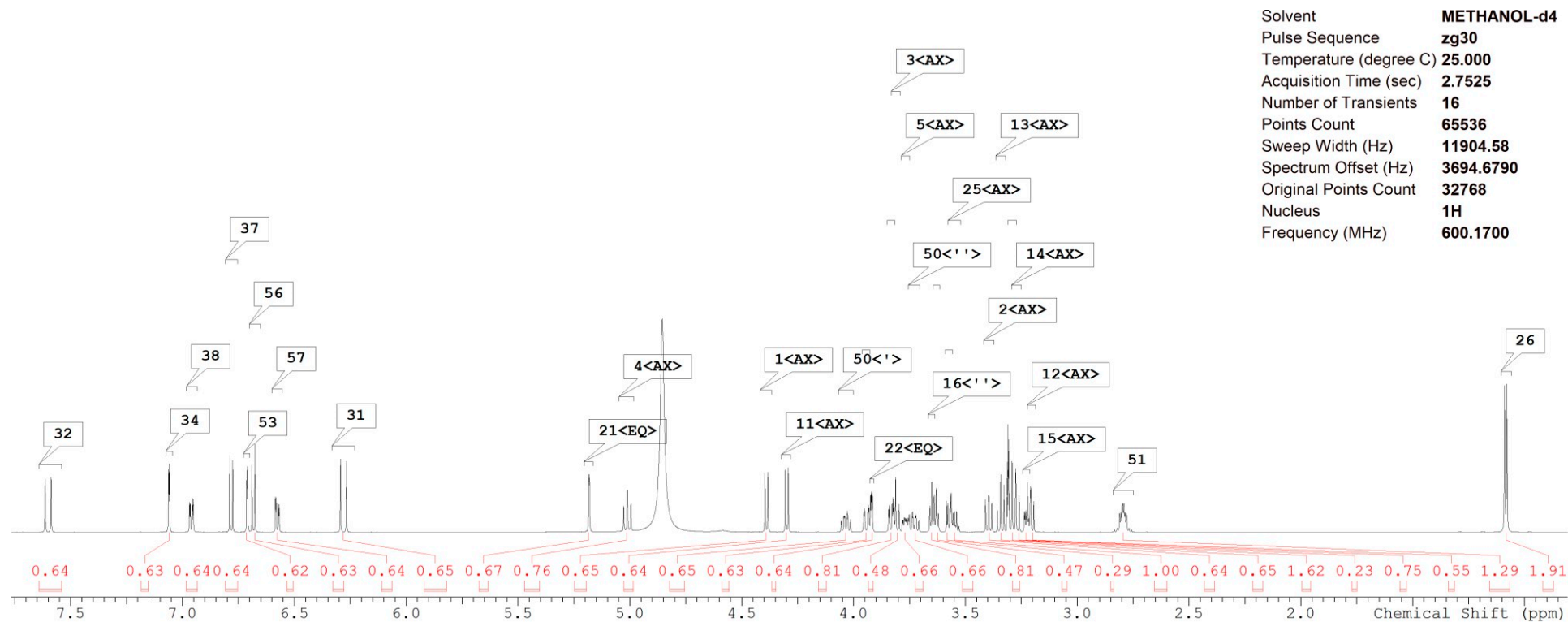
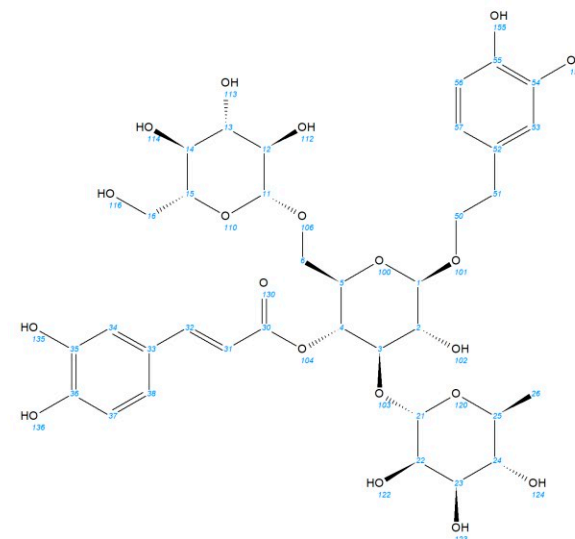


## Supplementary Materials

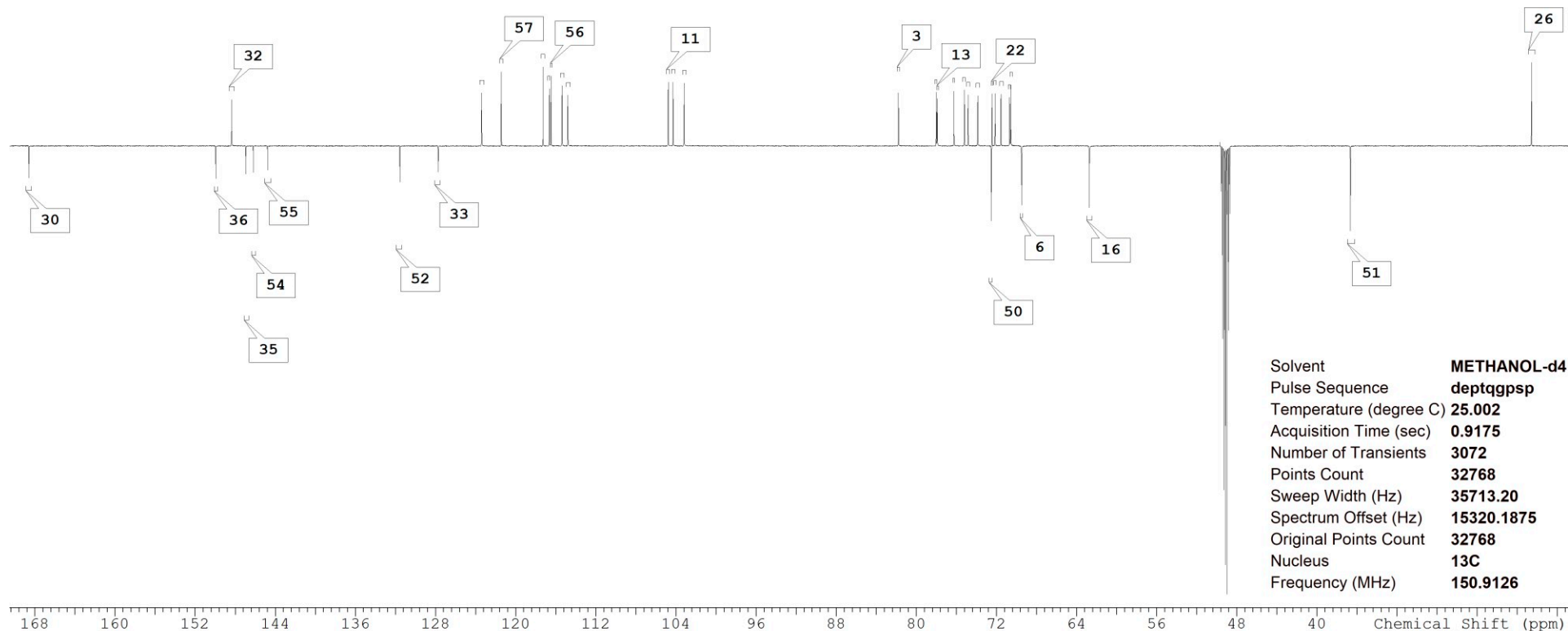
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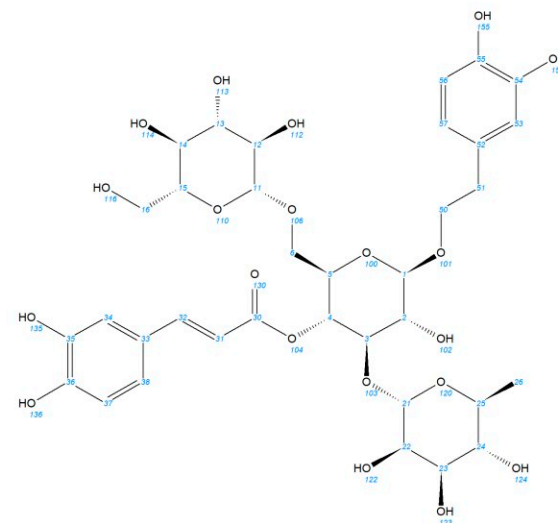
Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1	Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1
1.085	3.000	d	6.2	26	M31	3.920	1.000	dd	3.3, 1.8	22<EQ>	M15
2.796	2.000	m	-	51	M20	3.943	1.000	dd	11.4, 2.2	6<'>	M14
3.209	1.000	dd	9.3, 7.8	12<AX>	M26	4.035	1.000	ddd	9.6, 8.1, 7.0	50<'>	M13
3.223	1.000	ddd	9.4, 5.4, 2.2	15<AX>	M30	4.299	1.000	d	7.6	11<AX>	M12
3.276	1.000	t	8.9	14<AX>	M28	4.390	1.000	d	7.8	1<AX>	M11
3.292	1.000	t	9.6	24<AX>	M29	5.012	1.000	t	9.6	4<AX>	M10
3.343	1.000	t	9.1	13<AX>	M27	5.183	1.000	d	1.6	21<EQ>	M09
3.396	1.000	dd	9.1, 8.0	2<AX>	M25	6.281	1.000	d	16.0	31	M02
3.553	1.000	dq	9.6, 6.2	25<AX>	M24	6.577	1.000	dd	8.1, 2.1	57	M08
3.574	1.000	m	9.4, 3.3	23<AX>	M23	6.683	1.000	d	8.0	56	M07
3.636	1.000	t	11.4, 5.4	6<'>	M19	6.712	1.000	d	2.2	53	M06
3.645	1.000	t	11.9, 5.6	16<'>	M22	6.783	1.000	d	8.2	37	M05
3.730	1.000	m	9.6, 8.2, 6.7	50<'>	M18	6.961	1.000	dd	8.3, 2.1	38	M04
3.767	1.000	ddd	9.6, 5.4, 2.2	5<AX>	M21	7.061	1.000	d	2.0	34	M03
3.812	1.000	br t	9.3	3<AX>	M16	7.602	1.000	d	15.8	32	M01
3.832	1.000	dd	11.9, 2.3	16<'>	M17						



**Figure S1:** <sup>1</sup>H spectrum, structure, numbering and full assignment of **echinacoside** in methanol-d<sub>4</sub> at 25 °C



Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1
18.589	1.000	s	26	M35	78.020	1.000	s	15	M20	146.218	1.000	s	54	M04
36.680	1.000	s	51	M34	81.790	1.000	s	3	M19	146.955	1.000	s	35	M03
62.745	1.000	s	16	M33	103.196	1.000	s	21	M18	148.371	1.000	s	32	M08
69.498	1.000	s	6	M32	104.301	1.000	s	1	M17	149.967	1.000	s	36	M02
70.574	1.000	s	25	M30	104.778	1.000	s	11	M16	168.614	1.000	s	30	M01
70.696	1.000	s	4	M29	114.809	1.000	s	31	M15					
71.563	1.000	s	14	M28	115.387	1.000	s	34	M14					
72.163	1.000	s	23	M27	116.478	1.000	s	56	M13					
72.466	1.000	s	22	M26	116.651	1.000	s	37	M12					
72.524	1.000	s	50	M31	117.279	1.000	s	53	M11					
73.881	1.000	s	24	M25	121.454	1.000	s	57	M10					
74.849	1.000	s	5	M24	123.411	1.000	s	38	M09					
75.210	1.000	s	12	M23	127.759	1.000	s	33	M07					
76.257	1.000	s	2	M22	131.579	1.000	s	52	M06					
77.919	1.000	s	13	M21	144.788	1.000	s	55	M05					



**Figure S2:**  $^{13}\text{C}$  spectrum, structure, numbering and full assignment of **echinacoside** in methanol- $\text{d}_4$  at 25 °C

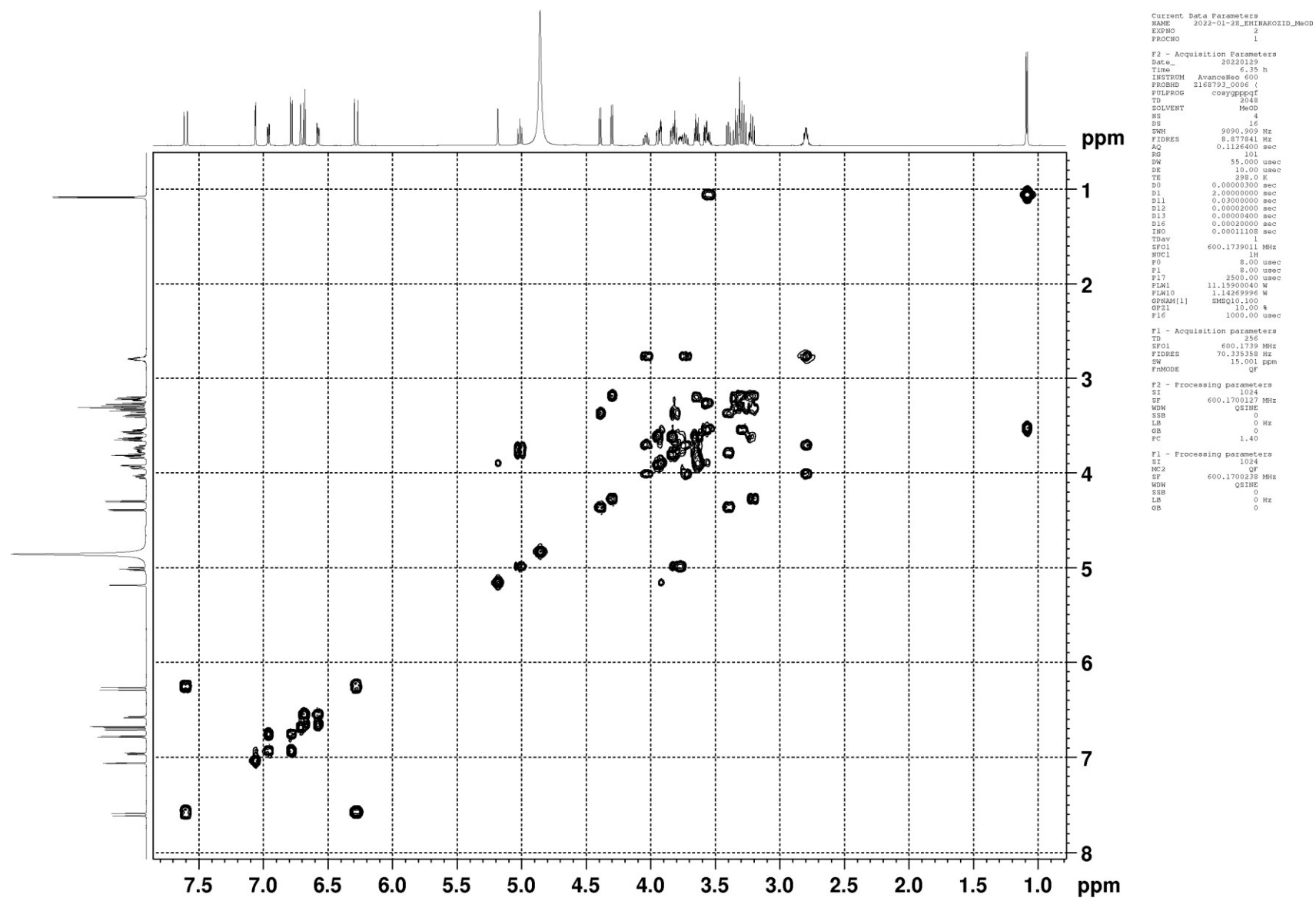
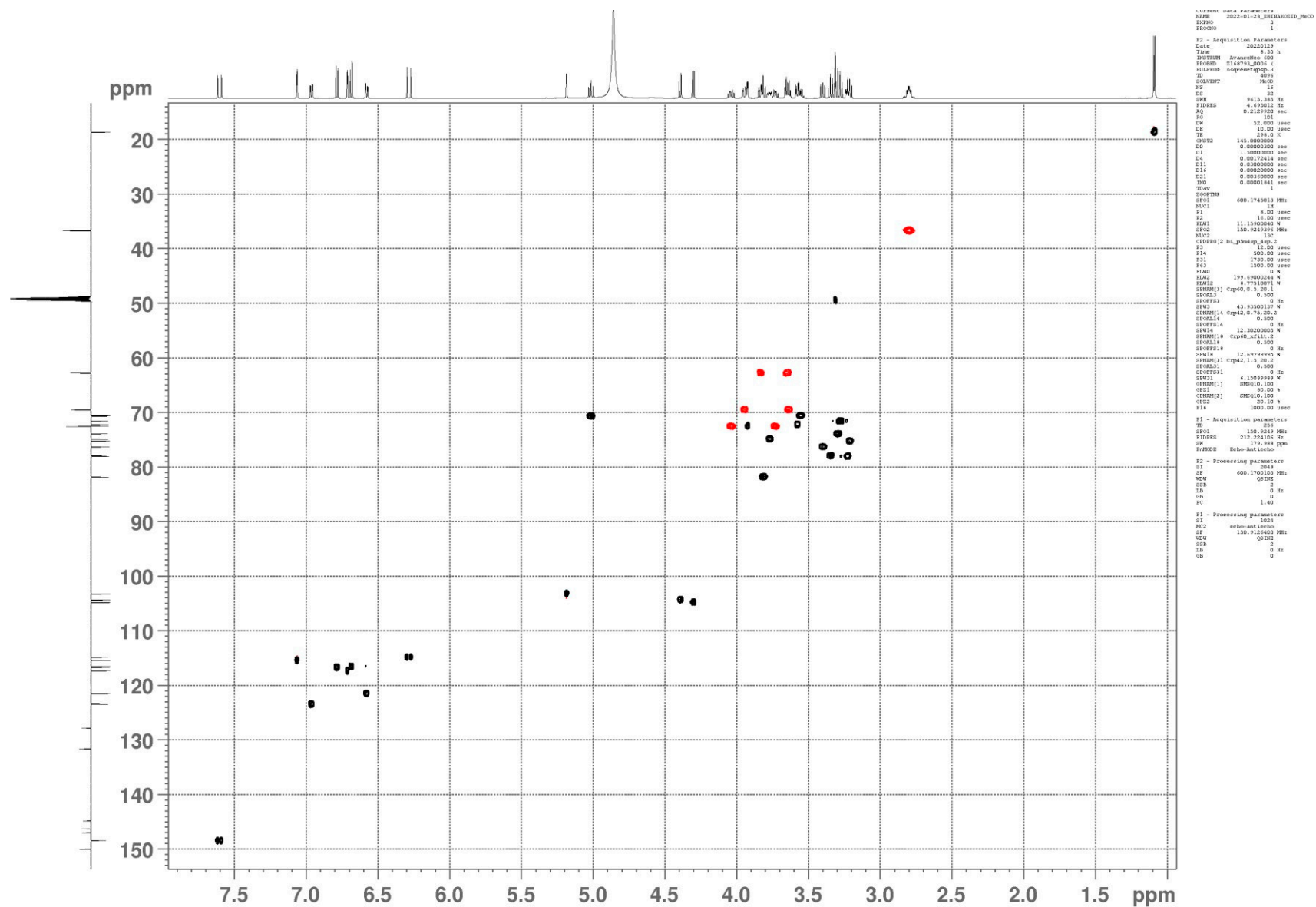
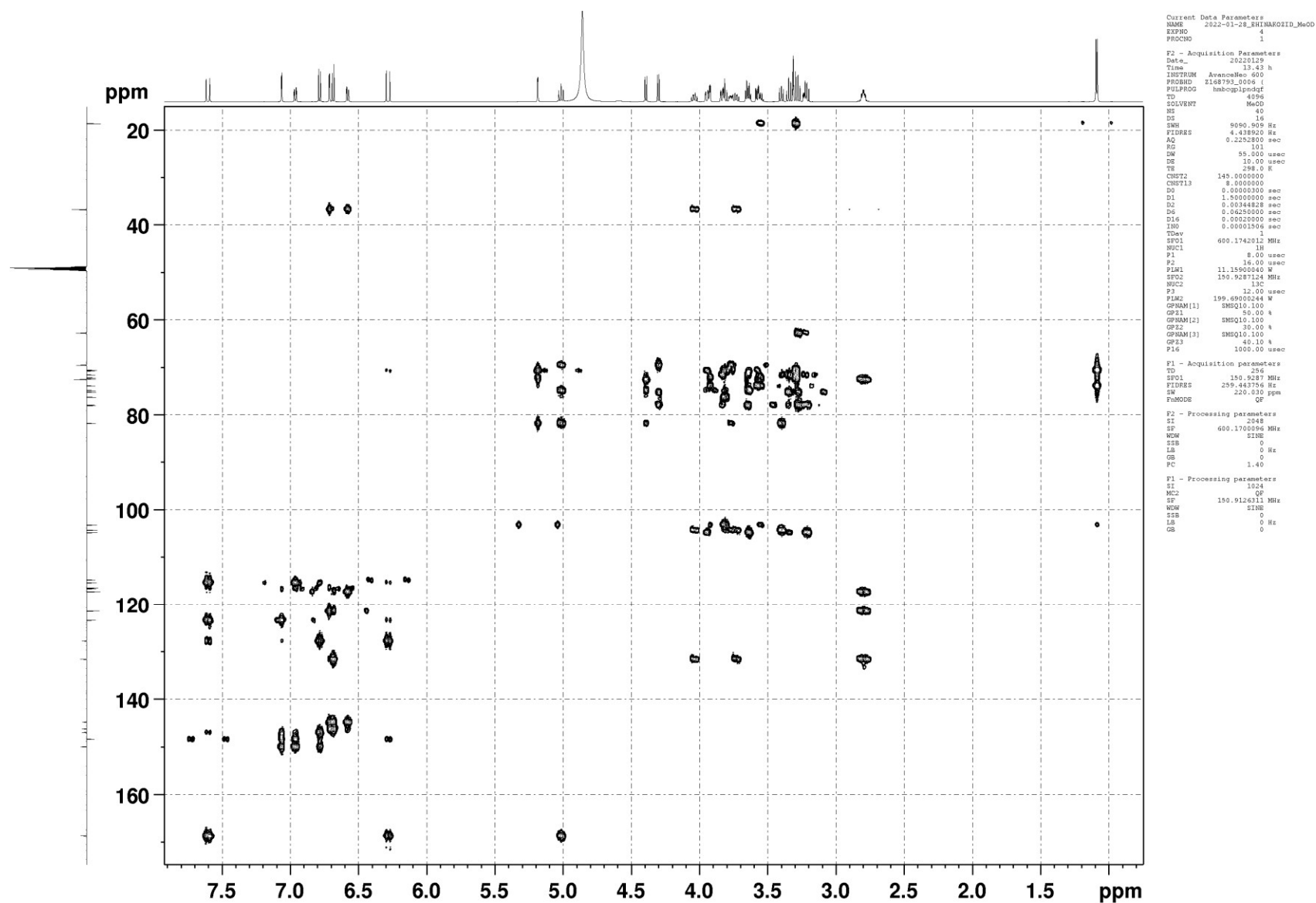


Figure S3: COSY spectrum of **echinacoside** in methanol- $d_4$  at 25 °C

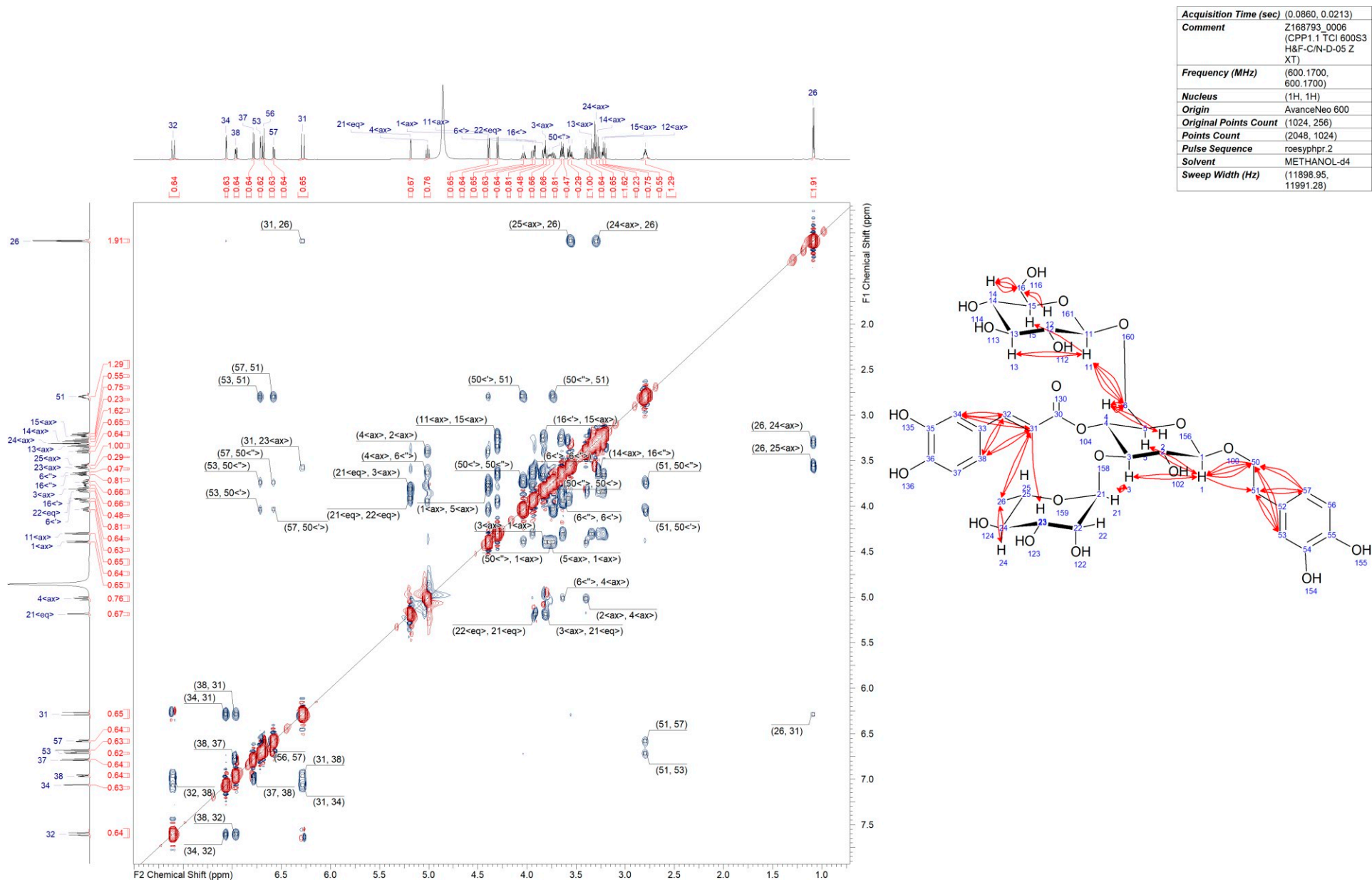




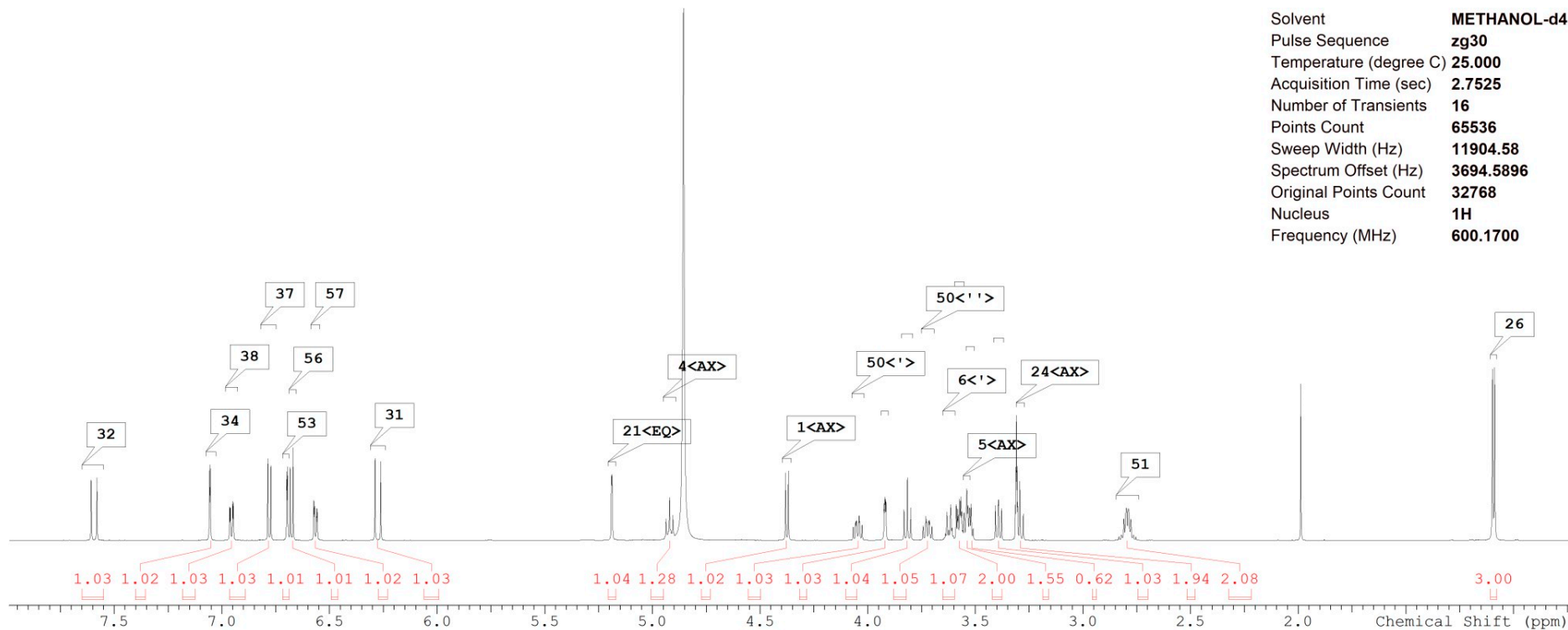
**Figure S4:**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of echinacoside in methanol- $\text{d}_4$  at 25 °C



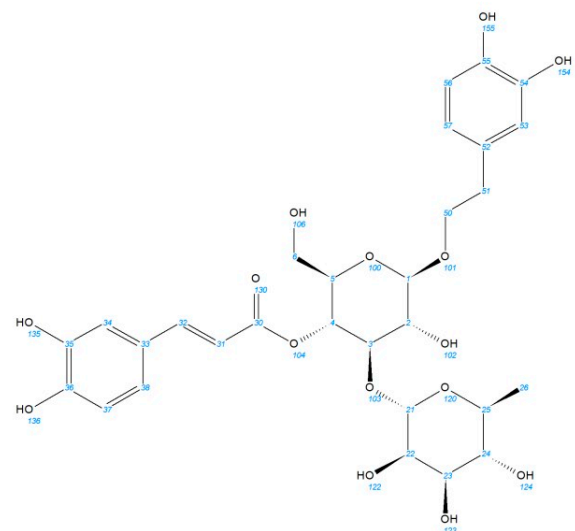
**Figure S5:**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of echinacoside in methanol- $\text{d}_4$  at 25  $^{\circ}\text{C}$



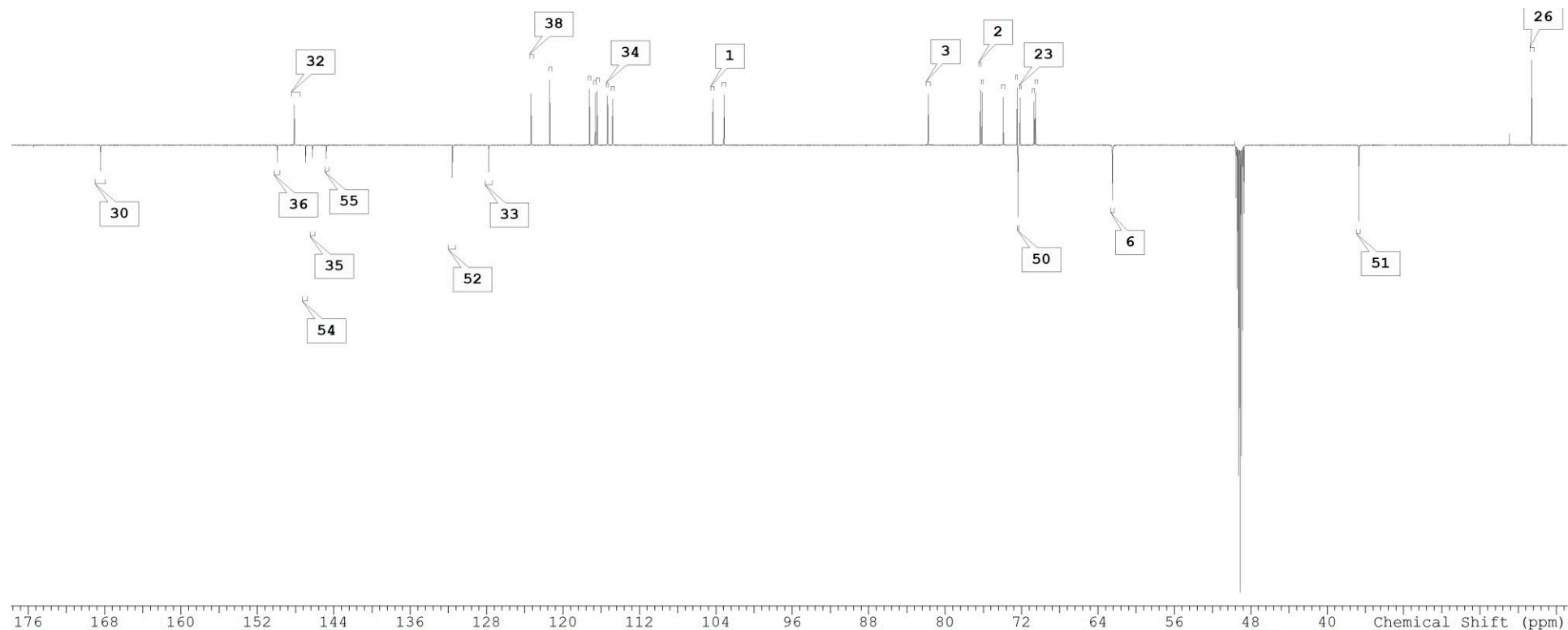
**Figure S6:** Fully assigned NOESY spectrum of **echinacoside** in methanol-d<sub>4</sub> at 25 °C



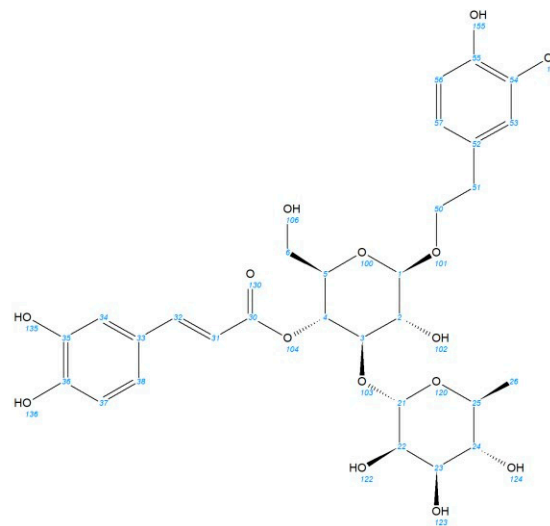
Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1	Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1
1.094	3.000	d	6.2	26	M19	6.276	1.000	d	15.8	31	M08
2.794	2.000	m	-	51	M17	6.566	1.000	dd	8.1, 2.1	57	M07
3.294	1.000	t	9.6	24<AX>	M18	6.677	1.000	d	8.0	56	M06
3.393	1.000	dd	9.2, 7.9	2<AX>	M20	6.698	1.000	d	2.0	53	M05
3.524	1.000	dd	10.2, 5.8	6<''>	M21	6.780	1.000	d	8.2	37	M04
3.542	1.000	m	-	5<AX>	M22	6.956	1.000	dd	8.2, 2.0	38	M03
3.572	2.000	m	-	23<AX>, 25<AX>	M23	7.057	1.000	d	2.0	34	M02
3.624	1.000	d	10.0	6<'>	M16	7.595	1.000	d	15.8	32	M01
3.723	1.000	ddd	9.6, 8.3, 6.8	50<'>	M15						
3.816	1.000	t	9.3	3<AX>	M14						
3.920	1.000	dd	3.2, 1.7	22<EQ>	M13						
4.047	1.000	ddd	9.5, 8.3, 6.7	50<'>	M12						
4.376	1.000	d	7.8	1<AX>	M11						
4.921	1.000	br t	9.4	4<AX>	M10						
5.189	1.000	d	1.6	21<EQ>	M09						



**Figure S7:** <sup>1</sup>H spectrum, structure, numbering and full assignment of **verbascoside** in methanol-d<sub>4</sub> at 25 °C



Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1
18.597	1.000	s	26	M29	115.352	1.000	s	34	M14
36.703	1.000	s	51	M28	116.436	1.000	s	56	M13
62.493	1.000	s	6	M27	116.645	1.000	s	37	M12
70.553	1.000	s	25	M25	117.244	1.000	s	53	M11
70.705	1.000	s	4	M24	121.397	1.000	s	57	M10
72.178	1.000	s	23	M23	123.362	1.000	s	38	M09
72.402	1.000	s	50	M26	127.789	1.000	s	33	M08
72.482	1.000	s	22	M22	131.595	1.000	s	52	M07
73.919	1.000	s	24	M21	144.811	1.000	s	55	M05
76.165	1.000	s	5	M20	146.263	1.000	s	35	M04
76.338	1.000	s	2	M19	146.964	1.000	s	54	M03
81.784	1.000	s	3	M18	148.155	1.000	s	32	M06
103.168	1.000	s	21	M17	149.925	1.000	s	36	M02
104.338	1.000	s	1	M16	168.428	1.000	s	30	M01
114.832	1.000	s	31	M15					



Solvent **METHANOL-d<sub>4</sub>**  
 Pulse Sequence **deptqgppsp**  
 Temperature (degree C) **25.000**  
 Acquisition Time (sec) **0.9175**  
 Number of Transients **3072**  
 Points Count **32768**  
 Sweep Width (Hz) **35713.20**  
 Spectrum Offset (Hz) **15322.5537**  
 Original Points Count **32768**  
 Nucleus **13C**  
 Frequency (MHz) **150.9126**

**Figure S8:** <sup>13</sup>C spectrum, structure, numbering and full assignment of **verbascoside** in methanol-d<sub>4</sub> at 25 °C



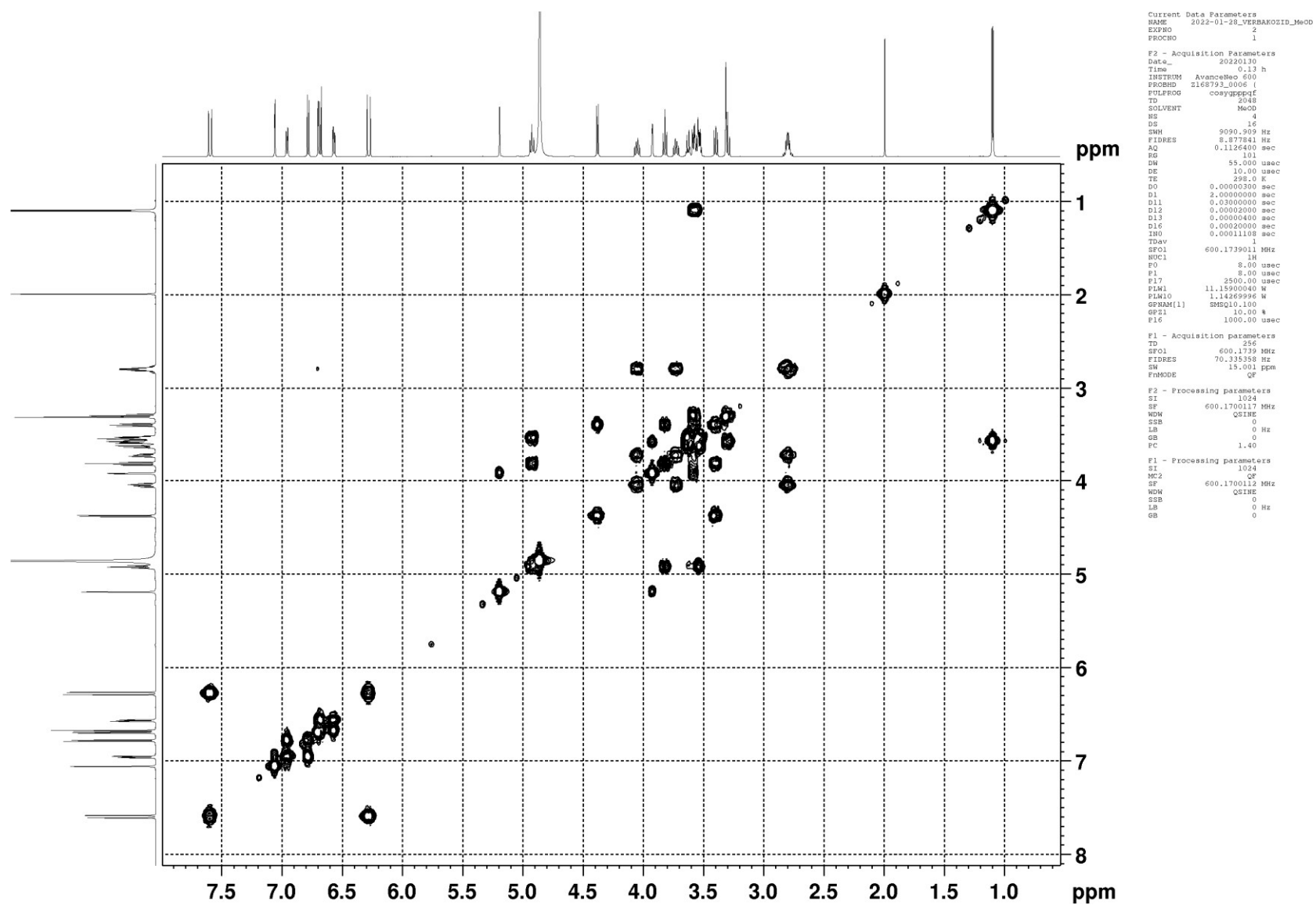


Figure S9: COSY spectrum of **verbascoside** in methanol- $d_4$  at 25 °C



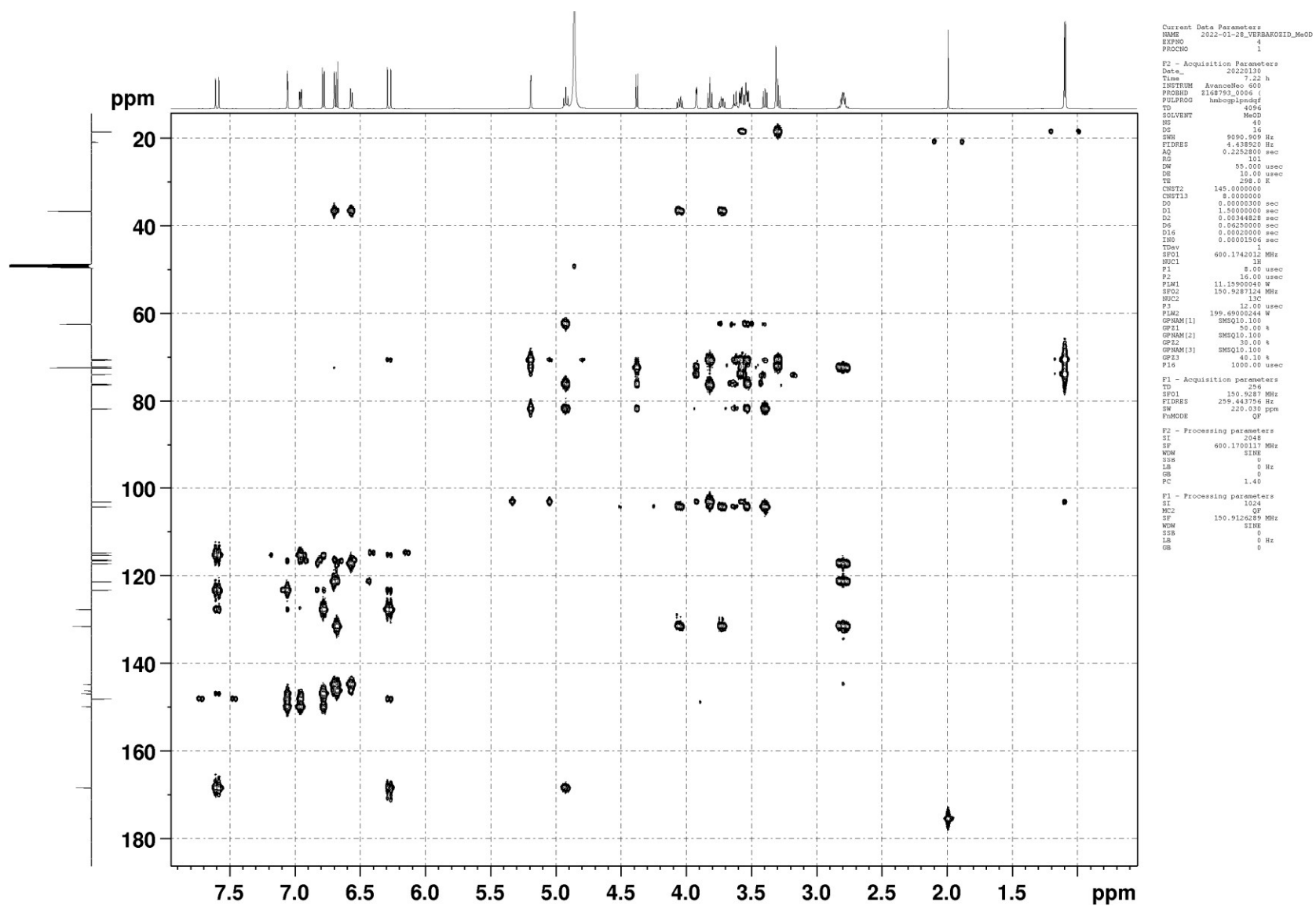
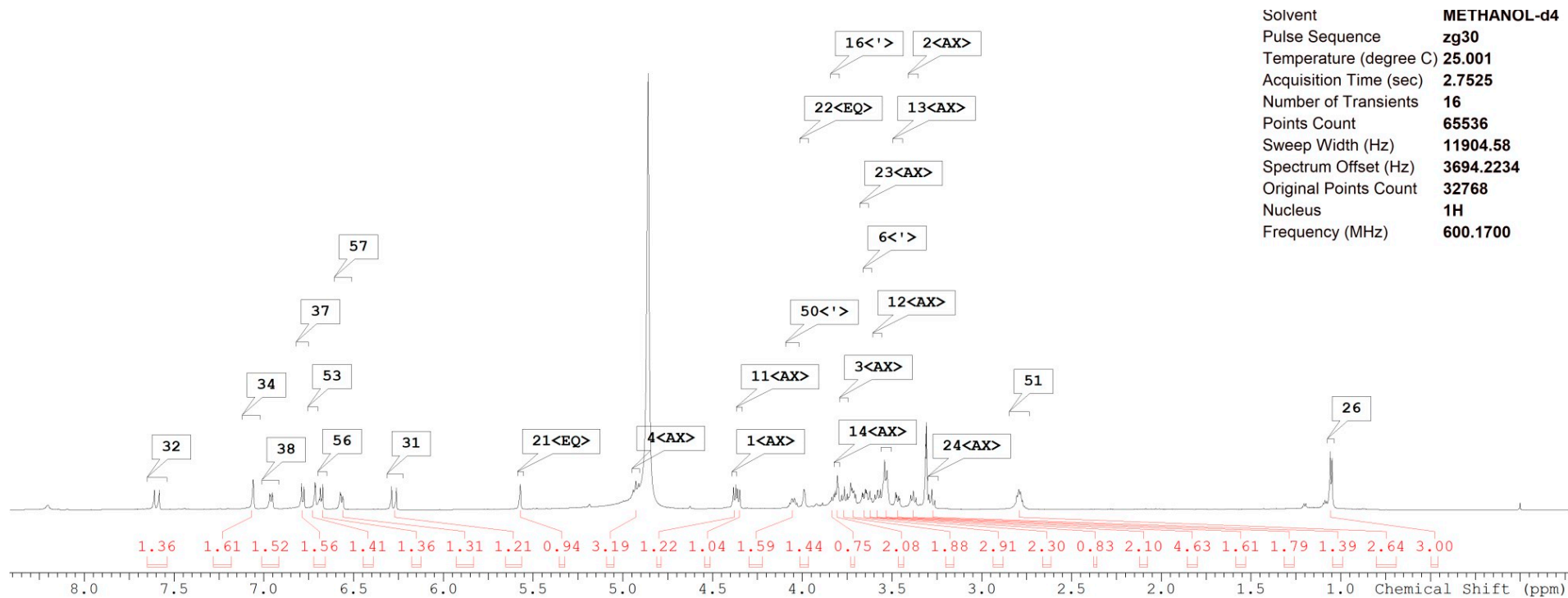
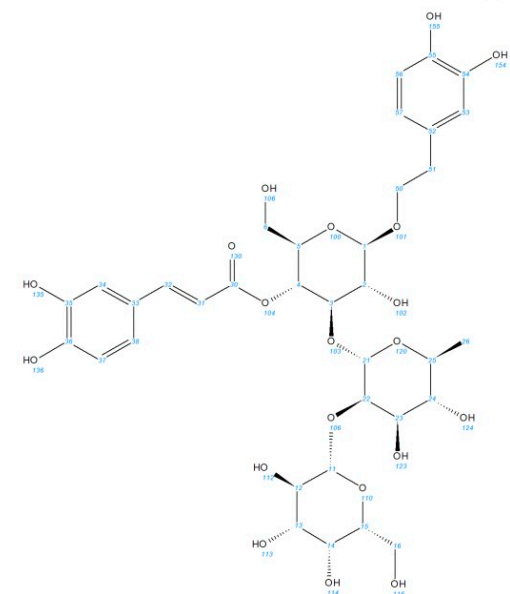


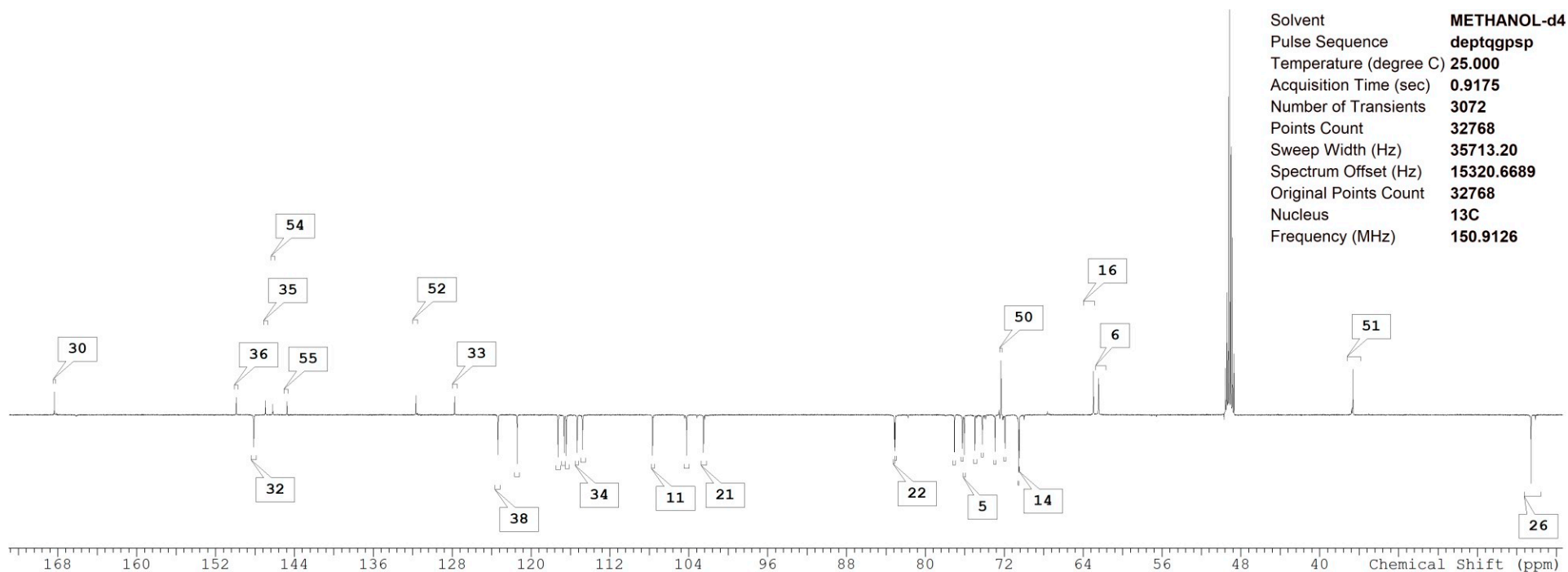
Figure S11:  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of verbascoside in methanol- $\text{d}_4$  at 25 °C



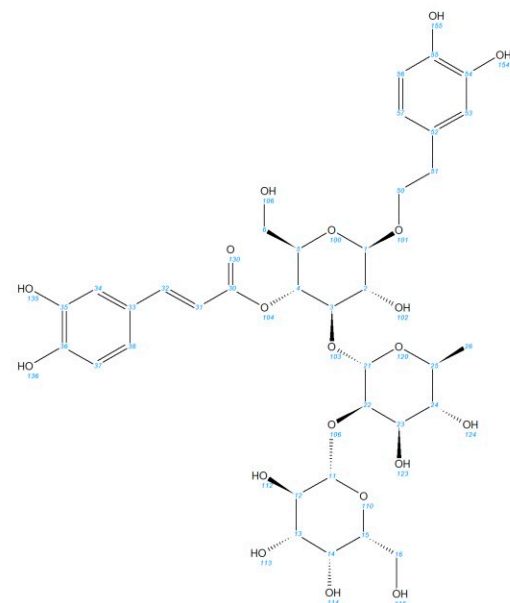
Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1	Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1
1.054	3.000	br d	6.0	26	M15	4.355	1.000	br d	7.6	11<AX>	M12
2.792	2.000	m	-	51	M16	4.378	1.000	br d	8.0	1<AX>	M11
3.279	1.000	br t	9.6	24<AX>	M17	4.928	1.000	br t	9.3	4<AX>	M10
3.382	1.000	br t	9.1	2<AX>	M18	5.573	1.000	s	-	21<EQ>	M09
3.470	1.000	br dd	9.7, 3.4	13<AX>	M19	6.276	1.000	br d	15.8	31	M02
3.536	4.000	m	-	5<AX>, 6<'>, 25<AX>, 15<AX>	M21	6.567	1.000	dd	8.0, 1.8	57	M08
3.582	1.000	br dd	9.6, 7.8	12<AX>	M20	6.680	1.000	br d	8.0	56	M07
3.635	1.000	br d	-	6<'>	M22	6.714	1.000	br d	1.8	53	M06
3.656	1.000	br dd	9.9, 3.4	23<AX>	M23	6.784	1.000	br d	8.2	37	M05
3.722	2.000	m	-	50<'>, 16<'>	M25	6.959	1.000	br dd	8.2, 1.8	38	M04
3.766	1.000	br t	9.3	3<AX>	M24	7.059	1.000	br d	1.8	34	M03
3.805	1.000	br s	3.4	14<AX>	M27	7.598	1.000	br d	15.8	32	M01
3.820	1.000	br dd	11.4, 7.3	16<'>	M26						
3.990	1.000	br dd	3.1, 1.3	22<EQ>	M14						
4.052	1.000	m	9.4, 7.8, 6.7	50<'>	M13						



**Figure S12:** <sup>1</sup>H spectrum, structure, numbering and full assignment of **PH5** in methanol-d<sub>4</sub> at 25 °C

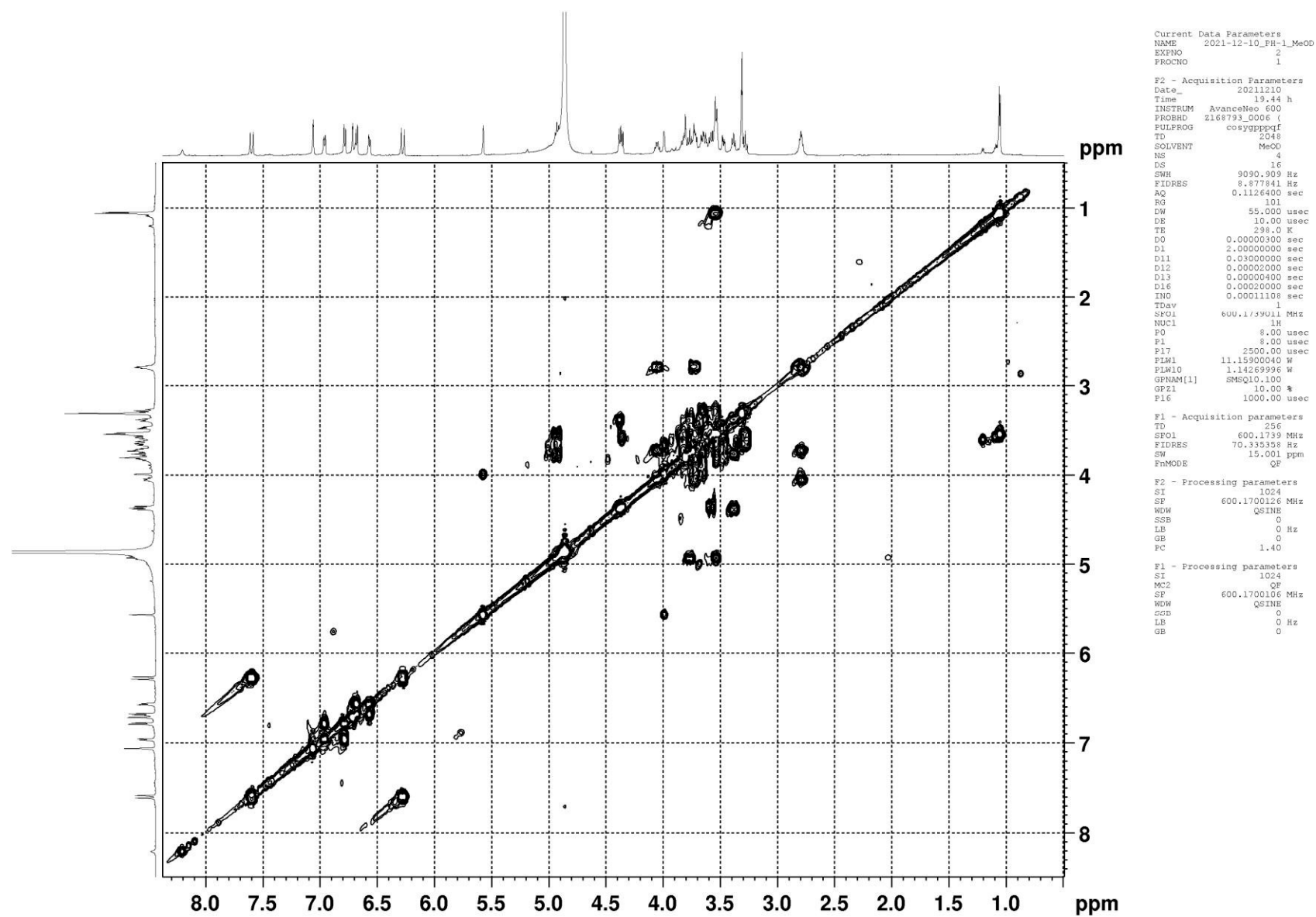


Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1
18.577	1.000	s	26	M31	83.151	1.000	s	22	M19	146.965	1.000	s	35	M03
36.640	1.000	s	51	M32	102.528	1.000	s	21	M18	148.143	1.000	s	32	M08
62.445	1.000	s	6	M33	104.239	1.000	s	1	M17	149.927	1.000	s	36	M02
62.979	1.000	s	16	M34	107.691	1.000	s	11	M16	168.379	1.000	s	30	M01
70.497	1.000	s	14	M29	114.784	1.000	s	31	M15					
70.548	2.000	s	4, 25	M30	115.332	1.000	s	34	M14					
71.942	1.000	s	23	M27	116.445	1.000	s	56	M13					
72.346	1.000	s	50	M28	116.661	1.000	s	37	M12					
72.953	1.000	s	12	M26	117.290	1.000	s	53	M11					
74.246	1.000	s	24	M25	121.428	1.000	s	57	M10					
74.990	1.000	s	13	M24	123.363	1.000	s	38	M09					
76.073	1.000	s	5	M23	127.776	1.000	s	33	M07					
76.261	1.000	s	2	M22	131.698	1.000	s	52	M06					
77.070	1.000	s	15	M21	144.777	1.000	s	55	M05					
83.093	1.000	s	3	M20	146.222	1.000	s	54	M04					



**Figure S13:** <sup>13</sup>C spectrum, structure, numbering and full assignment of **PH5** in methanol-d<sub>4</sub> at 25 °C





**Figure S14:** COSY spectrum of **PH5** in methanol- $d_4$  at 25 °C



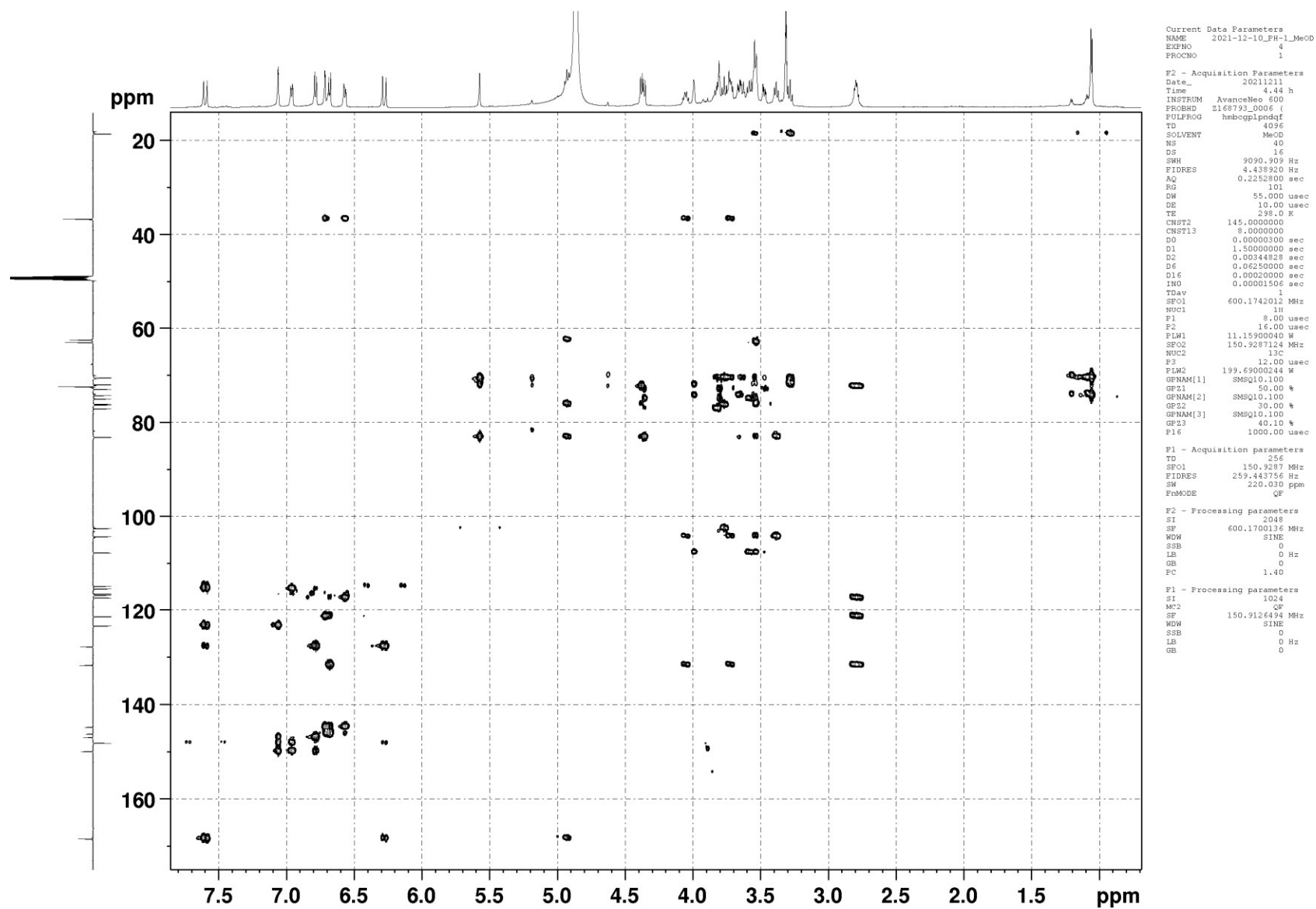
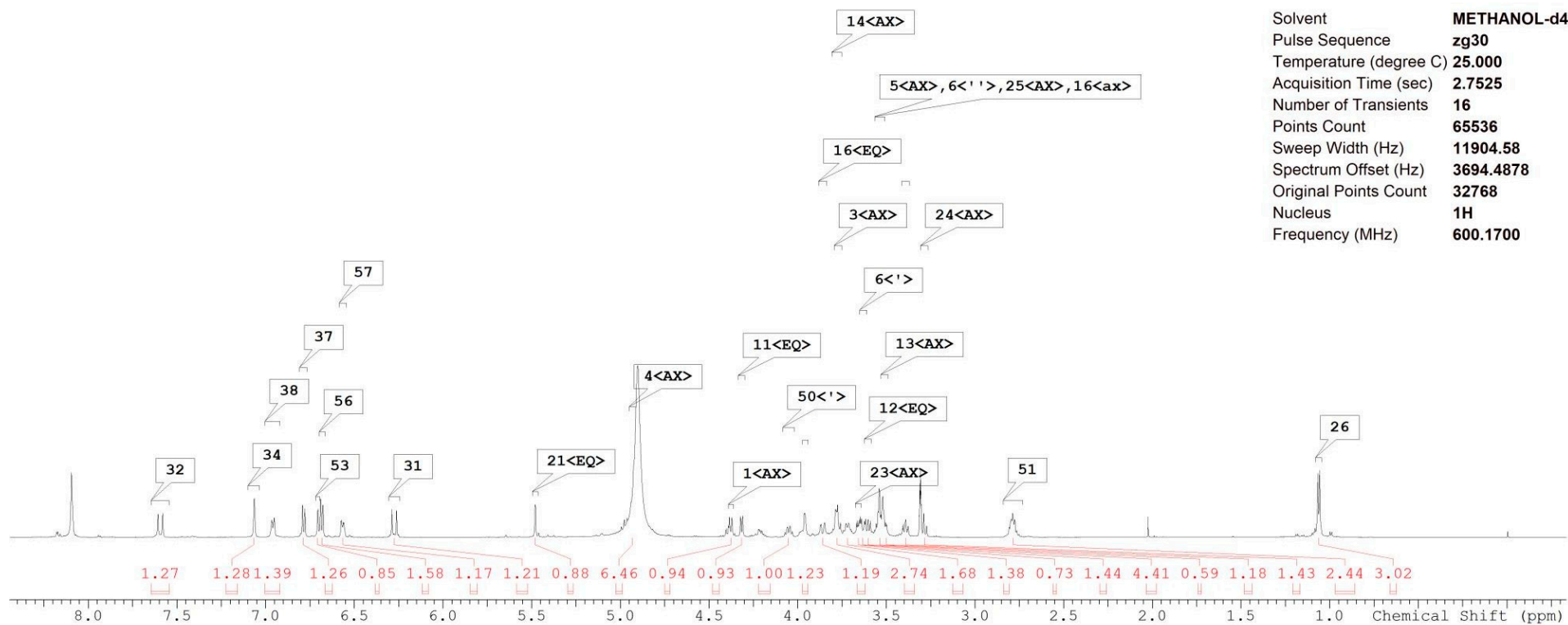
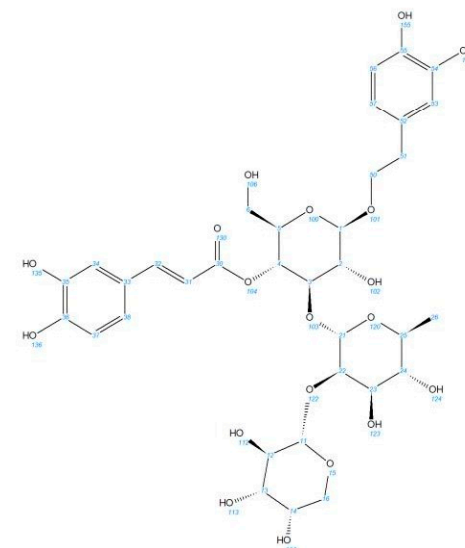


Figure S16:  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **PH5** in methanol- $d_4$  at 25 °C



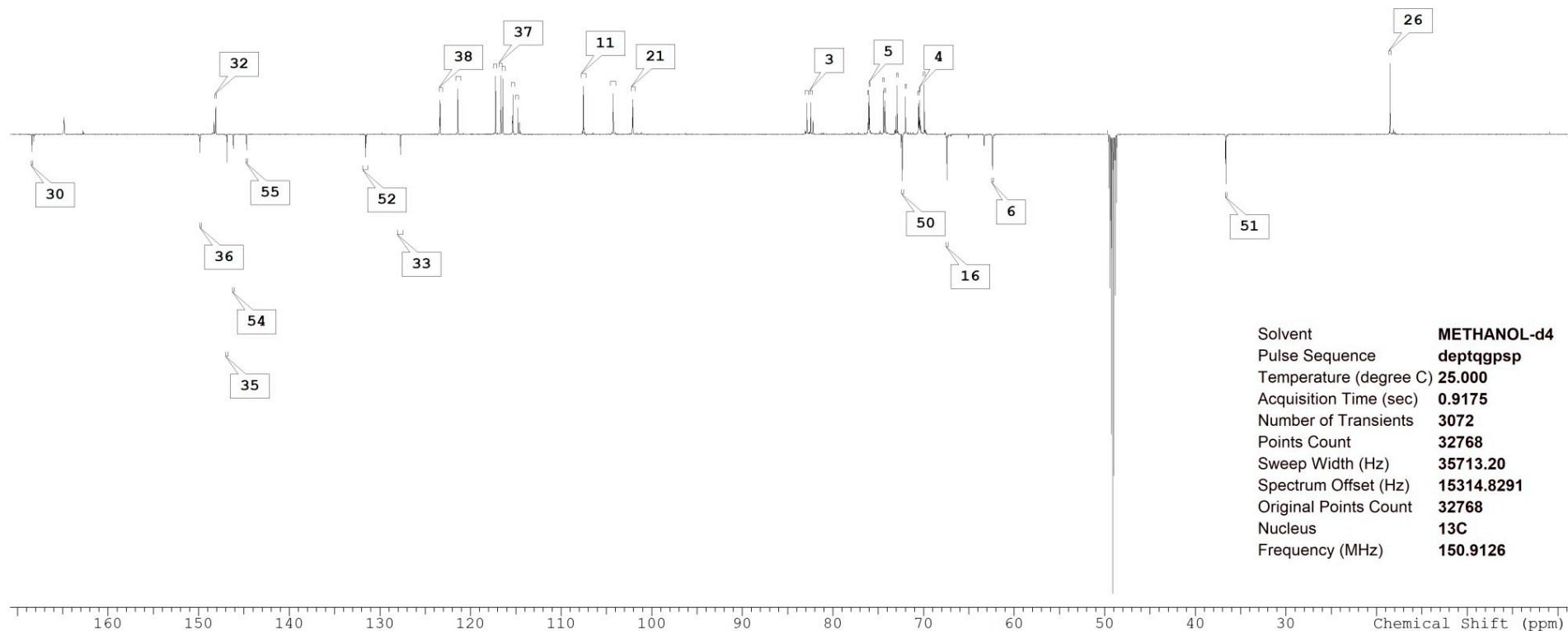


Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1	Shift1 (ppm)	H's	Type	J (Hz)	Atom1	Multiplet1
1.063	3.000	br d	6.2	26	M27	4.317	1.000	d	7.3	11<EQ>	M12
2.787	2.000	m	-	51	M26	4.379	1.000	br d	7.8	1<AX>	M11
3.290	1.000	t	9.6	24<AX>	M25	4.925	1.000	br s	9.3	4<AX>	M10
3.392	1.000	br t	9.3, 7.8	2<AX>	M24	5.482	1.000	s	-	21<EQ>	M09
3.510	1.000	br dd	9.0, 3.3	13<AX>	M23	6.276	1.000	d	15.8	31	M08
3.540	4.000	m	-	5<AX>, 6<'>, 25<AX>, 16<ax>	M22	6.568	1.000	br dd	8.0, 1.8	57	M07
3.605	1.000	br dd	9.0, 7.4	12<EQ>	M21	6.684	1.000	d	8.0	56	M06
3.633	1.000	br dd	13.6, 3.5	6<'>	M19	6.707	1.000	d	1.6	53	M05
3.658	1.000	br dd	9.6, 3.3	23<AX>	M20	6.786	1.000	d	8.2	37	M04
3.720	1.000	q	9.4	50<'>	M18	6.958	1.000	br dd	8.1, 1.9	38	M03
3.775	1.000	br t	9.3	3<AX>	M16	7.065	1.000	s	-	34	M02
3.783	1.000	br s	-	14<AX>	M17	7.594	1.000	br d	15.8	32	M01
3.860	1.000	br dd	12.8, 2.1	16<EQ>	M15						
3.961	1.000	br dd	3.0, 1.5	22<EQ>	M14						
4.052	1.000	q	8.4	50<'>	M13						

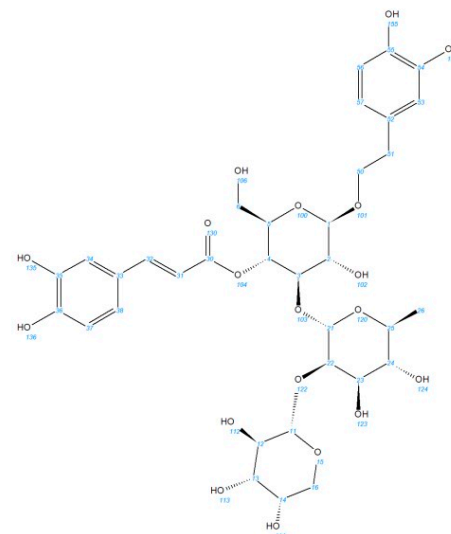


**Figure S18:** <sup>1</sup>H spectrum, structure, numbering and full assignment of PH6 in methanol-d<sub>4</sub> at 25 °C





Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1
18.546	1.000	s	26	M34	82.888	1.000	s	22	M19	146.898	1.000	s	35	M03
36.652	1.000	s	51	M33	102.106	1.000	s	21	M18	148.133	1.000	s	32	M06
62.413	1.000	s	6	M32	104.258	1.000	s	1	M17	149.859	1.000	s	36	M02
67.440	1.000	s	16	M31	107.552	1.000	s	11	M16	168.420	1.000	s	30	M01
69.953	1.000	s	14	M30	114.781	1.000	s	31	M15					
70.451	1.000	s	4	M29	115.352	1.000	s	34	M14					
70.574	1.000	s	25	M28	116.442	1.000	s	56	M13					
72.019	1.000	s	23	M27	116.659	1.000	s	37	M12					
72.286	1.000	m	50	M26	117.258	1.000	s	53	M11					
72.936	1.000	s	12	M25	121.418	1.000	s	57	M10					
74.294	1.000	s	24	M24	123.375	1.000	s	38	M09					
74.438	1.000	s	13	M23	127.752	1.000	s	33	M08					
76.034	1.000	s	5	M22	131.616	1.000	s	52	M07					
76.114	1.000	s	2	M21	144.731	1.000	s	55	M05					
82.484	1.000	s	3	M20	146.190	1.000	s	54	M04					



**Figure S19:**  $^{13}\text{C}$  spectrum, structure, numbering and full assignment of **PH6** in methanol- $\text{d}_4$  at 25  $^{\circ}\text{C}$

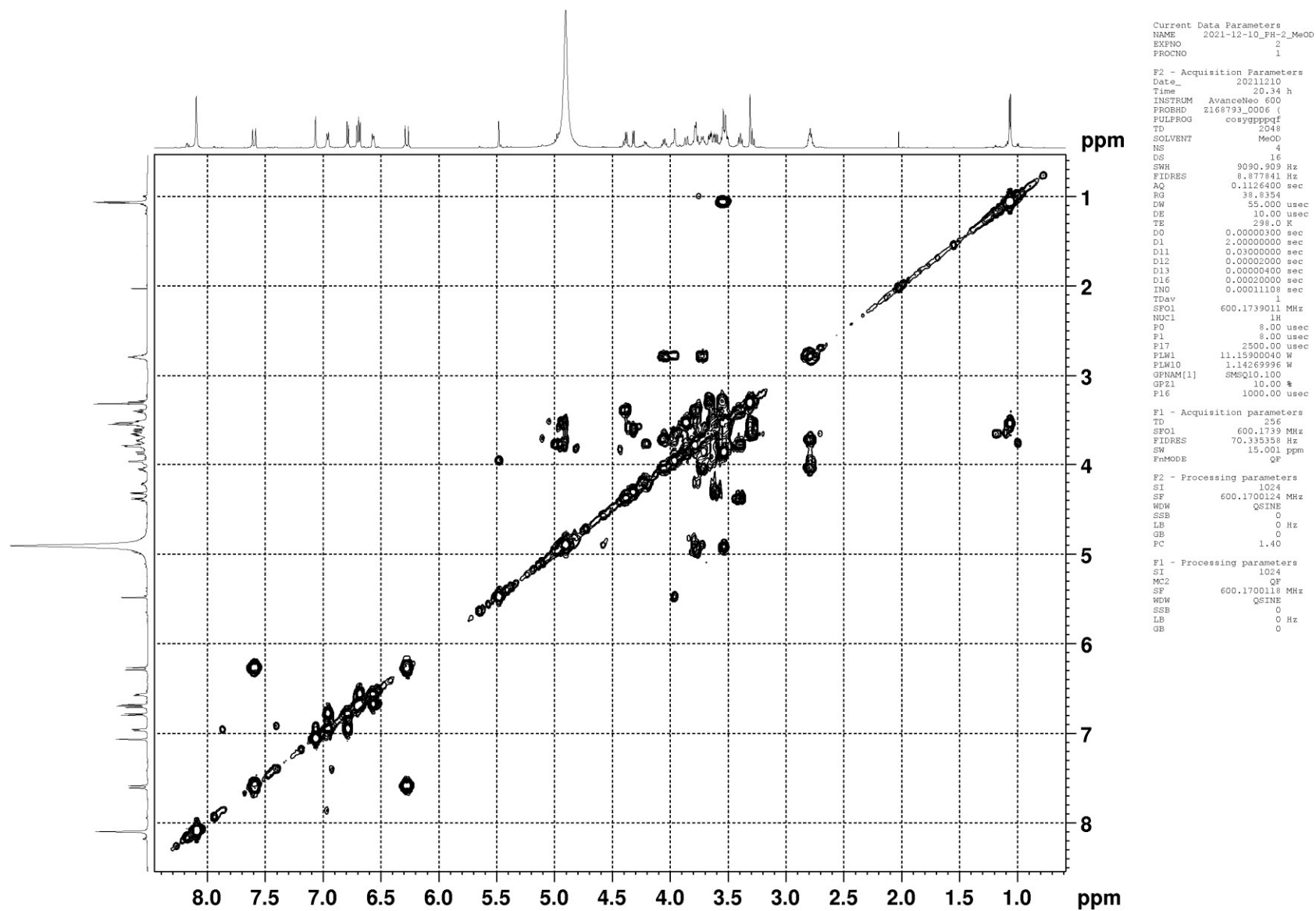


Figure S20: COSY spectrum of PH6 in methanol-d<sub>4</sub> at 25 °C



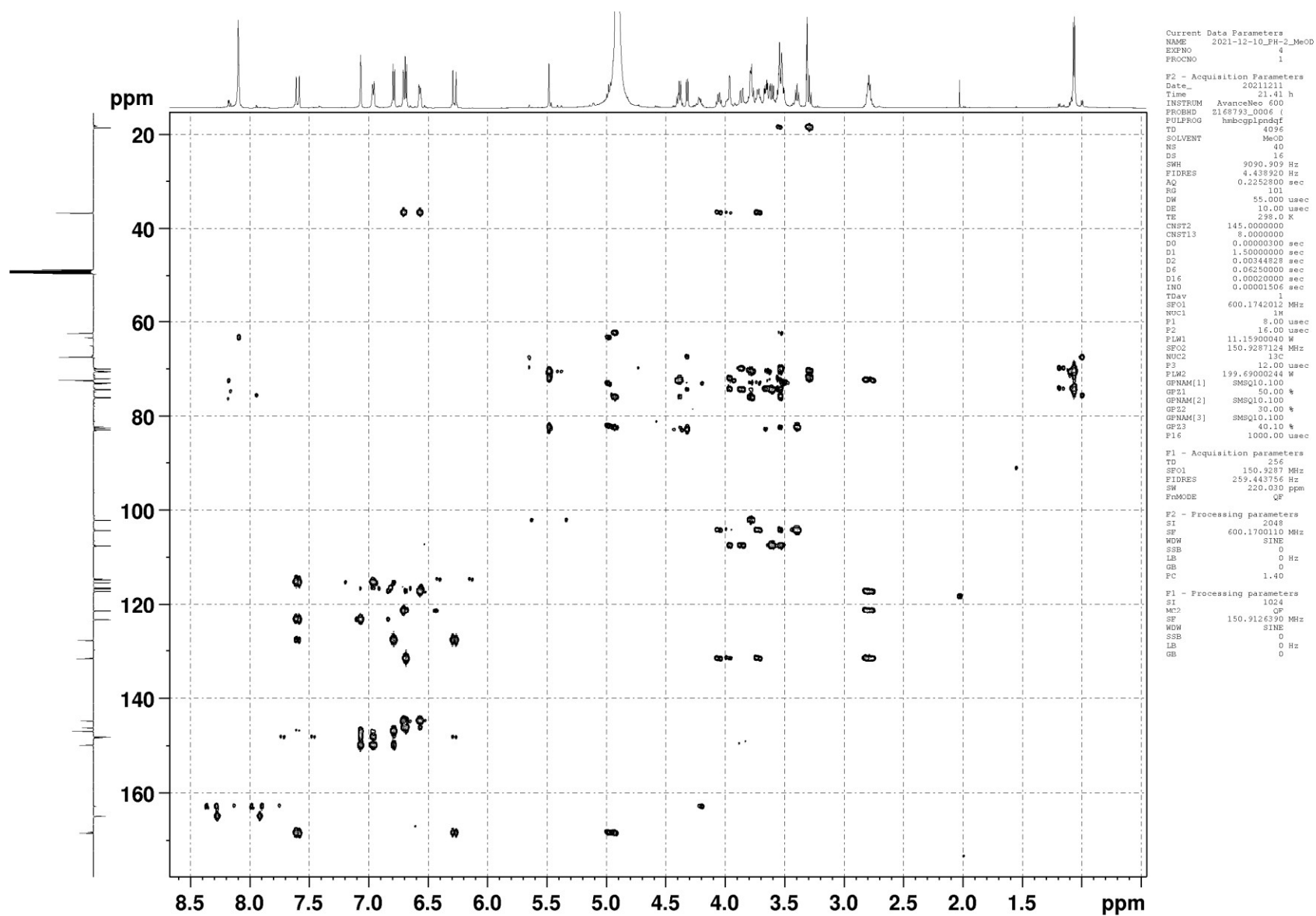
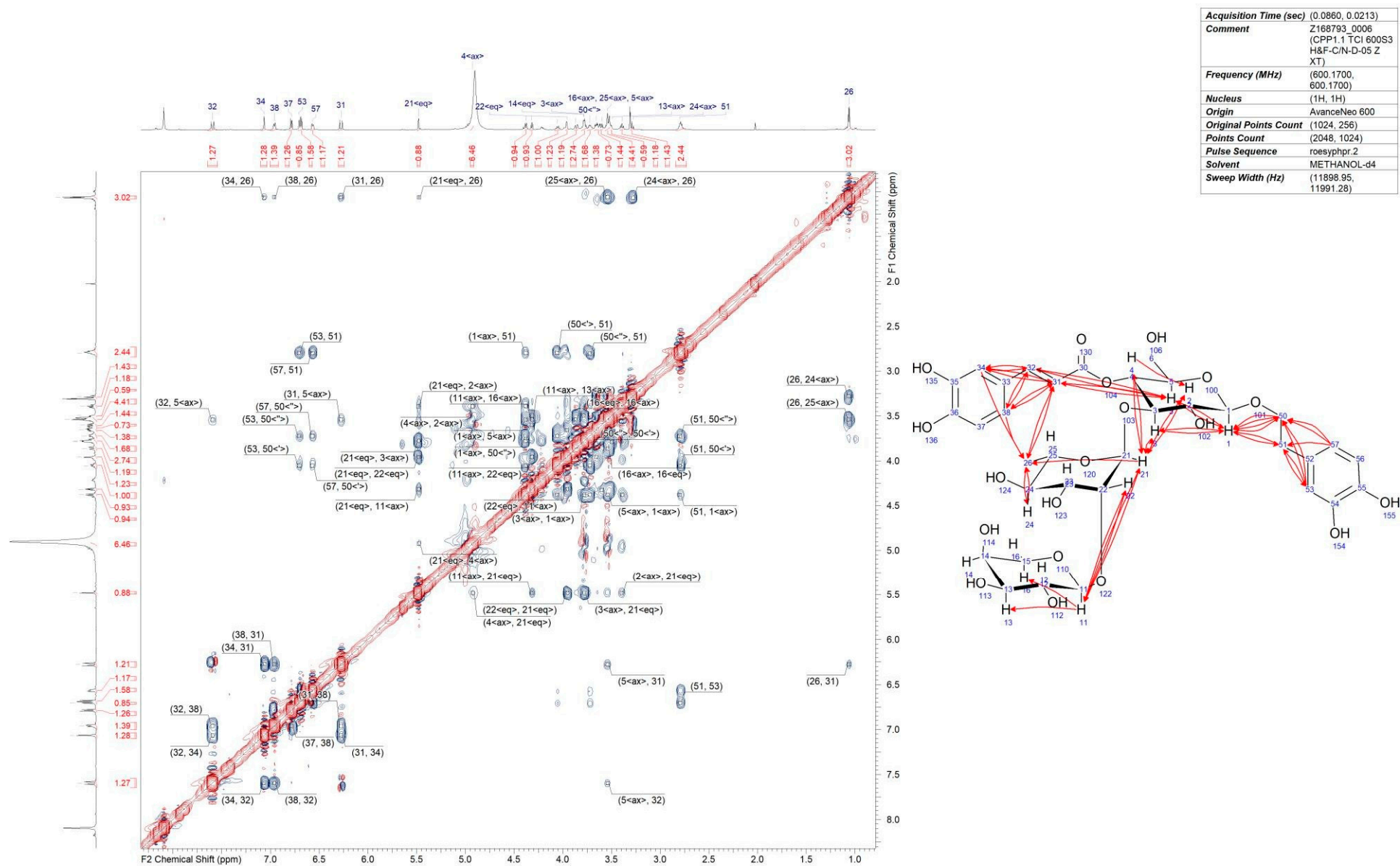
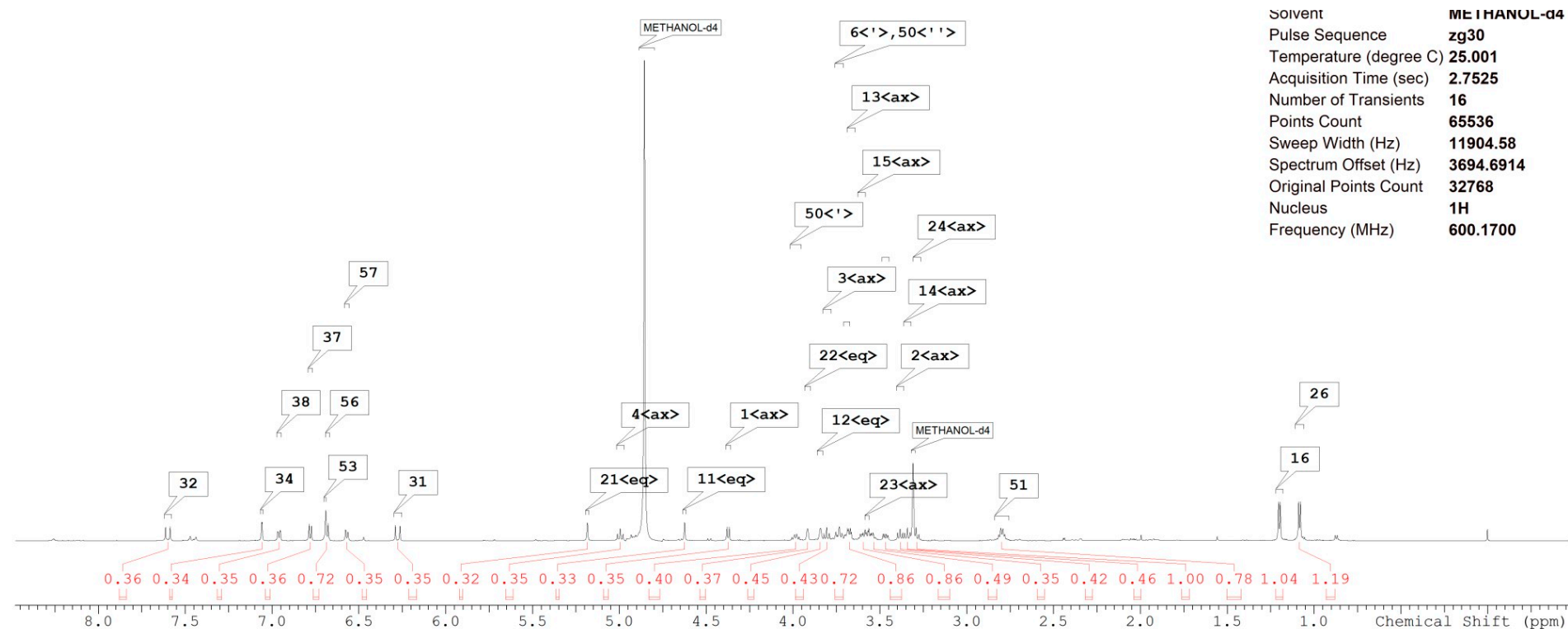


Figure S22:  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **PH6** in methanol- $\text{d}_4$  at 25 °C

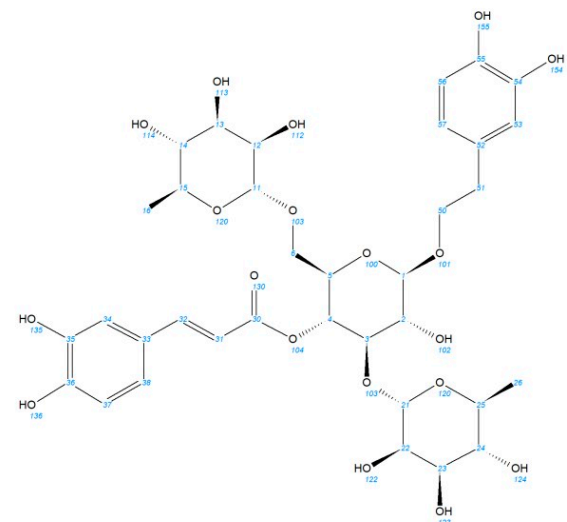


**Figure S23:** Fully assigned NOESY spectrum of **PH6** in methanol-d<sub>4</sub> at 25 °C

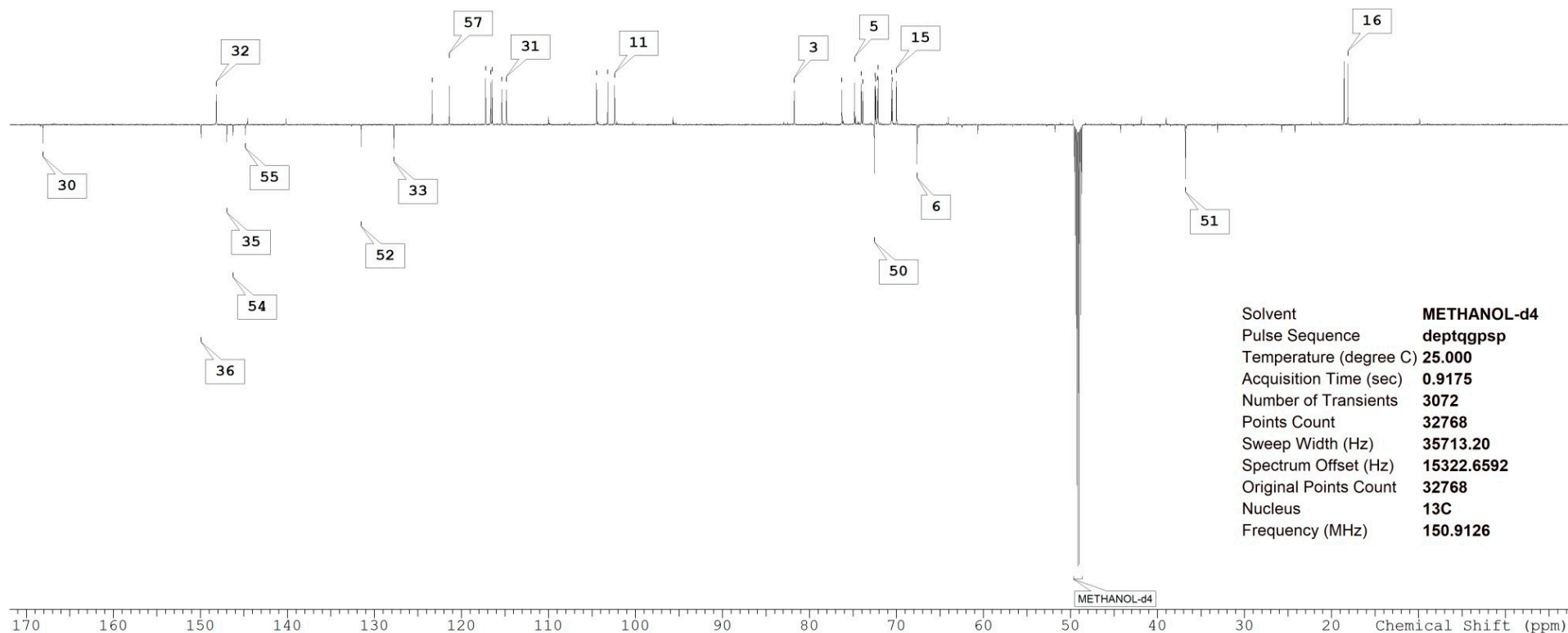




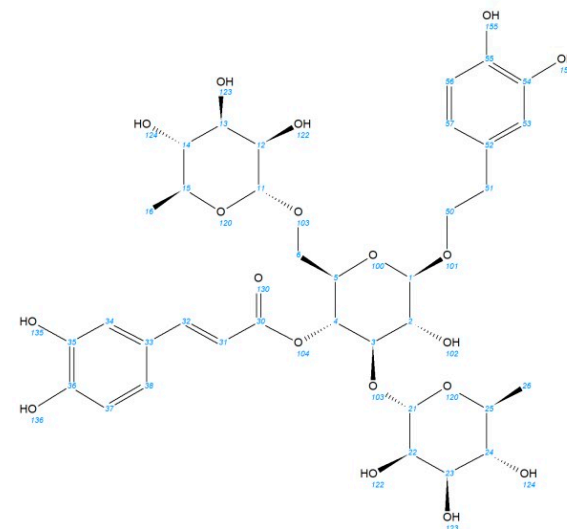
Shift1 (ppm)	H's	Type	J (Hz)	Connected Atoms	Atom1	Multiplet1	Shift1 (ppm)	H's	Type	J (Hz)	Connected Atoms	Atom1	Multiplet1
1.085	3.000	d	6.2	16	26	M02	3.917	1.000	dd	3.0, 1.5	-	22<eq>	M10
1.201	3.000	d	6.2	26	16	M03	3.986	1.000	ddd	9.5, 8.2, 6.9	-	50<'>	M13
2.799	2.000	br s	-	-	51	M04	4.375	1.000	d	8.0	57	1<ax>	M11
3.292	1.000	t	9.4	-	24<ax>	M05	4.626	1.000	d	1.2	-	11<eq>	M12
3.343	1.000	br t	9.5	-	14<ax>	M06	4.996	1.000	t	9.6	-	4<ax>	M14
3.384	1.000	t	8.5	-	2<ax>	M28	5.185	1.000	d	1.1	-	21<eq>	M15
3.468	1.000	dd	11.4, 5.4	-	6<'>	M27	6.278	1.000	d	16.0	-	31	M17
3.552	1.000	dq	9.3, 6.2	-	25<ax>	M07	6.571	1.000	dd	8.0, 1.6	1<ax>, 38	57	M18
3.575	1.000	dd	8.7, 2.5	-	23<ax>	M29	6.684	1.000	d	7.9	-	56	M19
3.601	1.000	dq	9.3, 6.2	-	15<ax>	M30	6.693	1.000	d	1.6	-	53	M24
3.677	1.000	br dd	9.4, 3.5	-	13<ax>	M08	6.781	1.000	d	8.2	38	37	M20
3.691	1.000	ddd	9.6, 4.4, 2.2	-	5<ax>	M26	6.960	1.000	dd	8.2, 1.8	37, 57	38	M21
3.737	2.000	m	-	-	6<'>, 50<'>	M25	7.059	1.000	d	1.8	-	34	M22
3.807	1.000	t	9.2	-	3<ax>	M09	7.601	1.000	d	15.8	-	32	M23
3.843	1.000	dd	3.2, 1.5	-	12<eq>	M16							



**Figure S24:** <sup>1</sup>H spectrum, structure, numbering and full assignment of PH7 in methanol-d4 at 25 °C



Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1	Shift1 (ppm)	C's	Type	Atom1	Multiplet1
18.150	1.000	s	16	M01	76.296	1.000	s	2	M23	146.264	1.000	s	54	M38
18.576	1.000	s	26	M02	81.763	1.000	s	3	M24	146.971	1.000	s	35	M39
36.805	1.000	s	51	M07	102.404	1.000	s	11	M25	148.192	1.000	s	32	M40
67.665	1.000	s	6	M11	103.205	1.000	s	21	M26	149.933	1.000	s	36	M41
70.019	1.000	s	15	M12	104.484	1.000	s	1	M27	168.125	1.000	s	30	M42
70.489	1.000	s	4	M13	114.840	1.000	s	31	M28					
70.576	1.000	s	25	M14	115.367	1.000	s	34	M29					
72.128	1.000	s	12	M15	116.494	1.000	s	56	M30					
72.186	1.000	s	23	M16	116.646	1.000	s	37	M31					
72.410	1.000	s	13	M17	117.238	1.000	s	53	M32					
72.475	1.000	s	22	M18	121.412	1.000	s	57	M33					
72.569	1.000	s	50	M19	123.377	1.000	s	38	M34					
73.891	1.000	s	24	M20	127.789	1.000	s	33	M35					
74.071	1.000	s	14	M21	131.531	1.000	s	52	M36					
74.837	1.000	s	5	M22	144.841	1.000	s	55	M37					



**Figure S25:**  $^{13}\text{C}$  spectrum, structure, numbering and full assignment of **PH7** in methanol- $\text{d}_4$  at 25  $^{\circ}\text{C}$

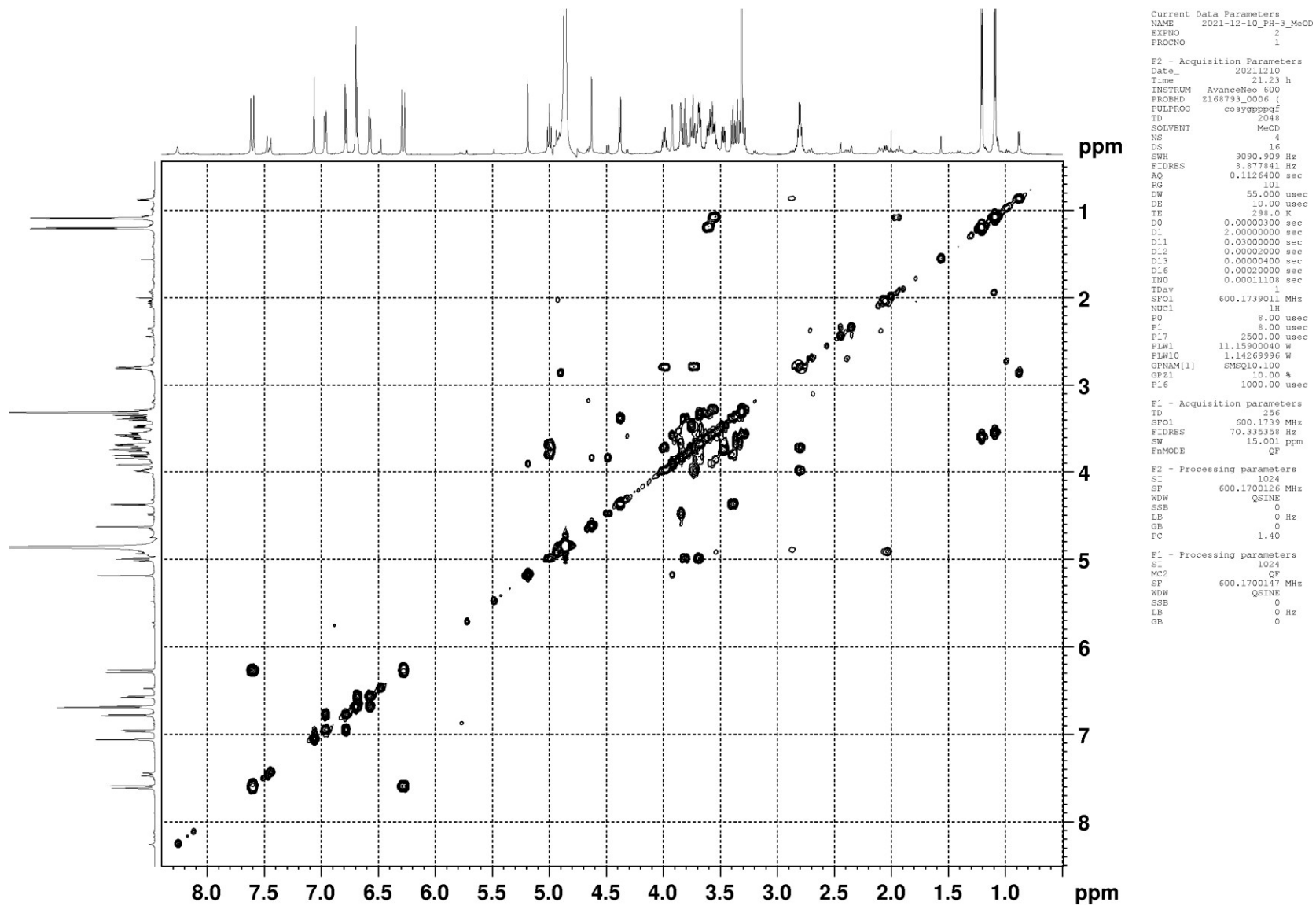


Figure S26: COSY spectrum of PH7 in methanol-d<sub>4</sub> at 25 °C



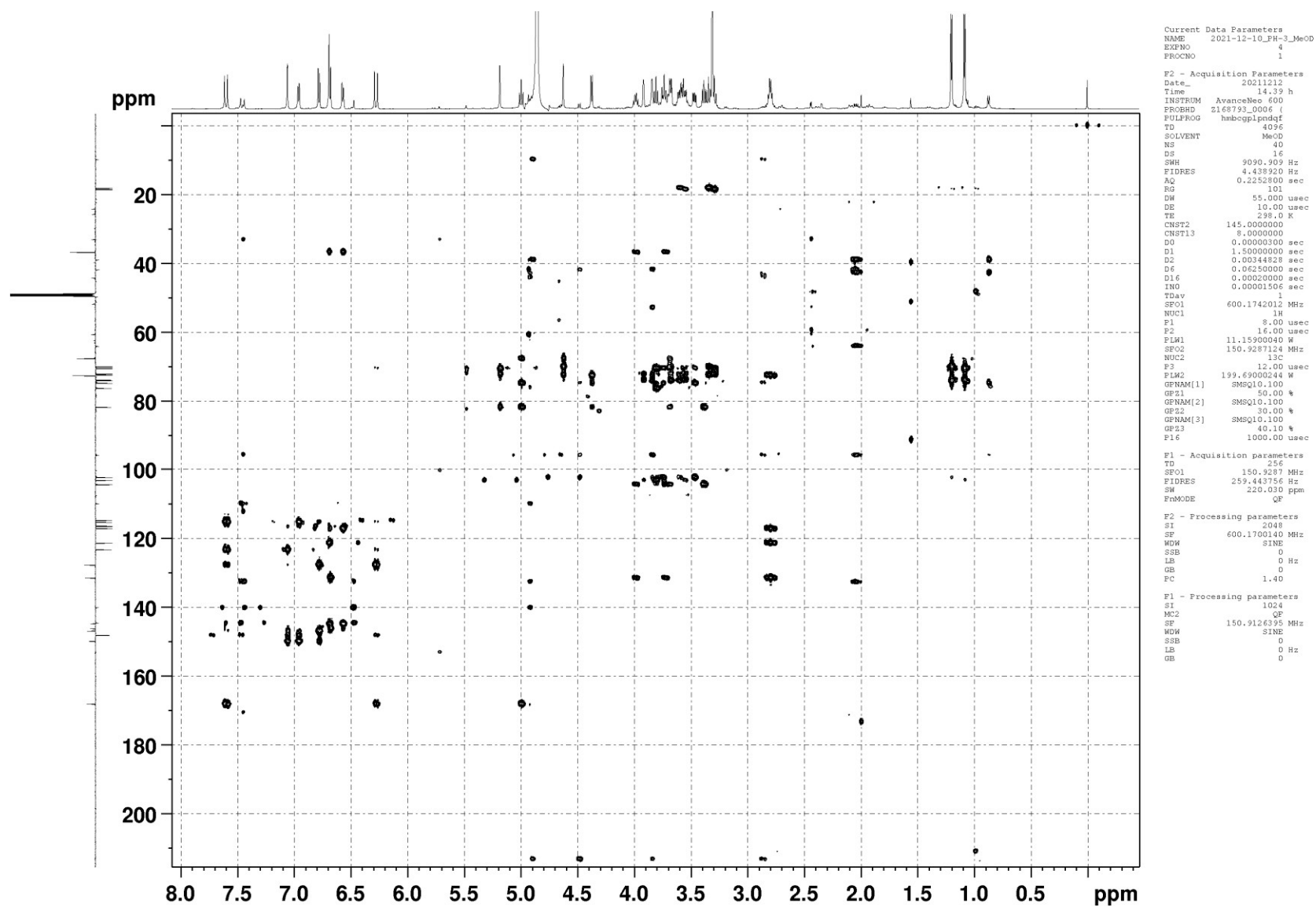


Figure S28:  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **PH7** in methanol- $\text{d}_4$  at 25 °C



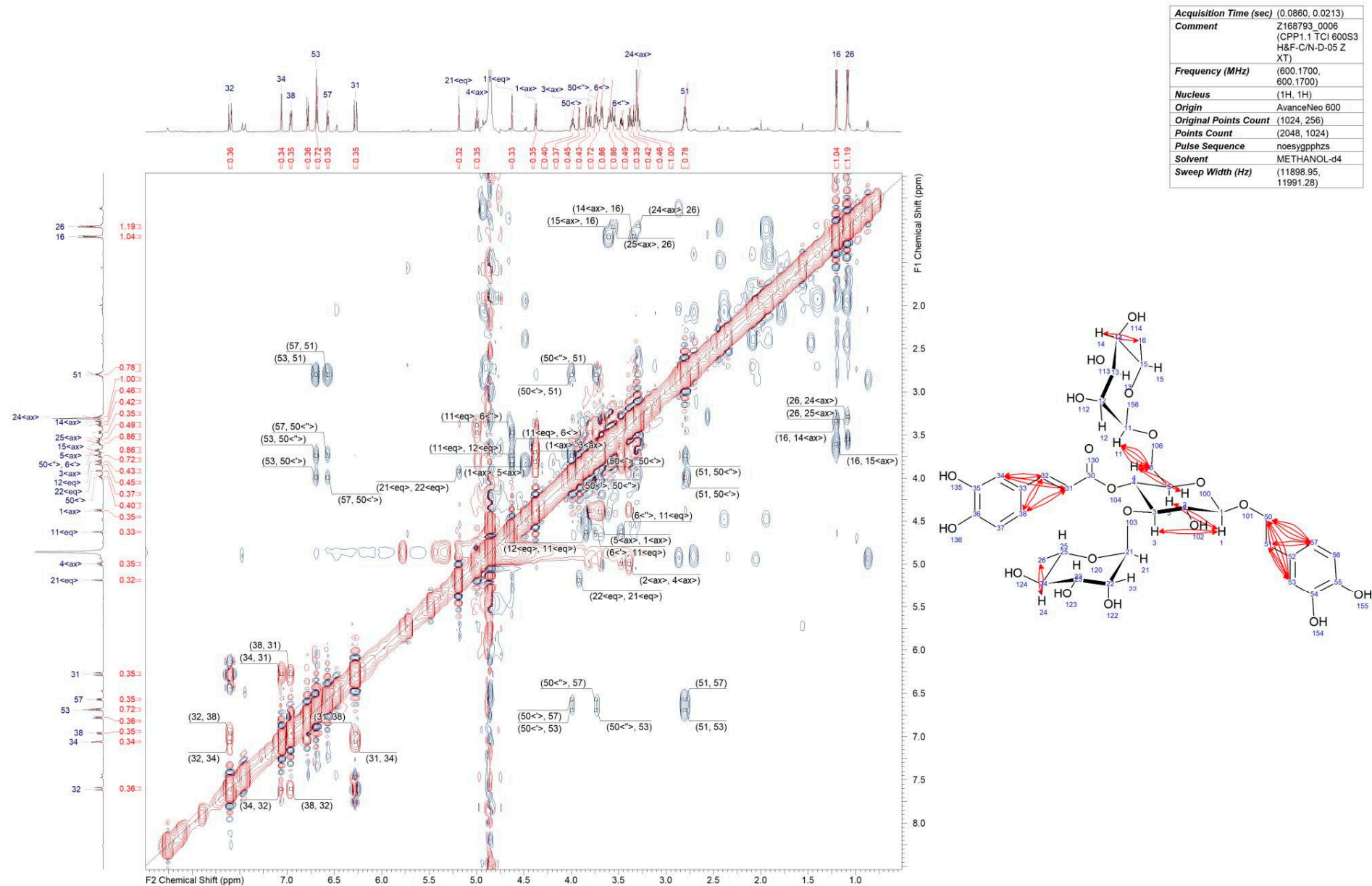


Figure S29: Fully assigned NOESY spectrum of PH7 in methanol-d<sub>4</sub> at 25 °C



**Table S1.** Comparison of proton chemical shifts for all analyzed compounds in methanol- d<sub>4</sub> at 25 °C, the biggest differences marked with superscripted mark “ \* ”.

Unit	Proton	Echinacoside	Verbascoside	PH5	PH6	PH7
<b>β-D-glucopyranose</b>	1<AX>	4.39	4.38	4.38	4.38	4.37
	2<AX>	3.40	3.39	3.38	3.39	3.38
	3<AX>	3.81	3.82	3.77	3.78	3.81
	4<AX>	5.01	4.92*	4.93*	4.93*	5.00
	5<AX>	3.77	3.54*	3.54*	3.54*	3.69
	6<'>	3.94	3.62*	3.64*	3.63*	3.47*
	6<">	3.64	3.52*	3.54*	3.54*	3.74*
<b>Second sugar</b>	11	4.30	n/a	4.36	4.32	4.63*
	12	3.21	n/a	3.58*	3.61*	3.84*
	13	3.34	n/a	3.47*	3.51*	3.68*
	14	3.28	n/a	3.81*	3.78*	3.34
	15	3.22	n/a	3.54*	n/a	3.60
	16<'>	3.83	n/a	3.82	3.86*	1.20
	16<">	3.65	n/a	3.72	3.54*	n/a
<b>α-L-rhamnose</b>	21<EQ>	5.18	5.19	5.57*	5.48*	5.18
	22<EQ>	3.92	3.92	3.99*	3.96*	3.92
	23<AX>	3.57	3.57	3.66*	3.66*	3.58
	24<AX>	3.29	3.29	3.28	3.29	3.29
	25<AX>	3.55	3.57	3.54	3.54	3.55
	26	1.09	1.09	1.05	1.06	1.08
<b>Caffeic acid</b>	31	6.28	6.28	6.28	6.28	6.28
	32	7.60	7.60	7.60	7.59	7.60
	34	7.06	7.06	7.06	7.07	7.06
	37	6.78	6.78	6.78	6.79	6.78
	38	6.96	6.96	6.96	6.96	6.96
<b>Hydroxytyrosol</b>	50<'>	4.04	4.05	4.05	4.05	3.99
	50<">	3.73	3.72	3.72	3.72	3.74
	51	2.80	2.79	2.79	2.79	2.80
	53	6.71	6.70	6.71	6.71	6.69
	56	6.68	6.68	6.68	6.68	6.68
	57	6.58	6.57	6.57	6.57	6.57

**Table S2.** Comparison of carbon chemical shifts for all analyzed compounds in methanol- d<sub>4</sub> at 25 °C, the biggest differences marked with superscripted mark “ \* ”.

Unit	Carbon	Echinacoside	Verbascoside	PH5	PH6	PH7
<b>β-D-glucopyranose</b>	1	104.3	104.3	104.2	104.3	104.5
	2	76.3	76.3	76.3	76.1	76.3
	3	81.8	81.8	83.1	82.5	81.8
	4	70.7	70.7	70.5	70.5	70.5
	5	74.8	76.2	76.1	76.0	74.8
	6	69.5	62.5*	62.4*	62.4*	67.7*
<b>second sugar</b>	11	104.8	n/a	107.7*	107.6*	102.4*
	12	75.2	n/a	73.0*	72.9*	72.1
	13	77.9	n/a	75.0*	74.4*	72.4
	14	71.6	n/a	70.5*	70.0*	74.1
	15	78.0	n/a	77.1		70.0
	16	62.7	n/a	63.0	67.4*	18.2
<b>α-L-rhamnose</b>	21	103.2	103.2	102.5	102.1	103.2
	22	72.5	72.5	83.2*	82.9*	72.5
	23	72.2	72.2	71.9	72.0	72.2
	24	73.9	73.9	74.2	74.3	73.9
	25	70.6	70.6	70.5	70.6	70.6
	26	18.6	18.6	18.6	18.5	18.6
<b>caffeic acid</b>	30	168.6	168.4	168.4	168.4	168.1
	31	114.8	114.8	114.8	114.8	114.8
	32	148.4	148.2	148.1	148.1	148.2
	33	127.8	127.8	127.8	127.8	127.8
	34	115.4	115.4	115.3	115.4	115.4
	35	147.0	146.3	147.0	146.9	147.0
	36	150.0	149.9	149.9	149.9	149.9
	37	116.7	116.6	116.7	116.7	116.6
	38	123.4	123.4	123.4	123.4	123.4
<b>hydroxytyrosol</b>	50	72.5	72.4	72.3	72.3	72.6
	51	36.7	36.7	36.6	36.7	36.8
	52	131.6	131.6	131.7	131.6	131.5
	53	117.3	117.2	117.3	117.3	117.2
	54	146.2	147.0	146.2	146.2	146.3
	55	144.8	144.8	144.8	144.7	144.8
	56	116.5	116.4	116.4	116.4	116.5
	57	121.5	121.4	121.4	121.4	121.4

**Table S3.** Comparison of coupling constants  $^nJ_{H,H}$  (Hz) for all analyzed compounds in methanol- $d_4$  at 25 °C, the biggest differences marked with superscripted mark “ \* ”.

$^nJ_{H,H}$ /Hz	Proton	Echinacoside	Verbascoside	PH5	PH6	PH7
<b><math>\beta</math>-D-glucopyranose</b>	1, 2	7.8	7.8	8.0	7.8	8.0
	2, 3	9.3	9.2	9.1	9.3	9.2
	3, 4	9.6	9.5	9.3	9.3	9.6
	4, 5	9.6	9.5	9.3	9.3	9.6
	5, 6a	2.2	<1*	overlap	3.5	2.2
	5, 6b	5.5	5.8	overlap	overlap	5.5
	6a, 6b	11.4	10.2	12.4	13.6	11.4
<b>second sugar</b>	11, 12	7.6	n/a	7.6	7.3	1.5
	12, 13	9.3	n/a	9.6	9.0	3.2
	13, 14	9.1	n/a	3.4*	3.3*	9.5
	14, 15	9.0	n/a	overlap (ca 2-3 Hz)*	n/a	9.3
	15, 16a	2.3	n/a	7.3*	n/a	6.2
	15, 16b	5.6	n/a	overlap	n/a	n/a
	16a, 16b	11.9	n/a	11.4	12.8*	n/a
	14, 16a	n/a	n/a	n/a	2.1*	n/a
<b><math>\alpha</math>-L-rhamnose</b>	14, 16b	n/a	n/a	n/a	overlap (ca 3-4 Hz)*	n/a
	21, 22	1.6	1.6	1.3	1.5	1.5
	22, 23	3.3	3.2	3.1	3.3	3.0
	23, 24	9.5	9.6	9.6	9.6	9.5
	24, 25	9.6	9.6	9.6	9.6	9.3
	25, 26	6.2	6.2	6.0	6.2	6.2
<b>caffeic acid</b>	31, 32	15.8	15.8	15.8		15.8
	34, 38	2.0	2.0	1.8	1.9	1.8
	37, 38	8.3	8.2	8.2	8.2	8.2
<b>hydroxytyrosol</b>	50a, 50b	9.6	9.6	9.5	9.5	9.5
	50a, 51a	7.0; 8.1	6.7; 8.3	6.7; 7.8	8.4	8.17; 6.9
	50a, 51b				8.4	
	50b, 51a	6.7; 8.2	6.8; 8.3	overlap	9.5	overlap
	50b, 51b			overlap	9.5	overlap
	53, 57	2.2	2.0	1.8	1.8	1.6
	56, 57	8.0	8.0	8.0	8.0	8.0