

Supplementary material

New 2-Methoxy Acetylenic Acids and Pyrazole Alkaloids from the Marine Sponge *Cinachyrella* sp.

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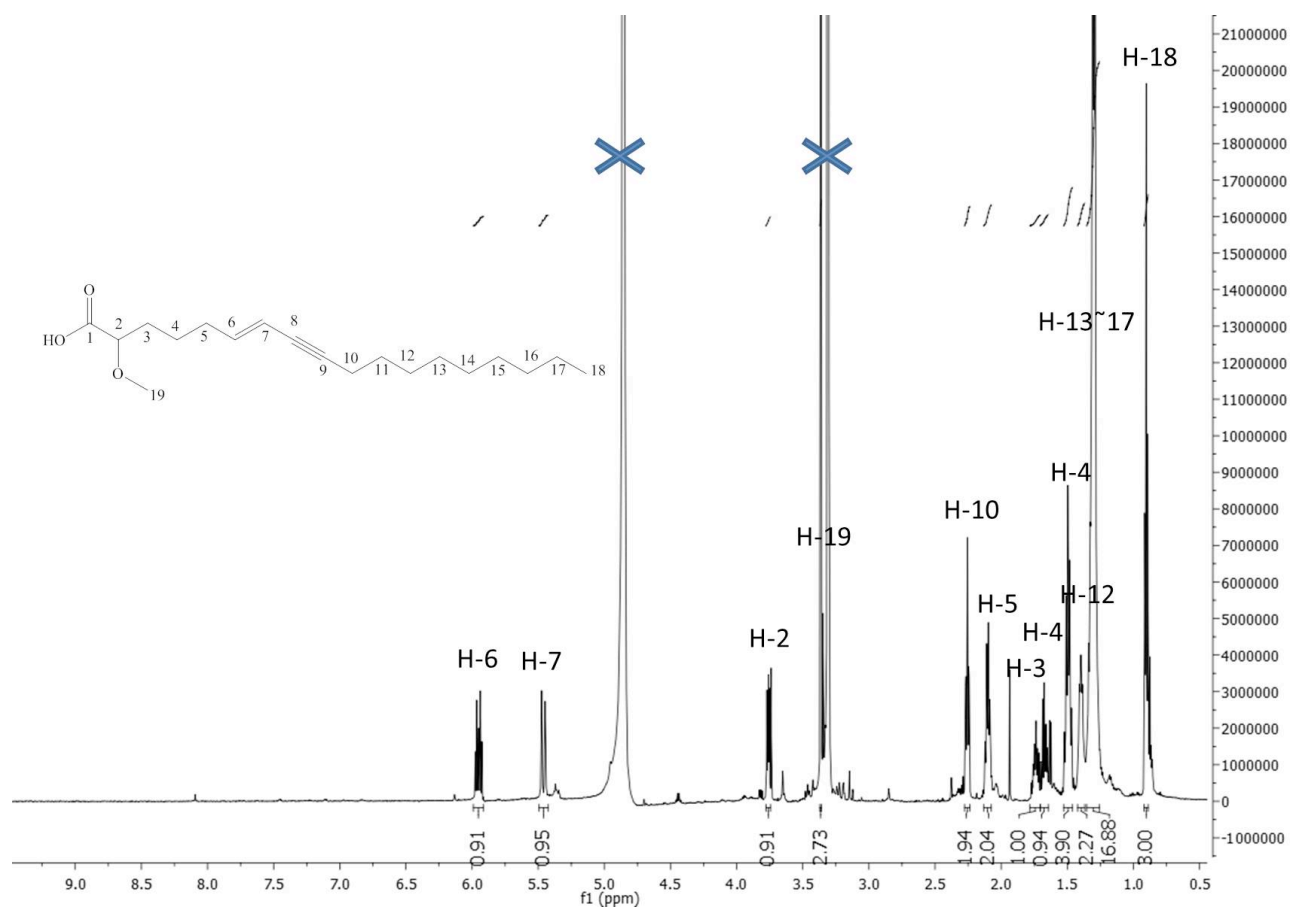
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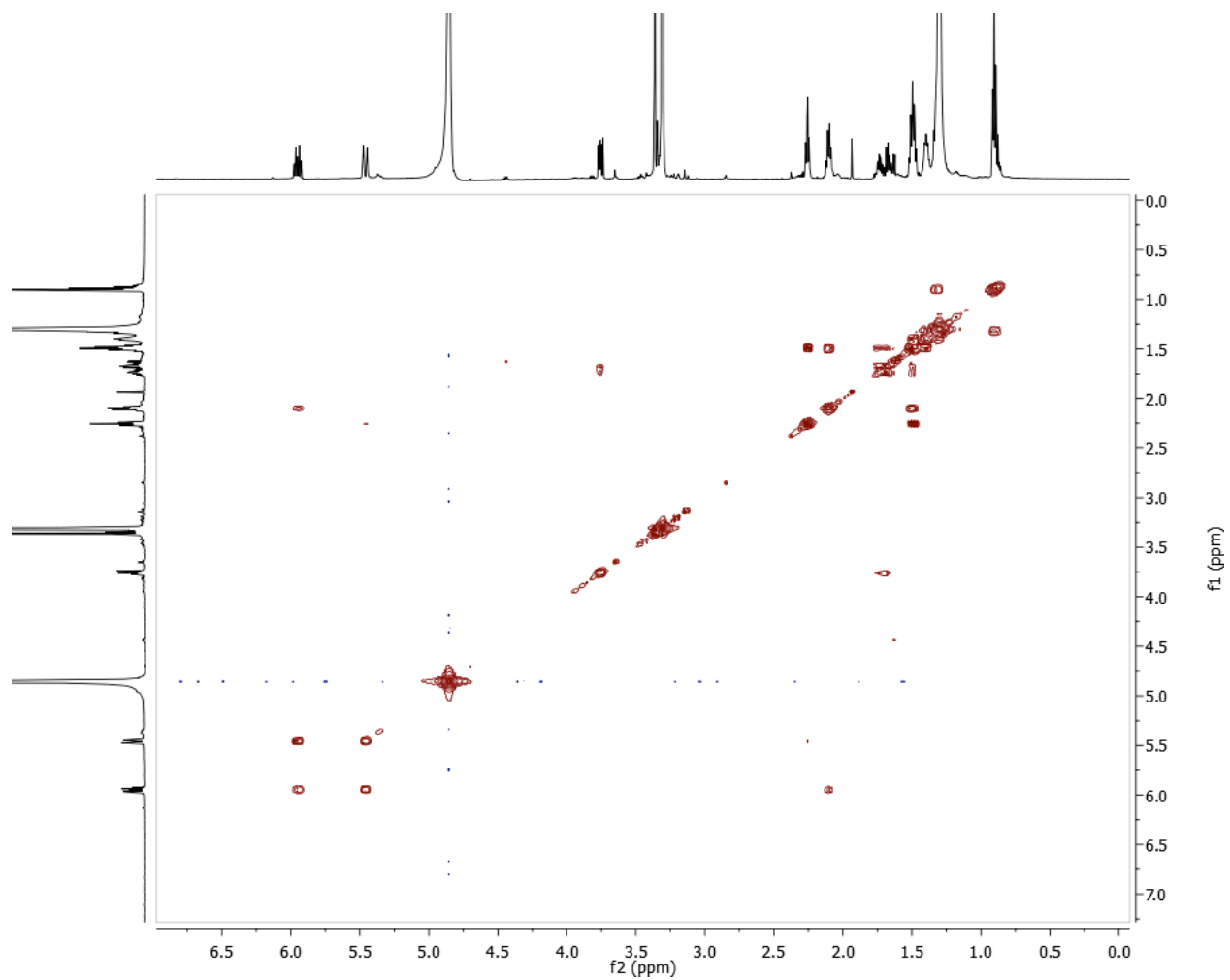
S7-6. HPLC chromatogram of 7 45

S7-7. UV spectrum of 7 45

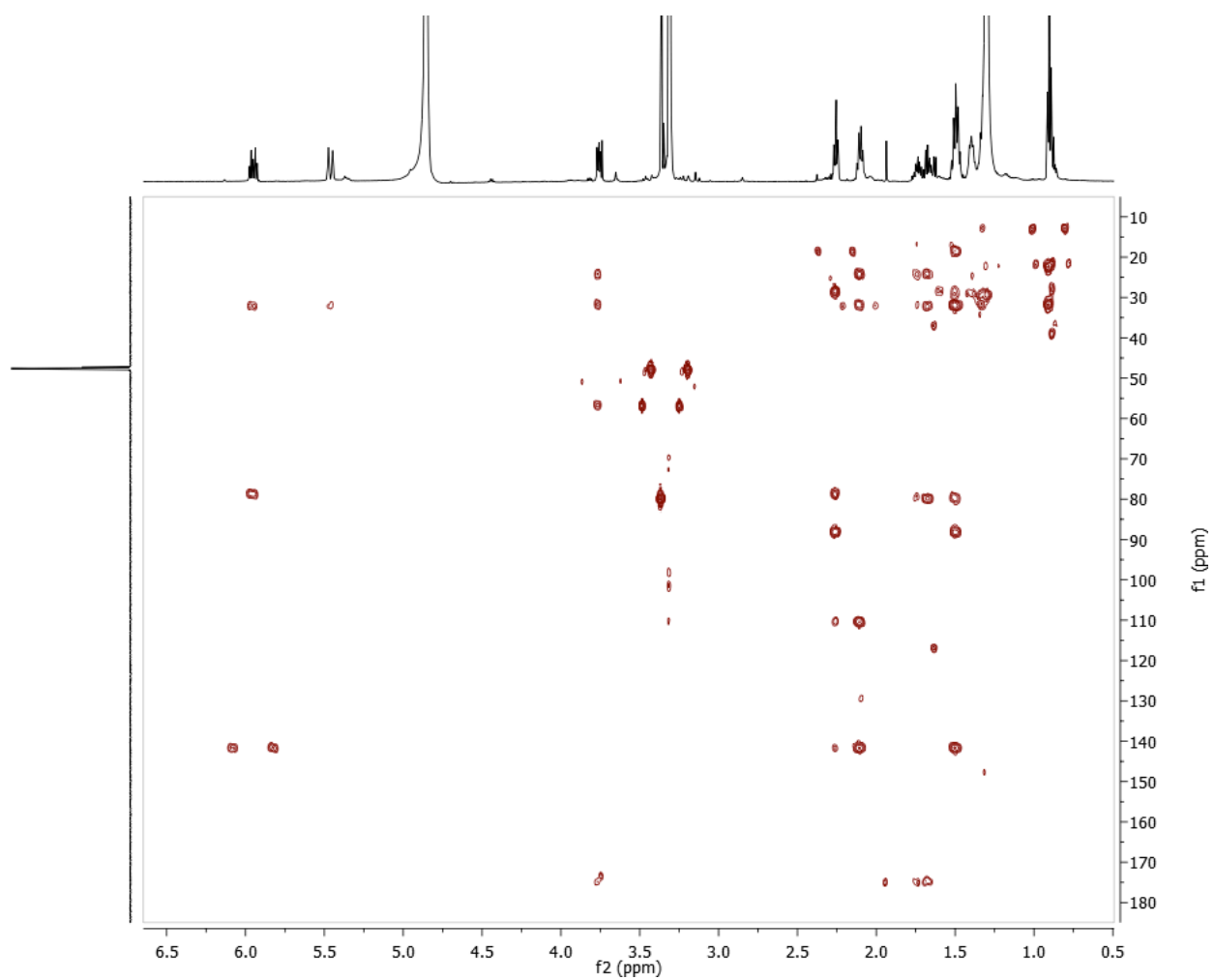
S1. Cinachylenic acid B (1)



S1-1. ¹H NMR (MeOH-d₄, 600 MHz) spectrum of 1



S1-2. COSY NMR (MeOH-*d*₄, 600 MHz) spectrum of **1**



S1-3. HMBC NMR (MeOH- d_4 , 600 MHz) spectrum of **1**

Mass Spectrum SmartFormula Report

Analysis Info

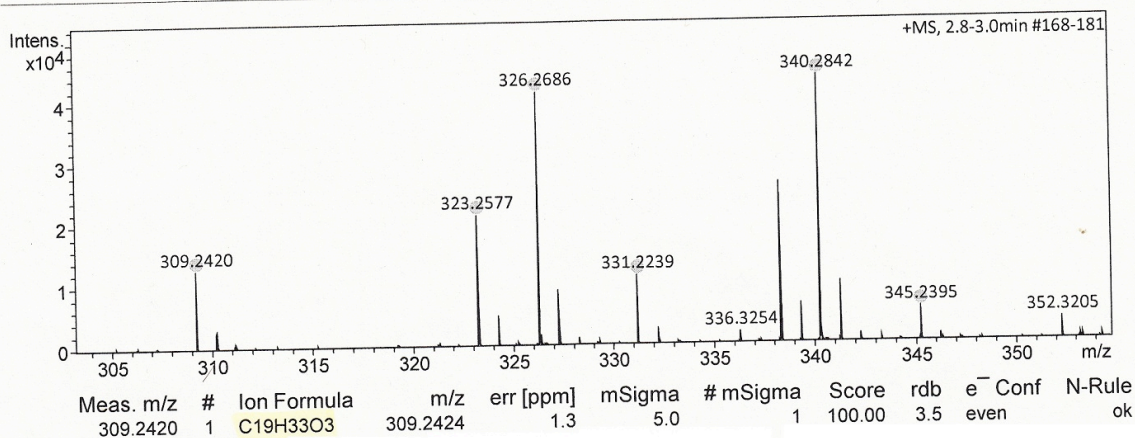
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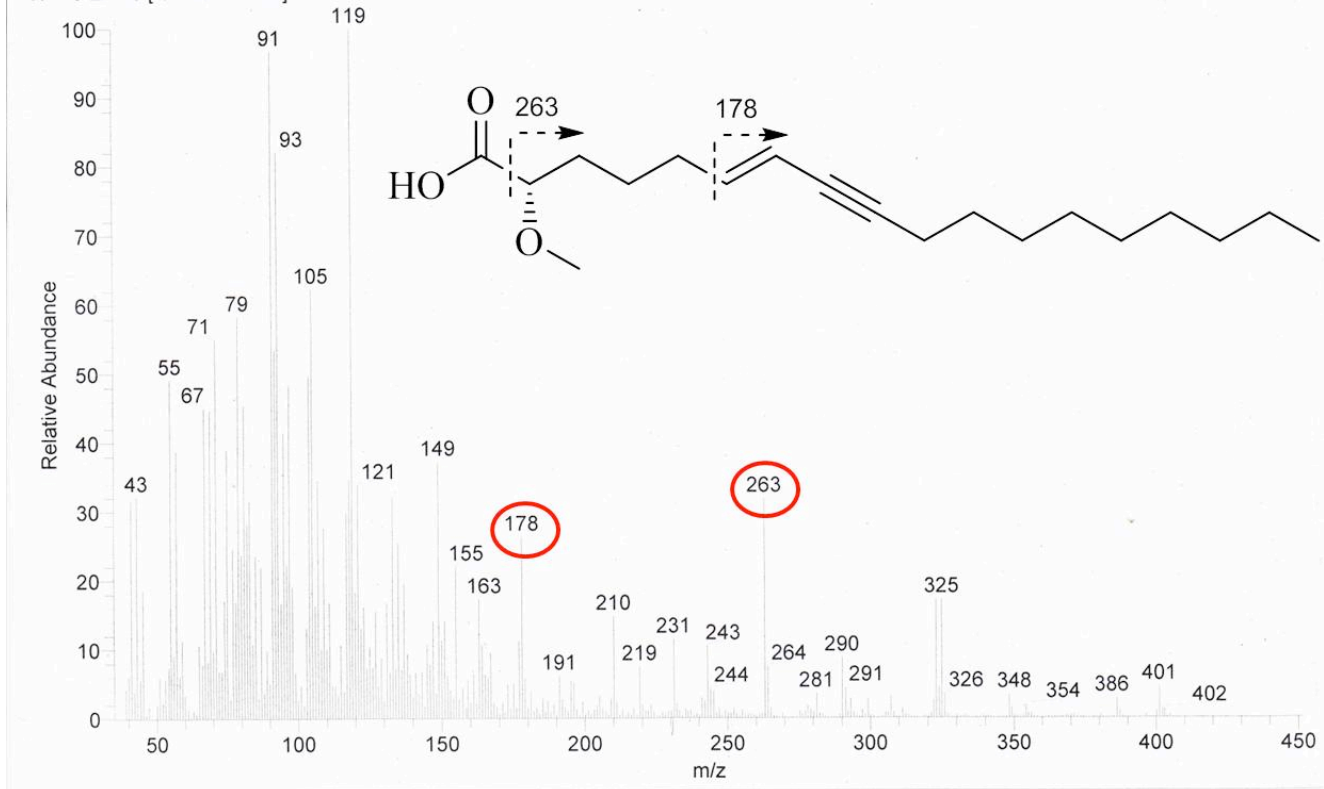
Operator Peter Tommes
Instrument maXis 288882.20213

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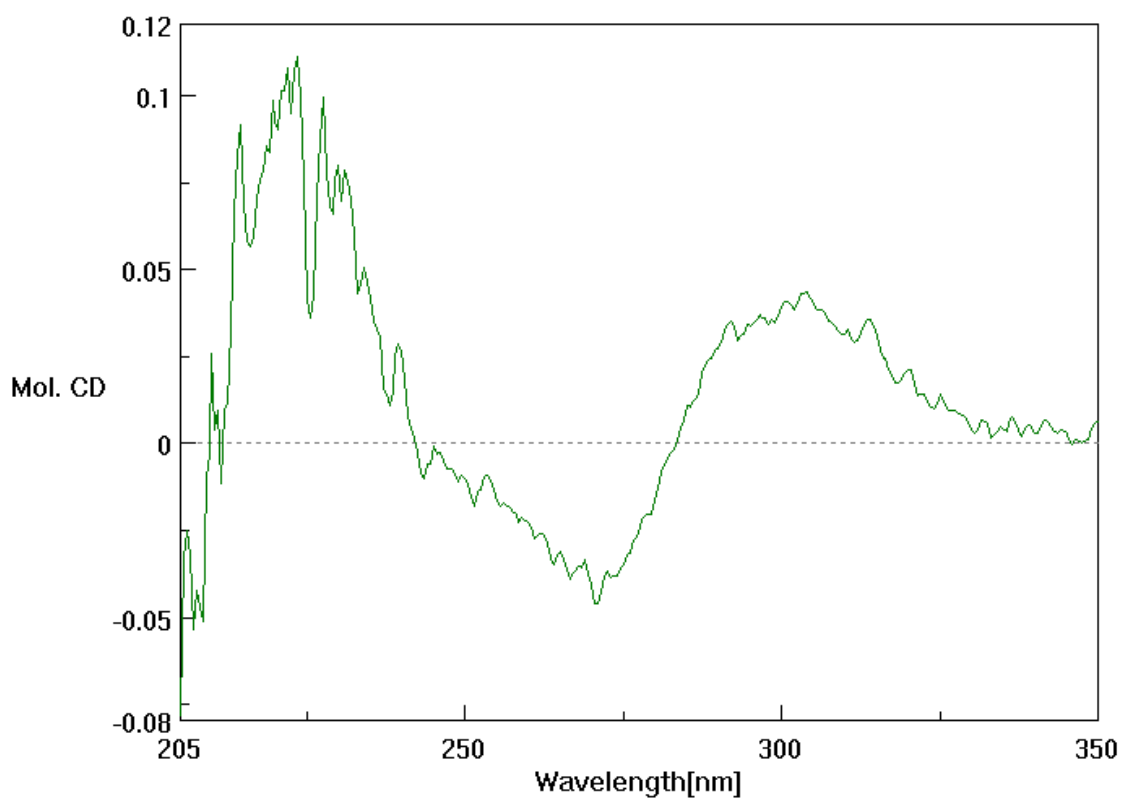
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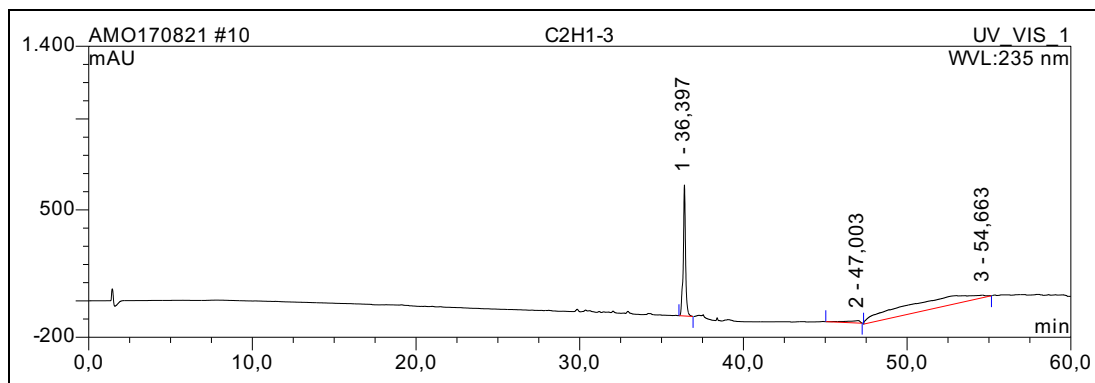
S1-4. HRESIMS spectrum of 1



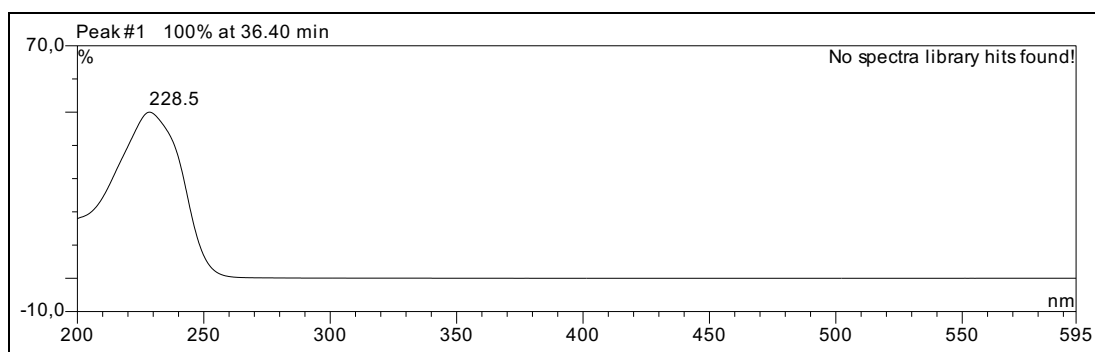
S1-5. EIMS spectrum of 1



S1-6. CD spectrum of **1**
0.3 mg in 1.5 mL MeOH
 $c = 6.4838 \times 10^{-4}$ M
cell length: 1 cm
accumulation: 5
sensitivity: high (5 mdeg)

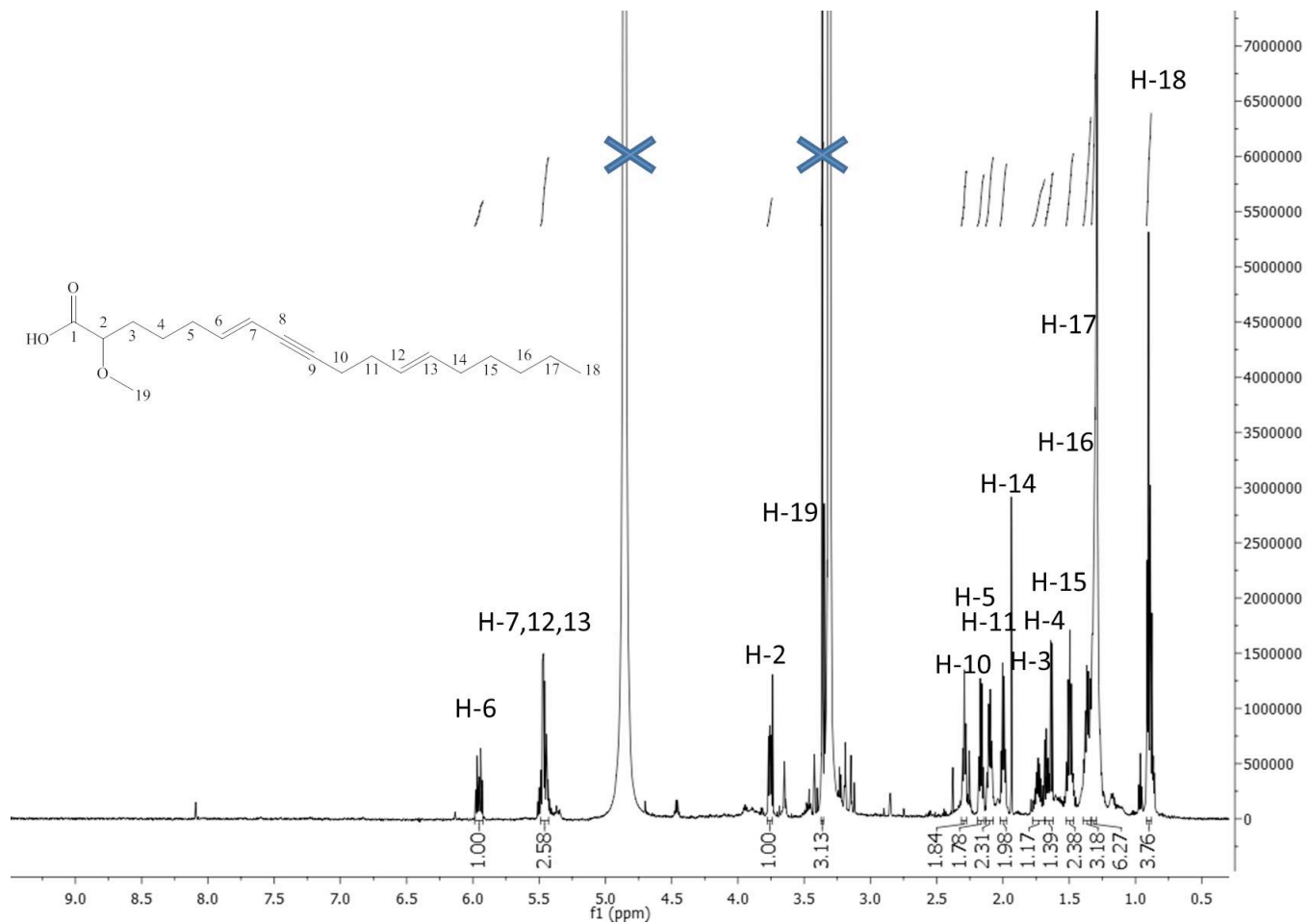


S1-7. HPLC chromatogram of **1**

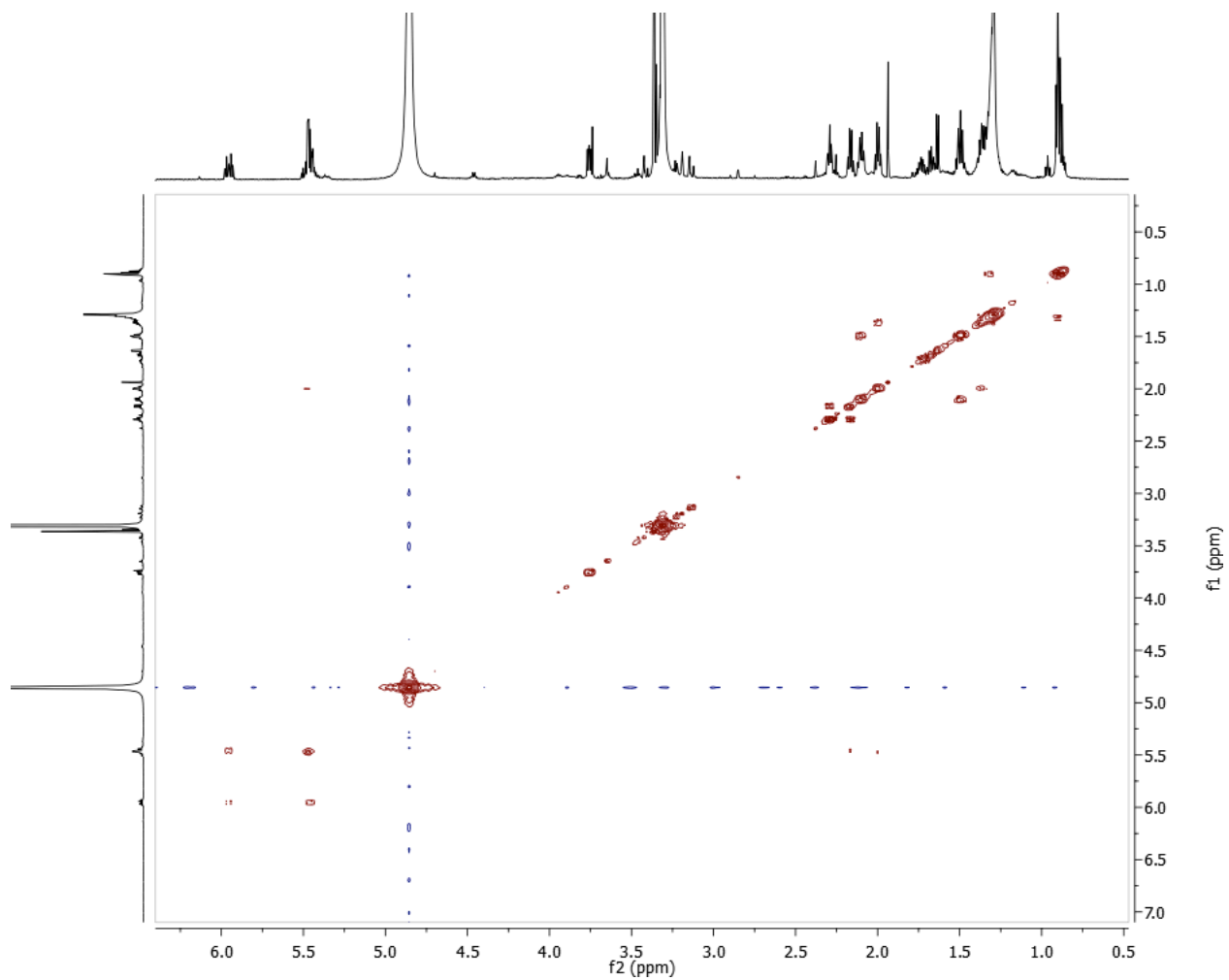


S1-8. UV spectrum of **1**

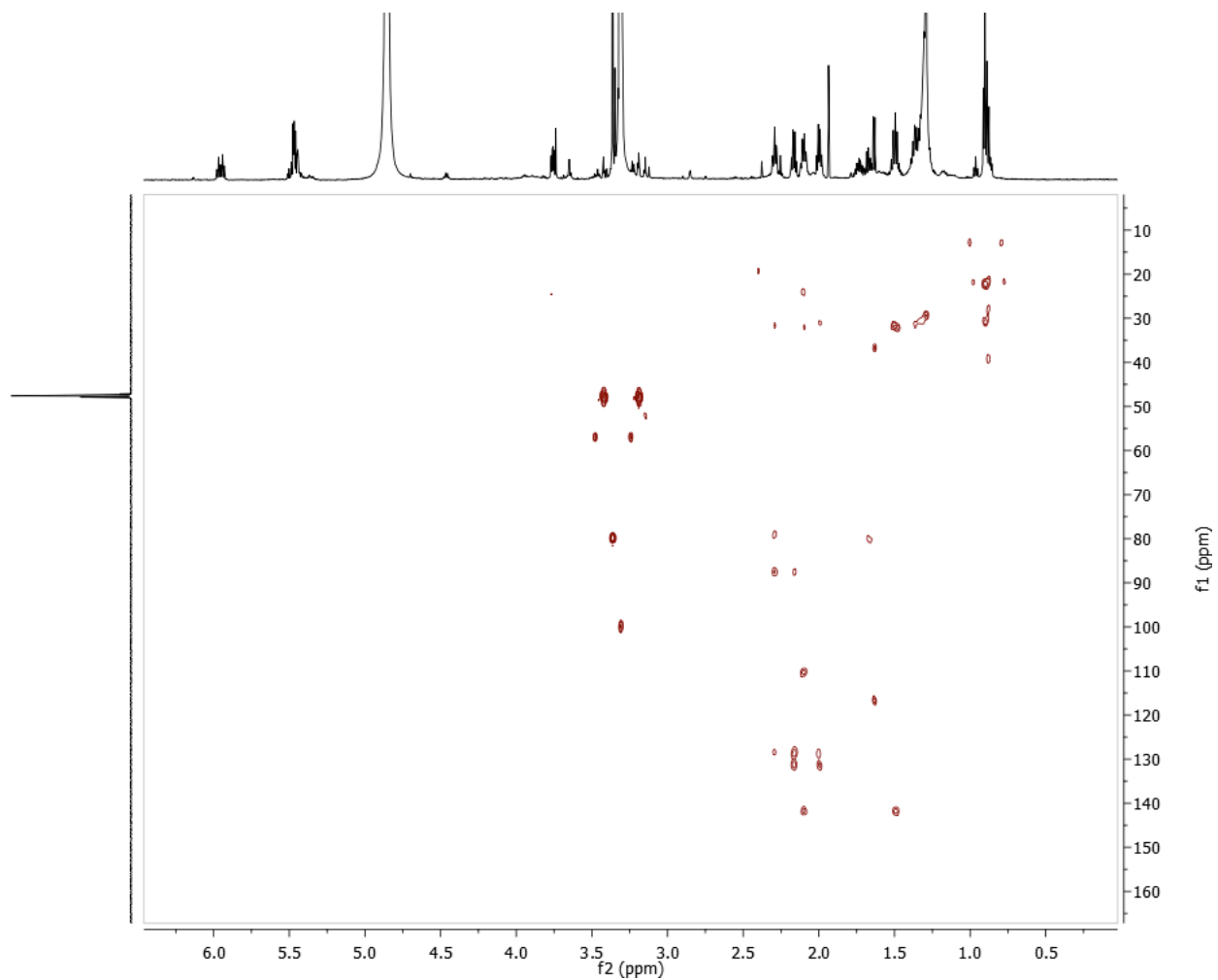
S2. Cinachylenic acid C (2)



S2-1. ^1H NMR ($\text{MeOH-}d_4$, 600 MHz) spectrum of 2



S2-2. COSY NMR (MeOH-*d*₄, 600 MHz) spectrum of 2



S2-3. HMBC NMR (MeOH- d_4 , 600 MHz) spectrum of **2**

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Analysis Info

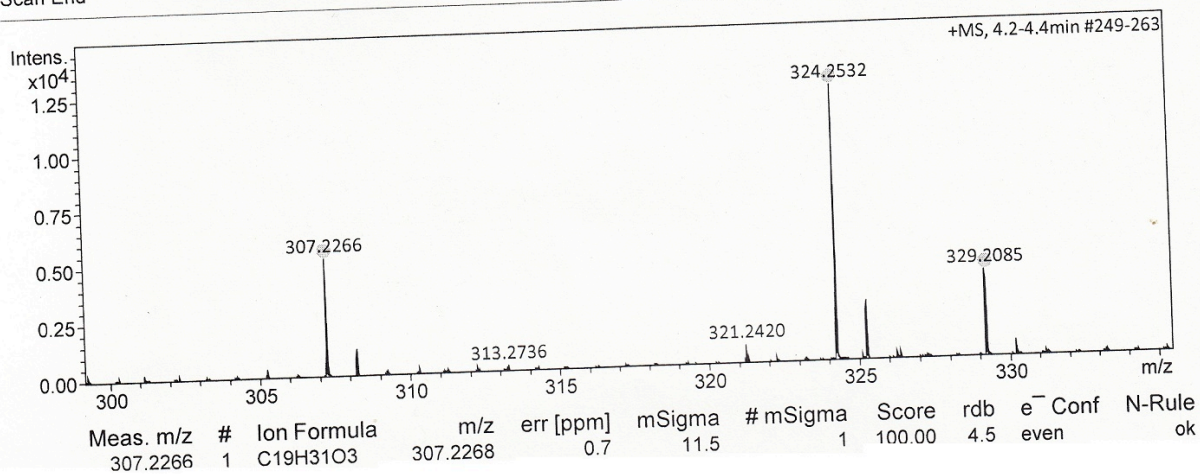
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Operator Peter Tommes
 Instrument maXis 288882.20213

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S2-4. HRESIMS spectrum of 2

C:\Xcalibur\user\finnigan\data\575-014

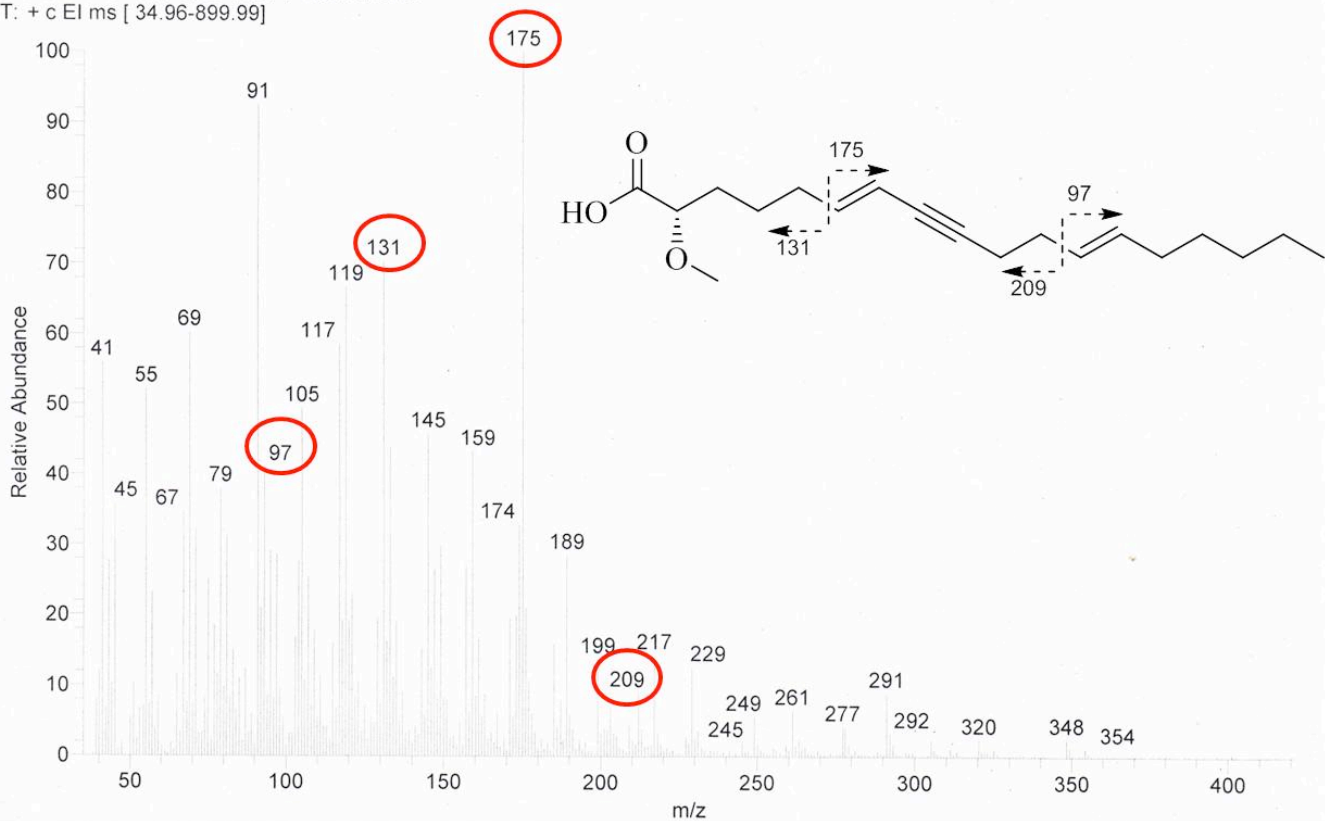
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Amin, C₂H₁-2+3

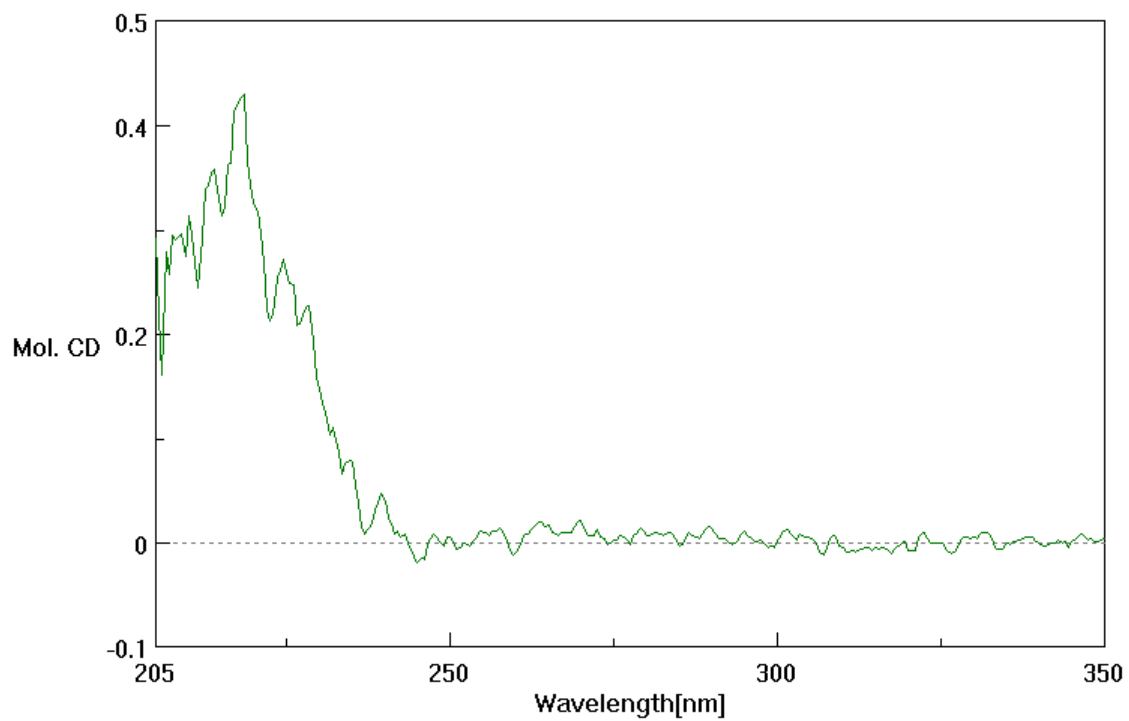
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575-014 #16 RT: 0.46 AV: 1 NL: 5.29E6

T: + c EI ms [34.96-899.99]



S2-5. EIMS spectrum of 2

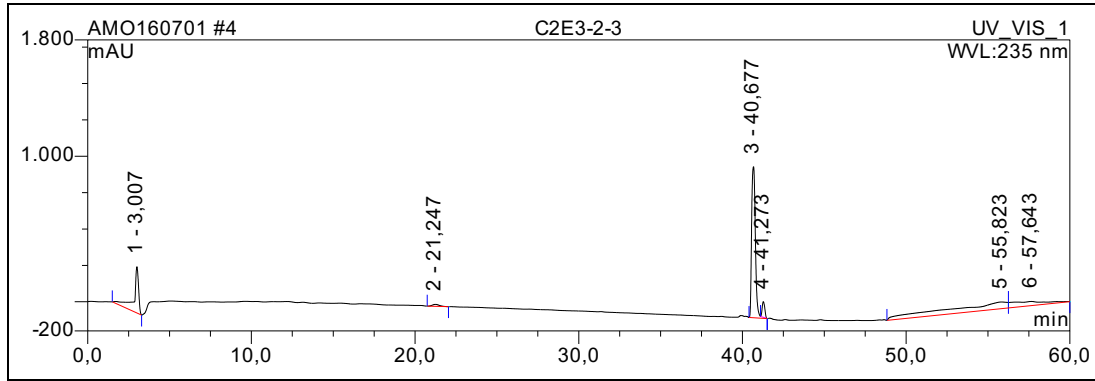


S2-6. CD spectrum of 2

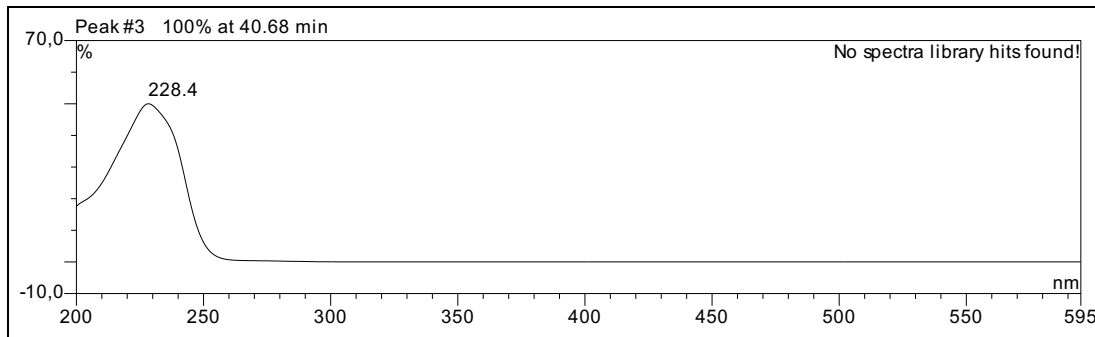
0.3 mg in 2.5 mL MeOH

$c = 3.9159 \times 10^{-4} \text{ M}$

cell length: 1 cm

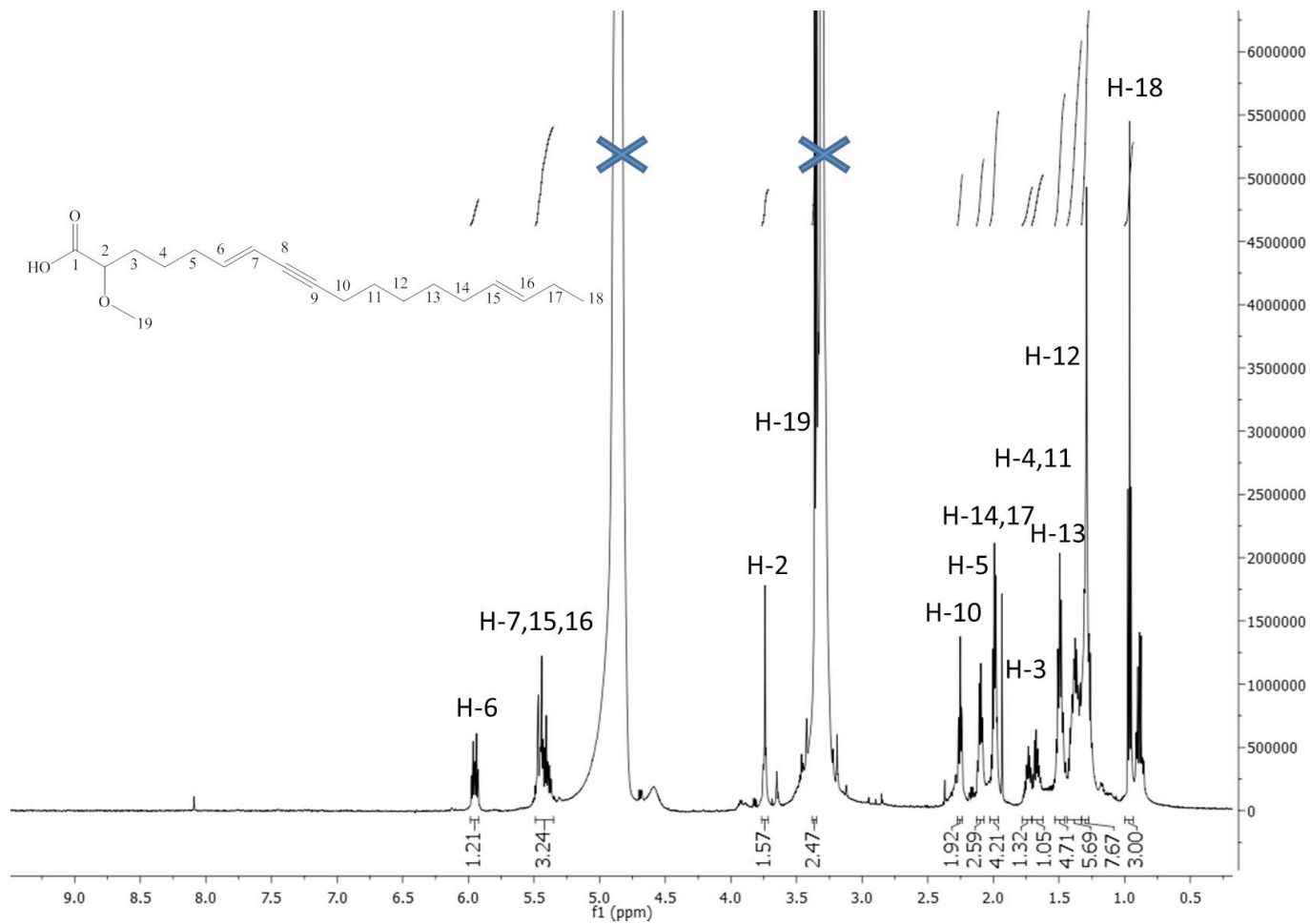


S2-7. HPLC chromatogram of 2

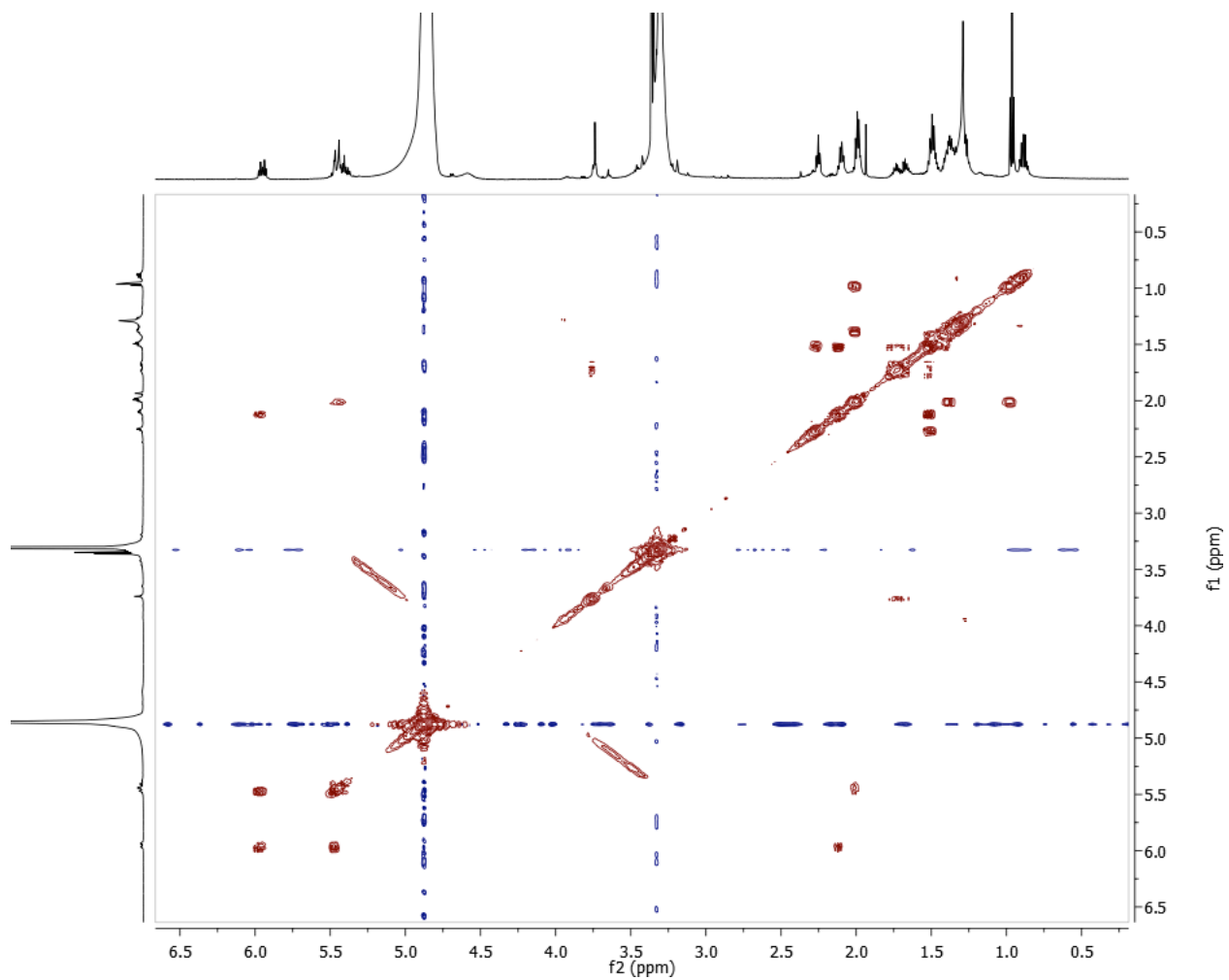


S2-8. UV spectrum of 2

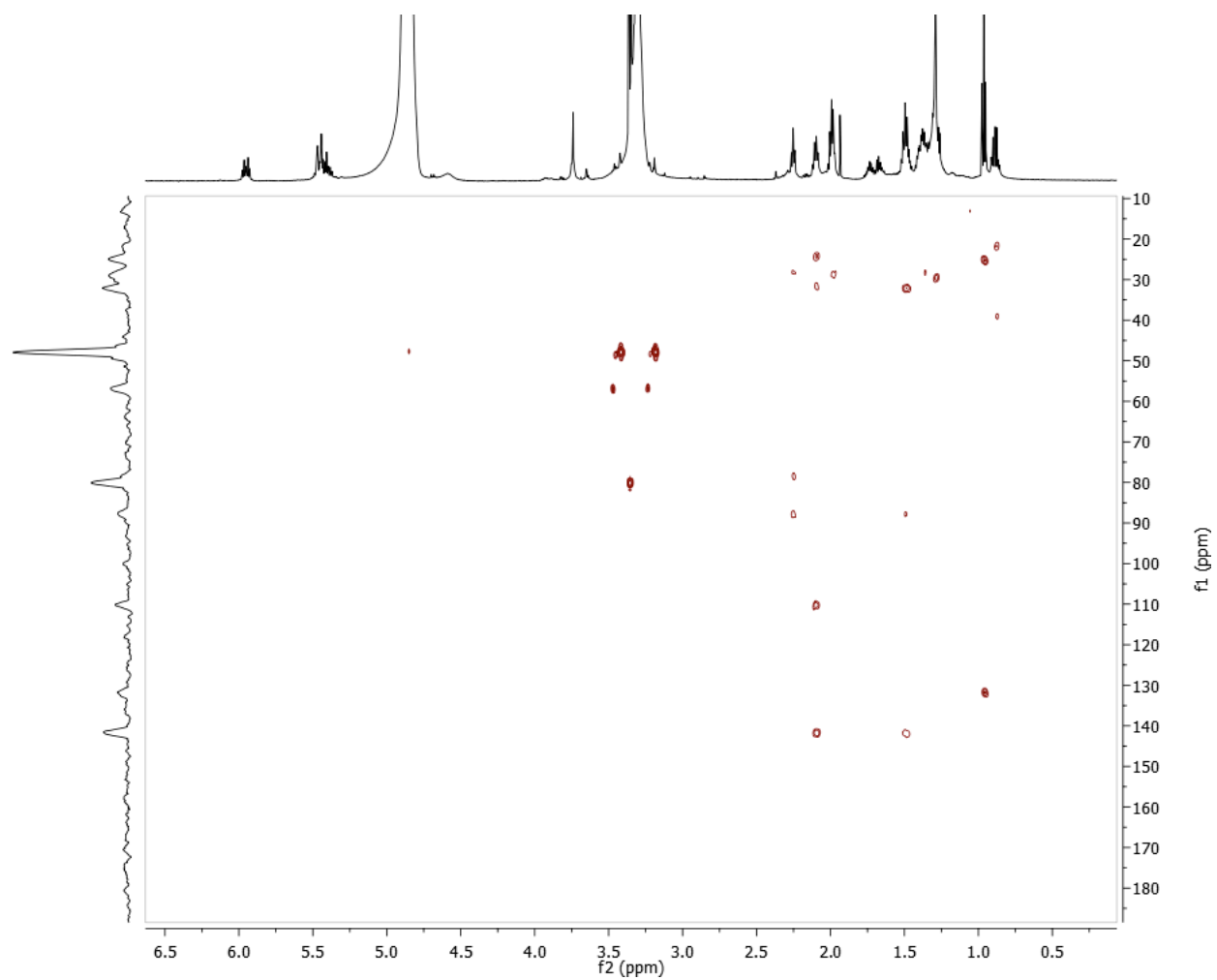
S3. Cinachylenic acid D (3)



S3-1. ¹H NMR (MeOH-d₄, 600 MHz) spectrum of 3



S3-2. COSY NMR (MeOH- d_4 , 600 MHz) spectrum of **3**



S3-3. HMBC NMR ($\text{MeOH-}d_4$, 600 MHz) spectrum of 3

Mass Spectrum SmartFormula Report

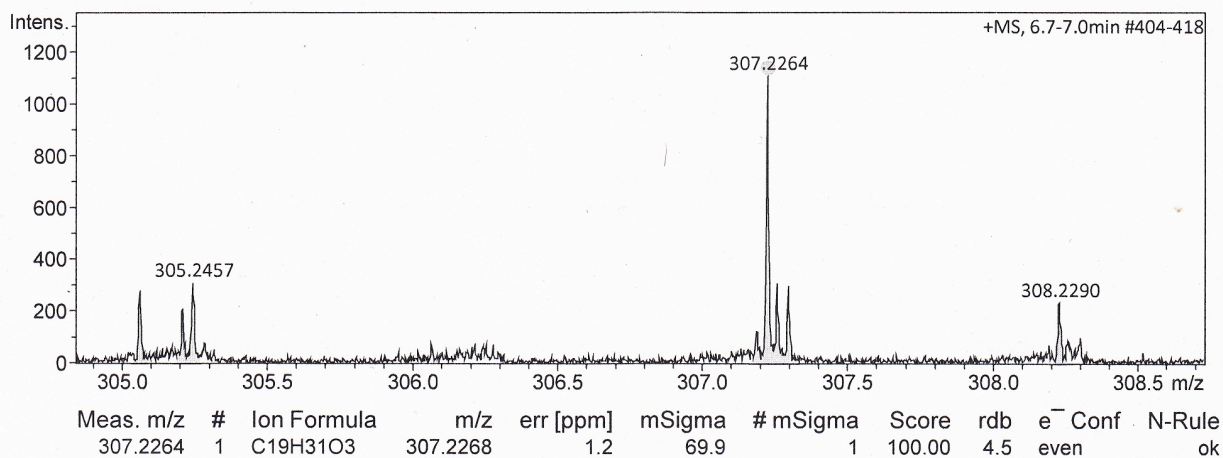
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Comment

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Operator Peter Tommes
Instrument maXis 288882.20213

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S3-4. HRESIMS spectrum of 3

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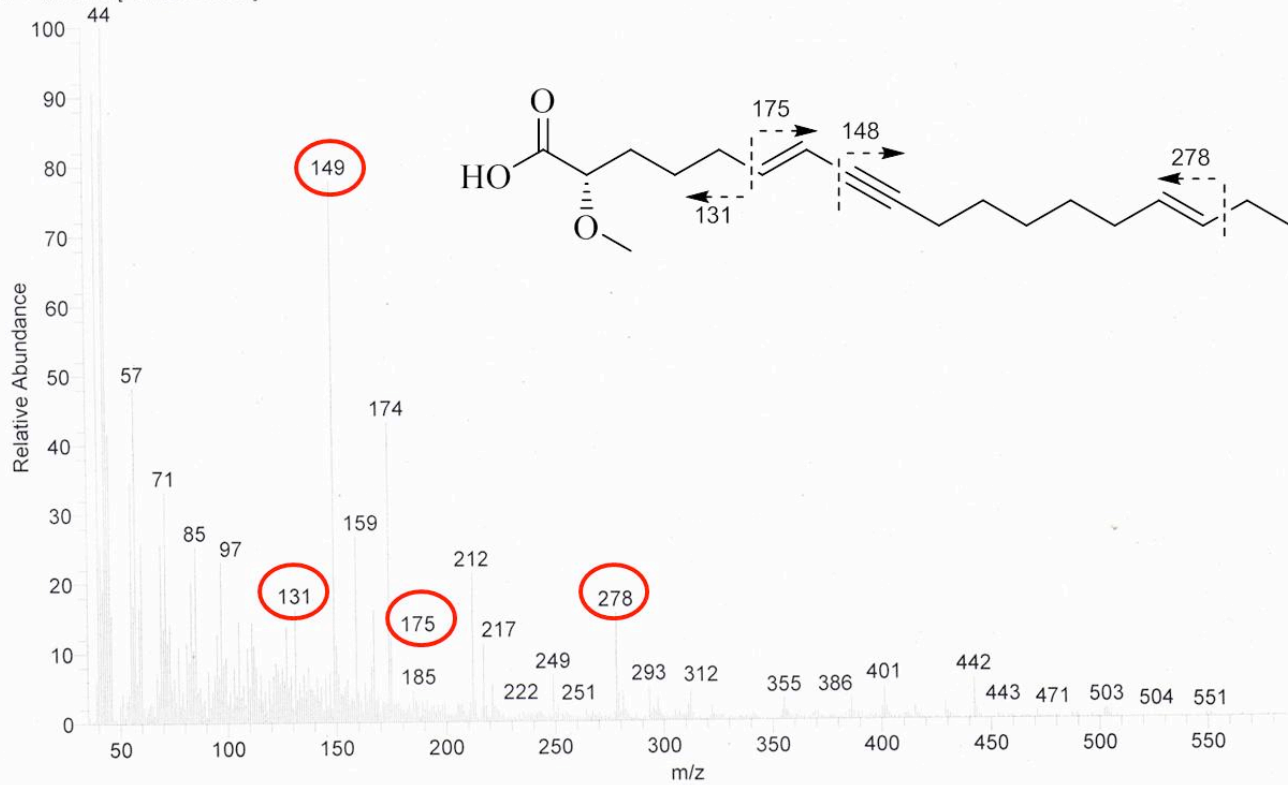
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Amin, C2H2-4-2

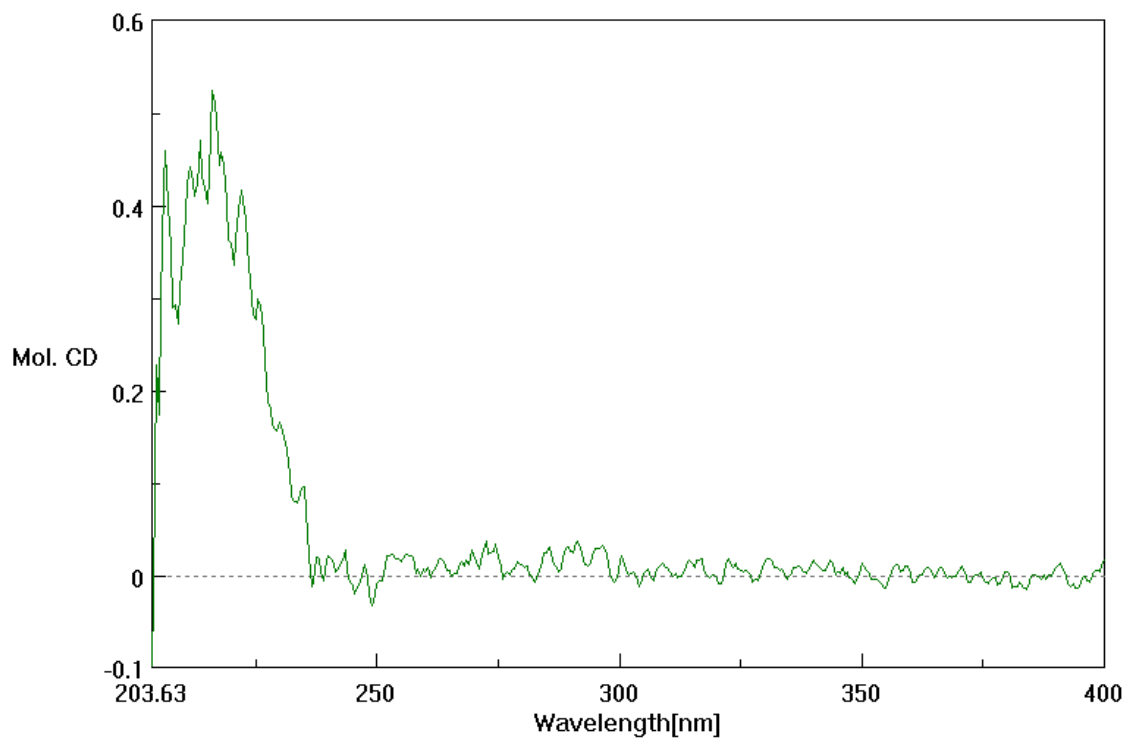
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S3-5. EIMS spectrum of 3

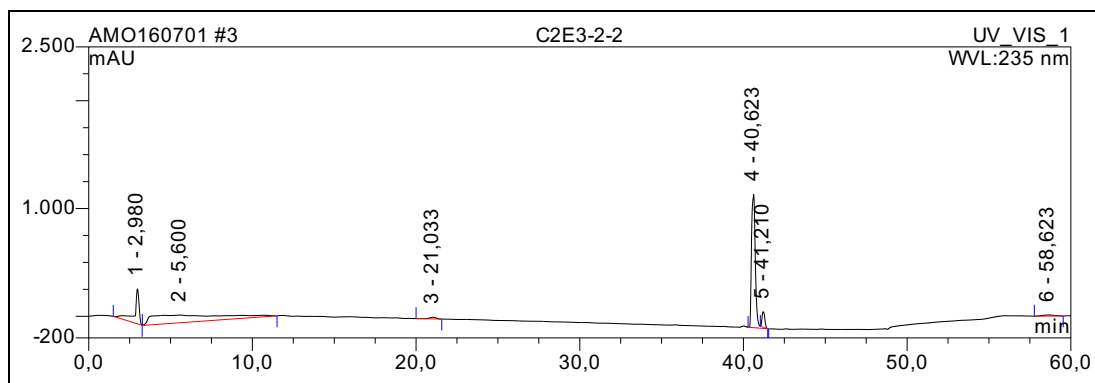


S3-6. CD spectrum of 3

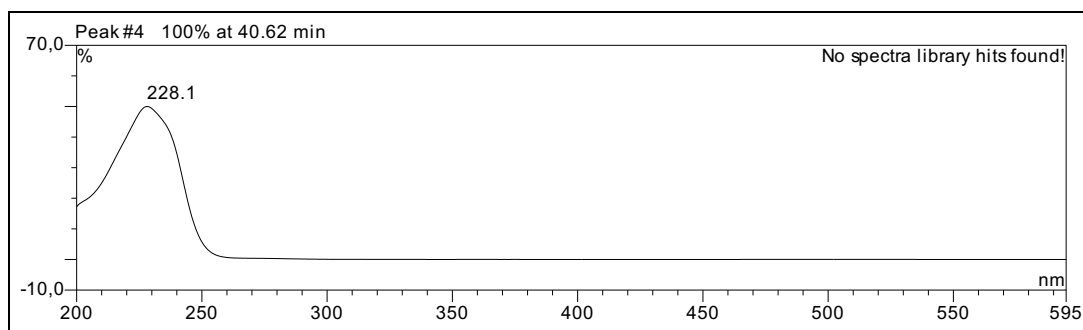
0.3 mg in 4 mL MeOH

$c = 2.4475 \times 10^{-4}$ M

cell length: 1 cm

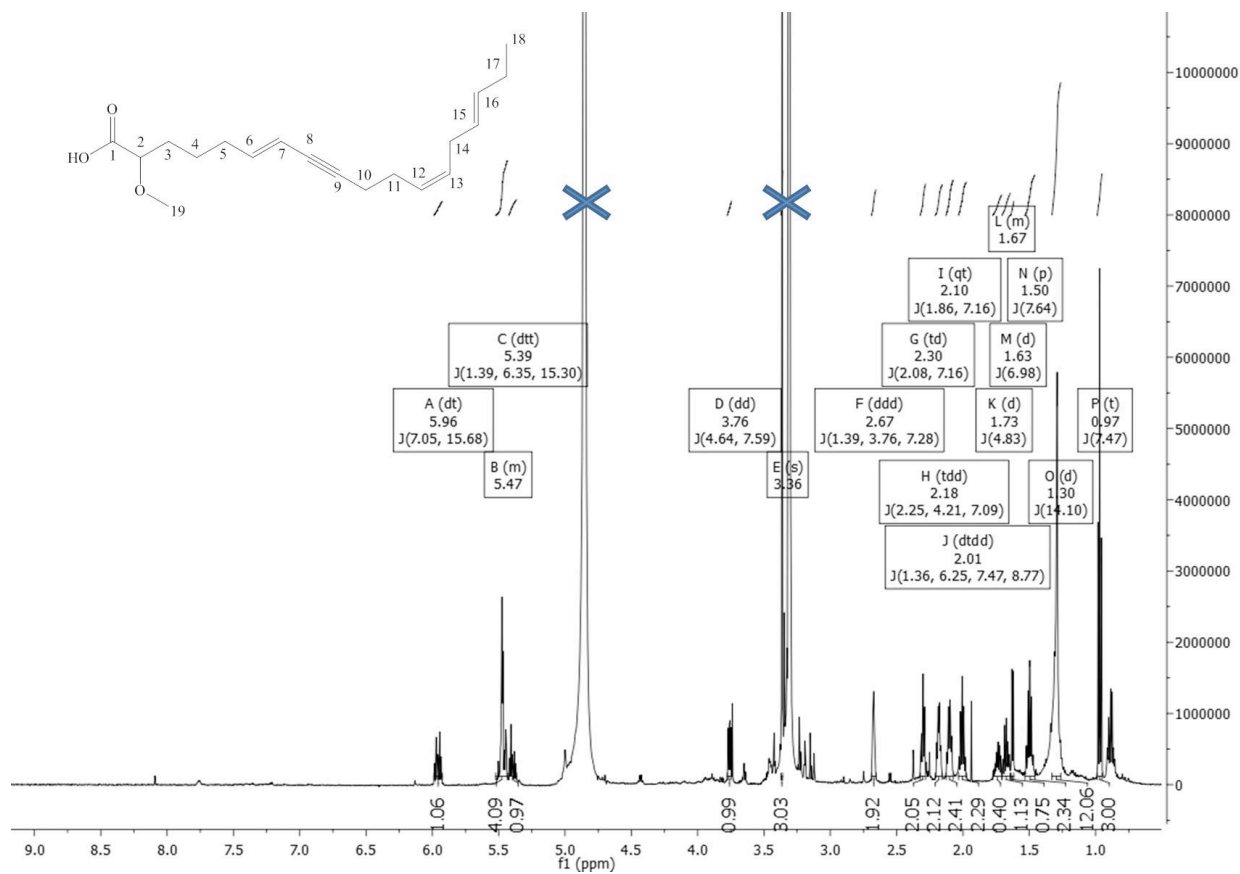


S3-7. HPLC chromatogram of 3



S3-8. UV spectrum of 3

S4. Cinachylenic acid A (4)



S4-1. ¹H NMR (MeOH-*d*₄, 600 MHz) spectrum of 4

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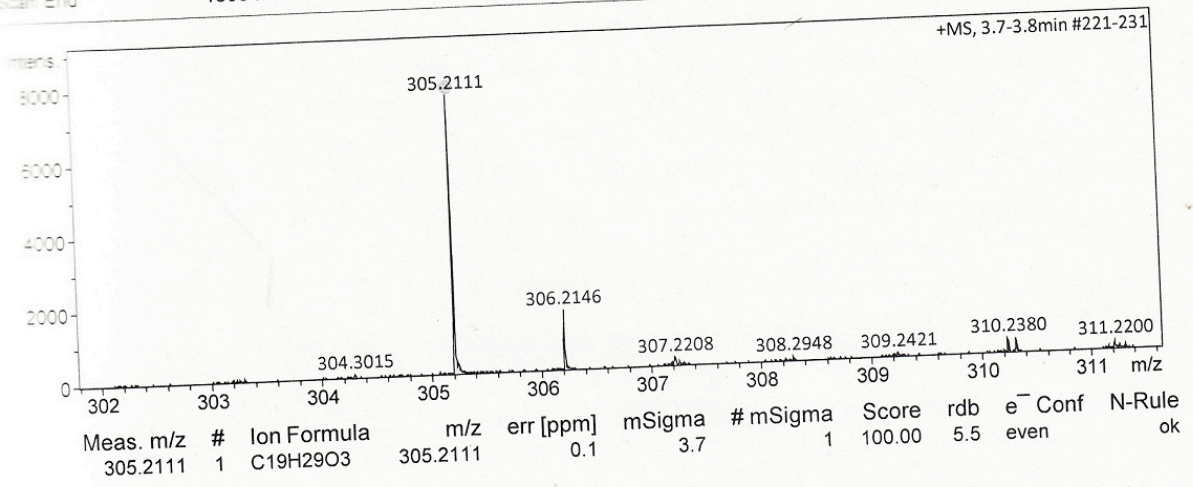
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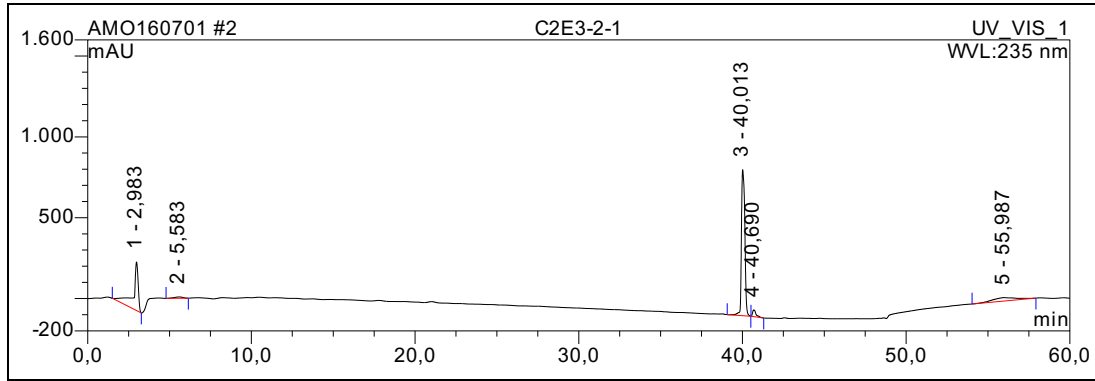
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 Instrument maXis 288882.20213

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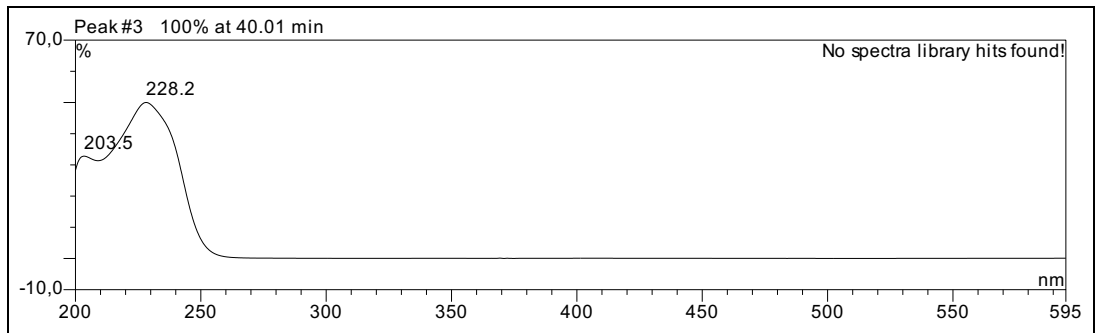
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S4-2. HRESIMS spectrum of 4

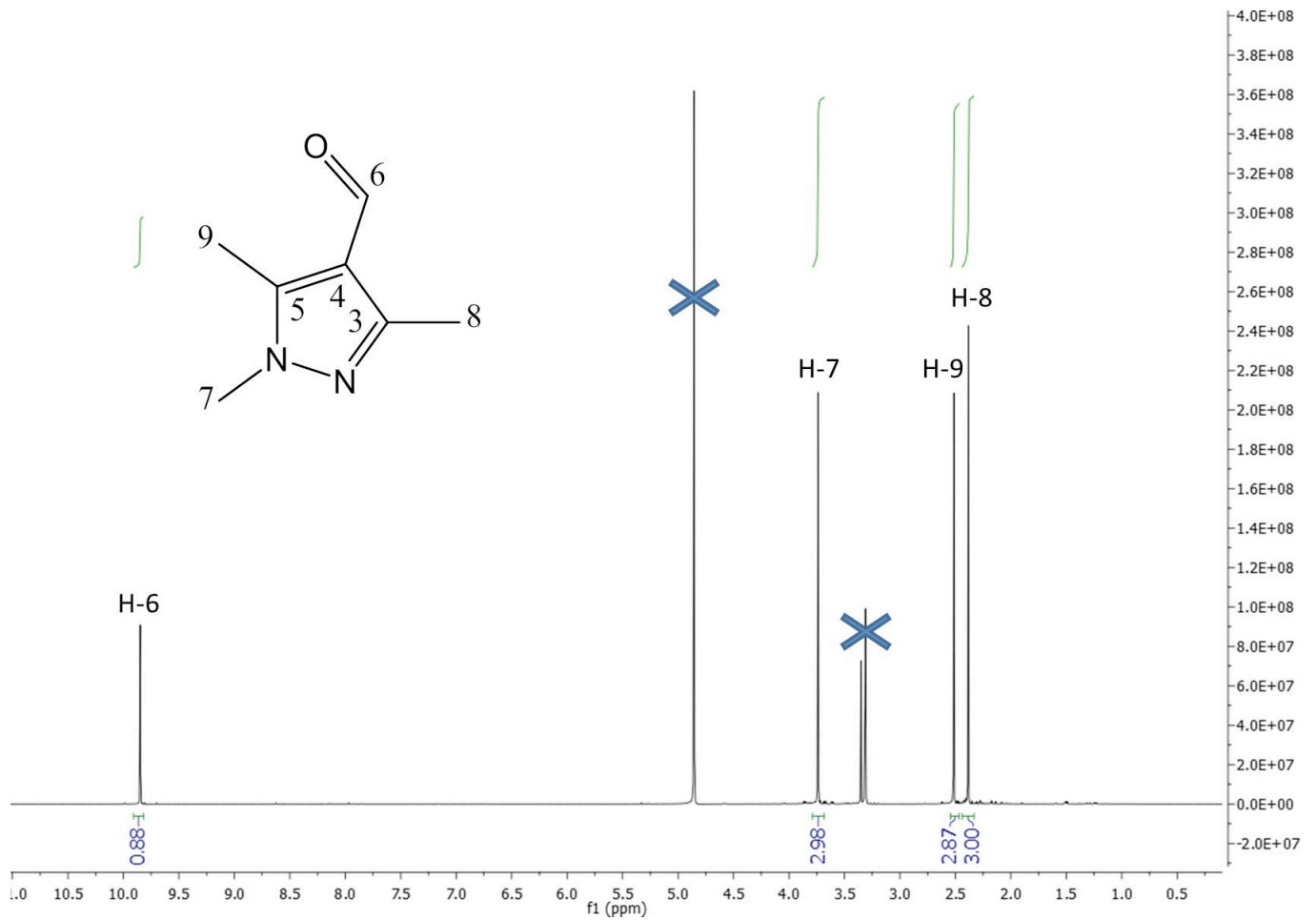


S4-3. HPLC chromatogram of 4

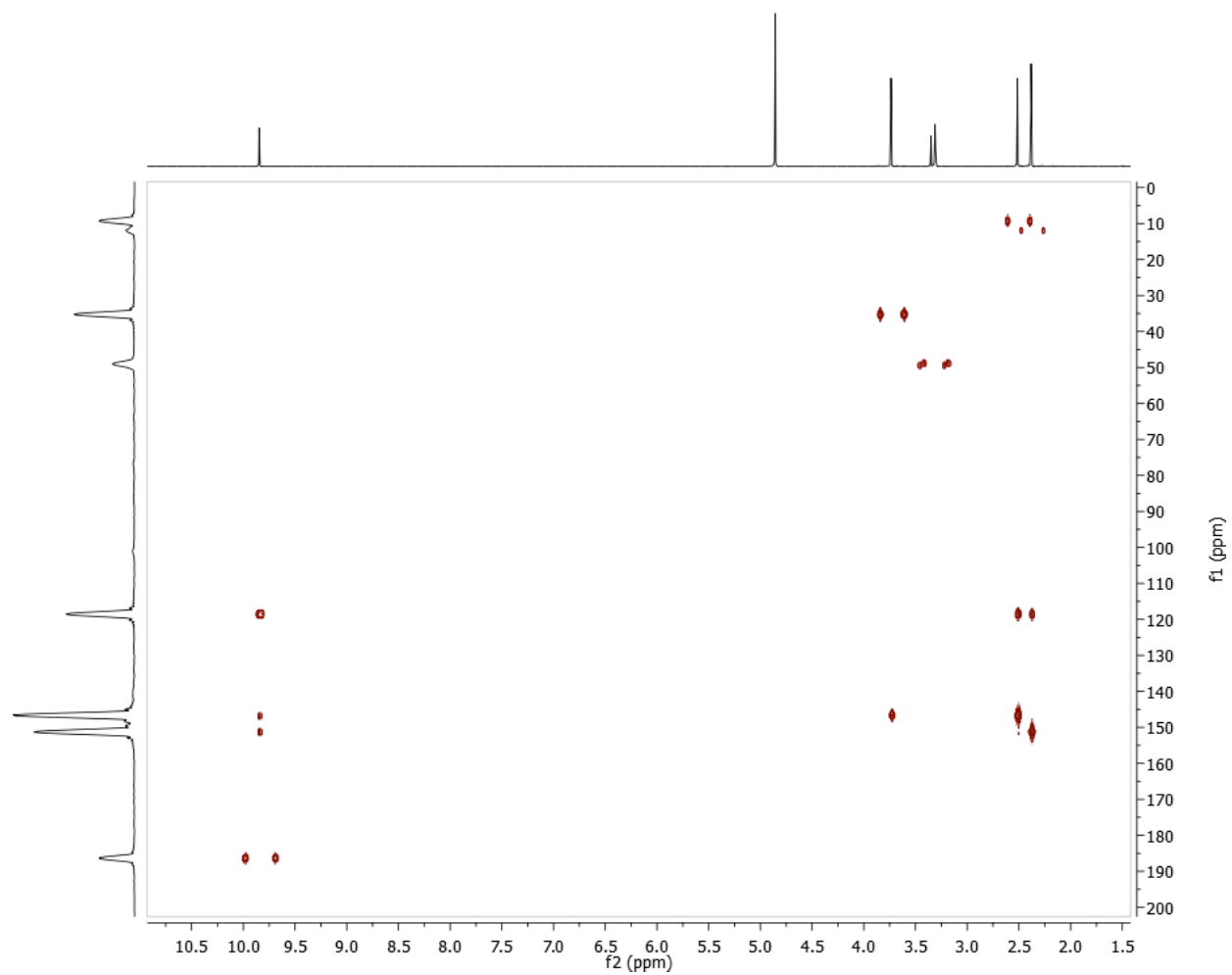


S4-4. UV spectrum of 4

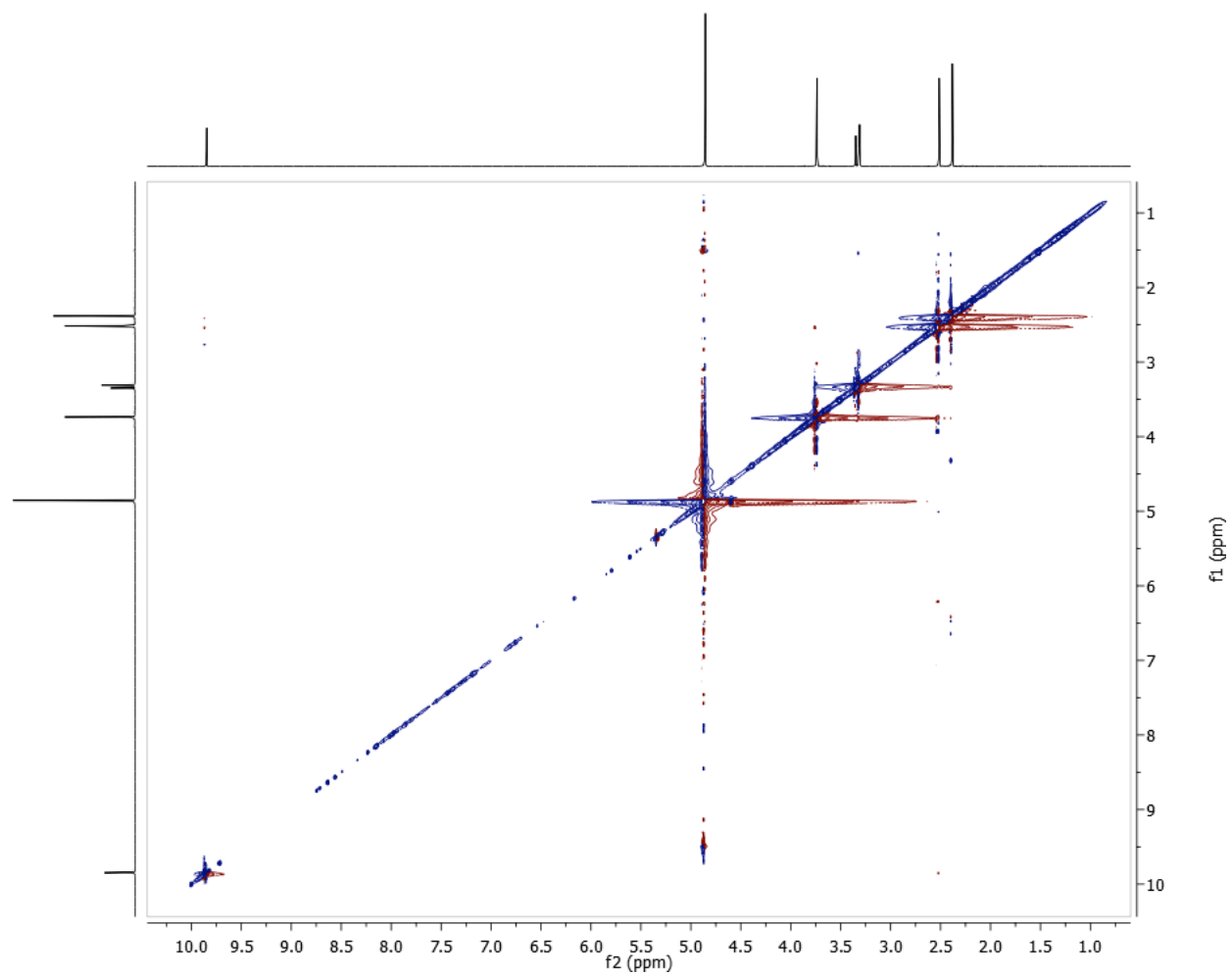
S5. Cinachyrazole A (5)



S5-1. ^1H NMR ($\text{MeOH-}d_4$, 600 MHz) spectrum of 5



S5-2. HMBC NMR (MeOH- d_4 , 600 MHz) spectrum of **5**



S5-3. ROESY NMR (MeOH-*d*₄, 600 MHz) spectrum of **5**

Mass Spectrum SmartFormula Report

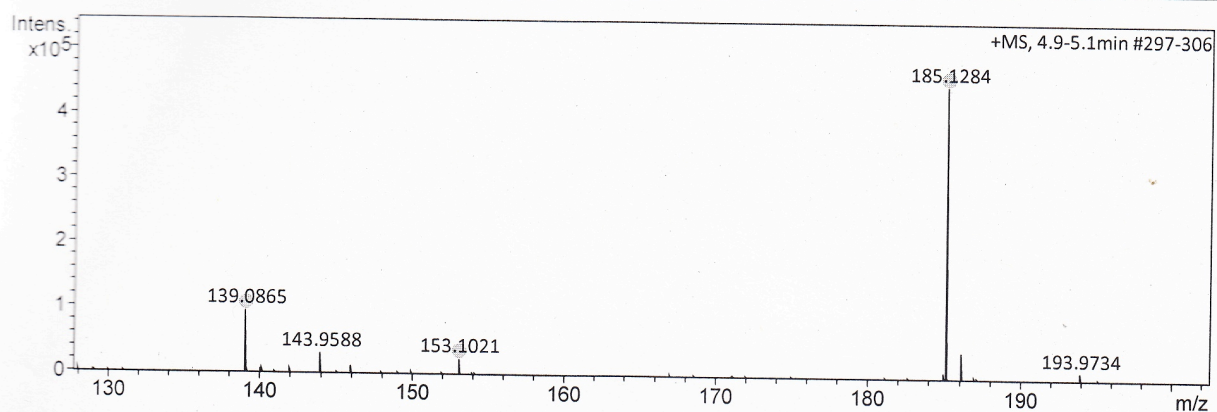
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Comment

Acquisition Date 1/9/2017 3:42:53 PM
Operator Peter Tommes
Instrument maXis 288882.20213

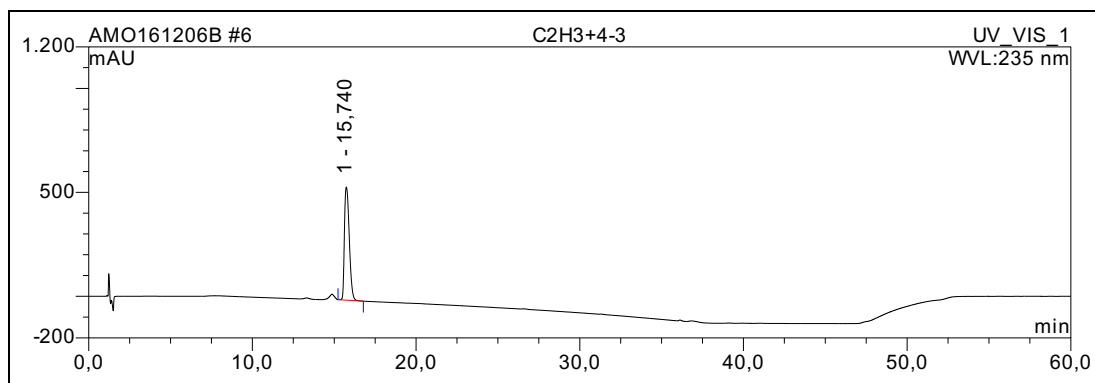
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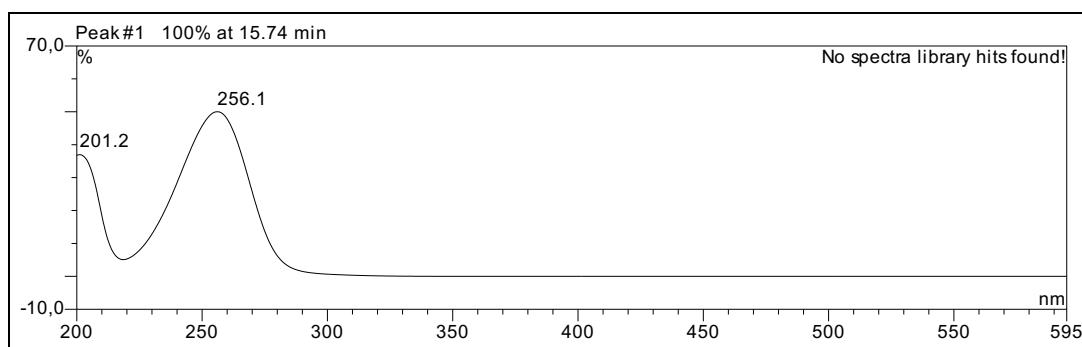


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
139.0865	1	C7H11N2O	139.0866	0.8	8.2	1	100.00	3.5	even	ok
153.1021	1	C8H13N2O	153.1022	1.0	3.8	1	100.00	3.5	even	ok
185.1284	1	C9H17N2O2	185.1285	0.0	10.3	1	100.00	2.5	even	ok

S5-4. HRESIMS spectrum of 5



S5-5. HPLC chromatogram of **5**



S5-6. UV spectrum of **5**

S5-7. Comparison of UV data of **5** with those reported in the literature

Compound	5 ¹	5 ²
UV (λ_{max} , MeOH)	201; 256	206; 252

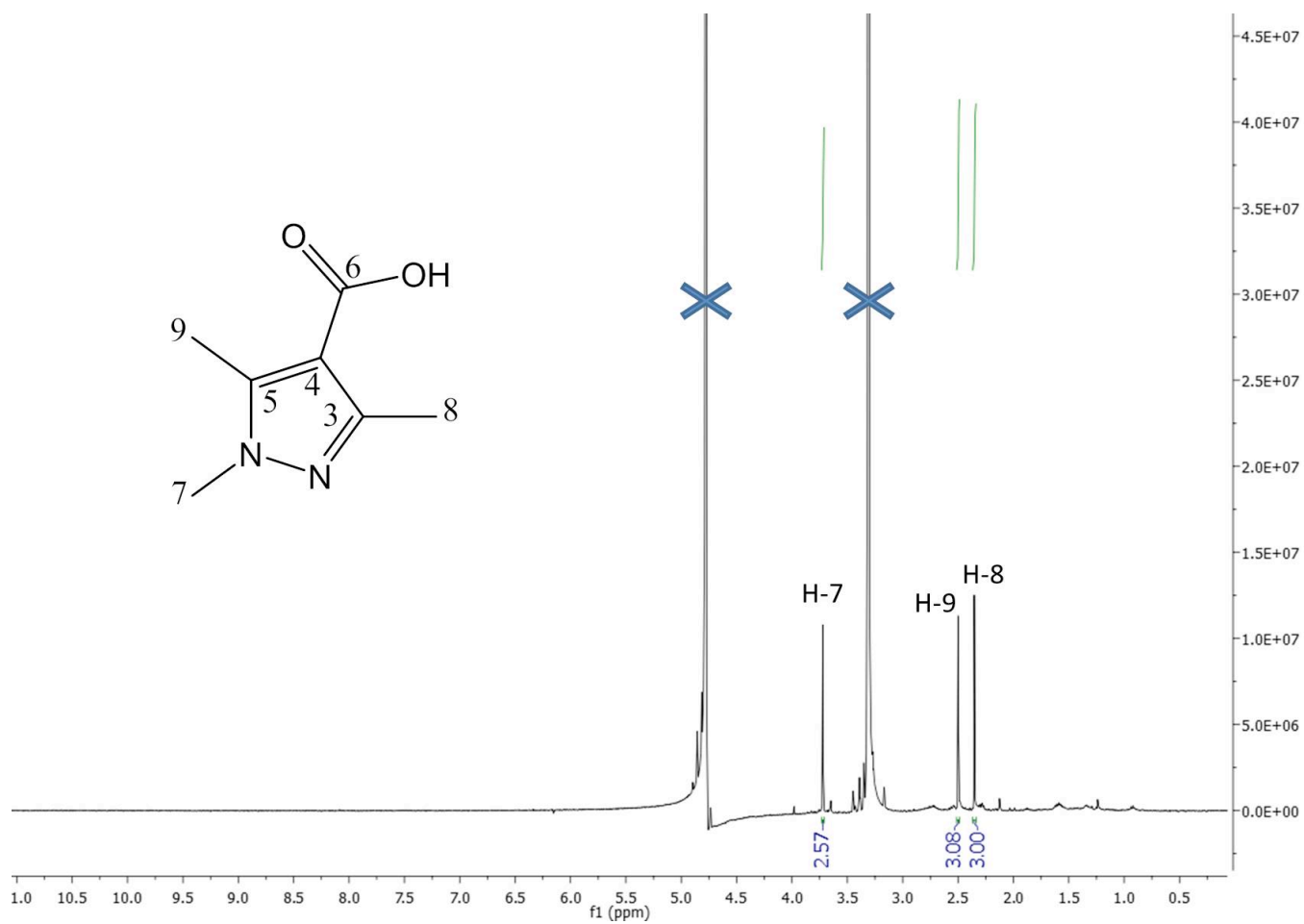
¹ Isolated in this study, ² UV data of **5** reported in the literature: Mortikov, V.Y.; Rodinovskaya, L.A.; Fedorov, A.E.; Shestopalov, A.M.; Belyakov, P.A. Synthesis of heterocyclic compounds from 4-formylpyrazoles. *Russian Chemical Bulletin* **2014**, 63, 443-456. DOI: 10.1007/s11172-014-0451-8.

S5-8. Comparison of ^1H NMR (600 MHz) data of **5** with those reported in the literature

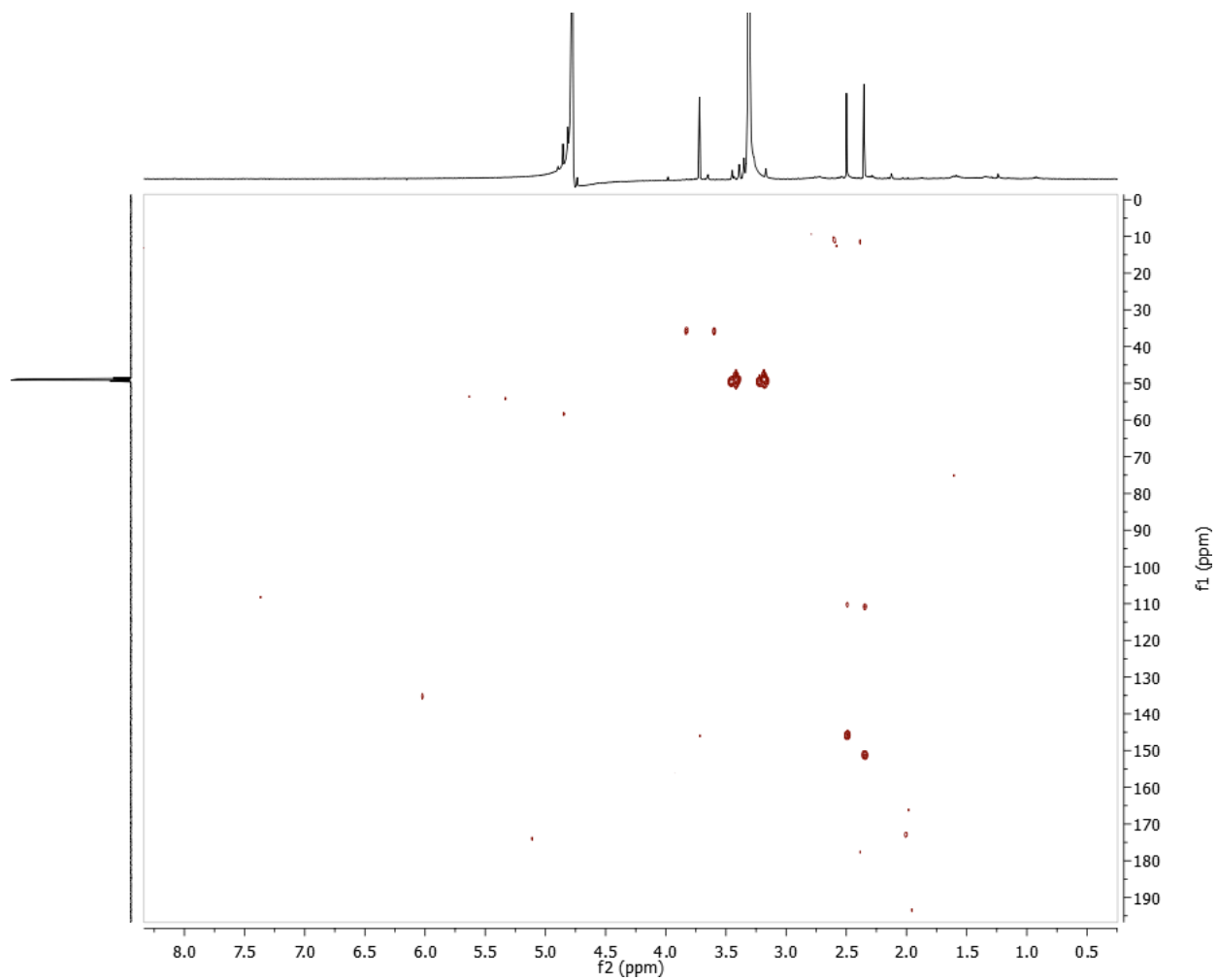
Position	5¹	5²
	(MeOH- <i>d</i> ₄ , δ in ppm) ^1H (<i>J</i> in Hz)	(DMSO- <i>d</i> ₆ , δ in ppm) ^1H (<i>J</i> in Hz)
6	9.85, s	9.81, s
7	3.74, s	3.68, s
8	2.38, s	2.29, s
9	2.51, s	2.45, s

¹ Isolated in this study, ² ^1H NMR data of **5** reported in the literature: Mortikov, V.Y.; Rodinovskaya, L.A.; Fedorov, A.E.; Shestopalov, A.M.; Belyakov, P.A. Synthesis of heterocyclic compounds from 4-formylpyrazoles. *Russian Chemical Bulletin* **2014**, 63, 443-456. DOI: 10.1007/s11172-014-0451-8.

S6. Cinachyrazole B (6)



S6-1. ¹H NMR (MeOH-d₄, 600 MHz) spectrum of 6



S6-2. HMBC NMR (MeOH- d_4 , 600 MHz) spectrum of **6**

Mass Spectrum SmartFormula Report

Analysis Info

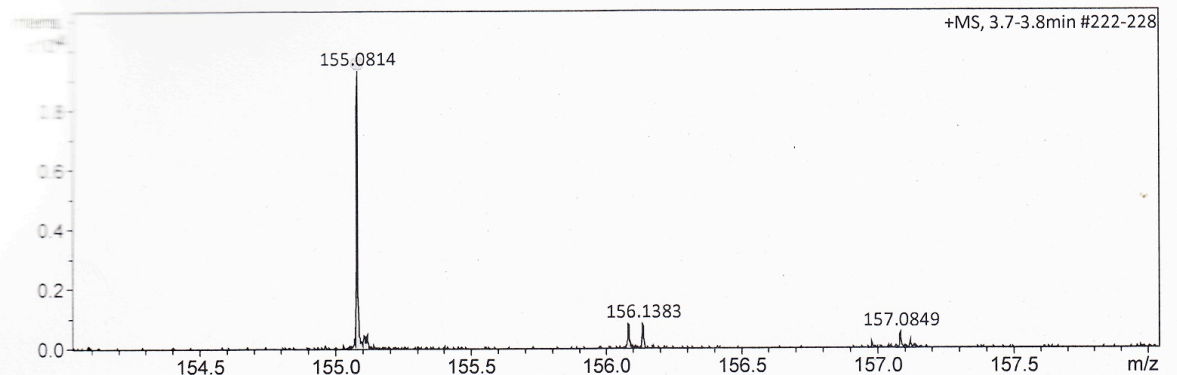
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Sample Name Amin-Mokhtesi C2B5-2 (CH3OH)
Comment

Acquisition Date 2/10/2017 9:29:17 AM

Operator Peter Tommes
Instrument maXis 288882.20213

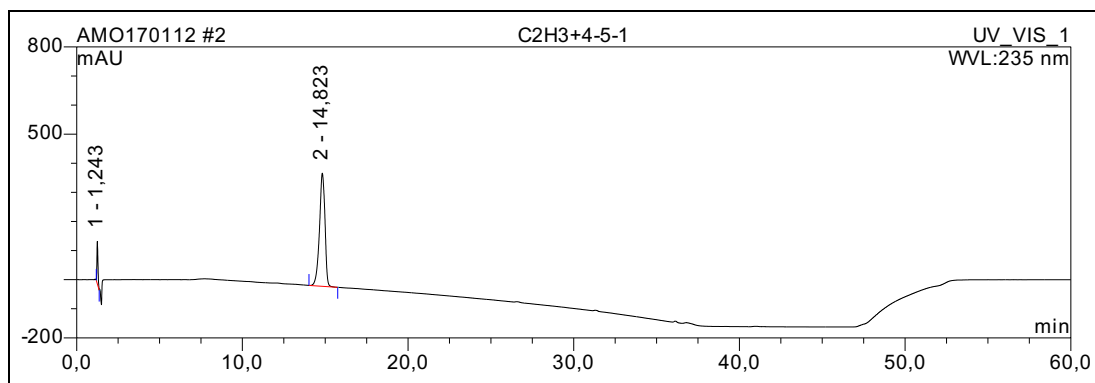
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Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

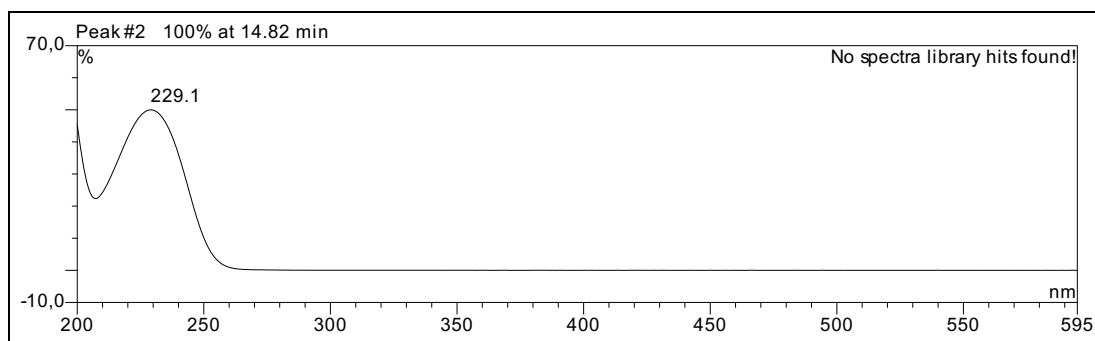


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
155.0814	1	C7H11N2O2	155.0815	0.6	27.8	1	100.00	3.5	even	ok

S6-3. HRESIMS spectrum of 6



S6-4. HPLC chromatogram of 6



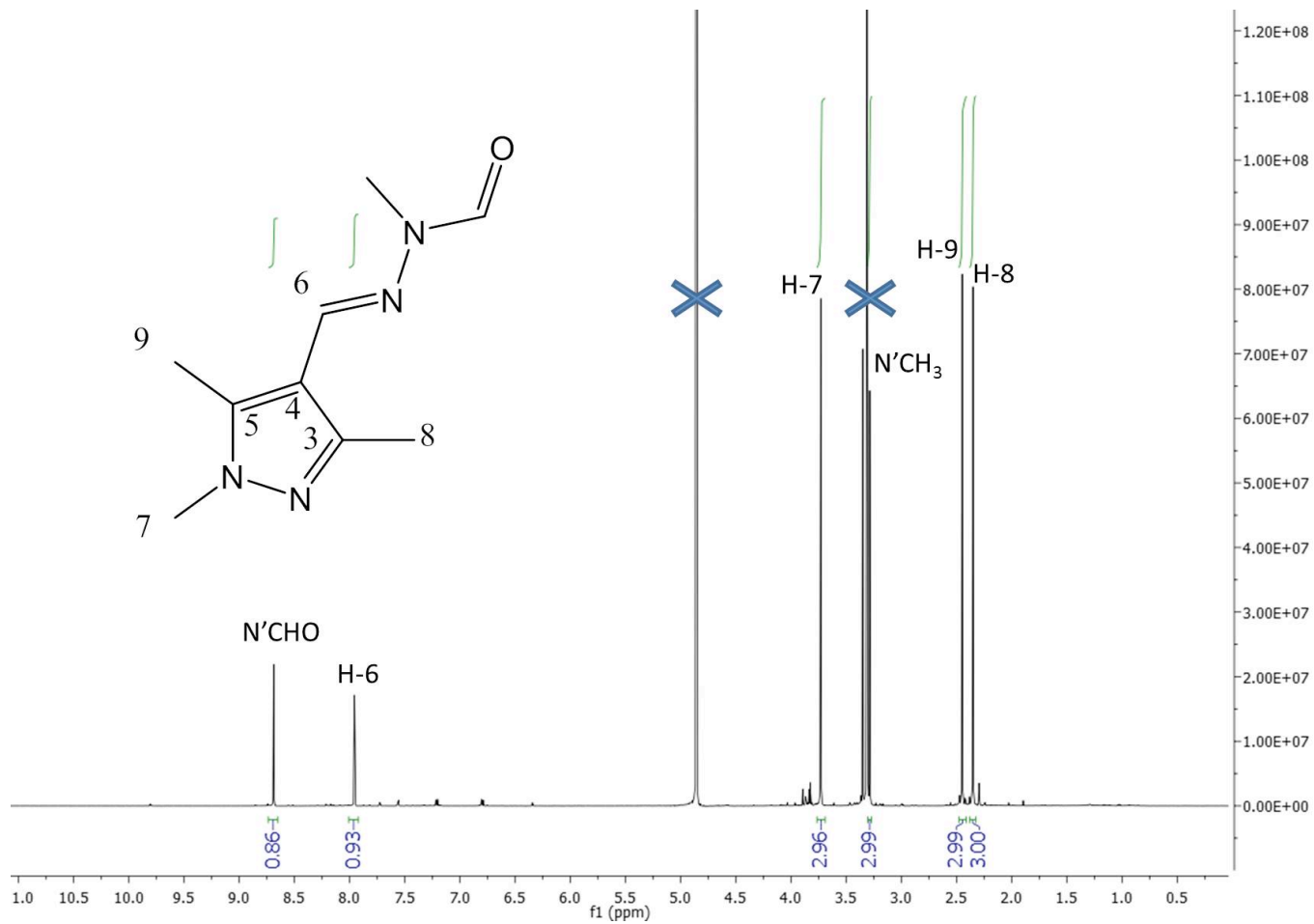
S6-5. UV spectrum of 6

S6-6. Comparison of the ^{13}C NMR (150 MHz) data of **6** with those reported in the literature

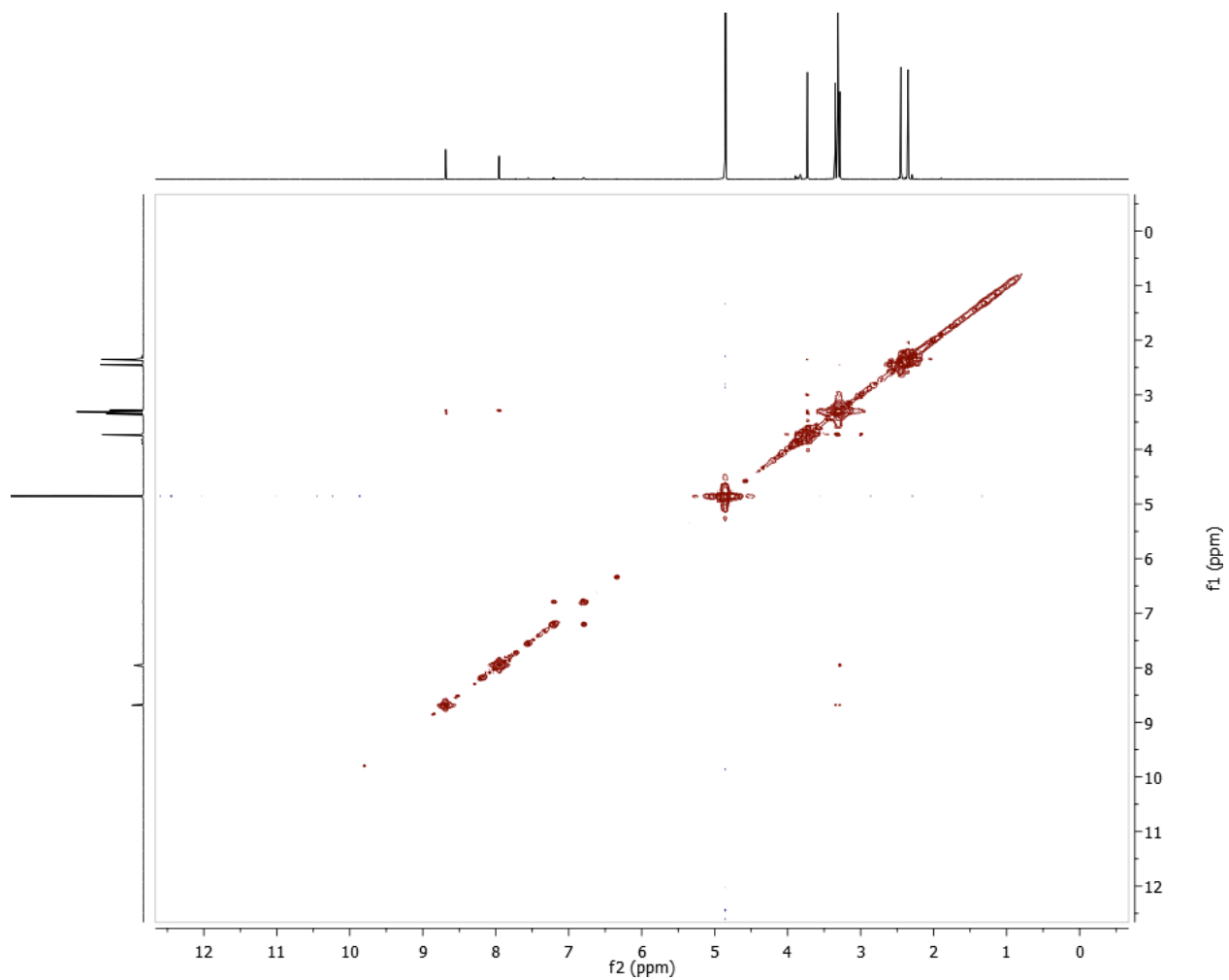
Position	6 ¹	6 ⁴
	^{13}C , type ² (MeOH- <i>d</i> ₄ , δ in ppm)	^{13}C , type (DMSO- <i>d</i> ₆ , δ in ppm)
3	151.2, C	148.7, C
4	110.5, C	109.1, C
5	145.7, C	143.5, C
6	– ³	– ⁵
7	35.8, CH ₃	35.6, CH ₃
8	– ³	– ⁵
9	11.5, CH ₃	– ⁵

¹ Isolated in this study, ² Data extracted from HMBC spectra, ³ Not observed, ⁴ ^{13}C NMR data of **6** reported in the literature: Begtrup, M., Boyer, G., Cabildo, P., Cativiela, C., Claramunt, R.M., Elguero, J., García, J.I., Toiron, C., Vedsø, P. ^{13}C NMR of pyrazoles. *Magnetic resonance in chemistry* **1993**, 31:107-68. DOI: 10.1002/mrc.1260310202, ⁵ Not reported.

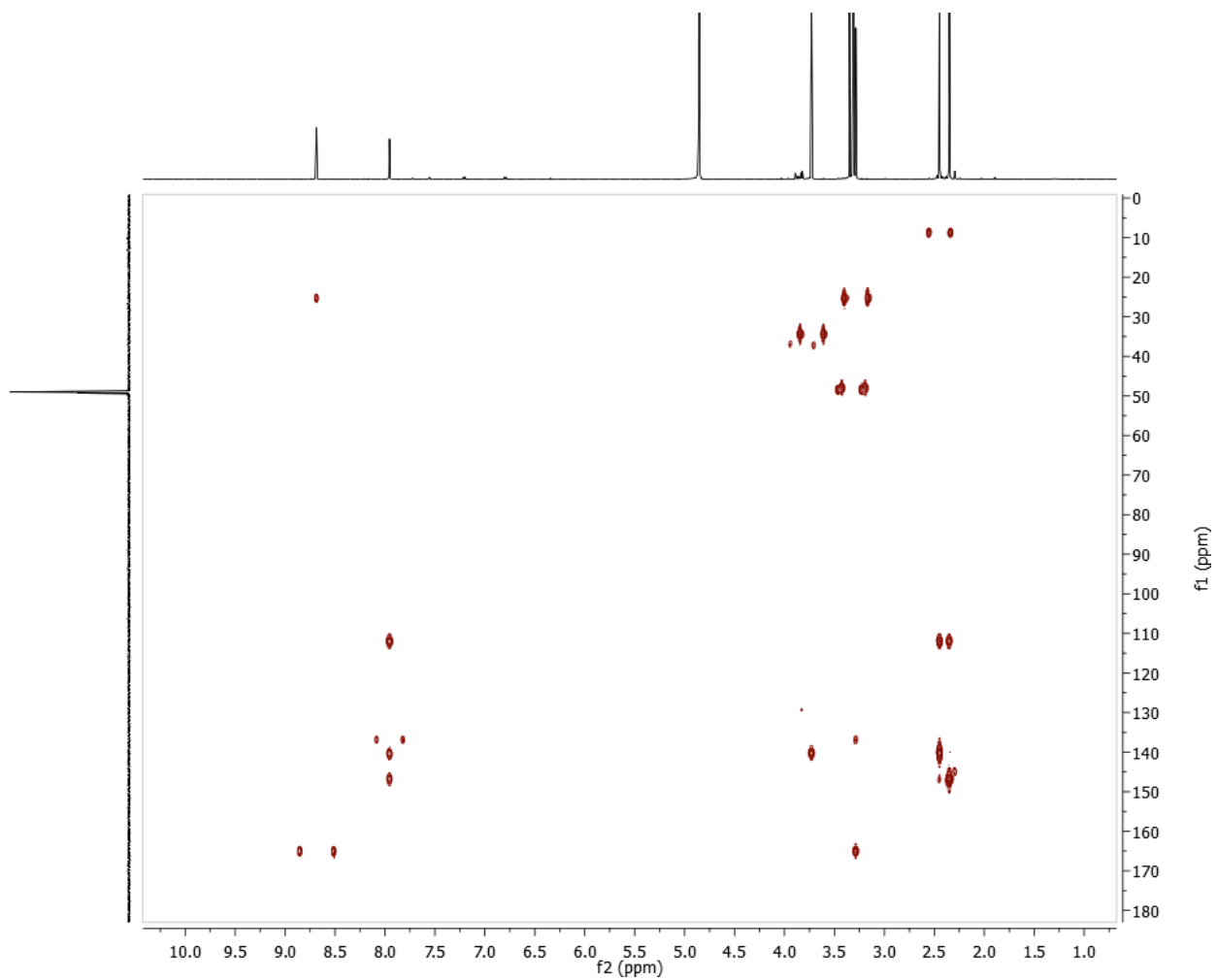
S7. Cinachyrazole C (7)



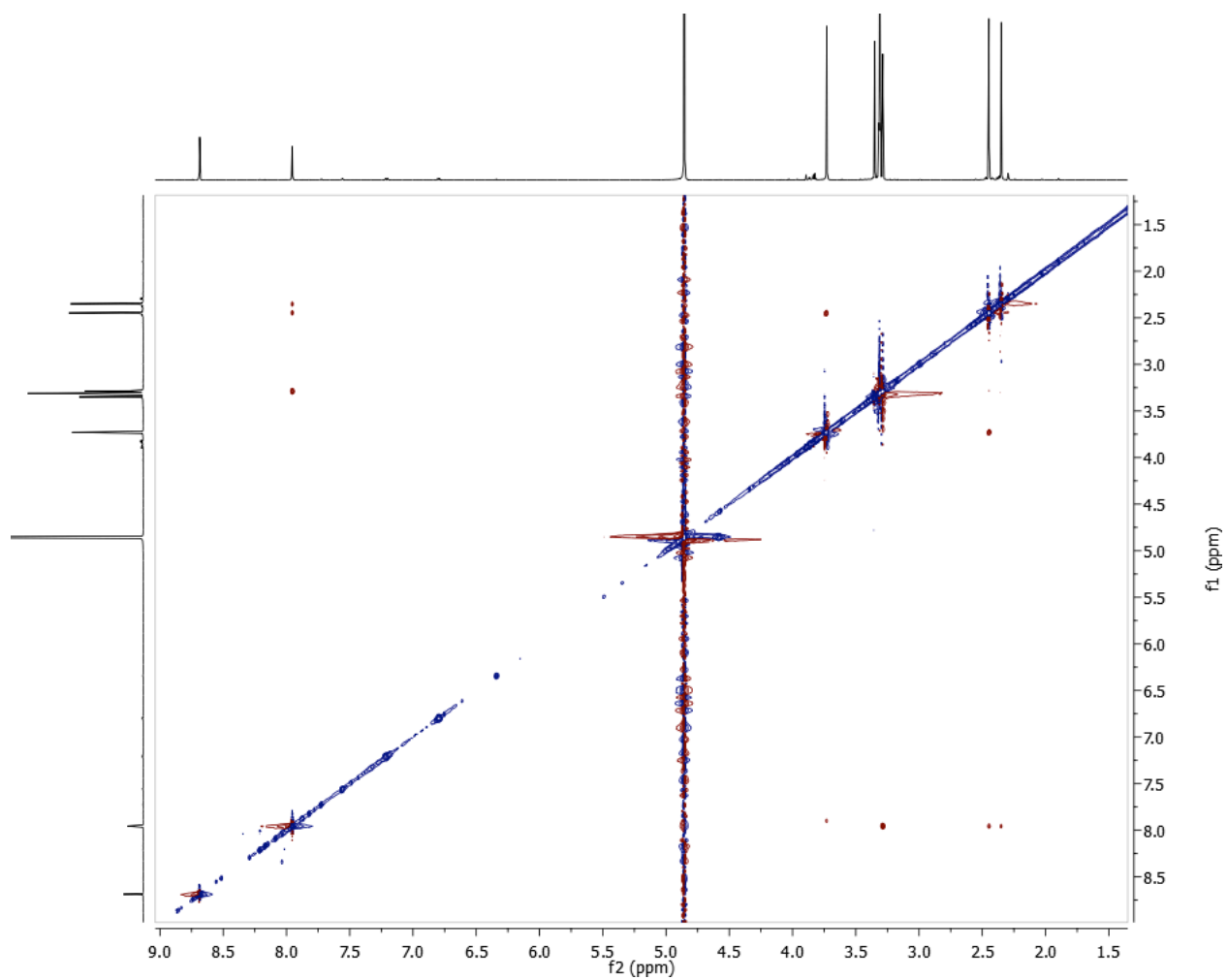
S7-1. ¹H NMR (MeOH-*d*₄, 600 MHz) spectrum of 7



S7-2. COSY NMR (MeOH- d_4 , 600 MHz) spectrum of 7



S7-3. HMBC NMR (MeOH- d_4 , 600 MHz) spectrum of 7



S7-4. ROESY NMR (MeOH-*d*₄, 600 MHz) spectrum of 7

Mass Spectrum SmartFormula Report

Analysis Info

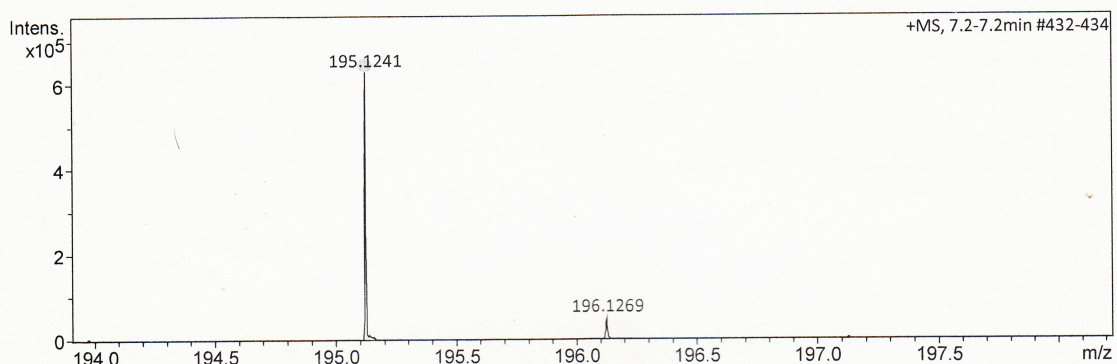
Analysis Name D:\Data\spektren2017\Proksch17HR000006.d
 Method tune_low_new.m
 Sample Name Amin Mokhlesi C2E5-3 (CH3OH)
 Comment

Acquisition Date 1/4/2017 3:09:42 PM

Operator Peter Tommes
 Instrument maXis 288882.20213

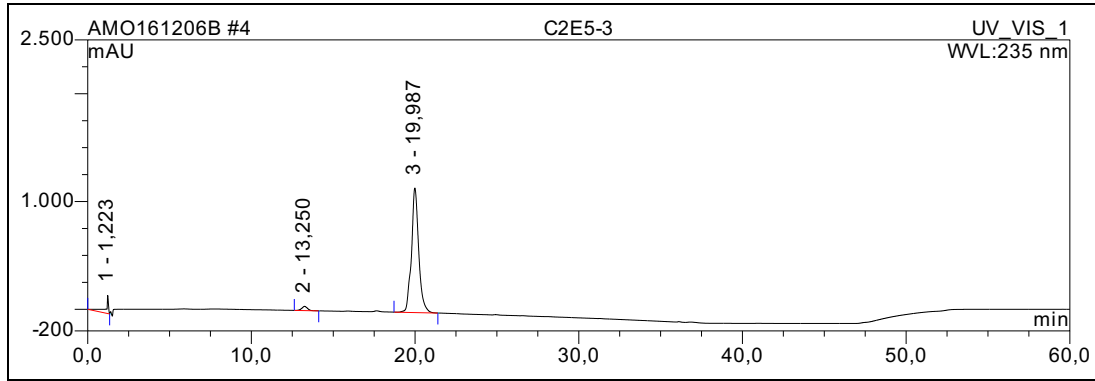
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

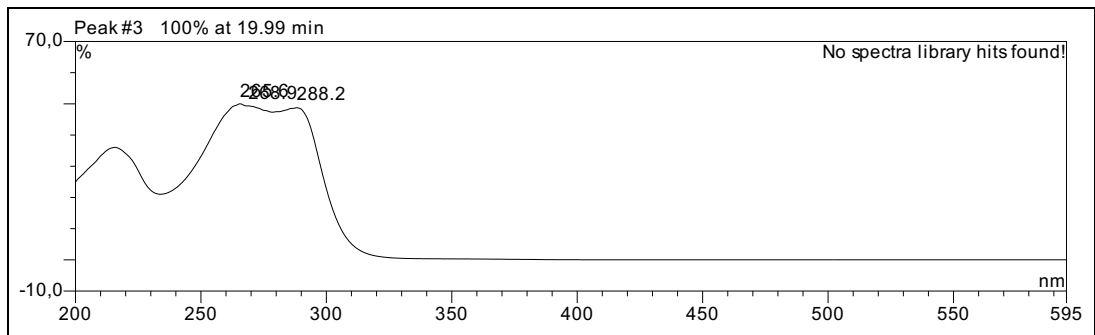


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
195.1241	1	C8H19O5	195.1227	-7.3	7.8	1	62.61	-0.5	even	ok
	2	C9H15N4O	195.1240	-0.4	19.8	2	100.00	4.5	even	ok

S7-5. HRESIMS spectrum of 7



S7-6. HPLC chromatogram of 7



S7-7. UV spectrum of 7