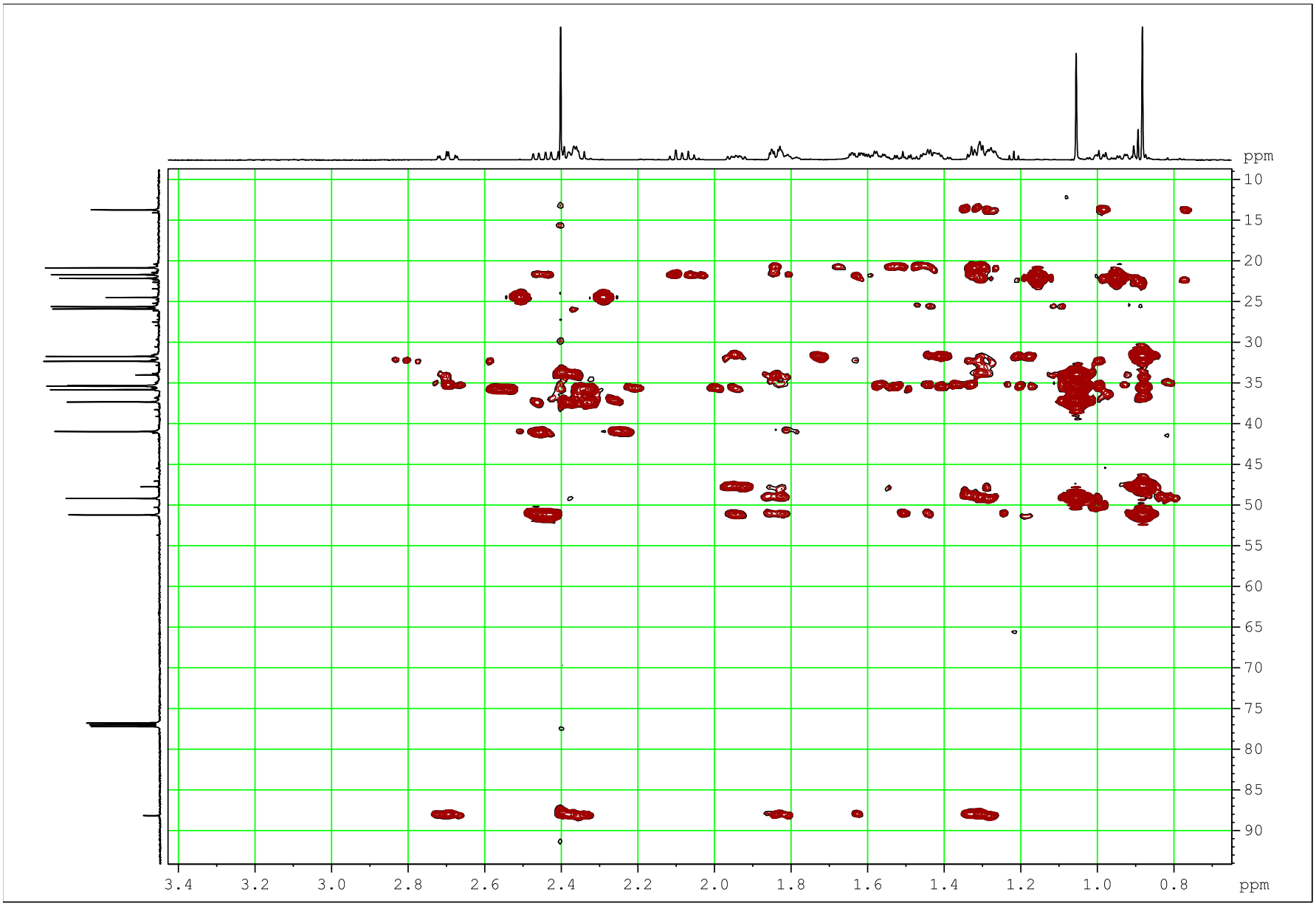

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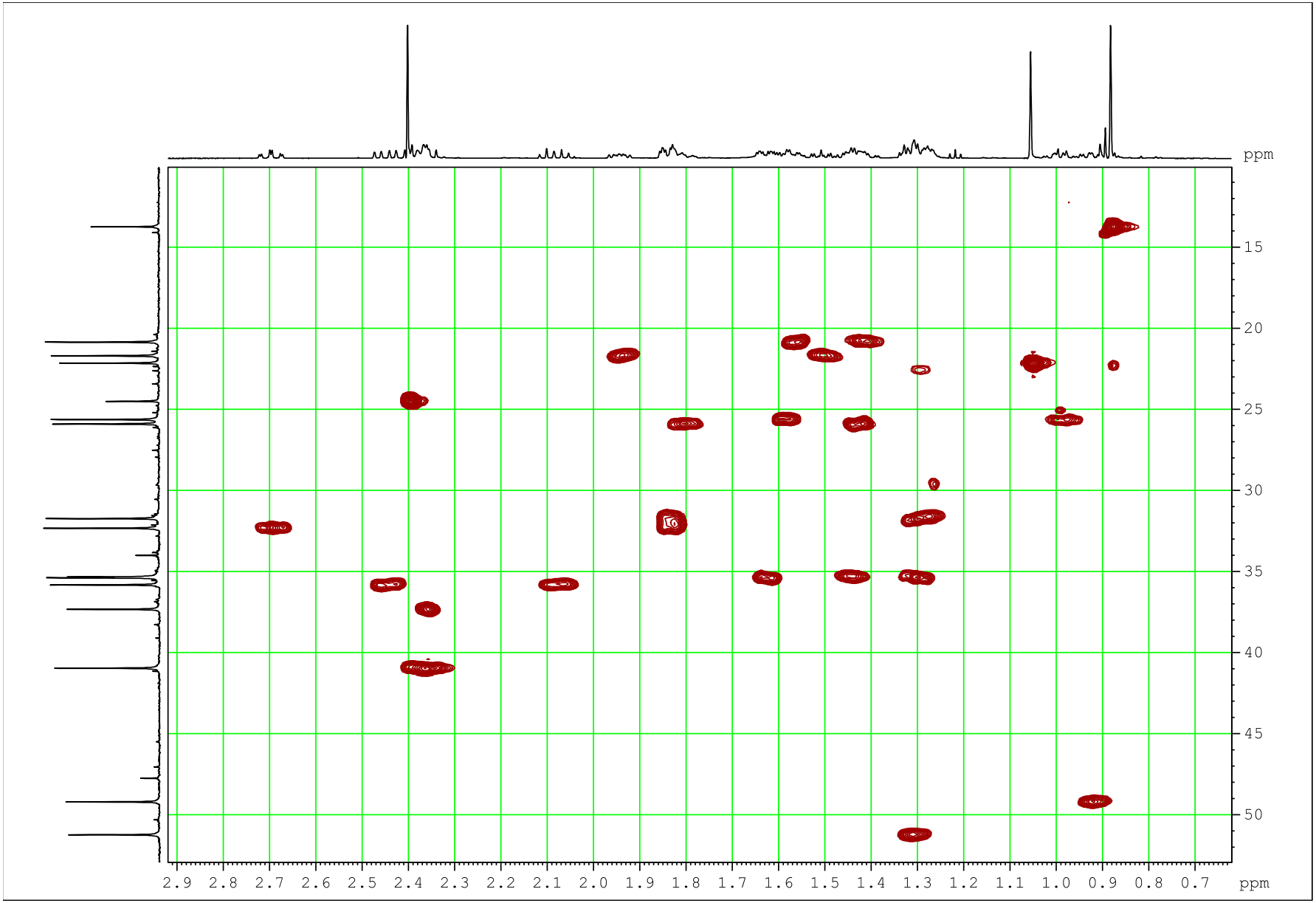

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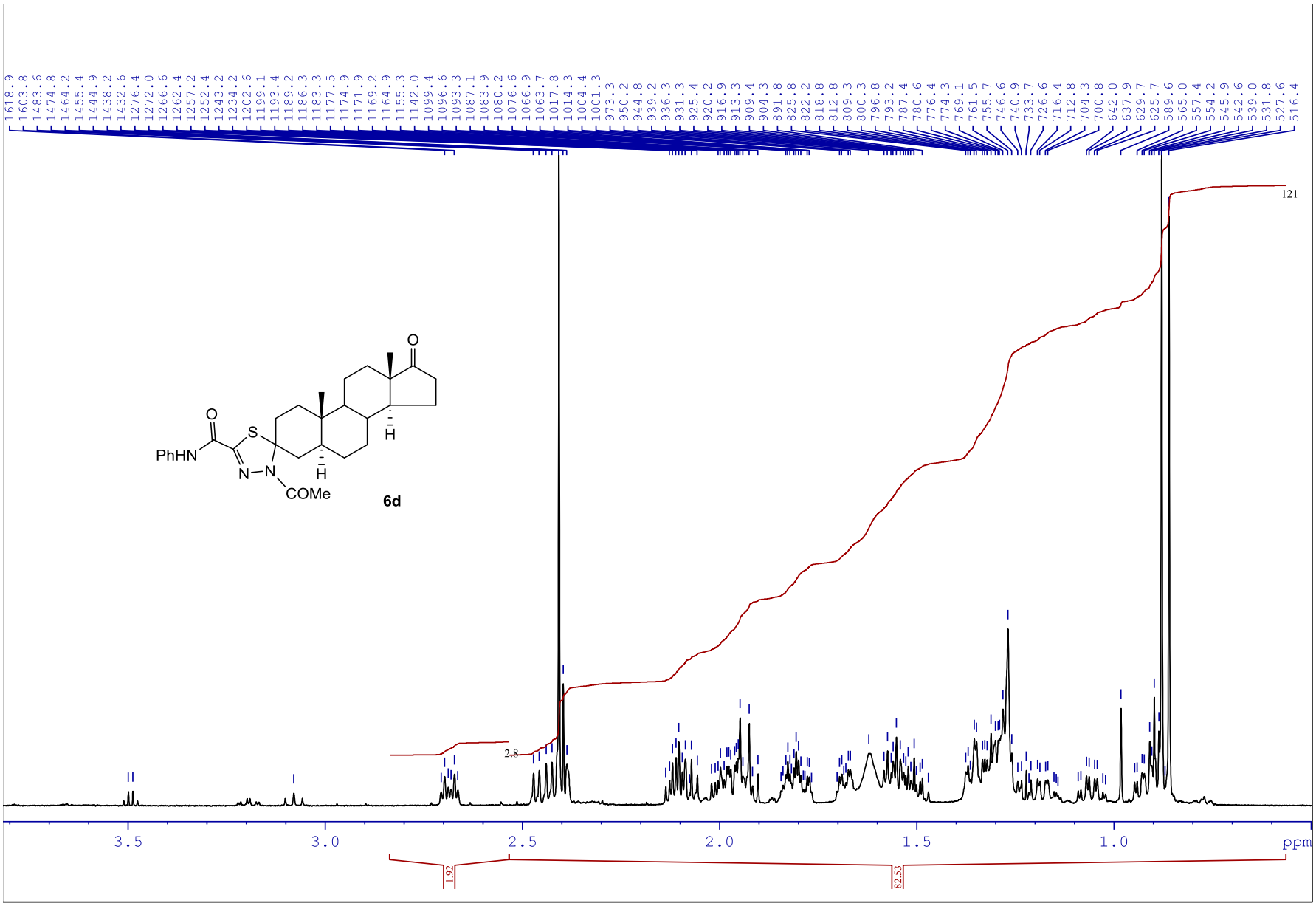
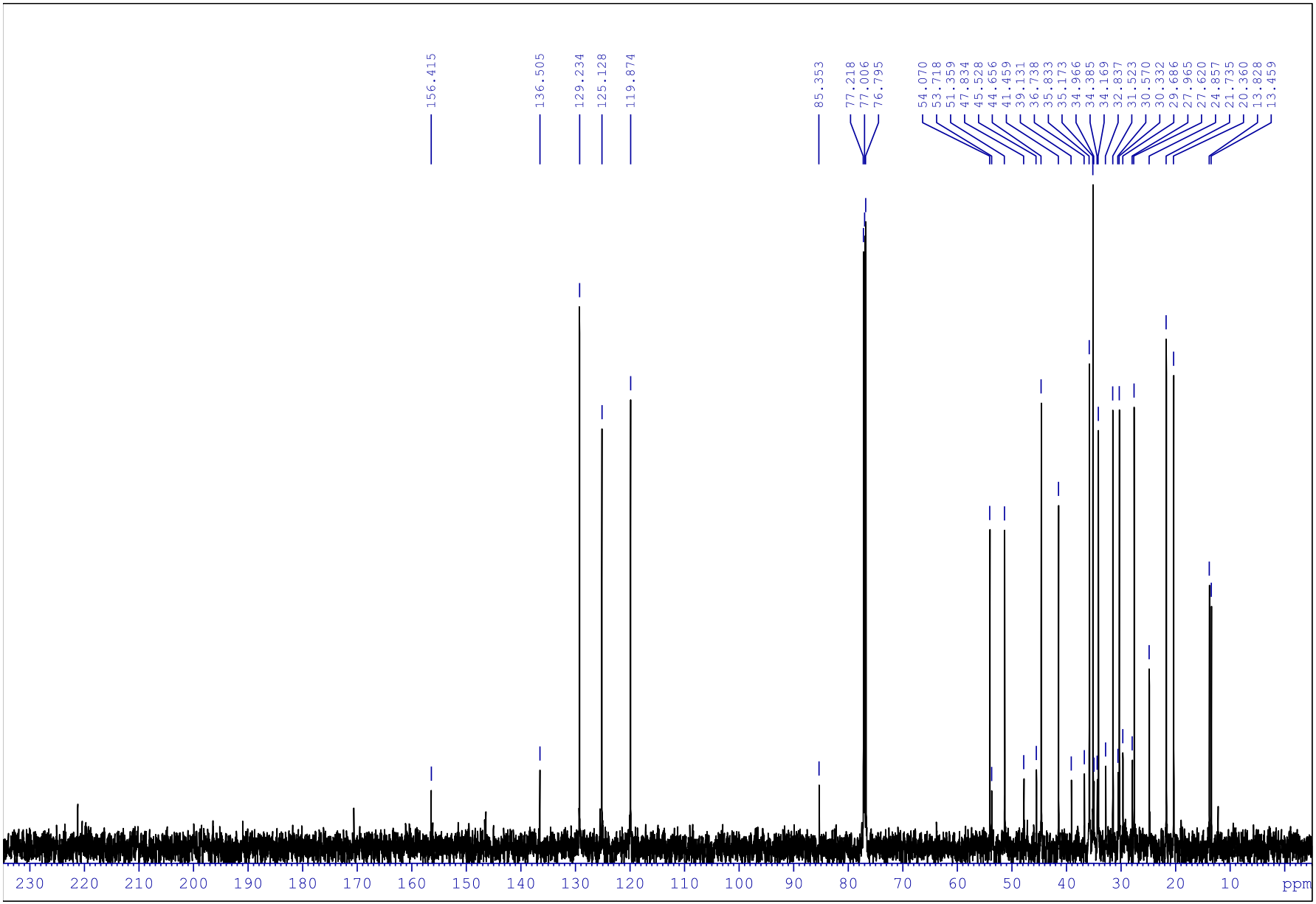
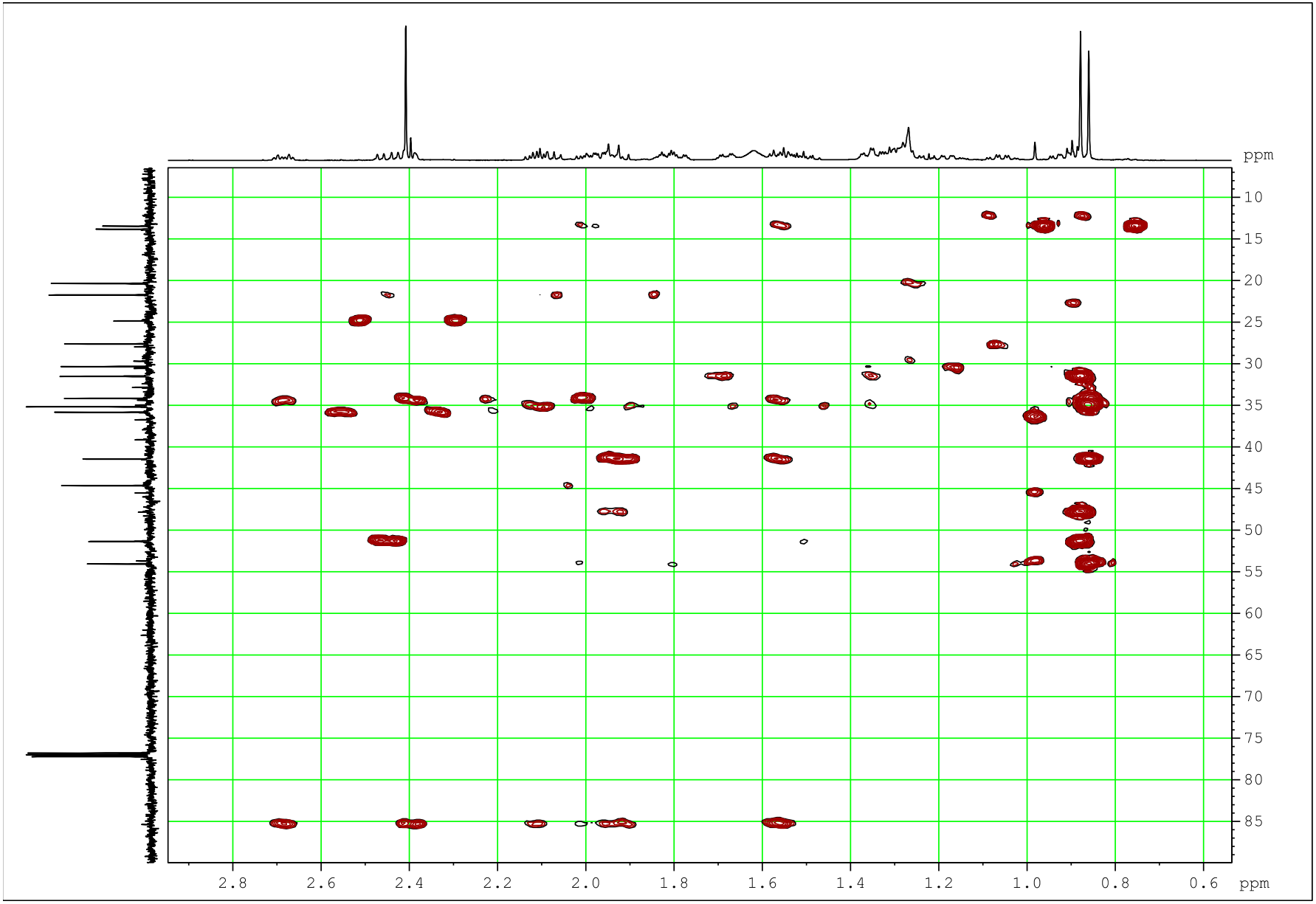


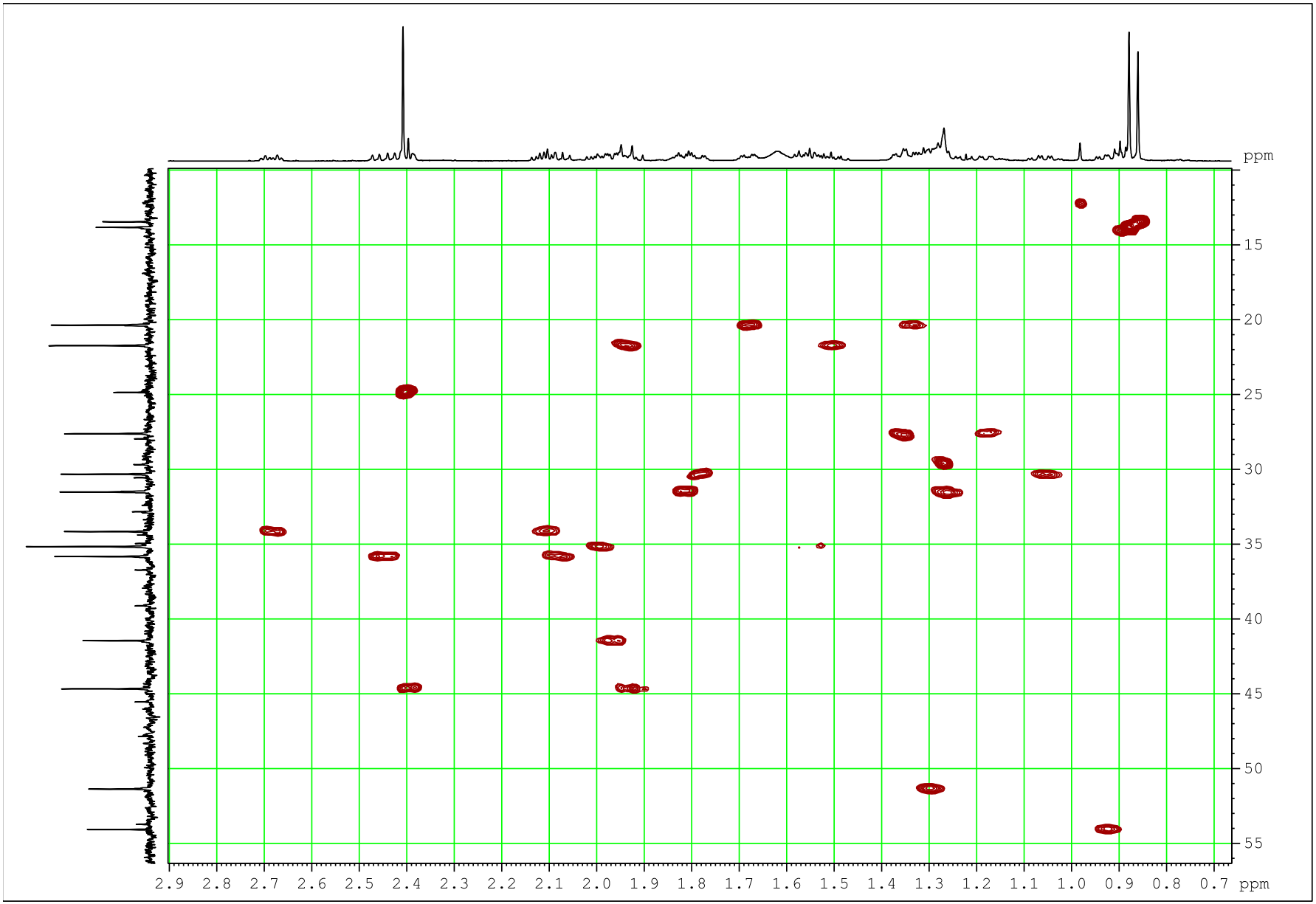
^{1}H NMR spectrum of **6d** ($CDCl_3$).



^{13}C NMR spectrum of **6d** ($CDCl_3$).

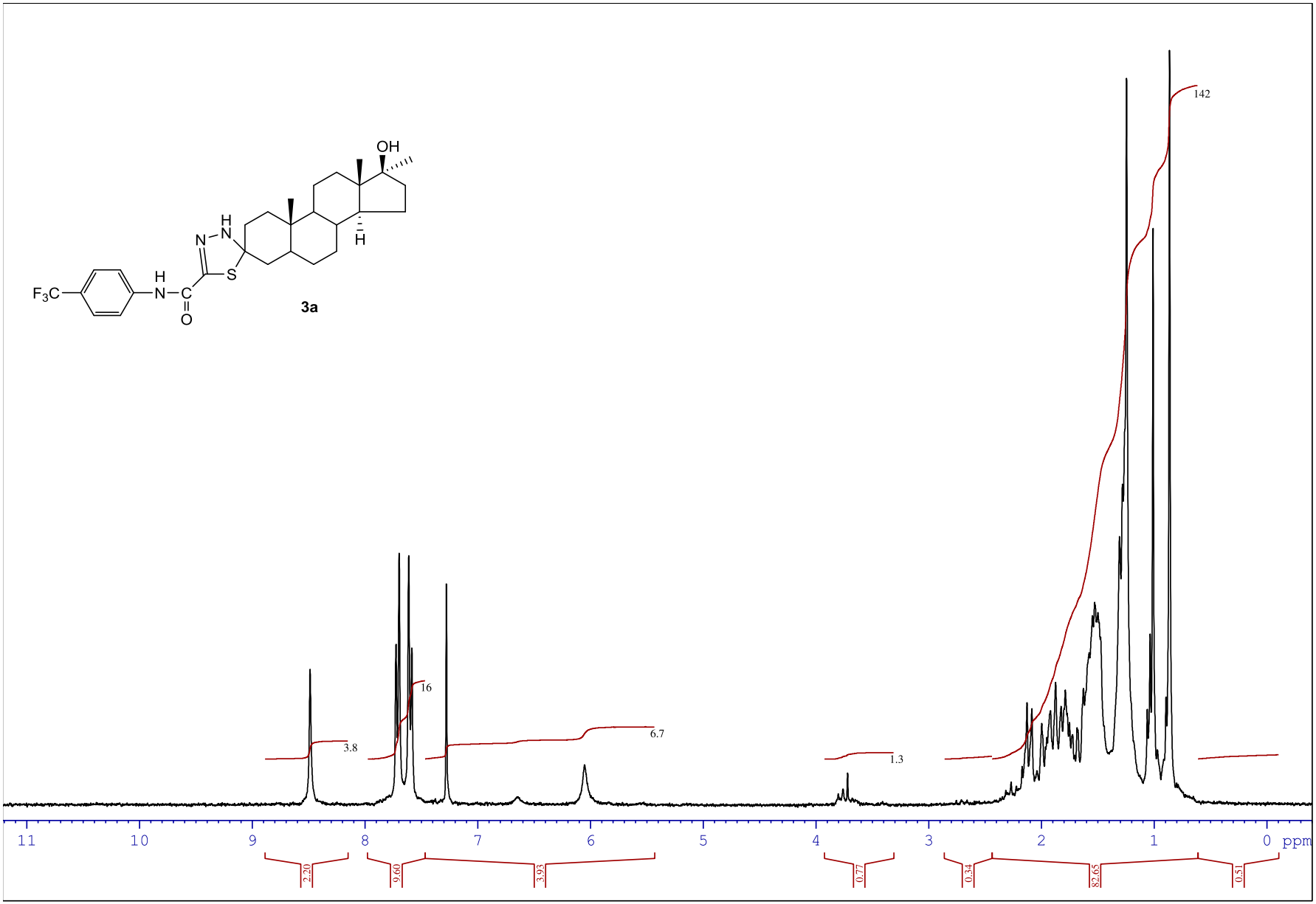


2D ^{1}H-^{13}C HMBC NMR spectrum of **6d** ($CDCl_3$).

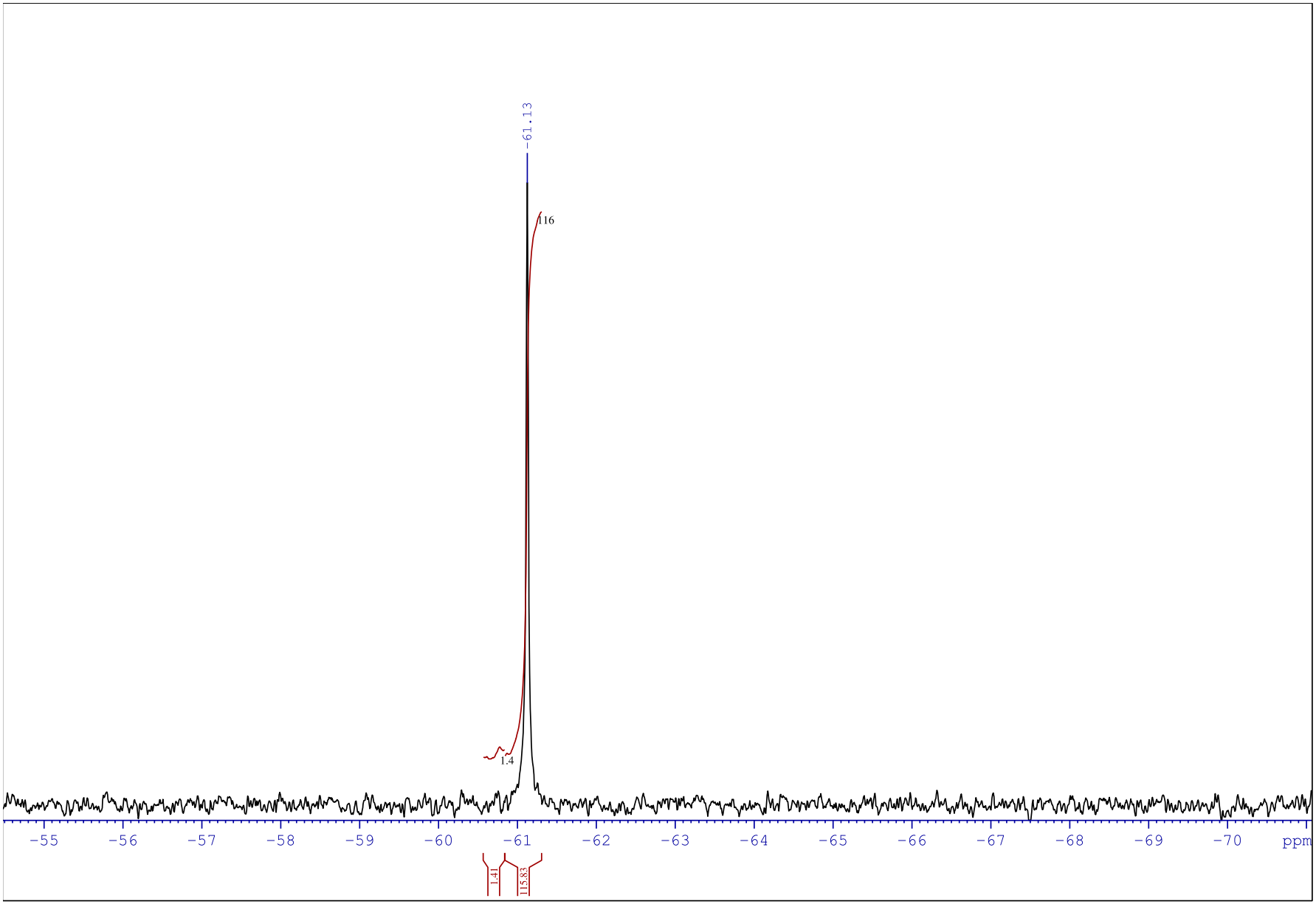


2D ^{1}H-^{13}C HSQC NMR spectrum of **6d** ($CDCl_3$).

2. NMR spectra (Bruker AM-300)

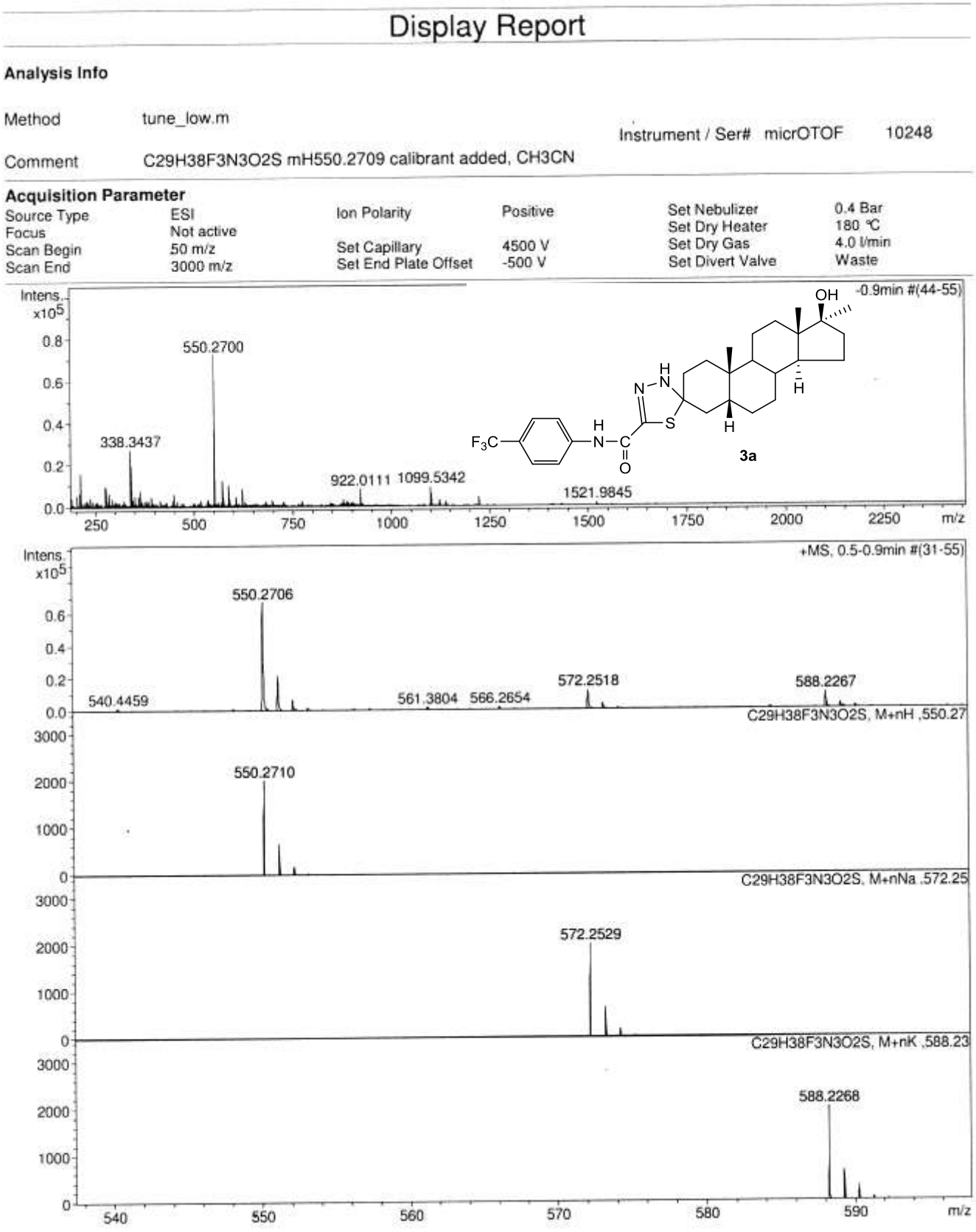


^{1}H NMR spectrum of **3a** ($CDCl_3$).



^{19}F NMR spectrum of **3a** (DMSO-d_6).

4. Mass spectra



Mass-spectra of **3a**.

Display Report

Analysis Info

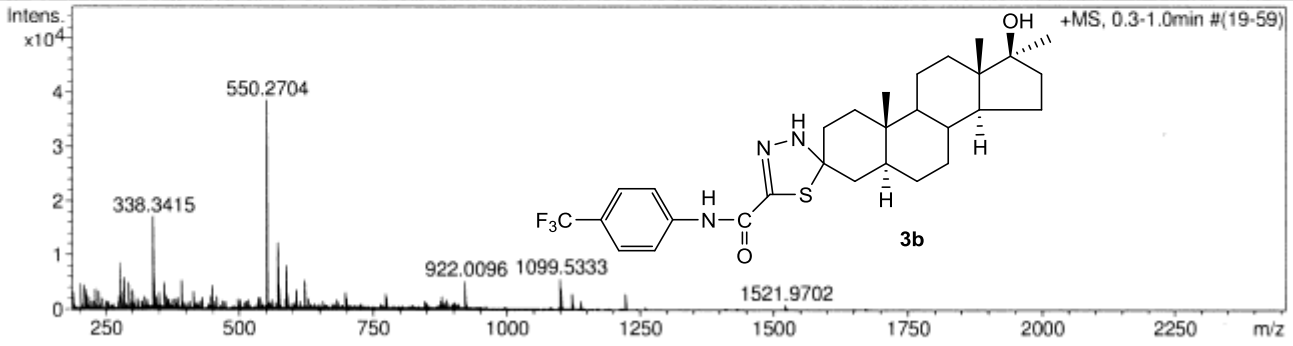
Method tune_low.m

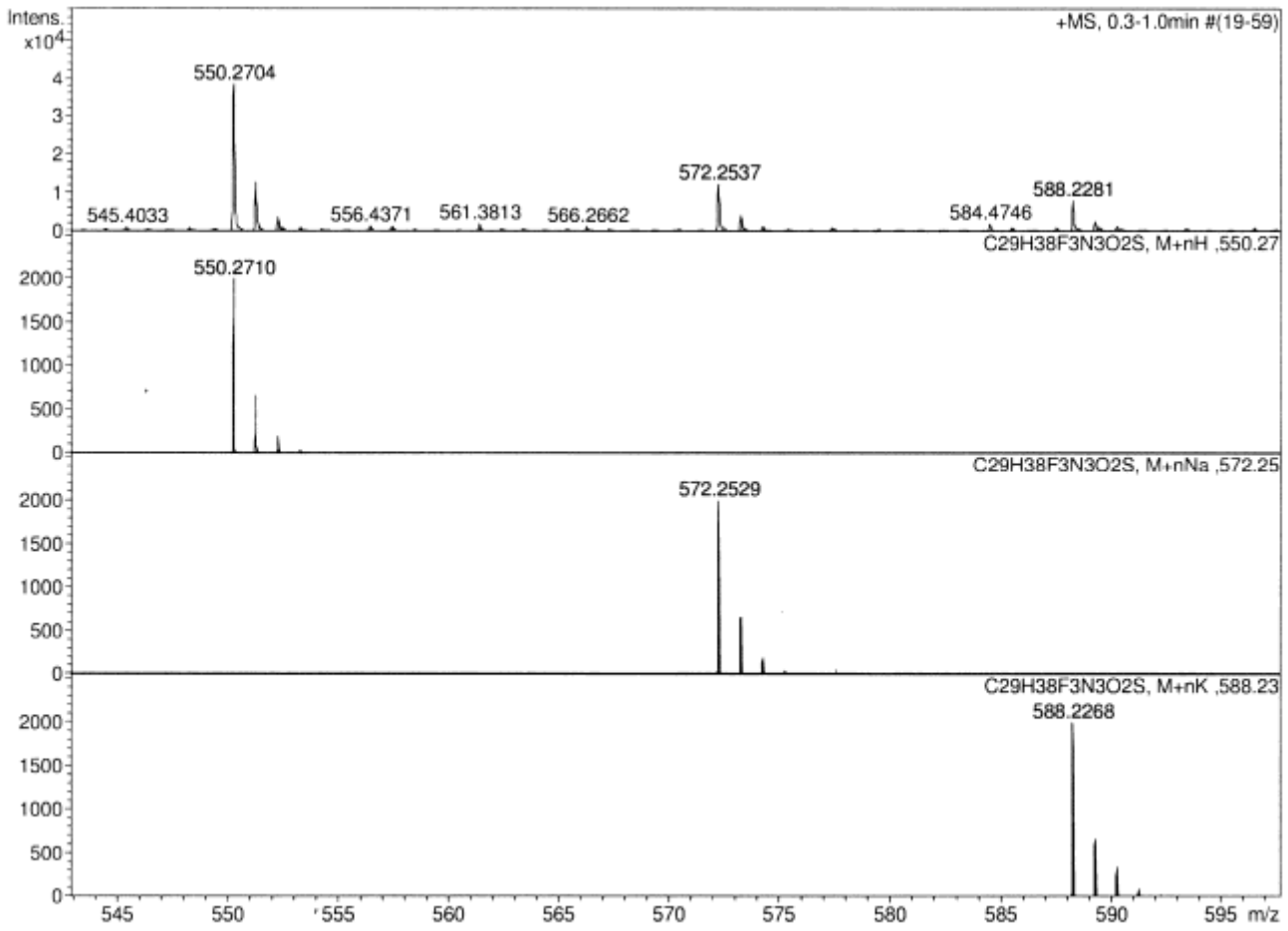
Instrument / Ser# micrOTOF 10248

Comment C29H38F3N3O2S mH550.2709 calibrant added, CH3CN

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





Mass-spectra of **3b**.

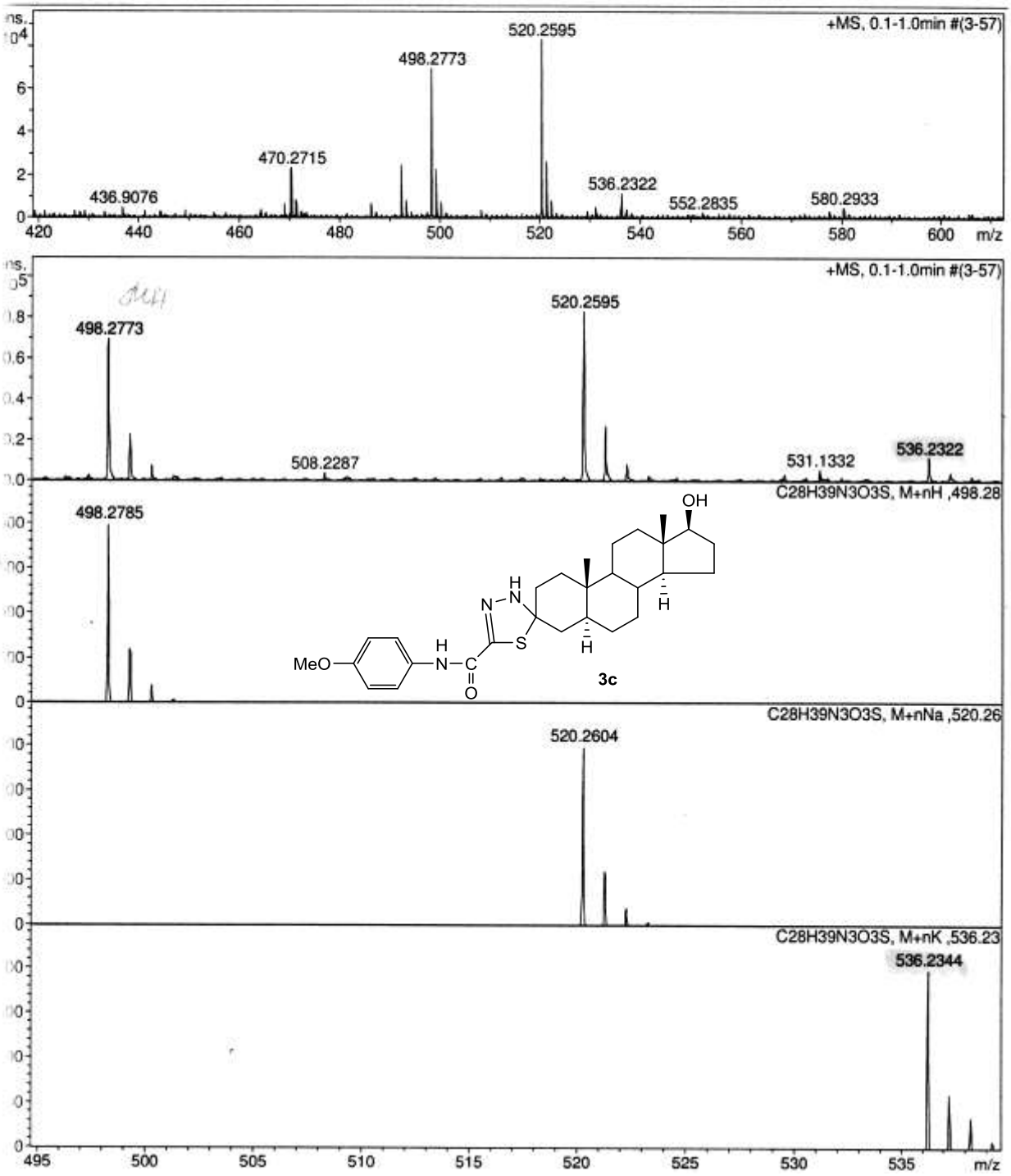
Display Report

ysis Info

sis Name	D:\Data\Kolotyrkina\2019\Komkov\0117001.d	Acquisition Date	17.01.2019 10:40:44
od	tune_50-1600.m	Operator	BDAL@DE
le Name	/CHER K-138	Instrument / Ser#	micrOTOF 10248
ment	C28H39N3O3S mH 498.2784 clb added		

isition Parameter

e Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
	Not active			Set Dry Heater	200 °C
Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **3c**.

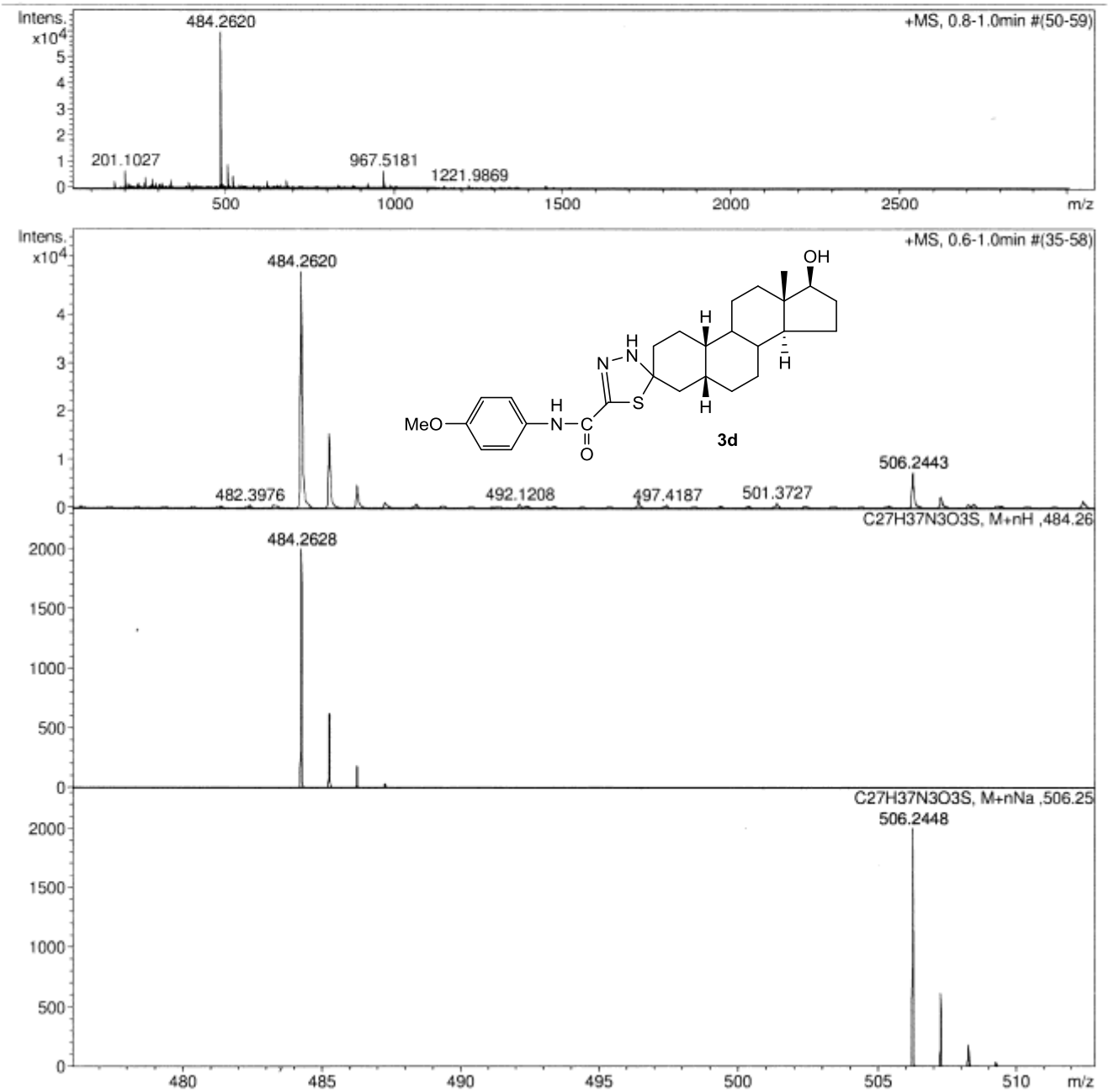
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2024\Komkov\0326031.d	Acquisition Date	26.03.2024 14:59:50
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHER K-139	Instrument / Ser#	micrOTOF 10248
Comment	C27H37N3O3S mH484.2628 calibrant added, CH3CN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **3d**.

Display Report

Analysis Info

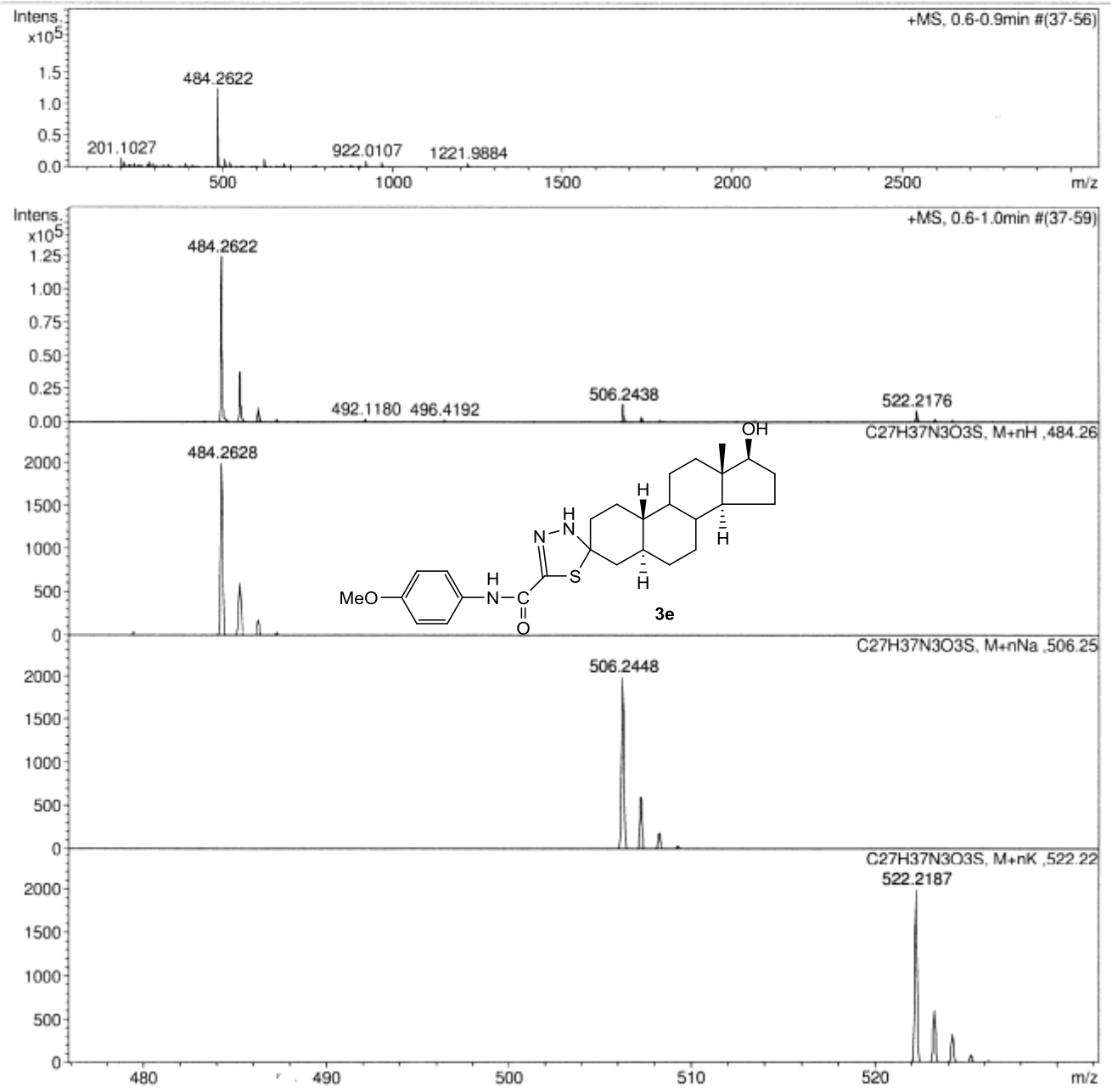
Method tune_low.m

Instrument / Ser# micrOTOF 10248

Comment C27H28N3O3S mH 484.2628 clb added CH3CN

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **3e**.

Display Report

Analysis Info

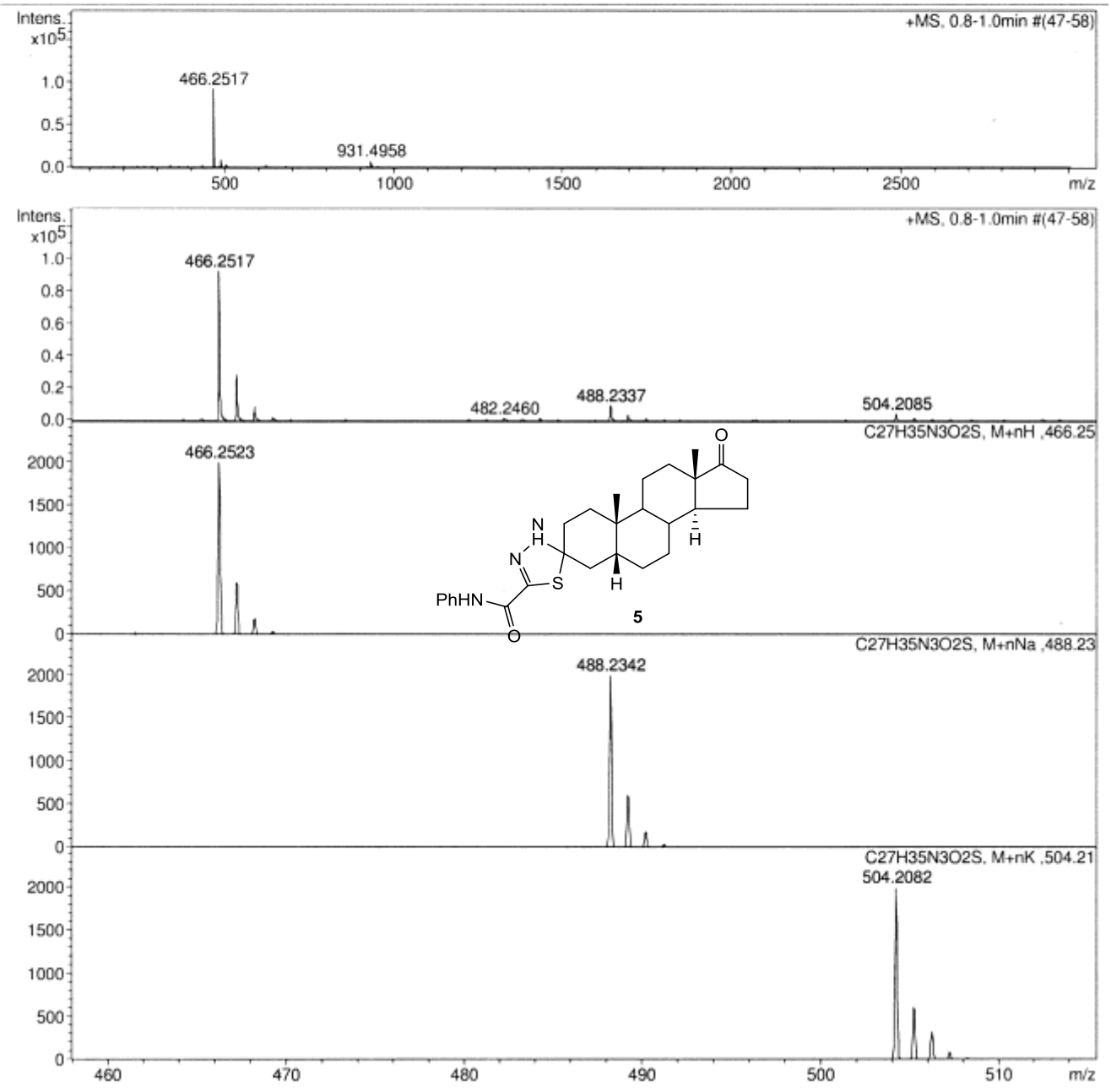
Method tune_low.m

Instrument / Ser# micrOTOF 10248

Comment C27H35N3O2S mH 466.2522 clb added CH3CN

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **5**.

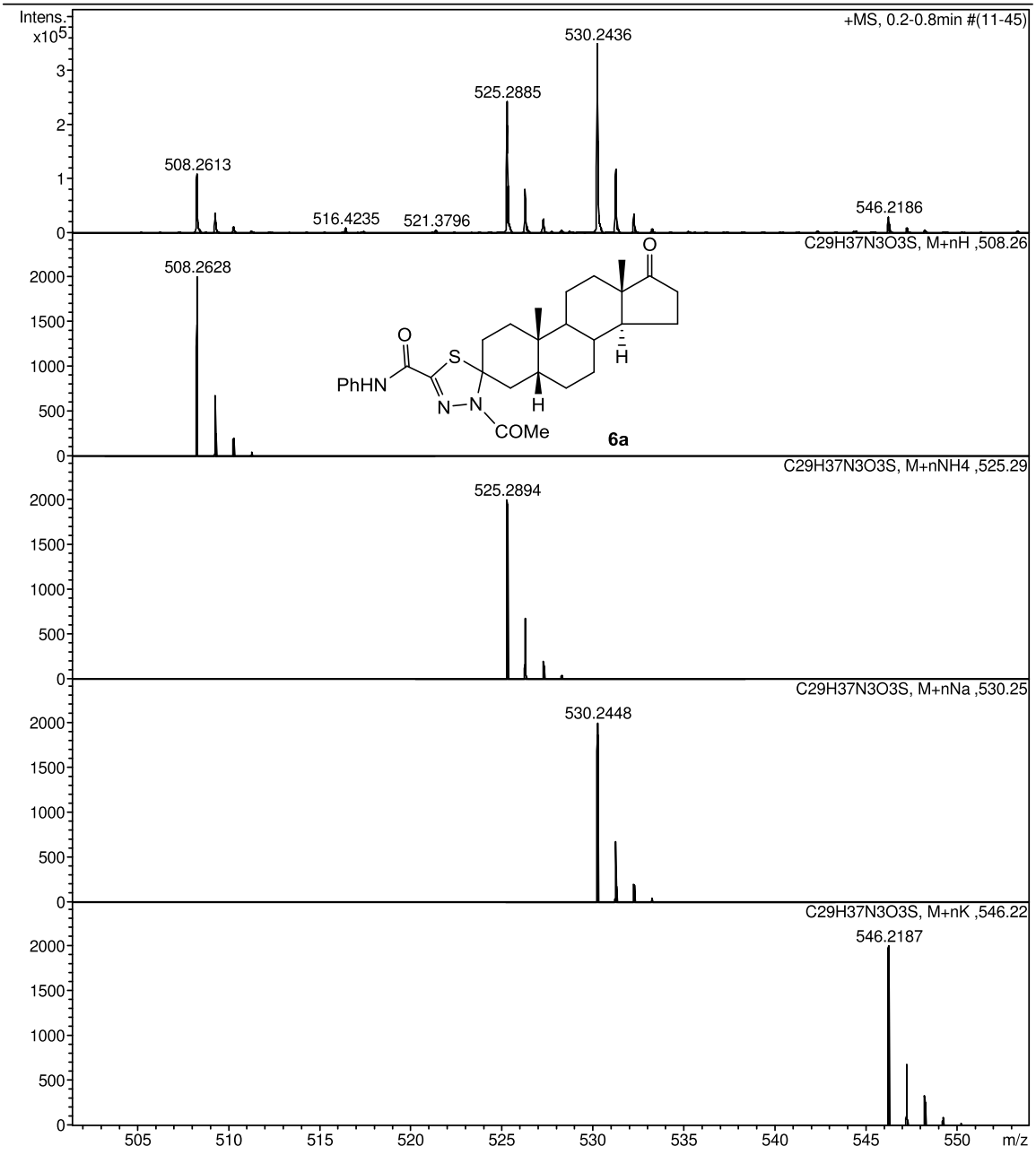
Display Report

Analysis Info

Method	tune_50-1600.m		
		Instrument / Ser#	micrOTOF 10248
Comment	C29H37N3O3S mH 508.2628, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **6a**.

Display Report

Analysis Info

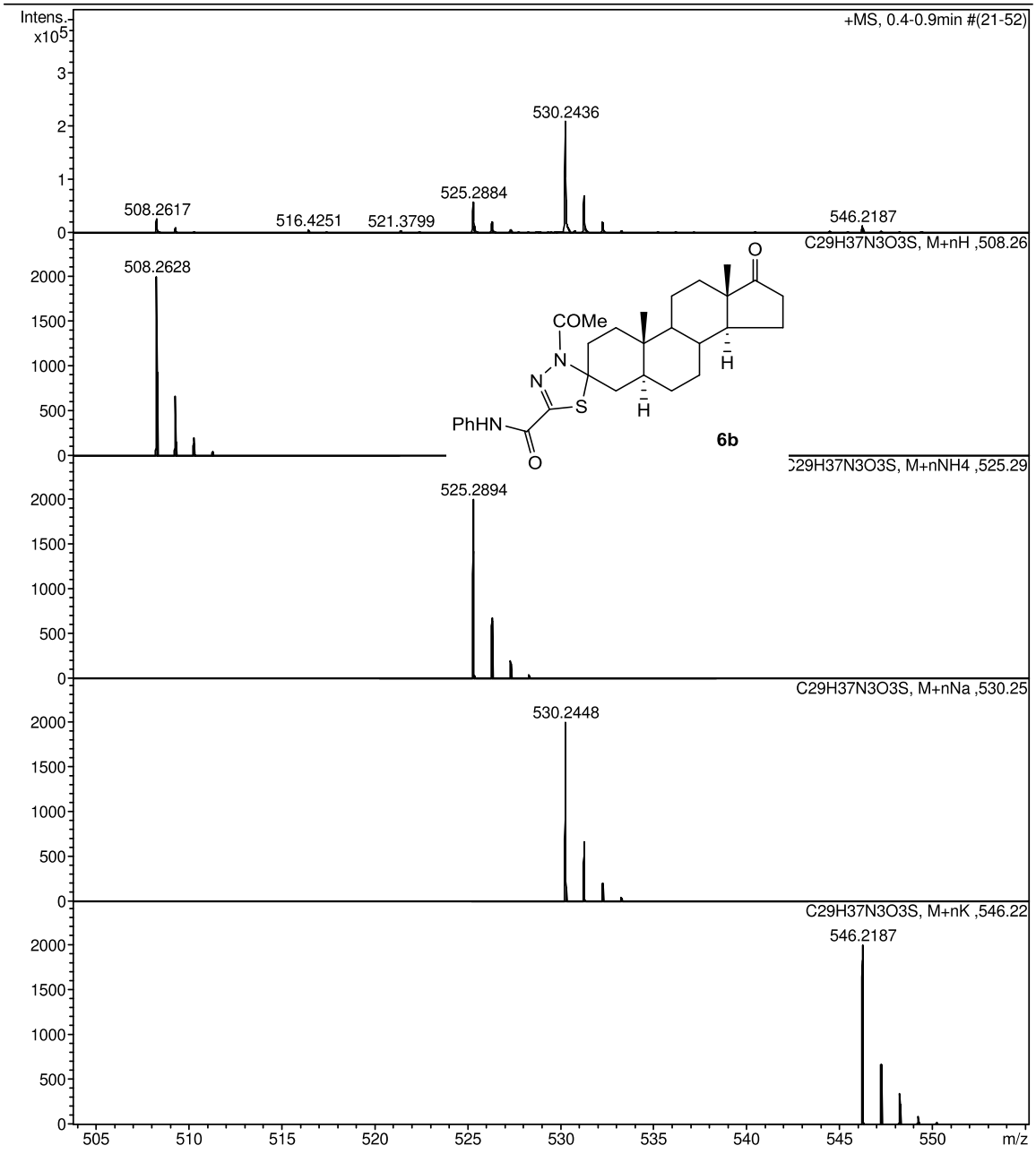
Method tune_50-1600.m

Instrument / Ser# micrOTOF 10248

Comment C29H37N3O3S mH 508.2628 calibrant added

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **6b**.

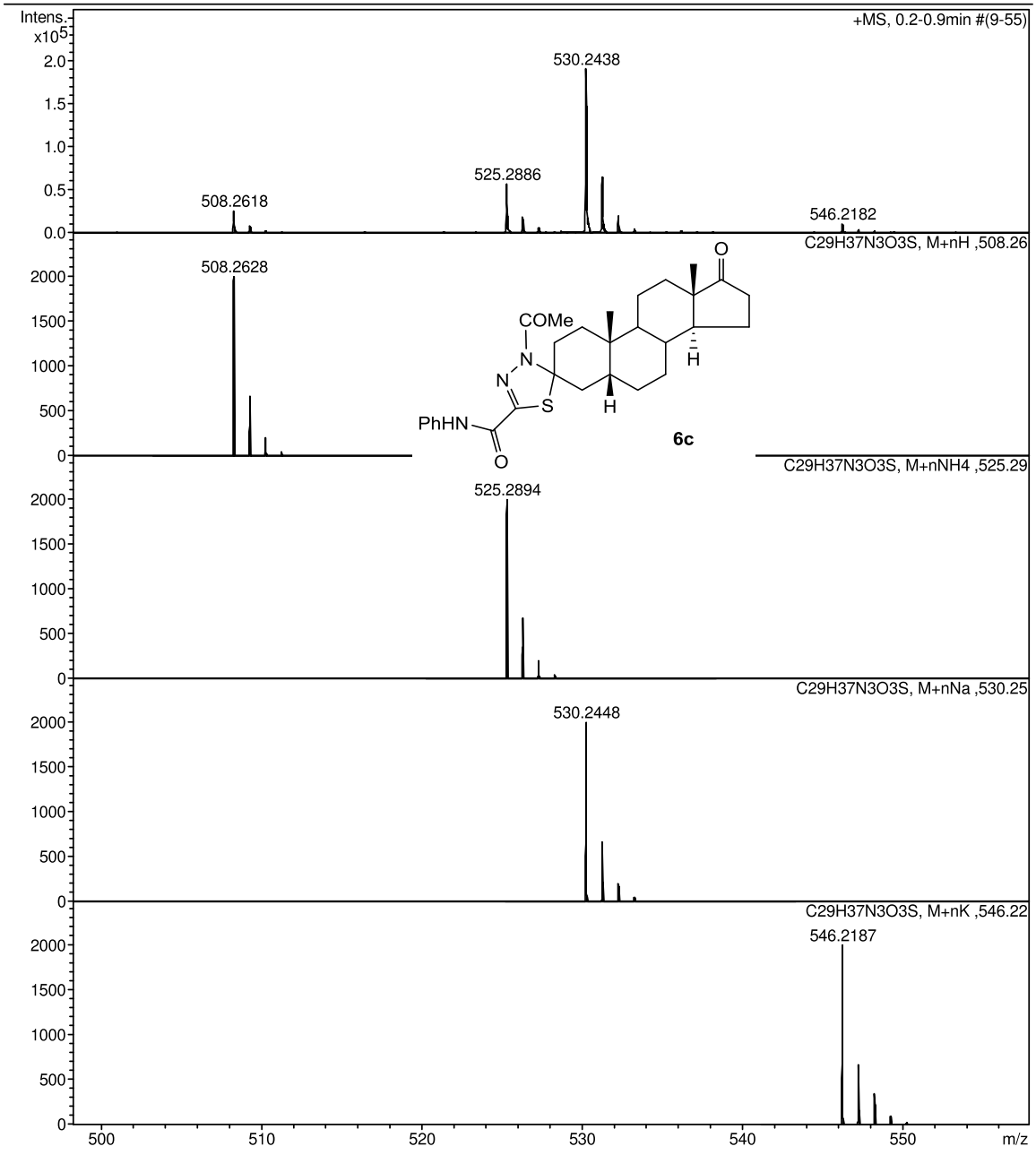
Display Report

Analysis Info

Method	tune_50-1600.m		
		Instrument / Ser#	micrOTOF 10248
Comment	C29H37N3O3S mH 508.2628 calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **6c**.

Display Report

Analysis Info

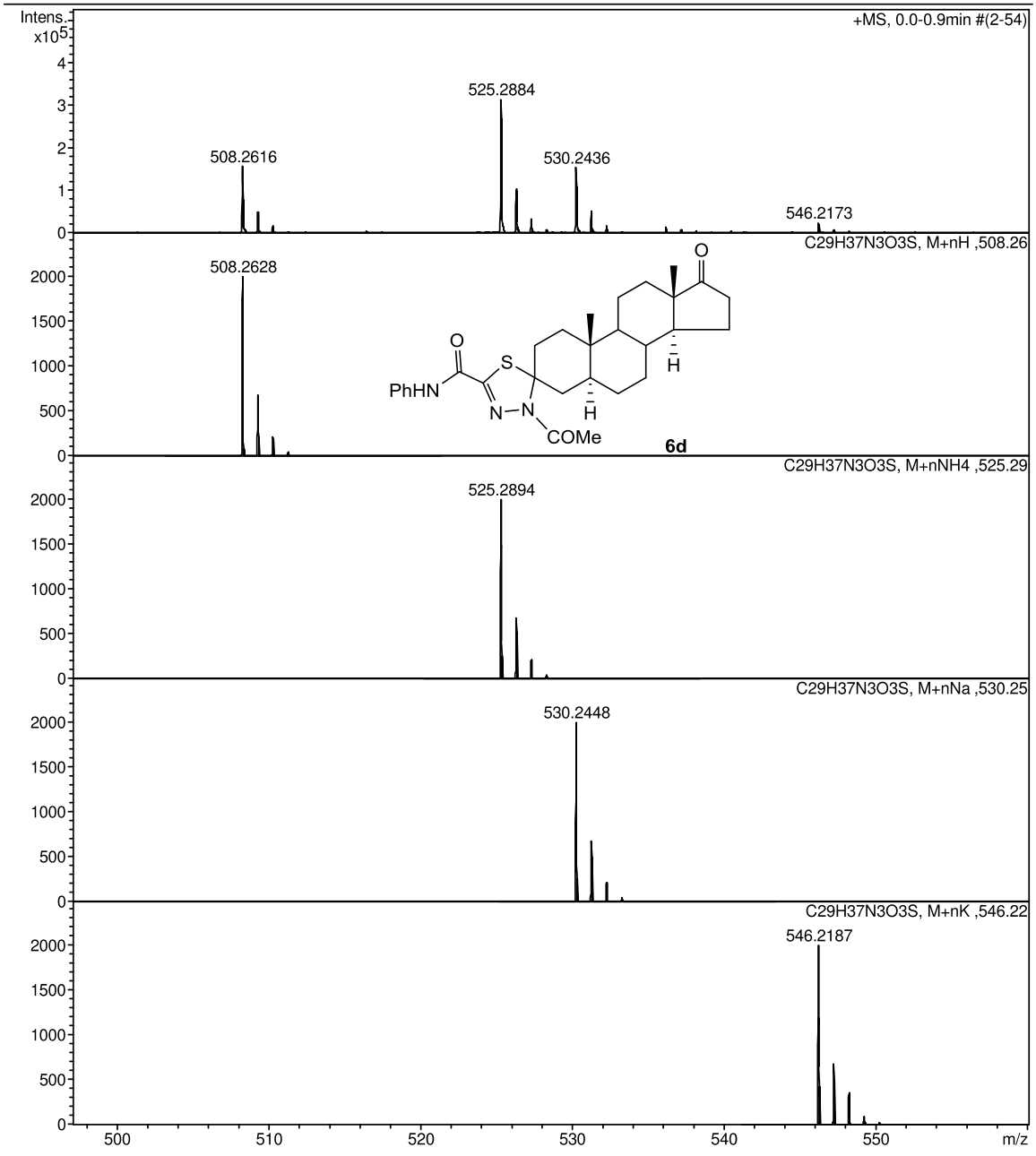
Method tune_50-1600.m

Instrument / Ser# micrOTOF 10248

Comment C29H37N3O3S mH 508.2628 calibrant added

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Mass-spectra of **6d**.