

# Supporting Information

for

## An improved preparation of phorbol from croton oil

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### ESI-HRMS and <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **1d** and **1e**

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**1. General Experimental Procedures.** 1D and 2D NMR spectra were recorded on a Bruker 700 Avance III HD ( $^1\text{H}$  NMR - 700.47 MHz;  $^{13}\text{C}$  NMR 176.13 MHz) in  $\text{CDCl}_3$ :  $\delta$  in ppm,  $J$  in Hz. Low resolution electrospray ionisation mass spectrometry measurements (LRESIMS) were recorded in positive or negative ionization mode on a Bruker Esquire HCT (High Capacity 3D ion trap) instrument with a Bruker ESI source. High resolution electrospray ionisation (HRESIMS) accurate mass measurements were recorded in positive mode on a Bruker MicrOTOF-Q (quadrupole – Time of Flight) instrument with a Bruker ESI source. Accurate mass measurements were carried out with external calibration using sodium formate as reference calibrant.

## 2. ESI HRMS of the sample **1d/1e** (2/1) in negative mode.

### Analysis Info

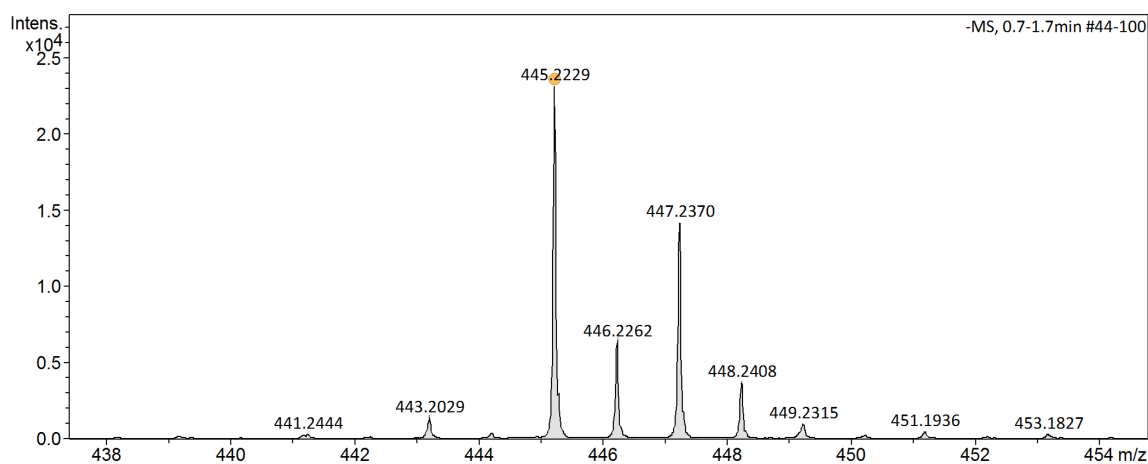
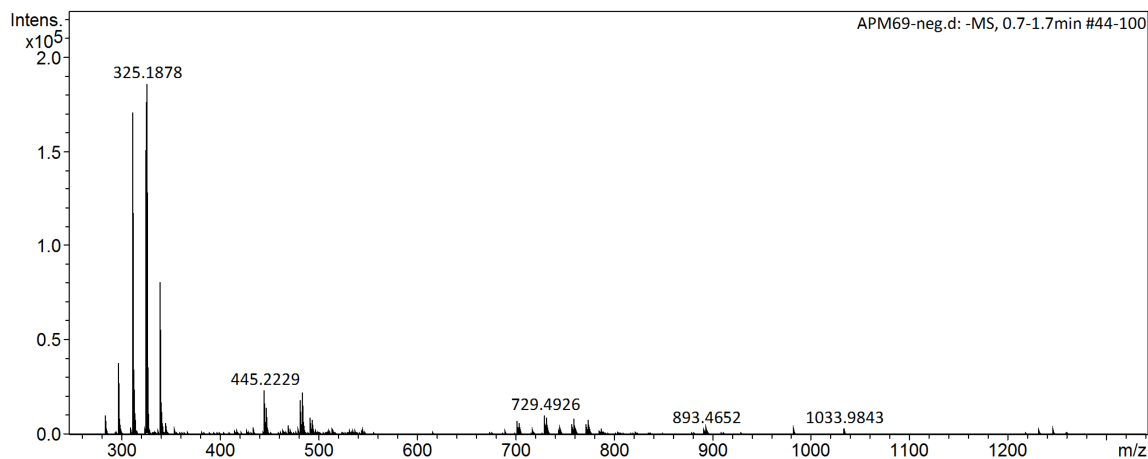
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 Sample Name  
 Comment

Acquisition Date 9/8/2016 4:49:05 PM

Operator BDAL@DE  
 Instrument micrOTOF-Q 228888.00070

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 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	3500 m/z	Set Collision Cell RF	550.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdB	e <sup>-</sup> Conf	N-Rule
445.2229	1	C25H33O7	445.2232	0.7	291.4	1	100.00	9.5	even	ok

### 3. ESI HRMS of the sample **1d/1e** (2/1) positive mode.

#### Analysis Info

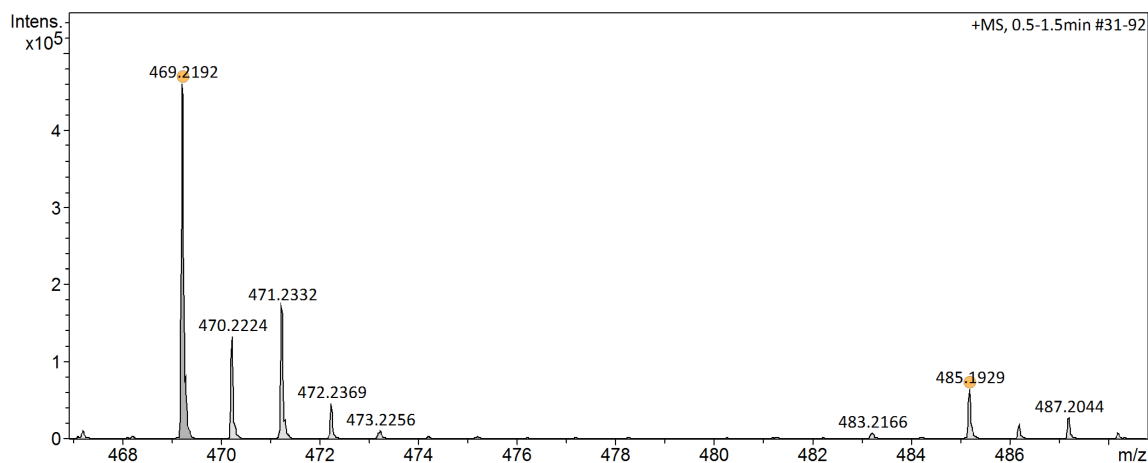
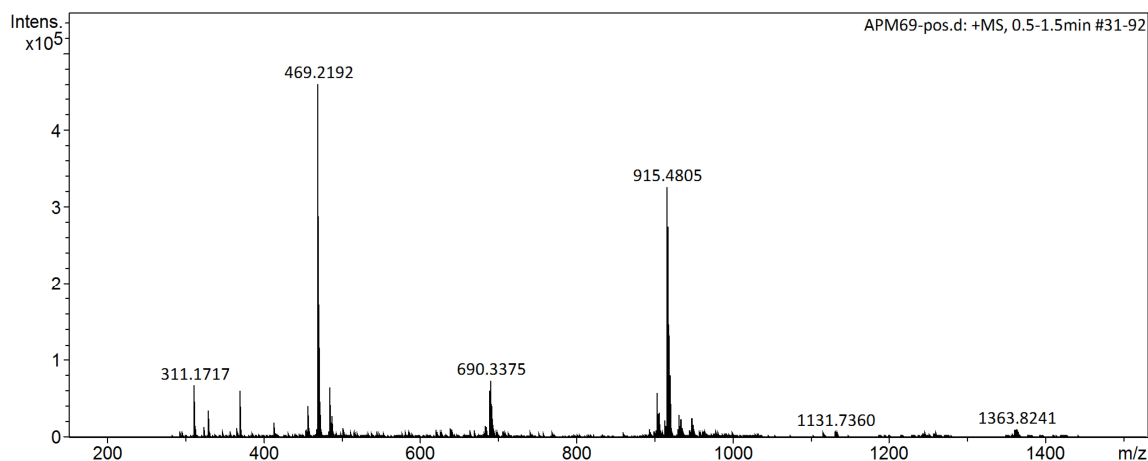
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 Sample Name  
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Acquisition Date 9/8/2016 4:54:41 PM

Operator BDAL@DE  
 Instrument micrOTOF-Q 228888.00070

#### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 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	3500 m/z	Set Collision Cell RF	550.0 Vpp	Set Divert Valve	Source



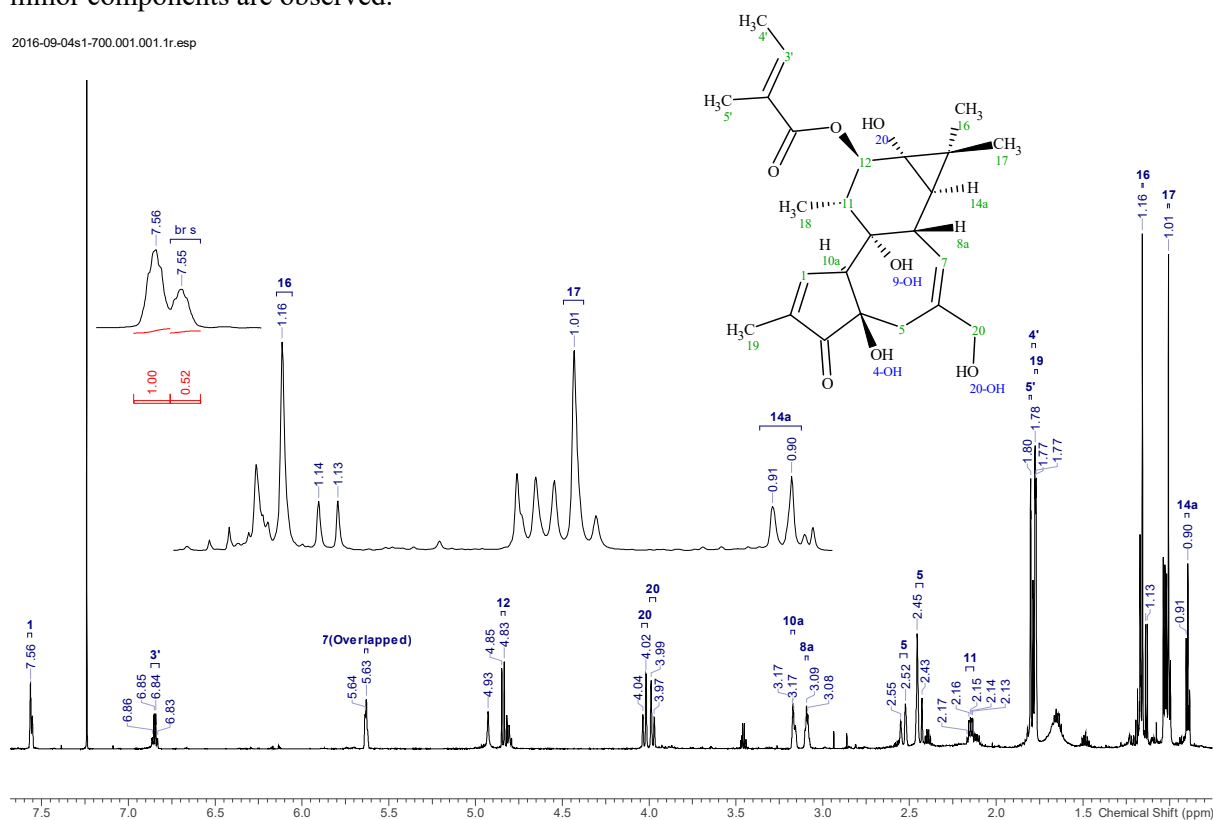
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
469.2192	1	C25H34NaO7	469.2197	1.1	166.9	1	100.00	8.5	even	ok
485.1929	1	C25H34KO7	485.1936	1.5	63.3	1	100.00	8.5	even	ok

4. Tabulated NMR data for **1d** compound recorded in CDCl<sub>3</sub> at 176/700 MHz.

No.	<sup>13</sup> C	<sup>1</sup> H	Multiplicity ( <i>J</i> in Hz)
1	160.28	7.56	s
2	133.41		
3	208.80		
4	73.49		
5a	38.74	2.44	m
5b	38.74	2.54	m
6	140.74		
7	129.29	5.63	m
8	38.99	3.09	m
9	79.17		
10	56.77	3.17	br d (2.54)
11	43.50	2.15	m
12	87.36	4.84	d (9.81)
13	60.83		
14	35.19	0.90	m
15	27.69		
16	22.27	1.16	s
17	17.03	1.01	s
18	16.08	1.03	u
19	10.14	1.77	dd (2.91, 1.27)
20a	67.97	3.98	m
20b	67.97	4.03	m
1'	170.51		
2'	128.13		
3'	138.66	6.85	qd (7.08, 1.27)
4'	14.51	1.78	m
5'	12.05	1.80	d (1.09)
9-OH		4.93	br s

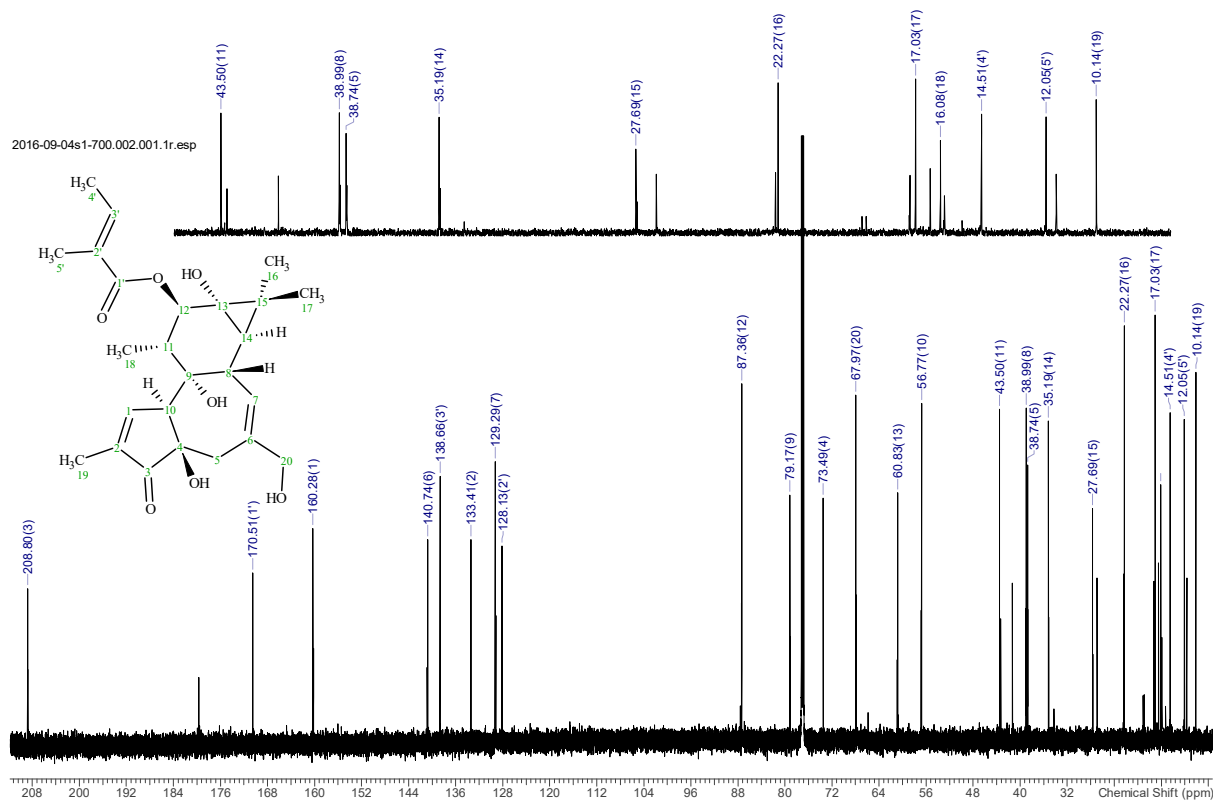
5.  $^1\text{H}$  NMR spectrum and assignments for **1d** recorded in  $\text{CDCl}_3$ . In expansions the signals of the minor components are observed.

2016-09-04s1-700.001.001.1r.esp



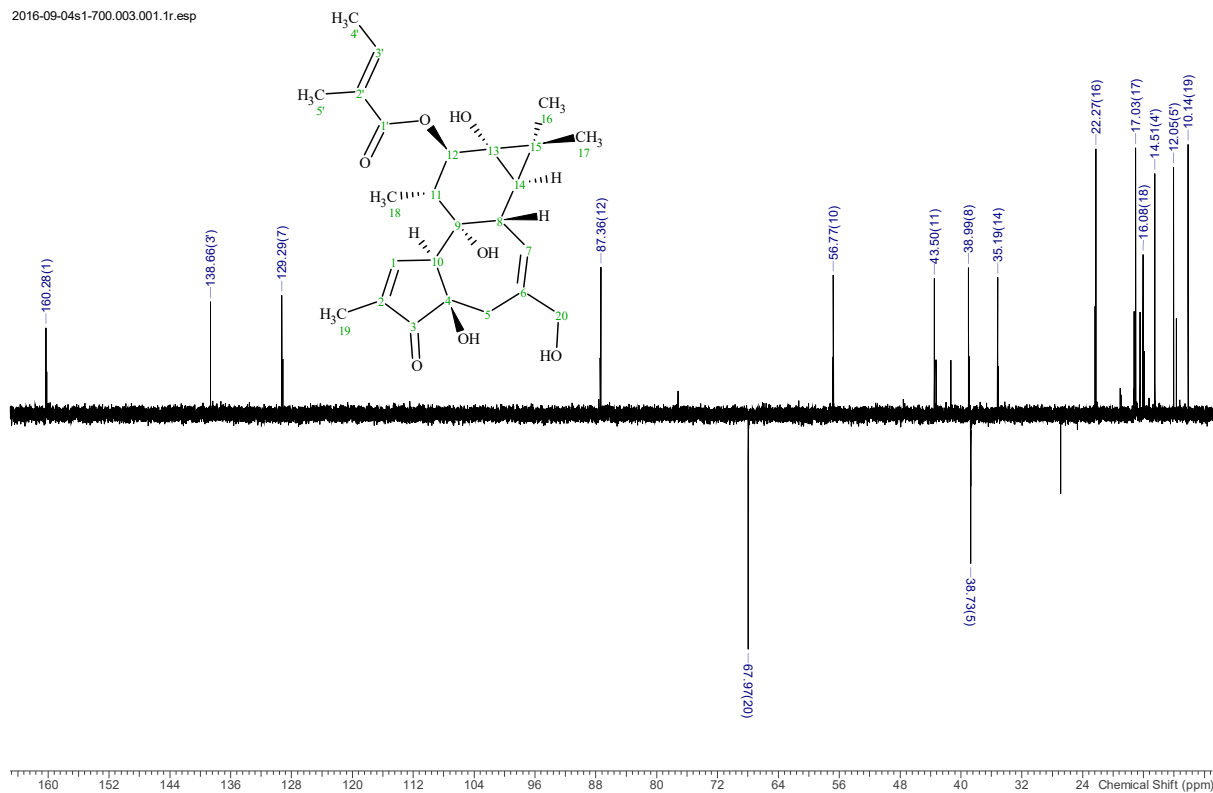
6.  $^{13}\text{C}$  NMR spectrum and assignments for **1d** recorded in  $\text{CDCl}_3$ . In expansions the signals of the minor components are observed.

2016-09-04s1-700.002.001.1r.esp



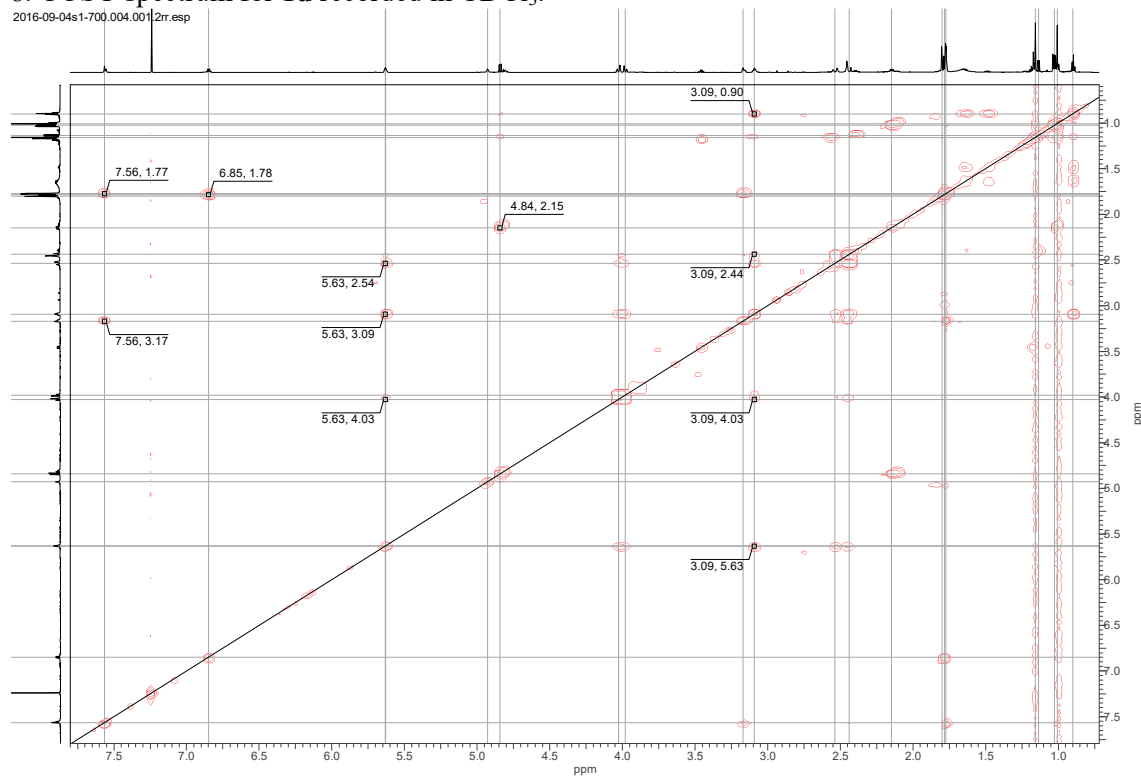
## 7. DEPT spectrum for **1d** recorded in CDCl<sub>3</sub>.

2016-09-04s1-700.003.001.1r.esp

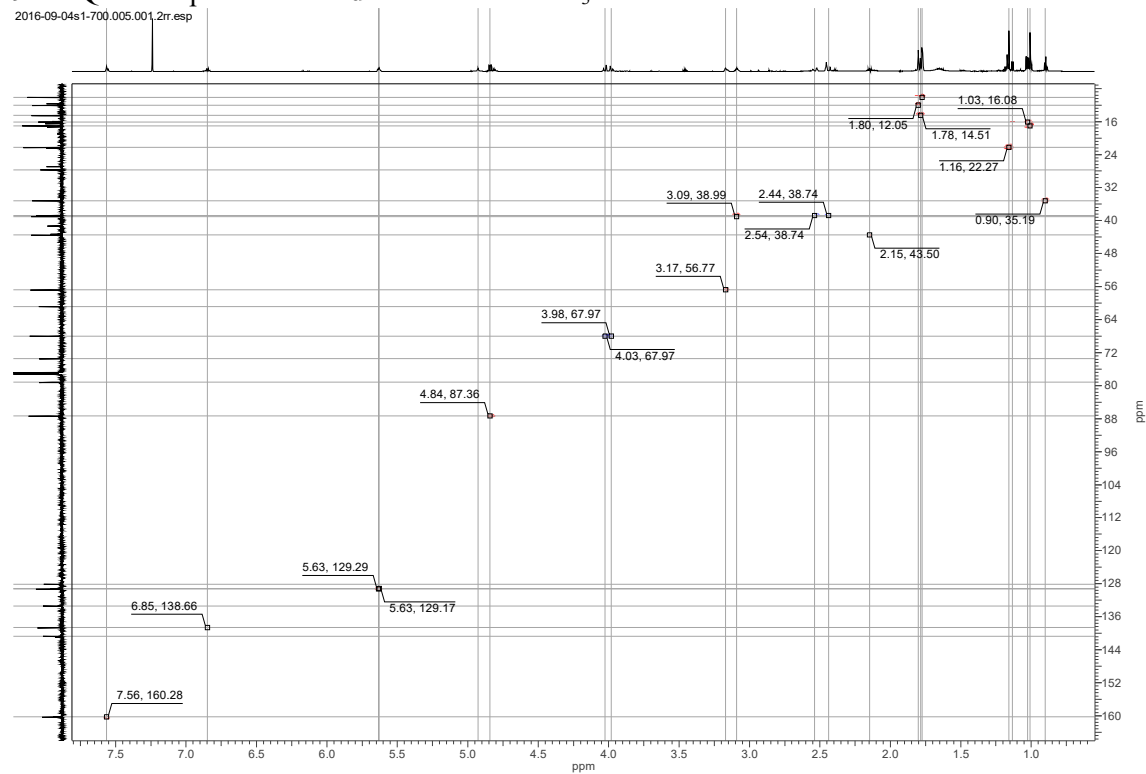


## 8. COSY spectrum for **1d** recorded in CDCl<sub>3</sub>.

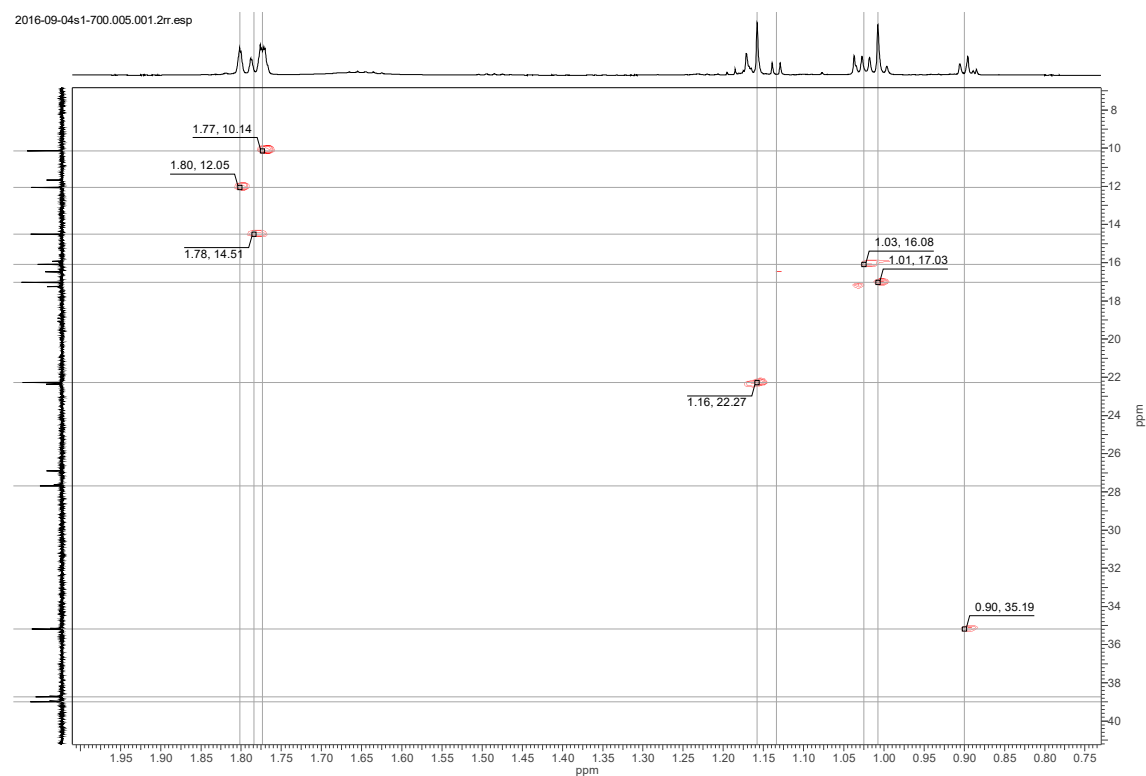
2016-09-04s1-700.004.001.2r.esp



9. HSQC edit spectrum for **1d** recorded in CDCl<sub>3</sub>.

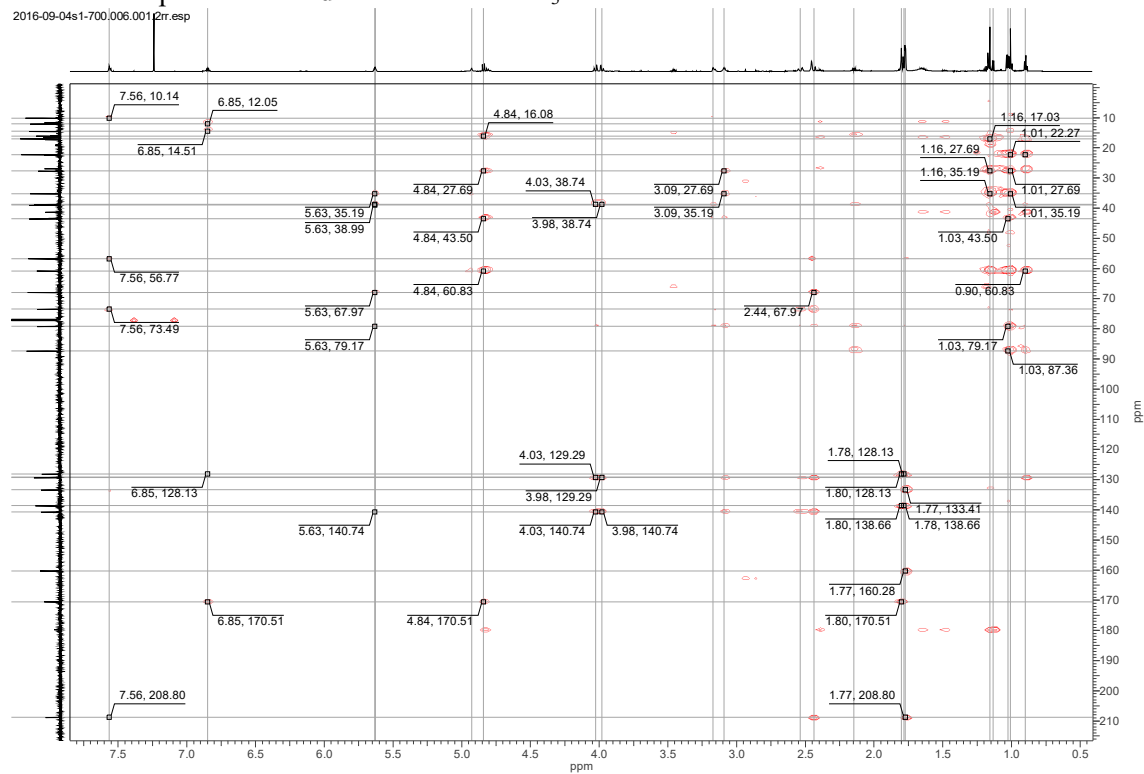


10. HSQC spectrum for **1d** recorded in CDCl<sub>3</sub>, 0.7-2.0×5-45 ppm expansion.

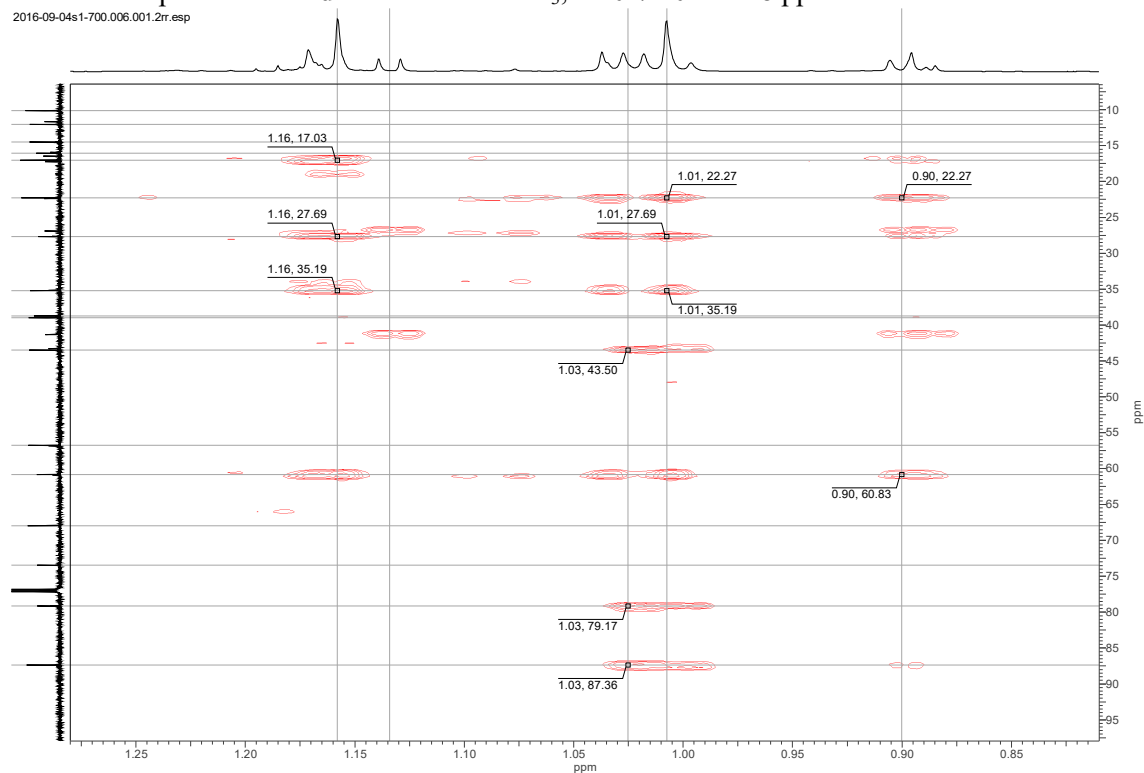




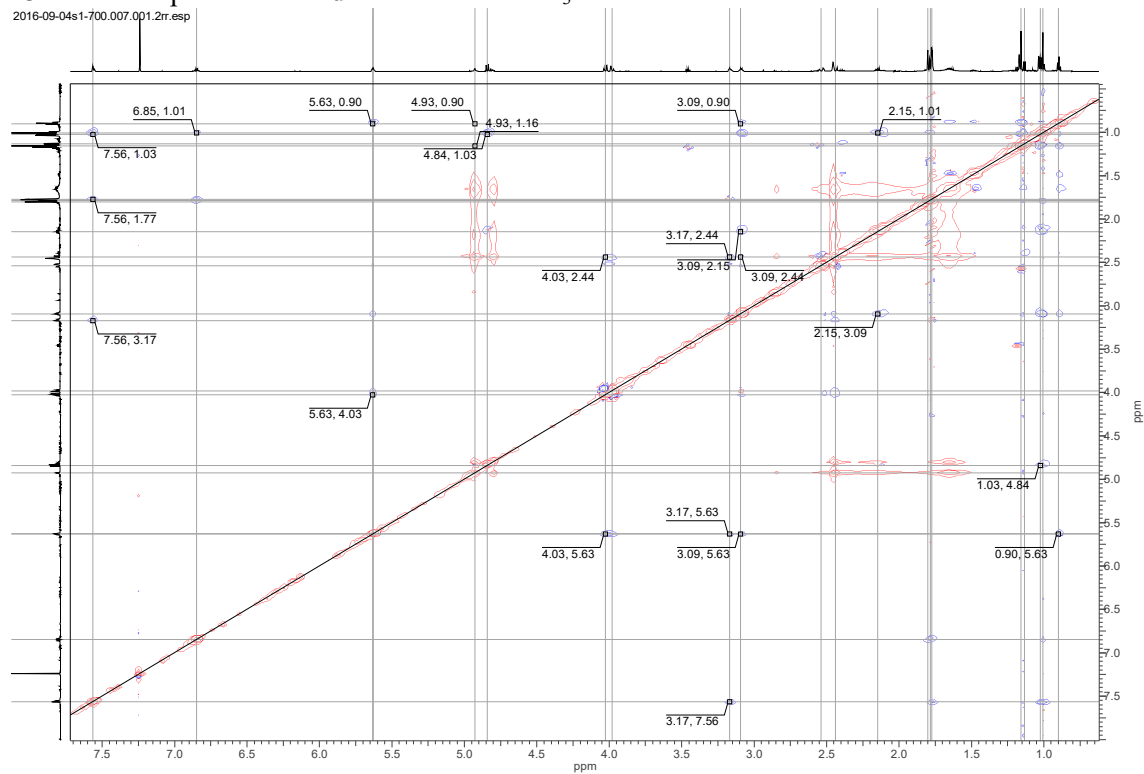
### 11. HMBC spectrum for **1d** recorded in CDCl<sub>3</sub>.



### 12. HMBC spectrum for **1d** recorded in CDCl<sub>3</sub>, 1.40-7.40×2-218 ppm.



### 13. NOESY spectrum for **1d** recorded in CDCl<sub>3</sub>.

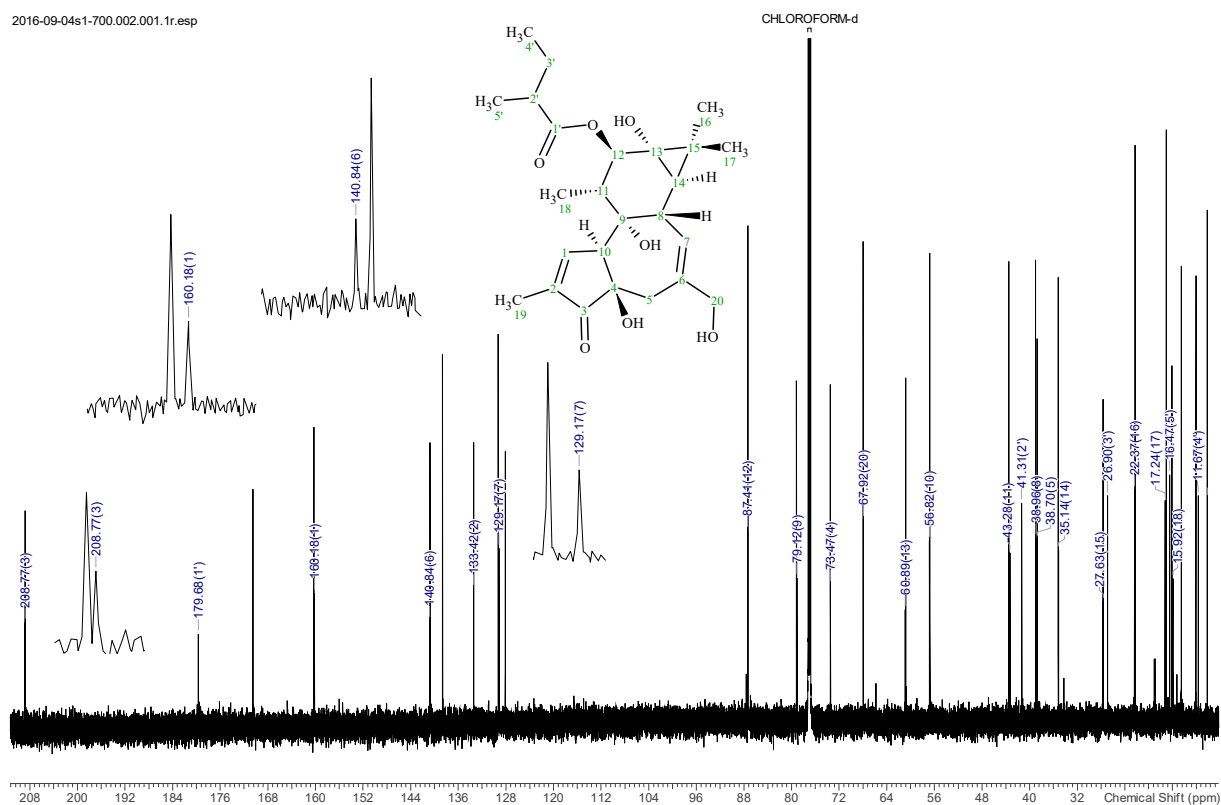


14. Tabulated NMR data for **1e** compound recorded in CDCl<sub>3</sub> at 176/700 MHz.

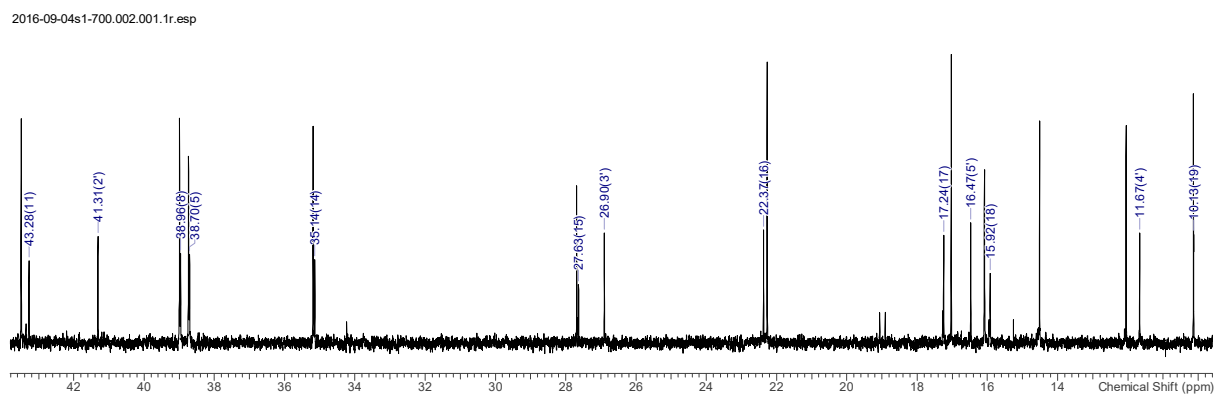
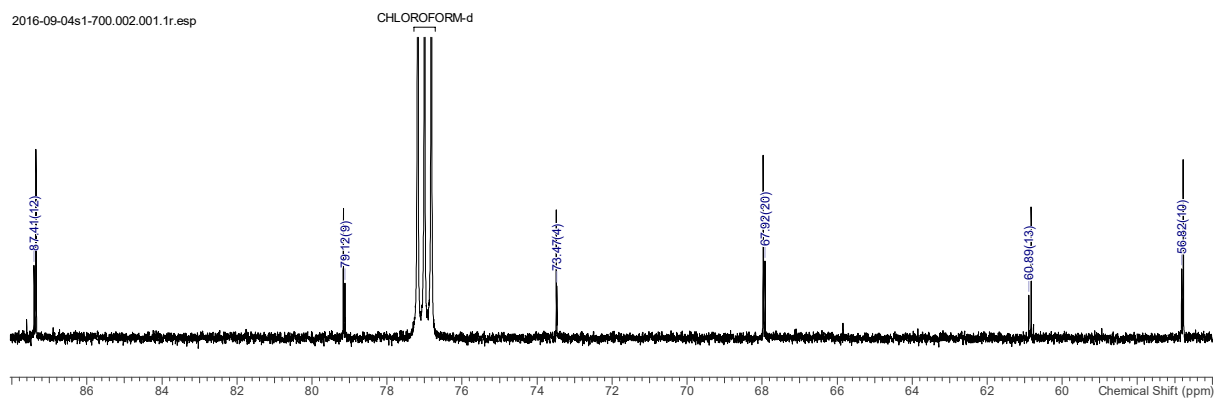
No.	<sup>13</sup> C	<sup>1</sup> H	Multiplicity ( <i>J</i> in Hz)
1	160.18	7.55	br s
2	133.42		
3	208.77		
4	73.47		
5a	38.70	2.44	br d (16.35)
5b	38.70	2.54	d (19.07)
6	140.84		
7	129.17	5.63	br d (5.09)
8a	38.96	3.09	br d (5.63)
9	79.12		
10a	56.82	3.16	br d (3.27)
11	43.28	2.11	dq (9.99, 6.72)
12	87.41	4.83	d (9.99)
13	60.89		
14a	35.14	0.89	d (7.63)
15	27.63		
16	22.37	1.17	s
17	17.24	1.04	s
18	15.92	1.00	d (6.50)
19	10.13	1.77	dd (2.91, 1.27)
20a	67.92	3.98	d (12.90)
20b	67.92	4.03	d (12.90)
1'	179.68		
2'	41.31	2.39	td (13.94, 6.99)
3'	26.90	1.65	m
3'	26.90	1.48	tt (13.74, 7.43)
4'	11.67	0.90	t (5.99)
5'	16.47	1.13	d (6.90)



17.  $^{13}\text{C}$  NMR spectrum and assignments for **1e** recorded in  $\text{CDCl}_3$ , expansions are shown for the selected carbons.

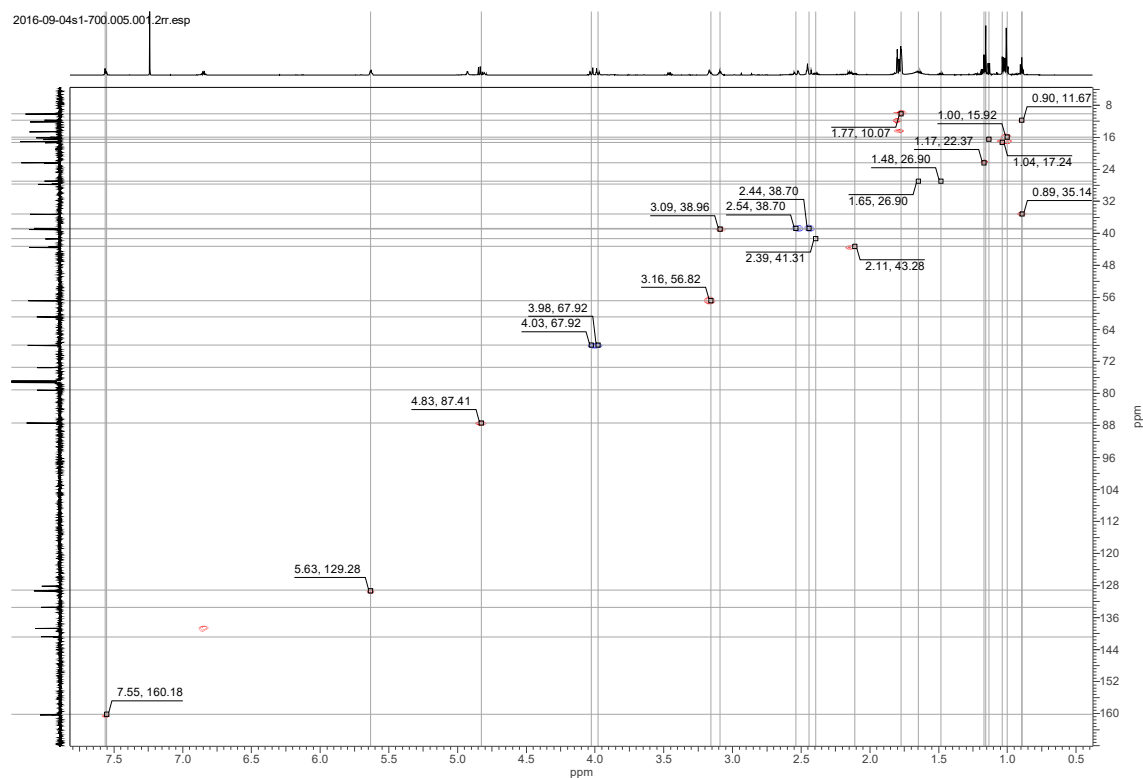


18.  $^{13}\text{C}$  NMR spectrum expansions for **1e** recorded in  $\text{CDCl}_3$ .

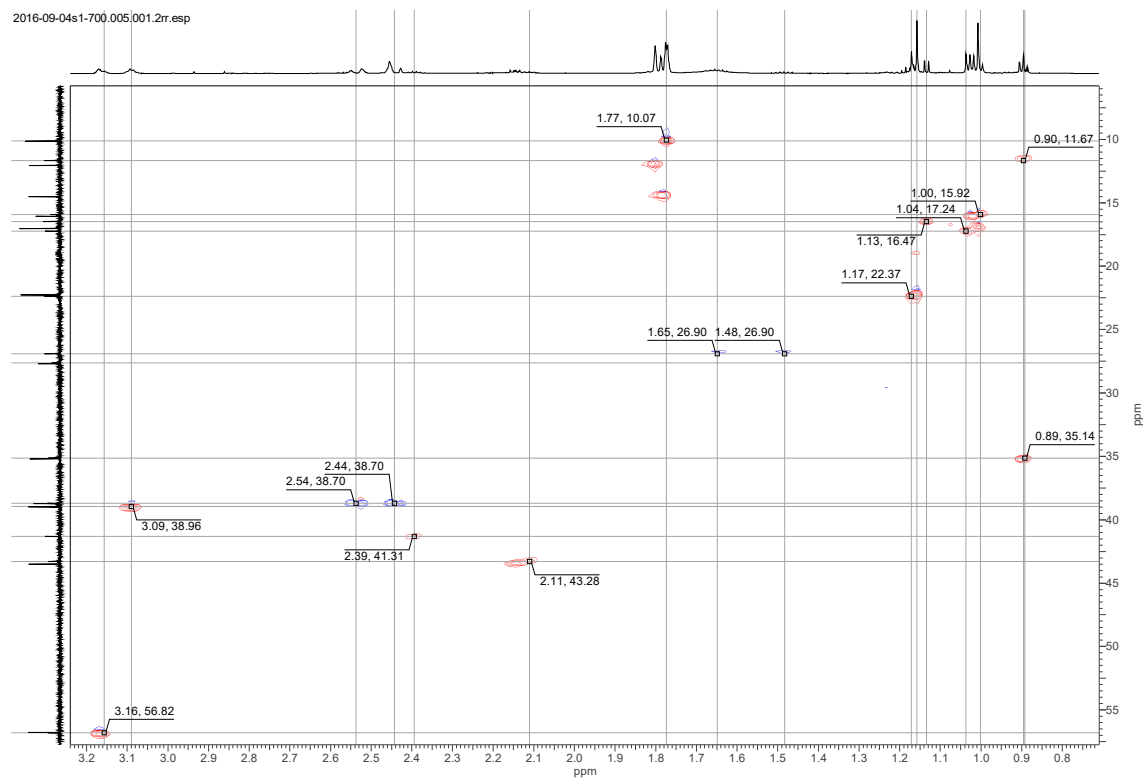




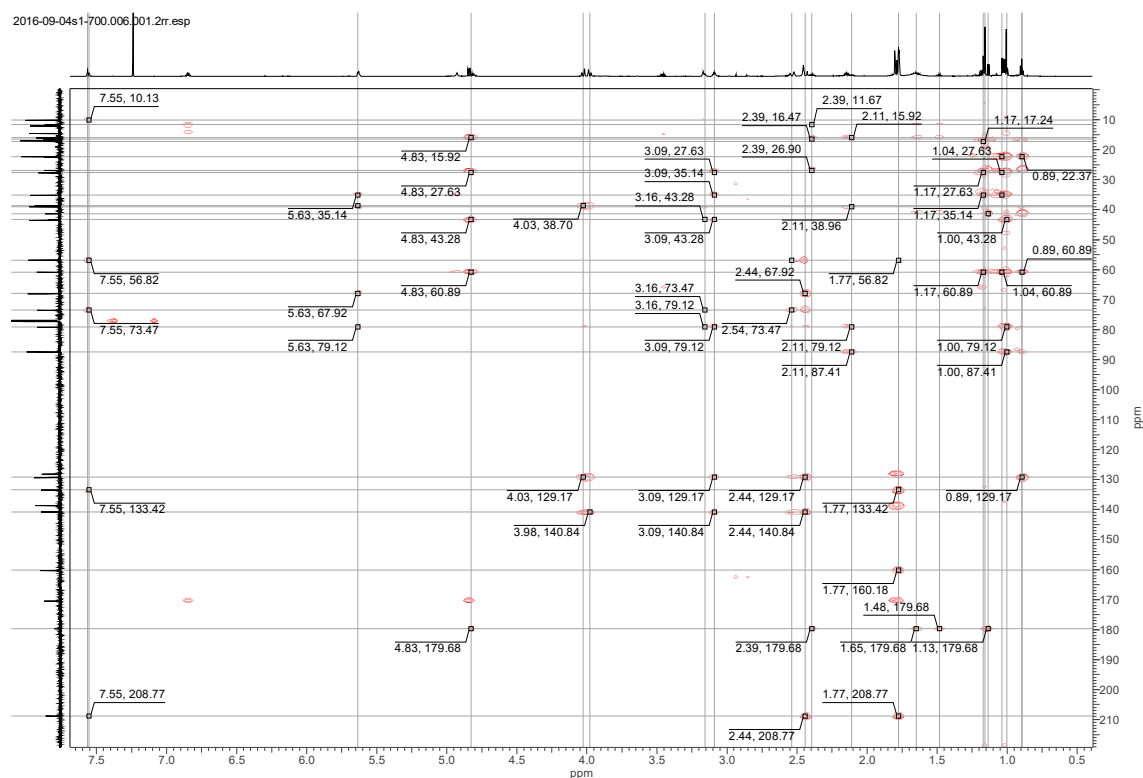
21. HSQC edit spectrum for **1e** recorded in CDCl<sub>3</sub>, peak picking was performed for the minor component.



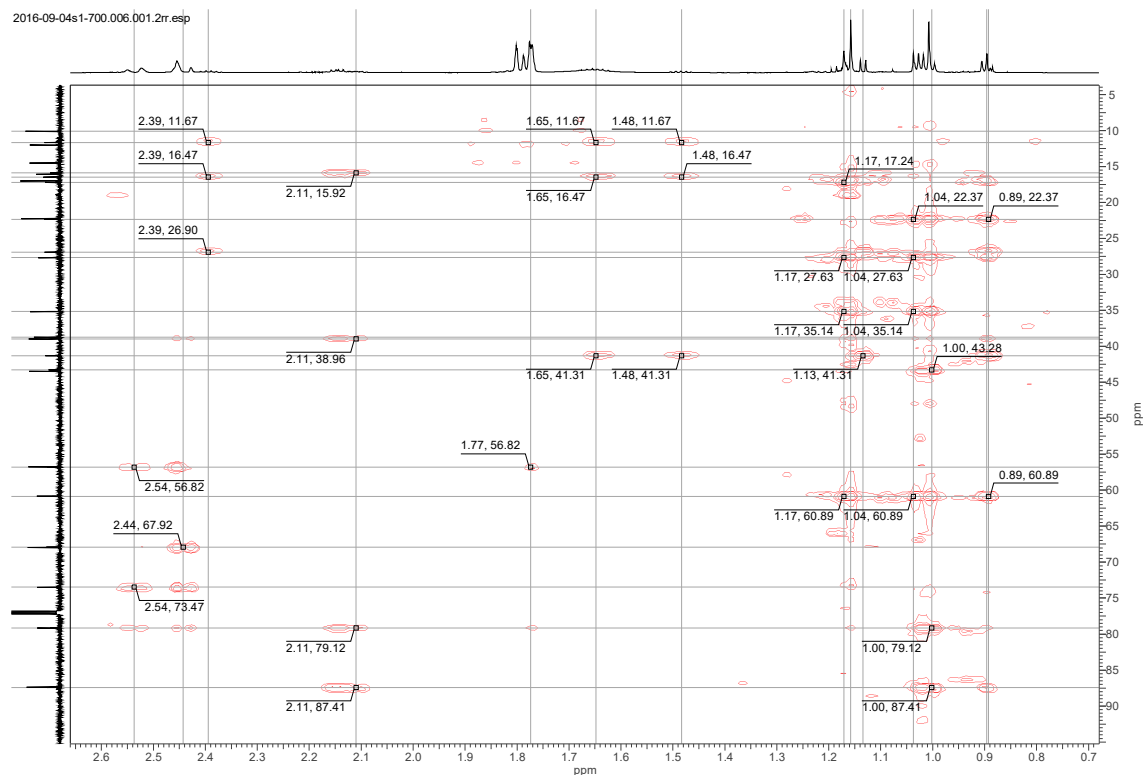
22. HSQC spectrum for **1e** recorded in CDCl<sub>3</sub>, 0.7-3.1×5-58 ppm expansion, peak picking was performed for the minor component.



23. HMBC spectrum for **1e** recorded in CDCl<sub>3</sub>, peak picking was performed for the minor component.

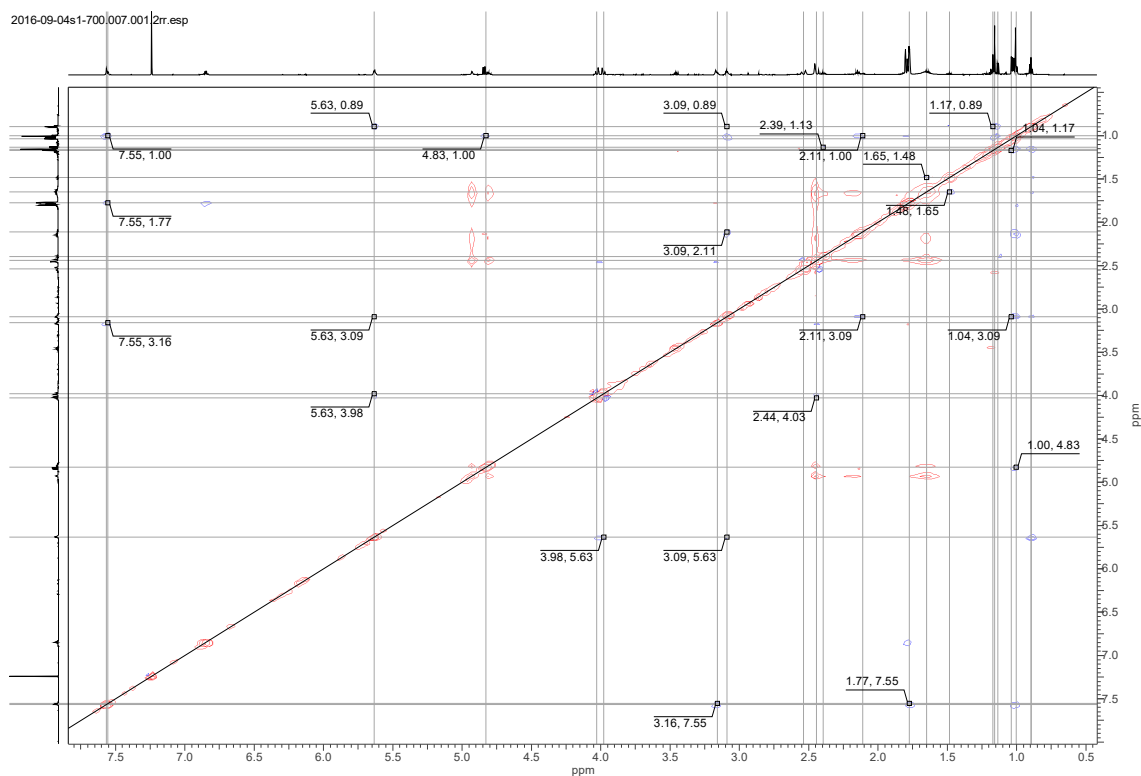


24. HMBC spectrum for **1e** recorded in CDCl<sub>3</sub>, 0.7-2.6×5-95 ppm expansion, peak picking was performed for the minor component.





25. NOESY spectrum for **1e** recorded in CDCl<sub>3</sub>, peak picking was performed for the minor component.



26. NOESY spectrum for **1e** recorded in CDCl<sub>3</sub>, 0.5-5.0×0.7-3.3 ppm expansion, peak picking was performed for the minor component.

