

Supporting Information for “Total synthesis and structural elucidation of spongisoritin A” L J Alcock, M D Norris and M V Perkins

Supporting Information for “Total synthesis and structural elucidation of spongisoritin A”

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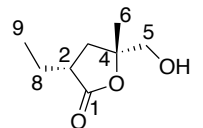
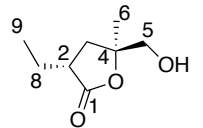
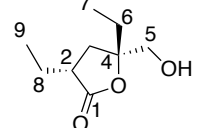
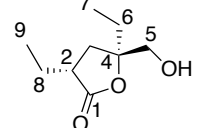
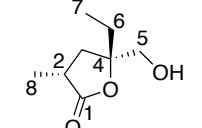
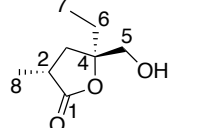
*mike.perkins@flinders.edu.au

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Assignment of syn and anti diastereomers for lactones **15a** & **15b**

Tabulated ¹H NMR data for the syn- (**15a**) and anti- (**15b**) lactones. Assignments were based on ¹H NMR comparison with previously reported analogous lactones by Brimble¹ and Perkins².

Carbon	 syn 15a (600 MHz, CDCl ₃)	 anti 15b (600 MHz, CDCl ₃)	 Perkins <i>syn</i> -isomer (500 MHz, CDCl ₃)	 Perkins <i>anti</i> -isomer (500 MHz, CDCl ₃)	 Brimble's <i>syn</i> -lactone (200 MHz, CDCl ₃)	 Brimble's <i>anti</i> -lactone (200 MHz, CDCl ₃)
5	3.72 (1H, d, <i>J</i> 12.5 Hz) 3.47 (1H, d, <i>J</i> 12.1 Hz)	3.66 (1H, d, <i>J</i> 11.7 Hz) 3.55 (1H, d, <i>J</i> 11.7 Hz)	3.75 (1H, dd, <i>J</i> 12.2, 4.3 Hz) 3.46 (1H, dd, <i>J</i> 12.2, 7.3 Hz)	3.70 (1H, dd, <i>J</i> 11.9, 5.0 Hz) 3.58 (1H, dd, <i>J</i> 11.9, 4.6 Hz)	3.75 (1H, dd, <i>J</i> 12.2, 4.8 Hz) 3.45 (1H, dd, <i>J</i> 12.2, 7.4 Hz)	3.72 (1H, d, <i>J</i> 12.0 Hz) 3.58 (1H, d, <i>J</i> 12.0 Hz)
2	2.73 (1H, m)	2.83 (1H, m)	2.67 (1H, tdd, <i>J</i> 10.2, 9.3, 4.7 Hz)	2.82 (1H, m)	2.91-2.69 (1H, m)	3.04–2.87 (1H, m)
3	2.08 (2H, m)	2.49 (1H, dd, AB distorted) 1.68 (1H, dd, AB distorted)	2.12 (1H, dd, <i>J</i> 12.9, 10.2 Hz) 1.99 (1H, dd, <i>J</i> 12.9, 10.2 Hz)	2.35 (1H, dd, <i>J</i> 13.0, 10.1 Hz) 1.72 (1H, dd, <i>J</i> 10.1, 6.0 Hz)	2.19 (1H, dd, <i>J</i> 12.9, 9.9 Hz) 1.95 (1H, dd, <i>J</i> 12.9, 9.9 Hz)	2.43 (1H, dd, <i>J</i> 13.0, 10.0 Hz) 1.76–1.66 (1H, overlapping)
8	1.51 (2H, m)	1.91 (2H, m)	1.91 (1H, dtd, <i>J</i> 13.8, 7.5, 4.6 Hz) 1.54 (1H, dtd, <i>J</i> 13.8, 9.3, 7.5 Hz)		1.29 (3H, d, <i>J</i> 7.0 Hz)	1.26 (3H, d, <i>J</i> 7.3 Hz)
6	1.35 (3H, s)	1.39 (3H, s)	1.69 (2H, q, <i>J</i> 7.6 Hz)		1.69 (2H, q, <i>J</i> 7.5 Hz)	1.76–1.66 (2H, overlapping)
9	0.98 (3H, t, <i>J</i> 7.3 Hz)	0.99 (3H, t, <i>J</i> 7.4 Hz)	0.99 (3H, t, <i>J</i> 7.5 Hz)		N/A	N/A
7	N/A	N/A	0.95 (3H, t, <i>J</i> 7.5 Hz)		0.94 (3H, t, <i>J</i> 7.5 Hz)	0.94 (3H, t, <i>J</i> 7.5 Hz)

All chemical shifts reported in ppm

(1) P. R. Allen, M. A. Brimble and H. Prabakaran, *J. Chem. Soc., Perkin Trans. I*, 2001, 379.

(2) M. D. Norris, M. V. Perkins and E. J. Sorensen, *Org. Lett.*, 2015, **17**, 668.

Comparison of ^{13}C and ^1H NMR data for reported natural product compared to synthetic syn-**1a** and anti-**1b**

Carbon no.	Natural product Capon ³		Natural product Epifanio ⁴		Synthetic syn 1a			Synthetic anti 1b		
	^{13}C (150 MHz, CDCl_3) (ppm)	^1H (600 MHz, CDCl_3) (ppm)	^{13}C (75.4 MHz, CDCl_3) (ppm)	^1H (300 MHz, CDCl_3) (ppm)	^{13}C (150 MHz, CDCl_3) (ppm)	^1H (600 MHz, CDCl_3) (ppm)	$\Delta\delta^{13}\text{C}^\#$	^{13}C (150 MHz, CDCl_3) (ppm)	^1H (600 MHz, CDCl_3) (ppm)	$\Delta\delta^{13}\text{C}^\#$
1	166.9		166.9		166.9		0	166.9		0
2	83.9	4.80	83.8	4.82	83.8	4.81	0.1	84	4.80	-0.1
3	171.5		171.5		171.5		0	171.1		0.4
4	138.2		138.1		138.1		0.1	138.3		-0.1
5	141.7	6.21	141.6	6.25	141.6	6.23	0.1	141.4	6.36	0.3
6	95.1		95.0*		95.1		0	95.2		-0.1
7a	45.0	1.76	44.9	1.76	45	1.76	0	44.8	1.87	0.2
7b		1.96		1.94		1.96				
8	40.1	1.76	40.0	1.78	40	1.76	0.1	41.4	1.72	-1.3
9	133.8	5.02	133.7	5.04	133.8	5.05	0	133.1	5.05	0.7
10	132.2	5.23	132.1	5.26	132.2	5.23	0	131.9	5.30	0.3
11	25.6	1.96	25.5	1.98	25.6	1.96	0	24.9	1.97	0.7
12	13.9	0.93	13.9	0.95	13.9	0.93	0	13.6	0.95	0.3
13	18.5	2.10	18.4	2.12	18.4	2.10	0.1	18.5	2.11	0
14	11.7	1.12	11.6	1.14	11.6	1.12	0.1	11.8	1.14	-0.1
15	26.3	1.40	26.3	1.42	26.3	1.41	0	25.5	1.41	0.8
16a	29.4	1.16	29.3	1.16	29.3	1.15	0.1	29.4	1.19	0
16b		1.36		1.36		1.40			1.36	
17	11.3	0.75	11.3	0.77	11.3	0.77	0	11.4	0.80	-0.1
OMe	50.5	3.70	50.5	3.64	50.5	3.69	0	50.5	3.67	0

(3) R. J. Capon, S. Singh, S. Ali and S. Sotheeswaran, *Aust. J. Chem.*, 2005, **58**, 18.

(4) R. d. A. Epifanio, L. S. Pinheiro and N. C. Alves, *J. Braz. Chem. Soc.*, 2005, **16**, 1367.

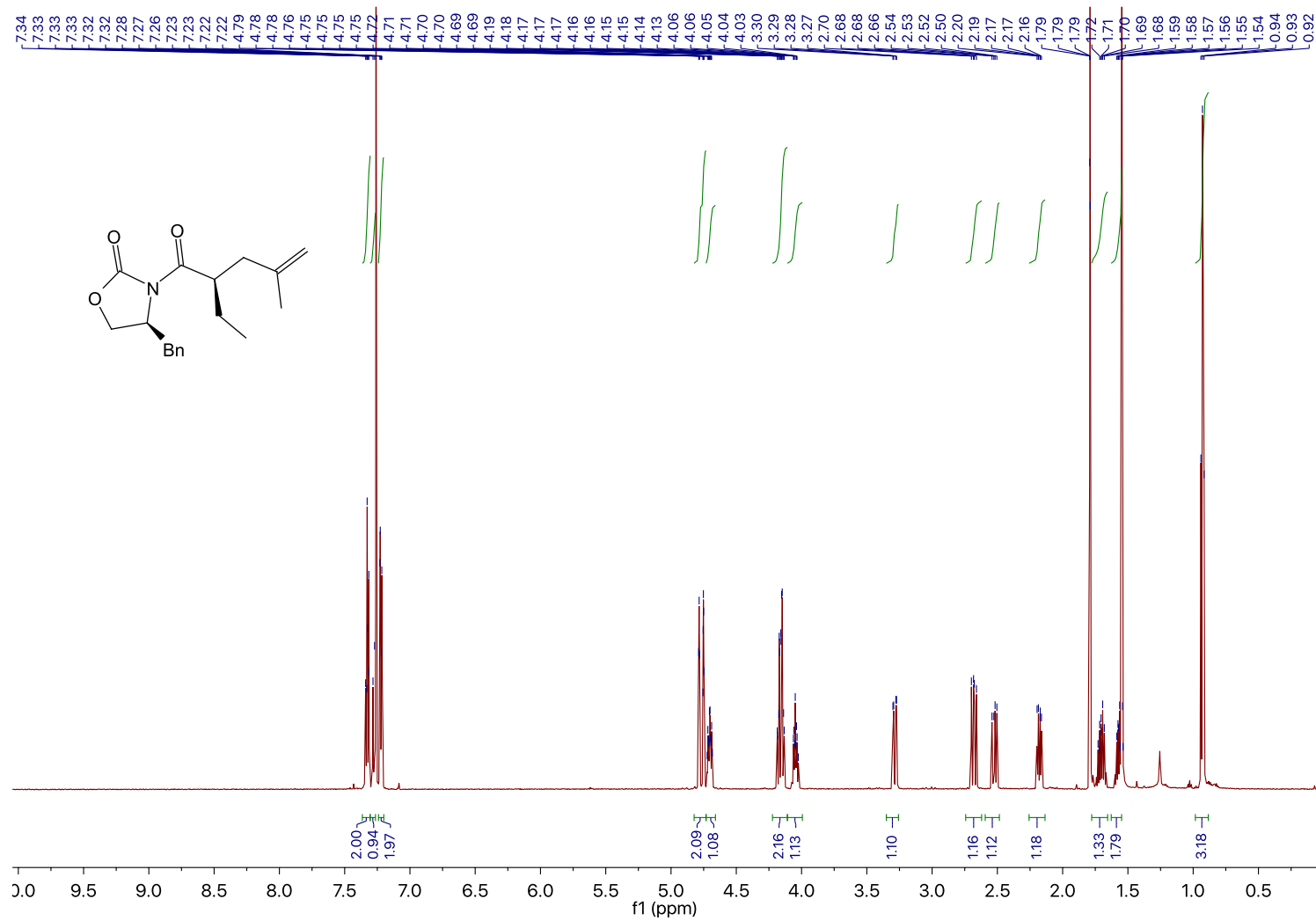
difference in ^{13}C chemical shift from the reported natural product¹ compared to the synthetic products

*reported as 5.0 ppm in original paper (4), but this is likely a typo which should read 95.0

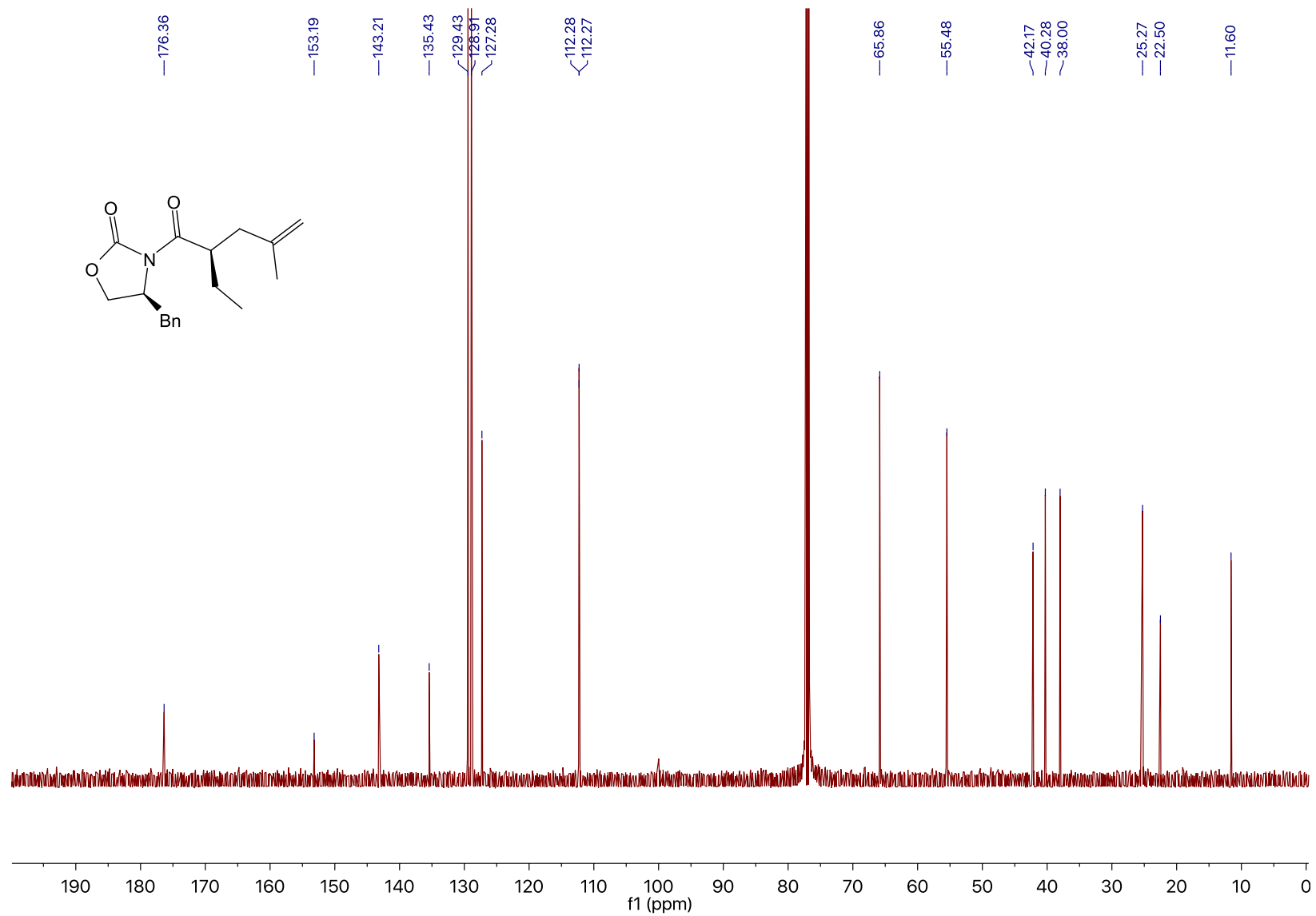
NMR and HRMS data for compounds **1a/1b**, **8a/8b**, **11a/11b**, **12**, **15-18**

^1H , ^{13}C NMR and HRMS (ESI) data for compound **12**

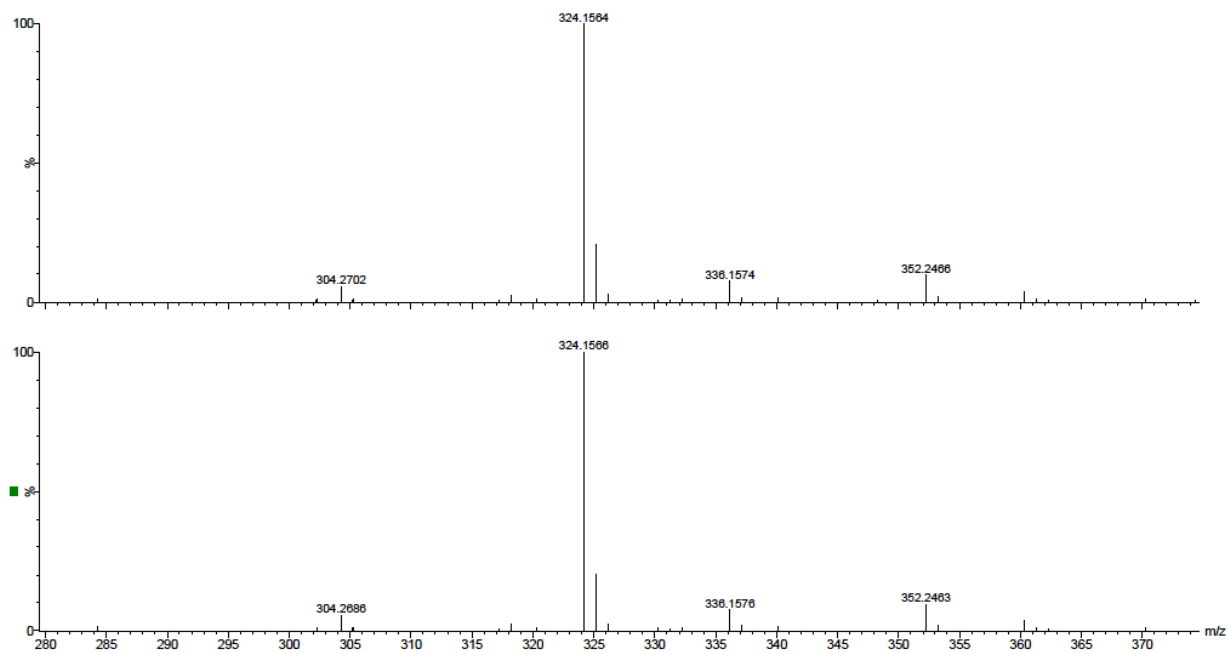
^1H NMR data



^{13}C NMR data



High Resolution Spectra
Positive ion



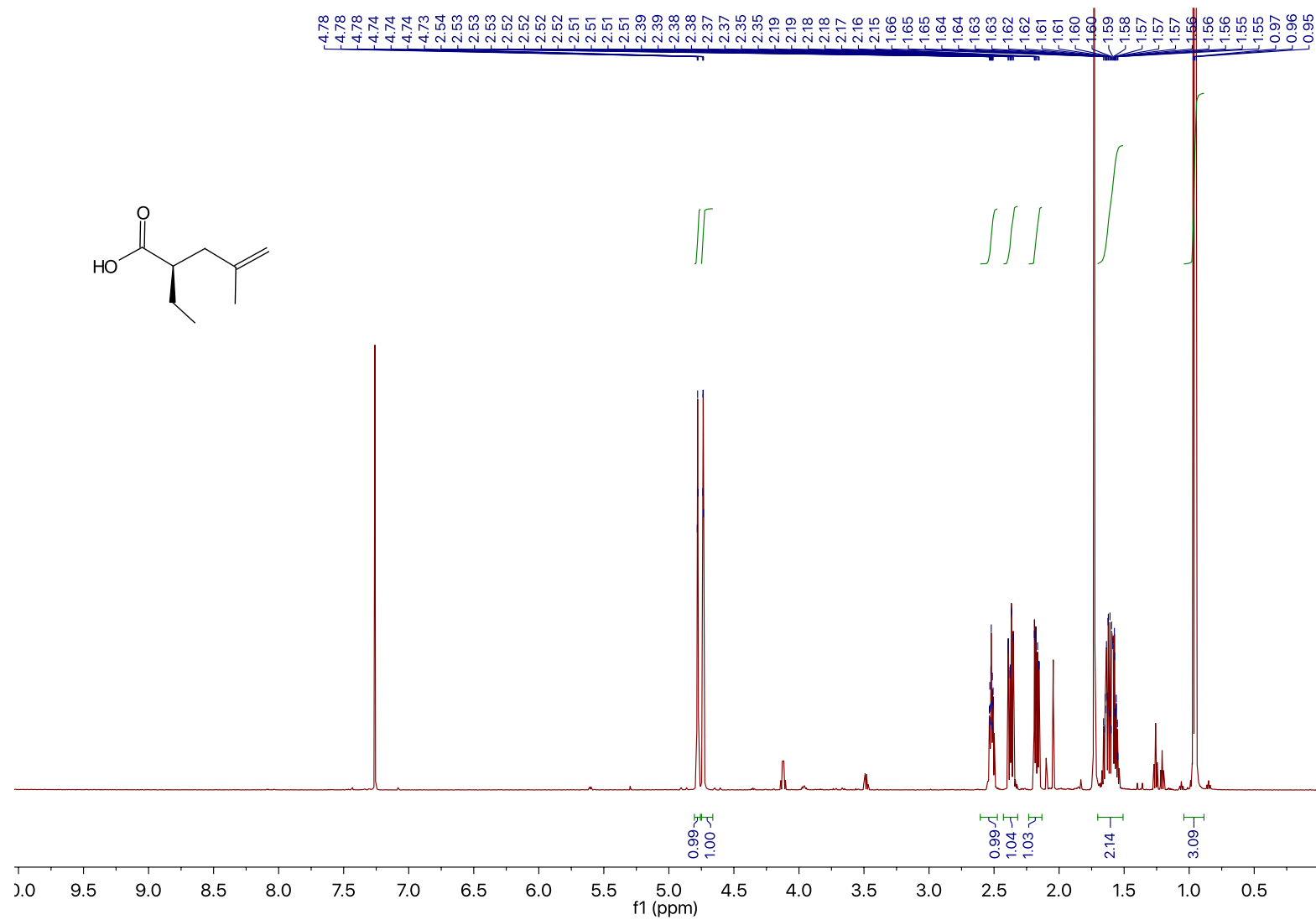
Accurate Mass Data

Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
324.1566	C ₁₈ H ₂₃ NO ₃ Na	324.1576	-3.1	1.8
324.1564	C ₁₈ H ₂₃ NO ₃ Na	324.1576	-3.7	1.2

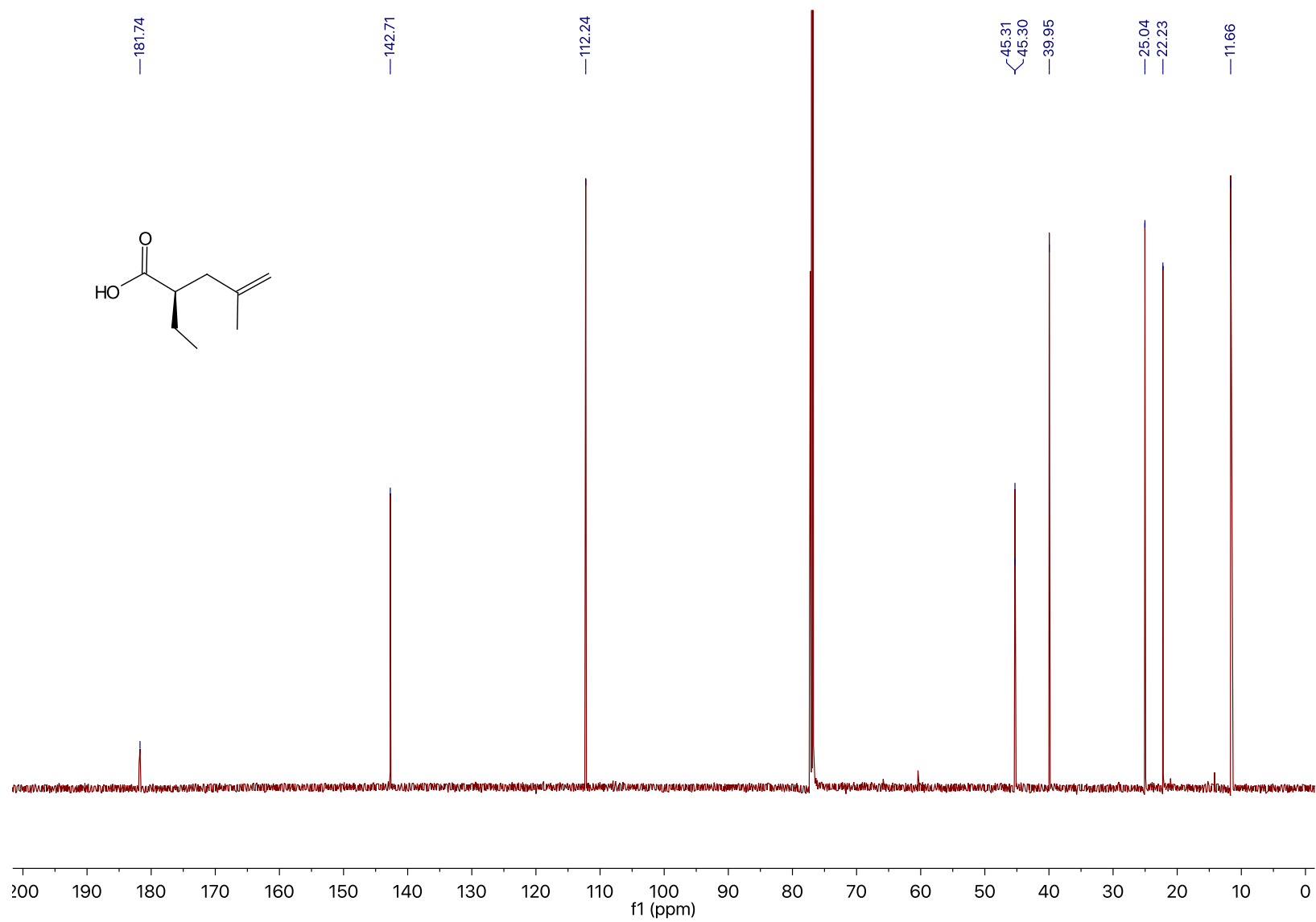
HRMS data

^1H , ^{13}C NMR and HRMS (ESI) data for compound **16**

^1H NMR data

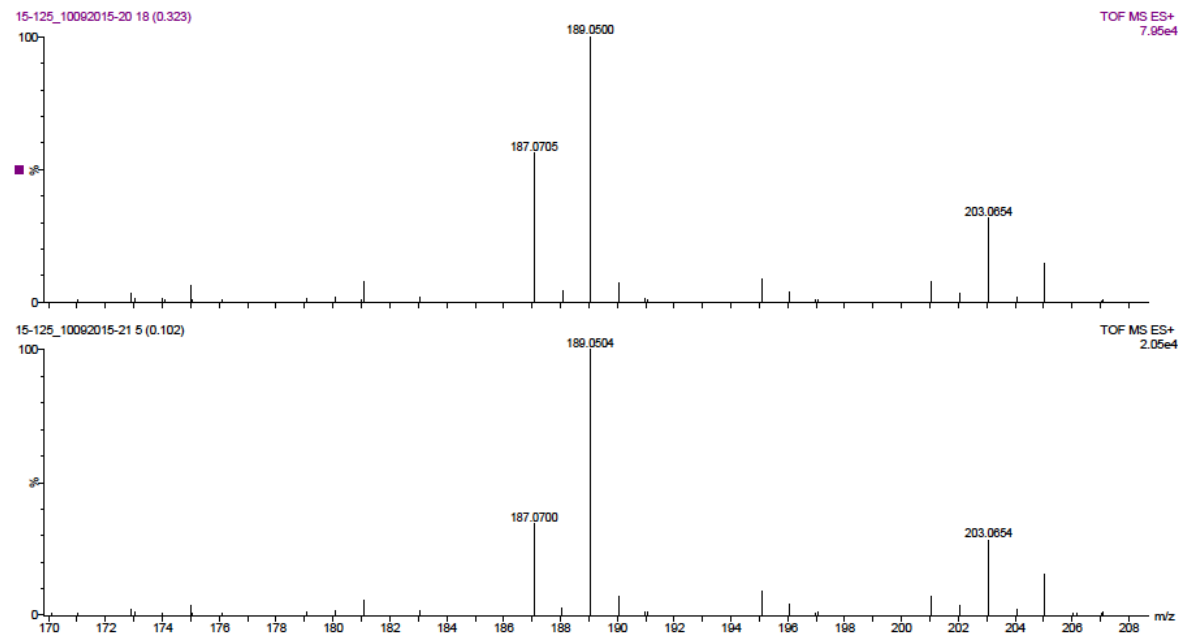


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

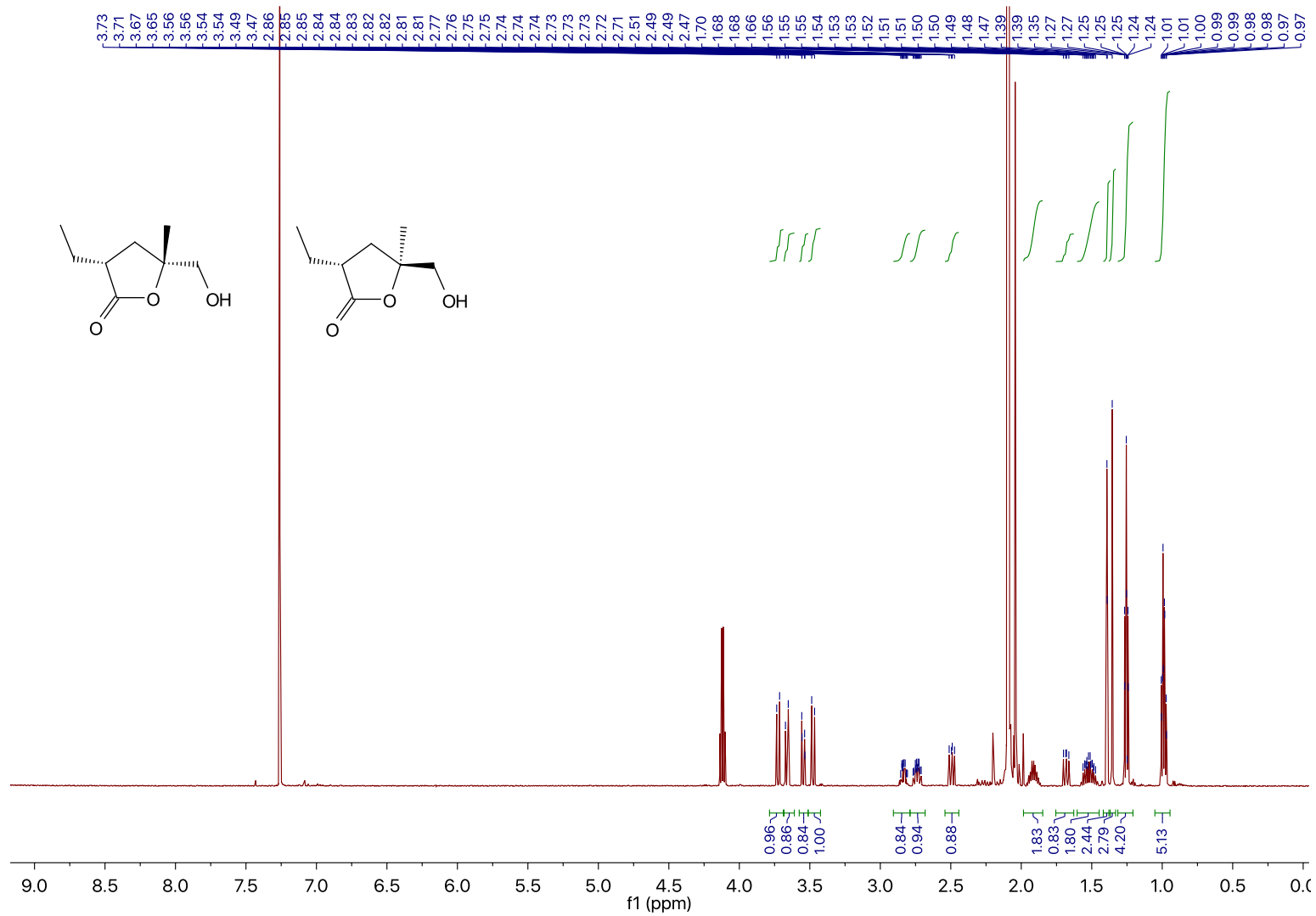


Accurate Mass Data

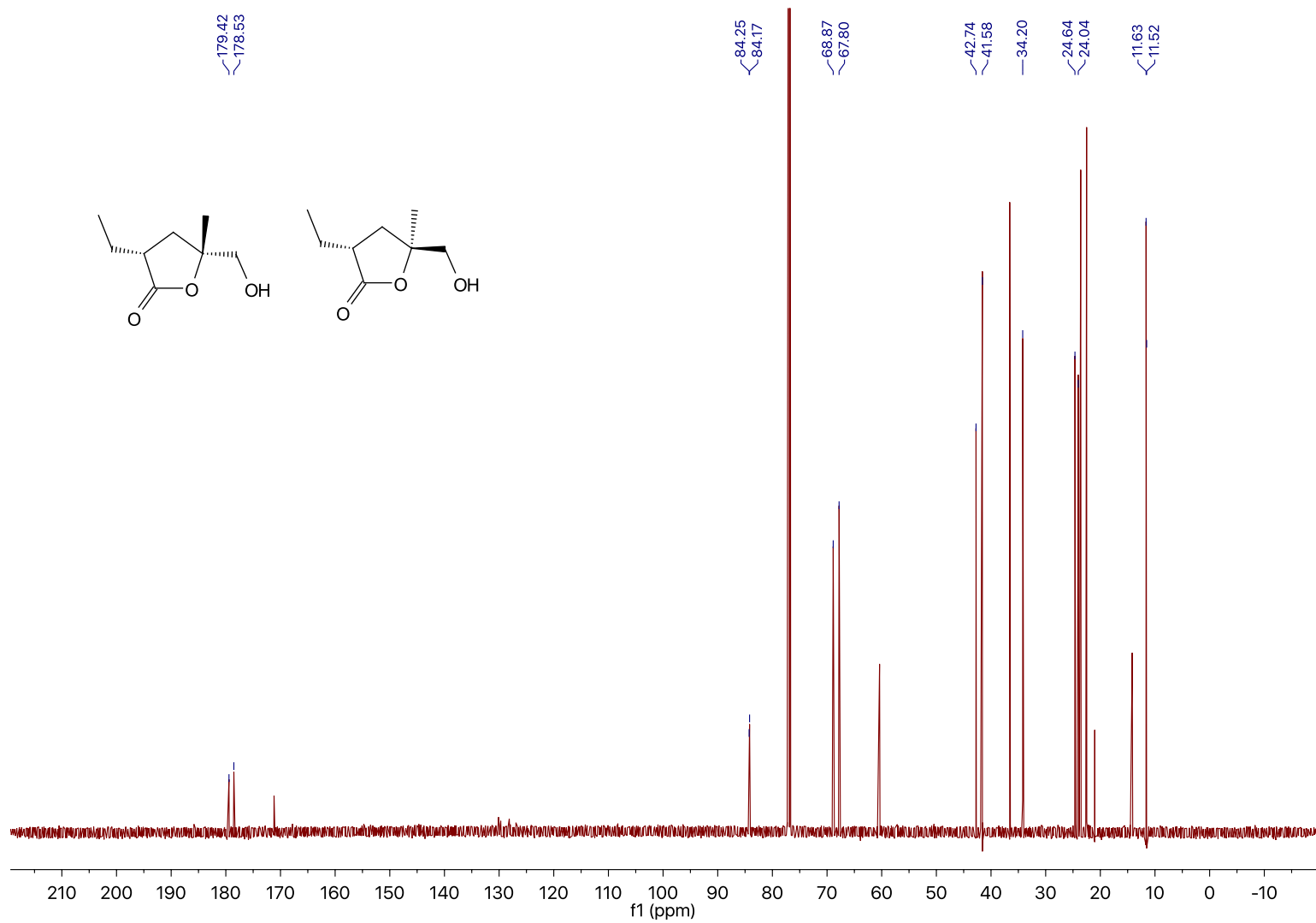
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
187.0700	C ₈ H ₁₃ O ₂ Na ₂	187.0711	-5.9	1.8
187.0705	C ₈ H ₁₃ O ₂ Na ₂	187.0711	-3.2	1.3

^1H , ^{13}C NMR and HRMS (ESI) data for compound **15a/15b**

^1H NMR data



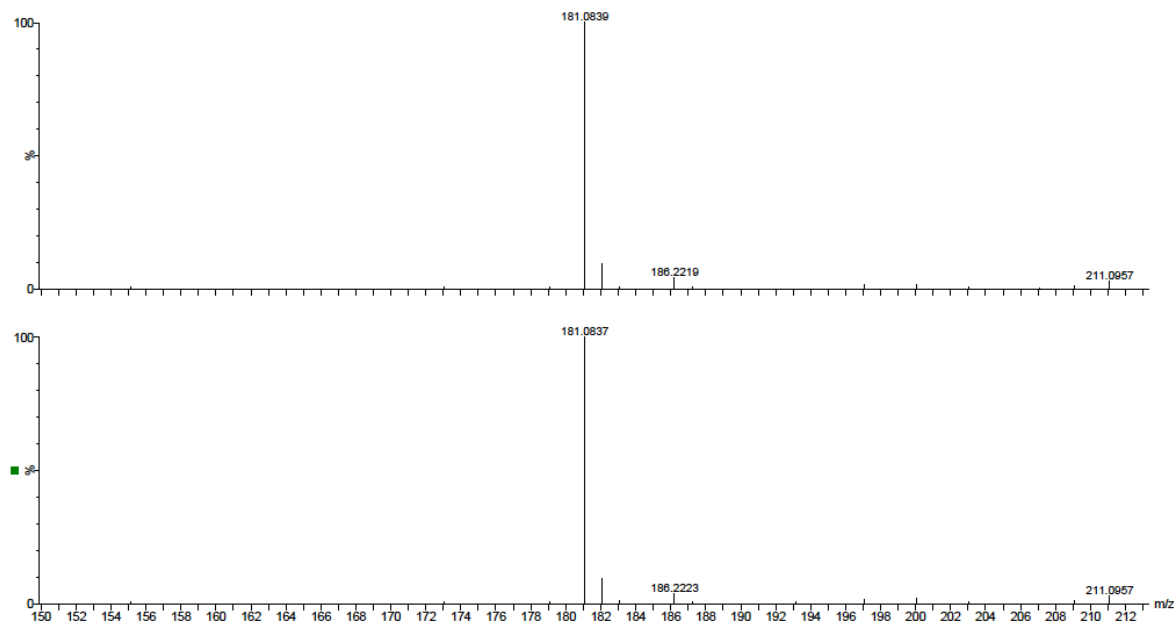
^{13}C NMR data



residual solvent peaks (EtOAc) present due to volatility of product

HRMS data

High Resolution Spectra
Positive ion

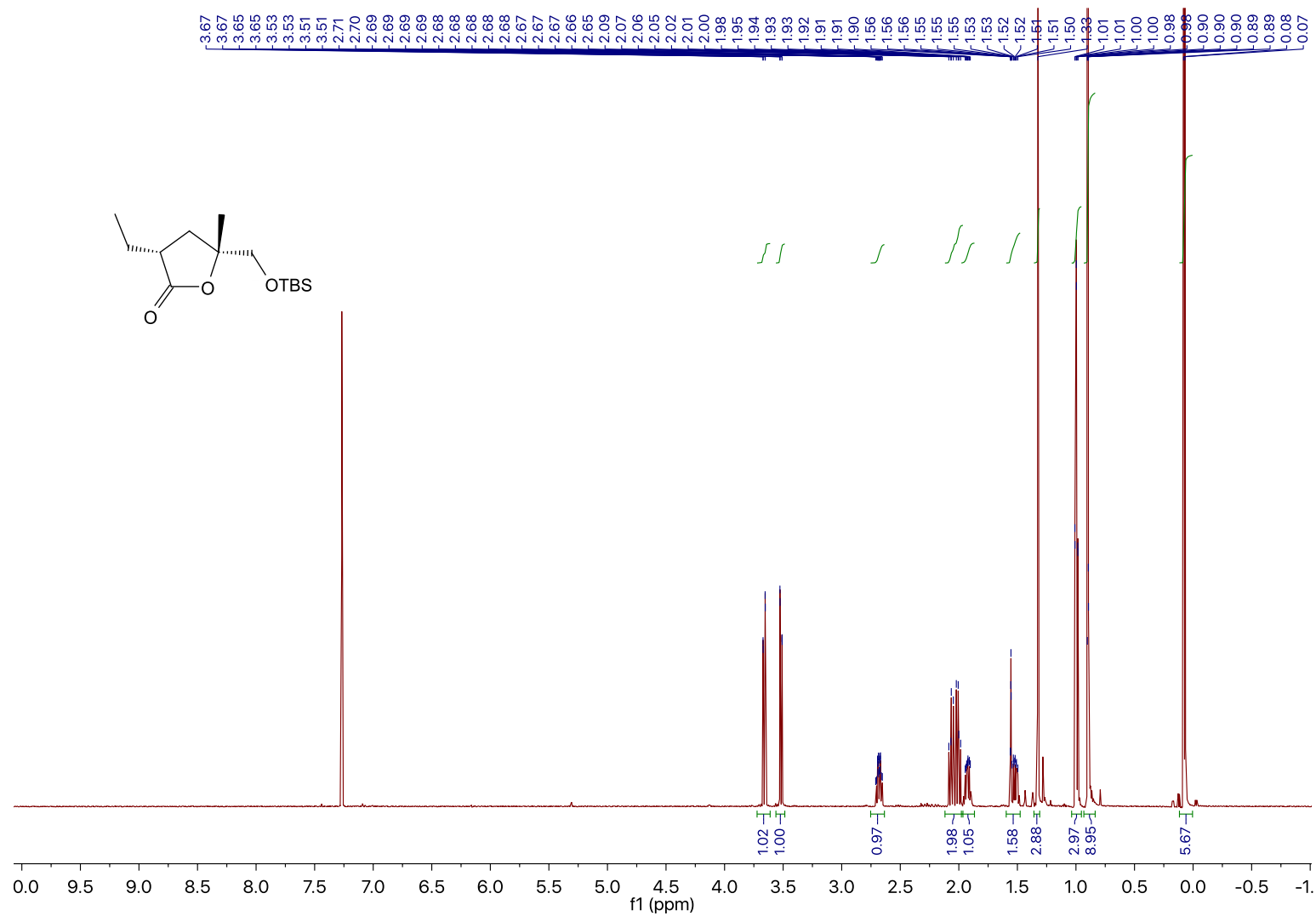


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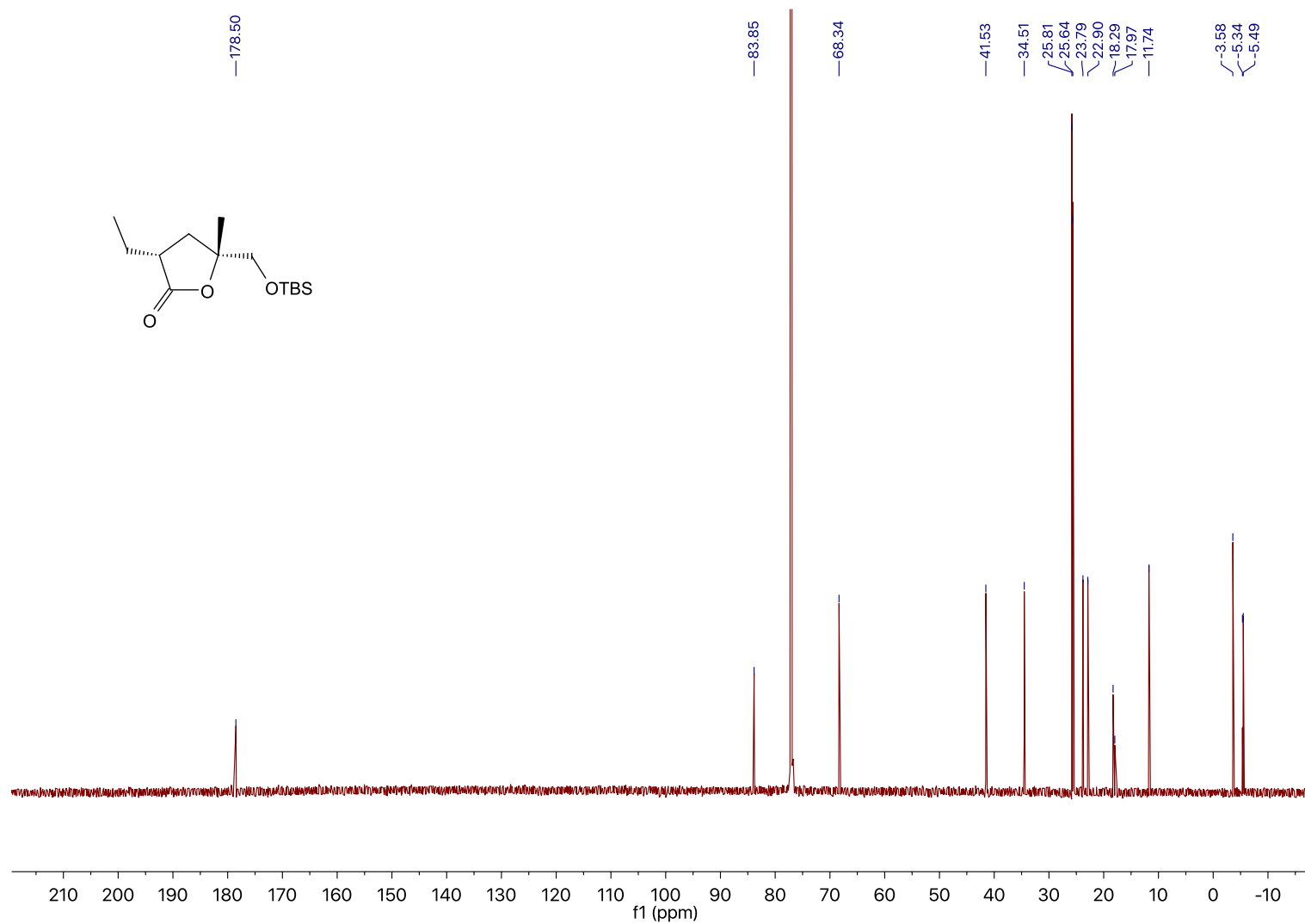
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
181.0837	C ₈ H ₁₄ O ₃ Na	181.0841	-2.2	0.0
181.0839	C ₈ H ₁₄ O ₃ Na	181.0841	-1.1	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **17a**

^1H NMR data

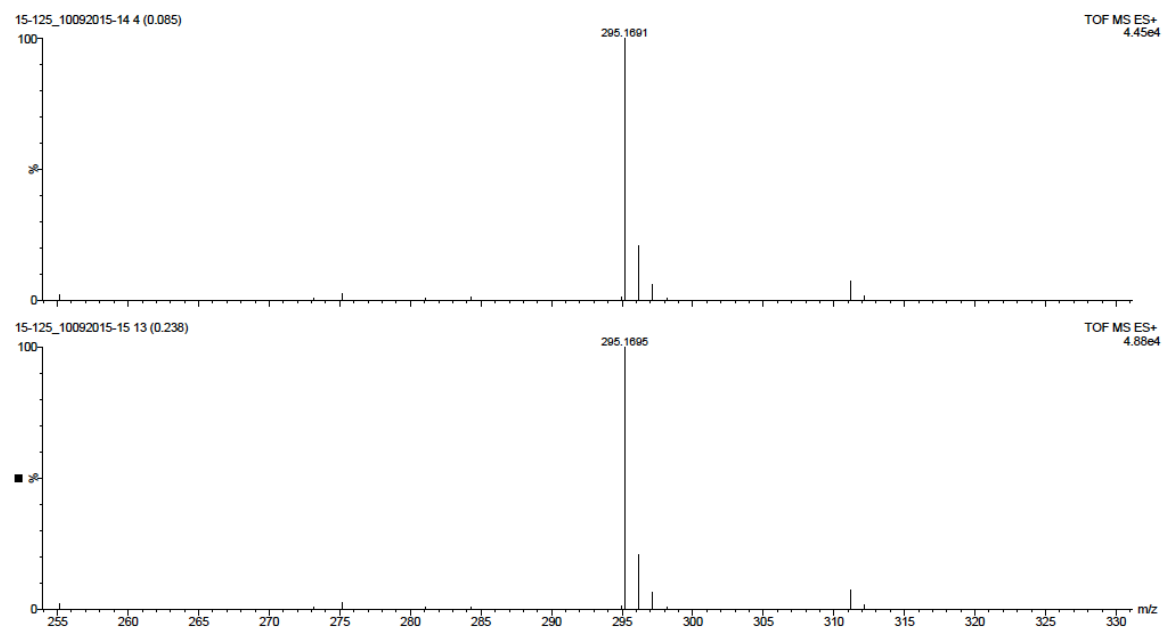


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

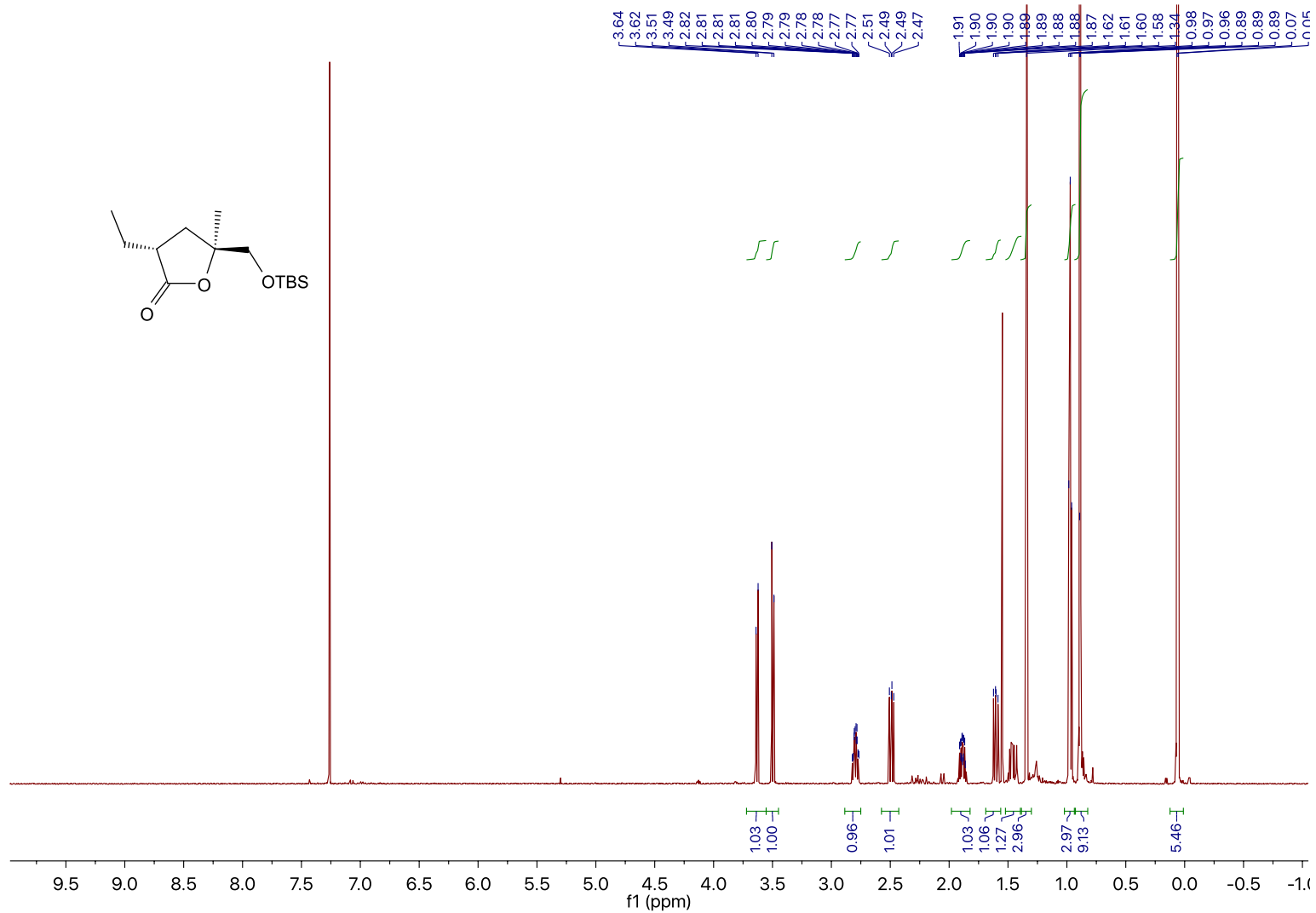


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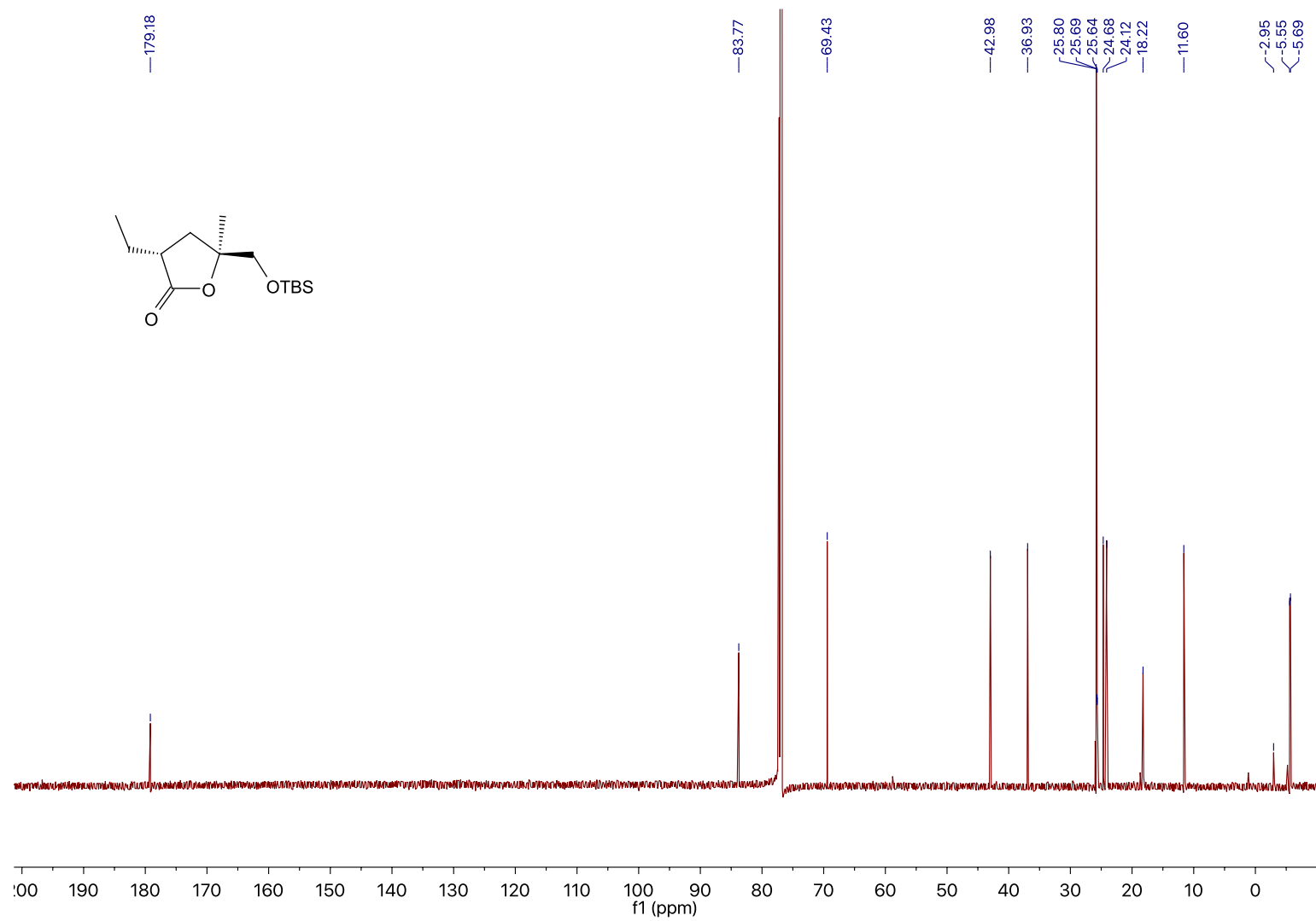
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFiT (norm)
295.1695	C ₁₄ H ₂₈ O ₃ SiNa	295.1705	-3.4	0.0
295.1691	C ₁₄ H ₂₈ O ₃ SiNa	295.1705	-4.7	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **17b**

^1H NMR data

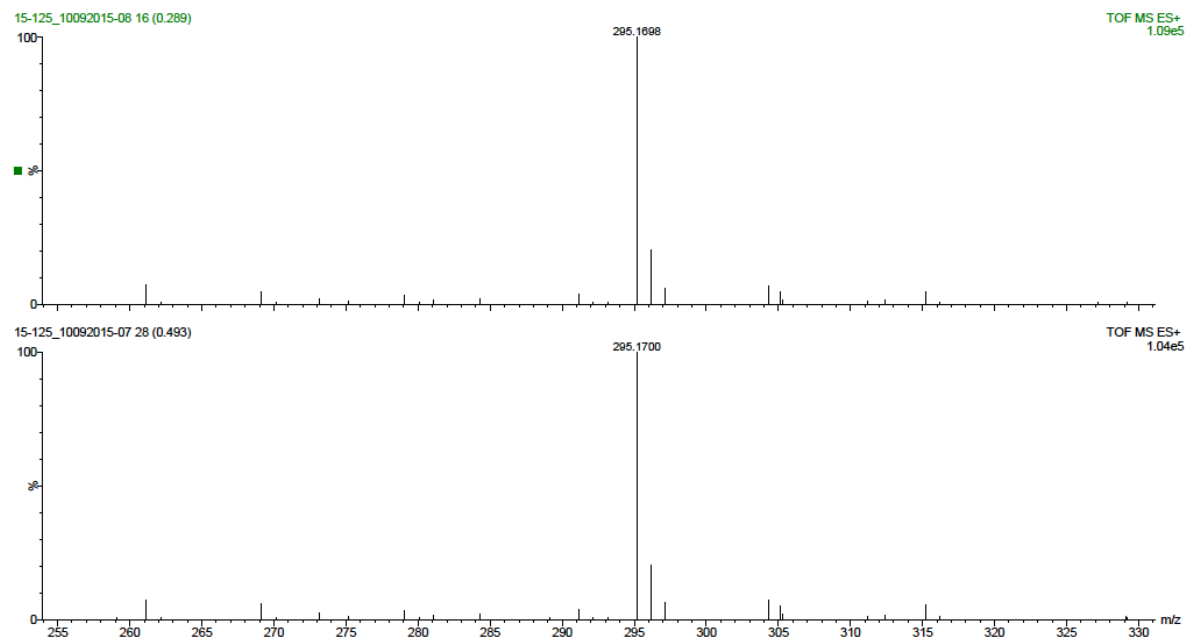


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

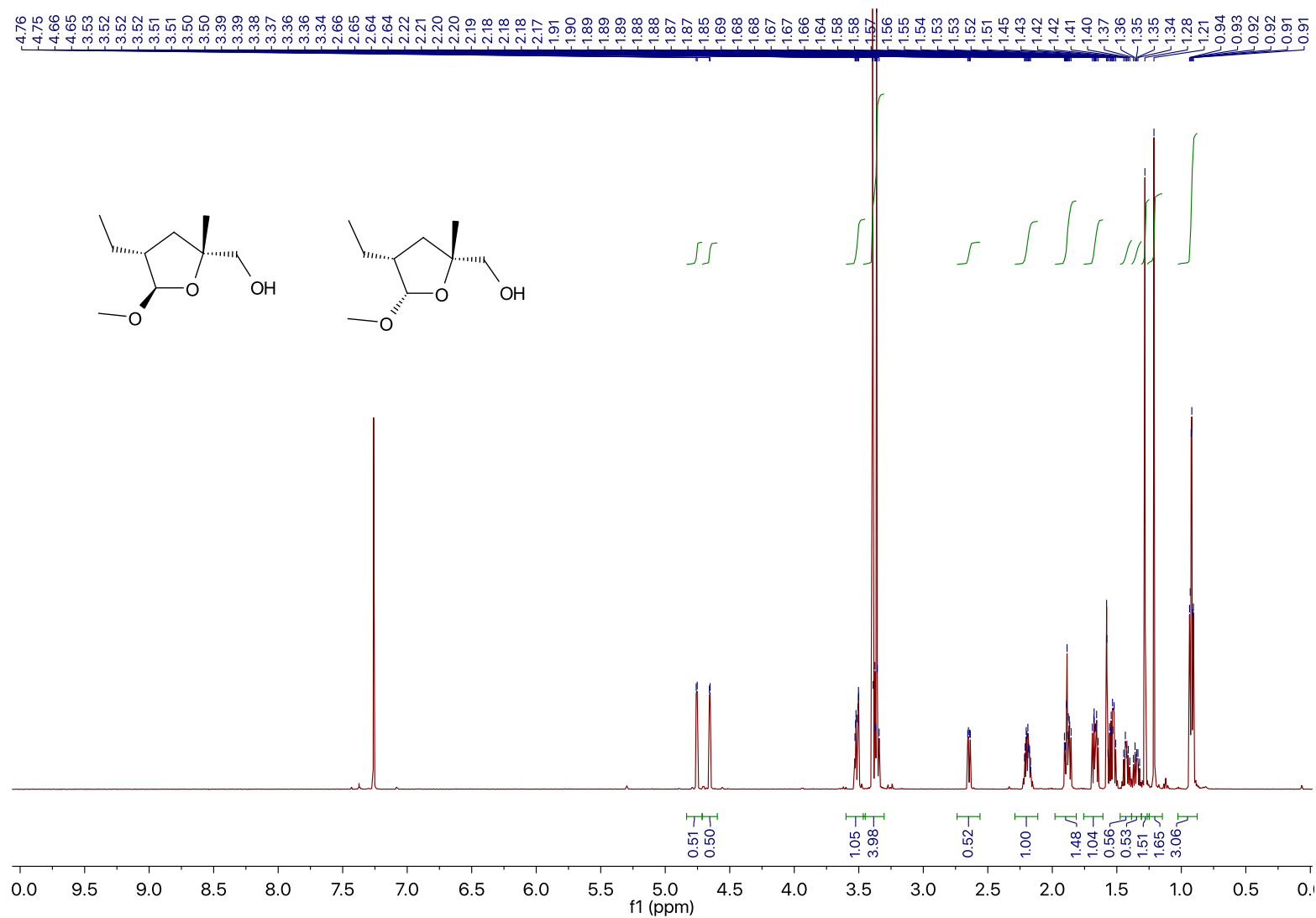


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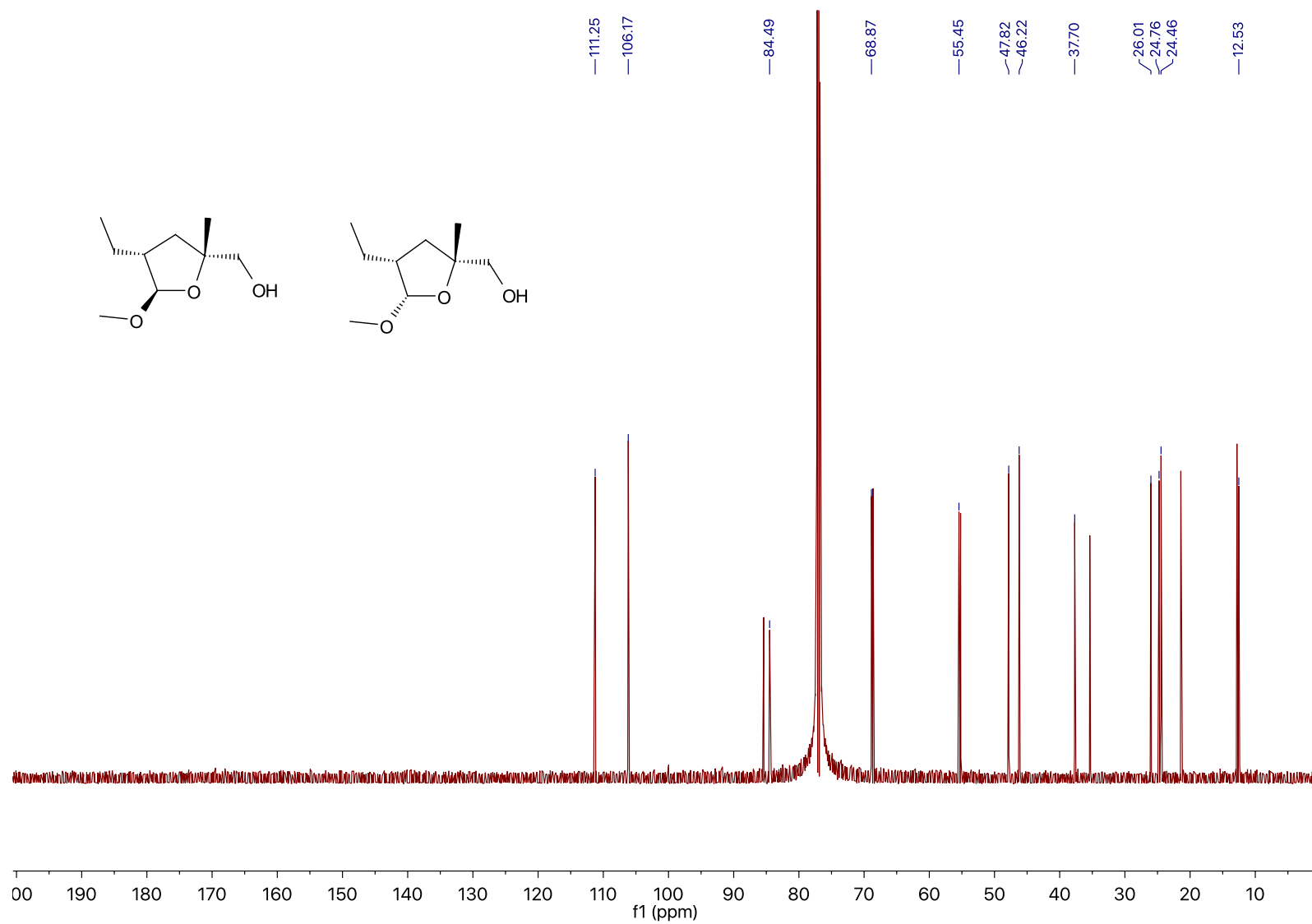
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
295.1700	C ₁₄ H ₂₈ O ₃ SiNa	295.1705	-1.7	5.2
295.1698	C ₁₄ H ₂₈ O ₃ SiNa	295.1705	-2.4	5.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **18a**

^1H NMR data

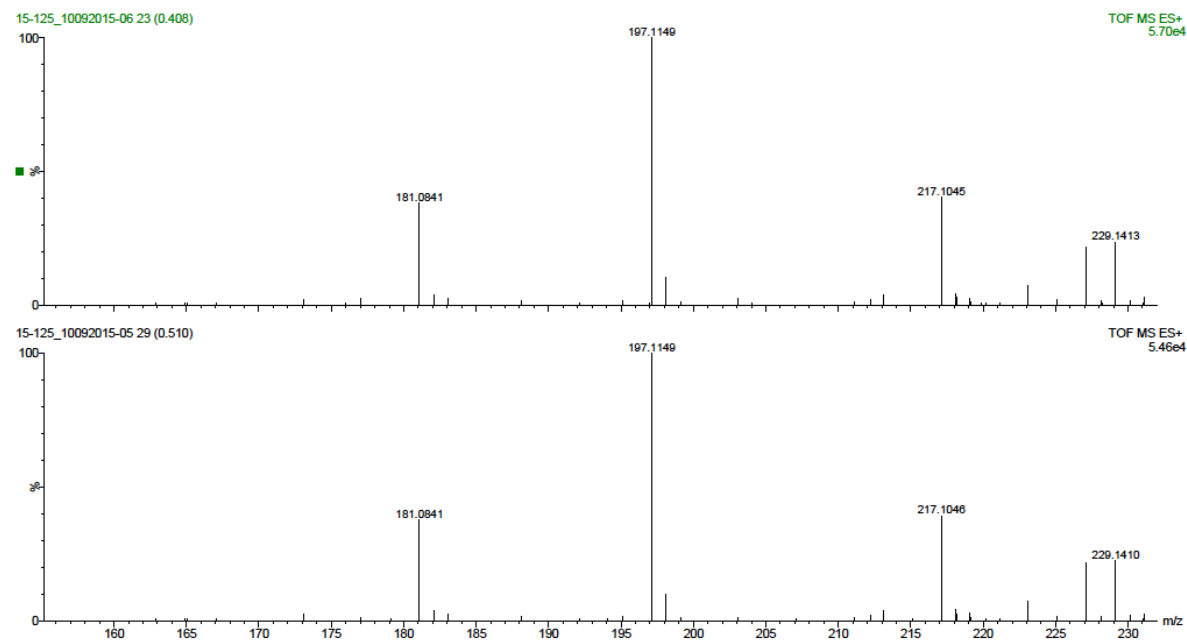


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

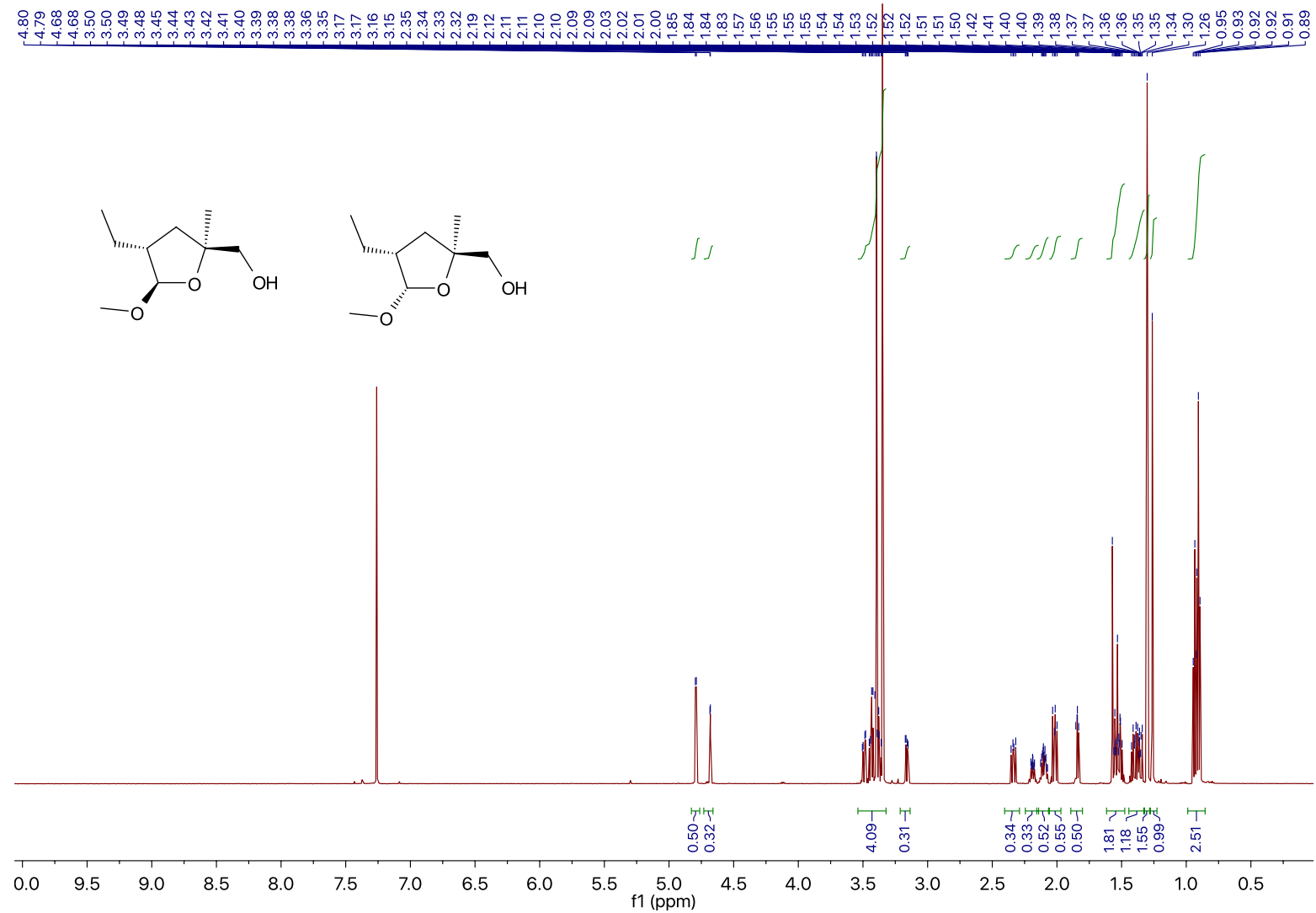


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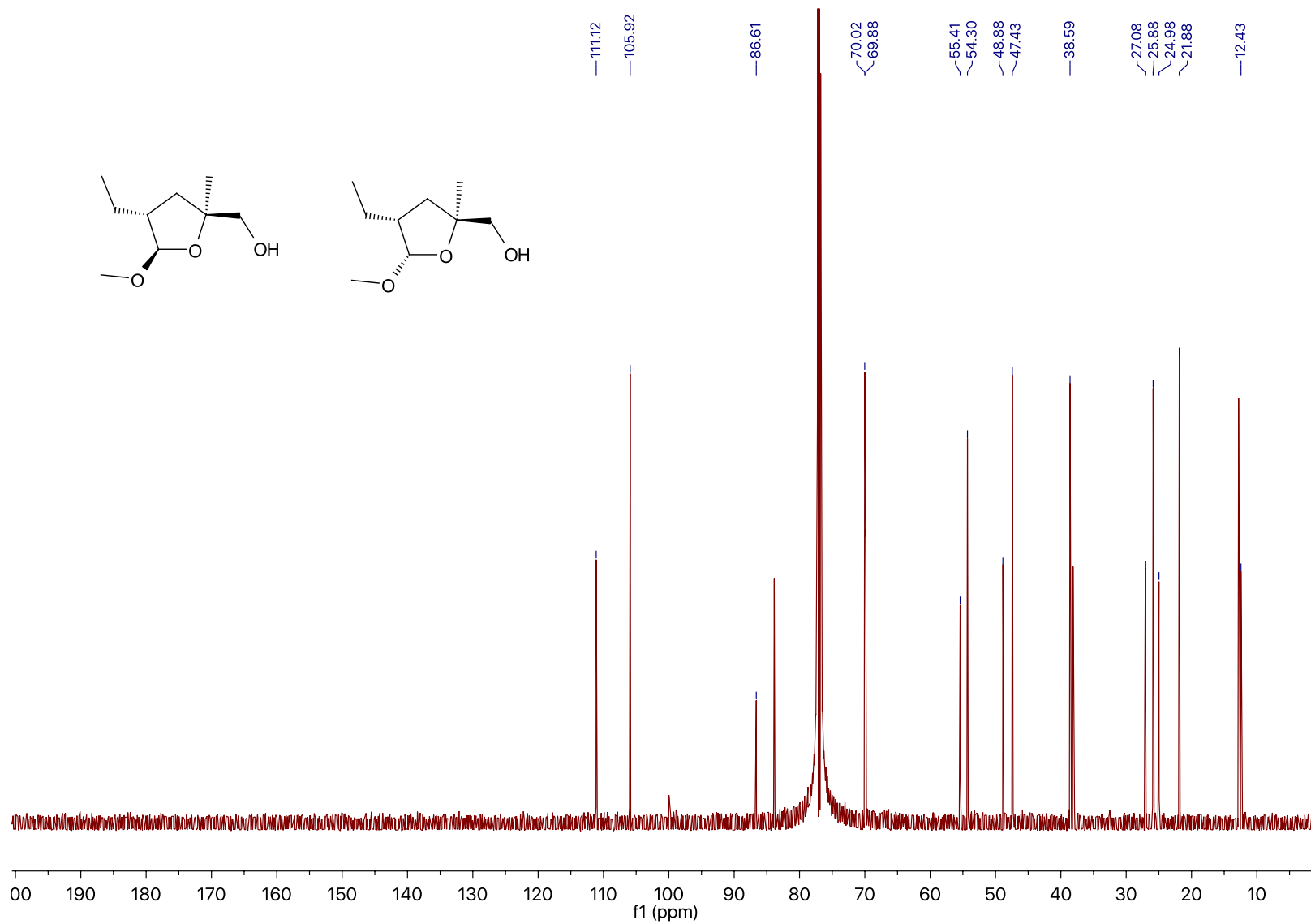
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
197.1149	C ₉ H ₁₈ O ₃ Na	197.1154	-2.5	0.0
197.1149	C ₉ H ₁₈ O ₃ Na	197.1154	-2.5	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **18b**

^1H NMR data

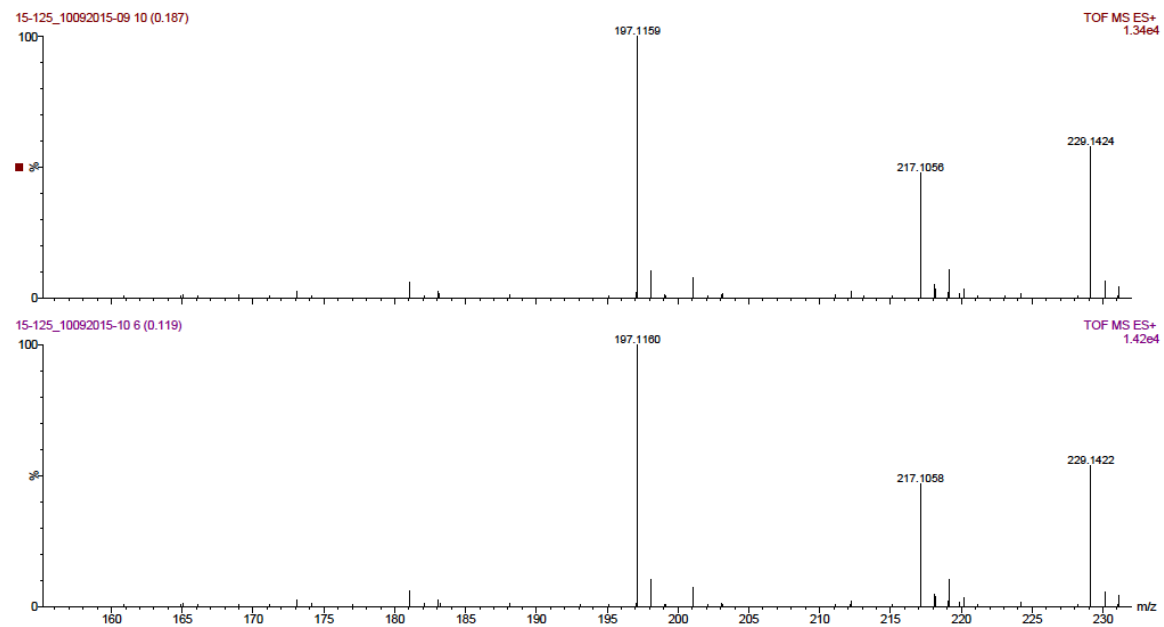


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

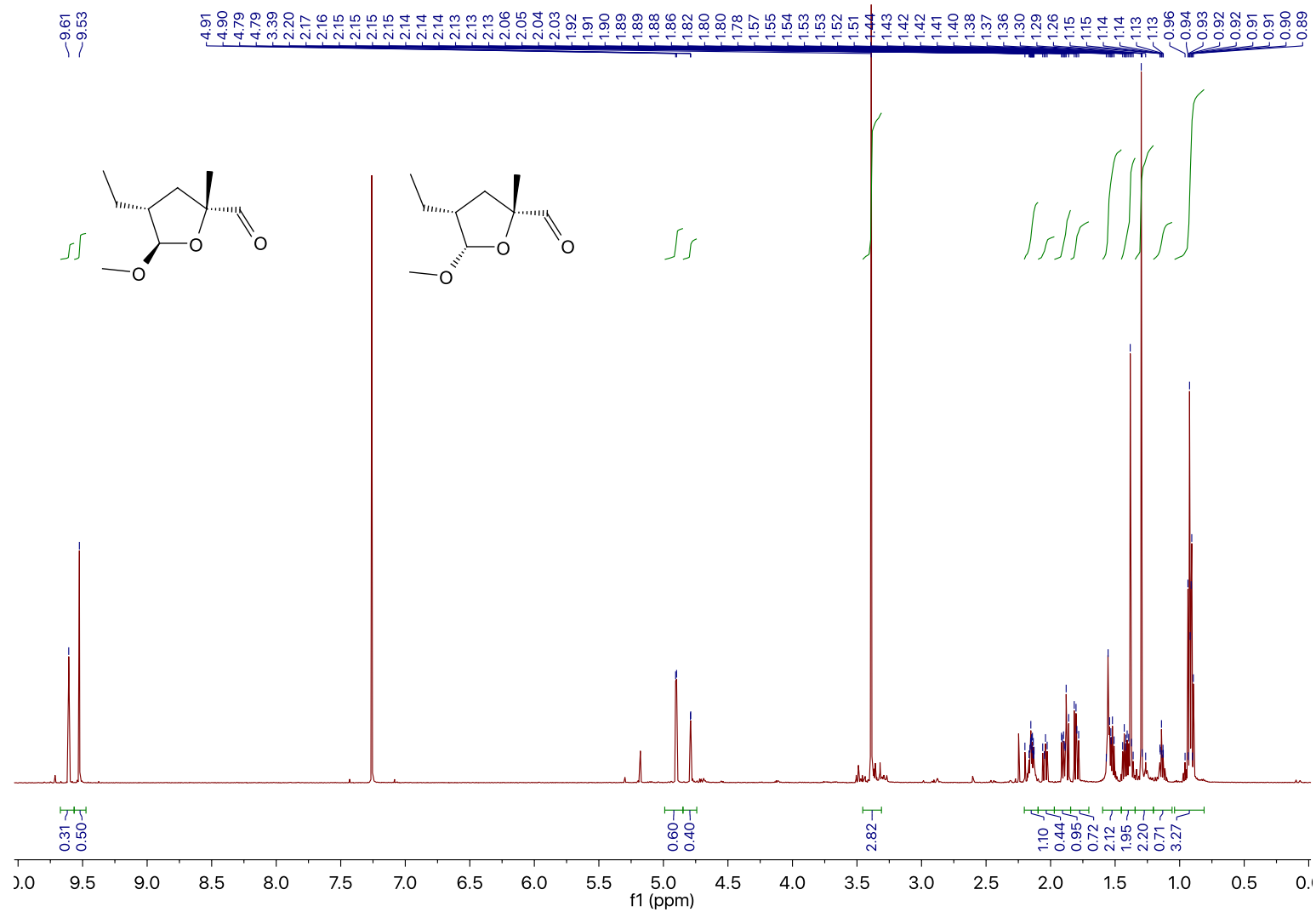


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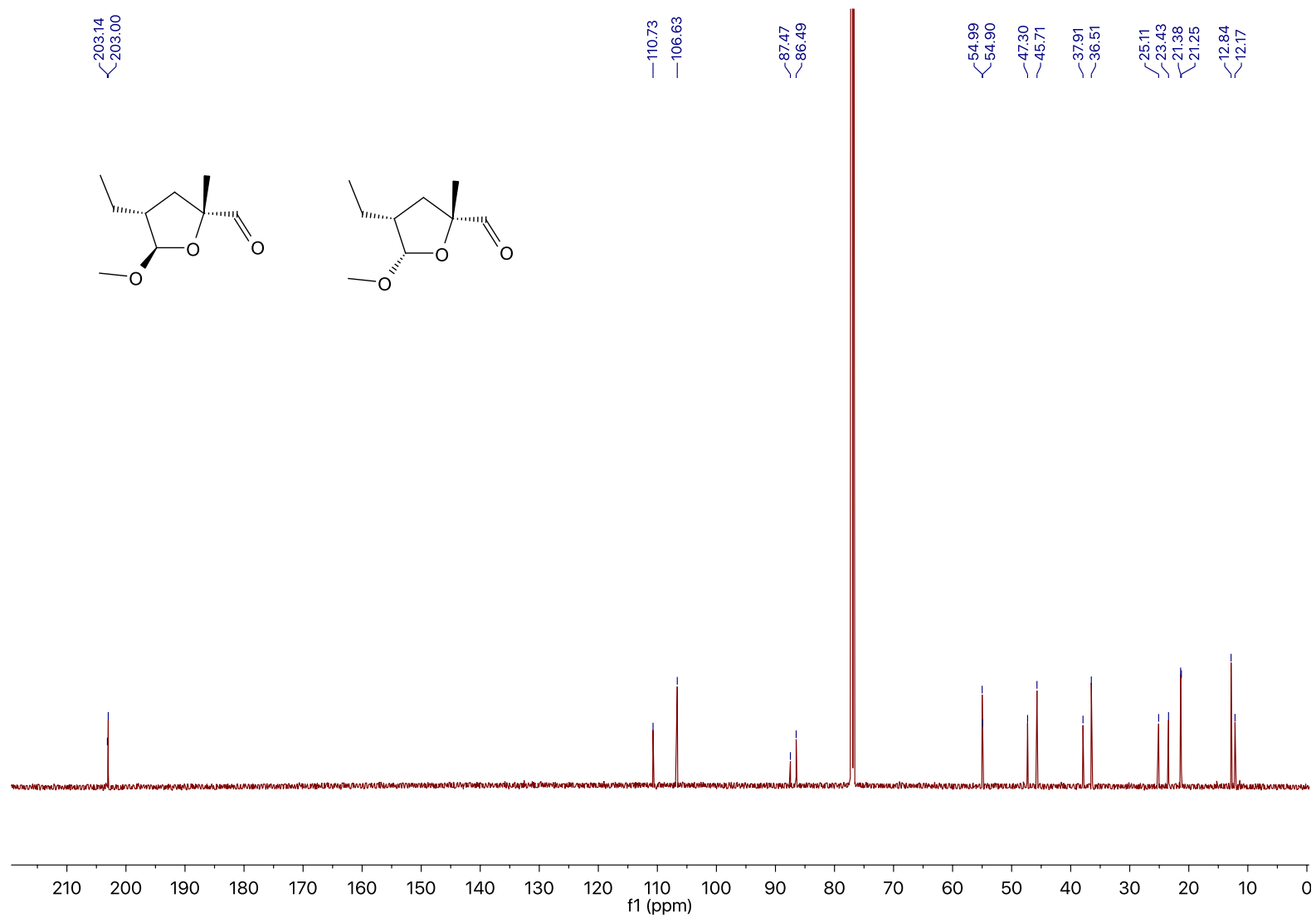
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
197.1160	C ₉ H ₁₈ O ₃ Na	197.1154	3.0	0.0
197.1159	C ₉ H ₁₈ O ₃ Na	197.1154	2.5	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **11a**

^1H NMR data

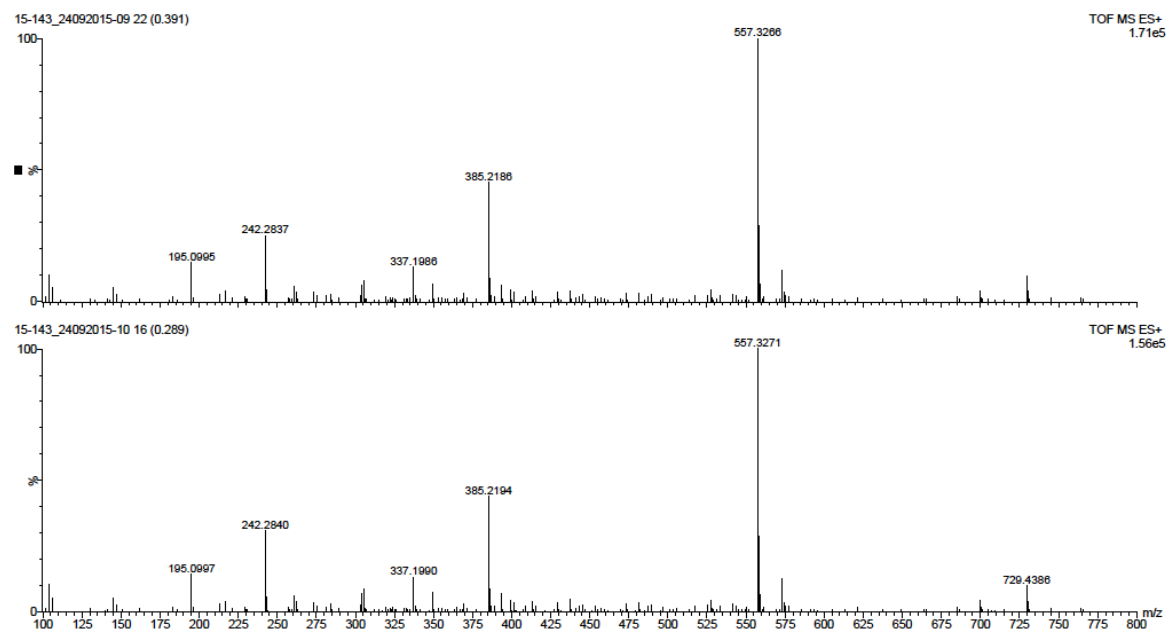


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

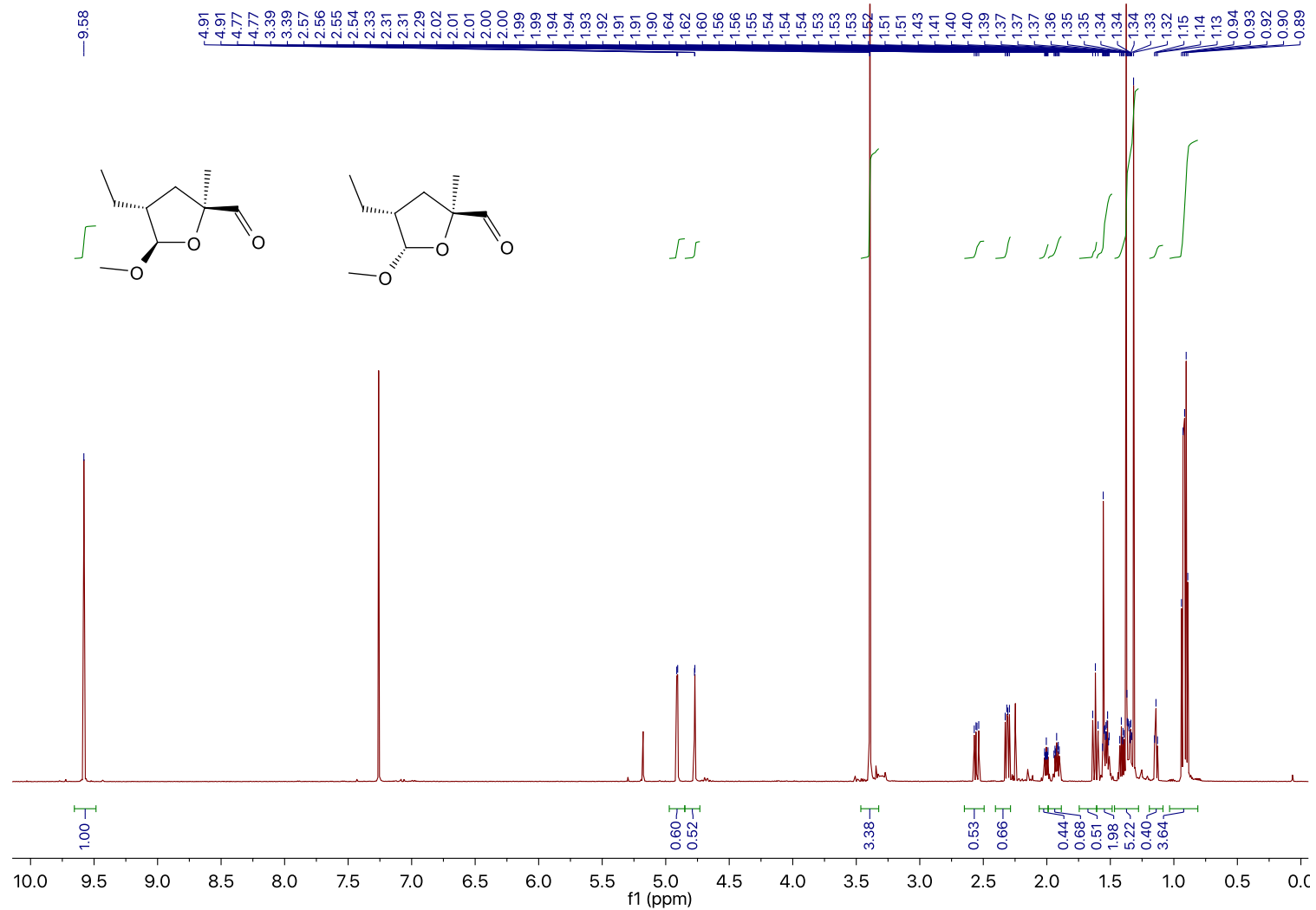


Accurate Mass Data

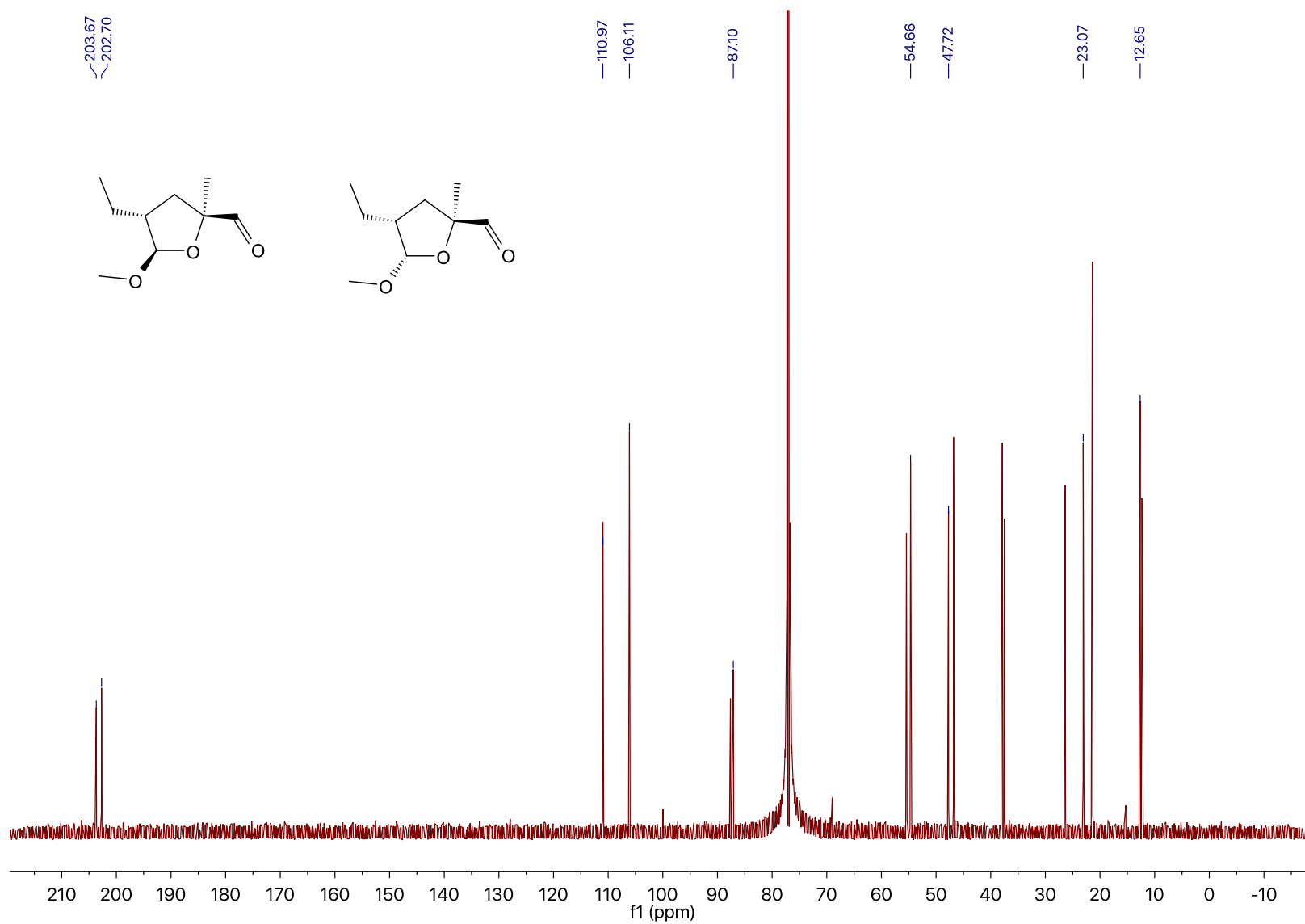
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFiT (norm)
195.0997	C ₉ H ₁₆ O ₃ Na	195.0997	0.0	0.0
195.0995	C ₉ H ₁₆ O ₃ Na	195.0997	-1.0	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **11b**

^1H NMR data

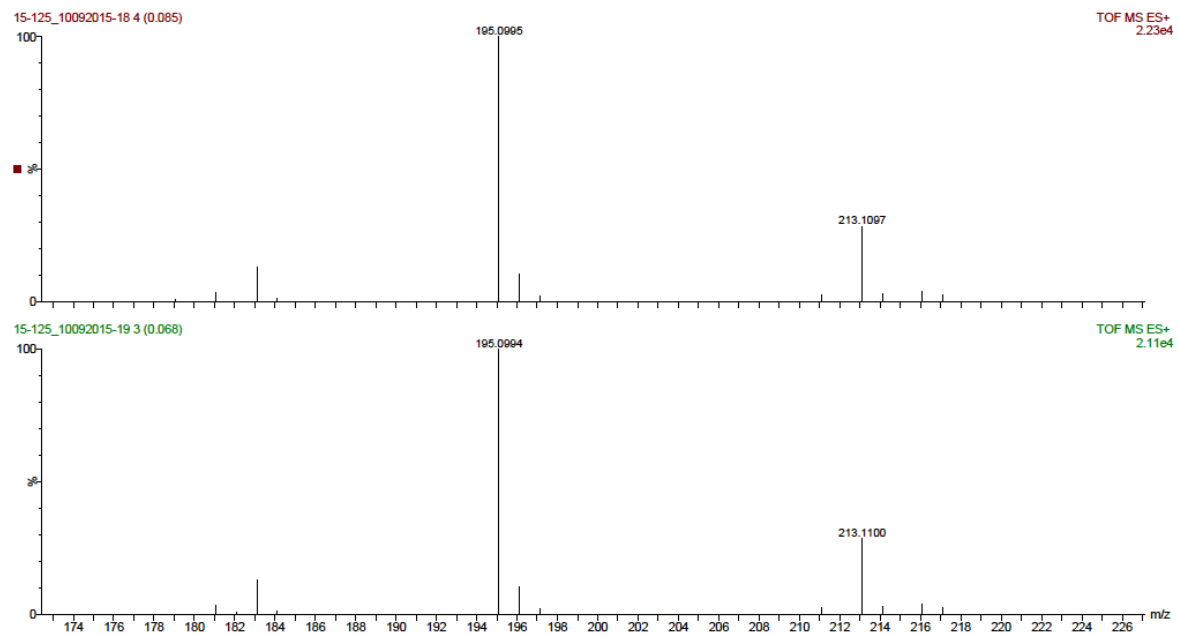


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

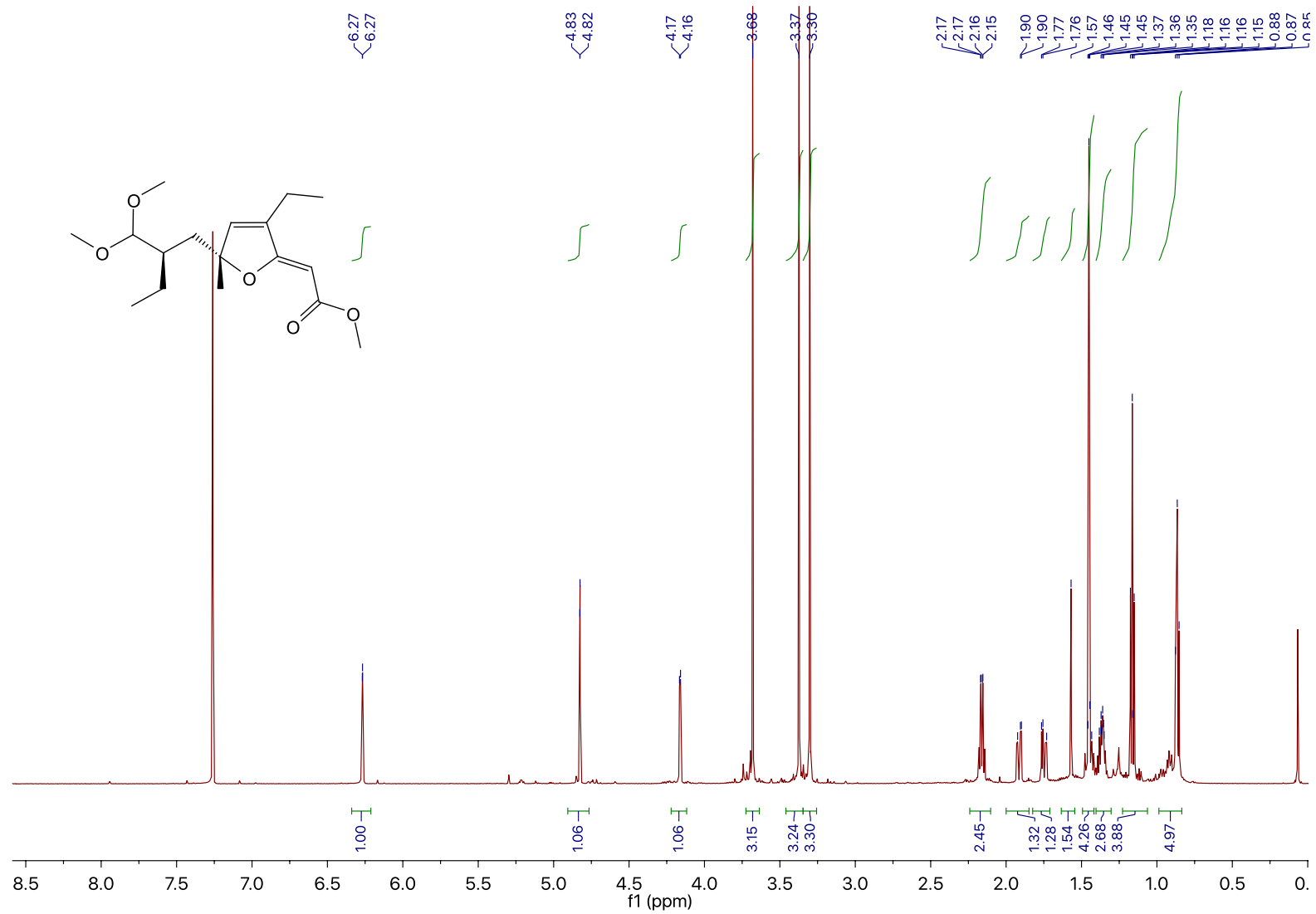


Accurate Mass Data

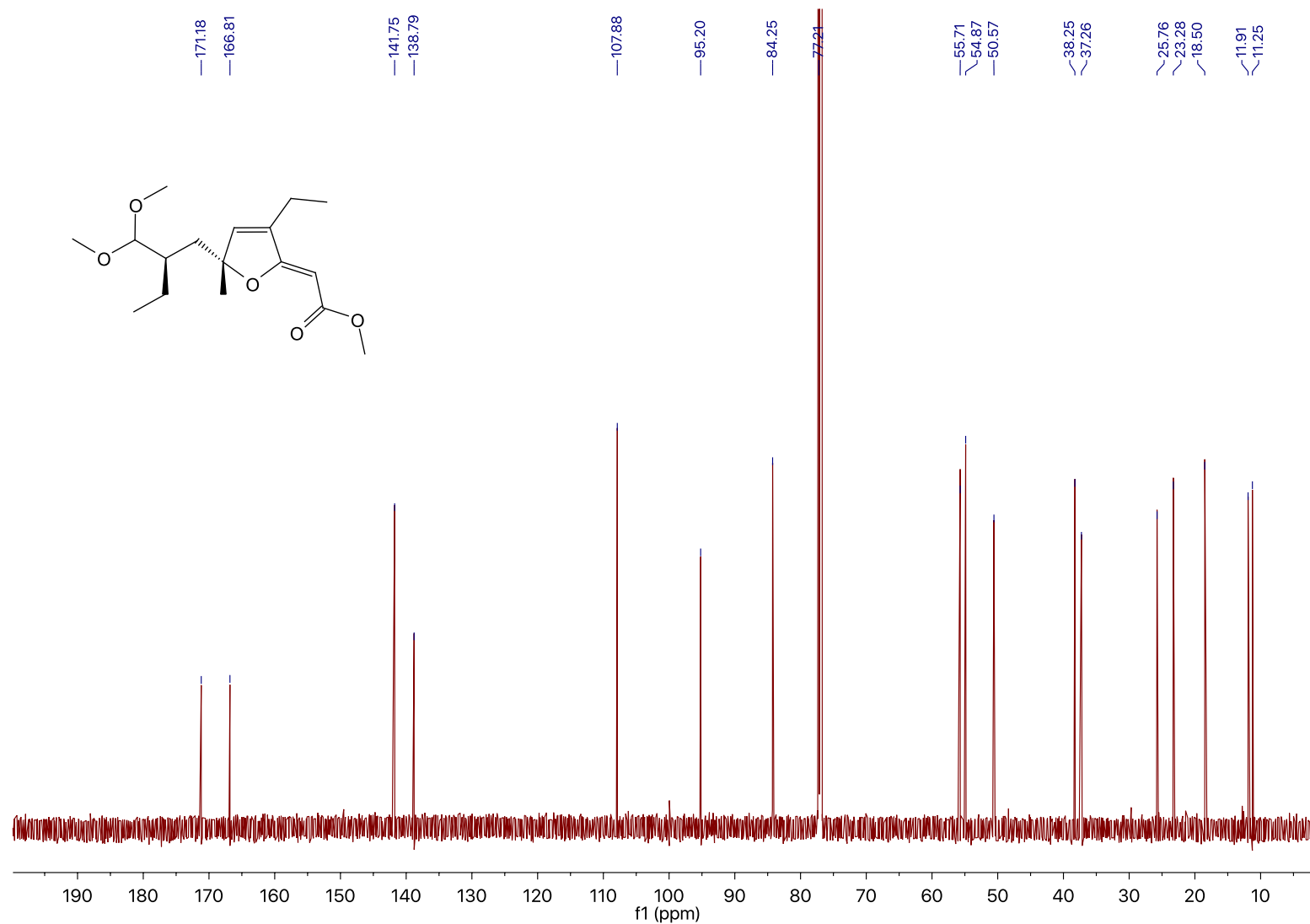
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
195.0994	C ₉ H ₁₆ O ₃ Na	195.0997	-1.5	0.0
195.0995	C ₉ H ₁₆ O ₃ Na	195.0997	-1.0	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **8a**

^1H NMR data

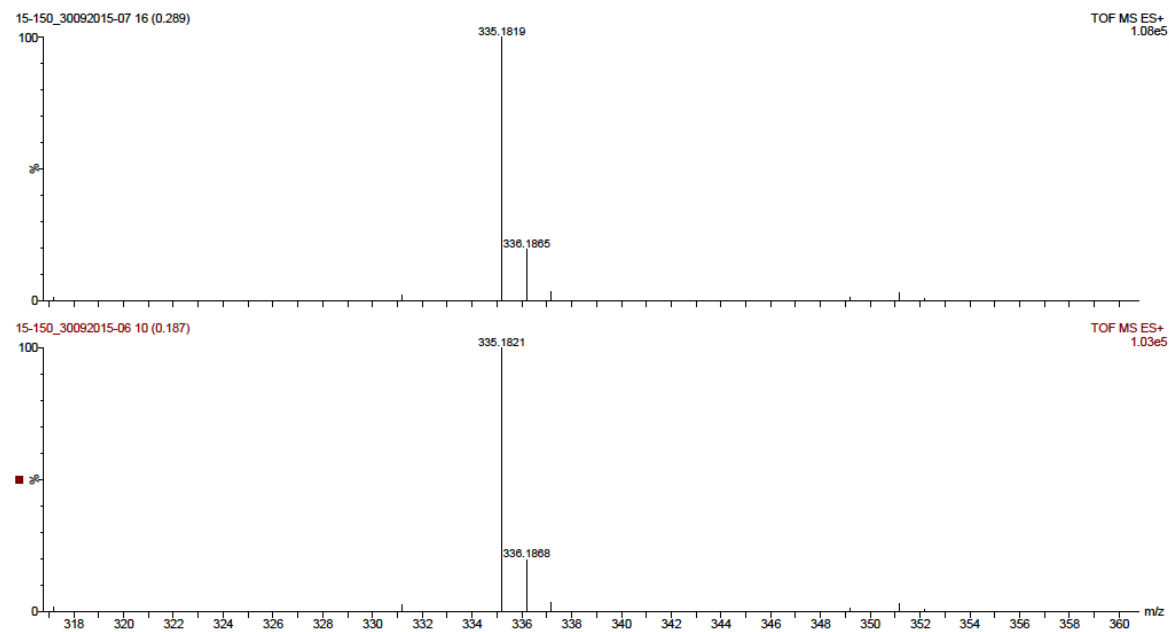


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

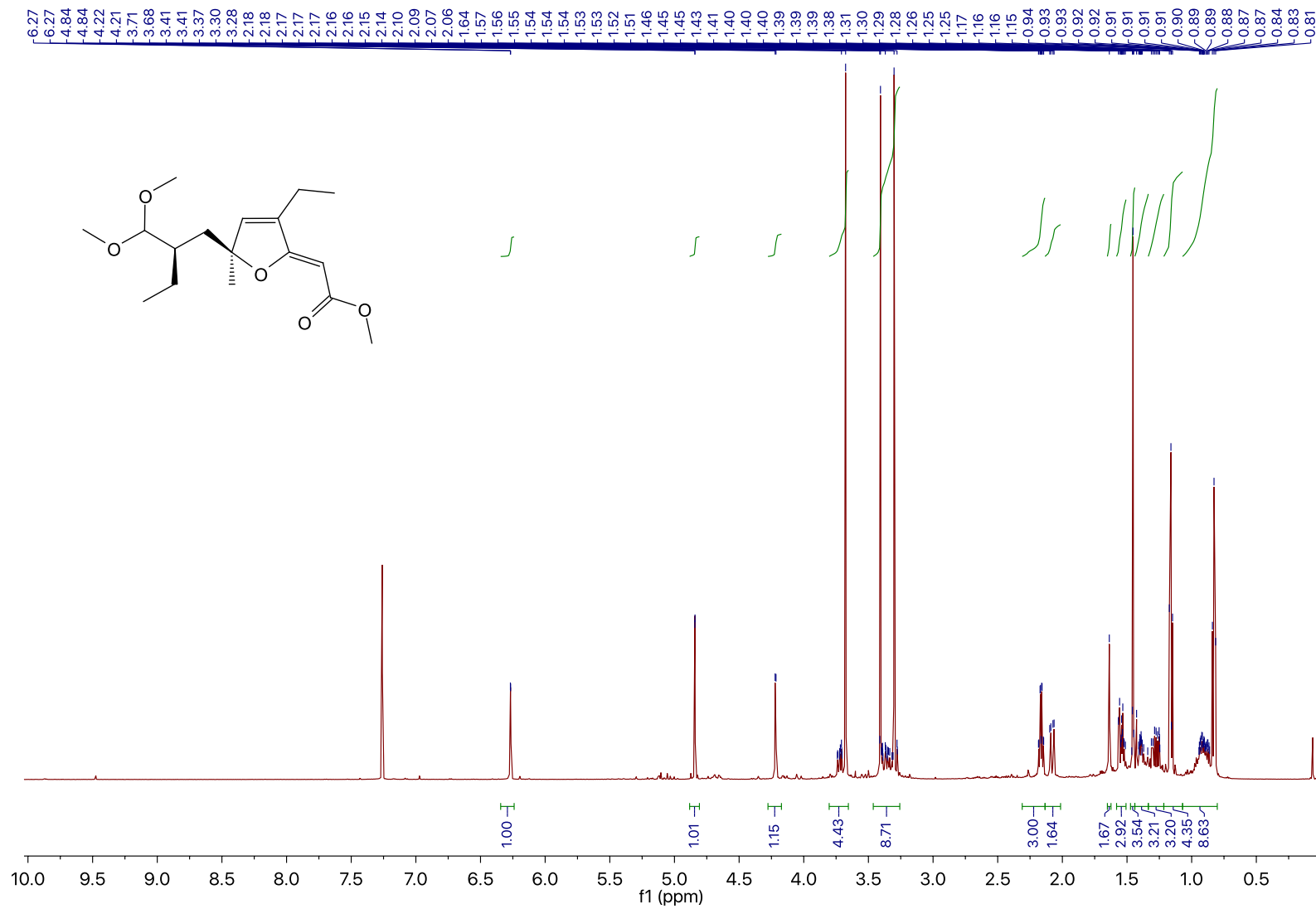


Accurate Mass Data

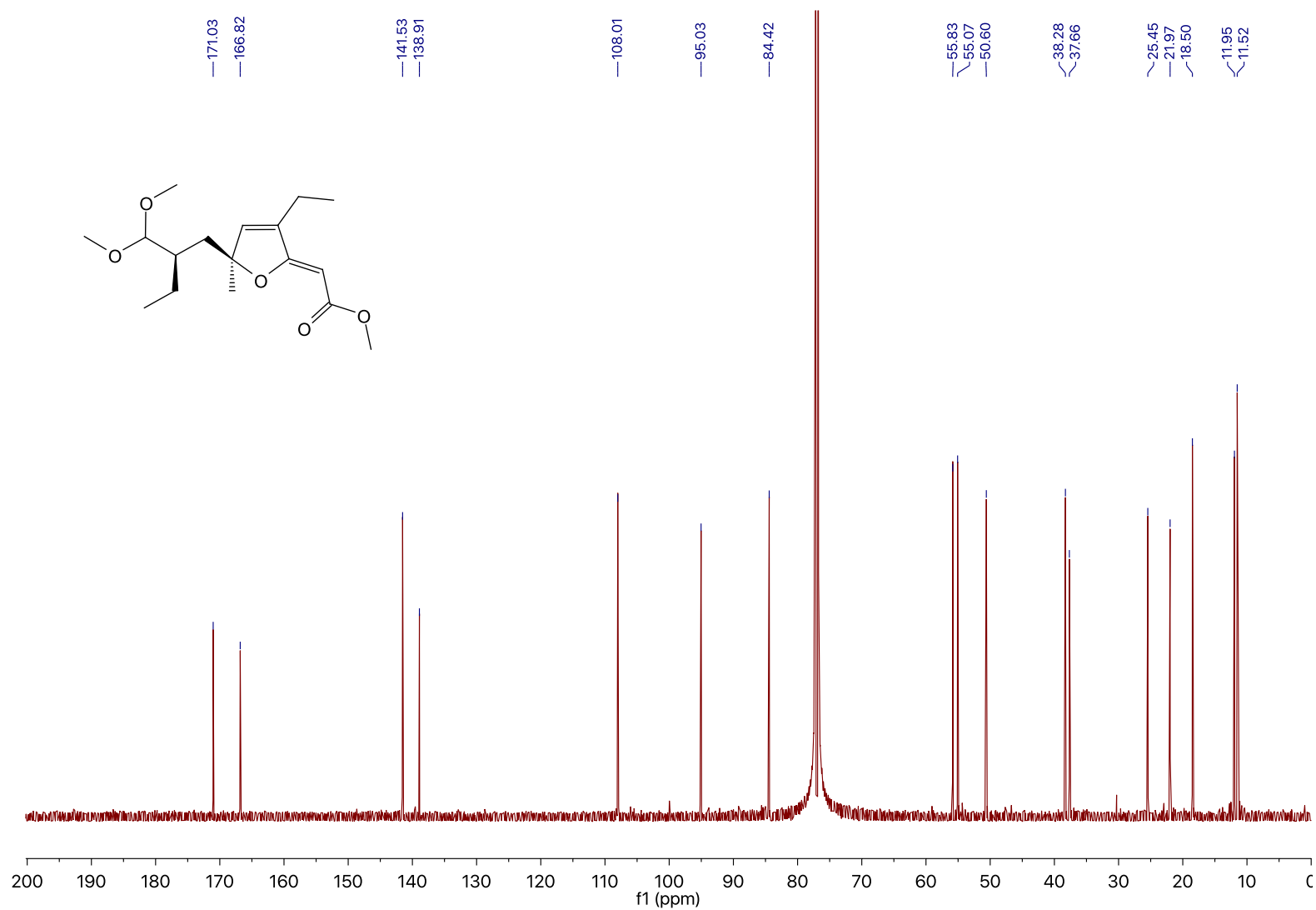
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
335.1821	C ₁₇ H ₂₈ O ₅ Na	335.1834	-3.9	0.0
335.1819	C ₁₇ H ₂₈ O ₅ Na	335.1834	-4.5	0.0

^1H , ^{13}C NMR and HRMS (ESI) data for compound **8b**

^1H NMR data

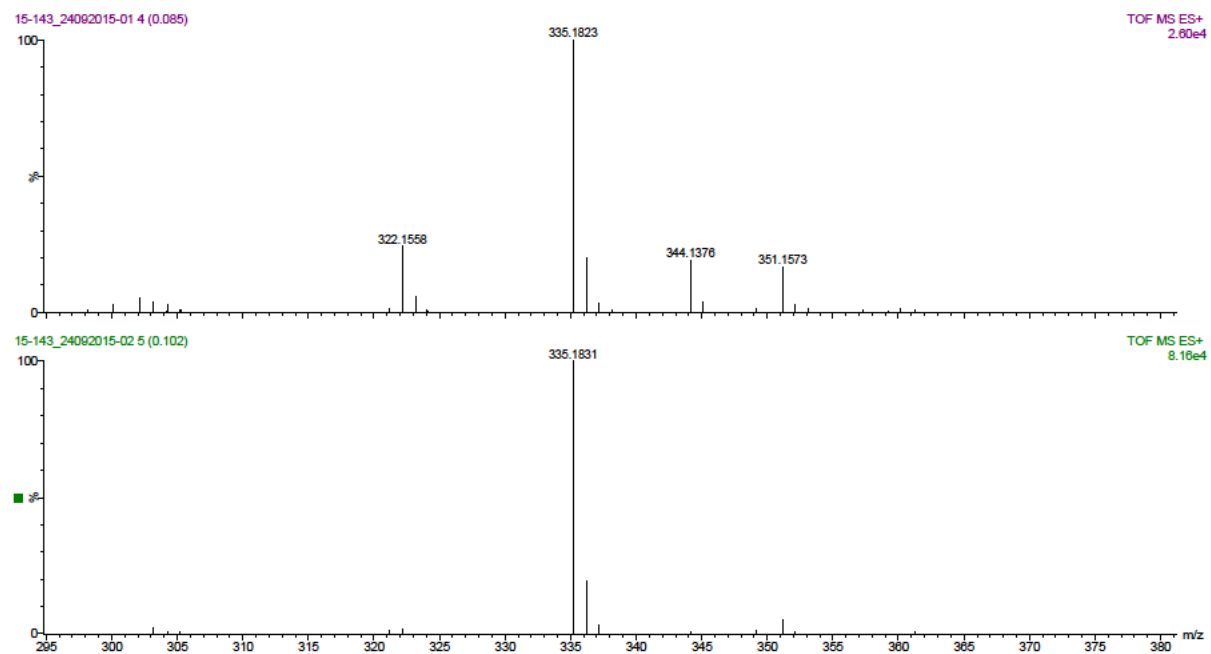


^{13}C NMR data



HRMS data

High Resolution Spectra
Positive ion

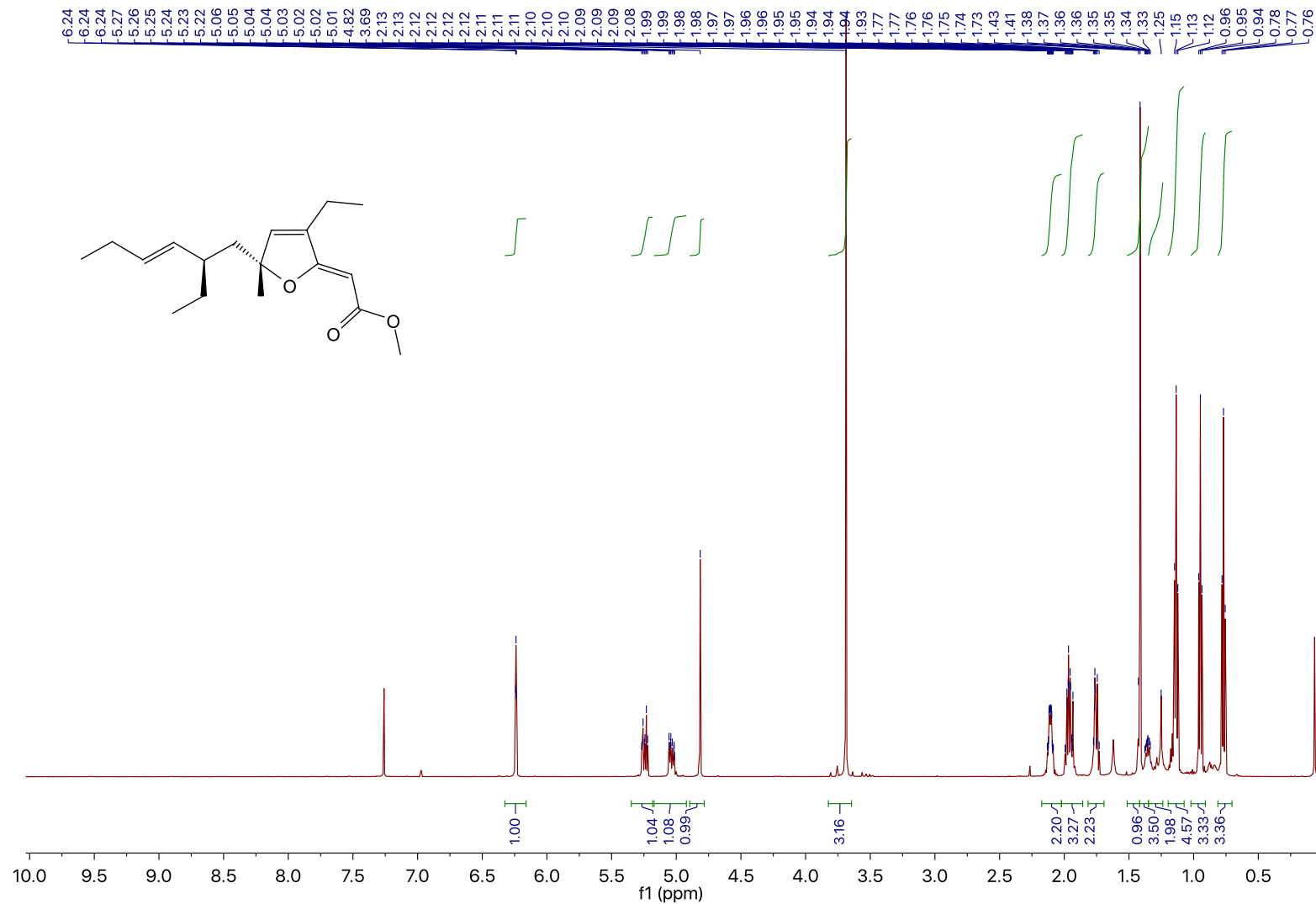


Accurate Mass Data

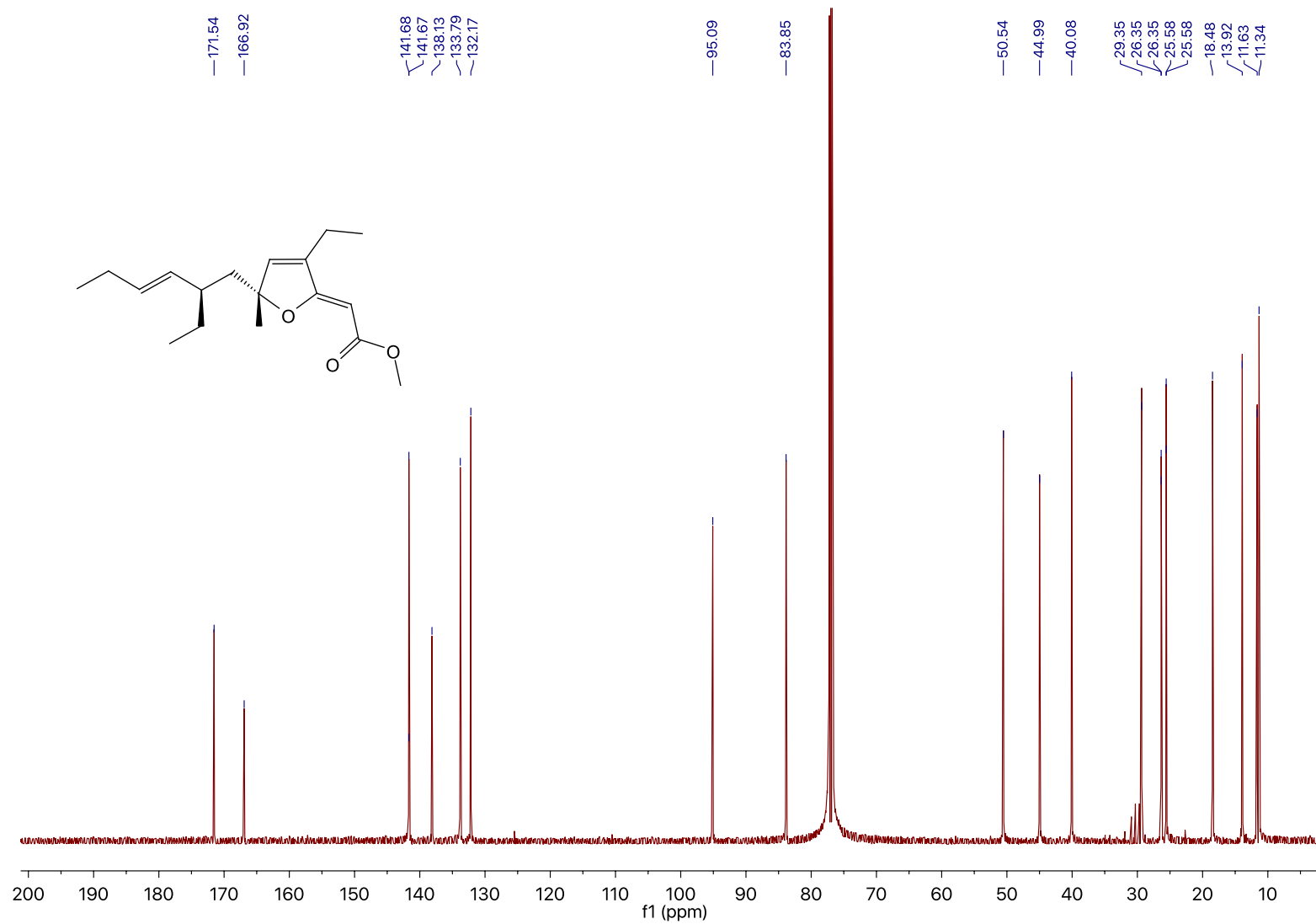
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
335.1831	C ₁₇ H ₂₈ O ₅ Na	335.1834	-0.9	2.0
335.1823	C ₁₇ H ₂₈ O ₅ Na	335.1834	-3.3	0.1

^1H , ^{13}C , COSY, HSQC NMR and HRMS (ESI) data for compound **1a**

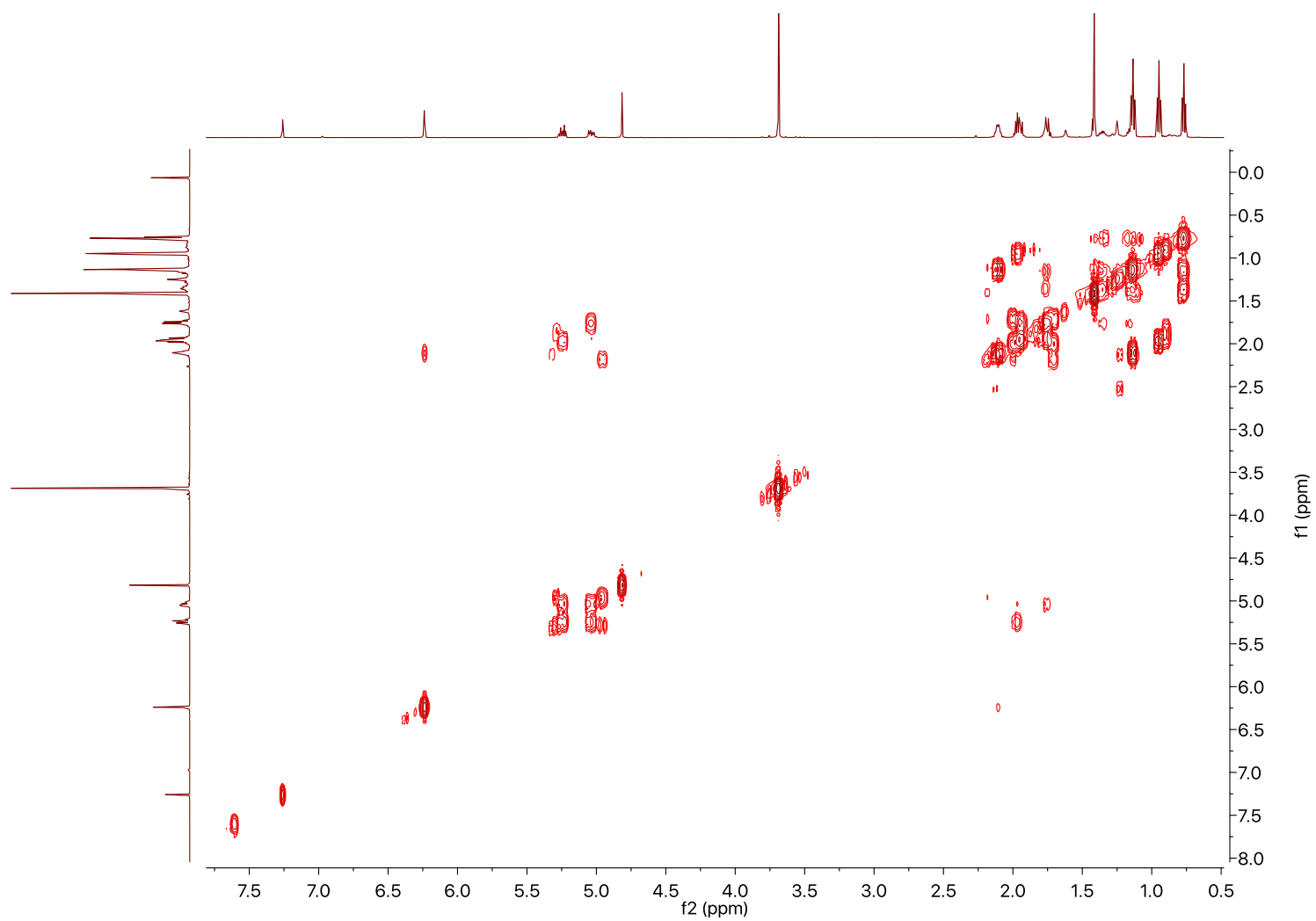
^1H NMR data



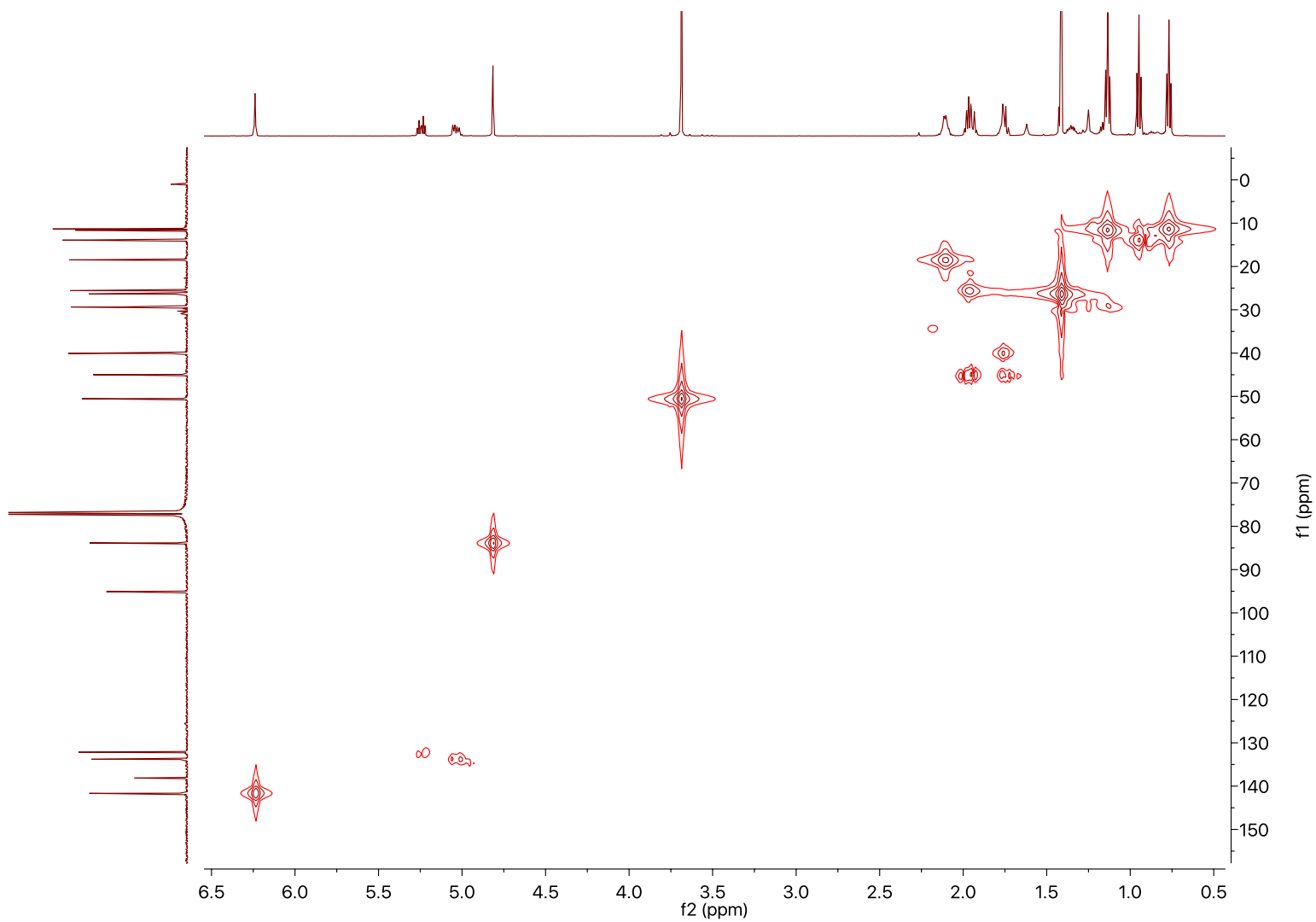
^{13}C NMR data



2D NMR Data **1a**
COSY

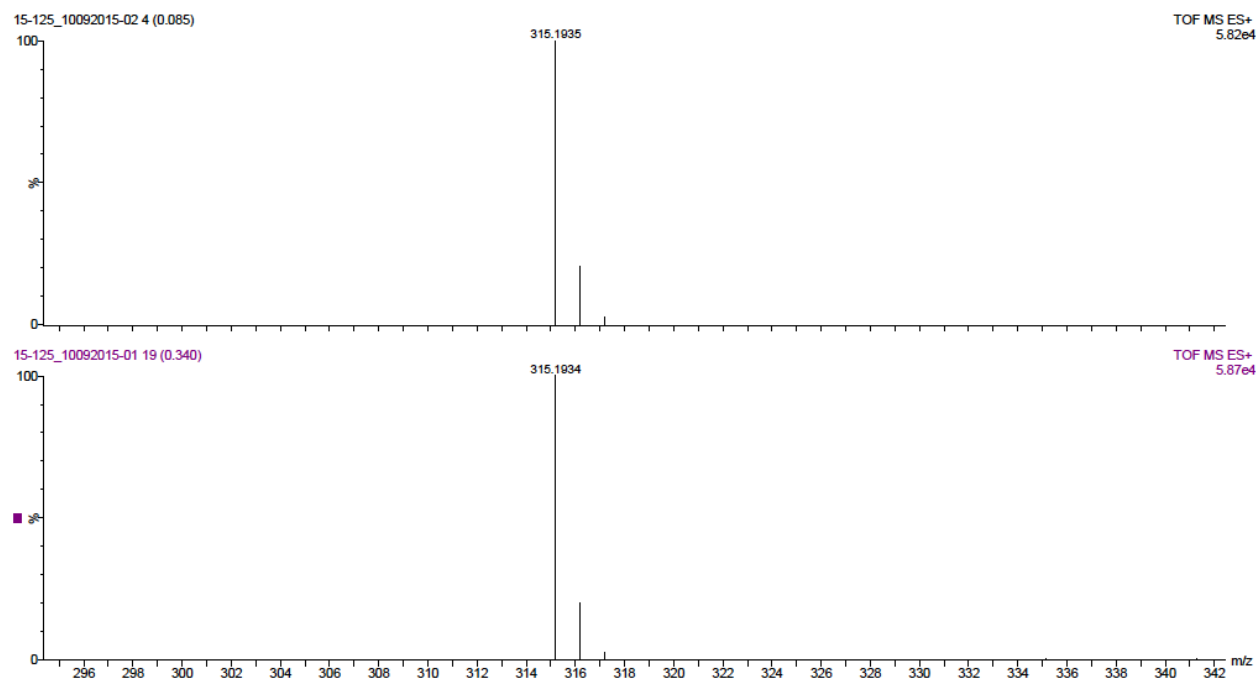


HSQC



HRMS data

High Resolution Spectra
Positive ion

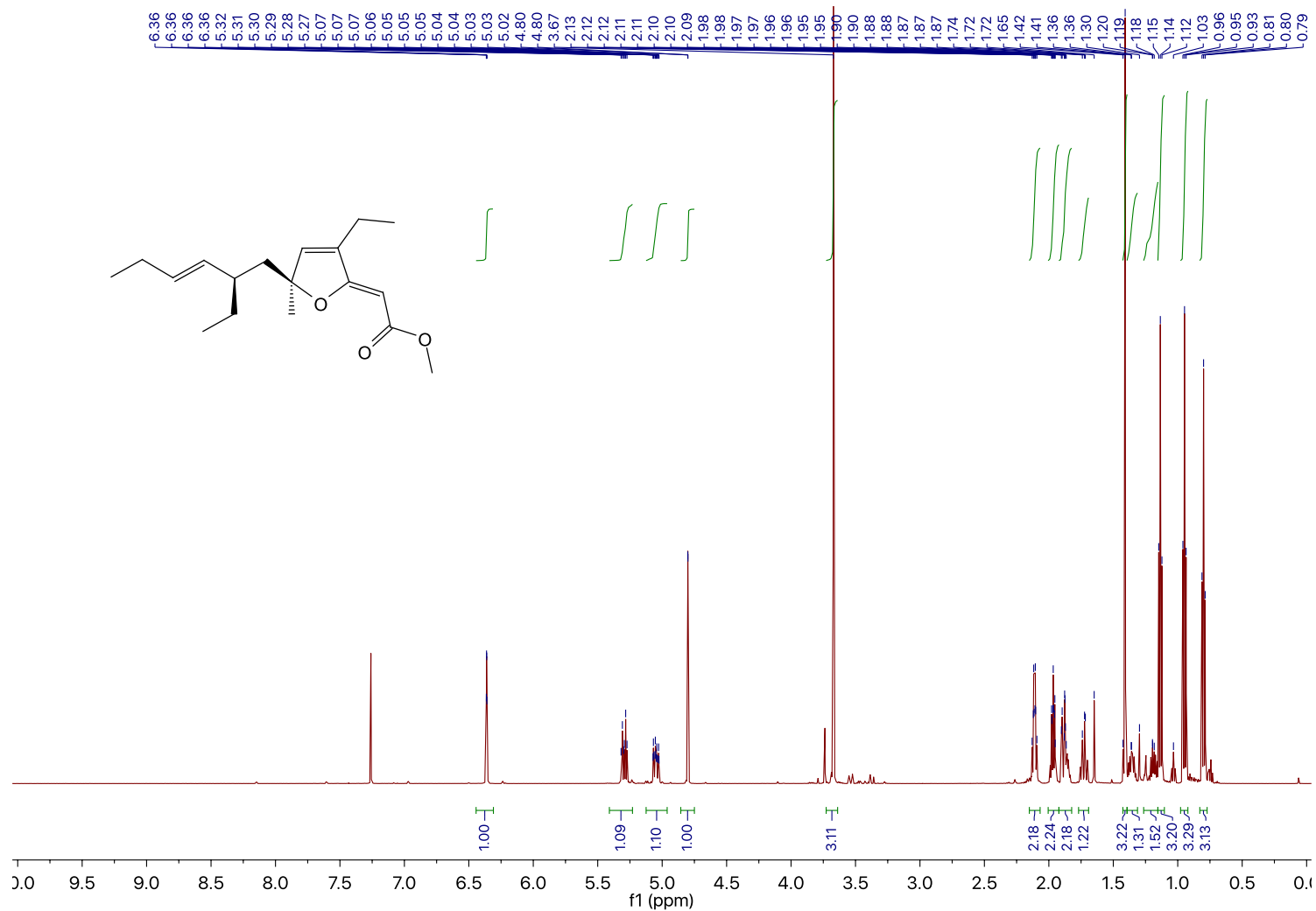


Accurate Mass Data

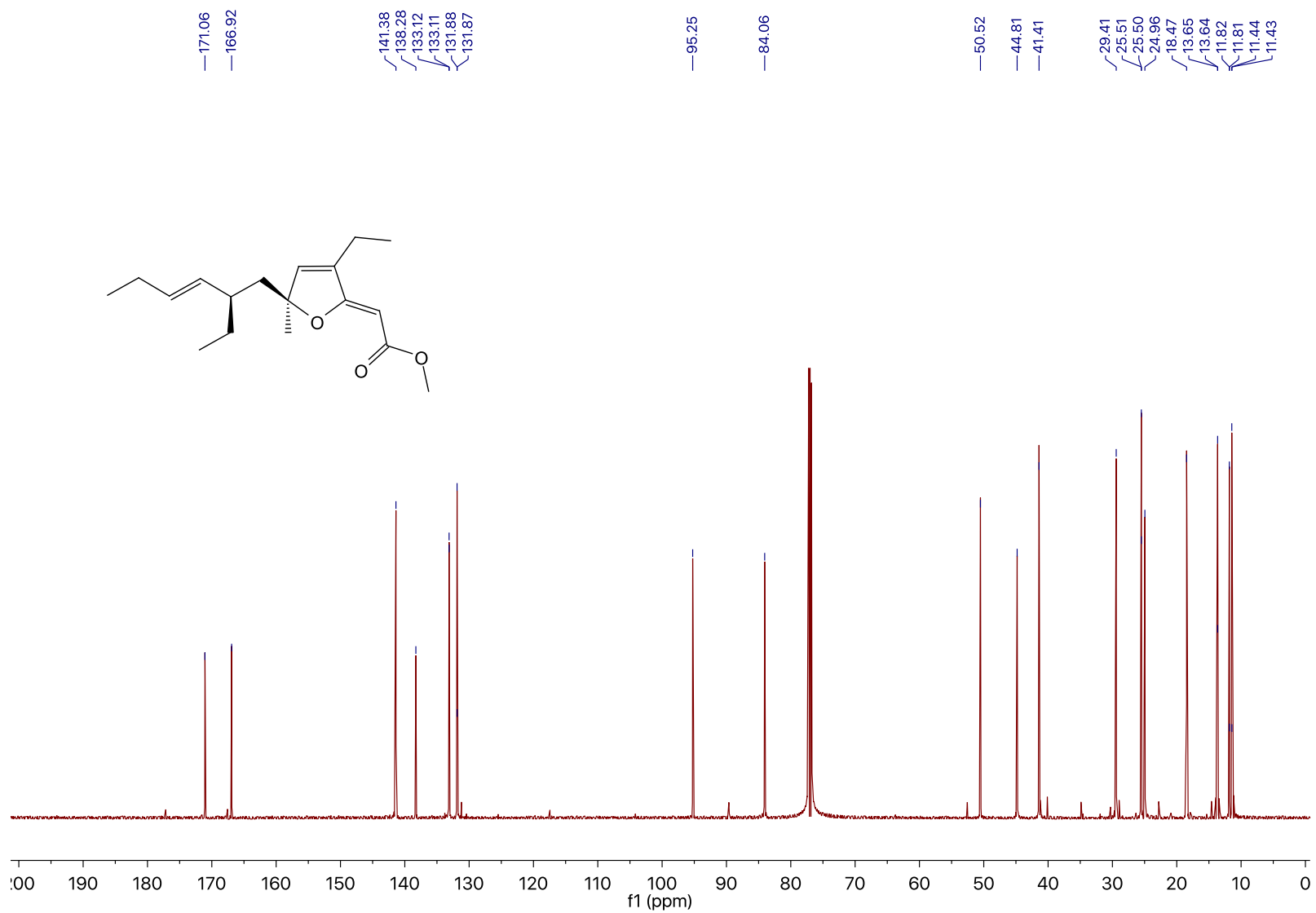
Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFiT (norm)
315.1934	C ₁₈ H ₂₈ O ₃ Na	315.1936	-0.6	1.0
315.1935	C ₁₈ H ₂₈ O ₃ Na	315.1936	-0.3	0.6

^1H , ^{13}C , COSY, HSQC NMR and HRMS (ESI) data for compound **1b**

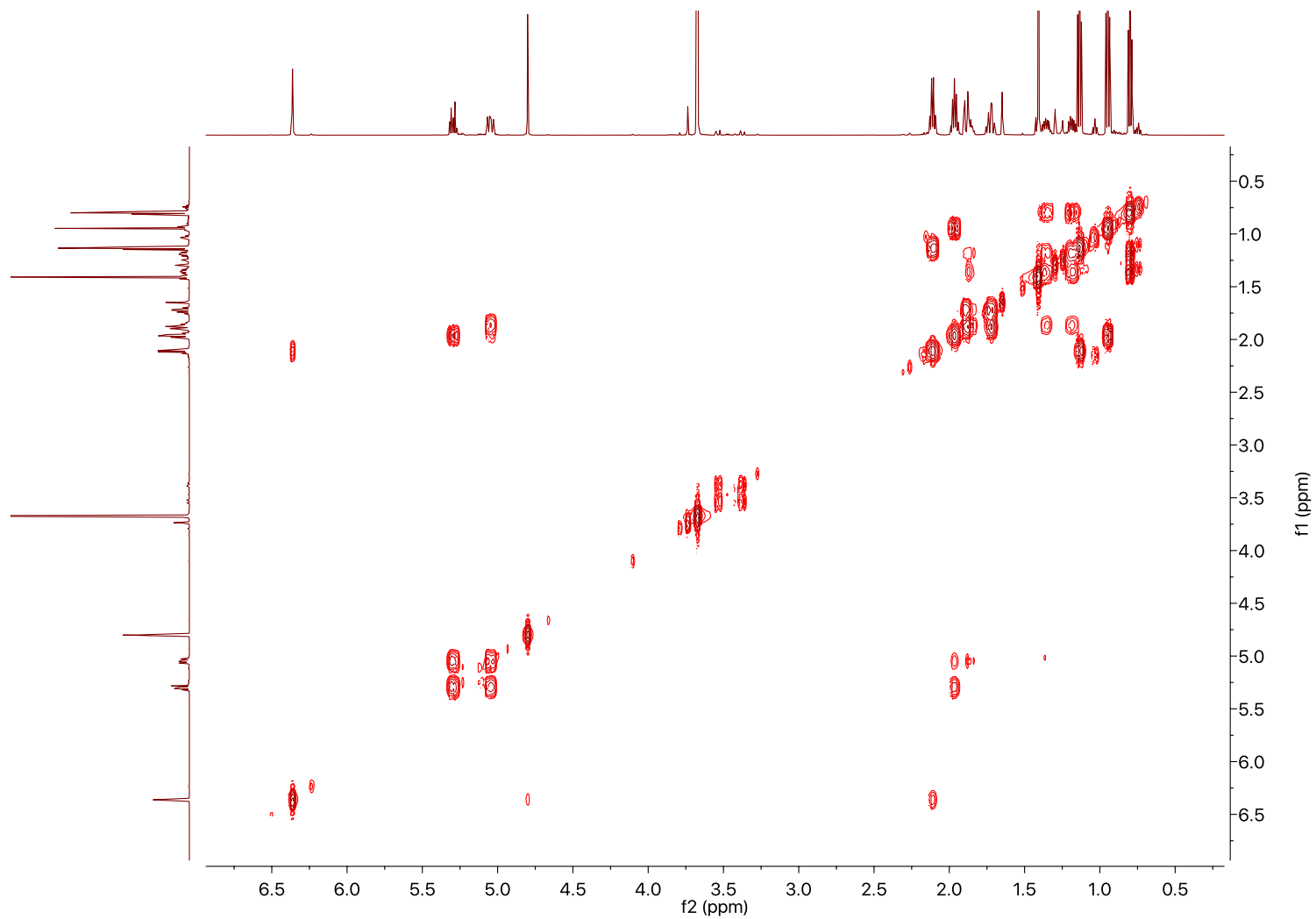
^1H NMR data



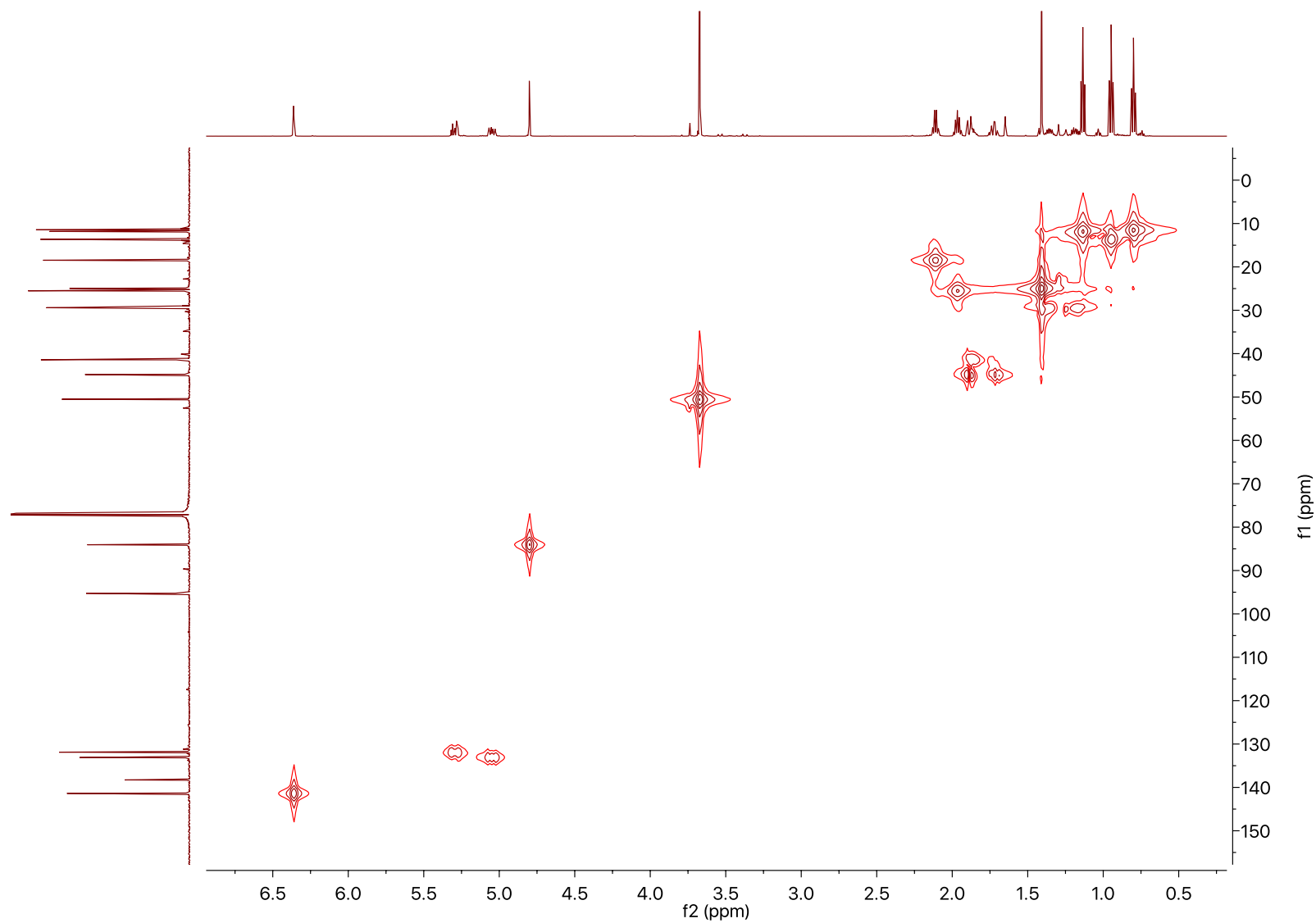
^{13}C NMR data



2D NMR Data **1b**
COSY

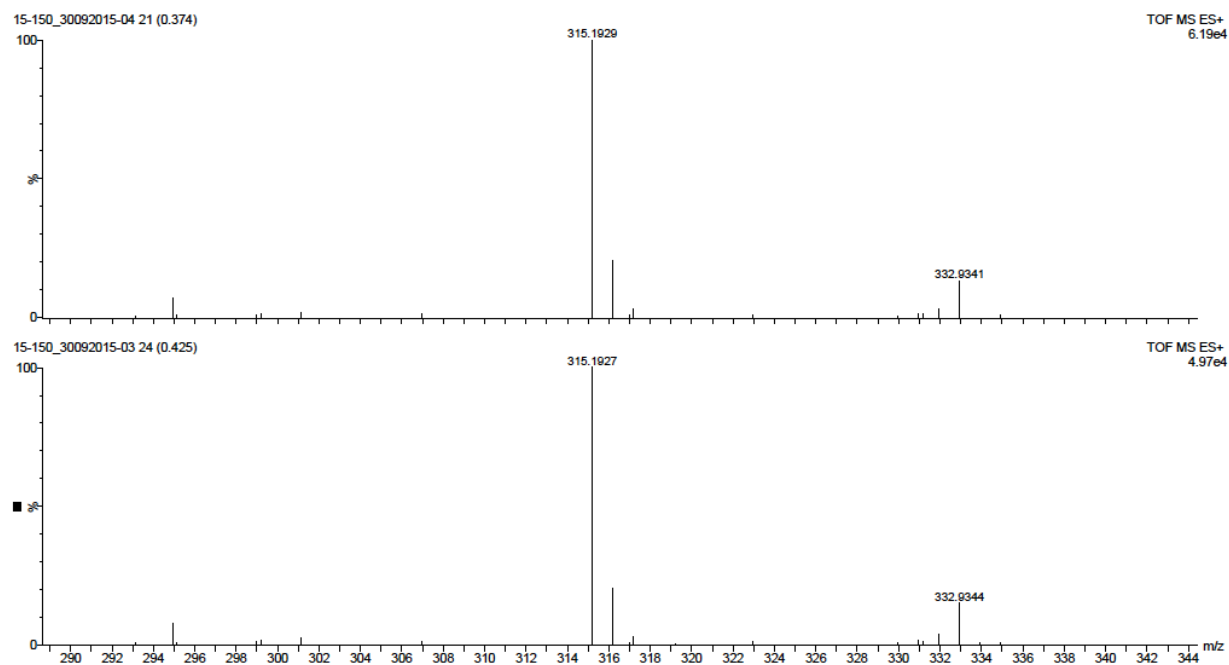


HSQC



HRMS data

High Resolution Spectra
Positive ion



Accurate Mass Data

Observed Mass	Formula [M+Na] ⁺	Calculated mass	Difference (ppm)	iFit (norm)
315.1927	C ₁₈ H ₂₈ O ₃ Na	315.1936	-2.9	0.0
315.1929	C ₁₈ H ₂₈ O ₃ Na	315.1936	-2.2	0.0