

## Supporting Information

### Cytotoxic Activity of Riccardin and Perrottetin Derivatives from the Liverwort *Lunularia cruciata*

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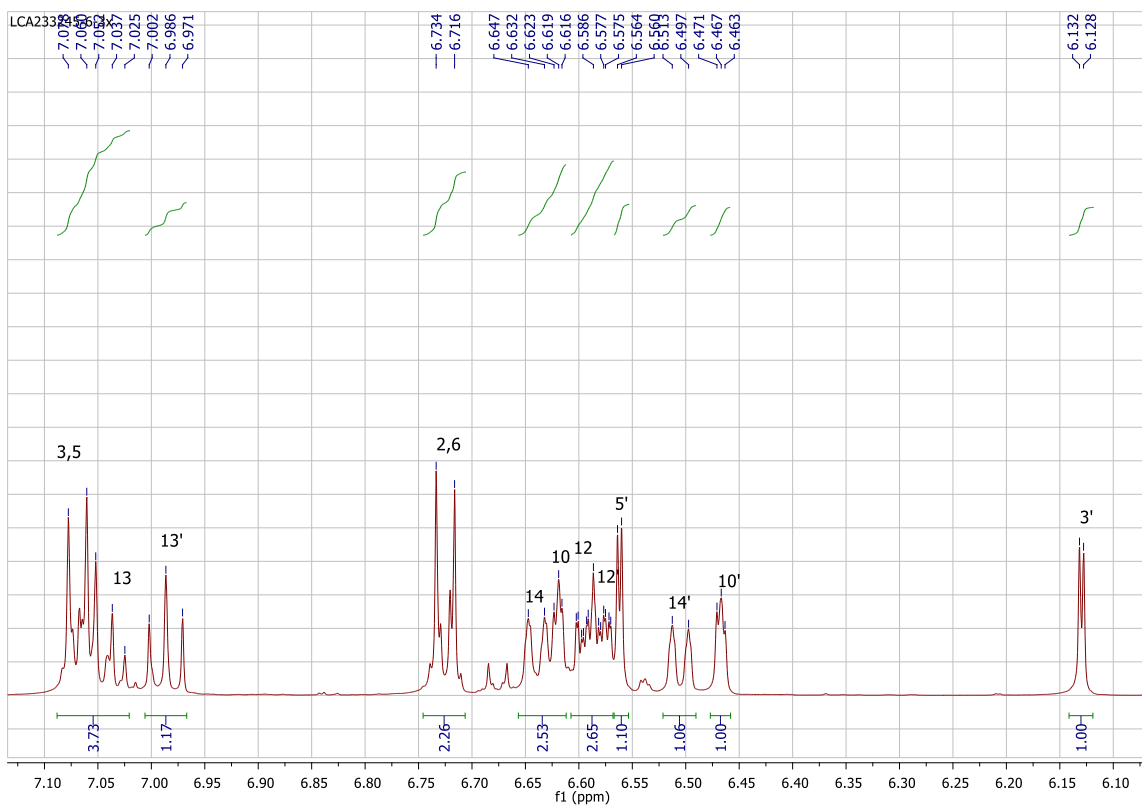
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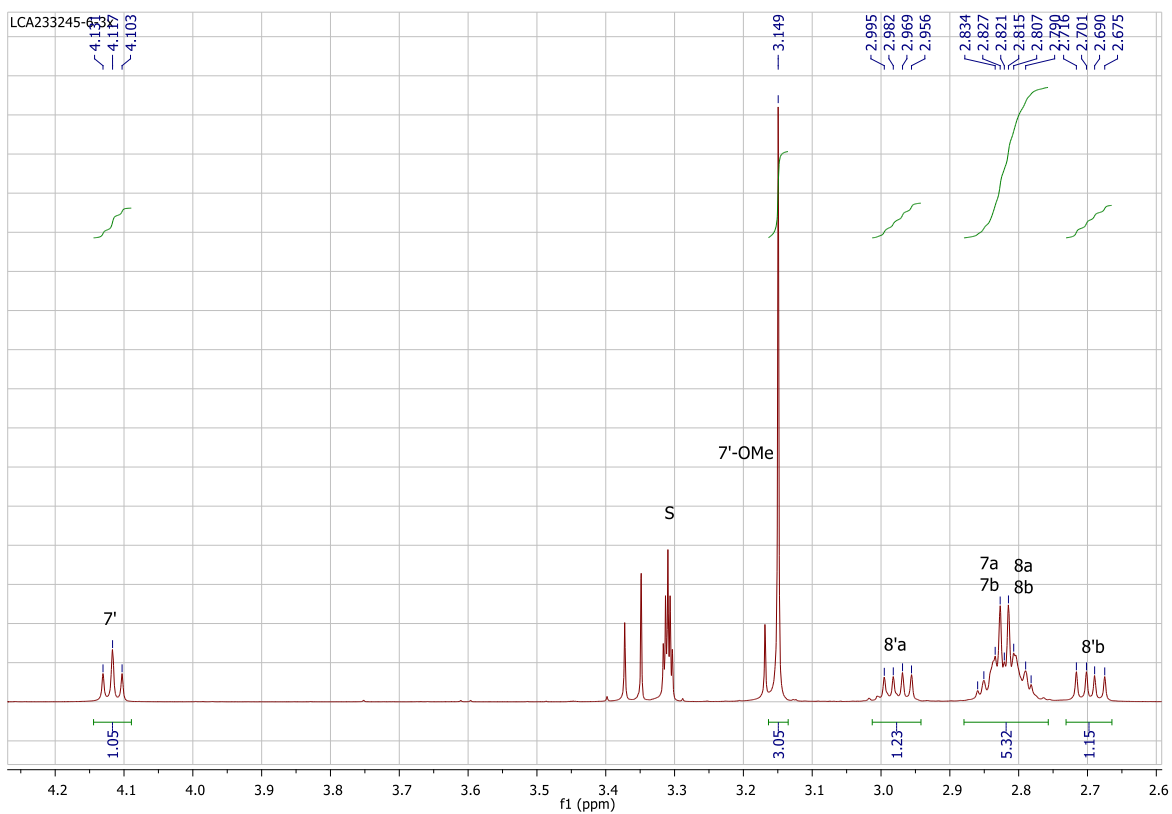
Table S1. Elution Program for the Silica Gel Column Separation

n-hexane	100	95	90	88	85	82	80	77	74	71	67
EtOAc	0	5	10	12	15	18	20	23	26	29	33
V (ml)	200	700	700	400	200	700	400	500	700	800	700
Fr. No.	-	-	-	-	-	0-46	47-62	63-82	83-113	114-148	149-182

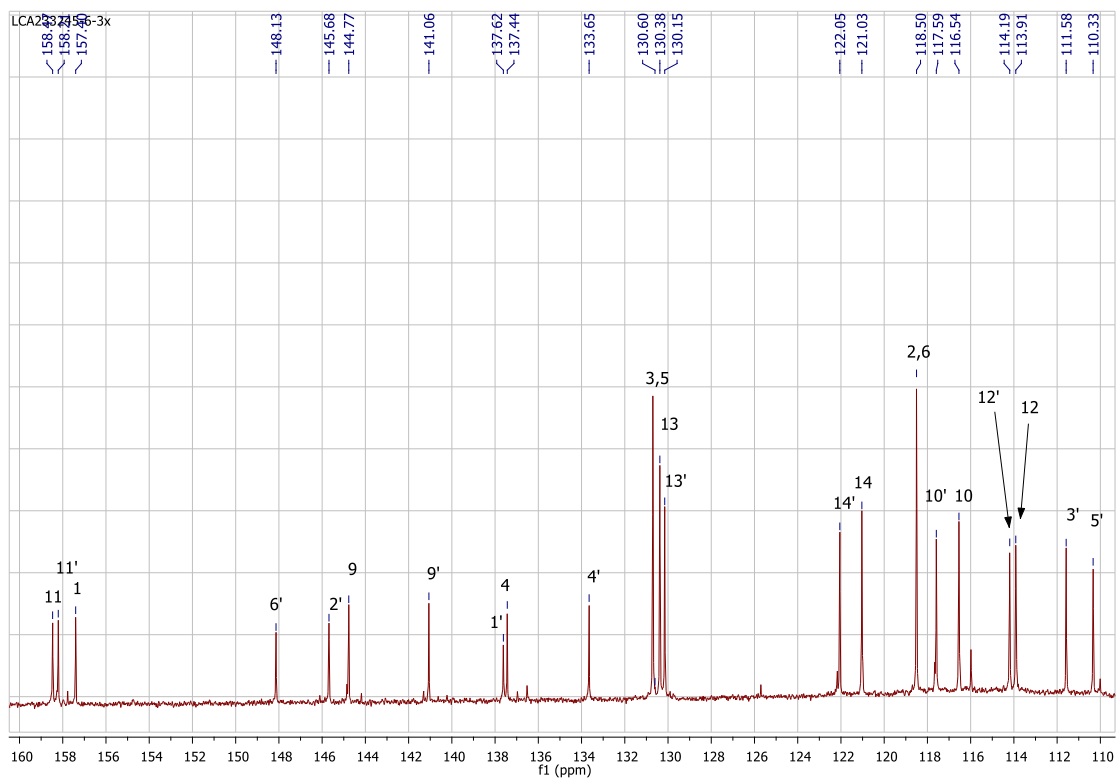
n-hexane	63	60	57	54	50	40	30	20	0
EtOAc	37	40	43	46	50	60	70	80	100
V (ml)	400	700	700	400	300	300	200	200	200
Fr. No.	183-200	201-229	230-260	261-277	278-290	291-305	306-315	316-330	331-339



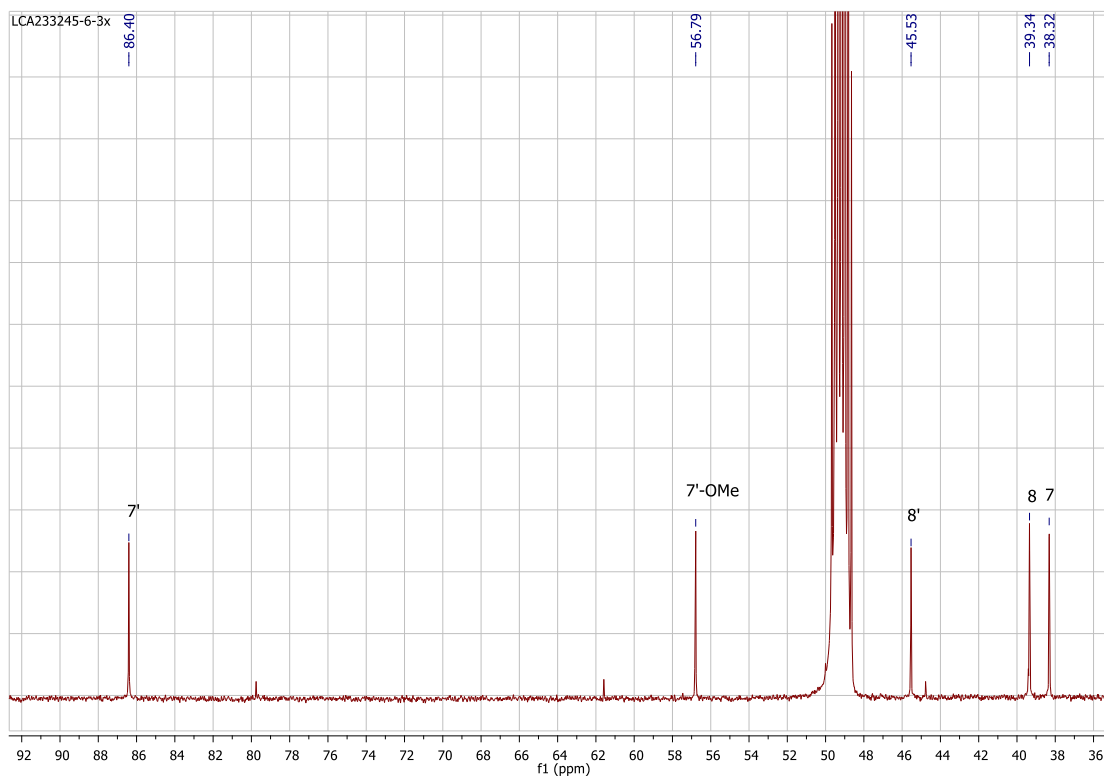
**Figure S1.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **1**



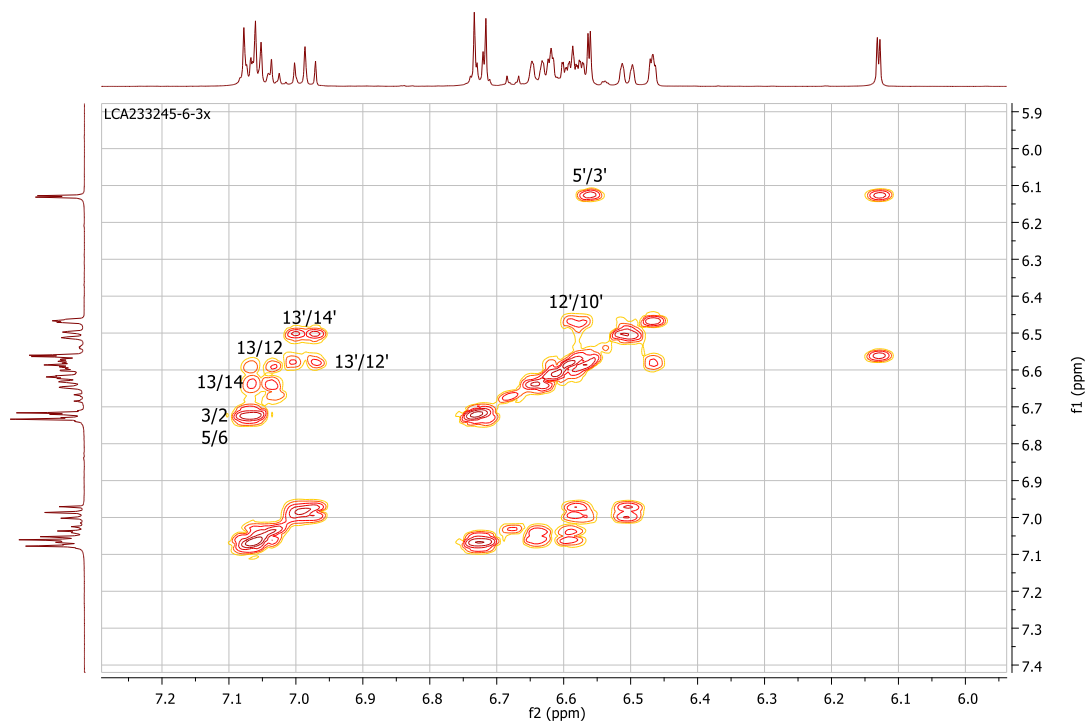
**Figure S2.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **1**



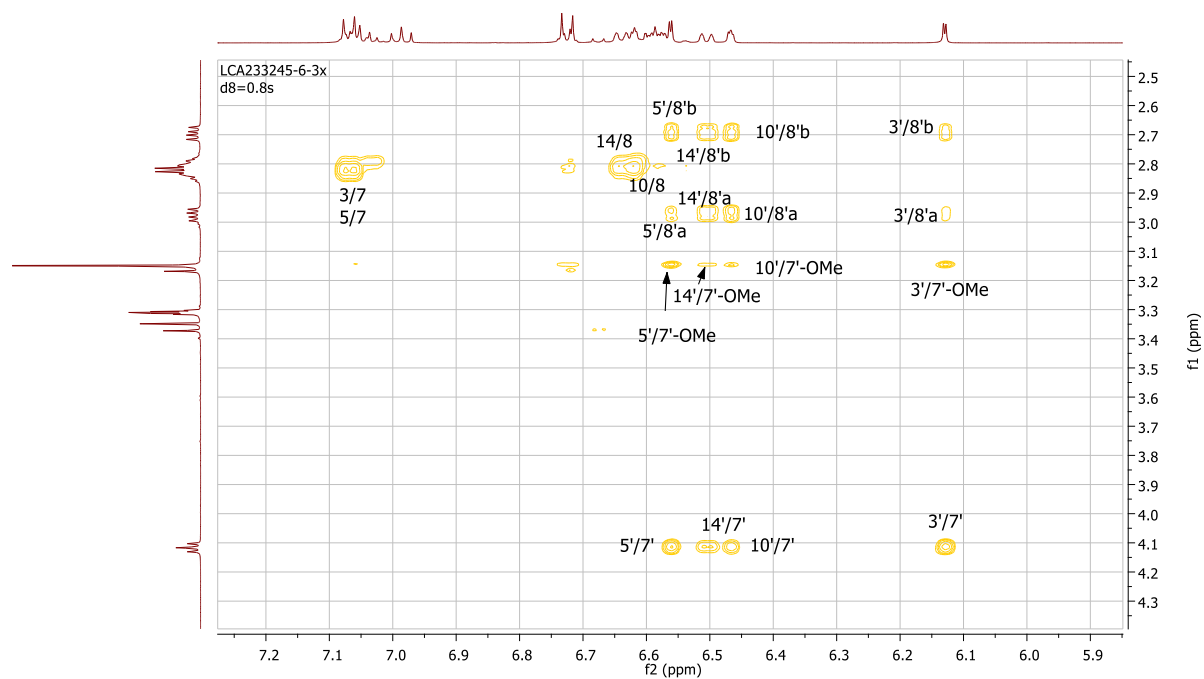
**Figure S3.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **1**



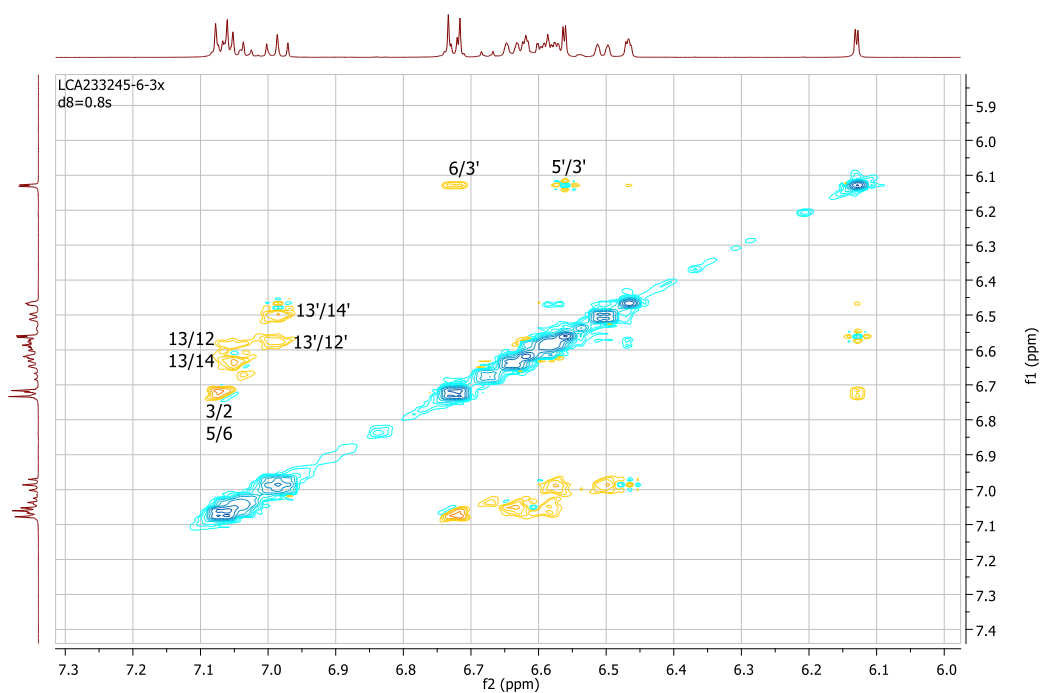
**Figure S4.** Aliphatic part of the  $^{13}\text{C}$  NMR spectrum of compound **1**



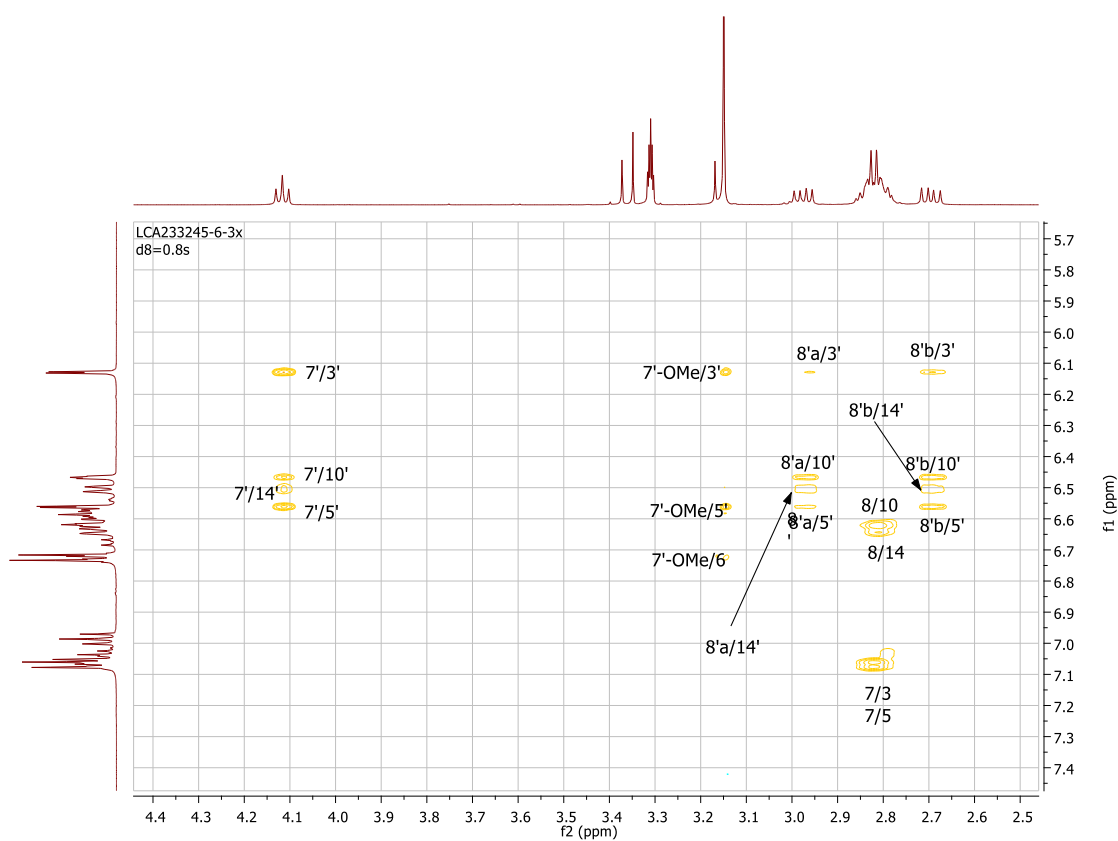
**Figure S5.** Aromatic part of the COSY spectrum of compound **1**



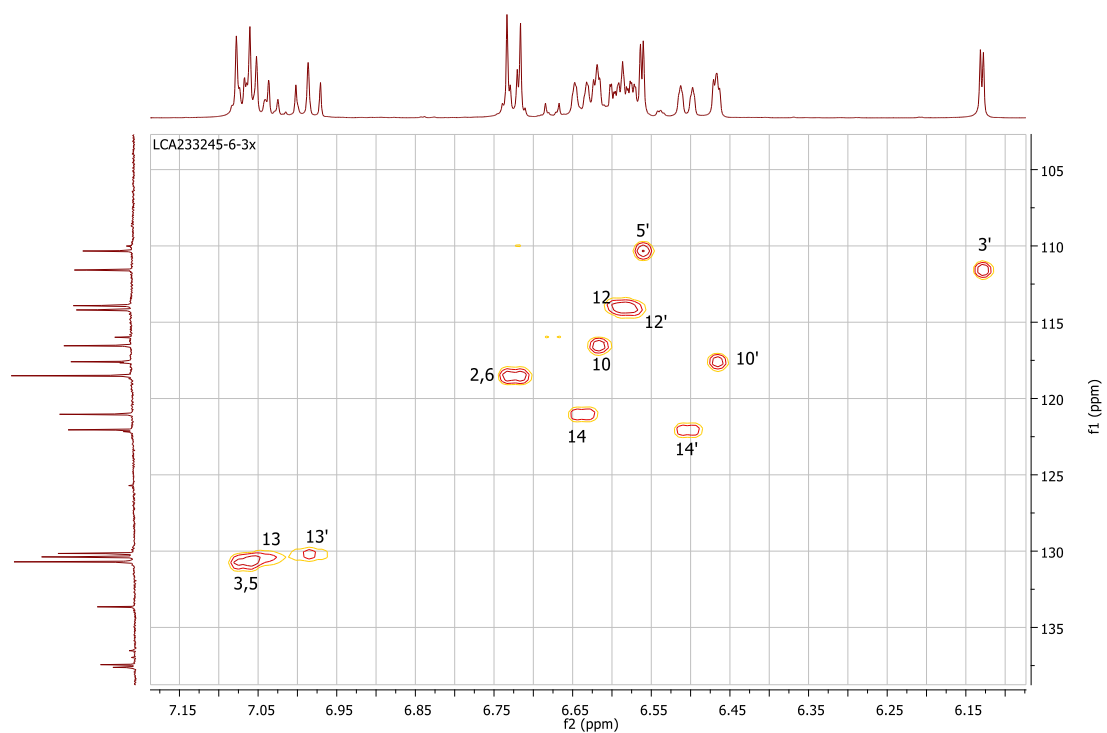
**Figure S6.** The first part of the NOESY spectrum of compound **1**



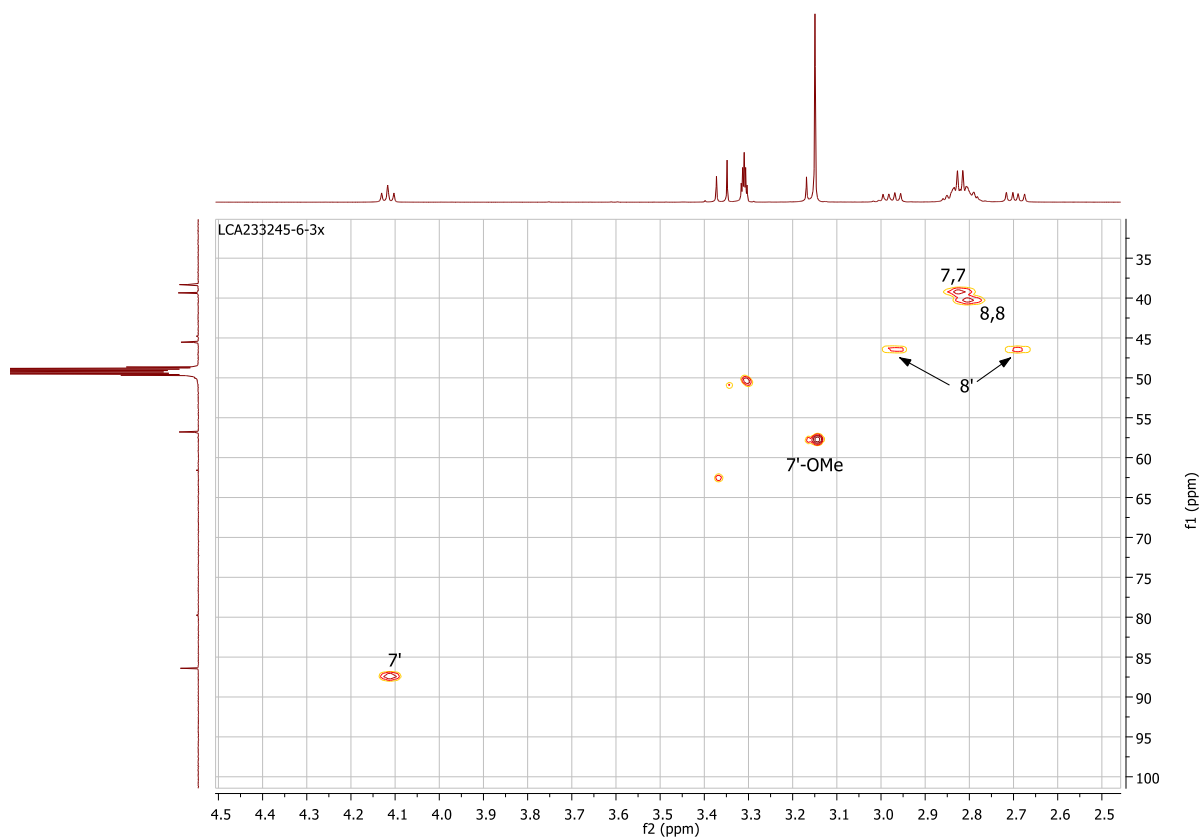
**Figure S7.** The second part of the NOESY spectrum of compound **1**



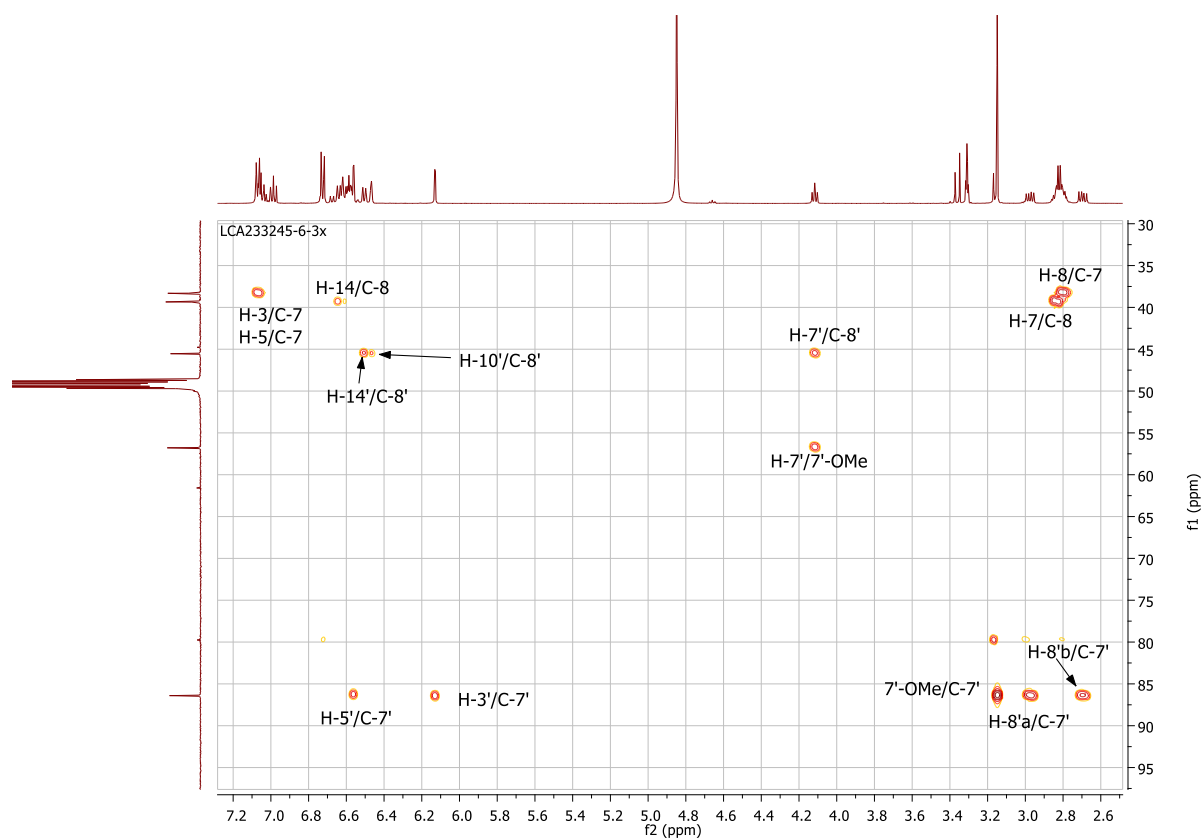
**Figure S8.** The third part of the NOESY spectrum of compound **1**



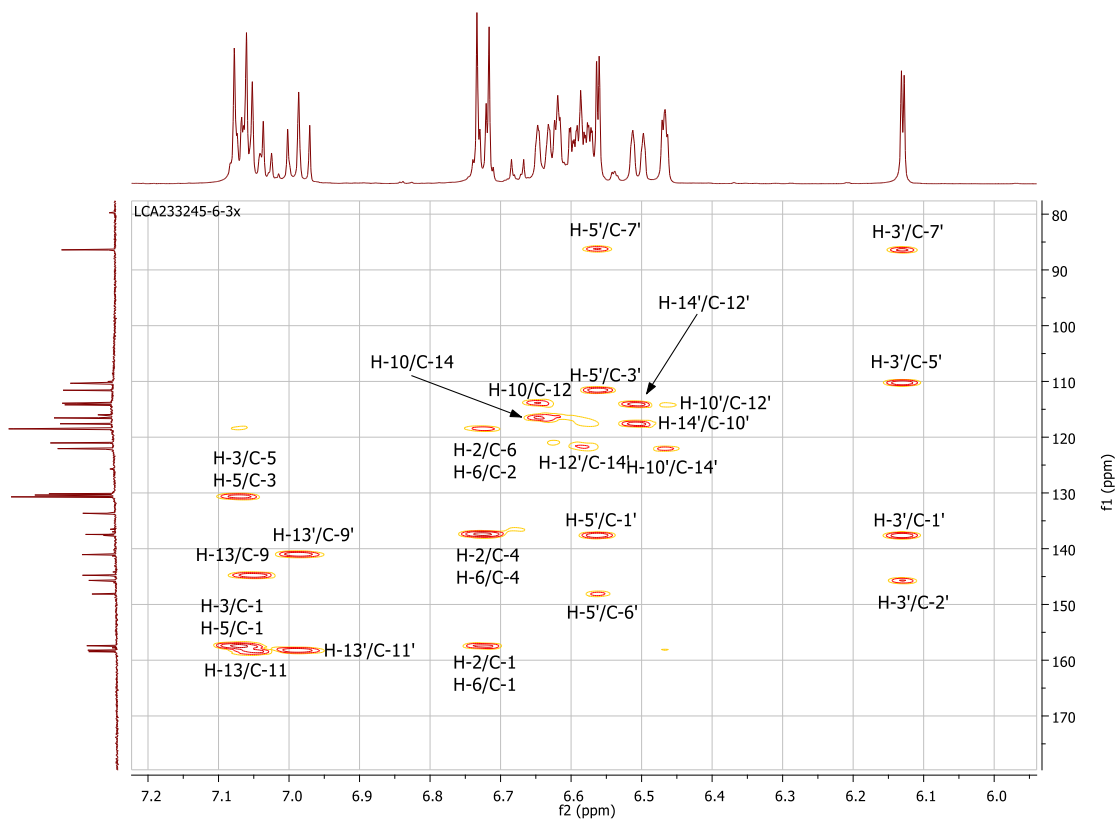
**Figure S9.** Aromatic part of the HSQC spectrum of compound **1**



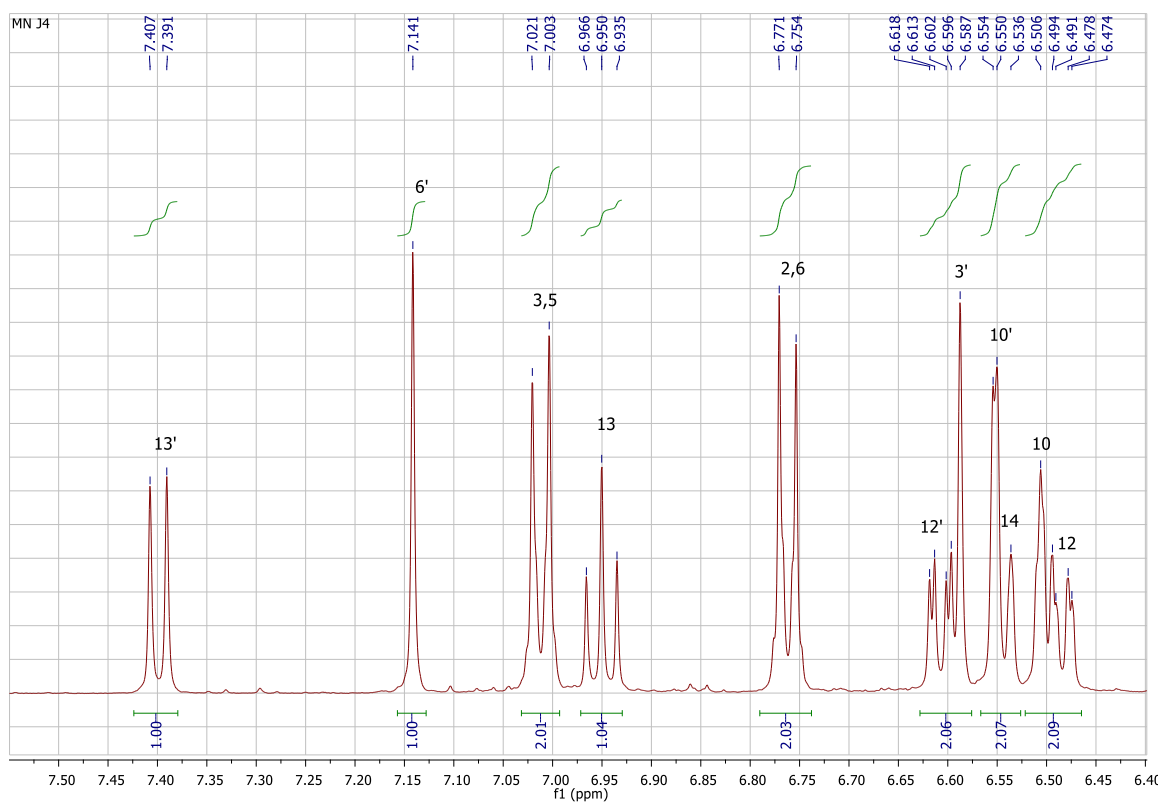
**Figure S10.** Aliphatic part of the HSQC spectrum of compound **1**



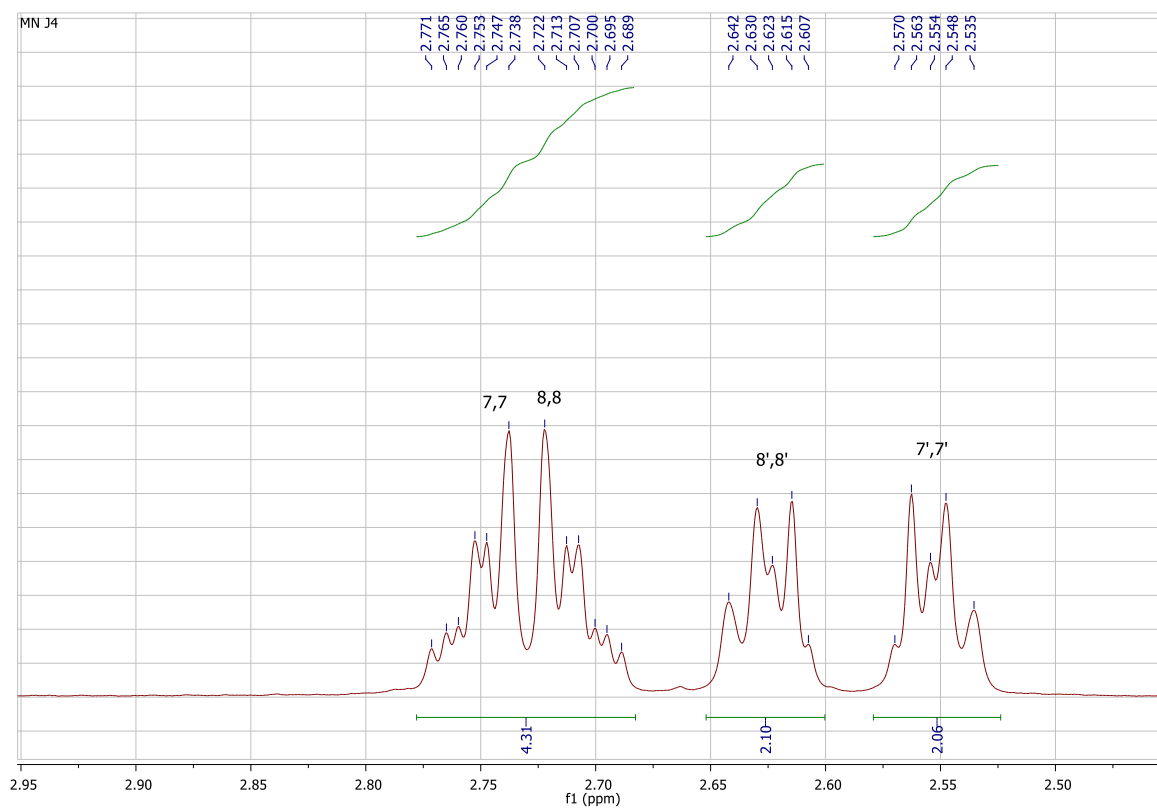
**Figure S11.** The first part of the HMBC spectrum of compound **1**



**Figure S12.** The second part of the HMBC spectrum of compound **1**

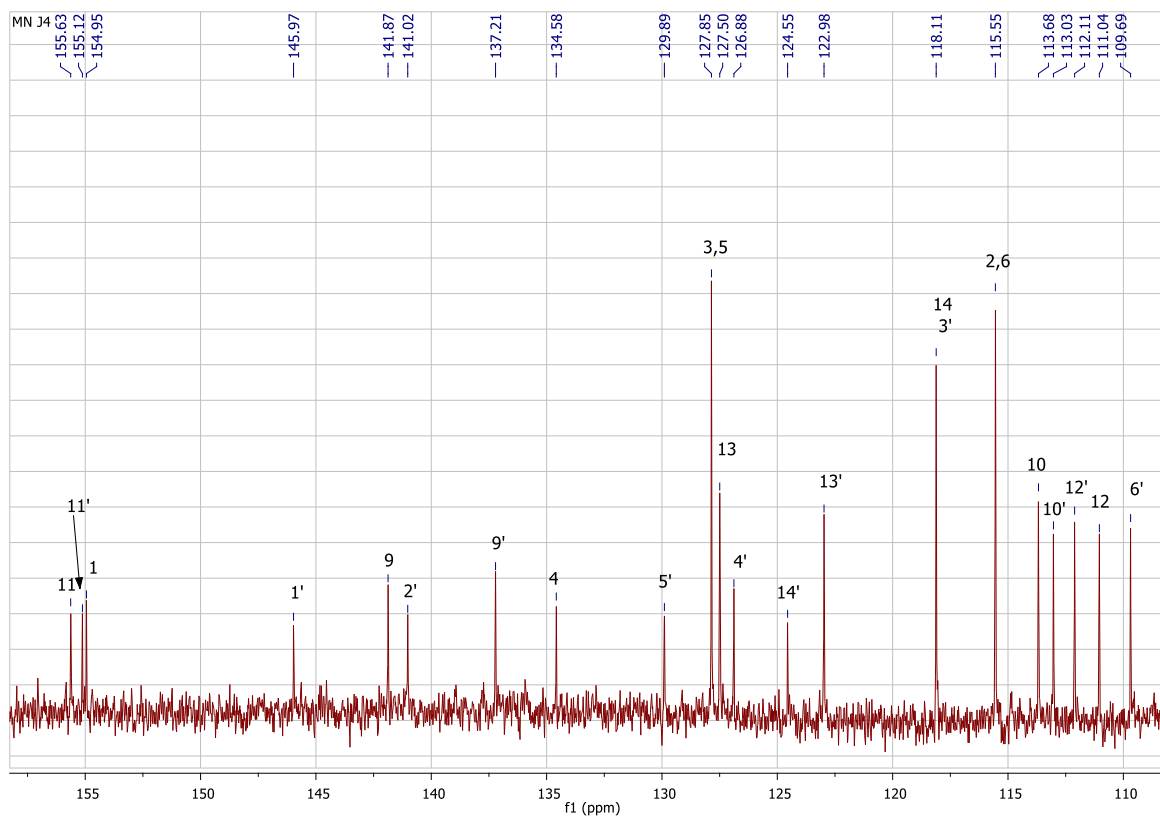


**Figure S13.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **2**

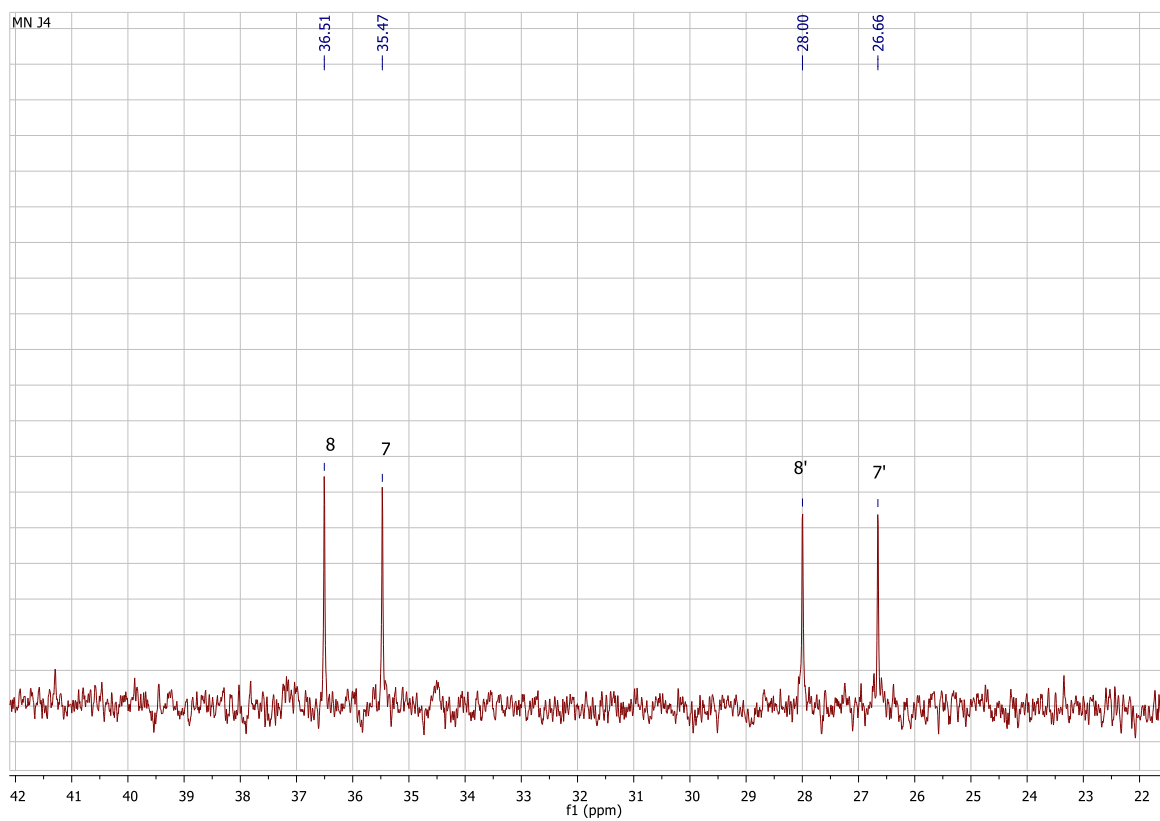


**Figure S14.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **2**

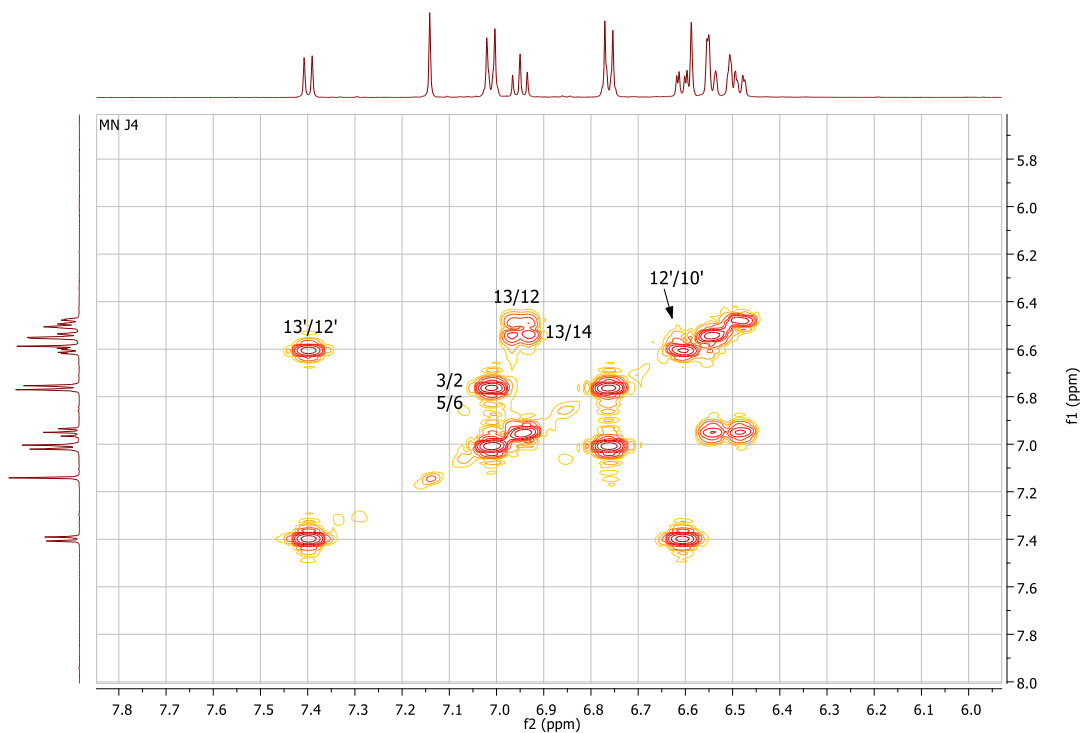




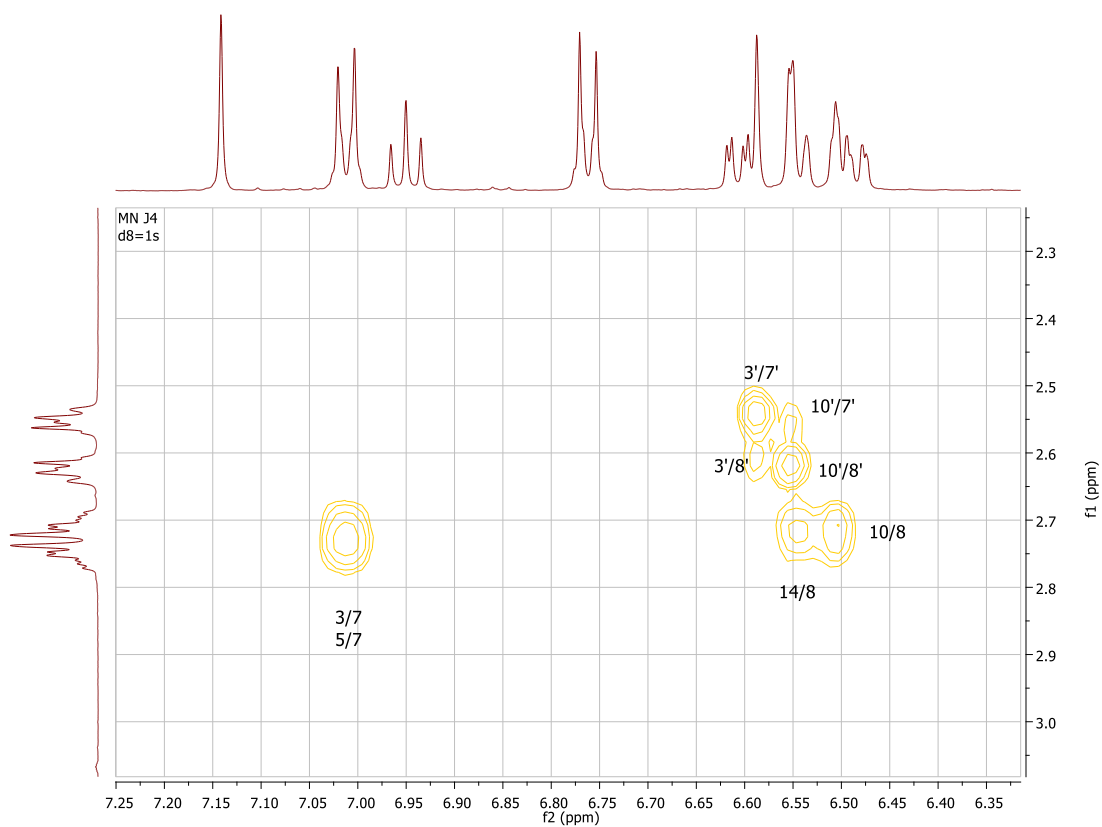
**Figure S15.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **2**



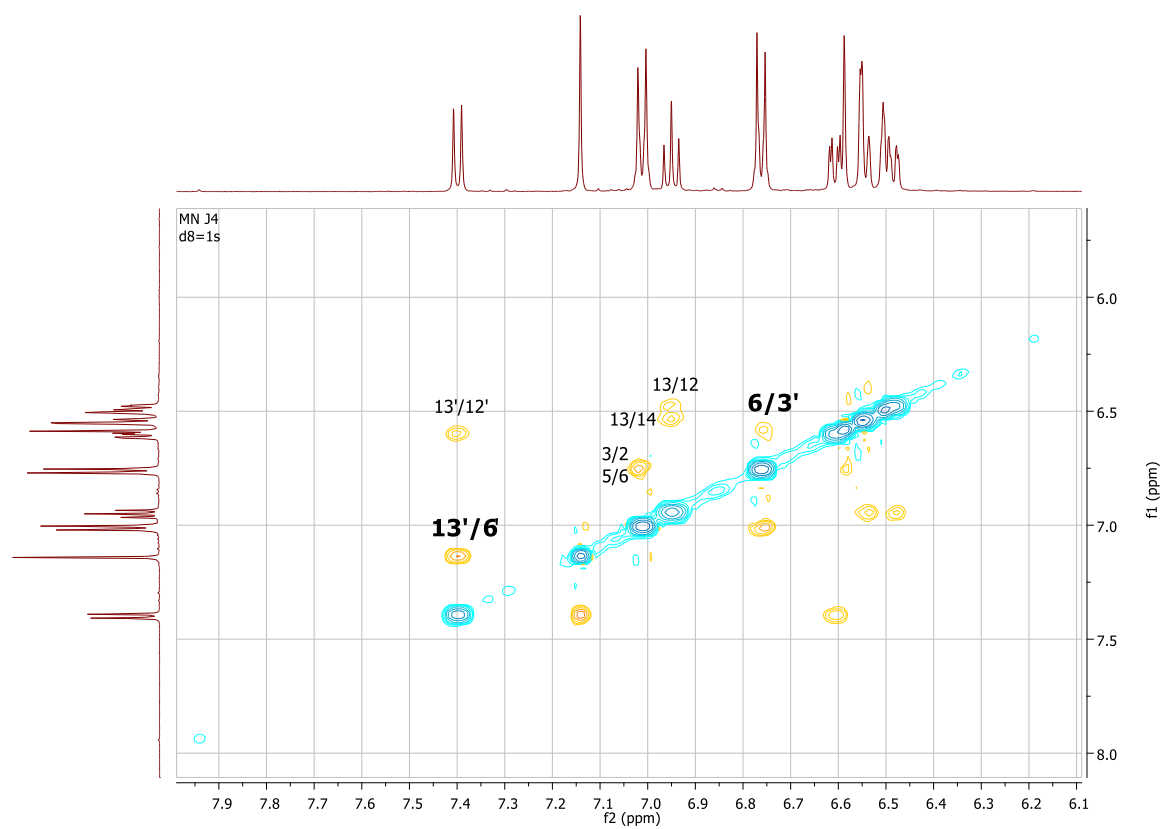
**Figure S16.** Aliphatic part of the  $^{13}\text{C}$  NMR spectrum of compound **2**



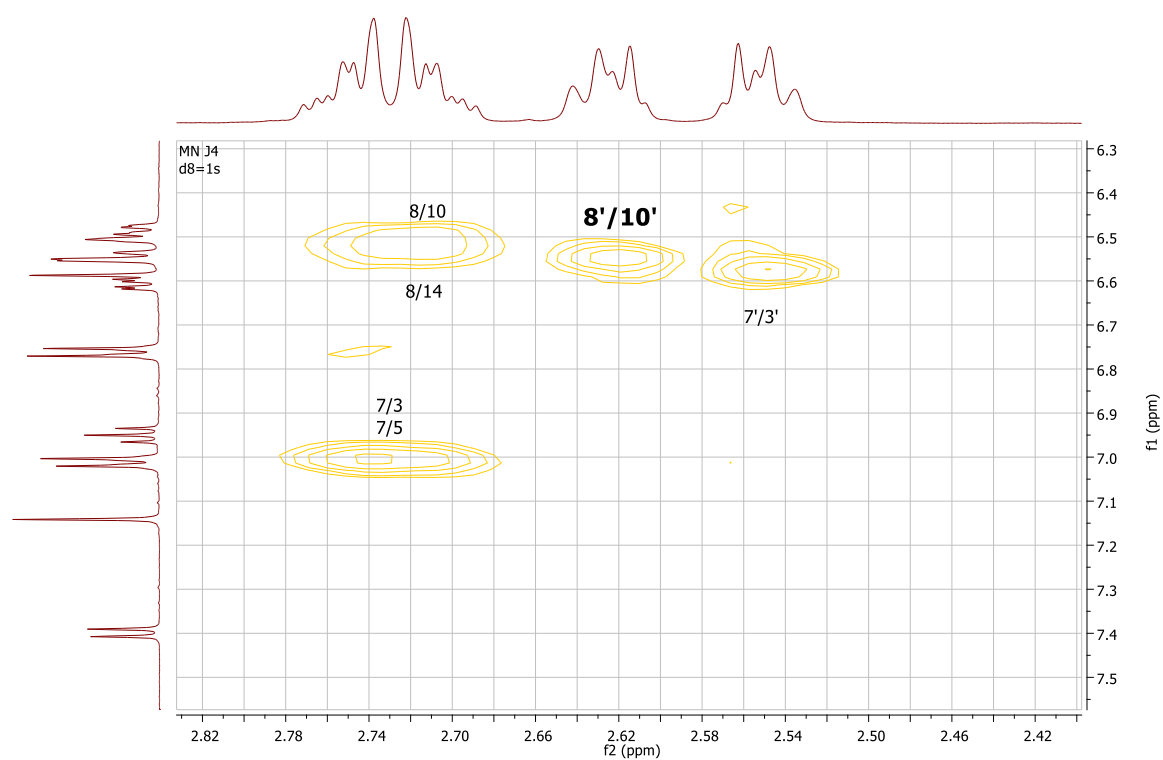
**Figure S17.** Aromatic part of the COSY spectrum of compound **2**



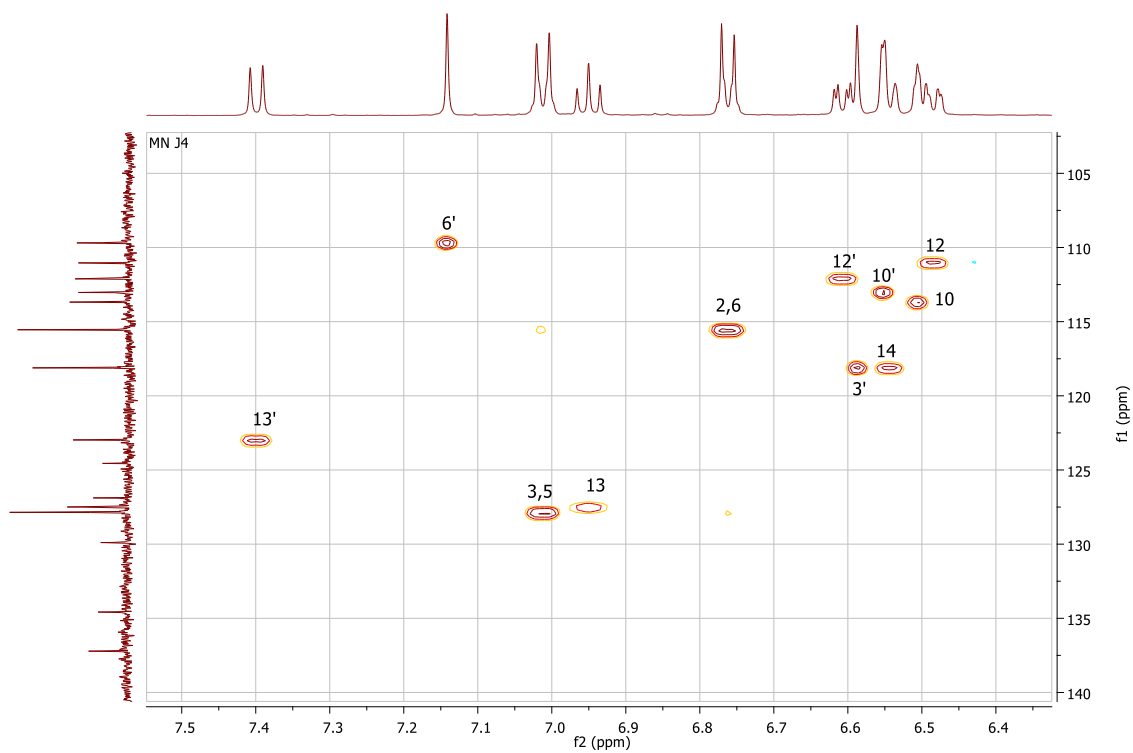
**Figure S18.** The first part of the NOESY spectrum of compound **2**



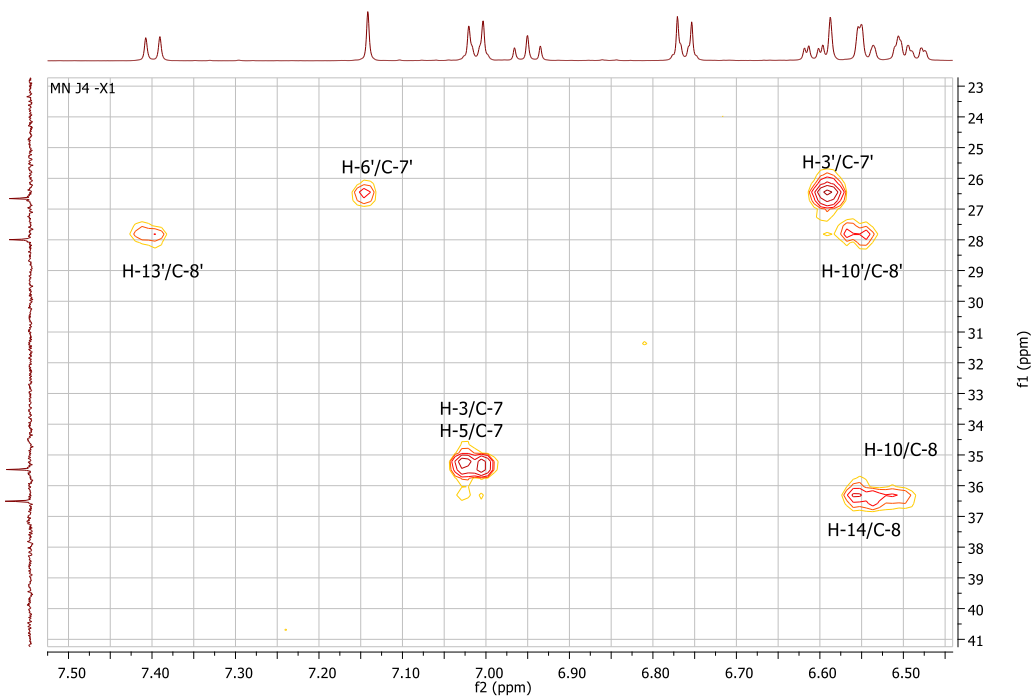
**Figure S19.** The second part of the NOESY spectrum of compound **2**



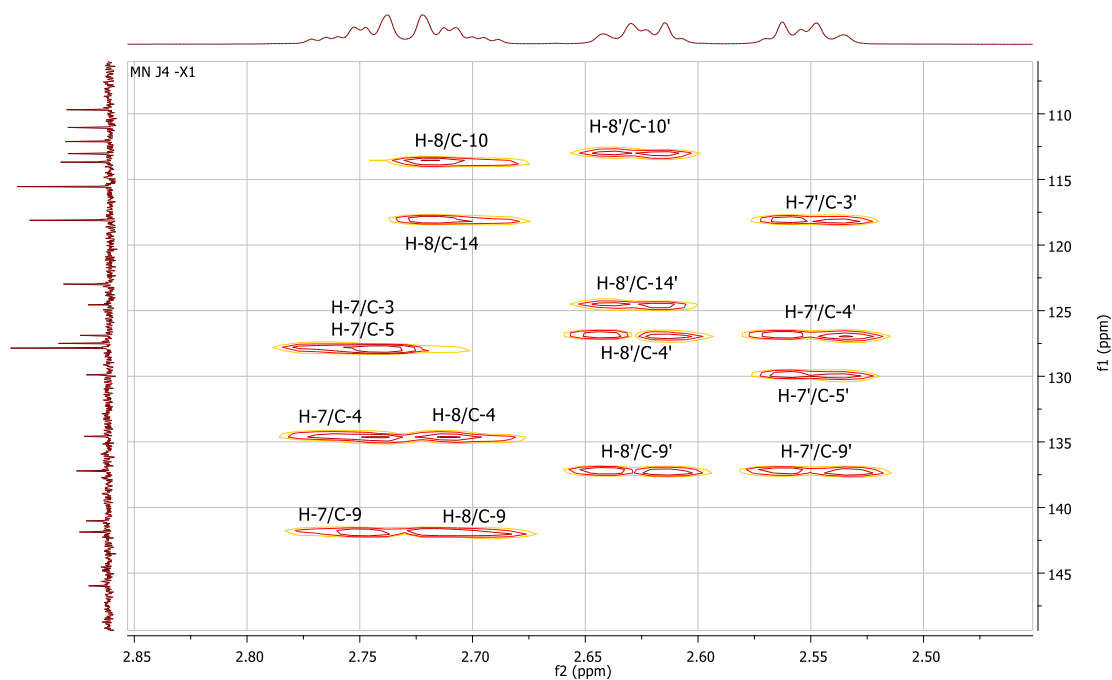
**Figure S20.** The third part of the NOESY spectrum of compound **2**



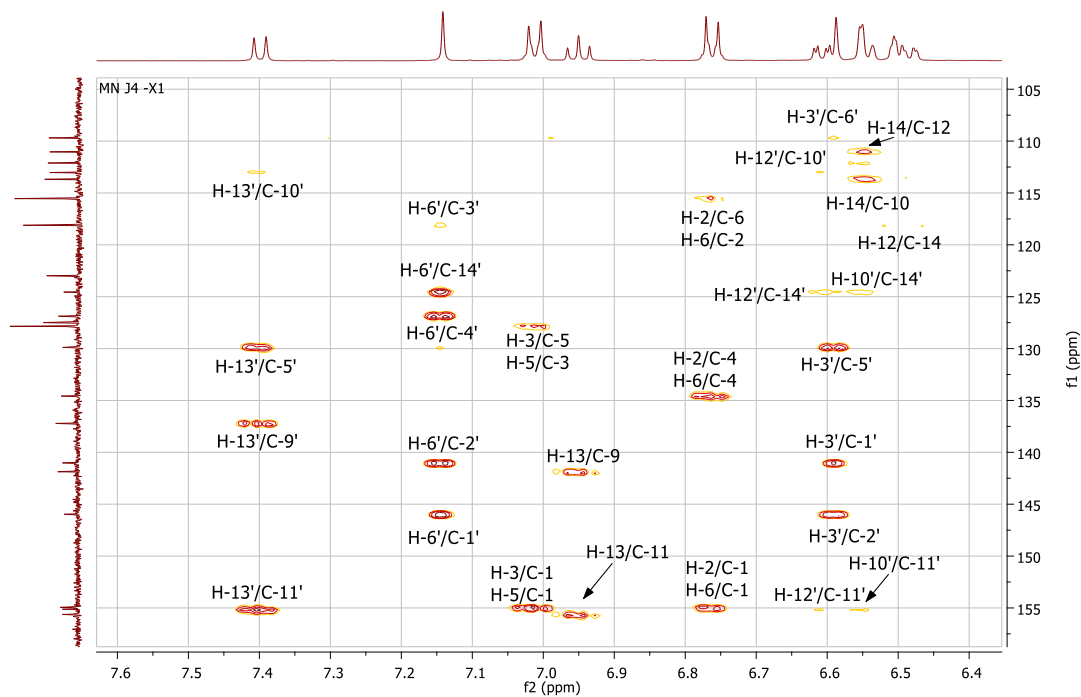
**Figure S21.** Aromatic part of the HSQC spectrum of compound **2**



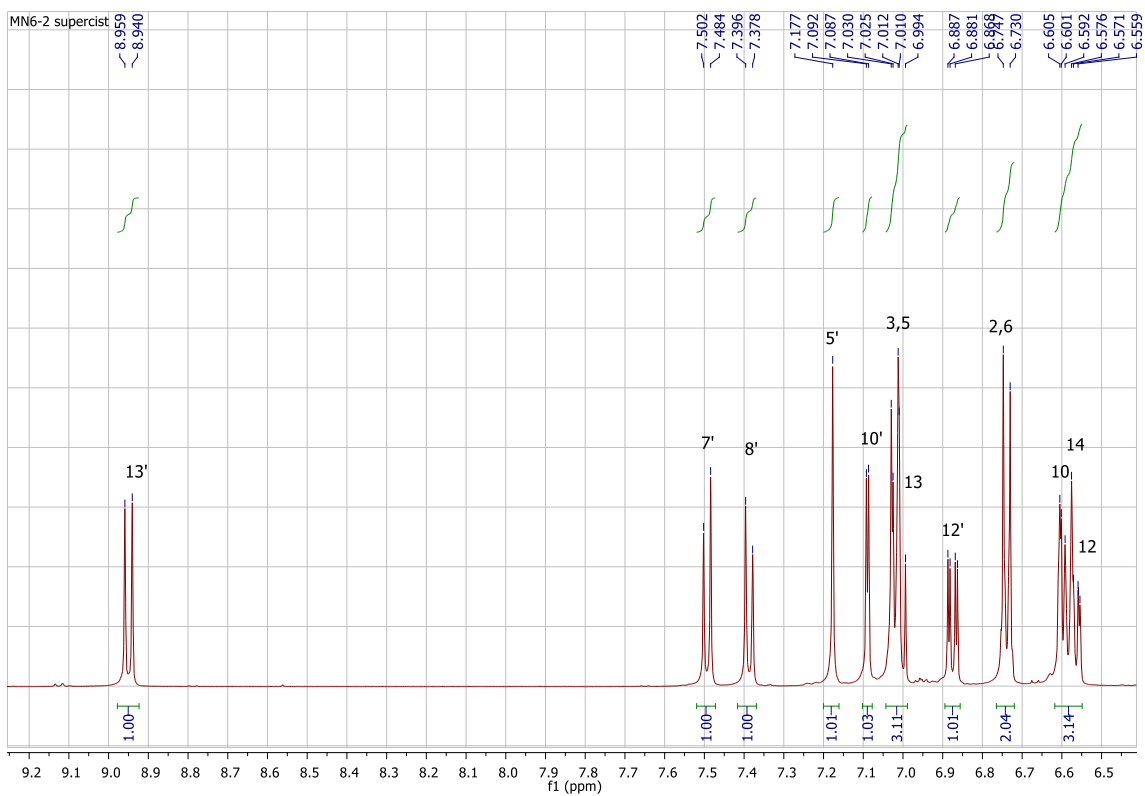
**Figure S22.** The first part of the HMBC spectrum of compound **2**



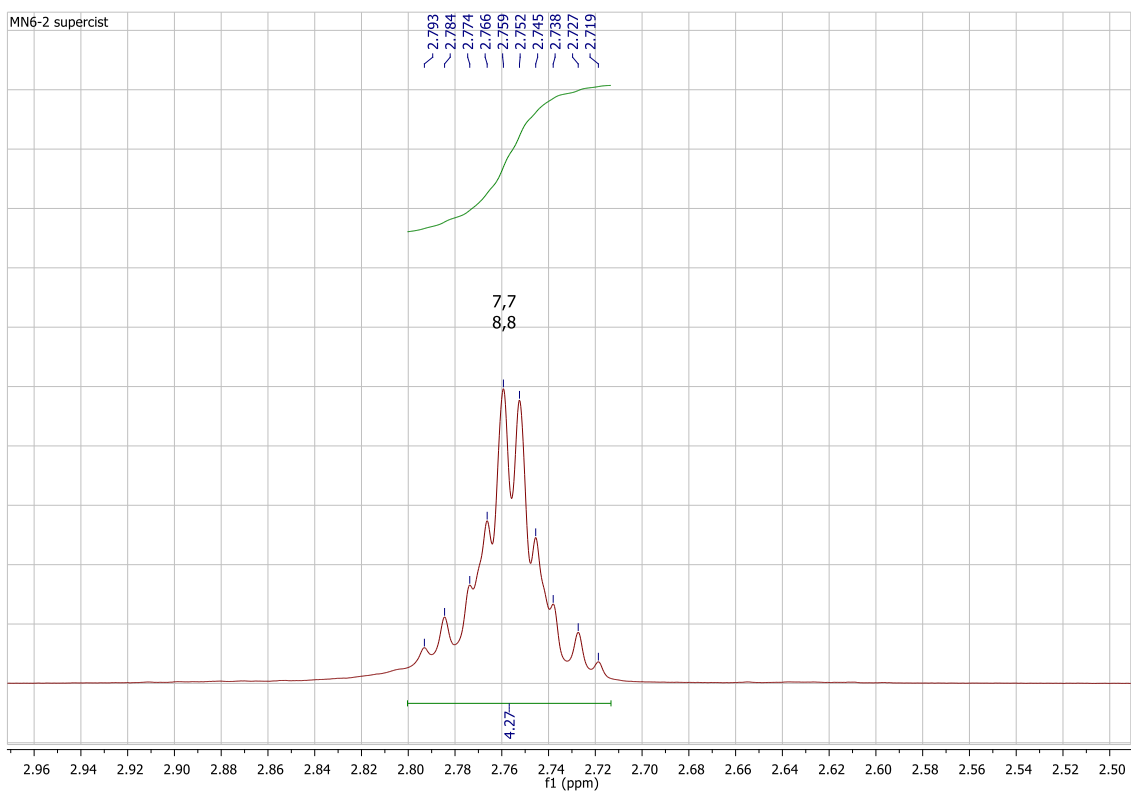
**Figure S23.** The second part of the HMBC spectrum of compound **2**



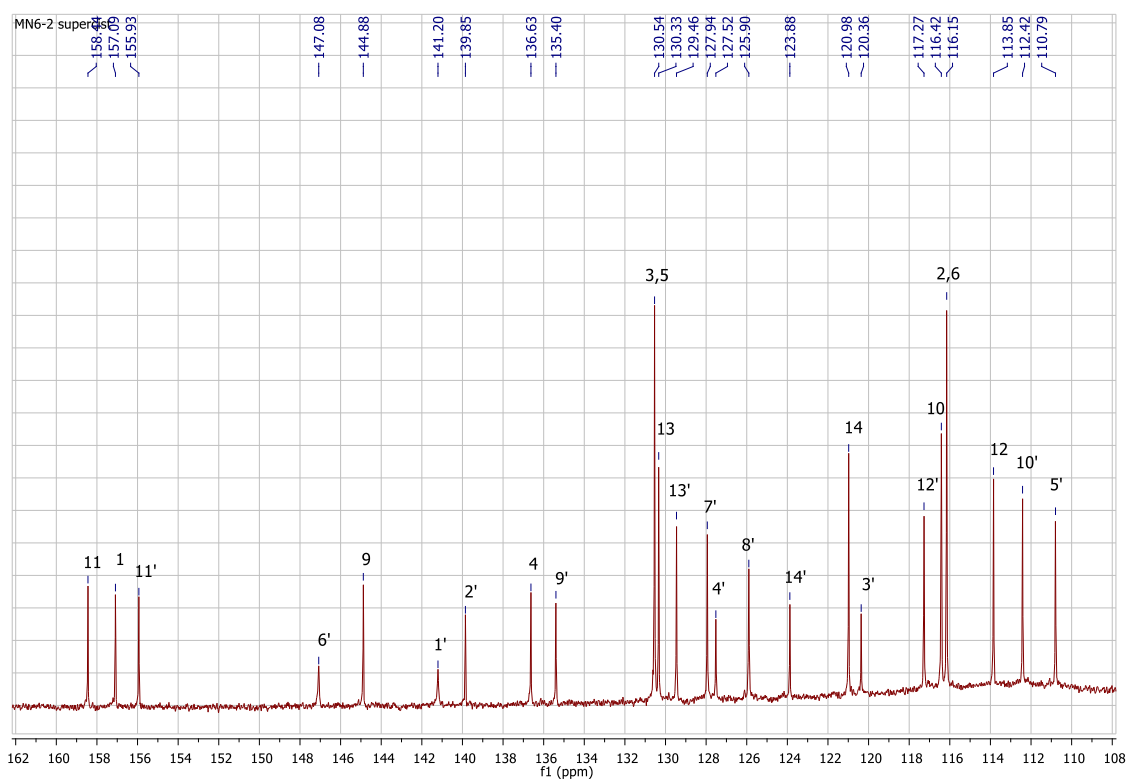
**Figure S24.** The third part of the HMBC spectrum of compound **2**



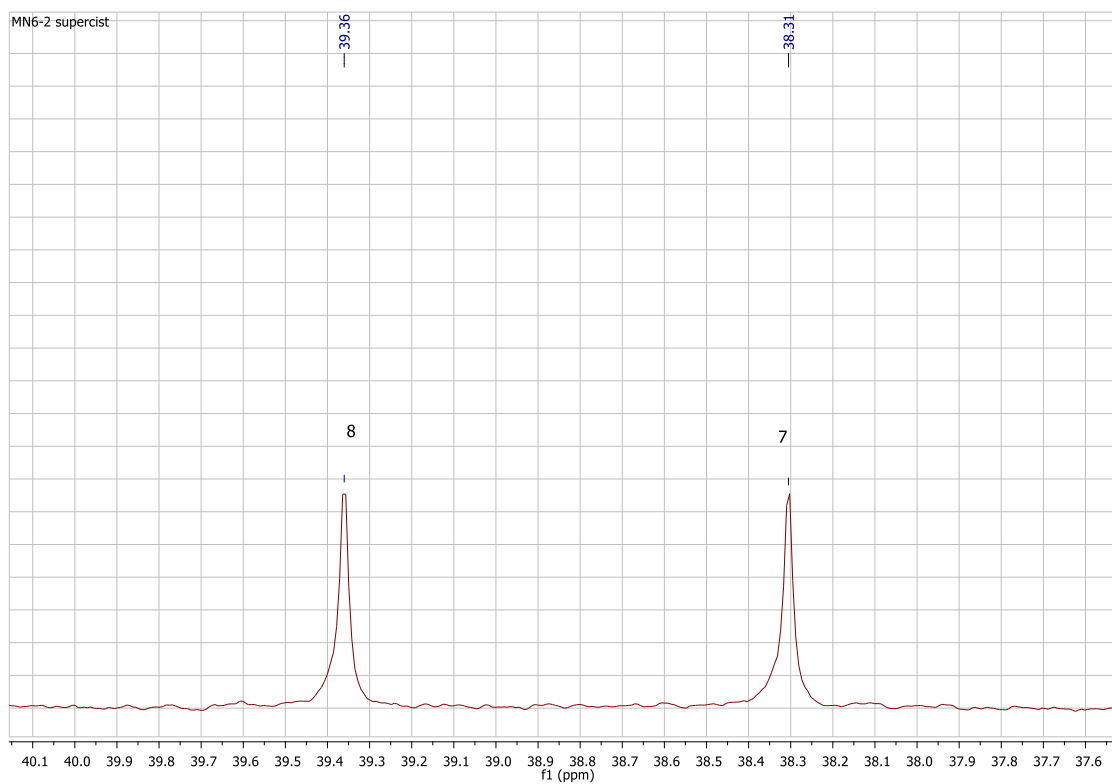
**Figure S25.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **3**



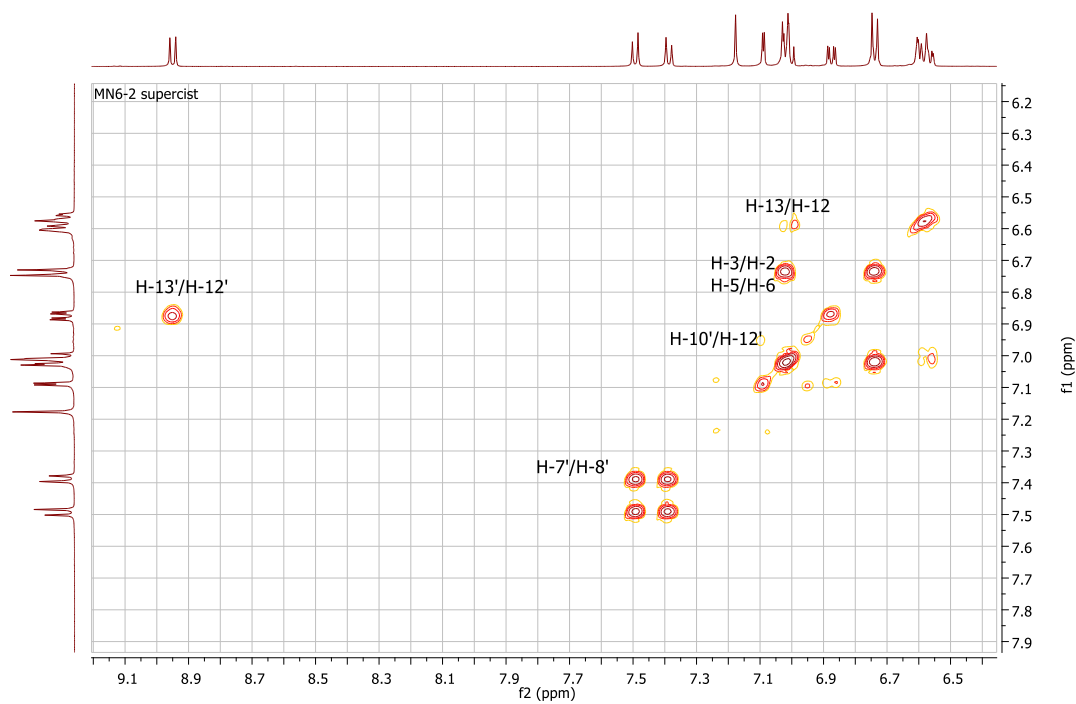
**Figure S26.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **3**



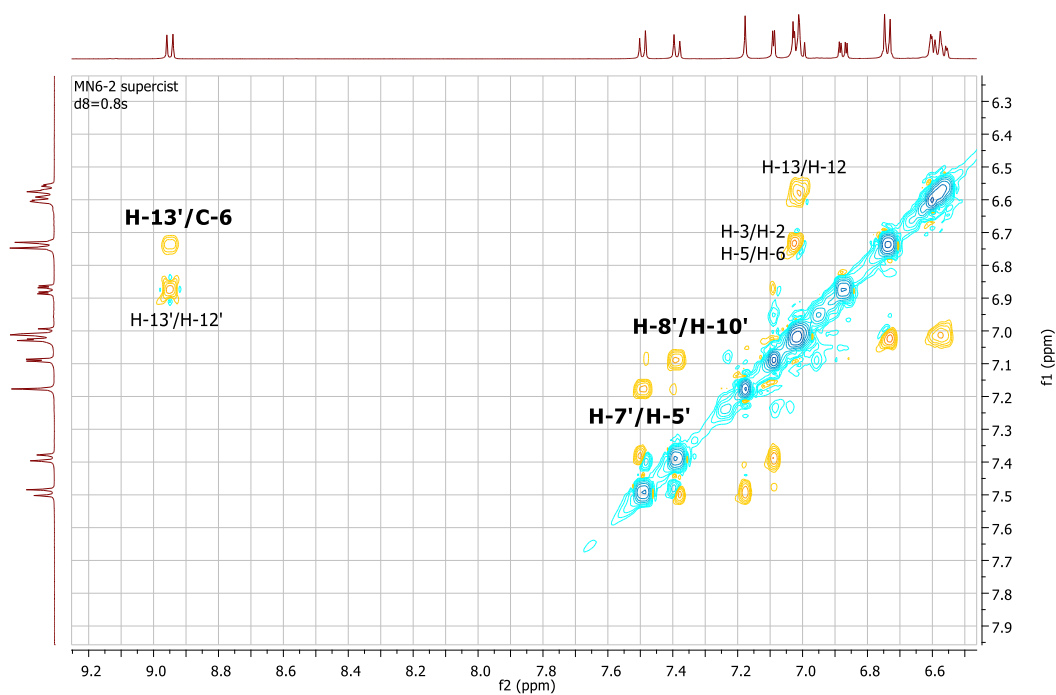
**Figure S27.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **3**



**Figure S28.** Aliphatic part of the  $^{13}\text{C}$  NMR spectrum of compound **3**

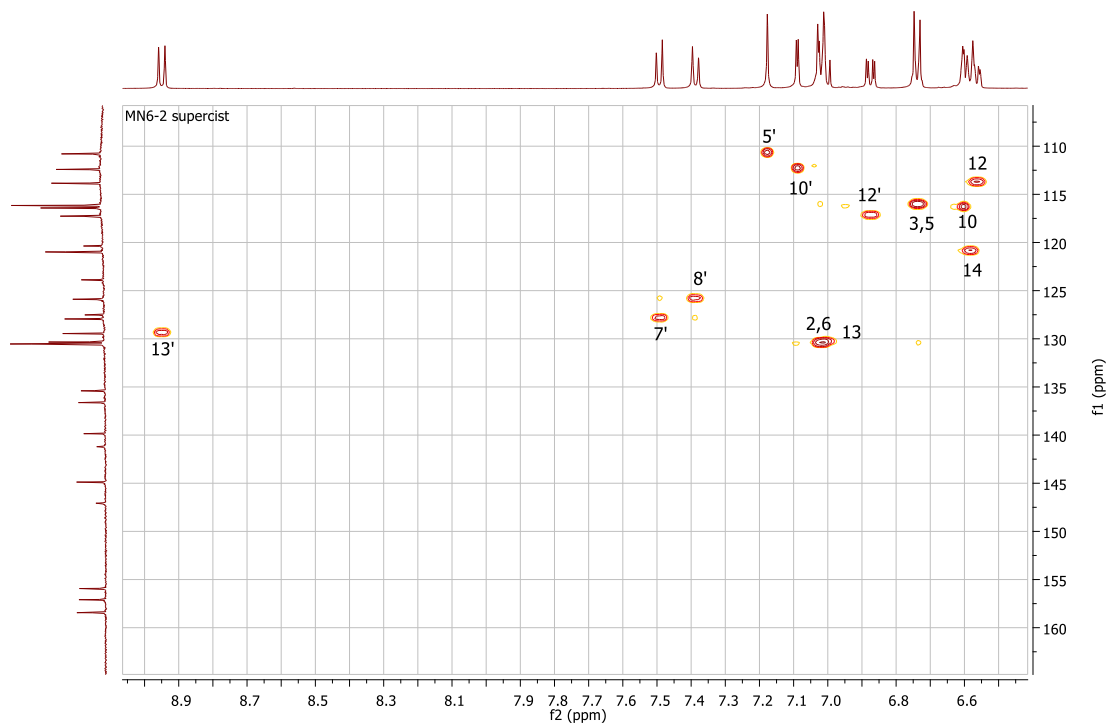


**Figure S29.** Aromatic part of the COSY spectrum of compound **3**

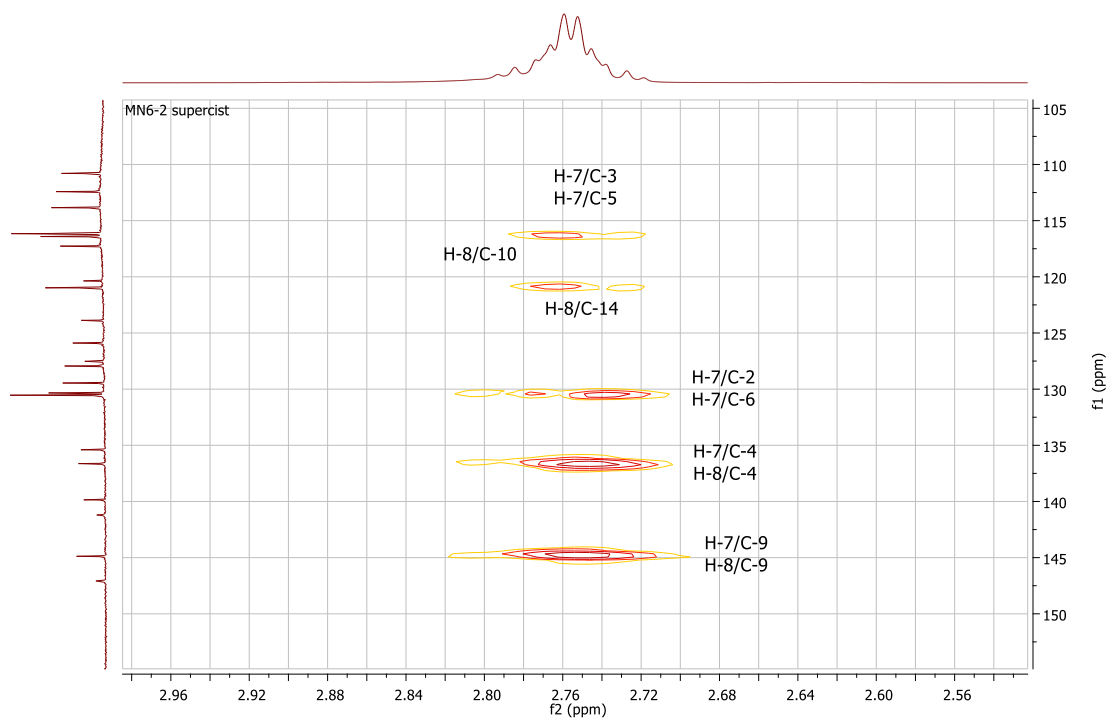


**Figure S30.** Aromatic part of the NOESY spectrum of compound **3**





**Figure S31.** Aromatic part of the HSQC spectrum of compound **3**



**Figure S32.** The first part of the **HMBC** spectrum of compound **3**

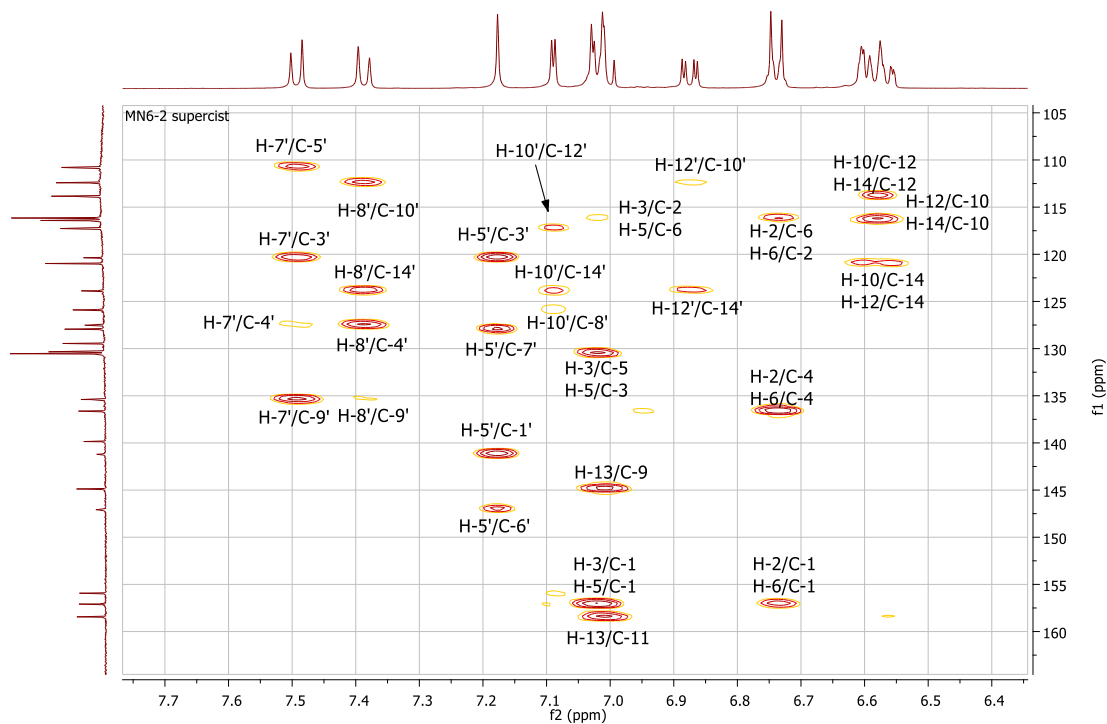


Figure S33. The second part of the **HMBC** spectrum of compound **3**

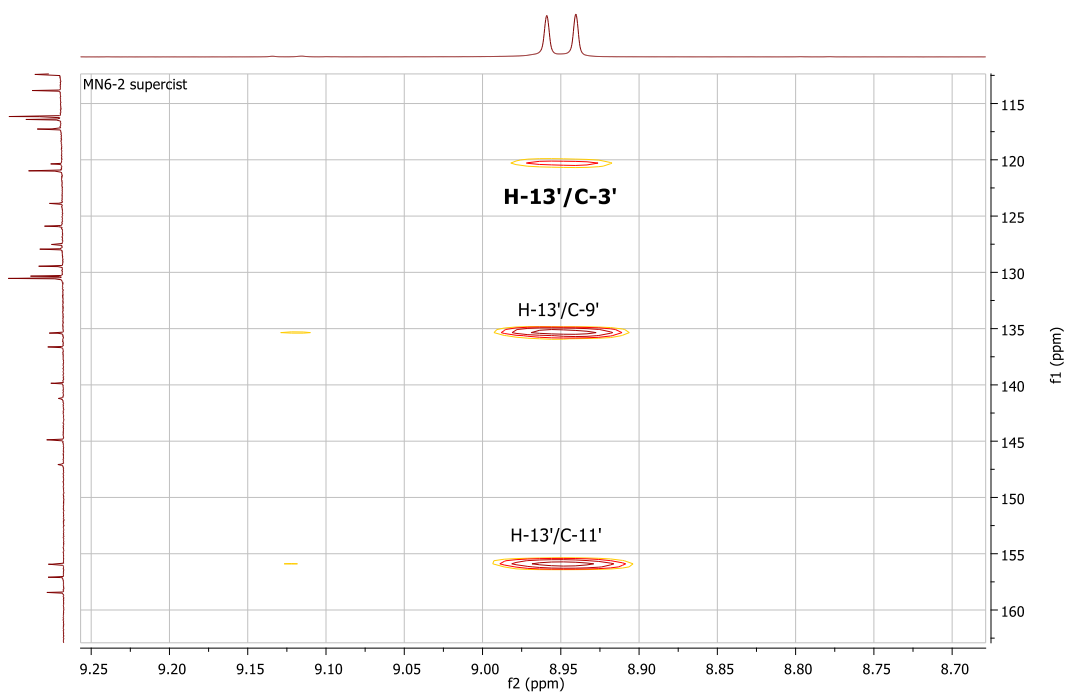
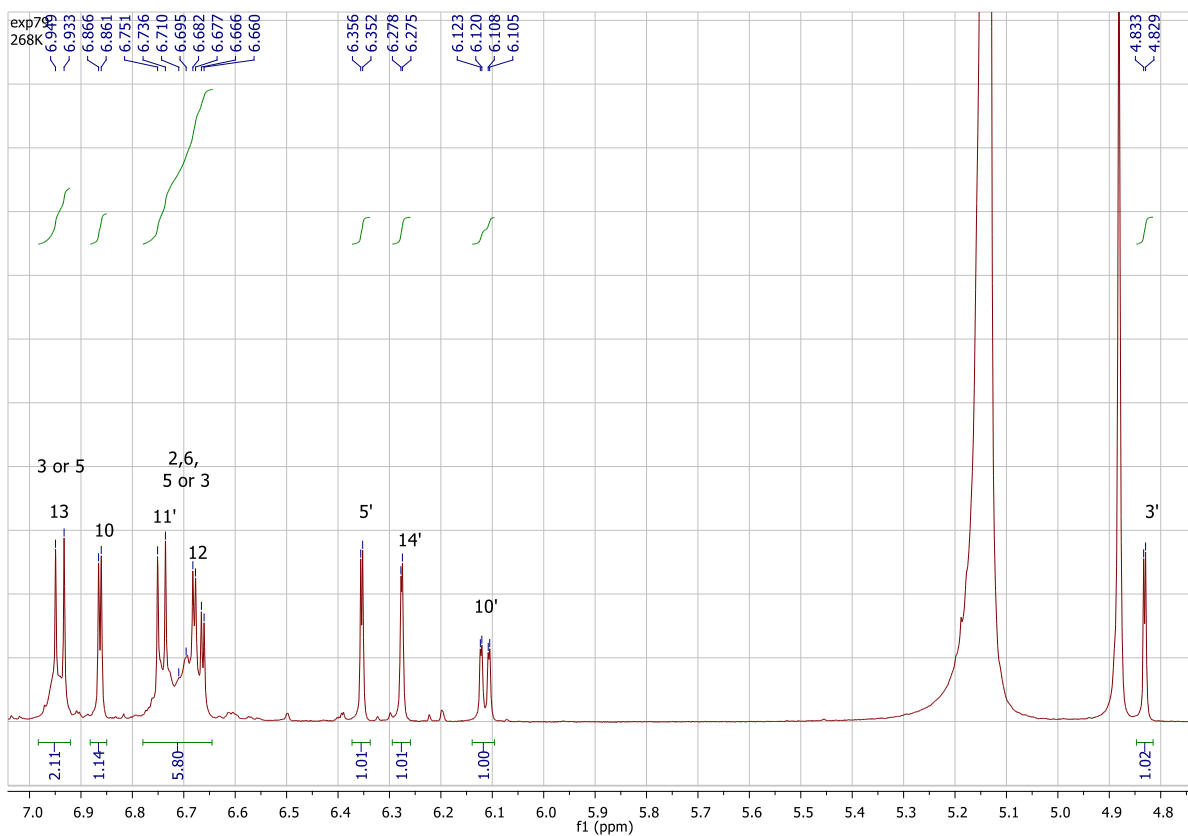
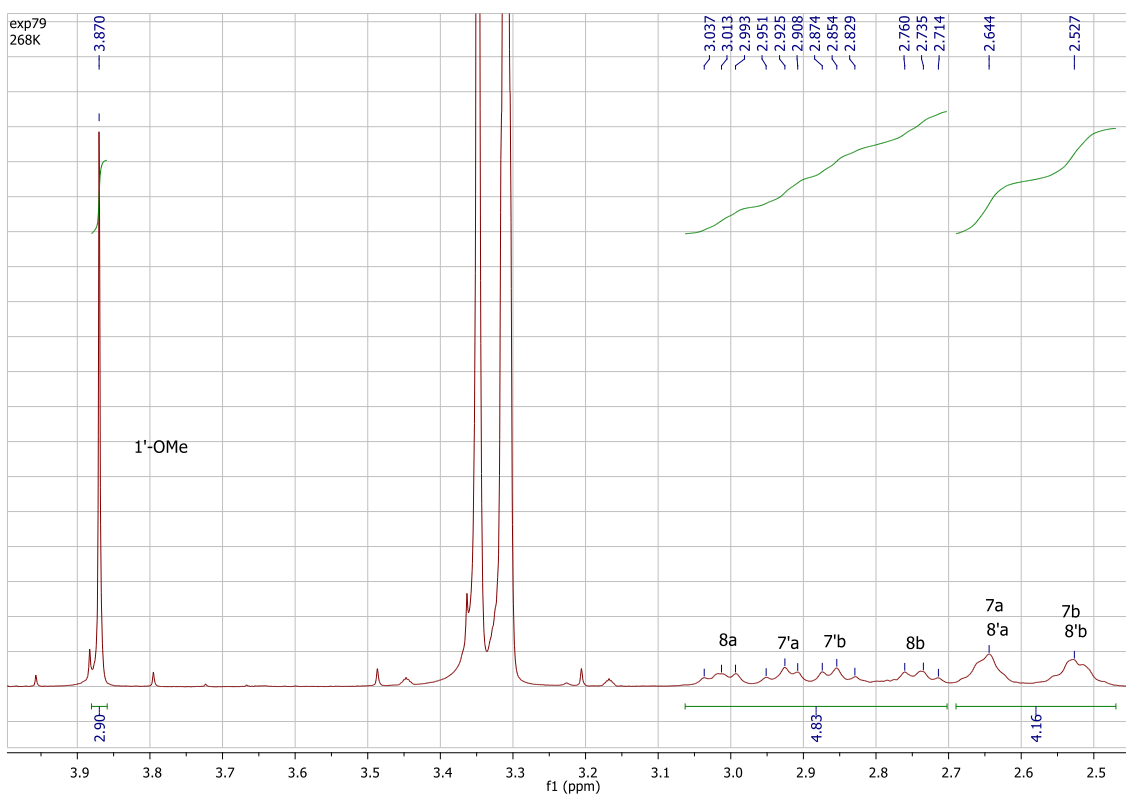


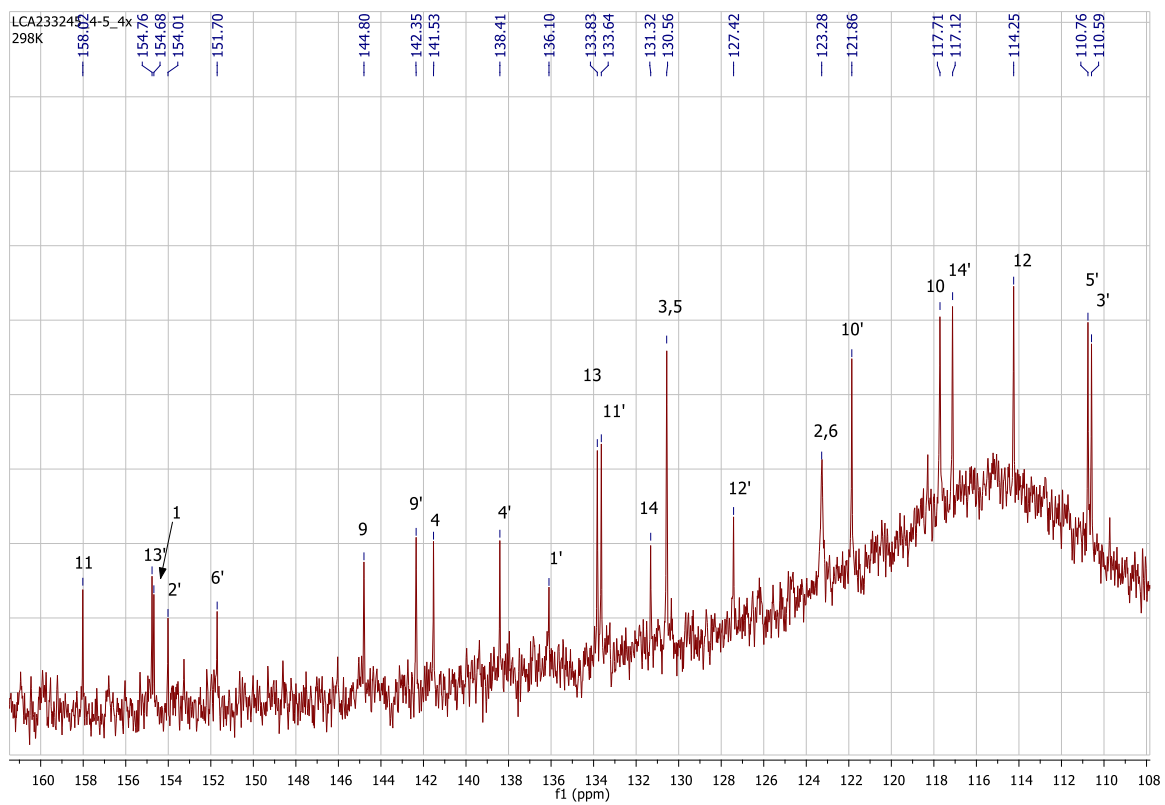
Figure S34. The third part of the **HMBC** spectrum of compound **3**



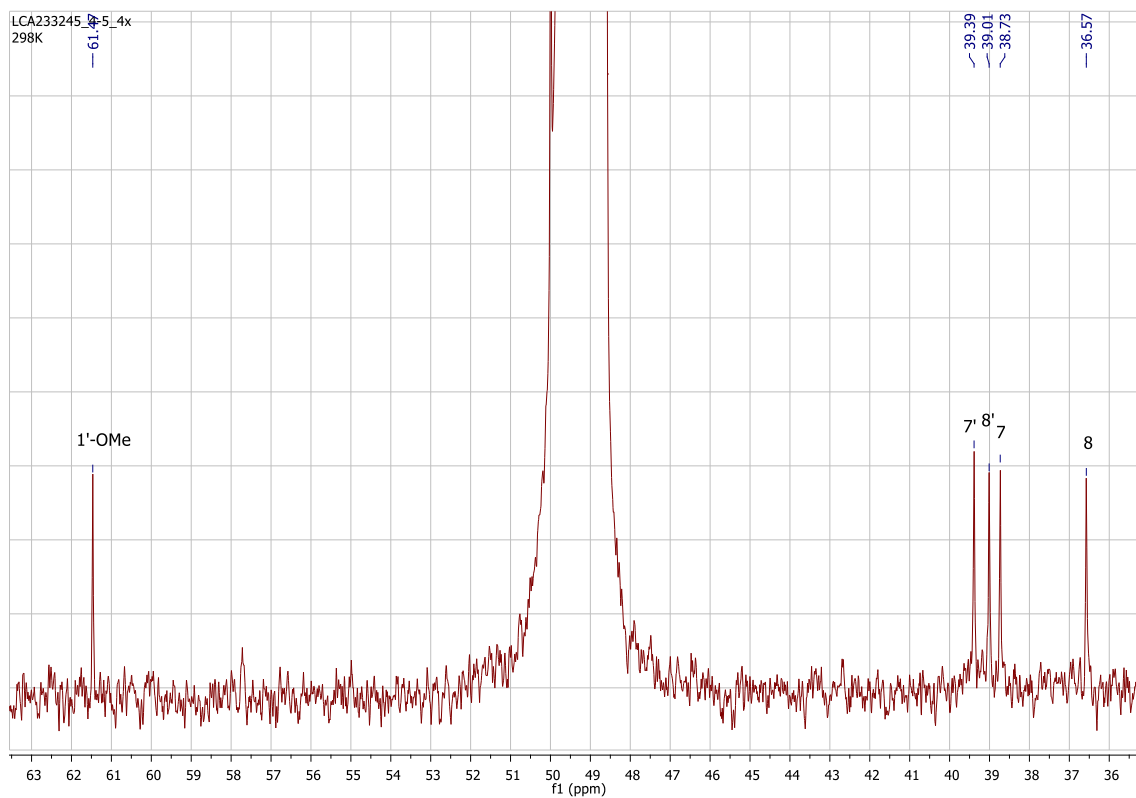
**Figure S35.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **4**



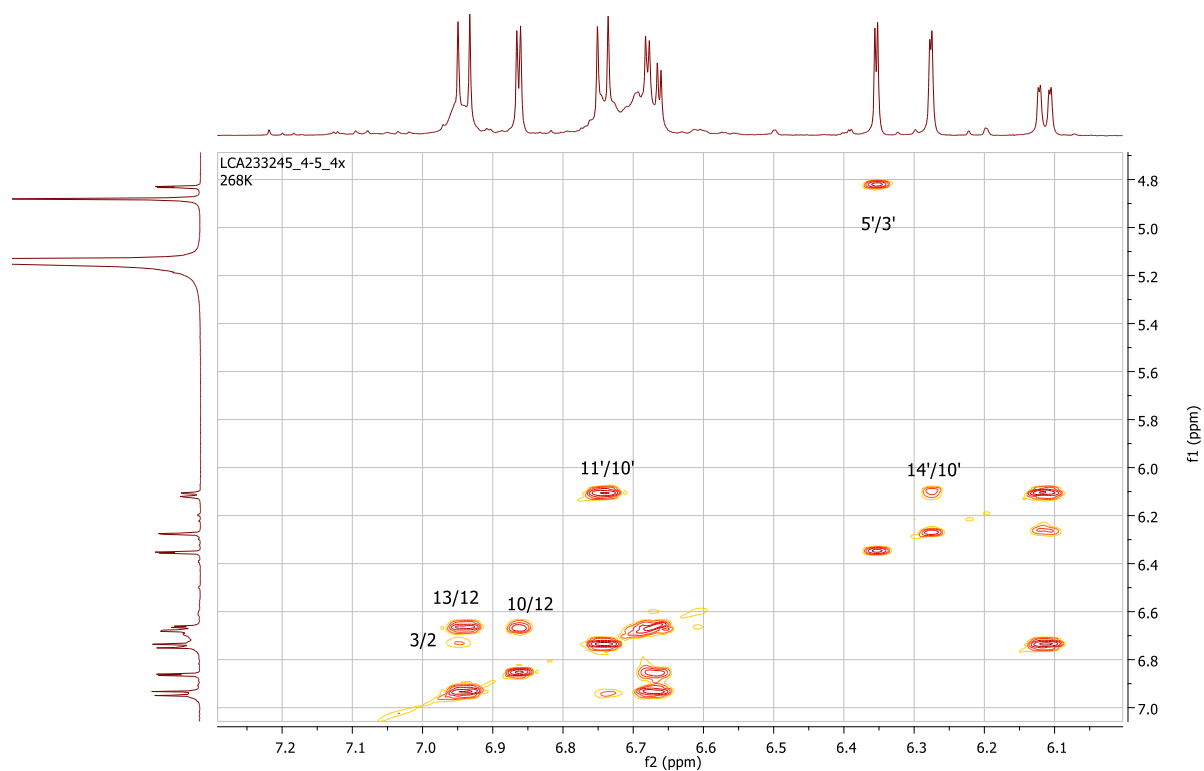
**Figure S36.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **4**



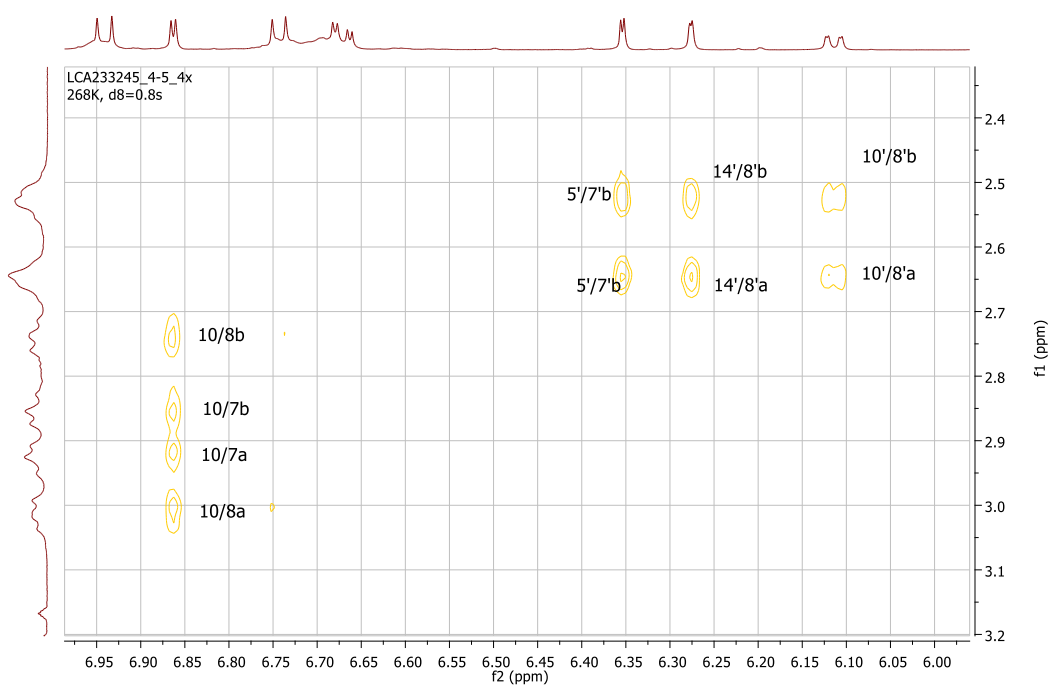
**Figure S37.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **4**



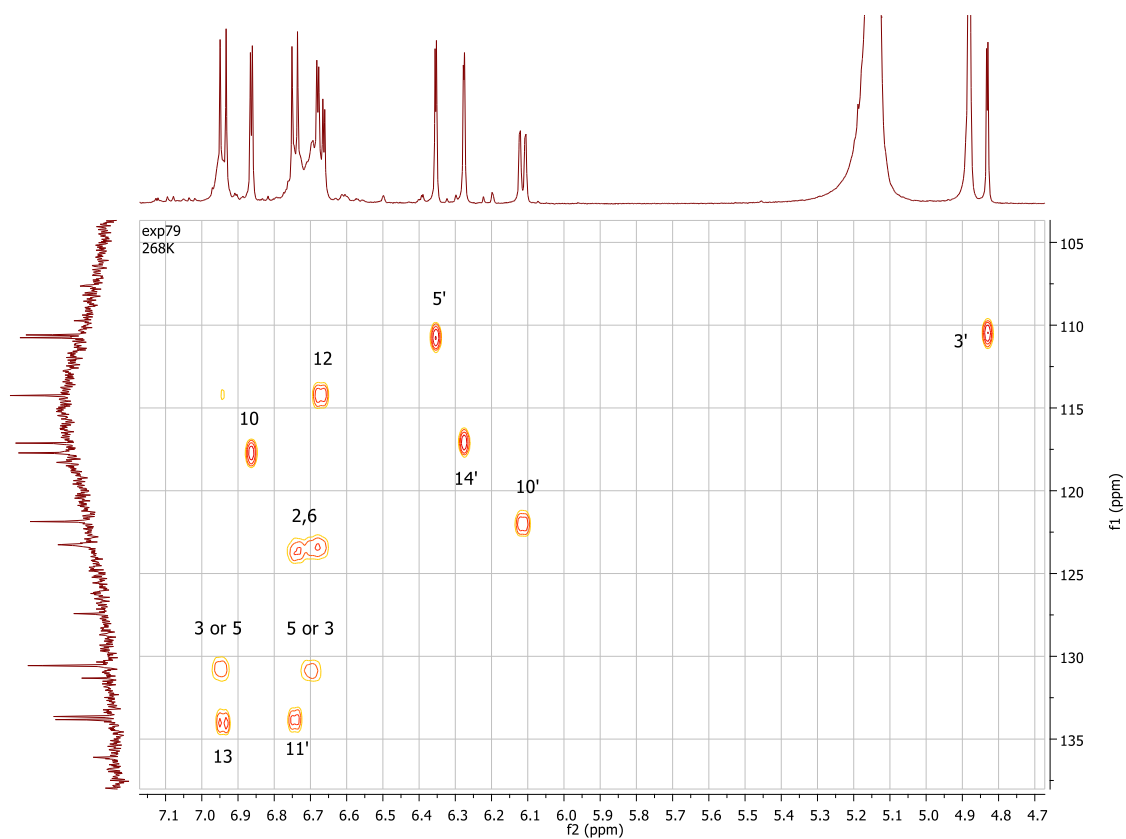
**Figure S38.** Aliphatic part of the  $^{13}\text{C}$  NMR spectrum of compound **4**



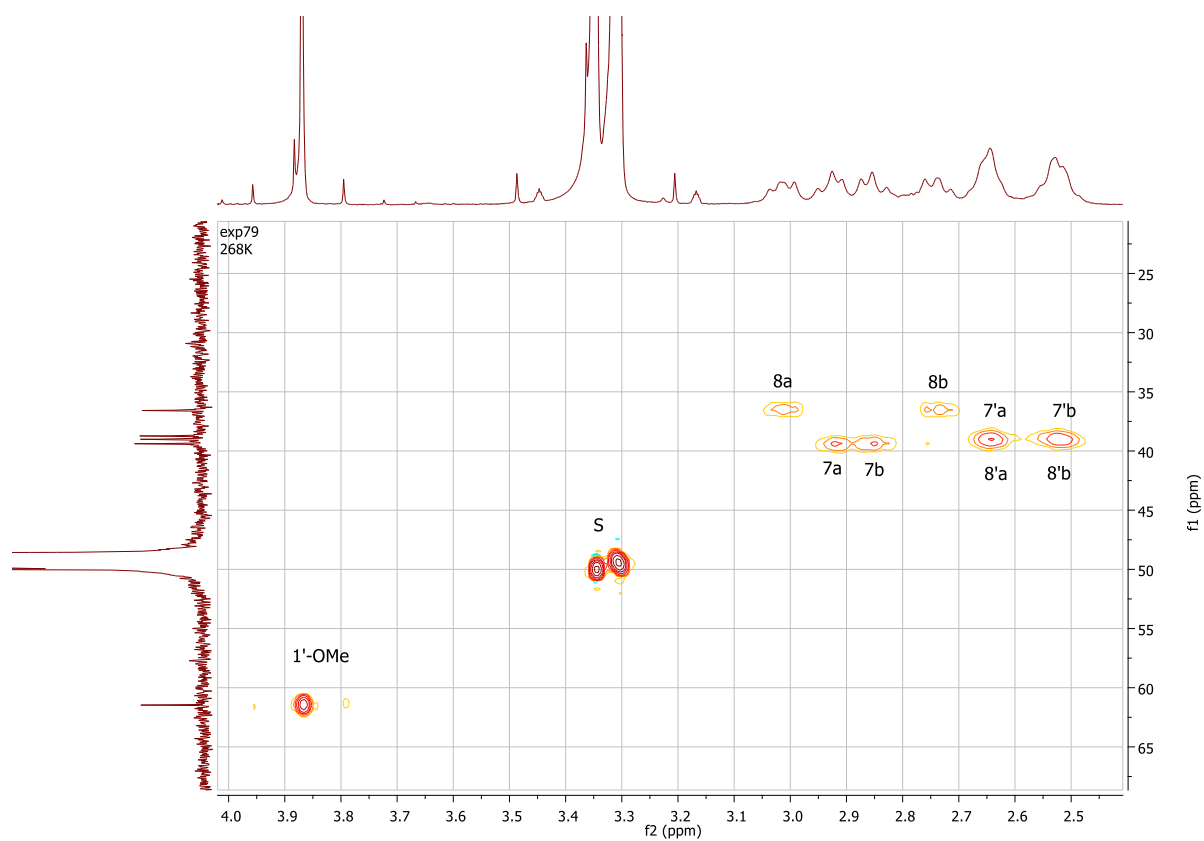
**Figure S39.** Aromatic part of the COSY spectrum of compound **4**



**Figure S40.** The first part of the NOESY spectrum of compound **4**



**Figure S41.** Aromatic part of the HSQC spectrum of compound **4**



**Figure S42.** Aliphatic part of the HSQC spectrum of compound **4**

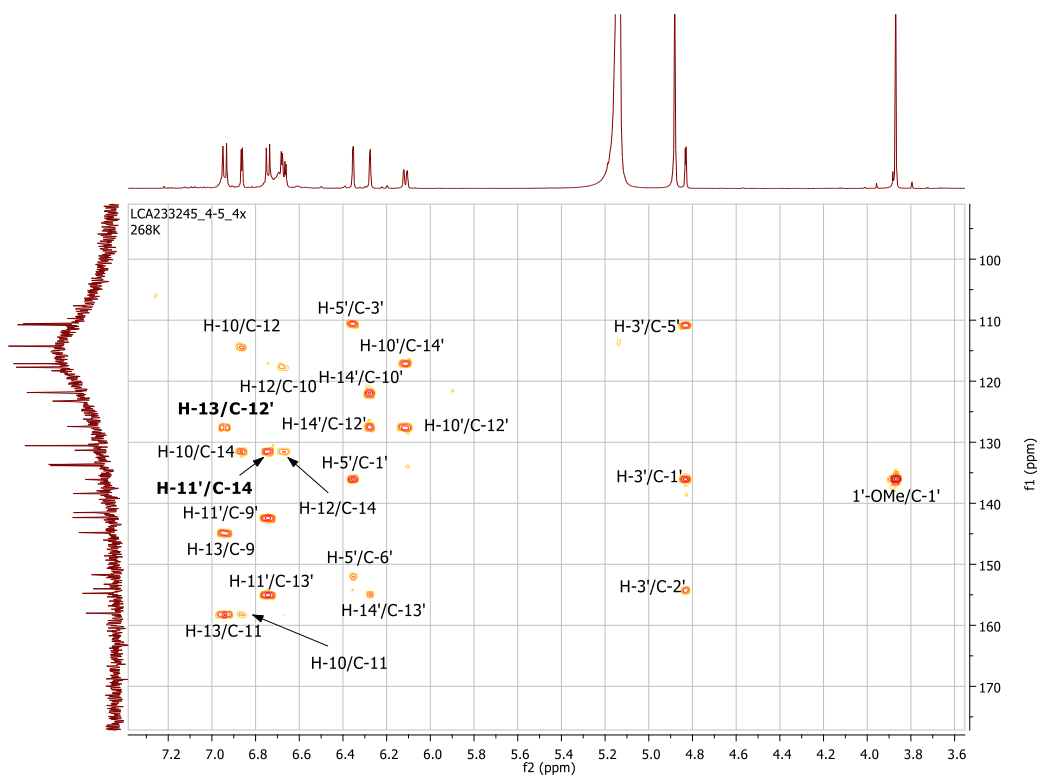


Figure S43. Aromatic part of the HMBC spectrum of compound 4

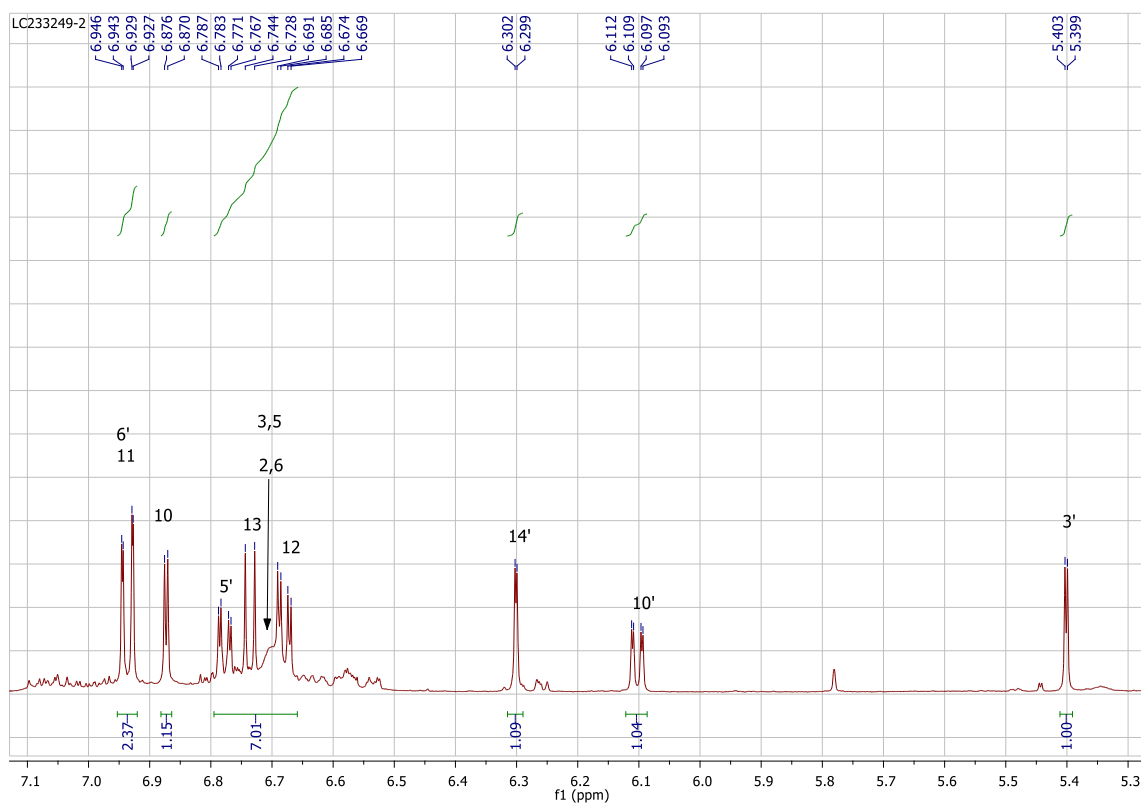
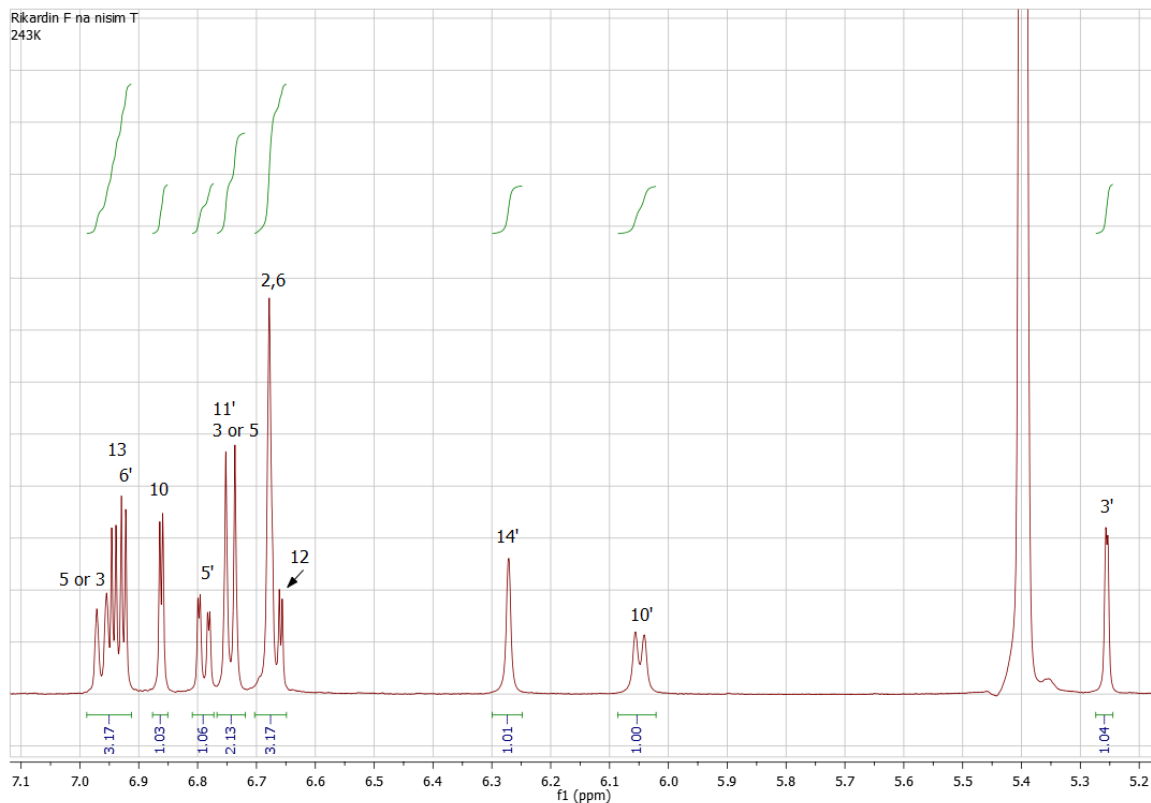
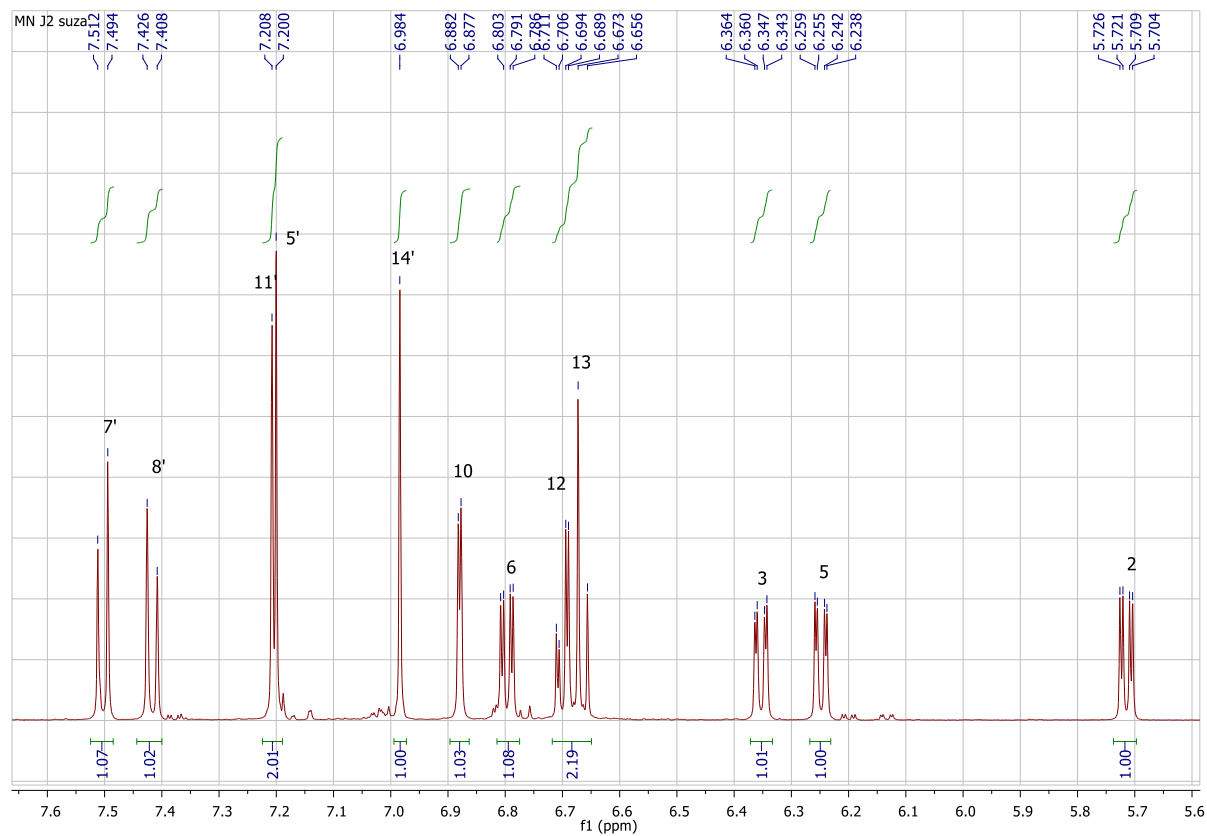


Figure S44. Aromatic part of the <sup>1</sup>H NMR spectrum of riccardin F at room temperature

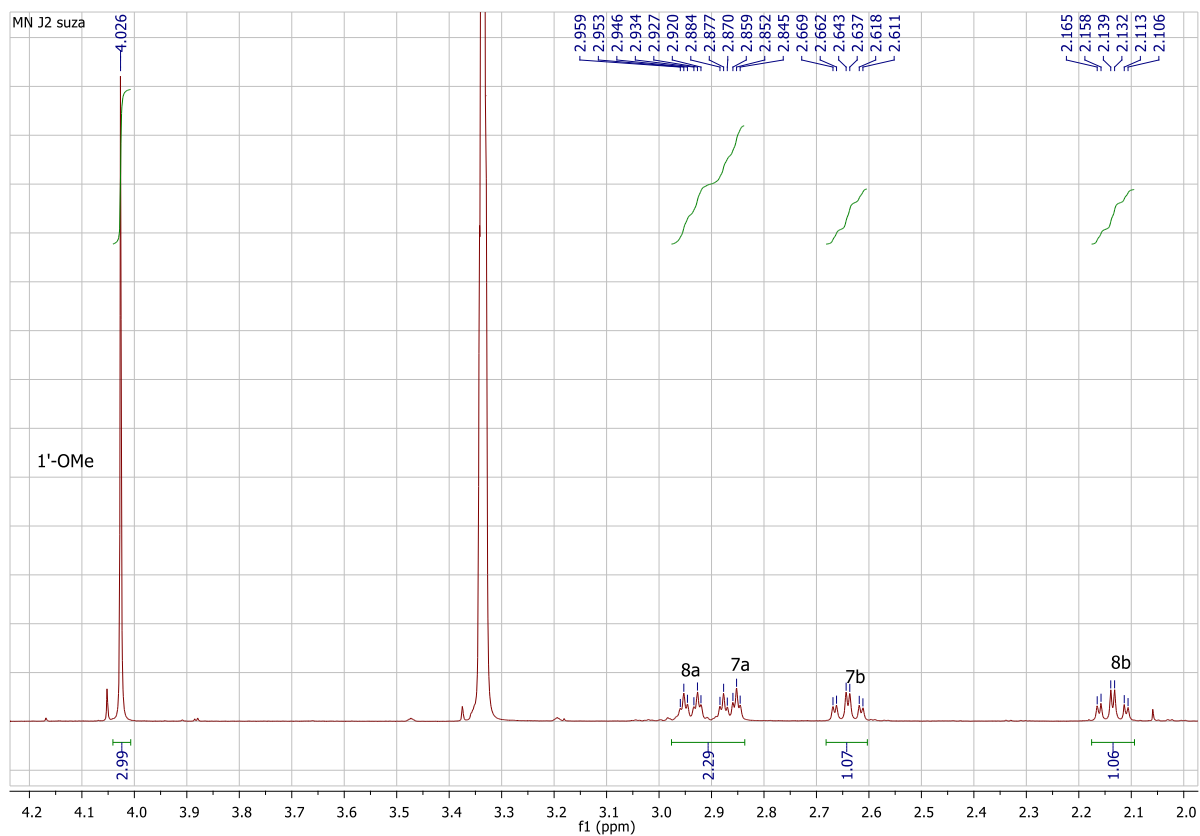


**Figure S45.** Aromatic part of  $^1\text{H}$  NMR spectrum of the purified riccardin F at 243K

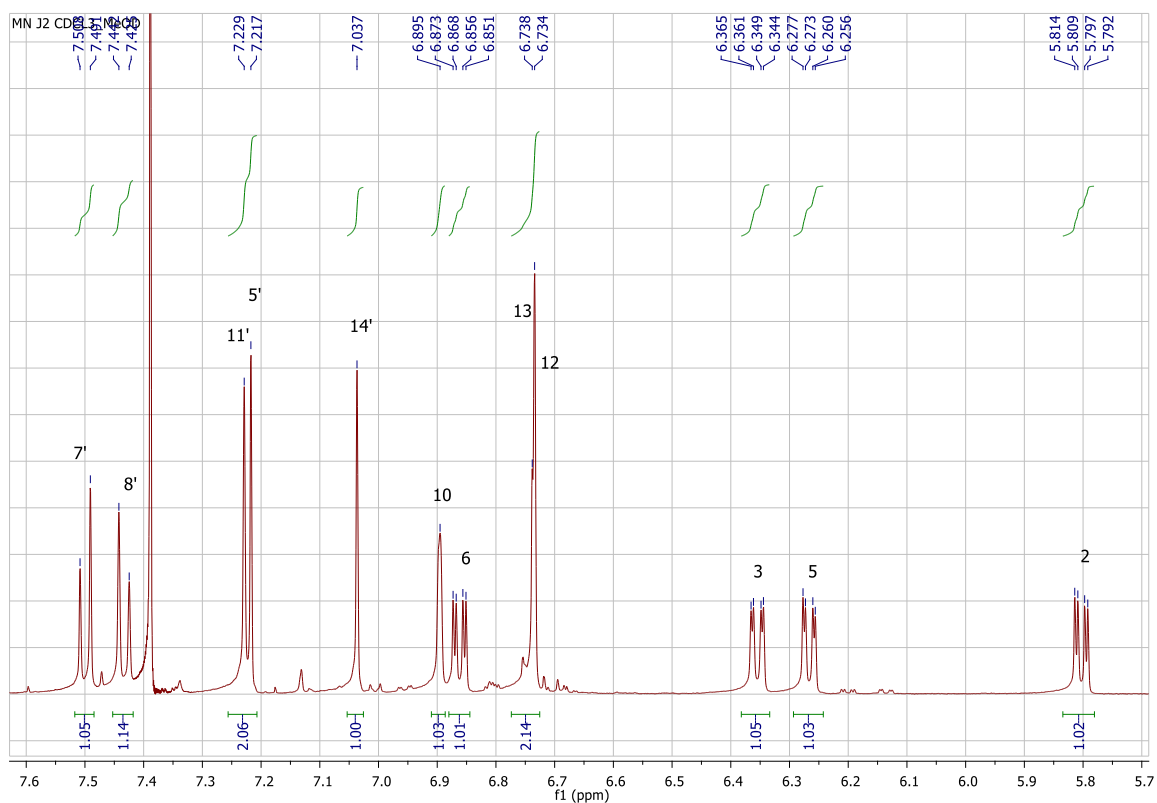


**Figure S46.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **5** recorded in  $\text{CD}_3\text{OD}$

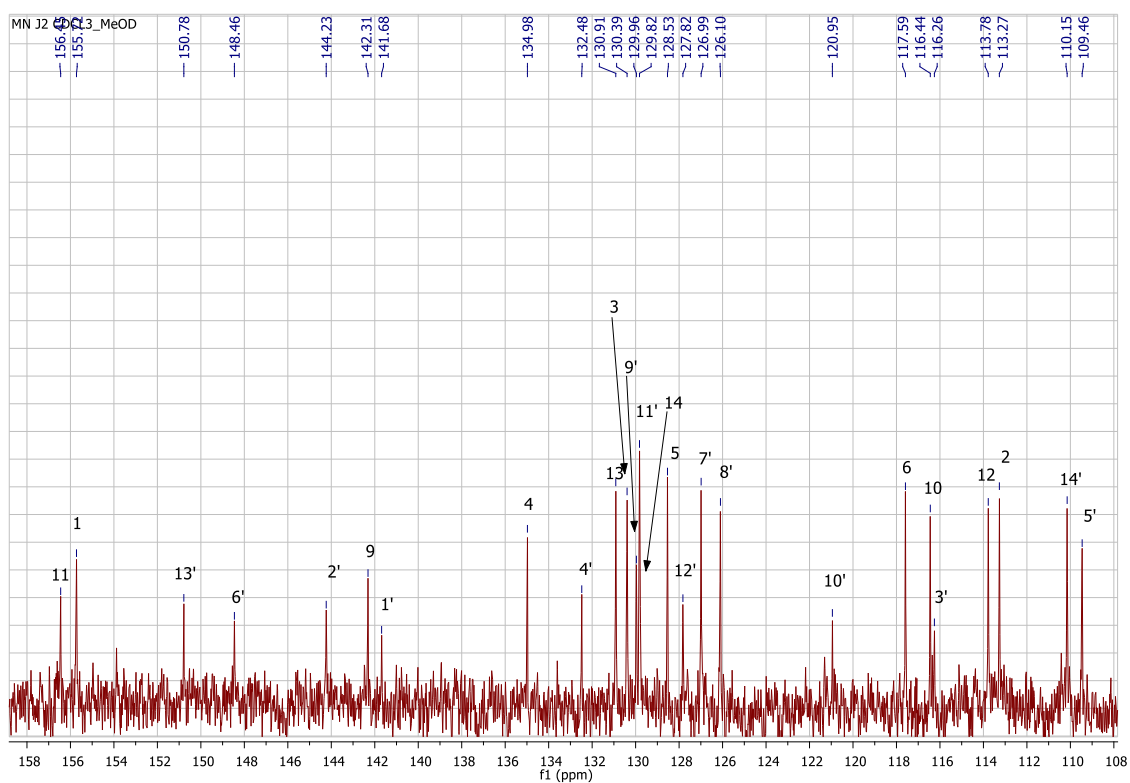




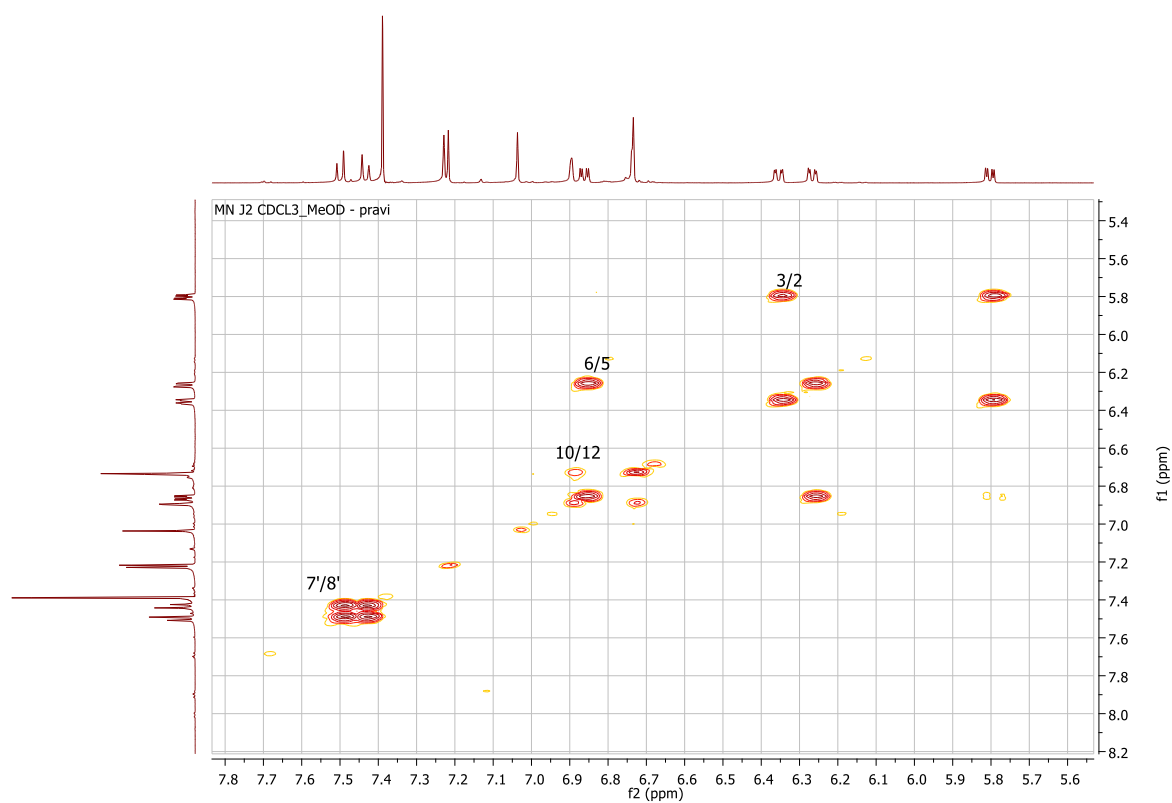
**Figure S47.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **5** recorded in  $\text{CD}_3\text{OD}$



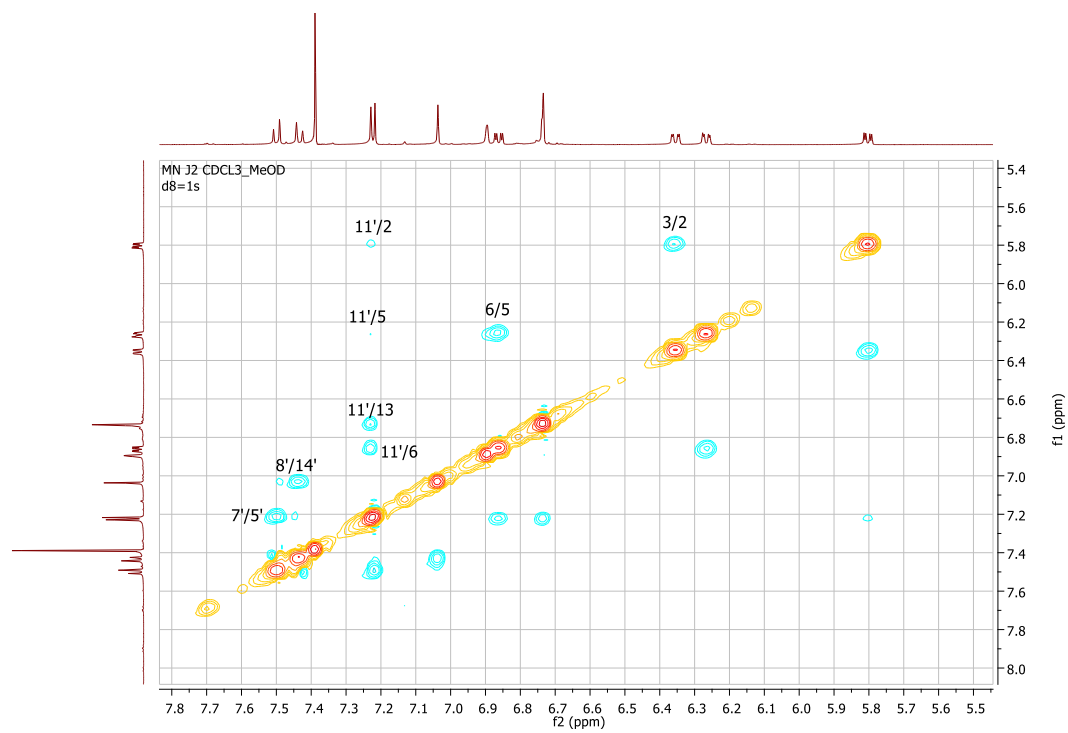
**Figure S48.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **5** recorded in mixture of  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$



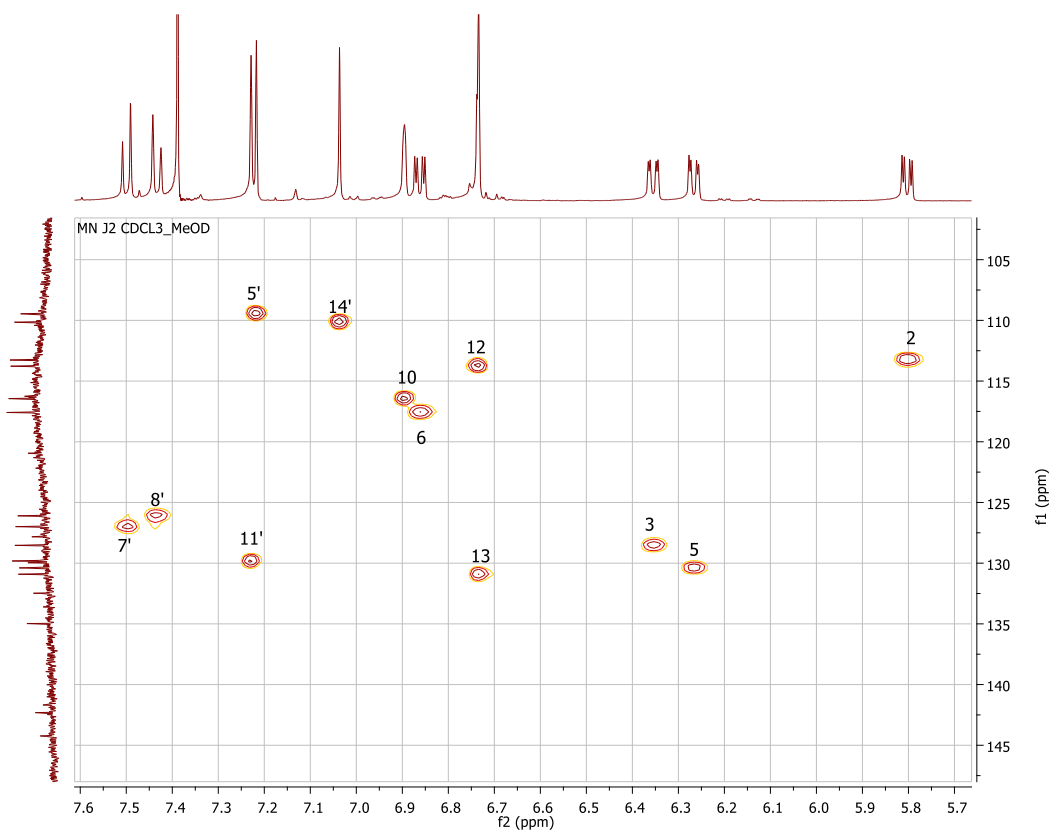
**Figure S49.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **5** recorded in mixture of  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$



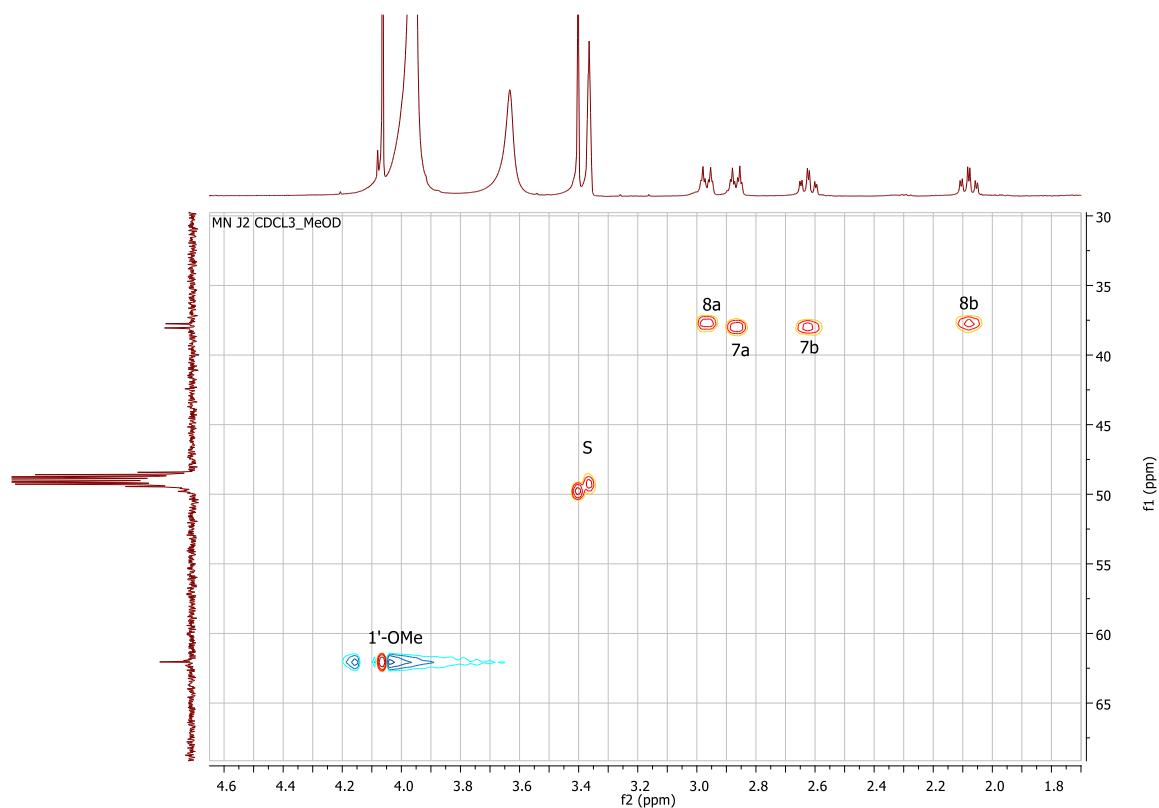
**Figure S50.** Aromatic part of the COSY spectrum of compound **11** recorded in mixture of  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$



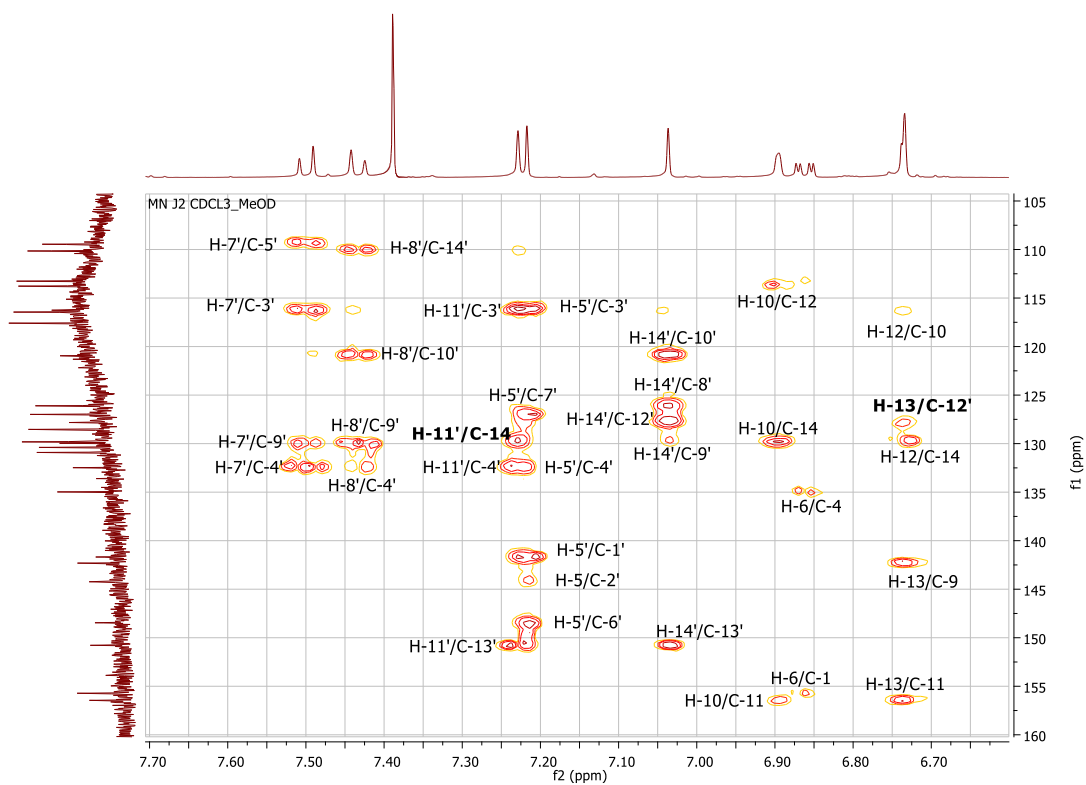
**Figure S51.** NOE correlations of aromatic protons of compound **5**



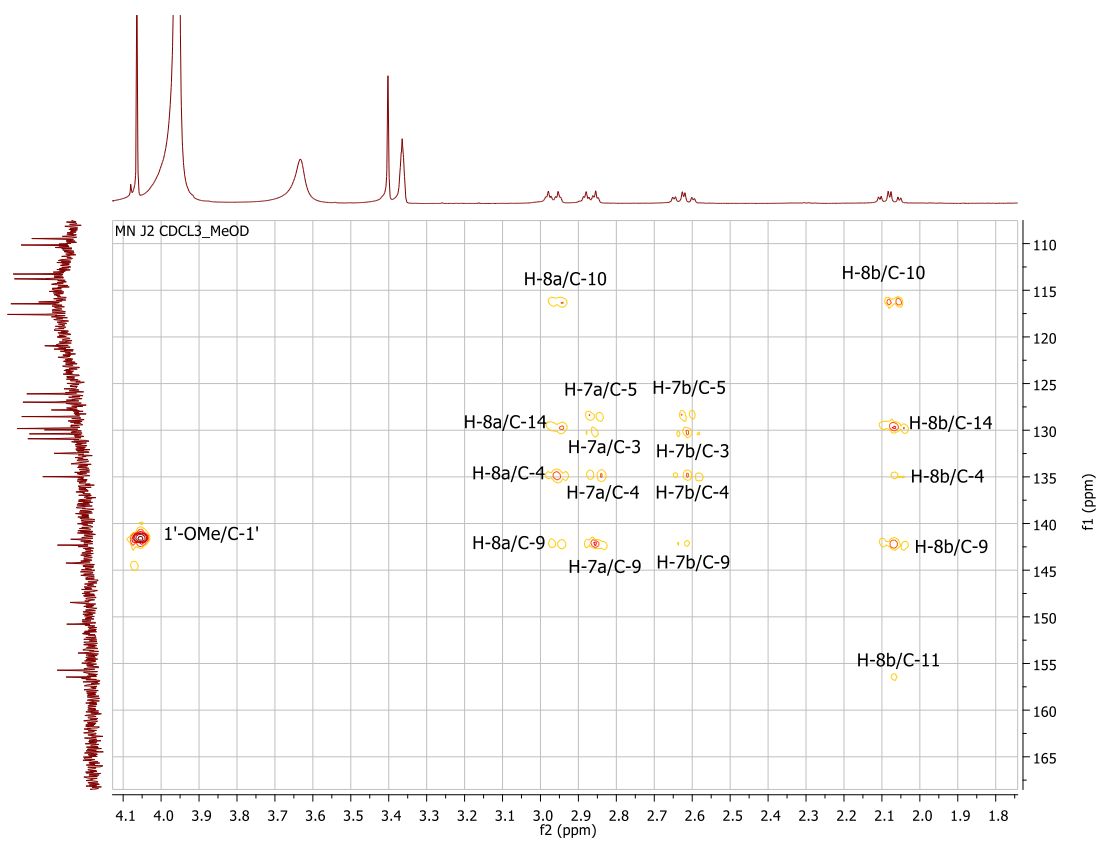
**Figure S52.** HSQC correlations of aromatic protons of compound **5**



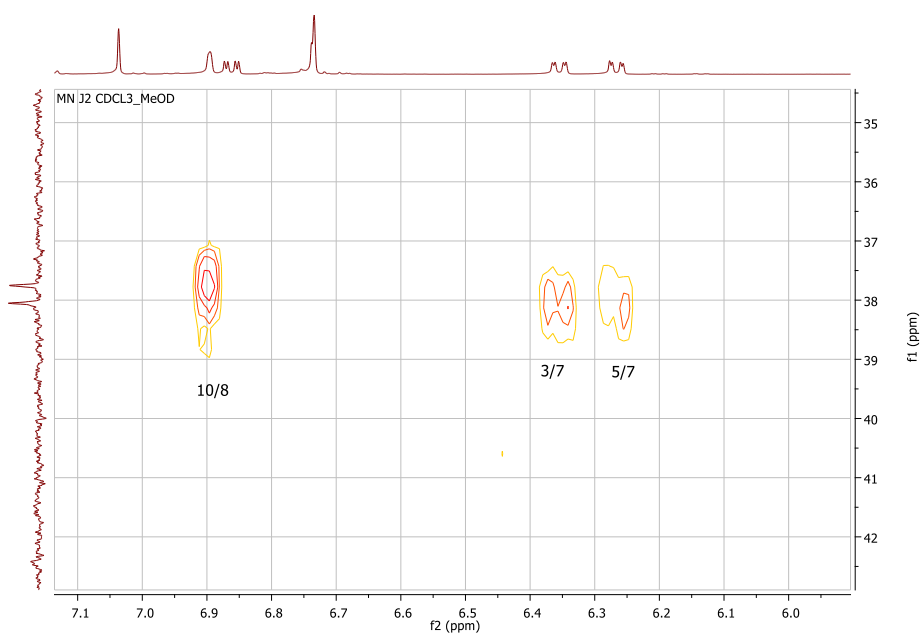
**Figure S53.** HSQC correlations of aliphatic protons of compound **5**



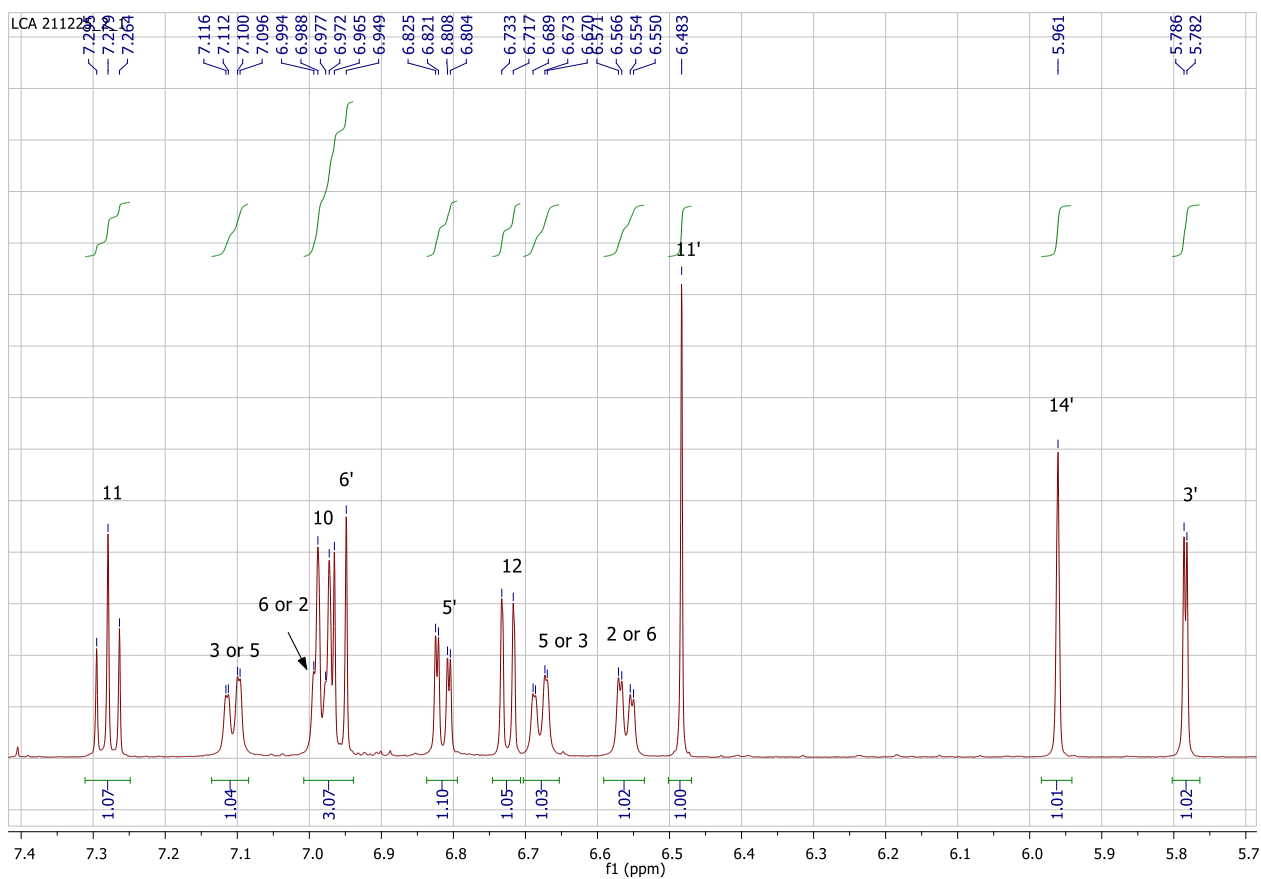
**Figure S54.** The first part of the HMBC spectrum of compound **5** recorded in mixture of CDCl<sub>3</sub> and CD<sub>3</sub>OD



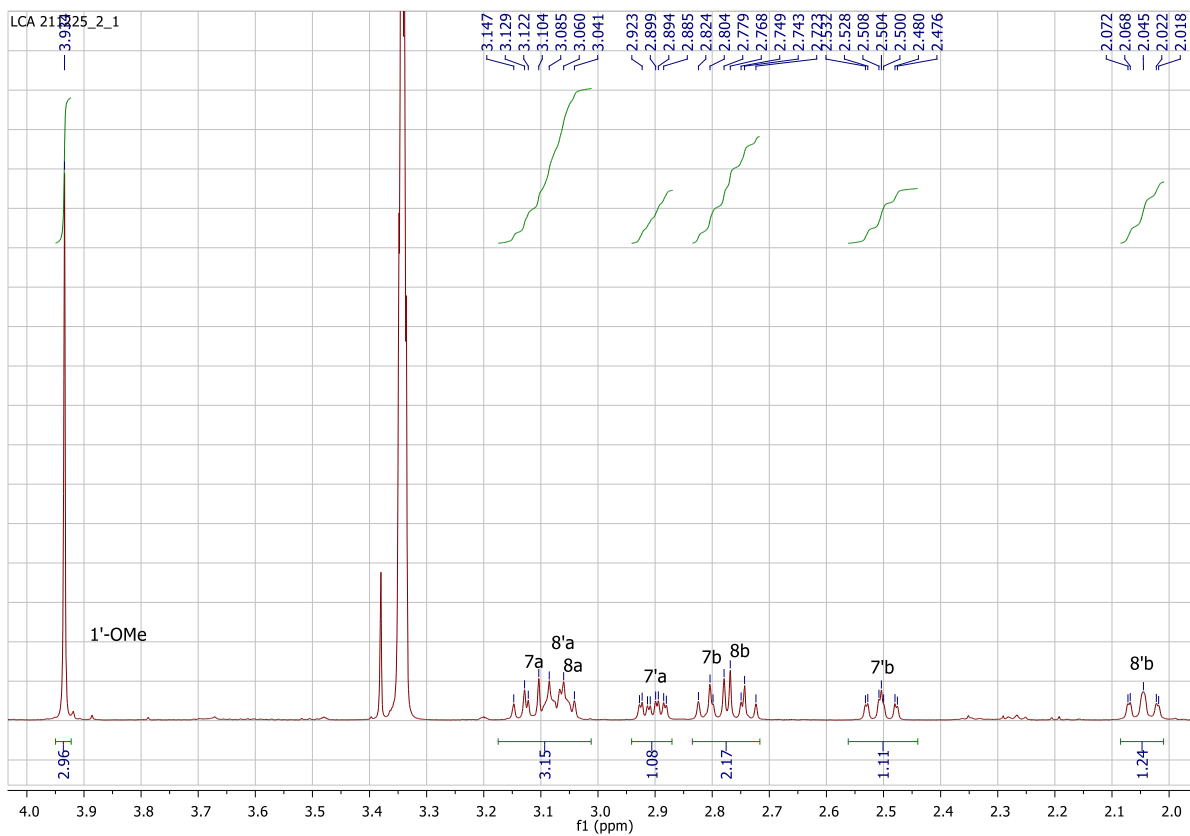
**Figure S55.** The second part of the HMBC spectrum of compound **5** recorded in mixture of  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$



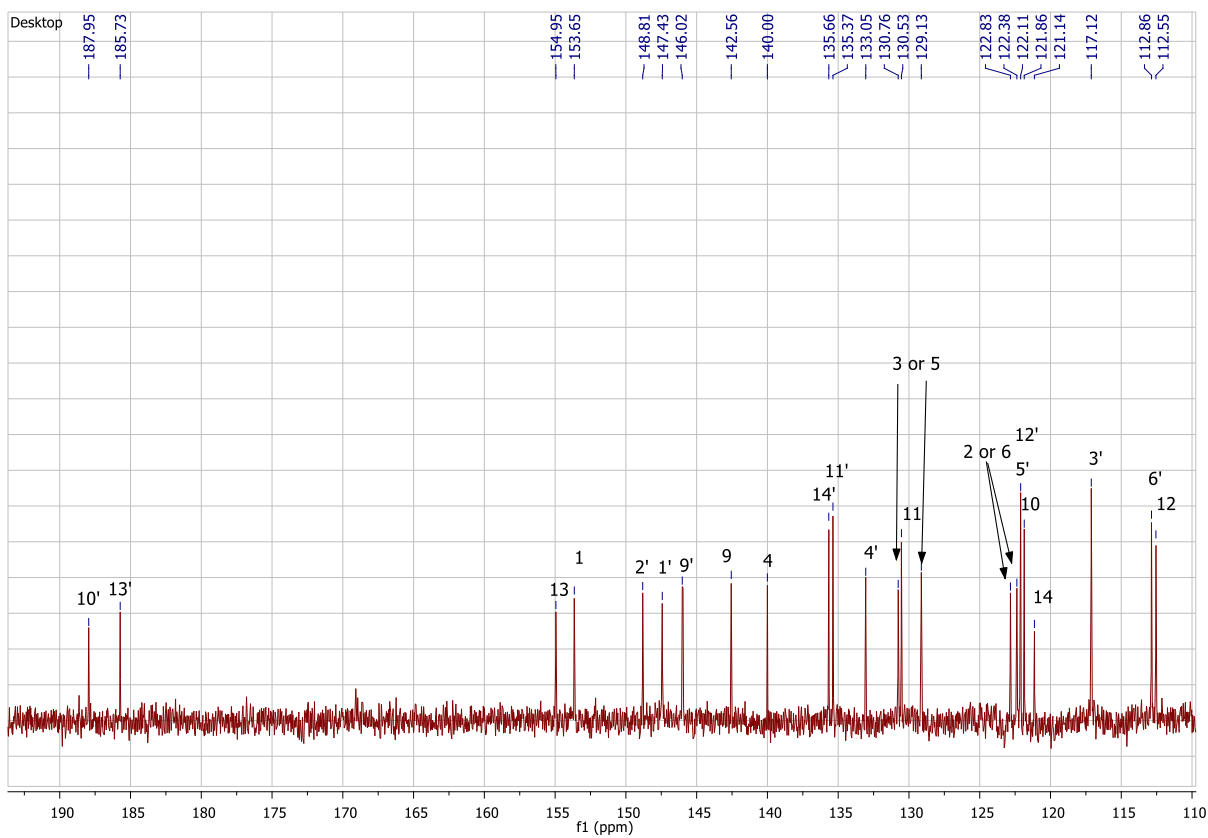
**Figure S56.** HMBC correlations of benzyl protons of compound **5**



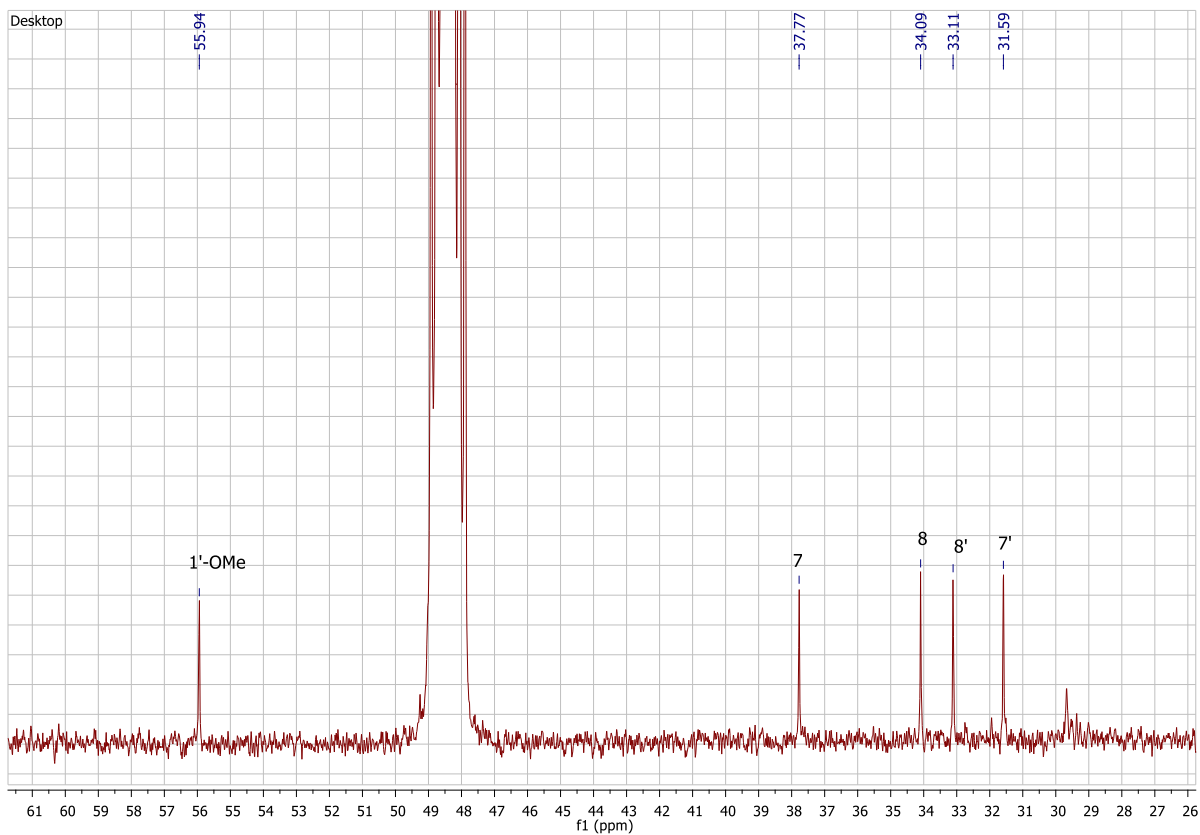
**Figure S57.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **6**



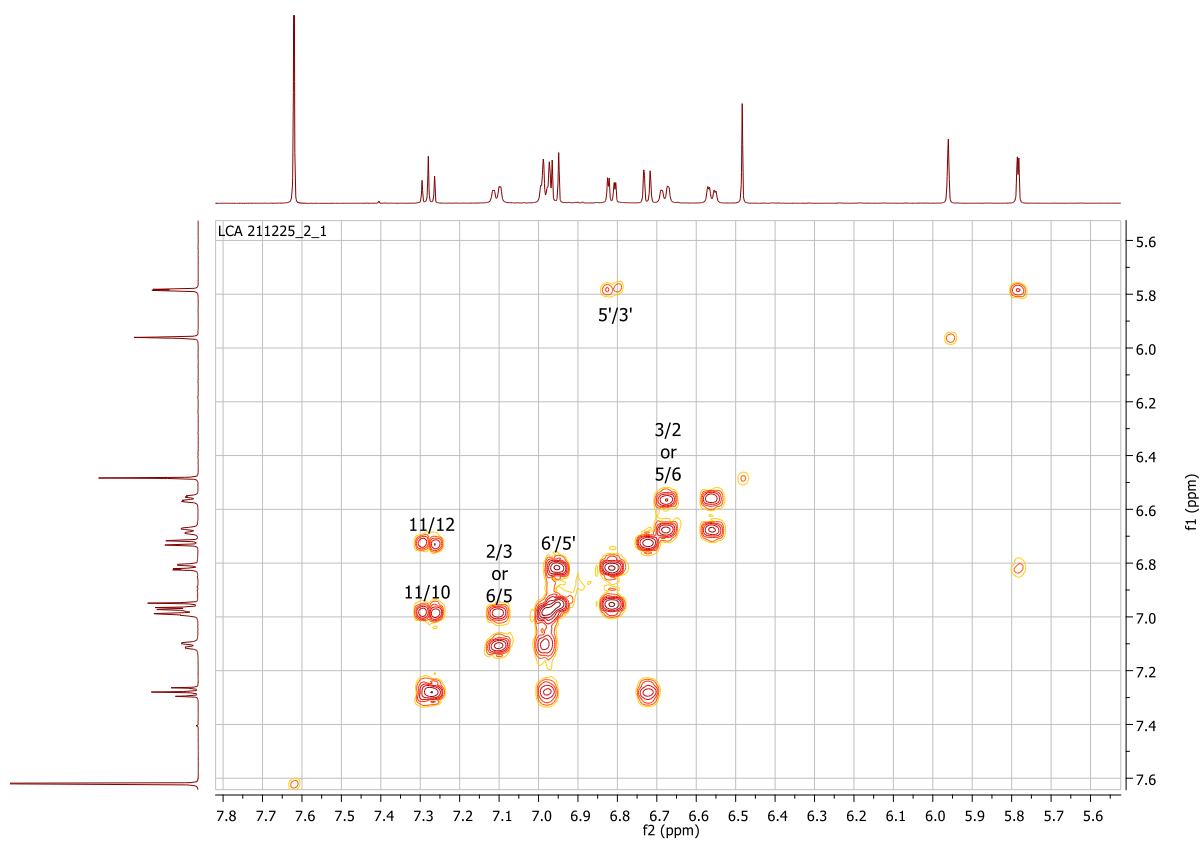
**Figure S58.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **6**



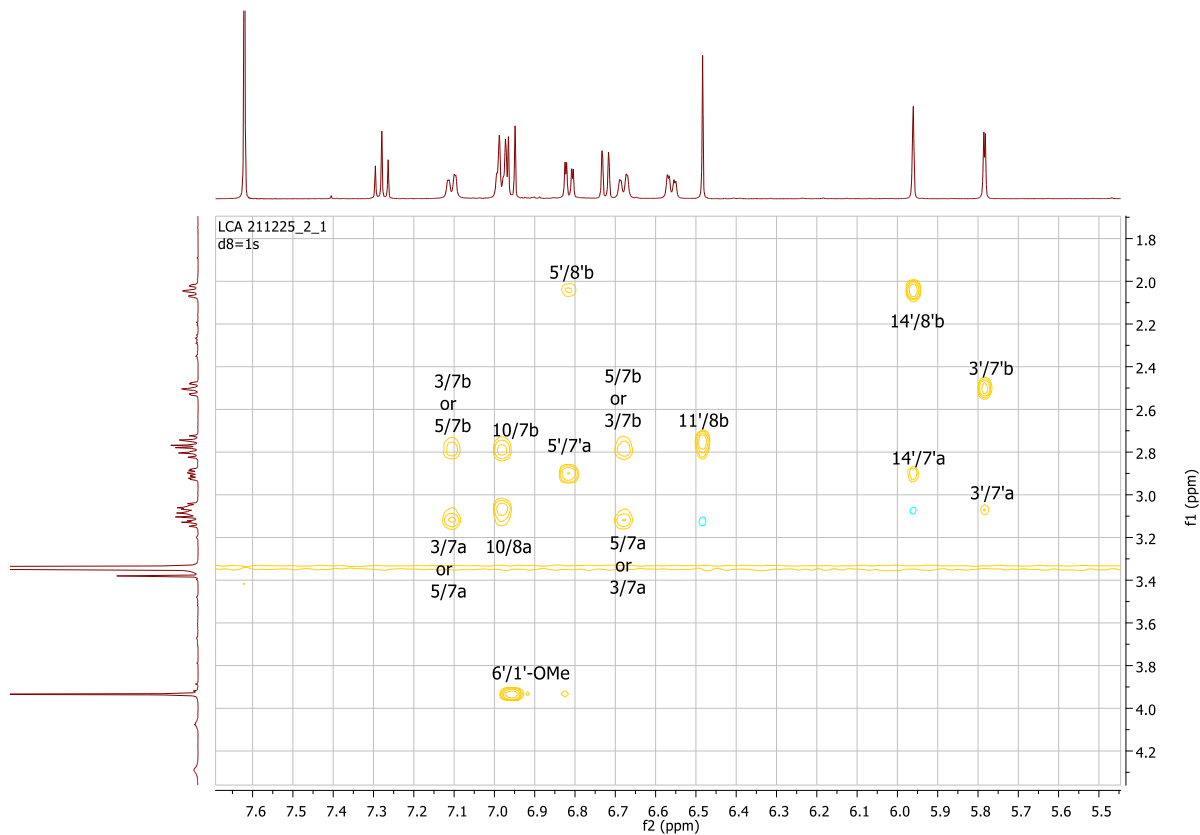
**Figure S59.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **6**



**Figure S60.** Aliphatic part of the  $^{13}\text{C}$  NMR spectrum of compound **6**

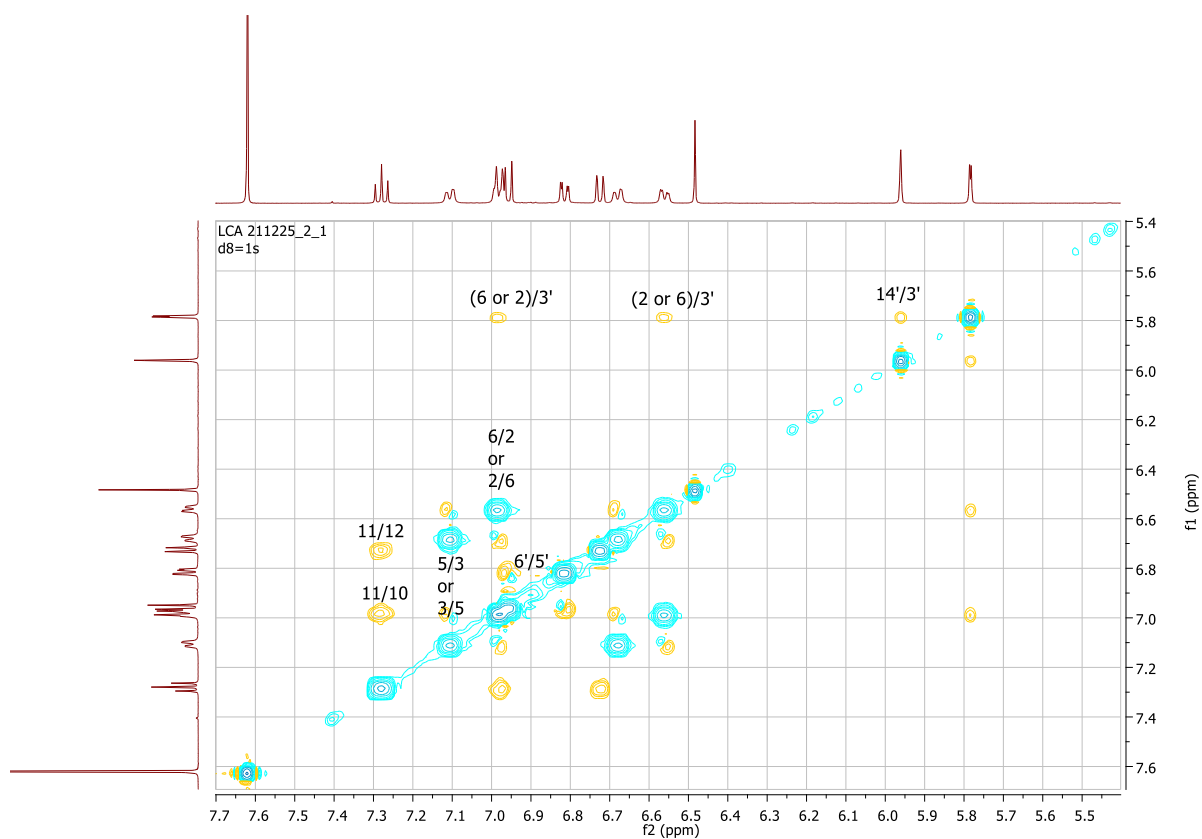


**Figure S61.** Aromatic part of the COSY spectrum of compound **6**

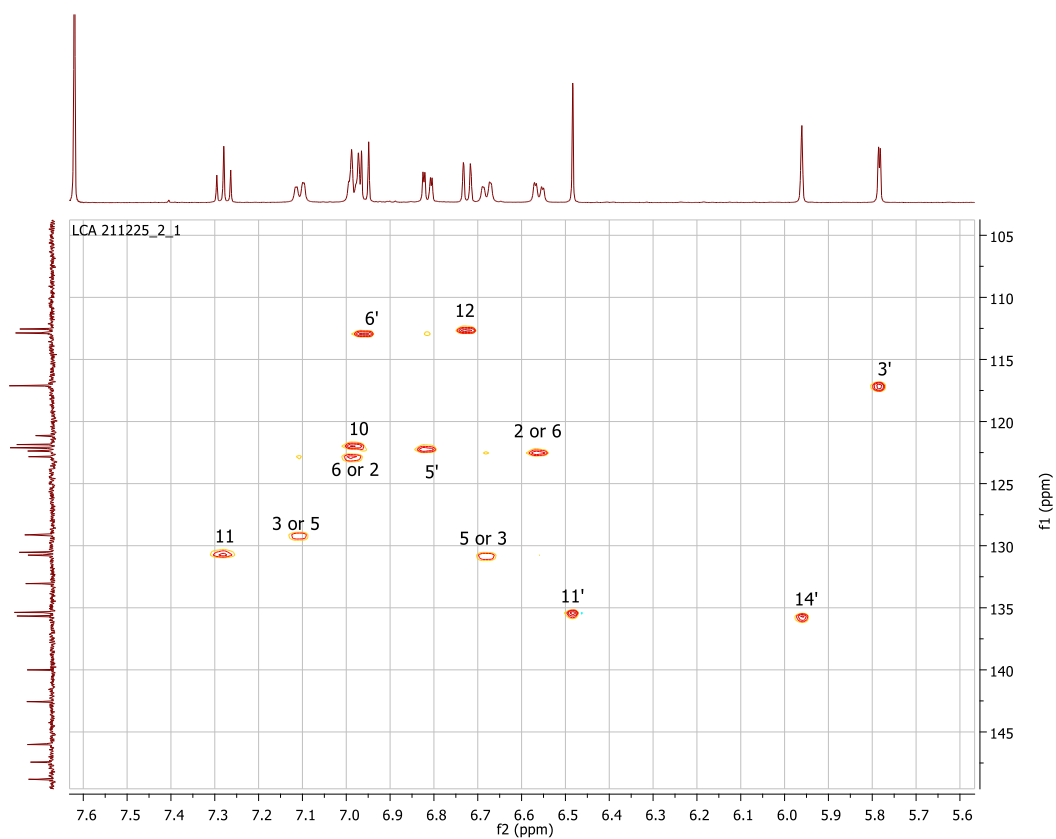


**Figure S62.** The first part of the NOESY spectrum of compound **6**



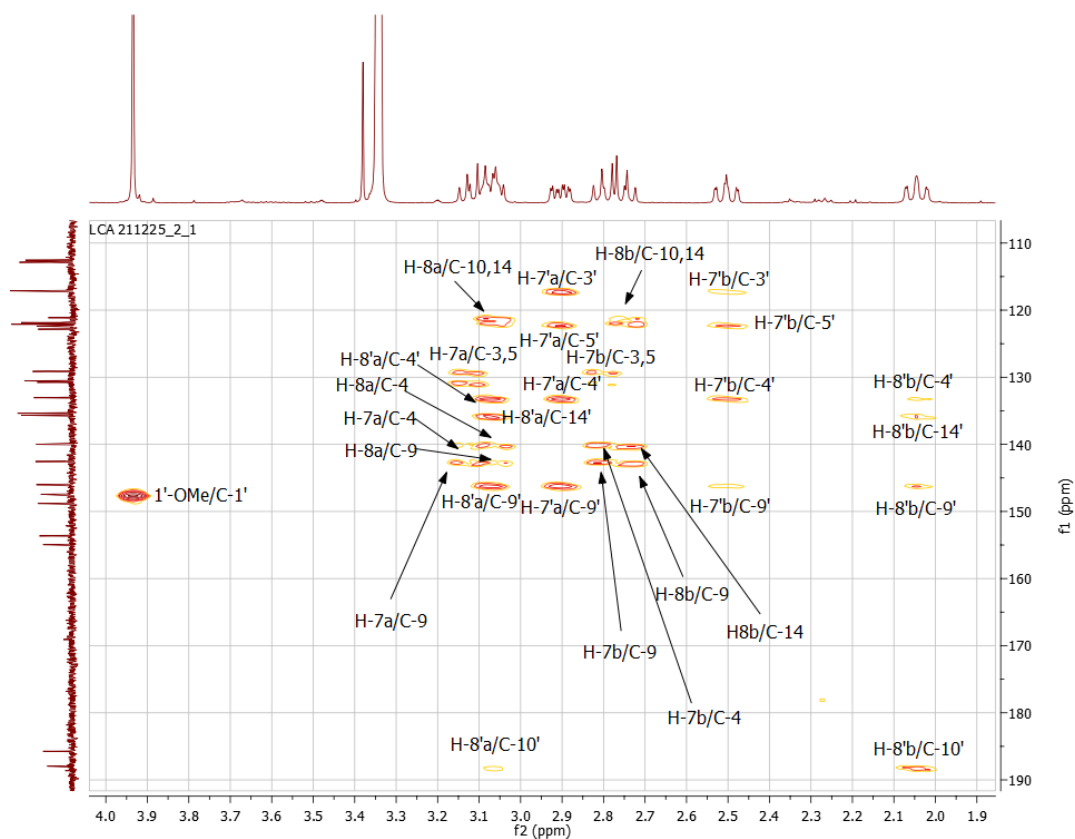


**Figure S63.** The second part of the NOESY spectrum of compound **6**

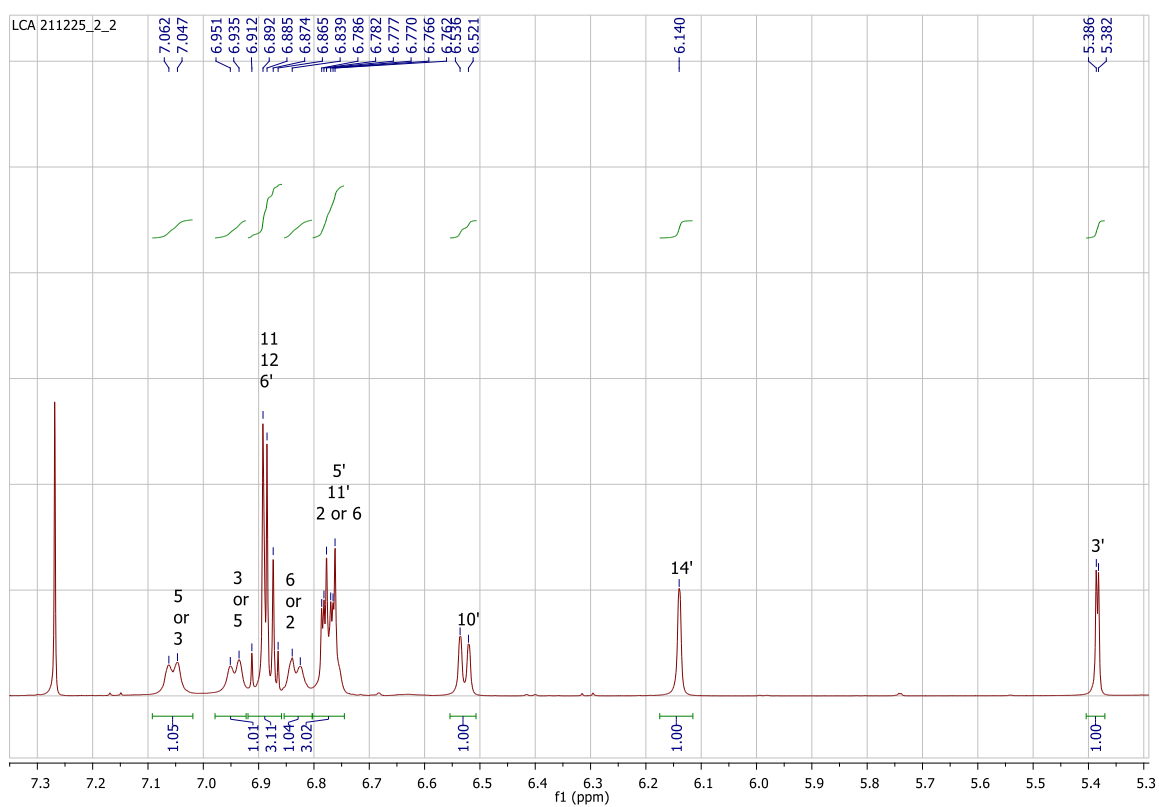


**Figure S64.** Aromatic part of the HSQC spectrum of compound **6**

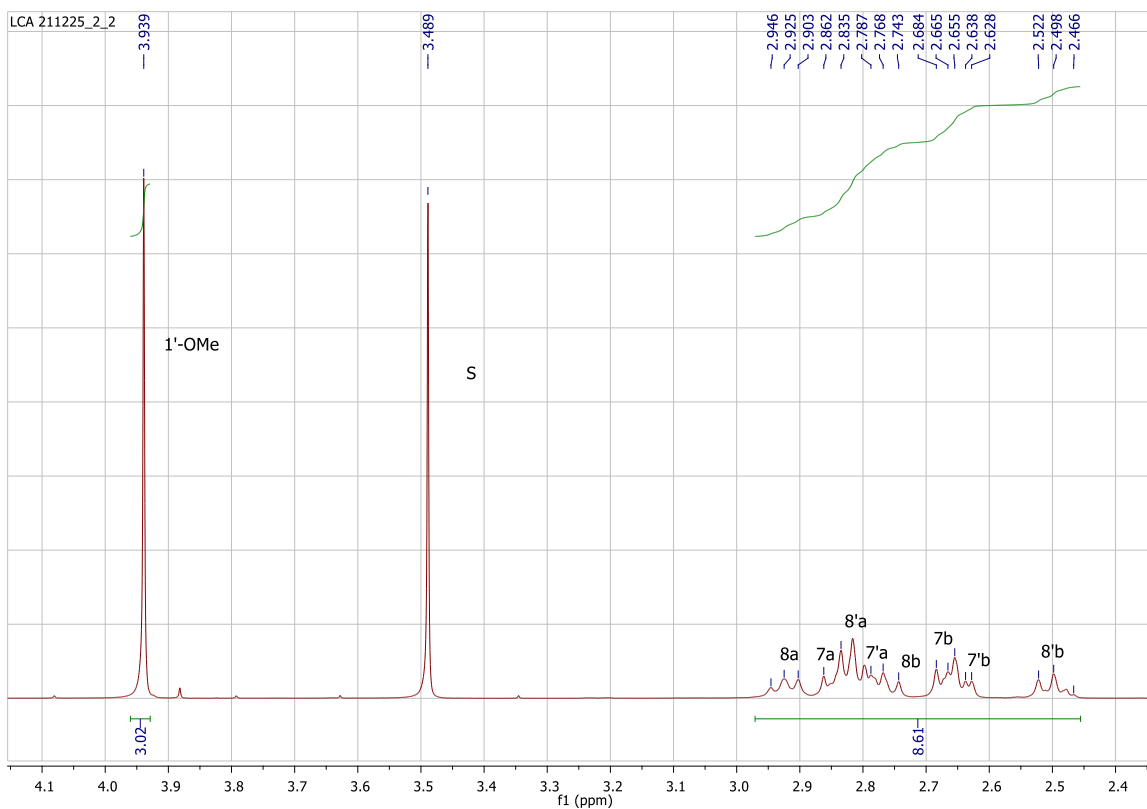




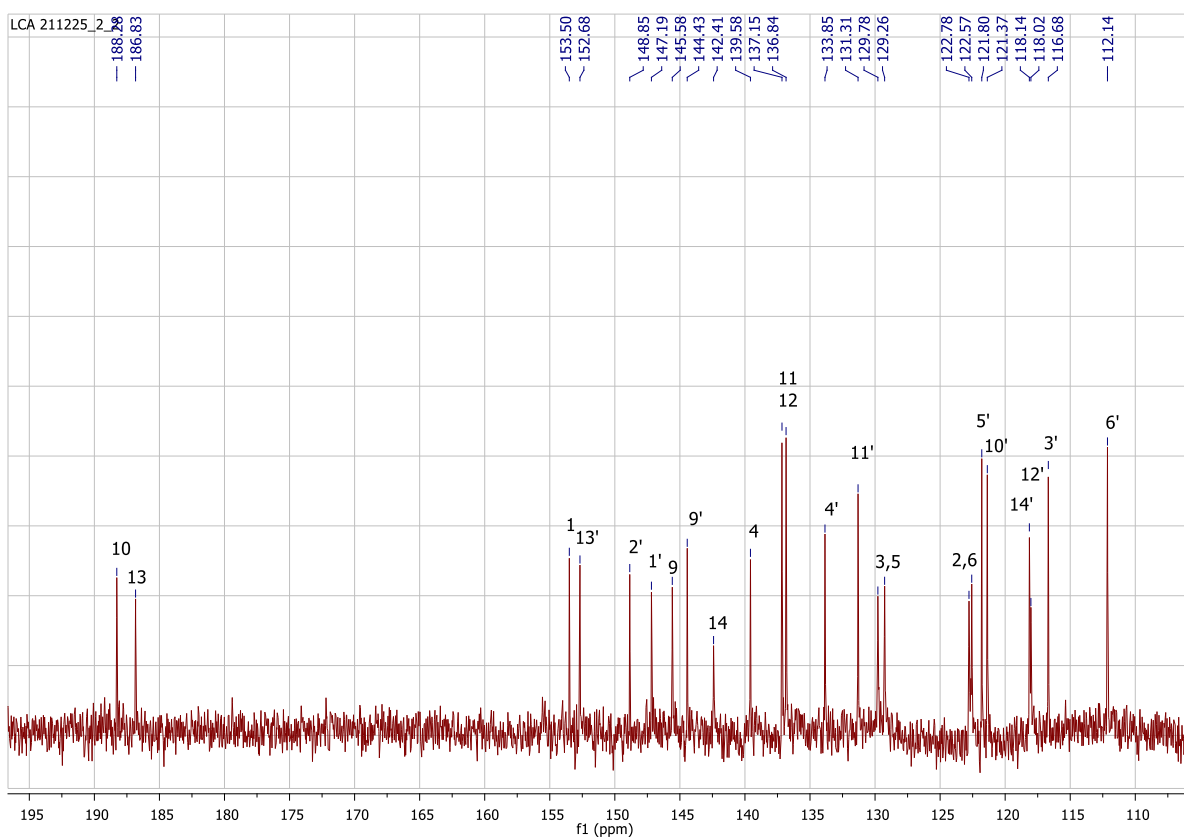
**Figure S67.** The second part of the HMBC spectrum of compound **6**



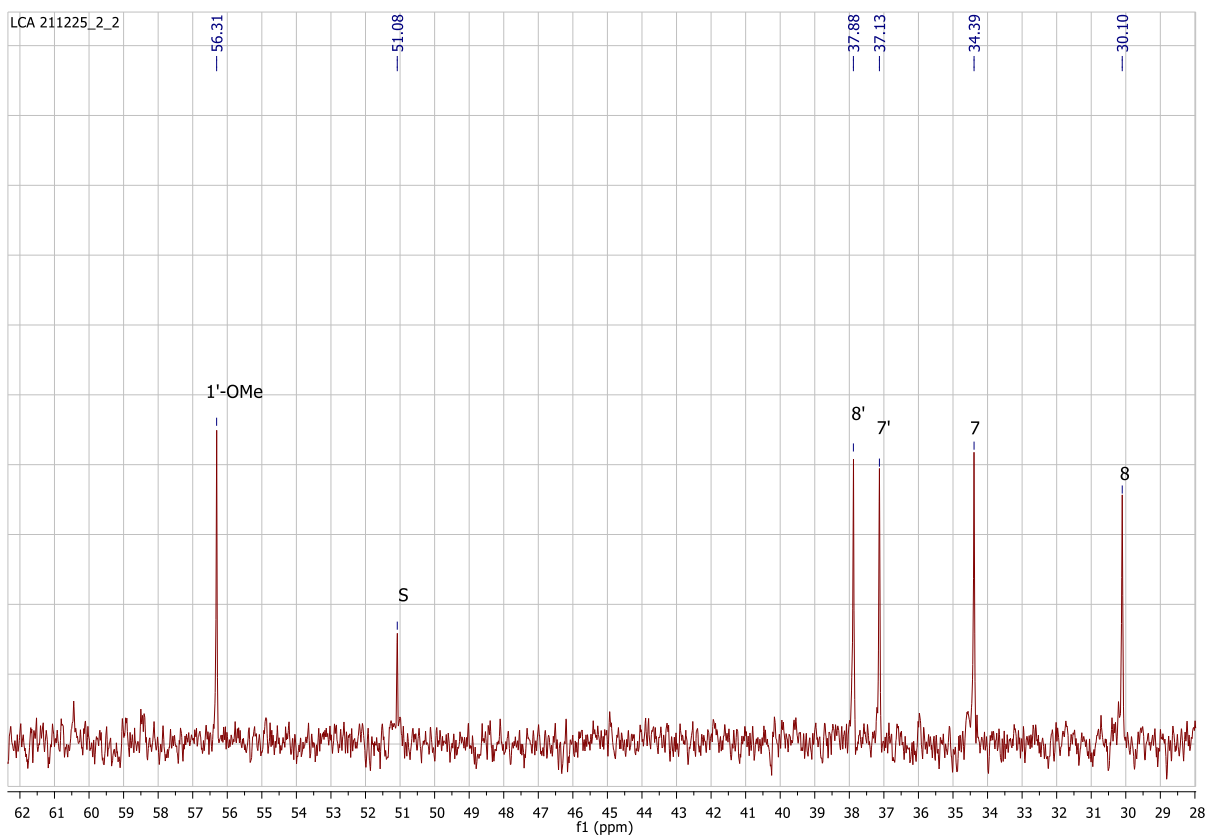
**Figure S68.** Aromatic part of the  $^1\text{H}$  NMR spectrum of compound **7**



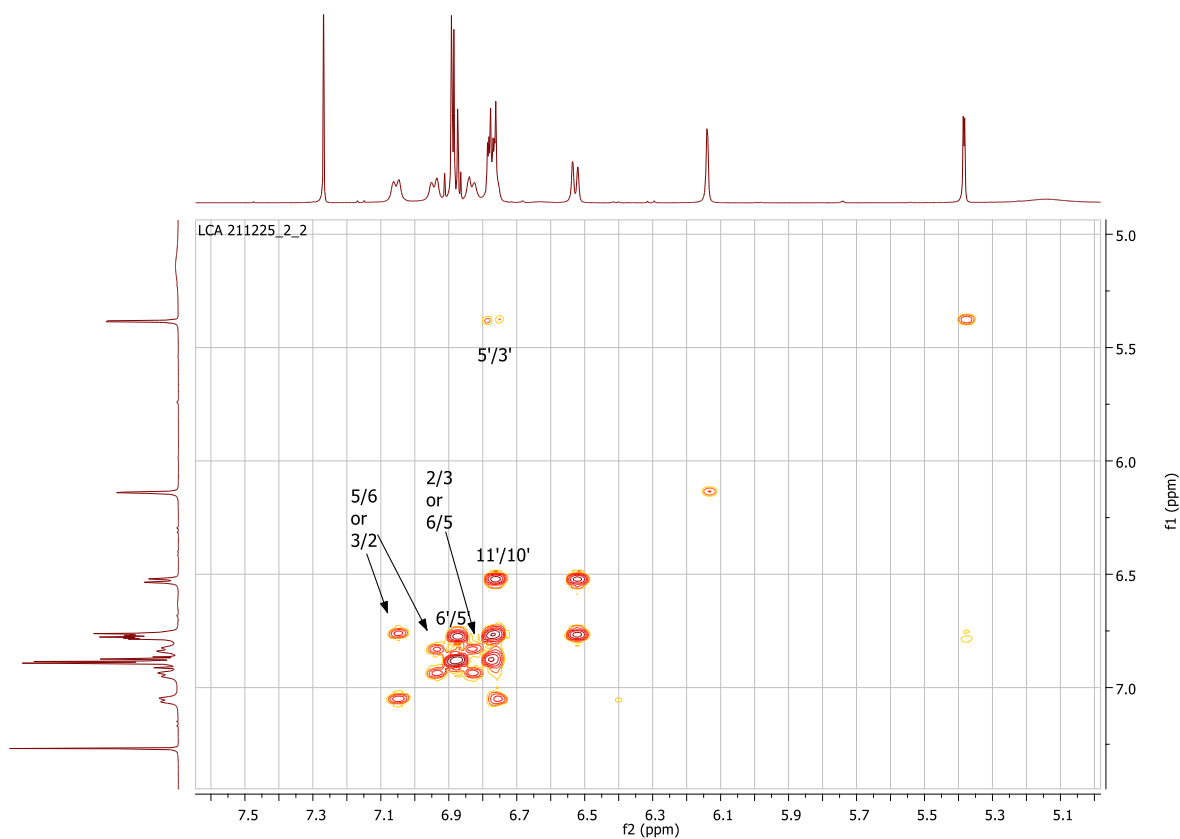
**Figure S69.** Aliphatic part of the  $^1\text{H}$  NMR spectrum of compound **7**



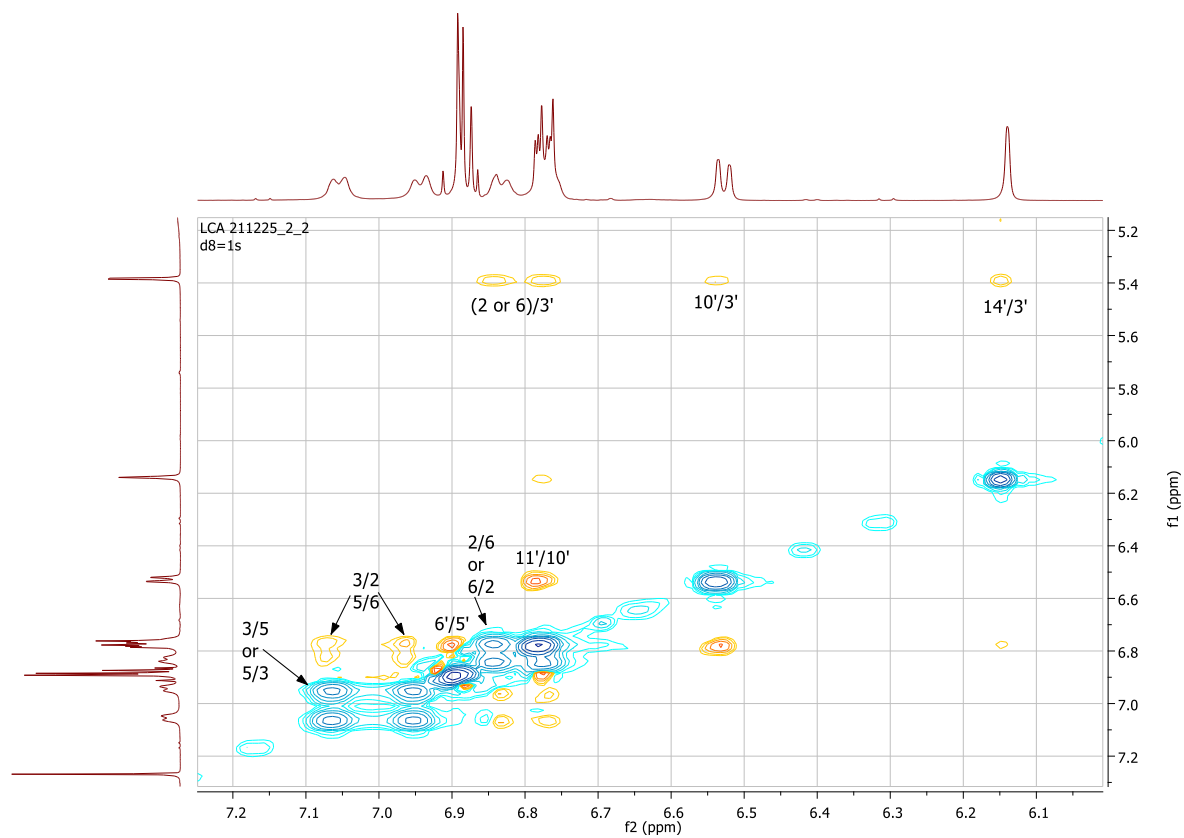
**Figure S70.** Aromatic part of the  $^{13}\text{C}$  NMR spectrum of compound **7**



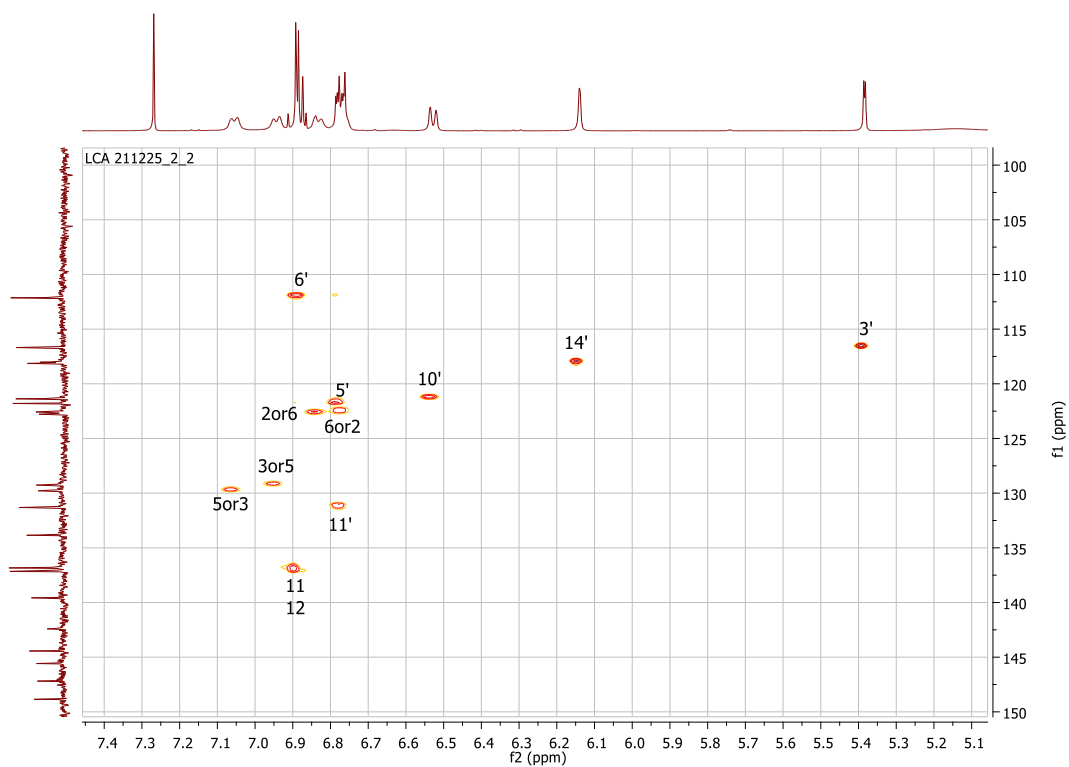
**Figure S71.** Aliphatic part of the  $^{13}\text{C}$  NMR spectrum of compound **7**



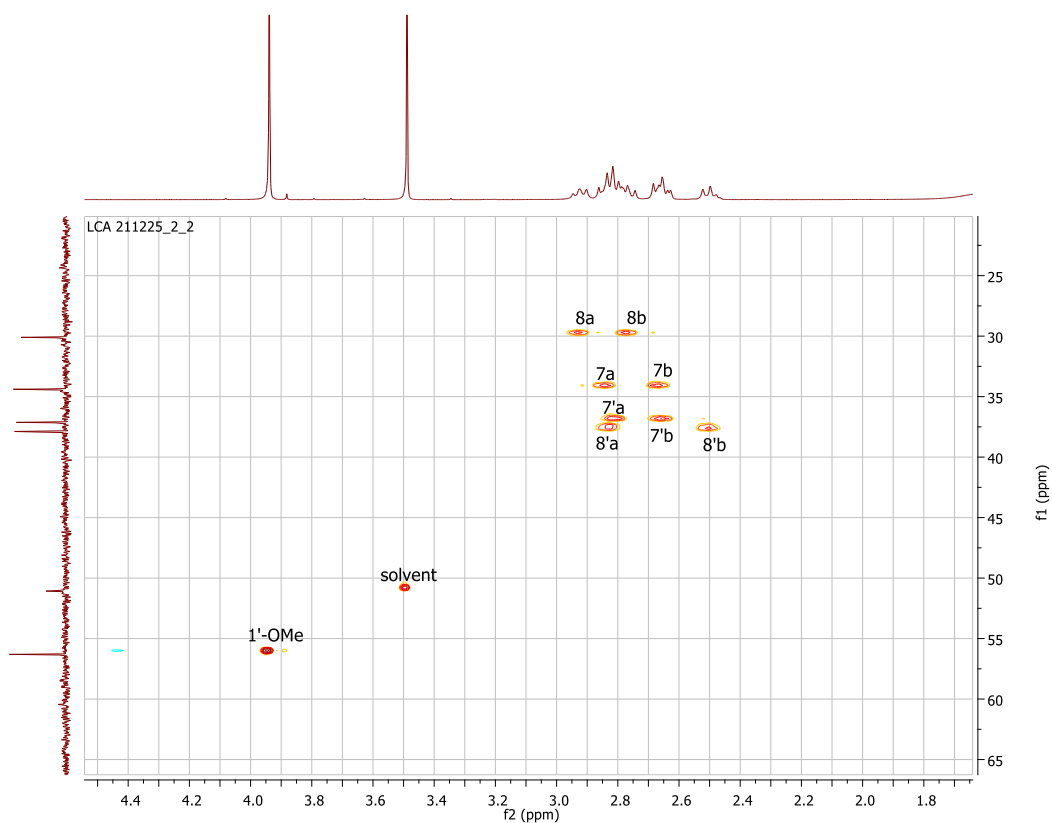
**Figure S72.** Aromatic part of the COSY spectrum of compound **7**



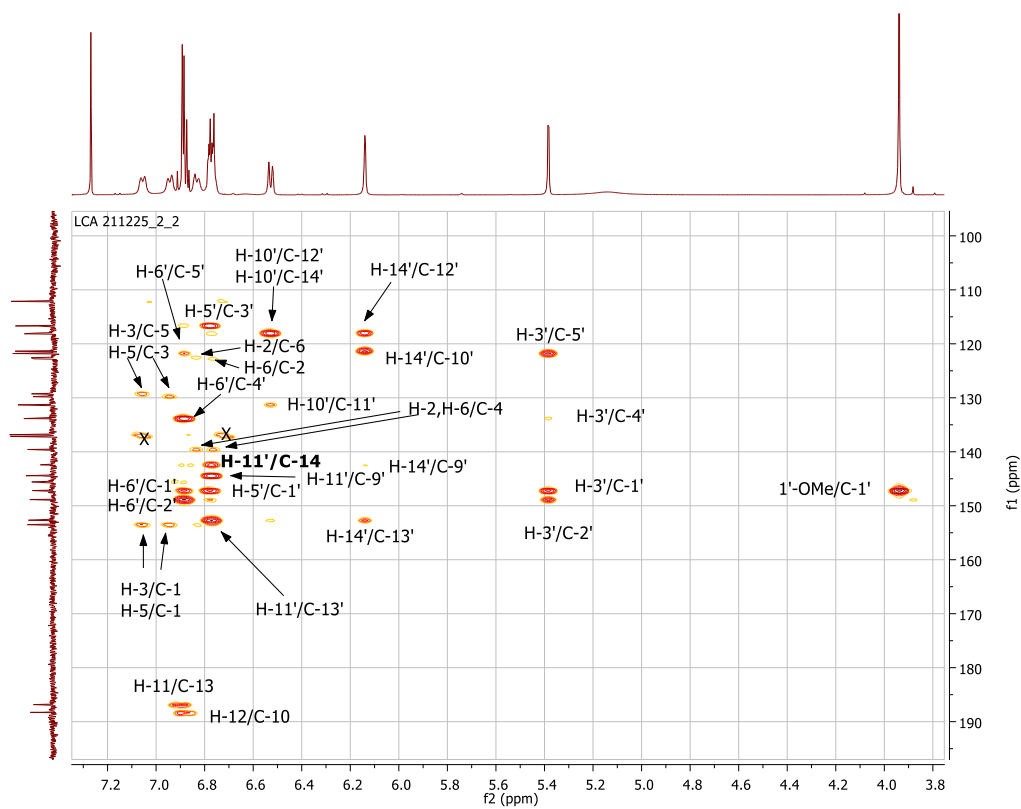
**Figure S73.** Aromatic part of the NOESY spectrum of compound **7**



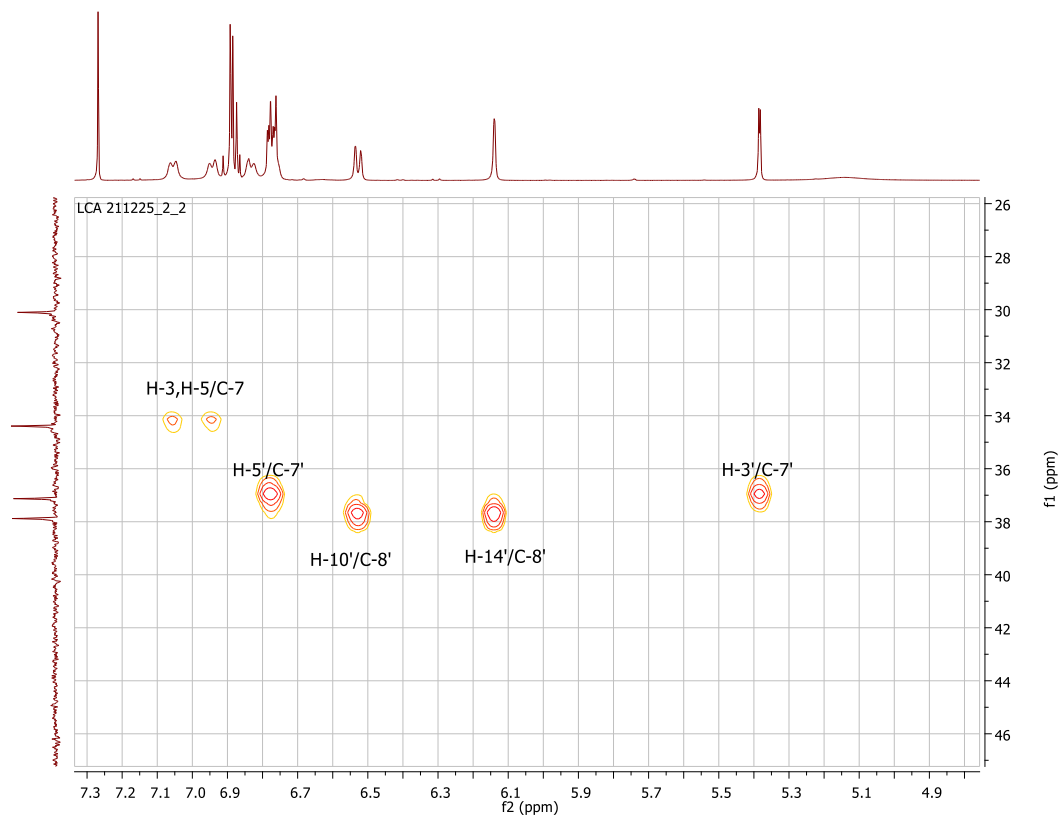
**Figure S74.** Aromatic part of the HSQC spectrum of compound **7**



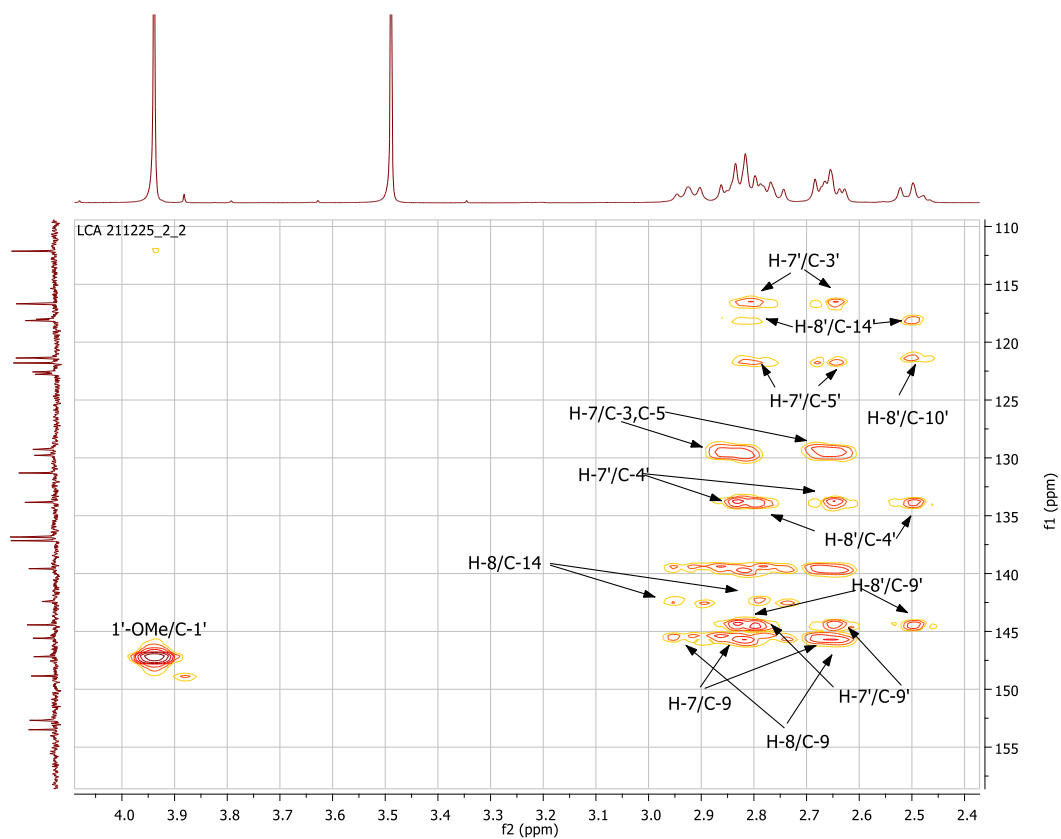
**Figure S75.** Aliphatic part of the HSQC spectrum of compound **7**



**Figure S76.** The first part of the HMBC spectrum of compound **7**

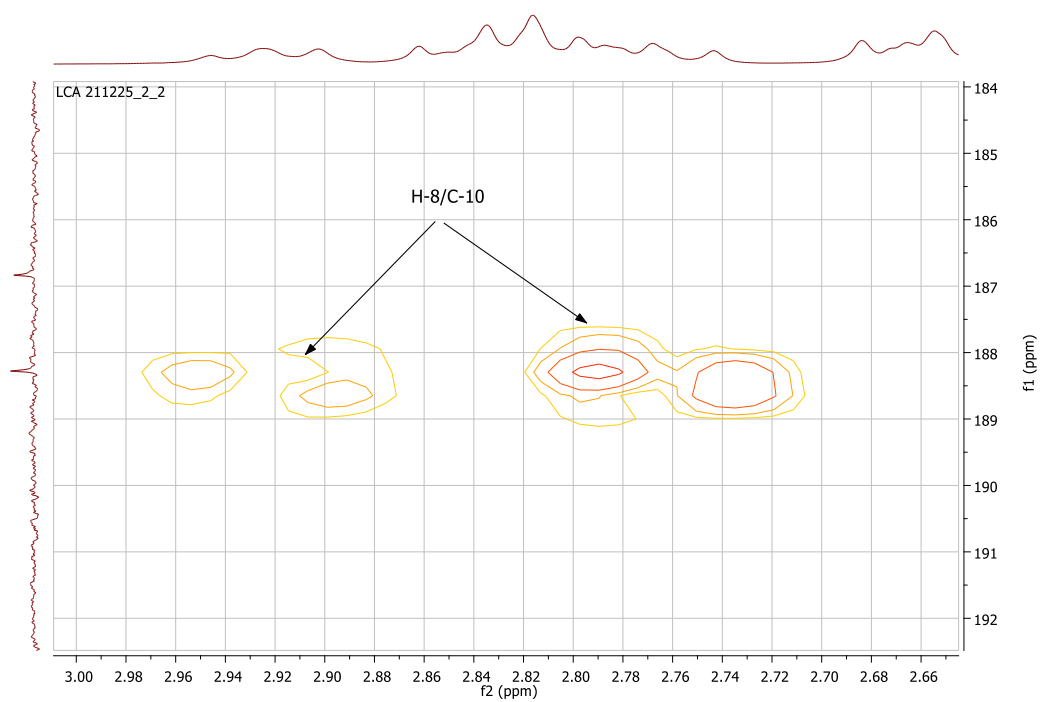


**Figure S77.** The second part of the HMBC spectrum of compound **7**



**Figure S78.** The third part of the HMBC spectrum of compound **7**





**Figure S79.** HMBC correlation H-8/C-10 in compound **7**

Table S2. Cytotoxicity (IC<sub>50</sub>, μM) of Bisbibenzyls on Two Human Cell Lines Determined by MTT Assay

Compound	Cell line		SI
	MRC5	A549	
<b>Lunularin</b>	200	150	
<b>Perrottetin E</b>	40.0	25.0	
<b>Perrottetin F</b>	30.0	15.0	
<b>Riccardin C</b>	15.0	22.5	
<b>Riccardin F</b>	15.0	30.0	
<b>Riccardin G</b>	7.5	2.5	3
<b>1</b>	40.0	10.0	4
<b>2</b>	60.0	10.0	6
<b>3</b>	5.0	5.0	1
<b>4</b>	15.0	10.0	1.5
<b>5</b>	3.0	5.0	0.6
<b>6</b>	30.0	60.0	
<b>7</b>	15.0	40.0	
<b>Methylated perrottetin E</b>	>120 <sup>b</sup>	>120	
<b>Methylated Perrottetin F</b>	>120	>120	
<b>Cisplatin</b>	3.5	2.5	1.4

<sup>a</sup> Results represent mean of three independent experiments done in quadruplicate, with standard deviation between 1-5%.

<sup>b</sup> not cytotoxic under tested conditions.

<sup>c</sup>SI – selectivity index