Supporting Information

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Carboxy Methyl and Carboxy Analogs Argaminolics B and C

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NMR Experimental

NMR spectra were acquired using a Bruker Avance II NMR spectrometer equipped with a 5-mm, inverse-configuration probe with triple-axis gradient capability at a field strength of 14.1 T operating at 600.1 and 150.9 MHz for the ^{1}H and ^{13}C nuclei, respectively, in CD_3OD at 303 K. Pulse widths were calibrated following the described protocol [1]. The chemical shifts of ^{1}H and ^{13}C nuclei are reported relative to TMS (δ = 0 ppm for both ^{1}H and ^{13}C) using the solvent signals as secondary internal references (δ_{CHD2OD} = 3.31 ppm for ^{1}H and δ_{CD3OD} = 49.05 ppm for ^{13}C). Chemical shifts for ^{13}C nuclei were obtained indirectly from 2D spectra. General NMR experimental and acquisition details for 1D ^{1}H, selective NOESY (τ_m, 0.3 and 0.5 s), selective ROESY (τ_m, 0.3 and 0.5 s), selective COSY (optimized for 3.5 and 10 Hz), and selective TOCSY (τ_m, 15 and 60 ms) and standard, gradient-selected 2D COSY, ^{1}H{^{13}C}-HSQC, ^{1}H{^{13}C}-HSQC-edit, and ^{1}H{^{13}C}-HMBC spectra have been previously described [2–5] for routine spectral assignment and structural analysis.

References

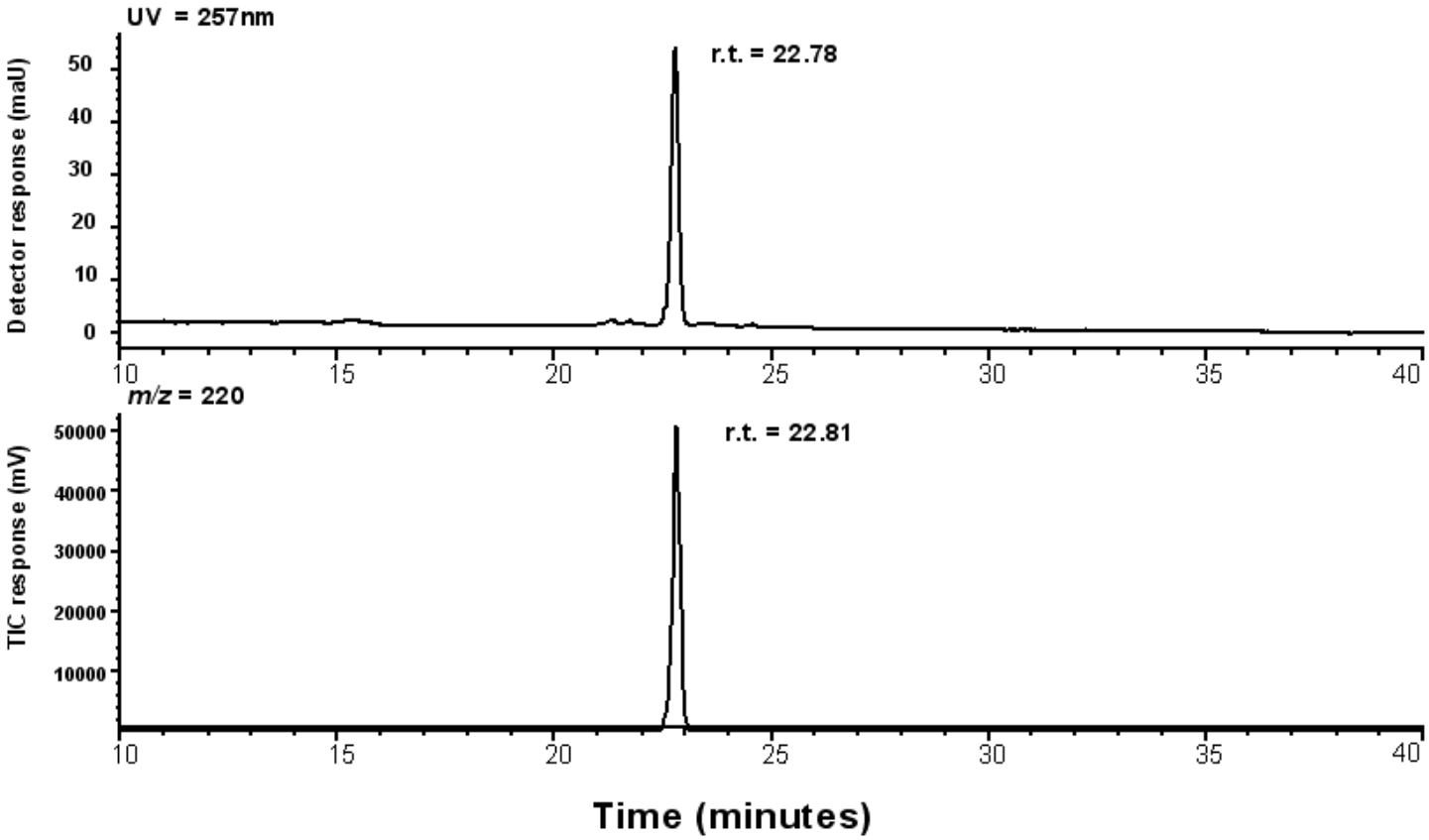
[1] K. D. Klika (2014). The application of simple and easy to implement decoupling pulse scheme combinations to effect decoupling of large *J* values with reduced artifacts, *Int. J. Spectr.* Art. 289638.

[2] P. Virta, A. Koch, M. U. Roslund, P. Mattjus, E. Kleinpeter, L. Kronberg, R. Sjöholm and K. D. Klika (2005). Synthesis, characterisation and theoretical calculations of 2,6-diaminopurine etheno derivatives, *Org. Biomol. Chem.* **3**, 2924–2929.

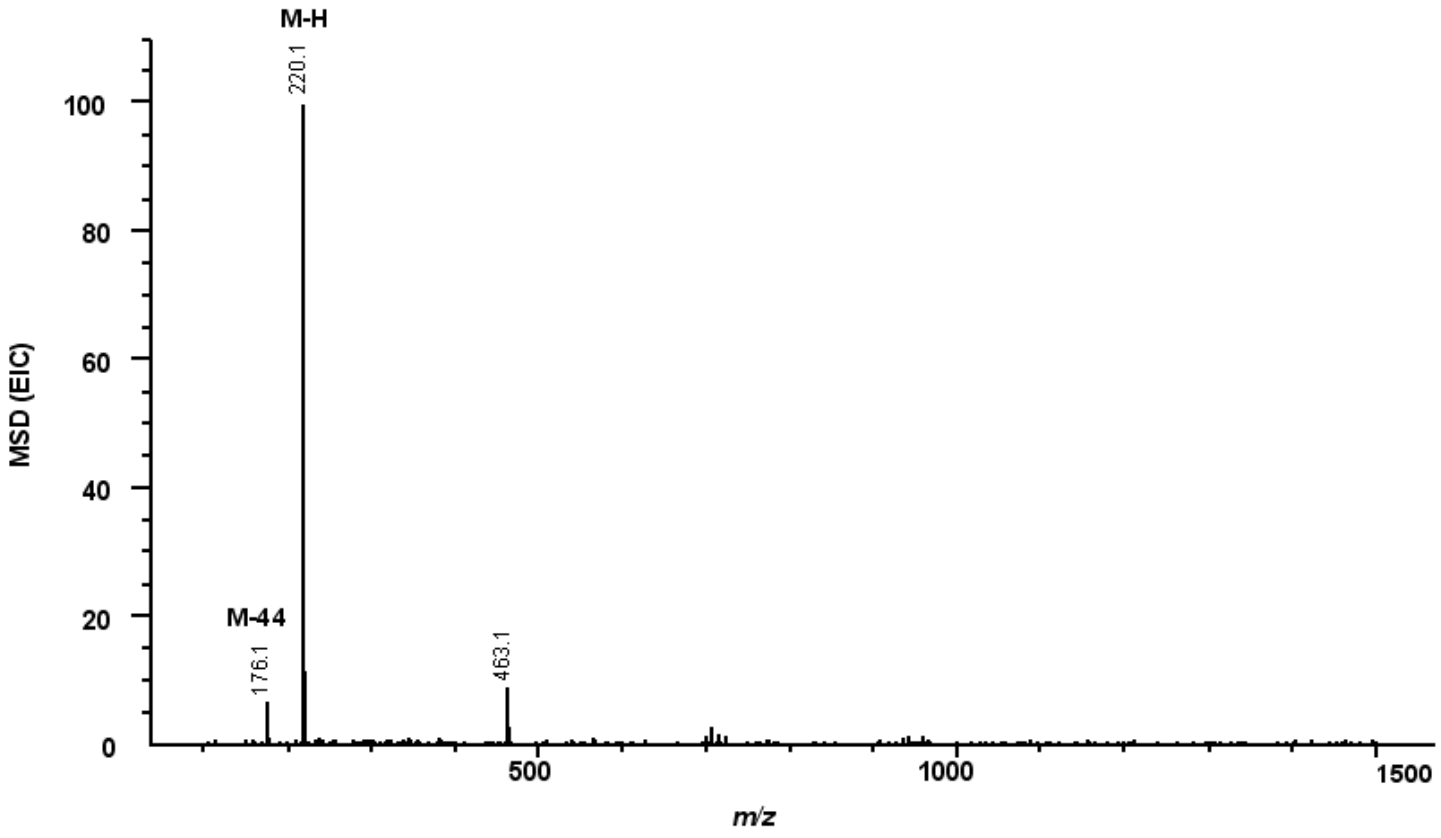
[3] K. D. Klika, J. Bernát, J. Imrich, I. Chomča, R. Sillanpää and K. Pihlaja (2001). Unexpected Formation of a Spiro Acridine and Fused Ring System from the Reaction Between an *N*-Acridinylmethyl Substituted Thiourea and Bromoacetonitrile Under Basic Conditions, *J. Org. Chem.* **66**, 4416–4418.

[4] E. Balentová, J. Imrich, J. Bernát, L. Suchá, M. Vilková, N. Prónayová, P. Kristian, K. Pihlaja and K. D. Klika (2006). Stereochemistry, Tautomerism, and Reactions of Acridinyl Thiosemicarbazides in the Synthesis of 1,3-Thiazolidines, *J. Heterocycl. Chem.* **43**, 645–656.

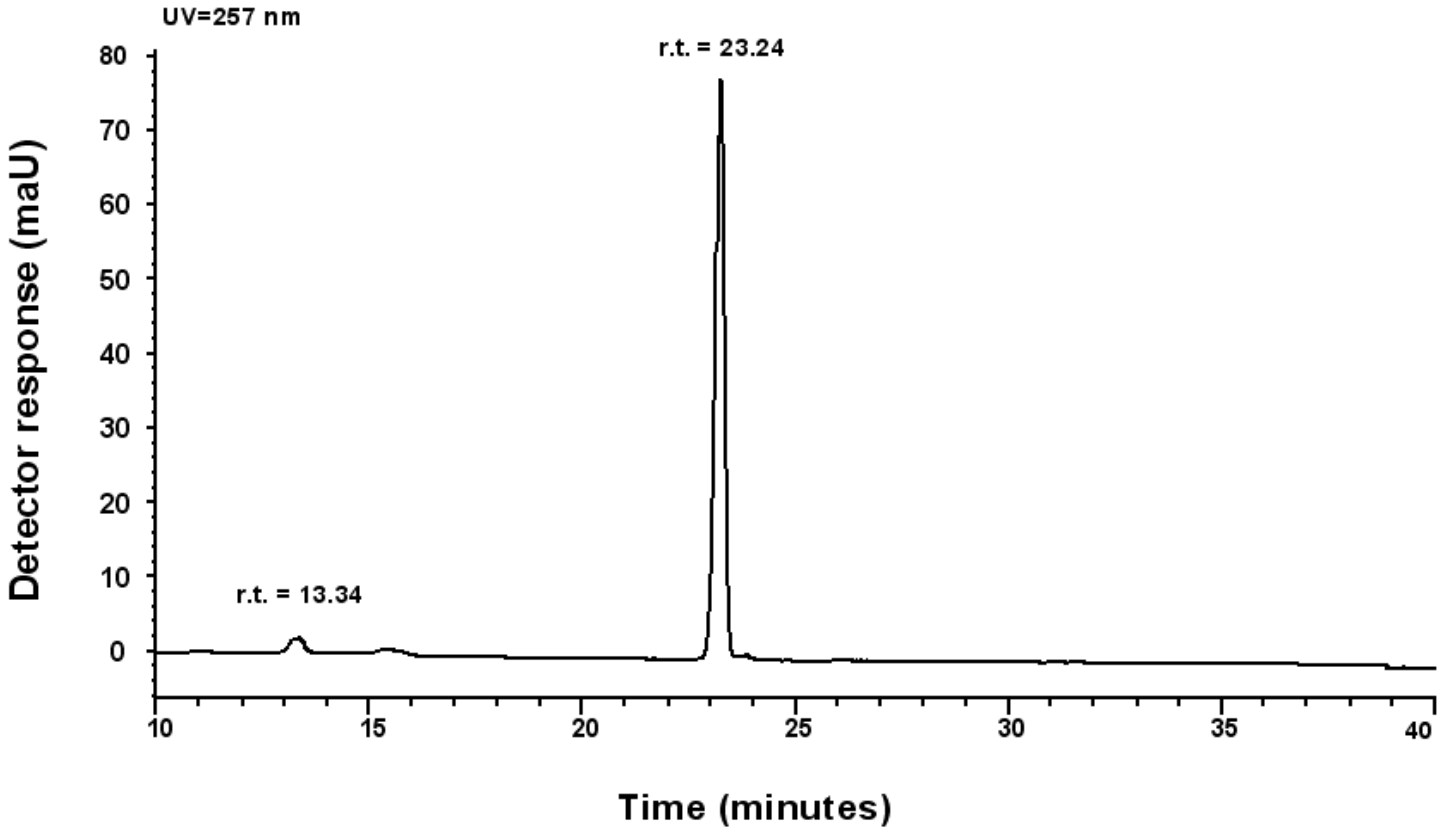
[5] J. Mäki, P. Tähtinen, L. Kronberg and K. D. Klika (2005). Restricted rotation/tautomeric equilibrium and determination of the site and extent of protonation in bi-imidazole nucleosides by multinuclear NMR and GIAO-DFT calculations, *J. Phys. Org. Chem.* **18**, 240–249.



S1: HPLC trace of Argaminolic A (**1**).



S2: ESI-MS of Argaminolic A (**1**) in negative-ion mode.



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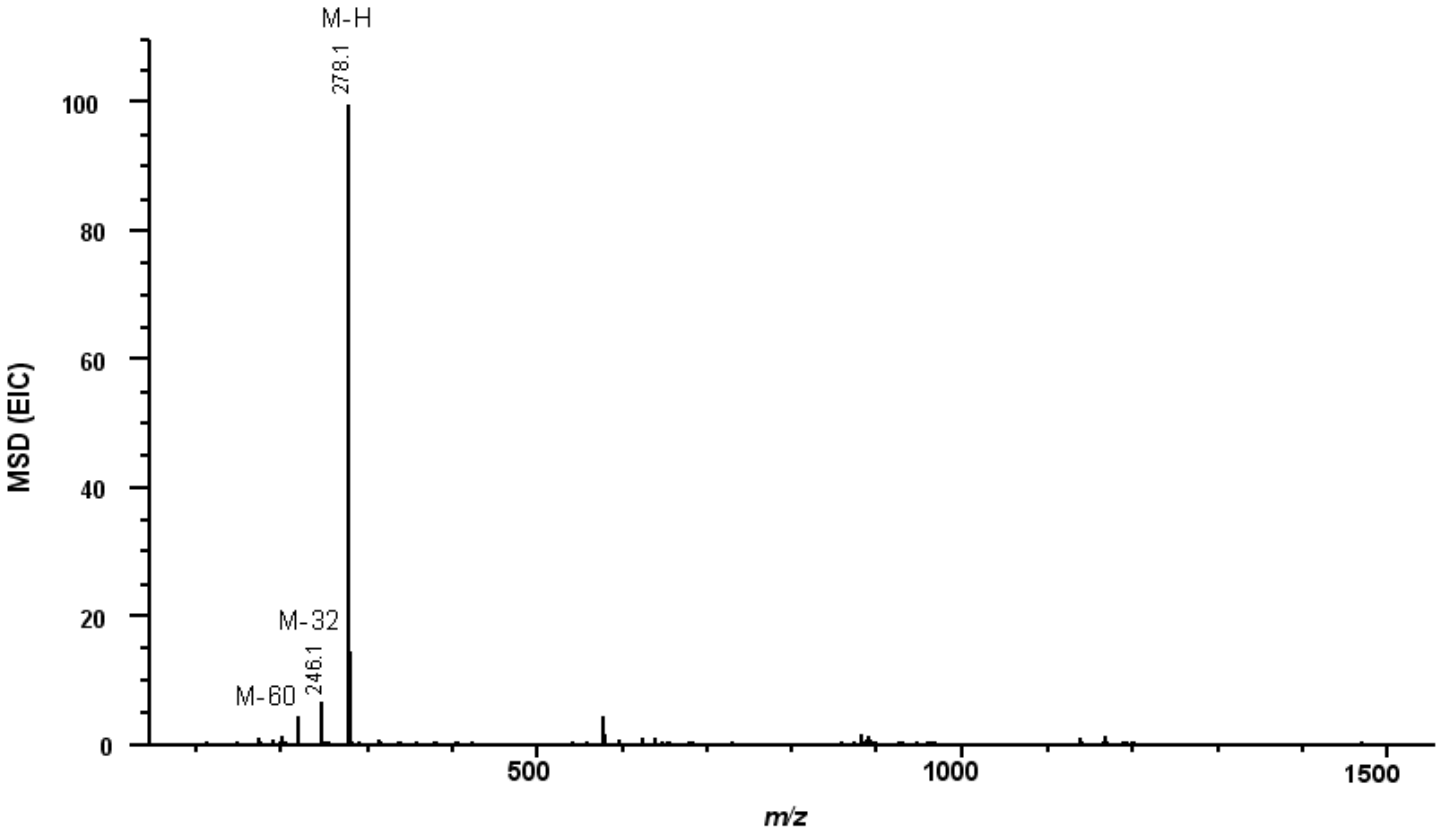
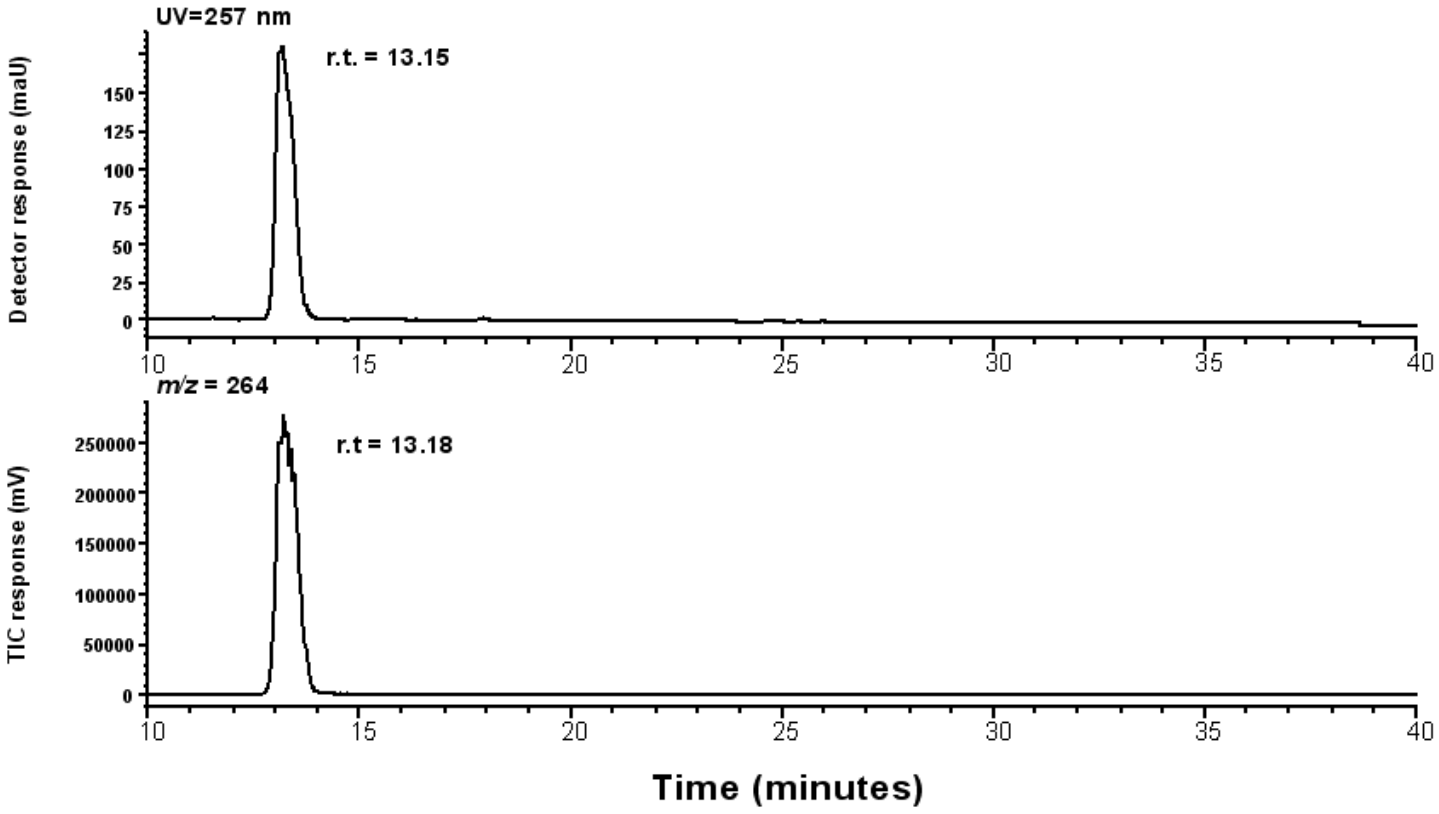
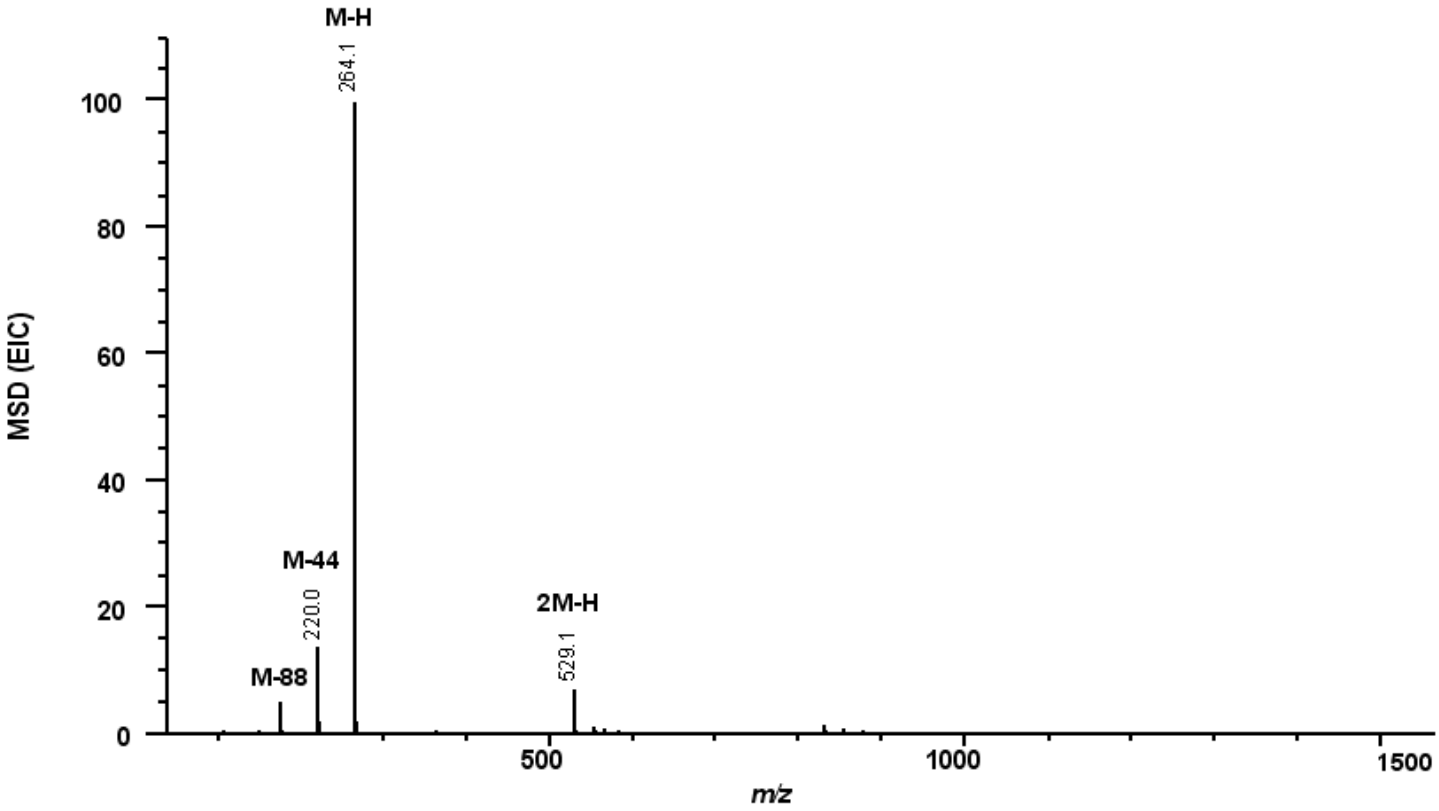


S4: ESI-MS of Argaminolic B (**2**) in negative-ion mode.



S5: HPLC trace of Argaminolic C (**3**).



S6: ESI-MS of Argaminolic C (**3**) in negative-ion mode.

Analysis Info

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Sample Name	Argannolic B	Operator	D.Lang
Comment	Klika, Dr Aubry Miller G404 DKFZ: Argannolic B in MeOH		

Acquisition Parameters

Accumulations	16	Collision Gas Flow Rate	0.3 L/sec	Capillary Entrance	3900.0 V
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Broadband High Mass	2200.0 m/z	Collision Cell RF	1100.0 V		
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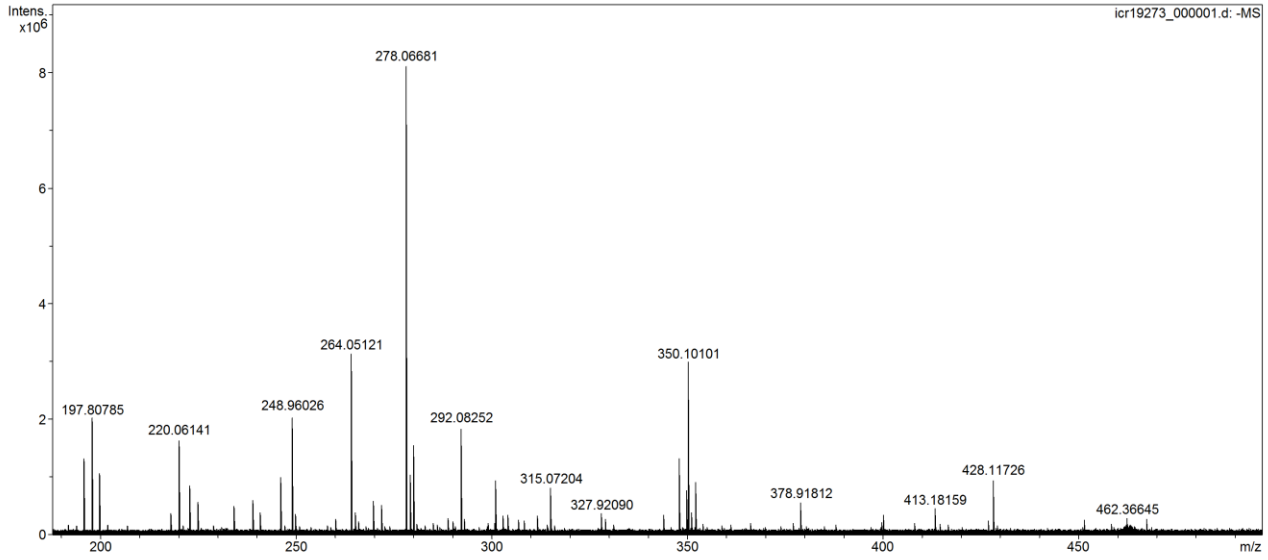
		Q1 Mass	200.000 m/z		



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Mass Spectrum Formula Report

Analysis Info

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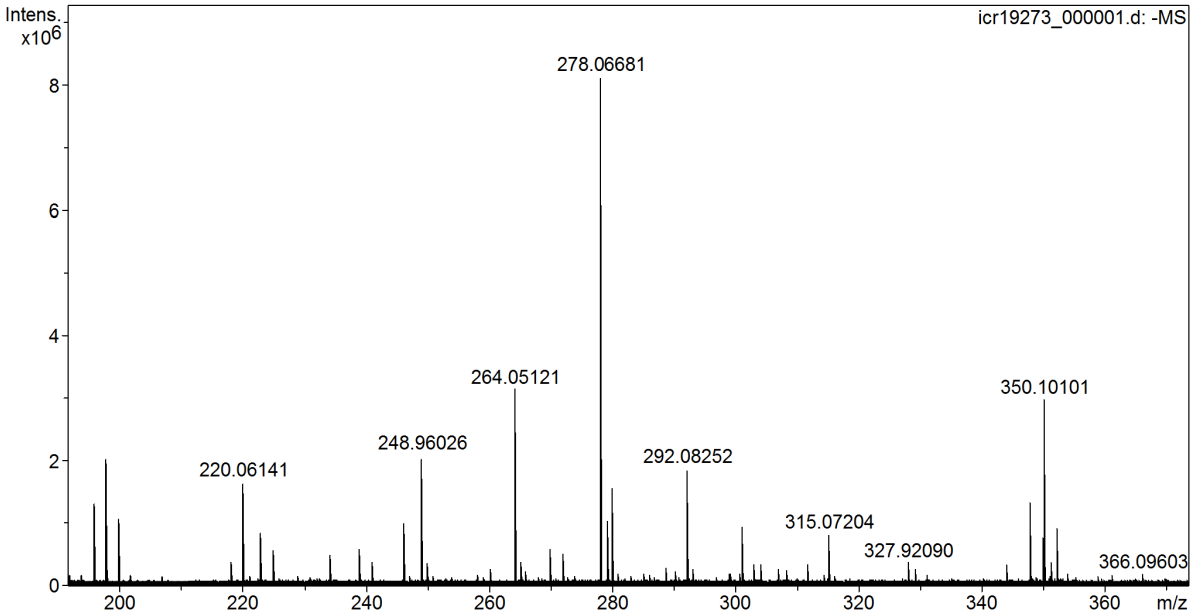

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	C 10 H 4 N 11	278.06566	0.1	0.5	614.0	14.5	ok	even

S7: ESI-HRMS of Argaminolic B (**2**) in negative-ion mode.

Analysis Info

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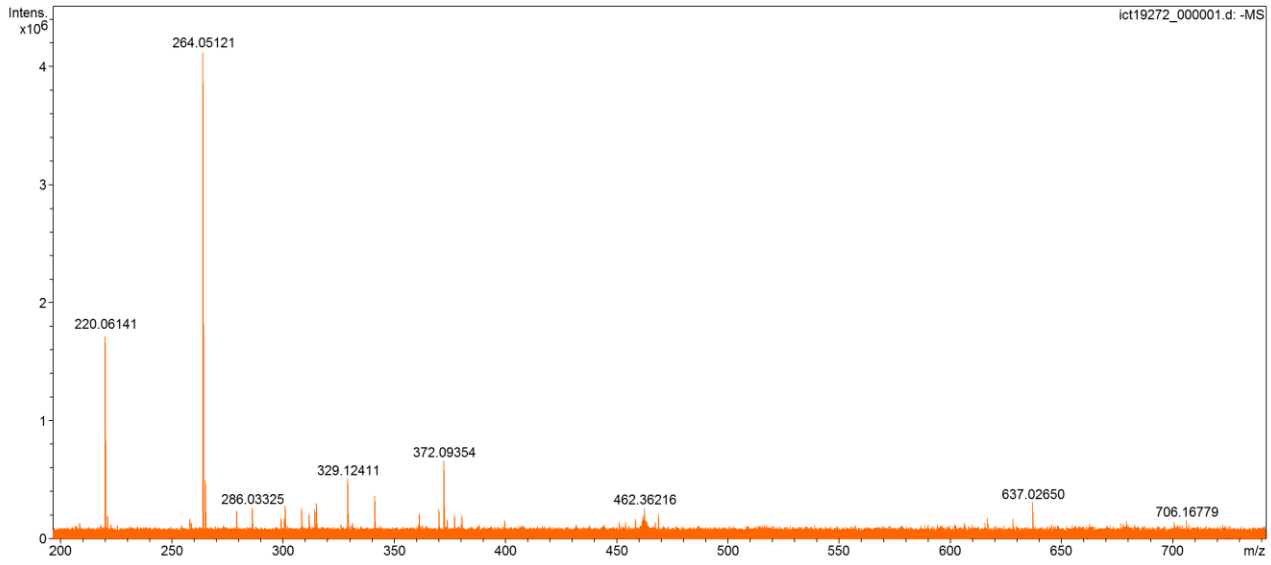
Sample Name	Argannolic C	Operator	D.Lang
Comment	Klika, Dr Aubry Miller G404 DKFZ: Argannolic C in MeOH		

Acquisition Parameters

Accumulations	16	Collision Gas Flow Rate	0.3 L/sec	Capillary Entrance	3900.0 V
Broadband Low Mass	187.7 m/z	Collision Energy	0.0 eV	Calibration Date	Thu Feb 19 11:25:10 2015
Broadband High Mass	2200.0 m/z	Collision Cell RF	1100.0 V		
Data Acquisition Size	2097152	Q1 Resolution	6.0		
		Q1 Mass	200.000 m/z		



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Mass Spectrum Formula Report

Analysis Info

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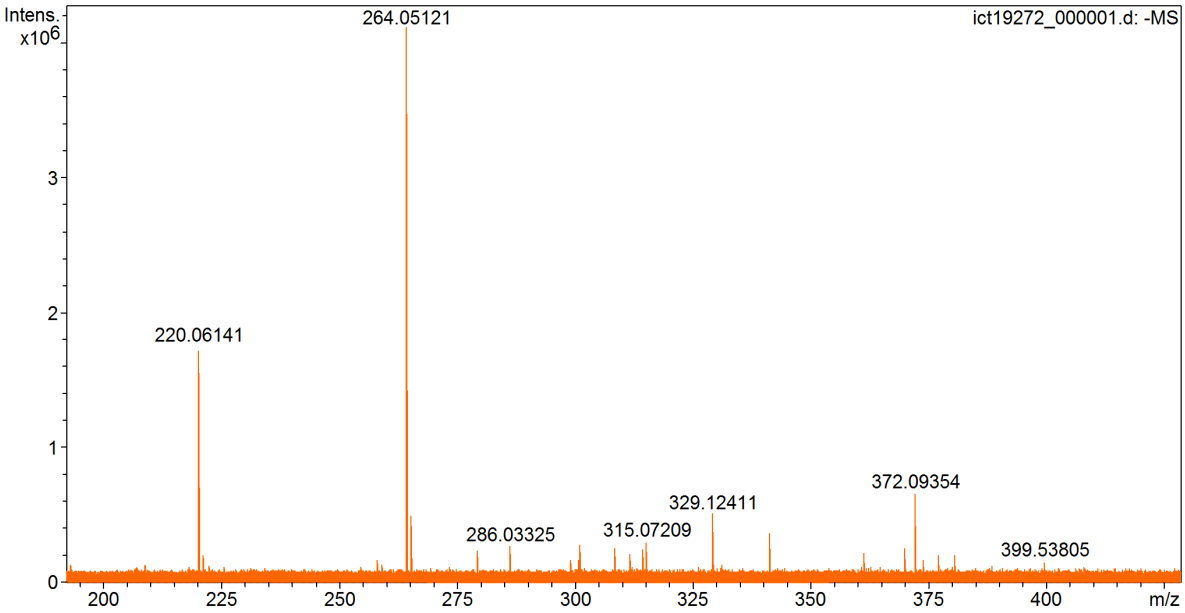

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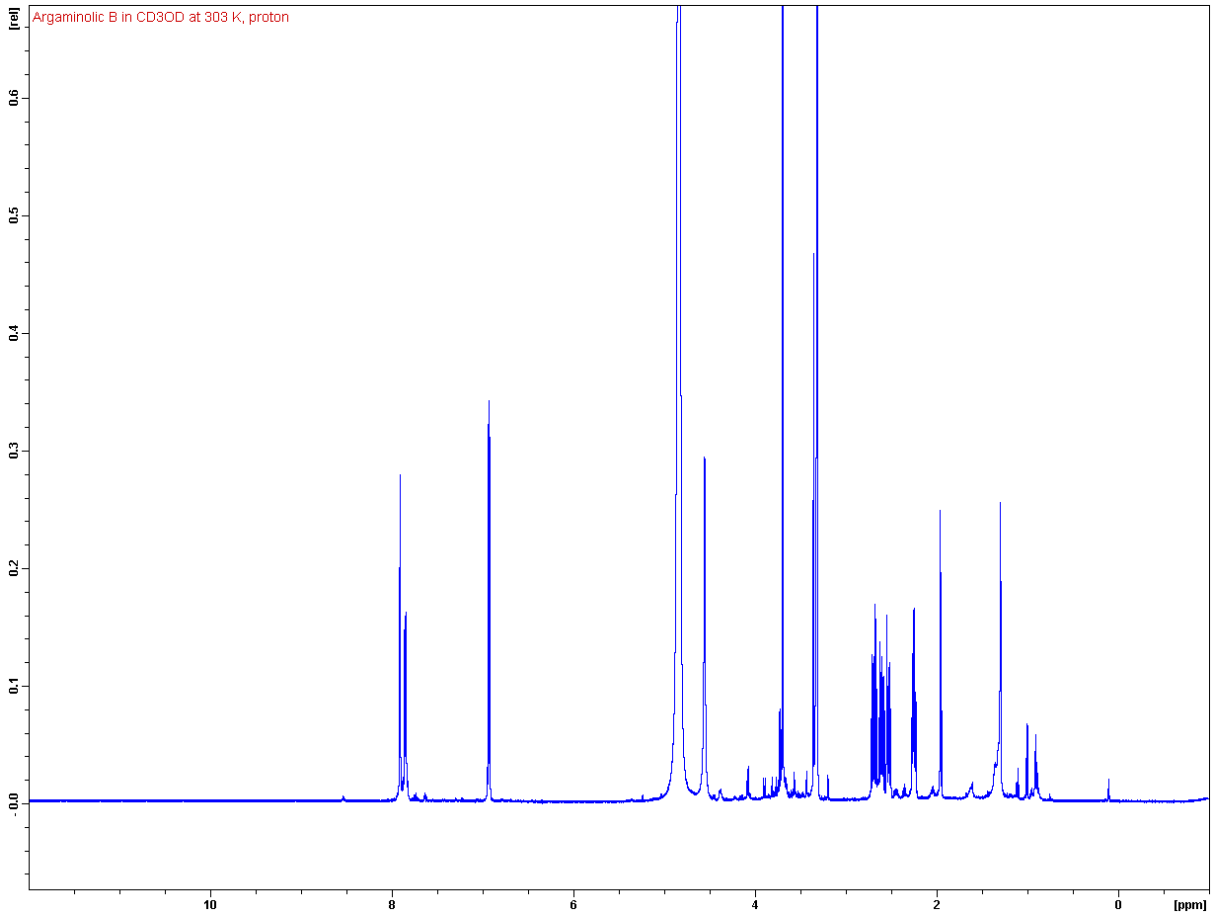
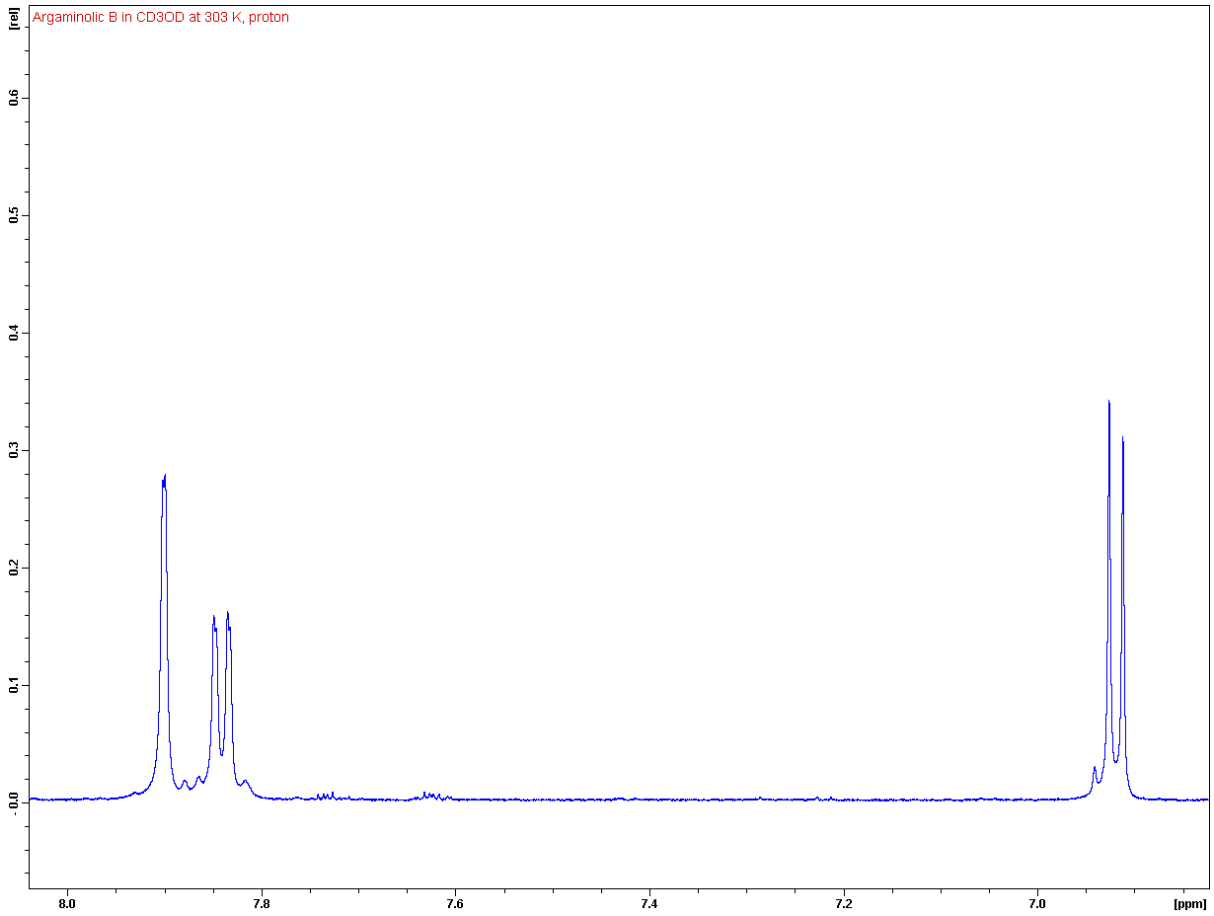
264.05121	C 12 H 10 N O 6	264.05136	0.1	0.6	14.2	8.5	ok	even
	C 11 H 4 N 8 O	264.05136	0.1	0.5	17.4	14.0	ok	odd

S8: ESI-HRMS of Argaminolic C (**3**) in negative-ion mode.



S9: ^{1}H NMR spectrum of Argaminolic B (**2**).



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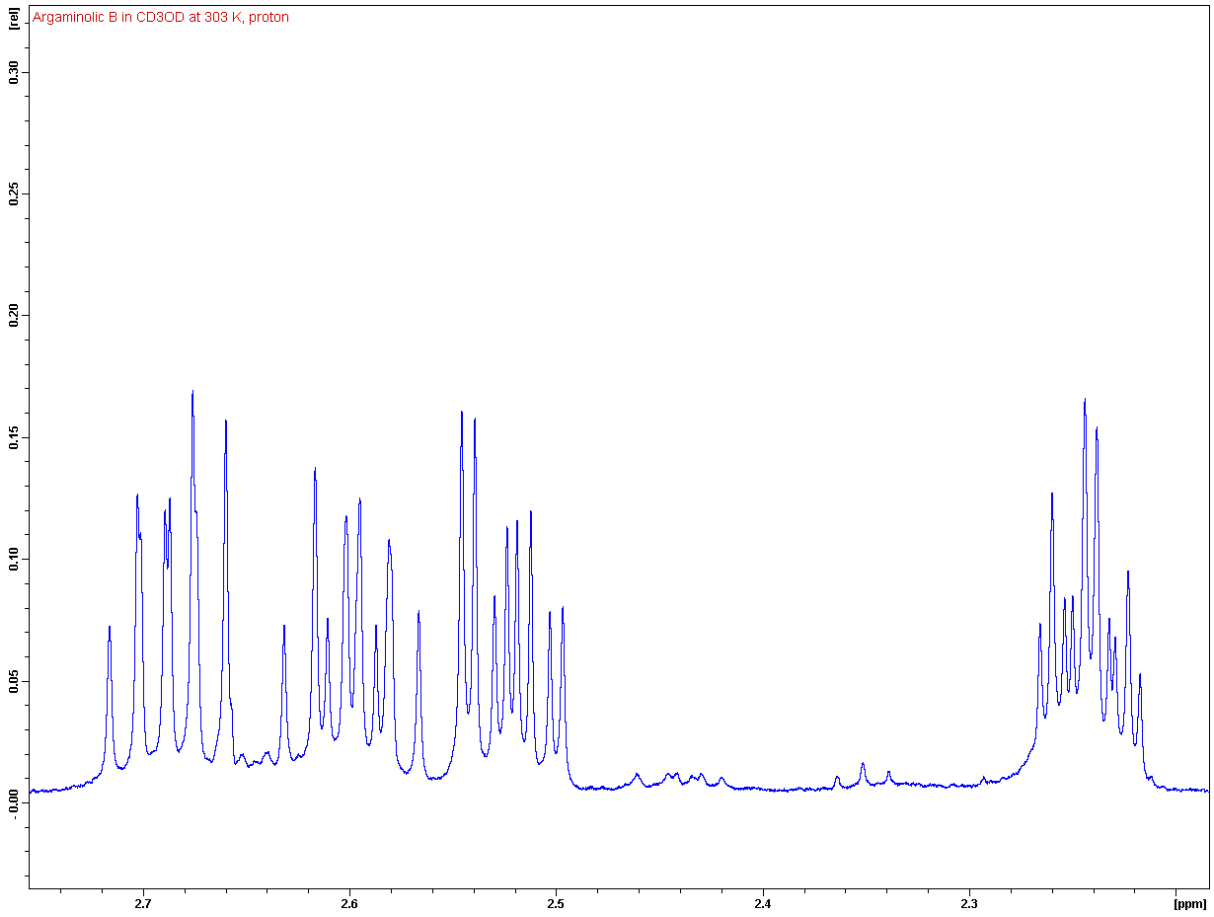

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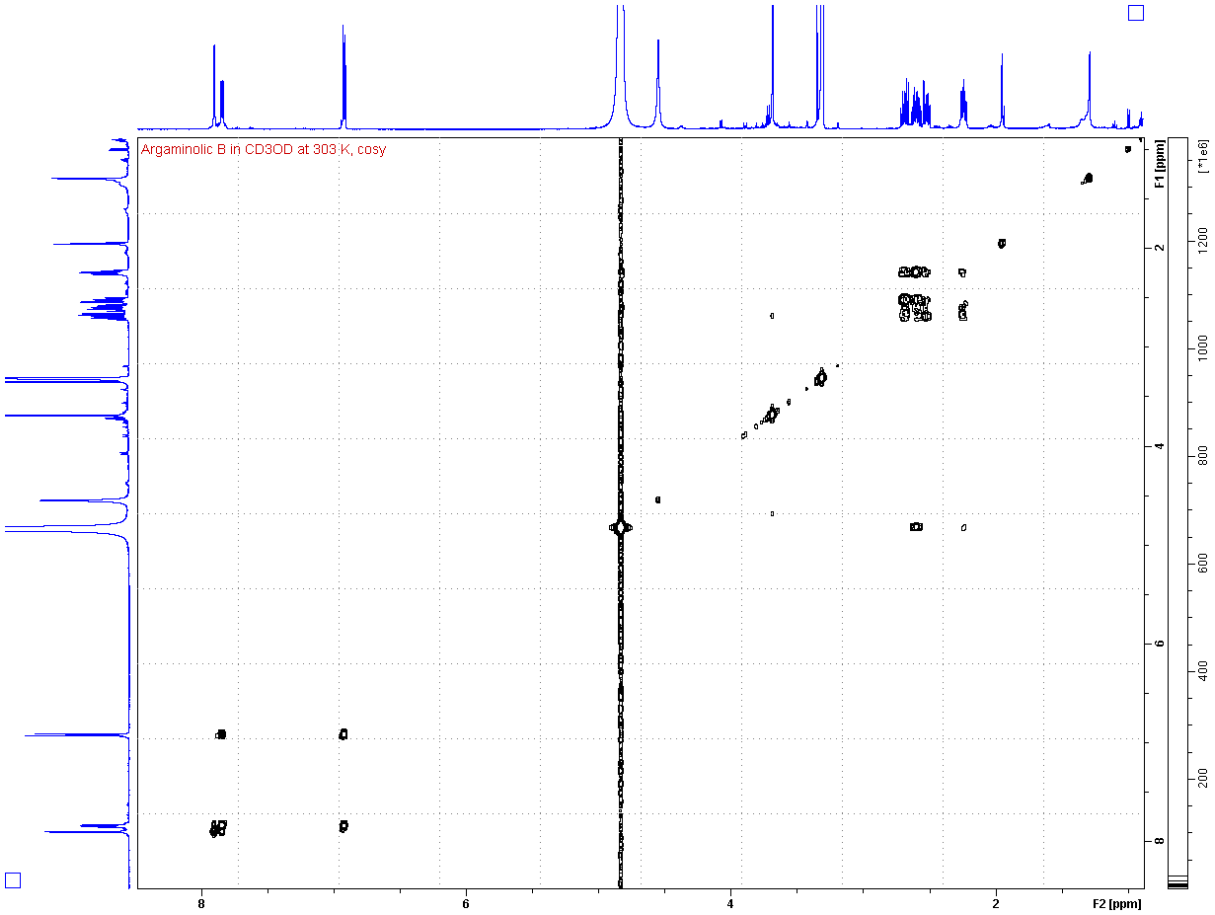

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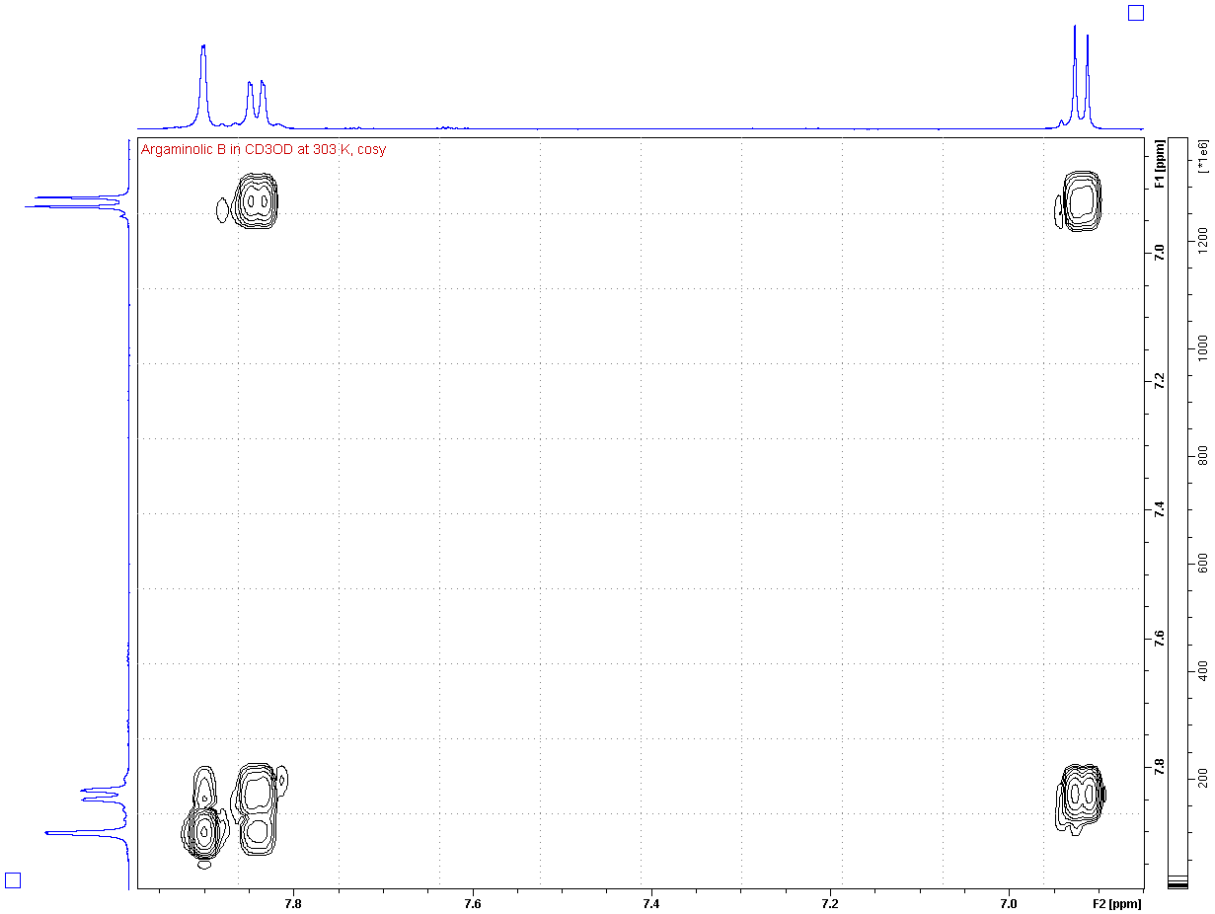

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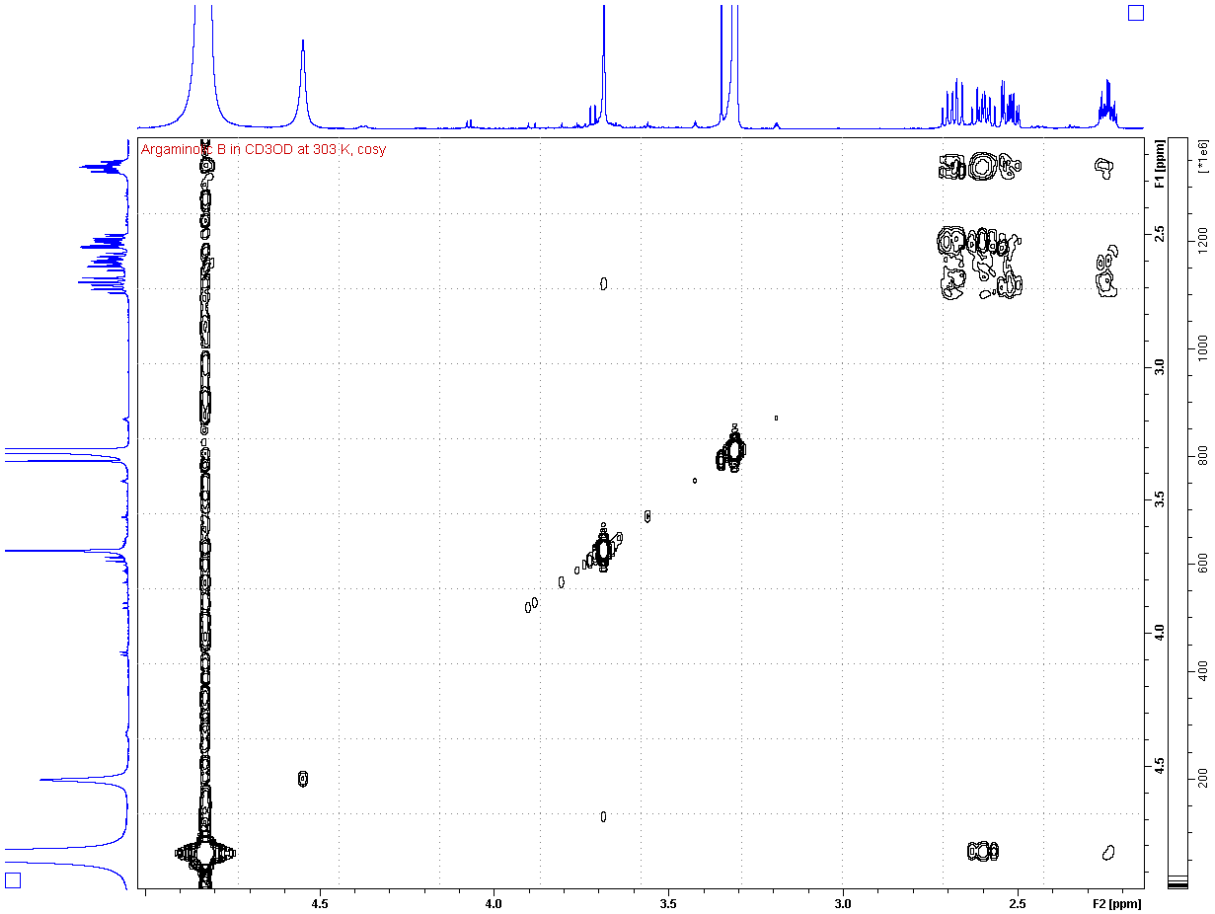

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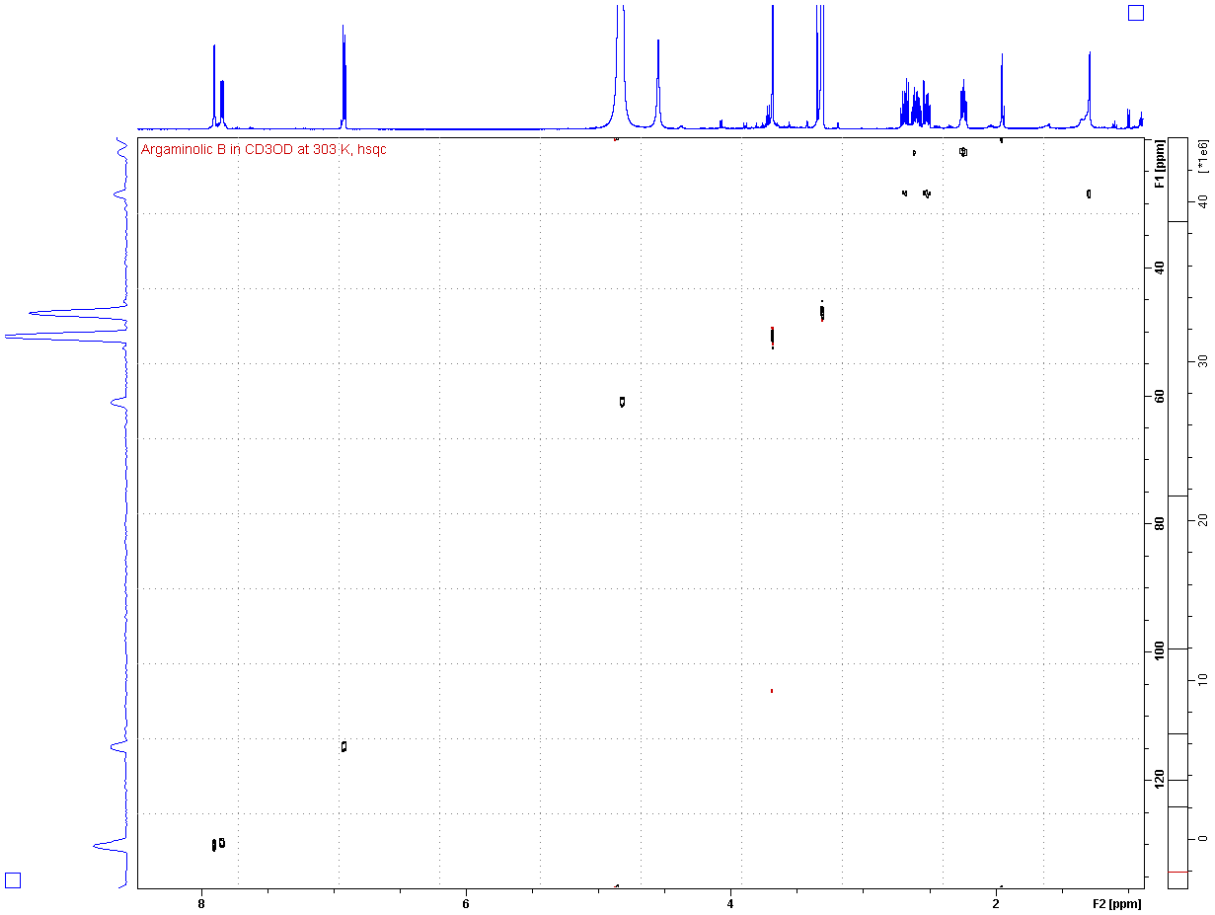

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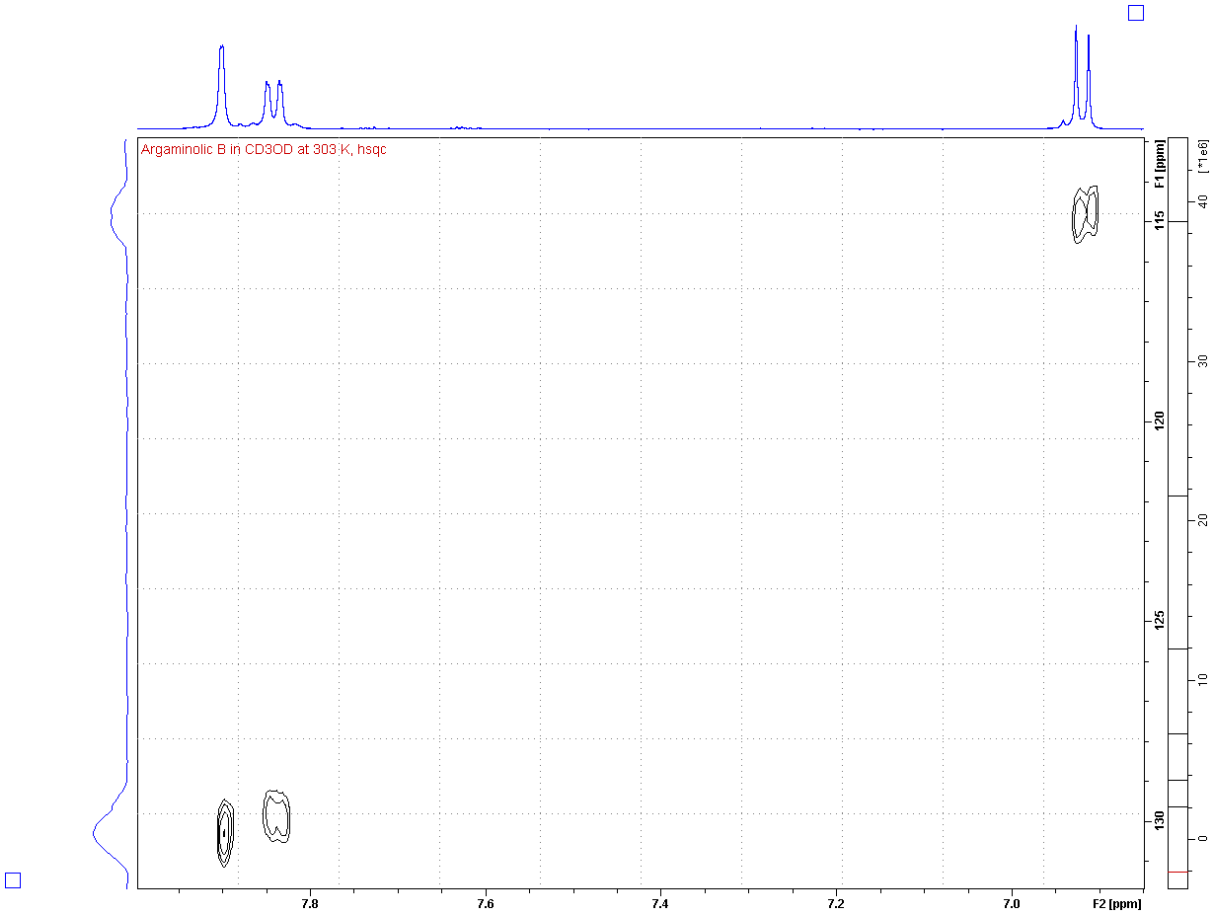

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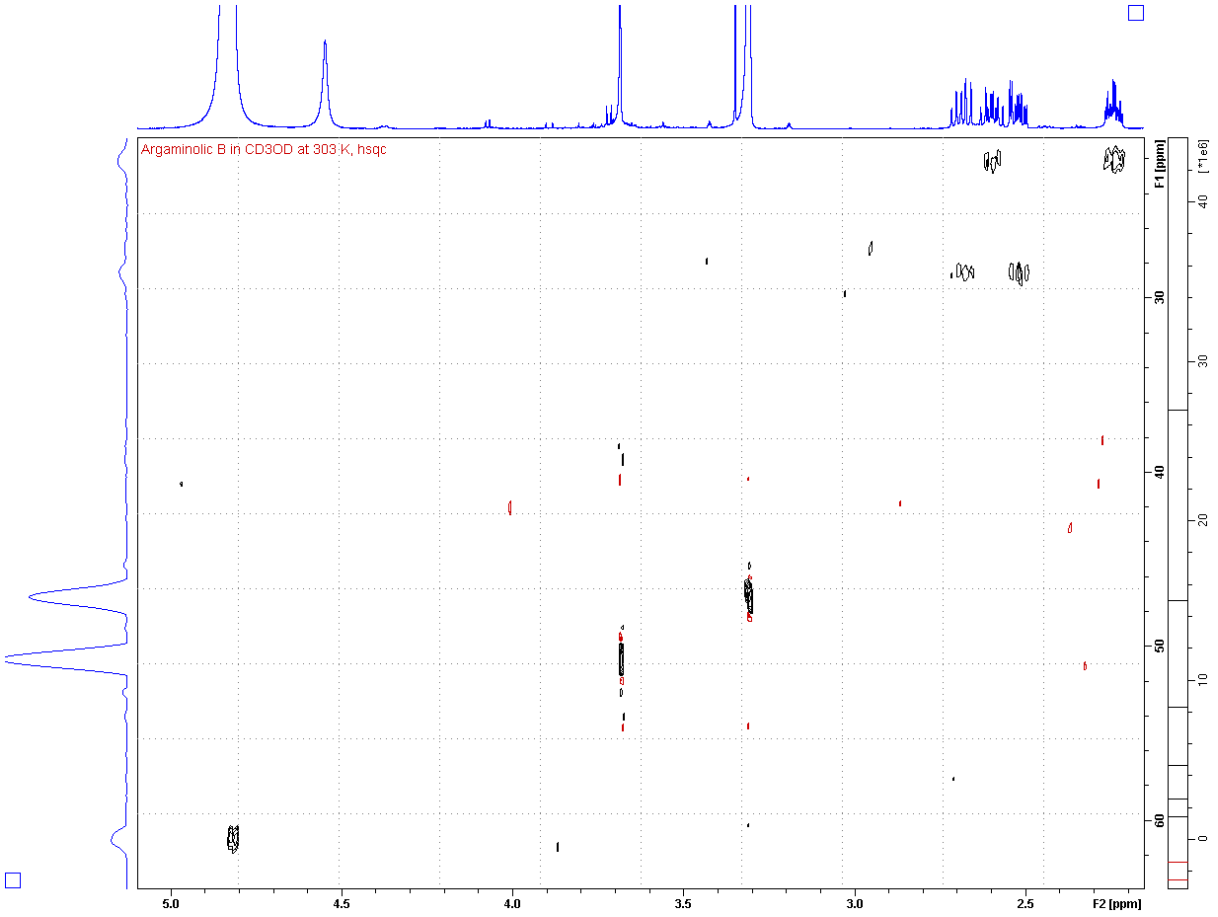

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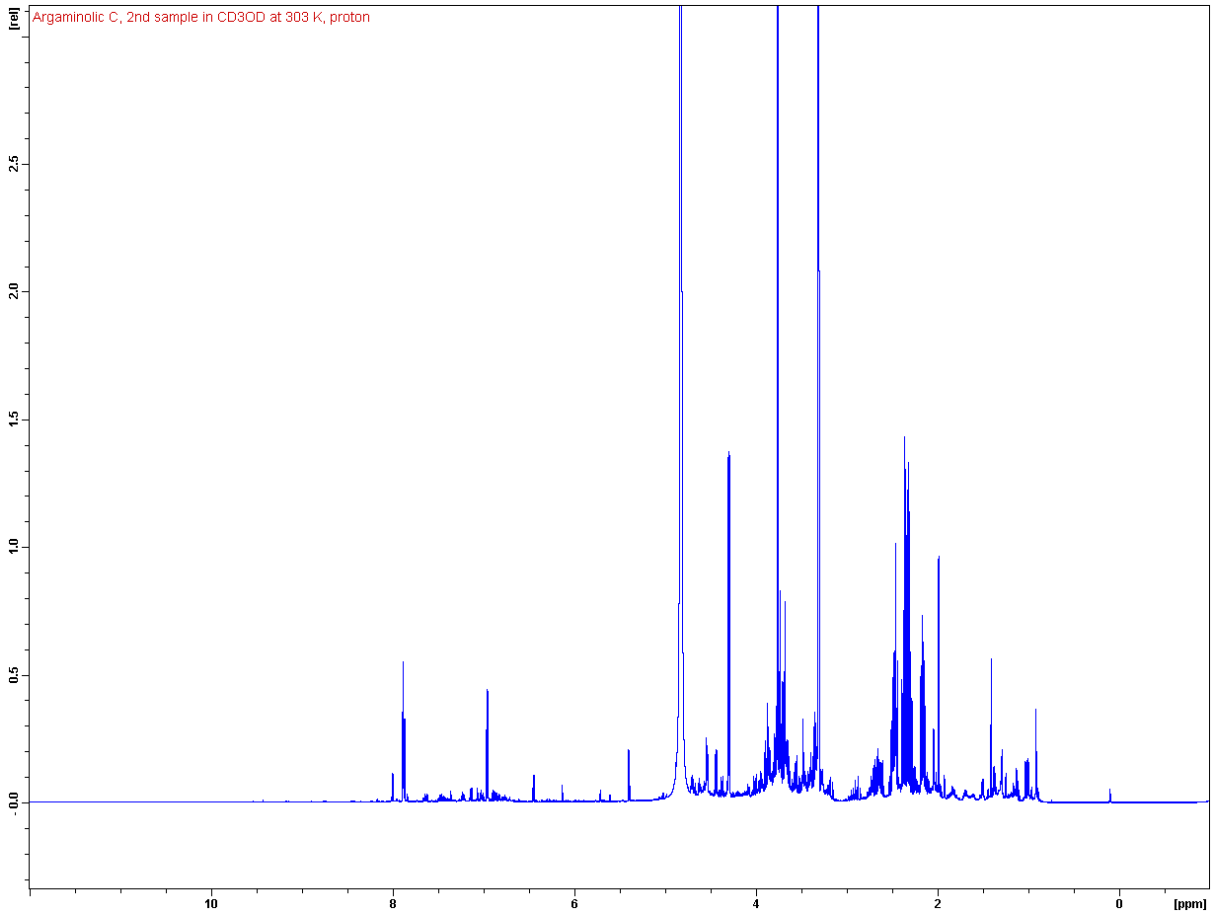
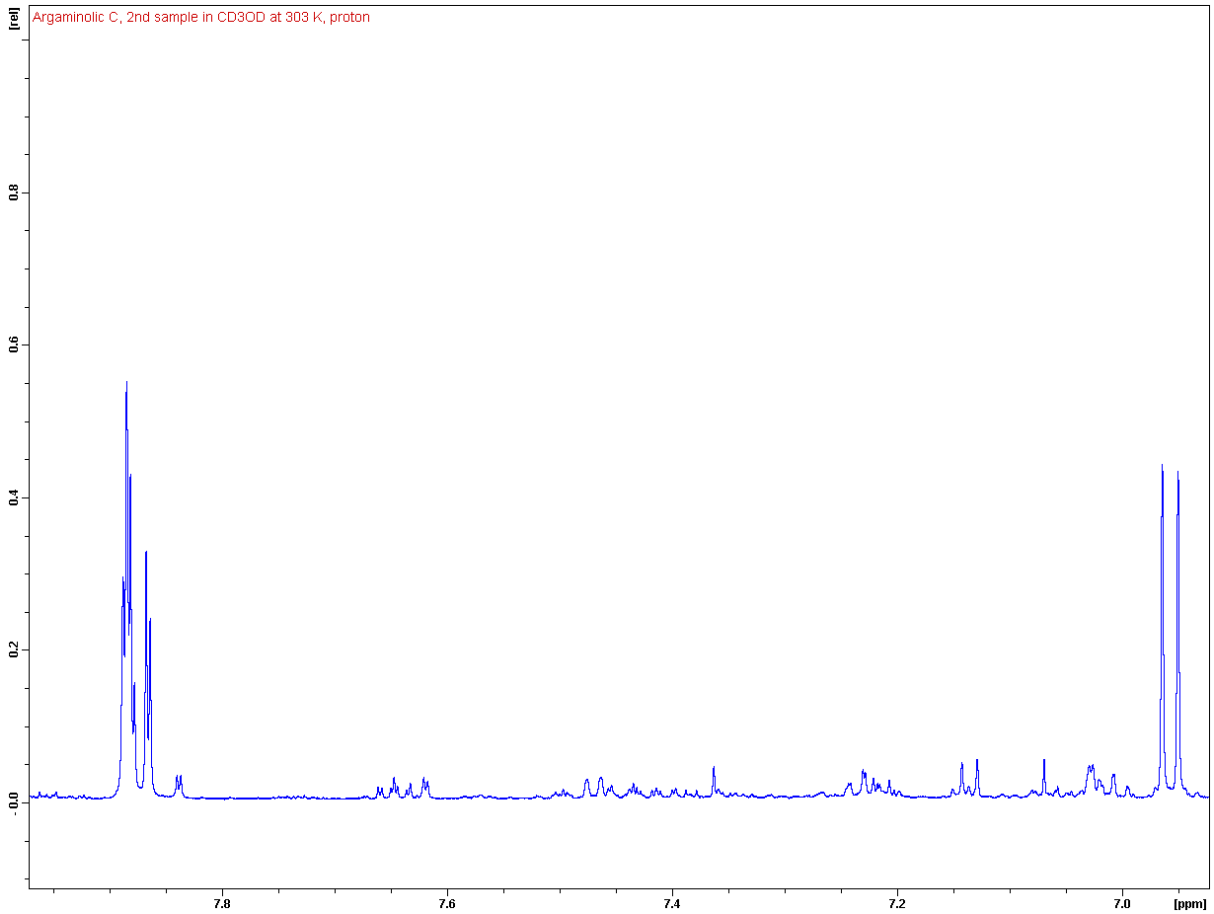


S18: ^{1}H NMR spectrum of Argaminolic C (**3**).



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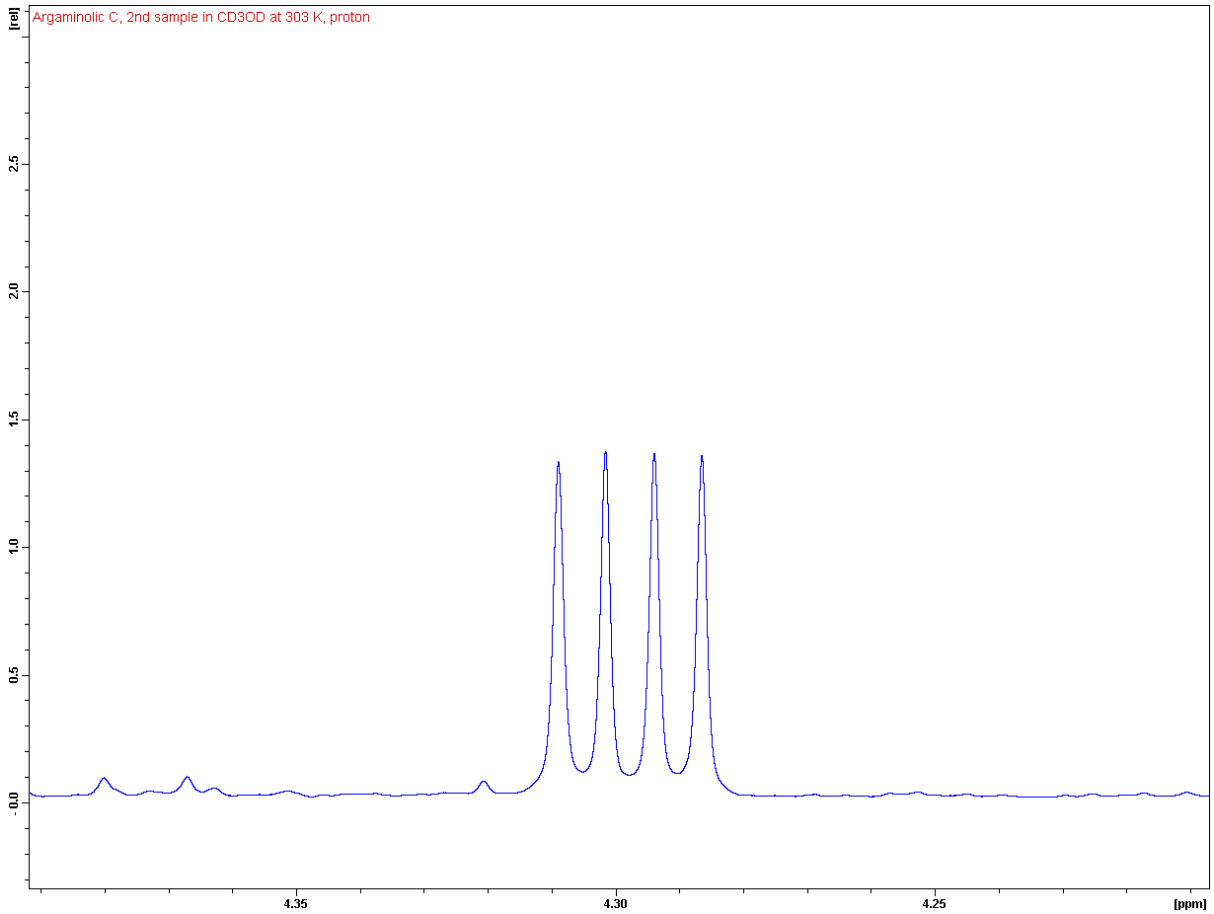

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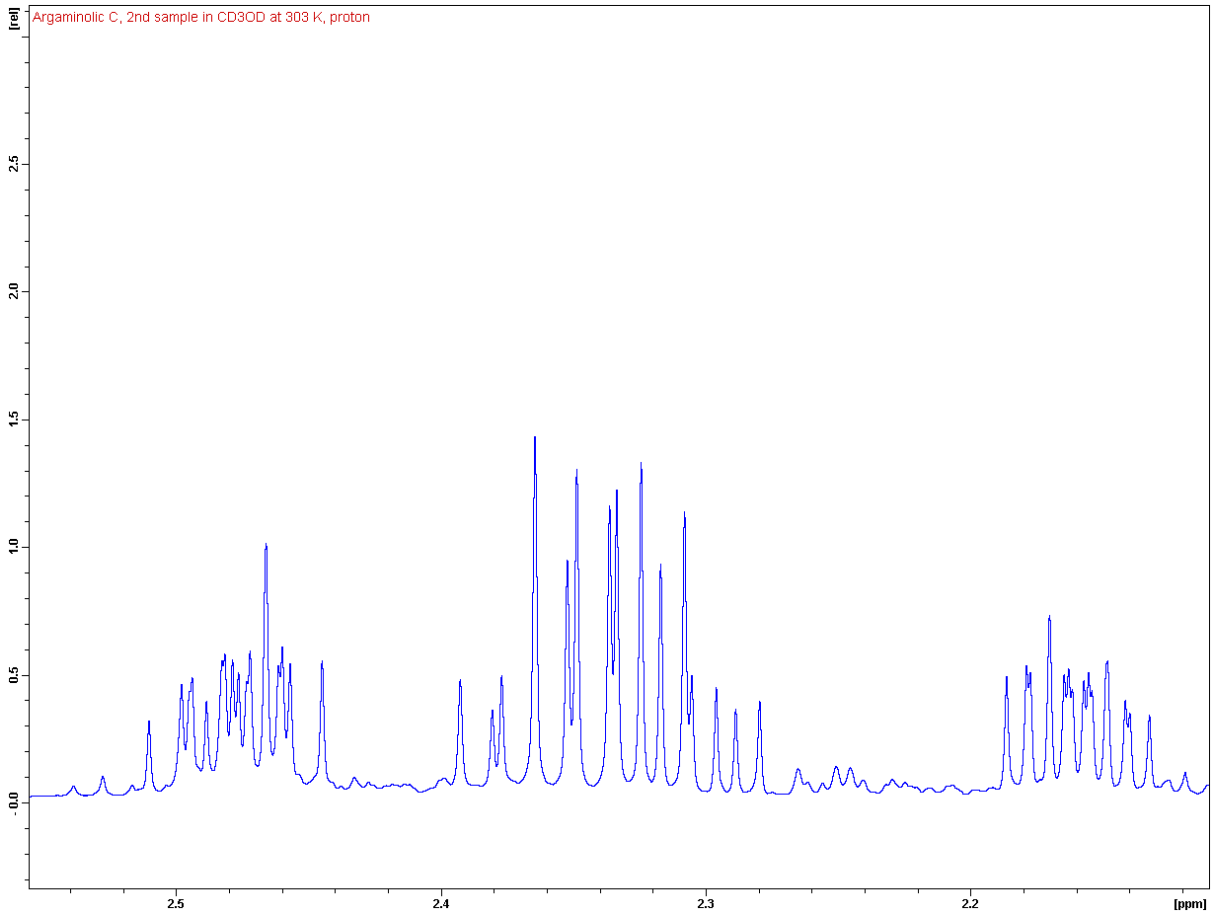

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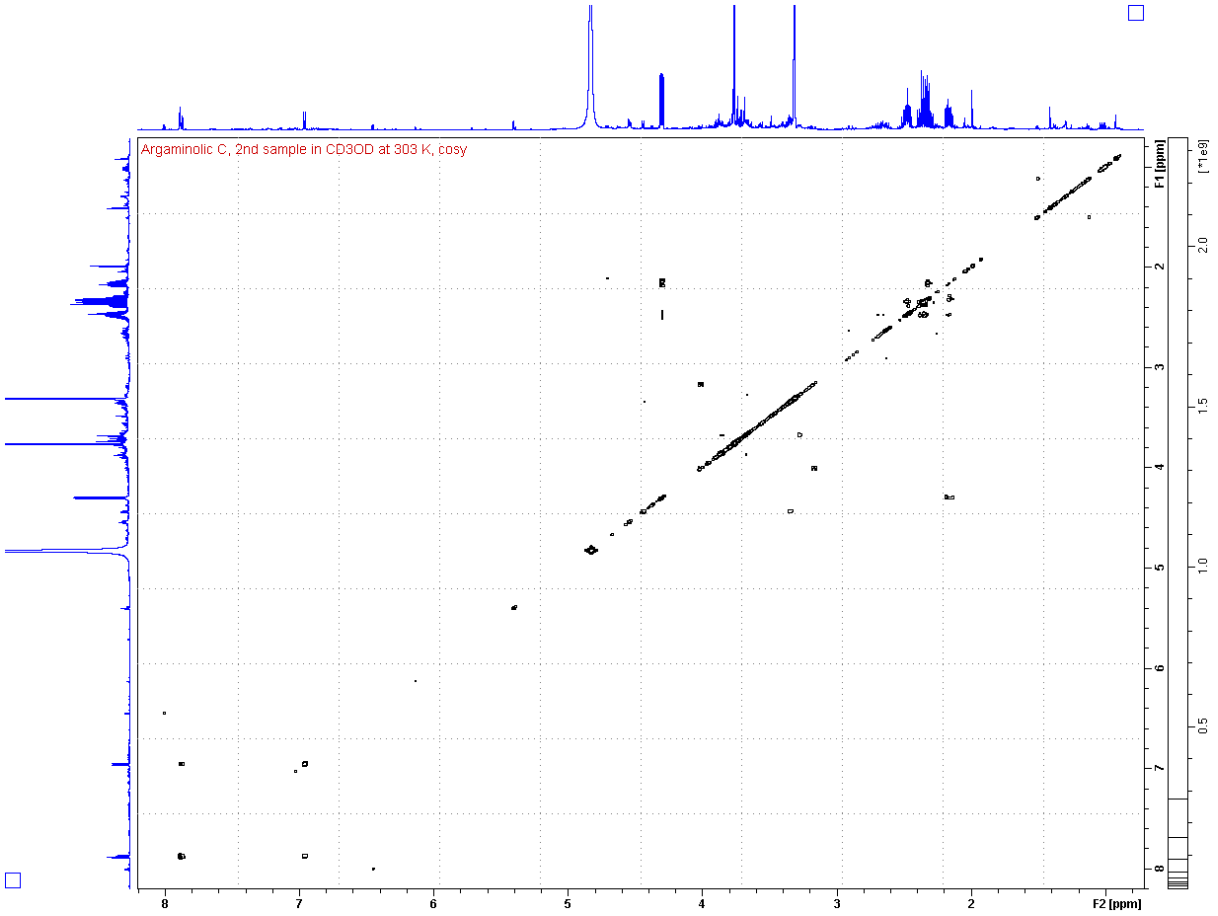

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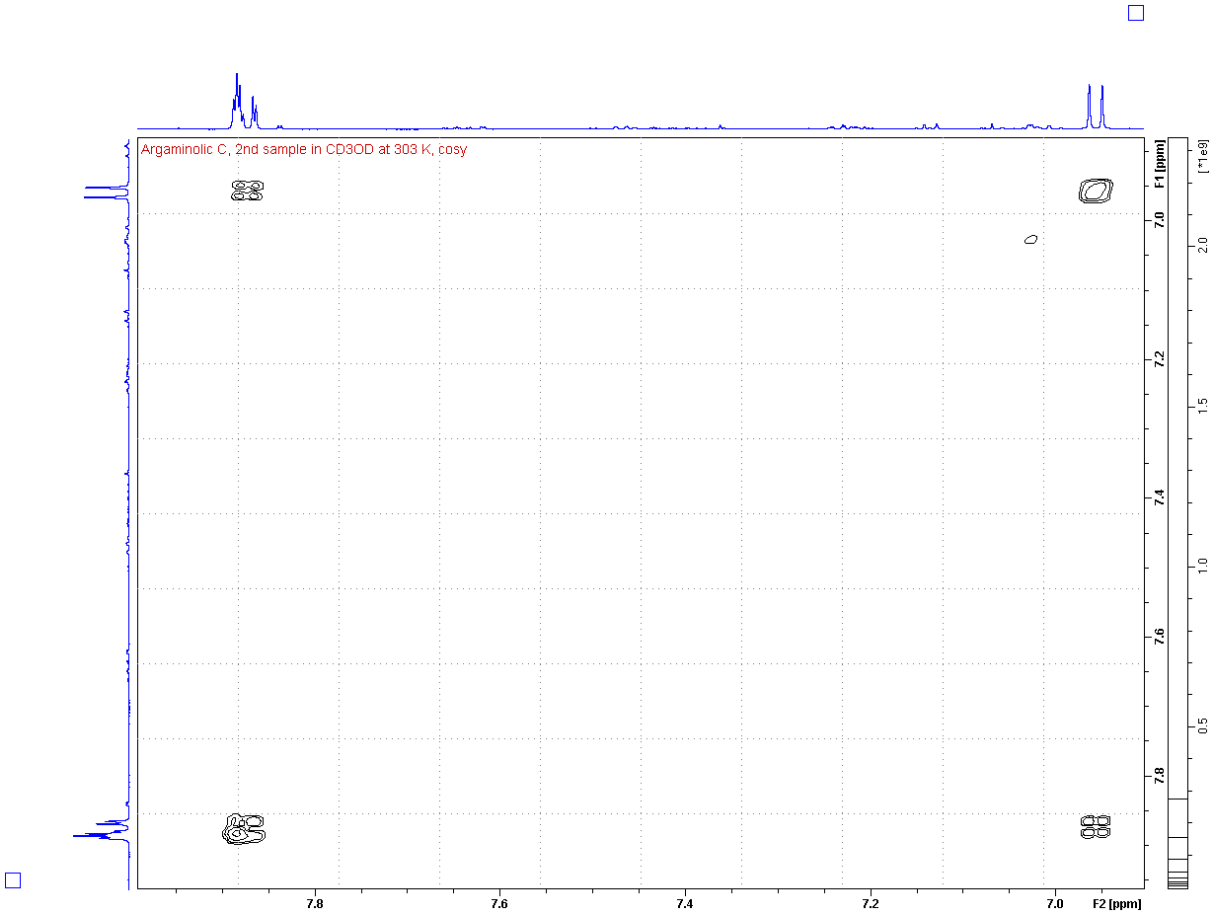

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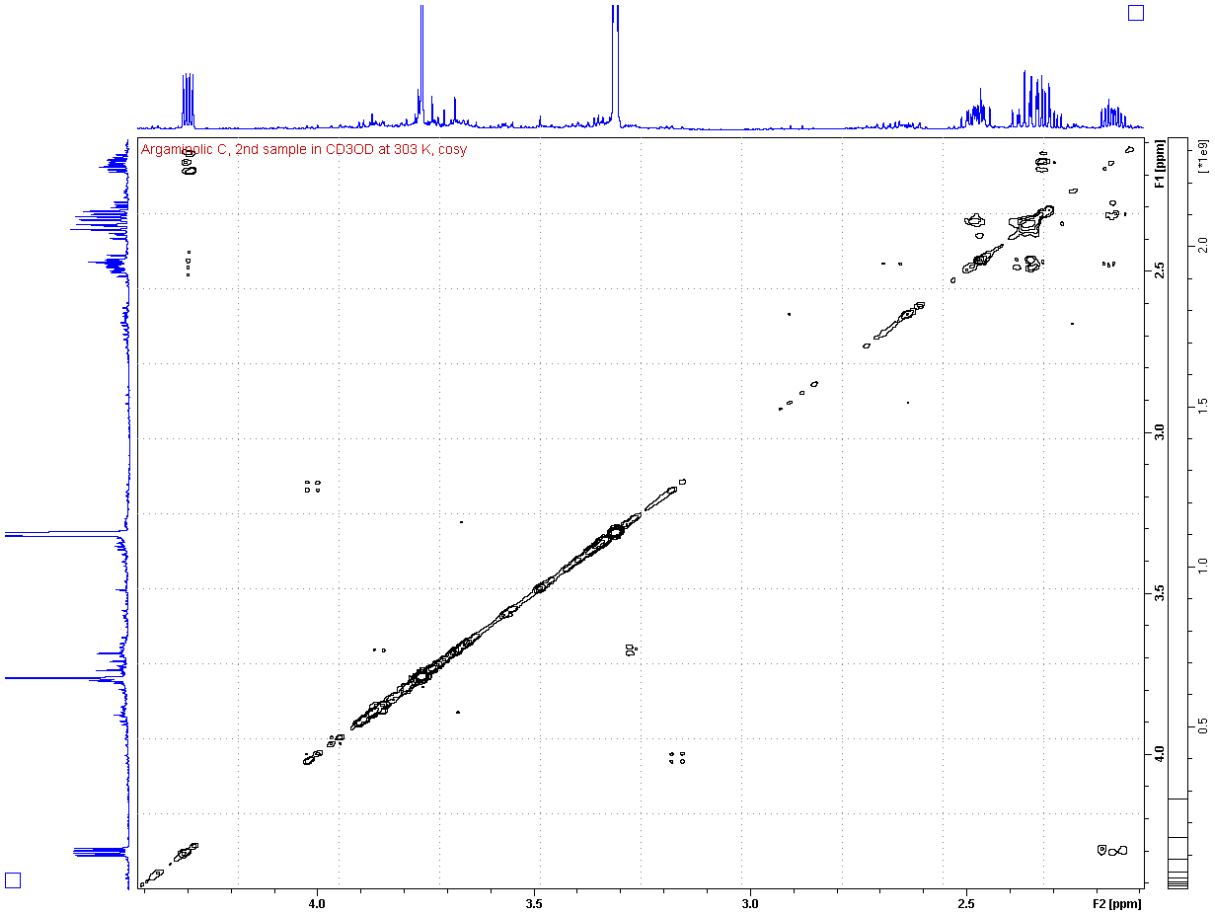
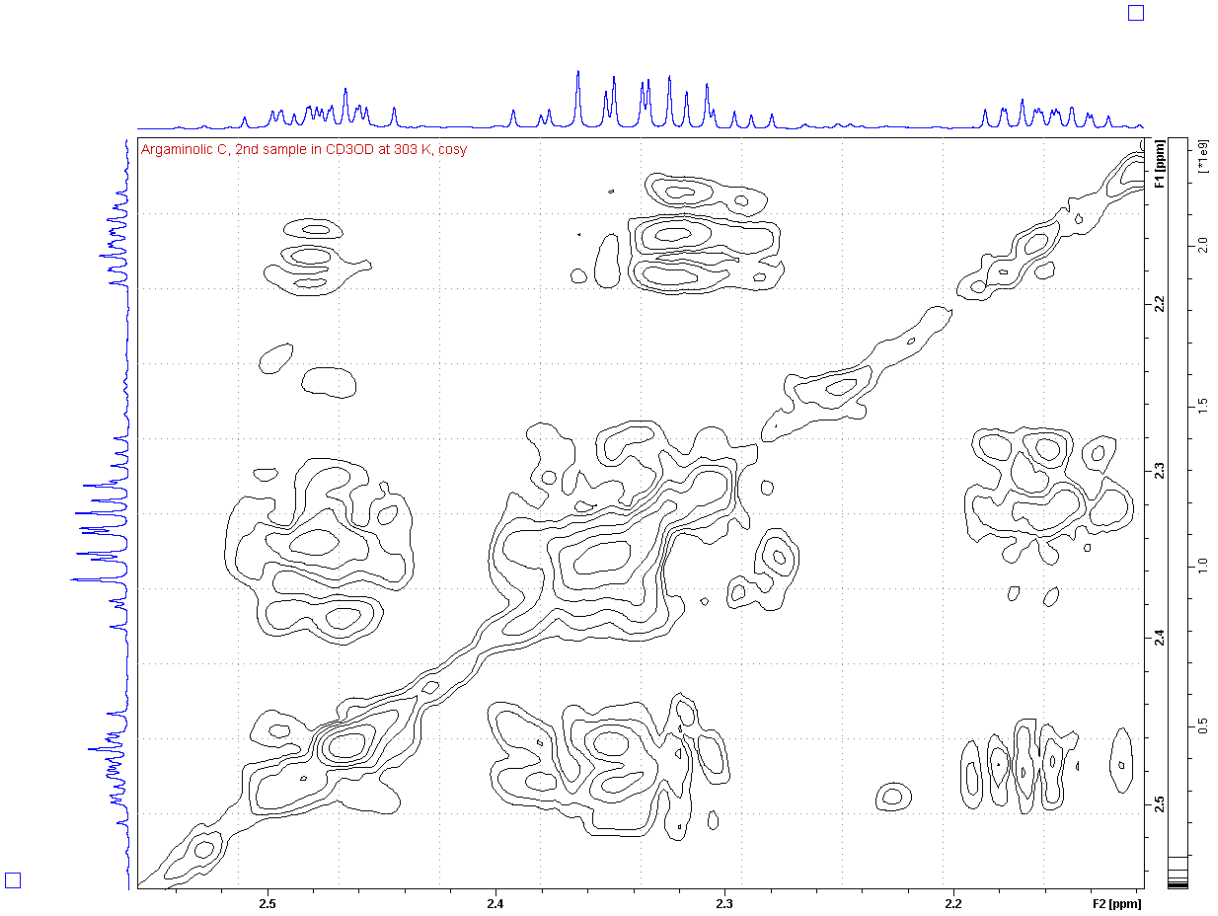


S24: COSY NMR spectrum of Argaminolic C (**3**).



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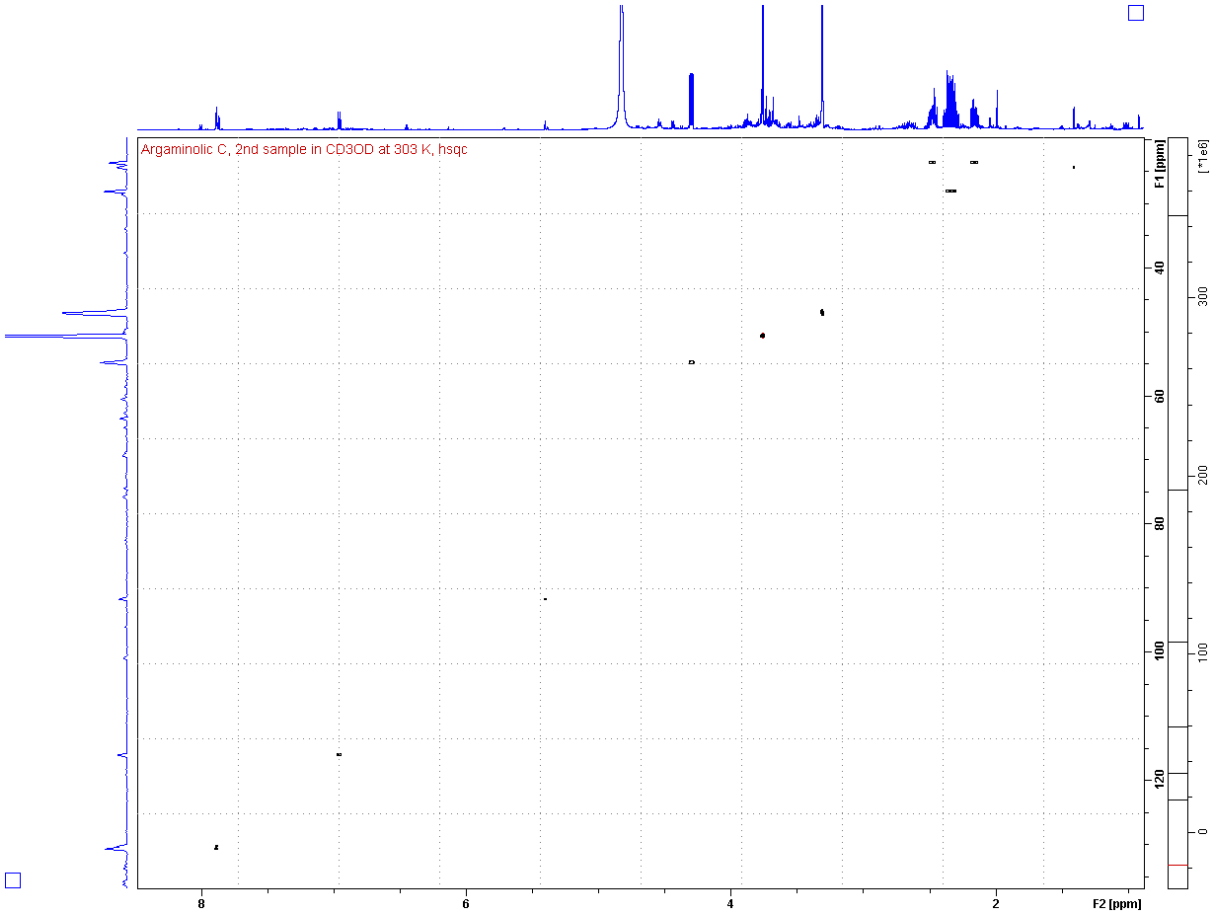

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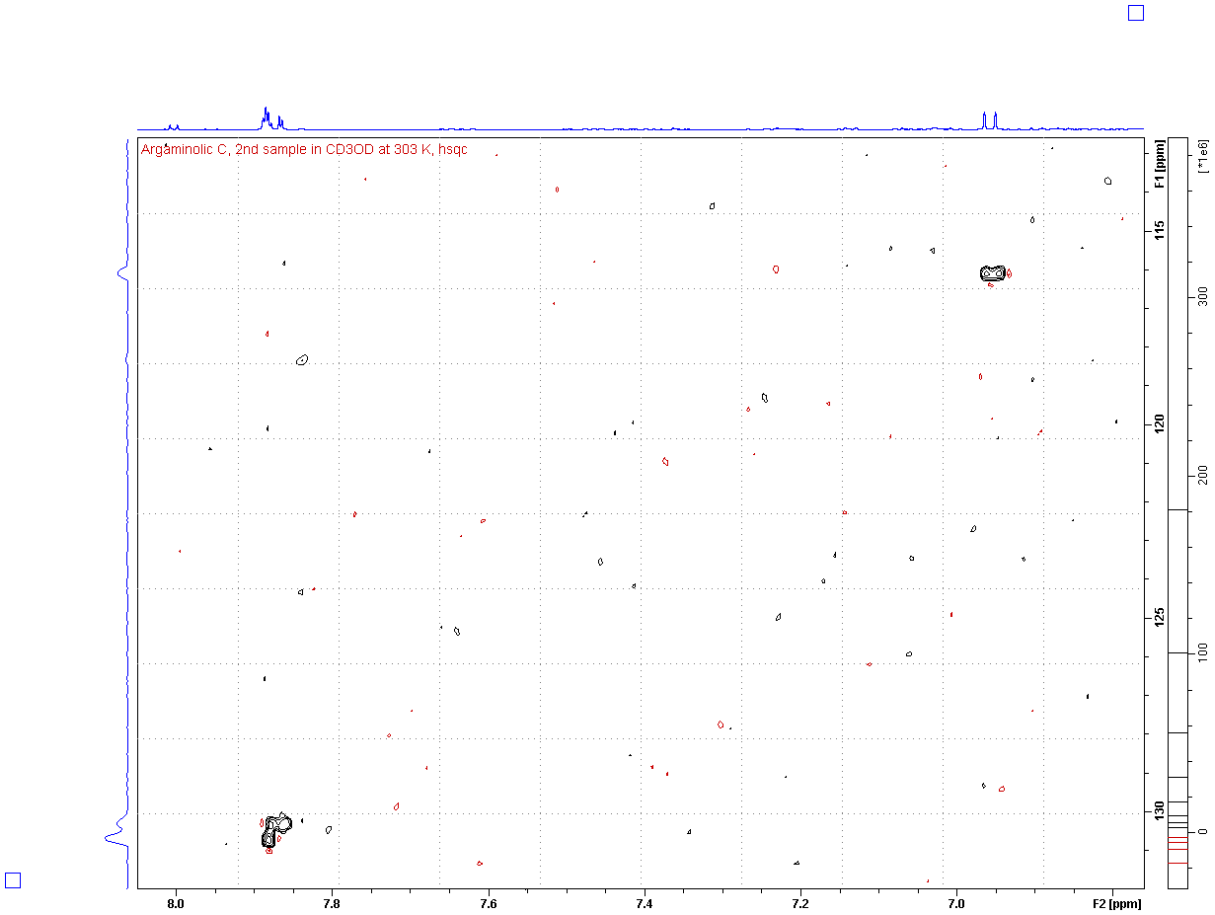

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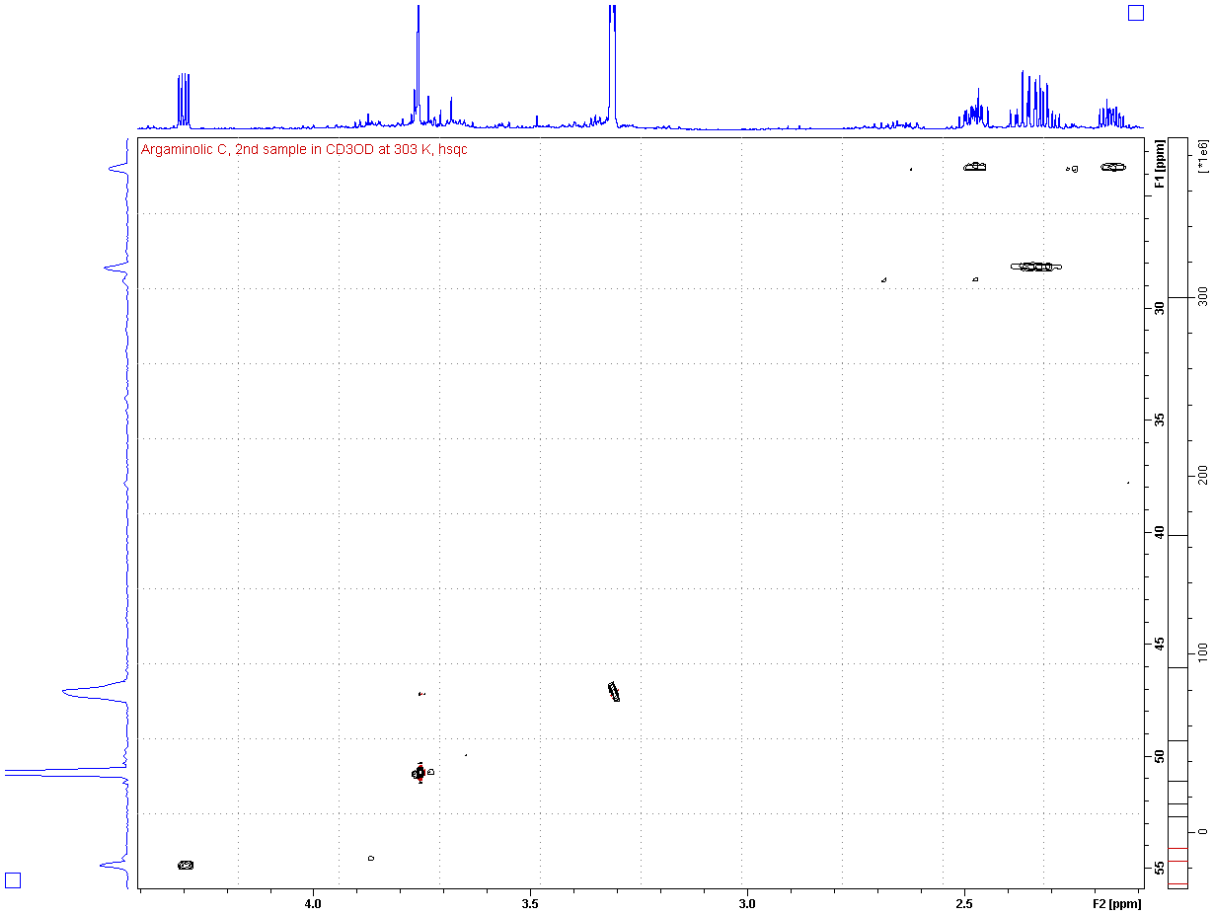
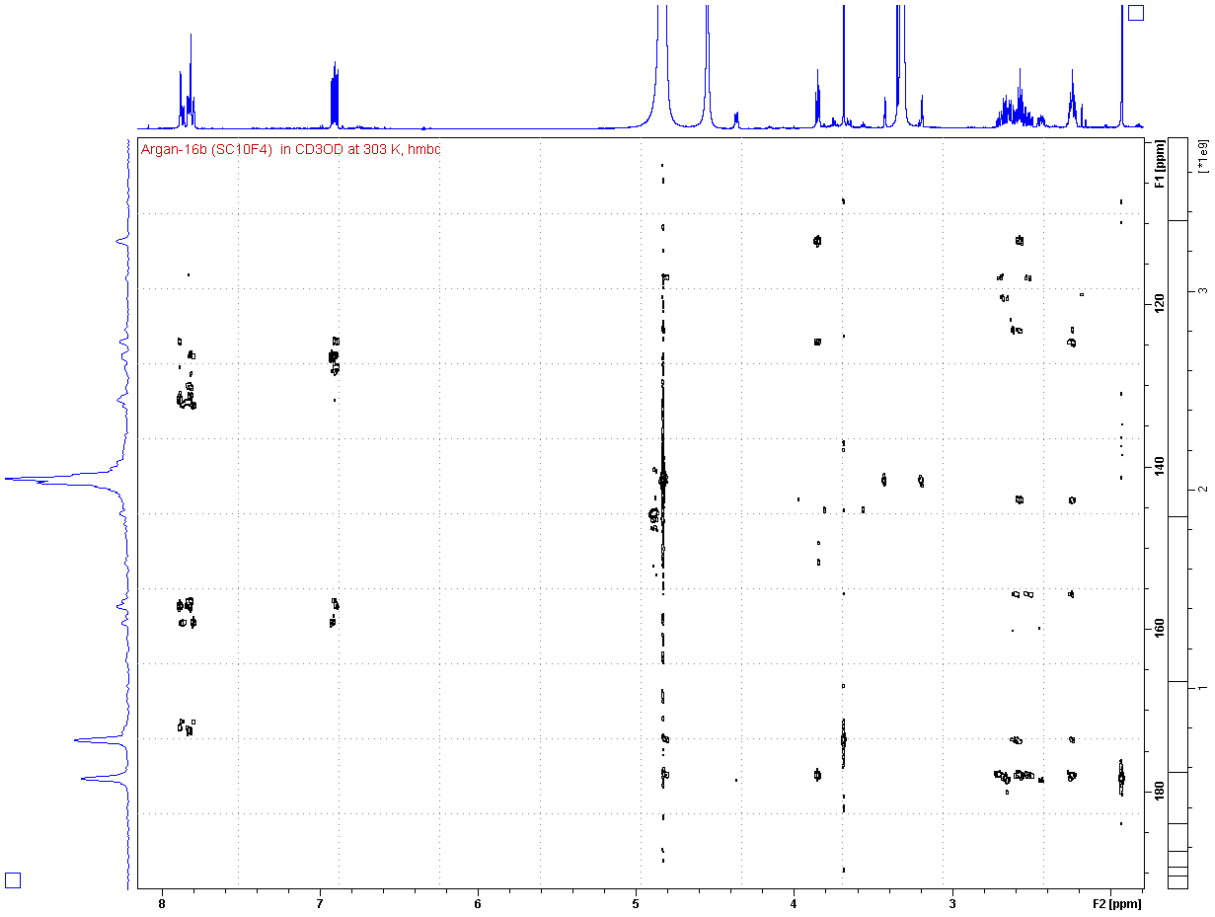
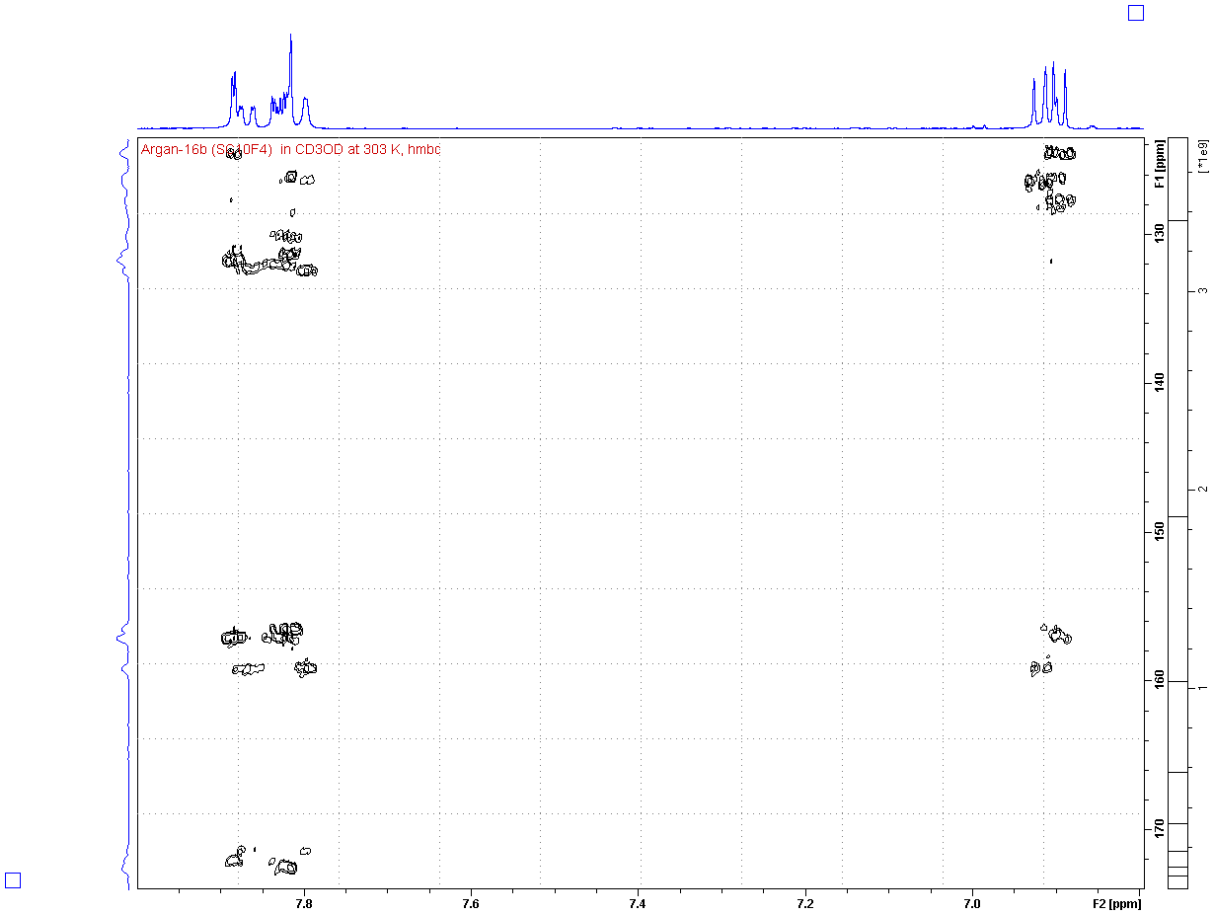


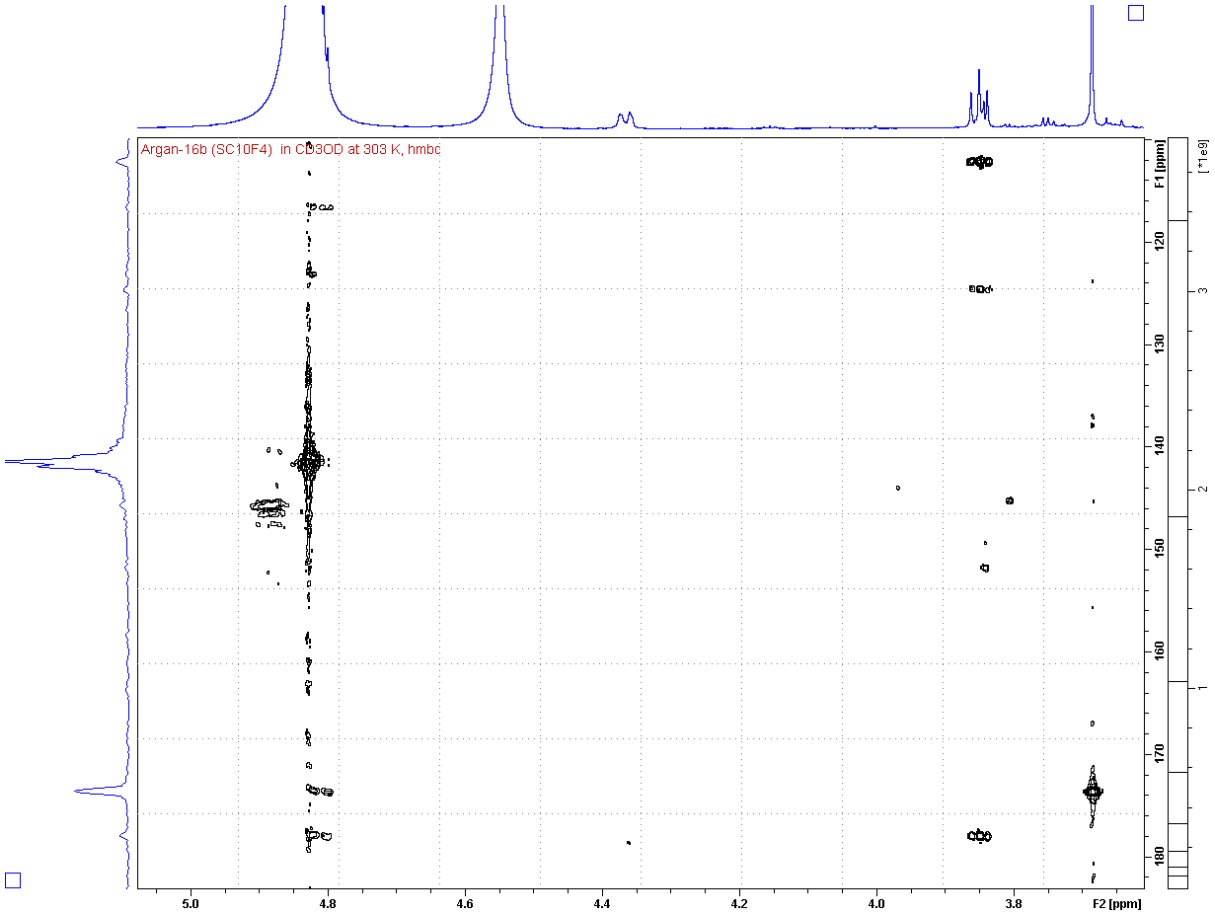
S28: HSQC NMR spectrum of Argaminolic C (**3**).



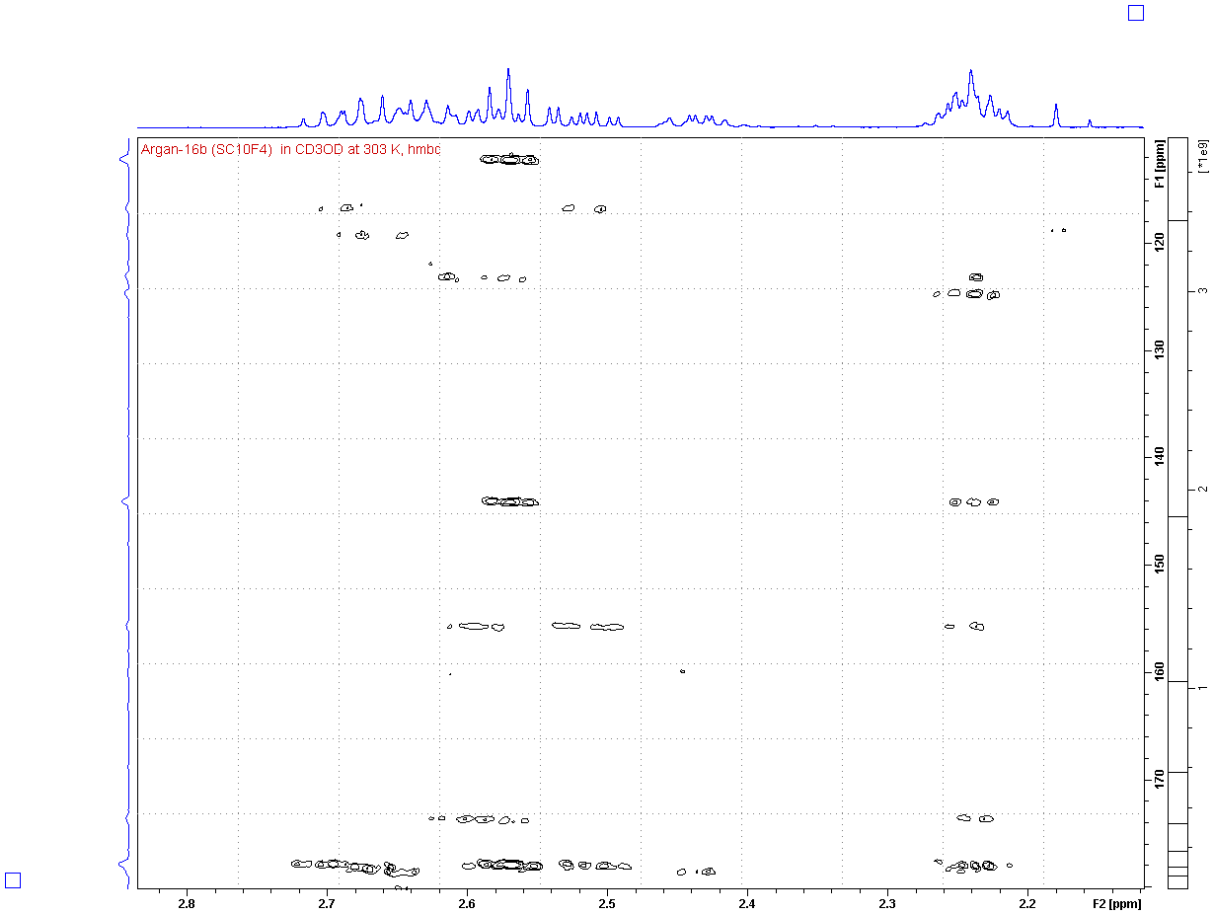
S29: HMBC NMR spectrum of Argaminolic B (**2**) and Argaminolic C (**3**).



S30: HMBC NMR spectrum of Argaminolic B (**2**) and Argaminolic C (**3**).



S31: HMBC NMR spectrum of Argaminolic B (**2**) and Argaminolic C (**3**).



S32: HMBC NMR spectrum of Argaminolic B (**2**) and Argaminolic C (**3**).